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Efeitos de Ligações de Hidrogênio em Propriedades de Aglomerados e de Líquidos Moleculares

Roberto Rivelino de Melo Moreno

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Orientador: Prof. Dr. Sylvio Roberto Accioly Canuto

Sylvio Canuto

Comissão Examinadora:

Prof. Dr. Adalberto Fazzio (IF-USP)

Profa. Dra. Márcia Cristina Bernardes Barbosa (UFRGS)

Prof. Dr. Paulo Sérgio Santos (IQ-USP)

Prof. Dr. Ricardo Bicca de Alencastro (UFRJ)

Prof. Dr. Sylvio Roberto Accioly Canuto (IF-USP)

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Voici un extrait de ma pensée profonde,
Ma guerre des nerfs parce que l'ignorance c'est le nerf de la guerre,
On nous dit, Dieu est lumière, nous sommes tous frères,
Mais on constate que la lumière est éteinte,
Je souhaite que nous ne fassions plus les mêmes erreurs,
C'est dur à dire, mais...

(C. M'Barali / Jimny Jay)

*Dedico esta tese a todos os
bolsistas, especialmente aos
do CNPq e da CAPES.*

Resumo

A influência da formação de ligações de hidrogênio (LHs) em sistemas moleculares é investigada analisando-se as propriedades de aglomerados próton-ligados e de moléculas em solventes próticos. As estruturas supermoleculares dos aglomerados são obtidas por otimização de geometria com diferentes métodos quânticos *ab initio*. Por sua vez, as estruturas supermoleculares dos solventes dependem de condições termodinâmicas e, portanto, são obtidas utilizando-se técnicas de simulação Monte Carlo, em que as interações intermoleculares são parametrizadas pelos potenciais de Lennard-Jones e de Coulomb. Os efeitos decorrentes da formação de LHs nos aglomerados moleculares são analisados a partir de suas propriedades: estabilidades, espectros vibracionais, constantes rotacionais e dipolos elétricos. Estas propriedades são calculadas usando-se métodos perturbativos (MBPT/CC) e teoria do funcional da densidade (DFT). Para as moléculas solvatadas em meio líquido, os efeitos das LHs são analisados na interação soluto-solvente durante o processo de equilíbrio conformacional de furfural em solventes próticos. A contribuição da interação do soluto com o meio também é investigada no espectro de absorção UV-vis do sistema furfural/água. Os resultados destes estudos mostram que a formação de LHs é importante para explicar o comportamento de algumas propriedades de sistemas moleculares próton-ligados, principalmente de aglomerados. No caso de sistemas em fase líquida, as LHs dependem, basicamente, do caráter prótico e da polaridade do solvente, propriedades que concorrem para a estabilização de possíveis formas conformacionais da molécula do soluto.

Abstract

The influence of hydrogen bond formation in molecular systems is investigated analysing the properties of both hydrogen-bonded clusters and molecules in protic solvents. The super-molecular structures of the clusters are obtained by optimizing the geometries with different *ab initio* quantum methods. On the other hand, the super-molecular structures of the solvents depend on thermodynamic conditions and, so, are obtained by using Monte Carlo simulation techniques, where the intermolecular interactions are accounted for the Lennard-Jones and Coulomb pair-potentials. The effects due to H-bond formation in the molecular clusters are analysed from their properties: stabilities, vibrational spectra, rotational constants, and electric dipoles. These properties are calculated using perturbation methods (MBPT/CC) and density functional theory (DFT). For the molecules in liquid solvents, the H-bond effects are analysed in the solute-solvent interaction during the conformational equilibrium process of furfural in protic solvents. The contribution of the interaction of the solute with the medium is also investigated in the UV-vis absorption spectrum of the furfural/water system. The results from these studies show that the H-bonding process is important to account for the behaviour of some properties of H-bonded molecular systems, mainly of clusters. In the case of liquid-phase systems, the H-bonds depend basically on both the protic nature and polarity of the solvent, properties that come together to stabilize possible conformational forms of the solute molecules.

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Capítulo 1

Introdução

Os primeiros desenvolvimentos de métodos quânticos para o estudo de sistemas moleculares e sólidos iniciaram-se a partir de 1926, com o trabalho de Schrödinger sobre a mecânica de átomos e moléculas [1], e 1927, com o trabalho de Born e Oppenheimer sobre a separação dos movimentos eletrônico e nuclear [2]. Nesta direção, Heitler e London [3] desenvolveram a **teoria de valência**, que mais tarde foi estendida por Pauling [4] e Coulson [5]. Paralelamente, a **teoria do orbital molecular** foi desenvolvida a partir dos trabalhos de Hund [6], Mulliken [7], Lennard-Jones [8], dentre outros autores importantes [9, 10]. Mais recentemente, a **teoria do funcional da densidade**, proveniente das idéias originais de Thomas, Fermi e Dirac [11], foi elaborada por Hohenberg, Kohn e Sham [12, 13] e vem sendo largamente usada para o cálculo de estrutura eletrônica de sólidos e moléculas.

No contexto da mecânica quântica, o estudo das interações intermoleculares surge com o trabalho de London e Eisenschitz sobre as interações de van der Waals [14]. A partir de então, outros trabalhos teóricos foram realizados com o objetivo de compreender melhor a natureza das interações entre moléculas [15]. Atualmente, tem-se concentrado grandes esforços para investigar as interações específicas, responsáveis pelas propriedades anômalas que algumas substâncias

apresentam. Nesta categoria de interações incluem-se as **ligações de hidrogênio** [16, 17]. Estas podem ser formadas internamente em moléculas isoladas (ditas ligações de hidrogênio intramoleculares) ou entre moléculas de aglomerados, sólidos e líquidos [18].

Os estudos dos mecanismos da formação de ligações de hidrogênio (LHs) são, sem dúvida, muito importantes para a compreensão das propriedades de diferentes tipos de sistemas moleculares. Como exemplo, o fenômeno de transferência protônica, responsável pela condutividade elétrica da água e do gelo [19, 20], está relacionado às LHs formadas entre as moléculas de água. Além disso, muitas bio-estruturas configuram-se em arquiteturas moleculares estabilizadas por LHs ou próton-ligadas [21]. De fato, as propriedades destes sistemas são regidas por efeitos não-aditivos [22, 23], originando, por exemplo, estruturas moleculares auto-organizadas [24] ou estruturas supramoleculares [25].

A investigação das propriedades de sistemas moleculares próton-ligados tem crescido bastante na físico-química de *clusters* e de líquidos [26, 27, 28]. E a potencial importância das LHs para a estabilização, bem como para a determinação das funções, de macromoléculas biológicas torna este estudo de grande interesse também em bioquímica. Por exemplo, sabe-se que a hélice dupla do DNA é estabilizada devido à formação de LHs e pelo efeito hidrofóbico [29, 30]. Assim, o meio em que estes sistemas estão imersos também desempenha um papel extremamente importante para a estabilização de um determinado soluto em um solvente específico.

O objetivo deste trabalho é investigar a estabilidade de sistemas próton-ligados e quantificar os efeitos das LHs em suas propriedades estruturais, energéticas e espectroscópicas. Nossos sistemas de interesse são aglomerados moleculares e moléculas imersas em solventes próticos. Para o tratamento de aglomerados utilizamos métodos quânticos de primeiros princípios, em que os efeitos eletrostáticos, de indução e de dispersão, decorrentes das interações intermoleculares, são computados apropriadamente. No caso de sistemas em fase líquida, utilizamos

uma metodologia sequencial de simulações Monte Carlo e cálculos quânticos [28], em que as estruturas estatisticamente descorrelacionadas do solvente são consideradas para a obtenção das propriedades eletrônicas do soluto.

Os métodos de estrutura eletrônica usados nesta tese são descritos no Capítulo 2 e uma breve introdução histórica, abordando os principais aspectos das LHs em sistemas moleculares, é feita no Capítulo 3. No Capítulo 4 discutimos as diferenças fundamentais entre as estruturas de aglomerados e de líquidos dentro da aproximação supermolecular. Uma apresentação sucinta do método Monte Carlo também é feita no Capítulo 4. A análise dos principais resultados dos nossos estudos é feita no Capítulo 5 e, finalmente, no Capítulo 6 concluímos o trabalho, lançando algumas perspectivas em trabalhos futuros. Alguns fatores de conversão de unidades que julgamos importantes são dados no Apêndice A. Nossas publicações são anexadas no Apêndice B e constituem uma parte essencial da tese.

Capítulo 2

Estrutura Eletrônica Molecular

O problema central da mecânica quântica molecular consiste em resolver a dinâmica de sistemas contendo muitas partículas interagentes. Devido à complexidade destes sistemas, a utilização de métodos aproximados torna-se necessária. Assim, um primeiro nível de aproximação adotado para se resolver o problema de moléculas com dois ou mais átomos é a separação de Born-Oppenheimer [2, 31]. Neste esquema, os núcleos podem ser tratados como se fossem fixos, criando apenas um campo externo ao qual os elétrons estão submetidos. Diz-se, portanto, que o movimento eletrônico foi desacoplado adiabaticamente do movimento nuclear [31].

A aproximação de Born-Oppenheimer leva ao conceito químico de **estrutura ou formação molecular**; para a qual o movimento nuclear fornece as propriedades ro-vibracionais, enquanto as propriedades eletrônicas podem ser determinadas a partir do problema de n elétrons movendo-se no campo eletrostático estacionário dos núcleos. Isto significa resolver a equação de Schrödinger eletrônica associada ao sistema molecular:

$$H\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n), \quad (2.1)$$

onde os $\mathbf{x}_i$ são coordenadas definidas como $\mathbf{x}_i = (\mathbf{r}_i, s_{zi})$, com os $\mathbf{r}_i$ sendo as coordenadas espaciais e os s_{zi} as coordenadas de spin ($\alpha \uparrow$ ou $\beta \downarrow$) do elétron i .

O hamiltoniano eletrônico descrito em unidades atômicas (*cf.* Apêndice A) é dado por:

$$H = \sum_i^n h(i) + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{r_{ij}} \quad (r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|), \quad (2.2)$$

ou seja, uma soma de hamiltonianos mono-eletrônicos do tipo

$$h(i) = -\frac{1}{2} \nabla^2(i) - \sum_{A=1}^M \frac{Z_A}{r_{Ai}} \quad (r_{Ai} = |\mathbf{r}_i - \mathbf{R}_A|), \quad (2.3)$$

com os termos de repulsão eletrônica, $1/r_{ij}$, para uma determinada configuração nuclear $\mathbf{R}$.

2.1 Aproximação de Hartree-Fock

Um primeiro passo em direção a resolver a equação eletrônica de Schrödinger (2.1) é a aproximação de Hartree-Fock [32, 33]. Nesta aproximação utiliza-se o método variacional para encontrar a melhor configuração de spin-orbitais $\{\chi_i\}_{i=1}^n$ em que o sistema multi-eletrônico seja descrito apenas com um determinante de Slater:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = (n!)^{-1/2} \det |\chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) \cdots \chi_n(\mathbf{x}_n)|. \quad (2.4)$$

Desta forma, o método de Hartree-Fock (HF) reduz o problema de n elétrons a n problemas de um elétron. Entretanto, a energia assim obtida, E_{HF} , não leva em conta a **correlação eletrônica**, uma vez que HF é uma aproximação de campo médio [34]. A energia de correlação pode ser definida como [35, 36]:

$$E_{\text{corr}} = E_{\text{exata}} - E_{\text{HF}}, \quad (2.5)$$

isto é, a diferença entre a energia exata não-relativística do sistema e a energia obtida com o método HF.

As equações de HF formam um conjunto de equações integro-diferenciais do tipo:

$$\left[h(1) + \sum_{j \neq i} J_j(1) - K_j(1) \right] \chi_i(1) = \varepsilon_i \chi_i(1) \quad i = 1, 2, \dots \quad (2.6)$$

onde

$$\begin{aligned} J_j(1)\chi_i(1) &= \left[\int \chi_j^*(2) r_{12}^{-1} \chi_j(2) d\mathbf{x}_2 \right] \chi_i(1) \\ K_j(1)\chi_i(1) &= \left[\int \chi_j^*(2) r_{12}^{-1} \chi_i(2) d\mathbf{x}_2 \right] \chi_j(1) \end{aligned} \quad (2.7)$$

são os operadores de Coulomb e de troca, respectivamente. Este é um problema de pseudo-autovalores, uma vez que o operador de Fock $F = h + \sum_j (J_j - K_j)$ depende das próprias funções χ_i que se pretende determinar. Sendo assim, as Eqs. (2.6) são resolvidas usualmente por um processo iterativo, e.g., o método do campo autoconsistente (SCF, *Self-Consistent Field*).

Uma maneira conveniente para resolver as equações de HF consiste em utilizar a aproximação de bases finitas. Por exemplo, no método HF restrito ($\chi_i = \psi_i^\alpha$ ou ψ_i^β) assume-se que os orbitais moleculares ψ_i sejam expressos em termos de um conjunto base de orbitais atômicos conhecidos $\{\phi_j\}_{j=1}^m$, contendo m ($m \geq n$) funções. Esta é a essência do método LCAO-MO (*Linear Combination of Atomic Orbitals - Molecular Orbital*):

$$\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}. \quad (2.8)$$

Com esta estratégia as equações de HF tomam a forma matricial:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}, \quad (2.9)$$

onde $\mathbf{C}$ é uma matriz retangular dos coeficientes de expansão dos orbitais moleculares, $\mathbf{S}$ é a matriz de *overlap* das funções ϕ_{μ} e $\boldsymbol{\varepsilon}$ é uma matriz diagonal contendo os autovalores ε_i . A Eq. (2.9) foi obtida independentemente por Roothaan [39] e por Hall [40], porém é referida comumente na literatura como equação de Hartree-Fock-Roothaan (HFR).

Na aproximação de HFR a energia total SCF para um sistema de camada fechada pode ser escrita como

$$E_{\text{SCF}} = 2 \sum_i h_{ii} + \sum_i \sum_j 2J_{ij} - K_{ij}, \quad (2.10)$$

onde os termos h_{ii} , J_{ij} e K_{ij} são expressos em função da base atômica $\{\phi_\mu\}$:

$$h_{ii} = \sum_{\mu\nu} C_{\mu i}^* C_{\nu i} \int \phi_\mu^*(1) h \phi_\nu(1) d\mathbf{r}_1, \quad (2.11)$$

$$J_{ij} = \sum_{\mu\lambda} \sum_{\nu\sigma} C_{\mu i}^* C_{\lambda j} C_{\nu i}^* C_{\sigma j} \langle \mu\lambda | \nu\sigma \rangle, \quad (2.12)$$

$$K_{ij} = \sum_{\mu\lambda} \sum_{\nu\sigma} C_{\mu i}^* C_{\lambda j} C_{\nu i}^* C_{\sigma j} \langle \mu\nu | \lambda\sigma \rangle, \quad (2.13)$$

com $\langle \mu\nu | \lambda\sigma \rangle$ representando as integrais de interação de dois elétrons sobre os orbitais atômicos

$$\langle \mu\nu | \lambda\sigma \rangle = \iint \phi_\mu(1) \phi_\lambda(2) r_{12}^{-1} \phi_\nu(1) \phi_\sigma(2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2.14)$$

A qualidade do cálculo HFR depende do conjunto base de orbitais atômicos escolhido. Por questões práticas, estes orbitais são usualmente escritos como combinações de funções gaussianas [37] (ou contrações) da forma:

$$\phi_\mu^{\text{CGF}}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^L d_{p\mu} g_p(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A), \quad (2.15)$$

em que L é o número de funções gaussianas primitivas, g_p ; $d_{p\mu}$ e $\alpha_{p\mu}$ são respectivamente coeficientes e expoentes da contração (2.15). Os cálculos de estrutura eletrônica molecular mais acurados envolvem muitas gaussianas, incluindo funções difusas e de polarização. Por exemplo, algumas destas bases atômicas usuais são denotadas como 6-31G, 6-311++G(d,p), aug-cc-pVDZ, etc [37, 38].

A Eq. (2.9) também pode ser resolvida utilizando-se procedimentos semi-empíricos [41], principalmente quando trata-se de sistemas com um número grande de elétrons. Neste nível de aproximação, as integrais contendo *overlap* do tipo $\phi_\mu^*(1) \phi_\nu(1)$ são consideradas nulas para $\mu \neq \nu$ (aproximação ZDO, *Zero-Differential Overlap*). Como consequência, as integrais de repulsão eletrônica (2.14) ficam dadas por:

$$\langle \mu\lambda | \nu\sigma \rangle = \langle \mu\lambda | \mu\lambda \rangle \delta_{\mu\nu} \delta_{\lambda\sigma}, \quad (2.16)$$

sendo δ_{ij} o delta de Kronecker, e as integrais do “caroço” atômico $h_{\mu\nu} = \int \phi_\mu^* h \phi_\nu d\mathbf{r}_1$ sendo determinadas como parâmetros semi-empíricos [41].

As diversas categorias de métodos semi-empíricos diferem basicamente na extensão em que a aproximação ZDO é considerada para as integrais de repulsão eletrônica. Assim, se todos os pares de orbitais atômicos satisfazem a Eq. (2.16), os elementos da matriz de Fock para um sistema de camada fechada tornam-se bastante simplificados:

$$\begin{aligned} F_{\mu\mu} &= h_{\mu\mu} - \frac{1}{2} P_{\mu\mu} \langle \mu\mu | \mu\mu \rangle + \sum_\lambda P_{\lambda\lambda} \langle \mu\lambda | \mu\lambda \rangle \\ F_{\mu\nu} &= h_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \langle \mu\nu | \mu\nu \rangle \quad (\phi_\mu \neq \phi_\nu) \end{aligned} \quad (2.17)$$

com os $P_{\mu\nu} = 2 \sum_i C_{\mu i}^* C_{\nu i}$. Além de considerarem a aproximação ZDO, os métodos semi-empíricos SCF levam em conta explicitamente apenas os elétrons de valência do sistema.

Dentre estes os modelos mais simplificados, destacam-se o CNDO (*Complete Neglect of Differential Overlap*), em que as integrais do tipo $\langle \mu\lambda | \mu\lambda \rangle$ (μ e ν centrados em átomos distintos, A e B) são substituídas por uma repulsão eletrostática média γ_{AB} ; o INDO (*Intermediate Neglect of Differential Overlap*), em que as integrais do tipo $\langle \mu\mu | \nu\nu \rangle$ ($\mu \neq \nu$) são todas computadas numericamente; e o NDDO (*Neglect of Diatomic Differential Overlap*) que despreza somente o *overlap* diferencial para os orbitais atômicos centrados em átomos distintos [41].

2.2 Métodos pós-Hartree-Fock

A descrição detalhada de processos químicos e físicos em escala atômica ou molecular requer que a energia de correlação eletrônica seja computada com grande precisão. Este é o objetivo maior dos métodos *ab initio* pós-HF para estados estacionários [37]. Partindo-se da aproximação HF, a correlação eletrônica pode ser incluída de forma variacional ou via um tratamento perturbativo [42].

Métodos variacionais

A utilização do princípio variacional para o cálculo da energia total de um sistema multi-eletrônico é a base de um dos métodos bastante utilizado em mecânica quântica molecular. Em princípio, a função de estado Ψ do sistema pode ser expandida num conjunto completo de funções multi-eletrônicas $\{\Psi_k\}$ ou CSFs (*Configuration State Functions*):

$$\Psi = \sum_k C_k \Psi_k. \quad (2.18)$$

Este tratamento dá origem aos métodos de interação de configurações (CI, *Configuration Interaction*), em que cada Ψ_k é um determinante de Slater construído a partir das soluções das equações de Hartree-Fock. Fazendo-se uma escolha de configurações adaptadas em simetrias de grupo espacial e de spin [32] torna-se possível obter expansões com um número finito de termos.

Como os orbitais moleculares de HF formam, em princípio, um conjunto completo de funções de uma partícula, então, a Eq. (2.18) pode ser reescrita como

$$\Psi = \Phi_{\text{SCF}} + \sum_i^a C_i^a \Phi_i^a + \sum_{\substack{i < j \\ a < b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \dots, \quad (2.19)$$

onde Φ_{SCF} é o determinante do estado de referência que contém os orbitais moleculares ocupados ψ_i, ψ_j, ψ_k , etc; enquanto Φ_i^a é a configuração obtida substituindo-se o orbital ψ_i por um orbital virtual (ou desocupado) ψ_a ; Φ_{ij}^{ab} contém as substituições duplas dos orbitais ψ_i e ψ_j pelos orbitais virtuais ψ_a e ψ_b , e assim sucessivamente para as substituições de ordens mais altas.

As funções-base da expansão CI são denominadas de configurações eletrônicas, determinadas pelos operadores de spin total S^2 e S_z . Neste sentido, diferentes determinantes podem pertencer a uma mesma configuração de orbitais. Os estados eletrônicos na aproximação CI são então determinados via o método variacional, o que é equivalente a resolver a equação:

$$\det |\mathbf{H} - E\mathbf{1}| = 0. \quad (2.20)$$

O método CI é conceitualmente simples e bastante utilizado para a inclusão da correlação eletrônica na energia do sistema [35, 36, 42]. Os autovalores da energia são obtidos pela diagonalização direta do hamiltoniano, sendo cada um deles um limite superior para a energia exata do sistema [43].

Métodos perturbativos

Uma abordagem usual para se resolver o problema de correlação eletrônica baseia-se na teoria de perturbação de muitos corpos [44, 45, 46]. Neste caso, a energia de correlação, Eq. (2.5), pode ser expandida numa série perturbativa [42]:

$$E_{\text{corr}} = \sum_{k=2}^{\infty} E^{(k)}, \quad (2.21)$$

onde $E^{(2)}$, $E^{(3)}$, etc são as correções de correlação em segunda ordem, terceira ordem, etc. Assim, a energia total do sistema multi-eletrônico pode ser escrita como

$$E = E_{\text{SCF}} + E_{\text{corr}}. \quad (2.22)$$

As contribuições de ordens maiores do que dois são calculadas usando-se a partição de Møller-Plesset [47], na qual o hamiltoniano não perturbado do sistema é escrito como uma soma de operadores de Fock, i.e., $H^{(0)} = \sum_i F_i$. Neste esquema, as contribuições de ordem k são denominadas de MP k e a primeira correção da energia Hartee-Fock aparece como uma perturbação de segunda ordem, i.e., MP2. Esta energia pode ser escrita como uma soma sobre todas as excitações duplas a partir da configuração de referência [42]:

$$E^{(2)} = \frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{|\langle ij||ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (2.23)$$

Outro formalismo bastante interessante para a obtenção sistemática da energia de correlação eletrônica é a teoria de *coupled-cluster* (CC). Os métodos de CC têm sua origem a

partir dos trabalhos de Coester [48] e Kümmel [49] e baseiam-se no *Ansatz* [50, 51]:

$$|\Psi\rangle = e^{T^{(A)}} |\Phi\rangle, \quad T^{(A)} = \sum_{k=1}^{m_A} T_k, \quad (2.24)$$

onde $|\Phi\rangle$ é um determinante de Slater representando o estado não perturbado do sistema e os T_k são definidos como operadores de *cluster*,

$$T_1 |\Phi\rangle = \sum_{\substack{i \\ a}} t_a^i |\Phi_i^a\rangle, \quad T_2 |\Phi\rangle = \sum_{\substack{i>j \\ a>b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad T_k |\Phi\rangle = \sum_{\substack{i_1>i_2>\dots>i_k \\ a_1>a_2>\dots>a_k}} t_{a_1 a_2 \dots a_k}^{i_1 i_2 \dots i_k} |\Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k}\rangle,$$

a partir dos quais obtém-se a teoria exata $m_A = n$ [52] e os métodos aproximados $m_A < n$ [36, 33], por exemplo:

$m_A = 2$	$T^{(A)} = T_1 + T_2$	CCSD
$m_A = 3$	$T^{(A)} = T_1 + T_2 + T_3$	CCSDT
$m_A = 4$	$T^{(A)} = T_1 + T_2 + T_3 + T_4$	CCSDTQ

As amplitudes de cluster $t_{ab\dots}^{ij\dots}$ devem ser tais que (2.24) seja uma solução da equação de Schrödinger (2.1),

$$He^T |\Psi\rangle = Ee^T |\Psi\rangle. \quad (2.25)$$

Então, multiplicando-se os dois lados da Eq. (2.25) por e^{-T} tem-se

$$e^{-T} He^T |\Psi\rangle = E |\Psi\rangle, \quad (2.26)$$

que pode ser expandida como

$$\{H + [H, T] + \frac{1}{2!}[[H, T], T] + \frac{1}{3!}[[[H, T], T], T] + \frac{1}{4!}[[[[H, T], T], T], T]\} |\Phi\rangle = E |\Phi\rangle. \quad (2.27)$$

Este resultado é uma consequência do fato de operador H envolver, no máximo, termos de dois elétrons [42, 53]. Na prática, as equações para a energia e para as amplitudes de *cluster* são obtidas multiplicando-se a Eq. (2.27) por $\langle\Phi|$ e pelos determinantes excitados até pequenas ordens [50, 51, 52].

É possível fazer uma conexão entre os métodos CC e CI escrevendo o vetor de estado $|\Psi\rangle$ com as excitações do mesmo tipo agrupadas [42], ou seja,

$$|\Psi\rangle = (1 + U_1 + U_2 + \dots) |\Phi\rangle \quad (2.28)$$

com

$$U_1 = T_1, \quad U_2 = T_2 + \frac{1}{2!}T_1^2, \quad U_3 = T_3 + \frac{1}{3!}T_1^3 + T_1T_2, \quad \text{etc}, \quad (2.29)$$

tal que U_i pode ser separado em duas partes:

$$U_i = T_i + Q_i, \quad (2.30)$$

sendo T_i o termo conexo, e Q_i o termo desconexo obtido a partir do produto de dois ou mais operadores de *cluster*.

A inclusão dos termos desconexos permite incorporar correções provenientes de excitações de ordens mais altas do que aquelas incluídas pelos operadores conexos [42]. Entretanto a teoria CC não é um método variacional, embora a expressão para o funcional da energia seja dada por

$$E = \frac{\langle \Psi | e^{T^+} H e^T | \Psi \rangle}{\langle \Psi | e^{T^+} e^T | \Psi \rangle}, \quad (2.31)$$

ela não é operacional porque a expansão dos operadores e^T e e^{T^+} não é truncada. Isto é, ao atuar à esquerda, o operador T torna-se T^+ , e assim tentará criar partículas em orbitais ocupados e destruir em orbitais virtuais. Por outro lado, $\langle \Psi | e^{T^+}$ será uma expansão do tipo $\langle \Psi | (1 + T + \frac{1}{2}T^2 + \dots)$ [42]. Uma das vantagens dos métodos MBPT/CC frente aos métodos variacionais truncados é a sua extensividade [42, 53], ou seja, energia é aditiva para subsistemas não interagentes.

2.3 Teoria do funcional da densidade

Uma formulação variacional alternativa para se resolver o problema eletrônico baseia-se na teoria do funcional da densidade (DFT, *Density Functional Theory*), na qual a energia total do sistema é expressa como um funcional da sua densidade eletrônica $\rho(\mathbf{r})$ [54]. Como proposto anteriormente por Thomas, Fermi e Dirac [11], a energia total de um sistema com muitos elétrons pode ser escrita como:

$$E[\rho] = C \int \rho(\mathbf{r})^{5/3} d\mathbf{r} - \sum_{A=1}^M Z_A \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}. \quad (2.32)$$

O primeiro termo na Eq. (2.32) representa a energia cinética, o segundo representa o potencial devido aos núcleos, o terceiro é a interação inter-eletrônica e, finalmente, o quarto termo refere-se à interação de troca [55].

A existência de um funcional único que determina a energia, bem como outras propriedades, do estado fundamental do sistema foi demonstrada por Hohenberg e Kohn (HK), usando o teorema variacional [12]. Então, em vez de se resolver a equação de Schrödinger para n elétrons (2.1), um problema de $3n$ coordenadas, a energia é obtida como solução de uma equação integral em três dimensões [56].

De acordo com o formalismo de HK [12] chega-se a um funcional energia mais geral da forma:

$$E[\rho] = T_0[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho] \quad (2.33)$$

onde $T_0[\rho]$ é a energia cinética para um sistema de partículas não interagentes com densidade $\rho(\mathbf{r})$, $v(\mathbf{r})$ é um potencial externo e $E_{xc}[\rho]$ é a energia de troca-correlação. Em termos práticos, a densidade

$$\rho(\mathbf{r}) = \sum_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) \quad (2.34)$$

é obtida pelo método de Kohn e Sham [13], de modo autoconsistente, i.e., minimizando-se

$E[\rho]$ juntamente com o vínculo da conservação do número de partículas, $n = \int \rho(\mathbf{r}) d\mathbf{r}$. Assim, obtém-se as equações de Kohn-Sham (KS):

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (2.35)$$

De fato, existe uma semelhança entre as equações de HF (2.6) e as de KS (2.35), entretanto não se pode atribuir formalmente o significado de orbitais moleculares e energias orbitais de Kohn-Sham, como no caso do método Hartree-Fock. O formalismo da DFT fornece, em princípio, a solução exata para o problema de n elétrons interagentes. A grande dificuldade desta formulação está na forma funcional de $E_{xc}[\rho]$, que não é conhecida exatamente.

No esquema de KS pode-se supor, como primeira aproximação, que $\rho(\mathbf{r})$ varia muito lentamente, tal que

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}^{LDA}(\rho(\mathbf{r})) d\mathbf{r} \quad (2.36)$$

onde ε_{xc}^{LDA} é a energia de troca-correlação por elétron para um gás eletrônico com densidade uniforme. Esta é a conhecida aproximação de densidade local (LDA, *Local Density Approximation*), para a qual se tem

$$\frac{\delta E_{xc}[\rho]}{\delta \rho} = \frac{d}{d\rho} [\rho \varepsilon_{xc}^{LDA}(\rho)] = v_{xc}^{LDA}(\rho) \quad (2.37)$$

que é o potencial de troca-correlação. A partir da LDA a Eq. (2.33) pode ser escrita como

$$E[\rho] = \sum_i \varepsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \rho(\mathbf{r}) [\varepsilon_{xc}^{LDA}(\rho) - v_{xc}^{LDA}(\rho)] d\mathbf{r} \quad (2.38)$$

Os métodos desenvolvidos para a obtenção das soluções das equações de KS, sem incluir parâmetros empíricos, pertencem à categoria dos métodos ditos *ab initio*. É muito comum também expressar a energia de troca-correlação como uma soma de dois termos:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (2.39)$$

assim, os funcionais de troca ($E_x[\rho]$) e de correlação ($E_c[\rho]$) podem ser modelados separadamente. Usualmente, correções de gradiente para a densidade, $\nabla\rho$, também podem ser incluídas, originando os métodos denominados GGAs (*Generalized-Gradient Approximation*). Nesta aproximação alguns funcionais de troca são bastante conhecidos [57], por exemplo, as correções de gradiente de Perdew e Wang (PW86) [58] e de Becke (B88) [59] tornaram-se bastante populares para o cálculo de propriedades eletrônicas de moléculas. Um funcional de correlação também bastante utilizado foi desenvolvido por Lee-Yang-Parr (LYP) [60]. Assim, o método referido como BLYP significa que se utiliza o termo de troca de Becke e o termo de correlação de LYP.

Atualmente, funcionais híbridos (que usam o termo de troca proveniente de outras aproximações, juntamente com o termo de Hartree-Fock) têm sido amplamente empregados no cálculo de propriedades moleculares. Como exemplo, tem-se o funcional B3LYP [61]:

$$E_{xc}^{\text{B3LYP}} = (1 - a_0 - a_x)E_x^{\text{LSDA}} + a_0E_x^{\text{HF}} + a_xE_x^{\text{B88}} + (1 - a_c)E_c^{\text{VWN}} + a_cE_c^{\text{LYP}}. \quad (2.40)$$

Os parâmetros a_0 , a_x e a_c são ajustados de acordo com energias de atomização moleculares experimentais [62] e servem para combinar os termos de troca LDA (de Slater), de HF, de Becke e os termos de correlação de LYP e de Vosko-Wilk-Nussair (VWN) [63]. Outro funcional híbrido de uso corrente na literatura é o B3P86, em que o termo E_c^{LYP} na Eq. (2.40) é substituído por E_c^{P86} [58].

Uma das grandes vantagens dos métodos da DFT é fornecer resultados para os cálculos de estrutura eletrônica mais acurados do que a aproximação HF, porém com um custo computacional equivalente. No caso da DFT, os termos que mais comprometem os atuais algoritmos computacionais do formalismo de KS são as integrais de Coulomb, que escalam quadraticamente com o tamanho do sistema. Neste sentido têm havido grandes esforços para o desenvolvimento de métodos que escalam linearmente [57, 64, 65].

Capítulo 3

Ligações de Hidrogênio

As primeiras evidências da existência de ligações de hidrogênio (LHs) foram documentadas depois dos trabalhos de Werner sobre a complexação de amônia com água em 1902 [66]:

A partir de então, muitos fenômenos químicos eram explicados utilizando-se os conceitos de formação de ligações “secundárias” ou “fracas” envolvendo a interação de um átomo de hidrogênio covalentemente ligado a um átomo de oxigênio ou nitrogênio [67, 68, 69]. Entretanto, somente em 1920, com a divulgação dos trabalhos de Latimer e Rodebush [70], é que o conceito de LH foi de fato estabelecido sob as bases da teoria do octeto de Lewis:

“Um par de elétrons livre em uma molécula de água pode exercer força suficiente sobre um átomo de hidrogênio ligado a uma outra molécula de água, levando a duas moléculas ligadas.... Tal explicação implica dizer que o núcleo de hidrogênio entre dois octetos constitui uma ligação fraca.”

Latimer e Rodebush propuseram modelos de redes quase-cristalinas para a água, i.e., “a água pode ser constituída de agregados moleculares que se quebram e se formam constantemente sob influência da agitação térmica”. Estes modelos foram utilizados para descrever a natureza das LHs como eram entendidas antes do desenvolvimento da mecânica quântica. A aceitação do

conceito de LH veio definitivamente com Pauling em 1931, depois da publicação de um artigo geral sobre a natureza das ligações químicas [4] que deu origem ao seu famoso livro [71]. Uma definição mais ampla para LH foi dada por Pimentel e McClellan em 1960 [72]:

“Uma ligação de hidrogênio existe entre um grupo funcional A—H e um átomo ou um grupo de átomos B, na mesma molécula ou em molécula distinta, quando (a) há evidência da formação de uma ligação (associação ou quelação), (b) há evidência que a nova ligação entre A—H e B envolve especificamente o átomo de hidrogênio já ligado à espécie A.”

Esta última definição generaliza o conceito de ligação de hidrogênio. De fato, recentemente tem se considerado a formação de ligações de hidrogênio não convencionais para uma série de compostos, tais como as ligações de hidrogênio com elétrons π em etileno ou em anéis benzênicos [18], ligações do tipo $C^\alpha-H$ na interação de aminoácidos com água [73] ou ligações do tipo $C-H \cdots O$ em complexos de aldeídos e CO_2 [74].

3.1 Definição de uma LH

Uma ligação de hidrogênio é formada quando um átomo de hidrogênio, H, covalentemente ligado a um átomo A (mais eletronegativo que H), forma uma segunda ligação com outro átomo B (e.g., um sítio doador de elétrons σ ou π), sendo esta ligação representada como $A-H \cdots B$ [75]. Este conceito simplificado de uma LH surge naturalmente das considerações de eletronegatividade de Pauling, porém a sua natureza eletrônica é bastante complexa. No modelo de valência de Coulson, a função de estado Ψ_{LH} de um sistema próton-ligado $A-H \cdots B$ pode ser particionada em cinco contribuições de valência distintas, combinadas linearmente, i.e.,

$$\Psi_{LH} = a\Psi_1 + b\Psi_2 + c\Psi_3 + d\Psi_4 + e\Psi_5, \quad (3.1)$$

em que cada função Ψ_i representa um estado específico do sistema próton-ligado:

De acordo com o modelo de Coulson, as componentes iônicas Ψ_2 e Ψ_4 dão a maior contribuição na maioria das LHs, refletindo o caráter eletrostático predominante envolvido na ligação. Usualmente, emprega-se os termos aceitador e doador para se referir respectivamente aos átomos ou grupos químicos que aceitam ou doam o próton na ligação de hidrogênio. Os doadores típicos incluem os átomos de oxigênio, nitrogênio, enxofre e alguns halogênios. Mas, mesmo os átomos de carbono, silício e fósforo podem funcionar como doadores (Tabela 3.1).

Do ponto de vista químico, os doadores de próton são simplesmente definidos como ácidos, enquanto os átomos ou grupos aceptadores são definidos como bases de Brønsted-Lewis [18]. Como já mencionado anteriormente, os aceptadores mais comuns vão desde átomos eletronegativos com pares de elétrons isolados a elétrons π em ligações insaturadas ou aromáticas. A Tabela 3.1 mostra alguns grupos funcionais doadores e aceptadores de próton comumente observados em ligações de hidrogênio [18].

Tabela 3.1: Alguns grupos funcionais que podem formar LH.

Doadores (A)	Aceptadores (B)
F-H, O-H, N-H	R-O-R (R = H, CH ₃ , etc)
Cl-H	F-C (?), R ₂ C=O
NC-H, CN-H	R ₃ N, -N=R
S-H	S=C<, SR ₂
P-H	>C=C<, anéis benzênicos
>CN-H	R-C≡C-R
C-H	R-X (X = F, Cl)
Si-H (?)	R-N=C

3.2 Energia de ligação

Uma das formas usuais de se medir a intensidade de uma LH é dada em termos da energia de ligação entre as moléculas envolvidas no processo de complexação. Em geral, os valores destas energias são estimados usando-se métodos termoquímicos associados ao equilíbrio

Então, medindo-se a constante de equilíbrio K_{LH} em função da temperatura, a entalpia ΔH° e a entropia ΔS° podem ser obtidas pela equação de Van't Hoff:

$$2,3 \log K_{LH} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{RT}. \quad (3.3)$$

Teoricamente, a energia da ligação $A-H \cdots B$ pode ser calculada como

$$\Delta E = E(A-H \cdots B) - [E(A-H) + E(B)]. \quad (3.4)$$

O cálculo da energia de ligação (Eq. (3.4)) a partir de métodos quânticos com bases finitas contém um erro inerente à superposição de base (BSSE), uma vez que as energias dos monômeros ($A-H$ e B) são usualmente determinadas utilizando-se conjuntos de funções-base menores que a do dímero ($A-H \cdots B$). A correção de BSSE pode ser feita com o método de *counterpoise* [76], i.e., recalculando-se a Eq. (3.4) como

$$\Delta E^{cp} = E(A-H \cdots B)_X - [E(A-H)_X + E(B)_X], \quad (3.5)$$

onde o índice X indica que o cálculo das energias dos monômeros é feito com a base do sistema $A-H \cdots B$. Portanto o erro de superposição de base fica dado por

$$BSSE = \Delta E^{cp} - \Delta E. \quad (3.6)$$

As LHs podem ser classificadas como fracas (2-20 kJ mol⁻¹), moderadas (20-40 kJ mol⁻¹) ou fortes (> 40 kJ mol⁻¹), dependendo da natureza das espécies A e B envolvidas na ligação. Nos casos extremos, quando os doadores e aceitadores são muito eletronegativos a ligação

de hidrogênio possui um caráter covalente, enquanto para espécies fracamente eletronegativas a ligação é preponderantemente eletrostática [5].

Os valores experimentais determinados para a entalpia de reação $A-H + B \rightarrow A-H \cdots B$ variam de aproximadamente -2 kJ mol^{-1} para a LH no sistema tiofenol-benzeno [77] até -155 kJ mol^{-1} para a LH em $(CH_3)_4N^+HF_2^-$ [78]. Entretanto, a maior parte das LHs situam-se em um intervalo de energia de 12 a 40 kJ mol^{-1} [79]. Para efeito de comparação com as LHs, na Tabela 3.2 é mostrado diferentes tipos de ligações químicas que ocorrem na natureza.

Tabela 3.2: Diferentes tipos de energia de ligação.

Tipo	Energia (kJ mol^{-1})	Sistema
van der Waals	$\lesssim 10$	$(CO_2)_n$
LH	12 – 40	$(H_2O)_n$
Covalente	200 – 900	C_{60}
Iônica	200 – 400	$(NaCl)_n$
Metálica	50 – 300	Na_n

3.3 Geometria de equilíbrio

As propriedades estruturais das LHs podem ser obtidas por técnicas de difração de raios-X ou de nêutrons [80, 81]. Os métodos de difração de raios-X são mais acurados para a determinação das distâncias médias entre os átomos pesados A e B envolvidos na LH, mas não detectam os átomos de hidrogênio. Assim, as distâncias de LH são às vezes reportadas na literatura como R_{AB} . A detecção da posição média dos hidrogênios pode ser obtida utilizando-se difração de nêutrons a baixas temperaturas. As principais características destas técnicas foram revisadas recentemente para a estrutura da água [82].

Com relação à geometria de equilíbrio das LHs pode-se distinguir as ligações curtas, cujo comprimento $H \cdots B$ varia entre 1,2 e 1,5 Å ($H \cdots B \approx A-H$) e o ângulo $A-\hat{H} \cdots B$ próximo de 180° . Estas são ligações bastante direcionais com energias superiores a 40 kJ mol^{-1} . Nor-

malmente as LHs são mais longas, com o comprimento $H \cdots B$ variando entre 1,5 e 3,0 Å ($H \cdots B > A-H$) e o ângulo $A-\hat{H} \cdots B$ de aproximadamente $160 \pm 20^\circ$. Neste caso, as LHs são pouco direcionais e possuem energias de ligação inferiores a 20 kJ mol^{-1} . As LHs ainda podem ser classificadas como intra ou intermoleculares, como mostradas na Figura 3.1 a seguir.

As geometrias de equilíbrio de sistemas próton-ligados também podem ser obtidas com boa precisão utilizando-se diferentes métodos quânticos. Isto é feito encontrando-se os mínimos de energia na superfície de potencial do sistema para um dado nível de cálculo, embora haja limitações técnicas para sistemas relativamente grandes. Os parâmetros geométricos assim obtidos variam com o nível de cálculo empregado. Em geral os métodos perturbativos, já em segunda ordem (MP2), fornecem bons parâmetros geométricos de equilíbrio em comparação com resultados experimentais. A Figura 3.1 mostra alguns exemplos típicos de ligações de hidrogênio obtidas por processos de otimização de geometria do sistema molecular.

3.4 Observações espectroscópicas

Uma das características mais marcantes que surge durante o processo de formação da LH é observada no espectro vibracional do sistema próton-ligado. Assim, as técnicas de espectroscopia de infravermelho (IV) são ferramentas bastante eficientes para a identificação dos modos vibracionais das LHs:

Frequência	Modo	Símbolo	Descrição
$3500 \sim 2500 \text{ cm}^{-1}$	$\overleftarrow{A} - \overrightarrow{H} \cdots \overrightarrow{B}$	ν_s	estiramento
$1700 \sim 1000 \text{ cm}^{-1}$	$A-H \uparrow \cdots B$	ν_b	deformação no plano
$900 \sim 300 \text{ cm}^{-1}$	$A-H \otimes \cdots B$	ν_t	deformação fora do plano
$250 \sim 100 \text{ cm}^{-1}$	$\overleftarrow{A} - \overleftarrow{H} \cdots \overrightarrow{B}$	ν_σ	estiramento da LH
$< 200 \text{ cm}^{-1}$	$A-H \cdots B \uparrow \otimes$	ν_β, ν_γ	deformação da LH

As maiores mudanças espectrais que ocorrem no espectro IV quando uma LH é formada são: (i) a diminuição da frequência de estiramento A—H (ν_s); (ii) o aumento da frequência de dobramento A—H (ν_b); e (iii) o aumento na intensidade da banda de absorção ν_s . O deslocamento de ν_s para frequências mais baixas é usualmente considerado como uma característica fundamental das LHs. Este deslocamento espectral resulta do alargamento da curva de energia potencial na direção A...B. Neste caso, os níveis vibracionais do estiramento A—H tornam-se mais próximos [18], permitindo um acoplamento anarmônico entre os modos ν_s e ν_σ [16, 72].

Por sua vez, o alargamento da banda do estiramento A—H também é atribuído a combinações do tipo $\nu_s \pm \nu_\sigma$. Entretanto, o aumento na intensidade da banda de absorção correspondente ao estiramento ν_s deve-se fundamentalmente à variação da polarização na ligação A—H, devido à redistribuição de carga que ocorre durante processo de ligação: $A-H^{\delta+} \cdots \delta^- B-H$. A intensidade da banda aumenta à medida que a força da LH aumenta e pode ser avaliada, a partir de métodos *ab initio*, calculando-se as derivadas do momento de dipolo com respeito às coordenadas nucleares. Na prática utiliza-se uma aproximação linear do dipolo com as coordenadas normais, de modo que as intensidades dos modos vibracionais são proporcionais aos quadrados das derivadas dipolares com respeito aos modos normais de vibração [16].

Os efeitos devidos à formação de LH são também característicos nos sinais de ressonância magnética nuclear (RMN) [83, 84]. O deslocamento químico para campos magnéticos mais altos pode ser observado aumentando-se a temperatura ou diluindo o sistema em um solvente apropriado. Este deslocamento de campo magnético no espectro de RMN é atribuído à quebra das ligações de hidrogênio por aquecimento ou diluição. As razões para um deslocamento químico para campos baixos, com a formação de LH, foram explicadas por Pople et al. [85], considerando a influência relativa de correntes magnéticas anisotrópicas no átomo B e a polarização da ligação A—H pelo átomo B.

Uma outra técnica espectroscópica de grande auxílio na identificação de pequenos aglomerados estabilizados por LHs é a espectroscopia rotacional de micro-ondas em fase gasosa [86]. Este método utiliza frequências de radiação na faixa de 10^9 a 10^{11} Hz e fornece informações sobre constantes rotacionais, distorção centrífuga, quadrupolo nuclear, etc [18]. Assim, parâmetros geométricos, constantes de força, momentos dipolares e outras grandezas de interesse podem ser obtidas indiretamente a partir dos espectros rotacionais.

Figura 3.1: Alguns exemplos típicos de LHs: (a) estrutura tetraédrica de H_2O , (b) ligação intramolecular em 7-hidróxi-1-naftilamina, (c) dímero de ácido acético, (d) cadeia em ziguezague de HF, (e) modelo de Watson-Crick do sistema guanina-citosina e (f) ligação intramolecular na molécula de ácido salicílico.

Capítulo 4

Estruturas Moleculares de Aglomerados e Líquidos

Os modelos mais apropriados para descrever as propriedades de agregados, sólidos ou líquidos consideram um sistema constituído de N átomos ou moléculas individuais interagentes. Naturalmente, os tipos de interações que mantêm esses sistemas estáveis são provenientes das forças eletrostáticas mútuas entre núcleos e elétrons. Nesta descrição atomística, as estruturas de agregados e líquidos moleculares são denominadas de estruturas supermoleculares. E, portanto, com este modelo as propriedades eletrônicas do sistema podem ser obtidas resolvendo-se a equação de Schrödinger (2.1). Esta metodologia é conhecida como aproximação supermolecular.

4.1 Aglomerados

Aglomerados ou agregados moleculares são sistemas ligados contendo entre 2 e $\sim 10^9$ moléculas. No laboratório os aglomerados são gerados por expansões supersônicas de um gás em câmara de vácuo [87]. O gás é expandido isentropicamente e mantido a baixíssimas condições de pressão e temperatura. Assim, as energias translacionais dos aglomerados atingem poucos eV e

as interações químicas tornam-se praticamente livres de condições termodinâmicas. Isto significa que a aproximação supermolecular, sem inclusão de temperatura, é suficientemente precisa para uma descrição quantitativa das propriedades de agregados.

4.1.1 Efeitos cooperativos

Muitos fenômenos físico-químicos interessantes estão associados à formação de aglomerados moleculares. No caso específico de agregados estabilizado por ligações de hidrogênio, suas propriedades podem ser compreendidas levando-se em conta as perturbações estruturais e eletrônicas envolvidas no processo de complexação molecular. Por exemplo, considerando a dimerização entre duas espécies A-H e B-H, é possível prever que a capacidade do dímero A-H...B-H interagir com uma outra espécie C-H será alterada após a formação da primeira LH [88].

Após a formação do dímero ocorre uma pequena transferência de carga eletrônica do tipo $A-H^{\delta+} \leftarrow \delta^- B-H$, o que torna o par B-H um melhor doador de próton, comparado ao seu estado isolado. Desta forma, a interação total em um trímero do tipo A-H...B-H...C-H é mais forte do que no dímero B-H...C-H. Por razões semelhantes, o par A-H em A-H...B-H torna-se um melhor aceitador de próton em relação à espécie isolada A-H. Este fenômeno reflete a natureza cooperativa das ligações de hidrogênio [16].

Entretanto, nem sempre a formação de LHs múltiplas leva a efeitos cooperativos "no sentido positivo". Ainda considerando o exemplo anterior, quando a densidade eletrônica δ^- é transferida a partir de B-H também torna este par um aceitador de próton mais fraco, de modo que a energia de interação no sistema

é menor do que as energias de interação nos dímeros $A-H \cdots B-H$ ou $C-H \cdots B-H$ isolados. Este efeito é designado na literatura como “cooperatividade negativa” ou anticooperatividade.

Uma maneira de estimar a energia cooperativa de um sistema ABC, por exemplo, é considerando um conjunto de reações de formação:

Neste esquema a energia de interação total é calculada somando-se as reações $R1$ com $R2$ ou $R3$ com $R4$:

$$\Delta E = (\Delta E_{AB} + \Delta E_{AB+C}) = (\Delta E_{BC} + \Delta E_{A+BC}), \quad (4.1)$$

enquanto o termo cooperativo é obtido subtraindo-se as reações $R3$ de $R2$ ou $R1$ de $R4$:

$$\Delta E_{coop} = (\Delta E_{AB+C} - \Delta E_{BC}) = (\Delta E_{A+BC} - \Delta E_{AB}). \quad (4.2)$$

Note-se que ΔE_{coop} leva em conta a relaxação da geometria de cada espécie: monômero, dímero e trímero. Também é possível avaliar a interação de três corpos na formação do trímero ABC calculando-se o termo

$$\Delta E_{ABC} = \Delta E - (\Delta E_{AB} + \Delta E_{AC} + \Delta E_{BC}), \quad (4.3)$$

com todas as interações de pares computadas na geometria do trímero. Aqui é importante salientar que para o cálculo das energias (4.1), (4.2) e (4.3), o erro de superposição de base, Eq. (3.6), é importante e, portanto, também deve ser levados em consideração. Os efeitos de BSSE tornam-se mais evidentes quando se utiliza um conjunto de funções-base pequeno, principalmente para sistemas estendidos.

4.1.2 Interação de muitos corpos

Além das orientações relativas das moléculas interagentes em aglomerados, os efeitos de muitos corpos, que aparecem quando grupos de três ou mais moléculas se juntam, também podem influenciar nas propriedades do sistema. Em primeira aproximação, a energia de interação total de um agregado molecular pode ser considerada como uma soma de interações de pares ou aditiva:

$$\Delta E = \sum_{i=1}^{N-1} \sum_{j>i}^N \Delta E_{ij} \quad (4.4)$$

Assim, os efeitos não-aditivos provenientes das interações de muitos corpos podem ser classificados como cooperativos, se $\Delta E < \sum_{ij} \Delta E_{ij}$, ou anti-cooperativos, se $\Delta E > \sum_{ij} \Delta E_{ij}$, para $\Delta E_{ij} < 0$ [22, 23]. Entretanto, em um nível de cálculo mais acurado, a interação envolvendo mais do que duas moléculas deve ser perturbada pela presença das moléculas vizinhas e, portanto, a energia de interação total do conjunto não é exatamente uma grandeza aditiva. Neste caso, a Eq. (4.4) deve ser expressa em função das interações de múltiplos corpos [17]:

$$\Delta E = \sum_{i=1}^{N-1} \sum_{j>i}^N \Delta E_{ij} + \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^N \Delta E_{ijk} + \dots \quad (4.5)$$

4.2 Líquidos

Diferentemente de um agregado, a dificuldade em modelar um líquido deve-se ao grande número de moléculas e aos efeitos térmicos aos quais o sistema está submetido. Portanto, um modelo simples para descrever o líquido molecular requer várias estruturas distintas e uma lei de interação entre seus constituintes. Neste sentido, é a mecânica estatística que fornece o modelo mais apropriado para o tratamento de um líquido. Assim, um sistema contendo N moléculas interagentes ocupando um volume V pode ser descrito classicamente:

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N). \quad (4.6)$$

No hamiltoniano (4.6), $U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ é a energia potencial de interação efetiva atuando entre todas as moléculas do sistema. As propriedades do líquido, quando em equilíbrio térmico, podem ser derivadas a partir da função de partição canônica

$$e^{-\beta F} = \frac{1}{N!} \left(\frac{m}{2\pi\hbar^2\beta} \right)^{\frac{3N}{2}} Q_N, \quad (4.7)$$

sendo β uma função da temperatura do sistema, i.e., $\beta = 1/k_B T$ e Q_N a integral configuracional

$$Q_N = \int e^{-\beta U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)} d\mathbf{R}_1 d\mathbf{R}_2 \dots d\mathbf{R}_N. \quad (4.8)$$

4.2.1 Interação intermolecular

Como primeira aproximação é possível assumir que a energia potencial em (4.6) pode ser escrita como uma soma de interações de pares:

$$U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = \sum_{i,j} U(R_{ij}), \quad (4.9)$$

embora a suposição de um potencial de força central $U(R_{ij})$ não seja justificada exatamente, uma vez que existe também um caráter orientacional nas interações intermoleculares [89]. Assim, um fator importante nas interações intermoleculares do líquido advém dos efeitos de muitos corpos. Analogamente ao caso das interações em aglomerados, a forma usual de recuperar as propriedades que dependem das interações não-aditivas considera a expansão [90]

$$U(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = \sum_{i=1} \sum_{j=i+1} U_{ij}(R_{ij}) + \sum_{i=1} \sum_{j=i+1} \sum_{k=j+1} U_{ijk}(R_{ij}, R_{ik}) + \dots \quad (4.10)$$

A estrutura do líquido pode ser caracterizada utilizando-se a função de distribuição radial de pares, definida como:

$$n_2(\mathbf{R}_1, \mathbf{R}_2) = \frac{N(N-1)}{Q_N} \int \exp[-\beta \sum_{i,j} U(R_{ij})] d\mathbf{R}_3 \dots d\mathbf{R}_N. \quad (4.11)$$

Para o líquido, $n_2(\mathbf{R}_1, \mathbf{R}_2)$ pode ser uma função apenas da distância entre os centros de massa de duas moléculas, ou quaisquer outros sítios de interesse, sendo denotada como

Figura 4.1: Forma típica da função de distribuição radial de pares para um líquido.

$n_2(\mathbf{R}_1, \mathbf{R}_2) = G(R)$. A partir da integração da $G(R)$ pode-se obter o número de moléculas contidas nas camadas de solvatação (a e b na Figura 4.1) de uma molécula de soluto.

A interação efetiva entre as moléculas de um líquido pode ser completamente parametrizada e, na aproximação de interação de pares, um dos modelos de potenciais que melhor descreve as propriedades do líquido é uma soma do potencial de Lennard-Jones com o potencial de Coulomb [91], definido por um conjunto de apenas três parâmetros $(\varepsilon_i, \sigma_i, q_i)$ em cada sítio nas moléculas A e B, i.e.,

$$U_{AB}(R_{ij}) = \sum_i^{\text{em A}} \sum_j^{\text{em B}} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] + \frac{q_i q_j}{R_{ij}} \right\}. \quad (4.12)$$

A regra de combinação geométrica para os parâmetros de Lennard-Jones pode ser escolhida como $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ e $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ ou $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ [92]. O potencial de Lennard-Jones possui um termo de longo alcance $1/R^6$, que descreve as interações intermoleculares atrativas, e um termo repulsivo $1/R^{12}$ para distâncias menores que σ , enquanto o potencial de Coulomb é responsável pelas interações entre os momentos de multipolos permanentes das moléculas.

Os graus de liberdade moleculares internos também podem ser tratados classicamente,

i.e., descritos por um potencial de interação intramolecular adicional, da forma

$$U_{\text{intra}}(r, \theta, \tau) = \sum_{\text{lig.}} \frac{k_r}{2} (r - r_{eq})^2 + \sum_{\text{ang.}} \frac{k_\theta}{2} (\theta - \theta_{eq})^2 + \sum_{\text{died.}} \frac{k_\tau}{2} [1 + \cos[m(\tau - \tau_0)]], \quad (4.13)$$

para o qual os dois primeiros termos descrevem os estiramentos e deformações angulares, na aproximação harmônica, enquanto o terceiro termo descreve as rotações internas.

4.2.2 Simulação Monte Carlo

As possíveis estruturas ou configurações do líquido podem ser obtidas utilizando-se o método Monte Carlo (MC) [93]. Na simulação MC o sistema é representado por N moléculas que interagem via o potencial efetivo (4.12) e as configurações $\{\Gamma_i(\mathbf{R})\}$ são geradas aleatoriamente, de acordo com a distribuição de probabilidade de Gibbs para uma dada temperatura T . A evolução da simulação (em passos MC) ocorre quando todas as N moléculas do sistema são visitadas. Então o movimento molecular é caracterizado por um conjunto de números gerados aleatoriamente. Estes números definem um movimento molecular aleatório composto por uma translação de $\delta r = (\delta x, \delta y, \delta z)$ e uma rotação de $\delta \Theta$ em torno de um eixo sorteado.

As regras de aceitação ou rejeição da nova configuração podem ser dadas de acordo com a amostragem de Metropolis [94], baseada na variação de energia entre as configurações. Para um ensemble canônico (NVT) as propriedades médias do sistema são calculadas como

$$\langle A \rangle_{NVT} = \frac{1}{M} \sum_{i=1}^M A(\mathbf{R}_i) P(\mathbf{R}_i), \quad (4.14)$$

onde $P(\mathbf{R}_k) = \exp[-\beta U(\mathbf{R}_k)]$ são os fatores de Boltzmann. No esquema de Metropolis, a Eq. (4.14) é calculada somente com as configurações $\mathbf{R}'_k$ geradas de acordo com estes fatores:

$$\langle A \rangle_{NVT} = \frac{1}{M} \sum_{k=1}^M A(\mathbf{R}'_k), \quad (4.15)$$

sendo M o número total de configurações.

Desta forma gera-se uma cadeia markoviana [95] de configurações para o líquido, tendo uma distribuição limite $e^{-\beta U_i}$. Portanto, se o sistema se move no espaço configuracional de Γ_i para Γ_j e $U_j \leq U_i$, então o movimento é aceito. Se $U_j \geq U_i$, a razão $\pi_{ij} = e^{-\beta U_j} / e^{-\beta U_i}$ é avaliada e comparada a um número aleatório x entre 0 e 1 e, se $\pi_{ij} \geq x$, o movimento também é aceito. Em outro caso a configuração Γ_j é rejeitada e um novo sorteio é realizado, partindo-se da configuração Γ_i . As cadeias de configurações obtidas desta maneira permitem que a média configuracional seja avaliada a partir da Eq. (4.15), obtendo-se, assim, as propriedades termodinâmicas do líquido.

Para o cálculo *a posteriori* das propriedades estruturais e eletrônicas, somente configurações estatisticamente descorrelacionadas fornecerão informações importantes [96]. Estas configurações reduzem consideravelmente a quantidade de estruturas supermoleculares que definem o líquido e, conseqüentemente, a quantidade de cálculos quânticos necessários para a obtenção de suas propriedades eletrônicas. Uma forma eficiente de otimizar a estatística configuracional do sistema baseia-se no cálculo da função de autocorrelação [97]. Para um processo markoviano esta função apresenta um decaimento exponencial:

$$C(\tau) = \sum c_i e^{-s/\tau_i}, \quad \tau = \int_0^\infty C(s) ds, \quad (4.16)$$

onde s é o intervalo de configurações Monte Carlo e τ é definido como o passo de correlação. A estatística configuracional para um líquido é considerada suficientemente boa quando $s > 3\tau$.

Assim, utilizando-se uma metodologia seqüencial de simulações Monte Carlo e cálculos de mecânica quântica [97, 98], é possível caracterizar os efeitos do solvente explicitamente em moléculas solvatados ou as propriedades eletrônicas de líquidos. Neste caso, as propriedades estruturais e eletrônicas do sistema são obtidas como médias configuracionais sobre dezenas ou centenas de estruturas supermoleculares que representam o líquido.

Capítulo 5

Aplicações e Resultados

As aplicações apresentadas neste capítulo baseiam-se nas publicações reproduzidas integralmente no Apêndice B. Nas seções subsequentes discutimos brevemente alguns resultados mais gerais sobre os efeitos das ligações de hidrogênio (LHs) em aglomerados e líquidos moleculares. Outros resultados complementares são discutidos nos Artigos B1 a B7, que abordam tanto os aspectos metodológicos quanto os aspectos fenomenológicos envolvendo sistemas próton-ligados. Estes artigos são uma parte essencial da tese e estão agrupados em ordem cronológica de seus desenvolvimentos.

No Artigo B1 apresentamos um estudo *ab initio* sobre dois isômeros intermoleculares obtidos como espécies estáveis: $\text{H}_2\text{O} \cdots \text{HCN}$ e $\text{HCN} \cdots \text{H}_2\text{O}$. Neste estudo as propriedades estruturais, energéticas e espectroscópicas são analisadas em função da formação de LHs intermoleculares. Outro estudo teórico complementar é tratado no Artigo B2, no qual discutimos os efeitos cooperativos em propriedades de agregados moleculares mistos de H_2O e HCN contendo mais do que dois monômeros em suas estruturas. A estabilidade desses possíveis aglomerados devido à formação de LHs dos tipos $\text{C}-\text{H} \cdots \text{O}$ e $\text{O}-\text{H} \cdots \text{N}$ também é analisada quantitativamente, dentro dos esquemas quânticos MBPT/CC e DFT/B3LYP.

No Artigo B3 métodos perturbativos e diferentes funcionais da densidade são utilizados para investigar a estabilidade de heterodímeros formados entre pequenas moléculas orgânicas e água. Estruturas, frequências vibracionais e dipolos elétricos também são investigadas à luz das LHs estabelecidas entre as moléculas. Um estudo metodológico, envolvendo diferentes funcionais da densidade, teoria de perturbação e interação de configurações, é feito no Artigo B4. Neste caso, os métodos são aplicados para calcular algumas propriedades de moléculas simples, com interesse, principalmente, em astrofísica, exigindo-se uma acurácia de $\pm 1\%$ dos valores experimentais das constantes rotacionais e $\pm 3\%$ para os momentos dipolares elétricos.

Os efeitos estatísticos de solventes próticos na estabilização de conformeros moleculares devido à formação de LHs são considerados no Artigo B5. Neste estudo fazemos uma análise conformacional da molécula de furfural em dois solventes próticos distintos (clorofórmio e água). Os efeitos estruturais do meio são levados em conta via simulações Monte Carlo em diferentes *ensembles*. Adicionalmente, discutimos a influência das LHs no espectro de absorção UV-vis de furfural em água, utilizando cálculos quânticos semi-empíricos INDO/CIS [99].

Estudamos também os efeitos de muitos corpos em cadeias lineares de HCN próton-ligadas no Artigo B6. Neste trabalho calculamos os termos de interação de dois até cinco corpos na energia de ligação de vários oligômeros de HCN. Além disso, quantificamos também os efeitos cooperativos na energia de ligação e nos dipolos elétricos em função do tamanho da cadeia. Finalmente, no Artigo B7, apresentamos um estudo *ab initio* sobre o uso de espalhamento Rayleigh como uma possível ferramenta auxiliar na identificação de aglomerados moleculares. Os graus de despolarização da luz são obtidos a partir das polarizabilidades elétricas, calculadas no nível MP2/aug-cc-pVDZ, usando o método de campo finito, para diferentes heterodímeros próton-ligados com água.

5.1 Isômeros intermoleculares próton-ligados

5.1.1 Introdução

A influência das LHs na estabilização de agregados moleculares é notável desde sistemas biológicos a sistemas interestelares (Artigo B1). Assim, os complexos moleculares formados entre HCN e H_2O são de grande importância para o estudo da formação de moléculas biológicas complexas em ambientes extraterrestres, principalmente devido à existência de moléculas de HCN aprisionadas nos cristais de gelo formados em caudas de cometas [100]. Duas possíveis formas de heterodímeros, envolvendo HCN e H_2O , são ilustradas na Figura 5.1.

Figura 5.1: Isômeros do sistema HCN- H_2O : (a) $\text{H}_2\text{O}\cdots\text{HCN}$ e (b) $\text{HCN}\cdots\text{H}_2\text{O}$.

No isômero $\text{H}_2\text{O}\cdots\text{HCN}$ (Figura 5.1 (a)) a molécula de HCN atua como doador e a molécula de H_2O atua como aceitador de próton, enquanto no isômero $\text{HCN}\cdots\text{H}_2\text{O}$ (Figura 5.1 (b)) essas moléculas exercem papéis contrários, i.e., H_2O atua como doador e HCN age como aceitador de próton. Apenas a primeira espécie tinha sido detectada por espectroscopia de micro-ondas, entretanto, recentemente, o segundo isômero foi detectado em matriz de argônio a baixas temperaturas [103]. Como ilustrado na Figura 5.2, no isômero (a) existe um ângulo fora do plano de ligação, $\delta(\text{H}_2\text{O}\cdots\text{H})$, que é determinado experimentalmente como sendo da ordem de 20° (Ref. [15] do Artigo B1). Nosso resultado calculado com o método MP2 e base atômica 6-311++G(d,p) dá um valor de 23° , estando em excelente concordância com o dado experimental.

Figura 5.2: Ângulo $\delta(\text{H}_2\text{O}\cdots\text{H})$ fora do plano da LH no isômero $\text{H}_2\text{O}\cdots\text{HCN}$.

A análise geométrica completa para essas duas espécies é feita no Artigo B1 em anexo. Aqui, vale mencionar que os comprimentos das LHs ($\text{O}\cdots\text{H}$ e $\text{N}\cdots\text{H}$), calculados com o método MP2/6-311++G(d,p), são respectivamente 2,068 e 2,169 Å, ou seja, o comprimento da LH no isômero (a) é 0,1 Å menor do que no isômero (b). O funcional B3LYP fornece valores de 2,028 Å para a distância $\text{O}\cdots\text{H}$ e 2,140 Å para a distância $\text{N}\cdots\text{H}$, com o mesmo conjunto de funções-base, o que está em bom acordo com o resultado MP2. Por outro lado, o ângulo $\delta(\text{H}_2\text{O}\cdots\text{H})$ calculado com B3LYP/6-311++G(d,p) é de aproximadamente 3°. Analisamos estes aspectos estruturais também no Artigo B2 para outros sistemas correlatos de $\text{HCN-H}_2\text{O}$.

5.1.2 Estabilidade relativa dos isômeros

A Tabela 5.1 fornece as energias de ligação para os dois isômeros intermoleculares calculadas com diferentes níveis de aproximação, incluindo métodos perturbativos e *coupled-cluster* contendo correções perturbativas para excitações triplas em CCSD(T). No melhor nível de cálculo considerado aqui, CCSD(T)/aug-cc-pVDZ (geometria otimizada com MP2/6-311++G(d,p)), o isômero (a) é mais ligado que o isômero (b) por 1,1 kcal mol⁻¹, embora ambos sejam obtidos como sistemas estáveis. As diferenças em energia vibracional de ponto zero (ZPE) para a formação dos isômeros (Figura 5.1) são respectivamente 1,59 e 1,24 kcal mol⁻¹, obtidas com MP2/6-311++G(d,p). Os valores da Tabela 5.1 não incluem as correções de ZPE.

Tabela 5.1: Comparação entre as energias de ligação (em kcal mol⁻¹) para os dois isômeros de HCN-H₂O. Todos os valores incluem correção de BSSE.

Método ^a	H ₂ O...HCN			HCN...H ₂ O		
	Base1 ^b	Base2 ^c	Base3 ^d	Base1	Base2	Base3
MP2	5,37	4,70	4,61	3,61	3,54	3,64
MP4	5,19	4,56	4,54	3,43	3,39	3,52
CCD	5,18	4,57	4,46	3,27	3,22	3,29
CCSD(T)	5,18	4,58	4,55	3,36	3,33	3,45

^a Geometrias otimizadas com o método MP2/6-311++G(d,p);

^b 6-311++G(d); ^c 6-311++G(d,p); ^d aug-cc-pVDZ.

5.1.3 Deslocamento das frequências vibracionais

Os deslocamentos vibracionais médios, $\langle \Delta\nu \rangle$, apresentados na Tabela 5.2, correspondem às diferenças das frequências vibracionais do dímero HCN...H₂O em relação às espécies isoladas. A notação utilizada para descrever os modos normais de vibração do complexo está de acordo com as observações espectroscópicas de IV apresentadas no Capítulo 3. Os $\langle \Delta\nu \rangle$ calculados são expressos como valores médios entre os resultados obtidos com os métodos B3LYP e MP2/6-311++G(d,p). A concordância entre os valores de $\langle \Delta\nu \rangle$ e os deslocamentos experimentais [103] mostram que a capacidade preditiva destes métodos teóricos é muito boa, o que os torna ferramentas bastante confiáveis para a caracterização de espécies ainda não detectadas.

Tabela 5.2: Frequências vibracionais intramoleculares calculadas e experimentais.

Modos	Monômeros isolados			HCN...H ₂ O			$\langle \Delta\nu \rangle$	$\Delta\nu^c$
	B3LYP ^a	MP2 ^a	Exp. ^b	B3LYP ^a	MP2 ^a	Exp. ^c		
$\nu_t(\pi)_{\text{HCN}}$	767	729	712	774	736	727	+7	+7
$\nu_t(\pi)_{\text{HCN}}$	767	729	712	775	738	728	+9	+8
$\nu_b(a_1)_{\text{HOH}}$	1602	1628	1590	1624	1654	1629	+24	+38
$\nu_s(\sigma)_{\text{CN}}$	2197	2016	2097	2209	2031	2109	+14	+16
$\nu_s(\sigma)_{\text{CH}}$	3452	3482	3311	3452	3481	3298	-1	-6
$\nu_s(a_1)_{\text{OH}}$	3817	3884	3638	3770	3851	3594	-40	-44
$\nu_s(b_2)_{\text{OH}}$	3922	4003	3733	3899	3979	3713	-24	-23

^a Base atômica utilizada: 6-311++G(d,p);

^b Refs. [29] e [30] do Artigo B1; ^c Ref. [103].

Como esperado, os nossos resultados corroboram as expectativas de que as frequências de estiramento, ν_s , diminuem e que as frequências de dobramento, ν_b , aumentam em sistemas estabilizados por LHs. É importante observar que os deslocamentos médios das frequências calculadas aqui são ligeiramente diferentes daqueles apresentados no Artigo B1, uma vez que aqui não consideramos os valores obtidos com o método MP2/aug-cc-pVDZ. Estes deslocamentos das frequências de estiramento para o vermelho e das frequências de dobramento para o azul dão indícios de formação de ligação de hidrogênio no complexo molecular. E como discutido no Capítulo 3, estas variações nas frequências vibracionais são bastante eficientes para caracterização e identificação de espécies isoméricas próton-ligadas.

5.1.4 Sumário

Nesta seção discutimos os principais resultados publicados no Artigo B1. Aqui mostramos que a utilização de métodos MBPT/CC e DFT é de grande valia para a caracterização de aglomerados moleculares. Em particular, investigamos as propriedades estruturais, energéticas e espectroscópicas de dois isômeros intermoleculares; $\text{H}_2\text{O} \cdots \text{HCN}$ e $\text{HCN} \cdots \text{H}_2\text{O}$. As questões relacionadas à formação de LH em heterodímeros têm sido uma preocupação frequente tanto para os teóricos quanto para os experimentais. Por exemplo, a interação entre HCN, ou moléculas orgânicas pequenas, com água vem sendo investigada utilizando-se diferentes metodologias. Nos Artigos B2, B3 e B7 continuaremos a tratar deste tema para outros sistemas moleculares de interesse, investigados com diferentes níveis de teoria.

Uma maneira usual de fazer a caracterização teórica de aglomerados moleculares é confrontando-se o espectro vibracional calculado com o espectro determinado experimentalmente. No caso de $\text{HCN} \cdots \text{H}_2\text{O}$ (isômero menos estável que $\text{H}_2\text{O} \cdots \text{HCN}$) comparamos as frequências vibracionais harmônicas com os espectros no infravermelho de HCN e H_2O isolados e

com o espectro infravermelho do próprio dímero em matriz de argônio [103]. Apesar dos valores absolutos das frequências de estiramento (ν_s) diferirem em mais de 100 cm^{-1} com relação aos resultados experimentais, nossos resultados para os deslocamentos vibracionais médios, apresentados na Tabela 5.2, estão em excelente acordo com os resultados experimentais. Aqui, também não consideramos os possíveis efeitos anarmônicos que podem chegar a 150 cm^{-1} para o modo de estiramento OH em aglomerados de água [101, 102], por exemplo.

5.2 Efeitos cooperativos em agregados mistos de H_2O e HCN

5.2.1 Introdução

A formação de LH em aglomerados moleculares modifica a geometria interna de cada monômero envolvido no processo de ligação. Conseqüentemente, a deformação das posições nucleares provoca uma redistribuição de carga na estrutura eletrônica de cada subunidade do sistema [16]. Como discutido no Capítulo 4, este efeito decorre basicamente devido à mudança de polarização do sistema e pode ser observado indiretamente em experimentos espectroscópicos, ou diretamente, via cálculos *ab initio*. À medida que mais moléculas vão se agregando, a mudança nos efeitos estruturais e eletrônicos do aglomerado tornam-se mais significativos. Então, muitas propriedades moleculares perdem o caráter aditivo. A seguir apresentamos brevemente alguns aspectos interessantes decorrentes dos efeitos cooperativos nas propriedades dos aglomerados mostrados na Figura 5.3.

5.2.2 $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$

Nesta subseção apresentamos os resultados dos efeitos cooperativos nas propriedades do trímero misto $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ (Figura 5.3 (a)). Mostramos também a influência de correlação eletrônica em diferentes ordens nos termos de energia cooperativa e de três corpos

Figura 5.3: Estruturas de possíveis agregados mistos de HCN-H₂O: (a) H₂O...HCN...H₂O e (b) H₂O...HCN...HCN...H₂O (b).

deste agregado. Para o cálculo da cooperatividade, consideramos a formação do trímero em dois caminhos distintos:

A energia de interação total independe do caminho escolhido (*I* ou *II*). Na Tabela 5.3 apresentamos as diferentes energias de complexação envolvidas na formação do agregado próton-ligado H₂O...HCN...H₂O.

Todos os valores das energias dadas na Tabela 5.3 são corrigidos para BSSE com o método de *counterpoise* [76]. Os diferentes termos da energia de complexação do trímero são obtidos de acordo com o esquema discutido na Seção 4.1. Por exemplo, a energia de interação total é calculada utilizando-se a Eq. (4.1), o termo cooperativo é obtido a partir da Eq. (4.2) e o

Tabela 5.3: Termos da energia de complexação (em kJ mol^{-1}) do trímero.

Interação	SCF	MP2	MP4	CCD	CCSDT	B3LYP
ΔE_{I-A}	-21,17	-19,48	-18,84	-18,84	-18,93	-21,80
ΔE_{I-B}	-15,32	-17,98	-17,36	-16,61	-17,11	-21,61
ΔE_{II-A}	-11,70	-14,59	-13,97	-13,21	-13,71	-14,61
ΔE_{II-B}	-24,79	-22,86	-22,23	-22,25	-22,33	-28,80
Total	-36,49	-37,45	-36,20	-35,45	-36,04	-43,41
Cooperativa	-3,62	-3,39	-3,39	-3,40	-3,41	-6,99
3 corpos	-2,42	-2,27	-2,31	-2,31	-2,32	-5,91

Cálculos feitos com a base atômica 6-311++G(d,p).

termo de três corpos com a Eq. (4.3). As variações de energia (I e II) têm o seguinte significado físico: quanto mais negativas, mais favoravelmente o processo pode ocorrer. Assim, a molécula de água ligando-se como aceitador de próton a HCN ($I - A$) libera cerca de 5 kJ mol^{-1} a mais do que como doador de próton ($II - A$), calculado com MP2 ou MP4.

A contribuição de três corpos é relativamente pequena, i.e., menor do que $2,5 \text{ kJ mol}^{-1}$ para todos os métodos MBPT/CC apresentados na Tabela 5.3, exceto no caso do método DFT/B3LYP. No caso dos métodos perturbativos esta contribuição corresponde a cerca de 6% da interação total; sendo o dobro com o funcional B3LYP. Como pode ser visto também na Tabela 5.3, os efeitos de correlação eletrônica são pouco relevantes para os termos de três corpos ou cooperativo. De fato, estas componentes energéticas são dominadas por interações eletrostáticas e, portanto, são bem descritas já no nível HF/SCF.

5.2.3 $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$

A estrutura do tetrâmero (Figura 5.3 (b)) é obtida a partir da complexação $\text{N} \cdots \text{H}$ entre os dois dímeros $\text{H}_2\text{O} \cdots \text{HCN}$ e $\text{HCN} \cdots \text{H}_2\text{O}$ (Figura 5.1). A geometria de equilíbrio do tetrâmero foi totalmente otimizada em dois níveis distintos de cálculo: MP2/6-311++G(d,p) e B3LYP/6-311++G(d,p). Todos os parâmetros geométricos, inter e intramoleculares, são dados no Artigo B2 para estes dois níveis de teoria. Os comprimentos das LHs, com relação às moléculas de

água terminais ($\text{O} \cdots \text{H}$ e $\text{N} \cdots \text{H}$), são calculadas, respectivamente, como sendo 2,015 e 2,140 Å (com MP2), e 2,093 e 1,969 Å (com B3LYP). Estes parâmetros são menores do que no caso dos dímeros isolados, refletindo, portanto, um efeito cooperativo nas distâncias intermoleculares.

A estabilidade relativa de $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$ com respeito aos dois heterodímeros de $\text{HCN-H}_2\text{O}$ é apresentada na Tabela 5.4. Os efeitos de correlação eletrônica na energia de ligação do tetrâmero são discutidos detalhadamente no Artigo B2. Aqui, como já apontamos nos casos dos dímeros e trímero, podemos afirmar que tais efeitos são desprezíveis para as energias de ligação do tetrâmero. É interessante também observar que o método DFT/B3LYP, além de fornecer parâmetros geométricos intermoleculares menores do que os obtidos com a aproximação MP2, parece superestimar a energia de ligação do sistema. Este resultado também pode ser visto na Tabela 5.4. Como mostraremos a seguir, uma conclusão similar também é obtida no Artigo B3, inclusive para outros tipos de funcionais da densidade.

Tabela 5.4: Influência de correlação eletrônica na energia de ligação do tetrâmero com respeito aos dois dímeros de $\text{HCN-H}_2\text{O}$ e $(\text{HCN})_2$. Valores calculados em kJ mol^{-1} com a base 6-311++G(d,p) e corrigidos para BSSE.

Método	$-\Delta E_1$	$-\Delta E_{(\text{HCN})_2}$	$-\Delta E_2$	$-\Delta E_{12}$
MP2	19,67	17,72	14,80	26,08
MP4	19,70	17,15	14,17	25,46
CCSD	19,10	16,62	13,46	24,89
CCSD(T)	19,16	16,81	13,96	25,12
B3LYP	22,27	17,96	15,13	27,73
Conversão: $1 \text{ kcal mol}^{-1} = 4,18 \text{ kJ mol}^{-1}$.				

Na Tabela 5.4, $-\Delta E_1$ corresponde à energia de ligação de $\text{H}_2\text{O} \cdots \text{HCN}$, $-\Delta E_{(\text{HCN})_2}$ é a energia de ligação do dímero $(\text{HCN})_2$, $-\Delta E_2$ corresponde à energia de ligação de $\text{HCN} \cdots \text{H}_2\text{O}$ e $-\Delta E_{12}$ é a energia de ligação do tetrâmero $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$ com respeito aos dois dímeros mistos de $\text{HCN-H}_2\text{O}$. Estes resultados mostram que a interação $\text{N} \cdots \text{H}$ é aumentada por, pelo menos, $8,3 \text{ kJ mol}^{-1}$ com teoria de perturbação e $9,8 \text{ kJ mol}^{-1}$ com o funcional B3LYP, em relação ao dímero de HCN isolado.

5.2.4 Sumário

Nesta seção apresentamos um estudo complementar à Seção 5.1, incluindo uma análise da influência das LHs para aglomerados contendo mais do que dois monômeros em suas estruturas. Nossos resultados mostram diversas nuances dos efeitos cooperativos nas propriedades dos complexos. De modo geral, o método DFT/B3LYP superestima os valores das energias de ligação e não descreve bem os ângulos fora do plano de ligação, $\delta(\text{H}_2\text{O}\cdots\text{H})$, obtidos experimentalmente como sendo da ordem de 20° para o isômero $\text{H}_2\text{O}\cdots\text{HCN}$. O funcional B3LYP fornece $3,2^\circ$ para o dímero (Figura 5.1 (a)), $7,8^\circ$ para o trímero (Figura 5.3 (a)) e somente $0,5^\circ$ para o tetrâmero (Figura 5.3 (b)). Utilizando o método MP2 com a mesma base atômica, 6-311++G(d,p), os valores calculados para os dímero, trímero e tetrâmero são, respectivamente, 23 , 24 e 21° . Este é um exemplo em que o funcional B3LYP falha para a determinação de estruturas moleculares precisas. Entretanto, como discutiremos mais adiante, este funcional fornece propriedades espectroscópicas bastante acuradas para pequenas moléculas (Artigo B4).

Além das geometrias e energias de ligação, calculamos também as frequências vibracionais dos sistemas $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ e $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. A discussão dos resultados para os deslocamentos espectrais é feita minuciosamente no Artigo B2. Nestes dois casos a interpretação dos deslocamentos vibracionais não é tão simples quanto no caso do dímero $\text{HCN}\cdots\text{H}_2\text{O}$ (cf. Tabela 5.2). No caso do trímero, embora os deslocamentos de $\nu_s(\sigma)_{\text{CN}}$ sejam pequenos, ainda podemos verificar que $\nu_s(\sigma)_{\text{CH}} = -126 \text{ cm}^{-1}$ (MP2) e -155 cm^{-1} (B3LYP), como esperado para sistemas próton-ligados. No caso do tetrâmero cada modo vibracional é duplicado, devido à presença de duas moléculas de água e duas de HCN na estrutura do aglomerado. Mesmo assim, pode-se observar que as frequências vibracionais referentes aos modos de estiramento da água diminuem, enquanto os modos de dobramento aumentam.

5.3 Caracterização de pequenos aglomerados moleculares

5.3.1 Introdução

Os mecanismos pelos quais a água interage com pequenas moléculas orgânicas são fundamentais para a compreensão dos fatores responsáveis pelas modificações das propriedades e da reatividade dessas moléculas em ambiente aquoso. Neste sentido, torna-se necessário obter informações quantitativas precisas sobre estrutura e energética de possíveis sistemas complexados com água. Em particular, as interações intermoleculares da água com nitrilas, moléculas orgânicas do tipo $R-CN$, são de grande interesse por formarem LHs ditas não usuais. Além disso, as ligações do tipo $O-H \cdots N$ também são bastante similares àsquelas de comum ocorrência em sistemas biológicos.

5.3.2 Aglomerados de $RCN \cdots H_2O$

Na Figura 5.4 apresentamos as estruturas de possíveis complexos moleculares formados entre nitrilas (ou cianetos) e água, os quais trataremos nesta seção. Os resultados obtidos para geometrias de equilíbrio, energética e espectros vibracionais destes agregados são discutidos no Artigo B3 em anexo. Aqui apresentamos os valores das energias de dissociação D_e e $D_0 = D_e + \Delta E_0$, em que ΔE_0 é a diferença em energia vibracional de ponto zero do agregado em relação às suas partes separadas. Estes valores são dados na Tabela 5.5 para os três sistemas mostrados na Figura 5.4.

Como pode ser lido na Tabela 5.5, estes sistemas podem formar complexos estabilizados por LHs do tipo $O-H \cdots N$. Dentre os complexos $R-CN \cdots H_2O$ mostrados na Figura 5.4, o sistema $(CH_3)CCN \cdots H_2O$ (c)-(d) é o mais fortemente ligado ($D_0 = 3,46 \text{ kcal mol}^{-1}$ no nível MP2). Em parte, isto decorre devido à possibilidade de formação de LHs adicionais, do tipo $C-H \cdots O$ com os grupos metilas. A menor diferença na estabilização deste complexo aparece

Figura 5.4: Estruturas dos aglomerados moleculares de $R-CN-H_2O$: (a) $HCN \cdots H_2O$, (b) $H_3CCN \cdots H_2O$ e (c)-(d) $(CH_3)_3CN \cdots H_2O$.

no nível DFT/PW91, cujo D_0 calculado é de 4,08 kcal mol⁻¹ em comparação com os 3,99 kcal mol⁻¹ de H₃CCN...H₂O (b).

O erro de superposição de base (BSSE) na energia de ligação é aproximadamente constante com o funcional PW91. Isto é, o BSSE calculado para os três complexos é da ordem de ~6%. Usando o funcional B3LYP este percentual cresce lentamente com o tamanho do sistema; os valores de BSSE são respectivamente 5, 6 e 8%. O maior erro na energia de ligação produzido com a base 6-311++G(d,p) ocorre para o método MP2. Neste caso o BSSE varia de 14% para HCN...H₂O (Figura 5.4 (a)), 17% para H₃CCN...H₂O (Figura 5.4 (b)) e 35% para (CH₃)₃CN...H₂O (Figura 5.4 (c)-(d)).

Tabela 5.5: Energias de dissociação para os complexos RCN-H₂O. Valores calculados em kcal mol⁻¹ com a base 6-311++G(d,p) e corrigidos para BSSE.

Método	HCN...H ₂ O		H ₃ CCN...H ₂ O		(CH ₃)CCN...H ₂ O	
	D_e	D_0	D_e	D_0	D_e	D_0
SCF	2,88	1,65	3,67	2,36	3,19	2,13
MP2	3,54	2,31	4,33	3,02	4,52	3,46
MP3	3,23	2,00	4,05	2,74	4,22	3,16
MP4(DQ)	3,22	1,99	3,97	2,66	4,03	2,97
MP4(SDQ)	3,26	2,03	4,03	2,74	4,12	3,06
MP4	3,39	2,16	4,19	2,88	4,39	3,33
CCD	3,22	1,99	3,99	2,68	4,07	3,01
CCSDT	3,34	2,11	4,13	2,82	4,32	3,26
B3LYP	3,62	2,33	4,56	3,17	4,08	2,75
PW91	4,28	2,99	5,37	3,99	5,40	4,08

5.3.3 Sumário

Aqui, investigamos as estruturas e as estabilidades de possíveis heterodímeros formados entre R-CN e H₂O (Artigo B3). Utilizamos métodos de MBPT/CC e DFT para determinar a influência da formação de LHs nas propriedades desses sistemas. Como discutido nas seções anteriores, esta metodologia tem se mostrado extremamente útil para ajudar na detecção de pequenos aglomerados moleculares existente somente sob certas condições especiais. Adi-

cionalmente, podemos explorar os limites quânticos de precisão dos cálculos, obtendo-se, assim, resultados bastante confiáveis para prever as propriedades destes complexos.

5.4 Moléculas importantes em astrofísica

5.4.1 Introdução

A confiabilidade nos métodos teóricos para auxiliar a caracterização de moléculas identificadas a partir de dados espectrais de radio-astronomia tem sido importante para os avanços em astrofísica molecular. Em particular, nestes estudos tem se utilizado com frequência a teoria do funcional da densidade para calcular as propriedades de moléculas interestelares. No Artigo B4 apresentamos um estudo sistemático, envolvendo diferentes funcionais da densidade e métodos pós-HF aplicados a moléculas simples, identificadas no espaço ou em condições especiais de laboratório via diferentes técnicas espectroscópicas. Algumas destas espécies são HCN, CH₃CN, CH₃CNH⁺, HCCCN, e HCCNC. Nosso principal interesse aqui é avaliar o desempenho de alguns métodos quânticos para o cálculo de propriedades moleculares dentro da precisão experimental.

5.4.2 Propriedades da molécula de HCN isolada

Na Tabela 5.6 apresentamos um resumo dos resultados obtidos com vários métodos utilizados para calcular a geometria de equilíbrio, a constante rotacional e momento dipolar da molécula de HCN. Aqui, mostramos somente aqueles métodos que estão dentro de uma margem de erro de $\pm 1\%$ para as constantes rotacionais e $\pm 3\%$ para os momentos dipolares elétricos obtidos experimentalmente. Entretanto, todos os resultados teóricos considerados em nosso estudo estão dentro de 5% em acurácia comparados ao resultado experimental da constante rotacional da molécula de HCN (44,51 GHz).

De acordo com os resultados do Artigo B4, dentre 39 procedimentos diferentes utiliza-

Tabela 5.6: Comparação dos resultados obtidos com diferentes métodos para geometria de equilíbrio, constante rotacional e momento dipolar elétrico da molécula de HCN isolada.

Método	Geometria(Å)		Const. rotacional		Momento dipolar	
	HC	CN	B (GHz)	Erro (%)	μ (D)	Erro (%)
BLYP/6-311++G(d)	1,067	1,148	44,85	0,8	3,10	3
B3LYP/6-31G(d)	1,070	1,157	44,20	0,7	2,90	3
B3LYP/6-31+G(d)	1,071	1,158	44,16	0,8	3,08	2
B3LYP/6-31++G(d,p)	1,070	1,158	44,16	0,8	3,08	2
B3LYP/6-311++G(d)	1,069	1,149	44,73	0,5	3,08	2
B3LYP/6-311++G(d,p)	1,067	1,149	44,76	0,6	3,05	1
B3P86/6-31+G(d)	1,072	1,156	44,23	0,6	3,08	2
B3P86/6-31G(d)	1,071	1,156	44,25	0,6	2,94	2
B3P86/6-311++G(d)	1,069	1,149	44,76	0,6	3,08	2
B3P86/6-311+G(d,p)	1,069	1,149	44,76	0,6	3,08	2
B3P86/6-311++G(d,p)	1,068	1,149	44,79	0,6	3,06	2
B3PW91/6-31G(d,p)	1,070	1,157	44,21	0,7	2,92	3
B3PW91/6-311++G(d)	1,069	1,150	44,70	0,4	3,07	2
CCD/6-311++G(d)	1,071	1,156	44,27	0,5	3,08	2
Experimental	1,065 ^a	1,153 ^a	44,51 ^a	-	2,99; 3,02 ^b	-

^a Ref. [12] do Artigo B4; ^b Refs. [67] e [68] do Artigo B4.

dos, 13 da DFT reproduzem o critério de acurácia ($\pm 1\%$ para a constante rotacional e $\pm 3\%$ para o dipolo experimentais). Por outro lado, dentre os métodos pós-HF, apenas a aproximação CCD/6-311++G(d) satisfaz este critério. Uma análise cuidadosa da performance dos métodos considerados aqui e no Artigo B4 mostra que os resultados obtidos com DFT são comparáveis, ou mesmo melhores, que o caso limite dos métodos pós-HF, como MP2 ou CCD, por exemplo. Uma excessão ocorre para o cálculo do momento de dipolo de HCN, quando se utiliza funcionais com base correlacionadas.

Podemos concluir também que os funcionais B3P86 e B3LYP fornecem constantes rotacionais bastante precisas, enquanto a aproximação MP2, mesmo com bases correlacionadas (cc-pVTZ ou aug-cc-pVDZ), dá valores muito pequenos. É também interessante notar que os resultados para os momentos dipolares obtidos com B3LYP são estáveis quando se emprega bases regulares mas deterioram com bases correlacionadas.

5.4.3 Isômeros de nitrilas e isonitrilas

Utilizando diferentes procedimentos teóricos, investigamos as propriedades de isômeros de nitrilas e isonitrilas. Em particular, estes compostos pertencem a uma classe de substâncias que nem sempre são acessíveis experimentalmente [104]. Aqui apresentamos a estabilidade relativa entre duas dessas espécies moleculares:

A molécula (1) possui a propriedade de formar longas cadeias estabilizadas por ligações de hidrogênio, assim como HCN (Artigo B6). Já a molécula (2), sintetizada em fase gasosa recentemente [104], exibe uma maior estabilidade frente a polimerização ou a isomerização. A diferença de energia entre (1) e (2), ΔE_{12} , calculada com métodos pós-HF e DFT é apresentada na Tabela 5.7.

Tabela 5.7: Estabilidade relativa (em eV) entre HCCCN e HCCNC.

HF e pós-HF	ΔE_{12}	DFT	ΔE_{12}
HF/6-31G(d)	0,951	BP86/6-31G(d)	1,156
HF/6-31+G(d)	0,903	BP86/6-31+G(d)	1,104
HF/6-31++G(d,p)	0,903	BP86/6-31++G(d,p)	1,103
MP2/6-31G(d)	1,441	BP86/cc-pVDZ	1,131
MP2/6-31+G(d)	1,373	BLYP/6-31+G(d)	1,109
MP2/6-31++G(d,p)	1,372	B3P86/6-31G(d)	1,116
MP2/cc-pVDZ	1,409	B3P86/6-31+G(d)	1,066
MP4(SDQ)//MP2/6-31++G(d,p)	1,131	B3P86/6-31++G(d,p)	1,065
MP4//MP2/6-31++G(d,p)	1,206	B3LYP/6-31G(d)	1,128
CCD//MP2/6-31++G(d,p)	1,129	B3LYP/6-31G(d,p)	1,122
CCSD//MP2/6-31++G(d,p)	1,126	B3LYP/6-31+G(d)	1,068
CCSD(T)//MP2/6-31++G(d,p)	1,156	B3LYP/6-31++G(d,p)	1,067
-	-	B3LYP/cc-pVDZ	1,101
-	-	B3LYP/aug-cc-pVDZ	1,087
-	-	B3PW91/6-31G(d,p)	1,122
-	-	B3PW91/6-31+G(d)	1,073
-	-	B3PW91/6-31++(d,p)	1,072

As barras duplas (//) indicam os níveis de otimização de geometria.

Conversão: 1 eV = 23,06 kcal mol⁻¹ = 96,48 kJ mol⁻¹.

A melhor estimativa considerada para esta diferença de energia está entre 1,1 e 1,2 eV (Refs. 42 e 43 do Artigo B4). Em nossos cálculos utilizamos diferentes funcionais com diversas bases gaussianas e comparamos os resultados com métodos HF e pós-HF. Todos os modelos da DFT analisados fornecem valores dentro do intervalo estimado, enquanto somente os métodos pós-HF, que incluem correlação eletrônica em altas ordens, dão bons resultados. Por exemplo, as diferenças de energia calculadas incluindo somente correlação eletrônica em segunda ordem (MP2) são mais altas, comparadas à estimativa de 1,1 a 1,2 eV. De outro lado, as diferenças de energia obtidas com HF são bem inferiores a este intervalo.

5.4.4 Sumário

Nesta seção resumimos alguns dos resultados mais importantes descritos nos Artigo B4. O trabalho apresenta um estudo metodológico, envolvendo basicamente DFT em comparação com métodos de MBPT/CC e dados experimentais. Revisitamos alguns sistemas simples de grande interesse em astrofísica, HCN, CH₃CN, CH₃CNH⁺, HCCCN, HCCNC, e avaliamos a performance dos diferentes níveis teóricos para a obtenção de constantes rotacionais, momentos dipolares elétricos e estabilidade entre isômeros configuracionais.

Em geral, os funcionais dão resultados dentro de $\pm 1\%$ dos valores experimentais para as constantes rotacionais e $\pm 3\%$ para os momentos dipolares. Considerando nossos níveis de cálculos, dentro da aproximação de Born-Oppenheimer não podemos esperar valores mais acurados do que estes. O desempenho dos funcionais considerados aqui é melhor do que poderíamos esperar para os limites dos métodos pós-HF, e.g., MP2 ou CCD. O funcional B3LYP com as bases 6-31++G(d,p) ou 6-31+G(d) fornece bons resultados para as constantes rotacionais ou momentos de dipolos. Entretanto, para esta última propriedade, o funcional B3P86 dá um melhor resultado. De fato, a melhor performance geral é obtida com o procedimento B3PW91/6-31G(d,p).

5.5 Equilíbrio conformacional de furfural em solventes próticos

5.5.1 Introdução

A estabilização de conforméromos moleculares em meio solvente é um dos principais aspectos que tem sido discutidos recentemente sobre as LHs. Este tópico é de crescente interesse em bioquímica, onde é sabido que a reatividade molecular em processos biológicos depende, em parte, de efeitos estéricos e da formação de LH com o meio aquoso. Portanto, uma avaliação teórica minuciosa dos efeitos de solvente sobre diferentes conforméromos moleculares requer a inclusão das moléculas do meio explicitamente. No caso de pequenas moléculas orgânicas, as diferenças de energia entre isômeros rotacionais são inferiores a $\sim 3 \text{ kcal mol}^{-1}$. Similarmente, as energias de solvatação de um soluto polar em solventes polares são também desta ordem de grandeza, de forma que pequenas mudanças do meio podem alterar consideravelmente o sentido do equilíbrio conformacional.

Existe uma variedade de compostos em que o rotâmero mais estável em solvente polar não é o mesmo encontrado em solventes apolares ou em fase de vapor. Em alguns casos um dos rotâmeros é preponderante em um meio específico, enquanto outros conforméromos são completamente escassos. As flutuações térmicas também são importantes para a concentração dos conforméromos. Para investigar este problema, realizamos um estudo dos efeitos de solventes próticos no equilíbrio conformacional da molécula de furfural, esquematizado na Figura 5.5.

Figura 5.5: Equilíbrio conformacional de furfural: OO-*cis* corresponde à conformação a 0° , TS corresponde à conformação a 90° e OO-*trans* corresponde à conformação a 180° .

O equilíbrio rotacional entre as duas formas planares de furfural (*OO-cis* $\rightleftharpoons$ *OO-trans*) tem sido assunto de numerosas investigações [105], desde a demonstração experimental deste equilíbrio feita por Allen e Bernstein [106]. Por exemplo, há mais de trinta anos discute-se acerca do equilíbrio rotacional de furfural em fases gasosa, líquida e também em diferentes soluções. A investigação de rotâmeros em meio solvente torna-se particularmente difícil quando a utilização de técnicas experimentais já não é capaz de fazer uma distinção entre os isômeros rotacionais sem qualquer ambigüidade [105].

Recentemente, Kaminski e Jorgensen [107] desenvolveram um procedimento combinado de simulação Monte Carlo e mecânica quântica para investigar a dependência do equilíbrio conformacional de furfural em tetracloreto de carbono (CCl_4), dimetóxi-etano (DME) e dimetil-sulfóxido (DMSO) (todos sendo solventes apróticos). Em outro estudo, Bain e Hazendonk [108] utilizaram uma combinação de experimentos de RMN e de cálculos *ab initio* para determinar os efeitos entrópicos na barreira rotacional de furfural em tolueno, acetona e metanol. Também, Baldrige e Jonas [109], usando métodos *ab initio*, realizaram uma análise conformacional de furfural em função da constante dielétrica do meio. Nosso interesse é investigar a influência de solventes próticos, em particular clorofórmio (CHCl_3) e água, na estabilização dos confórmeros de furfural, discutindo nossos resultados à luz de alguns resultados já existentes [107, 108, 109].

5.5.2 Influência do meio no equilíbrio conformacional

Usualmente, para um equilíbrio rotacional genérico $A \rightleftharpoons B$, a estabilização de um determinado confórmero é estimada em função da constante dielétrica do meio, ϵ , e dos momentos dipolares, μ , dos rotâmeros A e B de acordo com a expressão [110]:

$$\delta\Delta E_{sol} = (\mu_A^2 - \mu_B^2)\chi/r^3, \quad \chi = (\epsilon - 1)/(2\epsilon + 1). \quad (5.1)$$

Neste caso, a variação da energia de solvatação, Eq. (5.1), é inversamente proporcional ao volume molecular do soluto. Furfural, em solventes poucos polares ($\epsilon \leq 5$), é mais estável na conformação OO-*trans* ($\mu = 3,23$ D) do que na conformação OO-*cis* ($\mu = 3,76$ D) [105]. A pequena diferença de energia entre estes dois conformêros, a mudança da barreira rotacional em diferentes solventes e o papel das interações específicas entre soluto e solvente para a estabilização dos conformêros têm atraído a atenção de experimentalistas e teóricos. Algumas referências historicamente importantes sobre o equilíbrio OO-*cis* $\rightleftharpoons$ OO-*trans* são citadas no Artigo B5.

5.5.3 Inclusão explícita do solvente via simulação Monte Carlo

Uma das questões que nos interessa sobre o equilíbrio conformacional do furfural é a interação específica do soluto com solventes próticos, principalmente a contribuição das LHS na estabilização dos conformêros em solução. Para isto utilizamos dois sistemas distintos: furfural/água e furfural/clorofórmio. Nosso procedimento para gerar as estruturas do líquido utiliza a técnica de simulação Monte Carlo [111] descrita no Capítulo 4. Para o cálculo das propriedades estruturais e eletrônicas, somente as configurações MC estatisticamente descorrelacionadas [97] são analisadas. As camadas de solvatação dos solutos são então definidas utilizando-se as funções de distribuição radial de pares (com relação aos centros de massa soluto-solvente), a partir das quais obtemos as supermoléculas (Figura 5.6). A primeira camada de solvatação contém 1 molécula de furfural e 34 moléculas de H₂O.

As interações intermoleculares são totalmente parametrizadas de acordo com os potenciais de Lennard-Jones e Coulomb descritos na Eq. (4.12). As correções de longo alcance são feitas usando-se o método do campo de reação. A análise conformacional é feita realizando-se 20 simulações MC para cada um dos solventes (CHCl₃ e H₂O). Os solutos (diferentes conformêros de furfural) são definidos a partir da conformação inicial OO-*cis* (0°), variando-se o ângulo da

Figura 5.6: Ilustração de uma supermolécula do sistema furfural/água.

carbonila ($-\text{CHO}$) em relação ao anel furano ($-\text{C}_4\text{H}_3\text{O}$) de 9° , até atingir a conformação final *OO-trans* (180°), completando um total de 20 conformémeros distintos (Figura 5.5). Os parâmetros geométricos dos rotâmeros são obtidos via cálculos MP2/6-311G(d).

No caso de furfural em clorofórmio, as simulações foram feitas em *ensembles NVT* (canônico) com 343 moléculas de CHCl_3 e uma molécula de furfural, à temperatura de 298,15 K e densidade do clorofórmio de $1,480 \text{ g cm}^{-3}$. Inicialmente, fizemos 1×10^6 passos MC para a termalização, seguidos de 20×10^6 passos MC para atingir o equilíbrio termodinâmico. No caso de furfural em água utilizamos *ensembles NPT* (isobárico-isotérmico). Neste caso, 450 moléculas de H_2O foram empregadas para definir o solvente em torno de uma molécula de soluto. Para as 20 simulações, referentes a cada conformémero, a densidade média teve uma pequena variação entre $1,045 \text{ g cm}^{-3}$ e $1,055 \text{ g cm}^{-3}$. Na fase de termalização foram feitos 2×10^6 passos MC e na fase de equilíbrio termodinâmico, 27×10^6 passos MC.

5.5.4 Caracterização das LHs entre soluto e solvente

Os resultados para o número médio de LHs obtidas ao longo da interconversão OO-*cis* $\rightleftharpoons$ OO-*trans* são mostrados nas Tabelas 5.8 e 5.9. Esses valores foram obtidos a partir das configurações Monte Carlo, utilizando-se os critérios geométrico ($R_{OX} \leq 3,7 \text{ \AA}$; $\theta_{OXH} \leq 36^\circ$) e energético ($E_{LH} \leq -2 \text{ kcal mol}^{-1}$) para a definição das LHs [112]. Na Figura 5.7 apresentamos um esquema com os parâmetros geométricos envolvidos na LH e na Figura 5.8 mostramos os tipos de LHs mais prováveis de ocorrerem durante o processo de equilíbrio conformacional para os dois solventes próticos. Os valores médios das distâncias OX, ângulos OXH (X = O, C) e energias também são fornecidos para três conformêros distintos (0° , 90° e 180°) nos dois solventes (CHCl_3 e H_2O) nas Tabelas 5.8 e 5.9, respectivamente.

Figura 5.7: Parâmetros geométricos da LH. O átomo X representa o oxigênio no caso de H_2O e o carbono no caso de CHCl_3 .

Tabela 5.8: Número médio de LHs formadas entre furfural e clorofórmio de acordo com os critérios geométrico e energético.

Confórmero	No. de LHs	$\langle R_{OC} \rangle$, Å	$\langle \theta_{OCH} \rangle$, °	$\langle E_{LH} \rangle$, kcal mol $^{-1}$
OO- <i>cis</i>	1,07	$3,26 \pm 0,03$	$21,7 \pm 1,0$	$-3,26 \pm 0,09$
TS	0,97	$3,24 \pm 0,03$	$20,9 \pm 1,0$	$-3,21 \pm 0,07$
OO- <i>trans</i>	0,92	$3,27 \pm 0,03$	$20,7 \pm 1,0$	$-3,19 \pm 0,06$
Contribuição das LHs: $\Delta E(cis - trans) = +0,56 \text{ kcal mol}^{-1}$.				

Uma análise completa sobre o sistema furfural/água é feita no Artigo B5, onde verificamos a influência das LHs e o solvatocromismo ao longo do equilíbrio conformacional. Aqui é interessante observar que o número médio de LHs formadas com o soluto se mantém constante (em torno de 1 LH por rotâmero) ao longo do equilíbrio conformacional para os dois solventes

Tabela 5.9: Número médio de LHs formadas entre furfural e água de acordo com os critérios geométrico e energético.

Confórmero	No. de LHs	$\langle R_{OO} \rangle$, Å	$\langle \theta_{OOH} \rangle$, °	$\langle E_{LH} \rangle$, kcal mol ⁻¹
OO- <i>cis</i>	0,97	$3,03 \pm 0,03$	$19,5 \pm 1,0$	$-3,36 \pm 0,09$
TS	0,83	$2,98 \pm 0,03$	$20,8 \pm 1,0$	$-3,08 \pm 0,08$
OO- <i>trans</i>	1,13	$2,95 \pm 0,03$	$16,5 \pm 1,0$	$-3,45 \pm 0,09$
Contribuição das LHs: $\Delta E(cis - trans) = -0,64$ kcal mol ⁻¹ .				

investigados. A contribuição energética total de todas as LHs no processo *cis-trans* é de +0,54 kcal mol⁻¹ para o clorofórmio e de -0,64 kcal mol⁻¹ para a água. Estes resultados estão de acordo com as estabilidades dos confórmeros nos respectivos solventes, embora as LHs não desempenhem um papel decisivo para a estabilização de qualquer confórmero durante equilíbrio rotacional da carbonila. Como consequência, podemos inferir que a formação de LH contribui com uma pequena parcela entrópica para a barreira rotacional. Tal efeito foi anteriormente predito por Bain e Hazendonk [108] para o caso do sistema furfural/metanol.

Figura 5.8: Ligações de hidrogênio mais prováveis para os sistemas (a) furfural/CHCl₃ e (b) furfural/H₂O, obtidas via simulações Monte Carlo.

5.5.5 Solvatocromismo de furfural em água

Outra questão de interesse no estudo do equilíbrio *OO-cis* $\rightleftharpoons$ *OO-trans* de furfural diz respeito à influência do solvente no espectro de absorção UV-vis. Além disso, sabe-se que este espectro na região de 3000 a 3600 Å é de difícil acesso experimental em fase vapor e, em solventes polares, todo o espectro imerge em uma intensa banda de absorção (Ref. [22] do Artigo B5). Para a caracterização teórica do espectro de absorção UV-vis, utilizamos 60 configurações MC estatisticamente descorrelacionadas e fizemos os cálculos quânticos das energias de transição utilizando o método semi-empíricos INDO/CIS [99] para 60 supermoléculas (Figura 5.6).

Nossos resultados consideram apenas a primeira camada de solvatação do sistema furfural/água (1 molécula de soluto e 34 moléculas de solvente). O deslocamento solvatocrômico é calculado a partir dos valores médios das transições verticais (diferenças entre energia do primeiro estado excitado do soluto na supermolécula e a energia do primeiro estado excitado do soluto em fase gasosa). No Artigo B5 apresentamos uma resenha completa sobre o solvatocromismo do sistema furfural/água. Aqui, apresentamos a Tabela 5.10 com os valores calculados para os deslocamentos solvatocrômicos das absorções UV-vis mais baixas, $n - \pi^*$ e $\pi - \pi^*$, relativos às conformações mais estáveis de furfural. Como pode ser notado, nossos resultados estão em muito bom acordo com os experimentos.

Tabela 5.10: Deslocamentos solvatocrômicos (em cm^{-1}) calculados e experimentais.

Transição	Confórmero	Calculado	Experimental
$n - \pi^*$	<i>OO-cis</i>	1230 ± 45	1200^a ; 1350^b
$n - \pi^*$	<i>OO-trans</i>	1130 ± 43	-
$\pi - \pi^*$	<i>OO-cis</i>	-1005 ± 64	-1300^c
$\pi - \pi^*$	<i>OO-trans</i>	-950 ± 64	-

^a De ciclohexano para água, Ref. [22] do artigo B5;

^b De iso-octano para água, Ref. [22] do artigo B5;

^c De n-hexano para água, Ref. [21] do artigo B5.

5.5.6 Sumário

Nesta seção apresentamos um estudo dos efeitos de solvente próticos (incluídos explicitamente) durante o equilíbrio conformacional de furfural. Os efeitos estatísticos das LHs entre soluto e solvente também são avaliados nas simulações MC. Em média, apenas uma LH é formada com cada conformero analisado em água ou clorofórmio e a energia por LH não se modifica significativamente ao longo da interconversão *OO-cis* $\rightleftharpoons$ *OO-trans* (cf. Figura 5 do Artigo B5) nos dois solventes. Nossos resultados também indicam que as LHs não desempenham um papel crucial para a estabilização de qualquer rotâmero de furfural em solventes próticos. Isto leva a uma pequena contribuição entrópica para a barreira rotacional do sistema [108].

Os cálculos para o deslocamento solvatocrômico relativo ao espectro de absorção $n - \pi^*$ do rotâmero *OO-cis* em água fornecem $1230 \pm 45 \text{ cm}^{-1}$, estando em bom acordo com o resultado experimental de 1200 cm^{-1} (Ref. 22 do Artigo B5). No caso da primeira absorção $\pi - \pi^*$, o deslocamento calculado é de $-1005 \pm 64 \text{ cm}^{-1}$, sendo o resultado experimental de -1300 cm^{-1} . O comportamento do solvatocromismo ao longo do equilíbrio conformacional pode ser visto nas Figuras 6 e 7 do Artigo B5. Por exemplo, no caso da absorção $n - \pi^*$, o deslocamento solvatocrômico é independente de qualquer conformação específica do soluto.

Os resultados observados para o espectro UV-vis não são totalmente surpreendentes, uma vez que a interação do solvente com o o par eletrônico isolado do átomo de oxigênio da carbonila também não depende do ângulo de rotação. Portanto, a transição $n - \pi^*$ em meio solvente reflete apenas os efeitos estruturais que ocorrem naturalmente em fase gasosa (cf. Figura 6 do Artigo B5). Por outro lado, no caso da transição $\pi - \pi^*$, os efeitos estruturais causam mudanças mais drásticas no espectro de absorção UV-vis. Neste caso o solvatocromismo mostrado na Figura 7 do Artigo B5 não tem um padrão bem comportado, devido, principalmente, a uma quebra de simetria π que deve ocorrer ao longo do equilíbrio conformacional.

5.6 Efeito de muitos corpos em cadeias lineares de HCN

5.6.1 Introdução

Os mecanismos de reações para a formação de moléculas pré-bióticas a partir de moléculas simples têm sido propostos na literatura científica há pelo menos quatro décadas [113]. Em particular, a oligomerização de HCN fornece uma rota interessante para a evolução química de moléculas biológicas, como a adenina, por exemplo. Além disso, HCN é uma das moléculas mais abundantes em condições primitivas do universo e da Terra [114]. A molécula de adenina possui a mesma estequiometria de um pentâmero de HCN, i.e., $C_5H_5N_5$. Neste direção, Chakrabarti e Chakrabarti [115] propuseram recentemente um modelo para a produção de adenina a partir de reações de HCN em fase gasosa.

Outro fator importante na interação de moléculas de HCN é que as LHs do tipo $C-H \cdots N$ formadas em cadeias lineares são bastante semelhantes àsquelas formadas em sistemas biológicos [73]. Além disso, HCN forma sistemas fortemente polares (apresentando uma constante dielétrica de até 158), em que as LHs tornam-se surpreendentemente mais fortes do que o esperado. Assim, nos propomos investigar as interações intermoleculares em cadeias lineares de HCN próton-ligadas (Figura 5.9).

Nosso trabalho tem como objetivo central desenvolver um estudo sistemático, baseado em cálculos de primeiros princípios, para quantificar os termos de interação de muitos corpos nos oligômeros de HCN. Complementarmente, analisamos os efeitos cooperativos nas energias de ligação e nos dipolos elétricos desses sistemas. Os resultados obtidos são analisados em função do número de monômeros de HCN contidos nos aglomerados e comparados com alguns resultados experimentais disponíveis na literatura.

Figura 5.9: Cadeias lineares de HCN com diferentes tamanhos.

5.6.2 Energética dos oligômeros

Realizamos os cálculos quânticos dentro do esquema MBPT/CC com diferentes ordens de perturbação, otimizando as estruturas desde monômeros a heptâmeros no nível MP2. A escolha do conjunto de funções-base foi feita a partir de cálculos das propriedades estruturais e eletrônicas do dímero (HCN)₂. Investigamos três conjuntos de funções-base distintos: 6-311++G(d,p), aug-cc-pVDZ e aug-cc-pVTZ. Os resultados obtidos no Artigo B6 indicam que a base 6-311++G(d,p) fornece propriedades suficientemente acuradas, sendo portanto apropriada para o estudo de cadeias maiores. Na Tabela 5.11 apresentamos as energias de ligação e os efeitos cooperativos dos oligômeros (HCN)_{N=2-7} calculadas com MP2/6-311++G(d,p).

As primeiras duas colunas da Tabela 5.11 referentes aos $-\Delta E_N$ mostram as energias de ligação de cada oligômero. Como pode ser estimado, o erro devido à superposição de base (BSSE) afeta as energias de ligação dos dímero e trímero em aproximadamente 10%. Para as cadeias maiores, este erro é cerca de 9%. As colunas centrais mostram as energias de ligação do oligômero dividida pelo respectivo número de LHs em cada cadeia. Isto possibilita uma comparação direta das interações nos oligômeros com a energia de ligação do dímero. A influência de BSSE, neste caso, é cerca de 2 kJ mol⁻¹. A cooperatividade é dada nas últimas duas colunas da Tabela 5.11 a partir do trímero. Esta é computada como sendo a correção de duas vezes a energia do dímero ($2 \times \Delta E_2$) e normalizada pelo fator $(N - 2)$ para efeito de comparação. Assim, estes valores são

extrapolados convergindo para 5,8 kJ mol⁻¹ após correção de BSSE.

Tabela 5.11: Propriedades energéticas dos oligômeros de HCN. Valores calculados (em kJ mol⁻¹) nível MP2/6-311++G(d,p) com e sem BSSE.

N	$-\Delta E_N$		$-\Delta E_N/(N-1)$		Cooperatividade ^a	
	BSSE	<i>counterpoise</i>	BSSE	<i>counterpoise</i>	BSSE	<i>counterpoise</i>
2	19,49	17,72	19,49	17,72	-	-
3	43,27	39,47	21,63	19,73	4,03	4,29
4	68,46	62,59	22,82	20,86	4,99	4,72
5	94,24	86,29	23,56	21,57	5,43	5,14
6	120,32	110,28	24,06	22,06	5,72	5,42
7	146,55	134,43	24,43	22,40	5,92	5,62

^a A contribuição cooperativa é definida como $[\Delta E_N - (N-1)\Delta E_2]/(N-2)$.

Investigamos também as energias de fragmentação para as diversas cadeias de HCN:

com $N = 2 - 7$ e $K = 1 - 6$. Um histograma para o aumento percentual das energias de decomposição das LHs é mostrado na Figura 3 do Artigo B6, incluindo os respectivos valores após a correção de BSSE em dois níveis de cálculo (HF e MP2). Por exemplo, a dissociação do trímero $(\text{HCN})_3$ em $(\text{HCN})_2$ e HCN requer uma energia de 21,89 kJ mol⁻¹ (em MP2). Isto corresponde a 24% a mais do que a energia necessária para fragmentar o dímero $(\text{HCN})_2$, cuja energia é de 17,72 kJ mol⁻¹. O efeito cooperativo das LHs eleva esta energia em até 86% no caso da decomposição do heptâmero $(\text{HCN})_7$ em $(\text{HCN})_4$ e $(\text{HCN})_3$, com MP2/6-311++G(d,p).

5.6.3 Efeitos de muitos corpos

A energia de interação de um agregado formado por N moléculas interagentes (corpos), em uma dada configuração nuclear, pode ser decomposta de acordo com a Eq. (4.5):

$$\Delta E = \sum_{i=1}^{N-1} \sum_{j>i}^N \Delta E_2(i, j) + \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^N \Delta E_3(i, j, k) + \dots, \quad (5.2)$$

para a qual os termos ΔE_K ($K = 2 - N$) são as interações de múltiplos corpos. De fato, existem $N(N - 1)/(2!)$ termos de dois corpos, $N(N - 1)(N - 2)/(3!)$ termos de três corpos, $N(N - 1)(N - 2)(N - 3)/(4!)$ termos de quatro corpos, etc. No Artigo B6 calculamos explicitamente a contribuição dos termos de até cinco corpos na energia de interação de $(\text{HCN})_5$.

Tabela 5.12: Contribuição percentual dos termos de muitos corpos na energia de interação total de oligômeros de HCN. Valores calculados com MP2/6-311++G(d,p).

Oligômero	Tipo de interação	Contribuição
$(\text{HCN})_3$	$\sum_{ij} \Delta E_{ij}$	94%
	$\sum_{ijk} \Delta E_{ijk}$	6%
$(\text{HCN})_4$	$\sum_{ij} \Delta E_{ij}$	90%
	$\sum_{ijk} \Delta E_{ijk}$	9%
	$\sum_{ijkl} \Delta E_{ijkl}$	1%
$(\text{HCN})_5$	$\sum_{ij} \Delta E_{ij}$	88%
	$\sum_{ijk} \Delta E_{ijk}$	11%
	$\sum_{ijkl} \Delta E_{ijkl}$	<1%
	$\sum_{ijklm} \Delta E_{ijklm}$	~0%

As contribuições percentuais totais de múltiplos corpos calculadas com o método MP2/6-311++G(d,p) são mostradas na Tabela 5.12. Como pode ser visto, os termos de dois corpos diminuem à medida que a cadeia aumenta. Esta contribuição é de 94% no caso do trímero, 90% no caso do tetrâmero e 88% no caso do pentâmero (depois de corrigido o BSSE). Por outro lado, os termos de três corpos tendem a aumentar com N , correspondendo a 6% para o trímero, 9% para o tetrâmero e 11% para o pentâmero. Os termos de quatro corpos parecem permanecer constantes para cadeias contendo menos do que cinco unidades monoméricas, enquanto os termos de cinco corpos contribuem com menos de 1% na energia de interação total.

5.6.4 Efeitos cooperativos nos dipolos elétricos

Na Figura 5.10 mostramos a variação dos dipolos elétricos calculados com MP2/6-311++G(d,p) para os oligômeros de HCN. Comparando-se estes valores com as somas vetoriais dos dipolos de monômeros isolados, vemos que existe um incremento de 12% no dipolo do dímero e 18% no dipolo do trímero. Este incremento parece convergir para 28% no caso de oligômeros contendo mais do que 7 unidades de HCN. Os dipolos calculados também estão em bom acordo com os resultados experimentais. Por exemplo, o dipolo do monômero é calculado como 3,00 D, sendo o dipolo experimental de 2,99 D [116]. No caso do dímero o dipolo calculado é de 6,71 D, enquanto o experimental é estimado como 6,50 D [117]; e para o trímero nosso cálculo fornece 10,66 D, com o dipolo experimental sendo 10,6 D [118].

Figura 5.10: Variação do momento dipolar com o tamanho da cadeia de HCN. A linha tracejada corresponde a uma extrapolação ($N \rightarrow \infty$) com um valor limite de 3,87 D.

5.6.5 Sumário

Nesta seção apresentamos um esquema para investigar quantitativamente os efeitos cooperativos e de muitos corpos na energia de ligação de agregados moleculares. A energética dos vários oligômeros lineares de HCN é apresentada na Tabela 5.11, obtida com o método MP2/6-311++G(d,p). A obtenção dos termos de múltiplos corpos (Tabela 5.12) requer que uma grande quantidade de cálculos quânticos seja executada para as diversas combinações possíveis das unidades constituintes do agregado e, portanto, torna-se impraticável para sistemas estendidos. Calculamos todos os termos de dois até cinco corpos explicitamente para oligômeros de $(\text{HCN})_{N=3-5}$ e fizemos uma análise sistemática da influência destes termos na energia de interação dos aglomerados moleculares próton-ligados. Vimos que para as cadeias de HCN (sistemas fortemente polares) os termos de três corpos são relevantes para a estabilização do oligômero.

Os efeitos de muitos corpos na energia total de interação dos oligômeros de HCN são dominados por interações eletrostáticas. Isto pode ser observado pelos valores obtidos com o método HF/SCF. Os termos de dois e três corpos correspondem a 99% da interação total, sendo que a contribuição de três corpos tende a aumentar com o tamanho das cadeias, enquanto que a contribuição dos termos de quatro e cinco corpos é somente da ordem de 1%. Os momentos de dipolos calculados com esta metodologia também estão de acordo com dados experimentais disponíveis para distintos oligômeros de HCN, como pode ser visto no Artigo B6.

5.7 Espalhamento clássico da luz por agregados moleculares

5.7.1 Introdução

A formação de agregados moleculares estabilizados por LHs leva a supra-estruturas que apresentam propriedades eletrônicas de interesse. Por exemplo, complexos intermoleculares

quais envolvendo LHs simples do tipo $O-H \cdots O$ têm sido propostos recentemente por Portmann et al. [119]. Eles investigaram estes sistemas utilizando uma metodologia *ab initio* para calcular a energia de ligação entre diferentes enantiômeros intermoleculares. Como é sabido, as formas enantioméricas apresentam configurações absolutas tipo *R* ou *S*, de acordo com as rotações provocadas nos planos da luz polarizada e, portanto, podem, em princípio, ser identificadas analisando-se os estados de polarização da luz. Estes tipos de estudos são pioneiros e abrem perspectivas para a investigação de interações da radiação com agregados moleculares.

Assim, além das técnicas convencionais para a caracterização de agregados moleculares próton-ligados, o espalhamento Rayleigh da luz vem sendo empregado para o estudo de aspectos dinâmicos relacionados à formação de LHs entre moléculas de alcoóis em solução aquosa [120]. Ainda no âmbito do espalhamento clássico, estamos interessados na determinação das taxas de despolarização da luz espalhada em termos das polarizabilidades de pequenos agregados moleculares, incluindo possíveis formas isoméricas intermoleculares. Nesta direção, pretendemos investigar as modificações internas que ocorrem nestes sistemas a partir da radiação espalhada sobre eles. Este também é o objeto central do estudo apresentado no Artigo B7.

5.7.2 Espalhamento Rayleigh

No espalhamento clássico da luz, a radiação total emitida por unidade de ângulo sólido em uma determinada direção, por exemplo x , é dada por [122]

$$I = \frac{2\pi^3\nu^4}{3c^3}(\mu_y^2 + \mu_z^2), \quad (5.3)$$

para a qual ν é a frequência de oscilação da luz emitida, c é a velocidade da luz e $\mu_{\gamma=y,z}$ são as componentes do dipolo molecular induzido. A relação entre o dipolo induzido e o campo elétrico $\mathbf{E}$ da radiação é dado, na aproximação linear [121], por

$$\mu = \alpha \mathbf{E} \quad (5.4)$$

Neste sentido, as taxas de despolarização de Rayleigh (ou grau de despolarização) da radiação espalhada são dadas de acordo com as expressões [122]:

$$\sigma_n = \frac{6(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 7(\bar{\alpha})^2}, \quad \sigma_p = \frac{3(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 4(\bar{\alpha})^2} \quad \text{e} \quad \sigma_c = \frac{\sigma_n}{1 - \sigma_n}, \quad (5.5)$$

com os subíndices n , p e c nas Eqs. (5.5) referindo-se à luz natural, plano-polarizada e circularmente polarizada, respectivamente. Os invariantes da polarizabilidade são a polarizabilidade média,

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (5.6)$$

e anisotrópica,

$$\begin{aligned} \Delta\alpha = & \left\{ \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] \right. \\ & \left. + 3[(\alpha_{xy})^2 + (\alpha_{xz})^2 + (\alpha_{yz})^2] \right\}^{1/2} \end{aligned} \quad (5.7)$$

5.7.3 Cálculos da despolarização da luz

Usando a aproximação de campo finito [121] e cálculos *ab initio* MP2/aug-cc-pVDZ, obtivemos as polarizabilidades dipolares, α , bem como seus invariantes (polarizabilidade média e anisotropia) e determinamos as taxas de despolarização de Rayleigh para diversos tipos de complexos moleculares “hidratados”. Novamente, a principal motivação para a escolha de compostos do tipo $A-H \cdots H_2O$ deve-se à importância do ambiente aquoso para a modificação das propriedades e reatividades de muitos sistemas moleculares. As estruturas dos diferentes agregados moleculares são mostradas na Figura 5.11, para as quais analisamos as mudanças nos graus de despolarização Rayleigh das moléculas com respeito a formação de LHs.

Todos os complexos mostrados na Figura 5.11 são obtidos como estruturas estáveis no nível MP2/aug-cc-pVDZ. A partir dos resultados da Tabela 5.13 podemos ver que a formação de LH leva a um incremento (aditivo) da polarizabilidade média. Em contrapartida os valores

Figura 5.11: Estruturas dos aglomerados moleculares: (a) $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$, (b) $\text{HCHO}\cdots\text{H}_2\text{O}$, (c) $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$, (d) $\text{HCOOH}\cdots\text{H}_2\text{O}$, (e) $\text{CH}_3\text{CN}\cdots\text{H}_2\text{O}$, (f) $(\text{CH}_3)_2\text{CO}\cdots\text{H}_2\text{O}$. Comprimentos das LHs calculados com MP2/aug-cc-pVDZ e dados em Å.

das anisotropias dependem diretamente da simetria do sistema. Isto pode ser verificado para o caso das moléculas menos assimétricas, após a complexação com H_2O , em que a variação da anisotropia é inferior ao caso de CH_3CN , i.e., de 15,65 ua para 21,78 ua.

Tabela 5.13: Polarizabilidades, anisotropias (em unidades atômicas) e graus de despolarização Rayleigh, calculados com MP2/aug-cc-pVDZ.

Sistema	$\bar{\alpha}$	$\Delta\alpha$	$\sigma_n (\times 10^{-2})$	$\sigma_p (\times 10^{-2})$	$\sigma_c (\times 10^{-2})$
H_2O	9,30	1,04	0,17	0,08	0,17
$\text{H}_2\text{O} \cdots \text{H}_2\text{O}$	19,10	3,56	0,46	0,23	0,46
HCHO	17,58	8,57	3,05	1,55	3,15
$\text{HCHO} \cdots \text{H}_2\text{O}$	27,01	10,31	1,90	0,96	1,94
CH_3OH	21,22	3,38	0,34	0,17	0,34
$\text{CH}_3\text{OH} \cdots \text{H}_2\text{O}$	31,19	5,90	0,47	0,24	0,47
HCOOH	22,53	10,64	2,87	1,46	2,95
$\text{HCOOH} \cdots \text{H}_2\text{O}$	32,15	12,93	2,10	1,06	2,14
CH_3CN	29,43	15,65	3,61	1,84	3,74
$\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$	39,67	21,78	3,84	1,96	3,99
$(\text{CH}_3)_2\text{CO}$	42,38	12,38	1,12	0,56	1,13
$(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$	52,20	17,30	1,44	0,72	1,46

De acordo com as Eqs. (5.5), as variações das polarizabilidades e de suas anisotropias levam a variações nos graus de despolarização dos sistemas. Os valores calculados para estas grandezas são mostrados na Tabela 5.13. Como pode ser visto, após a complexação com H_2O , a luz passa a ser menos despolarizada somente nos casos de HCHO (formaldeído) e HCOOH (ácido fórmico). Isto é, as taxas de despolarização relativas da luz plano-polarizada variam (σ_p), respectivamente, -38% e -27% . Nos outros casos considerados aqui, a complexação leva a variações positivas nas taxas de despolarização; por exemplo, no dímero de água σ_p aumenta aproximadamente três vezes em relação ao monômero.

5.7.4 Caracterização de isômeros próton-ligados

O espectro Rayleigh de isômeros intermoleculares não é tão simples de ser analisado. No caso dos agregados de metanol-água as intensidades são muito similares, i.e., da ordem de

4424 ua para $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ e 4269 ua para $\text{CH}_3\text{OH}\cdots\text{OH}_2$. As estruturas destes dois isômeros intermoleculares são mostradas na Figura 5.12, sendo que o isômero (a) é mais estável que o isômero (b). Neste caso, os agregados produzem praticamente a mesma despolarização na luz natural, plano-polarizada ou circularmente polarizada. No Artigo B7 discutimos estes resultados, incluindo os sistemas $\text{HCN-H}_2\text{O}$ mostrados anteriormente na Figura 5.1.

Figura 5.12: Isômeros do sistema metanol-água: (a) $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ e (b) $\text{CH}_3\text{OH}\cdots\text{OH}_2$. Comprimentos das LHs calculados com MP2/aug-cc-pVDZ e dados em Å.

5.7.5 Sumário

Nesta seção utilizamos o espalhamento Rayleigh como uma possível ferramenta auxiliar no estudo de aglomerados moleculares. Em nossa metodologia determinamos as taxas de despolarização da luz (σ_n , σ_p e σ_c) para as moléculas isoladas e para seus complexos próton-ligados com água a partir de cálculos *ab initio*. Os maiores valores dos graus de despolarização ocorrem para os casos mais anisotrópicos. Verificamos que para os sistemas $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ e $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ essas taxas fornecem praticamente o mesmo valor. Como exemplo, os graus de despolarização da luz circularmente polarizada para estes dois dímeros são calculados como $0,46 \times 10^{-2}$ e $0,47 \times 10^{-2}$, respectivamente.

De fato, no caso de $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ e $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$, os valores de σ_n , σ_p e σ_c são muito próximos para podermos distinguir entre um e outro complexo, embora as intensidades do

espalhamento sejam diferentes para cada dímero. As intensidades Rayleigh são calculados como 1658 ua $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ e 4424 ua para $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$, o que corresponde, respectivamente, a incrementos de 424 e 217 ua depois da complexação com água. Já para o caso dos dois isômeros de metanol-água torna-se ainda mais difícil discernir as diferentes estruturas apenas com a atividade (intensidade) e/ou a taxa de despolarização Rayleigh.

Capítulo 6

Conclusões e Perspectivas

Nesta tese apresentamos um estudo sobre diversos efeitos das ligações de hidrogênio em aglomerados moleculares, bem como em processos moleculares em fase líquida. Abordamos alguns dos aspectos mais importantes decorrentes da formação de LHs, as quais são tratadas apropriadamente no contexto das interações intermoleculares. Para isto, utilizamos os conceitos usuais na literatura científica para a definição das LHs [16, 17, 18] e escolhemos sistemas de interesse, em que estas ligações são consideradas como um aspecto relevante para a caracterização das propriedades estruturais, energéticas e espectroscópicas do sistema (Artigos B1-B7).

No estudo dos aglomerados moleculares, os sistemas são descritos na aproximação supermolecular, sendo suas propriedades obtidas utilizando-se diferentes métodos de estrutura eletrônica e funções-base atômicas adequadas. Com esta metodologia investigamos as propriedades de vários heterodímeros, isômeros intermoleculares e oligômeros próton-ligados. Analisamos sistematicamente os efeitos cooperativos e de muitos corpos em sistemas contendo mais do que dois monômeros: $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{H}_2\text{O}$, $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$ e oligômeros de $(\text{HCN})_{N=1-7}$. Calculamos todos os termos de múltiplos corpos nas energias de interação de cadeias lineares de $(\text{HCN})_{N=3-5}$ e extrapolamos efeitos cooperativos para $N \rightarrow \infty$.

Os principais efeitos das LHs devem-se, em parte, à mudança de polarização do sistema, acompanhada de uma pequena transferência de carga no processo de ligação [16]. Desta forma verificamos as mudanças nos espectros vibracionais, nas geometrias de equilíbrio, na energética e nas propriedades dipolares após a formação das LHs. Em termos quantitativos, os deslocamentos das frequências vibracionais variam de poucas unidades a centenas de cm^{-1} , dependendo do modo normal analisado. Com relação às estruturas, as geometrias intramoleculares sofrem variações pequenas, da ordem de centésimos de Å. Por outro lado, as distâncias intermoleculares variam em até 0,1 Å, como observado para o sistema $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$ (Artigo B2). Em média, quando uma LH se forma, o momento dipolar do sistema sofre um acréscimo de $\sim 10\%$ em relação a adição dos dipolos dos monômeros envolvidos na complexação. Entretanto, para sistemas fortemente polares, como no caso de HCN, o incremento pode chegar até 28% para cadeias estendidas (Artigo B6). Em alguns casos podemos constatar que os nossos cálculos estão em boa concordância com os resultados experimentais.

Para investigar os efeitos estatísticos das ligações de hidrogênio nos processos moleculares em solução descrevemos os sistemas utilizando uma metodologia sequencial de simulações MC e cálculos quânticos (Artigo B5). Durante as simulações clássicas, as interações intermoleculares são parametrizadas via potenciais de Lennard-Jones e Coulomb. As estruturas do líquido são obtidas utilizando-se os conceitos de ineficiência estatística [97]. Isto reduz o espaço configuracional do líquido para dezenas ou centenas de estruturas estatisticamente descorrelacionadas. O número de moléculas de solvente em cada camada de solvatação do soluto é definido a partir das funções distribuição radial do sistema. Com esta metodologia viabilizamos os cálculos quânticos necessários para a obtenção das propriedades eletrônicas de moléculas solvatadas.

Assim, usando um modelo mecânico-estatístico para o solvente, escolhemos o equilíbrio conformacional de furfural em dois solventes próticos (clorofórmio e água) como principal pro-

blema a ser investigado. A quantidade de LHs formadas entre soluto (conformeros de furfural) e solvente foram determinadas utilizando-se critérios geométricos e energéticos clássicos. Nos dois solventes específicos, apenas uma ligação de hidrogênio é formada com cada conformero analisado. A energia de interação das LHs também não se modifica significativamente ao longo da interconversão *OO-cis* $\rightleftharpoons$ *OO-trans*. Estes resultados indicam que as LHs não desempenham um papel crucial para a estabilização de qualquer rotâmero no equilíbrio rotacional de furfural nos dois solventes próticos considerados.

Com as configurações MC descorrelacionadas, em torno de 60, analisamos os efeitos das interações específicas soluto-solvente e determinamos efeitos solvatocrômicos no espectro UV-vis de furfural em água a partir de cálculos quânticos semi-empíricos INDO/CIS [99]. Verificamos que o deslocamento solvatocrômico relativo ao espectro de absorção $n - \pi^*$ do rotâmero *OO-cis* em água é de $1230 \pm 45 \text{ cm}^{-1}$, estando em bom acordo com o resultado experimental de 1200 cm^{-1} . Neste caso, observamos também que o deslocamento solvatocrômico é independente de qualquer conformação específica do soluto (Artigo B5).

Como perspectiva, podemos utilizar as ferramentas teóricas apresentadas neste trabalho para investigar sistemas moleculares de interesse biológico; por exemplo, os efeitos das LHs na interação de aminoácidos em meio líquido [73]. Neste caso a influência do solventes podem ser investigado eficientemente empregando-se a metodologia sequencial Monte Carlo / Mecânica Quântica discutida no Artigo B5. Recentemente, outros sistemas que se tem dado bastante atenção são os nanotubos orgânicos [24]. Estes são supra-estruturas moleculares formadas por empilhamento de aminiácidos cíclicos estabilizadas por ligações de hidrogênio . Um tratamento de primeiros princípios para estes sistemas estendidos pode ser feito, por exemplo, utilizando-se a teoria do funcional da densidade. Nesta direção, alguns algoritmos que escalam linearmente com o tamanho do sistema têm sido desenvolvido [64, 65].

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Apêndice A

Conversão de Unidades

A.1 Unidades atômicas

No sistema de unidades atômicas (ua) as constantes e , $\hbar$, m e $\kappa_0 (= 4\pi\epsilon_0)$ possuem valores unitários. É também usual definir as quantidades “bohr” e “hartree”, dados respectivamente por:

$$a_0 = \hbar^2 \kappa_0 / m e^2, \quad E_h = m e^4 / \kappa_0^2 \hbar^2 \quad (\text{A.1})$$

e expressar outras quantidades em termos de combinações convenientes de e , $\hbar$, m , a_0 e E_h , como mostrado na Tabela A.1. Ainda em ua, o magneton de Bohr ($e\hbar/2m$) associado ao momento angular orbital assume o valor $\frac{1}{2}$ e a constante de estrutura fina,

$$\alpha = e^2 / \kappa_0 \hbar c = 1/137,030, \quad (\text{A.2})$$

que dá o valor de 137,030 para a velocidade da luz. Assim, expressando-se o hamiltoniano em ua, pode-se comparar as ordens de grandeza de pequenas perturbações com potências de $1/c$.

Tabela A.1: Equivalência entre unidades atômicas e o SI.

Grandeza	ua	SI
Massa	m	$9,1091 \times 10^{-31}$ kg
Carga	e	$1,6021 \times 10^{-19}$ C
Ação	$\hbar$	$1,0545 \times 10^{-34}$ J s
Permissividade	κ_0	$4\pi \times 8,8542 \times 10^{-12}$ F m $^{-1}$
Comprimento	a_0	$5,2916 \times 10^{-11}$ m
Energia	E_h	$4,3594 \times 10^{-18}$ J
Tempo	$\hbar E_h^{-1}$	$2,4189 \times 10^{-17}$ s
Velocidade	$E_h e \hbar^{-1}$	$2,1876 \times 10^6$ m s $^{-1}$
Força	$E_h a_0^{-1}$	$8,2383 \times 10^{-8}$ N
Potência	$E_h^2 \hbar^{-1}$	$1,8023 \times 10^{-1}$ W
Diferença de potencial	$E_h e^{-1}$	$2,7211 \times 10^1$ V
Intensidade de campo elétrico	$E_h e^{-1} a_0^{-1}$	$5,1422 \times 10^{11}$ V m $^{-1}$
Momento dipolar elétrico	$e a_0$	$8,4778 \times 10^{-30}$ C m
Polarizabilidade elétrica	$e^2 a_0^2 E_h^{-1}$	$1,6488 \times 10^{-41}$ C 2 m 2 J $^{-1}$
Densidade de fluxo magnético	$\hbar e^{-1} a_0^{-2}$	$2,3506 \times 10^5$ T
Momento dipolar magnético	$e \hbar m^{-1}$	$1,8546 \times 10^{-23}$ J T $^{-1}$

A.2 Fatores de conversão de energias

Apresentamos na Tabela A.2 alguns fatores de conversão para a energia. A conversão de e_1 para e_2 é feita da seguinte forma: $e_2 = \text{fator} \times e_1$. Estes fatores são baseados no número de Avogadro $6,022045 \times 10^{23}$. Para pequenas diferenças de energia é usual expressar os valores em unidades de kelvin, i.e., $1 \text{ eV}/k_B = 11604,45 \text{ K}$, onde $k_B = 1,381 \times 10^{-23} \text{ J K}^{-1}$ é a constante de Boltzmann. Outra grandeza que aparece comumente em unidades não convencionais é o momento de dipolo elétrico, i.e., uma unidade atômica de dipolo elétrico corresponde a 2,5418 debyes (D) ou $8,4778 \times 10^{-30} \text{ C m}$ no SI.

Tabela A.2: Fatores de conversão mais comuns para a energia.

$e_1 \backslash e_2$	E_h	eV	kcal mol $^{-1}$	kJ mol $^{-1}$	cm $^{-1}$
E_h	1,0000000				
eV	27,211625	1,000000			
kcal mol $^{-1}$	627,47237	23,05896	1,000000		
kJ mol $^{-1}$	2625,3444	96,47868	4,184000	1,000000	
cm $^{-1}$	219474,63	8065,465	349,7758	83,59842	1,000000

Apêndice B

Lista de Publicações

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B.1 An ab initio study of the hydrogen bonded $\text{H}_2\text{O}:\text{HCN}$ and $\text{HCN}:\text{H}_2\text{O}$ isomers.

R. Rivelino, S. Canuto.

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An ab initio study of the hydrogen-bonded $\text{H}_2\text{O}:\text{HCN}$ and $\text{HCN}:\text{H}_2\text{O}$ isomers

Roberto Rivelino, Sylvio Canuto*

Instituto de Física, Universidade de São Paulo, CP 66318 05315-970 São Paulo, SP, Brazil

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Abstract

Ab initio calculations are performed on the hydrogen bond interaction between HCN and water to analyze the structure, binding energy and change in vibrational frequencies of the $\text{HCN}:\text{H}_2\text{O}$ isomer. After geometry optimization, single-point calculations are made with many-body perturbation/coupled-cluster theories with different basis sets. At the highest level, CCSD(T), we find that the binding energy between HCN and water is 3.4 kcal/mol, after correcting for the basis-set-superposition error. Changes in intra-molecular vibrational frequencies are analyzed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogen bonding is a topic of considerable interest in physics, chemistry and biology [1–5]. Progress in cluster physical-chemistry [6,7] with laser vaporization and jet-cooling techniques, have produced a rich variety of water-bonded complexes. This leads to an increased interest in the theoretical investigation of both structure and spectroscopy of hydrogen-bonded systems [8–10].

The interaction between hydrogen cyanide, HCN, and water has been studied both experimentally [11] and theoretically [12–14]. The experimental microwave studies of Fillery–Travis [11] and Gutowski et al. [15] have established that the structure of the dimer is non-planar with the oxygen atom of water bonded to the hydrogen atom of HCN (Fig. 1a).

Thus the water molecule is the proton receptor. This has been confirmed theoretically both by molecular mechanics cluster [15] and explicit ab initio calculation [12,13]. Our interest in this system stems also from its extreme importance in astrophysics [16–20]. It is known that HCN may be trapped in water ice of comets and as such are pristine materials surviving from the time of Solar system formation [16–18]. The HCN–water complex is thus of extreme importance in pre-biotic and extra-terrestrial chemistry [18–20]. The possible existence of isomers of the hydrogen cyanide–water complex is of great importance. The complex already known is that one described above where water plays the role of proton acceptor. However, there might well be another one where water plays the role of proton donor. In this case, there would be a structure where the nitrogen atom of HCN is hydrogen-bonded to the hydrogen atom of water (as shown in Fig. 1b). This structure has never been observed in microwave experiments

* Corresponding author. Fax: +55-11-818-6831; e-mail: canuto@if.usp.br

Fig. 1. Calculated structures of the hydrogen cyanide–water complex.

[11,15], although it has been considered in a theoretical study of the electron affinities of $\text{HCN}:\text{H}_2\text{O}$ [14]. However, as we shall see it is a stable complex. In this paper we discuss the structure and energetics of the hydrogen cyanide–water, $\text{HCN}:\text{H}_2\text{O}$, as obtained from high-level *ab initio* calculations. From the viewpoint of astrophysics a millimeter wave description is necessary for radio-astronomy identification. We thus report the rotational constants of the $\text{HCN}:\text{H}_2\text{O}$ complex. In complement, we report the infrared spectrum of this complex and assign the transitions, including a comparison with the corresponding transitions of the separate moieties. We thus report geometry optimization, calculated binding energies and changes in the intra-molecular infrared spectrum of HCN and H_2O upon complex formation.

2. Methods of calculations

Geometry optimizations are performed at the second-order many-body perturbation theory, MBPT(2), best known as second-order Møller–Plesset theory, MP2. For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis set, so we use the so-called [21] 6-311+ +G** basis set. For comparison and to aid calculation of larger systems in the future we also test the density-functional Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional, B3LYP [22,23], in the same 6-311+ +G** basis set. After obtaining these optimized structures,

single-point calculations are performed using many-body perturbation/coupled-cluster theories [24] with the 6-311+ +G* and aug-cc-pVDZ basis sets. These include MP3 and MP4 as well as the more sophisticated coupled-cluster models such as CCSD [24] and CCSD(T) [25]. To analyze separately the influence of basis sets and electron correlation effects these calculations are supplemented by a correlated-consistent basis set, including diffuse functions, in the coupled-cluster calculations. Thus at the highest level, geometry optimization is performed at the MP2/aug-cc-pVDZ level and single-point calculations are further made up to the CCSD(T)/aug-cc-pVDZ level. Comparison between these results allows a systematic analysis of the electron correlation effects. The calculated binding energies are obtained with all the above theoretical models, correcting for the basis set superposition error (BSSE) [26]. This is done using the counterpoise method [27]. For the vibrational spectra we use the MP2/6-311+ +G**, B3LYP/6-311+ +G** and MP2/aug-cc-pVDZ models. Finally, all calculations are performed using the GAUSSIAN-98 program [28].

3. Results and discussion

3.1. $\text{HCN}:\text{H}_2\text{O}$ versus $\text{H}_2\text{O}:\text{HCN}$

The Fig. 1 illustrates the geometries of both isomers, $\text{H}_2\text{O}:\text{HCN}$ and $\text{HCN}:\text{H}_2\text{O}$, as obtained by MP2/6-311+ +G** and the results are compared in Table 1 with those obtained before [14]. The larger dipole moment for the isomer (1a) is expected as in this case the dipole moments of the two separate moieties are in the same direction and add to a larger value. Table 2 shows the calculated values for the binding energy, after correcting for BSSE. It is seen that the isomer (1b) is stable. Our calculated binding energy for $\text{H}_2\text{O}:\text{HCN}$ at the MP2 level is 5.36 kcal/mol, in very good agreement with the MP2/6-31G** value of 5.33 kcal/mol obtained by Tshchla and Ford [13]. At the highest level considered here, CCSD(T), the binding energy for $\text{H}_2\text{O}:\text{HCN}$ is calculated to be 5.17 kcal/mol. For $\text{HCN}:\text{H}_2\text{O}$ the binding energy is 3.38 kcal/mol; i.e. 1.8 kcal/mol smaller than that of isomer (1a). In agreement with

Table 1

Results for the geometry optimizations of the hydrogen cyanide–water clusters at the MP2/6-311+ +G** level

Geometry	H ₂ O:HCN (Fig. 1a)		Geometry	HCN:H ₂ O (Fig. 1b)	
	Present results	Ref. [14]		Present results	Ref. [14]
N1–C2	1.172	1.183	N1–C2	1.170	1.180
C2–H3	1.076	1.085	C2–H3	1.068	1.076
H3–O4	2.068	2.051	N1–H5	2.169	2.109
O4–H5	0.961	0.966	O4–H5	0.963	0.970
O4–H6	0.961	0.966	O4–H6	0.959	0.965
H5–O4–H6	104.1	104.5	H5–O4–H6	103.1	103.4
Energy MP2 (a.u.)	–169.4877623	–169.454127	Energy MP2 (a.u.)	–169.4846122	–169.452276
Dipole (D)	6.06	6.08	Dipole (D)	5.36	5.14

Distances in Å, angles in degrees. See Fig. 1.

previous studies [15,12,13] we find that isomer (1a) is non-planar and our calculated out-of-the-plane angle is 23°, in excellent agreement with the experimental result of 20° [15]. The structure of H₂O:HCN has been determined experimentally by rotational spectroscopy [15]. Similarly, the possible radio-astronomy detection of this complex, in whatever isomeric form, is facilitated by the knowledge of the rotational constants. Therefore the calculated rotational constants of both isomers are shown in Table 3 and compared with that obtained experimentally. As can be seen the results for isomer (1a) are in excellent agreement with those obtained experimentally [15]. Additionally, it shows that the distinction between the two isomers is more clearly seen using the I_A rotational constant.

3.2. Energetics and spectroscopy of HCN:H₂O

It is clear from the above results that the isomer (1b) is bound and a spectroscopic characterization, for further studies both in the laboratory and to aid in possible radio-astronomical detection, is timely and

relevant. We now concentrate on this form and study the energetics and spectroscopy of this species analyzing also the influence of basis set and electron correlation effects. In Table 4 we give the calculated geometrical parameters for both the complex HCN:H₂O and the separate moieties using different theoretical models. We note a similarity between the results obtained with the MP2 and B3LYP methods. The MP2/aug-cc-pVDZ gives a hydrogen-bond distance of 2.106 Å, that is smaller than that obtained by the other two procedures. All methods agree that HCN remains linear after the complex formation and there is a negligible decrease in the HOH bond angle. As expected, however, the OH bond distance involved in the bond formation is slightly increased. The results given for the rotational constants will be of help in a possible analysis of the millimeter-wave rotational spectrum of HCN:H₂O. The calculated rotational constants at the MP2 level agree better with one another than with the B3LYP results, particularly with respect to the larger I_A constant.

Table 5 gives the calculated binding energies for the complex, as compared with the separate

Table 2

Comparison between the calculated binding energies of HCN:H₂O and H₂O:HCN (in kcal/mol) including corrections for BSSE

	H ₂ O:HCN	HCN:H ₂ O
MP2	5.36	3.61
MP4	5.18	3.47
CCSD(T)	5.17	3.38

Geometries obtained with MP2/6-311+ +G**.

Table 3

Calculated rotational constants for the hydrogen cyanide–water complex and comparison with experimental results [15]

	I_A	I_B	I_C
H ₂ O:HCN (Fig. 1a)	402.514	3.046	3.026
HCN:H ₂ O (Fig. 1b)	481.461	3.176	3.155
Experimental [15]	–	3.046	3.020

The theoretical results are obtained with MP2/6-311+ +G**. All values in GHz.

Table 4

Optimized geometry of the HCN:H₂O complex in comparison with the isolated moieties

Geometry	MP2/aug-cc-pVDZ			MP2/6-311+ +G**			B3LYP/6-311+ +G**		
	HCN:H ₂ O	HCN	H ₂ O	HCN:H ₂ O	HCN	H ₂ O	HCN:H ₂ O	HCN	H ₂ O
C2–H3	1.078	1.078		1.068	1.068		1.067	1.067	
C2–N1	1.181	1.183		1.170	1.171		1.148	1.149	
N1–H5	2.106			2.169			2.140		
N1–O4–H5	3.7			0.8			1.0		
O4–H5	0.970		0.966	0.963		0.960	0.967		0.962
O4–H6	0.965		0.966	0.959		0.960	0.961		0.962
H5–O4–H6	103.9		103.9	103.1		103.5	104.8		105.1
O4–N1	3.073			3.132			3.107		
<i>I</i> _A	468.500			481.461			524.624		
<i>I</i> _B	3.254			3.176			3.235		
<i>I</i> _C	3.232			3.155			3.215		

Distances in Å, angles in degrees. See Fig. 1b. Also shown are the calculated rotational constants (in GHz).

monomers. These calculations are made at the corresponding geometries optimized at the MP2 and B3LYP levels. To correct for basis-set superposition error, the separate monomers are calculated using the entire basis set of the complex, as suggested by the counterpoise method [27]. In doing so, we use the optimized geometry of HCN:H₂O. We also report the result obtained at the B3LYP level with the 6-311+ +G** basis set. As can be seen in Table 5, B3LYP gives the largest binding energy, a value of 4.0 kcal/mol. Among the MBPT/CC result, MP2

Table 5

Influence of the basis sets and electron correlation effects on the calculated HCN:H₂O hydrogen binding energies (in kcal/mol) including corrections for BSSE

Basis set	6-311+ +G*	aug-cc-pVDZ
SCF	3.02	2.40
MP2	3.62	3.61
MP3	3.33	3.21
DQ-MP4	3.30	3.19
SDQ-MP4	3.33	3.26
MP4	3.44	3.47
CCSD	3.29	3.20
CCSD(T)	3.38	3.38
B3LYP	4.00	–

Geometries obtained with MP2/6-311+ +G**, MP2/aug-cc-pVDZ and B3LYP/6-311+ +G**. Corresponding differences in harmonic zero-point energies are given below.

Differences in ZPE are 1.23 kcal/mol, 1.31 kcal/mol and 1.40 kcal/mol for the calculated the frequencies at MP2/6-311+ +G**, B3LYP/6-311+ +G** and MP2/aug-cc-pVDZ levels, respectively.

gives the largest binding energy. This reinforces previous observations that B3LYP gives results similar to MP2. Comparison between the results obtained with SDQ-MP4 and full MP4 gives the contribution of triple excitations to fourth order. Using both basis sets this is a small number, 0.11 kcal/mol for the 6-311+ +G* basis set and 0.21 kcal/mol for the aug-cc-pVDZ basis set. Further comparison with the CCSD(T) gives the influence of triple-excitations at higher orders. The difference between SDQ-MP4 and CCSD(T) is only 0.05 kcal/mol for the 6-311+ +G* basis set and 0.12 kcal/mol for the aug-cc-pVDZ basis set. It is even more interesting to compare the results obtained by DQ-MP4 and CCSD, to obtain the influence of high-order double-excitations. As Table 5 shows this difference is only ± 0.01 kcal/mol, a negligible contribution. The difference in binding energy obtained by CCSD(T) and SCF (including the counterpoise correction) is only 0.36 kcal/mol for the 6-311+ +G* basis and 0.98 kcal/mol for the aug-cc-pVDZ basis sets, indicating that electron correlation effects do not contribute crucially to the binding energy. Indeed, most of the binding energy is obtained at the SCF level, showing the dominant participation of electrostatic interaction. At the highest level, CCSD(T), with either basis set, we obtain that the binding energy of HCN:H₂O is 3.38 kcal/mol. Clearly, this isomer is stable and may be detected experimentally. If one wants to go further in accuracy one should take into account the difference in zero-point vibrational energies. HCN

Table 6

Calculated vibrational frequencies of the HCN:H₂O complex and assignment with the calculated frequencies of the monomers

	HCN				H ₂ O				HCN:H ₂ O			<Δν>
	B3LYP ^a	MP2 ^a	MP2 ^b	Exp. ^c	B3LYP ^a	MP2 ^a	MP2 ^b	Exp. ^d	B3LYP ^a	MP2 ^a	MP2 ^b	
ν(π) bending	767	729	701	712					774	736	709	+8
ν(π) bending	767	729	701	712					775	738	710	+9
ν(a ₁) scissor					1602	1628	1622	1590	1624	1654	1642	+23
ν(σ) sym. stretch	2197	2016	1991	2097					2209	2031	2009	+15
ν(σ) asym. stretch	3452	3482	3455	3311					3452	3481	3458	+1
ν(a ₁) sym. stretch					3817	3884	3804	3638	3770	3851	3754	−36
ν(b ₂) asym. stretch					3922	4003	3938	3733	3899	3979	3911	−25

All frequencies in cm^{−1}. Basis sets used are 6-311+ +G** and aug-cc-pVDZ. <Δν> in the rightmost column is the average change, between all the calculations, in vibrational frequency due to the complex formation.

Basis sets are ^a6-311+ +G** and ^baug-cc-pVDZ.

Experimental results from ^cRef. [29] and ^dRef. [30].

and H₂O have in total seven vibrational modes. HCN:H₂O has in total twelve vibrational modes, an increase of five vibrational modes due to the inter-molecular vibrations. This difference, of course, influences the vibrationally corrected binding energy. The calculation of inter-molecular vibrational frequencies of hydrogen-bonded complexes is difficult because these modes are largely anharmonic. However, to obtain an estimate of these frequencies, and correct for the zero-point energy difference, we used the harmonic approximation both for the isolated monomers and the complex. The results indicate that the difference in total zero-point energy is small but it does influence the binding energy. For the MP2/6-311+ +G** this difference is 1.23 kcal/mol. For the B3LYP/6-311+ +G* it amounts to 1.31 kcal/mol and for the MP2/aug-cc-pVDZ it is slightly larger, 1.40 kcal/mol. Thus, correcting for this difference of zero-point energies, we find at the highest level of calculation that the binding energy involved in the hydrogen bonded system HCN:H₂O is close to 2.0 kcal/mol.

Table 6 shows the calculated vibrational frequencies. For the separate moieties we obtain a good agreement with the known experimental result. For water we obtain the frequencies of 1602, 1628 and 1622 cm^{−1} for the ν(a₁) symmetric scissors mode, as compared to the experimental result [30] of 1590 cm^{−1}, for instance. In the complex we find an average increase of 23 cm^{−1} in the vibrational frequency of this ν(a₁) scissors mode. Similarly, we find an average decrease of 36 cm^{−1} of the ν(a₁)

symmetric stretch frequency and a decrease of 25 cm^{−1} of the ν(b₂) frequency. For HCN, the calculated vibrational frequencies are also in very good agreement with the experimental results. After complex formation, the degenerate ν(π) mode increases in frequency and split. The average increase calculated here is less than 10 cm^{−1} with a negligible splitting. For the stretching modes there is an increase of 15 cm^{−1} in the frequency of the symmetric mode and a negligible change in the frequency of the asymmetric mode.

4. Summary and conclusions

The hydrogen bond interaction between HCN and water, where water is the proton donor, HCN:H₂O, has been analyzed by ab initio MBPT/CC. This isomer is found to be stable and may be observed experimentally. Electron correlation effects are relatively small but the basis set may influence this result considerably. The difference between the SCF and the highest correlated method considered here, CCSD(T), is 0.36 kcal/mol with the 6-311+ +G* basis set. The CCSD(T) result for the binding energy is 3.38 kcal/mol. We also find here that the zero point vibrational correction decreases the calculated binding energy by a value between 1.2 kcal/mol and 1.4 kcal/mol. The best result for the binding energy, after correcting for both BSSE and zero-point, at the highest level of calculation, CCSD(T), is only 2.0 kcal/mol. For comparison, the corresponding result

using B3LYP is 2.7 kcal/mol. Vibrational frequency analysis shows that some frequencies are decreased by complex binding whereas others are increased. The magnitudes of the shifts are small. The calculated change in the frequency of the symmetric stretch of HCN is 15 cm^{-1} . The calculated changes in the frequencies of the symmetric and asymmetric stretches of H_2O are, respectively, -36 cm^{-1} and -25 cm^{-1} . Finally, we have analyzed also the $\text{H}_2\text{O}:\text{HCN}$ isomer. We find it to lie energetically below the $\text{HCN}:\text{H}_2\text{O}$ isomer with a binding energy that is larger by 1.8 kcal/mol. The calculated rotational constants for this species are in excellent agreement with the experimental result and we find it to be non-planar with an out-of-plane H_2O bend angle of 23° , as compared with the experimental result of 20° .

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B.2 Theoretical study of mixed hydrogen-bonded complexes:

$\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HCN} \cdots \text{HCN} \cdots \text{H}_2\text{O}$.

R. Rivelino, S. Canuto.

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Theoretical Study of Mixed Hydrogen-Bonded Complexes: $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ and $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$

Roberto Rivelino[†] and Sylvio Canuto*

Instituto de Física, P.O. Box 66318, Universidade de São Paulo, 05315-970 São Paulo, SP, Brazil

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Mixed hydrogen-bonded clusters $\text{H}_2\text{O}\cdots\text{HCN}$, $\text{HCN}\cdots\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$, and $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ are studied by using ab initio calculations. The optimized structures and harmonic vibrational frequencies are obtained at the DFT/B3LYP and MBPT/MP2 levels with the 6-311++G(d,p) basis set. To investigate electron correlation effects on the binding energies, single-point calculations are also performed using the CCSD(T) method with the optimized MP2 geometries. The complexation energies are obtained for these systems including correction for basis set superposition error. In addition, the cooperative effects in the properties of the complexes are investigated quantitatively. We found a cooperativity contribution of around 10% relative to the total interaction energy of the complex $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. In the case of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$, the binding energy of the $\text{HCN}\cdots\text{HCN}$ is ca. 8 kJ/mol stronger in the mixed tetramer than in the corresponding isolated dimer. The effects of higher-order electron correlation are found to be mild, with MP2 giving a well-balanced result. Cooperative effects are predicted either by MP2 or by B3LYP in hydrogen bond distances and dipole moments of the clusters. In contrast, the B3LYP functional fails to account for the out-of-plane bend angle in $\text{H}_2\text{O}\cdots\text{HCN}$, which is well-described by the MP2 method.

1. Introduction

Experiments on photolysis of formaldoxime in an argon matrix¹ have led to the discovery of different complexes containing hydrogen cyanide and water. Other experimental works on microwave spectroscopy^{2,3} have aided characterization of HCN–water complexes. These methods, together with both millimeter-wave and infrared spectra, are also being used to observe a series of other gas-phase molecules existing under special conditions.^{4,5} In particular, HCN–water clusters are of great importance in the role of formation of the ancient organic compounds.^{6–8} From a theoretical point of view, ab initio calculations carried out with appropriate levels of theory have allowed determination of reliable information about rotational constants, infrared spectra, and structural properties of such complexes.^{9–13}

The possible existence of an HCN–water isomer in which the water molecule acts as a proton donor has recently been investigated.^{1,9,14} This isomer ($\text{HCN}\cdots\text{H}_2\text{O}$) was experimentally observed and computationally calculated to be less stable than the ordinary hydrogen-bonded mixed dimer ($\text{H}_2\text{O}\cdots\text{HCN}$) by 5.3 kJ/mol¹. Other theoretical studies have been made by Heikkilä and Lundell¹⁰ for investigating pure dimers of HCN and HNC, Smith et al.,¹¹ Tshela and Ford,¹² and Turi and Dannenberg¹³ performed detailed ab initio calculations on HCN–water mixed dimers. In our previous work,⁹ we have analyzed the equilibrium structures and changes in intramolecular vibrational frequencies of the isomers $\text{HCN}\cdots\text{H}_2\text{O}$ and $\text{H}_2\text{O}\cdots\text{HCN}$ with the many-body perturbation (MBPT) and density-functional theories (DFT). To evaluate the electron correlation effects on binding energies of these dimers, we performed single-point calculations employing the coupled-cluster method, carried out with different basis sets.

The formation of a hydrogen-bonded system, involving two species capable of donating and accepting a proton simultaneously, provides a complex that is both a stronger proton donor and a stronger proton acceptor. This effect is currently attributed to an electron density transfer from the acceptor to the donor across the hydrogen bonding, which can extend itself for a long range of intermolecular interaction, forming chains or cycles, and it is usually known as cooperativity.^{15,16} Experimentally, the cooperative effect can be observed in several hydrogen-bonded systems, including liquids and crystal structures.^{17,18} Theoretically, such interactions have been described as σ -bond cooperativity, in contrast to those with multiple bonds, which are known as π -bond cooperativity.¹⁹ It is common in the literature to employ the term nonadditivity to express the cooperativity quantitatively, as the total interaction energy of a hydrogen-bonded complex on one hand and the sum of all pairwise interactions on the other.²⁰ Further evidence of the cooperative effects arises from consideration of the geometry, dipole moment, and vibration frequencies of hydrogen-bonded clusters. Theoretical studies taking into account of these effects have become an important subject to understand the nature of interactions in many-molecule clusters as they occur in biological, chemical, and physical systems.^{21–23}

This paper is an extension of our previous study on HCN–water complexes to other theoretically predicted linear clusters, namely, the mixed trimer $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ and the mixed tetramer $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. This tetramer is a possible product of the interaction between the two isomers $\text{H}_2\text{O}\cdots\text{HCN}$ and $\text{HCN}\cdots\text{H}_2\text{O}$. Thus, we have made a detailed analysis of the structures, harmonic vibrational frequencies, energetics, and effects of cooperativity on the properties of these complexes. The ab initio calculations used here are the DFT and MBPT/coupled-cluster theories successfully used to investigate HCN–water isomers.⁹

* To whom correspondence should be addressed. E-mail: canuto@if.usp.br. Fax: +55.11.3818-6831.

[†] E-mail: rivelino@if.usp.br.

Figure 1. Structure of the trimer $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$.

2. Computational Aspects

Quantum chemistry computations have been applied to the systems $\text{H}_2\text{O}\cdots\text{HCN}$, $\text{HCN}\cdots\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$, and $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ using the Gaussian 98 program.²⁴ These are the density functional theory with gradient-corrected exchange-correlation (DFT/B3LYP)^{25,26} and the second-order many-body perturbation theory (MBPT/MP2), both carried out with the 6-311++G(d,p) basis set to full optimization of the geometries. After the equilibrium structures are found, at the MP2 and B3LYP levels of theory, we have calculated their vibrational spectra. This guarantees that each optimized structure corresponds to an energy minimum. The MP2 energies have been improved for electron correlation effects by performing single-point calculations with many-body perturbation/coupled cluster methods carried out with the same basis set. These include MP3, MP4, CCSD, and CCSD(T)^{27,28} calculations.

The interaction energies of the clusters have been corrected for basis set superposition error (BSSE) using the counterpoise correction method (CP).^{29,30} The cooperative energy component of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ is defined in the usual manner,²⁰ by considering two reaction routes for obtaining the trimer. The three-body term is computed as the difference between the binding energy of the trimer and the pairwise interaction energies:

$$E_{\text{ABC}} = \Delta E - [\Delta E(\text{AB}) + \Delta E(\text{AC}) + \Delta E(\text{BC})]$$

To evaluate the energetics of the mixed tetramer $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$, we have used a two-body approximation in such a way that the basic moieties are considered as being the dimers $\text{H}_2\text{O}\cdots\text{HCN}$ and $\text{HCN}\cdots\text{H}_2\text{O}$. In this case, the binding energy is computed as the total energy of the tetramer minus the energy sum of the separate dimers. Corrections for zero-point vibration energy are also calculated from the harmonic frequency analysis.

3. Results and Discussion

Geometrical Features of the Mixed Trimer. The optimized geometry of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ is illustrated in Figure 1, and its geometrical parameters are presented in Table 1 at the two levels of calculation (MP2 and B3LYP). The main difference between the results of these methods is the out-of-plane bend angle, δ , that the water molecule forms when it acts as a proton acceptor in the complex. Our calculated MP2 value for δ in $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ is 24° , whereas the B3LYP value is only 7.8° .

As we shall see later, the out-of-plane bend angle calculated in $\text{H}_2\text{O}\cdots\text{HCN}$ at the MP2 level is 23° (see Table 3). This value is in good agreement with the rotational spectroscopy experiments, which furnish 20° .³ For this reason, we believe that in the case of the trimer the MP2 calculations provide more reliable potential surfaces than the B3LYP ones. Another interesting feature observed in the geometry of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ is that the intermolecular distances ($\text{O}\cdots\text{H}$ and $\text{N}\cdots\text{H}$) are shorter at the B3LYP level than those obtained from MP2 calculations. The cooperativity in the hydrogen bond distances appears when we compare the $\text{O7}\cdots\text{H6}$ distance in the trimer with the

TABLE 1: Geometry of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$ Complex Computed with Different Methods^a

geometry	MP2/6-311++G(d,p)	B3LYP/6-311++G(d,p)
O2-H1	0.959	0.961
O2-H3	0.964	0.968
N4-H3	2.128	2.098
C5-N4	1.170	1.149
C5-H6	1.077	1.079
O7-H6	2.031	1.987
O7-H8	0.961	0.963
O7-H9	0.961	0.963
H1-O2-H3	103.0	104.6
H8-O7-H9	104.2	106.0
δ (deg)	24.0	7.8
μ (D)	7.86	7.93
I_A (GHz)	150.405	200.700
I_B (GHz)	1.007	1.026
I_C (GHz)	1.005	1.026

^a Distances are given in Å, and angles are given in deg. The out-of-plane angle, δ , dipole moment, μ , and rotational constants (I_A , I_B , I_C) are also shown.

corresponding one in the dimer $\text{H}_2\text{O}\cdots\text{HCN}$. The latter distance has been computed as 2.067 Å (at the MP2 level), showing that when a second H_2O molecule is added as a proton donor, it contracts the $\text{O7}\cdots\text{H6}$ distance by about 0.04 Å.

Table 1 also gives the dipole moments of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. The dipole moment of the complex is slightly larger than the dipole sum of the three individual monomers. For example, at the MP2 level, the sum is 7.84 D, compared to the calculated value of 7.86 D for the trimer. At the B3LYP level, this increase becomes more meaningful, from 7.37 to 7.93 D, respectively. This dipole increment can be understood by cooperative polarization effect when the hydrogen-bonded chain grows. Rotational constants are also shown in Table 1. Because the trimer has not been observed experimentally, a direct comparison with observed rotational constants cannot be made. Judging from our previous result on the $\text{H}_2\text{O}\cdots\text{HCN}$ isomer,⁹ we believe that the I_B and I_C constants are accurate within 1% or less.

Complexation Energies of $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. The components of the complexation energy of the mixed trimer are reported in Table 2. Comparison with the SCF results allows separation of the contribution of the electron correlation effects. All results were corrected for BSSE using the counterpoise method. They are organized in two different paths for obtaining the trimer, $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$. First, we combine a H_2O molecule with HCN forming the most stable dimer, $\text{H}_2\text{O}\cdots\text{HCN}$, which we call dimer I. This is added to another H_2O molecule acting as a proton donor (Path I). The same complex is obtained in Path II, in which one combines HCN plus H_2O , forming the less stable dimer, $\text{HCN}\cdots\text{H}_2\text{O}$ or dimer II, and then adds the second H_2O molecule as a proton acceptor. The two procedures are given in the following scheme:

Path I

Path II

The total energy of the trimer is, of course, the same, regardless of the path chosen. Comparison of reactions I-B and II-A at

TABLE 2: Complexation Energies (in kJ/mol) and Cooperative Effect in H₂O...HCN...H₂O Complex Computed with the 6-311++G(d,p) Basis Set^a

energy	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4	CCSD	CCSD(T)	B3LYP
E(I-A)	-21.17	-19.48	-19.73	-19.05	-18.93	-18.84	-18.84	-18.93	-21.80
E(I-B)	-15.32	-17.98	-16.69	-16.58	-16.79	-17.36	-16.61	-17.11	-21.61
E(II-A)	-11.70	-14.59	-13.27	-13.19	-13.39	-13.97	-13.21	-13.71	-14.61
E(II-B)	-24.79	-22.86	-23.16	-22.44	-22.33	-22.23	-22.25	-22.33	-28.80
total ^b	-36.49	-37.45	-36.42	-35.63	-35.71	-36.20	-35.45	-36.04	-43.41
cooperative ^c	-3.62	-3.39	-3.42	-3.39	-3.40	-3.39	-3.40	-3.41	-6.99
three-body ^d	-2.42	-2.27	-2.32	-2.29	-2.31	-2.31	-2.31	-2.32	-5.91

^a All results are corrected for BSSE. ^b $E(\text{I-A} + \text{I-B}) = E(\text{II-A} + \text{II-B})$. ^c $E(\text{I-B} - \text{II-A}) = E(\text{II-B} - \text{I-A})$. ^d $E_{\text{ABC}} = E(\text{ABC}) - [E(\text{AB}) + E(\text{AC}) + E(\text{BC})] + [E(\text{A}) + E(\text{B}) + E(\text{C})]$.

Figure 2. Calculated structures of the HCN–water complexes: (a) the less stable dimer II; (b) the more stable dimer I; (c) the tetramer.

the MP2 level shows that H₂O, acting as a proton donor, bonds more strongly to the dimer I (17.98 kJ/mol) than to the isolated HCN molecule (14.59 kJ/mol), as indicated by the energy differences in Table 2. A similar comparison between reactions I-A and II-B shows that the H₂O molecule is a better proton acceptor when it is added first to the dimer II (22.86 kJ/mol) than to a single HCN molecule (19.48 kJ/mol). The energy enhancement in the trimer formation is better described by the cooperative energy (Table 2) of 3.4 kJ/mol, calculated with the MP2 method (and about twice that amount for the B3LYP level).

It is interesting to note that in this case the cooperative effects are not very much dependent on the electron correlation contribution beyond MP2. For instance, one can note that the binding energy changes from 35.7 kJ/mol to 36.2 kJ/mol by including triple excitation in fourth-order. However, the contribution to the cooperative effects is only 0.01 kJ/mol. Similarly, the cooperativity contribution using CCSD or CCSD(T) is the same. By far, most of the cooperativity is obtained already in MP2. On the other hand, the DFT/B3LYP model seems to overestimate significantly these quantities, giving results that are more than twice those obtained at the CCSD(T) level.

The cooperative energy terms calculated in Table 2 take into account the contributions arising from the interaction between the two terminal water molecules. Thus, we have also computed the three-body term by defining it as the total binding energy of the trimer minus the interaction energy of each pair of monomers with all of them frozen in the geometry of the trimer.²⁰ As it can be seen, the three-body contribution is small, being less than 2.5 kJ/mol, in all theoretical models considered here, except to the B3LYP level. This corresponds to only ~6% of the total complexation energy. Again, electron correlation effects seem to be less important for the three-body terms reported in Table 2. As noted before by Chalasinski and Szczesniak,³¹ these energy components are reasonably well-described at the SCF level. In fact, the cooperative energy is

computed as being -3.62 kJ/mol (and -2.42 kJ/mol for the three-body term) with SCF calculation, while at the highest level, CCSD(T), these terms are -3.41 kJ/mol (and -2.32 kJ/mol). This behavior holds for any level of higher-order electron correlation calculated in the MBPT/coupled-cluster series (Table 2).

Dimer and Tetramer Geometries. The structures of the mixed dimers, H₂O...HCN and HCN...H₂O, and the tetramer, H₂O...HCN...HCN...H₂O, are shown in Figure 2. The geometries of these systems are also fully optimized at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. The geometrical parameters for their equilibrium structures are presented in Table 3. We observe that the O10...H9 bonding is shorter in the resultant tetramer by 0.05 Å at the MP2 level and 0.06 Å at the B3LYP level relative to the dimer I. A similar result is also obtained when H₂O acts as a proton donor. For this case, an enhancement in the calculated N4...H3 distance (0.03 Å with MP2 and 0.05 Å with B3LYP) can still be seen. A more significant decrease is observed in the N7...H6 bonding; it is 0.1 Å with respect to the corresponding bonding in the HCN...HCN dimer (calculated as 2.271 Å at the MP2 level).

These effects of cooperativity are less apparent in the intramolecular geometry (Table 3). For instance, the H–O–H angle remains essentially constant when the complex increases. On the other hand, the intermolecular O2–H3–N4 angle is slightly more sensitive; it varies 3.5° from the dimer II to the tetramer with either MP2 or B3LYP. Conversely, as we have discussed previously, the δ bend angle (which indicates how the proton acceptor H₂O molecule is out-of-plane in the complex) is better described with the MP2 method. For this level of theory, our calculated δ is 23° in the dimer I and 21° in the tetramer (Table 3). The values obtained with the B3LYP calculations are only 3.2° and 0.5°, respectively. Indeed, experimental results for the dimer I give an angle of 20°.³ It is also interesting to observe here a cooperative polarization effect

TABLE 3: Optimized Geometries of the HCN–Water Dimers and Tetramer^a

geometry	MP2/6-311++G(d,p)			B3LYP/6-311++G(d,p)		
	dimer I	dimer II	tetramer	dimer I	dimer II	tetramer
O2–H1		0.959	0.959		0.961	0.961
O2–H3		0.963	0.965		0.967	0.968
N4...H3		2.167	2.140		2.140	2.093
C5–N4		1.170	1.170		1.480	1.149
C5–H6		1.068	1.077		1.067	1.078
N7...H6			2.173			2.129
C8–N7	1.172		1.170	1.150		1.149
C8–H9	1.076		1.078	1.077		1.080
O10...H9	2.067		2.015	2.028		1.969
O10–H11	0.961		0.961	0.963		0.963
O10–H12	0.961		0.961	0.963		0.963
H1–O2–H3		103.2	102.9		104.8	104.6
O2–H3–N4		179.1	175.5		178.5	175.1
H11–O10–H12	104.1		104.2	105.9		106.2
δ (deg)	23.0		21.0	3.2		0.5
μ (D)	6.06	5.36	12.34	5.85	5.11	12.17
I_A (GHz)	401.031	481.461	124.641	423.923	524.624	181.396
I_B (GHz)	3.046	3.176	0.329	3.121	3.235	0.337
I_C (GHz)	3.027	3.155	0.329	3.099	3.215	0.337

^aDistances are given in Å and angles are given in deg. The out-of-plane angle, δ , dipole moment, μ , and rotational constants (I_A , I_B , I_C) are also shown.

TABLE 4: Influence of Electron Correlation and Counterpoise Correction on the Binding Energies (in kJ/mol) of the Mixed Tetramer Relative to the Separate Dimers I and II and (HCN)₂^a

method	no counterpoise correction				counterpoise correction			
	tetramer	dimer I	(HCN) ₂	dimer II	tetramer	dimer I	(HCN) ₂	dimer II
SCF	27.82	23.13	18.90	13.50	26.84	21.41	17.67	12.04
MP2	28.58	25.25	19.49	16.97	26.08	19.67	17.72	14.80
MP3	27.66	24.97	18.83	16.05	25.13	19.94	16.73	13.50
DQ-MP4	27.56	24.34	18.84	15.84	25.09	19.30	16.84	13.46
SDQ-MP4	27.77	24.51	18.91	16.05	25.25	19.18	16.94	13.63
MP4	28.22	25.15	19.16	16.68	25.46	19.07	17.15	14.17
CCSD	27.39	24.32	18.63	15.93	24.89	19.10	16.62	13.46
CCSD(T)	27.82	24.98	18.89	16.47	25.12	19.16	16.81	13.96
B3LYP	28.54	24.45	19.99	15.84	27.73	22.27	17.96	15.13

^a Values were computed with the 6-311++G(d,p) basis set. Differences in zero-point vibration energy in the tetramer are 3.75 and 4.77 kJ/mol for the calculated frequencies with the MP2 and B3LYP methods, respectively.

on the dipole moment of H₂O...HCN...HCN...H₂O. The additive MP2 dipole moment of the two HCN–water dimers gives 11.42 D, while the dipole moment of the tetramer is 12.34 D (these are 10.96 and 12.17 D, respectively, with the B3LYP functional). This formation of the tetramer leads to an increase of about 10% in the combined dipole moment.

H₂O...HCN...HCN...H₂O. The full treatment of the interaction energy of H₂O...HCN...H₂O has shown that the three-body contribution to its total binding energy amounts to only 6%. In previous investigations, it has also been noted that four-body contribution is negligible in the water tetramer¹⁵ and is only ~10% of the three-body contribution.^{16,20} Although the partitioning of the energy in the many-body components is an important issue, our major interest lies in the cooperative effects in the HCN...HCN binding. Here, we are interested in obtaining the interaction energy between the two mixed dimers, HCN...H₂O (Figure 2a) and H₂O...HCN (Figure 2b), leading to the formation of H₂O...HCN...HCN...H₂O and then making a direct comparison with the simpler HCN...HCN, as well as the isolated dimers I and II. Thus, the energetics to form the tetramer (in the fully optimized MP2 and B3LYP geometries) are reported in Table 4 and compared with (HCN)₂.

We can see that the B3LYP method gives the largest binding energy for the tetramer, 27.73 kJ/mol, whereas the MP2 result is 26.08 kJ/mol after counterpoise correction. This result reinforces the trend that DFT overestimates binding energies.³² Our values for the binding energies increase when various

hydrogen bonds are involved in the cluster formation. For comparison, the calculated binding energy of the HCN...HCN dimer is 17.72 kJ/mol at the MP2 level with counterpoise correction. This result reflects the electron charge redistribution in the electronic structure of each subunit making the dimer I a stronger proton acceptor and the dimer II a better proton donor when they interact to form the tetramer. Here, the correlation effects investigated with the MBPT/coupled-cluster methods also seem to be not very important. After counterpoise correction, the result obtained with CCSD(T) differs from SCF by less than 2 kJ/mol. In any case, the effect of electron correlation decreases the calculated binding energy. We observe that the contribution of triple excitation at higher order, as obtained from the difference between MP4 and CCSD(T), is only 0.34 kJ/mol. On the other hand, the basis set superposition error gives a larger variation on the binding energies. The counterpoise correction with the MBPT methods is 2.5 kJ/mol, although with the B3LYP functional this effect is only 0.8 kJ/mol. Considering the correction due to zero-point vibration (3.75 kJ/mol at MP2 level), we estimate a binding energy of 22.3 kJ/mol with respect to dissociation of the tetramer into two dimers, H₂O...HCN and HCN...H₂O, after breaking the HCN...HCN bond. This illustrates the large cooperative effect derived from the water molecules because this value is more than 8 kJ/mol higher than in the isolated HCN...HCN dimer dissociation (for which the calculated zero-point vibration energy is 3.43 kJ/mol at the MP2 level). Indeed, this cooperative effect is large and essentially

TABLE 5: Computed Frequencies (in cm^{-1}) of Intramolecular Vibrational Modes in the Trimer Compared to HCN and H_2O Molecules^a

normal modes ^c	basic moieties ^b			$\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$	
	MP2	B3LYP	expt ^d	MP2	B3LYP
HCN stretching (π)	729	767	712	888	897
HCN bending (π)	729	767	712	924	930
H_2O scissor (a_1)	1628	1602	1590	1664 (1661)	1628 (1633)
HCN stretching (σ)	2016	2197	2097	2029	2192
HCN asym stretch (σ)	3482	3452	3311	3356	3297
H_2O stretching (a_1)	3884	3817	3638	3835 (3872)	3746 (3817)
H_2O asym stretch (b_2)	4003	3923	3733	3975 (3983)	3894 (3918)

^a Data were obtained with the 6-311++G(d,p) basis set. ^b Refer to the H_2O and HCN molecules. ^c Relative to the isolated moieties. ^d References 33 and 34.

TABLE 6: Frequency (in cm^{-1}) Shifts in the Tetramer Relative to the Dimers^a

normal modes ^b	$\text{H}_2\text{O}\cdots\text{HCN}$		$\text{HCN}\cdots\text{H}_2\text{O}$		$\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}_2\text{O}$			
	MP2	B3LYP	MP2	B3LYP	MP2		B3LYP	
$\nu(\pi)$ bending	877	880	736	774	890	869	908	894
$\nu(\pi)$ bending	908	909	738	775	929	873	941	896
$\nu(a_1)$ scissor	1642	1627	1654	1625	1665	1645	1636	1629
$\nu(\sigma)$ sym stretch	2015	2182	2031	2209	2043	2030	2195	2189
$\nu(\sigma)$ asym stretch	3375	3321	3481	3452	3349	3334	3308	3279
$\nu(a_1)$ sym stretch	3874	3818	3851	3769	3872	3832	3814	3743
$\nu(b_2)$ asym stretch	3989	3921	3979	3898	3987	3974	3917	3893

^a Data were computed with the 6-311++G(d,p) basis set. ^b Relative to H_2O and HCN vibrational modes.

independent of the electron correlation effects. For instance, it amounts to 8.36 (MP2), 8.31 (MP4), and 8.31 kJ/mol (CCSD(T)) in different treatments. At the SCF level, it gives an over-estimated value of 9.17 kJ/mol. The B3LYP results are closer to the SCF than the MBPT/CC values, giving a cooperative effect of 9.77 kJ/mol. For comparison, we also report in Table 4 the binding energy calculated at MBPT/coupled-cluster level for the dimers I and II. Our best result of 16.8 kJ/mol for $(\text{HCN})_2$ agrees very well with the one of Heikkilä and Lundell¹⁰ (also 16.8 kJ/mol) using a larger basis set 6-311++G(2d,2p).

Vibrational Analysis of the Complexes. The frequency shift in infrared spectroscopy is a very useful tool for the characterization of hydrogen-bonded clusters. In the systems studied here, water acts as both acceptor and donor of proton. When it is a proton donor, there appears a large negative shift of the O—H stretching vibrations. In both trimer and tetramer, H_2O acts as a proton donor at one end and a proton acceptor at the other. The calculated vibrational modes for these complexes are given in Tables 5 and 6, respectively. Table 5 shows that the degenerate π mode of HCN splits in the trimer, but both undergo a large positive shift. The σ stretching vibrations change a little for the symmetric case but undergo a large red shift in the case of the asymmetric stretching. The magnitude of this shift is -126 (MP2) and -155 cm^{-1} (B3LYP).

The changes in the water spectrum are now interesting because of the vibration split of the separate molecules. The bending (scissor) mode of H_2O shows a small splitting of 3 (MP2) and 5 cm^{-1} (B3LYP), which are blue-shifted compared to the individual vibrations. These shifts are $+36$ (MP2) and $+26$ cm^{-1} (B3LYP) when H_2O acts as a proton donor and $+32$ (MP2) and 31 cm^{-1} (B3LYP) when it acts as a proton acceptor. More pronounced splitting is found for the stretching vibration of water. In this case (at the MP2 level), the symmetric stretching of H_2O splits by $+37$ cm^{-1} corresponding to shifts of -49 and -12 cm^{-1} of the individual molecules. The respective B3LYP calculated shifts are larger, except when water is a proton acceptor, for which no shift is calculated. A very similar behavior is also obtained for the asymmetric vibrational mode at the two levels of theory.

In Table 6, the calculated frequencies are shown for the tetramer in comparison with those of the two HCN—water dimers. Each vibrational frequency is split because of the presence of these dimers in the complex. For this reason, we analyzed the vibrational changes based on the average frequencies for the dimers I and II and the average frequency splitting in the tetramer spectrum. At the MP2 level of calculation, the average symmetric and asymmetric stretching modes of H_2O are -11 and -4 cm^{-1} , respectively, whereas for the scissor mode, the value is $+7$ cm^{-1} . All of the average bending vibrational frequencies are positively shifted by 73 and 78 cm^{-1} . The average symmetric stretching of HCN is also blue-shifted by 14 cm^{-1} . However, the asymmetric mode is considerably red-shifted by 87 cm^{-1} .

At the B3LYP level, the average frequency shifts from the separate moieties to the tetramer spectrum are in agreement with the MP2 calculations, except for the symmetric stretching of HCN, calculated as -4 cm^{-1} (while the corresponding MP2 value is $+14$ cm^{-1}). Our calculated B3LYP average changes are the blue shifts of 74 and 77 cm^{-1} for the bending modes and the red shifts of 93 cm^{-1} for the asymmetric stretching mode of HCN and 15 and 5 cm^{-1} for the symmetric and asymmetric stretching modes, respectively, of H_2O .

4. Conclusion

Ab initio calculations at the MBPT/MP2 and DFT/B3LYP levels of theory with the 6-311++G(d,p) basis set have been performed for investigating equilibrium structures, vibrational spectra, energetics, and cooperative effects on the properties of mixed HCN—water clusters. Correlation effects and counterpoise correction have been systematically analyzed. High-order electron correlation effects are found to give only a minor contribution to the binding. The contribution beyond fourth-order, as obtained by the difference between MP4 and CCSD(T), decreased the binding energy by 0.16 kJ/mol in $\text{H}_2\text{O}\cdots\text{HCN}\cdots\text{H}_2\text{O}$, 0.27 kJ/mol in $\text{HCN}\cdots\text{HCN}$, and 0.34 kJ/mol in $\text{H}_2\text{O}\cdots\text{HCN}$ and $\text{HCN}\cdots\text{H}_2\text{O}$. From CCSD to CCSD(T), the correlation contribution amounted to only 0.60, 0.26, and 0.23

kJ/mol, respectively, in the interaction of these clusters. Counterpoise correction amounts to 2.5 kJ/mol in the binding energies of both the tetramer and (HCN)₂.

The B3LYP results for the binding energies of the trimer and tetramer have been larger than those calculated with MP2. The intermolecular distances were also calculated to be shorter with the B3LYP functional. This trend observed in applying DFT/B3LYP for the hydrogen-bonded clusters has also been noted before.³² Also in this present study, we note that this functional has not described correctly the out-of-plane bend angle, present in the complexes when H₂O acts a proton acceptor. This angle is known in the case of the H₂O...HCN dimer and is correctly described by MP2. By using different correlated methods, we could verify that most of the cooperative effects were already obtained at the MP2 level and that the high-order correlation effects were less important. The electrostatic contribution in the hydrogen-bonded clusters has led to increased dipole moments. For instance, the dipole moments of the trimer and tetramer were larger than the sum of the separate moieties by about 1 D. We have estimated that the cooperativity contribution to the binding energy of the mixed trimer accounts for about 10% of the total interaction energy, which is in agreement with other recent studies.²² In the case of the mixed tetramer, H₂O...HCN...HCN...H₂O, the energy associated with the HCN...HCN hydrogen bonding is ca. 8 kJ/mol larger than that in the corresponding isolated dimer. This cooperative effect is well-described by the MBPT/CC methods, and the large-order electron correlation effects are found to be very small, being well-described by MP2. The cooperative effects are more difficult to be described in the vibrational spectra of the complexes studied here. The calculated intramolecular harmonic frequencies changed little by the presence of the hydrogen bonds. However, we note that all of the O—H...N stretching bands were shifted to lower frequencies. Finally, this study presents a systematic analysis of hydrogen-bonded HCN—water clusters and the effects on structures, binding, infrared spectra, and cooperativity.

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**B.3 Theoretical studies of hydrogen bonding in water-cyanides
and in the base pair Gu-Cy.**

R. Rivelino, V. Ludwig, E. Rissi, S. Canuto.

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Theoretical studies of hydrogen bonding in water–cyanides and in the base pair Gu–Cy

Roberto Rivelino, Valdemir Ludwig, Eduardo Rissi, Sylvio Canuto*

Instituto de Física, P.O. Box 66318, Universidade de São Paulo, 05315-970 São Paulo, SP, Brazil

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Abstract

Density-functional (DFT) and many-body-perturbation theories (MBPT/CC) are used to study the hydrogen bonding in the water–cyanide complexes $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ and $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$. Structures, binding energies and changes in vibrational frequencies are analyzed. The calculated $\text{C}\equiv\text{N}$ stretching frequency is found to shift to the blue upon complexation in $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ and $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$. To investigate electron correlation effects on the binding energies of these complexes, single-point calculations are performed at the MBPT/CC (MP2, MP3, MP4, CCSD and CCSD(T)) levels using the optimized MP2 geometries. Binding energies are also obtained at different levels of DFT (B3LYP and PW91) and compared with the MBPT/CC results. All calculations include corrections for basis set superposition error (BSSE) and zero-point vibrational energies. Additionally, the triple hydrogen-bonded guanine–cytosine (Gu–Cy) base pair is analyzed. The binding energy of the Watson–Crick model for Gu–Cy is calculated using the Hartree–Fock calculations and DFT (B3LYP and BP86) methods. The results for the hydrogen bonding distances and binding energies are in good agreement with experimental and recent theoretical values. The calculated dipole moment of the Gu–Cy complex is compared with the direct vector sum of the isolated bases. After taking into account the BSSE effects we find that the electron polarization due to the hydrogen binding leads to an increase of $\sim 20\%$ of the calculated dipole moment of the complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio; Hydrogen bond; Water–cyanides; Base pair

1. Introduction

In recent years quantum-mechanical calculations of hydrogen bonding have attracted theoretical chemists, physicists and biologists [1–3]. The importance of hydrogen-bonded systems has long been known, although the understanding of its nature is not yet complete. It has been recognized that non-conventional hydrogen bonds can be formed by C^αH

groups in peptides [4]. These non-conventional bonds are also known to be valuable in folding of polysaccharides [5] and nucleic acids [6,7]. Hydrogen bonding is indeed an important type of intermolecular interaction that is responsible for remarkable changes in the properties of various complexes. These can be solids, liquids, or large clusters [2,8]. However, most theoretical studies have concentrated in relatively small hydrogen-bonded clusters, because they allow investigation at high-level quantum-chemical calculations. There is a wide range of phenomena involving hydrogen-bonded systems, which can be accounted for by means of quantum-mechanical calculations.

* Corresponding author. Tel.: +55-11-3818-6983; fax: +55-11-3818-6831.

E-mail address: canuto@if.usp.br (S. Canuto).

For example, chirality on the intermolecular interactions [9], cooperativity or non-additivity phenomenon [10–13] and solvatochromic shift in absorption transition [14–22], have been consistently investigated in the framework of hydrogen bonding.

The appropriate level of theory to provide reliable information for the hydrogen-bonded complexes has been another interesting subject [23]. It has greatly increased the use of density functional theory (DFT) in the calculations of structure and energetics of hydrogen-bonded systems [23–30]. The main advantage in utilizing DFT is the lower computational effort compared to high-level *ab initio* quantum-chemical calculations. For this reason, density-functional methods with linear scaling to treat very large systems have consistently been implemented [25,26,31,32]. On the other hand, for smaller systems, the many-body perturbation theory (MBPT) [33] offers the possibility to investigate separate many-body energy contributions and polarizations involved in the binding interaction of molecular clusters [3,34]. Understanding the many-body effects is also very useful to describe parameterized force fields for using in computational simulations of larger scale processes [26,31].

In this work, we study the influence of hydrogen-bonding in the structures, vibrational spectra, dipole moments, and binding energies of small molecular complexes based on MBPT [33] and DFT [35] calculations. The present study focuses on the structural and energetic aspects of hydrogen-bonded clusters. The influence of electron correlation effects and basis set superposition error (BSSE) on the binding energies are systematically analyzed. Of particular interest in the experimental characterization of hydrogen-bonded systems is the change in the vibrational frequencies due to the complexation. Thus, frequency calculations for the three hydrogen-bonded water–cyanide complexes $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ are performed. The vibrational frequency shifts of $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ compared to isolated $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ have special interest [36,37]. Additional interest lies also in the Watson–Crick [38] model for triple hydrogen-bonded guanine–cytosine (Gu–Cy) base pair. Considerable effort has been dedicated to the proper theoretical treatment to describe the hydrogen bond lengths and binding energy. Studies carried at both the

DFT and MP2 levels were able to obtain a reasonably accurate description. Here we want to analyze the electron correlation effects obtained at the DFT level by comparing the results with the Hartree–Fock level. Recent studies of stacking of DNA basis have emphasized the role of dispersion interaction [28]. Another interesting aspect of the Gu–Cy complexation is the mutual orientation of the dipole moments with the possible additivity to give the total dipole moment of the complex. Hence we compare the dipole moment of the complex with the vector sum of the dipole moment of the isolated monomers. In this we also take into account the BSSE effects.

2. Computational details

We have employed both many-body perturbation/coupled-cluster theories (MBPT/CC) [33,39] and DFT [35,40–45] to calculate the optimized structures, binding energies and dipole moments of the $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, and $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ systems. Geometry optimizations are performed at the second-order Møller–Plesset theory (MP2), as well as DFT, with the 6-311++G(d,p) basis set, that includes diffuse and specially polarization functions, known to be necessary for a proper treatment of hydrogen-bonded complexes at the correlated levels of theory [13,46,47]. At DFT level, we have employed the Becke's three-parameter hybrid functional combining Lee–Yang–Parr correlation term (B3LYP) [42], and the Perdew–Wang's exchange and correlation functionals (PW91) [44], with the same 6-311++G(d,p) basis set. From the optimized structures we have also calculated the vibrational spectra of all the cyanide–water systems. After obtaining the optimized structures and harmonic normal modes at the MP2 level, single-point calculations are performed using MBPT/CC theories, which includes MP3 and MP4 as well as the more sophisticated coupled-cluster models such CCSD [39] and CCSD(T) [33]. At the highest level, the calculations are carried out at the CCSD(T) level from optimized geometry obtained at the MP2 level. This is normally termed as CCSD(T)//MP2/6-311++G(d,p). For the multiple hydrogen-bonded Gu–Cy complex Hartree–Fock (HF) calculations, as well as Becke's one-parameter hybrid functional with

Table 1
Bond lengths (in Å), rotational constants (in GHz) and dipole moments (in D) for the different water–cyanide complexes. Bond lengths for the isolated cyanides are given in parenthesis. Data computed with the 6-311++G(d,p) basis set

	H–C≡N···H ₂ O			H ₃ C–C≡N···H ₂ O			(CH ₃) ₃ C–C≡N···H ₂ O		
	MP2	B3LYP	PW91	MP2	B3LYP	PW91	MP2	B3LYP	PW91
N···H	2.167	2.138	2.081	2.108	2.080	2.021	2.346	2.283	2.241
C≡N	1.170(1.171)	1.147(1.149)	1.158(1.160)	1.172(1.174)	1.151(1.153)	1.162(1.164)	1.177(1.176)	1.155(1.154)	1.166(1.165)
H–C	1.068(1.066)	1.067(1.067)	1.074(1.074)	–	–	–	–	–	–
C–C	–	–	–	1.463(1.463)	1.455(1.457)	1.452(1.454)	1.473(1.473)	1.473(1.474)	1.470(1.472)
B	3.046	3.238	3.306	1.747	1.762	1.790	1.655	1.553	1.604
A	3.026	3.218	3.285	1.733	1.752	1.779	1.412	1.354	1.388
μ(complex)	5.36	5.10	5.07	6.26	6.15	6.18	2.47	2.31	2.29
μ(cyanide)	3.32	3.06	2.98	4.30	4.05	4.02	4.48	4.19	4.14

Perdew correlation term (BP86) [40,43], MP2//HF/6-31G(d,p), and B3LYP/6-31G(d,p) are performed to study the binding energy and the combined dipole moment, in terms of the dipole moment of the separate parts. For this, we have employed the 6-31G(d,p) basis set leading to a total of 335 contracted Gaussian basis functions. Binding energies and dipole moments of the hydrogen-bonded complexes, obtained with all above methods, are corrected for BSSE [48] with the counterpoise method (CP) [49], and zero-point vibrational energy (ZPE) from the harmonic frequency analysis. All calculations have been performed with the GAUSSIAN-98 program [50].

3. Results and discussion

3.1. Water–cyanide complexes

Water and organic cyanides are known to form hydrogen-bonded complexes of great interest in the physical chemistry of the interstellar space [51]. Water–cyanide complexes are also of great importance in the study of hydrogen bonds of polar molecules. H₃C–C≡N···H₂O, in particular, has been detected experimentally in super-sonic beam expansion experiment [36] and the dipole moment of the complex has been used in the possible characterization of its isomeric form. Here, following our previous studies on HCN–water complexes [13,34], we investigate the structures and properties of three hydrogen-bonded systems with the cyanides H–C≡N (hydrogen cyanide), H₃C–C≡N (methyl cyanide), and (CH₃)₃C–C≡N (*t*-butyl cyanide). The results for the optimized geometries of these complexes are summarized in Table 1. It is interesting to note that while the OH distance is increased upon complexation, the calculated C≡N distances in the hydrogen-bonded cyanides are slightly shorter than in the isolated species, except in the (CH₃)₃C–C≡N case. This will have consequences in the calculated vibrational frequency shifts. All the hydrogen bond distances calculated with DFT methods are shorter than that calculated at the MP2 level. To aid on possible identification of these species by millimeter wave we also give the calculated rotational constants. The calculated dipole moments of the three complexes are also given. The vector addition of the

Table 2

Influence of counterpoise (CP) correction and electron correlation on the binding energies (BE in kcal/mol) in three water–cyanide complexes. Data computed with MBPT/CC and DFT employing the 6-311++G(d,p) basis set

Method	HCN··H ₂ O		H ₃ CCN··H ₂ O		(CH ₃) ₃ CCN··H ₂ O	
	BE	BE + CP	BE	BE + CP	BE	BE + CP
HF	3.23	2.88	4.03	3.67	3.43	3.19
MP2 ^a	4.06	3.54	5.05	4.33	6.11	4.52
MP3	3.84	3.23	4.81	4.05	5.69	4.22
DQ-MP4	3.79	3.22	4.71	3.97	5.44	4.03
SDQ-MP4	3.84	3.26	4.77	4.03	5.56	4.12
MP4	3.99	3.39	4.97	4.19	6.08	4.39
CCSD	3.81	3.22	4.73	3.99	5.49	4.07
CCSD(T)	3.94	3.34	4.92	4.13	5.95	4.32
B3LYP ^b	3.79	3.62	4.82	4.56	4.42	4.08
PW91 ^c	4.52	4.28	5.68	5.37	5.73	5.40

^a ZPE = 1.23, 1.31, 1.06 kcal/mol, respectively.

^b ZPE = 1.29, 1.39, 1.33 kcal/mol, respectively.

^c ZPE = 1.29, 1.38, 1.32 kcal/mol, respectively.

individual dipole moments gives more than 90% of the total calculated dipole moment of the complex in the case of H–C≡N··H₂O and H₃C–C≡N··H₂O. Inclusion of CP correction leads to only minor changes in the dipole moments of the cyanides. The magnitude order of these typical changes is of 0.01 D. In the case of (CH₃)₃C–C≡N··H₂O the dipole moments have a large anti-parallel component. The optimized geometries described in Table 1 were next used to calculate the binding energies of all the three complexes using different theoretical models. Table 2 shows the calculated binding energies. As it can be seen they are all stable complexes but the (CH₃)₃C–C≡N··H₂O is more strongly bound. At the CCSD(T) level it is more bound than H–C≡N··H₂O by 0.98 kcal/mol and more bound than H₃C–C≡N··H₂O by 0.19 kcal/mol, after CP correcting for BSSE. These energy differences increase after considering the contribution of ZPEs. As Fig. 1 suggests, in this isomer we are considering the water molecule playing not only the role of the hydrogen donor but also some acceptor role, with the oxygen atom of water connecting with the CH₃ of *t*-butyl cyanide. A similar isomer has been suggested to exist, based on HF calculations [37], in the case of methyl cyanide but this was calculated here to be unbound at a higher level of theory such as simple MP2. The CCSD(T) calculations are made at the geometries optimized at the MP2 level. As the structures are

calculated at the MP2 level we first analyze the results obtained at this level. They show that electron correlation effects increase the binding energy and BSSE amounts to less than 1 kcal/mol for H–C≡N··H₂O and H₃C–C≡N··H₂O. For (CH₃)₃C–C≡N··H₂O this error is found to be larger amounting to 1.6 kcal/mol at the MP2 level. Higher-order correlation contribution, as obtained by CCSD(T), systematically decreases the binding energies obtained at the MP2 level by 0.2 kcal/mol (CP corrected). It is worth noting that high-order triple excitation obtained by the difference between the CCSD(T) and CCSD results leads to an increase in binding energy of 0.12 kcal/mol (H–C≡N··H₂O), 0.14 kcal/mol (H₃C–C≡N··H₂O) and 0.25 kcal/mol ((CH₃)₃C–C≡N··H₂O). These values are equivalent to those obtained by fourth-order triple-excitations; i.e. 0.13, 0.16 and 0.27 kcal/mol, respectively. Hence, the contribution of triple excitations to the binding energy is already well obtained at fourth-order in perturbation theory. High-order single- and double-excitations, in turn, can be separated using the difference between the CCSD and MP2 results. These give values that are negative and more significant for the larger systems; i.e. –0.32, –0.34 and –0.54 kcal/mol, respectively. As it can be seen, the difference between the MP2 and the CCSD(T) results is a constant value of 0.2 kcal/mol. As a conclusion, higher-order electron correlation effects

Fig. 1. Structures of the water–cyanide complexes.

are partially cancelled and this explains why MP2 calculations [4,34] are a viable alternative to the theoretical calculation of hydrogen-bonded systems. As to the DFT results we can note in Table 2 that B3LYP gives values that are similar to the MP2 results. The PW91 results for the binding energies are slightly higher, by $\sim 20\%$. Tsuzuki and Lüthi [52] have argued based on systematic calculations that the PW91 functional works better than most current functionals for obtaining binding energies of van der Waals and hydrogen-bonded complexes. They found an average difference of approximately 30% in binding energy between MP2 and PW91 in reasonably good agreement with the experimental data [52]. These theoretical results obtained here predict that the

$\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ is stable with a binding energy of ~ 3.0 kcal/mol (after correcting for the difference in ZPEs) and a dipole moment of ~ 6.0 D which is only slightly higher than the experimentally inferred value of 5.5 D [36]. Similar conclusions can be reached for the other species.

The changes in vibrational frequencies due to the complexation are a useful tool to characterize the species [36]. The hydrogen-bonded species has six vibrational modes that do not correspond to any vibrations of the isolated molecules. These are the intermolecular and anharmonic vibrations that are located in the lowest part of the infrared spectrum. In fact most of these transitions lies below the usual 400 cm^{-1} limit of most spectrometers. The $\text{C}\equiv\text{N}$

Table 3
Harmonic frequencies (in cm^{-1}) of intra-molecular vibrational modes in water–cyanide complexes. Data computed with the 6-311++G(d,p) basis set

Vibrational modes	H–C≡N···H ₂ O			H ₃ C–C≡N···H ₂ O			(CH ₃) ₃ C–C≡N···H ₂ O		
	MP2	B3LYP	PW91	MP2	B3LYP	PW91	MP2	B3LYP	PW91
HOH-bending	1654(25)	1625(22)	1589(20)	1662(33)	1632(29)	1598(29)	1639(10)	1615(12)	1578(9)
OH-sym. stretch.	3851(–34)	3769(–48)	3648(–75)	3829(–56)	3739(–78)	3610(–113)	3844(–41)	3765(–52)	3647(–76)
OH-asym. stretch.	3979(–24)	3898(–24)	3803(–29)	3974(–29)	3894(–28)	3800(–32)	3975(–28)	3900(–22)	3805(–27)
C≡N-stretch.	2031(15)	2209(15)	2138(17)	2223(12)	2373(11)	2298(14)	2170(–2)	2328(–8)	2247(–10)

Values in parenthesis refer to the frequency shifts from free moieties.

stretch is of greater interest because it lies in the region of 2000 cm^{-1} , has intensity, and is common to the three species considered here. Table 3 shows that upon complexation, the C≡N stretch frequencies shift to the high energy side of the spectrum by $\sim 15\text{ cm}^{-1}$ in H–C≡N···H₂O and $\sim 12\text{ cm}^{-1}$ in H₃C–C≡N···H₂O. Similar results are obtained using MP2 and DFT methods. For (CH₃)₃C–C≡N···H₂O the results indicate that the C≡N stretch frequency shifts to the lower side. It is normally expected that stretching frequencies shift to the red upon hydrogen bond. As it was noted before, in Table 1, the C≡N distances are calculated to slightly decrease after complexation in the cases of H–C≡N···H₂O and H₃C–C≡N···H₂O. So the frequency shifts are compatible with the bond length changes and the improper blue shift pointed out by Hobza and Havlas [53]. As Fig. 1 indicates, in the isomer considered here the larger shift should appear in the CH₃ stretching mode. Indeed, the MP2 results indicate that this degenerate frequency changes from 3167 to 3177 cm^{-1} upon complexation, thus leading to a shift of 10 cm^{-1} , with a small (3 cm^{-1}) calculated splitting. All the vibrational frequencies of the water molecule are calculated to present larger shifts, as seen in Table 3. The largest shift is calculated for the symmetric stretching frequency and it is larger for the H₃C–C≡N···H₂O than for the H–C≡N···H₂O.

3.2. Guanine–cytosine base pair

The importance of hydrogen bonding in biological structures has been realized long before crystallographic structure determinations of carbohydrates, proteins, and nucleic acids were reported [1,2]. In particular, the interest on the role of hydrogen bonding in chains of nucleotides has significantly increased [32]. The Watson–Crick model [38] for hydrogen-bonded base pairs in nucleotides has been shown to be a feature of all known double helical structures of ribonucleic and deoxyribonucleic acids (RNA and DNA, respectively). Guerra et al. [54] have investigated various base pairs using DFT combined with different Slater-type orbital basis sets to confront their calculated hydrogen bond lengths with recent experimental results. Another systematic quantum-chemical study on nucleotide base pairs was performed by Šponer et al. [55] and Gould and

Fig. 2. Guanine–cytosine hydrogen-bonded base pair in the Watson–Crick structure.

Kollman [56]. Here we perform calculations at the HF and DFT (BP86 and B3LYP) methods for the guanine–cytosine (Gu–Cy) system (Fig. 2). Geometries are optimized using these methods with the 6-31G(d,p) basis set. Additionally, we have performed single-point MP2 calculations at the optimized HF structure, namely, MP2//HF/6-31G(d,p), to obtain the binding energy. Of particular interest is the analysis of the combined dipole moment of the Gu–Cy pair in terms of the isolated guanine and cytosine.

In Table 4 we present the interatomic distances of the triple bonded Gu–Cy complex as obtained at the HF, BP86 and B3LYP levels of theory. Our results obtained with the two functionals, are in good agreement with the experimental data [57], as well as other previous calculations [32,54–57]. The distances obtained by Guerra et al. [54] with the BP86/DZVP are similar to our B3LYP/6-31G(d,p) results (Table 4). For instance, the N···O and O···N distances differ by only 0.01 Å and the calculated N···N has the same value. As for the result obtained with BP86/6-31G(d,p) they differ in the N···N and O···N distances from the results of Guerra et al. [54] by 0.04 Å. Among the DFT methods presented, the

values calculated by Sánchez-Portal et al. [32] with LDA deviate by as much as -0.35 Å from the experimental data. On the other hand, the MP2 results of Gould and Kollman [56] differ by about $+0.09$ Å. Comparing our results obtained at the HF and DFT levels with the same basis set it is possible to separate the influence of electron correlation effects as obtained with BP86/6-31G(d) and B3LYP/6-31G(d). As expected, all correlated results give hydrogen bond distances that are shorter than those obtained by HF. The LDA results of Ref. [32] give systematically too short distances for all the hydrogen bonds. It can be noted that the N···N distance is reasonably well described by all correlated calculations but the N···O and O···N distances are more difficult and all theoretical results are either too short or too long. The experimental structure is obtained from X-ray diffraction on crystals and as discussed by Guerra et al. [54] a better agreement between theory and experiment would require the consideration of the interaction with the environment.

Table 5 gives the calculated binding energies (BE) with four different methodologies for the Gu–Cy complex. To compare the calculated values with the gas-phase experimental enthalpy (ΔH) [58], we have obtained the ZPE difference in every case. Using this we can estimate the enthalpy using $\Delta H \approx -(\text{BE} + \text{ZPE})$. The stabilization energy of the complex depends on the deformation of the isolated base pairs (Gu or Cy) upon Gu–Cy complex formation. In Table 5 it is shown that HF/6-31G(d,p) gives a binding energy (after zero-point and CP corrections) of 20.77 kcal/mol, which agrees within 0.3 kcal/mol with the experimental bond enthalpy (-21.0 kcal/mol) [58]. Using this geometry (HF/6-31G(d,p)) and including correlation energy at the second-order, MP2, the result seems to overestimate the

Table 4

Distances (in Å) between guanine (Gu) and cytosine (Cy) in the isolated base pair Gu–Cy. Our results are obtained with the 6-31G(d,p) basis set

Gu–Cy	HF	BP86	B3LYP	BP86 ^a	LDA ^b	MP2 ^c	Exp. ^d
N···O	3.03	2.93	2.92	2.93	2.53	3.01	2.86
N···N	3.04	2.89	2.93	2.93	2.61	3.05	2.95
O···N	2.92	2.74	2.79	2.78	2.51	2.93	2.91

^a BP86/DZVP from Guerra et al. [54].

^b Fully self-consistent local-density-functional with linear scaling from Sánchez-Portal et al. [32].

^c Second-order Møller–Plesset calculation from Gould and Kollman [56].

^d Experimental data from Saenger [57].

Table 5

Calculated binding energies (in kcal/mol) for the H-bonded Gu–Cy complex

Methods	BE	BE + CP	BE + CP + ZPE
HF/6-31G(d,p)	25.4	22.8	20.8
MP2//HF/6-31G(d,p)	30.2	24.3	22.3
BP86/6-31G(d,p)	29.5	24.9	23.2
B3LYP/6-31G(d,p)	30.3	25.7	24.2
DFT with STO basis [54]			$-\Delta H_{298}$
BP86/TZ2P	26.1	25.2	23.8
BP86/DZP	28.8	25.1	
PW91/TZ2P	28.5	27.7	26.3
BLYP/TZ2P	28.3	27.4	26.0
DFT with GTO basis			$-\Delta H_{298}$
BP86/DZVP [59]		27.7	
B3LYP/6-31G(d,p) [60]		25.5	24.0
Other calculations			$-\Delta H_{298}$
MP2/DZP//HF/6-31G(d) [56]		28.0	25.4
MP2/6-31G(d)(0.25)//HF/6-31G(d,p) [55]		23.4	20.8
Experimental enthalpy ($-\Delta H_{298}$) [58]			21.0

binding energy, by 1.3 kcal/mol. Also, the BP86/6-31G(d,p) and B3LYP/6-31G(d,p) calculations yield binding energies that differ slightly more from the experimental value, by giving 2.2 and 3.3 kcal/mol, respectively. The BSSE is relatively large at the correlated level. At the HF level it is 2.6 kcal/mol, but at the MP2//HF, this value reaches 6.0 kcal/mol and in the DFT methods it is 4.6 kcal/mol.

Another important aspect in the interaction of the pair guanine–cytosine is the resultant dipole moment of the complex. It is known that the polarities of the molecules involved in a hydrogen bond increase. It is expected that the dipole moments of hydrogen-bonded complexes are slightly larger than the vector sum of the monomers [3,61]. For small systems such as $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ we find that the vector sum of the separate dipole moments accounts for $\sim 95\%$ of the total calculated dipole moment of the complex. For the pair Gu–Cy this is probably smaller because one

should expect a larger polarization. Secondary BSSE has been investigated before for the dipole moments [61–63]. In Table 6 we give the calculated dipole moments of guanine, cytosine and the complex Gu–Cy as obtained with BSSE and after CP correcting for this. The dipole moment of guanine and cytosine are now calculated at the geometries obtained in the complex. There are several interesting aspects worth noting. First, the CP correcting values show that BSSE is quite appreciable in the monomers increasing the dipole moment by about 12%. Similar result is obtained for the vector sum of the individual dipole moments. Finally, it can be seen that the vector sum of dipole moments of guanine and cytosine gives only $\sim 80\%$ of the total dipole moment of the Gu–Cy complex. Thus the electron polarization leads to an increase of 20% in the dipole moment. Table 7 and Fig. 3 give details about the precise vector location of the individual dipole moments.

Table 6

Comparison of the dipole moments (in D) of Gu–Cy complex with the vector sum of isolated moieties (vsim), guanine (Gu) and cytosine (Cy), at different methods. See Fig. 3 for definitions

Method	Gu	Gu ^a	Cy	Cy ^a	Gu–Cy	VSIM	VSIM ^a
HF/6-31G(d,p)	6.84	7.45	7.12	7.67	6.43	4.63	5.27
BP86/6-31G(d,p)	6.42	7.15	6.05	6.87	5.83	3.94	4.50
B3LYP/6-31G(d,p)	6.50	7.31	6.29	7.03	6.10	4.24	4.66

^a CP corrected.

Table 7

Angles (in °) between the individual vector dipole moments of guanine (Gu) and cytosine (Cy). See Fig. 3 for definitions

Method	θ	θ^a
HF/6-31G(d,p)	141.3	139.5
BP86/6-31G(d,p)	143.3	142.4
B3LYP/6-31G(d,p)	141.2	142.3

^a CP corrected.

4. Summary

The water–cyanides hydrogen-bonded systems $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ and $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ were studied using MBPT and DFT. Full geometry optimizations were made using the MP2, B3LYP and PW91 methods. In addition, single-point calculations were made at the CCSD(T) level to analyze the role of electron correlation effects on the binding energies. It is found that high-order effects partially cancel leading to a good description at the second-order MP2 level. The changes in vibrational frequencies due to the complexation were examined. The $\text{C}\equiv\text{N}$ stretch mode is found to shift towards the blue side by $\sim 12\text{--}15\text{ cm}^{-1}$ in the case of $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ and $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$. This type of blue shift, opposite to the expected red shift, has been analyzed by Hobza and Havlas [53]. All systems are found to be bound and the structures considered here are true energy minima. The best estimate obtained for the binding energy at the CCSD(T) level, after correcting for BSSE and ZPE difference, is 2.1, 2.8 and 3.3 kcal/mol for $\text{H}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ and $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$, respectively.

Fig. 3. Relative positions of the calculated dipole moments of guanine (μ_G) and cytosine (μ_C). θ is the angle between the vectors.

The density-functional results are similar to the MP2 but the PW91 results are slightly higher.

The Gu–Cy pair has also been examined obtaining optimized geometries and binding energies using the HF and DFT methods. Of particular interest in this study is the contribution of polarization to the total dipole moment. It is found that the dipole moment of the complex Gu–Cy is $\sim 20\%$ larger than the vector sum of the individual guanine and cytosine (in the corresponding geometries of the complex) after taking into account BSSE. This indicates that there is indeed a large reciprocal electrostatic polarization that contributes to the binding energy.

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B.4 Application of density functional theory methods in millimeterwave spectroscopy.

E. Rissi, R. Rivelino, S. Canuto.

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Applications of Density Functional Theory Methods in Millimeter-Wave Spectroscopy

EDUARDO RISSI, ROBERTO RIVELINO, SYLVIO CANUTO

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

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ABSTRACT: Density functional theory (DFT), using the most common functionals, and ab initio quantum chemistry methods are used to calculate the rotational constants and dipole moments of the astrophysically important molecules HCN, CH₃CN, CH₃CNH⁺, HCCCN, and HCCNC. As far as millimeter-wave spectroscopy is of interest the DFT methods performed well with most functionals, giving results within $\pm 1\%$ of experiments for rotational constants and $\pm 3\%$ for dipole moments. Analyzing the results obtained with all theoretical models, it may be concluded that the Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang, and Paar (B3LYP) and Becke's three-parameter functional with Perdew–Wang correlational functional [B3PW91/6-31G(d, p)] give the best performances. A detailed analysis of the electron correlation effects shows that HCCCN is more stable than is HCCNC, by 1.16 eV, with important contribution arising from triple excitations. This result is also compared with those obtained with DFT methods. Despite occasional difficulties, DFT with the currently available functionals are of great utility in quickly assessing spectroscopic parameters of astrophysical interest. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 91: 575–585, 2003

Key words: astrophysics; B3LYP; B3PW; density functional theory; millimeter-wave; spectroscopy

Introduction

Ab initio molecular quantum mechanics is an important tool in calculating spectroscopic constants of astrophysically interesting molecules [1]. Indeed, the detection of interstellar molecules has been very much aided by the availability of

their spectroscopic constants. Microwave spectroscopy is an important tool in the identification of new molecular species in both laboratory and space. One well-known example where theory [2] has greatly aided the identification in the interstellar medium is HCO⁺ [3]. The accurate calculations on HCO⁺ [2–4] for the X-ogen line have been used in the experimental identification of the millimeter-wave observations [3–5]. Similarly, the identification [6] of HCCNC has benefited from the previous

Correspondence to: S. Canuto; e-mail: canuto@if.usp.br
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existence of theoretical rotational constants [7]. More recently, SiC, the first metal carbide, was detected [8] both in laboratory and in space and this observation relied on previous calculations [9]. Theoretical calculations of other metal carbides aimed at helping possible identification of CaC [10], MgC [11, 12], and AlC [13] have appeared. In the last few years the computational possibilities for calculating spectroscopic constants of small molecules have considerably expanded. On one side, the increase in computer power allowed the use of more sophisticated many-body theories, such as higher-order perturbation and coupled-cluster theory [14, 15]. On the other side, there has been an increase in the methodological possibilities also. More specifically, the use of density functional theory (DFT) methods [16–18] is in clear expansion. Although DFT has been extensively used in solid-state and condensed-matter physics [18, 19], only recently has its reputation sufficiently improved to be used in theoretical quantum chemistry. The possibility of use in astrophysics and, in particular, radioastronomy, is of relevance [20]. As there is no exact density functional known, even for the simplest of the molecules, most applications in molecular properties make use of some approximation of the exchange-correlation term. There is indeed an enormous variety of possible functionals available, including hybrid functionals [21]. With this there appears a wide range of possibilities to be used and the necessity of assessing the capability and possible accuracy of these methods for specific interests. Thus, in related fields these methods have been confronted to understand their ability to describe hydrogen bonds [22–26] and van der Waals [26–29] interactions, for instance. Similar systematic attempt in millimeter-wave spectroscopy is the aim of this article. Several different DFT methods have been used to obtain the rotational and vibrational properties of HCN-related systems. These methods differ in the systematic change of functional and basis sets. To have an indication of their performance traditional quantum chemical calculations are also made. Thus, most of the more commonly used functionals and methods have been used. One of the aims of this contribution is to assess typical results that could be expected from these theoretically exact but in practice only approximate methodologies. In this direction, HCN is an important and first example where theoretical results have been very important for proper characterization of the radioastronomy observations. Hence, we confront the results obtained using present-day methodologies with those found

before [2] to be accurate enough for characterizing observations of HCN. In total, as many as 39 methods have been used for the confrontation of the current results for the rotational constants of HCN. This is perhaps the most thorough study of the performance of DFT methods in molecular systems. Other important molecules are CH_3CN and CH_3CNH^+ . Our selection for CH_3CN and CH_3CNH^+ stems from the fact that CH_3CN is well known both theoretically and experimentally [30–33], whereas CH_3CNH^+ is known theoretically [34] and has been detected in laboratory [35, 36] but not conclusively in the interstellar medium [33]. Thus, they are not only molecules related by protonation but also molecules of enormous astrophysical interest. As H_3^+ , CH_3^+ , CH_3CN , and HCN have been detected in the interstellar medium, CH_3CNH^+ may be formed by either radiative association reaction [37] such as $\text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\text{CNH}^+ + h\nu$ or exothermic proton transfer [38] $\text{CH}_3\text{CN} + \text{H}_3^+ \rightarrow \text{CH}_3\text{CNH}^+ + \text{H}_2$. Quantum chemical wavefunction-based and DFT methods are considered to obtain the rotational constants, and the dipole moment for both CH_3CN and CH_3CNH^+ . As many as 23 representative calculations (with 14 DFT) will be reported and compared with the benchmark result of Botschwina [34]. These two molecules belong to the C_{3v} point group symmetry and thus behave as a prolate rotational species. The B rotational constant of CH_3CNH^+ has been measured [36] in laboratory and calculated [34] with high-order electron correlation effects included. These results will serve as a benchmark for a comparison of our results. Similarly, the isomers HCCCN and HCCNC are important molecules, detected in both laboratory and interstellar media [6, 39–49]. These are two linear molecules with well-known rotational constants and dipole moments. It is known that the HCCCN species is more stable than the HCCNC isomer [7]. The differences in calculated total energies will then be used as an additional test of DFT methods in predicting relative stability of isomers. As an additional test we discuss the hydrogen-bonded system $\text{H}_2\text{O}:\text{HCN}$. As HCN may be trapped in water ice of comets, this hydrogen-bonded system is of importance in prebiotic and extraterrestrial chemistry [50–52].

Methods

Seven functionals, which can be seen as representative among the most common approaches in

density functional theory, have been applied. First, we used the local spin density exchange with correlation functional fitted to the uniform electron gas, best known as Slater exchange combined with Vosko, Wilk, and Nusair correlation functional, SVWN, or the slightly modified SVWN5 [53]. Second, we employed gradient-corrected exchange-correlation functionals: Becke's one- and three-parameter hybrid functionals combining Lee–Yang–Parr correlation term, namely BLYP and B3LYP, respectively [54, 55]; and Becke's one- and three-parameter hybrid functionals with Perdew [56], BP86 and B3P86, respectively, and Perdew–Wang, B3PW91 [57, 58] correlation terms. On the other side, as a comparative study, we also performed the calculations with some wavefunction methods. These were the Hartree–Fock approximation, second-order Møller–Plesset perturbation theory (MP2), double-excitation coupled-cluster method (CCD) [14, 15], and quadratic configuration interaction with single and double substitutions (QCISD) [15, 59, 60]. These methods were used with the most common Gaussian basis sets [61] and with correlated-consistent (cc) augmented or not with diffuse functions (aug-cc), as proposed by Dunning [62, 63]. Full geometry optimization was performed in all cases and the rotational constants and dipole moments were calculated in the equilibrium geometries. In addition, the energetics of two reactive processes were considered: $\text{CH}_3\text{CN} + \text{H}^+ \rightarrow \text{CH}_3\text{CNH}^+$ and $\text{H}_3^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{H}_2$. The binding energies in these cases were properly corrected for the difference in zero-point energy vibrations. The electron correlation effects on the relative stability of the HCCCN isomer over the HCCNC form was systematically analyzed using quantum-chemical coupled-cluster single-, double-, and partial triple-excitation theory, CCSD(T) [15], and the results were compared with DFT results. All calculations were performed with the Gaussian 98 program [64]. The theoretical calculations were not corrected here to include vibrational–rotational interaction [65].

Results

HCN

Table I shows the results for the geometry and corresponding rotational constants of HCN. In total 39 different methods are reported and compared with two previous benchmark calculations [2] and

TABLE I

Comparison of the results from different methods to calculate the geometry and rotational constant of HCN.

Method	Geometry (Å)		Rotational constant (GHz)
	HC	CN	B
HF/6-31G(d)	1.059	1.133	45.98
HF/6-31G(d, p)	1.059	1.133	45.97
MP2/6-31G(d)	1.069	1.178	42.92
MP2/6-311++G(d)	1.068	1.171	43.32
MP2/cc-pVDZ	1.079	1.182	42.53
MP2/aug-cc-pVDZ	1.078	1.183	42.49
MP2/cc-pVTZ	1.064	1.167	43.65
BLYP/6-311++G(d)	1.067	1.148	44.85 ^a
BLYP/6-31G(d)	1.078	1.169	43.34
B3LYP/6-31G(d)	1.070	1.157	44.20 ^a
B3LYP/6-31+G(d)	1.071	1.158	44.16 ^a
B3LYP/6-31++G(d, p)	1.070	1.158	44.16 ^a
B3LYP/6-311++G(d)	1.069	1.149	44.73 ^a
B3LYP/6-311++G(d, p)	1.067	1.149	44.76 ^a
B3LYP/cc-pVDZ	1.077	1.158	44.06 ^a
BP86/6-31G(d)	1.080	1.170	43.29
BP86/6-31+G(d)	1.081	1.170	43.27
B3P86/6-31+G(d)	1.072	1.156	44.23 ^a
BP86/6-311++G(d, p)	1.076	1.162	43.85
B3P86/6-31G(d)	1.071	1.156	44.25 ^a
B3P86/6-311++G(d)	1.069	1.149	44.76 ^a
B3P86/6-311+G(d, p)	1.069	1.149	44.76 ^a
B3P86/6-311++G(d, p)	1.068	1.149	44.79 ^a
B3PW91/6-31G(d, p)	1.070	1.157	44.21 ^a
B3PW91/6-311++G(d)	1.069	1.150	44.70 ^a
SVWN/6-31G(d)	1.081	1.162	43.74
CISD/6-31G(d)	1.068	1.157	44.25 ^a
CISD/6-311++G(d)	1.066	1.150	44.71 ^a
CISD/cc-pVDZ	1.077	1.161	43.89
SDQMP4/6-31G(d)	1.071	1.167	43.57
SDQMP4/cc-pVDZ	1.081	1.171	43.19
QCISD/6-31G(d)	1.072	1.166	43.62
QCISD/6-311++G(d)	1.072	1.160	44.03
QCISD/cc-pVDZ	1.081	1.170	43.24
CCD/6-31G(d)	1.071	1.162	43.85
CCD/6-31G(d, p)	1.065	1.163	43.91
CCD/6-311++G(d)	1.071	1.156	44.27 ^a
CCD/cc-pVDZ	1.080	1.167	43.47
CCD/aug-cc-pVDZ	1.080	1.167	43.48
Cl (Ref. [2])	1.064	1.150	44.74 ^a
Experiment (Ref. [66])	1.065	1.153	44.51

^a Results within 1% of the given experimental value.

the experimental [66] result of 44.51 GHz. All theoretical results are within 5% accuracy compared with the experimental result. This testifies the util-

TABLE II
Calculated dipole moment of HCN.

Method	Dipole moment (D)
HF/6-31G(d)	3.21
HF/6-31G(d, p)	3.20
MP2/6-31G(d)	2.95 ^a
MP2/6-311++G(d)	3.07 ^a
BLYP/6-311++G(d)	3.10 ^a
BLYP/6-31G(d)	2.80
B3LYP/6-31G(d)	2.90 ^a
B3LYP/6-31+G(d)	3.08 ^a
B3LYP/6-31++G(d, p)	3.08 ^a
B3LYP/6-311++G(d)	3.08 ^a
B3LYP/6-311++G(d, p)	3.05 ^a
B3LYP/cc-pVDZ	2.80
BP86/6-31G(d)	2.84
BP86/6-31+G(d)	3.01 ^a
B3P86/6-31+G(d)	3.08 ^a
BP86/6-311++G(d, p)	2.98 ^a
B3P86/6-31G(d)	2.94 ^a
B3P86/6-311++G(d)	3.08 ^a
B3P86/6-311+G(d, p)	3.08 ^a
B3P86/6-311++G(d, p)	3.06 ^a
B3PW91/6-31G(d, p)	2.92 ^a
B3PW91/6-311++G(d)	3.07 ^a
SVWN/6-31G(d)	2.88
QCISD/6-311++G(d)	3.09 ^a
CCD/6-31G(d)	2.98 ^a
CCD/6-31G(d, p)	2.93 ^a
CCD/6-311++G(d)	3.08 ^a
Experiment	2.99 ^b ; 3.02 ^c

^a Results within 3% of the given experimental values.^b Ref. [67].^c Ref. [68].

ity of these quantum methods. To compare the relative accuracy of these methods we test the results within an accuracy of 1%. Several methods are remarkably accurate, in particular, the DFT methods with the B3LYP and B3P86 functionals. The tendency of considering that DFT methods perform within the MP2 accuracy is not reproduced here for HCN and, in fact, none of the MP2 methods employed here are within this $\pm 1\%$ window of accuracy. Interesting enough, all B3P86 and B3LYP results are sufficiently accurate, but the MP2 model, even with the cc-pVTZ or aug-cc-pVDZ basis, gives rotational constants that are too small. As can be seen, this can be traced to very long calculated bond lengths. The MP2 method overcorrects the very short bond lengths obtained by the HF method. In Table II we show that the DFT methods also give good results for the dipole moments of HCN [67,

68]. Almost all results are within 3% accuracy. The exceptions are the BLYP and BP86 with the 6-31G(d) basis and B3LYP/cc-pVDZ. It is interesting to note how the dipole moment results with B3LYP are stable with regular basis sets but deteriorate with the correlated-consistent cc-pVDZ basis set. The BP86/6-311++G(d, p) performs poorly for the rotational constant but gives a very good dipole moment, in considerable improvement over the same functional without diffuse functions, BP86/6-31G(d). This improvement will not occur in other systems. As we shall see later, the dipole moment obtained for HCCNC with the BP86/6-31G(d) is very good, whereas that obtained with BP86/6-31+G(d) is too high. The MP2 results for the dipole moments may be considered very good.

CH₃CN AND CH₃CNH⁺

Next we consider the CH₃CN and CH₃CNH⁺ systems. The rotational constant of CH₃CN is known experimentally [35, 69] to be 9199 MHz, whereas for CH₃CNH⁺ it has been measured [36] as 8591 MHz. Table III gives the calculated rotational constants and dipole moments. There has been a general tendency to consider the B3LYP/6-31+G(d) one of the best compromises among the available functionals for molecular calculations. The results of Table III show that for CH₃CN it gives a good value for rotational constant. Improving the basis set to B3LYP/6-31++G(d, p) makes only a minor change in the rotational constant. However, the B3LYP/6-311++G(d, p) shows a sudden change just by modifying the flexibility in the contracted basis (from 6-31 to 6-311). The result of 9247 MHz may be considered only reasonable but it gives a better description for the dipole moment. At this level it is reasonably well calculated as 4.05 D, as compared with 3.92 D, obtained experimentally [29]. The sensitivity to basis set improvement is large also in the many-body theories, such as MP2. At the highest level considered here, CCD/cc-pVDZ, the rotational constant is still off by 178 MHz. Similar analysis can be made for CH₃CNH⁺, with a similar conclusion. However, the performance of the DFT methods for the rotational constants of both CH₃CN and CH₃CNH⁺ is noteworthy. All results match the 1% accuracy test. Note that the best DFT result is obtained with the B3PW91/6-31G(d, p) both for the rotational constants and dipole moments. At the high-order CCSD(T)/cc-pVQZ the results [34] obtained for CH₃CNH⁺ are very good. The B3LYP/6-31+G(d)

TABLE III
Rotational constants and dipole moments of CH₃CN and CH₃CNH⁺.

Method	CH ₃ CN		CH ₃ CNH ⁺	
	Rotational constant (MHz)	Dipole moment (D)	Rotational constant (MHz)	Dipole moment (D)
BLYP/6-31+G(<i>d</i>)	9158 ^a	4.07	8549 ^a	1.08
B3LYP/6-31+G(<i>d</i>)	9151 ^a	4.07	8548 ^a	1.06
B3LYP/6-31G(<i>d</i> , <i>p</i>)	9168 ^a	3.83 ^b	8562 ^a	1.06
B3LYP/6-31++G(<i>d</i> , <i>p</i>)	9161 ^a	4.08	8561 ^a	1.00 ^b
B3LYP/6-311++G(<i>d</i>)	9239 ^a	4.04 ^b	8629 ^a	1.07
B3LYP/6-311++G(<i>d</i> , <i>p</i>)	9247 ^a	4.05	8639 ^a	1.00 ^b
B3PW91/6-311++G(<i>d</i> , <i>p</i>)	9279 ^a	4.05	8674 ^a	0.98 ^b
B3P86/6-31+G(<i>d</i>)	9203 ^a	4.07	8604 ^a	1.03 ^b
B3PW91/6-31+G(<i>d</i>)	9185 ^a	4.06	8586 ^a	1.04 ^b
B3P86/6-31G(<i>d</i> , <i>p</i>)	9218 ^a	3.88 ^b	8617 ^a	1.00 ^b
B3PW91/6-31G(<i>d</i> , <i>p</i>)	9199 ^a	3.87 ^b	8604 ^a	1.01 ^b
B3P86/6-31++G(<i>d</i> , <i>p</i>)	9215 ^a	4.08	8614 ^a	0.97
SVWN/6-31+G(<i>d</i>)	9240 ^a	4.14	8657 ^a	0.83
SVWN5/6-31+G(<i>d</i>)	9215 ^a	4.14	8636 ^a	0.84
HF/6-31G	9283 ^a	4.13	8569 ^a	1.09
HF/6-31+G(<i>d</i>)	9292 ^a	4.20	8588 ^a	1.22
HF/6-311++G(<i>d</i>)	9352	4.18	8647 ^a	1.20
MP2/6-31+G(<i>d</i>)	9028	4.30	8451	1.09
MP2/6-31G(<i>d</i> , <i>p</i>)	9052	4.15	8460	1.04 ^b
MP2/6-311++G(<i>d</i>)	9083	4.28	8503	1.07
MP2/cc-pVDZ	8965	4.11	8396	1.00 ^b
CCD/cc-pVDZ	9021	4.08	8402	1.06
QCISD/cc-pVDZ	8988	4.09	8370	1.04 ^b
CCSD(T)/cc-pCVQZ ^c	—	—	8600 ^a	—
CCSD(T)/cc-pVQZ ^c	—	—	8564 ^a	1.01
Experiment	9199 ^d	3.92 ^e	8591 ^f	—

^a Results within 1% of the given experimental value for the rotational constant.

^b Results within 3% of the given experimental value (or best calculation, for CH₃CNH⁺) for the dipole moment.

^c Ref. [34].

^d Ref. [69].

^e Ref. [29].

^f Refs. [35] and [36].

gives a rotational constant of 8548 MHz and a dipole moment of 1.06 D, as compared with the experimental result of 8591 MHz and best theoretical result available of 1.01D [34]. The SVWN functional has a worse performance, with rotational constants that are too high and dipole moments that are too high or too low. But the performances of the Becke-Perdew or Becke-Perdew-Wang functionals are very good. Indeed the B3PW91/6-31+G(*d*) and B3PW91/6-31G(*d*, *p*) (or B3P86/6-31+G(*d*)) give the best rotational constants of 8586 MHz and 8604 MHz, respectively, comparable to the more computationally involved CCSD(T)/cc-pCVQZ calculation [34] that gives 8600 MHz. It is clear (see Table III) that at these levels of calculations and systems,

the DFT methods perform better than any MP2 calculation, particularly for CH₃CNH⁺.

As CH₃CNH⁺ has not been observed in the interstellar medium, its formation is not known. In interstellar conditions it is believed that it may be formed by the unusually fast radiative reaction CH₃⁺ + HCN → CH₃CNH⁺ + *hν*. Two other processes may not be discarded, such as CH₃CN + H⁺ → CH₃CNH⁺ and H₃⁺ + CH₃CN → CH₃CNH⁺ + H₂. Table IV gives the energetics of formation from these two latter processes. All the binding energies given in this table have been properly corrected for the differences in zero-point energies of the incoming and outgoing reactive channels. Direct protonation leads to a binding energy of around 8 eV.

TABLE IV

Calculated binding energy (kcal/mol) for two different processes of formation of CH_3CNH^+ using different theoretical methods.^a

Method	$\text{CH}_3\text{CN} + \text{H}^+ \rightarrow \text{CH}_3\text{CNH}^+$		$\text{H}_3^+ + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{H}_2$	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
BLYP/6-31+G(d)	-190.38	-184.30	-94.92	-94.79
B3LYP/6-31+G(d)	-190.61	-184.58	-94.69	-94.59
B3LYP/6-31G(d, p)	-196.69	-190.72	-93.21	-93.05
B3LYP/6-31++G(d, p)	-193.23	-187.23	-89.64	-89.44
B3LYP/6-311++G(d)	-190.54	-184.55	-94.84	-93.85
B3LYP/6-311++G(d, p)	-193.21	-187.20	-88.64	-88.17
B3PW91/6-311++G(d, p)	-195.06	-189.03	-88.05	-87.66
B3P86/6-31+G(d)	-191.80	-185.76	-94.33	-94.46
B3PW91/6-31+G(d)	-192.25	-186.21	-94.37	-94.48
B3P86/6-31G(d, p)	-196.98	-191.00	-92.03	-92.03
B3PW91/6-31G(d, p)	-197.54	-191.54	-92.12	-92.10
B3P86/6-31++G(d, p)	-194.41	-188.40	-89.10	-89.05
SVWN/6-31+G(d)	-188.73	-182.96	-93.53	-93.55
SVWN5/6-31+G(d)	-188.18	-182.42	-93.23	-93.23
HF/6-31G	-197.77	-190.91	-105.20	-104.81
HF/6-31+G(d)	-192.07	-185.45	-99.55	-99.40
HF/6-311++G(d)	-192.33	-185.68	-98.99	-97.63
MP2/6-31+G(d)	-192.94	-186.77	-97.39	-97.69
MP2/6-31G(d, p)	-197.90	-191.75	-93.36	-93.48
MP2/6-311++G(d)	-193.19	-187.04	-96.96	-96.15
MP2/cc-pVDZ	-196.24	-190.10	-90.79	-90.44
CCD/cc-pVDZ	-195.52	-189.31	-89.78	-89.31
QCISD/cc-pVDZ	-195.53	-189.39	-89.81	-89.44

^a In each case the first column gives difference in total energies, whereas the right column includes corrections due to vibrational zero-point and thermal energies.

Conversion units: 1 eV = 8067 cm^{-1} = 23.065 kcal/mol.

Reaction involving H_3^+ leads to a lower binding of around 4 eV. The numbers change depending on the theoretical model employed but the result obtained using CCD/cc-pVDZ or QCISD/cc-pVDZ should be among the most accurate ones. Interestingly, the B3LYP/6-31++G(d, p) gives a result that is very close to these two models.

HC_3N AND HC_2NC

Both HCCCN and HCCNC have been detected in laboratory and space [39–49] and have recently been the subject of intense experimental and theoretical work. Recent millimeter-wave spectra studies of HCCCN have been performed by Mbosei et al. [45] and Thorwirth et al. [47] and for HCCNC by Vigouroux et al. [44]. Although first synthesized in 1991 [6], the existence of HCCNC was anticipated in an earlier work by Wilson [7] and first detected in

the interstellar cloud in a subsequent work by Kawaguchi et al. [39]. Chains of carbon molecules in the interstellar medium have attracted considerable interest in astrochemistry. Among these, the cyanopolynes occupy a special place. In particular, HCCCN and HCCNC are isomers that were both identified in the space and other similar species will certainly come to be known. Theoretical methods will be of great assistance in the identification of these new species. Hence, we have tested the DFT methods also for these systems. The BP86, B3P86, B3LYP, and B3PW91 functionals were used in different gaussian basis sets, such as 6-31G(d), 6-31G(d, p), 6-31+G(d), 6-31++G(d, p), and cc-pVDZ and compared with some commonly used quantum chemical methods and experimental results. The results of 24 different theoretical models are discussed. The calculated and experimental results for the rotational constants and dipole moments are

TABLE V
Rotational constants and dipole moments of HCCNC and HCCCN.

Method	HCCNC		HCCCN	
	Rotational constant (MHz)	Dipole moment (D)	Rotational constant (MHz)	Dipole moment (D)
HF/6-31G(<i>d</i>)	5038	2.51	4605	4.09
MP2/6-31G(<i>d</i>)	4862	3.19	4455	3.78 ^b
BP86/6-31G(<i>d</i>)	4876	2.94 ^b	4481	3.79 ^b
B3P86/6-31G(<i>d</i>)	4957 ^a	2.85 ^b	4548 ^a	3.87
B3LYP/6-31G(<i>d</i>)	4942 ^a	2.84 ^b	4539 ^a	3.83 ^b
HF/6-31+G(<i>d</i>)	5040	2.61	4600	4.15
MP2/6-31+G(<i>d</i>)	4862	3.38	4449	3.90
BP86/6-31+G(<i>d</i>)	4879	3.10	4477	3.93
B3P86/6-31+G(<i>d</i>)	4959 ^a	3.00 ^b	4545 ^a	3.98
BLYP/6-31+G(<i>d</i>)	4873	3.09	4476	3.92
B3LYP/6-31+G(<i>d</i>)	4943 ^a	2.99 ^b	4534 ^a	3.98
B3PW91/6-31G(<i>d</i> , <i>p</i>)	4949 ^a	2.84 ^b	4540 ^a	3.84 ^b
B3PW91/6-31+G(<i>d</i>)	4952 ^a	2.99 ^a	4539 ^a	3.97
HF/6-31++G(<i>d</i> , <i>p</i>)	5039	2.60	4600	4.14
MP2/6-31++G(<i>d</i> , <i>p</i>)	4862	3.31	4448	3.83 ^b
BP86/6-31++G(<i>d</i> , <i>p</i>)	4879	3.08	4477	3.91
B3P86/6-31++G(<i>d</i> , <i>p</i>)	4959 ^a	2.97 ^b	4544 ^a	3.97
B3LYP/6-31++G(<i>d</i> , <i>p</i>)	4944 ^a	2.97 ^b	4534 ^a	3.96
B3PW91/6-31++G(<i>d</i> , <i>p</i>)	4952 ^a	2.97 ^b	4538 ^a	3.95
MP2/cc-pVDZ	4812	3.19	4394	3.54
BP86/cc-pVDZ	4857	2.97 ^b	4460	3.60
B3LYP/cc-pVDZ	4922 ^a	2.88 ^b	4514 ^a	3.65 ^b
MP2/aug-cc-pVDZ	4815	3.27	4391	3.79 ^b
B3LYP/aug-cc-pVDZ	4937 ^a	2.96 ^b	4521 ^a	3.91
Experiment	4968 ^c	2.93 ^d	4549 ^e	3.73 ^f

^a Results within 1% of the given experimental value for the rotational constant.

^b Results within 3% of the given experimental value for the dipole moment.

^c Refs. [6] and [48].

^d Ref. [6].

^e Ref. [45].

^f Ref. [49].

shown in Table V. Only three theoretical methods satisfy the accuracy criteria for rotational constants and dipole moments for both HCCCN and HCCNC. These are the B3LYP/6-31G(*d*), B3LYP/cc-pVDZ, and B3PW91/6-31G(*d*, *p*). Three other aspects are worth noticing. First, none of the MP2 results match the 1% accuracy, even with the largest basis sets. Higher-order electron correlation effects are necessary. However, the MP2 method gives good results for the dipole moments. Overall, the performance of B3LYP is better than that of MP2, even for the correlated-consistent basis sets. Second, the performance of the B3LYP functional is indeed very good, but improving the basis set does not improve the results systematically. Again, this is one aspect of DFT methods where the systematic

improvement is not clear and a hierarchy of approximations is not available. Here it is clear that the use of better basis sets does not necessarily lead to better densities in these parameterized functionals. Third, the B3PW91/6-31G(*d*, *p*) method satisfies again the accuracy tests and is the only method that satisfies this accuracy for all systems considered here.

Another test case for the DFT methods is the relative stability energy of HCCCN with respect to HCCNC (Table VI). An early estimate at the HF level [7] gives 0.8 eV. Our HF calculations also give less than 1.0 eV with all basis sets. A better estimate for this relative energy is 1.1 eV–1.2 eV, as derived from two works of Botschwina et al. [42, 43]. Correcting the HF value with MP2 gives a relative

TABLE VI
Calculated relative stability energy of HCCCN with respect to HCCNC.

Method	Energy difference (eV)
HF/6-31G(d)	0.951
MP2/6-31G(d)	1.441
BP86/6-31G(d)	1.156
B3P86/6-31G(d)	1.116
B3LYP/6-31G(d)	1.128
HF/6-31+G(d)	0.903
MP2/6-31+G(d)	1.373
BP86/6-31+G(d)	1.104
B3P86/6-31+G(d)	1.066
B3LYP/6-31+G(d)	1.109
B3LYP/6-31+G(d)	1.068
B3PW91/6-31+G(d)	1.073
HF/6-31++G(d, p)	0.903
MP2/6-31++G(d, p)	1.372
BP86/6-31++G(d, p)	1.103
B3P86/6-31++G(d, p)	1.065
B3LYP/6-31++G(d, p)	1.067
B3PW91/6-31G(d, p)	1.122
B3PW91/6-31++G(d, p)	1.072
MP2/cc-pVDZ	1.409
BP86/cc-pVDZ	1.131
B3LYP/cc-pVDZ	1.101
B3LYP/aug-cc-pVDZ	1.087
SDQ-MP4//MP2/6-31++G(d, p)	1.131
SDTQ-MP4//MP2/6-31++G(d, p)	1.206
CCD//MP2/6-31++G(d, p)	1.129
CCSD//MP2/6-31++G(d, p)	1.126
CCSD(T)//MP2/6-31++G(d, p)	1.156

energy that is around 1.4 eV, which seems too high. To analyze systematically the electron correlation effects full (including all single-double-triple and quadruple excitations) SDTQ-MP4, and CCSD and CCSD(T) calculations were performed using the geometry optimized at the MP2/6-31++G(d, p) level. These are termed as CCSD(T)//MP2/6-31++G(d, p), for instance, on the bottom of Table VI. The results show that high-order electron correlation effects decrease the MP2 estimate. High-order single and double excitations are very important and CCSD decreases the MP2 result by 0.246 eV. In fact, the CCD result shows that high-order single-excitation contribution is small (−0.003 eV) and double excitations are the most important (−0.243 eV). A comparison between SDTQ-MP4 and SDQ-MP4 shows that the triple excitations in fourth order contribute 0.075 eV for the relative energy. Including higher-order triple-excitation

TABLE VII
Calculated rotational constant (GHz) of H₂O:HCN with the 6/311++G(d, p) basis.

Method	B	A
MP2	3.046 ^a	3.026 ^a
SDQ-MP4	3.032 ^a	3.013 ^a
CCD	3.027 ^a	3.007 ^a
QCISD	3.024 ^a	3.005 ^a
BLYP	3.125	3.103
B3LYP	3.121	3.099
B3P86	3.199	3.176
B3PW91	3.137	3.114
Experiment ^b	3.046	3.020

^a Results within 1% of the given experimental value.

^b Ref. [72].

contribution in a perturbative manner [15], CCSD(T), decreases the contribution to 0.030 eV. Thus, the systematic quantum-chemical analysis shows that high-order single excitations contributes only −0.003 eV but double and triple excitations are important, contributing −0.243 eV and 0.030 eV for the relative stability of HCCCN over HCCNC. So the best theoretical estimate of this energy would be 1.16 eV. This is in very good agreement with the result of 1.15 eV that can be inferred from the calculations of Botschwina et al. [42, 43]. The total energies of either of the two isomers using DFT are exaggerated, with very large electron correlation contribution, but the relative energy is only slightly lower and in some cases surprisingly good. It is worth noting the result of 1.12 eV obtained with the B3PW91/6-31G(d, p).

H₂O:HCN

It is interesting to discuss the case of the hydrogen-bonded H₂O:HCN system. It is known that HCN may be trapped in water ice of comets and is of great importance as pristine material surviving from the time of solar system formation. The hydrogen-bonded HCN-water system exists in two forms. The most stable [70, 71] has the H₂O:HCN bond (Fig. 1), where the water acts as the proton

FIGURE 1. The most stable isomer of the hydrogen-bonded H₂O:HCN system.

acceptor. This structure has an experimental [72] out-of-plane H_2O bend angle of 20° . The calculated result using the B3LYP/6-311++G(*d, p*) gives an angle of only 3° . For comparison, using the same basis set, the MP2/6-311++G(*d, p*) result is 23° , in excellent agreement with experiment. Table VII illustrates the results obtained for the calculated rotational constants using some of these models. The superiority of the MP2 and CC methods, in this case, is clear and the DFT methods employed here cannot treat adequately the out-of-plane hydrogen bond, leading to rotational constants that are too high. In fact the use of DFT methods to describe hydrogen bonds, with currently available functionals, has been subjected to some criticism [25, 73]. Recent applications, however, claim good agreement [22–24, 26]. The use of DFT methods in proton transfer is also subjected to limitations [74] and relative success [75]. Details of the potential energy surface are difficult to obtain by DFT methods [76]. It seems the use of DFT methods will continue to increase, mostly because of their computational appeal. Other functionals, such as the Wilson–Levy [77] correlation functional, that are still not in widespread use, seem to perform better [27] in van der Waals interactions. Analyzing the results obtained with all theoretical models, one may conclude that indeed the B3LYP gives one of the best overall performance among the most commonly used functionals, but its general use cannot be recommended without some warning [26, 77–79], as can be seen from the results for the hydrogen-bonded $\text{H}_2\text{O}:\text{HCN}$ system. Overall, the best performance obtained here is that using the B3PW91/6-31G(*d, p*). A similar conclusion regarding the Perdew–Wang exchange-correlation has been obtained for intermolecular interaction [26].

Summary and Conclusions

One of our goals here was to make a direct test between the most commonly used DFT methods and to try to assess their relative accuracy for molecular astrophysics, and millimeter-wave spectroscopy, in particular. As far as rotational constants are of interest, the DFT methods performed surprisingly well, with most functionals giving results within $\pm 1\%$ of experiments for rotational constants and $\pm 3\%$ for dipole moments. With the usual nonrelativistic and Born–Oppenheimer approximations, we should not expect more accuracy than this. Vibrational–rotational

interactions are important but were not included in a “large-sample” study such as that presented here. In general, the performance of the DFT methods considered here is comparable to or even better than that which could be expected in limited quantum chemical calculations, such as MP2, and in some cases even CCD. Exceptions do occur, however, and in particular, the use of correlated consistent basis in the DFT methods gave inconsistent results for the dipole moment of HCN. For HCCCN, however, very good results were obtained with B3LYP/aug-cc-pVDZ. For the HCN-like systems considered here, such as HCN, CH_3CN , CH_3CNH^+ , HC_2NC , and HC_3N , the B3LYP/6-31++G(*d, p*), or even the B3LYP/6-31+G(*d*), method performed well for both rotational constants and dipole moments. The B3P86 functional presented improved values of the dipole moment. But the best performance is obtained with the B3PW91/6-31G(*d, p*). It is clear that DFT methods with these basis sets and functionals are indeed of enormous interest in quickly assessing spectroscopic parameters of astrophysical interest. However, the improvement in accuracy of the calculated DFT result is not clear-cut and for high-precision results the use of sophisticated and hierarchically structured quantum chemical methods, though very costly computationally, should still be favored. On the predictive side, we find that the direct proton transfer reaction $\text{CH}_3\text{CN} + \text{H}^+ \rightarrow \text{CH}_3\text{CNH}^+$ is energetically more favorable than is the exothermic proton transfer $\text{CH}_3\text{CN} + \text{H}_3^+ \rightarrow \text{CH}_3\text{CNH}^+ + \text{H}_2$ by 4.3 eV, with the proton transfer having a stabilization energy of around 8.2 eV. In addition, we also state that the HC_3N , the more stable isomer, has a relative energy of -1.16 eV compared with HC_2NC . This value is obtained with a careful analysis of the electron-correlation effects obtained at the coupled-cluster level.

Finally, this article presents a lengthy analysis on the performance of DFT methods for HCN, CH_3CN , CH_3CNH^+ , HCCCN, and HCCNC and the hydrogen-bonded $\text{HCN}:\text{H}_2\text{O}$. Despite occasional difficulties, the DFT methods are a viable alternative to quickly obtain theoretical rotational constants and dipole moments useful in millimeter-wave spectroscopy.

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B.5 A Monte Carlo - quantum mechanics study of the solvent-induced spectral shift of different conformations of furfural in water.

R. Rivelino, K. Coutinho, S. Canuto.

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A Monte Carlo-Quantum Mechanics Study of the Solvent-Induced Spectral Shift and the Specific Role of Hydrogen Bonds in the Conformational Equilibrium of Furfural in Water

Roberto Rivelino[†]

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

Kaline Coutinho[‡]

CIIB, Universidade de Mogi das Cruzes, CP 411, 08701-970 Mogi das Cruzes, SP, Brazil

Sylvio Canuto*

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

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The solvation shift of the lowest absorption transition of furfural in water is analyzed as a function of the rotation angle for the interconversion between the two conformations, OO-cis and OO-trans, of furfural. In total, 20 Monte Carlo NPT simulations are performed, corresponding to different rotation angles of the carbonyl group. The solvation shift of the $n-\pi^*$ state is calculated to be $1230 \pm 45 \text{ cm}^{-1}$ in the most stable OO-cis form. This calculated shift is found to be essentially independent of the rotation angle. The hydrogen bonds between furfural and water are also analyzed along the interconversion path. These hydrogen bonds are found to be equivalent, both in number and in binding energy, for all rotation angles. The results for the solvent-induced spectral shift and the hydrogen bond interactions confirm that in water they make no preference for any rotamer of furfural and lead to small contribution to the entropic activation barrier of furfural in protic solvents.

Introduction

Conformation equilibrium of organic molecules in different solvents is a topic of great importance.¹ In this direction furfural is an interesting system that may exist in two possible conformations corresponding to a OO-cis and a OO-trans conformer² (Figure 1). In the gas phase it is known that the OO-trans is more stable than the OO-cis with an energy difference³ that is less than 1.0 kcal/mol. Between these two forms there is a large interconversion barrier that has been determined^{3,4} to be 9.3 kcal/mol. The conformational equilibrium of furfural, however, has a strong solvent dependence.^{5,6} In neat furfural the barrier is³ 11.0 kcal/mol. The barrier has also been determined for a few other solvents and it has been the subject of intense theoretical and experimental investigations.^{1–20} The recent and interesting work of Baldrige, Jonas, and Bain⁷ gives an overview of previous works on the energetics of furfural in the gas phase and in different solvents. The conformer with the larger dipole moment, OO-cis, dominates in polar solvents over the OO-trans conformer, which is, however, more stable in the gas phase or in low-polarity solvents (dielectric constant smaller than 5). The small energy difference between the two conformations and the activation barrier of furfural in different solvents have attracted both experimental^{2–15} and theoretical investigations.^{15–20} Bain and Hazendonk¹⁴ have used combined NMR experiments to determine the activation barrier of furfural in toluene, acetone, and methanol. They have found that the behavior of the enthalpies of activation for the cis–trans process

Figure 1. Conformational equilibrium of furfural. The carbonyl group rotates relative to the furan ring.

does not obey a simple relationship with the dielectric constant. This, of course, indicates that the solvent effects are more complex than could be inferred by a simple reaction field. In addition, they also emphasized the existence of entropic aspects in the activation barrier. There is a large entropy activation in the case of toluene and acetone, for instance.¹⁴ In the first solvent the variation is positive, indicating that the transition state is disordered compared to the planar form. For acetone, the reverse occurs, with the planar form more disordered than the transition state. For methanol, however, there is no significant entropy of activation, meaning that there is no preferred interaction between the solute and the solvent.¹⁴ This is of great interest because one could at first expect that in protic solvents the hydrogen bonds, formed in the oxygen atoms of furfural should give a preferred structure along the rotation of the carbonyl group. This is the major interest of this present paper. Here we will give a very detailed theoretical analysis of the hydrogen bonds formed between furfural and water, a very protic solvent, along the cis–trans rotational interconversion, including the transition state. The selection for water is interesting because any hydrogen bond effect will be enhanced by this strong protic solvent. We shall consider the number of hydrogen bonds formed and the corresponding binding energies, as a function of the rotation

* Corresponding author. E-mail: canuto@if.usp.br.

[†] E-mail: rivelino@if.usp.br.

[‡] E-mail: kaline@umc.br.

angle. With this we analyze possible preferences of the solute form.

The solvent dependence of the UV-vis absorption spectrum of furfural is much less known despite its great importance as an additional aid to the conformation dynamics.^{21,22} The ultraviolet absorption spectrum of furfural vapor is quite weak to be accurately measured, whereas in polar solvents the whole spectrum merges into a strong absorption.^{21,22} The influence of polar solvents, e.g., water, on the $n-\pi^*$ transition of furfural is known to give a blue shift, as normally expected. The $\pi-\pi^*$ transition, instead, suffers a red shift.^{21,22} It is important to understand the role of the conformers on the solvent-induced spectral shift of furfural during the internal rotation of the carbonyl group. In particular, the effect of the solvent on the $n-\pi^*$ transition gives additional information on the possible preference of the solute form, because the lone pair of furfural is located in the same atom that is the proton acceptor of the hydrogen bond.

Thus, the major interest here is to investigate the hydrogen bonds formed between furfural and water and the solvent effects on the absorption spectrum of furfural in aqueous solution. We use a sequential Monte Carlo (MC) quantum mechanics (QM) methodology,²³⁻²⁵ where we first generate the structures of the liquid by using MC simulations. The advantage of using a sequential procedure has been discussed before.²⁵⁻²⁷ Supermolecular structures are extracted from the MC simulations and only statistically uncorrelated configurations are used. As we shall demonstrate, this leads to converged results for all calculations presented here.

The solvation shifts and the analysis of the hydrogen bonds are made for several rotation angles, starting with the OO-cis conformation and changing the dihedral angle until the OO-trans structure is reached (Figure 1). Note that the use of isolated cluster calculations is not recommended in this case. For one side there is no a priori indication of how many hydrogen bonds are formed. The change of the number of hydrogen bonds along the cis-trans interconversion is precisely the subject of interest here. On the other, geometry-optimized clusters cannot reproduce the liquid situation.^{26,28} Instead, the use of computer simulation of liquids is more appropriate. We use MC simulation to generate the liquid structure. In total, 20 different conformations of furfural are used, with the dihedral angles changed by 9° between successive simulations. The QM calculations are performed in several supermolecular structures of each of these 20 conformations of furfural in aqueous solution obtained from the MC simulations. In every conformation singly excited configuration interaction calculations at the INDO/CIS^{29,30} level are performed to obtain the solvatochromic shifts of the $n-\pi^*$ and $\pi-\pi^*$ electronic transitions during the conformational changes of furfural in water. Each supermolecule included in the QM calculation is composed of the solute furfural and all molecules up to the first solvation shell. The use of this supermolecular approach incorporates in a natural way the solute-solvent interaction because it is treated by quantum mechanics.

Monte Carlo Simulation and Computational Details

Monte Carlo (MC) statistical mechanics simulations are carried out by employing standard procedures,³¹ including the Metropolis sampling technique³² and periodic boundary conditions using the minimum image method in a cubic box. The simulations are performed in *NPT* ensembles. The system consists of one furfural molecule plus 450 water molecules at temperature of 298.15 K and pressure of 1 atm. In total, 20

Figure 2. Geometrical parameters (Å) for the conformers of furfural.

TABLE 1: Potential Parameters Used in the Monte Carlo Simulations (q in Elementary Charge Unit, ϵ in kcal/mol, and σ in Å)^a

atom	ϵ	σ	atomic charge q in conformation:		
			OO-cis ($\varphi = 0^\circ$)	TS ($\varphi = 90^\circ$)	OO-trans ($\varphi = 180^\circ$)
O ₄	0.140	2.90	-0.113742	-0.140933	-0.186419
C ₁	0.070	3.55	-0.229589	-0.236743	-0.152939
C ₂	0.070	3.55	-0.092507	-0.109888	-0.182596
C ₃	0.070	3.55	-0.066166	-0.080331	0.013224
C ₅	0.070	3.55	0.093111	0.070219	0.096797
H ₁	0.030	2.42	0.154373	0.152396	0.150293
H ₂	0.030	2.42	0.123161	0.128195	0.146217
H ₃	0.030	2.42	0.160697	0.158236	0.141872
C ₆	0.105	3.75	0.378572	0.528755	0.382465
O ₆	0.210	2.96	-0.403259	-0.413801	-0.416096
H ₆	0.030	2.42	-0.004650	-0.056105	0.007182

^a Atomic indices are defined in Figure 2. The parameters ϵ and σ are taken from ref 16, and the atomic charges are obtained from CHELPG calculations using MP2/6-311+G(d).

different MC simulations of furfural in water are performed for a fixed dihedral angle φ (O₄C₅C₆O₆, in Figure 2) with $\Delta\varphi = 9^\circ$, from 0° (OO-cis or syn-furfural) to 180° (OO-trans or anti-furfural). The intermolecular interactions are described by the standard Lennard-Jones plus Coulomb potential with three parameters for each atom i (ϵ_i , σ_i , and q_i). The atomic parameters are combined by geometric average to generate the pair parameters $\epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i\sigma_j)^{1/2}$. For the water molecules we use the SPC potential developed by van Gunsteren et al.³³ For furfural, we use the OPLS-AA potential previously used to study the free energy of its interconversion in different solvents.^{16,34} The atomic charges of furfural have been obtained by fitting the electrostatic potential at points selected according to the CHELPG scheme,³⁵ using an ab initio second-order Møller-Plesset perturbation theory (MP2) with the 6-311+G(d) basis set,^{36,37} as implemented in the Gaussian98.³⁸ The sets of intermolecular potential parameters employed in the simulations are shown in Table 1. As the atomic charges are different for the different rotational angles we obtain 20 sets of atomic charges from the MP2/6-311+G(d) calculations. In Table 1 we only show the charges for the planar OO-cis conformation ($\varphi = 0^\circ$), the nearest conformation of the transition state ($\varphi = 90^\circ$), and OO-trans conformation ($\varphi = 180^\circ$). As can be seen, they do not differ much. However, it is interesting to note that the oxygen atom of the carbonyl has a larger negative charge than the oxygen in the furan ring. This aspect is seen here even when using other ab initio theoretical models. Thus the carbonyl group is more apt to make hydrogen bonds with the solvent water than the furan ring. In the 20 simulations, the averaged density has a small variation. The smaller value of the averaged density $\rho = 1.045$ g/cm³ was found to conformation at $\varphi = 117^\circ$ and the larger value $\rho = 1.055$ g/cm³ was found at $\varphi = 63^\circ$. This means that in the average the smallest cubic box has size of $L = 21.46$ Å and the largest 21.52 Å. The intermolecular interactions are spherically truncated within a center of mass

separation smaller than the cutoff radius, $r_c = L/2$. Long-range corrections were calculated beyond this cutoff distance.³¹ The Lennard-Jones potential contribution is estimated assuming an uniform distribution $G(r) \approx 1$ after the cutoff radius and the electrostatic potential contribution is estimated with the reaction field method of the dipolar interaction. In the simulation the molecules are kept with rigid geometries for the different conformations of furfural. The geometrical parameters used for furfural in the simulations are given in Figure 2. Using these parameters, we find that the dipole moments of the OO-cis and OO-trans configurations at the ab initio MP2/6-311G(d) level are 3.76 and 3.24 D, respectively. These compare very well with the corresponding experimental³⁹ values of 3.97 and 3.23 D. During the classical simulation the water molecules are kept in their C_{2v} structure with $r_{OH} = 1.000$ Å and $\theta(HOH) = 109.47^\circ$.

The initial configurations are generated randomly, considering the position and orientation of each molecule. One MC step is performed after one water molecule randomly attempts to translate in the Cartesian directions and also attempts to rotate around a randomly chosen axis. The maximum allowed displacement of the molecules and of the box size are self-adjusted after 50 configurations to give an acceptance ratio of new configurations around 50%. The maximum rotation angle was fixed during the simulation in $\delta\theta = \pm 15^\circ$. The simulations consisted of a thermalization phase of 2.0×10^6 MC steps, followed by an averaging stage of 27.0×10^6 MC steps.

As quantum mechanical calculations will be performed on the configurations generated by the MC simulations it is very important to optimize the statistics. Successive configuration, which are statistically highly correlated, will not give important additional information. Therefore we calculate the interval of statistical correlation using the autocorrelation function of the energy.^{23–25,40,41} Essentially, it gives the interval of MC steps in which the statistically uncorrelated configuration can be sampled. For the simulations presented here, we obtain that configurations separated by 450×10^3 MC steps are statistically less than 10% correlated. Then, the total of 27×10^6 successive configurations generated in each simulation can be drastically reduced to 60 nearly uncorrelated configurations without loss of statistical information.^{26,40,41} Thus, after each simulation corresponding to the different rotation angles, 60 uncorrelated configurations are sampled to be used in further quantum mechanical supermolecular calculations. Each supermolecule is composed of the chromophore (furfural) and all solvent molecules up to the first solvation shell of the radial distribution function. This gives a number of 34 water molecules surrounding furfural. Then, for each QM calculation there are 308 valence electrons included. In total, 20 sets of configurations are generated by the MC simulations, corresponding to the different dihedral angles. This means that 60 QM calculations are performed for the supermolecules composed of one furfural and 34 water molecules. A more detailed discussion on the efficiency of the sampling procedure will be given below and demonstrate that statistically converged results are obtained.

All simulations are performed with the DICE⁴² Monte Carlo statistical mechanics program. DICE is a general program for MC simulation with a graphical interface that calculates thermodynamic properties and generates structures for using in most conventional quantum chemistry program.

Results and Discussion

Hydrogen Bond Analysis. In this section we analyze the number of hydrogen bonds formed between furfural and water

TABLE 2: Statistics of the Hydrogen Bonds Formed between Furfural and Water

no. of HB	OO-cis ($\varphi = 0^\circ$)		TS ($\varphi = 90^\circ$)		OO-trans ($\varphi = 180^\circ$)	
0	23%		28%		8%	
1	58%		60%		72%	
2	17%		12%		18%	
3	2%				2%	
average	0.97		0.84		1.13	
proton acceptor	O _c	O ₄	O _c	O ₄	O _c	O ₄
	0.87	0.10	0.82	0.02	1.13	0.00

and the energy of these bonds for each of the 20 different conformations used here. These will give microscopic detailed information of the specific interaction involving the proton acceptor furfural and the proton donor water clarifying the specific role played by the hydrogen bonds in the rotational interconversion between the two extreme OO-cis and OO-trans conformers.

A common procedure to identify hydrogen bonds is by using the radial distribution function. In this case spherical integration of the first peak of the radial distribution function between the oxygen atom of furfural and the hydrogen atom of water would give the coordination number; i.e., the number of hydrogen bonds formed. The uncertainty associated with this procedure is that it cannot be assured that all nearest-neighbor structures are indeed associated with hydrogen bonds.^{24,26,43} An efficient and more correct way to extract the hydrogen-bonded structures has been presented by Stlinger and Rahman^{44–46} and Mezei and Beveridge.⁴⁷ They have discussed the directional and energetic aspects of hydrogen bonds and its usefulness in identifying hydrogen bonds in computer simulation of liquids. Hydrogen bonds are indeed better obtained using the geometric and energetic criteria.^{24,26,43,48} We consider a hydrogen bond formation when the distance $R(O-O_w) \leq 3.7$ Å, the angle $\theta(OO_wH_w) \leq 36^\circ$, and the binding energy is positive. Again, as there are 20 simulations performed, corresponding to the 20 rotation angles selected, it is cumbersome to give detailed information for all cases. Let us then first consider the most important cases of the OO-cis, OO-trans, and the transition state. It is of great importance to clarify the specific role played by the hydrogen bonds in the rotational interconversion between the two extreme OO-cis and OO-trans forms. Table 2 gives the detailed statistics of the hydrogen bonds. In the OO-cis case 23% of the configurations make no hydrogen bonds, 58% makes one, 17% makes two, and 2% makes even three hydrogen bonds. Table 2 shows that out of the 60 configurations selected there are 58 hydrogen bonds in the OO-cis conformation, thus making, on average, 0.97 hydrogen bond. These are averages for the liquid. Almost all the hydrogen bonds formed have the oxygen of the carbonyl as the proton acceptor. For instance, in this case of OO-cis, 0.87 is formed in the oxygen of the carbonyl, the O_c site, and a negligible number of 0.10 in the oxygen atom O₄ of the furan ring. Similar results can be obtained for the OO-trans and even for the transition state. In these cases we find that furfural makes, on average, 1.13 hydrogen bonds in the OO-trans case and a slightly smaller number of 0.84 for the transition state. In the case of OO-trans 72% of the configurations make one hydrogen bond. In total, there are 1.13 hydrogen bonds and all these have the O_c site as the proton acceptor. Figure 3 illustrates the hydrogen bond formed between furfural and water for an arbitrarily selected angle ($\varphi = 36^\circ$). This is very indicative that the hydrogen bonds do not contribute to any preferred orientation of furfural in water. To have the overall picture of the number of hydrogen bonds in the different conformations, Figure 4 shows the average number as a function of the rotation angle. As can be seen the total number of hydrogen bonds is

Figure 3. Illustration of the hydrogen bond formed between furfural and water for a rotation angle of 36° .

Figure 4. Calculated number of hydrogen bonds between furfural and water as a function of the rotation angle.

Figure 5. Binding energy per hydrogen bond as a function of the rotation angle.

remarkably stable, varying between a minimum of 0.75 hydrogen bond (for $\varphi = 135^\circ$) and a maximum of 1.25 hydrogen bonds (for $\varphi = 45^\circ$). A consequence of this result is, of course, that hydrogen bonds do not contribute much to the energy change along the rotational interconversion. Hence, hydrogen bonds do not give rise to any preferred solute-solvent structure. To make this assertion even more emphatic, we show in Figure 5 the hydrogen bond energies. In the OO-cis case the binding energy is calculated as 3.36 kcal/mol . The maximum binding is $3.58 \pm 0.10 \text{ kcal/mol}$, obtained for $\varphi = 162^\circ$. For comparison, the minimum binding is $2.83 \pm 0.10 \text{ kcal/mol}$, obtained for $\varphi = 63^\circ$. In complement, the binding energy for the OO-trans case is $3.45 \pm 0.10 \text{ kcal/mol}$, 0.1 kcal/mol stronger than in the case of the OO-cis case. As the statistical error in the calculations is 0.1 kcal/mol , we cannot, in fact, distinguish between the OO-cis and OO-trans cases. For the transition state the binding energy is only 0.5 kcal/mol weaker than in the planar forms. The conclusion is that hydrogen bonds between furfural and

TABLE 3: Calculated Solvatochromic Shifts (cm^{-1}) and Comparison with Experimental Data^a

transition	solvatochromism	experiment
$n \rightarrow \pi^*$ (OO-cis)	1230 ± 45	$1200^a, 1350^b$
$n \rightarrow \pi^*$ (OO-trans)	1130 ± 43	
$\pi \rightarrow \pi^*$ (OO-cis)	-1005 ± 64	-1300^c
$\pi \rightarrow \pi^*$ (OO-trans)	-950 ± 64	

^a From cyclohexane to water, ref 22. ^b From isooctane to water, ref 22. ^c From *n*-hexane to water, ref 21.

Figure 6. First absorption transition of furfural in the gas phase and in water as a function of the rotational angle. Lines shown are best fits to the calculated points. The lower curve corresponds to the transition shift of furfural in gas phase. The upper curve is the same transition shift in explicit water environment.

water are essentially equivalent for all rotation angles and therefore they make no contribution to a particular preference for any rotamer. This is in agreement with what could be expected from the experimental NMR measurements of Bain and Hazendonk.¹⁴

Solvatochromic Shifts. Now we analyze the solvation shifts of furfural in water. The UV-vis absorption spectrum of furfural in the gas phase shows a very weak $n \rightarrow \pi^*$ and a strong $\pi \rightarrow \pi^*$ electronic transitions.^{21,22} The solvation shift of the $n \rightarrow \pi^*$ in water is thus measured from cyclohexane and isooctane, leading to an observed blue shift of $1350 \pm 150 \text{ cm}^{-1}$. As both solvents have a low polarity and low dielectric constant, we compare these values with those obtained here for the gas phase. For the $\pi \rightarrow \pi^*$ electronic transition the shift from *n*-hexane to water has been measured as -1300 cm^{-1} . Again, we take this value for a comparison of our results for the solvation shift from gas to water. Table 3 shows a comparison of our calculated results and the experimental values available for the OO-cis conformation for both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. As can be seen, the agreement is very good. The blue shift of the $n \rightarrow \pi^*$ transition is calculated as $1230 \pm 45 \text{ cm}^{-1}$, whereas the red shift of the $\pi \rightarrow \pi^*$ electronic transition is calculated as $-1005 \pm 64 \text{ cm}^{-1}$. These compare very well with the above-quoted experimental results of 1350 and -1300 cm^{-1} , respectively.

It is now of interest to analyze the solvation shifts for the different conformations of furfural. This is shown in Figure 6 for the $n \rightarrow \pi^*$ transition. In the gas phase (lower curve) the transition is blue shifted by as much as 1700 cm^{-1} , in going from the OO-cis to the transition state. This maximum in the transition state is not due to the solvent interaction because it occurs for the gas phase. This is only a structural effect. Next in the rotation, the gas-phase absorption decreases and reaches the value corresponding to the OO-trans case. Thus the gas-phase absorption $n \rightarrow \pi^*$ transition shows a clear structural dependence and reaches its maximum close to the transition state where the absorption increases by 1700 cm^{-1} . However, there is an interesting aspect in the analysis of the solvation

Figure 7. Second absorption transition of furfural in the gas phase and in water as a function of the rotational angle. Full line is the best fit for the transition in the gas phase. The dotted line is for visualization of a constant shift of -1000 cm^{-1} for the transition shift in explicit water environment. Comparison of the calculated points (full circles) with the dotted line shows the discrepancy from a constant solvation shift.

shift. As Figure 6 shows, the *solvation shift* (difference between the two curves) is essentially independent of the conformation. This is not surprising because, as noted in the previous section, the solvent environment in the oxygen atom of the carbonyl is not very dependent on the rotation angle. As the lone pair of this atom is the one involved in the promotion of the $n-\pi^*$ transition, it follows the same pattern along the rotation and gives a constant shift of about 1200 cm^{-1} . Even in the other extreme, the OO-trans conformation, the shift is 1130 cm^{-1} , only 100 cm^{-1} less than in the more favorable OO-cis conformation. The constant solvatochromic shift of the $n-\pi^*$ transition is thus related to the nonexistence of a preferred angle for the interaction of hydrogen bonds and the carbonyl group. Therefore, this should not occur in the strong $\pi-\pi^*$ transition. Indeed, as shown in Figure 7, the $\pi-\pi^*$ transition shows a more erratic behavior. The π^* orbital is more localized in the furan ring but during the rotation of the carbonyl group the occupied π orbital becomes less defined and is not delocalized over the entire molecule because it loses planarity. The largest variations form a constant shift (dotted line) are found close to the transition state. At the other extreme, the OO-trans planar conformation, the solvation shift is a red shift of 1130 cm^{-1} , only 100 cm^{-1} less than in the case of OO-cis.

Every point in Figures 6 and 7 is the result of an average over 60 quantum mechanical calculations. It is clear that if each of these numbers is not properly converged a wrong picture could emerge. We shall show below that the use of an efficient sampling procedure, as adopted here, guarantees converged results for a relatively small number of quantum mechanical calculations. This is of course an important point not only for the general QM/MM methodology but also because using 20 different simulations each entry in Figures 6 and 7 requires an average value for each rotation angle, amounting here to a total of 1200 quantum mechanical calculations.

Statistical Convergence Analysis. The question of sampling configurations from statistical simulations has been recognized to be a very important issue and it is crucial for the efficiency of QM/MM methods. We have addressed this issue several times before.^{23–27} Instead of performing a quantum mechanical calculation on every configuration generated by the MC simulation, we use the interval of statistical correlation and the statistical inefficiency, to select the configuration that gives relevant statistical information.^{23–27,40,41,48} We have shown numerically that performing average over thousands of successive configurations generated in the MC simulation, gives the

Figure 8. Convergence of the (a) calculated solvation shift and (b) hydrogen binding energy for the OO-cis case.

same result as averaging over only a few statistically uncorrelated configurations.⁴⁰ This is a very efficient way to sample configurations. It is statistically sound, and as we demonstrate, now it gives statistically converged results.

Now we analyze the dependence of our calculated average values on the set of values used in the calculation. As discussed before, the configurations separated from the MC simulation are statistically uncorrelated and therefore the average value should converge fast and systematically and should be independent of the particular choice of the set of MC configurations selected for the QM calculations. The statistical error of the average, however, depends on the total number of uncorrelated configurations (l) used to calculate the average; i.e., on the total size of the simulation. Figure 8a shows the calculated average solvation shift of the $n-\pi^*$ transition of the OO-cis conformation of furfural in water as the number of configurations used for the average is increased. This corresponds to the zero rotation angle of Figure 6. There are 20 averages of this type obtained for the analysis of the rotation effect on the $n-\pi^*$ transition. Of course, only one case is given for illustration. Figure 8a clearly shows that the solvatochromic shift reported is a statistically converged value. In complement, Figure 8b shows the same convergence analysis for the hydrogen binding energy of the OO-cis case. The results clearly demonstrate that all average values considered here are statistically converged with only 60 uncorrelated structures of the MC simulation. This is again a demonstration of the efficiency of the sampling procedure used here that only $l = 60$ instantaneous values give statistically converged results. Increasing further the number of calculations does not change the average, but of course, the statistical error, which depends on $1/\sqrt{l}$, decreases.

Summary and Conclusions

The conformation equilibrium of furfural has been of great interest and the subject of several theoretical and experimental studies. It is known that it may exist in two conformations, the OO-cis and the OO-trans conformers, that are separated by a large interconversion barrier. In water, the conformer with the higher dipole moment, the OO-cis, is the most stable. In this investigation we have considered the role of hydrogen bonds in the conformational equilibrium and in the solvation shift of the $n-\pi^*$ and $\pi-\pi^*$ transitions of furfural in water.

A detailed analysis is made of the hydrogen bonds formed. To verify the dependence on the rotation angle, 20 different rotamers were considered. Thus 20 different Monte Carlo simulation were performed. On average one hydrogen bond is formed in the most stable OO-cis form. The number and strength of these hydrogen bonds do not vary much along the interconversion, thus suggesting that this interaction makes no preference for any particular rotamer. This is in agreement with experimental results obtained for furfural in a protic solvent.

Using a combined Monte Carlo and quantum mechanics methodology, the structure of the liquid composed of one furfural molecule and the first solvation shell of water is subjected to the calculation of the absorption spectrum. From the 20 different Monte Carlo simulations a total of 60 structures are sampled for each case for subsequent quantum mechanical calculations. It is found that the $n-\pi^*$ absorption transition shifts by $1230 \pm 45 \text{ cm}^{-1}$ in the OO-cis form, in good agreement with the experimental result of 1350 cm^{-1} . The solvatochromic shift of this $n-\pi^*$ transition does not depend on the particular rotation angle. This is supplementary strong evidence that the hydrogen bonds have no preference for any particular rotamer of the solute and leads to small contribution to the entropic activation barrier. Before concluding, we should mention that the selection of water for this study is also related to the existence of the UV-vis experiment of furfural in water. Similar to the case of water we also found that the number and strength of hydrogen bonds formed between chloroform (a weaker protic solvent) and furfural is essentially constant along the rotational interconversion giving again no contribution to the entropic activation barrier.

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B.6 Quantifying multiple-body interaction terms in H-bonded HCN chains with many-body perturbation/coupled-cluster theories.

R. Rivelino, P. Chaudhuri, S. Canuto.

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Quantifying multiple-body interaction terms in H-bonded HCN chains with many-body perturbation/coupled-cluster theories

Roberto Rivelino[†], Puspitapallab Chaudhuri and Sylvio Canuto^{*}

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

Abstract

Many-body perturbation/coupled-cluster calculations have been carried out to investigate the magnitudes of the multiple-body energy terms and their contribution to the interaction energy of linear (HCN)_N chains. All minimum energy geometries of the clusters ($N = 2-7$) are obtained at the second-order many-body perturbation (MP2) levels of theory. Electron correlation and cooperative effects in the C–H · · · N hydrogen bonds are also quantitatively characterized during the aggregation process. It is found that the two- and three-body terms account for nearly all of the total interaction energy, but all high-body terms increase with the size of the cluster. Detailed numerical values are given for all the many-body contributions of the (HCN)_N chains. Electron correlation effects are found to be important for the two- and three-body terms but have decreased importance for the higher-body terms. Cooperative effects are also investigated for the binding energy and dipole moment. The dipole moments of the HCN oligomers are larger than the sum of the individual monomers with differences ranging between 12% ($N = 2$) and 28% ($N = 7$). The limiting values for the binding energy and dipole moment of (HCN)_N, corresponding to very large N values, are estimated to be 22.9 kJ/mol and 3.87 D, per monomer, respectively. These results correspond to cooperative contributions of 5.8 kJ/mol to the energy, and 1.0 D to the dipole moment.

Keywords: Multiple-body interaction terms; hydrogen bonding; cooperative effects.

^{*} Corresponding author. E-mail: canuto@if.usp.br, Fax: + 55 11 3091 6831.

[†] E-mail: rivelino@if.usp.br.

I. INTRODUCTION

Hydrogen-bonded molecular complexes are species of considerable interest in cluster researches^{1,2}. Investigation on the structures and interactions of molecular clusters provides important information on the properties of both single particles and condensed materials. In recent years the progress in physical-chemistry techniques and quantum-chemistry calculations permitted to systematically investigate the properties of hydrogen-bonded clusters in gas phase, by first considering only the two-body interactions in binary complexes, and then proceeding to three- and many-body interactions through the study of ternary and larger complexes³⁻⁸. Computing the contribution of multiple-body interactions of these aggregates is important for understanding the nonadditive nature of the hydrogen bonds in a great variety of interesting systems⁹⁻¹¹. The anisotropic character of the hydrogen bonds can lead to assembling supramolecular structures by linking molecules via intermolecular interactions¹². These constitute interesting systems to enhance our understanding of bonding properties in biological structures.

The ability of small molecules such as hydrogen cyanide to form long hydrogen-bonded chains is well known¹³. Because this molecule is rather abundant under primitive conditions of pre-biotic Earth^{14,15} and Space¹⁶⁻¹⁹, its oligomerization mechanism is of great relevance for studying the chemical evolution of biologically important molecules²⁰. Recently, Smith *et al.*²¹ investigated the first step of a proposed synthesis of adenine in dense interstellar clouds²², by analyzing the possible products of the dimerization of HCN forming chemically bound isomers. Several features such as the small size of the HCN monomer, structural linearity in different phases, low-polarity of the C-H $\cdots$ N bonds, single lone pair of the HCN molecule, and strong ability to form large molecular chains make the hydrogen cyanide clusters very interesting systems for quantitative characterization of the physical and chemical properties. For instance, structures, spectra, and kinetics can be assessed by different spectroscopic techniques, such as Fourier transform microwave spectroscopy (FTMW)²³, photoacoustic Raman spectroscopy (PARS)²⁴, tunable far-infrared Stark spectroscopy²⁵, superfluid helium droplet spectroscopy (SHEDS)²⁶, mass spectrometric methods¹⁴, and electron mobility measurements by the pulsed Townsend method²⁷.

Besides the experimental investigations, several theoretical studies have also been performed in the last few years on HCN systems. Kofraneck *et al.*²⁸ have performed quantum-mechanical calculations to obtain structures and vibrational spectra of HCN oligomers up to five molecules utilizing various extended basis sets. They have obtained the equilibrium geometries of the clusters at the Hartree-Fock (HF-SCF) level and performed the vibrational analyses using the harmonic approximation. In another paper²⁹ they have also examined the harmonic frequencies of the HCN dimer and trimer, including electron correlation in the calculations obtained from the coupled pair functional (CPF) method, combined with polarized basis sets. The binding energies and electric properties have also been estimated with these levels of theory. Later on, the investigation was extended by King and Weinhold³⁰ using the second-order Møller-Plesset (MP2) method, with the 6-31+G(d) basis set. In this case, the emphasis was centered on cooperative effects of the HCN trimer and tetramer. According to these authors most of the cooperativity arises from the donor-acceptor ($n_N \rightarrow \sigma_{CH}^*$) interaction in the C-H $\cdots$ N bonding. Even though this can be interpreted as a propagation of electron density from the acceptor to the donor along the hydrogen-bonded chains, the polarization of the hydrogen bonding could not be thought in terms of the "classical electrostatic sense". However, Buckingham *et al.*³¹ have argued against a "quantum charge transfer" between acceptor and donor as providing the major nonadditivity contribution of the hydrogen bond. Instead, they suggested that an approach based on electrostatic interactions, including induction by means of distributed polarizabilities, is rather reliable for a quantitative description of the cooperative effects in linear HCN clusters. More importantly, they have concluded that cooperativity is given by induction effects and not due to charge transfer.

With all these theoretical discussions and several available experimental data, it is now opportune to establish a systematic study of the multiple-body contributions and the influence of electron correlation on these multiple-body energy terms, involving the interaction of all monomers in the oligomer configuration of HCN linear chains. These are difficult to be directly obtained from experimental measurements, since this requires a fine interpretation of the magnitude and origin of the explicit multiple-body interactions. The present work focuses on these aspects, in which we will discuss the multiple-body interactions based on many-body perturbation/coupled-cluster calculations¹¹. The total interaction energy of a cluster formed with N interacting molecules can be decomposed into a sum of multiple-body terms, according to the partition scheme³²:

$$U = \sum_{i=1}^{N-1} \sum_{j>i}^N U_2(i,j) + \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^N U_3(i,j,k) + \dots \quad (1)$$

In Eq. (1) the U_K ($K = 2-N$) terms correspond to the two- through N -body single contributions in the total interaction energy of the aggregate. The multiple-body terms are recursively obtained by considering the energy of doublets, $E_2(i,j)$, triplets, $E_3(i,j,k)$, and etc., defined as

$$\left. \begin{aligned} U_2(i,j) &= E_2(i,j) - [E_1(i) + E_1(j)], \\ U_3(i,j,k) &= E_3(i,j,k) - [U_2(i,j) + U_2(i,k) + U_2(j,k)] \\ &\quad - [E_1(i) + E_1(j) + E_1(k)], \\ U_4(i,j,k,l) &= E_4(i,j,k,l) - [U_3(i,j,k) + U_3(i,j,l) + U_3(i,k,l) + U_3(j,k,l)] \\ &\quad - [U_2(i,j) + U_2(i,k) + U_2(i,l) + U_2(j,k) + U_2(j,l) + U_2(k,l)] \\ &\quad - [E_1(i) + E_1(j) + E_1(k) + E_1(l)], \\ &\dots \end{aligned} \right\} \quad (2)$$

In fact, there are $N(N-1)/(2!)$ two-body terms, $N(N-1)(N-2)/(3!)$ three-body terms, $N(N-1)(N-2)(N-3)/(4!)$ four-body terms, and so on. Most of the present theories of liquids are based upon the assumption of pairwise additivity for the overall interaction potential ($U_K = 0$ for $K \geq 3$)³³. The main characteristic feature of the HCN molecule pair potential, U_2 , is the ability to form single lone pair hydrogen bonds. Because of the possibility of resonance with the $\text{H}-\text{C}^+::\text{N}^-$ structure, involving a positive formal charge on the carbon atom, the H-bonds are strong enough to stabilize the linear polymers of hydrogen cyanide, even in condensed phase³⁴. However, it is well accepted that hydrogen bond formation in HCN clusters possesses a cooperative character¹³. Thus, once the first H-bond is established, the subsequent contiguous bonds become gradually stronger. This phenomenon is largely associated with nonadditive potentials, such as U_3 , U_4 , etc., which provide the many-body effects in the total interaction. Then, in this work we will systematically quantify the magnitudes of the multiple-body interaction terms in different sizes of H-bonded HCN clusters.

II. METHODS AND COMPUTATIONAL PROCEDURE

The first-principle calculations are performed in the supermolecular approach for $(\text{HCN})_N$ linear chains $N = 2-7$. All cluster geometries are optimized at the second-order Møller-Plesset (MP2) method. For $N = 2$, the calculations are carried out using three gaussian-type basis sets: the standard split-valence diffuse-polarized³⁵ 6-311++G(d,p) and augmented correlation-consistent with polarized valence³⁶ of double (aug-cc-pVDZ) and triple (aug-cc-pVTZ) zeta quality. After obtaining the equilibrium structure of $(\text{HCN})_2$ with these three different basis sets, single-point calculations are performed within the many-body perturbation/coupled-cluster theories (MBPT/CC)^{37,38}. Thus, we are able to separately analyze the influence of basis sets and high-order electron correlation effects in assembling the complex from its isolated monomers. For $N = 3-7$, only the 6-311++G(d,p) basis set is employed. This set includes only 51 basis functions per monomer but allows reliable quantitative characterization of the multiple-body terms in the total interaction energies, including the limiting behavior in larger HCN clusters. The decomposition of total energies of the $(\text{HCN})_N$ oligomers, $N = 3, 4$, into multiple-body contributions has also been improved for higher-order electron correlation by performing single-point calculations beyond MP2/6-311++G(d,p). These include MP3, MP4, CCSD, and the highest level, CCSD(T)³⁸. For $(\text{HCN})_5$ the energy decomposition scheme is carried out at the HF-SCF and MP2 levels. The fragmentation of the H-bond energies, according to the processes $(\text{HCN})_N \rightarrow (\text{HCN})_{N-K} + (\text{HCN})_K$ for $N = 2-7$ and $K = 1-6$, has also been performed at the HF-SCF and MP2 levels. All interaction energies and the multiple-body terms are calculated with all the above methods correcting for full basis set superposition error (BSSE). This correction is done using the Boys and Bernardi³⁹ counterpoise (CP) technique. The influence of CP correction is also verified for the energetic cooperativity upon complexation and dipole moments of the HCN chains. The latter has been calculated using the MP2/6-311++G(d,p) charge densities. All these quantum-mechanical calculations, including analytical derivatives for obtaining optimizations and harmonic zero-point vibrational energies (ZPE), have been performed with the GAUSSIAN 98 program⁴⁰.

III. ENERGETIC AND HIGHER-ORDER ELECTRON CORRELATION

A. Basis set and correlation effects on the HCN dimer

The calculated binding energies, BE_2 , of $(HCN)_2$ at different levels of theory are given in Table I. The full BSSE counterpoise-corrected values are presented as $BE_2 + CP$. As can be seen for the three basis sets employed here, BE_2 changes by only 1.0 kJ/mol with the size of the basis functions (at the MP2 level, after CP corrections). At the highest level considered here, CCSD(T), the binding energy is calculated to be 16.81 kJ/mol (with 6-311++G(d,p)), 17.60 kJ/mol (with aug-cc-pVDZ), and 18.98 kJ/mol (with aug-cc-pVTZ). Comparison between the results obtained with MP4-SDQ and full MP4 gives the electron correlation contribution of triple-excitations at fourth-order. This is a small value of 0.21 kJ/mol for the 6-311++G(d,p), 0.58 kJ/mol for the aug-cc-pVDZ, and 0.60 kJ/mol for the aug-cc-pVTZ basis sets. However, analyzing the influence of higher-order triple-excitation by directly comparing the results obtained with MP4-SDQ and CCSD(T), these differences are larger using the correlation-consistent basis set with triple zeta quality, which gives 0.29 kJ/mol, while the basis set with double-zeta quality gives only 0.07 kJ/mol. In the case of the 6-311++G(d,p) basis set, the high-order triple excitation is found here to be negligible. The effect of high-order double excitation is less important. Comparing the results obtained going from MP4-DQ to CCSD levels, the influence of higher-order double-excitations is seen to be only ± 0.3 kJ/mol. Using the correlated methods, BSSE is 2.0 kJ/mol (6-311++G(d,p)), 4.7 kJ/mol (aug-cc-pVDZ), and 2.6 kJ/mol (aug-cc-pVTZ). At the HF-SCF level these values are smaller, i.e., 1.23, 2.56, and 1.40 kJ/mol, respectively, as we can obtain from Table I. Therefore, the small difference in BE_2 and the smallest value of BSSE, with respect to the basis set dependence, reinforce that MP2/6-311++G(d,p) is an appropriate method to investigate the properties of larger complexes of HCN. A comparison between our calculated binding energy, using different correlated methods carried out with the 6-311++G(d,p), and the results obtained by Heikkilä and Lundell⁴, with the 6-311++G(2d,2p) basis set, shows an excellent agreement, differing by less than 0.03 kJ/mol.

TABLE I. Influence of basis sets, BSSE, and electron correlation effects on the calculated $(HCN)_2$ hydrogen binding energies (BE_2 in kJ/mol).

Method	6-311++G(d,p)		aug-cc-pVDZ		aug-cc-pVTZ	
	BE_2	$BE_2 + CP$	BE_2	$BE_2 + CP$	BE_2	$BE_2 + CP$
HF-SCF	18.90	17.67	19.19	16.64	18.03	16.63
MP2	19.49	17.72	23.19	18.76	22.23	19.74
MP3	18.83	16.73	22.25	17.39	21.52	18.76
MP4-DQ	18.84	16.84	22.04	17.39	21.31	18.69
MP4-SDQ	18.91	16.94	22.14	17.53	21.22	18.69
MP4	19.16	17.15	22.95	18.11	21.82	19.30
CCSD	18.63	16.62	22.15	17.51	21.03	18.42
CCSD(T)	18.89	16.81	22.48	17.60	21.61	18.98

Geometries obtained at the MP2/6-311++G(d,p), MP2/aug-cc-pVDZ, and MP2/aug-cc-pVTZ levels of calculations. Corresponding differences in harmonic zero-point energies (ZPE) are respectively 3.43 kJ/mol, 3.79 kJ/mol, and 3.49 kJ/mol.

Considering the difference of BE_2 between HF-SCF and MP2 with the 6-311++G(d,p) basis set, most of the binding energy (including CP correction) is obtained at the HF-SCF level, showing the dominant character of the electrostatic interaction. For the correlation-consistent basis sets the second-order electron correlation is calculated to be 2.12 kJ/mol (aug-cc-pVDZ) and 3.11 kJ/mol (aug-cc-pVTZ). For more accuracy in the binding energy, we take into account the difference in zero-point vibrational energies (ZPE). The calculation of intermolecular vibrational frequencies of hydrogen-bonded complexes is difficult because these modes are largely anharmonic. To obtain an estimate of the correction for ZPE difference, we have used the harmonic approximation. The results indicate that the total difference of ZPE is small but it slightly influences the binding energy. For the MP2/6-311++G(d,p) this difference is 3.43 kJ/mol; for the MP2/aug-cc-pVDZ it amounts to 3.79 kJ/mol and for MP2/aug-cc-pVTZ it is slightly smaller, 3.49 kJ/mol. Our best agreement with the experimental data⁴¹ of 18.39 kJ/mol is obtained with the CCSD(T)/aug-cc-pVTZ level (16.49 kJ/mol, after both BSSE and ZPE corrections). The experimental intermolecular distance (C-H $\cdots$ N) is found to be 2.265 Å, while our best value is calculated to be 2.271 Å at the MP2/6-311++G(d,p) level. The calculated values with correlation-consistent basis sets are shorter, i.e., 2.180 Å (aug-cc-pVDZ) and 2.181 Å

(aug-cc-pVTZ). Finally, the binding energy and structure obtained for the dimer (HCN)₂ at the MP2/6-311++G(d,p) are comparable to the best theoretical results available and will be used for the larger systems. The MP2/6-311++G(d,p) is indeed found to be a feasible theoretical model for the calculations of the cooperative effects and multiple-body energy terms in HCN oligomers.

B. BSSE and correlation effects on the HCN trimer and tetramer

Before discussing the multiple-body decomposition analysis of the HCN oligomers, it is interesting to investigate the importance of BSSE and electron correlation effects on the binding energies and cooperativity. These properties are calculated from the MP2 up to the CCSD(T) level, as listed in Table II and III for (HCN)₃ and (HCN)₄, respectively. The first two columns report the binding energies (BE_N , $N = 3, 4$) related to assembling each complex from its isolated monomers. For instance, at the MP2/6-311++G(d,p) level, the binding energies are 43.27 kJ/mol for the trimer and 68.46 kJ/mol for the tetramer. After the inclusion of ZPE and CP corrections for basis set superposition error, we obtain, respectively, these quantities, as 31.85 and 51.05 kJ/mol. Electron correlation effects beyond second-order are not very important if an accuracy of ~1.0 kJ/mol is required. The total binding energy of the trimer (39.47 kJ/mol) is more than twice that for the dimer case (17.72 kJ/mol). This increase in strength indicates that the two H-bonds appearing in (HCN)₃ are stronger than two isolated H-bonds. Similarly, the bond between two isolated HCN dimers is weaker than in (HCN)₄ by around 10 kJ/mol, as obtained at the MP2 level. The next two columns in Tables II and III refer to the binding energy per H-bond¹³ in the oligomer [$BE_N/(N - 1)$]. For example, while BE_2 is 17.72 kJ/mol, $BE_3/2$ and $BE_4/3$ increase to 19.73 and 20.86 kJ/mol, respectively. The increments in binding energy are better described in the last two columns, as cooperativity. The CP-corrected values of the cooperativity is around 4 kJ/mol for the trimer at the correlated levels of theory, while for the tetramer it increases slightly to ~5 kJ/mol. BSSE effect on cooperativity is fairly a negligible quantity. We can estimate that this effect accounts for about 5% of the cooperativity. The result obtained for the cooperative energy contribution at the HF-SCF level overestimates the final result.

TABLE II. Electron correlation effects on the binding energy and cooperativity (kJ/mol) of (HCN)₃ calculated at different levels with the 6-311++G(d,p) basis set.

Method	BE ₃		BE ₃ /2		Cooperativity*	
	No CP	CP	No CP	CP	No CP	CP
HF-SCF	41.87	39.92	20.94	19.96	4.08	4.58
MP2	43.27	39.47	21.63	19.73	4.29	4.03
MP3	41.77	37.47	20.89	18.74	4.11	4.02
MP4-DQ	41.75	37.60	20.87	18.80	4.07	3.92
MP4-SDQ	42.00	37.85	21.00	18.92	4.17	3.97
MP4	42.66	38.28	21.33	19.14	4.33	3.99
CCSD	41.38	37.18	20.69	18.59	4.11	3.93
CCSD(T)	42.02	37.58	21.01	18.79	4.25	3.97

*Cooperativity is evaluated as $(BE_3 - 2BE_2)$ [Ref.13]. Corresponding differences in harmonic zero-point energies (ZPE) is estimated to be 7.62 kJ/mol.

TABLE III. Electron correlation on the binding energy and cooperativity (kJ/mol) of (HCN)₄ calculated at different levels with the 6-311++G(d,p) basis set.

Method	BE ₄		BE ₄ /3		Cooperativity*	
	No CP	CP	No CP	CP	No CP	CP
HF-SCF	66.92	63.80	22.31	21.27	5.11	5.40
MP2	68.46	62.59	22.82	20.86	4.99	4.72
MP3	66.36	59.61	22.12	19.87	4.93	4.71
MP4-DQ	66.20	59.71	22.07	19.90	4.85	4.60
MP4-SDQ	66.60	60.13	22.20	20.04	4.93	4.66
MP4	67.57	60.79	22.52	20.26	5.04	4.67
CCSD	65.66	59.09	21.89	19.70	4.88	4.61
CCSD(T)	66.65	59.73	22.22	19.91	5.00	4.66

*Cooperativity is evaluated as $(BE_4 - 3BE_3)/2$ [Ref. 13]. Corresponding differences in harmonic zero-point energies (ZPE) is estimated to be 11.54 kJ/mol.

IV. MULTIPLE-BODY DECOMPOSITION ANALYSIS

A. HCN trimer

It is now of interest to analyze the multiple-body contribution to the total interaction energies of the HCN oligomers. In the trimer structure [Fig. 1 (a)] the central HCN molecule (2) simultaneously acts as proton donor and proton acceptor, while the edge HCN molecules are either a proton acceptor (1) or a proton donor (3). These three molecules form a sequential trimer containing two non-symmetrical C-H $\cdots$ N bonds, (1-2) and (2-3), which we have calculated, in the MP2/6-311++G(d,p) geometry, as being 2.212 and 2.223 Å, respectively. By considering the H-bond distance in the dimer (2.271 Å), the length of these bonds decreases systematically when more HCN molecules are added to the cluster. This trend is usually interpreted as a cooperative effect of hydrogen bonding.

The two- and three-body energy contributions referring to (HCN) $_3$ are reported in Table IV at eight different and complementary levels of theory including the electron correlation effects. These energy terms are taken to be negative, since their sum together with the monomer energy contributions give the total energy of the system. The U_K ($K=2,3$) terms give the contributions in the total interaction energy and are organized according to Eq. (1). All calculated terms are also corrected for BSSE. Among the MBPT/CC results, MP2 gives the largest total two-body contribution (-36.984 kJ/mol). Also in this case correlation effects at higher-order do not contribute crucially to the pairwise additive term. For instance, at the highest level, CCSD(T), the total two-body contribution is calculated as -34.961 kJ/mol, i.e., it decreases ca. 2.0 kJ/mol. Although this fact is also valid for the terms of the nearest-neighbor pair interactions, $U_2(1,2)$ and $U_2(2,3)$, the same does not hold for the nearest second neighbor pair interaction $U_2(1,3)$, which depends strongly on long range interactions. As we can see in Table IV, the HF-SCF value for $U_2(1,3)$ is of -2.080 kJ/mol, while its corresponding MP2 value is -1.746 kJ/mol. On the other hand, the nearest-neighbor interactions are higher at the MP2 level by only 0.1 and 0.2 kJ/mol, respectively. The total two-body interaction accounts for 94% of the total trimer interaction energy, calculated as -39.47 kJ/mol (MP2).

FIG. 1: Chemical structures of the linear H-bonded chains: (a) trimer, (b) tetramer, and (c) pentamer.

For the three-body term $U_3(1,2,3)$, unique in the trimer energy decomposition scheme, the highest value is obtained at the HF-SCF level (-3.014 kJ/mol) showing a dominant participation of electrostatic interactions. At the MP2 level, $U_3(1,2,3)$ corresponds approximately to 6% of the total interaction energy. Analyzing the results for U_3 we can see that high-order electron correlation effects are negligible. For instance, the influence of higher-order double excitations obtained comparing MP4-DQ and CCSD yields only 0.05 kJ/mol. Considering the difference between HF-SCF and MP2 results, we observe that the electrostatic influence is more pronounced in the three-body term $U_3(1,2,3)$ than in the two-body term $U_2(1,3)$. However, while the variation of electron correlation increases with the higher-order excitations in $U_3(1,2,3)$, this seems not to be very important for $U_2(1,3)$.

TABLE IV. Correlation effects on the decomposition of interaction energy (kJ/mol) for (HCN)₃. All energies are counterpoise corrected for BSSE.

Terms	HF-SCF	MP2	MP3	MP4-DQ	MP4-SDQ	MP4	CCSD	CCSD(T)
$U_2(1,2)$	-17.338	-17.574	-16.477	-16.578	-16.690	-16.950	-16.339	-16.563
$U_2(1,3)$	-2.080	-1.746	-1.753	-1.753	-1.753	-1.704	-1.758	-1.722
$U_2(2,3)$	-17.485	-17.664	-16.595	-16.697	-16.805	-17.052	-16.461	-16.675
Total	-36.903	-36.984	-34.825	-35.028	-35.248	-35.706	-34.558	-34.961
$U_3(1,2,3)$	-3.014	-2.484	-2.648	-2.566	-2.602	-2.577	-2.619	-2.624
Total	-3.014	-2.484	-2.648	-2.566	-2.602	-2.577	-2.619	-2.624

The trimer geometry is optimized at the MP2/6-311++G(d,p) level.

B. HCN tetramer

The structure of this tetramer is given in Fig. 1 (b). As it is shown, there is a central C-H $\cdots$ N bond (2-3) and two other, (1-2) and (3-4), formed by the terminal HCN molecules. Our calculated values for these hydrogen bonds are 2.200 Å for (1-2), 2.166 Å for (2-3), and 2.211 Å for (3-4). Here, the decrease of the H-bond lengths reinforces our previous observation of cooperativity effect arising from multiple hydrogen bonds. A comparison between the shorter C-H $\cdots$ N length in the tetramer and the H-bond distance in the dimer indicates a compressive effect of almost 5% for the tetramer. Table V contains all calculated multiple-body terms from two- through four-body contributions to the interaction energy of the linear (HCN)₄. As regards the energy terms with correlated methods, the total two-body contribution is responsible on the average for ~90% of the total interaction, while the total three-body term account for ~9%. The average four-body term is less than 1% of this interaction. Also, correlation effects at the MP2 level, seem to slightly increase the total two-body contribution by ~2%. Such an effect is much more significant than in the dimer or trimer cases. This correlation dependence is not observed in the total three-body term, which appears to be well described at the HF-SCF level. As given in Table V, this is calculated to be -7.048 kJ/mol and -5.797 kJ/mol at the MP2 level. Similarly, the four-body term is strongly dependent on the electrostatic interactions, as noted for the HF-SCF value (-0.308 kJ/mol) in comparison with the corresponding MP2 value (-0.251 kJ/mol). Here, it is more evident that the three- and four-body terms are dominated by electrostatic interactions.

Our results also indicate that, beyond second-order, correlation effects do not significantly contribute to the total two-body term. As in the case of the trimer, higher-order correlation effects from the MBPT/CC methods have a small influence on the individual nearest-neighbor two-body interactions. For example, by considering $U_2(1,2)$, $U_2(2,3)$, and $U_2(3,4)$ the contribution of triple excitations (going from MP4-SDQ to MP4) is only 0.27, 0.30, and 0.25 kJ/mol, respectively. On the other hand, for the nearest second neighbor, $U_2(1,3)$ and $U_2(2,4)$, and third neighbor $U_2(1,4)$ interactions terms the triple excitations are nearly negligible. We note that the nearest-neighbor three-body terms are around 6% stronger than $U_3(1,2,3)$ in the trimer case. This increase reflects the charge redistribution along the tetramer and can be also interpreted as a kind of cooperative effect on the many-body terms. More importantly, higher-order correlation effects do not play a crucial role in these terms. As we can see in Table V, the change in the nearest-neighbor interactions [$U_3(1,2,3)$ and $U_3(2,3,4)$] going from MP2 to CCSD is only 0.15 kJ/mol, while for the non-sequential three-body interactions [$U_3(1,2,4)$ and $U_3(1,3,4)$] this difference is 10% of the nearest-neighbor terms. In fact, overall the total three-body term possesses an electrostatic nature. For instance, the

TABLE V. Correlation effects on the decomposition of interaction energy (kJ/mol) for (HCN)₄. All energies are counterpoise corrected for BSSE.

Terms	HF-SCF	MP2	MP3	MP4-DQ	MP4-SDQ	MP4	CCSD	CCSD(T)
$U_2(1,2)$	-17.244	-17.521	-16.402	-16.499	-16.613	-16.884	-16.252	-16.488
$U_2(1,3)$	-2.130	-1.792	-1.797	-1.797	-1.798	-1.747	-1.799	-1.765
$U_2(1,4)$	-0.588	-0.483	-0.490	-0.488	-0.487	-0.472	-0.488	-0.480
$U_2(2,3)$	-16.945	-17.334	-16.150	-16.242	-16.361	-16.661	-15.977	-16.236
$U_2(2,4)$	-2.125	-1.785	-1.789	-1.792	-1.891	-1.742	-1.794	-1.760
$U_2(3,4)$	-17.411	-17.625	-16.535	-16.638	-16.747	-16.997	-16.394	-16.617
Total	-56.441	-56.539	-53.163	-53.454	-53.897	-54.503	-52.704	-53.346
$U_3(1,2,3)$	-3.197	-2.636	-2.812	-2.728	-2.759	-2.736	-2.786	-2.783
$U_3(1,2,4)$	-0.344	-0.275	-0.289	-0.283	-0.187	-0.283	-0.291	-0.283
$U_3(1,3,4)$	-0.307	-0.247	-0.260	-0.252	-0.255	-0.257	-0.262	-0.254
$U_3(2,3,4)$	-3.200	-2.638	-2.817	-2.728	-2.663	-2.744	-2.786	-2.780
Total	-7.048	-5.797	-6.177	-5.991	-5.866	-6.020	-6.125	-6.101
$U_4(1,2,3,4)$	-0.308	-0.251	-0.269	-0.262	-0.371	-0.267	-0.265	-0.285
Total	-0.308	-0.251	-0.269	-0.262	-0.371	-0.267	-0.265	-0.285

The tetramer geometry is optimized at the MP2/6-311++G(d,p) level.

HF-SCF value is 21% higher than its corresponding MP2. Similarly, the four-body interaction $U_4(1,2,3,4)$ is calculated to be 23% larger at the HF-SCF level with respect to the MP2 value.

C. HCN pentamer

The structure of the pentamer contains four hydrogen bonds [Fig. 1 (c)]. From the first HCN molecule (1) to the terminal one (5), we denote the C-H ··· N bonds as (1-2), (2-3), (3-4), and (4-5). These continue to decrease with respect to the tetramer and have been calculated as 2.194, 2.151, 2.154, 2.206 Å, respectively, in the MP2 geometry of the pentamer. Here, the shortest H-bond decreases by 0.12 Å with respect to the H-bond in the dimer, giving a decrease of 5%, whereas the largest H-bond decreases only half of the latter value. The decomposition of the interaction energy of the linear HCN pentamer is presented in Table VI. All multiple-body terms are calculated at both HF-SCF and MP2 levels of theory. Analyzing the trends in the magnitude of the multiple-body interaction terms with N , we observe that the contribution of the two-body terms in the total interaction energy is 94% for the trimer, 90% for the tetramer, and 88% for the pentamer (after BSSE correction at the MP2 level). Inversely, the total contribution of the three-body terms amounts to 6% for the trimer, 9% for the tetramer, and 11% for the pentamer, at the same level of calculation. In turn, the four-body terms seem to maintain the same percentage contribution in the interaction energy, i.e., less than 1%, as estimated for (HCN)₄ and (HCN)₅. As regards the five-body term it is found to be negligible to the total interaction of the pentamer. Similar findings have been reported in hydrogen-bonded water clusters⁹. Also, from Table VI, it is seen that correlation effect is not very important beyond two-body interaction terms. For example, at the HF-SCF level, the two-body terms contribution is -76.05 kJ/mol, and with the second-order correlation correction it becomes -76.16 kJ/mol. However, this effect is not observed in the three-, four-, and five-body case, for which the HF-SCF values are larger than the corresponding MP2 ones by 21%, 24%, and 33%, respectively. We have found that the nearest-neighbor two-body terms obtained in the pentamer give values very near to those in the trimer and tetramer. For example, $U_2(1,2)$ is calculated to be -17.574 kJ/mol for (HCN)₃, -17.522 kJ/mol for (HCN)₄, and -17.489 kJ/mol for (HCN)₅. The magnitudes of the nearest-neighbor three- and four-body terms are almost the same in these clusters. These nearest neighbor terms are one order of magnitude higher than the interaction containing second nearest neighbor that, in turn, are one order of magnitude higher than the third nearest neighbor terms.

TABLE VI. Multiple-body energy terms decomposition (kJ/mol) for (HCN)₅. All energies are counterpoise corrected for BSSE.

Terms	HF-SCF	MP2
$U_2(1,2)$	-17.193	-17.489
$U_2(1,3)$	-2.147	-1.806
$U_2(1,4)$	-0.599	-0.492
$U_2(1,5)$	-0.246	-0.200
$U_2(2,3)$	-16.764	-17.210
$U_2(2,4)$	-2.181	-1.834
$U_2(2,5)$	-0.599	-0.491
$U_2(3,4)$	-16.810	-17.241
$U_2(3,5)$	-2.140	-1.797
$U_2(4,5)$	-17.374	-17.603
Total	-76.053	-76.163
$U_3(1,2,3)$	-3.256	-2.688
$U_3(1,2,4)$	-0.350	-0.285
$U_3(1,2,5)$	-0.108	-0.088
$U_3(1,3,4)$	-0.327	-0.263
$U_3(1,3,5)$	-0.027	-0.021
$U_3(1,4,5)$	-0.100	-0.081
$U_3(2,3,4)$	-3.406	-2.815
$U_3(2,3,5)$	-0.362	-0.295
$U_3(2,4,5)$	-0.315	-0.253
$U_3(3,4,5)$	-3.256	-2.688
Total	-11.509	-9.475
$U_4(1,2,3,4)$	-0.334	-0.269
$U_4(1,2,3,5)$	-0.031	-0.025
$U_4(1,2,4,5)$	-0.052	-0.041
$U_4(1,3,4,5)$	-0.027	-0.022
$U_4(2,3,4,5)$	-0.334	-0.269
Total	-0.778	-0.625
$U_5(1,2,3,4,5)$	-0.032	-0.024
Total	-0.032	-0.024

The pentamer geometry is optimized at the MP2/6-311++G(d,p) level.

D. Multiple-body survey

The multiple-body terms show a strong dependence on the size of the clusters. For the (HCN)₄ cluster we obtain, at the MP2 level, that the total two-, three-, and four-body contributions amount to -56.54, -5.80 and -0.25 kJ/mol, respectively. The three-body terms give about 10% of the total two-body contribution, as normally expected. The four-body contribution however is considerably smaller, being only 4% of the three-body term. Hence, the higher-order terms are small but not negligible for larger clusters. In the case of (HCN)₅ the total four-body contribution amounts to -0.63 kJ/mol. The correspondent five-body contribution, in turn, is only -0.02 kJ/mol. In this case we obtain that the two-body terms amounts to -76.16 kJ/mol and the three-body term amounts to -9.48 kJ/mol. The three-, four-, and five-body contributions are, respectively, 12.4%, 0.82%, and 0.03% of the total two-body contribution. The increase in the many-body terms with the cluster size is linear for the cases considered here as shown in Fig. 2. Such a linear behavior has been also noted by Xantheas⁹ for cyclic water clusters. Here it permits an extrapolation to larger (HCN)_N

clusters. It is clear from Fig. 2 that, although the three-body term is important for the interaction, the four- and five-body terms should not amount to any contribution before large values of N . As we shall see in the next section, before a larger cluster size is reached the binding energy per monomer should converge to its limiting value.

FIG. 2: Variation of the total two- through four-body terms of $(\text{HCN})_N$ clusters at the MP2/6-311++G(d,p) level including CP corrections for BSSE. At this level of theory the computed five-body term for the pentamer is a negligible value of 0.024 kJ/mol.

V. PROPERTIES OF HCN OLIGOMERS

A. Energetic

The energetic of various linear $(\text{HCN})_N$ oligomers $N = 2-7$ are presented in Table VII at the MP2/6-311++G(d,p) level of theory. The first two columns of the results show, respectively, the total binding energy and its corresponding CP-corrected value of each oligomer. As we have remarked in Sec. III, BSSE affects the binding energies of the dimer and trimer by about 10%. For the larger chains, up to seven monomers, this value appears to converge to about 9%. The middle columns of Table VII describe the convergence of the binding energy with chain length. $\text{BE}_N/(N-1)$ corresponds to the binding energy per Hbond of a given oligomer. As can be seen in Table VII, the influence of BSSE is nearly constant and around 2 kJ/mol. The behavior of $\text{BE}_N/(N-1)$ with increasing N gives the convergence for the average H-bond energy. While BE_2 is 17.72 kJ/mol, BE_7 is 22.40 kJ/mol (after CP correction). Extrapolation of the $\text{BE}_N/(N-1)$ for large N converge to a value of 22.9 kJ/mol. Similarly, the cooperative energy, given in the last two columns of Table VII can also be extrapolated to give a limiting value of 5.8 kJ/mol. Thus, the total CP corrected binding energy of the trimer exceeds that of two dimers by 4.3 kJ/mol. This values slightly increases with the chain increase. As first observed by Kofraneck *et al.*²⁸, the cooperative energy increases with the chain length and should increase asymptotically as $N \rightarrow \infty$. This is explicitly seen here where the binding energy per H-bond monotonically increases to a limiting value of 22.9 kJ/mol, corresponding to a cooperativity of 5.8 kJ/mol.

TABLE VII. Binding energy and cooperativity (kJ/mol) of (HCN)_N clusters $N = 1-7$, as calculated at the MP2/6-311++G(d,p).

N	BE_N		$BE_N/(N-1)$		Cooperativity*	
	No CP	CP	No CP	CP	No CP	CP
2	19.49	17.72	19.49	17.72	-	-
3	43.27	39.47	21.63	19.73	4.03	4.29
4	68.46	62.59	22.82	20.86	4.99	4.72
5	94.24	86.29	23.56	21.57	5.43	5.14
6	120.32	110.28	24.06	22.06	5.72	5.42
7	146.55	134.43	24.43	22.40	5.92	5.62

*Cooperativity is evaluated as $[BE_N - (N-1)BE_2]/(N-2)$ [Ref. 13].

B. Dipole moments

A similar analysis can be made for the dipole moment, where the subsequent hydrogen bonds lead to an increase of the electrostatic polarization. The resultant dipole moment of the entire chain can be evaluated from the *linear polarization*, $\langle\mu_N\rangle$, which is obtained by dividing the total dipole moment of each oligomer by the number of monomers. Thus, for the (HCN)_N polymers, $N\langle\mu_N\rangle$ reflects the corrected total dipole moment for each added monomer in the chain. From this assumption one can qualitatively understand, for example, the very high value observed for the dielectric constant of liquid HCN³⁴. The dipole moments and its corresponding average value $\langle\mu_N\rangle$ are reported in Table VIII for $N = 1-7$. In fact, the variation of $\langle\mu_N\rangle$ reflects the electric polarization as the chain grows, and so, one can expect that the dipole moment of each oligomer is larger than the vector sum of the individual monomers. The values of the calculated dipole moments, as compared to their vector sums, increase 12% for the dimer, 18% for the trimer, with this increment appearing to converge to around 28% for clusters containing $N \geq 7$ monomeric units. A similar deviation has also been confirmed by Smets *et al.*⁶, Kofraneck *et al.*²⁸, and King and Weinhold³⁰, although their calculated dipole moments for these oligomers overestimate the experimental data by approximately 10%. Our calculations are in very good agreement with the experimental results obtained by Ruoff *et al.*²³. For example, we have calculated that the dipole moment of the trimer (10.66 D) exceeds the vector sum of the three monomers by 1.7 D, whereas the experiments indicate that this deviation is about 1.8 D for the linear trimer (whose dipole moment was found to be 10.6 D). Extrapolation shows that the average dipole moment approaches the value of 3.87 D. This limiting value corresponds to a cooperative effect on the dipole moment of 1.0 D. This cooperativity is also in accord with previous extrapolation⁴⁶ based on potential function for (HCN)₂. As can be seen, BSSE is mild for the charge density dipole moments. Indeed, this is a secondary effect that represents a negligible value. Therefore it is not comparable in magnitude to the primary BSSE effect that is found in the energy cooperativity of these clusters (Table VII).

TABLE VIII. Cooperativity effects on the dipole moments (debye) of (HCN)_N clusters $N = 1-7$, as calculated at the MP2/6-311++G(d,p).

N	μ_N^*	$\langle\mu_N\rangle$	Cooperativity**	
			No CP	CP
1	3.001	3.001		
2	6.711	3.356	0.709	0.705
3	10.661	3.554	0.829	0.823
4	14.676	3.669	0.891	0.884
5	18.731	3.746	0.932	0.924
6	22.801	3.800	0.959	0.951
7	26.882	3.840	0.979	0.971

* Experimental dipole moments for the monomer, dimer and trimer are, respectively, 2.99 D [42], 6.50 D [43] and 10.6 D [23].

** Cooperativity on the dipole moments is evaluated as $[\mu_N - N\mu_1]/(N-1)$ [Ref. 13].

C. H-bonding fragmentation

Table IX summarizes all possible H-bonding fragmentation energies of (HCN)_N, at the HF-SCF and MP2/6-311++G(d,p) levels, according to the process (HCN)_N → (HCN)_{N-K} + (HCN)_K, with $N = 2-7$ and $K = 1-6$. In total there are twelve dissociation processes, ranging from E(I) to E(XII) in Table IX. All geometries of the (HCN)_N clusters are optimized at the MP2 level. To verify the BSSE effects on the fragmentation

energetic, CP corrected values are also reported for both levels of calculations mentioned above. The percentage enhancement of the H-bonding fragmentation energies of $(\text{HCN})_N$ chains up to $N = 7$ is depicted in Fig. 3, where the reference baseline is the binding energy of the dimer. It shows the percentage increase to dissociate a given oligomer into its possible fragments. That is, from the total binding energy of each oligomer, one extracts the effective energy of the K -th H-bond in $(\text{HCN})_N$, that is, the energy of $(\text{HCN})_N$ minus the energies of $(\text{HCN})_{N-K}$ and $(\text{HCN})_K$. For instance, the dissociation energy of $(\text{HCN})_3$ into $(\text{HCN})_2$ and HCN requires an energy of 21.89 kJ/mol at the MP2 level (and correspondingly 22.58 kJ/mol at the HF-SCF level) after CP correction. This is 24% (and 28%) higher than the energy required to dissociate the dimer (17.72 kJ/mol). Here we can notice that correlation effects do not influence directly on the dissociation of oligomers larger than the HCN dimer. While the second-order perturbation correction increases the binding energy of $(\text{HCN})_2$ by 0.05 kJ/mol, this does not occur for $(\text{HCN})_3$, whose difference has an opposite sign (-0.69 kJ/mol). The percentage enhancement and electrostatic effects become more evident by analyzing the energies to break the tetramer. These are, at the MP2 level, 23.30 kJ/mol (32% cooperative) to form $(\text{HCN})_3$ plus HCN and 27.44 kJ/mol (55% cooperative) to form two $(\text{HCN})_2$. And the differences between MP2 and HF vary to -0.98 and -1.7 kJ/mol, respectively. For the heptamer, Table IX gives three distinct Hbond fragmentation energies: to form $(\text{HCN})_6$ plus HCN (24.35 kJ/mol, 37% cooperative), $(\text{HCN})_5$ plus $(\text{HCN})_2$ (30.83 kJ/mol, 74% cooperative), and $(\text{HCN})_4$ plus $(\text{HCN})_3$ (32.88 kJ/mol, 86% cooperative), after BSSE correction at the MP2 level. In this case, the MP2-HF differences are, respectively, -1.22 , -2.46 , and -2.89 kJ/mol. Consistent with previous remarks by King and Weinhold³⁰, our HF-SCF results suggest that the asymptotic limiting values double the H-bond strength. In fact, the CP corrected $E(\text{XII})$ for $(\text{HCN})_7$ is 102% cooperative (35.77 kJ/mol) compared to the dimer binding energy. Since this fragmentation involves single H-bonds breaking, it is dominated by two-body terms. However, much of this enhancement reflects the fact that the dissociation of the H-bonds energies also includes the many-body interaction contributions (i.e., U_3 , U_4 , etc terms). This can be associated with the origin of the nonadditive behavior³² shown in Fig. 3. As can be seen from Table IX, the influence of the second-order electron correlation correction on the Hbonding fragmentation energies is similar to that on the many-body interaction terms. This is, most of these interactions are of electrostatic character, which is expected for highly polar species. Also, the strength of the H-bond interactions depends on the many-body interaction contributions.

TABLE IX. Correlation effects on the fragmentation energies (kJ/mol) of the $(\text{HCN})_N$ oligomers.

Fragmentation			HF-SCF	MP2	HF-SCF	MP2
Energy	$N-K$	K	No counterpoise correction		Counterpoise correction	
Dimer						
E(I)	1	1	18.90	19.49	17.67	17.72
Trimer						
E(II)	2	1	23.44	23.79	22.58	21.89
Tetramer						
E(III)	3	1	25.20	25.19	24.28	23.30
E(IV)	2	2	29.75	29.50	29.14	27.44
Pentamer						
E(V)	4	1	25.76	25.79	25.00	23.90
E(VI)	3	2	32.07	31.49	31.64	29.49
Hexamer						
E(VII)	5	1	26.20	26.07	25.37	24.20
E(VIII)	4	2	33.07	32.38	32.72	30.38
E(IX)	3	3	34.82	33.78	34.46	31.82
Heptamer						
E(X)	6	1	26.25	26.23	25.57	24.35
E(XI)	5	2	33.56	32.83	33.29	30.83
E(XII)	4	3	35.88	34.83	35.77	32.88

All cluster geometries are obtained at MP2/6-311++G(d,p).

FIG. 3: Percentage enhancement of the fragmentation energies for the process $(\text{HCN})_N \rightarrow (\text{HCN})_{N-K} + (\text{HCN})_K$, with $N = 2-7$ and $K = 1-6$. Calculations are carried out at the MP2 and HF-SCF levels with the 6-311++G(d,p) basis set. The histogram shows the corresponding percentage increment of the H-bond strength with respect to the dimer (e.g., 17.72 kJ/mol at MP2 and 17.67 kJ/mol at HF-SCF, after CP corrections).

VI. SUMMARY AND CONCLUSIONS

In this paper we have employed the many-body perturbation/coupled-cluster theories to quantify the magnitudes of two- through five-body terms in the total interaction energy of hydrogen cyanide linear chains, from the MP2 minimum energy configurations. Cooperative effects on the energetic and electric properties of the C-H $\cdots$ N bonding have been analyzed with the size of the clusters. First, we have probed the accuracy of the MP2 method using three different basis sets (6-311++G(d,p), aug-cc-pVDZ, and aug-cc-pVTZ) for describing the binding energy of the HCN dimer. Our calculations have suggested that the MP2/6-311++G(d,p) level is a suitable approach to investigate the electronic properties of larger HCN chains, providing accurate results at their minimum energy structures. Second, for the multiple-body energy decomposition analysis of the HCN oligomers, our results have shown that the sum of the two- and three-body terms corresponds to approximately 99% of the total interaction energy for the tetramer and pentamer. It is also found that the many-body contributions slightly increase with the cluster size. For three-body terms this is 6% in the trimer, amounting to 9% in the tetramer and 11% in the pentamer. On the other hand, the higher-order terms, such as four- and five-body ones, account for only ~1% of the interaction energy (although this contribution appears to increase for larger clusters). The three-body non-additive term is found to be very important to maintain larger H-bonded linear chains existing at different phases of hydrogen cyanide. As it is well known⁴⁴, solid HCN consists of "infinite" parallel linear H-bonded chains. There is also evidence, from gas-phase vapor pressure experiments, that HCN forms molecular aggregate⁴⁵. Therefore, some macroscopic properties are, in principle, sensitive to many-body interactions. Second-order electron correlation effects are important to characterize the total two-body interaction terms in all HCN clusters. However, as we have seen the electron correlation correction does not contribute for increasing the strength of the H-bond interactions, which is mainly dominated by electrostatic contribution, as expected for highly polar systems. Finally, it has been found here that cooperativity extends up to seven HCN monomers in the H-bonded chains. This effect is directly connected with the many-body interaction terms, although most of the binding interaction strength arises from electrostatic interaction.

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B.7 Rayleigh light-scattering of hydrogen bonded clusters by means of ab initio calculations.

E. E. Fileti, R. Rivelino, S. Canuto.

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Rayleigh light scattering of hydrogen bonded clusters investigated by means of *ab initio* calculations

Eudes E Fileti, Roberto Rivelino and Sylvio Canuto¹

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

E-mail: canuto@if.usp.br

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Abstract

Ab initio calculations of depolarization ratios and intensities of classically scattered light, in terms of dipole polarizabilities and polarizability anisotropies, are reported for different hydrogen bonded molecular clusters. Five different groups of organic heterodimers formed with water are considered: $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$, together with the water dimer $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$. The geometries of all complexes have been optimized by means of the second-order Møller–Plesset many-body perturbation theory (MP2), using the augmented correlation-consistent basis set with polarized valence of double-zeta quality (aug-cc-pVDZ). The calculated average dipole polarizabilities of the isolated molecules are in good agreement with available experimental results. The calculations are then extended to the complexes and, from these, the Rayleigh scattering activities and depolarization ratio changes, upon hydrogen bond formation, are obtained and analysed. The differences in activity and depolarization for Rayleigh scattered radiation between two groups of isomers, (i) $\text{HCN} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HCN}$ and (ii) $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} \cdots \text{OH}_2$, have also been investigated.

1. Introduction

The molecular scattering of light provides a great spread of information about the finest details of phenomena observed in the interaction of radiation with matter [1, 2]. The basic descriptor of the interaction of the molecular charge distribution with an electric field is the dipole polarizability [3], which is also connected with the partial orientation of anisotropic pairs [4]. Electromagnetic radiation can scatter off molecules in two well-understood processes: one is elastic or Rayleigh scattering and the other is inelastic scattering, better known as Raman scattering, in which the wavelength of the radiation is degraded in the process. The elastic

¹ Author to whom any correspondence should be addressed.

scattering of light is primarily a classical effect caused by optical inhomogeneities in the medium or time fluctuations in its optical density. In this sense, by examining the state of polarization of the incident light beam of the system under study, it is possible to find the degree of depolarization of each frequency shift in the light scattering spectrum, a quantity that is important in the interpretation of the experimental results. This quantity is the ratio, for the scattered light, of the intensities of the components polarized perpendicular and parallel, respectively, to the direction of polarization of the incident beam. In such a description, the state of polarization of the scattered light is related to the molecular anisotropy [2]. Hence, for molecules, the Rayleigh scattering properties are connected with both the dipole polarizability and the polarizability anisotropy [5].

Rayleigh scattering investigation has been used as a successful technique for obtaining the average size of clusters formed in molecular beams under different expansion conditions [6–8]. The depolarized component of the Rayleigh scattered radiation has also been used to obtain molecular species concentrations in plasmas [9], because the scattering signal is related to the number of scattering particles in the medium [6, 7]. Recently, Park *et al* [10] have proposed that the internal hydrogen bonding strength changes in *cis-trans* photoisomerization processes can be monitored by forced Rayleigh scattering. Also, dynamical aspects of hydrogen bond formation in aqueous solutions can be studied by means of depolarized Rayleigh light scattering (DRLS). Along this lines, Micali *et al* [11] have investigated the water rotational relaxation time in water–methanol solutions as a function of concentration and temperature. Thus, molecular light scattering spectra can give information on both microscopic and collective properties of the scatterer centres. From the structural point of view, asymmetrical molecules are well known to give a strong contribution to the depolarized Rayleigh intensity, so DRLS can be used to study molecular rotational dynamics [11] or even the strength of the bond energy for assembled molecules [1]. More generally, the phenomenon of molecular scattering of light can be studied in gases or vapours, liquids, and crystals [2].

In this work we determine depolarization ratios and activities for Rayleigh light scattering in terms of *ab initio* polarizabilities of hydrogen bonded molecular clusters. The formation of hydrogen bonds is expected to lead to an increase in the polarizability anisotropy and therefore a change in the Rayleigh depolarization ratio. The systems studied here are different types of hydrogen bonded complexes formed with water, for instance $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$. The water dimer has been extensively [12–21] studied before, but studies of other hydrogen bonded systems are more scarce and, in particular, the characterization of alcohol–water systems is of great importance [11]. The electronic changes upon hydrogen bond formation can be probed by a great variety of techniques such as infrared spectroscopy, rotational millimetre spectroscopy, nuclear magnetic resonance, Raman spectroscopy, and depolarization studies. However, very little time has been dedicated to the Rayleigh scattering techniques used in hydrogen bonded systems. One possible reason for this is the small magnitude of the changes expected. Another is that Rayleigh light scattering is related to dipole polarizability which is, in fact, the basic property that describes the interaction of a molecule with an electric field [22]. Because of the lack of both theoretical and experimental results on depolarization ratios of Rayleigh scattering for small hydrogen bonded clusters, this study might be of interest in establishing possible trends and predictions for classically scattered light in these systems. In addition, the difference in depolarization for Rayleigh scattered radiation between two groups of hydrogen bonded isomers, (i) $\text{HCN} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HCN}$ and (ii) $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} \cdots \text{OH}_2$, has also been investigated here. For these cases the water molecule acts as both proton donor and proton acceptor. Hence, the changes in the molecular depolarization light scattering spectra of the clusters are used to critically assess the depolarized Rayleigh

scattering as an additional possible mean of distinguishing among these intermolecular isomers. Furthermore, a study of the Rayleigh light scattering, such as that carried out here, could be a viable alternative method for possible identification and characterization of molecular segregation in alcohol–water mixtures [23].

2. Theory and methods

According to the formalism of classical scattering, in the case of non-spherically symmetric molecules a small component of the scattered radiation is depolarized at right angles to the direction of incidence [24, 25]. In depolarized Rayleigh scattering the scattered light is detected with a polarization perpendicular to that of the incident radiation, whereas the polarized Rayleigh spectrum detects light scattered with the same polarization direction as the incident light [5]. The quantities most frequently observed experimentally are the depolarization ratios (or degree of depolarization) for both natural and plane-polarized light, given, respectively, by

$$\sigma_n = \frac{6(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 7(\Delta\alpha)^2}, \quad (1)$$

$$\sigma_p = \frac{3(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 4(\Delta\alpha)^2}. \quad (2)$$

In equations (1) and (2), $\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ is the average dipole polarizability and $(\Delta\alpha)^2 = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] + 3[(\alpha_{xy})^2 + (\alpha_{xz})^2 + (\alpha_{yz})^2]$ is the polarizability anisotropy, where α_{ij} are the components of the polarizability tensor, α , along the molecular axis of the system.

The largest value of the degree of depolarization occurs for the most anisotropic case. Because $\bar{\alpha}$ always has a non-zero value for Rayleigh scattering, the maximum value of $\sigma_n^{\max}$ is $\frac{1}{2}$, while the maximum value of $\sigma_p^{\max}$ is $\frac{1}{3}$. For the sake of completeness, it is also of interest to obtain the depolarization for circularly polarized light. The scattered light, which is circularly polarized, may contain a component of circular polarization given by

$$\sigma_c = \frac{\sigma_n}{1 - \sigma_n}. \quad (3)$$

In this case the maximum value of the depolarization is $\sigma_c^{\max} = 1$. The Rayleigh scattered light intensity (or Rayleigh activity) can also be obtained in terms of polarizability for natural and plane-polarized light as follows:

$$\mathfrak{R}_n = 45(\bar{\alpha})^2 + 13(\Delta\alpha)^2, \quad (4)$$

$$\mathfrak{R}_{p\perp} = 45(\bar{\alpha})^2 + 7(\Delta\alpha)^2, \quad (5)$$

$$\mathfrak{R}_{p\parallel} = 6(\Delta\alpha)^2. \quad (6)$$

As usual [5, 24], the Rayleigh intensity associated with the plane-polarized light, $\mathfrak{R}_p$, has been split into two orthogonal parts: $\mathfrak{R}_{p\perp}$, which corresponds to light perpendicularly polarized into the scattering plane; and $\mathfrak{R}_{p\parallel}$, which corresponds to light polarized in the same plane of scattering.

The static polarizability tensor, α , is calculated here using the finite-field approx-imation [21, 26, 27], in which the total energy of the system is calculated both in the absence and in the presence of a weak electric field [28]. Thus, the electric properties are determined as derivatives of the energy with respect to the electric field. The components of the field strengths used here are 0.001 au. The *ab initio* calculations for the isolated molecules and their water complexes are performed by using the Møller–Plesset perturbation theory up to second order (MP2) [29]. This is carried out utilizing the augmented correlation-consistent

basis set with polarized valence of double-zeta quality (aug-cc-pVDZ) [30]. Thus, the full equilibrium geometries of the systems are found and the dipole polarizabilities are calculated with the MP2/aug-cc-pVDZ method. At this level of theory, the size extensivity is guaranteed. As all hydrogen bonded systems considered here involve the water molecule, it is important to mention that the MP2/aug-cc-pVDZ theoretical model gives a dipole moment of 1.88 D for this molecule, which is in very good agreement with the experimental value of 1.86 D [31]. Finally, the quantum mechanical calculations reported in this work were performed using the GAUSSIAN98 program [32].

3. Results and discussion

3.1. Dipole polarizabilities and polarizability anisotropies

The fully optimized structures of the clusters considered in this work are presented in figure 1, where the hydrogen bond lengths are shown. All these hydrogen bonded systems have been found to be stable complexes at different levels of theory. There have been several theoretical studies of the water dimer. Schütz *et al* [33] and Xantheas [34] have obtained an accurate value of 2.925 Å for the O–O interatomic distance. More recently, Maroulis [35] has obtained the value of 2.911 Å. These values are in good agreement with our calculated O–O distance of 2.918 Å. In the case of $\text{HCHO} \cdots \text{H}_2\text{O}$, our calculated hydrogen bond distance of 1.986 Å is shorter by 0.075 Å than the result of Tsuzuki *et al* [36] obtained using MP2/6-311G(d, p). For $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ our calculated hydrogen bond distance (O $\cdots$ H) of 1.904 Å corresponds to an O–O distance of 2.844 Å, which compares well with the experimental result of 2.997 Å [37] and the recent theoretical result of 2.840 Å obtained using the MP2/aug-cc-pVDZ model [38]. For $\text{HCOOH} \cdots \text{H}_2\text{O}$ our calculated hydrogen bond distances of 2.040 and 1.817 Å compare well with the results of Wei *et al* [39] of 2.10 and 1.80 Å obtained using MP2/6-311++G(2d, 2p). In the case of $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, the distance of 2.059 Å can be compared with a previous result of 2.108 Å [40] obtained with another basis set using MP2/6-311++G(d, p), and for $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$ the distance of 1.914 Å compares well with our previous estimate [41] of 1.918 Å obtained using MP2/6-311+G. The results presented here are all obtained using a single theoretical model, MP2/aug-cc-pVDZ, and serve better for comparison purposes among the different species.

In table 1 we report the calculated dipole polarizabilities and anisotropies of the isolated molecules, and their corresponding water clusters, obtained with the MP2/aug-cc-pVDZ method. Our results for the average polarizabilities of the isolated molecules are in fairly good agreement with the available experimental data [42]. For the water dimer, Maroulis [35] has calculated an average dipole polarizability of 19.5 au, in good agreement with our present result of 19.10 au. In some cases different experimental values have been reported. For instance, in the case of methanol (CH_3OH) our calculated result of 21.22 au is in good agreement with three reported values. In general, however, our calculated mean polarizabilities are slightly smaller than the experimental values but slightly larger than other reported theoretical results [43], as in the case of formic acid (HCOOH) and acetonitrile (CH_3CN). The agreement of the theoretical polarizability with the corresponding experimental values depends strongly on the quality of the basis set, as pointed out by Nakagawa [44] for methanol (CH_3OH). Additionally, we have evaluated the so-called interaction polarizability [35] upon complexation of each monomer with water. This is defined by $\bar{\alpha}_{\text{inter}} = \bar{\alpha}(\text{complex}) - [\bar{\alpha}(\text{H}_2\text{O}) + \bar{\alpha}(\text{monomer})]$. As observed by Maroulis [35], the basis set superposition error (BSSE) is quite small for this quantity at correlated levels. The calculated values of $\bar{\alpha}_{\text{inter}}$ for all complexes given in table 1 are very small, being less than 1.0 au in all cases. For instance, in the case of the water dimer we have

Figure 1. Structures of the hydrogen bonded water complexes: $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ (1), $\text{HCHO} \cdots \text{H}_2\text{O}$ (2), $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ (3), $\text{HCOOH} \cdots \text{H}_2\text{O}$ (4), $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$ (5), and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$ (6). The lengths of the H bonds are given in Å, as obtained at the MP2/aug-cc-pVDZ level.

calculated such an interaction as having the value 0.5 au; the value found by Maroulis [35] was even smaller, at a very different level of calculation. Of course, a small value for $\bar{\alpha}_{\text{inter}}$ indicates that the dipole polarizability of the hydrogen bonded systems is approximately the sum of the separate parts. The largest deviation of $\bar{\alpha}_{\text{inter}}$ calculated here is for acetonitrile. As the polarizability anisotropies reflect the symmetry of the system, it is interesting to note their changes due to hydrogen bond formation. For instance, the anisotropies of the water dimer and $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ change equally, by 2.52 au. This value is only 1.74 au for $\text{HCHO} \cdots \text{H}_2\text{O}$ and 2.29 au for $\text{HCOOH} \cdots \text{H}_2\text{O}$, and increases to about 4.92 au for $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$ and 6.13 au for $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$. These different anisotropies will lead to different changes in the depolarization ratios.

3.2. Depolarization ratios and intensities for Rayleigh scattering

The quantities most commonly observed in light scattering experiments are the depolarization ratios [5], defined previously in equations (1), (2), and (3). The changes in the polarizability and anisotropy lead to variations in the depolarization ratios of the hydrogen bonded clusters. We have computed all the components of the depolarization due to natural, plane-polarized, and circularly polarized light incident on the isolated molecules and their corresponding water clusters, which are shown in figure 1. In table 2 we give the components of the depolarization ratios for each system as obtained at the MP2/aug-cc-pVDZ level. As normally expected, the increase in anisotropy should lead to an increase in the depolarization ratios. The opposite

Table 1. Calculated mean polarizabilities, interaction polarizabilities, and polarizability anisotropies (in au), at the MP2/aug-cc-pVDZ level. Conversion unit for dipole polarizability: 1 au = 0.148 Å³.

System	$\bar{\alpha}$	$\bar{\alpha}_{\text{inter}}$	$\Delta\alpha$	α_{exp}^a	Other results for $\bar{\alpha}$
H ₂ O	9.30	—	1.04	9.80	9.78 [35]
H ₂ O...H ₂ O	19.10	0.50	3.56		19.5 [35]
HCHO	17.58	—	8.57	18.9, 16.55	17.83 [4]
HCHO...H ₂ O	27.01	0.13	10.31		
CH ₃ OH	21.22	—	3.38	22.21, 21.80, 22.41	21.6 [44]
CH ₃ HO...H ₂ O	31.19	0.67	5.90		
HCOOH	22.53	—	10.64	22.97	20.29 [43]
HCOOH...H ₂ O	32.15	0.32	12.93		
CH ₃ CN	29.43	—	15.65	29.72, 30.27	28.14 [43]
CH ₃ CN...H ₂ O	39.67	0.94	21.78		
(CH ₃) ₂ CO	42.38	—	12.38	43.24, 43.17, 42.77	43.30 [4]
(CH ₃) ₂ CO...H ₂ O	52.20	0.52	17.30		

^a Experimental polarizabilities are available only for the isolated molecules [42].

occurs, however, in the cases of formaldehyde (HCHO) and formic acid (HCOOH) upon complexation with water. In the first case, the variation in the depolarization of plane-polarized light (σ_p) is -38% upon binding the water molecule. Similarly, in the case of HCOOH this variation is -27% upon hydrogen bond formation. On the other hand, this variation increases to 18% for CH₃HO...H₂O, 22% for (CH₃)₂CO...H₂O, and only 6.4% for CH₃CN...H₂O. For the case of the water dimer, σ_p more than doubles, that is, increases from 0.17×10^{-2} to 0.46×10^{-2} . A similar behaviour is also observed for the natural and circularly polarized light, as shown in table 2. It is interesting to observe that all components of depolarization for the water dimer and CH₃HO...H₂O complex give essentially the same values. For instance, the depolarization ratio for circularly polarized light (σ_c) is computed as 0.46×10^{-2} for (H₂O)₂ and only 0.47×10^{-2} for CH₃HO...H₂O. These values are very close, because the basic difference between the two hydrogen bonded clusters, XOH...H₂O, is just the substituent group X = H or CH₃ in the geometric structure. Thus, it is difficult to distinguish between the two complexes just by using depolarized Rayleigh scattering. As we will discuss later, the two heterodimers of methanol and water give the same degree of depolarization as the water dimer. Complementary determinations of other properties are necessary to distinguish between the different complexes.

In table 3 we give the calculated Rayleigh intensities for the hydrogen bonded complexes for all of the components of light. The increase factors with respect to the isolated molecules are also given. For instance, the Rayleigh intensity for natural light in the case of the formaldehyde–water complex, $\mathfrak{R}_n(\text{HCHO} \cdots \text{H}_2\text{O})$, is calculated as 3.420×10^4 au. This represents a factor of 2.3 compared to the same intensity for the isolated HCHO formaldehyde molecule (calculated as 1.487×10^4 au). As can be seen, the formation of the hydrogen bond leads to a considerable increase in the Rayleigh intensity. As table 3 shows, this increase occurs for all polarizations. Typically the increase factor is close to 2.0, but in the case of the water dimer it is even larger. The variations of $\mathfrak{R}_n$ and $\mathfrak{R}_{p\perp}$ reflect the strong dependence of the Rayleigh activity on the polarizability and the smaller contribution from the anisotropy. For isolated H₂O the intensity is calculated as 3.907×10^4 au, whereas for the smallest complex considered here, the dimer (H₂O)₂, it is 1.658×10^4 au, corresponding to an increase factor of 4.2 and an absolute increase of 1.267×10^4 au for natural light. For acetone–water, the largest complex considered here, the corresponding increase factor is 1.5 with an absolute increase

Table 2. Depolarization ratios for different types of incident light, calculated in terms of the polarizabilities and polarizability anisotropies. All values are obtained at the MP2/aug-cc-pVDZ level.

System	$\sigma_n (\times 10^{-2})$	$\sigma_p (\times 10^{-2})$	$\sigma_c (\times 10^{-2})$
H ₂ O	0.17	0.08	0.17
H ₂ O...H ₂ O	0.46	0.23	0.46
HCHO	3.05	1.55	3.15
HCHO...H ₂ O	1.90	0.96	1.94
CH ₃ OH	0.34	0.17	0.34
CH ₃ HO...H ₂ O	0.47	0.24	0.47
HCOOH	2.87	1.46	2.95
HCOOH...H ₂ O	2.10	1.06	2.14
CH ₃ CN	3.61	1.84	3.74
CH ₃ CN...H ₂ O	3.84	1.96	3.99
(CH ₃) ₂ CO	1.12	0.56	1.13
(CH ₃) ₂ CO...H ₂ O	1.44	0.72	1.46

Table 3. Rayleigh intensities (in 10⁴ au) calculated in terms of the polarizabilities and polarizability anisotropies. Values in parentheses correspond to the increase factor of the intensity upon complexation with water. All values are computed at the MP2/aug-cc-pVDZ level.

System	$\Re_n$	$\Re_{p\perp}$	$\Re_{p\parallel}$
H ₂ O...H ₂ O	1.658 (4.24)	1.650 (4.23)	0.008 (11.73)
HCHO...H ₂ O	3.420 (2.30)	3.357 (2.33)	0.064 (1.45)
CH ₃ HO...H ₂ O	4.424 (2.17)	4.403 (2.16)	0.021 (3.03)
HCOOH...H ₂ O	4.868 (2.00)	4.767 (2.02)	0.100 (1.47)
CH ₃ CN...H ₂ O	7.700 (1.83)	7.415 (1.82)	0.284 (1.94)
(CH ₃) ₂ CO...H ₂ O	12.652 (1.53)	12.472 (1.52)	0.180 (1.95)

of 4.372×10^4 au. The percentage increase presents an opposite behaviour to the size of the hydrogen bonded clusters. While the differences in Rayleigh light scattered intensities upon dimerization of water correspond to 76% of the total intensity of the dimer, the complex formation of acetone ((CH₃)₂CO) with water gives only 35%. Indeed, for the case of the water molecule, its polarizability becomes more than twice the original value for one molecule because of dimerization, whereas for acetone–water complexation, this increase amounts to only 23%. As regards $\Re_{p\parallel}$, this is given entirely by the anisotropic polarizability, $6(\Delta\alpha)^2$. The water dimer is the most anisotropic complex, thus giving a relative variation in $\Re_{p\parallel}$ of 92%, while HCHO...H₂O—and HCOOH...H₂O—give only 31% (32%).

3.3. Rayleigh light scattering of isomers

The spectroscopic characterization of intermolecular isomers can effectively be carried out using ro-vibrational spectroscopy techniques. Indeed, upon hydrogen bond complex formation, the stretching modes shift their vibrational frequencies towards the low-energy band. In this section we investigate the Rayleigh light scattering properties for two groups of hydrogen bonded isomers: (i) HCN...H₂O and H₂O...HCN and (ii) CH₃HO...H₂O and CH₃OH...OH₂, where the water molecule acts as both proton donor and proton acceptor.

The MP2/aug-cc-pVDZ optimized geometries of the two possible heterodimers, hydrogen cyanide–water and methanol–water, are given schematically in figure 2. In a previous work, we calculated the stability of the hydrogen cyanide–water isomers using CCSD(T)/MP2/6-

Table 4. Calculated mean polarizabilities and polarizability anisotropies (in au), and Rayleigh depolarization ratios. All values are computed at the MP2/aug-cc-pVDZ level.

Isomers	$\bar{\alpha}$	$\Delta\alpha$	$\sigma_n (\times 10^{-2})$	$\sigma_p (\times 10^{-2})$	$\sigma_c (\times 10^{-2})$
H ₂ O...HCN	26.74	13.74	3.38	1.72	3.49
HCN...H ₂ O	22.60	15.37	5.75	2.96	6.10
CH ₃ HO...H ₂ O	31.19	5.90	0.47	0.24	0.47
CH ₃ OH...OH ₂	30.67	5.25	0.40	0.20	0.40

Table 5. Rayleigh intensities (in 10⁴ au) calculated in terms of the polarizabilities and polarizability anisotropies. Values in parentheses correspond to the increase factor of the intensity upon complexation with water. All values are computed at the MP2/aug-cc-pVDZ level. I_A , I_B , and I_C are the calculated rotational constants given in GHz.

Isomer	$\Re_n$	$\Re_{p\perp}$	$\Re_{p\parallel}$	I_A	I_B	I_C
H ₂ O...HCN	3.463 (2.51)	3.350 (2.52)	0.113 (2.35)	429.98	3.04	3.01
HCN...H ₂ O	2.606 (1.89)	2.464 (1.85)	0.142 (2.95)	476.62	3.25	3.23
CH ₃ HO...H ₂ O	4.424 (2.17)	4.403 (2.16)	0.021 (3.03)	24.92	4.62	4.05
CH ₃ OH...OH ₂	4.269 (2.09)	4.252 (2.09)	0.016 (2.39)	31.96	3.80	3.23

311 ++ G(d, p) [45]. For H₂O...HCN the binding energy has been obtained as 5.17 kcal mol⁻¹, whereas for HCN...H₂O the binding energy is found to be 3.38 kcal mol⁻¹, that is, 1.8 kcal mol⁻¹ smaller than for the first isomer. The existence of these isomers has also been detected by photolysis of formaldoxime [46]. In the case of the methanol-water isomers, both experimental techniques [47–49] and theoretical calculations [50] have predicted the existence of two stable heterodimers (figure 2). In this case, the CH₃HO...H₂O complex is found to be more stable than the CH₃OH...OH₂ isomer by an estimated amount less than 1 kcal mol⁻¹, or 0.7 kcal mol⁻¹ using the hybrid density-functional theory B3LYP/6-311 + G(3df, 2p) [50]. Here we find that CH₃HO...H₂O is more stable by 0.8 kcal mol⁻¹. In the theoretical study of these heterodimers by González *et al* [50], they obtained a hydrogen bond distance (O...H) in the case of CH₃HO...H₂O of 1.890 Å, and in the case of CH₃OH...OH₂ their value is 1.937 Å. These results compare favourably with our corresponding results of 1.904 and 1.942 Å, although our distances are slightly longer—by 0.014 and 0.005 Å, respectively. Our calculated Rayleigh scattering properties corresponding to these two groups of hydrogen bonded isomers are presented in tables 4 and 5.

As can be seen in table 4, although the polarizabilities and polarizability anisotropies of the hydrogen cyanide-water isomers are rather similar, the depolarization components of HCN...H₂O differ from those of H₂O...HCN by a factor of 1.7. However, this finding is not verified for the methanol-water isomers, for which the polarizabilities, anisotropies, and all components of the depolarization ratios have similar values. The variations in Rayleigh activities of the two groups of isomers are given in table 5. Again, the observed effect for $\Re_n$ and $\Re_{p\perp}$ is strongly dominated by the $(\bar{\alpha})^2$ term, with a smaller contribution from the $(\Delta\alpha)^2$ term, whereas $\Re_{p\parallel}$ depends solely on the latter term. After complexation, these systems are of nearly-prolate rotor type, as indicated by the rotational constants (I_A , I_B , I_C) in table 5. These quantities are relevant for a millimetre wave description and have also been obtained previously, both theoretically [50] and experimentally [49]. In addition, the present accuracy might be useful in aiding possible detection of hydrogen bonded complexes [45].

Figure 2. Structures of the HCN–water and methanol–water complexes. The lengths of the H bonds are given in Å, and were obtained at the MP2/aug-cc-pVDZ level.

4. Summary

A classical light scattering investigation has been made to analyse small hydrogen bonded clusters. Using *ab initio* calculations at the MP2/aug-cc-pVDZ level, full-geometry optimizations for different water complexes ($\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$) have been performed. The dipole polarizabilities and polarizability anisotropies have been calculated for the separate molecules and the complexes. From these calculations, Rayleigh light scattering properties have been determined and compared, to analyse the changes upon hydrogen bond formation. The Rayleigh intensity is considerably increased by a factor of nearly two in most cases, with the exception of those of $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$ and $(\text{H}_2\text{O})_2$. Different degrees of polarization have been considered (i.e., natural, plane-polarized, and circularly polarized light) to analyse the depolarization ratios. To assess depolarized Rayleigh scattering as a possible means of identifying intermolecular isomers, we have investigated the interaction between hydrogen cyanide (HCN) and water as well as methanol (CH_3OH) and water. Possible detections of these clusters have recently been of great interest in physical chemistry [46–49]. In the case of HCN the different isomers respond differently to light scattering, but in the case of methanol the distinction between the isomers is more difficult to discern in the scattering activity and in the depolarization.

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