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APLICAÇÃO DE MÉTODOS DA QUÍMICA QUÂNTICA
NA DESCRIÇÃO DE ESTRUTURA ELETRÔNICA
MOLECULAR E DE PROPRIEDADES ESPECTROSCÓPICAS
DE SISTEMAS DIATÔMICOS

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*Aos meus pais, Isabel e Roberto, como
gratidão pelo muito que fizeram por mim.*

*À Emília, minha esposa, pelos
aborrecimentos que meu corre-corre
diário lhe trouxe.*

*Ao Frederico, meu filho, como um exemplo de
que deve acreditar em si mesmo e lutar.*

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quando mais preciso.*

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I. INTRODUÇÃO

Sob a denominação de Química Quântica agrupa-se hoje uma variedade enorme de atividades de pesquisa. Num extremo, encontramos aquelas totalmente voltadas ao desenvolvimento de novas metodologias para a descrição da estrutura eletrônica em átomos e moléculas e propriedades em geral e, no outro, temos aquelas nas quais indivíduos se servindo de implementações computacionais dos vários métodos propostos os aplicam na elucidação dos mais diversos problemas estruturais e espectroscópicos. Entre esses extremos de químicos quânticos, a diversificação de atividades é enorme. Por exemplo, existem indivíduos que se dedicam à resolução de problemas numéricos como a elaboração de algoritmos eficientes para a diagonalização de matrizes e outros que se especializam no cálculo de integrais moleculares. Encontramos, ainda, aqueles que se dedicam quase que exclusivamente à programação de códigos e outros que se ocupam com a construção de bases atômicas apropriadas para cálculos moleculares. Entre os usuários de códigos de terceiros, os sistemas de interesse variam desde a descrição rigorosa de átomos com poucos elétrons até moléculas relativamente complexas de interesse bioquímico ou farmacológico. Essa diversificação de atividades poderia ser ilustrada ainda com vários outros casos, entretanto, gostaria de enfatizar um ponto negativo decorrente da proliferação de programas e computadores no meio acadêmico. Hoje, infelizmente, muitos indivíduos se servem de programas de terceiros sem que tenham tido uma formação adequada na área. Passam a ser meros usuários de uma caixa preta sem que tenham o espírito crítico necessário para avaliar, dentro de um contexto mais amplo, a ferramenta que estão usando e a qualidade do produto que essa ferramenta gera. A consequência pode ser uma enorme proliferação de meias-verdades ou conclusões totalmente erradas.

Neste texto procuraremos sistematizar de forma crítica parte de nossa contribuição como químicos quânticos para o desenvolvimento da área no país procurando enfatizar a filosofia que nos tem guiado nesse tipo de trabalho. Porém, antes de analisarmos os

trabalhos especificamente, gostaríamos de procurar situar nossas atividades dentro dessa enorme gama de opções mencionadas há pouco. Para tal, na secção II apresentamos uma exposição sucinta de algumas das diferentes metodologias e discutimos as limitações de suas aplicações. Finalmente, na secção III, agrupando os artigos de forma a caracterizar diferentes etapas de nossas atividades de pesquisa, procuramos enfatizar e discutir de forma crítica sua relevância tanto num contexto nacional como internacional.

II. METODOLOGIAS DA QUÍMICA QUÂNTICA

Sendo as propriedades químicas de uma substância um reflexo de sua estrutura eletrônica, do ponto de vista da mecânica quântica não-relativista, bastaria explicitar no hamiltoniano todas as interações ocorrendo no sistema, no caso atrações e repulsões coulombianas, e resolver a equação de Schrödinger que, em princípio, as informações necessárias para caracterizar esse sistema estariam contidas na solução dessa equação. Na prática, porém, esse é um problema extremamente complicado. Os diferentes métodos para a descrição da estrutura eletrônica de átomos e moléculas exatamente refletem as várias propostas de resolução dessa equação.

Nas sub-seções seguintes, apresentamos um retrospecto de alguns pontos fundamentais de diferentes metodologias sem a preocupação de fazer uma apresentação formal e detalhada das mesmas, visto que isso pode ser encontrado em textos especializados. Nosso propósito é procurar fornecer alguns elementos que nos possibilitem caracterizar aspectos positivos e negativos de sua utilização, bem como para que possam servir como um guia para que nossa contribuição na área possa ser melhor avaliada.

II. 1 O Método Hartree-Fock

Neste método a idéia central é procurar reduzir a equação de Schrödinger, que descreve um conjunto de átomos com N -elétrons, a um conjunto de N equações de um elétron, onde cada uma delas tem embutida no seu hamiltoniano um potencial efetivo que representa uma interação média de um elétron com os outros $N-1$ elétrons restantes. Neste método a função de onda é dada por um produto antisimetrizado de funções de um elétron, chamadas de orbitais, e é normalmente escrita na forma de um determinante de Slater,

$$\Psi(1, 2, \dots, N) = D = |\phi_1(1)\bar{\phi}_2(2)\phi_3(3)\dots\bar{\phi}_N(N)|$$

A minimização da energia do sistema através de variações na forma dos orbitais conduz a um conjunto ótimo de funções conhecidas como orbitais Hartree-Fock (ou canônicos).

Uma versão matricial das equações de Hartree-Fock, proposta por Roothaan em 1951, acabou sendo um dos marcos na história da Química Quântica. Com a disseminação dos computadores no meio acadêmico nas décadas que se seguiram, o método Hartree-Fock-Roothaan passou a ser uma espécie de padrão relativamente ao qual outras metodologias passaram a se referir. A implementação computacional desse método envolve a codificação de várias etapas, as quais apresentamos de forma esquematizada na Fig. 1.

E desnecessário frizar que essa tarefa está longe de ser um problema trivial e que obviamente não é um trabalho para uma única pessoa. O esquema da Fig. 1 ilustra claramente um dos pontos mencionados na Introdução relativamente às várias atuações do químico quântico. Temos o idealizador do método, temos os indivíduos que se especializam no cálculo das integrais, uns naquelas que usam orbitais do tipo Slater, outros naquelas que usam funções gaussianas, temos as pessoas envolvidas com problemas numéricos como diagonalização de matrizes, problemas de dependência linear, ortogonalização e outros, além obviamente, daqueles que vão aplicar o código como um todo.

A posse de um desses programas é uma condição necessária, mas não suficiente, para que um grupo possa usá-los. Tendo sido projetados para computadores específicos, a incompatibilidade software-hardware foi, e tem sido, um grande obstáculo para muitos grupos no que diz respeito a sua utilização.

Um outro problema diz respeito ao tamanho do sistema que se deseja estudar e o menor ou maior grau de sofisticação dos recursos computacionais existentes. A relativa complexidade de muitas moléculas e a não disponibilidade de computadores com os recursos apropriados fizeram com que alternativas a um cálculo *ab initio* do tipo Hartree-Fock-Roothaan fossem desenvolvidas de uma forma semi-empírica. Aproximações como CNDO/2, MINDO/3, MNDO e outras que reduzem de forma significativa o número de integrais calculadas se tornaram bastante populares. No Brasil, em particular, a inexis-

Figura 1. Seqüência esquemática de um cálculo Hartree-Fock

tência de bons computadores fez desses métodos as únicas ferramentas de trabalho de muitos grupos e por muitos anos.

Quanto aos resultados obtidos a nível Hartree-Fock, sabemos que o erro na energia é relativamente pequeno, da ordem de 1% da energia total, entretanto, essa discrepância é suficientemente grande para que propriedades que envolvam diferenças de energia, como por exemplo, a energia de dissociação, sejam mal descritas. Propriedades outras como o momento de dipolo ou o momento de transição são bastante sensíveis à qualidade da função de onda, e para um grande número de moléculas sua descrição não é boa.

Pelo fato de a função de onda Hartree-Fock ser representada por um único determinante de Slater, sistemas nos quais todos os orbitais estão duplamente ocupados tenderão a se dissociar incorretamente. Lembramos o caso da molécula de H_2 que deveria se dissociar em dois átomos de hidrogênio, mas que descrita pela metodologia Hartree-Fock-Roothaan se dissocia em H^+ e H^- .

Se a descrição do estado fundamental já deixa a desejar, sua aplicação a estados excitados, ou seja, para descrever de forma rigorosa e detalhada a espectroscopia de um sistema molecular é de menor sucesso ainda.

II. 2 O Método Interação de Configurações

Parte da deficiência do método Hartree-Fock relativa à dissociação incorreta de uma molécula pode ser corrigida através de versões não-restritas do método, ou seja, permitindo que os elétrons ocupem orbitais distintos, entretanto, como o potencial na equação de Hartree-Fock reflete uma interação média entre os elétrons, suas interações instantâneas não são apropriadamente descritas. A inclusão dessa correlação dinâmica entre os elétrons tem sido feita com muito sucesso através do método Interação de Configurações.

De uma forma simples, podemos dizer que a idéia central do método interação de configurações (CI) é expandir a função de onda de N -elétrons numa base de funções

devidamente definidas. Ocorre, entretanto, que os determinantes formados pelas diferentes ocupações de todos os orbitais virtuais gerados num cálculo Hartree-Fock definem uma tal base de N-elétrons.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_i c_i D_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

Obviamente, essa expansão pode ser reestruturada para que cada um de seus termos reflita um dado estado de spin e uma dada simetria molecular

$$\Psi_k(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_i c_{ik} \Phi_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

com

$$\Phi_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_j d_{ij} D_{ij}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

Essas funções Φ_i 's são normalmente chamadas de funções de configurações. Os coeficientes $\{d_{ij}\}$ são conhecidos a priori, pois definem o estado de spin do sistema, e os coeficientes $\{c_{ik}\}$ são obtidos variacionalmente pela minimização da energia. Formalmente, o método CI é relativamente simples, pois sendo uma aplicação direta do método variacional de Ritz, a solução da equação de Schrödinger fica reduzida à resolução de uma equação matricial

$$(\mathbf{H} - 1\varepsilon) \mathbf{C} = 0$$

onde,

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$$

Pode-se facilmente ver que limitações práticas também surgem para a aplicação deste método. Por exemplo, para uma base relativamente pequena com 30 orbitais moleculares e um sistema com dez elétrons, existem cerca de $\binom{60}{10} \simeq 10^{11}$ possíveis determinantes que

poderão ser formados pela distribuição de 10 elétrons em 60 spin orbitais. É óbvio que esse número é intratável. Entretanto, técnicas existem para reduzir esse problema a dimensões aceitáveis pelos padrões de computadores existentes.

Apesar de seu formalismo ser bem mais simples que o do método Hartree-Fock-Roothaan, a implementação computacional do método CI é um problema difícil. A figura 2 esquematiza as diferentes etapas desse cálculo. É importante ressaltar que, ao longo de sua história, programas computacionais foram desenvolvidos por diversos grupos que, se servindo de recursos específicos existentes em cada tipo de computador, tornaram a adaptação desses códigos a outras máquinas um problema extremamente extenuoso, senão, quase que impossível. Fica evidente, que a aplicação rigorosa desse método está limitada a uma classe de moléculas com alguns poucos átomos e da ordem de três dezenas de elétrons. Se para o uso da metodologia Hartree-Fock barreiras diversas foram encontradas, a condução de um cálculo a nível CI se constitui um problema pelo menos uma ordem de magnitude mais complexo. Talvez, menos de 10% de colegas na área de química quântica no país disponham hoje de software e/ou computador para conduzir um estudo a nível interação de configurações.

Ressaltamos, novamente, que essas rápidas considerações têm o propósito de procurar auxiliar a situar apropriadamente nosso trabalho num contexto mais amplo facilitando assim uma compreensão melhor das razões que nos levaram a tratar os casos aqui discutidos

Figura 2. Sequência esquematizada de um cálculo CI, Passo 1,

Figura 2(cont). Seqüência esquematizada de um cálculo CI. Passo 2.

Figura 2(cont.). Sequência esquematizada de um cálculo CI. Passo 3.

III. APLICAÇÕES

Nesta seção agrupamos os trabalhos que refletem nossa produção na área de tal forma que as diferentes fases do progresso realizado possam ser caracterizadas. Precedendo cada grupo de artigos, procuramos discutí-los criticamente de modo a enfatizar sua relevância num contexto tanto nacional como internacional.

Para efeito organizacional, essas etapas foram rotuladas conforme mostrado abaixo :

- A Adaptação de Programas e os Primeiros Cálculos do Tipo Interação de Configurações;
- Descrição Rigorosa de Estados Eletrônicos e Vibracionais de Moléculas Diatômicas:
o Íon BeH^+ ;
- Descrição Rigorosa de Estados Eletrônicos e Vibracionais de Moléculas Diatômicas:
as Moléculas CH^+ e BeF ;
- Abordagens Ab Initio e Semi-Empíricas a Sistemas Poliatômicos: Acetonas Substituídas, Mercaptoetanol, $\text{H}_2\text{P}_2\text{F}_2$, Nitroanilinas Substituídas e P_2O ;
- Abordagens Educacionais a Conceitos e Técnicas da Química Quântica.

**A Adaptação de Programas e os Primeiros Cálculos
do Tipo Interação de Configurações**

Artigos

Configuration Interaction: Molecular Orbitals for Accurate Calculations on Diatomics

F. R. Ornellas e S. Hagstrom, *Theoret. Chim. Acta (Berlim)*, **62**, 87-92 (1982)

Potential Energy Curves and Spectroscopic Constants for the $X^1\Sigma^+$ and $A^1\Sigma^+$ States
of the BeH^+ Molecule

F. R. Ornellas, *J. Phys. B: At. Mol. Phys.*, **15**, 1977-1980 (1982)

A relevância desses artigos está no fato de serem esses trabalhos os primeiros cálculos do tipo interação de configurações feitos totalmente no país. Tendo trabalhado durante o doutorado no planejamento e codificação de todas as etapas de um cálculo do tipo interação de configurações, como mostradas na Fig. 2, pude sem grandes problemas adaptar tais programas no computador Cyber 170/730, da então Divisão de Estudos Avançados (EAV), do Instituto de Atividades Espaciais, do CTA, em São José dos Campos. Note que aqui, foi a combinação de fatores como a experiência no desenvolvimento desses programas e disponibilidade de recursos computacionais como os existentes no EAV que viabilizaram tais cálculos.

No primeiro desses artigos procuramos abordar o problema da construção de uma base atômica apropriada, por se tratar de um passo crítico nas etapas seguintes do cálculo CI. Ele procura apresentar um procedimento no qual o tamanho do conjunto base de orbitais moleculares (MO's) e conseqüentemente o tamanho da função de onda não são estabelecidos no começo do cálculo, mas sim após uma série de pequenos cálculos CI nos quais informações sobre a importância dos orbitais naturais são obtidas.

Esse procedimento tem a vantagem de nos permitir testar os expoentes das funções do tipo Slater para cada orbital molecular. Isso é viável pois as expansões da função de onda são pequenas e os cálculos podem ser feitos relativamente rápidos. Como conseqüência o conjunto de orbitais moleculares fica menor e a função de onda mais compacta, sem que perca em qualidade. A aplicação dessa técnica no cálculo da energia da molécula LiH ilustra muito bem sua potencialidade. Nossos resultados, -8.06347 u.a., obtidos com uma função de onda com 1852 termos são de mesma qualidade que os obtidos pelo grupo de química quântica da NASA, -8.0640 u.a., com uma função de onda com 6514 termos, na época o cálculo mais rigoroso para esse sistema.

Enquanto procedíamos aos cálculos para a molécula LiH, percebemos a existência de um outro sistema diatômico de quatro elétrons pouco explorado experimentalmente, e muito menos teoricamente. Tratava-se do íon BeH^+ . No segundo trabalho, nossa pre-

ocupação foi garantir de imediato nossa prioridade na descrição das curvas de potencial para os dois primeiros estados de simetria $^1\Sigma^+$ dessa molécula. Apesar de ser um cálculo CI do tipo simples e duplas a partir de uma única referência e, portanto, apresentar falhas na descrição da região de dissociação e do estado excitado, esse trabalho teve o mérito de ser o melhor estudo desse sistema na ocasião.

Configuration Interaction: Molecular Orbitals for Accurate Calculations on Diatomics

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A procedure is developed to construct an optimum set of molecular orbitals (MO's) to be used in large scale configuration interaction expansion for diatomics. The set is optimum in the sense that a significant energy improvement can be obtained for a relatively short wavefunction expansion. Application of this methodology to the ground state of the LiH molecule gave an energy of -8.06345 a.u. for an expansion with 1852 terms obtained from a set with 16σ -, 12π -, and 6δ -type MO's.

Key words: Configuration interaction – Molecular orbitals – Lithium hydride.

1. Introduction

The virtual Self-Consistent Field-Linear Combination of Atomic Orbitals (SCF-LCAO) Molecular Orbitals (MO's), although known for quite some time as not good correlating orbitals, have been used in several configuration interaction [1] studies. Schemes to transform these virtual orbitals to increase their effectiveness have also been discussed in the literature [2]. Of these, the Iterative Approximate Natural Orbitals (IANO's) procedure, as developed by Bender and Davidson [3], seems to have been the most successful. A scheme that also uses this iterative approach but employs first-order perturbation theory (of the wavefunction) to construct approximate CI expansions is discussed by Jafri and Whitten [4]. It is

worth-recalling that Bender and Davidson's IANO's approach involves the substitution of the starting set of MO's by Natural Orbitals (NO's), but they go through a large CI calculation before using the NO's, so if the starting MO set is not of "good quality" the iterative process will cause a minimum of improvement or none at all. In fact, studies by Thunemann [5] et al. have also shown the possibility of the calculation getting worse after the iteration.

Recently, Ermler and McLean [6] stressed the "critical importance of the use of adequate one-particle basis sets to provide the starting point for any *ab-initio* method", and in this connection we can notice that in several CI studies reported in the literature, the number of Slater-type functions (STF's), some of the exponents in these functions (for extended basis sets), and the number of MO's used have some arbitrariness in their choice. Clearly, a blind choice in the number of MO's can lead to the construction of maybe an unnecessarily large formula tape for the CI matrix elements.

In this paper, we propose a procedure in which the size of the MO set and consequently the size of the formula tape are not established at the outset of the calculation, but are determined after a series of small CI calculations giving enough information about the importance of the different natural orbital types that are being selected to make up the working MO set. Since the CI expansions during this stage are very small, we also have the possibility of experimenting with the orbital exponents and/or increasing the number of STF's for each MO type.

2. Procedure

Our scheme is a normal CI approach organized in such a way that all the two-electrons integrals can be computed and transformed according to their symmetry types. Having the orbitals grouped according to their symmetry, we carry out small CI calculations within each group in such a way that, besides the occupied MO's, only σ -MO's are used as virtual orbitals in one set of calculation, then π -MO's only, and then δ -MO's only. These small CI expansions in each group correspond, in one case, to the freezing of the core electrons, and in a second case to the freezing of the valence electrons. For each one of these expansions the first-order density matrix is generated and the corresponding NO's computed. The MO's for each expansion within a given symmetry type of virtual orbitals are ordered according to their occupation numbers, and those with occupation numbers below a specified threshold neglected. At this stage we expect to obtain an indication of the importance of a given NO by the magnitude of its occupation number. The next step consists of merging the selected NO's into a single set. This new set will consist of the occupied SCF orbitals and the virtual NO's grouped in decreasing value of their occupation numbers. If the number of selected NO's in this new set exceeds the number of MO's in the original set, we take this information as an indication that the original set should be augmented by this extra number of MO's. This, of course, implies a corresponding increase in the number of STF's.

The generation of an additional number of MO's and/or a variation in the exponents of the added STF's makes this procedure clearly dependent on the efficiency of the routines that calculates the two-electron integrals. In this respect we "armed" ourselves by transforming the efficient "in-core" diatomic integral routine DERIC developed many years ago by Hagstrom [7], into an "out-of-core" disk-file oriented package [8] whose efficiency becomes greater the larger the number of integrals being calculated, specially with the new computers with array processing hardware. As to the two-electron integral transformation, since we have all the integrals grouped according to their symmetry type, this step is not time consuming. Once this selection procedure has been conducted for each symmetry type of MO's, they are combined into a single set with which a large scale CI is carried out. The final CI expansion besides all singles and doubles also includes some selected triples and quadruples; this selection procedure is discussed in the next section.

3. Results and Discussion

The ideas put forth in Sect. 2 were tested in the calculation of the ground state energy of the lithium hydride (LiH) molecule. Representative calculations on this molecule are collected in Table 1; they all employed Slater type functions (STF's). The STF's used in this work are those given in Table 2. The exponents for the $nl\sigma$ functions are those given by Cade and Huo [9]. For the $nl\pi$ functions we started with the nine exponents given by Bender and Davidson [3], and then, after experimenting with them, the set given in Table 2 was generated. The exponents in parentheses were added to augment Bender and Davidson's modified set of $nl\pi$ functions. The exponents for the $nl\delta$ functions are also the ones given by Bender and Davidson, they were changed also, but no significant

Table 1. Representative studies[†] of the ground state of the LiH molecule; $R = 3.015$ bohr

(AO's/MO's) ^a	Number of terms	-Energy (Hartree)
(12-4/16) ^b	1	7.98731
(12-4, 6-3, 4-2, 1-1/not reported) ^c	939	8.0606
Hylleraas-type ^d	119	8.0630
(15-7, 8-4, 4-3/not reported) ^e	6514	8.0640
CEPA ^f	non-variational	8.0660
(12-4/16)	435	8.03262
(12-4, 6-3/16, 9)	606	8.06011
(12-4, 6-3, 4-2/16, 9, 6)	684	8.06165
(12-4, 6-3, 4-2/16, 9, 6)	684	8.06166
(12-4, 6-3, 4-2/16, 9, 6)	1517	8.06206
(12-4, 8-4, 4-2/16, 12, 6)	813	8.06265
(12-4, 8-4, 4-2/16, 12, 6)	1852	8.06317
(12-4, 8-4, 4-2/16, 12, 6)	1852	8.06347
"experimental"		8.0704 ^b

[†] See text for explanation on the unreferenced results.

^a Ref. [14]; ^b Ref. [9]; ^c Ref. [3]; ^d Ref. [15]; ^e Ref. [11]; ^f Ref. [16].

Table 2. Orbital exponents for the Slater type functions

	Lithium	Hydrogen
1s	4.699, 2.52117	1.56567, 0.88775
2s	1.200, 0.79722	2.200
3s	2.750	
2p σ	2.750, 1.200, 0.73691	1.37646
3p σ	3.200	
3d σ	1.200, 0.64232	
4f σ	0.92480	
2p π	4.789, 2.600, (1.274)	1.000, (0.600)
3d π	5.500, 3.000, (1.274)	1.200
4f π	7.200, 4.789	1.622
3d δ	6.3852, 1.6984	2.1626
4f δ	6.3852, 1.6984	2.1626

improvement was obtained. The starting MO's comprised the 1 σ , 2 σ and 3 σ orbitals given by Cade and Huo and the remaining ones were generated by Schmidt orthonormalization, with the order of orthonormalization being that of the atomic functions given in Table 2. The orbitals centered on the hydrogen atom follow the ones centered on the lithium atom.

In Table 1 the results of this work are compared with previous calculations. Although the basis set preparatory stage had indicated that the π -MO's set should contain more than the nine functions as we originally started, the decision was made to carry out a series of calculations with this smaller basis set to better assess the improvement in subsequent results. First of all, we can notice that from an all σ -MO's, singles and doubles, 435-term CI, an all σ -, and π -MO's 606-term CI, and finally from a 684-term CI with 16 σ , 9 π , 6 δ MO's, the correlation energy recovered (0.07434 a.u.) can be partitioned into the following contributions: 0.04531 a.u. from σ -MO's, 0.02749 a.u. from π -MO's, and 0.00154 a.u. from δ -MO's, which amounts to 60.9%, 37.0% and 2.1% respectively of the total recovered. Before working with the larger set we tried to improve this energy first by an iterative process like Bender and Davidson's approach, and second by the inclusion of selected triples and quadruples. With just one iteration the energy lowered by 1.0×10^{-5} a.u., a small improvement. As to the triples and quadruples their generation was done as single and double excitations from a reference set of seven configurations which, based on the magnitude of their coefficients, were selected as most important. For a final expansion with 1517 terms the energy obtained, -8.06206 a.u., is just 4.0×10^{-4} a.u. below the all singles and doubles value, and in our opinion reflects a deficiency in the one-particle basis.

The larger atomic basis set essentially contains three more STF's, and the improvement obtained from this addition is evident in Table 1. The correlation energy now recovered is 0.0754 a.u. (90.7%) and the total energy for an all

singles and doubles 813-term CI is -8.06265 a.u. Note that this number is below the one from the previous calculation which had also included selected triples and quadruples. It is important to point out that to test the accuracy of our results for the all singles and doubles CI's we verified the invariance of the energy upon a transformation among the set of virtual orbitals [10].

In going beyond the singles and doubles level, the generation of triples and quadruples was done as single and double excitations from a reference set of 25 configurations with the constraint that these excitations would involve only the first few most important natural orbitals of each symmetry type. This constraint, although logical was also done to keep the expansion within the present limits of our computer codes. Also, due to computer time availability we did not calculate part of the matrix elements in the symbolic matrix, that is, every matrix element resultant from a triply or a quadruply excited configuration and a singly or doubly excited configuration whose coefficient in the all singles and doubles CI was less than $|1.0 \times 10^{-4}|$ was set equal to zero. Also, in the triples and quadruples block only the diagonal elements were kept. The results obtained, -8.06265 a.u. and -8.06317 a.u., respectively, represent a considerable improvement over the value -8.0606 a.u. obtained by Bender and Davidson with an atomic basis of almost equal size. Next, using the IANO's approach an attempt was made to improve the best value we had obtained so far. With one iteration the energy lowered to -8.06347 a.u.

The significance of the approach used in this work can be better evaluated if these results are compared with the ones reported by Langhoff and Chong [11]. Using an atomic basis with 22 $nl\sigma$, 12 $nl\pi$ and 7 $nl\delta$ STF's they generated a CI expansion with 6514 terms giving an energy of -8.0640 a.u. More recently, using the orbital exponents given by Langhoff and Chong [11], with the exception of the 4f8 STO on the hydrogen, Partridge and Langhoff [12] obtained an energy of -8.06385 a.u. for an interatomic distance of 3.00 bohr. Clearly, for an almost equal energy, we have achieved a considerable compaction in the wavefunction. This result certainly shows the importance of adequately constructing the one-particle basis. A careful natural orbital study of the first row atoms in the manner done by Bunge [13] would certainly be useful in this regard, especially in the construction of the MO's to describe the core correlation.

In connection with this work, a study is now under progress to determine for the few electrons diatomics an optimum size set of MO's that guarantees the attainability of the all singles and doubles energy limit before going to triple and quadruple excitations.

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Potential energy curves and spectroscopic constants for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of the BeH^+ molecule

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Abstract. Using a 1322-term configuration interaction wavefunction, potential energy curves were computed for the ground ($X^1\Sigma^+$) and first excited ($A^1\Sigma^+$) states of the BeH^+ molecule. Spectroscopic constants were obtained by means of a Dunham analysis.

The beryllium hydride ion, BeH^+ , although isoelectronic with LiH , has not been as exhaustively investigated as this latter molecule. Previous *ab initio* studies on the ground state of BeH^+ are those of Jenč *et al* (1962), Brown (1969), Cade and Huo (1973) and Banyard and Taylor (1975). In this letter we report the theoretical potential energy curves and spectroscopic constants for the ground state ($X^1\Sigma^+$) and the first excited state ($A^1\Sigma^+$) of BeH^+ using a 1322-term (singles and doubles) configuration interaction wavefunction.

The calculation presented here is a normal configuration interaction (CI) approach where the configuration functions are generated as all the single and double excitations relative to the reference configuration ($1\sigma^2 2\sigma^2$) that could be obtained from a molecular orbital (MO) set containing 22 σ -, 14 π -, and 5 δ -type functions. The Slater-type functions (STF) used in the construction of these MO are those given in table 1. Notice that the set of functions with $m_l = 0$ is that of Cade and Huo (1973) augmented by six other functions.

Table 1. Orbital exponents for the Slater-type functions.

Orbital	Beryllium	Hydrogen
1s σ	2.9447, 5.748	1.06491, 3.200
2s σ	0.89249, 1.27381, 7.450	2.500
3s σ	3.630, 8.800	
2p σ	0.80799, 1.0459, 1.500, 4.100, 5.900, 7.450	0.800, 1.450
3d σ	0.96654, 1.700, 7.410	
4f σ	1.24389	
2p π	0.900, 2.000, 3.500, 5.000, 6.500	0.400, 0.700, 1.200
3d π	3.000, 5.900, 8.500	1.500
4f π	2.500, 7.000	
3d δ	1.000, 4.000, 9.500	2.800
4f δ	9.000	

The potential energy curves were obtained in a two-step process. First, keeping the 1σ and 2σ MO of Cade and Huo fixed the remaining of the σ MO were generated by Schmidt orthonormalisation; the π and δ MO were also obtained by Schmidt orthonormalisation with the order of orthonormalisation being that of the STF given in table 1. This orbital space was then used to obtain a first approximation to the energy of the ground state at all the internuclear distances. In a second step the natural orbitals were obtained for every point in the curve and used as input orbitals in a second CI. The final energies obtained are those given in table 2. Also listed in table 2 are the energies of the first excited state ($A^1\Sigma^+$) obtained as the second root of the Hamiltonian matrix. In figure 1 our results are compared with the experimental ones and with other theoretical calculations.

Table 2. Energies, in hartrees, of the BeH^+ molecule.

Internuclear distance (Bohr)	$X^1\Sigma^+$	$A^1\Sigma^+$
1.60	-14.792 04	-14.502 12
1.80	-14.865 53	-14.584 19
2.00	-14.906 82	-14.637 78
2.20	-14.927 54	-14.672 45
2.40	-14.935 12	-14.694 26
2.479	-14.935 61	-14.700 26
2.60	-14.934 35	-14.707 20
2.80	-14.928 44	-14.713 88
3.00	-14.919 50	-14.716 12
3.20	-14.909 01	-14.715 18
3.50	-14.892 40	-14.709 73
4.00	-14.866 70	-14.694 78
5.00	-14.831 35	-14.662 77
6.00	-14.814 21	-14.643 93
7.00	-14.806 84	-14.636 77
8.50	-14.802 90	-14.631 03
9.25	-14.802 15	-14.630 52

Although these results certainly represent the best energies now available, notice that at large internuclear distances this one-reference-root CI does not recover most of the correlation energy as it does at the equilibrium distance. At this distance 90% of the correlation energy is recovered compared with the estimate of 47% at 9.25 Bohr. This is not so surprising since the equilibrium configuration $1\sigma^2 2\sigma^2$ is not the most appropriate reference for large internuclear distances. Notice also that while the energy at the equilibrium distance for the ground state is in error by 0.063%, the error in the minimum of the excited state is 0.33%, a reflection also of the inadequacy of the configuration $1\sigma^2 2\sigma^2$ as a reference configuration for this state.

The experimental energies were computed according to the formulae (Cade and Huo 1967)

$$E(X^1\Sigma^+) = E_{\text{exact}}(\text{Be}^{2+}) + \text{IP}(\text{Be}^+) + D_e$$

$$E(A^1\Sigma^+) = E(X^1\Sigma^+) + T_e$$

where $E_{\text{exact}}(\text{Be}^{2+})$ is the exact energy of the two-electron system Be^{2+} given by

Figure 1. Potential energy curves for the first excited state (a) and the ground state (b) of the BeH^+ molecule derived from a CI calculation. In (a) $E_{\text{exp}}(R = 3.040 \text{ Bohr}) = -14.76547 \text{ au}$. In (b): x, SCF-LCAO (Cade and Huo 1973), -14.85396 au ; o, CI (Brown 1969), -14.92126 au ; □, experimental, -14.94505 au .

Pekeris (1958) and $\text{IP}(\text{Be}^+)$ is the ionisation potential of Be^+ given by Moore (1971). D_e is the dissociation energy and is given by $D_0 + \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$. All unnamed constants have their usual meanings as given by Huber and Herzberg (1979).

The spectroscopic constants were obtained by means of a Dunham (1932) analysis and are given in table 3. They represent the average of three different fittings by a fifth-degree polynomial over the intervals (1.8–3.5), (2.0–3.2) and (2.0–3.5) for the ground state, and over the intervals (2.2–5.0), (2.2–4.0) and (2.4–4.0) for the excited state. The agreement with the experimental values is very good.

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Table 3. Spectroscopic constants for BeH⁺. With the exception of R (Bohr) all the constants are given in cm⁻¹.

	X ¹ Σ ⁺			A ¹ Σ ⁺	
	Banyard Taylor (1975)	This work	Experimental ^a	This work	Experimental ^a
R_e	2.52	2.473	2.479	3.030	3.040
ω_e	2146	2243.1	2221.7	1468.0	1476.1
$\omega_e x_e$	40	40.19	39.79	14.05	14.80
α_e	—	0.322	0.294	0.157	0.125
B_e	10.42	10.862	10.800	7.232	7.184
$\tilde{D}_e(\times 10^{-4})$	—	10.2	9.9	7.0	6.1

^a Huber and Herzberg (1979).

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Descrição Rigorosa de Estados Eletrônicos e Vibracionais de
Moléculas Diatômicas : o Íon BeH^+

Artigos

A Vibration-Rotation Analysis of the Beryllium Hydride Ion $(\text{BeH})^+$ in the $X^1\Sigma^+$ State

F. R. Ornellas, *J. Mol. Struct. (Theochem)*, **92**, 337-345 (1982)

Radiative Transition Probabilities, Lifetimes, and Dipole Moments for all Vibrational Levels in the $X^1\Sigma^+$ State of the Beryllium Hydride Ion

F. R. Ornellas, W. C. Stwalley e W. T. Zemke, *J. Chem. Phys.*, **79**, 5311-5315 (1983)

A Theoretical Study of the $(\text{BeH})^+$ Molecule in the $A^1\Sigma^+$ State

F. R. Ornellas, *J. Chem. Phys.*, **82**, 379-383 (1985)

Theoretical Transition Probabilities and Lifetimes for the BeH^+ ($A^1\Sigma^+ - X^1\Sigma^+$) Band System

F. B. C. Machado e F. R. Ornellas, *J. Mol. Struct. (Theochem)*, em impressão, 1990

Esses trabalhos representam o estudo mais detalhado e rigoroso existente na literatura sobre o íon molecular BeH^+ . Nele são apresentadas curvas de potencial para os dois estados eletrônicos conhecidos e, para cada um deles, todos os níveis vibracionais até o limite de dissociação são calculados tanto para o BeH^+ como para a espécie deuterada BeD^+ . Em função desses níveis, constantes vibracionais e rotacionais são também obtidas.

Além disso, servindo-nos da função momento de dipolo e das funções de onda vibracionais, ainda desconhecidas na literatura, pudemos calcular o momento dipolar médio para cada estado vibracional e probabilidades de transições radiativas vibro-rotacionais. Completando ainda mais essa descrição, tempos de vida radiativa para cada estado vibracionalmente excitado em função do número quântico rotacional foram também calculados. Esses resultados eram totalmente inéditos.

Esse tipo de trabalho reflete uma de nossas opções de trabalho em química quântica que é a descrição o mais rigorosa possível de sistemas diatômicos tal que as informações espectroscópicas obtidas sejam de alta qualidade. Note que há oito anos atrás já tínhamos feitos cálculos de quantidades como D_0 , por exemplo, com o rigor que ultimamente se convencionou chamar de precisão química (erros da ordem de 1 kcal/mol). Quanto aos espaçamentos entre os níveis vibracionais, nossos erros são inferiores a 9 cm^{-1} .

Essa boa qualidade dos resultados para os estados sobre os quais informações experimentais são conhecidas nos permite extrapolar com confiança nossos valores para os níveis ainda desconhecidos. O difícil trato experimental de espécies iônicas, associado à toxidez dos compostos de berílio, faz desses trabalhos uma peça importante na caracterização espectroscópica dessas moléculas.

Esses cálculos só foram viáveis porque dispúnhamos das facilidades computacionais do IEAv, de nossos próprios programas para o cálculo do tipo interação de configurações e de outro programa (INTENSITY) para a resolução da equação de Schrödinger para o movimento dos núcleos e cálculos de probabilidades de transições que adaptamos ao Cyber 170/750, após gentil cessão por parte do Prof. William Stwalley, da Universidade de Iowa,

E.U.A..

Mais recentemente, em função de novo software (Programa MELD desenvolvido por E. Davidson e colaboradores) para cálculos de estrutura eletrônica, que adaptamos ao computador Cyber, pudemos começar a explorar também o problema das transições eletrônicas através de cálculos de probabilidades de transições radiativas e conseqüentemente a obtenção dos tempos de vida radiativa para estados excitados eletronicamente e vibracionalmente. A aplicação natural desses novos recursos era obviamente para o estudo das transições do sistema de bandas $A^1\Sigma^+ - X^1\Sigma^+$ do íon molecular BeH^+ para o qual nosso estudo anterior era o mais completo existente. O último trabalho da série acima veio completar ainda mais a caracterização espectroscópica desse sistema e em vista de sua importância serviu-nos como forte motivador para que estudos semelhantes fossem estendidos a outros sistemas.

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THEOCHEM

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A VIBRATION–ROTATION ANALYSIS OF THE BERYLLIUM HYDRIDE ION (BeH)⁺ IN THE $X^1\Sigma^+$ STATE

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ABSTRACT

Using a 1857-term configuration interaction wavefunction an accurate potential energy curve has been calculated for the ground state ($X^1\Sigma^+$) of the beryllium hydride ion-molecule. Vibrational levels were determined by solving the radial Schrödinger equation and all vibration–rotation constants for (Be^1H)⁺ as well as (Be^2H)⁺ were obtained via a least squares fit of standard expressions to theoretical data.

INTRODUCTION

This study is part of a long-term project embarked upon with the aim of understanding the spectroscopy of the few-electron diatomics completely from first principles. We report the construction of a very accurate potential energy curve for the beryllium hydride ion in the $X^1\Sigma^+$ state and the corresponding vibration–rotation energy levels and spectroscopic constants for the (BeH)⁺ and (BeD)⁺ species.

In contrast to LiH, which has been so exhaustively studied, the only theoretical studies on the isoelectronic (BeH)⁺ molecule are those of Jenč et al. [1], Brown [2], Cade and Huo [3], Banyard and Taylor [4], Rosmus and Meyer [5] and Ornellas [6]. Experimentally, the only available information is the relatively old studies of Knave [7], Koontz [8] and Watson and Humphreys [9].

RESULTS

Potential construction

To generate the potential energy curve a configuration interaction (CI) calculation was first carried out at twenty internuclear distances covering the region from 1.0 to 10.0 a_0 . Based on a previous all singles and doubles CI study [6] of this molecule, care has been taken to include reference configurations other than $1\sigma^2 2\sigma^2$ which could more appropriately describe the correlation effects throughout the potential curve. Seven more reference

configurations have been added and selected single and double excitations relative to these configurations have been generated involving only what was judged to be the relevant part of the orbital space. A final 1857-term wavefunction was then obtained which besides the 1321 all singles and doubles configuration functions generated from the $1\sigma^2 2\sigma^2$ reference configuration, also contained 535 selected triple and quadruple excitations. The molecular orbital (MO) set consisted of 22σ -, 14π -, and 5δ -type and the Slater type functions used in the construction of these MOs as well as the general procedure to generate the final MO set and wavefunctions is described by Ornellas [6]. The total energies obtained are listed in Table 1.

The remaining points in the potential energy curve were obtained by a cubic spline [10] fit to the points listed in Table 1. A total of 2800 points was generated at a distance of $0.005 a_0$ from each other.

The potential for internuclear distances smaller than $1.0 a_0$ was constructed assuming that it could be approximated by the function $E(R) = A + B \exp(-C.R)$ where the coefficients were determined by requiring that $E(R)$ matches the computed energy at $1.0, 1.6$ and $1.8 a_0$. For internuclear distances greater than $10.0 a_0$ the approximation function used was

$$E(R) = D + ER^{-6} + FR^{-8}$$

where the coefficients were determined by requiring that $E(R)$ matches the theoretical values at R equals $8.5, 9.25$ and $10.0 a_0$. The values obtained for these coefficients are: $A = -14.975831, B = 11.143187, C = -2.568199, D = -14.818463, E = 227.2941$ and $F = -29783.26$.

Vibration-rotation levels and spectroscopic constants

With the potential derived above the radial Schrödinger equation was then solved numerically for the vibration-rotation eigenvalues by the Numerov-

TABLE 1

Theoretical total energies (in hartree) for the beryllium hydride ion in the $X^1\Sigma^+$ state

$R(a_0)$	Energy	$R(a_0)$	Energy
1.00	-14.121444	3.20	-14.910812
1.60	-14.792835	3.50	-14.894789
1.80	-14.866342	4.00	-14.870493
2.00	-14.907669	4.50	-14.851897
2.20	-14.928456	5.00	-14.839116
2.40	-14.936122	6.00	-14.825953
2.479 ^a	-14.936654	7.00	-14.820866
2.60	-14.935480	8.50	-14.818954
2.80	-14.929727	9.25	-14.818656
3.00	-14.921016	10.00	-14.818534

^aOther theoretical energies at this R are: SCF-LCAO, -14.85396 a.u., ref. 3; CI, -14.92126 a.u., ref. 2; CEPA, -14.936011 a.u., ref. 5; $E_{\text{exp}} = -14.94505$ a.u., refs. 3, 6.

Cooley method using a computer program kindly supplied by Stwalley and Zemke [11]. The vibrational levels for the isotopic species $(\text{BeH})^+$ and $(\text{BeD})^+$ are listed in Table 2, and plotted in Fig. 1. For a more direct comparison with experimental data the vibrational level spacings

$$\Delta G_{v+1/2} = G(v+1) - G(v)$$

are listed in Table 3 together with the available experimental results [7-9].

For the same vibrational state we have also computed the difference in energy between adjacent rotational levels for $(\text{BeH})^+$ and $(\text{BeD})^+$. These differences as given by the expression [12]

$$F_v(J+1) - F_v(J) = 2(J+1)B_v - 4(J+1)^3D_v \quad (1)$$

allow one to obtain the rotational constants B_v and D_v , listed in Table 4, by a least square fit to the theoretical values. From these values the spectroscopic constants B_e , α_e , γ , D_e and β_e can be obtained by a least squares fit of the

TABLE 2

Vibrational energy levels in (cm^{-1}) for the beryllium hydride ion in the $X^1\Sigma^+$ state with respect to the bottom of the curve

$(\text{BeH})^+$		$(\text{BeD})^+$	
v	$E(v)$	v	$E(v)$
0	1105.0	0	821.8
1	3253.4	1	2431.6
2	5320.3	2	3996.5
3	7304.5	3	5516.4
4	9204.4	4	6991.0
5	11018.4	5	8419.2
6	12743.3	6	9800.7
7	14378.4	7	11133.9
8	15921.6	8	12417.9
9	17369.3	9	13652.8
10	18719.2	10	14837.9
11	19968.3	11	15971.6
12	21112.3	12	17052.5
13	22147.0	13	18080.4
14	23066.9	14	19053.6
15	23866.6	15	19970.5
16	24543.7	16	20829.6
17	25101.1	27	21629.2
18	25534.0	18	22367.2
19	25816.5	19	23041.2
		20	23649.0
		21	24189.1
		22	24662.3
		23	25070.5
		24	25410.6
		25	25674.5
		26	25845.3

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Fig. 1. Potential energy curve for the $X^1\Sigma^+$ state of $(\text{BeH})^+$. The horizontal solid and dashed lines represent the vibrational levels of $(\text{Be}^1\text{H})^+$ and $(\text{Be}^2\text{H})^+$ respectively.

TABLE 3

Comparison of calculated and observed vibrational level spacings (in cm^{-1}), $G(v+1) - G(v)$, in the $X^1\Sigma^+$ state of the $(\text{BeH})^+$ and $(\text{BeD})^+$ molecules^a

$(\text{BeH})^+$			$(\text{BeD})^+$	
v	This work	Expt.	This work	Expt.
0	2148.4	2139.9	1609.8	1602.8
1	2066.9	2059.0	1564.9	1559.5
2	1984.2	1977.2	1519.9	1514.9
3	1899.9	1893.5	1474.6	
4	1814.0	1810.4	1428.2	
5	1724.2	1722.0	1381.5	
6	1635.1	1633.6	1333.9	
7	1543.2	1545.0	1284.0	
8	1447.7		1234.9	
9	1350.0		1185.1	

^a $\Delta G_{1/2} = 2141.4 \text{ cm}^{-1}$, ref. 5.

TABLE 4

Rotational constants (in cm^{-1}) for beryllium hydride in the $X^1\Sigma^+$ state^a

v	(BeH) ⁺				(BeD) ⁺			
	B_v (calc.)	B_v (expt.) ^b	D_v (calc.)	D_v (expt.) ^b	B_v (calc.)	B_v (expt.) ^c	D_v (calc.)	D_v (expt.) ^c
0	10.667	10.659	9.81		5.897	5.893	3.02	2.91
1	10.354	10.346	9.77		5.770	5.771	3.01	2.99
2	10.035	10.028	9.74		5.641	5.646	3.00	3.04
3	9.707	9.701	9.70		5.510	5.504	2.99	2.78
4	9.369	9.373	9.58		5.375		2.97	
5	9.031	9.019	9.78	9.3	5.240		2.97	
6	8.681	8.684	9.81	9.9	5.102		2.99	
7	8.325	8.333	9.93	9.8	4.961		3.00	
8	7.953	7.955	10.11	9.7	4.819		3.01	
9	7.562	7.586	10.02	10.3	4.675		3.03	
10	7.166	7.185	10.51	10.6	4.526		3.06	
11	6.745		10.92		4.373		3.08	
12	6.301		11.39		4.215		3.11	

^aThe D_v constants should be multiplied by 10^{-4} . ^bRef. 9. ^cRef. 8.

expressions [12] below to the points in Table 4. These constants are collected in Table 5.

$$B_v = B_e - \alpha_e(v + 1/2) + \gamma(v + 1/2)^2 \quad (2)$$

$$D_v = D_e + \beta_e(v + 1/2) \quad (3)$$

The vibrational constants were obtained by a least squares fit of the expression [12] to the theoretical level spacings of Table 3.

$$\begin{aligned} \Delta G_{v+1/2} = & \omega_e - 2\omega_e x_e(v + 1) + \omega_e y_e[1 + 3(v + \frac{1}{2}) + 3(v + \frac{1}{2})^2] \\ & + \omega_e z_e[1 + 4(v + \frac{1}{2}) + 6(v + \frac{1}{2})^2 + 4(v + \frac{1}{2})^3] \end{aligned} \quad (4)$$

DISCUSSION AND CONCLUSIONS

The energies listed in Table 1 represent the best currently available calculation on the beryllium hydride ion molecule. The correlation energy now recovered is 91% at $R = 2.479 a_0$ and 87% at $R = 9.25 a_0$, an increase of 1% and 40% respectively over our previous work [6]. This 1% increase is almost uniform from $1.5 a_0$ to approximately $3.8 a_0$, and clearly indicates that around the minimum the one-reference root CI is a good description of this system. Notice in Fig. 1 that for (BeH)⁺ this region can hold seven vibrational levels, which makes the spectroscopic constants obtained by our previous Dunham analysis very reliable.

TABLE 5

Spectroscopic constants^a for (BeH)⁺ in the X ¹Σ⁺ state

	(Be ¹ H) ⁺				(Be ² H) ⁺	
	Ref. 4	Ref. 5	This work	Expt. (ref. 8)	This work	Expt. (ref. 7)
R_e	2.52	2.479	2.487 ^b	2.479	2.487 ^a	2.478 ^a
B_e	10.42	10.79	10.732	10.800	5.911	5.955
α_e		0.310	0.256	0.294	0.104	0.123
$-\gamma$			0.0082	0.0049	0.0025	
D_e			0.00080	0.00099	0.00026	0.00029
β_e			3.7×10^{-6}		7×10^{-6}	

^aWith the exception of R_e (in a_0) all the constants are given in cm^{-1} .^bCalculated using the relation $R_e = (h/8\pi^2 c \mu B_e)^{1/2}$.

The solution of the radial equation for the nuclear motion yielded 20 and 27 vibrational levels for (BeH)⁺ and (BeD)⁺ respectively. Although an error analysis of all the steps involved in the calculation as a whole is relatively complex to carry out, it is known however, that the computed energies have a numerical error in the sixth decimal place for the few largest values of R . This error combined with the one due to the interpolation procedure might bring an uncertainty in the fifth and maybe in the fourth decimal place in the potential energy in this region. As a consequence, an error of about 50 cm^{-1} would certainly be introduced in the energy levels, and this becomes very crucial in the calculation of $\Delta G_{v+1/2}$ for these highest levels.

Experimentally, only 8 and 3 $\Delta G_{v+1/2}$ values have been obtained for the (BeH)⁺ and (BeD)⁺ species, respectively. Our values are greater than the experimental ones by no more than 9 cm^{-1} for the (BeH)⁺ molecule, and smaller by no more than 7 cm^{-1} for (BeD)⁺.

As shown in Table 6 the calculation of the spectroscopic constants as given by eq. (4) is very sensitive to the number of $\Delta G_{v+1/2}$ values in the least squares fit, a fact also pointed out by Docken and Hinze [13] in their study of the LiH molecule. This behavior is also manifested in the experimental values as shown in Table 7. In trying to reproduce the experimentally determined constants the $w_e z_e$ contribution was neglected as in ref. 9, and only 8 $\Delta G_{v+1/2}$ values were used. Notice that when using the experimental $\Delta G_{v+1/2}$ values it was not possible to reproduce the reported experimental constants via a least squares fit [14].

Since the experimental constants have been determined, "from the combination differences by the usual semigraphical method" [9], Table 7 is probably more representative of a comparison between theoretical and the available experimental values, since the same fitting procedure was used for both cases.

Neglecting the last four $\Delta G_{v+1/2}$ values in Table 6 for which the above error considerations might apply, there seems to be a convergence pattern

TABLE 6

Theoretical spectroscopic constants (in cm^{-1}) as a function of the number of level spacings ($\Delta G_{v+1/2}$) for the $(\text{BeH})^+$ molecule in the $X^1\Sigma^+$ state^a

No. of level spacings	ω_e		$\omega_e x_e$		$-\omega_e y_e$		$-\omega_e z_e$	
	(BeH) ⁺	(BeD) ⁺	(BeH) ⁺	(BeD) ⁺	(BeH) ⁺	(BeD) ⁺	(BeH) ⁺	(BeD) ⁺
4	2229.0	1654.8	40.14	22.68	0.087	0.117	0.015	0.0167
5	2228.7	1654.8	39.84	22.75	0.182	0.137	0.005	0.0188
6	2228.7	1654.1	40.60	22.20	0.026	0.011	0.023	0.0058
7	2228.4	1654.4	39.74	22.38	0.179	0.031	0.008	0.0090
8	2227.9	1654.2	39.42	22.28	0.248	0.010	0.003	0.0076
9	2228.4	1653.6	39.71	21.91	0.193	0.062	0.006	0.0032
10	2228.6	1653.1	39.82	21.66	0.173	0.106	0.008	0.0008
11	2228.8	1653.1	39.88	21.66	0.163	0.106	0.008	0.0008
12	2229.2	1653.3	40.09	21.74	0.132	0.094	0.010	0.0014
13	2229.8	1653.5	40.33	21.81	0.097	0.084	0.011	0.0018
14	2230.5	1653.5	40.65	21.84	0.057	0.081	0.013	0.0020
15	2231.3	1653.7	40.96	21.92	0.019	0.071	0.014	0.0023
16	2231.2	1654.0	40.91	22.01	0.024	0.061	0.014	0.0027
17	2228.9	1654.2	40.09	22.10	0.114	0.051	0.011	0.0030
18	2226.4	1654.5	39.24	22.21	0.201	0.039	0.008	0.0034
19	2228.9	1655.0	40.05	22.35	0.122	0.026	0.010	0.0038
20		1655.4		22.48		0.013		0.0041
21		1655.6		22.56		0.006		0.0043

^aExperimental constants for $(\text{BeD})^+$: $\omega_e = 1647.6 \text{ cm}^{-1}$, $\omega_e x_e = 21.9 \text{ cm}^{-1}$, $\omega_e y_e = -0.06 \text{ cm}^{-1}$ (ref 8).

TABLE 7

Experimental and theoretical spectroscopic constants (in cm^{-1}) as a function of the number of vibrational level spacings for the $(\text{Be}^1\text{H})^+$ molecule in the $X^1\Sigma^+$ state^a

No. of level spacings	ω_e		$\omega_e x_e$		$-\omega_e y_e$	
	Expt. ^b	Calc.	Expt. ^b	Calc.	Expt. ^b	Calc.
3	2219.9	2228.7	39.78	39.82	0.150	0.207
4	2219.2	2228.4	39.30	39.64	0.233	0.237
5	2220.3	2228.4	39.89	39.59	0.148	0.244
6	2218.5	2227.4	39.03	39.13	0.254	0.302
7	2218.1	2227.4	38.83	39.11	0.276	0.304
8	2218.5	2227.3	39.00	39.10	0.259	0.305

^aExperimental values determined by combination differences (ref. 9) are: $\omega_e = 2221.7 \text{ cm}^{-1}$, $\omega_e x_e = 39.79 \text{ cm}^{-1}$ and $\omega_e y_e = -0.21 \text{ cm}^{-1}$.

^bObtained by fitting eqn. (4) to the experimental $\Delta G_{v+1/2}$ values with $\omega_e z_e$ neglected.

for these constants with w_e and $w_e x_e$ increasing slightly after an initial irregular pattern, and $w_e z_e$ and $w_e y_e$ increasing and decreasing, respectively, more markedly with the number of level differences and reaching values of the same order of magnitude.

The rotational constants listed in Table 4 show a very good agreement with the experimental values. Notice that for $(\text{BeH})^+$ the calculated B_v values are slightly greater than the experimental quantities for the first four levels, and slightly smaller for the remaining levels. The first five values are taken from the work of Knave [7] and the remaining ones from the work of Koontz [8] and Watson and Humphreys [19]. The D_v values differ by about 5%.

The constants in eqns. (2) and (3) are collected in Table 5 where they are compared with other theoretical and experimental values. Although the agreement is good in general, the existing differences in these quantities obviously reflect the influence of the added data, a fact also pointed out by Koontz [8] and Watson and Humphreys [9] relative to their experiment and Knave's work [7].

The equilibrium distance computed via the relation $R_e = (h/8\pi^2 c \mu B_e)^{1/2}$ is slightly greater (0.3%) than the experimental value, and the dissociation energy (D_e) is underestimated by 503 cm^{-1} (0.0623 eV). The "experimental" value was defined as the energy of Be^+ and H in their ground states minus the energy of $(\text{BeH})^+$ at $2.479 a_0$, and is equal to 0.2041 a.u. (3.276 eV). Finally, the computed bond dissociation energy (D_0) equals 3.077 eV (experimental [15] 3.14 eV) for $(\text{BeH})^+$ and 3.112 eV (experimental [15] 3.18 eV) for $(\text{BeD})^+$.

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Radiative transition probabilities, lifetimes, and dipole moments for all vibrational levels in the $X^1\Sigma^+$ state of the beryllium hydride ion

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The dipole moment function, vibrationally averaged dipole moment, radiative transition probabilities and radiative lifetimes are computed for all vibrational levels and selected rotational levels of the beryllium hydride molecule ion in the $X^1\Sigma^+$ state.

I. INTRODUCTION

This study is part of a long-term project we have embarked on with the purpose of understanding the spectroscopy of the few electron diatomics completely from first principles. We report our calculations for the dipole moment function, vibrationally averaged dipole moments, radiative transition probabilities, and lifetimes for all vibrational levels ($v=0-19$) in the $X^1\Sigma^+$ state of the $(\text{BeH})^+$ molecule. Radiative lifetimes and averaged dipole moments for all vib-rotational levels with $J=0, 1, 5$, and 10 are also presented. So far as we know no detailed studies have been carried out on this molecule in a manner similar to that done by Zemke and Stwalley¹ on the isoelectronic LiH molecule. This work is part of such a study. For the spectroscopic constants, vibrational levels and potential energy curve see Ref. 2 and references therein. It should be noted that charge-induced multipole terms [e.g., $(-\alpha_H/2)R^{-4}$] were left out of the long-range expansion in that work.²

II. THE DIPOLE MOMENT FUNCTION

The dipole moment for ionized molecules is dependent on the choice of the origin of the coordinate system,⁴ and its value relative to an origin at the center of mass should be used in the computation of the transition probabilities¹⁰ to be discussed in Sec. III. Calculated values of the dipole moment relative to the geometric center (GC) and relative to the center of mass (c.m.) of the molecule for internuclear distances (R) ranging from 1.0 to $10.0a_0$ are listed in Table I (see also Fig. 1) for the molecules $(\text{BeH})^+$ and $(\text{BeD})^+$. These quantities were obtained using a very accurate configuration interaction wave function computed by Ornellas.³ This wave function is such that approximately 91% and 87% of the correlation energy was recovered at $R=2.479$ and $R=10.0a_0$, respectively.

The center of mass dipole moment function for BeH^+ approximately parallels that for LiH^+ (shifted downwards

by ~ 3 a.u. in the $1-6a_0$ region), except that it does not vanish at large R as it does for LiH . It is interesting to note in Fig. 1 that the geometric center dipole moment curve (GC) increases linearly in magnitude at large R following the relationship $\mu \approx R/2$ (note that both μ and R are in a.u.). This behavior can be explained by

TABLE I. The dipole moment function $\mu(R)$ in (a.u.)^a for the beryllium hydride ion in the $X^1\Sigma^+$ state.

$R(a_0)$	$-\mu(R)^b$		
	GC ^b	CM ^c	CM ^d
1.00	1.6947	1.2953	1.3774
1.60	1.9189	1.2799	1.4112
1.80	2.0055	1.2866	1.4343
2.00	2.0893	1.2905	1.4546
2.20	2.1655	1.2865	1.4671
2.40	2.2293	1.2707	1.4677
2.479	2.2507	1.2606	1.4640
2.60	2.2787	1.2403	1.4536
2.80	2.3114	1.1931	1.4228
3.00	2.3265	1.1283	1.3745
3.20	2.3248	1.0467	1.3093
3.50	2.2976	0.8997	1.1869
4.00	2.2357	0.6381	0.9663
4.50	2.2387	0.4414	0.8107
5.00	2.3566	0.3596	0.7699
6.00	2.8409	0.4445	0.9369
7.00	3.4102	0.6144	1.1888
8.50	4.2183	0.8234	1.5209
9.25	4.6075	0.9131	1.6721
10.00	4.9916	0.9976	1.8182

^a1 a.u. = 2,5418 D.

^bRelative to the geometric center (GC).

^c $(\text{BeH})^+$; relative to the center of mass (c.m.).

^d $(\text{BeD})^+$; relative to the c.m.

^e $\mu_{GC}(2.479) = -2.296$ a.u. (Ref. 7);

$\mu_{GC}(2.4795) = -2.238$ a.u. (Ref. 8);

$\mu_{GC}(2.48) = -2.142$ a.u. (Ref. 9).

FIG 1. The dipole moment function $\mu(R)$, in ea_0 units, for the beryllium hydride ion $(\text{BeH})^+$: —, relative to the geometric center; ---, relative to the center of mass for $(\text{BeH})^+$; - · - ·, relative to the center-of-mass for $(\text{BeD})^+$.

the following picture: The only important configuration at large R is Be^+H (Be^+ and H being the proper asymptotic species) and thus the total dipole moment at large R is just the dipole moment contribution from the center of the molecule to the Be^+ ion, i.e., just one-half the distance R . In the case of the $X^1\Sigma^+$ state of LiH ,^{1,11,12} at large R covalent bonding of neutral atoms predominates and the dipole moment vanishes since there is no ionic contribution to the dipole moment.

Using this same picture, at intermediate distances the Be^{2+}H^- configuration becomes important and one predicts the dipole to vary according to the steeper relationship $\mu \approx (3/2)R$ ($2 \times R/2$ from the Be^{2+} ion plus $R/2$ from the H^- ion). The "crossover" from $3R/2$ dependence at intermediate distance to $R/2$ dependence at large distance explains the minimum in the GC dipole moment function in the $4a_0$ region.

The dipole moment function $\mu(R)$ for this interval, which is the region of predominant significance, was obtained from a cubic spline fit³ to the center of mass values given in Table I. For $(\text{BeH})^+$, $\mu(R)$ was set equal to -1.2953 a.u. for $R < 1.0a_0$, and for $R > 10.0a_0$ $\mu(R)$ was approximated by the function $\mu(R) = 0.12910 - 0.11267R$. For $(\text{BeD})^+$, $\mu(R)$ was set equal to -1.3774 a.u. for $R < 1.0a_0$, and for $R > 10.0a_0$ $\mu(R)$ was approximated by the function $\mu(R) = 0.12980 - 0.19480R$.

III. RADIATIVE TRANSITION PROBABILITIES AND LIFETIMES

The transition probabilities for emission and for photon detectors is usually expressed by the Einstein A coefficient

$$A_{ki} = 7.2356 \times 10^{-6} \nu_{ki}^3 |\mu_{ki}|^2 (\text{s}^{-1}),$$

where the constant in front includes the conversion from μ_{ki} matrix elements in eÅ units⁵ to A_{ki} in s^{-1} ; $k = (v', J')$ and $i = (v'', J'')$ stand for the upper and lower vib-rotational states respectively; ν_{ki} is the transition fre-

quency given by $[E'(v', J') - E''(v'', J'')]/h$ in cm^{-1} and μ_{ki} is the dipole moment matrix element

$$\mu_{ki} = \int_0^\infty \psi_k(R) \mu(R) \psi_i(R) dR.$$

The upper (ψ_k) and lower (ψ_i) states are normalized, and $\mu(R)$ is the dipole moment function discussed in Sec. II.

Note that for $k = i$, $\mu_{kk} = \langle \mu \rangle$ is the dipole moment expectation value for the system in the k th state.

The radiative lifetimes $\tau_{v', J'}$ were obtained as the reciprocals of the total Einstein $A_{v', J'}$ coefficients, which are given by the expression

$$A_{v', J'} = \frac{1}{2J' + 1} \left\{ J' \sum_{J''=0}^{J'-1} A_{v', J'; v'', J''-1} + (J' + 1) \sum_{J''=0}^{J'-1} A_{v', J'; v'', J''+1} \right\}.$$

IV. RESULTS AND DISCUSSION

With the exception of the dipole moment function the calculations reported here were carried out using the INTENSITY Program developed by Stwalley and Zemke.⁵ This program is an extensively modified version of the diatomic intensity factor program of Zare and co-workers⁶ based on the Numerov-Cooley numerical solution of the radial equation.

The dipole moment expectation values for $J' = J'' = 0, 1, 5$, and 10 and all vibrational levels of the $(\text{BeH})^+$ and $(\text{BeD})^+$ molecules are collected in Tables II and III, respectively. This variation in $\langle \mu(R) \rangle$ with the vibrational quantum number v and $J' = J'' = 0$ is shown also in Fig. 2, and is to be contrasted with the isoelectronic

TABLE II. The dipole moment function expectation values $\langle \mu(R) \rangle$ (in eÅ) for all vibrational and selected rotational levels in the $X^1\Sigma^+$ state of $(\text{BeH})^+$.

v	$J=0$	$J=1$	$J=5$	$J=10$
0	-0.6611	-0.6611	-0.6605	-0.6588
1	-0.6476	-0.6475	-0.6467	-0.6445
2	-0.6319	-0.6318	-0.6308	-0.6280
3	-0.6140	-0.6139	-0.6127	-0.6092
4	-0.5938	-0.5937	-0.5923	-0.5881
5	-0.5715	-0.5714	-0.5697	-0.5648
6	-0.5471	-0.5470	-0.5451	-0.5395
7	-0.5210	-0.5209	-0.5187	-0.5125
8	-0.4933	-0.4931	-0.4908	-0.4840
9	-0.4645	-0.4643	-0.4618	-0.4545
10	-0.4352	-0.4350	-0.4324	-0.4248
11	-0.4062	-0.4060	-0.4033	-0.3955
12	-0.3782	-0.3780	-0.3754	-0.3678
13	-0.3526	-0.3524	-0.3499	-0.3429
14	-0.3305	-0.3304	-0.3282	-0.3224
15	-0.3143	-0.3142	-0.3127	-0.3090
16	-0.3066	-0.3065	-0.3061	-0.3056
17	-0.3092	-0.3093	-0.3102	-0.3142
18	-0.3253	-0.3255	-0.3292	-0.3452
19	-0.3731	-0.3740	-0.3879

FIG. 2. Vibrationally averaged dipole moments, in eÅ units, relative to the center of mass: ●●●, for levels $v=0-19$ (all $J=0$) in the $X^1\Sigma^+$ state of (BeH)⁺; ▲▲▲, for levels $v=0-26$ (all $J=0$) in the $X^1\Sigma^+$ state of (BeD)⁺.

molecule LiH¹ for which $\langle\mu\rangle \sim 0$. Note in Table II that for (BeH)⁺ the decrease of $|\langle\mu\rangle|$ with the rotational quantum number J is less than 3% for most of the cases, while the magnitude of $\langle\mu\rangle$ decreases by about 50% in going from the vibrational ground state to the highest

TABLE III. The dipole moment function expectation values $\langle\mu\rangle$ (in eÅ) for all vibrational and selected rotational levels in the $X^1\Sigma^+$ state of the (BeD)⁺ molecule.

v	$J=0$	$J=1$	$J=5$	$J=10$
0	-0.7715	-0.7715	-0.7713	-0.7709
1	-0.7642	-0.7642	-0.7640	-0.7633
2	-0.7559	-0.7558	-0.7555	-0.7547
3	-0.7464	-0.7464	-0.7460	-0.7449
4	-0.7358	-0.7358	-0.7353	-0.7340
5	-0.7241	-0.7241	-0.7235	-0.7219
6	-0.7113	-0.7113	-0.7106	-0.7088
7	-0.6974	-0.6974	-0.6967	-0.6946
8	-0.6826	-0.6826	-0.6818	-0.6794
9	-0.6670	-0.6669	-0.6660	-0.6635
10	-0.6506	-0.6505	-0.6496	-0.6468
11	-0.6336	-0.6336	-0.6325	-0.6296
12	-0.6163	-0.6162	-0.6152	-0.6121
13	-0.5990	-0.5989	-0.5978	-0.5947
14	-0.5819	-0.5818	-0.5807	-0.5775
15	-0.5654	-0.5654	-0.5643	-0.5612
16	-0.5501	-0.5500	-0.5490	-0.5461
17	-0.5365	-0.5364	-0.5355	-0.5328
18	-0.5251	-0.5250	-0.5242	-0.5221
19	-0.5168	-0.5168	-0.5162	-0.5148
20	-0.5128	-0.5128	-0.5126	-0.5123
21	-0.5143	-0.5144	-0.5147	-0.5160
22	-0.5227	-0.5227	-0.5237	-0.5269
23	-0.5387	-0.5388	-0.5406	-0.5465
24	-0.5655	-0.5657	-0.5690	-0.5799
25	-0.6121	-0.6126	-0.6196	-0.6449
26	-0.7059	-0.7070	-0.7225	...

TABLE IV. Spontaneous radiative lifetimes (in ns) calculated for various (v', J') levels of the $X^1\Sigma^+$ state of (BeH)⁺.

v'	J'			
	0	1	5	10
0	∞	97.643	581.7	72.80
1	64.40	64.27	48.32	24.09
2	22.91	22.64	19.03	12.25
3	12.16	12.05	10.61	7.656
4	7.867	7.811	7.054	5.433
5	5.754	5.719	5.250	4.217
6	4.615	4.579	4.250	3.513
7	3.930	3.911	3.659	3.089
8	3.541	3.525	3.318	2.847
9	3.332	3.318	3.137	2.724
10	3.238	3.226	3.060	2.684
11	3.232	3.220	3.065	2.713
12	3.297	3.285	3.136	2.801
13	3.425	3.414	3.272	2.957
14	3.643	3.633	3.500	3.210
15	3.990	3.981	3.859	3.606
16	4.520	4.512	4.406	4.207
17	5.347	5.341	5.280	5.720
18	7.061	7.069	7.209	8.275
19	12.94	13.05	15.27	...

levels. For (BeD)⁺, Table III shows that $|\langle\mu\rangle|$ decreases with J by less than 1%, and also decreases with v by about 30%. For the uppermost levels $|\langle\mu\rangle|$ increases with J and v for both molecules.

So far as we know no experimental values are available for a comparison with our calculation.

The dipole moment function matrix elements $\mu_{v',0;v'',1}$ are collected in the upper right section of Table V. Note that for the case of absorption measured by a decrease in photon flux, the transition probability is proportional to the square of this quantity. The lower left section of Table V contains the Einstein A spontaneous emission coefficients $A_{v',0;v'',1}$. In the diagonal are the pure rotational matrix elements $\mu_{v,0;v,1}$.

As mentioned in Sec. III, the spontaneous radiative lifetimes were computed as the reciprocals of the total Einstein $A_{v',J';v'',J''}$ coefficients arising from all bound to bound transitions of the $X^1\Sigma^+ - X^1\Sigma^+$ band system; they are collected in Table IV for $J'=0, 1, 5$, and 10.

As previously noticed for the lithium hydride molecule¹ the effect of rotation on the radiative lifetime is small for all but the first few levels. Contrary to LiH for which the lifetime increases with increasing J' for v' greater than 3, Table IV shows that there is a decrease in the radiative lifetime with increasing J' up to v' equal to 17. Also for the same J' the radiative lifetime decreases until $v'=11$ for $J'=0, 1$, and $v'=10$ for $J'=5, 10$, and then it starts to increase again. For the pure rotational transitions the emission rate follows the same trend as the LiH molecule, i.e., it increases by almost three orders of magnitude in going from $J'=1$ to $J'=10$.

TABLE V. Dipole moment absorption matrix elements $\mu_{v',0;v'',1}$ (in eÅ units, in upper right and pure rotational transitions on the diagonal) and Einstein A spontaneous emission coefficients $A_{v',0;v'',1}$ (in s^{-1} units, in lower left) for the $X^1\Sigma^+-X^1\Sigma^+$ bands of $(BeH)^+$.

Initial state $v'(J'=0)$	Final state $v''(J''=1)$									
	0	1	2	3	4	5	6	7	8	9
0	-0.661 122	0.016 604	0.002 806	-0.000 615	0.000 067	0.000 003	-0.000 006	0.000 002	0.000 001	-0.000 003
1	1.529 2(1)	-0.647 550	0.027 429	0.004 548	-0.001 341	0.000 193	-0.000 012	-0.000 005	0.000 006	-0.000 005
2	5.093 7(0)	3.856 1(1)	-0.631 864	0.038 581	-0.002 302	0.005 797	0.000 421	-0.000 040	-0.000 011	0.000 012
3	7.335 5(-1)	1.209 3(1)	6.942 3(1)	-0.613 928	0.050 372	0.006 378	-0.003 470	0.000 787	-0.000 111	-0.000 004
4	2.169 6(-2)	3.071 4(0)	1.781 5(1)	1.062 0(2)	-0.593 776	0.062 746	0.006 050	-0.004 815	0.001 354	-0.000 248
5	1.450 5(-7)	1.507 0(-1)	7.927 3(0)	1.974 1(1)	1.459 8(2)	-0.571 434	0.075 504	0.004 553	-0.006 186	0.002 162
6	3.080 2(-4)	2.206 2(-3)	6.051 7(-1)	1.565 8(1)	1.673 2(1)	1.842 5(2)	-0.547 032	0.088 241	0.001 642	-0.007 427
7	5.882 0(-5)	6.529 1(-5)	1.439 7(-2)	1.793 9(0)	2.602 8(1)	9.878 0(0)	2.167 6(2)	-0.520 924	0.100 487	-0.003 029
8	5.641 3(-5)	2.934 5(-4)	2.505 0(-4)	7.773 2(-2)	4.471 2(0)	3.684 1(1)	2.650 9(0)	2.384 1(2)	-0.493 217	0.111 682
9	2.579 7(-4)	4.030 9(-4)	1.057 7(-3)	1.938 3(-4)	2.986 6(-1)	9.534 4(0)	4.522 3(1)	1.884 6(-1)	2.448 9(2)	-0.464 379
10	1.753 3(-4)	3.398 7(-4)	7.685 7(-4)	1.560 2(-3)	3.899 9(-3)	1.039 7(0)	1.758 9(1)	4.716 9(1)	8.381 7(0)	2.346 2(2)
11	3.669 6(-6)	1.551 4(-4)	4.856 0(-4)	2.696 1(-3)	1.574 8(-3)	4.487 0(-2)	2.932 7(0)	2.849 5(1)	3.938 4(1)	3.048 1(1)
12	1.300 0(-4)	2.832 1(-5)	4.045 1(-4)	2.710 1(-3)	2.743 8(-3)	5.392 9(-4)	2.731 0(-1)	7.067 9(0)	3.944 8(1)	2.339 2(1)
13	4.504 6(-4)	2.699 2(-7)	4.362 8(-4)	1.986 8(-3)	2.944 7(-3)	4.826 1(-3)	7.031 4(-3)	1.104 6(0)	1.468 8(1)	4.448 7(1)
14	6.399 4(-4)	2.609 1(-7)	4.686 4(-4)	1.182 6(-3)	3.100 6(-3)	4.611 2(-3)	2.763 6(-3)	1.140 6(-1)	3.572 9(0)	2.489 8(1)
15	5.903 2(-4)	2.034 8(-6)	4.330 4(-4)	6.572 2(-4)	2.946 8(-3)	3.638 1(-3)	6.879 8(-3)	3.906 9(-3)	6.760 9(-1)	9.281 8(0)
16	4.137 8(-4)	2.054 2(-5)	3.405 2(-4)	3.901 6(-4)	2.451 8(-3)	3.000 0(-3)	6.352 0(-3)	1.369 6(-3)	1.064 5(-1)	2.894 5(0)
17	2.383 8(-4)	5.308 0(-5)	2.360 6(-4)	2.611 6(-4)	1.826 3(-3)	2.531 8(-3)	4.662 7(-3)	4.804 4(-3)	1.272 5(-2)	8.344 8(-1)
18	1.136 6(-4)	7.407 8(-5)	1.429 1(-4)	1.799 5(-4)	1.193 0(-3)	1.948 8(-3)	3.043 6(-3)	5.217 7(-3)	6.380 3(-4)	2.294 3(-1)
19	4.094 0(-5)	5.537 0(-5)	6.517 0(-5)	9.633 5(-5)	5.784 8(-4)	1.075 0(-3)	1.510 0(-3)	3.160 1(-3)	1.896 1(-5)	5.759 0(-2)

Initial state $v'(J'=0)$	Final state $v''(J''=1)$									
	10	11	12	13	14	15	16	17	18	19
0	0.000 002	0.000 000	-0.000 001	0.000 003	-0.000 003	0.000 003	-0.000 002	0.000 002	-0.000 001	0.000 001
1	0.000 004	-0.000 002	0.000 001	0.000 000	0.000 000	0.000 000	0.000 001	-0.000 001	0.000 001	-0.000 001
2	-0.000 008	0.000 005	-0.000 004	0.000 004	-0.000 004	0.000 003	-0.000 003	0.000 002	-0.000 002	0.000 001
3	0.000 017	-0.000 016	0.000 014	-0.000 010	0.000 007	-0.000 005	0.000 004	-0.000 003	0.000 002	-0.000 002
4	0.000 011	0.000 021	-0.000 020	0.000 017	-0.000 015	0.000 013	-0.000 011	0.000 009	-0.000 007	0.000 005
5	0.000 522	0.000 073	0.000 020	-0.000 030	0.000 024	-0.000 019	0.000 015	-0.000 013	0.000 011	-0.000 008
6	0.003 223	-0.000 982	0.000 227	-0.000 018	-0.000 030	0.000 034	-0.000 029	0.000 023	-0.000 017	0.000 012
7	-0.008 255	0.004 531	-0.001 710	0.000 534	-0.000 133	0.000 010	0.000 025	-0.000 032	0.000 029	-0.000 021
8	-0.009 631	-0.008 178	0.005 933	-0.002 785	0.001 111	-0.000 402	0.000 131	-0.000 033	-0.000 001	0.000 009
9	0.121 075	-0.018 159	-0.006 725	0.007 065	-0.004 135	0.002 083	-0.000 998	0.000 473	-0.000 223	0.000 103
10	-0.435 114	-0.127 839	-0.028 568	-0.003 324	0.007 400	-0.005 461	0.003 368	-0.001 997	0.001 173	-0.000 652
11	2.080 5(2)	-0.406 043	0.130 973	-0.040 434	0.002 702	0.008 098	-0.008 191	0.004 632	-0.003 148	0.001 918
12	6.502 1(1)	1.681 4(2)	-0.378 125	0.129 415	-0.052 714	0.011 692	0.002 037	-0.005 149	-0.003 826	-0.003 381
13	6.524 3(0)	1.036 6(2)	1.215 0(2)	-0.352 473	0.122 145	-0.063 875	0.023 214	-0.005 477	-0.000 893	0.002 150
14	3.832 0(1)	2.094 0(-1)	1.314 6(2)	7.589 4(1)	-0.330 447	0.108 150	-0.071 567	0.035 435	-0.015 695	0.006 396
15	3.252 8(1)	2.081 1(1)	1.412 9(1)	1.343 9(2)	3.881 2(1)	-0.314 208	0.087 325	-0.072 694	0.044 084	-0.023 647
16	1.753 3(1)	3.049 1(1)	3.003 6(0)	4.363 1(1)	1.084 9(2)	1.509 5(1)	-0.306 516	0.061 018	-0.063 494	0.041 057
17	8.042 4(0)	2.317 8(1)	1.558 1(1)	2.977 0(0)	6.640 8(1)	6.605 2(1)	3.940 4(0)	-0.309 255	-0.030 088	-0.039 446
18	3.378 4(0)	1.342 1(1)	1.708 2(1)	9.498 9(-1)	2.133 2(1)	5.867 9(1)	2.615 5(1)	3.804 0(-1)	-0.325 359	-0.004 705
19	1.187 7(0)	5.752 2(0)	9.853 4(0)	2.643 7(0)	4.300 3(0)	2.640 9(1)	2.327 7(1)	3.780 8(0)	1.431 3(-2)	-0.373 440

TABLE VI. Deviations from the harmonic oscillator selection rule ($\Delta v = \pm 1$) for absorption (largest $|\mu|^2$) and for emission (largest A) involving transitions among the vibrational levels ($J' = 0, J'' = 1$) of the $X^1\Sigma^+$ state of $(\text{BeH})^+$.

$\Delta v =$	Largest $ \mu ^2$		Largest A coefficient			
	1	2	-1	-2	-3	-4
0	x					
1	x		x			
2	x		x			
3	x		x			
4	x		x			
5	x		x			
6	x		x			
7	x		x			
8	x		x			
9	x		x			
10	x		x			
11	x		x			
12	x		x			
13	x		x			
14	x			x		
15	x			x		
16		x		x		
17		x			x	
18	x				x	
19						x

V. CONCLUSION

This study reports for the first time the dipole moment function, averaged dipole moments, transition probabilities, and lifetimes for the vibrational levels in

the $X^1\Sigma^+$ state of the beryllium hydride ion molecule. It complements previous work² on this molecule and adds information to our search to find out how realistic diatomic molecules behave. In this regard, the results in Table V can be contrasted with the harmonic oscillator selection rule $\Delta v = \pm 1$. This is done in Table VI where it is shown that the strongest absorption (largest $|\mu|^2$ value) and the strongest emission (largest A value) among the vibrational levels of the $X^1\Sigma^+$ state of $(\text{BeH})^+$ do not correspond to $\Delta v = \pm 1$ for a significant number of levels, especially for emission.

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A theoretical study of the $(\text{BeH})^+$ molecule in the $A\ ^1\Sigma^+$ state

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A theoretical study of the $(\text{BeH})^+$ molecule ion in the $A\ ^1\Sigma^+$ state is performed using a potential energy curve and a dipole moment function calculated with a configuration interaction wave function. Averaged dipole moments, radiative transition probabilities, and radiative lifetimes are presented for the lower vibrational levels. Spectroscopic constants are obtained by standard fitting procedures.

I. INTRODUCTION

The spectroscopy of the beryllium hydride ion, $(\text{BeH})^+$, has not been extensively studied, either experimentally or theoretically as has its isoelectronic counterpart LiH . Beryllium compounds are known to cause serious lung complications,¹ a fact which might well be one of the reasons for the existence of only a few experimental studies on $(\text{BeH})^+$. To our knowledge the only experimental studies on this species are those of Koontz,² Watson and Humphreys,³ and Knave.⁴ Theoretically, only the fundamental $X\ ^1\Sigma^+$ state has been investigated in detail.⁵⁻¹² For the first excited state, a potential energy curve and the corresponding spectroscopic constants obtained via a Dunham analysis comprise the only information available.¹⁰

In this paper we present a detailed investigation of the $A\ ^1\Sigma^+$ state from first principles. We report a potential energy curve and a dipole moment function computed using a configuration interaction wave function with selected triple and quadruple excitations. The vibrational energy levels are obtained as solutions of the radial Schrödinger equation, and radiative transition probabilities, lifetimes, and averaged dipole moments are calculated for the lower vibrational levels. Spectroscopic constants are obtained by standard fitting procedures.

II. METHODS

A. Potential energy curve

In a previous exploratory theoretical study¹⁰ of the $(\text{BeH})^+$ ion, the energy of the $A\ ^1\Sigma^+$ state was obtained as the second root of an eigenvalue equation assembled with the purpose of studying the ground electronic state in the region of the equilibrium internuclear distance. Although the second root is an upper bound to the exact energy of the $A\ ^1\Sigma^+$ state, we do not expect it to be very accurate due to the lack of appropriate reference configurations in the CI expansion.

A standard procedure in the generation of potential curves is to choose all the dominant configurations for the range of internuclear distances of interest and then carry out a singles and doubles CI. However, computer codes limitation in our program has restricted the number

of single and double excitations relative to configurations other than the $1\sigma^2 2\sigma^2$ reference. Analyzing the contribution of each configuration for $R = 2.137, 3.0, 6.0$, and $10.0a_0$ obtained from our previous study¹⁰ of this molecule, seven references have been chosen from which limited single and double excitations were carried out. These references include the configurations $1\sigma^2 3\sigma^2$, $1\sigma^2 4\sigma^2$, $1\sigma^2 1\pi, 1\pi_-$, and $1\sigma^2 3\pi, 3\pi_-$ to describe the proper dissociation, and the configurations $5\sigma^2 2\sigma^2$, $6\sigma^2 2\sigma^2$, $2\pi, 2\pi_- 2\sigma^2$ to account for the core correlation. Excitations up to the eighth most important natural orbital for the σ set, and the third one for the π set were allowed. This restriction is not a rule in our procedure, and as mentioned before it had to be imposed to keep the calculation within the limits of our codes. Its generalization to many electron systems has no guarantee of success. With a molecular orbital (MO) set consisting of 22σ -, 14π -, and 5δ -type orbitals, a total of 1857 CSFs were used for the ground and excited states calculation. The Slater-type functions used in the construction of the MO's as well as the general procedure for generating the MO set for the ground state are described in Refs. 10 and 11.

For the ground state, after one natural orbital iteration the new wave function recovered about 87% of the correlation energy at $R = 9.25a_0$, a significant improvement compared to the 47% obtained in a previous calculation. It was then used in a rotation-vibration analysis of the ground state,¹¹ and to calculate radiative transition probabilities, lifetimes, and average dipole moments.¹²

To construct the wave function for the $A\ ^1\Sigma^+$ state we first used the second eigenfunction obtained from the calculation of the ground state to generate natural orbitals (NO) for the $A\ ^1\Sigma^+$ state. These NO's were then used in the configuration functions for the final wave function. The total energies obtained are listed in Table I (see also Fig. 1). We have listed also the values from our previous calculations. The remaining points in the interval $1.6-9.25a_0$ were obtained by a cubic spline¹³ fit to the points listed in Table I. For internuclear distances smaller than $1.6a_0$ the potential curve was approximated by the function $E(R) = 1/R - 25.120\ 425R + 13.8183R^2 - 2.525\ 628R^3$. For internuclear distances greater than $9.25a_0$ the approximation used was $E(R) = -14.668\ 793 - 2.25/R^4 - 2124.05/R^6 + 72\ 107.193/R^8$. With the exception of

TABLE I. Energies (in hartree) for (BeH)⁺ in the *A* ¹Σ⁺ state.

Internuclear distance (<i>a</i> ₀)	SD ^a	This work ^b
1.60	-14.502 12	-14.537 84
1.80	-14.584 19	-14.619 25
2.00	-14.637 78	-14.672 73
2.20	-14.672 45	-14.707 36
2.40	-14.694 26	-14.729 34
2.479	-14.700 26	-14.735 45
2.60	-14.707 20	-14.742 58
2.80	-14.713 88	-14.749 67
3.00	-14.716 12	-14.752 39
3.20	-14.715 18	-14.751 94
3.50	-14.709 73	-14.747 17
4.00	-14.694 78	-14.732 95
5.00	-14.662 77	-14.701 36
6.00	-14.643 93	-14.681 93
7.00	-14.636 77	-14.675 28
8.50	-14.631 03	-14.672 21
9.25	-14.630 52	-14.671 15

^a 1322 terms (singles and doubles) (Ref. 10).^b 1857 terms (1322 SD + 535 triples and quadruples).

the R^{-4} coefficient, which was set equal to half the polarizability of the hydrogen, all the others were chosen such that $E(R)$ matches three computed energies in Table I in the small and large R ranges.

B. The dipole moment function

The dipole moment for ionized molecules depends on the choice of origin of the coordinate system.¹⁴ Its

FIG. 1. Potential energy curve for the *A* ¹Σ⁺ state of (BeH)⁺, including calculated vibrational levels ($v = 0-23$): ---, 1322 terms (singles and doubles), Ref. 10; —, 1857 terms (1322 SD + 535 triples and quadruples).

value relative to an origin at the center of mass is used in the computation of the transition probabilities to be discussed in Sec. II D. Calculated values of the dipole moment relative to the geometric center (CG) and relative to the center of mass (CM) of the molecule for internuclear distances (R) ranging from 1.6 to 9.25 a_0 are listed in Table II (see also Fig. 2) for the molecules (BeH)⁺ and (BeD)⁺.

For $R > 5.0a_0$ the dipole moment exhibits the same behavior as that for the ground state, following, relative to the GC, the relationship $\mu \approx -R/2$ due to the contribution of the charge on the ion Be⁺ to the dipole moment. The charge distribution does not show as accentuated a change in polarity as it does for LiH.¹⁵ It shows a slight Be-H⁺ polarization for $R < 2.5a_0$ which changes to Be²⁺-H⁻ at moderate distances, and to Be⁺-H at large distances.

The dipole moment function between 1.6 and 9.25 a_0 was obtained from a cubic spline¹³ fit to the center of mass values given in Table II. Outside these limits, the approximation used was $\mu(R) = 0.3021R + 0.11292R^2$ for $R < 1.6a_0$, and $\mu(R) = -0.1006R$ for $R > 9.25a_0$, for the (BeH)⁺ species.

C. Vibration-rotation levels, spectroscopic constants

With the potential energy curve derived above the radial Schrödinger equation was then solved numerically for the vibration-rotation eigenvalues by the Numerov-Cooley method using a computer program kindly supplied by Stwalley and Zemke.¹⁶ Vibrational levels for the molecule (BeH)⁺ are listed in Table III, and plotted in Fig. 2. The vibrational levels spacings

$$\Delta G_{v+1/2} = G(v+1) - G(v)$$

TABLE II. The dipole moment function $\mu(R)$ (in a.u.)^a for the beryllium hydride ion in the *A* ¹Σ⁺ state.

<i>R</i> (<i>a</i> ₀)	$\mu(R)$ ^c		
	GC ^b	CM ^c	CM ^d
1.60	0.1334	0.7724	0.6354
1.80	0.1907	0.9096	0.7554
2.00	0.1789	0.9777	0.8064
2.20	0.1193	0.9980	0.8095
2.40	0.0266	0.9851	0.7796
2.479	-0.0191	0.9710	0.7587
2.60	-0.0975	0.9410	0.7182
2.80	-0.2478	0.8705	0.6307
3.00	-0.4240	0.7742	0.5172
3.20	-0.6212	0.6569	0.3828
3.50	-0.9470	0.4509	0.1511
4.00	-1.5089	0.0887	-0.2539
5.00	-2.3316	-0.3346	-0.7629
6.00	-2.7964	-0.4000	-0.9140
7.00	-3.2918	-0.4960	-1.0956
8.50	-4.1388	-0.7439	-1.4720
9.25	-4.5471	-0.8526	-1.6450

^a 1 a.u. = 2.5418 D.^b Relative to the geometric center (GC).^c (BeH)⁺; relative to the center of mass (CM).^d (BeD)⁺; relative to the CM.^e $\mu_{CM}(R) = \mu_{GC}(R) + 0.39940R$; see Ref. 14.

FIG. 2. The dipole moment function $\mu(R)$, in ea_0 units, for the beryllium hydride ion $(\text{BeH})^+$: —, relative to the geometric center; ---, relative to the center of mass for $(\text{BeH})^+$; - · - ·, relative to the center of mass for $(\text{BeD})^+$.

are also listed in Table III together with the experimental data.²⁻⁴

For specific vibrational states of $(\text{BeH})^+$ we have computed the difference in energy between adjacent rotational levels. These differences may be represented by the expression¹⁷

$$F_v(J+1) - F_v(J) = 2(J+1)B_v - 4(J+1)^3D_v.$$

The rotational constants B_v and D_v obtained by a least squares fit to the theoretical values are listed in Table IV. From them the spectroscopic constants B_e , α_e , γ , D_e , and β_e can be obtained by a least squares fit of the expressions¹⁷

$$B_v = B_e - \alpha_e(v + 1/2) + \gamma(v + 1/2)^2,$$

$$D_v = D_e + \beta_e(v + 1/2)$$

TABLE III. Vibrational levels $G(v)$ and vibrational level spacings $\Delta G_{v+1/2}$ (in cm^{-1}) for the beryllium hydride ion in the $A^1\Sigma^+$ state.

v	$G(v)^a$	$\Delta G_{v+1/2}^b$	v	$G(v)$	$\Delta G_{v+1/2}$
0	715.4 (734.4)	1407.5 (1445)	12	14 839.7	788.8
1	2 122.9 (2179)	1378.2 (1412)	13	15 628.5	684.2
2	3 501.1 (3591)	1343.8 (1377)	14	16 312.7	551.7
3	4 844.9 (4968)	1304.3 (1337)	15	16 864.4	409.3
4	6 149.2 (6305)	1262.0	16	17 273.7	301.7
5	7 411.2	1219.8	17	17 575.4	231.4
6	8 631.0	1175.4	18	17 806.8	198.1
7	9 806.4	1127.1	19	18 004.9	151.5
8	10 933.5	1073.3	20	18 156.4	106.9
9	12 006.8	1013.0	21	18 263.3	67.0
10	13 019.8	946.5	22	18 330.3	51.1
11	13 966.3	873.4	23	18 381.4	...

^a Experimental values in parentheses, Ref. 5.

^b Experimental values in parentheses, Ref. 3.

TABLE IV. Rotational constants (in cm^{-1}), averaged dipole moments (in $e \text{ \AA}$) and radiative lifetime ($A^1\Sigma^+ - A^1\Sigma^+$ band only) (in ms) for the beryllium hydride ion in the $A^1\Sigma^+$ state.

v	B_v		$D_v (\times 10^4)$		$\langle \mu \rangle$	τ
	Calc.	Expt. ^a	Calc.	Expt. ^a		
0	6.999	7.129	6.42		0.3563	∞
1	6.868	6.988	6.33		0.3354	16.28
2	6.730	6.835	6.32	6.0	0.2992	5.37
3	6.579	6.680	6.37	6.0	0.2650	3.35
4	6.415	6.521	6.35	6.0	0.2350	3.15
5	6.248	6.353	6.38	6.2	0.2047	2.35
6	6.077	6.158	6.38	6.2	0.1750	1.43
7	5.895		6.50		0.1463	1.63
8	5.700		6.77		0.1182	1.81

^a Reference 3.

to the points in Table IV. The constants are collected in Table V.

The vibrational constants were obtained by a least squares fit of the expression

$$\begin{aligned} \Delta G_{v+1/2} = & \omega_e - 2\omega_e x_e(v + 1) + \omega_e y_e[1 + 3(v + 1/2) \\ & + 3(v + 1/2)^2] + \omega_e z_e[1 + 4(v + 1/2) \\ & + 6(v + 1/2)^2 + 4(v + 1/2)^3] \end{aligned}$$

to the points in Table III.

D. Radiative transition probabilities and lifetimes

The radiative transition probabilities for emission are given by

$$A_{kl} = 7.2356 \times 10^{-6} \nu_{kl}^3 |\mu_{kl}|^2 (\text{s}^{-1}),$$

where the constant in front includes the conversion from μ_{kl} matrix elements in $e \text{ \AA}$ units,¹⁶ $k \equiv (v', J')$ and $l \equiv (v'', J'')$ stand for the upper and lower vibrotational states respectively, ν_{kl} is the transition frequency given by $[E'(v', J') - E''(v'', J'')]/h$ in cm^{-1} , and μ_{kl} is the dipole moment matrix element

$$\mu_{kl} = \int_0^\infty \psi_k(R) \mu(R) \psi_l(R) dR,$$

measured in $e \text{ \AA}$. The upper (ψ_k) and lower (ψ_l) state vibrational eigenfunctions are normalized to unity and $\mu(R)$ is the dipole moment function.

For $k = l$, $\mu_{kk} = \langle \mu \rangle$ is the expectation value of the dipole moment for the system in the k th state. Values of $\langle \mu \rangle$ are collected in Table IV for $J' = J'' = 0$.

The radiative lifetimes $\tau_{v,J}$ are the reciprocals of the

TABLE V. Spectroscopic constants for $(\text{BeH})^+$ in the $A^1\Sigma^+$ state.

	Ref. 10	This work	Expt. Ref. 3
B_e	7.232	7.045	7.184
α_e	0.157	0.1101	0.125
$-\gamma$	...	5.91×10^{-3}	5.4×10^{-3}
D_e	7.0×10^{-4}	5.97×10^{-4}	6.08×10^{-4}
β_e	...	1.2×10^{-3}	...

total Einstein $A_{\nu',J'}$ coefficients, which are given by the expression

$$A_{\nu',J'} = \frac{1}{2J'+1} \left\{ J' \sum_{\nu''=0}^{\nu'} A_{\nu',J';\nu'',J'-1} + (J'+1) \sum_{\nu''=0}^{\nu'-1} A_{\nu',J';\nu'',J'+1} \right\}.$$

III. DISCUSSION AND CONCLUSIONS

The energies listed in Table I are the results of our most elaborate calculation on the $A \ ^1\Sigma^+$ state of the beryllium hydride ion. As can be seen in Fig. 1, the introduction of triple and quadruple excitations changes significantly the total energies. The energy at the theoretical minimum differs by only 0.09% from the estimated experimental value. The extrapolated energy of the separated atoms is -14.668 793 a.u., compared to the experimental value of -14.679 15 a.u. which is the sum of the energies of the $\text{Be}^+(^2P)$ ion and a hydrogen atom $\text{H}(^2S)$. The theoretical dissociation energy (D_e) is 2.279 eV, compared to the experimental value of 2.348 eV. The error at the minimum of the potential curve for both the ground (0.06%) and the first excited state (0.09%) is reflected in the theoretical electronic term $T_e = 40\,407 \text{ cm}^{-1}$ compared to the experimental value $39\,417 \text{ cm}^{-1}$. Relative to the ground state calculation the minimum of the $A \ ^1\Sigma^+$ potential energy curve is still 990 cm^{-1} higher. The theoretical and experimental separated-atom limits, relative to the ground state, are 4.074 and 3.959 eV, respectively.

Although an error analysis of all the steps involved in the generation of the potential curve as a whole is relatively complex to carry out, an estimate of it can, however, be given. For a molecular orbital set with no large coefficients (~ 100) it is expected that one digit will be lost during the process of transforming an integral over atomic orbitals to one over molecular orbitals. Another digit can be lost during the diagonalization step. The energies will be, therefore, two digits less precise than the atomic integrals calculated at an initial stage. The

atomic integrals set a bound to the precision of the calculation. These integrals were computed with an "out-of-core" disk-file oriented modification²⁰ of the well-known "in-core" diatomic integral routine developed by Hagstrom.²¹ Even though no integral convergence test was made to check the precision in the energies, it is expected that 17 terms in the Neumann sum for the two-electron, two-center integrals are sufficient to give energies with five/six decimals precision all over the internuclear distance range. A greater precision, however, would be required for a reliable fitting of the curve in the asymptotic region.

The accuracy of the calculations is obviously less than the quoted precision, due to basis set limitation and CI truncation.

As shown in Table VI the calculation of the vibrational constants is sensitive to the number of $\Delta G_{v+1/2}$ values, and to the number of parameters used in the least squares fit, as was found by Docken and Hinze¹⁸ in their study of the LiH molecule. It was not straightforward to fit the theoretical $\Delta G_{v+1/2}$ values to a power series in v . To keep the difference between the inputted and the adjusted values within 1 cm^{-1} we had to restrict the fitting to only $10\Delta G_{v+1/2}$ values. Contrary to our study of the ground state no convergence pattern as a function of the number of level spacings is observed for the constants in Table VI. This might partly be due to perturbations in the $A \ ^1\Sigma^+$ state caused by a higher energy state. The separated-atom limit pair $\text{Be}(^1S) + \text{H}^+$ is just 0.33 eV above the $\text{Be}^+(^2P) + \text{H}$ asymptote. Although this behavior is indicative of a perturbation, the fact the potential energy curve does not show an anomalous square-well shape as was the case for LiH,¹⁵ suggests that this interaction is not so strong as the one for LiH. For LiH the avoided crossing between the covalent and ionic curves is also manifested in the relatively large variation of the dipole moment function with internuclear distance, whereas this variation is significantly lower for $(\text{BeH})^+$.

In Table III the experimental vibrational levels obtained by Jenc⁵ using the RKR method are compared with our results. Only four experimental $\Delta G_{v+1/2}$ values are available for a comparison. Surprisingly, our value of

TABLE VI. Theoretical spectroscopic constants (in cm^{-1}) as a function of the number of levels spacings ($\Delta G_{v+1/2}$) for the $(\text{BeH})^+$ molecule in the $A \ ^1\Sigma^+$ state.^{a,b}

No. of levels spacings	ω_e		$\omega_e x_e$		$\omega_e y_e$		$\omega_e Z_e$
	F3	F4	F3	F4	F3	F4	F4
3	1431.8	...	10.78	...	-0.853	...	...
4	1431.7	1431.8	10.75	10.83	-0.858	-0.833	-0.0025
5	1433.1	1429.9	11.54	9.22	-0.744	-1.341	0.0498
6	1435.9	1428.5	12.01	8.09	-0.575	-1.648	0.0766
7	1438.0	1430.0	13.81	9.18	-0.479	-1.388	0.0568
8	1438.7	1433.0	14.10	11.07	-0.451	-0.982	0.0295
9	1438.1	1436.4	13.87	13.05	-0.471	-0.601	0.0065
10	1436.2	1439.6	13.23	14.78	-0.520	-0.295	-0.0102

^a Experimental values (Ref. 19): $\omega_e = 1476.1$ (1475.4) cm^{-1} , $\omega_e x_e = 14.8$ (14.40) cm^{-1} , $\omega_e y_e = -0.380$ (-0.475) cm^{-1} . Values in parenthesis correspond to a three-parameter least square fit to the experimental $\Delta G_{v+1/2}$ values.

^b F3 and F4 stand for a three-, and four-parameter least squares fit, respectively.

TABLE VII. Dipole moment matrix elements $\mu_{v',0;v'',1}$ (in $e \text{ \AA}$ units, in upper right, and pure rotational transitions on the diagonal) and Einstein A spontaneous emission coefficients $A_{v',0;v'',1}$ (in s^{-1} units, in lower left) for the $A \text{ } ^1\Sigma^+-A \text{ } ^1\Sigma^+$ bands of (BeH)⁺.

Initial state $v' (J' = 0)$	Final state $v'' (J'' = 1)$					
	0	1	2	3	4	5
0	0.356 182	-0.056 969	0.003 855	-0.011 096	0.004 793	0.006 204
1	6.142 37 (1)	0.335 282	-0.101 362	0.001 202	0.001 502	0.001 016
2	1.919 68 (0)	1.841 89 (2)	0.299 108	-0.119 424	0.002 541	0.004 857
3	6.142 66 (1)	4.802 05 (-2)	2.373 28 (2)	0.264 938	-0.137 960	0.009 165
4	2.573 92 (1)	1.213 70 (0)	3.636 90 (-1)	2.902 05 (2)	0.234 852	-0.153 568
5	7.985 21 (1)	1.020 73 (0)	1.091 35 (1)	7.777 55 (0)	3.264 25 (2)	0.204 620

$\Delta G_{v+1/2}$ is 38 cm^{-1} ($0.000 173 \text{ a.u.}$) smaller than the experimental one. These $\Delta G_{v+1/2}$ values and the vibrational constants in Table VI suggest that the new potential curve although significantly lower in energy has a slightly different shape around the minimum. The energy differences between the theoretical and experimental values at the minimum and at large R are approximately 0.0129 and 0.0104 a.u., respectively, in the two calculations. Thus, the effect of the consecutive unitary transformations is apparently to change the molecular orbitals in such a way that the structure Be-H⁺ is overemphasized around R_e in the CI expansion for the excited state. A competition between the structures Be-H⁺ and Be²⁺-H⁻ might be responsible for the lower dipole moment around the equilibrium distance, $\mu_{GC} = 0.4240ea_0$, compared to that of lithium hydride, $\mu = 1.2575ea_0$. The change in polarity as the internuclear distance increases is also manifested in the average dipole moment which takes on positive values up to $v = 12$ [$\langle \mu (v = 12) \rangle = 0.099e \text{ \AA}$] and then changes sign, increasing. It is interesting to observe in Table II the dependence of the polarity on the reference system. For the geometric center the molecule looks like Be²⁺-H⁻, but from the center of mass it looks like Be-H⁺.

We have collected the dipole moment function matrix elements $\mu_{v',0;v'',1}$ for v' up to 5 in the upper right section of Table VII. For the case of absorption the transition probability is proportional to the square of $\mu_{v',J';v'',J''}$. The lower left section contains the Einstein spontaneous emission coefficient $A_{v',0;v'',1}$. In the diagonal are the pure rotational matrix elements $\mu_{v,0;v,1}$. For the states shown in Table VII the fundamental transitions are the strongest both in emission and absorption. The strongest single emission transition is the transition 5, 0-4, 1 and the strongest single absorption transition is the transition 5, 1-4, 0. The spontaneous radiative lifetimes are collected in Table IV for $J' = 0$. They show a behavior found for LiH and for the ground state of (BeH)⁺ in that they decrease up to a certain vibrational level and then increase.

The rotational constants listed in Table IV show a very good agreement with the experimental values. The

calculated B_v values differ by no more than 2% from the experimental ones, while for the D_v values this difference increases to no more than 6%. For B_e and D_e this error is less than 2%, and for α_e and γ it is less than 9%.

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THEORETICAL TRANSITION PROBABILITIES AND LIFETIMES FOR THE BeH^+ ($A^1\Sigma^+ - X^1\Sigma^+$) BAND SYSTEM

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ABSTRACT

New potential energy curves and transition-moment functions are calculated using the multi-reference single and double configuration-interaction approach with the aim of the determination of the transition-moment probabilities and radiative lifetimes for the $A^1\Sigma^+ - X^1\Sigma^+$ emission band. The calculated transition moment is in good agreement with experimental values for the Be^+ ($^2S - ^2P$) transition. Total transition probabilities and radiative lifetimes for bound-bound transitions show only a slight variation for the first ten vibrational levels, and there is a decrease in transitional probabilities with v' .

INTRODUCTION

This study is part of a long-term project we have embarked upon with the aim of a complete understanding of the spectroscopy of the few-electron diatomics from first principles. In previous works [1-4] one of us has reported potential-energy curves, dipole-moment functions, radiative transition probabilities and radiative lifetimes for the infrared transition of the $X^1\Sigma^+$ and $A^1\Sigma^+$ electronic states of BeH^+ molecule.

In this paper we report the determination of the transition-moment probabilities and radiative lifetimes of the $A^1\Sigma^+ - X^1\Sigma^+$ emission band. To this end we have calculated new potential-energy curves and transition-moment functions using the multireference single and double configuration-interaction approach.

To our knowledge, neither an experimental nor a theoretical study for the transition probabilities in this band system has been reported. The lack of

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experimental data are probably due to the fact that beryllium compounds cause serious lung complications [5].

METHODS AND RESULTS

Potential-energy curves

The potential-energy curves for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of the BeH^+ molecule and the transition-moment function were calculated using the same set of molecular orbitals for both states, e.g. the SCF molecular orbitals calculated for the $X^1\Sigma^+$ state. The one-particle basis sets employed for beryllium and hydrogen were derived from the 13s and 8s set of Cartesian Gaussian orbitals of van Duijneveldt [6] contracted to 8s and 5s [7], respectively, and augmented with the primitive polarization sets 6p, 4d for Be and 2p, 2d for H used by Larsson in his study of the BeH molecule [8]. One more set of *f* functions ($\alpha=0.56$) was also added to the beryllium atom. The final basis set can be written as (13s6p4d1f/8s2p2d)/[8s6p4d1f/5s2p2d].

The multi-reference single and double configuration-interaction approach (MR-SD-CI) as implemented in the MELD codes [9] was used to generate the final wavefunction at 20 internuclear distances covering the region from 1.6 to 10.0 a_0 . The 21 reference-state configurations used in the MRSD-CI calculations were selected on the basis of the size of the configuration coefficients in a previous Hartree-Fock single and double configuration-interaction (HFSD-CI) calculation at five internuclear distances ($R=1.8, 2.479, 3.2, 5.5$, and $8.0 a_0$). Only contributions with coefficients greater than 0.05 were included in the reference space. The sum of squares of these reference configuration coefficients, Σc_i^2 , was 0.99 for all distances and for both states, which is considered good as a rough measure of the quality of the reference space [10].

From this set of reference configurations the MRSD-CI program generated 61 174 spin and space adapted state functions. Due to the limitation of the computer hardware (CYBER 170/750) perturbation theory with an energy threshold of 10^{-7} hartree was used to keep the final wavefunction within 8000–10 800 terms. The calculations were carried out in the C_{2v} point-group symmetry due to a restriction in the MELD programs.

Total electronic energies for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states are listed in Table 1 together with previous results [2,4] and plotted in Fig. 1 for several internuclear separations. It should be noted that Ornellas used an extensive Slater-type set and natural orbitals constructed for each individual state; however, we obtained slightly better results. The energy values calculated at the theoretical minimum differ by 0.05% from the estimated experimental values [1,11] for both states, compared with 0.06% and 0.09% obtained by Ornellas [2,4]. At $R=9.25 a_0$ the differences are 0.016% and 0.020% for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states, compared with the values 0.041% and 0.054% calculated by Ornellas,

TABLE 1

Total energy (E), dipole moment (μ) and transition moment (TM) for the BeH^+ molecule in the $X^1\Sigma^+$ and $A^1\Sigma^+$ states: energy values are relative to -14.0 hartree

$R (a_0)$	$X^1\Sigma^+$			$A^1\Sigma^+$			$X-A$	
	$-E$ (hartree)		μ (a.u.)	$-E$ (hartree)		μ (a.u.)	TM	
	This work	[2]	This work	[3]	This work	[4]	This work	[4]
1.6	0.793062	0.792835	-1.2651	-1.2799	0.544482	0.53784	1.0570	0.7724
1.7	0.834838		-1.2623		0.589812		1.0694	0.5944
1.8	0.866639	0.866342	-1.2577	-1.2866	0.626455	0.61925	1.0766	0.9096
2.0	0.908001	0.907669	-1.2439	-1.2905	0.679993	0.67273	1.0745	0.9777
2.2	0.928828	0.928458	-1.2209	-1.2965	0.714617	0.70736	1.0520	0.9980
2.4	0.936546	0.936122	-1.1858	-1.2707	0.736384	0.72934	1.0107	0.9851
2.479	0.937109	0.936654	-1.1681	-1.2608	0.742345	0.73545	0.9890	0.9710
2.6	0.935985	0.935480	-1.1366	-1.2403	0.749198	0.74258	0.9496	0.9410
2.8	0.930333	0.929727	-1.0717	-1.1931	0.755741	0.74967	0.8696	0.8705
3.0	0.921767	0.921016	-0.9908	-1.1283	0.758006	0.75239	0.7661	0.7742
3.2	0.911733	0.910812	-0.8964	-1.0467	0.756966	0.75194	0.6474	0.6569
3.5	0.895980	0.894789	-0.7373	-0.8997	0.751392	0.74717	0.4404	0.4509
4.0	0.871861	0.870493	-0.4767	-0.6381	0.736196	0.73295	0.0954	0.0887
4.5	0.853522	0.851897	-0.3008	-0.4414	0.719221		-0.1712	1.6432
5.0	0.840842	0.839116	-0.2494	-0.3596	0.704336	0.70138	-0.3150	-0.3346
5.5	0.832790		-0.2935		0.693298		-0.3428	1.5900
6.0	0.827968	0.825953	-0.3766	-0.4445	0.685959	0.68193	-0.3332	-0.4000
7.0	0.823822	0.820866	-0.5655	-0.6144	0.679140	0.67528	-0.3411	-0.4960
8.0	0.822676		-0.7208		0.676920		-0.6255	1.3741
9.25	0.822211	0.818656	-0.8782	-0.9131	0.676044	0.67115	-0.8641	-0.8526
10.0	0.822106	0.818534	-0.9642	-0.9976	0.675912		-0.9690	1.3237

Fig. 1. Potential-energy curves for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of the BeH^+ molecule.

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respectively. These differences are reflected in the calculated value for $T_e = 39\,308\text{ cm}^{-1}$ and in the value of energy at the separated-atom limit relative to the ground state, which is equal to 3.978 eV. Experimental values are $39\,417\text{ cm}^{-1}$ [12] and 3.959 eV [13], respectively. The values obtained by Ornellas are $40\,407\text{ cm}^{-1}$ and 4.074 eV, respectively. The calculated dissociation energies (D_e) are 3.213 eV and 2.234 eV for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states. These results can be compared with the experimental ones of 3.276 and 2.348 eV and with Ornellas' values of 3.214 and 2.279 eV, respectively. The "experimental" values were defined as the energies of Be^+ in the states of 2S and 2P and the energy of H in the ground state minus the energy of BeH^+ at the calculated minimum.

Dipole-moment and transition-moment functions

The calculated dipole-moment functions for the $X^1\Sigma^+$ states and the $A^1\Sigma^+$ states of the BeH^+ molecule and the transition-moment function between these states, calculated with the origin at the centre of mass, are listed in Table 1 and plotted in Fig. 2. As can be seen, our results for the dipole-moment function agree closely with those obtained by Ornellas [3,4]. The transition moment was calculated using the operator z , for parallel transitions, according to the convention of Whiting et al. [14]. The transition moment goes through a maximum between $R = 4.5$ and $5.0 a_0$ where the $A^1\Sigma^+$ state changes its polarity. In the asymptotic limit the calculated value is 1.328 a.u. ($R = 10.0 a_0$) which agrees quite well with the experimental value (1.31 a.u.) for the $\text{Be}^+ (^2S - ^2P)$ transition [15].

The transition probabilities for emission as given by the Einstein A coefficient are listed in Table 2

Fig. 2. Dipole-moment functions for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of BeH^+ and the transition-moment function for the $A^1\Sigma^+ - X^1\Sigma^+$ band system.

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TABLE 2

Einstein coefficients (s^{-1}) for the $A^1\Sigma^+ - X^1\Sigma^+$ band system of the BeH^+ molecule*

v'	v''										
		0	1	2	3	4	5	6	7	8	9
0	2.229(7)	4.952(7)	5.094(7)	2.792(6)	6.969(6)	6.790(5)	1.618(4)	2.353(1)	1.641(1)	8.327(-1)	
1	3.791(7)	2.110(7)	5.602(5)	3.397(7)	4.483(7)	1.625(7)	1.792(6)	2.879(4)	7.949(2)	4.394(3)	
2	3.721(7)	5.294(5)	2.062(7)	1.011(7)	1.056(7)	4.763(7)	2.403(7)	2.753(6)	1.794(4)	4.394(3)	
3	2.745(7)	5.051(6)	1.620(7)	3.250(6)	2.022(7)	2.026(6)	4.532(7)	2.998(7)	3.267(6)	4.775(2)	
4	1.719(7)	1.454(7)	2.799(6)	1.609(7)	3.160(5)	2.019(7)	5.775(3)	4.246(7)	3.444(7)	3.264(6)	
5	9.743(6)	1.816(7)	4.930(5)	1.214(7)	7.431(6)	4.034(6)	1.599(7)	5.741(5)	4.065(7)	3.767(7)	
6	5.196(6)	1.632(7)	5.563(6)	2.848(6)	1.335(7)	1.837(6)	7.691(6)	1.132(5)	1.499(6)	3.928(7)	
7	2.690(6)	1.234(7)	1.031(7)	4.206(4)	7.880(6)	9.721(6)	4.160(4)	9.621(6)	7.295(6)	2.209(6)	
8	1.390(6)	8.477(6)	1.188(7)	2.655(6)	1.570(6)	9.673(6)	5.445(6)	4.896(5)	9.876(6)	3.941(6)	
9	7.349(5)	5.533(6)	1.091(7)	6.079(6)	6.358(4)	4.307(6)	8.715(6)	2.179(6)	1.915(6)	8.771(6)	
10	4.044(5)	3.434(6)	8.800(6)	7.875(6)	1.858(6)	5.750(5)	6.024(6)	6.283(6)	3.716(5)	3.561(6)	
v'		10	11	12	13	14	15	16	17	18	
0	3.819(-2)	1.049(-1)	1.945(-2)	6.328(-4)	6.770(-3)	6.346(-3)	3.528(-3)	1.542(-3)	5.620(-4)		
1	7.343(0)	2.887(-2)	3.435(-1)	8.838(-2)	6.301(-3)	9.741(-4)	5.937(-3)	6.961(-3)	4.409(-3)		
2	8.077(0)	4.449(1)	3.473(-1)	8.283(-1)	2.604(-1)	3.136(-2)	2.324(-3)	3.264(-5)	4.056(-5)		
3	1.285(4)	6.284(1)	2.159(2)	2.537(1)	4.663(-2)	8.739(-1)	3.506(-1)	7.754(-2)	1.402(-2)		
4	1.995(4)	2.962(4)	1.344(3)	4.013(2)	2.207(2)	2.844(1)	1.052(0)	6.154(-2)	1.616(-1)		
5	3.073(6)	1.082(5)	5.941(1)	1.064(4)	3.248(-1)	3.864(2)	2.187(2)	7.133(1)	1.955(1)		
6	4.044(7)	3.384(6)	3.706(5)	6.116(1)	3.471(4)	4.021(3)	3.784(1)	8.571(1)	9.103(1)		
7	3.570(7)	4.548(7)	4.033(6)	1.119(6)	3.503(3)	5.107(4)	2.198(4)	5.555(3)	1.193(3)		
8	3.028(6)	2.877(7)	5.572(7)	2.798(6)	2.329(6)	1.366(5)	4.695(3)	1.961(4)	1.159(4)		
9	1.176(6)	4.221(6)	2.461(7)	6.496(7)	2.883(5)	2.783(6)	8.134(5)	1.179(5)	1.154(4)		
10	6.291(6)	3.597(3)	4.561(6)	2.825(7)	6.503(7)	1.508(6)	1.163(6)	1.177(6)	4.750(5)		

*The values in parentheses are the exponents, e.g. 2.229(7) is 2.229×10^7 .

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TABLE 3

Transition probabilities (A_v) and radiative lifetimes (τ_v) for the $A^1\Sigma^+ - X^1\Sigma^+$ band system

v'	A_v (10^6 s^{-1})	τ_v (ns)	v'	A_v (10^6 s^{-1})	τ_v (ns)
0	1.583	6.316	9	1.482	6.748
1	1.564	6.394	10	1.476	6.773
2	1.535	6.516	11	1.464	6.829
3	1.528	6.545	12	1.447	6.913
4	1.513	6.607	13	1.228	8.141
5	1.501	6.661	14	1.214	8.240
6	1.492	6.702	15	0.839	11.923
7	1.486	6.731	16	0.770	12.985
8	1.482	6.747	17	0.296	33.751

$$A_{v'v''} (\text{s}^{-1}) = (7.2356 \times 10^{-6}) \nu_{v'v''}^3 (\text{cm}^{-1})^3 |D_{v'v''}|^2 (e \text{ \AA})^2 \quad (1)$$

where $\nu_{v'v''}$ is the transition frequency between the electronic states and the electronic transition dipole matrix element $D_{v'v''}$ is given by

$$D_{v'v''} = \int_0^\infty \Psi_{v'}(R) D(R) \Psi_{v''}(R) dR \quad (2)$$

where $\Psi_{v'}$ and $\Psi_{v''}$ are the upper and lower vibrational wavefunction, respectively and $D(R)$ is the electronic transition moment as a function of the internuclear distance. It should be noted that we neglect rotation ($J' = J'' = 0$). The contributions arising from all bound-bound transitions are given by the expression

$$A_v = \sum_{v''}^N A_{v'v''} \quad (3)$$

and are listed in Table 3 together with the radiative lifetimes for several vibrational levels which are given as the inverse of the total bound-bound transition probabilities. We assumed the bound-free contributions to be small for these levels. These calculations were done with the INTENSITY program [16].

DISCUSSION AND CONCLUSIONS

The energies listed in Table 1 represent the best currently available calculations on the beryllium hydride ion molecule in the $X^1\Sigma^+$ and $A^1\Sigma^+$ states. Compared with the estimated experimental values the differences at the minimum and at $R = 9.25 a_0$ are 0.05% and 0.02% for both states, respectively. The calculated wavefunctions show the expected behaviour of the dipole moment, e.g. for small internuclear distance it tends to zero and for large distances it reflects the proper asymptotic species ($\text{Be}^+ + \text{H}$).

In addition the transition moment reported here, the first calculation ever done, seems to be very good since in the asymptotic limit our result differs from the experimental value for the transition $\text{Be}^+ (^2S-^2P)$ by only 0.7% [15].

The Einstein coefficients, $A_{v'v''}$ (Table 2) give a good idea of the relative intensity of the various transitions. Since the equilibrium internuclear distances for the two states do not differ very much, strong transitions are expected to occur involving the lowest vibrational levels of both electronic states. As pointed out by Zemke and Stwalley [17], a rough criterion for a reasonable intensity transition is that the outer turning points of the lower levels be between the inner and outer turning points of the upper levels. The dip in intensity for the $v' = 1, v'' = 2$ transition, for example, is associated with the fact that the node in the $v' = 1$ wavefunction is at a distance close to the turning point of the $v'' = 2$ state. The total transition probabilities and radiative lifetimes for the bound-bound transitions listed in Table 3 show the same tendency as those calculated for the LiH molecule [18], i.e. there is only a slight variation for the first ten vibrational levels and the transition probabilities decrease slowly with v' . Although in the long-range molecular region we have the most intense transition, $A_{v'v''}$ ($v' = 16, v'' = 18$), the value for $A_{v'}$ is small compared with the experimental value for the transition $\text{Be}^+ (^2S-^2P)$, i.e. $1.15 \times 10^9 \text{ s}^{-1}$ [15]. In this region the bound-free transitions are expected to be important.

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**Descrição Rigorosa de Estados Eletrônicos e Vibracionais de
Moléculas Diatômicas : CH^+ e BeF**

Artigos

The Dipole Moment Function and Spectroscopic Constants for the CH^+ and CD^+
Ion-Molecules

F. R. Ornellas e F. B. C. Machado, *J. Mol. Struct. (Theochem)*, **120**, 149–156 (1985)

A Theoretical Study of the Infrared Transition Matrix Elements for the $\text{X}^1\Sigma^+$ State
of the CH^+ and CD^+ Molecules

F. R. Ornellas e F. B. C. Machado, *J. Chem. Phys.*, **84**, 1296–1301 (1986)

A Theoretical Study of the BeF Molecule in the $\text{X}^2\Sigma^+$ State

F. B. C. Machado e F. R. Ornellas, *Mol. Phys.*, **67**, 1129–1140 (1989)

Contrariamente à espécie BeH^+ , a molécula CH^+ era relativamente bem conhecida teoricamente, principalmente no que diz respeito à descrição de seus diferentes estados eletrônicos e as possíveis transições entre esses estados. Percebemos na época, então, que essa caracterização não estava completa pois faltava descrever propriedades vibracionais e rotacionais para um dado estado eletrônico, bem como a função momento de dipolo.

Nesses dois trabalhos, parte da dissertação de mestrado do aluno F. B. C. Machado, procuramos completar a caracterização do estado eletrônico fundamental de forma semelhante à que havíamos feito para a molécula BeH^+ . A qualidade de nossos resultados pode ser inferida pela excelente concordância de nossas curvas de potencial com as publicadas por B. Liu e colaboradores do grupo de Química Quântica da IBM nos E.U.A..

Quanto às informações espectroscópicas obtidas nesse trabalho, fomos um pouco mais além do que no caso do BeH^+ e calculamos as forças (ou intensidades de linha) para algumas bandas no infravermelho para as moléculas CH^+ e CD^+ no estado fundamental.

Mais uma vez, é importante ressaltar que o cálculo da energia eletrônica e da função momento de dipolo só se viabilizaram por causa dos programas que havíamos desenvolvido anteriormente.

Relativamente à molécula BeF , esse trabalho representa nossa primeira tentativa de descrever rigorosamente um sistema diatômico mais complexo que os até então estudados. Com ele estávamos chegando próximos ao limit e de memória e de disco do computador. Sua relevância está no fato de caracterizar de forma rigorosa e detalhada o estado eletrônico fundamental e os respectivos estados vibro-rotacionais. É o primeiro trabalho a descrever a função momento de dipolo e o momento dipolar médio para cada nível vibracional, assim como probabilidades de transições e tempos de vida radiativa. O alto nível dos cálculos fez da energia de dissociação obtida um valor muito mais confiável que a de estudos anteriores. De passagem mostramos, também, que a energia de dissociação experimental, obtida pelo técnica de extrapolação de Birge-Sponer, é acidentalmente boa, pois nesse procedimento deveria se esperar um valor superestimado.

O artigo sobre o BeF é resultado de parte da tese de doutorado do aluno F. B. C. Machado.

THE DIPOLE MOMENT FUNCTION AND SPECTROSCOPIC CONSTANTS FOR THE CH^+ AND CD^+ ION-MOLECULES

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ABSTRACT

Potential energy curves, dipole moment functions, dipole moment expectation values, vibrational and rotational constants are computed for CH^+ and CD^+ with a configuration interaction wavefunction.

INTRODUCTION

The CH^+ is a molecule of fundamental importance in astrophysics where it plays a key role in the chemistry of diffuse interstellar clouds [1-3]. Despite its importance, only recently a direct determination of the vibration constants for the ground state has been performed by Carrington and Ramsay [4]. Laser induced fluorescence studies have also contributed additional spectroscopic data for CH^+ [5] and CD^+ [6,7].

Theoretically, the small number of electrons has allowed large scale configuration interaction calculations to be carried out in this molecule [8-10]. These studies have been focused mainly on the computation of potential curves for the ground state and several excited states. Transition moments between the ground electronic state and the first two excited states of $^1\Sigma^+$ and $^1\Pi$ symmetry have been also computed by Saxon et.al. [10]. Oscillator strengths calculation for the $X^1\Sigma^+ - A^1\Pi$ system has been performed by Yoshimine et.al. [12] and radiative lifetime of the $A^1\Pi$ state has been computed by Larsson and Siegbahn [11]. Some spectroscopic constants have been obtained in these studies only for the CH^+ species. No theoretical data for CD^+ have been found in the literature.

This paper aims at complementing the available studies about this molecule by presenting the dipole moment function for the ground electronic state and the first two excited states of $^1\Sigma^+$ symmetry. Also reported are vibrational energies, vibrational level spacings, vibrationally averaged dipole moments and spectroscopic constants for both CH^+ and CD^+ . Absorption matrix

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elements, Einstein A spontaneous emission coefficients and radiative lifetimes for all vibrational levels and selected rotational levels will be presented in a forthcoming paper.

METHODS AND RESULTS

Potential Energy Curve

Using the configuration interaction (CI) method, energies and dipole moments as a function of the internuclear distance (R) have been calculated for the $X^1\Sigma^+$, $2^1\Sigma^+$ and $3^1\Sigma^+$ electronic states. In our approach, for a reference set consisting of four configurations, namely, $1\sigma^2 2\sigma^2 3\sigma^2$, $1\sigma^2 2\sigma^2 3\sigma 4\sigma$, $1\sigma^2 2\sigma^2 4\sigma^2$, and $1\sigma^2 2\sigma^2 1\pi_+ 1\pi_-$, appropriate for the correct asymptotic behaviour of the potential energy curve, a total of 2116 configuration state functions (CSF) were generated as single and double excitations relative to this set. The 1σ electrons were kept frozen. In the absence of a multiconfiguration self-consistent field package to generate molecular orbitals (MO) for the whole range of R , the following procedure was carried out. Previous experience with the BeH^+ molecule [13] has shown that a singles and doubles CI is quite good to describe the potential energy around the minimum. With this in mind, a 861-term singles and doubles expansion was generated from a molecular orbital set consisting of $20\sigma^-$, $10\pi^-$, and $3\delta^-$ -type functions. The atomic orbitals employed are the Slater type functions of Cade and Huo [14] augmented by the functions: $3s_C(\alpha = 2.0)$, $2s_H(\alpha = 1.0)$, $2p_H(\alpha = 1.3)$ and $2p_H(\alpha = 0.5)$. Using the three MO's given by Cade and Huo [14] as a starting point, an initial set was generated by Schmidt orthonormalization, where for the virtual orbitals a value of 1 was given for the diagonal elements in the coefficients matrix. This set was used in the 861-term expansion to calculate the energy and wavefunction, and from this wavefunction natural orbitals were generated for the larger expansion at $R = 2.137 a_0$.

One more iteration with the larger expansion gave the energy for $R = 2.137 a_0$ and a new set of natural orbitals. The next adjacent point to be calculated used as input orbitals the natural orbitals from the previous calculation. With this wavefunction a new set of natural orbitals is computed and used as input in the next point, and an iterated energy is obtained for the former point. This procedure is then extended for the whole range of R from $1.40 a_0$ to $12.0 a_0$. The calculated energies are listed in Table 1.

The remaining points in the potential energy curve were obtained by a cubic spline fit [15] to the points listed in Table 1. A total of 2500 points was generated at a distance of $0.00424 a_0$ from each other. These curves are displayed in Fig. 1 together with the results of Saxon et. al. [10].

TABLE 1

Theoretical energies (in hartree) and dipole moment function $D(R)$ (in a.u.)^a for CH^+ in the $X^1\Sigma^+$ state

R(a ₀)	energy			D(R)		
	$X^1\Sigma^+$	$2^1\Sigma^+$	$3^1\Sigma^+$	GC ^b	CM ^c	CD ^d
1.4	-37.83890	-37.47772	-37.25150	0.0385	0.6301	0.5373
1.5	.90184	.54595	.32248	0.0000	0.6339	0.5344
1.6	.94645	.59601	.37586	-0.0394	0.6367	0.5307
1.7	.97738	.63249	.41647	-0.0792	0.6392	0.5264
1.8	.99804	.65880	.44795	-0.1193	0.6414	0.5221
1.9	-38.01103	.67518	.47298	-0.1592	0.6437	0.5177
2.0	.01826	.69056	.49353	-0.1990	0.6461	0.5135
2.137	.02138	.70169	.51667	-0.2530	0.6501	0.5084
2.2	.02088	.70491	.52595	-0.2776	0.6521	0.5062
2.4	.01390	.70969	.55135	-0.3547	0.6595	0.5004
2.6	.00198	.70944	.57208	-0.4307	0.6680	0.4956
2.8	-37.98793	.70681	.58933	-0.5069	0.6763	0.4907
3.0	.97338	.70345	.60398	-0.5854	0.6824	0.4835
3.2	.95926	.70039	.61662	-0.6689	0.6834	0.4712
3.4	.94613	.69834	.62772	-0.7605	0.6763	0.4509
3.6	.93421	.69781	.63726	-0.8629	0.6584	0.4197
3.8	.92362	.69908	.64495	-0.9784	0.6274	0.3754
4.0	.91435	.70213	.65064	-1.1082	0.5821	0.3169
4.5	.89658	.71370	.65798	-1.4900	0.4116	0.1133
5.0	.88525	.72383	.66076	-1.9209	0.1920	-0.1395
5.5	.87858	.72958	.66215	-2.3455	-0.0213	-0.3860
6.0	.87488	.73186	.66292	-2.7291	-0.1936	-0.5914
6.5	.87291	.73211	.66334	-3.0673	-0.3205	-0.7515
7.0	.87187	.73144	.66352	-3.3713	-0.4133	-0.8774
8.0	.87100	.72945	.66351	-3.9237	-0.5431	-1.0737
9.0	.87067	.72727	.66335	-4.4455	-0.6423	-1.2390
10.0	.87052	.72664	.66320	-4.9572	-0.7314	-1.3944
11.0	.87042	.72589	.66310	-5.4649	-0.8165	-1.5458
12.0	.87038	.72540	.66305	-5.9706	-0.8997	-1.6953

^a 1 a.u.=2.5418 D. ^b CH^+ , GC. ^c CH^+ , CM. ^d CD^+ , CM.

The Dipole Moment Function

The dipole moment for ionized molecules depends on the choice of origin of the coordinate system[16]. Its value relative to an origin at the center of mass is used in the computation of the transition probabilities. Calculated values of the dipole moment for internuclear distances (R) ranging from 1.4 to 12.0 a₀ are listed in Table 1. Fig. 2 displays the dipole moment function relative to the geometric center (GC) and relative to the center of mass (CM) for CH^+ and CD^+ in the ground electronic state $X^1\Sigma^+$ and also the dipole moment function for CH^+ in the states $2^1\Sigma^+$ and $3^1\Sigma^+$.

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Fig. 1. Comparison of $1\Sigma^+$ potential energy curves of CH^+ calculated in this work (solid lines) and the results of Ref. 10 (points).

Fig. 2. The dipole moment function of CH^+ and CD^+ .

Spectroscopic properties

Using the potential energy function derived above, the radial equation was solved numerically [17]. Vibrational levels and their spacings for CH^+ and CD^+ are listed in Table 2.

For each vibrational state the difference in energy between adjacent rotational levels was next used to compute the rotational constants B_v and D_v which are listed in Table 2. From these constants the values of $B_e, \alpha_e, \gamma_e, D_e$ and E_e (listed in Table 4) were obtained by a least square fit. The vibrational constants (listed in Table 3) were also obtained by standard fitting procedure. See Ref. [13] for explicit expressions used in the calculation of these constants. Complementing these properties, average dipole moments, as described in Ref. [19], are also listed in Table 5.

DISCUSSION AND CONCLUSIONS

The calculated potential energy curves are compared in Fig. 1 with the CI results of Saxon et.al. [10]. Their calculation was meant to cover five $1\pi^+$ states, whence the relatively large number of configuration state functions (6808) and molecular basis orbitals (24, 12, 38). Fig. 1 clearly shows that for the ground state our 2116-term CI gives also equally good results. A slight discrepancy exists around the minimum which, as will be shown later, is reflected in a 20-30 cm^{-1} error in the $\Delta G_{v+1/2}$ values. For the $2\pi^+$ state both calculations practically agree for $R > 4.5 a_0$. For $R < 4.5 a_0$ our curve is slightly parallel to that of Ref. [10], but the hump due to the avoided crossing of the $2\pi^+$ and $3\pi^+$ states is correctly described. A height of $\approx 2600 \text{ cm}^{-1}$ was obtained, compared with $\approx 2800 \text{ cm}^{-1}$ of Ref. [10].

TABLE 2
Vibration energies, levels spacings, rotation constants^a

v	CH^+				CD^+			
	G(v)	ΔG	B_v^b	$10^3 D_v^b$	G(v)	ΔG	B_v^c	$10^4 D_v^c$
0	1403.2		13.904	1.356	1032.6		7.533	4.01
1	4119.2	2716.0	13.410	1.336	3049.8	2017.2	7.337	3.96
2	6716.5	2597.3	12.914	1.316	5003.6	1953.8	7.140	3.92
3	9195.2	2478.7	12.426	1.299	6892.5	1888.9	6.946	3.88
4	11557.3	2362.1	11.937	1.278	8717.8	1825.3	6.752	3.83
5	13804.2	2246.9	11.447	1.258	10480.2	1762.4	6.559	3.79
6	15936.4	2132.2	10.955	1.237	12179.9	1699.4	6.366	3.75
7	17954.8	2018.4	10.459	1.211	13817.4	1637.5	6.173	3.72
8	19860.2	1905.4	9.957	1.181	15392.9	1575.5	5.980	3.69

^a Exper.: 2739.7, 2623.1, 2507.8, Ref. 4

Theor.: 2743.4, 2610.2, 2473.5, Ref. 11; 2742.9, 2625.3, 2507.9, Ref. 10

^b Exper.: 13.930, 13.441, 12.956, 12.476; 1.365, 1.342, 1.322, 1.308, Ref. 4

^c Exper.: 7.583, 7.402, 7.22; 5.819, 1.126, 12, Ref. 6, 7

For the $3^1\Sigma^+$ state, although the two calculations differ all over the range of R , the general shape of our curve follows that of Ref. [10]. The differences are certainly due to the inclusion of configurations in the reference set where both valence and Rydberg orbitals are occupied, and also to their more elaborate choice of those orbitals. It is important to recall that the procedure we followed was essentially based on the non-availability of a multiconfiguration self-consistent package for preliminary calculations. One aspect of our approach worth mentioning is that although for every point two CI's were carried out, the iteration changed the energies only in the fifth decimal place, implying that the calculation time could have been reduced to half the time actually spent.

Note in Fig.2 that relative to the CM and for large R the dipole moment function $D(R)$ behaves as $\sim -R/2$ and as $\sim +R/2$ for the fundamental and excited states, respectively, in accordance with the contribution of the charge on the ion C^+ to the dipole moment of the fundamental state, and the contribution of the charge on the ion H^+ to the dipole moment of the excited states. An almost linear relationship is also followed by $D(R)$ for small values of the internuclear distance. A sizeable change in polarity is, however, shown by CH^+ in the $3^1\Sigma^+$ state. The molecule changes from C^+-H at small R , to $C^{+2}-H^-$ at moderate distances, and to $C-H^+$ at large distances.

As discussed by Cade[16] the dipole moment is origin dependent for ionized molecules. Fig.2 shows this dependence for CH^+ and CD^+ in their fundamental electronic states. The molecules have the same dipole moment relative to the GC, but since their masses enter into the definition of the CM, they will obviously have different dipole moment values relative to this center. The implications of the origin dependence is that besides the usual

TABLE 3
Dependence of vibration constants on number of spacings

Number of Spacings	w_e		$w_e x_e$		$w_e y_e$		$w_e z_e$	
	CH^+	CD^+	CH^+	CD^+	CH^+	CD^+	CH^+	CD^+
4	2833.3	2076.9	57.97	28.23	-0.543	-1.148	0.0721	0.1137
5	2835.0	2079.3	59.41	30.31	-0.090	-0.495	0.0254	0.0465
6	2836.4	2081.1	60.51	31.67	0.209	-0.125	-0.0008	0.0141
7	2836.8	2081.8	60.76	32.14	0.269	-0.013	-0.0053	0.0056
8	2836.8	2082.3	60.77	32.47	0.270	0.059	-0.0054	0.0008
3 ^{a,b}	2834.9	2079.4	59.52	30.67	0.033	-0.238		
4	2836.2	2081.4	60.34	31.97	0.178	-0.011		
5	2836.6	2082.3	60.60	32.48	0.215	0.063		

^aTheoret.: 2873.4, 64.1, -0.568, Ref.11; 2861.0, 59.0, -0.083, Ref.10

Exerim.: 2857.6, 59.3, 0.226, Ref.4; 2850.1, 52.9, Ref.6,7

^bExerim.: 2092, 28.5, Ref.6,7

TABLE 4
Theoretical and experimental spectroscopic constants

	CH ⁺				CD ⁺	
	Ref.10	Ref.11	This work	Exp.Ref.4	This work	Exp.Ref.6,7
$R_e(a_0)$	2.134	2.132	2.143	2.137		2.109
B_e	14.2009	14.2372	14.0212	14.1766	7.435	7.763
α_e	0.4806	0.5231	0.4256	0.4939	0.133	0.18
γ_e	-0.0021	-0.0037	-0.0057	0.0023	-0.0032	
$10^3 D_e$	1.22	1.27	1.10	1.373	0.321	
$10^3 J_e$	0.26	-0.94	0.25	-0.193	0.06	

difference in vibrational wavefunctions between CH⁺ and CD⁺ this new factor will contribute further to differentiate those properties like the transition probability that have the dipole moment function in their definition.

The solution of the radial equation[17] for the nuclear motion has yielded 22 and 29 vibrational levels for CH⁺ and CD⁺, respectively. These energy levels and their difference ($\Delta G_{v+1/2}$) are listed in Table 2, and compared with available experimental and theoretical data. For CD⁺ neither experimental nor theoretical values were found and only three experimental values were found for CH⁺.

Table 3 lists vibrational constants for CH⁺ and CD⁺, obtained by standard fitting procedure[13], as a function of the number of vibrational spacings. As was found by Docken and Hinze [18] in their study of LiH and by Ornellas[13] in his study of BeH⁺, the vibrational constants are sensitive to the number of $\Delta G_{v+1/2}$ values and to the number of parameters used in the least squares fit. Table 3 shows that this is also the case for CH⁺. For space saving reasons, most of the vibrational dependent properties are listed only up to 8 levels. The remaining values are available upon request. For the sake of comparison, the lower part of Table 3 lists spectroscopic constants obtained by a 3-parameter least squares fit, and other theoretical values. The overall agreement is very good.

TABLE 5
Dipole moment expectation values (in eA)

v	CH ⁺			CD ⁺		
	J=0	J=5	J=10	J=0	J=5	J=10
0	0.3448	0.3449	0.3453	0.2687	0.2686	0.2684
1	0.3465	0.3467	0.3470	0.2681	0.2680	0.2678
2	0.3483	0.3484	0.3488	0.2674	0.2674	0.2672
3	0.3500	0.3501	0.3505	0.2668	0.2667	0.2665
4	0.3515	0.3516	0.3519	0.2660	0.2659	0.2657
5	0.3525	0.3526	0.3528	0.2650	0.2649	0.2647
6	0.3529	0.3529	0.3530	0.2638	0.2637	0.2634
7	0.3523	0.3522	0.3520	0.2622	0.2621	0.2618
8	0.3504	0.3501	0.3495	0.2602	0.2601	0.2597

The rotational constants B_v and D_v are listed in Table 2. They are the result of a least squares fit [13] involving fifteen rotational levels for each vibrational state. The agreement with experimental data is in general very good, the only exception being the experimental D_v values for CD^+ which seem to be too large. The remaining spectroscopic constants are collected in Table 4. There is no concordance on the value of 3_e . The general agreement among the theoretical γ_e values suggest that the experimental one should also be negative. Finally, the dipole moment expectation values listed in Table 5 show practically no dependence on the rotational levels.

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A theoretical study of the infrared transition matrix elements for the $X^1\Sigma^+$ state of the CH^+ and CD^+ molecules

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Theoretical results for the absorption matrix elements, Einstein A spontaneous emission coefficients, and radiative lifetimes for all vibrational levels and selected rotational levels are reported for the CH^+ and CD^+ molecules in the $X^1\Sigma^+$ state.

I. INTRODUCTION

The key role played by the CH^+ molecule in the chemistry of diffuse interstellar clouds^{1,2} has motivated theoreticians to carry out large scale configuration interaction calculations on these few electron systems.³⁻⁸ From the experimental point of view the CH^+ molecule has recently received special attention by Carrington and Ramsay⁹ and has been, together with CD^+ , the object of laser induced fluorescence studies by Mahan and O'Keefe.^{10,11} The theoretical studies have concentrated mainly on calculations of potential energy curves for the ground and several excited states, also on oscillator strengths for the $X^1\Sigma^+ \rightarrow A^1\Pi$ and $X^1\Sigma^+ \rightarrow i\Sigma^+$ ($i = 2,3$) transitions, and on radiative lifetime of the $A^1\Pi$ state.

Recently, we have contributed additional theoretical information about this molecule by calculating the dipole moment functions, vibrationally averaged dipole moments, and a complete set of rotational and vibrational constants for both CH^+ and CD^+ .¹² In this paper, we are concerned with the infrared spectra of these systems along the lines of approach used by Stwalley and collaborators.¹³ Theoretical results are reported for the absorption matrix elements, Einstein A spontaneous emission coefficients, and radiative lifetimes for all vibrational levels and selected rotational levels.

II. RADIATIVE TRANSITION PROBABILITIES AND LIFETIMES

The calculation of the radiative transition probability for emission, usually expressed as the Einstein A_{kl} coefficient,

depends upon the dipole moment matrix elements μ_{kl} and the transition frequency ν_{kl} between the two states:

$$A_{kl} = 7.2356 \times 10^{-6} \nu_{kl}^3 |\mu_{kl}|^2. \quad (1)$$

For ν_{kl} given in cm^{-1} and μ_{kl} in $e \text{ Å}$, the constant in Eq. (1) is the conversion factor necessary to express A_{kl} in s^{-1} .^{13,14}

The dipole moment matrix element given in Eq. (2),

$$\mu_{kl} = \int_0^\infty \psi_k(R) \mu(R) \psi_l(R) dR, \quad (2)$$

is dependent upon the vibrational wave functions and the dipole moment function. Its evaluation involves, in a first step, the solution of an eigenvalue equation for the electronic motion for several internuclear distances. In a second step, the electronic eigenfunctions are used to compute the dipole moment function, and the energy eigenvalues are then used to construct a potential energy function which is used in the radial equation for the nuclear motion. The solution to this equation provides the vibrational wave functions which appear in Eq. (2) and the frequencies needed in Eq. (1).

The total Einstein $A_{\nu', J'}$ coefficient is the sum of all possible transition probabilities starting from the state (ν', J') ,

$$A_{\nu', J'} = \frac{1}{2J' + 1} \left\{ J' \sum_{\nu''=0}^{\nu'} A_{\nu', J'; \nu'', J'-1} + (J' + 1) \sum_{\nu''=0}^{\nu'-1} A_{\nu', J'; \nu'', J'+1} \right\}, \quad (3)$$

where, J' and $J' + 1$ are, respectively, the Hönl-London factors for the R and P branches and $2J' + 1$ is the statistical weight for the rotational level.¹⁵⁻¹⁸

TABLE I. Dipole moment matrix elements $\mu_{\nu', 0, \nu'', 1}$ (in $e \text{ Å}$ units, in upper right, and pure rotational transitions on the diagonal) and Einstein A spontaneous emission coefficients $A_{\nu', 0, \nu'', 1}$ (in s^{-1} units, in lower left) for the $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ bands of CH^+ .

Initial state $\nu' (J' = 0)$	Final state $\nu'' (J'' = 1)$							
	0	1	2	3	4	5	6	7
0	0.344 833	0.002 190	0.000 049	-0.000 051	-0.000 007	0.000 008	-0.000 001	-0.000 002
1	1.408 2(0)	0.346 546	0.003 332	-0.000 033	-0.000 131	0.000 006	0.000 013	-0.000 008
2	4.608 6(-3)	2.735 9(0)	0.348 304	0.004 233	-0.000 254	-0.000 230	0.000 035	0.000 015
3	2.220 8(-3)	4.929 2(-2)	3.771 0(0)	0.349 988	0.004 868	-0.000 662	-0.000 336	0.000 088
4	1.667 6(-3)	1.953 8(-2)	2.286 8(-1)	4.342 690	0.351 455	0.005 127	-0.001 299	-0.000 427
5	1.434 4(-3)	7.417 9(-4)	6.021 6(-2)	0.728 700	4.311 340	0.352 514	0.004 857	-0.002 199
6	8.447 6(-5)	4.324 5(-3)	2.228 2(-4)	1.170 3(-1)	1.816 4(0)	3.641 5(0)	0.352 906	0.003 868
7	1.262 5(-4)	1.917 9(-3)	6.964 2(-3)	9.858 5(-3)	0.158 2(0)	3.799 8(0)	2.467 3(0)	0.352 315

TABLE II. Dipole moment matrix elements $\mu_{v',0,v'',1}$ (in $e \text{ \AA}$ units, in upper right, and pure rotational transitions on the diagonal) and Einstein A spontaneous emission coefficients $A_{v',0,v'',1}$ (in s^{-1} units, in lower left) for the $X^1\Sigma^+-X^1\Sigma^+$ bands of CD^+ .

Initial state $v'(J' = 0)$	Final state $v''(J'' = 1)$							
	0	1	2	3	4	5	6	7
0	0.268 673	− 0.002 561	0.000 466	− 0.000 093	0.000 008	− 0.000 001	0.000 002	− 0.000 001
1	0.252 280	0.268 064	− 0.003 494	0.000 763	− 0.000 206	0.000 027	0.000 000	− 0.000 001
2	7.441 8(− 2)	0.420 240	0.267 438	− 0.004 183	0.000 995	− 0.000 343	0.000 055	0.000 000
3	9.593 0(− 3)	0.178 430	0.538 300	0.266 757	− 0.004 786	0.001 151	− 0.000 502	0.000 100
4	7.985 9(− 5)	4.350 8(− 2)	0.267 730	0.633 560	0.265 963	− 0.005 403	0.001 216	− 0.000 681
5	5.681 6(− 7)	1.146 4(− 3)	0.110 780	0.311 130	0.730 510	0.265 001	− 0.006 113	0.001 178
6	2.099 8(− 5)	3.516 8(− 5)	5.062 2(− 3)	0.216 730	0.294 390	0.852 500	0.263 792	− 0.006 994
7	2.313 2(− 5)	4.151 2(− 5)	7.838 3(− 5)	1.607 2(− 2)	0.391 160	0.223 910	1.024 8(0)	0.262 242

The radiative lifetimes are computed as the reciprocals of the total Einstein $A_{v',J'}$ coefficients.

III. RESULTS

The potential energy function and the dipole moment function used in this work were obtained by a 2116-term CI wave function and have been discussed in detail in Ref. 12. In the calculation of the transition probabilities, besides the difference in the vibrational wave functions of CH^+ and CD^+ due to their different reduced masses, there is also a contri-

bution from the dipole moment function itself, which in the case of ionized species is dependent on the choice of the origin of the coordinate system. Having chosen this origin at the center of mass, CH^+ and CD^+ will also differ with respect to their dipole moments.

Dipole moment matrix elements $\mu_{v',0,v'',1}$ for v' up to 7 are collected in the upper right section of Table I for CH^+ and of Table II for CD^+ . The lower left section of these tables contains the Einstein spontaneous emission coefficient $A_{v',0,v'',1}$. In the diagonal are the pure rotational matrix elements $\mu_{v',0,v',1}$.

FIG. 1. Einstein $A_{v',0,v'',1}$ coefficients for emission from the vibrational level v' to the level v'' ; $\Delta v = v' - v''$.

FIG. 2. Einstein $A_{v',0,v'',1}$ coefficients for emission from the vibrational level v' to the level v'' ; $\Delta v = v' - v''$.

The variation in $A_{v',0,v'',1}$ with v' and v'' for $\Delta v = v' - v'' = 1, 2, 3$ is better seen in Figs. 1 and 2 for CH^+ and CD^+ , respectively. Also plotted is the quantity $A_{Total} = \sum_{\Delta v=1}^{\infty} A_{v',0,v'',1}$. The difference between A_{Total} and $A_{v',0,v'',1}$ for $\Delta v = 1, 2, 3$ is a direct measure of the contribution of overtones with $\Delta v > 3$.

Total transition probabilities for emission and radiative lifetimes for selected rotational levels ($J' = 0, 1, 5$, and 10) and all vibrational levels are collected in Table III for CH^+ and in Table IV for CD^+ .

Finally, Table V shows the line strengths without the Hönl-London factor, $|\langle v'', J'' | \mu(R) | v', J' \rangle|^2$ for CH^+ and CD^+ and the bands 1-0, 2-0, 3-0, and 2-1 of the $X^1\Sigma^+$ state. This definition of line strength is that of Refs. 16 and 19.

The solution of the radial equation and the calculation of transition probabilities have been carried out using the INTENSITY computer program developed by Zemke and Stwalley.²⁰

IV. DISCUSSION AND CONCLUSIONS

An analysis of the emission transition probabilities shows that for CD^+ the fundamental transition ($\Delta v = 1$) is dominant for $v' < 25$. For CH^+ , transitions with $\Delta v = 1$ are dominant for v' up to 6, then in the range $7 < v' < 13$ there is a predominance of transitions with $\Delta v = 2$, and then for $v' > 13$ there is a competition between the fundamental and the first and second overtone transitions. As to A_{Total} , it reaches a maximum at $v' = 16$ for CH^+ and at $v' = 21$ for CD^+ . The radiative lifetime will have the opposite behavior, first decreasing and then increasing. It is usually expected that the higher v' , the higher the transition probability for emission will be, with a corresponding decrease in the lifetime of that state. However, this behavior is not observed for the very high vibrational levels of both CH^+ and CD^+ . In these states we have a kind of long-range molecule^{13(a)} which exhibits quite a different behavior than normal molecules. A discussion of this behavior in terms of the detailed nature of

TABLE III. Total transition probabilities for emission (in s^{-1} units) and spontaneous radiative lifetimes (in ms) calculated for various (v', J') levels of the $X^1\Sigma^+$ state of CH^+ .

v	$A_{v,0}$	$A_{v,1}$	$A_{v,3}$	$A_{v,10}$	$\tau_{v,0}$	$\tau_{v,1}$	$\tau_{v,3}$	$\tau_{v,10}$
0		6.2(-3)	1.0370	8.3202		162080	964.3	120.2
1	1.4082	1.4567	2.9853	11.2231	710.1	686.5	335.0	89.1
2	2.7405	2.8250	4.7705	13.7651	364.9	354.0	209.6	72.6
3	3.8225	3.9381	6.2382	15.8471	261.6	253.9	160.3	63.1
4	4.5925	4.7352	7.3402	17.4539	217.7	211.2	136.2	57.3
5	5.1024	5.2699	8.1506	18.7112	196.0	189.8	122.7	53.4
6	5.5796	5.7710	8.9190	19.9323	179.2	173.3	112.1	50.2
7	6.4441	6.6596	10.0806	21.5922	155.2	150.2	99.2	46.3
8	8.2515	8.4917	12.1995	24.2717	121.2	117.8	82.0	41.2
9	11.5879	11.8534	15.8596	28.5431	86.3	84.4	63.1	35.0
10	16.9310	17.2206	21.5166	34.7907	59.1	58.1	46.5	28.7
11	24.4418	24.7528	29.2857	42.9899	40.9	40.4	34.2	23.3
12	33.7586	34.0816	38.7356	52.5086	29.6	29.3	25.8	19.0
13	43.8001	44.1211	48.6988	61.9416	22.8	22.7	20.5	16.1
14	52.8876	53.1886	57.2907	69.4009	18.9	18.8	17.6	14.4
15	59.0956	59.3555	62.9686	72.7395	16.9	16.9	15.9	13.8
16	60.4187	60.6144	63.2797	70.0111	16.6	16.5	15.8	14.3
17	55.9124	56.0296	57.5606	60.6597	17.9	17.9	17.4	16.5
18	46.0126	38.5745	46.2086	45.1750	21.7	25.9	21.6	22.1
19	31.7559	31.6885	30.5372	24.8557	31.5	31.6	32.8	40.2
20	16.0457	15.9009	13.6926		62.3	62.9	73.0	
21	16.2402				160.2			

the long-range forces is presented by Stwalley.^{13(a)} Recent studies on LiH ¹³ and on BeH^+ ¹⁴ have also confirmed his prediction of an increase in radiative lifetimes for these long-range molecules. Examining the vibrational wave functions

of the LiH molecule, Stwalley^{13(a)} has noticed that contrary to ordinarily excited molecules which show rapid oscillations with somewhat greater amplitude near R_{v+} than R_{v-} (classical turning points), the very high levels are distinct in

TABLE IV. Total transition probabilities for emission (in s^{-1} units) and spontaneous radiative lifetimes (in ms) calculated for various (v', J') levels of the $X^1\Sigma^+$ state of CD^+ .

v	$A_{v,0}$	$A_{v,1}$	$A_{v,3}$	$A_{v,10}$	$\tau_{v,0}$	$\tau_{v,1}$	$\tau_{v,3}$	$\tau_{v,10}$
0		6.0(-4)	0.1007	0.8223		1679562	9934	1216
1	0.2523	0.2621	0.4823	1.5028	3964	3816	2073	665.4
2	0.4947	0.5128	0.8418	2.1307	2022	1950	1188	469.3
3	0.7263	0.7520	1.1796	2.7111	1377	1330	847.8	368.9
4	0.9449	0.9774	1.4943	3.2445	1058	1023	669.2	308.2
5	1.1536	1.1924	1.7908	3.7396	866.9	838.7	558.4	267.4
6	1.3687	1.4133	2.0862	4.2164	730.6	707.6	479.3	237.2
7	1.6561	1.6760	2.4180	4.7162	603.8	596.7	413.6	212.0
8	1.9737	2.0287	2.8365	5.2947	506.7	492.9	352.6	188.9
9	2.4753	2.5353	3.4064	6.0197	404.0	394.4	293.6	166.1
10	3.2045	3.2692	4.2023	6.9688	312.1	305.9	238.0	143.5
11	4.2404	4.3097	5.3074	8.2212	235.8	232.0	188.4	121.6
12	5.6601	5.7339	6.7863	9.8503	176.7	174.4	147.4	101.5
13	7.5253	7.6033	8.6772	11.9088	132.9	131.5	115.2	84.0
14	9.8615	9.9432	11.0967	14.4095	101.4	100.6	90.1	69.4
15	12.6506	12.7348	13.9232	17.3161	79.1	78.5	71.8	57.8
16	15.8032	16.1537	17.0930	20.5117	63.3	61.9	58.5	48.8
17	19.1400	19.2256	20.4208	23.7911	52.3	52.0	49.0	42.0
18	22.4081	22.4910	23.6465	26.8809	44.6	44.5	42.3	37.2
19	25.3238	24.8730	26.4841	29.4865	39.5	40.2	37.8	33.9
20	27.5703	27.6403	28.6096	31.2658	36.3	36.2	35.0	32.0
21	28.7992	28.8562	29.6760	31.8724	34.7	34.7	33.7	31.4
22	28.7474	28.7822	29.4254	31.0682	34.8	34.8	34.0	32.2
23	27.3011	27.3321	27.7540	28.7773	36.6	36.6	36.0	34.8
24	24.5047	24.5202	24.7147	25.0641	40.8	40.8	40.5	39.9
25	20.4842	20.4827	20.4350	20.0793	48.8	48.8	48.9	49.8
26	15.4895	15.4700	15.1713	14.0378	64.6	64.6	65.9	71.2
27	9.9909	9.9559	9.4373	7.6343	100.1	100.4	106.0	131.0
28	5.0987	5.0625	4.5512		196.1	197.5	219.7	

TABLE V. Line strengths $|\langle \nu'', J'' | \mu(R) | \nu', J' \rangle|^2$ for four infrared bands of the ground state of CH^+ and CD^+ (in $10^{-9} \text{e}^2 \text{\AA}^2$).

J	CH^+							
	1-0		2-0		3-0		2-1	
	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$
0		4 796.4		2.362		2.5837		11 101
1	10 019	2 907.8	4.314	11.422	0.6558	4.1075	22 264	6 981.8
2	13 363	1 494.1	14.804	27.517	0.1862	6.0505	29 327	3 823.5
3	17 202	549.71	31.288	50.901	0.0045	8.4485	37 390	1 615.7
4	21 539	68.89	53.518	81.810	0.8079	11.340	46 461	347.4
5	26 380	45.93	81.236	120.49	0.3864	14.763	56 550	8.0
6	31 729	474.57	114.21	167.18	0.8941	18.757	67 665	586.2
7	37 589	1 348.7	152.19	222.07	1.5760	23.371	79 815	2 071.0
8	43 965	2 661.9	194.99	285.33	2.4080	28.637	93 006	4 451.4
9	50 861	4 407.6	242.38	357.23	3.3644	34.609	107 250	7 715.6
10	58 282	6 579.3	294.20	437.87	4.4218	41.4218	122 550	11 854
11	66 230	9 170.7	350.30	527.39	5.5560	48.858	138 910	16 856
12	74 713	12 175	410.51	625.96	6.7529	57.237	156 350	22 713
13	83 732	15 587	474.81	733.62	7.9888	66.512	174 880	29 416
14	93 295	19 400	543.09	850.49	9.2441	76.746	194 490	36 957

J	CD^+							
	1-0		2-0		3-0		2-1	
	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$
0		6 556.9		216.86		8.705		12 210
1	4343.8	7 830.3	166.12	245.22	6.6398	9.887	7965.5	14 665
2	3405.6	9 213.9	143.64	275.64	5.7455	11.175	6178.2	17 339
3	2580.3	10 707	123.02	308.18	4.9366	12.576	4615.9	20 231
4	1868.8	12 308	104.21	342.87	4.2083	14.095	3279.4	23 339
5	1270.9	14 016	87.16	379.79	3.5570	15.740	2169.8	26 661
6	787.9	15 831	71.78	418.90	2.9749	17.513	1288.2	30 196
7	419.5	17 751	58.07	460.31	2.4604	19.423	634.60	33 941
8	166.1	19 774	47.94	504.06	2.0083	21.477	209.82	37 894
9	28.0	21 900	35.36	550.15	1.6138	23.681	14.25	42 053
10	5.3	24 127	26.26	598.66	1.2739	26.045	48.14	46 416
11	98.12	26 454	18.61	649.61	0.9842	28.577	311.69	50 981
12	306.45	28 880	12.32	702.96	0.7379	31.274	804.94	55 745
13	630.38	31 403	7.40	758.84	0.5365	34.156	1527.8	60 705
14	1069.8	34 021	3.75	817.20	0.3725	37.228	2480.3	65 862

that they show a diminished wave function amplitude over the deep part of the potential well, and a dominant contribution of the outermost portion of the wave function outside the last node. The overall result is that transitions for which ν could be large are made unlikely by the $|\mu_{kl}|^2$ factor, and on the other hand, transitions for which $|\mu_{kl}|^2$ can be significant (between the very high levels) have their contribution diminished by the small ν factor. The net effect is a decrease in the total transition probability. Although we have not carried an analysis of the vibrational wave functions for the systems studied here, it seems that the above rationale for the increase in the radiative lifetimes can also be extended to CH^+ and CD^+ .

The data in Tables III and IV show that the effect of rotation on the radiative lifetimes is significant for the first ten vibrational levels in CH^+ and the first 15 in CD^+ . In general, for a given vibrational level the radiative lifetime decreases with increasing rotational levels.

Note also in Tables III and IV that a significant difference is observed between the radiative lifetimes of the two species. For a given ν' and J' the radiative lifetime of CD^+ is approximately five times greater than the corresponding one

in CH^+ , and this factor goes up to 10 for $\nu' = 0$ and $J = 1, 5$, and 10. Similar results have also been obtained for $(\text{BeH})^+$ and $(\text{BeD})^+$.²¹

Concentrating now on the results of Table V it is observed that for a given J the line strengths decrease in going from the 1-0 band to the 2-0 band and to the 3-0 band; however, the ones in the 2-1 band are in general greater than the corresponding ones in the 1-0 band by a factor of 2. In the absence of any other theoretical or experimental data for comparison, we noticed, however, that a similar behavior has been observed by Docken and Hinze²² for LiH and by Lie¹⁶ for HF .

Finally, notice that for CH^+ the line strength increases with J in the P branch, with the exception of the second overtone. In the R branch, it increases with increasing J for the first and second overtones, and decreases up to $J = 5$ and then increases for the two fundamental transitions 1-0 and 2-1. For CD^+ , the line strengths decrease with increasing J in the P branch for the 2-0 and 3-0 transition. For the 1-0 and 2-1 transitions this decrease reaches a minimum for $J = 10$ and 9, respectively, and starts to increase again. In the R branch, the line strengths increase with increasing J .

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A theoretical study of the BeF molecule in the $X^2\Sigma^+$ state

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A potential energy curve and a dipole moment function are computed for the $X^2\Sigma^+$ state of the BeF molecule using the multi-reference singles and doubles configuration interaction approach. Vibrationally averaged dipole moments, radiative transition probabilities and radiative lifetimes are reported for several vibrational levels and selected rotational levels together with the corresponding spectroscopic constants. Agreement of the vibrational spacings with the available experimental ones is 15 cm^{-1} on the average. A value of 5.92 eV is also obtained for the dissociation energy D_0 .

1. Introduction

Starting from first principles, accurate potential energy curves, dipole moment functions and radiative transition probabilities can be calculated with the current methodology of theoretical chemistry. For few electron diatomics, calculations have been reported for molecules such as LiH [1-4], BeH⁺ [5, 6], BeH [7], BH⁺ [8], CH⁺ [9], HF [10], OH [11-13], OH⁺, OH⁻ [12], and CN⁻, NH⁻ [14].

In this work is presented an investigation of the spectroscopic properties of the $X^2\Sigma^+$ state of the BeF molecule from first principles. Using the multireference singles and doubles configuration interaction approach, an accurate potential energy curve and dipole moment function are computed and therefrom vibrationally averaged dipole moments, radiative transition probabilities and lifetimes for several vibrational levels and selected rotational levels, the corresponding vibrational and rotational constants, and the dissociation energy are calculated.

To our knowledge, the dipole moment has been reported only at the equilibrium distance [15]. The existing theoretical dissociation energies (D_e) differ significantly, 3.94 eV [16], 5.5 eV [17] and 6.02 eV [18] and the use of different experimental techniques has resulted in values for D_0 ranging from 5.4 eV to 6.26 eV [19-24].

2. Theoretical approach

The electronic energies and the dipole moments were computed by the configuration interaction method as implemented in the MELD codes [25]. With the exception of the three innermost molecular orbitals which were kept frozen, all single and double excitations from a multi-reference set of ten configuration state functions were allowed. Perturbation theory with an energy threshold of 10^{-7} hartree was used to keep the length of the final wavefunction (5000-10 000 terms) manageable within the limitations of the computer hardware (CYBER 170/

750). Due to a restriction in the MELD programs the calculation was carried out in the C_{2v} point group symmetry. The molecular orbitals (MOs) used in the excitation process to generate the $X^2\Sigma^+$ wavefunction were those resulting from an SCF calculation for the excited $^2\Pi$ state. The reason for that was the need to use a single set of MOs for both states that could make viable the calculation of transition moments in a future step. Also, in a preliminary study, the increase in the energy of the $^2\Pi$ state using the $X^2\Sigma^+$ MOs was greater than that resulting from the use of the $^2\Pi$ MOs in the calculation of the $X^2\Sigma^+$ state.

For beryllium, the 10s, 5p set of cartesian gaussian contracted to 5s, 3p [26] plus one set of *d*-functions ($\alpha = 0.80$) was employed, whereas for fluorine, the 13s, 8p set of Duijneveldt contracted to 7s, 4p [27] plus two sets of *d*-functions with exponents 1.89 and 0.56 [28] was used.

With energies and dipole moments calculated for several internuclear distances ranging from 1.8 to $10.0 a_0$, numerical interpolations (~ 2500 points) were carried out next to generate numerical functions. These functions were used as input in the PROGRAM INTENSITY [29] which calculates the vibrational energies by the Numerov-Cooley method and also computes the transition probabilities.

3. Results and discussion

3.1. Electronic and vibrational energies

Total electronic energies are listed in table 1 and plotted in figure 1 for several internuclear separations. Beyond the Hartree-Fock level no explicit value was found in the literature for a comparison with our calculation. Inspection of figure 1 in [17] leads one to infer that for the equilibrium and intermediate internuclear distances both calculations seem to be in very good agreement. For distances greater than $5.0 a_0$ our values are slightly higher. Around $6.5 a_0$, the sharp change in the shape of the potential energy curve is attributed to an avoided crossing with the $B^2\Sigma^+$ state. In this region, a very small barrier is observed and beyond it the curve is marginally

Table 1. Total electronic energies (in hartree) for the BeF molecule in the $X^2\Sigma^+$ state. Energy values are relative to -114.0 hartree.[†]

$R(a_0)$	$-E$	$R(a_0)$	$-E$
1.8	0.041 037	3.5	0.275 996
1.9	0.143 292	3.7	0.256 561
2.0	0.216 122	4.0	0.229 386
2.1	0.267 132	4.2	0.212 726
2.2	0.301 633	4.5	0.189 999
2.3	0.324 043	4.8	0.170 019
2.4	0.337 370	5.0	0.157 934
2.5	0.343 959	5.5	0.131 870
2.6	0.345 447	6.0	0.120 975
2.7	0.343 334	6.5	0.116 447
2.8	0.338 642	7.0	0.117 061
2.9	0.332 031	8.0	0.117 852
3.0	0.324 087	10.0	0.120 335
3.2	0.305 827	25.0	0.124 851

[†] 1 hartree = $4.359 75 \times 10^{-18}$ J; $1 a_0 = 5.2918 \times 10^{-11}$ m.

Figure 1. Potential energy curve for the $X^2\Sigma^+$ state of BeF, including calculated vibrational levels.

repulsive. A similar trend was also observed by Roach and Kuntz [16] but not by Marian [17]. Considering that 42 reference state functions were used by Marian to generate the CI wavefunction in the crossing region, compared to ten in this work, one can certainly explain the reason for such discrepancies. Marian was mainly interested in the calculation of the spin-orbit couplings. Besides this fact, it is known that the $X^2\Sigma^+$ and $A^2\Pi$ states have the same dissociation limit, however a calculated splitting of $\sim 1000\text{ cm}^{-1}$ is observed, with the $A^2\Pi$ state lower in energy. Since the molecular orbitals used in the $X^2\Sigma^+$ state energy calculation are those generated in a calculation for the $A^2\Pi$ state, the discrepancy between this work and that of [17] can also be attributed in part to a basis set deficiency.

The calculated differences in vibrational energies are listed in table 2 together with the available experimental data which were obtained from the heads of the Q_1^x branches reported in [24]. Notice that the agreement of our results with these data is very good, the average deviation being 15 cm^{-1} .

With the purpose of checking the arguments presented in [16] questioning the validity of the spectroscopic determination of the dissociation energy, based on their valence bond calculation of the potential energy and vibrational levels, the vibrational spacings of table 2 were next plotted as a function of the vibrational quantum number v in figure 2. The graph also shows the straight line obtained by extrapolation of the first 16 spacings (number of available experimental points) and also the extrapolation of the curve passing through all the vibrational spacings. The Birge-Sponer procedure yields values for D_0 equal to 5.96 eV and 5.54 eV , respectively for the theoretical and for the experimental data. These values should be contrasted

Table 2. Comparison of calculated and observed vibrational level spacings (in cm^{-1}), $G(v+1) - G(v)$, for the $X^2\Sigma^+$ state of BeF.[†]

v	This work	Exp. [24]	v	This work	Exp. [24]
0	1255.6	1247.2	13	1041.3	1020.2
1	1239.5	1229.0	14	1024.4	1003.7
2	1221.6	1210.8	15	1007.7	987.4
3	1202.9	1192.8	16	991.5	
4	1184.8	1175.0	17	975.7	
5	1167.7	1157.4	18	960.4	
6	1151.9	1139.5	19	945.6	
7	1136.6	1122.2	20	931.3	
8	1121.4	1104.9	21	917.5	
9	1106.2	1086.8	22	904.0	
10	1090.6	1070.6	23	890.8	
11	1074.6	1053.7	24	877.8	
12	1058.2	1036.9	25	865.1	

[†] $G(0) = 634.4 \text{ cm}^{-1}$

with the poor result of 3.94 eV for D_e reported in [16] and also with the mass spectrometric result of Hildenbrand and Murad, 5.85 eV [22]. Although the Birge-Sponer linear extrapolation is sensitive to the shape of the potential energy curve and leads in general to overestimated values, a glance at figure 2 shows clearly that the areas under both curves are approximately equal, a fact that makes the reported experimental spectroscopic result [19–21] accidentally very close to the true value. In this work, the dissociation energy (D_0) calculated from the computed energies at $R = 25.0 a_0$ and $R = R_e = 2.591 a_0$ and the zero point energy (634.4 cm^{-1}) gives 5.92 eV ($D_e = 6.00 \text{ eV}$). This result is in excellent agreement with the value of 5.94 eV

Figure 2. Theoretical vibrational energy spacings as a function of v of the BeF molecule in the $X^2\Sigma^+$ state.

Table 3. Self-consistent field and singles and doubles configuration interaction energies for Be, F and BeF, including also ghost orbitals. Energies are given in hartree. For BeF and the ghost orbitals calculations the internuclear distance is $2.572 a_0$.

	SCF	CI
Be	-14.572 246	-14.616 844
F	-99.409 973	-99.526 514
Be + ghost	-14.572 252	-14.617 134
F + ghost	-99.410 016	-99.526 694
BeF	-114.166 371	-114.341 087
D_e	0.184 151	0.197 722
$D_e(\text{ghost})$	0.184 103	0.197 252
BSSE (in eV)	0.001	0.013

obtained by Langhoff *et al.* [18] in a recent study where a methodology which combines experimental data and theoretical energies is successfully tested for the determination of the dissociation energies of the alkali and alkali-earth monofluorides and monochlorides. Arguments presented in references [15] and [18] and quoted works therein indicate that a saturation of the one-particle and n -particle bases might increase D_e by approximately 0.3 eV.

If the long range energy is corrected by the difference observed between the $X^2\Sigma^+$ and $A^2\Pi$ states the new D_0 obtained, 5.80 eV, is still quite concordant with that of [22]. An estimate of the correction for basis set superposition error (BSSE) was carried out using the counterpoise method [30]. To avoid truncating the CI expansion due to size limitation of the computer central processing unit this estimate was based in a single-reference function singles and doubles CI. The results are presented in table 3. Note that at the Hartree-Fock level the BSSE is practically non-existent, whereas at the CI level it amounts to about 0.01 eV.

3.2. The dipole moment function, averaged dipole moments, radiative transition probabilities and lifetimes

The dipole moments for internuclear distances ranging from 1.8 to $10.0 a_0$ of the $X^2\Sigma^+$ state are listed in table 4 and plotted in figure 3. As expected the dipole

Table 4. The dipole moment function $\mu(R)$ (in a.u.) for the beryllium monofluoride in the $X^2\Sigma^+$ state.†‡

$R(a_0)$	$\mu(R)$	$R(a_0)$	$\mu(R)$	$R(a_0)$	$\mu(R)$
1.8	0.1963	2.8	-0.6722	5.0	-2.7501
1.9	0.1233	2.9	-0.7710	5.5	-3.1396
2.0	0.0479	3.0	-0.8710	5.8	-2.1483
2.1	-0.0329	3.2	-1.0747	6.0	-1.5309
2.2	-0.1164	3.5	-1.3821	6.5	-0.4063
2.3	-0.2036	3.7	-1.5901	7.0	0.0104
2.4	-0.2937	4.0	-1.8981	8.0	0.1528
2.5	-0.3861	4.2	-2.0933	10.0	0.1081
2.6	-0.4793	4.5	-2.3673		
2.7	-0.5755	4.8	-2.6056		

† 1 a.u. = $2.5418 D = 8.4784 \times 10^{-30} \text{ C m}$.

‡ $\mu(\text{SDCI}) = 0.4450 \text{ a.u.}$, $\mu(\text{CPF}) = 0.4273 \text{ a.u.}$ at $R = 2.572 a_0$, [15].

Figure 3. The dipole moment function (in $e a_0$) of the BeF molecule in the $X^2\Sigma^+$ state.

moment approaches zero for large internuclear distances, reflecting the fact that the molecule dissociates to neutral species in this state. In the intermediate region, the dipole moment function takes on negatively increasing values until about $5.5 a_0$ where, due to an avoided crossing of the $X^2\Sigma^+$ and $B^2\Sigma^+$ potential curves, it abruptly changes, decreasing then to zero to allow for the proper dissociation to Be(1S) and F(2P). In all that region the molecule has the polarity $\text{Be}^+ \text{F}^-$.

No experimental data were found for comparison, and the only theoretical values are 1.131 D ($0.445 e a_0$) and 1.086 D ($0.427 e a_0$) calculated at the experimental R ($2.572 a_0$) by the SDCI and CPF approaches, respectively [15]. Although we have no dipole moment calculated at this point, the SDCI value of Langhoff *et al.* [15] fits perfectly the curve shown in figure 3. It is also worth pointing out here the striking similarity of this curve with the one reported by Larsson [7] and by Cooper [31] for the $X^2\Sigma^+$ state of BeH, where the same kind of avoided crossing, as observed here, gives that curve its final shape.

With the dipole moment function obtained in this work, the dipole moment matrix elements involving the upper and lower vibrational states were computed and therefrom the radiative transition probability as given by the expression

$$A_{kl} = 7.25356 \times 10^{-6} \nu_{kl}^3 |\mu_{kl}|^2.$$

For μ_{kl} given in units of $e \text{Å}$ and ν_{kl} given in cm^{-1} , the above constant is the conversion factor necessary to express A_{kl} in s^{-1} [4–6, 9].

The vibrationally averaged dipole moment for the system in the k th state is simply given by the expectation value $\mu_{kk} = \langle \mu \rangle$. Values of $\langle \mu \rangle$ for several vibrational levels and $J' = J'' = 0, 1, 5$ and 10 are given in table 5. Almost no dependence on the rotational levels is observed.

Table 5. The dipole moment expectation values in ($e \text{ \AA}$) for selected vibrational and rotational levels in the $X^2\Sigma^+$ state of the BeF molecule.†

v	$J = 0$	$J = 1$	$J = 5$	$J = 10$
0	-0.2537	-0.2537	-0.2538	-0.2544
1	-0.2675	-0.2675	-0.2676	-0.2682
2	-0.2805	-0.2805	-0.2806	-0.2812
3	-0.2936	-0.2936	-0.2938	-0.2943
4	-0.3071	-0.3071	-0.3073	-0.3079
5	-0.3209	-0.3210	-0.3211	-0.3217
6	-0.3349	-0.3350	-0.3351	-0.3357
7	-0.3489	-0.3489	-0.3491	-0.3497
8	-0.3628	-0.3629	-0.3630	-0.3636
9	-0.3766	-0.3767	-0.3768	-0.3775
14	-0.4477	-0.4477	-0.4479	-0.4486
19	-0.5293	-0.5293	-0.5295	-0.5301
24	-0.6162	-0.6162	-0.6164	-0.6171

† $1 e \text{ \AA} = 4.8033 \text{ D} = 1.6022 \times 10^{-29} \text{ C m}$.

The radiative lifetimes $\tau_{v', J'}$ can be obtained as the reciprocals of the Einstein $A_{v', J'}$ coefficients, which are given by the expression

$$A_{v', J'} = \frac{1}{2J' + 1} \left\{ J' \sum_{v''=0}^{v'} A_{v', J'; v'', J'-1} + (J' + 1) \sum_{v''=0}^{v'-1} A_{v', J'; v'', J'+1} \right\}.$$

The relevant information for absorption and emission processes is collected in table 6. The upper right section of this table brings the dipole moment function matrix elements $\mu_{v', 0; v'', 1}$ for v' up to 12 and the lower left section contains the Einstein spontaneous emission coefficients $A_{v', 0; v'', 1}$. The diagonal elements are the pure rotational matrix elements $\mu_{v', 0; v'', 1}$. For the states shown in table 6 the fundamental transitions are the strongest both in emission and absorption. Overtones make significant contributions for high ($v > 5$) vibrational levels.

Total transition probabilities for emission and spontaneous radiative lifetimes (see table 7) show that the dependence of the radiative lifetime on the rotational state ($J = 0, 1, 5$ and 10) is significant only for the first vibrational level, being practically constant within other levels. For the levels studied (about 25) the radiative lifetime decreases almost monotonically, the slight deviation being the levels 18, 19 and 20. Previous studies on LiH [1], BeH⁺ [5] and CH⁺ [9] have shown that the radiative lifetime decreases up to a certain level and then increases.

3.3. Spectroscopic constants

From the experimental [24] and theoretical vibrational levels, spectroscopic constants were obtained by a least squares fit of the expression [19] below to the corresponding levels spacings

$$\Delta G_{v+1/2} = \omega_e - 2\omega_e x_e(v+1) + \omega_e y_e[1 + 3(v + \frac{1}{2}) + 3(v + \frac{1}{2})^2].$$

The constants ω_e , $\omega_e x_e$ and $\omega_e y_e$ are collected in table 8.

Table 6. Dipole moment absorption matrix elements $\mu_{v',0;v'',1}$ (in $e\text{\AA}$ units†, in upper right and pure rotational transitions on the diagonal) and Einstein A spontaneous emission coefficients $A_{v',0;v'',1}$ (in s^{-1} units, in lower left) for the $X^2\Sigma^+ - X^2\Sigma^+$ bands of BeF.

Initial state $v' (J' = 0)$	Final state $v'' (J'' = 1)$						
	0	1	2	3	4	5	6
0	-0.25367	-0.04417	0.00247	-0.00024	0.00009	-0.000116	0.000063
1	2.7850 (1)	-0.267469	-0.062791	0.004301	-0.000617	0.000170	-0.000056
2	0.678989	5.4154 (1)	-0.280469	-0.07757	0.006075	-0.000857	0.000138
3	2.1889 (-2)	1.9661 (0)	7.9107 (1)	-0.293593	-0.090151	0.007757	-0.000996
4	7.5351 (-3)	1.3319 (-1)	3.7509 (0)	1.0206 (2)	-0.307107	-0.101264	0.009280
5	2.2028 (-2)	2.3589 (-2)	2.4525 (-1)	5.8398 (0)	1.2307 (2)	-0.320948	-0.111381
6	1.0895 (-2)	4.8160 (-3)	1.4648 (-1)	3.1520 (-1)	7.9924 (0)	1.4256 (2)	-0.334938
7	6.4029 (-3)	2.2637 (-3)	9.0242 (-3)	1.3577 (-4)	3.8619 (-1)	1.0435 (1)	1.6103 (2)
8	6.2356 (-2)	5.7883 (-2)	9.1545 (-2)	7.9114 (-2)	7.0434 (-3)	5.4120 (-1)	1.3473 (1)
9	6.7333 (-2)	1.7664 (-1)	2.027 (-1)	1.8875 (-1)	1.3244 (-1)	2.1941 (-4)	9.0033 (-1)
10	1.4593 (-2)	1.7137 (-1)	2.0671 (-1)	2.2304 (-1)	1.4654 (-1)	6.0680 (-2)	4.8428 (-2)
11	2.5164 (-3)	2.2351 (-2)	7.9237 (-2)	9.2514 (-2)	5.3191 (-2)	1.2863 (-2)	4.5343 (-3)
12	2.6521 (-2)	5.6048 (-2)	5.9082 (-3)	5.1378 (-3)	1.0411 (-2)	5.1700 (-2)	9.8238 (-2)

Initial state $v' (J' = 0)$	Final state $v'' (J'' = 1)$					
	7	8	9	10	11	12
0	0.000038	-0.000099	0.000087	-0.000035	-0.000013	0.000037
1	-0.000029	0.000118	-0.000171	0.000143	-0.000044	-0.000061
2	0.000077	-0.000189	0.000225	-0.000189	0.000099	0.000023
3	-0.000011	0.000234	-0.000278	0.000242	-0.000129	-0.000026
4	-0.001128	-0.000096	0.000309	-0.000250	0.000121	0.000044
5	0.010831	-0.001364	-0.000014	0.000213	-0.000076	-0.000121
6	-0.120821	0.012558	-0.001794	0.000275	-0.000061	0.000214
7	-0.348919	-0.129862	0.014546	0.002429	0.000729	-0.000462
8	1.7873 (2)	-0.362827	-0.138645	0.016762	-0.003226	0.001251
9	1.7370 (1)	1.9571 (2)	-0.376641	-0.147220	0.019101	-0.004085
10	1.5906 (0)	2.2160 (1)	2.1186 (2)	-0.390404	-0.155591	0.021443
11	3.3305 (-1)	2.6976 (0)	2.7610 (0)	2.2681 (2)	-0.404248	-0.163711
12	2.5826 (-1)	9.4613 (-1)	4.1519 (0)	3.3330 (1)	2.4024 (2)	-0.418326

† $1e\text{\AA} = 4.8033\text{D} = 1.6022 \times 10^{-29}\text{Cm}$.

Table 7. Total transition probabilities for emission (in s^{-1}) and spontaneous radiative lifetimes (in ms) calculated for various (v' , J') levels of the BeF molecule in the $X^2\Sigma^+$ state.

v	$A_{v',0}$	$A_{v',1}$	$A_{v',5}$	$A_{v',10}$	$\tau_{v',0}$	$\tau_{v',1}$	$\tau_{v',5}$	$\tau_{v',10}$
0	—	3.888(−6)	6.631(−4)	5.567(−3)	∞	2.572(8)	1.508(6)	1.796(5)
1	27.85	27.84	27.83	27.79	27.79	35.91	35.93	35.98
2	54.83	54.83	54.80	54.72	18.24	18.24	18.25	18.27
3	81.10	81.09	81.05	80.93	12.33	12.33	12.34	12.36
4	105.95	105.96	105.90	105.75	9.44	9.44	9.44	9.46
5	129.20	129.20	129.14	128.98	7.74	7.74	7.74	7.75
6	151.03	150.89	150.83	150.65	6.62	6.63	6.63	6.64
7	171.87	171.86	171.78	171.55	5.82	5.82	5.82	5.83
8	193.04	193.04	192.92	192.59	5.18	5.18	5.18	5.19
9	214.75	214.74	214.58	214.15	4.66	4.66	4.66	4.67
14	325.77	325.74	325.37	324.29	3.07	3.07	3.07	3.08
17	360.47	360.49	360.81	361.66	2.77	2.77	2.77	2.77
18	352.09	352.12	352.59	353.92	2.84	2.84	2.84	2.83
19	345.69	345.70	345.85	346.40	2.89	2.89	2.89	2.89
20	358.87	358.81	357.99	355.87	2.79	2.79	2.79	2.81
21	409.86	409.68	407.20	400.50	2.44	2.44	2.46	2.50
24	851.32	850.64	842.64	820.00	1.17	1.18	1.19	1.22

The differences between adjacent rotational levels for a given vibrational level are given by the expression [19]

$$F_v(J+1) - F_v(J) = 2(J+1)B_v - 4(J+1)^3D_v.$$

A least squares fit of this expression to the theoretical differences gives the values of B_v and D_v which are listed in table 9. Fourteen rotational levels have been used at all for each vibrational level.

Table 8. Theoretical and experimental spectroscopic constants (in cm^{-1}) as a function of the number of vibrational levels spacings for the BeF molecule in the $X^2\Sigma^+$ state.

No. of levels spacings	ω_e		$\omega_e x_e$		$\omega_e y_e$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
3	1265.4	1269.8	9.10	6.65	0.0	−0.3067
4	1265.6	1270.6	9.20	7.15	0.0167	−0.2183
5	1265.6	1271.9	9.24	7.85	0.0238	−0.1167
6	1265.7	1273.2	9.27	8.50	0.0274	−0.0371
7	1265.5	1274.5	9.20	9.06	0.0194	0.0237
8	1265.6	1275.4	9.22	9.42	0.0212	0.0580
9	1265.6	1275.9	9.23	9.59	0.0221	0.0726
10	1265.3	1276.0	9.14	9.62	0.0155	0.0751
11	1265.6	1275.7	9.21	9.55	0.0200	0.0698
12	1265.7	1275.2	9.24	9.40	0.0221	0.0601
13	1265.7	1274.5	9.25	9.21	0.0230	0.0486
14	1265.7	1273.7	9.26	9.01	0.0231	0.0372
15	1265.7	1272.8	9.26	8.82	0.0232	0.0271
16	1265.8	1272.1	9.26	8.66	0.0233	0.0194

Table 9. Rotational constants for BeF (in cm^{-1}) in the $X^2\Sigma^+$ state.

v	B_v	$D_v(\times 10^{-6})$
0	1.463	7.367
1	1.444	7.630
2	1.427	7.647
3	1.411	7.419
4	1.394	7.366
5	1.377	6.406
6	1.361	7.506
7	1.345	6.988
8	1.329	7.366
9	1.313	7.688
10	1.297	6.406

Finally, a least squares fit of the calculated B_v and D_v values to the expressions [19]

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma(v + \frac{1}{2})^2,$$

$$D_v = D_e - \beta_e(v + \frac{1}{2}),$$

allows for the calculation of the remaining spectroscopic constants B_e , α_e , γ , D_e and β_e which are collected in table 10.

The routine ICSUKU from the IMS library [32] has been used in all the least square fits.

The data in table 8 show how sensitive the spectroscopic constants are relative to the number of points used in the fitting procedure and the care one must take when comparing experimental and theoretical results. Similar observations have been reported before for LiH [1], BeH [7] and BeH⁺ [33]. Experimental results reported by Novikov and Gurvich [34] based on the data of Tatevskii *et al.* [24] give: $\omega_e = 1265.9 \text{ cm}^{-1}$, $\omega_e x_e = 9.35 \text{ cm}^{-1}$ and $\omega_e y_e = 0.033 \text{ cm}^{-1}$. The available theoretical values are: $\omega_e = 1258 \text{ cm}^{-1}$, $\omega_e x_e = 8.8 \text{ cm}^{-1}$ [17], $\omega_e = 1250 \text{ cm}^{-1}$, using a SDCI wavefunction [15] and $\omega_e = 1239 \text{ cm}^{-1}$ using the coupled pair functional (CPF) approach [15]. The latter values were based on a parabolic fit (in $1/r$) to the lowest energy points on a 0.1 bohr grid. Based on the fitting involving all the experimental spacings we come out with the following values for the spectroscopic constants: $\omega_e = 1265.7 \text{ cm}^{-1}$, $\omega_e x_e = 9.26 \text{ cm}^{-1}$ and $\omega_e y_e = 0.0233 \text{ cm}^{-1}$. The small discrepancy between our theoretical values and the experimental ones, and the 10–20 cm^{-1} error between the theoretical and experimental vibrational levels seem to indicate that the right-hand side of our calculated potential curve is slightly steeper than it should be.

To the best of our knowledge no explicit B_v and D_v values are available in the literature for a comparison with this work. For remaining constants the agreement is good in general, with the exception of β_e , which due to its very small magnitude has an inherent large error.

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Table 10. Theoretical and experimental spectroscopic constants for BeF in the $X^2\Sigma^+$ state†.

	This work	Exp. [34]	Exp. [24]	Exp. [21]	Exp. [19]	Theor. [17]	Theor. [15]
B_e	1.469	1.4911	1.4793	1.489	1.4889	1.472	
α_e	1.692(-2)	1.7(-2)	1.685(-2)	1.76(-2)	1.76(-2)		
γ	6.424(-5)						
D_e	7.730(-6)	0.58(-6)	8.209(-6)		8.28(-6)		
β_e	-5.451(-8)		2.903(-8)				
R_e	2.591	2.572					2.577‡/2.583§

† With the exception of R_e , given in a_0 ($1 a_0 = 5.2918 \times 10^{-11}$ m) all the constants are given in cm^{-1} .

‡ SDCI.

§ CPF.

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Abordagens Ab Initio e Semi-Empíricas a Sistemas Poliatômicos :

Acetonas Substituídas, Mercaptoetanol, $\text{H}_2\text{P}_2\text{F}_2$,

Nitroanilinas Substituídas e P_2O

Artigos

Conformational Studies of α -Substituted Carbonyl Compounds by the Molecular Orbital Method CNDO/2

F. R. Ornellas e P. R. Olivato, *Rev. Bras. Fis.*, **15**, 235-246 (1985)

A Theoretical Study of the Intramolecular Hydrogen Bond in 2-Mercaptoethanol

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Phosphinodifluorophosphine ($\text{H}_2\text{P}_2\text{F}_2$) : Is There a Stable Gauche Conformer ?

An Ab Initio Study

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Teorias Moleculares do Sabor Doce. Análise do Modelo de Shallenberger via Cálculos Mecânico-Quânticos de Propriedades Moleculares das 2-R-5-Nitroanilinas

Orlando Roberto Neto e F. R. Ornellas, *Química Nova*, **11**, 272-274 (1988)

An Ab Initio Study of the Molecules P_2O and P_2O^+

F. R. Ornellas e A. J. A. Aquino, *Theor. Chim. Acta (Berlim)*, aceito para publicação, 1990.

Os trabalhos aqui abordados situam-se, em termos de rigor quantitativo na sua descrição, em situações intermediárias ou opostas às já vistas para os sistemas diatômicos. Obviamente, a relativa complexidade desses sistemas delimita a metodologia que pode ser empregada. Em quase todos eles, o problema dos possíveis arranjos conformacionais da molécula é o ponto central do trabalho. No caso das acetonas substituídas empregamos o método semi-empírico CNDO/2, que também foi usado para o estudo do 2-mercaptoetanol, juntamente com o método Hartree-Fock-Roothaan com uma base mínima do tipo STO-4G.

Embora para problemas conformacionais muitos autores justifiquem o uso de cálculos não correlacionados argumentando que, não havendo quebra de ligações, os erros devido à correlação eletrônica se cancelam, o que é observado num grande número de casos, a escolha da base atômica, entretanto, é um fator crucial, e o terceiro artigo sobre a fosfinodifluorofosfina ilustra claramente esse ponto.

O trabalho sobre as nitroanilinas substituídas, parte da dissertação de mestrado do aluno Orlando Roberto Neto, é representativo de uma incursão que fizemos na área das relações entre estrutura e atividade de uma molécula, com ênfase nas suas propriedades edulcorantes. Nele, a análise de vários cálculos leva-nos a apresentar argumentos que não apoiam a hipótese convencional de Shallenberger para a interação de uma substância edulcorante com seu sítio receptor. Esse artigo, juntamente com a dissertação de mestrado que lhe originou, constituem certamente o que de mais completo existe publicado sobre os aspectos estruturais e eletrônicos dessa classe de compostos.

Relativamente à molécula P_2O , ela nos traz uma ponta de orgulho, pois chegamos a postular sua existência por analogia com a espécie N_2O . Sua descrição, bem como a do íon P_2O^+ , é bem mais rigorosa que a dos casos anteriores, trazendo inclusive um tratamento a nível de cálculo interação de configurações. Este é um caso em que as enormes dificuldades existentes para a execução dos programas afetou de forma significativa o andamento do trabalho e nos tiraram o privilégio de termos registrados oficialmente nossos nomes como

os proponentes da molécula. Entretanto, mesmo assim, na sua forma presente, é o estudo teórico com a descrição mais completa sobre esses sistemas. Juntamente com as moléculas N_2S , N_2S^+ e N_2O , esse trabalho é parte da tese de doutorado da aluna Adélia J. A. Aquino sob nossa orientação.

Hoje, ao escolhermos um problema para estudo, nossa filosofia tem sido decidir sobre aquele em que possamos tratá-lo da forma ab initio, preferencialmente, com bases estendidas. A experiência que tivemos com os casos acima e outros mais faz-nos sentirmos muito mais seguros com os resultados dos cálculos ab initio pois, em caso de problemas, o direcionamento a ser dado neles é bem mais claro.

Com a recente instalação de um supercomputador no Centro de Computação Eletrônica desta Universidade, a perspectiva de se estudar novos sistemas é bem mais ampla, entretanto, nosso guia na escolha e descrição de um problema será o rigor que poderemos dar a seu tratamento teórico, pois esse é, segundo nosso ponto de vista, um dos caminhos para que nossos trabalhos venham a ter aceitação internacional.

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Conformational Studies of α -Substituted Carbonyl Compounds by the Molecular Orbital Method CNDO/2

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Abstract Within the framework of the CNDO/2 method, the energies and dipole moments computed as a function of a rotation angle are used to analyse the population ratios of *cis* and *gauche* conformers of five α -substituted acetones. The polar solvent effect is taken into account via a supermolecule model. UV and IR frequency shifts are discussed in terms of energy levels and hyperconjugation, respectively.

1. INTRODUCTION

Recently, Olivato¹ and coworkers have performed a systematic conformational analysis of some α -substituted acetones by IR measurements in solvents of increasing polarity and by UV measurements of the $n \rightarrow \pi^*$ carbonyl transitions in *n*-hexane. Their paper attempts to offer a qualitative explanation for both the relative stabilities of the *cis* and *gauche* conformers and for the carbonyl frequency shifts of both rotamers in relation to the parent compound. Moreover, the energies of the $n \rightarrow \pi^*$ transitions of the carbonyl group are discussed as well as the corresponding band intensities.

In this paper we have attempted to discuss Olivato *et al.*¹ conformational ratios and frequency shifts on more quantitative grounds using the molecular orbital method CNDO/2 as developed by Pople² and coworkers. Due to the parametrization restriction existent in the CNDO/2 version distributed by QCPE³, only five α -substituted acetones, namely, fluoroacetone, chloroacetone, methoxyacetone, ethylthioacetone, and dimethylaminoacetone have been studied in this paper although experimental results are available for bromoacetone and iodoacetone also.

2. THE CALCULATION

With the exception of fluoroacetone⁸, experimentally determined geometries were found for these molecules. In trying to use a consistent set of atomic coordinates for these molecules, the decision was made to use that geometry that minimizes the energy in the CNDO/2 approximation. Only interatomic distances considered as relevant were varied in this minimization process. They are the carbon-oxygen distance in the carbonyl group, the carbon-heteroatom, and the carbon-carbon bonds. Standard tetrahedral (109.5°) and trigonal (120°) angles were employed were needed. Carbon-hydrogen bonds were set equal to 1.095 Å. The calculated distances for the fluoroacetone for which experimental distances were found are: $R(C-C) = 1.46 \text{ Å}$ (1.507 Å), $R(C=O) = 1.27 \text{ Å}$ (1.222 Å), $R(C-F) = 1.35 \text{ Å}$ (1.398 Å); the values in parenthesis are the experimental ones. Note that there is an error smaller than 4% in the calculated distances.

Within two decimals precision the optimum values for the carbon-oxygen and carbon-carbon distances in the compounds were found to be the same as the ones quoted above. The other calculated distances are: Carbon-chlorine, 1.67 Å; carbon-nitrogen, 1.42 Å; carbon-oxygen (methoxy-group), 1.38 Å; and carbon-sulphur, 1.75 Å.

For the geometry given in Fig. 1, the energy and the dipole moment for every molecular species as a function of the rotation angle (ϕ) were computed and are graphically displayed in Figs. 2 and 3, respectively. In Fig. 2 the energy of the most stable conformer was chosen as the zero of energy, so that these curves can be seen as rotational barriers.

Fig.1 - The dihedral (rotation) angle ϕ .

Fig.2 - The energy as a function of the rotation angle: — fluoroacetone; --- chloroacetone; -.-dimethylaminoacetone; ——— methoxyacetone; ethylthioacetone.

3. RESULTS AND DISCUSSION

A. Conformational analysis

The rotational barriers shown in Fig. 2 clearly indicate that the energetically favourable geometries are the ones corresponding to molecules in the gauche (trans) conformation. The curves for fluoroacetone and methoxyacetone exhibit each two deep minima, the lowest one around 180° and the highest one around 0° . These minima are separated by relatively high barriers (about 6 kcal/mol for fluoroacetone and about 3.8 kcal/mol for methoxyacetone). The curve for ethylthioacetone shows a very wide minimum in the region $135^\circ < \phi < 215^\circ$, and a high maxi-

Fig. 3 - The dipole moment as a function of the rotation angle: — fluoroacetone; --- chloroacetone; dimethylaminoacetone; -...- methoxyacetone; ethylthioacetone.

mum of about 4.2 kcal/mol around $\phi=0$. Notice in Table 1 that fluoroacetone (the highest barrier) and ethylthioacetone (high barrier and wide minimum) are the compounds with the smallest (0.07) cis/gauche ratios. For chloroacetone, besides the global minimum at about $\phi=180^\circ$, only a very shallow and relatively high minimum around $\phi=0^\circ$ is predicted by the CN00/2 calculation. The approximate nature of the molecular orbital approach being used makes it difficult to tell whether the non-existence of a more pronounced minimum around $\phi=0^\circ$ for the two compounds with second row elements (S, Cl) is a fact of nature or an artifact of the CN00/2 method. Finally, dimethylaminoacetone shows the least energetic rotational barrier. Its height is only 0.5 kcal/mol, but its minimum

Table 1 - Conformational population ratios of some α -substituted acetones.

	This work	CIS/GAUCHE RATIO	
		Exp. ^a	Exp. ^b
Fluoroacetone	0.064	0.07	1.81
Chloroacetone	0.012	0.22	0.53
Dimethylaminoacetone	0.454	0.29	1.57
Ethylthioacetone	0.047	0.07	0.23
Methoxyacetone	0.105	0.19	1.86

a) Non-polar solvent, *n*-hexane, Ref. (1). b) Polar solvent, chloroform, Ref. (1).

extends practically from $\phi=115^\circ$ to $\phi=245^\circ$. This molecule shows the highest (0.29) *cis/gauche* ratio, but the *gauche* conformation is still the dominant one.

Experimentally, Olivato *et al*¹ defined a *cis/gauche* ratio as the ratio of the apparent molar absorptivities at the absorption maxima of the carbonyl stretching bands observed in the IR spectra. Can the *cis/gauche* ratio be inferred from our calculations? It is expected that the ratio of the probability of finding the molecule with an angle ϕ ranging from 0° to 90° over the probability of finding the molecule with an angle ϕ ranging from 90° to $\phi=180^\circ$ can approximately give the observed ratios of Olivato *et al*¹. This probability was estimated using the standard Boltzmann distribution

$$P(\phi) = \int_0^{\phi^1} \exp[-E(\phi)/kT] d\phi / \int_0^{180} \exp[-E(\phi)/kT] d\phi$$

where, k is the Boltzmann constant, T the temperature, assumed equal to 300 K, and $E(\phi)$ is the energy as a function of the rotation angle ϕ as given in Fig. 2. An analytical expression for $E(\phi)$ was obtained using a least square fit, and the integrals were solved numerically. The calculated ratios are collected in Table 1, which also shows the experimental results of Olivato *et al*¹.

The quantitative agreement with experimental results is poor,

specially for chloroacetone, however the *gauche* conformation is predicted to be the preferred one in non-polar solvents, in qualitative agreement with the experimental trend. In the particular case of chloroacetone, this failure can certainly in part be attributed to parametrization problems in the CNDO/2 method. The overall results, however, may indicate that other factors besides free molecule rotation barrier must play an important role in the determination of the *cis-gauche* ratio.

In a polar solvent the experimental data show a reversion in the ratios for methoxyacetone, fluoroacetone, and dimethylaminoacetone, implying now a predominance of the *cis* conformation, while for chloroacetone and ethylthioacetone there is still a preference for the *gauche* conformation, although there has been an increase in the population of the *cis* conformer.

At first, one might be tempted to say that this reversion in the ratios can be attributed to the dipole-dipole interaction between solvent and solute. A glance at Fig. 3 shows, however, that all five species have about the same dipole moment at small values of the rotation angle. These data imply that the dipole-dipole interaction is certainly not the major effect responsible for the stabilization of the *cis* conformer relative to the *gauche* one.

The next step was to investigate how hydrogen bonding affects the stabilization of both conformers. Only hydrogen binding to the carbonyl oxygen was investigated, and fluoroacetone was taken as the prototype molecule. The approach used was the supermolecule method as extensively used by Pullmann⁵ and coworkers. Essentially, one views the fluoroacetone and the chloroform molecule as a single unit forming a "supermolecule", as shown in Fig. 4.

The energy of the system is then calculated as a function of the angle α between the line joining the atoms C and H in the chloroform molecule, and the line joining the atoms C and O in fluoroacetone. Fig. 5 shows this energy for both *cis* and *gauche* conformers and for the oxygen and hydrogen atoms 1.70 Å apart. The energy curve in Fig. 5 clearly indicates that *cis* conformation is energetically favoured when hydrogen bonding is taken into account. An energy minimum occurs at $\alpha \sim 75^\circ$ for the *cis* conformer, and at $\alpha \sim 85^\circ$ for the *gauche* one. Obviously, the carbonyl is not the only site for hydrogen bonding. The heteroatom can

Fig. 4 - The "supermolecule": α -substituted acetone-chloroform.

Fig.5 - Relative energies of the *cis* and *trans* conformers of the supermolecule fluoroacetone-chloroform.

also play such a role, and in fact the data in Table 1 seem to be consistent with the view that a second chloroform molecule is interacting via hydrogen bonding with the heteroatom. The stronger the binding the more stable the supermolecule, and it is a well known fact that the strength of a hydrogen bond is greater when O, F and N atoms are involved in the binding, then when Cl and S are the atoms involved. Therefore, although a single chloroform molecule hydrogen bonded to the carbonyl oxygen stabilizes the *cis* conformer relative to the *gauche* one, it is certainly the strength of a second hydrogen bond involving the heteroatom that makes the *cis* conformer of the compounds containing the elements F, O, and N much more stable than those involving Cl and S. And this is exactly the trend observed in Table 1.

B. Ultraviolet frequency shifts

Since the energies of two different electronic states should really be known in order to accurately obtain the transition frequency, and since this procedure is impractical for molecules of the size being studied, one frequently resorts to simple models where one hopes to predict at least the general trend of the shifts. One general practice is simply to calculate the difference in energies between the LUMO(π^*_{CO}) and the HOMO (π_0)⁶. If the Coulomb (J_{ij}) and exchange (K_{ij}) integrals over the molecular orbitals are available, the former difference can be corrected upon addition of the term $2K_{ik} - J_{ij}$ ⁷. Even for this latter case, care must be taken in the conclusion since that formula is based on a frozen orbital single configuration description of the excited state, which is often inadequate. In Table 2 are listed the experimentally observed $\pi \rightarrow \pi^*$ frequencies¹ and estimates based on the two approaches mentioned above.

The differences in energies of the LUMO and HOMO are indicative that for fluoroacetone, methoxyacetone and chloroacetone there should be a red shift relative to acetone, whereas for dimethylaminoacetone and ethylthioacetone there should be a blue shift. The blue shift conclusion although in direct conflict with the experimental data is in complete agreement with earlier calculation of Allinger *et al.*⁸ on cyclohexanones. These authors have concluded that the red shift induced in cyclohexanone $\pi \rightarrow \pi^*$ transition by axial halogen substituents

Table 2 - Experimental $\pi \rightarrow \pi^*$ transition energies and estimates based on CNDO/2 method.

	$\nu_{\max}^{**}/\text{cm}^{-1}$	$\Delta E^+/\text{cm}^{-1}$	$\Delta E^{++}/\text{cm}^{-1}$
pentan-2-one	35,842	135,152*	44,393*
fluoroacetone	35,714	134,011	44,266
methoxyacetone	35,335	133,001	45,915
dimethylaminoacetone	34,364	139,168	
chloroacetone	34,364	130,982	59,142
ethylthioacetone	33,222	137,961	

* Calculations done for acetone. ** Experimental Ref. 1. $^+ \Delta E = \epsilon_j - \epsilon_i$. See text. $^{++} \Delta E = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij}$. See text.

is due to an interaction between the carbonyl π_{CO}^* orbital and the $\sigma_{\text{C-X}}^*$ orbital, with a consequent lowering of the π_{CO}^* energy level. This should happen if either X is electronegative ($\sigma_{\text{C-X}}^*$ lower in energy) or if the bond is weak, so that the σ and σ^* energy levels are not very far apart. In Fig. 6 as a function of the rotation angle ϕ are plotted the energy levels of the π_{CO}^* , π_0 , and π_{CO} orbitals. These curves exactly reflect Allinger's *et al.*⁸ conclusion. For fluoroacetone, methoxyacetone, and chloroacetone there is a lowering of the π_{CO}^* energy level, and for dimethylaminoacetone and ethylthioacetone there is a raising of the π_{CO}^* level. We recall that in the Pauling scale, the electronegativities for the heteroatoms are: F (3.98), O (3.44), Cl (3.16), N (3.04), S (2.58) and H (2.20). The results discussed above seem to indicate that conclusions about red or blue shifts based on the lowering or raising of orbital energy levels calculated for the molecule in the ground state should be taken with reserve, specially if approximate methods are involved. The experimental results for dimethylaminoacetone and ethylthioacetone clearly cannot be explained by the approximate model invoked here.

C. Carbonyl stretching frequency shifts

A thorough discussion of the different effects that might be

Fig.6 - Orbital energies as a function of the rotation angle.

involved in the carbonyl stretching frequency shifts in the species considered here has been done by Olivato *et al.*¹. In this section we want to complement his view of a hyperconjugative interaction using information obtained from the molecular orbital calculation.

In Table 3 we have summarized the populations of the 2p atomic orbitals of the carbonyl carbon (π_C) and carbonyl oxygen (π_O), and also the charge on the oxygen (Q_O) for several dihedral angles. There is also a Δ value included which represents the variations of the populations of the 2p atomic orbitals on the carbonyl oxygen and carbonyl carbon in comparison with the corresponding orbitals in fluoroacetone which was taken as the reference compound.

Table 3 - Populations of the $2p\pi$ atomic orbitals of the carbonyl carbon and oxygen atoms (π_C , π_O) and the charge (Q_O) on the carbonyl oxygen (in units of 10^{-3} electrons).

Degree		S	Cl	N	O	F
0°	π_C	0.807	0.817	0.814	0.817	0.823
	π_O	1.274	1.263	1.268	1.262	1.256
	Δ^a	2	3	1	0	0
	Q_O	238	269	279	270	258
90°	π_C	0.797	0.814	0.805	0.818	0.833
	π_O	1.308	1.272	1.278	1.252	1.227
	Δ^a	45	26	23	10	0
	Q_O	308	280	287	272	254
120°	π_C	0.798	0.811	0.808	0.808	0.826
	π_O	1.302	1.273	1.273	1.257	1.240
	Δ^a	34	18	15	6	0
	Q_O	305	281	261	275	286
150°	π_C	0.798	0.805	0.809	0.809	0.814
	π_O	1.294	1.282	1.275	1.273	1.267
	Δ^a	11	6	3	1	0
	Q_O	301	286	289	285	275
180°	π_C	0.797	0.801	0.810	0.805	0.808
	π_O	1.292	1.291	1.277	1.282	1.280
	Δ	1	4	1	1	0
	Q_O	300	292	291	290	283

$$^a = |\pi_O(x) - \pi_O(F)| - |\pi_C(x) - \pi_C(F)|, x = S, Cl, N, O, F$$

One can notice in Table 3 that for the *cis* and *trans* conformers the decrease in population of the $2p\pi$ atomic orbitals on the carbonyl carbon relative to fluoroacetone along the series F, O, N, Cl, S is approximately equal to the increase in the $2p\pi$ atomic orbital population on the carbonyl oxygen. But, one can also notice that as the dihedral angle changes to 150° , 120° and 90° , the decreases in population of the

2p π atomic orbitals on the carbonyl carbon is less than the corresponding increases in the population of the 2p π atomic orbitals on the carbonyl oxygen. This fact, as discussed by Pople⁹, is indicative of a transfer of π -electrons from the CH₂-X group into the carbonyl group by hyperconjugation. This electron transfer is maximum at 90°, and is also more prominent for the S and Cl compounds, and practically inexistent for fluoroacetone. It is noteworthy that this result is well in accord with the estimates of Olivato *et al.*¹ for the frequency shifts (in cm⁻¹) of the carbonyl group due to the hyperconjugation effect ($\Delta\nu_H$) which follows the order F (0.0), O (-2.1), N (-4.2), Cl (-8.1) and S (-15.5).

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Resumo

Através da parametrização do método CNDO/2 foi possível analisar a população relativa dos conformeros *cis* e *gauche* de 5 acetonas α -heterossustituídas, através do cálculo das energias e dos momentos dipolares em função do ângulo de rotação ϕ . O efeito do solvente foi estimado via o modelo de uma supermolécula e os deslocamentos de frequência tanto no U.V. quanto no I.V. são discutidos em termos dos níveis de energia e da hiperconjugação respectivamente.

A THEORETICAL STUDY OF INTRAMOLECULAR HYDROGEN BOND IN 2-MERCAPTOETHANOL

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ABSTRACT

The CNDO/2 and ab initio molecular orbital methods are used to study the conformational structure and the formation of the intramolecular hydrogen bond in 2-mercaptoethanol. The CNDO/2 calculations yield the *Cis* conformation about the C-C (σ , -0°) bond to be more stable, whereas it is sterically unfavored. The ab initio results using the STO-4G basis set were able to predict the experimental conformation.

INTRODUCTION

The conformational structure of 2-mercaptoethanol in its liquid state has been studied by Nardy et al. (1-2) using Raman and Infrared techniques. More recently, Sung and Harmony (3) carried out a gas-phase microwave study of this same structure.

About the C-C bond, in all 1,2-disubstituted ethanes, one obtains various stable *trans* or *gauche* rotamers, while *cis* forms are sterically unfavored. Conformers with lower energy in the *gauche* forms have been attributed to an intramolecular hydrogen bond, as investigated experimentally by Azrak and Wilson (4) in 2-haloethanols.

We have begun a study to verify the evidency for the intramolecular hydrogen bond involving sulfur atoms using the molecular orbital calculation method. In this paper, we discuss the case of 2-mercaptoethanol, describing our calculations performed at the semi-empirical level, using the CNDO/2 (5) method, and at the ab initio level with the program HONDO/5 (6).

THE CALCULATIONS

The 2-mercaptoethanol molecule has the capacity for rotational isomerism about three bonds. We can thus classify the various possible conformers of type *gauche* (G), *cis* (C) and

trans (T) about these bonds, through the dihedrals HS-CC (θ_1), SC-CO (θ_2) and CC-OH (θ_3) as shown in Figure 1. The SCF-MO calculations for the CNDO/2 level as for the ab initio level, using the HONDO/5 program with a minimal STO-4G (7) basis set, have been carried out by varying the dihedral angles θ_1 , θ_2 and θ_3 in steps of 60 degrees.

From the results of the ab initio level calculations using the minimal STO-4G basis set, the six conformers of lower energy were selected. Using these, two more levels of calculation were carried out. On one level, the geometrical optimization was performed using the minimal STO-4G basis set. The other calculations were performed with the split valency 4-31G (8-9) basis set with no geometrical optimization.

The results obtained are compared with the experimental values and discussed in the next section.

Fig. 1 A model showing the dihedral angles in 2 - mercaptoethanol. The dihedral angles (AB-CD) are measured clockwise about the B to C bond.

RESULTS AND DISCUSSION

Figures 2 to 5 and Figures 6 to 9 show the total energy as a function of the dihedral angles θ_1 - θ_2 - θ_3 for the 2-mercaptoethanol molecule when calculated at the ab initio level, using the STO-4G basis set, and at the semi-empirical level, using the CNDO/2 method, respectively. As previously mentioned, the dihedral angles θ_1 - θ_2 - θ_3 were varied in 60 degrees steps. In the figures the curves were visually fitted to the calculated points.

In Figures 6 to 9 we can verify that, for the CNDO/2 results, the cis (C) conformation about C-C ($\theta_2 = 0^\circ$) bond, i. e., trans-cis-cis (TCC) ($\theta_1 = 180^\circ$, $\theta_2 = 0^\circ$ and $\theta_3 = 0^\circ$) seems to

Fig. 2

Fig. 4

Fig. 3

Fig. 5

Figs. 2 to 5 Total Energy as a function of the dihedral angles $\theta_1 - \theta_2 - \theta_3$, for the 2-mercaptoethanol, when calculated for the STO-4G level. In all, $\square$ for $\theta_3 = 0^\circ$, $\circ$ for $\theta_3 = 60^\circ$, Δ for $\theta_3 = 120^\circ$, $\blacksquare$ for $\theta_3 = 180^\circ$, $\bullet$ for $\theta_3 = 240^\circ$ and $\blacktriangle$ for $\theta_3 = 300^\circ$.

Fig. 6

Fig. 8

Fig. 7

Fig. 9

Fig. 6 to 9 as in Figures 2 to 5 except for the CNDO/2 level.

be more stable, whereas this molecular conformation is unfavored from the point of view of steric interactions. At the STO-4G level, Figures 2 to 5 show that the all gauche (GGG) ($\theta_1=60^\circ$, $\theta_2=60^\circ$ and $\theta_3=300^\circ$) conformations are more stable. This greater stability is attributed to the formation of an intramolecular hydrogen bond and this result is in perfect agreement with the experimental results of Sung and Harmony (3) ($\theta_1=67.1^\circ$, $\theta_2=58.3^\circ$ and $\theta_3=307.3^\circ$).

The six conformers of lower energy obtained from the ab initio results using the STO-4G basis set are presented in Table I together with the results obtained using the 4-31G basis set, and those obtained at the STO-4G level with geometrical optimization. As we can verify, all levels of calculations show the same trend for the stability of the conformers studied. The GGG and GTG conformations are found to be more stable, the former being more stable by 502.0, 1725.6 and 420.4 cal/mol for the STO-4G, 4-31G and STO-4G with optimization levels, respectively. These results differ from those obtained experimentally in the liquid-phase (1-2) which suggest the trans conformation to be 600 cal/mol more stable than the gauche one. In gas-phase study of the Sung and Harmony (3), it was not possible to observe the trans isomer, which suggests that it is less stable than indicated by Nandy et al.

From the point of view of steric interactions, the TGT molecular conformation is expected to be the most stable. However, for all levels of calculation, as shown in Table I, this conformation is the least stable.

The results for the dipole moment, given in Table I, do not differ practically when the optimization is performed at the STO-4G level. However, some conformers when calculated at the 4-31G level yield dipole moments approximately 30% larger than those at the STO-4G level. The STO-4G results agree well with the experimental data (3) (1.871D) for the GGG conformation. The semi-empirical, CNDO/2 results behave like those at the 4-31G level, overestimating the dipole moment.

CONCLUSION

From the results presented above, it is apparent that the CNDO/2 method is not adequate to describe the conformational structure of 2-mercaptoethanol and consequently can not be considered to investigate the formation of an intramolecular hydrogen bond in like systems. On other hand, the results in ab initio level with a minimal STO-4G basis set, do not differ from the results with a split valency basis set, and are in perfect agreement with the experimental data (3), i. e., for 2-mercaptoethanol, the ab initio calculations with a minimal basis set were sufficient to reproduce its experimental

conformational structure.

Table I. Energy (hartrees) and Dipole moment (Debye) for 2-mercaptoethanol for some selected conformers

$\theta_1 - \theta_2 - \theta_3$ (Degrees)*	STO-4G not optimizat. (387 sec)†	STO-4G with optimizat. (4520 sec)	4-31G not optimizat. (838 sec)	CNDO/2 (8 sec)
(60.6-59.5-60.6)	-548.64172	-548.64341	-550.88937	-48.1716
60-60-60	1.8357	1.8542	3.1737	3.0854
(60.5-59.5-300.1)	-548.64325	-548.64489	-550.89503	-48.1736
60-60-300	1.6725	1.6994	2.7315	1.6253
(179.7-60.3-180.1)	-548.63877	-548.64073	-550.88712	-48.1743
180-60-180	1.9700	1.9754	3.4059	3.0830
(60.1-179.8-60.1)	-548.64236	-548.64406	-550.89212	-48.1710
60-180-60	1.6091	1.6389	2.4240	1.6929
(60.6-179.8-301.0)	-548.64245	-548.64422	-550.89228	-48.1710
60-180-300	0.6124	0.6397	0.6493	1.6080
(180-180-180)	-548.63920	-548.64161	-550.88877	-48.1734
180-180-180	0.5186	0.5506	0.7048	1.4595

* Values in parenthesis refer to conformers obtained when the optimization were requested.

† CPU time (10)

From these results, it is also dangerous to affirm that the minimal STO-4G basis set calculations are able to describe the preferred conformational structure of the 1,2-disubstituted ethanes, such as ethanedithiol, ethylene glycol, etc. If were to be the case, it would imply a great economy in computational effort, as shown in Table I where the central processing unit (CPU) time (10) is also listed. The computer time using the minimal basis set is two times that using the split valency basis set, while when the geometrical optimization is requested, the computer time rises by a factor of twelve.

Carlsen et. al. (11) in their study of the structure of formamide have shown the necessity of using the double zeta plus polarization basis set in order to reproduce the experimental geometry there. We believe that the use of this basis set would not change our results for 2-mercaptoethanol, but would certainly give us more accurate results. However, the computational effort would be very great. Preliminary studies in ethanedithiol have indicated the need of a basis set more sophisticated than those we have used here.

Finally, we would like to reaffirm that the formation of an intramolecular hydrogen bond is responsible for the stability of the GGG conformer, in detriment of the TGT conformer, which is sterically favored. Observing the OH...S (2.645 Å) and SH...O (3.491 Å) distances in GGG conformer, we

can affirm that the intramolecular hydrogen bond involving the sulphur atom in 2-mercaptoethanol is of type OH...S, i.e., the SH group acts as a donor of the electronic pair.

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PHOSPHINODIFLUOROPHOSPHINE (H_2PPF_2): IS THERE A STABLE GAUCHE CONFORMER? AN AB-INITIO STUDY

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ABSTRACT

The effect of the use of different basis sets on the conformation stability and on the dipole moment of phosphinodifluorophosphine has been studied at the ab-initio HF-SCF-LCAO level. Geometry optimization has been carried out with the 6-31G** basis. Although the *trans* and *gauche* (70.8°) conformers are predicted to be equally stable relative to the *cis* conformer, the small barrier of $0.9 \text{ kcal mol}^{-1}$ for the *gauche*–*trans* interconversion and zero-point energy arguments do not seem to agree with the experimental observation of a stable *gauche* conformer.

INTRODUCTION

The conformation of phosphinodifluorophosphine, H_2PPF_2 , has been predicted experimentally to be *trans* [1]. However, a recent theoretical study [2] with a 6-31G basis set with polarization functions on the phosphorus atoms alone points out that a *gauche* conformation should also be observed because it is equally stable. Since the assumptions made in the experimental study leave open the question whether that is the only possible conformation, they suggest the need for a more accurate experimental investigation of the gas-phase structure of H_2PPF_2 [2].

We have reinvestigated theoretically the existence of a *gauche* conformation by examining the dependence of the conformation and of the dipole moment on the basis set employed, and also the role played by the zero-point energies. Moments of inertia and the components of the dipole moment along the principal axes for the different conformations are also calculated. The possible existence of an intra-molecular hydrogen bond and the participation of *d*-orbitals in bonding are also examined.

Electron correlation effects have not been considered in this study since the results from ref. 2, with a smaller basis set, show that they are small ($\sim 0.2 \text{ kcal mol}^{-1}$) and affect both conformers equally.

METHOD OF CALCULATION

The calculations were based on the Hartree-Fock-Roothaan [3] formalism and used the HONDO/5 set of programs [4]. Five different basis sets have been employed: 4-31G [5], 6-31G [6], 6-31G plus a set of d -functions ($\alpha_P = 0.62$) on the phosphorus atoms alone, 6-31G plus a set of d -functions on the phosphorus and fluorine atoms ($\alpha_P = 0.62$ and $\alpha_F = 0.8$) and finally the 6-31G** set, which comprises the previous set plus a set of p -functions ($\alpha_H = 1.1$) on the hydrogen atoms.

A complete geometry optimization was done only at the 6-31G** level. The optimization was carried out until the components of the gradient were less than 10^{-3} hartree bohr $^{-1}$. For the non-optimized calculations the different conformers have the geometric parameters of the *trans* conformer with exception, of course, of the HPPF dihedral angle. The effect of this constraint is discussed in the next section.

RESULTS AND DISCUSSION

Relative energies and equilibrium geometries

The energy of a conformer relative to the *cis* form and as a function of the dihedral angle is displayed in Fig. 1 for all five basis sets employed.

Figure 1 shows the shift in relative stability going from the 4-31G to the 6-31G** basis sets. Observe that the addition of d -functions on the phosphorus atoms is the main factor responsible for this shift. A further extension

Fig. 1. Energies relative to the *cis* conformer for phosphinodifluorophosphine as a function of the dihedral angle calculated with different basis sets: $\circ$, 4-31G; $\bullet$, 6-31G; $\blacktriangle$, 6-31G (P^*); $\times$ 6-31G (P^* , F^*); $\square$, 6-31G**; and $+$, 6-31G** with geometry optimization.

of the fluorine basis set by a set of *d*-functions and of the hydrogen basis set by a set of *p*-functions causes almost no sensible changes in the relative energies.

Either with the 4-31G or the 6-31G basis, a *gauche* conformer with a dihedral angle of about 65° is predicted to be more stable by approximately 1.8 and 1.0 kcal mol⁻¹, respectively, than the *trans* conformer. The barrier for the *gauche*—*trans* interconversion is about 2.1 and 1.8 kcal mol⁻¹, respectively. With the addition of polarization functions on the phosphorus atoms, the *trans* conformer now becomes more stable than the *gauche* by about 0.6 kcal mol⁻¹. The barrier for the *gauche*—*trans* interconversion is about 1.3 kcal mol⁻¹.

Although the inclusion of polarization functions on the fluorine and hydrogen atoms does not change the relative stability, their relative decrease in energy per atom is about 12.3 and 1.7 kcal mol⁻¹, respectively. The energy decrease per atom is about 576 and 44 kcal mol⁻¹ when going from the 4-31G to the 6-31G basis set, and from the 6-31G to the 6-31G extended with *d*-functions on the phosphorus atoms, respectively.

The energies for some of the optimized geometries calculated at the 6-31G** level are: -881.513285 hartree (*cis*), -881.519069 hartree (*gauche*, 70.8°), -881.518398 hartree (*gauche*, 93.6°), -881.517794 hartree (*gauche*, 134.8°) and -881.519033 hartree (*trans*). This optimization yields a *gauche* (70.8°) and a *trans* conformer lower in energy by 3.63 and 3.61 kcal mol⁻¹ than the *cis* form. Clearly, the *gauche* and *trans* conformers are equally stable, a fact that apparently conflicts with the experimental finding of only

TABLE 1

Optimized and experimental geometric parameters for H₂PPF₂. Angles are given in degrees and bond distances in angstroms^a

Experimental (ref. 1)	<i>Trans</i>		<i>Gauche</i>	
	6-31G** This study	6-31G(P*) Ref. 2	6-31G** This study	6-31G(P*) Ref. 2
P—P 2.218	2.205	1.209	2.196	2.201
P—F ⁱ 1.587	1.582	1.609	1.584	1.610
P—F ^e 1.587	1.582	1.609	1.583	1.610
P—H ⁱ 1.42(ass.)	1.405	1.404	1.400	1.400
P—H ^e 1.42(ass.)	1.405	1.404	1.401	1.402
∠PPH ⁱ 90.3	95.2	94.7	97.1	97.4
∠PPH ^e 90.3	95.2	94.7	95.3	95.1
∠HPH 93.2	95.0	94.7	96.4	96.5
∠PPF ⁱ 97.2	96.6	96.4	100.8	101.0
∠PPF ^e 97.2	96.6	97.0	97.0	96.5
∠PPF 98.2	98.8	98.3	97.2	96.9
∠HPPF <i>trans</i>	177.9	178.0	70.8	71.6

^aOptimized geometries for the other conformations are available upon request.

one (*trans*) stable conformer. The optimized equilibrium geometries for these species calculated with the 6-31G** basis are presented in Table 1. The minima are now separated by a hump of about 0.9 kcal mol⁻¹ located at 122°.

The relaxation of the geometric parameters was responsible for a lowering of about 1.6, 1.5 and 0.9 kcal mol⁻¹ in the total energies of the *cis*, *gauche* and *trans* conformers, respectively. These numbers suggest that the constancy of the bond angles and bond lengths for different values of the dihedral angle HPPF may affect the relative energies by an amount of the order of 1.0 kcal mol⁻¹, a value that can be very significant depending on the species involved. In this study, by virtue of the initial input for the geometries, the relaxation brought extra stability to the *gauche* and *cis* conformers.

The geometric parameters in Table 1 show that the extension of the basis set beyond the 6-31G (P*) level of ref. 2 has a net effect of decreasing the P—P and the P—F bond lengths. For the P—Fⁱ (i stands for internal) bond this decrease is more pronounced relative to the previous study.

Notice that the optimized bond distances in taking the values 1.581 Å for the *cis*, 1.584 Å for the *gauche* and 1.582 Å for the *trans* conformers are very close to the known value for PHF₂, 1.582 Å [7]. The PH bond lengths for the *trans* conformer are practically the same in both calculations (1.405 Å). It is also slightly larger than the other conformers and lesser than the experimentally determined conformer 1.42 Å.

It is interesting to note that the bond angles PPH and PPF in the *gauche* conformer are larger than those involving the external hydrogen and fluorine atoms. This might be an indication of a slight hydrogen attraction for the lone pair of the adjacent phosphorus atom, with a consequent stabilization of the *gauche* conformer. In this respect it might be worth recalling that H₂P₂F₂ readily decomposes to HPF₂ [1].

As evidence of a possible existence of an intramolecular hydrogen bond we would expect a lengthening of both PH and PF bond lengths in the *cis* and *gauche* conformers. Table 1 shows that this is not the case; in fact the *cis* conformer has the shortest PH bond distance. For the PF bond there is a slight increase.

For the P—P bond, Table 1 shows a longer bond distance for the *cis* conformer, which might reflect a repulsion between the lone pairs on the phosphorus atoms. This repulsion seems to be the major factor destabilizing the *cis* conformer.

The atomic gross charges, obtained from a Mulliken population analysis [8] (Fig. 2) show that in going from the *trans* to the *cis* conformer there is a charge rearrangement which involves mainly the hydrogens and the phosphorus atoms. Also, an analysis of the total gross population of the *d* orbitals shows a larger contribution of these orbitals for the phosphorus atom connected to the fluorine atoms. These populations, are almost unvarying from one conformer to the other (0.23 e and 0.13 e). The fluorine *d* orbitals have a population of 0.13 e and the hydrogen *p* orbitals a population of 0.011 e.

Fig. 2. Atomic gross charges (in milli-electrons) obtained via a Mulliken population analysis.

Dipole moments

The dipole moment as a function of the dihedral angle is displayed in Fig. 3 for all five basis sets employed.

As was the case for the energies, there is a significant change in the magnitude of the dipole moments as polarization functions are included in the basis sets. As expected, the dipole moment functions obtained with the 4-31G and 6-31G bases exhibit the same behavior and have about the same magnitude. The overall effect of including polarization functions on the phosphorus and fluorine atoms is to reduce the dipole moments to about half the value calculated with the 4-31G and 6-31G basis sets. Additional inclusion of *p*-functions on the hydrogen atoms causes a very slight increase in the dipole moments. This is not perceptible with the scale used to draw the curves in Fig. 3. Addition of *d*-functions on the phosphorus atoms only is insufficient to describe the dipole moment for small value of the dihedral angle properly.

Listed in Table 2 are the total dipole moments, their components along

Fig. 3. Dipole moments for phosphinodifluorophosphine as a function of the dihedral angle.

TABLE 2

Dipole moments (in Debye) and moments of inertia (in AMU Å²) for different conformers of H₂PPF₂

	μ_{Total}	μ_a	μ_b	μ_c	I_a	I_b	I_c
<i>Cis</i>	0.77	0.75	0.0	0.13	72.3854	151.4174	191.5705
<i>Gauche</i> (70.8°)	1.49	1.02	0.84	0.67	71.7227	149.7864	188.5532
<i>Trans</i>	2.23	1.24	0.0	1.85	72.7919	147.5754	188.7530
Experimental	1.71	1.24	0.11	1.16	73.0902	149.8784	190.8679

the principal axes, and the moments of inertia for three conformers where a geometry optimization was carried out with the 6-31G** basis set. A glance at the non-zero and larger components of the dipole moments along the principal axes for the *gauche* and *trans* conformers apparently points to a wealth of possible transitions. This seems to suggest that a reinvestigation of the microwave spectrum of H₂PPF₂ should be carried out in order to search for the *gauche* conformer. Although this might be the case, a knowledge of the zero-point energies of the potential wells in Fig. 1 would certainly be very helpful in interpreting the data observed. Were this level situated well above the humps there would be no hindered internal rotation for the *gauche*—*trans*—*gauche* interconversion, and the maximum probability of observing that state would correspond to a *trans* conformation. The measured quantities would be averages of the possible values the system can take within the classical turning points. Note, in this respect, that the observed dipole moment (1.71 D) is in fact very close to the average of the *trans* and *gauche* dipole moments ($(2 \times 1.49 + 2.23) \text{ D}/3 = 1.74 \text{ D}$). A second possibility to examine would be the one corresponding to zero-point energies below the internal barrier maximum. Here, the different shapes of the potential wells imply different zero-point energies, the broader curve having a lower zero-point energy. Considering that the calculation with geometry optimization gives a relative small hump of about $0.9 \text{ kcal mol}^{-1}$, and that the inclusion of the zero-point energies reduces that barrier still more, the *gauche*—*trans* interconversion will certainly have a high tunnelling frequency, and the *trans* conformation will be favoured, since the *gauche* form has a higher zero-point energy.

CONCLUSION

This study clearly shows that the use of a split-valence type basis set with no polarization functions can lead to incorrect prediction of conformation stability. The inclusion of *d*-functions on the phosphorus atoms although predicting the same relative stability as the more extended basis set still fails to account for the dipole moment properly. Polarization functions on all the heavy atoms are needed.

The constraint of keeping constant the geometrical parameters during the rotation along the P—P bond is critical. Relaxation of these parameters changes the relative energies by approximately 1 kcal mol⁻¹ which is already higher than the final optimized hump of 0.9 kcal mol⁻¹.

As to the existence of a stable *gauche* conformer we are led to conclude that it seems unlikely to be detected. The small hump and zero-point energy arguments seem to favour the experimental observation of a *trans* conformation.

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TEORIAS MOLECULARES DO SABOR DOCE. ANÁLISE DO MODELO DE SHALLENBERGER VIA CÁLCULOS MECÂNICO-QUÂNTICOS DE PROPRIEDADES MOLECULARES DAS 2-R-5-NITROANILINAS

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ABSTRACT

A theoretical analysis of the basic assumption in Shallenberger's model of a simultaneous two hydrogen bonds interaction between the sweet agent and the receptor is performed based on quantum mechanical calculations of several molecular properties of 2-R-5-nitroanilines. The results obtained do not favour Shallenberger hypothesis of a gluco group interaction in this class of molecules.

1. INTRODUÇÃO

Substâncias doces, também denominadas edulcorantes, são encontradas nas mais diversas classes químicas¹. Em razão dessa diversidade estrutural, muito esforço tem sido dispendido com o propósito de descobrir qual é a relação existente entre as propriedades físico-químicas e o sabor doce exibido por essas substâncias^{1,2}. Uma apresentação da evolução histórica e, também, uma crítica das diferentes teorias do sabor doce podem ser encontradas de forma detalhada na ref. 3.

Dentre as várias teorias existentes, aquela apresentada por Shallenberger^{4,5} e complementada por Kier^{6,7} teve ampla divulgação na literatura, e exatamente sua hipótese central constitui o objeto de estudo neste artigo.

A suposição fundamental nessa teoria é que a atividade edulcorante é uma propriedade biológica estruturalmente específica, e que o evento principal para a manifestação do sabor doce depende do "encaixe" do edulcorante ao sítio receptor a fim de que se formem duas ligações de hidrogênio através das unidades bifuncionais complementares AH/B (Figura 1). Kier procurou complementar a hipótese de Shallenberger propondo que a alta atividade edulcorante mostrada por certas substâncias dependeria também, da existência de uma terceira posição de ligação, a qual participaria de interações de dispersão com uma região hidrofóbica do sítio receptor. (Círculos tracejados na Figura 1)

No exame da plausibilidade desse modelo, escolhemos para estudo a classe das 2-R-5-nitroanilinas, na qual a unidade glucofórica AH é o grupo CH do anel aromático na posição para ao grupo amino, e o elemento B é o oxigênio do grupo nitro (Figura 1). Para essa classe, uma série de cálculos usando métodos da mecânica quântica molecular

foram realizados. Esses cálculos tiveram como objetivo: 1) a análise do efeito dos substituintes sobre as propriedades eletrônicas e estruturais; 2) a análise da capacidade de formação de ligações de hidrogênio nas posições propostas por Shallenberger, além da interação via terceiro centro; 3) a correlação de todos esses efeitos com a atividade edulcorante.

2. MÉTODOS

Os cálculos realizados neste estudo foram feitos ao nível semi-empírico usando-se o método e o programa computacional CNDO/2^{8,9}, e ao nível ab-initio, usando-se o método Hartree-Fock-Roothaan¹⁰, implementado no programa computacional HONDO/5¹¹. Neste último caso trabalhou-se com uma base mínima STO-3G¹⁰.

Propriedades moleculares como energia total, potencial de ionização, geometria de equilíbrio, e cargas eletrônicas líquidas foram calculadas para as 2-R-5-nitroanilinas e outros derivados benzênicos, além da energia de estabilização intermolecular para vários complexos.

Figura 1. Edulcorantes e as atribuições de seus respectivos glucóforos segundo Shallenberger (Ref. 4) e Kier (Ref. 6).

3. RESULTADOS E DISCUSSÃO

3.1. Formação de Ligações de Hidrogênio Através do Grupo CH

Enquanto os grupos OH e NH estão bem caracterizados como doadores de prótons em ligações de hidrogênio, o mesmo não pode ser dito do grupo CH. Estudos experimentais^{12,13} e teóricos^{14,15} mostram que a capacidade de doação protônica do grupo CH depende do estado de hibridização do átomo de carbono e do efeito do substituinte. A capacidade de formação de ligação de hidrogênio através do grupo CH, em relação a um doador fixo, é dada por¹⁴:

No caso de derivados benzênicos, Allerhand e Schleyer¹² conseguiram detectar a formação de ligação através do grupo CH observando o deslocamento espectral de complexos formados com bases fortes como piridina e dimetilsulfóxido. Tal evidência de doação protônica depende da presença de ao menos três grupos substituintes fortemente captores de elétrons no anel benzênico.

Nas 2-R-5-nitroanilinas há grupos doadores e receptores de elétrons competindo na distribuição eletrônica no anel benzênico. O resultado global do efeito dos substituintes sobre o anel benzênico pode ser analisado comparando-se as cargas positivas sobre os hidrogênios das ligações CH e NH. Tais valores de cargas, juntamente com a atividade edulcorante de uma série de derivados benzênicos são mostrados na Tabela 1.

Desses resultados notamos que, relativamente à ligação CH no benzeno, há um incremento de carga líquida no hidrogênio, entretanto, no grupo de derivados doces não há uma correlação entre as cargas positivas nos hidrogênios

e as respectivas atividades edulcorantes. As cargas positivas sobre os hidrogênios do triclouro e tetraclorobenzeno podem ser consideradas como limites inferiores para que um derivado benzênico seja capaz de formar uma ligação de hidrogênio fraca. Notamos na Tabela 1 que, relativamente ao grupo CH, as cargas líquidas nos derivados doces e insípidos das nitroanilinas estão abaixo do limiar necessário para que ocorra a formação de ligação de hidrogênio. Tal conclusão é reforçada quando observamos os valores das cargas no hidrogênio do grupo NH, o qual está bem caracterizado como participante em ligações de hidrogênio.

3.2. Correlação da Atividade Edulcorante com a Interação de Dispersão

Uma comparação entre a atividade edulcorante e a interação de dispersão pode ser feita através da equação de London^{16,17} utilizando o produto αI , onde α é a polarizabilidade e I é o potencial de ionização calculado através do teorema de Koopmans¹⁰. A Tabela 2 contém os valores de αI , assim como as respectivas atividades edulcorantes da benzonitrila, do nitrobenzeno, e das 2-R-5-nitroanilinas ($R = \text{H}, \text{F}, \text{NH}_2, \text{OH}, \text{CH}_3$, e OCH_3). Nessa tabela, α representa a polarizabilidade do grupo R, ou das 2-R-5-nitroanilinas, ou do nitrobenzeno, ou da benzonitrila.

Esses resultados podem ser discutidos de duas formas distintas. Se não considerarmos a 2-amino-5-nitroanilina, notaremos uma correlação entre duas faixas de intensidades edulcorantes. A primeira, incluindo os derivados com hidrogênio, flúor, hidroxila, benzonitrila e nitrobenzeno, e a segunda, envolvendo os grupos metoxila, metila e cloro. Tais resultados são, qualitativamente, análogos aos obtidos por Kier⁷, que também assume a constância do termo entrópico na expressão da energia livre. Por outro lado, a inclusão da 2-amino-5-nitroanilina, bem como de outros derivados com substituintes como metilamino, dimetilamino, ciclohexilamino enfraquece a coerência da correlação e sugere a ação de outras propriedades moleculares ou macroscópicas influenciando a atividade edulcorante.

A correlação encontrada neste trabalho e, também, por Kier entre a atividade edulcorante e a energia de dispersão pode sugerir que esse fenômeno não seja estruturalmente específico. Isso deve-se à possibilidade de podermos reunir um conjunto de moléculas distintas estruturalmente, mas com valores de polarizabilidades tais que nos induzam a falsas correlações.

3.3. Simulação da Formação de Ligação de Hidrogênio Através do Método da Supermolécula

Outra forma de analisar a viabilidade do glucóforo CH/O das nitroanilinas em formar ligações com o sítio receptor é através da obtenção da energia de estabilização e cargas eletrônicas líquidas dos complexos ou supermoléculas formamida/2-R-5-nitroanilinas. A formamida foi usada como modelo de receptor porque apresenta características estruturais e eletrônicas que permitem simular a formação simultânea de duas ligações de hidrogênio,

Tabela 1. Atividade edulcorante, cargas líquidas nos hidrogênios das ligações C-H e N-H. Cálculos efetuados com a base STO-3G.

Derivado	AE*	qH (C-H) ¹	qH (N-H) ²
benzeno	0	0,063	—
o-nitroanilina	0	0,096	0,259
p-nitroanilina	0	0,098	0,203
2-amino-5-nitroanilina	0	0,094	0,200
benzonitrila	11	0,080 ⁴	—
m-nitroanilina	40	0,093	0,200
2-flúor-5-nitroanilina	40	0,098	0,200
nitrobenzeno	95	0,100	—
2-hidroxi-5-nitroanilina	120	0,096	0,200
2-metoxi-5-nitroanilina	220	0,095	0,200
2-metil-5-nitroanilina	330	0,094	0,201
2-cloro-5-nitroanilina	400	0,102	0,200
1,3,5-triclorobenzeno	—	0,111 ³	—
1,3,4,6-tetraclorobenzeno	—	0,117 ³	—

¹ Ligação adjacente ao grupo nitro. ² Ligação mais próxima ao grupo nitro. ³ Maior valor da carga líquida. * Atividade edulcorante em relação a sacarose (Ref. 1). ⁴ Ligação adjacente ao grupo CN.

Tabela 2. Correlação da atividade edulcorante (AE) com as polarizabilidades das 2-R-5-nitroanilinas (2-R-NA), benzonitrila (BNA), nitrobenzeno (NB) e dos respectivos grupos R com a energia de dispersão (α I). A polarizabilidade é medida em $\text{\AA}^3$ e o potencial de ionização em eV.

R	α (R)*	α I	Edulcorante	α (Edulcorante)*	α I	AE
—	—	—	BNA	9,98	80,94	11
H	0,394	2,65	2-H-NA	13,05	87,70	40
F	0,486	3,28	2-F-NA	12,89	86,88	40
—	—	—	NB	11,88	86,84	96
OH	1,143	7,23	2-OH-NA	13,80	87,35	120
NH ₂	1,518	9,03	2-NH ₂ -NA	14,21	84,55	0
OCH ₃	2,925	17,84	2-OCH ₃ -NA	15,62	95,28	220
CH ₃	2,222	14,80	2-CH ₃ -NA	14,87	98,59	330
Cl	2,305	16,39	2-Cl-NA	14,96	106,37	400

* Polarizabilidade do substituinte, ref. 17.

* Polarizabilidade do edulcorante, ref. 17.

segundo a suposição fundamental do modelo de Shallenberger. Além disso, apresenta alta capacidade para formar ligações de hidrogênio e ainda é utilizada como modelo de ligação peptídica no estudo da estabilidade das estruturas secundárias e terciárias de proteínas¹⁸. A estrutura da supermolécula está esquematizada na Figura 2.

Os valores dos parâmetros geométricos foram obtidos através de extensa exploração da superfície de potencial no plano do anel benzênico utilizando os programas computacionais CNDO/2 e HONDO/5. Os resultados finais da energia de estabilização e valores das cargas eletrônicas líquidas estão arrolados na Tabela 3.

Objetivando escolher uma referência para analisar os resultados dos complexos formamida/2-R-5-nitroanilinas, utilizamos o complexo formamida/água por causa da sua capacidade de formar ligações de hidrogênio¹⁹. A estrutura desse complexo (Figura 3) foi construída usando os mesmos parâmetros intermoleculares empregados nos complexos formamida/2-R-5-nitroanilinas. Os valores das cargas líquidas e energia de estabilização estão na Tabela 4.

A partir dos resultados da Tabela 3 notamos que as cargas nas moléculas isoladas e nos complexos são aproximadamente constantes, não guardando correlação com a

variação da atividade edulcorante das 2-R-5-nitroanilinas. Além disso, os valores das cargas estão abaixo daqueles encontrados no complexo formamida/água e nas respectivas moléculas isoladas (Tabela 4). Do ponto de vista

Figura 2. Estrutura da supermolécula utilizada nos cálculos de energia (Ref. 3).

Tabela 3. Atividade edulcorante (AE), energia de estabilização (ΔE) (Kcal/mol) e cargas eletrônicas líquidas do glucóforo AH/B das 2-R-5-nitroanilinas (R = NH₂, H, F, OH, OCH₃ e CH₃) e de seus respectivos complexos formados com a formamida. Cálculos realizados com a base STO-3G.

Edulcorante			Complexo Edulcorante/Receptor					
R	qH ₉	qO ₁₆	qH ₉	QO ₁₀	qH ₁₅	qH ₁₆	Δ E	AE
NH ₂	0,094	-0,195	0,130	-0,290	0,247	-0,214	-0,27	0
H	0,093	-0,186	0,130	-0,290	0,246	-0,204	0,26	40
F	0,098	-0,187	0,134	-0,291	0,246	-0,205	0,06	40
OH	0,096	-0,191	0,132	-0,292	0,246	-0,210	-0,72	120
OCH ₃	0,095	-0,191	0,132	-0,291	0,246	-0,209	-0,32	220
CH ₃	0,094	-0,188	0,129	-0,290	0,246	-0,207	-0,02	330

* Cargas na formamida isolada qH = -0,269, qH = 0,201.

Tabela 4. Energia de estabilização (ΔE) (Kcal/mol), cargas eletrônicas líquidas da água, da formamida e do complexo formado entre elas. (Ref. 3)

Formamida			Formamida/Água			
qO_4	qH_9	qH_3	qO_4	qH_9	qO_{10}	ΔE^*
-0,269	0,201	0,215	-0,292	0,240	-0,376	-5,52

* Molécula de água isolada: $qH = 0,183$, $qO = -0,367$.

Figura 3. Estrutura do complexo formamida/água (Ref. 3).

energético, as ligações CH (AH) das 2-R-5-nitroanilinas, mesmo com a participação da ligação NO(B), indicam fraca estabilização ou repulsão, pois as variações energéticas estão bem abaixo das encontradas no complexo formamida/água.

4. CONCLUSÕES

Os resultados aqui apresentados levam-nos a concluir que o glucóforo proposto por Shallenberger para a classe das 2-R-5-nitroanilinas não apresenta características eletrônicas de grupos capazes de participarem de ligações de hidrogênio. Tanto as cargas líquidas das ligações CH como as energias de estabilização do complexo, simulando a interação receptor-edulcorante, estão abaixo dos valores correspondentes de moléculas ou complexos que formam ligações de hidrogênio. A única correlação encontrada é entre a intensidade edulcorante e a energia de dispersão (proporcional ao produto αI), sendo os resultados análogos aos encontrados por Kier. Por outro lado, é possível anular essa correlação comparando-se as energias de dispersão de moléculas não-doces como as 2-R-5-nitroanilinas, onde R pode ser tanto o grupo amino, como o grupo metilamino, ou ainda os grupos dimetilamino e ciclohexilamino. Este resultado pode indicar a participação de outras propriedades moleculares ou macroscópicas.

A deficiência do modelo de Shallenberger em justificar a doçura das 2-R-5-nitroanilinas através do sistema glucofórico AH/B e os conceitos e resultados envolvidos no modelo de hidratação²⁰ levam-nos a considerar seriamente, também, a possibilidade do sabor doce ser controlado, predominantemente, por propriedades macroscópicas e, portanto, ser considerado uma propriedade biológica estruturalmente não-específica.

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AN AB INITIO STUDY OF THE
MOLECULES P_2O AND P_2O^+

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SUMMARY

This paper presents a detailed study at the Hartree-Fock and Multi-Reference Singles and Doubles Configuration Interaction levels of the molecules P_2O and P_2O^+ . An analysis of the geometries and relative stabilities of both molecules is presented together with a discussion of the dissociation channels and of the electronic spectrum of linear P_2O . The results for the ionic species P_2O^+ are the first ever presented and suggest the existence of this molecule in a cyclic geometry, as indicated by the calculated vibrational frequencies. Results are also presented which indicate a surface crossing at a relatively low energy which might lead to P_2O dissociation and hence be one of the factors contributing for its non-observation at room temperatures.

KEY WORDS: phosphorus(I) oxide, geometry optimization, dissociation channels, excitation energies, electronic spectrum, vibrational frequencies

1. Introduction

Contrary to the stable and quite well known N_2O molecule [1-3], P_2O is practically an unknown species. Experimentally, a first mention to P_2O was made by Besson [4] at the turn of last century, but the results of his experiments have been questioned by Chapman and Lidbury [5] who were unable to have them reproduced. The issue of the existence of P_2O was again addressed by Michaelis and Pitsch [6] and by Besson [7]. Based on these old papers, inorganic texts today, in the rare occasions in which a mention is made to P_2O , refer to Besson's suboxide as a mixture [8]. Note that P_2O is the supposed anhydride of hypophosphorous acid (H_3PO_2) which is well known as are its salts.

Recently, Andrews and Whithnall [9], using matrix isolation techniques to study the reaction of P_4 with oxygen, have recorded the infrared spectra of several oxides including the suboxides P_2O and P_4O proposed by Besson about 90 years ago. In their study a sharp 1197.3 cm^{-1} band attributed to an almost pure $\text{P}=\text{O}$ stretching was the only fundamental assigned to a linear P_2O structure.

On the theoretical side, preliminary results of a prediction on the existence of P_2O have been reported by Ornellas [10]. After having completed these calculations, we became aware of the work of Busch and Schoeller [11] on the theoretical evaluation of bonding properties of cyclic and linear analogues of N_2O . Although no particular discussion of P_2O is presented in that work, results of predicted geometries and relative stabilities obtained at the self-consistent field (SCF) and single-reference singles and doubles configuration interaction levels are presented which are quite concordant with ours.

After a new manuscript was prepared making proper reference to the work of Busch and Schoeller [11], to our surprise, a new study on P_2O was announced [12]. Besides presenting also results for the linear and cyclic structures, that paper mainly addresses the calculation of harmonic frequencies at the SCF and MP2 levels.

In this paper we complement these previous studies with calculations at the SCF and multi-reference singles and doubles configuration interaction (MR-SDCI) levels of the species P_2O and also of its ion P_2O^+ . A detailed analysis of the geometries, relative stabilities, binding, dissociation channels and of the electronic spectrum is presented. The problem of the non-observation of P_2O at room temperature is also addressed.

2. Computational Methods

This study has been carried out both at the SCF and at the multi-reference singles and doubles configuration interaction (MR-SDCI) levels. At the SCF level the geometries were optimized using the gradient of the energy with respect to the nuclear coordinates as implemented in the Hondo/5 program [13]. The optimization was considered complete for changes in the energy gradient smaller than 10^{-4} hartree/ a_0 . At the MR-SDCI level the geometries were obtained as the minima in a potential energy surface constructed by varying the phosphorus-phosphorus and phosphorus-oxygen internuclear distances for fixed bond angles. Since these calculations are very time-consuming, this search was done only for the linear structure. The MR-SDCI results have been obtained with the Meld codes developed by Davidson and collaborators [14].

Huzinaga's (9s,5p) set of cartesian gaussians [15] contracted to [4s,3p] by Dunning [16], plus a set of d-type ($\alpha = 0.85$) polarization functions comprised the oxygen basis set. For phosphorus, Huzinaga's (11s,7p) set of cartesian gaussians contracted to [6s,4p] by Dunning, plus a set of d-type ($\alpha = 0.62$) polarization functions were employed.

Due to symmetry restrictions in the Meld codes this study was carried out both in the C_{2v} and C_s point group symmetries. The MR-SDCI calculations were made freezing the canonical molecular orbitals (MO's) corresponding to the 1s, 2s, 2p atomic orbitals on phosphorus and the 1s atomic orbital on oxygen. A total of 16 electrons was correlated as single and double excitations from a set of reference configuration state functions considered relevant for the description of the multiple bond character and of the excited states of these

molecules. Due to hardware limitations (CYBER 170/730), perturbation theory with energies thresholds of the order of 5×10^{-5} hartree was used to keep the final wavefunction expansion within 14000 terms. For the same reason, only one set of d-type functions was used in the basis sets.

3. Results and Discussions

A. P_2O , Geometries and Energetics

Total energies for the optimized geometries of P_2O are presented in Table I. The corresponding structure parameters are given in Table II. Of the three converged calculations at the SCF level, a force constant calculation indicates that the species with higher energy is unstable. Vibrational frequencies corresponding to the true local minima of both linear and cyclic species are listed in Table III. As discussed in ref. [12] these unscaled harmonic frequencies are expected to be overestimated by about 30 %.

First of all, note that the SCF energies of this study are lower than any of the previous works. In particular, it is interesting to compare with the calculation of Busch and Schoeller [11] which also used Huzinaga's basis but with a different choice of contraction, [5s,4p], and a relatively high exponent, 1.25, for the oxygen d-function. This choice of exponent makes the d-function tighter than the one used in this work, (0.85), also recommended by Dunning and Hay [16], and is certainly the cause of their calculated higher energies and slightly longer bond distances. Although of double-zeta size, that basis set is of the same quality as the split-valence 6-31G* basis set used by Jarret-Sprague et al. [12].

Table I includes SDCI [11] and MR-SDCI energies, and perturbation results at the MP2 level [12]. In this study, only the linear structure was optimized at the CI level. The correlated energies for the other structures were calculated at SCF optimized geometries. The MP2 results correspond to optimized geometries. With the exception of the extended basis entries, our results are systematically lower than those published previously. A more

useful visualization of the results of Table I in the form of relative energies is presented in Fig. 1. Notice that the inclusion of correlation effects reduces the energy difference of the cyclic species relative to the linear one by only about 10%, as compared to the SCF value. For the transition state structure (C_s symmetry), hardware limitations has forced us to raise the energy threshold to 2.0×10^{-5} hartree for configuration selection. This threshold is about an order of magnitude higher than the ones used for the linear and cyclic structures and is responsible for the relatively high value of the non-corrected CI result which reflects the lack of a significant number of doubles and quadruples excitations in the wavefunction.

As to the MP2 result of ref. [12], it seems to be overestimating the energy of the linear form and/or underestimating the energy of the cyclic structure. Their value of 10.4 kcal/mol is about twice the result obtained in this study, 5.5 kcal/mol, using a MR-SDCI plus Davidson correction calculation. Since the SCF results are quite close, we are inclined to believe that these structures are not being properly described at the MP2 level. Correlation effects lengthen the SCF bond distances by about 2% at the CI level and by about 4% at the MP2 level. Bond angles are practically unaffected.

In the absence of experimental bond distances and angles it is worth-comparing the calculated results with the corresponding ones in known phosphorus and oxygen compounds. The experimental bond distances of P_2 and PO are, respectively, 1.894 Å [17] and 1.476 Å [18]. Note that our correlated results, 1.887 Å and 1.468 Å, are quite close to these bond distances which are characteristic of the triple bond in P_2 and of the double bond in PO. As pointed out before, the MP2 results (1.922 Å and 1.503 Å, [12]) are certainly overestimated.

As to the binding in the linear molecule, there is a neat evidence of the participation of all valence orbitals of the phosphorus atoms (see Table IV). In order of increasing stability, the first six molecular orbitals are : $(4b_1, 4b_2)$, $11a_1$, $(3b_1, 3b_2)$ and $10a_1$ (4π , 11σ , 3π and 10σ in the $C_{\infty v}$ notation). The atomic coefficients of these MO's, listed in Table V, show

that for the degenerate pair ($4b_1, 4b_2$) the contribution of the d-type function of the central phosphorus atom is significant to the π -type bonding orbitals between the two phosphorus atoms. On the other hand, for the degenerate pair ($3b_1, 3b_2$), the small magnitude of the coefficients of the functions centered on the peripheral phosphorus atom give to this pair a bonding π -type character involving the central phosphorus and the oxygen atom. As to the $a_1(\sigma)$ orbitals, they seem to be delocalized between the three atoms. This picture is consistent with the valence bond structure $P \equiv P \equiv O$. Table IV also suggests the structure $P \equiv P^+ - O^-$.

As to the cyclic structure, the SCF PP bond distance of 1.933 Å although lying between the triple bond in P_2 (1.894 Å) and the single bond in P_4 (2.21 Å, [19]), but much closer to that associated with a triple bond, does in fact correspond to a "cyclic double bond". Here also the molecular orbitals have significant contributions of the d-type atomic orbitals as shown by the Mulliken gross atomic populations listed in Table IV. The calculated PO bond distance, 1.709 Å, is comparable to the observed PO single bond in P_4O_6 , 1.65 Å [8].

B. P_2O^+ , Geometries and Energetics

To our knowledge, the results in this section represent the first calculations reported for this ionized species. The methodology and basis sets are the same as the ones used for the neutral molecule. Geometry optimization at the SCF level leads to two stationary points corresponding to a linear and a cyclic structure. Subsequent force constant calculations rule out the linear structure as a minimum. Vibrational harmonic frequencies are listed in Table III. The geometrical parameters and energies are shown in Fig. 2 together with the Mulliken gross atomic charges for both the ionic and neutral molecules. Atomic populations are shown in Table IV.

Despite the fact that the ionized electron is removed from a bonding $\pi(PP)$ molecular orbital, note that the new PP bond length (2.009 Å) is not very different from the corre-

sponding one in the neutral species (1.933 Å). This might imply that the sigma skeleton is the structure determining factor in the molecule. Also, the approximately 6° increase in the $\widehat{POP}$ bond angle brings a simultaneous overlap increase between the orbitals describing the PO bonds with a concomitant bond length shortening, 1.646 Å now, compared to 1.709 Å in the neutral molecule. Note also that the gross atomic charges clearly increase on the phosphorus atoms in going from the neutral to the ionic molecule. Despite the loss of one electron, this increase is not exactly half an electron for each phosphorus atom because of a partial electron migration from the oxygen atom.

Despite the fact that no experimental evidence has been found for the ionized molecule, as far as we know, the SCF energy difference between the linear structure of the neutral species and the cyclic structure of the cation allows us to estimate the adiabatic ionization potential of P_2O to be about 7.5 eV. We remember that the linear neutral molecule structure is less than 0.3 eV more stable than the cyclic one.

C. Dissociation Channels

In this section we examine the possible outcomes of the dissociation of P_2O in its linear geometry. Binding energies were calculated at the SCF and MR-SDCI levels using the counterpoise procedure to correct for basis set superposition errors [20,21]. Table VI collects the energies of the fragments allowed by the Wigner-Witmer rule and Fig. 3 shows schematically various states of P_2O and their dissociation products. Note that the molecular ground state correlates with excited atomic states.

At the SCF level, relative to the excited atomic states, binding energies of 36.8 and 67.6 kcal/mol (1.60 and 2.93 eV) were predicted for the PP and PO bonds, respectively, in P_2O . Inclusion of the zero-point energy decreases these values to 33.3 and 64.6 kcal/mol (1.44 and 2.80 eV). Notice that the use of correlated wavefunctions decreases the energy of the dissociation products of the two different channels by about the same value, 230 kcal/mol (9.97 eV), so that the increase in the binding energy at the CI level relative to the

SCF result, 17 kcal/mol (0.74 eV), comes from an increase in the correlation energy of P_2O relative to that of the products. An assessment of the accuracy of our calculations can be made by comparison of our results for the binding energies (D_e) of the molecules P_2 and PO with the experimentally known values of D_0 , 116 and 143 kcal/mol (5.03 and 6.20 eV), respectively [17]. The results of Table VI show that our calculations underestimate the dissociation energy of P_2 and PO by about 40 kcal/mol (1.73 eV). Extension of the atomic basis sets to at least a triple zeta level plus another d-type function and eventually an f-type function plus an enlarged set of configuration state functions would allow a better description of the valence correlation and certainly reduce the above discrepancy. An error of this magnitude has also been found by Lohr [22] for the dissociation energy of PO. In his study, using a 6-31G* basis set augmented by diffuse s- and p-type basis functions for both P and O atoms, values for D_e of 108 and 99 kcal/mol (4.68 and 4.29 eV) have been obtained at the MP3 and CISD levels, respectively.

Fig. 3 clearly shows that the energy difference between the two lowest P_2+O dissociation channels is essentially that for the energy separation between the 1D and 3P states of oxygen. Table VI gives 15240 cm^{-1} (1.89 eV) for this difference, a value quite good if compared with the experimental one of 15868 cm^{-1} (1.97 eV) [23]. Similarly, for the other two dissociation channels ($P + PO$), the energy difference is that for the separation between the 4S and 2D states of phosphorus, 13671 cm^{-1} (1.69 eV) (exp., 11377 cm^{-1} (1.41 eV) [23]). Thus, for the two dissociation channels of $P_2 + O$, the error in their relative energy is expected to be very small, less than 2 kcal/mol, whereas that for the $P + PO$ channels is about 6 kcal/mol. If the energy of the $P(^4S) + PO(^2\Pi)$ channel is corrected by this amount, its separation from the $^1\Sigma^+$ state of P_2O would fall below 10 kcal/mol. Since the errors in the dissociation energies of P_2 and PO are about the same, 40 kcal/mol, it is expected that the relative ordering of these four channels will not change very much with improvements in the wavefunction.

Still with reference to Fig. 3 it is important to notice that the dissociation channel

$P(^4S) + PO(X^2\Pi)$ is about 7.5 kcal/mol lower in energy, at the SCF level, and about 15 kcal/mol higher in energy, at the CI level, than the linear P_2O molecule at the equilibrium geometry. Inclusion of the zero-point energy (3.4 kcal/mol) makes the separation between the ground state and this dissociation limit equal to about 4000 cm^{-1} (11.5 kcal/mol) for the correlated wavefunction calculation. These figures suggest that a surface crossing between the $^3\Pi$ and $X^1\Sigma^+$ states might exist at a not so high energy. Depending on the exothermicity of the reaction leading to the formation of P_2O , a number of excited vibrational levels could then be populated reducing thus the barrier for the new formed molecule to dissociate via that channel.

Contrasting with this situation, in the case of N_2O , we remember that it dissociates into N_2 and O [2]. Here, the dissociation limit $N(^2D) + NO(X^2\Pi)$, which correlates with N_2O in its ground state is about 169 kcal/mol (7.31 eV) high in energy. The next lowest dissociation limit, $N(^4S) + NO(X^2\Pi)$, is also about 114 kcal/mol (4.93 eV) higher in energy than the ground state. As to the dissociation into $N_2 + O$, the lowest channel, $N_2(X^1\Sigma^+) + O(^3P)$ is about 39 kcal/mol (1.68 eV) high in energy and the next one, which correlates with ground state, is about 84 kcal/mol (3.64 eV) higher in energy than the ground state [2]. For N_2O , an MCSCF/CI-4s3p1d treatment of the $X^1\Sigma^+$ state has resulted in 72.0 kcal/mol (3.12 eV) for the NN-O binding energy, which compared with the experimental value, 86.7 kcal/mol (3.76 eV), represents a recovery of 83% of the binding energy [2]. In the case of P_2O , any further improvements in the wavefunction is likely to change the binding energy by only a fraction of the change observed in going from the SCF to the correlated results. An estimate of 40% of that value, 6.8 kcal/mol, would increase the P-PO and the PP-O binding energies to about 61 and 91 kcal/mol (2.65 and 3.95 eV), respectively. Contrasting these figures with the ones for P_2O , one can rationalize the stability of the N_2O molecule and the non-observation of P_2O at room temperature.

Due to the small amount of CPU memory in the Cyber 170 computer, the $^3\Pi$ potential energy surface could not be generated with the same accuracy as the one for the ground

state. This fact has prevented us of precisely locating the region of crossing of the two potential surfaces.

D. Excited Electronic States

The first few excited electronic states arise as promotions from electrons in the 4π molecular orbital (MO) into the 12σ and 5π MO's. These configurations and the associated states are

... $3\pi^4 11\sigma^2 4\pi^1$	$X^1\Sigma^+$
... $3\pi^4 11\sigma^2 4\pi^3 12\sigma^1$	$1,3\Pi$
... $3\pi^4 11\sigma^2 4\pi^3 5\pi^1$	$1,3\Sigma^-, 1,3\Delta, 1,3\Sigma^+$

The relative order of these states and the vertical excitation energies are shown in Fig. 3 and were obtained at the MR-SDCI level after a preliminary SCF calculation and using the ground state equilibrium geometry. For a given symmetry, the estimated energies of the excited states were obtained as the first few eigenvalues of the hamiltonian matrix. Again, the small main memory of the Cyber 170 computer imposed severe limitations on the final wavefunctions. A relative high energy threshold (6.5×10^{-5} hartree) had to be used in the configuration selection by perturbation theory limiting the size of the wavefunction to less than 14000 terms. Therefore, although we believe the ordering to be correct, its relative spacings might be subjected to small changes.

With respect to this spectrum, two comparisons with the corresponding one for N_2O are worth-making. First, as mentioned in the previous section and in contrast with P_2O (first excited state $^3\Pi$), that for N_2O is a $^3\Sigma^+$. For N_2O , this latter state is about 6.5 eV high relative to the ground state and correlates with a dissociative state ($N(^2D) + NO(X^2\Pi)$) that is about 0.8 eV higher in energy. Second, the first vertical transition fully allowed by the dipole selection rule is predicted to require 5.57 eV, whereas that for N_2O involves about 8.4 eV [2].

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Figure Captions

Fig. 1. Relative energies (in kcal/mol) for the optimized structures of P_2O .

Fig. 2. Geometrical parameters, SCF energies and Mulliken gross atomic charges for P_2O and P_2O^+ . $E_{CI}(\text{P}_2\text{O}^+) = -756.31570$ a.u..

Fig. 3. Energy correlation diagram and vertical excitation energies (in parenthesis) for P_2O . Energies for the system PPO are given relative to -756.0 a.u.. Values in parenthesis and in brackets are given in eV.

Fig. 1

$$E_{\text{SCF}} = -758.23817 \text{ a.u.}$$

$$E_{\text{SCF}} = -755.98260 \text{ a.u.}$$

$$E_{\text{SCF}} = -756.24814 \text{ a.u.}$$

Fig. 2

P + PO

P₂OP₂ + O

FIG. 3

Table I. Total energies (in a.u.) for P_2O . Values in parenthesis include Davidson correction. Values listed should be added to -756.0 .

	LINEAR		CYCLIC		TRANSITION STATE	
	SCF	Correlated	SCF	Correlated	SCF	Correlated
This Study	-0.248135	-0.640799 (-0.705375)	-0.238168	-0.632736 ^e (-0.696550)	-0.218487	-0.550636 ^e (-0.652728)
Ref. [11] ^a	-0.2390		-0.2256		-0.2003	
		(-0.6858)		(-0.6742)		(-0.6317)
Ref. [12] ^b	-0.2318	-0.6739	-0.2233	-0.6573 -0.8112 ^c -0.9083 ^d		

^aBasis set: (9s,5p)/ [5s,3p] plus d(1.25) for oxygen and (11s,7p)/ [7s,4p] plus d(0.5) for phosphorus. Single-reference CI results.

^bBasis set: Pople's 6-31G* . Correlated results at the MP2 level.

^cBasis set: DZ of Huzinaga plus d(1.28) for oxygen and d(0.465) for phosphorus.

^dBasis set: TZ2P of Huzinaga, ref. [15].

^eSCF optimized geometry was used.

Table II. Optimized geometries for P_2O .

	PP bond length, Å		PO bond length, Å		PPO bond angle	
	SCF	Correlated	SCF	Correlated	SCF	Correlated
LINEAR						
This study	1.846	1.887	1.438	1.468	180	180
Ref. [11] ^a	1.852		1.446		180	
Ref. [12] ^b	1.852	1.922	1.446	1.503	180	180
CYCLIC						
This study	1.933		1.709		55.6	
Ref. [11] ^a	1.938		1.721		55.7	
Ref. [12] ^b	1.939	2.012	1.726	1.776	55.9	55.5
		2.007		1.770		55.5
		2.018		1.762		55.1
TRANSITION STATE						
This study	2.110		1.472		95.2	
Ref. [11] ^a	2.118		1.479		95.6	

^aCorrelated results obtained at the single-reference CI.^bCorrelated results obtained at the MP2 level.

Table III. Unscaled harmonic vibrational frequencies (in cm^{-1}) calculated at the SCF level for P_2O and P_2O^+ .

<u>P_2O, linear</u>		<u>P_2O, cyclic</u>		<u>P_2O^+, cyclic</u>
201 ^a	213 ^b	270 ^a	303 ^b	663 ^b
749 ^a	752 ^b	734 ^a	741 ^b	977 ^b
1429 ^a	1451 ^{b,c}	925 ^a	938 ^b	1098 ^b

^a Ref. [12]

^b This study

^c Exp. 1197.3 cm^{-1} , ref. [9]

Table IV. Mulliken gross atomic populations for P_2O and P_2O^+ .

	P_2O , cyclic ^a		P_2O , linear ^b			P_2O^+ , cyclic ^a	
	P	O	P	P	O	P	O
s	5.640	3.889	5.818	5.086	3.845	5.658	3.852
p_x	3.054	1.469	3.203	2.953	1.708	2.641	1.645
p_y	2.999	1.935	3.203	2.953	1.708	2.988	1.487
p_z	2.583	1.426	2.642	2.751	1.405	2.545	1.512
d	0.342	0.027	0.148	0.528	0.050	0.386	0.069

^a The molecule is on the yz plane^b The z-axis contains the internuclear distance

Table V. Atomic coefficients for some molecular orbitals of the linear structure of P_2O .

	10a ₁ (-0.679 a.u.)			11a ₁ (-0.518 a.u.)		
	P1	P2	O	P1	P2	O
s	0.014	-0.014	-0.053	-0.017	0.009	-0.009
s	0.043	-0.044	-0.074	-0.053	0.027	-0.014
s	-0.093	0.095	0.220	0.115	-0.060	0.037
s	-0.175	0.184	0.286	0.224	-0.114	0.077
s	0.305	-0.357		-0.391	0.199	
s	0.310	0.154		-0.505	0.294	
p _z	0.016	0.094	0.243	-0.135	0.125	0.150
p _z	0.002	0.012	0.305	-0.021	0.019	0.189
p _z	-0.033	-0.195	0.201	0.285	-0.287	0.145
p _z	-0.000	0.038		0.167	-0.121	
d _{zz}	-0.007	-0.014	-0.032	0.060	-0.026	-0.018
d _{yy}	-0.007	0.021	0.007	0.004	0.011	0.002
d _{xx}	-0.007	0.021	0.007	0.004	0.011	0.002

	3b ₁ (3b ₂) (-0.574 a.u.)			4b ₁ (4b ₂) (-0.378 a.u.)		
	P1	P2	O	P1	P2	O
p _x (y)	-0.032	-0.119	0.289	0.167	0.100	0.139
p _x (y)	-0.006	-0.019	0.385	0.025	0.016	0.168
p _x (y)	0.072	0.254	0.295	-0.358	-0.222	0.233
p _x (y)	0.041	0.183		-0.424	-0.274	
d _x (y,z)	0.018	0.059	-0.043	-0.065	0.115	-0.014

Table VI. Energies (in a.u.) of various fragments of the dissociation of P_2O .

	SCF	CI
P (2D)	-340.618382	-340.702552
P (4S)	-340.689187	-340.764845
PO ($^2\Pi$)	-415.571191	-415.852109
P ₂ ($^1\Sigma_g^+$)	-681.421143	-681.653007
O (1D)	-74.719285	-74.853417
O (3P)	-74.801240	-74.922855
P (2D) + PO	-756.189573	-756.554661
P (4S) + PO	-756.260378	-756.616954
P ₂ O ($X^1\Sigma^+$)	-756.248135	-756.640799
ΔE (P—P) ^a	36.75	54.08
ΔE (P—O) ^a	67.59	84.32

^a in kcal/mol

Abordagens Educacionais a Conceitos e Técnicas da Química Quântica

Artigos

The Integral Transform Approach : The Electron-Repulsion Integral and the Helium Atom

F. R. Ornellas, *J. Chem. Educ.*, **62**, 378 (1985)

Why is the Momentum Operator Given by $-\hbar\partial/\partial x$?

F. R. Ornellas, submetido para publicação na revista Química Nova.

O ensino da Química Quântica foi sempre uma preocupação constante que tivemos e continuamos tendo. Ele representa um grande desafio pois a mecânica quântica forma a base das explicações microscópicas dos fenômenos químicos. Entretanto, por razões diversas, a forma de apresentação de conceitos e técnicas matemáticas necessárias para a compreensão dos fenômenos a nível molecular nem sempre é feita de forma tal que incentive o aluno a superar suas dificuldades de conteúdo matemático e, principalmente, a vencer a barreira psicológica que cria perante o assunto.

O fato de vivermos a Química Quântica de forma intensa nos levou a escrever esses dois artigos que abordam tópicos que desenvolvemos em ocasiões distintas em que estávamos ministrando o curso Química Quântica I. O primeiro ilustra uma técnica para a resolução de integrais de dois elétrons que surgem quando se resolve a equação de Schrödinger para o átomo de hélio. Esse procedimento não existe em nenhum livro-texto e surgiu da fusão de nossa vivência com o átomo de hélio na forma como é tratado nas salas de aula com a experiência que tínhamos com técnicas de resolução de integrais dispersas na literatura.

No segundo artigo, como muitos livros que introduzem a mecânica quântica para os químicos a fazem postulando a existência de vários operadores, cuja forma parece ter algo de mágico, resolvemos ir um pouco além e mostrar porque o operador do momento linear é representado dessa forma usual baseando-nos na argumentação dada por D. Bohm em seu livro *Quantum Theory*, que infelizmente, de um modo geral, não é do conhecimento dos químicos.

É nosso sentimento que esses dois trabalhos representam apenas o começo de uma série de muitos outros com enfoque pedagógico, que temos aflorados à mente, mas que, devido à sobrecarga de atividades, acabamos sempre adiando o seu registro no papel.

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The Integral Transform Approach

The Electron-Repulsion Integral and the Helium Atom

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When a student is introduced to the quantum mechanical methods for treating the helium atom, he or she is always faced with the problem of evaluating the electron-repulsion integral

$$I = \iint d^3r_1 d^3r_2 \phi^2(r_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi^2(r_2) \quad (1)$$

where,

$$\phi(r) = Z^{3/2} \pi^{-1/2} e^{-Zr}$$

Most standard texts usually evaluate this integral by one of the following methods: (1) an expansion of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ in terms of spherical harmonics (1, 3); (2) an explication of the coordinates of the second electron relative to that of the first electron (4a, 5); or (3) the use of physical arguments that this integral represents the interaction electrostatic energy of two spherically symmetric electronic densities $\phi^2(r_1)$ and $\phi^2(r_2)$ (6, 7). A discussion of the consistent way in which the integral given by eqn. (1) should be evaluated by the second method has recently been discussed by Lee (8).

In what follows we show that the integral I can still be evaluated by another method, namely, the Fourier transform method (FTM) (9). The merits of the FTM are that it introduces the students both to a technique that is used to compute electron-repulsion integrals involving orbitals on different atoms and also to a technique of evaluating integrals where the orbitals contain explicitly the interelectronic distance r_{ij} (Hylleraas-type functions). For a recent detailed presentation of the Fourier transform method in the context of multi-center electron repulsion integrals, the reader is referred to the work of Partridge (10). An example of this same technique in the construction of correlated wavefunctions for the ground state of helium-like atoms is given by Bonham and Kohl (11). Still in the context of the helium atom we can also mention another merit of the FTM, namely, its applicability to the calculation of exchange integrals arising in such states as $1s2s\ ^1S$ and $1s2s\ ^3S$.

The basic step in the evaluation of eqn. (1) is to realize that $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ can be written as a Fourier transform

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{2\pi^2} \int d^3t \frac{\exp(i\mathbf{t} \cdot (\mathbf{r}_1 - \mathbf{r}_2))}{t^2} \quad (2)$$

Substituting eqn. (2) into eqn. (1) gives

$$I = \frac{Z^6}{2\pi^4} \int \frac{d^3t}{t^2} \int d^3r_1 e^{-2Zr_1 + i\mathbf{t} \cdot \mathbf{r}_1} \int d^3r_2 e^{-2Zr_2 - i\mathbf{t} \cdot \mathbf{r}_2} \quad (3)$$

The integrals over the coordinates r_1 and r_2 are equal and can be found in a table of integrals or be easily evaluated (choose the vector $\mathbf{t}$ parallel to the Z axis). They are given by

$$\int d^3x e^{-ax + i\mathbf{x} \cdot \mathbf{b}} = \frac{8\pi a}{(a^2 + b^2)^2} \quad (4)$$

Making use of eqn. (4) and carrying out the integration over the angular coordinates of the vector $\mathbf{t}$, eqn. (3) reduces to

$$I = \frac{512Z^8}{\pi} \int_0^\infty \frac{dt}{(4Z^2 + t^2)^4} \quad (5)$$

The integral in eqn. (5) is again easily found in any table of integrals or directly evaluated by contour integration (4b). Its value is $5\pi Z^{-7/2} 12^{-12}$. Substitution of this value into eqn. (5) gives the well-known result

$$I = \frac{Z^6}{\pi} \iint d^3r_1 d^3r_2 \frac{e^{-2Z(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5Z}{8}$$

Finally, as mentioned in the introduction, this technique can also be extended to calculations related to excited states of helium. For example, the energy difference between the singlet state ($1s2s\ ^1S$) and the triplet state ($1s2s\ ^3S$) is equal to $2K_{12}$, where K_{12} is the exchange integral (12). If the $1s$ and $2s$ functions are represented by hydrogen-like functions, a straightforward application of the procedure described here yields $K_{12} = 16Z/729$.

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WHY IS THE MOMENTUM OPERATOR
GIVEN BY $-i\hbar\partial/\partial x$?

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The teaching of a quantum chemistry course is always a challenge. By its own nature, concepts can not be easily visualized in terms of macroscopic images and the written language requires a minimum of mathematical skills. In all the different presentations, one certainly emphasizes that the quantities that can be measured, the *observables*, will be represented by mathematical entities called *hermitian operators*, and that the solution of the Schrödinger equation, the *wavefunction* Ψ , is such that $\Psi^*\Psi$ represents a *probability distribution*.

The determinism, typical of classical physics, is then replaced by a statistical description of the system, and the average value of an observable is now the quantity of interest. The particle in a one-dimensional box is the first model studied and average values of the position and the momentum of the particle calculated using the relations

$$\bar{x} = \int_{-\infty}^{+\infty} \Psi^*(x) \hat{x} \Psi(x) dx = \int_{-\infty}^{+\infty} \Psi^*(x) x \Psi(x) dx \quad (1)$$

$$\bar{p}_x = \int_{-\infty}^{+\infty} \Psi^*(x) \hat{p}_x \Psi(x) dx = \int_{-\infty}^{+\infty} \Psi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right) \Psi(x) dx \quad (2)$$

At this point, whether or not grasping the logic of quantum mechanics, the student certainly asks the question: *Why is the momentum operator given by $-i\hbar\partial/\partial x$? How was it "invented"?*

The purpose of this paper is to present what we judge to be a beautiful answer to these questions. We will show that the form of the operator given in (2) arises naturally if one realizes that, similarly to (1), the average value of the momentum can also be calculated by the expression

$$\bar{p}_x = \int_{-\infty}^{+\infty} \Phi^*(p_x) \hat{p}_x \Phi(p_x) dp_x = \int_{-\infty}^{+\infty} \Phi^*(p_x) p_x \Phi(p_x) dp_x \quad (3)$$

where, $\Phi(p_x)$ is the wavefunction expressed in terms of the momentum of the particle and $\hat{p}_x$ is simply a multiplicative operator, the number p_x . For simplicity, we will omit the subscript x in what follows.

Since the momentum is related to the wave vector k by the relation $p = k\hbar$, the normalization condition

$$\int_{-\infty}^{+\infty} \Phi^*(p) \Phi(p) dp = \int_{-\infty}^{+\infty} \phi^*(k) \phi(k) dk = 1 \quad (4)$$

implies that

$$\phi(k) = \hbar^{1/2} \Phi(p) \quad (5)$$

A key point to answer the above question is to realize that a wavefunction can be expanded in the form of a Fourier integral

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{ikx} \phi(k) dk \quad (6)$$

where the coefficients $\phi(k)$ can also be obtained as an inverse Fourier integral

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-ikx} \Psi(x) dx \quad (7)$$

Substituting (4) and (7) into (3) and rearranging, one obtains

$$\bar{p} = \frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{ikx'} \Psi^*(x') k e^{-ikx} \Psi(x) dx dx' dk \quad (8)$$

Noticing that

$$k e^{-ikx} = i \frac{\partial}{\partial x} e^{-ikx}, \quad (9)$$

integration by parts over the variable x in equation (8) can be carried out after substitution of (9) into (8). Using also the fact that $\Psi(\pm\infty) = 0$ equation (8) can be rewritten as

$$\bar{p} = \int_{-\infty}^{+\infty} dx (-i\hbar) \frac{\partial \Psi(x)}{\partial x} \int_{-\infty}^{+\infty} dx' \Psi^*(x') \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{ik(x'-x)} \quad (10)$$

Equation (10) now reduces to

$$\bar{p} = \int_{-\infty}^{+\infty} \Psi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x) dx \quad (11)$$

if recurrence is made to the Fourier integral theorem

$$\Psi(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{ik(x-x')} \Psi(x') dx' dk \quad (12)$$

Notice that the integral over k in expression (12) is the integral representation of the Dirac's delta function

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ik(x-x')} dk \quad (13)$$

and

$$\Psi(x) = \int_{-\infty}^{+\infty} \Psi(x') \delta(x - x') dx' \quad (14)$$

Expression (11) clearly shows that the operator $\hat{p}$ should be represented by $-\hbar\partial/\partial x$. This last statement to be entirely correct should specify that one is working in the *coordinate or position representation*, that is, the wavefunction is expressed as a function of the position of the particle. On the other hand, if one writes the wavefunction as a function of the momentum of the particle, the so called *momentum representation*, the momentum operator is simply given by the number p , and the position operator becomes now the differential operator $\hbar\partial/\partial p$, as could be proved by a procedure similar to the one shown above.

Depending on the level of the course being taught one can go through all the mathematical details of the derivation or explain the logical connection of these steps. This approach clearly shows that $-\hbar\partial/\partial x$ is not a mysterious entity. Its origin is firmly rooted in the fundamentals of quantum mechanics.

This derivation is based essentially on that given by Bohm(1) in his excellent and concepts-rich textbook *Quantum Theory* which I highly recommend for those teaching quantum chemistry.

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