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Two-photon two-atom processes

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Two-photon two-atom processes

Tese apresentada ao programa de Pós-Graduação em Física do Instituto de Física de São Carlos da Universidade de São Paulo, para obtenção do título de Doutor em Ciências.

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Orientador: Prof. Dr. Vanderlei Salvador Bag-nato

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*“We choose to go to the moon in this decade and do the other things,
not because they are easy, but because they are hard,
because that goal will serve to organize
and measure the best of our energies and skills,
because that challenge is one that we are willing to accept,
one we are unwilling to postpone,
and one we intend to win ... “*

- John Fitzgerald Kennedy

Resumo

PAIVA, R. R. **Processos envolvendo a interação de dois fótons com dois átomos** 2013. 95 p. Tese (Doutorado em ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2013.

No campo da física atômica, molecular e ótica processos envolvendo dois fótons são bem compreendidos e usados em diversas aplicações. Nesta tese apresentamos o estudo e a realização experimental de dois processos de dois-fótons. Usando átomos de sódio aprisionados em uma armadilha magneto ótica, demonstramos a absorção cooperativa de dois fótons e que a criação de um estado ligado molecular usando somente campos de luz, ou estado ligado fotônico, é possível. Absorção cooperativa de dois fótons, um processo bem comum em física de estado sólido, acontece quando um par de átomos inicialmente no estado fundamental é excitado para o estado duplamente excitado, via absorção de dois fótons de frequência não ressonante com a dos estados excitado. A realização experimental deste processo em um sistema de átomos frios pode abrir novas, e excitantes possibilidades para entender melhor processos não lineares, e é um novo método de criar átomos e fótons correlacionados. Essa absorção foi observada através da ionização do par depois da absorção, e um modelo simples que considera somente interação dipolo-dipolo entre os dois átomos nós ajuda entender as características básicas dos dados obtidos. Um estado ligado fotônico usa dois fótons para criar as duas características básicas dos estados ligados moleculares: a parte repulsiva e a parte atrativa. Um fóton “azul”, deslocado para o azul da transição atômica, conecta o estado fundamental do par a parte repulsiva do primeira estado excitado molecular 1_g , e um fóton “vermelho”, deslocado para o vermelho da transição atômica, conecta o estado fundamental a parte atrativa do deslocado para o azul da transição atômica. No contexto de estados vestidos, quando os campos de luz são intensos, esses sistema de três estados e dois fótons cria potenciais ligantes adiabáticos que são fortemente dependentes das propriedades desses fótons. Usando um modelo teórico para esses potenciais pudemos estudar como é essa dependência, com as características do fótons, e os dados experimentais mostram que esses fótons estão de fato vestindo os estados com uma eficiência que viabiliza a criação de moléculas fotônicas

Palavras-chaves: Átomos frios. Processos de dois fótons. Efeitos não-lineares. Absorção cooperativa . Moléculas fotônicas.

Abstract

PAIVA, R. R. **Two-photon two-atom processes**. 2013. 95 p. Tese (Doutorado em ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2013

In the atomic, molecular, optical physics field, processes involving two photons are very well understood and used in applications ranging from spectroscopy to laser cooling techniques. In this thesis is presented the study and experimental realization of two two-photon processes. Using sodium atoms trapped in a magnetic optical trap we could demonstrate two-photon cooperative absorption, and that the creation of a molecular bound state using only light fields, or photonic bound state, is possible. Two-photon cooperative absorption, very common in solid-state physics, is a process where a pair of atoms initially in the ground state is excited to the double excited state, via absorption of two photons with frequency that is not resonant with any excited state. Its experimental realization with cold atoms may open new and exciting possibilities to better understand nonlinear effects, and it is a new way to create correlated atoms and photons in cold atomic physics. This absorption was observed by ionization of the pair after the excitation. A simple model that considers only dipole-dipole interactions between the atoms allows us to understand the basic features observed in the experimental data. A photonic bound state uses two photons to create the two basic features of a molecular bound state: a repulsive part and an attractive part. A “blue” photon, blue detuned from the atomic transition, connects the ground state of the pair to the repulsive part of the first excited molecular state 1_g , and a “red” photon, red detuned from the atomic transition, connects the ground state of the pair to the attractive part of the first excited molecular state. In the dressed state picture, when the light fields are strong, this three-states-two-photon system creates adiabatic bound potentials that are strongly dependent of the photon properties. Using a theoretical model we could study how this bound energies changes when we change the photon properties, and the experimental data shows that this photons are indeed dressing the potentials with a efficiency that would enable the creation of photonic molecules.

Key-words: Cold atoms. Two-photon process. Nonlinear effects. Two-photon cooperative absorption. Photonic molecules.

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List of abbreviations and acronyms

TPA	Two-photon absorption
OPT	One-photon transition
AMO	atomic molecular and optical
PA	Photoassociation
PAPI	Photoassociative photoionization
PAI	Photoassociative ionization
MOT	Magneto optical trap
Dark SPOT	Dark Spontaneous optical trap
EOM	Electro optical modulator
AOM	Acoustic optical modulators
CCD	Charge-coupled device
PD	Photo detector
TP	Transition probability

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An introduction to two-photon two-atom processes

In cold collision process, it is common for a pair of atoms or molecules to absorb a single photon. In fact, such processes were fundamental to the development of the understanding of cold collisions (?) and the determination of scattering length values (?), among others. It is possible, however, that the pair interacts with two photons, simultaneously or not. In this thesis we will present two experiments in a sample of cold sodium atoms that use two-photon absorption in different ways. This first is simultaneously absorption of two photons by a pair of atoms, or cooperative two-photon absorption. The second uses absorption of two photons with different colors at different times to create, in the dressed picture, a molecular bound state.

Coherent two-photon absorption (TPA) is a process where two photons are simultaneously absorbed to excite an atom or ion to a higher-lying state, with the energy increase being equal to the sum of the photon energies. TPA is a third-order nonlinear susceptibility process that is several orders of magnitude weaker than linear absorption. As one would expect its absorption strength depends on the square of the light intensity, which is different from the linear absorption. Since it uses two photons it can promote transitions forbidden easily by one-photon transitions (OPT), which allows spectroscopy of states that cannot easily be reached via OPT.

TPA was originally predicted by Maria Goeppert-Mayer (?), and was first observed in a europium-doped crystal (?). After that it was widely used and tested in different kind of crystals (?), semiconductors (?) and a cesium vapor (?). Recently two-photon spectroscopy has been used in magneto optical traps, which allowed high resolution spectroscopy. Also there are proposals to use TPA as a cooling technique.

Cooperative effects studies were carried out simultaneously with TPA. And due to the interaction between atoms, ions and others were the subject of those researches. The

first experiment that shows one-photon cooperative absorption by two-atoms was done by F. Varsanyi and G.H. Dieke in 1961 (?). In solids, important results were obtained by D. L. Dexter (?) where it was shown that the cooperative effect favors an energy transfer between the atoms enabling the simultaneous one-photon absorption. Recently Xingcan Dai and collaborators (?) have observed a double-quantum coherence signal (two-atoms one-photon transition) in a gas of potassium at twice the frequency of the one-quantum coherences (one-photon one-atom transition), where one would naively expect no available transition, since there is no atomic level with such energy. They show that collective resonances resulting from interatomic interactions can induce double-quantum coherences. The authors proposed a theoretical treatment including dipole-dipole interactions in gas of atoms combined with molecular dynamics simulations to reproduce the experimental results. It has been suggested that interaction-induced double-quantum coherences may play a role in photoprocesses such as light harvesting (?). Furthermore, quantum information processing schemes exploiting the collective resonances due to long-range dipole-dipole coupling have been proposed (?).

Two-photon cooperative absorption is a TPA where a atom pair absorbs two photons and goes to a combination of two higher excited state. It relies on the pair interaction for the absorption to happen, because the sum of the photon energies is not equal to any atomic state. TPA cooperative absorption was first observed in mixture of Ba/Tl, where a pair of atoms were simultaneously excited by a cooperative-absorption process (?). The problem has also been considered theoretically by a few authors (?, ?).

Colliding cold atoms have been a test bench for many studies (?), but nonlinear optical effects involving two-photon absorption have not been deeply investigated in this kind of low density system. In a sample of cold atoms, the absence of motion and the long-range part of the interaction provide the necessary ingredients for a two-photon cooperative absorption, making this sample adequate for studying cooperative transitions near resonances. The first experiment presented here demonstrates the occurrence of a two-photon cooperative absorption in a pair of colliding cold Na atoms kept in a magneto-optical trap (?). Two photons from a strong laser having a frequency ω are absorbed by a

cooperating pair of atoms producing $3P_{1/2}$ and $3P_{3/2}$ excited atoms when the relationship $2\omega = \omega_{s_{1/2} \rightarrow P_{1/2}} + \omega_{s_{1/2} \rightarrow P_{3/2}}$ between the laser frequency ω and the atomic transition frequencies is satisfied.

The experimental data shown in this thesis demonstrate that simultaneous two-photon absorption is possible in a sample of cold sodium atoms. Two-photon cooperative absorption in cold atoms may open up a new, exciting nonlinear type of effect which may allow investigation into the process of cold-atom interactions in classical or quantum degenerate samples. The process is by itself a way to generate entanglement (?) of atoms in the excited state as well as to produce correlated photons with different frequencies (?,?). Both of those effects may find interesting applications in the future.

The second part of this work is concerned to the production of ultracold molecules. Starting from a few research groups in the late 90's the field of *cold* ($1 \text{ mK} < T < 1 \text{ K}$) and *ultracold* ($T < 1 \text{ mK}$) molecules has grown to comprise hundreds of researches. The production of ultracold ensembles of atoms has revolutionized the field of AMO physics. The impact of creating ultracold molecules is expected to be a large and profound as that made by the work performed with ultracold atoms. The rich internal structure combined with low translational and rotational energy enables high resolution spectroscopic measurements, high precision control of chemical reactions (?), studying new low energy collision dynamics (?), quantum-phase transitions (?), among others (?).

The cold molecules field joins two of the three main branches of modern atomic, molecular and optical (AMO) physics: the ultracold and the ultraprecise. It also brings together many areas of knowledge AMO physics, chemistry, quantum information science, quantum simulation, condensed matter physics, nuclear physics and astrophysics. In order to study such exciting applications, it is essential to produce large samples of molecules at temperatures below 1 K .

The complex molecular energy level structure has so far prevented a straightforward extension of laser cooling to molecules, although several proposals for direct (?, ?, ?) or cavity-enhanced laser cooling (?, ?, ?) have emerged. Instead, the production of cold and ultra cold molecules have focused on two main routes with successful results. The

first is the direct cooling of existent “hot” ground-state stable molecules via sympathetic cooling, such as buffer gas cooling (?), or using external electric (?), magnetic (?), or optical fields (?) to do a phase space-conservative deceleration of the molecular beams. The second widely used approach is to associate ultracold atoms. These techniques take advantage of the enormous power of existing methods in laser cooling and evaporative cooling (?, ?, ?) for producing samples of ultracold atoms.

The earliest experiments in forming ultracold molecules from laser-cooled atoms used the indirect method of photoassociation (PA) (?). In PA, a laser is tuned to resonance with with a transition from the free (scattering) state of two ultracold ground (S) state atoms, to a bound level of the excited ($S + P$) potential.

Another increasingly common associating technique involves sweeping a magnetic field through a Fano-Feshbach resonance, such that atom pairs are adiabatically transferred from an unbound state to a weakly bound state (?). This kind of magneto-association process, has been demonstrated with near-unit efficiency for both homonuclear and heteronuclear species (?, ?)

In this thesis we proposed a new way to associate a pair of atoms. Starting from a cold sample of sodium atoms, we use two strong photons, with different wavelengths, to create a bound state. A interatomic binding potential consists of an attractive part at large separations, approaching a minimum in the region of equilibrium separation, then becoming repulsive. The different photons connect the Na pairs to the attractive and to the repulsive part of the $3S_{1/2} + 3P_{3/2}$ excited molecular state, creating a molecular bound state. The proposed model for this molecubr creation process, presented in this thesis, shows how one can create a bound potential with any desirable low state energy, and energy separation. The experimental data shows that the creation of such molecules are viable.

This thesis is divided into 5 chapters. The first being the theoretical considerations

where I explain the basic concepts for the understanding of both experimental results. These concepts include: Light-matter interaction, two-photon processes, internuclear interactions, Born-Oppenheimer approximation, electronic states of diatomic molecules, electronic state transitions and formation of molecules and ions.

Chapter 2 covers the experimental setup. Since both experiments were carried out in the same experimental setup, and its composition was well described in many works from our group (tese edwin, tese franklin) (? , ? , ? , ? , ? , ?), only the main features of the system are going to be addressed: The atomic source, the magneto optical trap, dark spontaneous optical trap, lasers and frequencies used in the experiments, vacuum system, the system measurement control and the kind of information that was acquired.

The two-photon cooperative absorption experiment is presented in chapter 3. The experimental data shows an indirect measurement of the phenomena along with a intensity dependent plot that gives us the necessary elements to confirm that we are indeed observing a TPA. Also a theoretical model based on the long-range potentials is given to explain the TPA peak asymmetry.

Chapter 4 describes the photonic molecule creation. A theoretical description of the molecule is given, including the basic phenomenon and observations necessary for the bound potential formation. Since the model was proposed by us, a thorough study on how its parameters change the molecular potential was done and is shown in a series of graphs. The experimental data points show in three different ways that the production of such molecules is possible.

In the final chapter the conclusions and perspectives for both experiments are given.

1 Theoretical Considerations

1.1 Fundaments of light-atom interaction

One approach to treat the light-matter interaction in the quantum mechanic picture is to consider the classical mechanic Hamiltonian, that describes a particle with charge e and mass m in the presence of an electromagnetic field and an external conservative potential, in terms of the vector and scalar potentials and replace $\mathbf{r}$ and $\mathbf{p}$ by the observables $\mathbf{R}$ and $\mathbf{P}$, respectively, obtaining:

$$\hat{H} = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - e\mathbf{A} \right)^2 + e\phi + V \quad (1.1)$$

which may be expanded into

$$\hat{H} = \frac{1}{2m} \left(-\hbar^2 \nabla^2 - \frac{\hbar}{i} \nabla \cdot \mathbf{A} - \frac{2\hbar e}{i} (\mathbf{A} \cdot \nabla) + e^2 \mathbf{A}^2 \right) + e\phi + V \quad (1.2)$$

The choice of Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) for electromagnetic waves propagating in the free space ($\phi = 0$) simplifies the Hamiltonian to

$$\hat{H} = \left[\frac{-\hbar^2}{2m} \nabla^2 + V \right] + \left[\frac{-e^2 \mathbf{A}^2}{2m} - \frac{e\hbar}{im} (\mathbf{A} \cdot \nabla) \right] \equiv \hat{H}_0 + W. \quad (1.3)$$

This can be viewed as composition between a zero-order Hamiltonian ($\hat{H}_0$) for the unperturbed particle with an external field, and the term arising from the radiation-matter interaction W , for particles bound in atoms or molecules experiencing ordinary electromagnetic waves. When the light field is quantized (?) we can rewrite the time dependent vector potential as:

$$\mathbf{A} = C \sum_{\mathbf{k}} \sum_{\alpha} \frac{1}{\sqrt{\omega}} \left[a_{\mathbf{k},\alpha}(t) \epsilon^{(\alpha)} e^{i\mathbf{k} \cdot \mathbf{x}} + a_{\mathbf{k},\alpha}^{\dagger}(t) \epsilon^{(\alpha)} e^{-i\mathbf{k} \cdot \mathbf{x}} \right] \quad (1.4)$$

where C is a normalization constant, ω is the light frequency, $\epsilon^{(\alpha)}$ is the polarization vector, and $a_{\mathbf{k},\alpha}^\dagger(t)$ ($a_{\mathbf{k},\alpha}(t)$) is the creation (annihilation) operator that creates (annihilates) a photon with momentum $\mathbf{k}$ and polarization α at a time t . Our quantum state can be written in terms of the atomic state and the number of photons, e.g. $|u_{\mathbf{k}} ; N\rangle$ describes a system with N photons where the atom is in the state $u_{\mathbf{k}}$ with momentum $\mathbf{k}$. In this formalism one can see that the term $\frac{-e^2 \mathbf{A}^2}{2m}$ in Equation 1.3 will contribute only when the state of the atom was kept the same, since it acts only on the photon state. While the term $\mathbf{A} \cdot \nabla$ acts on everything because of the differential operator.

For particles bound in atoms or molecules experiencing ordinary electromagnetic waves, the internal electric fields due to V are order of magnitude larger than the external fields. Therefore the W term in Equation 1.3 can be treated as a perturbation. An atomic wave function ψ can be expanded as

$$|\psi ; N\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}(t) |u_{\mathbf{k}} ; N\rangle e^{-iE_{\mathbf{k}}t/\hbar} \quad (1.5)$$

where $|u_{\mathbf{k}} ; N\rangle \equiv u_k$ are the wave functions for the unperturbed Hamiltonian ($\hat{H}_0 u_k = E_k u_k$) ($\hat{H}_0$ only acts on the atomic state). Using that wave function in the Schrodinger Equation 1.3 we have

$$\begin{aligned} [\hat{H}_0 + W] |\psi ; N\rangle &= \sum_{\mathbf{k}} c_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} \hat{H}_0 u_k + \sum_{\mathbf{k}} c_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} W(t) u_k(x) \\ &= i\hbar \left[\sum_{\mathbf{k}} \dot{c}_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} u_k - \frac{i}{\hbar} \sum_{\mathbf{k}} E_k c_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} u_k \right] \\ &= i\hbar \frac{\partial |\psi ; N\rangle}{\partial t} \end{aligned} \quad (1.6)$$

The term that contains $\hat{H}_0 u_k$ cancels the term $\frac{i}{\hbar} \sum_{\mathbf{k}} E_k c_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} u_k$ and we obtain:

$$i\hbar \sum_{\mathbf{k}} \dot{c}_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} u_k = \sum_{\mathbf{k}} W c_{\mathbf{k}}(t) e^{-iE_{\mathbf{k}}t/\hbar} u_k \quad (1.7)$$

Now we can use the fact that functions u_k constitute an orthonormal set and we can multiply Equation 1.7 by $u_k e^{iE_m t/\hbar}$ and we have:

$$i\hbar \sum_{\mathbf{k}} \dot{c}_{\mathbf{k}}(t) e^{-i(E_k - E_m)t/\hbar} \langle u_{\mathbf{m}} | u_{\mathbf{k}} \rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}(t) e^{-i(E_k - E_m)t/\hbar} W_{m,k}(t) \quad (1.8)$$

$$i\hbar \sum_{\mathbf{k}} \dot{c}_{\mathbf{k}}(t) e^{-i(E_k - E_m)t/\hbar} \delta(k, m) = \sum_{\mathbf{k}} c_{\mathbf{k}}(t) e^{-i(E_k - E_m)t/\hbar} W_{m,k}(t) \quad (1.9)$$

$$\dot{c}_{\mathbf{m}}(t) = \frac{1}{i\hbar} \sum_{\mathbf{k}} c_{\mathbf{k}}(t) e^{-i(E_k - E_m)t/\hbar} W_{m,k}(t) \quad (1.10)$$

where $W_{m,k}(t) \equiv \langle u_{\mathbf{m}} | W(t) | u_{\mathbf{k}} \rangle$. This expression is exact. We can now introduce the perturbation theory by assuming that all the population is in the initial state state $|u_1; N\rangle$, and the transition probability from this state to some other state $|u_{\mathbf{k}}; N\rangle$ is small. This would imply that at zeroth order approximation we have:

$$c_1^{(0)}(t) = 1 \quad (1.11)$$

$$c_{\mathbf{k} \neq 1}^{(0)}(t) = 0 \quad (1.12)$$

With this we can now get the first order approximation of:

$$\dot{c}_{\mathbf{m}}^{(1)}(t) = \frac{1}{i\hbar} \sum_{\mathbf{k}} \delta(\mathbf{k}, 1) e^{-i(E_k - E_m)t/\hbar} W_{m,k}(t) \quad (1.13)$$

$$\dot{c}_{\mathbf{m}}^{(1)}(t) = \frac{1}{i\hbar} e^{-i(E_l - E_m)t/\hbar} W_{m,k}(t) \quad (1.14)$$

$$c_{\mathbf{m}}^{(1)}(t) = \frac{1}{i\hbar} \int_0^\infty dt' e^{-i(E_l - E_m)t'/\hbar} W_{m,k}(t) \quad (1.15)$$

If $c_{\mathbf{m}}^{(1)}$ vanishes or if a better approximation is called for, we use

$$c_{\mathbf{m}} \cong c_{\mathbf{m}}^{(0)}(t) + c_{\mathbf{m}}^{(1)} + c_{\mathbf{m}}^{(2)}$$

where:

$$\dot{c}_{\mathbf{m}}^{(2)}(t) = \frac{1}{i\hbar} \sum_{\mathbf{n}} c_{\mathbf{n}}^{(1)}(t) e^{-i(E_n - E_m)t/\hbar} W_{m,k}(t) \quad (1.16)$$

$$\begin{aligned}\dot{c}_{\mathbf{m}}^{(2)}(t) &= \frac{1}{i\hbar} \sum_{\mathbf{n}} e^{-i(E_n - E_m)t/\hbar} W_{m,k}(t) \\ &\times \frac{1}{i\hbar} \int_0^\infty dt' e^{-i(E_l - E_n)t'/\hbar} W_{n,l}(t')\end{aligned}\quad (1.17)$$

$$\begin{aligned}c_{\mathbf{m}}^{(2)}(t) &= \frac{1}{i\hbar} \sum_{\mathbf{n}} \int_0^\infty dt'' e^{-i(E_n - E_m)t''/\hbar} W_{m,n}(t'') \\ &\times \frac{1}{i\hbar} \int_0^\infty dt' e^{-i(E_l - E_n)t'/\hbar} W_{n,l}(t')\end{aligned}\quad (1.18)$$

and so on.

From Equations 1.3 and 1.4 we can see that the first order approximation has terms from one and two photon transitions. But the two-photon term doesn't change the atomic state. Since the scope of this thesis is two-photon absorption with change in the atomic (or molecular) state the $\mathbf{A} \cdot \mathbf{A}$ term will not be considered. The term $\mathbf{A} \cdot \nabla$ taken twice (second order perturbation) is two-photon process that changes the atomic state. The vector potential acting twice can change the net number of photons by: $-2, 0$, or 2 therefore we can either have a two-photon absorption, an absorption followed by an emission (or the other way around) or a two-photon emission.

1.2 Atomic structure - alkali-metal atoms

Alkali atoms are very popular in atomic molecular optics (AMO) physics, they were the first ones to be cooled and trapped, and are widely used for most of the present experiments. Two important features that made them so popular in the AMO field is that the excitation frequency from the ground-state to the first excited state is in the visible region, which makes it relatively simple to generate light for the optical transition. And the other reason is that it is easy to generate an atomic beam with large vapor pressure with a few hundred of degrees Centigrade.

One key point to understand alkali-metal atoms structure is the fact that their ground-state have a closed shell with one valence electron. For sodium the electron configuration is $^{23}\text{Na} (1s)^2 (2s)^2 (2p)^6 (3s)$. Because of the closed shell the core doesn't contribute to the atom orbital angular momentum, and there remains only the outer,

valence electron. The state this electron is completely determined by its spin angular momentum (s) and orbital angular momentum (l). The coupling of this two in the usual way forms the electron total angular momentum (j).

$$|l - s| \leq j \leq l + s \quad (1.19)$$

Since the core is shielding the contribution the the angular momenta from the other electron, the total orbital angular momentum is $\vec{L} = \vec{l}$, spin angular momentum $\vec{S} = \vec{s}$, and total angular momentum $\vec{J} = \vec{j}$. The fine structure is given by the spin-orbit interaction $V_{so} \propto \vec{J} \cdot \vec{S}$, that depends on the interaction of $\vec{S}$ with respect to $\vec{L}$ the different energy values os the states are given by different values of $\vec{J}$. This coupling is only valid if the spin-orbit interaction is small compared to the level separation of the states.

The atomic electronic states are fully specified in the Russell-Saunders notation as $n^{(2s+1)}L_j$ where n is the principal quantum number of the valence electron. In Na case the angular momentum $L = 1$ can couple with the total spin $S = 1/2$ to form either $J_e = 1/2$ or $J_e = 3/2$. The fine structure splitting between these two states is $\approx 515 \text{ GHz}$. The lowest state ($L = 0$) for Na is the $3^2S_{1/2}$ state, whereas the first excited ($L = 1$) state are $3^2P_{1/2,3/2}$ states, where the valence electron is excited to the $(3p)$ -state.

When the interaction of the nuclear spin $\vec{I}$ with the total angular momentum electron $\vec{J}$ is included, the structure of the alkali-metal atoms becomes somewhat more complicated. These angular momenta couple in the usual way to form the total angular momentum as $\vec{F} = \vec{I} + \vec{J}$. Different values of $\vec{F}$ for the same values of both $\vec{I}$ and $\vec{J}$ are split by the interaction between the nuclear spin and the electronic angular momentum. The resulting structure is called the hyperfine structure, and because of the much smaller size of the nuclear magnetic moment it is much smaller than the fine structure. For Na , with a nuclear spin of $I = 3/2$, the ground state has $F_g = 1$ or 2 and the hyperfine splitting is $\approx 1.77 \text{ GHz}$. The excited state has $F_e = 0, 1, 2$, and 3 , and the resulting hyperfine splitting is $\approx 100 \text{ MHz}$. In general, the shift of energy levels because of the hyperfine

interaction can be written as (?)

$$\Delta E_{hfs} = \frac{1}{2}hAK + hB \frac{3/2K(K+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)} \quad (1.20)$$

where $K = F(F+1) - I(I+1) - J(J+1)$ and A and B are two parameters, that are adjusted using experimental data. And as it is well explained in Ref (?) each of these states can be further splinted into $(2I+1) \times (2J+1)$ Zeeman sub-levels when there is an external magnetic field present.

1.3 Atom-atom interactions

One key point to understand the two-photon two-atom absorption, and the creation of a photonic potential is the interaction between the atoms.

An atom is made up of a central nucleus and orbital electrons, discounting any subnuclear phenomena (since they have different nature and are orders of magnitude stronger than any interatomic force) we can consider the nucleus being a solid body of diameter $\approx 10^{-12}$ cm with a positive charge. If there where no orbital electrons the force between two nuclei would be Coulombic: $F_{N-N}(r) = Z_1 Z_2 e^2 / r^2$ where Z_1 and Z_2 are the number of protons contained in the nucleus.

If the orbital electrons are considered the atom size is $\approx 10^{-8}$ cm. The effect of the electrons is to neutralize the charges of the nucleus. If two atoms are far from each other, they can be considered as two entities with an effective null charge (when considering neutral atoms), consequently there are no interatomic forces. When the separation is comparable with the atomic diameter the Coulomb interactions of the outer electrons of atom 1 with those of atom 2 and with the nucleus of atom 2 (and vice versa) have a significant effect. The two atoms no longer view each other as separate entities and the interaction becomes a rather complicated many-body problem.

Lets consider the Hamiltonian of a system containing N nuclei and I electrons whose polar coordinates are $\mathbf{R}_n$ and $\mathbf{r}_i$ respectively ($n = 1$ to N and $i = 1$ to I)

$$H = - \sum_{n=1}^N \frac{\hbar}{2M_n} \frac{\partial^2}{\partial \mathbf{R}_n^2} - \sum_{i=1}^I \frac{\hbar}{2m_e} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V = T_N + T_e + V \quad (1.21)$$

where T_n is the nucleus kinetic energy, T_e is the electrons kinetic energy, and V Coulomb interaction potential given by:

$$V = \frac{1}{2} \sum_{i \neq j=1} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{n=1}^N \sum_{i=1}^I \frac{Z_n e^2}{|\mathbf{R}_n - \mathbf{r}_i|} + \frac{1}{2} \sum_{n \neq l=1}^N \frac{Z_n Z_l e^2}{|\mathbf{R}_n - \mathbf{R}_l|} \quad (1.22)$$

This many-body problem can be simplified if we adopt the Born-Oppenheimer approximation, which takes advantage of the large difference in the masses of the electrons and nuclei. Because of this, the electrons respond almost instantaneously to nuclei displacement. Therefore instead of trying to solve the Schrodinger equation for all particles simultaneously, we regard the nuclei as fixed in position and solve the Schrodinger equation for the electrons in the static electric potential arising from the nuclei in that particular arrangement.

The electronic part of Equation 1.21 can be seen as a nuclei position dependent Hamiltonian:

$$H_e \Phi_q = (T_e + V) \Phi_q = E_q(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \Phi_q \quad (1.23)$$

where $\Phi_q = \Phi_q(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_I)$ is the electronic wave function for a specified nuclear configuration, and these solutions form an orthonormal set of equations. The solutions to the Schrodinger equation arising from the Hamiltonian in 1.21:

$$H \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_I) = E \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_I) \quad (1.24)$$

can be expanded in terms of the electronic wave function

$$\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_I) = \sum_q F_q(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \Phi_q \quad (1.25)$$

when substituting Equation 1.25 in 1.21 we obtain:

$$\sum_q \left\{ - \sum_{n=1}^N \frac{\hbar}{2M_n} \frac{\partial^2}{\partial \mathbf{R}_n^2} (F_q \Phi_q) - F_q \sum_{j=i}^I \frac{\hbar}{2m_e} \frac{\partial^2 \Phi_q}{\partial \mathbf{r}_j^2} + V F_q \Phi_q \right\} = E \sum_q F_q \Phi_q \quad (1.26)$$

The nuclei kinetic energy operator as a function of F_q and Φ_q is

$$\begin{aligned} - \sum_{n=1}^N \frac{\hbar}{2M_n} \frac{\partial^2}{\partial \mathbf{R}_n^2} (F_q \Phi_q) &= - \frac{\hbar}{2\mu} \left(\Phi_q - \sum_{n=1}^N \frac{\hbar}{2M_n} \frac{\partial^2}{\partial \mathbf{R}_n^2} + 2 \sum_{n=1}^N \frac{\partial F_q}{\partial \mathbf{R}_n} \frac{\partial \Phi_q}{\partial \mathbf{R}_n} \right) \\ &\quad - \frac{\hbar}{2\mu} F_q \sum_{n=1}^N \frac{\partial^2 \Phi_q}{\partial \mathbf{R}_n^2} \end{aligned} \quad (1.27)$$

Now we can use the Born-Oppenheimer approximation:

$$|\nabla_{\mathbf{R}_n} F_q| \gg |\nabla_{\mathbf{R}_n} \Phi_q| \quad (1.28)$$

and neglect the term that contains $\nabla_{\mathbf{R}_n} \Phi_q$ in 1.27 and we obtain for the Schrodinger equation:

$$\sum_q \{ \Phi_q (T_N F_q) + F_q (T_e \Phi_q + V \Phi_q) \} = E \sum_{q'} F_{q'} \Phi_{q'} \quad (1.29)$$

Using the fact that Φ_q form an orthonormal set of equations:

$$\sum_q \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi_p^* \Phi_q = \delta_{pq} \quad (1.30)$$

we can multiply Equation 1.29 by Φ_p and integrate over all electronic coordinates

$$\Phi_p (T_N F_p) + F_p \Phi_p E_p(\mathbf{R}) = E F_p \Phi_p \quad (1.31)$$

and we obtain a Hamiltonian for the nuclei:

$$T_N F_p + E_p F_p = H_N F_p = E F_p \quad (1.32)$$

As it also can be shown that the nuclear wave function can be separated in vibration and rotational motion.

The Born-Oppenheimer approximation has divided the Schrodinger equation into two parts: electrons (Equation 1.23) and nuclei (Equation 1.32). As it was mentioned Equation 1.23 the Schrodinger equation for the electron in a potential V depends on the fixed locations of the nuclei. The solution is the electronic wavefunction Φ_p , and the eigenvalue E_p is the electronic contribution to the total energy of the system plus the potential energy of internuclear repulsion at the predetermined nuclear position. When the the energy is plotted against the nuclear position we obtain the interatomic potential energy curve. Since the sum of the potentials have bound states the interacting atoms can be seen as molecules.

1.3.1 Electronic states of diatomic molecules

The interatomic potential energy curves (or electronic states) can be calculated through a series of methods: Thomas-Fermi model (?), Thomas-Fermi-Dirac (?), empirically (?), Valece bound method (?), Molecular orbital method (?) and others.

The idea is not to obtain such curves, but use them so we can understand some collision properties. Therefore an important characteristic worth viewing is how these states are classified. Also let's focus on the interaction of a diatomic pair, which is more suitable for the experiments that we performed.

For an atom pair the interatomic axis can naturally be taken as the symmetry axis. The allowed symmetries can be inferred from the atomic properties at the dissociation limit. In the nonrotating, nonrelativistic approximation, the total electron spin $\vec{S}$, which is the sum of the individual electron spin from each atom ($\vec{S} = \vec{s}_a + \vec{s}_b$), is conserved. The total electronic orbital angular momentum ($\vec{L} = \vec{l}_a + \vec{l}_b$) is not conserved, as a frozen dimer is not spherically symmetric in space. The molecule presents a cylindrical symmetry around the internuclear axis, this makes the projection of the angular momenta onto the symmetry axis, Λ a good quantum number, since it is conserved. Thus we can name our molecular state based on the atomic Russel-Saunders coupling

$$^{2S+1}\Lambda^{\pm} \text{ or } ^{2S+1}\Lambda_{g/u}^{\pm} \quad (1.33)$$

where Λ is encoded as $\Sigma, \Pi, \Delta, \dots$ for $|\Lambda| = 0, 1, 2, \dots$. The $\pm$ superscript indicates a reflection symmetry of the spatial component of the electronic wavefunction through a plane containing the internuclear axis. This symmetry only exists for Σ states. The g/u (gerade / ungerade) subscript indicates the inversion of all electrons through the center of charge. It only exists for homonuclear dimer.

The nonrelativistic description determines the largest energy scales in molecules, which occurs when the atoms are interacting at short-range, where the interatomic distance (R) is smaller than $30a_0$ (a_0 is the Borh radius). When we are in the long-range part of the interaction ($R > 30a_0$) the weaker relativistic interactions, such as spin-orbit and hyperfine interactions, play an important role in the electronic states, since they are still vastly larger than the kinetic energy of the colliding atoms.

Regardless of the detailed form of the spin-orbit interaction, these “relativistic adiabatic” potential are labeled by $\Omega_{g/u}^{\pm}$, where Ω is the absolute value of the projection the total angular momentum $\vec{j} = \vec{j}_a + \vec{j}_b = \vec{L} + \vec{S}$ in the internuclear axis. The superscript, $\pm$, which differs from the nonrelativistic case, is a reflection symmetry of the total electron wavefunction (not only the spatial part) through a plane containing the internuclear axis.

Figure 1 taken from Ref (?) show the potentials for a sodium dimer. Figure 1 (a) are the short-range potentials and (b) are the long-range ones. One can see that the energy scale is a factor of 100 times smaller for the long-range potentials while the internuclear separation is 10 times bigger. Each curve of the long-range will approach one of the short-range. There are 16 long-range potentials and only 8 short range potentials dissociating to $^2S + ^2P$, hence several of the relativistic adiabatic potentials approach one short-range potential. For example, four relativistic adiabatic potentials, with symmetries 0_u^+ , 0_u^- , 1_u and 2_u approach the short-range state labeled $^3\Pi_u$. Within the relativistic calculation these four will not be exactly degenerate but will be split by the spin-orbit interaction. However on the scale of Figure 1 (a) this splitting (roughly 10 cm^{-1} for Na_2) would hardly be noticeable.

Figure 1 – Interatomic potentials for a sodium dimer. (a) Short-range potentials. (b) Long-range potentials. (?).

Table 1 – Long-range potentials can be expanded in power series. This table shows which coefficient corresponds to each interaction

Interaction Coefficient	Interaction
C_1	Ion-Ion
C_2	Ion-Dipole
C_3	Dipole-Dipole
C_4	Ion-Dipole
C_5	Dipole-Dipole
C_6	Dipole*-Dipole*
C_7	Quadrupole-Quadrupole
C_8	Dipole*-Quadrupole*
C_9	Quadrupole - Octopole
C_{10}	Quadrupole* - Quadrupole*

Long-range potentials can be expanded in power series:

$$V(R) = D - \sum_n \frac{C_n}{R^n} \quad (1.34)$$

where D is the dissociation energy and R is the interatomic distance. The C_n coefficients are calculated via perturbation theory through the multipolar expansion. Table 1 shows which coefficient correspond to each interaction.

When dealing with alkali-metal homonuclear pairs one important interaction is the

dipole-dipole interaction. The excited state $S^2 + P^2$ has a $1/R^3$ behavior resulting from the sharing of the excitation back and forth between the two atoms. A useful semiclassical picture of this resonant dipole interaction is that each atom is in a superposition of ground and excited state and has a real oscillating dipole moment. Depending on how the dipoles are oriented, the interaction can be attractive or repulsive. For example, two dipoles oscillating perpendicular to the molecular axis will have an interaction which is either $\pm C_3/R^3$ depending on whether the dipoles are in phase or 180° out of phase.

1.3.2 Electronic state transitions

The main basis of the experiments here presented is the interaction between a colliding pair and light. Therefore, is useful to understand some concepts used in understanding cold collisions in a light field. Figure 2 gives a schematic description of the key features of these collisions. The ground state potential, $V_g(R)$, is connected to the excited one, $V_e(R)$, via an optical coupling, a light field with frequency ω , which is detuned by $\Delta = \omega - \omega_0$ from the frequency of the atomic resonance ω_0 . The detuning can be to the blue or to the red of the resonance, corresponding to a positive or negative value of Δ , respectively. In Figure 2 is also indicated the Condon point, R_C , for the optical transition. The Condon point is the position at which the internuclear distance of the pair enables the optical resonance with the light field, i.e.,

$$V_e(R_C) - V_g(R_C) = \hbar\omega \quad (1.35)$$

The Condon point is based on the Franck-Condon principle, which, similarly to the Born-Oppenheimer approximation, because nuclear masses are so much larger than the mass of an electron, an electron transition occurs within a stationary nuclear framework. As a result, the internuclear separation remains unchanged during the actual transition, but then readjust once the electrons have adopted their final distribution.

The quantum description of this process is similar to the classical one. Qualitatively, the transition occurs from the initial vibrational state to the vibrational state that

Figure 2 – Schematic description of the key features of pair-photon collisions. The ground state potential ($V_g(R)$) is connected to the excited one ($V_e(R)$) via an optical coupling, a light field with frequency ω , which is detuned by $\Delta = \omega - \omega_0$ from the frequency of the atomic resonance ω_0 .

it most resembles in the final state. In that way, the vibrational wavefunction undergoes least change, which corresponds to the preservation of the dynamical state of the nuclei as required by the Franck-Condon principle.

A quantitative quantum mechanical description is based on the evaluation of the electric dipole transition moment between the initial vibronic state $\psi_a = |\xi\nu\rangle$ and the excited vibronic state $\psi_b = |\xi'\nu'\rangle$. In a molecule, the electric dipole moment operator depends on the locations and charges of electrons, and the nuclei:

$$\mu = -e \sum_j^I r_j + e \sum_n^N Z_n R_n = \mu_e + \mu_N \quad (1.36)$$

In the Born-Oppenheimer approximation the transition amplitude is given by:

$$\langle \psi_b | D | \psi_a \rangle = e \int dR \int dr F_B^*(R) \Phi_B^*(R, r_1, \dots, r_n) \left(\sum_{i=1}^2 Z_i R_i - \sum_j r_j \right) F_A(R) \Phi_A(R, r_1, \dots, r_n) \quad (1.37)$$

Using the orthogonality of the electronic wave functions, the first term in the expression above is zero. The integral over all electron coordinates in the final term is the dipole moment for the transition when the nuclei have coordinates $\mathbf{R}$. To a reasonable first approximation, this transition moment is independent of the locations of the nuclei so long as they are not displaced by a constant $\mu_{\xi', \xi}$. Therefore, the overall electric dipole transition moment is

$$\langle \psi_b | D | \psi_a \rangle = \mu_{\xi', \xi} \int F_B^*(R) F_A(R) dR \quad (1.38)$$

where the integral is the overlap integral between the two vibrational state in their respective electronic states. Therefore the transition probability is proportional to the overlapping between the initial and the final states.

1.3.2.1 Formation of molecules and ions

One technique used to study ultracold collisions is the photoassociation of ultracold atoms. Photoassociation (PA) is the process in which two colliding atoms absorb a photon to form an excited molecule:

The high resolution of PA spectroscopy in ultracold atoms ($T < 1 \text{ mK}$) enables us to study how this molecule formation is changed in the presence of light. One way to monitor this process is to photoionize the cold excited molecules and detect the resulting ions. For Na, there are two pathways leading to ionization:

1. The cold excited molecule is directly photoionized at short internuclear distances, which is termed photoassociative photoionization (PAPI) :

Figure 3 – Photoassociative Ionization diagram. This process was explained semiclassically in four steps by Gallagher (?) : 1) the pair in the ground state absorbs a photon and goes to the first excited state. 2) In the excited state the pair goes from $R_C(\omega_1)$ to $R_C(\omega_2)$. 3) When the pair reach $R_C(\omega_2)$ it absorbs ω_2 and goes to the doubly-excited state. 4) The velocity gained in step 2 due to the attractive interaction of the first excited state enables the pair to reach short-range internuclear distances, and goes to the ionizing state

2. The cold excited molecule is promoted to a doubly-excited autoionizing state, which is termed photoassociative ionization (PAI).

It has been shown that PAI is dominant when energetically allowed (?). This process was explained semiclassically in four steps by Gallagher (?) and is diagrammatically shown in Figure 3: 1) the pair in the ground state absorbs a photon and goes to the first excited state. 2) In the excited state the pair goes from $R_C(\omega_1)$ to $R_C(\omega_2)$. 3) When the pair reach $R_C(\omega_2)$ it absorbs ω_2 and goes to the doubly-excited state. 4) The velocity

gained in step 2 due to the attractive interaction of the first excited state enables the pair to reach short-range internuclear distances, and goes to the ionizing state. The steps 1 and 3 can be done with the same frequency, namely 1 color PAI, or with two different frequencies (2-color PAI)

2 Experimental system

Our system is based in a magneto optical trap (MOT) (1,2) that catches the atoms released by the atomic source, creating a sample of cold atoms ($\approx 270\mu K$). Lasers probe this sample and the ions that are formed by this interaction are measured as function of the intensity or frequency of the probe beam. The setup here presented was used for both experiments carried during my Ph.D., two-photon cooperative absorption and the photonic molecule, with minor differences between them. Besides ions, other information of our sample is acquired, such as: number of trapped atoms, volume of the sample and frequency of the probe laser. The experimental setup was well described in many published materials (3,4,5,6,7,8) so in this chapter I'll do a brief explanation of the main components, and how the data is taken.

2.1 Atomic source

In studies previously realized in our group (9) we concluded that for sodium, the oven combined with a Zeeman Slower (10) was the best (in comparison with a dispenser) source of atoms for the MOT. Therefore our system is composed by an oven that operates at $\approx 550 K$ and a water cooled Zeeman slower in a spin flip configuration. The design of this part was based on the ones presented by Naik on his Ph.D. thesis (11). The Zeeman slower is used to obtain a beam of atoms moving with a speed near the capture velocity, which in case of sodium is $\approx 20 m/s$, in the science chamber region. It consists of a slowing light beam, that is counterpropagated to the atomic flux, and a magnetic field that is designed to compensate the Doppler effect experienced by the atoms as they are slowed. Therefore enabling the atoms to absorb the slowing light all the way to the science chamber.

The formula of the magnetic is given by:

Figure 4 – Magnetic field as a function of the distance. The red line shows the theoretical calculation. The black points is the measured data.

$$B(z) = \frac{\hbar\Delta}{\mu} - \left(\frac{\hbar k v_{ini}}{\mu} \right) \sqrt{1 - \left(\frac{z}{z_0} \right)^2} \quad (2.1)$$

where Δ is the light detuning from the resonance, $z_0 = M v_0^2 / \eta \hbar k \gamma$ is the length of the magnet, M is the atomic mass and k is the wavenumber. The spin flip configuration consists on having a magnetic field that crosses zero. As one can see from Equation 2.1 the detuning from the resonance of the slowing beam is directly proportional to difference between the final and the initial magnetic field. Making magnetic fields that crosses zero gives the possibility to have a large detuning without the need of big magnetic fields.

Our Zeeman slower was built using a square cross-section cooper tube. The choice of this kind of wire was based on the fact that it could be water-cooled and the winding was easier since it has no gaps between the turns. The theoretical field (figure 4) was calculated for slowing atoms with 900 m/s, or less, with a 170 MHz detuning from the atomic transition $3S_{1/2}(F=2) \rightarrow 3P_{3/2}(F'=3)$. Two sets of coils were designed to match the positive and the negative part of the field.

2.2 Magneto-optical trap

A magnto-optical trap is a hybrid trap design to trap neutral atoms. It employs circularly polarized counter propagating beams along the 3 cartesian axes (trap beams) and a linearly inhomogeneous magnetic field to create a trapping potential for the atoms. For sodium the trap frequency is tuned to the red of the atomic transition $3S_{1/2}(F = 2) \rightarrow 3P_{3/2}(F' = 3)$, the cycling transition of the D_2 line.

The hyperfine splitting between the $3P_{3/2}(F = 3)$ state and the $3P_{3/2}(F = 2)$ state is $\approx 58 \text{ MHz}$ so the trap frequency overlaps with the $F' = 2$ state and atoms are pumped to this state. The selections rules of parity forbids the atoms to decay from the exited $3P_{3/2}(F = 2)$ to the $3P_{1/2}$ and from the momentum selection rules they can decay to the $3S_{1/2}(F = 2)$ state or the $3S_{1/2}(F = 1)$ “dark” state. When the atoms are in the dark state they are not affected by the trapping light. A repump frequency ($3S_{1/2}(F = 1) \rightarrow 3P_{3/2}(F' = 2)$) is needed to put the atoms back into the cycling transition so that the cooling can continue.

2.2.1 Dark spontaneous optical trap (SPOT)

The MOT density is limited by two process: i) collision losses, ii) repulsive forces between atoms due to reabsorption of scattered photons inside the trap. The radiation trapping or photon induced repulsion occurs when atoms near the trap center spontaneously emit a photon which is absorbed by another atom before leaving the MOT volume. This absorption increases the relative momentum between the atoms by an amount $2\hbar k$ and produces a repulsive force proportional to the absorption cross-section of the incident beam. The equilibrium between this internal force and the confining force leads to bigger atomic clouds.

To overcome the radiation trapping one can pump the trapped atoms to a dark hyperfine level, that will not interact with the trapping light. Therefore the spontaneously

Figure 5 – MOT absorption image, when the trap in the “bright” and in the “Dark SPOT” configuration.

emitted photon is not seen by any trapped atoms. This can be done by putting a real dark spot in the center of the repumping beam. The atoms in the trap center are not repumped to the $3S_{1/2}(F = 2)$ state and therefore are transparent to the trapping frequency ($3S_{1/2}(F = 2) \rightarrow 3P_{3/2}(F' = 3)$).

Figure 5 shows pictures of the MOT done in the “Bright” configuration, no dark spot, and in the Dark SPOT. Both pictures were taken in the same way and the number of trapped atoms is approximately the same $\approx 2 \times 10^9$ therefore they show that this technique enables the creation of denser samples. In addition, the sample population is 99% in the $3S_{1/2}(F = 1)$ state (?) which allows a better understanding of the spectroscopic data.

2.3 Lasers and frequencies

To perform our experiments we had available 1 solid state laser, 3 dye lasers and 1 diode laser. To obtain the sample of cold atoms we need 4 different frequencies:

1. Cooling frequency ($\approx -10 MHz$ from the $3S_{1/2}(F = 2)$ to $3P_{3/2}(F' = 3)$ transition)
2. Repumping frequency (the $3S_{1/2}(F = 1)$ to $3P_{3/2}(F' = 2)$ transition frequency)
3. Slowing frequency ($\approx -170 MHz$ from the $3S_{1/2}(F = 2)$ to $3P_{3/2}(F' = 3)$ transition)

4. Slowing repumper ($\approx -170 MHz$ from the $3S_{1/2}(F = 1)$ to $3P_{3/2}(F' = 2)$ transition frequency))

These frequencies were obtained in three differently ways. The first one used in the two-photon experiment used two different dye laser, one to obtain the trap frequencies and another to the slower frequencies. Both beams passed through $1.77 GHz$ electro optical modulators (EOM) so in the same beam we could get the repumping frequencies. And the second way was done using only one laser to obtain all 4 frequencies. First the laser beam passed through a $1.77 GHz$ EOM and then through an $170 MHz$ acoustic optical modulator (AOM) producing two spatially separated beams, one used for trapping and another uses for slowing. The third and last setup, schematically shown in Figure 6, also used only one laser to obtain the frequencies, but the difference is that the repumping beam is spatially separated from the cooling beam, to do so we used an AOM instead of the EOM. The beam goes through an $1.77 GHz$ AOM to obtain the repumping beam, then to another $170 MHz$ AOM to obtain the slower beam. The cooling beam is expanded and sent to the main chamber, the slowing beam passes through a $1.77 GHz$ EOM and then is expanded and sent to the oven.

Other frequencies that were relevant to the experiment were the probe frequency, which was a tunable frequency provided by a dye laser, used to probe the pair state, and the frequencies necessary to create the photonic bound state, that also were taken from separate dye lasers.

2.4 Vacuum system

As mentioned, the number of trapped atoms is limited by collision loses. So if the background pressure is too high the background gas will kick the sodium atoms out of the MOT. A vacuum bellow $8 \times 10^{-8} Torr$ in the science chamber is needed lower to enable the trapping, and also to assure a good lifetime of the atoms in the trap.

The MOT is loaded from an atomic beam, the oven is at $550 K$ and according to

Figure 6 – Schematic representation of the experimental system.

the to the vapor-pressure model for sodium at liquid phase ($370\text{ K} < T_{Na} < 1156$), given by (?), which is

$$\log_{10} P_v = 10.86423 - \frac{5619.406}{T} + 0.00000345 T - 1.04111 \log_{10} T \quad (2.2)$$

where P_v is given in Torr, and T is in K . This rough model predicts a pressure of $\approx 6 \times 10^{-3}$ Torr in the oven. Therefore we need a differential pumping scheme to shield the vacuum in the science chamber. It can be separated into 3 parts.

1. oven: composed by the oven a nozzle and a turbo pump.
2. Ion pump: a 6-way and a ion pump.
3. The science chamber: Zeeman Slower, science chamber and ion pump.

each of this parts have there own pumping system and are connected through a differential pumping tube with a diameter of $\approx 6\text{ mm}$ and a length of $\approx 15\text{ cm}$. Due to this tube, the pressure in the second part is $\approx 3 \times 10^{-8}$ Torr, and in the chamber is of the order of 10^{-9} Torr.

2.5 Measurements

In order to measure how light affects the collision process via photoassociative ionization (PAI), or PAPI. We analyzed the ion formation as a function of the intensity or frequency of this light beam. Therefore we needed to measure the ion formation per time, the number of trapped atoms, as well as taking an image of the MOT..

2.5.1 Counting ions

The way we choose to study how the pair collision is affected with the addition of a light beam, was to analyze the ion formation as a function of the intensity or frequency of this light beam. Our choice was based in the fact the Na atoms in a MOT have an ion formation route, the PAI (mentioned in Chapter 2). Therefore using this route to study how collisions are affected was a natural choice. In the case of the two-photon absorption, PAI was not effective due to the low probability that this absorption occurs. So we used the fact that our system was ready to count ions and we added a diode laser with wavelength $\approx 405 \text{ nm}$ to ionize the atoms.

The ion counting is done in two steps, the formed ions are accelerated towards the *channeltron* multiplier using a 2.5 kV electric potential difference between the counter and a grid inside the chamber, followed by the the channeltron sending a pulse to the pulse counter. The number of pulses that are counted during a time interval gives the ions per time formation.

2.5.2 Number of atoms and image.

The number of atoms was taken from a standard procedure using a calibrated photo detector (PD). An image of the MOT is projected onto the PD and we could infer the number of atoms through the brightness of that image.

There were two ways that we could take an image of the MOT: i) emission image. ii) absorption image . The first type of image (Figure 5) is obtained the same way as the number of atoms, but instead of using a set of lenses to project it onto the PD, we do it on a CCD image sensor. After calibrating it (which can be done by taken a picture of a ruler with the same set of lens, and putting the ruler at the same distance that the center of the MOT will be) the picture can give us the size of the atomic cloud.

The absorption image uses a beam that goes through the MOT and it is imaged into a CCD. This type of image gives extra information, the density of the cloud, via the Beer-Lambert law. But it is a little bit trickier to implement. In our setup, it was only implemented when we were taking the data for the photonic molecule. A small part of the repump beam was taken and it passed through two 80 *MHz* AOMs. We used the first positive order from the first AOM and the first negative order from the second AOM. So we could tune the frequency of image beam to obtain the maximum absorption. After the beam was expanded and sent through the MOT, the beam stuck a CCD sensor on the other side of the chamber and an image was captured.

2.5.3 Timing sequence

In order to minimize the number of frequencies present in the sample while the ions are counted, to maintain the same number of atoms during the data count and the background count, a timing sequence was implemented. For both experiments we used the same basic idea, do a background count without the probe laser, then do a measurement with the probe beam. The time between those measurements was only to recover the number of trapped atoms lost while the slower beam was closed. This was done in order to have the same configurations when both measures are taken.

2.5.4 Control and analysis

Figure 7 – Timing sequence for both experiments. We used the same basic idea, do a background count without the probe laser, then do a measure with the probe beam.

The timing sequence, ion counting, laser frequency and frequency measurement were all controlled by a Labview program developed by me. The user interface is shown in Figure 8. All the relevant parameters to do the measurement could be changed, such as delay between shutting the slower off and opening the ionization and probe beam. This was done at first by optical shutters, (which have a response time of the order of $200 \mu s$) and afterward by Uniblitzs (response time of the order of $80 \mu s$). Also there is the possibility to add a delay in the counting start. The measurement time, the time between measurements and the number of measurements were also changeable parameters. The program was designed to have a precision of $0.1 ms$ in the time sequence.

The program also had a settable threshold for the number of atoms to validate the measurement. If either the background data or the full data (data point taken in the presence of the probe laser) displayed a number of trapped atoms below the setting, the data point (background - "full" data) was not saved. All valid data was saved in a .dat file. The user could also set how many data points he wanted to take, which influences the number of steps required to change the laser frequency. The user can also set the number of times the measurement is repeated. During the entire measurement the MOT

Figure 8 – Labview program user interface. This program controls the time sequence and the ion counter.

was observed through a CCD camera to make sure it didn't change position or shape, but the program didn't take any pictures.

The data saved in the file was composed of: probe laser frequency, number of atoms (background count), ion count (background count), number of atoms ("full" data count), ion count ("full" data count). The data was then imported by a Mathematica program, developed by me, that would separate the data points by probe frequency and do an average of the data points in the defined range of frequencies.

3 Two-photon cooperative absorption

The first two-photon experiment realized in our system, as it is presented here, was the cooperative absorption of two photons by two sodium atoms in a collision process. This nonlinear process, widely investigated in solids, had never been realized with cold atoms, but cold atoms hold the key ingredient for cooperative effects: long-range interactions (?)

The idea is to have two photons from a strong laser with frequency ω absorbed by a pair of sodium atoms in the ground state $3S_{1/2} + 3S_{1/2}$ and promoting them to the doubly excited state $3P_{1/2} + 3P_{3/2}$, when the relationship $2\omega = \omega_{s_{1/2} \rightarrow P_{1/2}} + \omega_{s_{1/2} \rightarrow P_{3/2}}$ between the laser frequency and the atomic transitions is satisfied (figure 9).

3.1 Theoretical model

Consider two noninteracting sodium atoms in a collision process interacting with one photon with frequency ω_p . The transition probability (TP) for a two-photon absorption by the pair as a function of ω_p will be the product of the two independent one-photon, one-atom transition probabilities

$$TP(\omega_p) \propto \left[\frac{(\mu_{P_{1/2}} E / 2\hbar)}{(\omega_{P_{1/2}} - \omega_p)^2 + (\Gamma/2)^2} \right] \times \left[\frac{(\mu_{P_{3/2}} E / 2\hbar)}{(\omega_{P_{3/2}} - \omega_p)^2 + (\Gamma/2)^2} \right] \quad (3.1)$$

where $\hbar\Gamma$ is the line width for both transitions, $\mu_{P_{1/2}}$ ($\mu_{P_{3/2}}$) is the dipole matrix element for the transition $3S_{1/2} \rightarrow 3P_{1/2}$ ($3S_{1/2} \rightarrow 3P_{3/2}$). This function has a Lorentzian shape that peaks when ω_p is resonant with any of the atomic transitions.

When the interaction between the atoms is considered, a new scenario arises. Let H_{int} be the perturbation term in the Hamiltonian describing the atom-atom interaction. We can describe the coupled two-atom system in the framework of first-order perturbation

Figure 9 – Relevant energy levels in the atomic and in the molecular structure, for simplicity the hyperfine splitting was not consider.

theory as

$$\chi_{ij} = |i, j\rangle + \sum_{(k,l) \neq (i,j)} \frac{|kl\rangle \langle kl | H_{int} | ij\rangle}{\hbar\omega_{kl} - \hbar\omega_{ij}} \quad (3.2)$$

where $|ij\rangle$ are the non-interacting eigenfunctions. From now on lets consider $3S_{1/2} = 0$, $3P_{1/2} = A$ and $3P_{3/2} = B$. Therefore non-interacting eigenfunctions are equal to

$$|ij\rangle = |0, 0\rangle, |0, A\rangle, |0, B\rangle, |A, A\rangle, |A, B\rangle, |B, B\rangle. \quad (3.3)$$

In this approximation, the wavefunctions are modified while the energy levels remain unshifted. Although the atom-atom interaction has an electrostatic origin, and in general all multipole orders, only dipole-dipole interactions are considered here. So H_{int} assumes the form

$$H_{int} = \frac{e^2}{K\rho^3} [R_a \cdot R_b - 3(R_a \cdot \rho)(R_b \cdot \rho) / \rho^2] \quad (3.4)$$

where K is the host dielectric constant, ρ is the separation between the ions, $R_a = \sum_{l=1}^{\alpha} r_l$ and $R_b = \sum_{l=1}^{\beta} r_l$.

The calculation performed in Ref (?) considers the interatomic interaction to be strong, enabling the two-photon absorption, but weak enough to give a negligible change to the atom energies. The interaction with the incident light and the atoms is treated in the dipole approximation $\sum_l e \epsilon \cdot r_l$ where r_l is the position of the l th electron, ϵ is the electric field and e is the electron charge. To account for the two photon transition, one should consider second-order perturbation theory in the external field amplitude and one will obtain for the two-photon transition probability (TP_{int})

$$TP_{int} \propto \left[1 + \frac{4 \langle H_{int} \rangle^2 / \hbar^2}{(2\omega_p - \omega_{P_{1/2}} - \omega_{P_{3/2}})^2 + \Gamma^2} + \frac{4 (2\omega_p - \omega_{P_{1/2}} - \omega_{P_{3/2}}) \langle H_{int} \rangle / \hbar}{(2\omega_p - \omega_{P_{1/2}} - \omega_{P_{3/2}})^2 + \Gamma^2} \right] \times TP \quad (3.5)$$

for simplification it was assumed that $\langle A, 0 | H_{int} | 0, B \rangle = \langle 0, B | H_{int} | A, 0 \rangle$. As it was expected, the first term in the brackets accounts for one one-photon transition probabilities (eq.3.1) for atom A and B. The second and third terms in the bracket presents an asymmetric resonance lineshape when ω_p is near $(\omega_{P_{1/2}} + \omega_{P_{3/2}}) / 2$. These terms are the responsible for the cooperative two-photon absorption. The first contribution, proportional to $\langle H_{int} \rangle^2$, has a Lorentzian lineshape and is proportional to the transition probability of energy exchange between atom a and b . Assuming that one atom a (or b) is not much influenced in its transition the of charge distribution in the other atom. The energy difference (ΔE figure 9) between the incident photon and the level A is transferred to atom b enabling both atoms to absorb the atom with frequency ω_p even though neither of the photon are resonant with that transition. This effect is enhanced when $2\omega_p = \omega_{P_{1/2}} + \omega_{P_{3/2}}$ one can see in figure 10 c. The second contribution to the two photon absorption comes from a dispersion-like resonance lineshape proportional to $\langle H_{int} \rangle$. The two-photon resonance lineshape has an asymmetric shape due to the dispersion-like contribution that shows an increase in transition probability to the blue of the two photon transition and a decrease to the red. The data shown in figure 10 was plotted using an interaction strength equal to $\langle H_{int} \rangle = 5\hbar\Gamma$.

Figure 10 – Shows the plotted function of equation 3.1 as a function of the detuning, with an interaction strength equal to $\langle H_{int} \rangle = 5\hbar\Gamma$. The first two peaks show the one photon one atom transition $3S_{1/2} \rightarrow 3P_{1/2}$ and $3S_{1/2} \rightarrow 3P_{3/2}$. The last peak is the two-photon absorption contribution to the transition probability. It is composed of two contributions a Lorentzian and a dispersive one.

3.2 Experimental data

The measurement of the transition probability was taken indirectly in a two step process. First the atoms were probed with a continuous wave dye laser that takes them to an excited state ($3P_{1/2}$ or $3P_{3/2}$). In the second step, the population of the excited states was ionized by a diode laser with wavelength 405 nm. This wavelength can ionize atoms that are in the $3P_{1/2}$ state or higher. The probe laser was scanned through the $3S_{1/2} \rightarrow 3P_{1/2}$ transition, the $3S_{1/2} \rightarrow 3P_{3/2}$ and in between where the two-photon contribution was expected.

For an interaction strength of $50\Gamma\hbar$, the transition probability of the two-photon absorption is $\approx 0.005\%$ of probability of a one-photon transition, so each data point

Figure 11 – The data represents the ion count as function of the probe beam frequency. The first (last) peak is due to the one-photon transition $3S_{1/2} \rightarrow 3P_{1/2}$ ($3S_{1/2} \rightarrow 3P_{3/2}$). The *shoulder*-like structure is due to hyperfine transition.

presented here is a average of 300 measurements. Background data consists of ions formed by atoms that had their first step done by the trap laser. It was taken immediately after each ion count with the probe to account for any possible laser power fluctuations, or small frequency changes.

In figure 11 the data presents the ion count as function of the probe beam frequency. The first (last) peak is due to the one-photon transition $3S_{1/2} \rightarrow 3P_{1/2}$ ($3S_{1/2} \rightarrow 3P_{3/2}$). The *shoulder*-like structure is due to hyperfine transition. The aspects of those one-photon transition are presented in details in Ref (?). The novelty was the observation of a small peak when the probe frequency is $2\omega_p = \omega_{P_{1/2}} + \omega_{P_{3/2}}$.

The data presented in figure 12 demonstrates that the observed peak is due to a two-photon transition. With the probe laser frequency fixed at the center of the middle peak we changed the intensity of the probe laser, and as one should expect for a two-photon process, we observed a quadratic behavior for the middle peak while for the others peaks we observed a linear behavior (?).

As one can observe in the center of figure 11, the cooperative two-photon transition peak presents an evident asymmetry extending to the red part, although the model shows an asymmetry to the blue side.

Figure 12 – The data presented demonstrates that the observed peak is due to a two-photon transition. With the probe laser frequency fixed at the center of the middle peak, we changed the intensity of the probe laser, and as one should expect for a two-photon process, we observed a quadratic behavior.

The Rios Leite model does not take potentials of that form into account. In an attempt to better understand the shape, we produced a simple model equivalent to the photoassociative ionization calculation presented by Gallagher (?). As previously presented, the ground state depends on the internuclear separation, R , as R^{-6} , whereas the excited-state potential goes as R^{-3} . Since we are considering only long-range interactions, we can consider the ground state to be constant, and we can also consider that the excited states have only the attractive part of the potential. Considering these, we have $\omega'_{P_i} = \omega_{P_i} + C_i^{(3)}/R^3$ with $i = 1/2$ or $3/2$ and the ionization rate, which is proportional to two-photon transition probability (TP_{int}) can be written as

$$I_{rate} = A \int_0^\infty dR \left[1 + \frac{4 \langle H_{int} \rangle^2 / \hbar^2}{(\Delta\omega)^2 + \Gamma^2} + \frac{4(\Delta\omega) \langle H_{int} \rangle / \hbar}{(\Delta\omega)^2 + -\Gamma^2} \right] \times TP(\omega'_{P_{3/2}}, \omega'_{P_{1/2}}) \quad (3.6)$$

Figure 13 – Shows the data points (bars), the theoretical model from equation 3.5 (black points) and the prediction from equation 3.6 (red line).

where $\Delta\omega = 2\omega_p - \omega'_{P_{1/2}} - \omega'_{P_{3/2}}$ and A is the proportionality constant.

Considering a uniform density distribution of the pairs, a numerical integration of equation 3.6 was made using *Mathematica* and plotted with the data points. Figure 13 shows the data points (bars), the theoretical model from equation 3.5 (black points), and well as the prediction from equation 3.6 (red line). One can observe that taking into account the form of the potentials results in an asymmetry to the red side.

Although the theoretical curve has a good agreement with the lineshape of the data, the constructed model predicts a much faster increase around the peak, and the frequency where the maximum is obtained appears to be displaced further to the blue in the model. In reality, the considerations made for the form the potentials was simplified. In this region, the complex combination of the molecular levels produces a spaghetti of levels (?) and to construct a better model, that should be taken into account.

4 Photonic molecule

When considering molecular states of neutral atoms a good question to be asked is: “Why can two neutral atoms combine to form a stable molecule?”. The answer depends on the specific atoms and on the internuclear distance R .

Let’s consider a molecule made by two alkali atoms. For internuclear distances $R < \langle r_a \rangle + \langle r_b \rangle$ that are smaller than the sum of the mean atomic radii, two effects contribute to the binding. The first one is the sharing of electrons in a hydrogenlike fashion. It occurs when both atoms share the valence electron. This results in an electrostatic attraction between the positive cores of two atoms and the negative electron charge distribution between them. The second reason is the exchange interaction. Because the two electrons in the atomic orbitals can not be distinguished in their common molecular orbital, they can be exchanged. This increases the spatial uncertainty for the electrons and therefore decreases their average momentum and their kinetic energy. The combination of both effects leads to a minimum in the potential energy curve, since it contains the average kinetic energy of the electrons. For large internuclear distances $R > \langle r_a \rangle + \langle r_b \rangle$, where the electron cloud of the two atoms no longer overlap, the covalent binding described above loses its importance. Nevertheless stable molecules are possible with such large internuclear distances due to the multipolar interactions, although their binding energy is smaller.

In summary a typical two-body interatomic binding potential consists of an attractive part at large separations, approaching a minimum in the region of equilibrium separation, then becoming repulsive. Therefore, there is no reason why one could not tailor a potential to have these same properties. Consider the combination of two strong laser fields coupled to attractive and repulsive quasi-molecular states of sodium (Figure 14). A strong blue detuned laser connecting the ground state to the repulsive state, is nothing more than an optical shield preventing the pair from getting closer (repulsive part), but the red detuned laser that connects the ground state to the attractive part

Figure 14 – Diagrammatic representation of two strong laser fields coupled to attractive and repulsive quasi-molecular states of sodium. The strong blue detuned laser connects the ground state to the repulsive state, which is nothing more than an optical shield preventing the pair from getting closer, but the red detuned laser that connects the ground state to the attractive part, creates conditions for the formation of a bound potential. The semiclassical representation of the pair motion is presented with the green arrows.

(large separations attractive interaction) creates conditions for the formation of a bound potential.

In a semi-classical picture one can see in 8 steps the vibrational movement of the pair, also depicted in (Figure 14):

1. the pair starts in the attractive potential, before the Condon point of the red detuned laser (let's call it the red laser from now on).
2. the pair emits a red photon, via stimulated or spontaneous emission, and goes to the ground state
3. the energy gain in the first step enables the atoms to be reach the Condon point of the blue detuned laser (blue from now on)
4. the pair absorbs the blue photon
5. the pair climbs the repulsive potential and starts to move away from each other
6. the pair emits a blue photon, via stimulated or spontaneous emission, and goes to the ground state

7. the energy gain in the last step enables the atoms to be reach the Condon point of the red laser
8. the pair climbs the attractive potential and starts to move towards each other, reaching the start position

As one can see these molecular bound states will exist only in the presence of the light fields. Therefore, we can call them photonic states or photonic molecules.

A theoretical model of the potential, proposed by us in collaboration with Yehuda B. Band, considering the dressed states picture and the experimental data. The data supports the possibility of creating a photonic bound state but a direct measurement of the bound states was not taken due to technical difficulties. The effects of high laser power connecting states will also be presented this chapter.

4.1 Theoretical arguments

Optical-shielding is the starting point for the ideas presented here, I'll present a brief description of this effect. Using an intense bluer tuned light field during the atomic pair collision, a rerouting of the ground state entrance channel can take place, transferring the scattering flux to the excited state. The process is schematically represented in Figure 15. Particles initially in the ground state approaching each other with little kinetic energy are excited to the repulsive excited state, stopping the collision process. The shielding can be adequately described using Landau-Zener avoided crossing treatment (?) as represented in Figure 15. The dressing picture involves the two ground state atoms in the presence of the field $|3S_{1/2} + 3S_{1/2}, N\rangle$ and the ground-excited state atoms in the presence of one photon less in the field $|3S_{1/2} + 3P_{3/2}, N - 1\rangle$. The flux of colliding atoms enters in the $|3S_{1/2} + 3S_{1/2}, N\rangle$ channel and moves adiabatically through the optical coupling region feeling the repulsion and exits again on the $|3S_{1/2} + 3S_{1/2}, N\rangle$ state. As the intensity of the optical field increases, the population actually transferred to the excited state decreases, turning the process into truly elastic one.

Figure 15 – Schematic representation of optical shielding. Using an intense bluer tuned light field during the atomic pair collision, a rerouting of the ground state entrance channel can take place, transferring the scattering flux to the excited state. Landau-Zener avoided crossing.

Consider now the situation described in Figure 14. The combination of levels and light fields correspond now to a ground state $|3S_{1/2} + 3S_{1/2}, N\rangle$, and two excited states: $|3S_{1/2} + 3P_{3/2}, N\rangle_a$ attractive and $|3S_{1/2} + 3P_{3/2}, N\rangle_r$ repulsive and two light fields. One blue with a Condon point R_{blue} and a second is red with a Condon point R_{red} . The situation demands now a dressing picture involving the three level and the two optical fields that can be described by the interaction matrix 3×3 , $V(R)$.

$$V(R) = \begin{bmatrix} V_g(R) & V_{g \rightarrow a} & V_{g \rightarrow r} \\ V_{g \rightarrow a} & V_a(R) - \hbar\omega_{red} & 0 \\ V_{g \rightarrow r} & 0 & V_r(R) - \hbar\omega_{blue} \end{bmatrix} \quad (4.1)$$

This can be diagonalized providing the description for the potentials. We explicitly consider the states 0_g^- and 1_g states connecting to the $S_{1/2} + P_{3/2}$ asymptotes, and use these potentials in the diagonal elements V_a (attractive potential) and V_r (repulsive potential) respectively on equation 4.1. The 1_g state behaves asymptotically as $\frac{C'}{R^3}$ and the 0_g^- potential must be evaluated using Movre-Prichler procedure (?). In this case, the 0_g^- state is constructed first identifying the states $|L\Lambda\delta\Sigma q\rangle$ with $\Lambda + \Sigma = 0$ and generate gerade symmetry ($q = g$). The following combination of these states having odd parity $|\Sigma\rangle$ can

be formed:

$$|\Sigma\rangle \equiv \frac{1}{2} (|11 - 1 g\rangle + |-111 g\rangle)$$

The ${}^3\Pi_g$ state, $|\Pi\rangle \equiv |-111 g\rangle$ interacts with the $|\Sigma\rangle$ via spin-orbit coupling. Diagonalizing the Movre-Pichler potential matrix containing spin-orbit interaction and long range R^{-3} potential,

$$V_{mp} = \begin{bmatrix} \frac{C_3}{R^3} - \frac{2\delta}{3} & \frac{\sqrt{2}}{3}\delta \\ \frac{\sqrt{2}}{3}\delta & -\frac{2C_3}{R^3} + \frac{\delta}{3} \end{bmatrix} \quad (4.2)$$

where δ is the atomic spin-orbit splitting ($\delta = 17.2 \text{ cm}^{-1} = 512.52 \text{ GHz}$ for Na case). From equation 4.2 we obtain the 0_g^- states to be used. The upper eigenvalue is the 0_g^- state asymptotically connecting to $S_{1/2} + P_{3/2}$. In Figure 16 we represent the obtained 0_g^- state.

Instead of a state going asymptotically like $-\frac{C_3}{R^3} + \Delta_{12}$ we take the 0_g^- state, having a potential denoted by $V_{0_g^-}(R)$.

All these considerations make the system closer to the real experimental system. The matrix to be diagonalized is written as

$$V(R) = \begin{bmatrix} -\frac{C_6}{R^6} & V_{g \rightarrow a} & V_{g \rightarrow r} \\ V_{g \rightarrow a} & V_{0_g^-}(R) + \hbar\Delta_{red} & 0 \\ V_{g \rightarrow r} & 0 & \frac{C'_3}{R^3} + \hbar\Delta_{blue} \end{bmatrix} \quad (4.3)$$

the diagonalization of equation 4.3 allows the potentials, U_j , where $j = 1, 2, 3$, to be obtained. The U_j potentials correspond to the dressed states for the situation outlined in Figure 14. Considering the specific conditions for $\Delta_{red} = -19 \text{ GHz}$, $\Delta_{blue} = 30 \text{ GHz}$, and $I_{g \rightarrow a} = 8.8 \times 10^3 \frac{W}{cm^2}$, and $I_{g \rightarrow r} = 8.8 \times 10^3 \frac{W}{cm^2}$ we obtain the potentials presented in Figure 16. The U_1 state is mainly the 0_g^- potential taht is slightly broadening at the bottom of the potential, which would only lead to some shift in the vibrational levels of the 0_g^- state, and the presented shape seems to be only due to an avoided crossing between the attractive and repulsive state. If so, the ground state would not take part in

Figure 16 – Theoretical plot of the ground state, attractive state 0_g^- , repulsive state 1_g and the adiabatic potentials calculated by diagonalization of equation 4.3. Considering $\Delta_{red} = -19 \text{ GHz}$, $\Delta_{blue} = 30 \text{ GHz}$, and $I_{g \rightarrow a} = 8.8 \times 10^3 \frac{W}{cm^2}$, and $I_{g \rightarrow r} = 8.8 \times 10^3 \frac{W}{cm^2}$.

Table 2 – Energy of the bound levels for the U_3 potential considering $\Delta_{red} = -19 \text{ GHz}$, $\Delta_{blue} = 30 \text{ GHz}$, and $I_{g \rightarrow a} = 8.8 \times 10^3 \frac{W}{cm^2}$, and $I_{g \rightarrow r} = 8.8 \times 10^3 \frac{W}{cm^2}$. Bound levels are calculated using *Level 8* program.

Vibrational Level with $J = 0$	Energy (detuned from the $3S_{1/2} + 3P_{1/2}$)
0	-0.3290 cm^{-1}
1	-0.2771 cm^{-1}
2	-0.2319 cm^{-1}
3	-0.1928 cm^{-1}
4	-0.1592 cm^{-1}
5	-0.1305 cm^{-1}
6	-0.1061 cm^{-1}
7	-0.0855 cm^{-1}
8	-0.0684 cm^{-1}
9	-0.0541 cm^{-1}

the bound process. The U_2 state supports some bound states but is too shallow. Since our idea is to have a tailored potential that has a reasonable number of bound states, let's concentrate on the upper, U_3 , state. The adiabatic potential calculated was used in *Level 8* program so we could obtain the vibrational levels. The potential U_3 is 0.35 cm^{-1} deep ($\approx 10 \text{ GHz}$) and accommodates 9 states with the energies presented in table 2 .

To demonstrate that the potential aspects are greatly dependent on the frequency and intensity used in the light fields, Figure 17 shows a series of 4 graphs. First, the U_3 potential is plotted versus the intensity of the blue laser, the second the intensity of the red that was changed. Next Δ_{red} is varied, Finally is the dependence of the adiabatic potential with Δ_{blue} is depicted. The U_3 potential in red with triangular dots in all graphs is the same plotted in 16 where $\Delta_{red} = -19 \text{ GHz}$, $\Delta_{blue} = 30 \text{ GHz}$, and $I_{red} = 8.8 \times 10^3 \frac{W}{cm^2}$, and $I_{blue} = 8.8 \times 10^3 \frac{W}{cm^2}$.

This method of creating bound states is interesting because of the freedom that one has to modify the number of bound states, the average separation between them, the depth of the potential. Basically one can create the best potential to fit one's needs. In Figures 19 and 18, the effect of the blue and the red detuning, respectively, in the bound levels was studied. With constant values for the intensities, the properties of the bound states were compared: (a) Level energy vs Vibrational number, (b) laser detuning vs number of vibrational levels, (c) laser detuning vs energy of the lowest vibrational

Figure 17 – Series of 4 graphs, the U_3 potential is plotted versus the intensity of the blue laser, the second was the intensity of the red that was changed, in the third was Δ_{red} and in the final one is the dependence of the adiabatic potential with Δ_{blue} that is depicted. The U_3 potential in red with triangular dots in all graphs is the same plotted in 16 where $\Delta_{\text{red}} = -19 \text{ GHz}$, $\Delta_{\text{blue}} = 30 \text{ GHz}$, and $I_{\text{red}} = 8.8 \times 10^3 \frac{\text{W}}{\text{cm}^2}$, and $I_{\text{blue}} = 8.8 \times 10^3 \frac{\text{W}}{\text{cm}^2}$.

Figure 18 – The effect of the red detuning in the bound levels. With constant values for the intensities the properties of the bound states were compared: (a) Level energy vs Vibrational number, (b) laser detuning vs number of vibrational levels, (c) laser detuning vs energy of the lowest vibrational level and (d) laser detuning vs average level separation.

level and (d) laser detuning vs average level separation. As one can see the potential is more sensitive to the effect of the red detuning. The number of bound levels, the depth, and the average separation are greatly dependent on the red laser frequency, while the blue one only shifts these parameters by small amounts. One could think of it as the red frequency being a course adjustment of the bound energies, and the blue detuning as a fine adjustment.

Figure 19 – The effect of the blue detuning in the bound levels. With constant values for the intensities the properties of the bound states were compared: (a) Level energy vs Vibrational number, (b) laser detuning vs number of vibrational levels, (c) laser detuning vs energy of the lowest vibrational level and (d) laser detuning vs average level separation.

4.2 Experimental data

The experimental data is composed of 3 sets. The first one is the ionization spectra due to the probe laser only. The second is the effect of the blue detuned laser, and the last is the combined effect of the red and the blue laser. The first and second parts are detailed in Franklin's master dissertation (?), so I'll just briefly go through the main results.

4.2.1 Photoassociative Ionization ($\Delta_{probe} = 0 \rightarrow -30 \text{ GHz}$)

The first part of the experiment was done to understand which potentials are involved in the collision process when a red detuned laser, from 0 GHz to -30 GHz of the $3P_{3/2} + 3S_{1/2}$ asymptote, is present. The way we used to measure the effect of the probe laser was through observing changes in the photoassociative ionization (PAI) formation rate constant as a function of the probe frequency. As mentioned before, PAI is a two photon process that promotes the atom pairs to an autoionizing state. The formed ions are then collected with the channeltron and changes can be observed by comparing the data with the probe and without it. Figure 20(a) shows the diagrammatic representation of the frequencies involved in the process. In this case, the first excitation was done by absorption of the probe laser ($I_{probe} \approx 35 \text{ W/cm}^2$), and the second by the blue detuned photon ($\Delta_{PI} \approx 30 \text{ GHz}$) with intensity of $I_{PI} \approx 1.3 \times 10^4 \text{ W/cm}^2$.

The resulting spectrum is shown in Figure 20(b). The peaks in the ions count are due to bound states. One interesting piece of information that this spectroscopic data can give us is which long-range potentials are participating in the collisional process in this region. Using the ideas presented by Stwalley et. al (?), that long-range potential energy curves with R^{-3} behavior, at large internuclear distance, have the energy of one vibrational level (ν) given by:

$$\nu_D - \nu \approx \frac{\pi^{1/2}}{2} \frac{\Gamma(\frac{5}{6})}{\Gamma(\frac{4}{3})} \frac{4}{h} (2\mu)^{1/2} C_3^{1/3} \epsilon^{1/6} \quad (4.4)$$

where h is the Planck's constant, μ is the reduced mass of the molecular pair, ν_D is the

(a) Ionization routes diagrammatic representation

(b) Experimental data

Figure 20 – (a) diagrammatic representation of the frequencies involved in photoassociative ionization steps. (b) Ion count as a function of the probe laser frequency.

effective vibrational quantum number at dissociation D , and the binding energy $\epsilon_\nu \equiv E_D - E(\nu, 0)$. One can see that the separation between two consecutive vibrational levels, of the same molecular potential, will be a constant. With that information we could group the peaks of Figure 20 b into 3 sets, corresponding to 3 different long-range potentials (Figure 21) (?). The correspondence was made by comparing our experimental data for the peaks with experimental measurements, we could label the 0_g^- , 1_g and 0_u^+ potentials along with 2 other peaks that could not be identified.

4.2.2 The pure repulsive state ($1g$)

The effect of the repulsive state in the photonic molecular potential is to prevent the atoms from reaching an internuclear distance smaller than the blue laser Condon point R_{blue} , and also to dress the ground state in way such that we have a good percentage of pairs in the ground-state after going to the repulsive state.

The effect of the repulsive state dressing the ground state in a sodium MOT was previously studied by our group (?) in the region from 0 to -3 GHz. We just extended that study for our working region and with our typical laser powers. Again we used a change in the PAI rate of ion formation to see the suppression of the pair collision. We measured the ion count as a function of the intensity of the blue laser (Figure 22 a). The idea is that the probe laser does the first excitation of the pair, then the pair absorbs the ω_{PI} photon and goes to the doubly-excited state. From there it can form an ion, but if the ω_{Blue} laser is intense enough, the ion formation through that route can be suppressed.

One simple two level semiclassical model can be used to treat the dressed state: the Landau-Zener model. This semiclassical approach considers the pair movement to follow classical trajectories: its motion on each state takes place under the force exerted by the potential curve of that particular state and obeys the laws of Newton.

When the pairs in the ground-state reach the avoided crossing point $R_C(Blue)$, and passes by it with momentum p , some pairs will enter the excited state and the rest will remain in the ground-state. The semiclassical approach is to assume that the interaction

Figure 21 – Ion count as a function of the energy difference from the dissociation energy to the peak energy, for each long-range potential contribution to the spectroscopy data taken when the probe laser was scanned.

region where the potential curves are strongly coupled is narrow and inside it the potential surfaces can be replaced by their tangents at the Condon point. Under these conditions, the classical trajectory becomes simply $dR/dt = p/\mu$, where μ is the effective mass, and we can put it into the Landau-Zener model to replace the linear time dependence in the energy level structure with a spatial dependence. According to this model, the probability the pairs exit in the excited state is:

$$P_e = 1 - \exp\left(\frac{2\pi\Omega^2}{\alpha v}\right) \quad (4.5)$$

where α is the slope difference potential evaluated at the Condon point, v is the local approach velocity of the pair, and Ω the Rabi frequency of the optical coupling

$$\frac{\Omega_{eg}}{2\pi} = 17.35 \text{ MHz} \times \sqrt{I(W \text{ cm}^{-2})} \times d_{eg} \quad (4.6)$$

In Equation 4.6, I is the intensity of the red field and d_{eg} is the transition dipole moment in atomic units. The probability that the pair stays in the ground-state is given by:

$$P_{L-Z} = \exp\left(\frac{-2\pi\hbar\Omega^2}{\alpha v}\right) \quad (4.7)$$

Since the ion formation depends linearly with the Landau-Zener probability, one should expect an exponential decay of the ion count as a the intensity of the blue laser increases.

In the experimental setup blue laser was tuned 24 GHz from the atomic transition $3S_{1/2} + 3P_{1/2}$, and focused into the MOT with a beam waist of $\approx 85 \mu m$. The PI laser was overlapping the blue, with a constant power of 4 mW and a detuning of 30 GHz . The probe laser had also constant power of 15 mW and was scanned through the region of $-30 \rightarrow -24 \text{ GHz}$. The maximum ion counts of one peak, located at -28.65 GHz , as a function of blue laser intensity is shown in Figure 22 a. An exponential decay function was fitted to show that, indeed, the data behaves as expected. The key point is that each time the pair passes $R_C(blue)$, there is the probability that some will continue in the ground-

(a) Experiment diagrammatic representatio

(b) Experimental data

Figure 22 – (a) Diagrammatic representation of the ion route formation when a blue detuned laser is present in the PAI process. (b) Normalized ion count as a function of the blue laser power. A exponential fit was plotted to show the Landau-Zener behavior of the process.

state, thus leaving the photonic potential. That excitation efficiency was calculated from the fitted curve, $y = e^{-ax}$ with $a = 1/138$, and we obtain 98% with a 600 *mW* blue laser, which is a good efficiency with an achievable laser power.

4.2.3 Adding the red laser

The last set of data is conclusive for the experimental demonstration of the viability to create the photonic molecule. From our semi-classical picture (Figure 14) the role of the red detuned laser is to bring the pair to the ground state when they are approaching each other, and when the atoms are moving apart in the ground state, the red photon should excite the pair to the $3S_{1/2} + 3P_{3/2}$ state. In other words, we need to show that that the red intense beam is dressing the ground state.

In order to fully determine the role of the red detuned laser we compared the following ionization routes:

- Route 1 (Figure 23 a) - The pair starts in the ground-state and absorbs the probe. In the excited-state it absorbs the blue laser and goes to the autoionizing doubly-excited state.
- Route 2 (Figure 23 b) - The pair starts in the ground state and absorbs the red laser. In the excited-state it can either spontaneously decay to the ground state, or continue in the excited state. If it decays, it has a probability to absorb the probe. In the excited state it absorbs the blue laser and goes to the autoionizing doubly-excited state.
- Route 3 (Figure 23 c) - The pair starts in the ground state and absorbs the probe. In the excited-state, it can either decay (spontaneously or stimulated) to the ground state, or continue in the excited state. If it decays, it has a probability to absorb the red. In the excited state, it absorbs the blue laser and goes to the autoionizing doubly-excited state.

Figure 23 – Ionization Routes (a) Blue laser before the red laser (b) Probe laser after the red laser, (c) Red laser after the probe

The measurement process only takes into account the routes where the probe is involved, since one data point is given by the difference between counts without the probe and with it. Therefore, Route 1 should give us no change at all when the red laser is on. In the dressed state picture, the strong red photon dresses the ground-state creating two adiabatic potentials Figure 24 (b), if the pair starts in the ground-state the dressed potential enables the pair to absorb the blue photon and goes to the doubly-excited autoionizing state Figure 24 (c). If the pairs starts in the attractive excited, state the blue photon is no longer absorbed by the pair Figure 24 (d). Therefore, if the red detuned field is dressing the potential when the intensity is high enough, one should expect a suppression in the ion formation.

The spectroscopic data (Figure 20 b) shows that for a large detuning ($> -8 \text{ GHz}$),

Figure 24 – Diagrammatic Ionization routes in the dressed state picture (a) Red and Blue laser connecting the pair to the excited and double-excited state respectively. (b) Dressed state picture due to the strong red laser. (c) Ionization route when the pair starts in the ground-state. (d) Ionization route when the pair starts in the excited-state.

the effect of a red detuned laser is almost none if its frequency is not near the resonance of a vibrational level. Therefore, for all experiments the red frequency was tuned $\approx -19 \text{ GHz}$, in the top of the peak that exists in this region. In order to maximize the overlapping region between the red, the blue and the probe laser, all of them are aligned, focused and enter the science chamber through the same window. The beam waist in the MOT region is $\approx 85 \text{ }\mu\text{m}$ so from now on I'll only talk about laser power.

The first set of data shows the suppression. The powers of the probe ($P_{probe} = 10 \text{ mW}$) and the blue ($P_{blue} = 130 \text{ mW}$) lasers were kept fixed while we changed the power of the red laser. The scanned region was one peak of the 0_g^- long-ranged potential, centered $\approx -15.4 \text{ GHz}$ from the $3S_{1/2} + 3P_{3/2}$ state. Figure 25 (a) shows how the peak

changes with the red laser intensity.

The suppression in the ion counts is due to the decrease in the number of pairs in the excited state that reach the Condon point of the blue laser ($R_C(blue)$). Figures 24 (b),(c) and (d) show how this picture can be represented as a Landau-Zener avoided crossing of field-dressed potentials. As the red detuned laser intensity increases the avoided crossing gap around the Condon point of the red laser ($R_C(red)$) widens, and the semi-classical pair moves through the optical coupling region adiabatically. As mentioned for the blue laser, the Landau-Zener probability that the pair remains on the excited-state as it passes once through the interaction region is

$$P_{L-Z} = \exp\left(\frac{-2\pi\hbar\Omega^2}{\alpha v}\right) \quad (4.8)$$

Since the ion formation depends on the Landau-Zener probability, we would expect an exponential decay of the ion count as a function of the red laser power, and that's exactly what is shown in Figure 25 (b). The peak's ion count is shown as a function of the laser power. As one can see the exponential decay fit agrees with the data, showing that the red photon is dressing the potential. The efficiency of the suppression was also calculated from the fitted curve ($y = e^{-ax}$ where $a = 9.6$) and for 100 mW it is 99% is obtained.

The comparison between route 2 and route 3 (Figure 26) supports the idea of the dressed state. When the probe detuning is bigger than of the red laser, a decay in the ion count is also expected. The same idea of the Landau-Zener probability can be applied for the ground state. The probability of the pair to stay in the ground state, after passing the interaction point ($R_C(red)$), should decay exactly with the same exponential dependence of the probability to the pair stay in excited state. The data presented (Figure 26 a) shows that change in counting for route 2. When compared with route 3 (Figure 26 a), in the same conditions, it shows that route 2 is much less sensitive to the red laser power. This is because the probe intensity was lower (≈ 7 mW), and the transition from ground to excited state via the probe laser was not saturated. Therefore the loss in the number of pairs in the ground-state getting in the Condon point of the probe laser ($R_C(probe)$),

(a) Ion Count as a function of the probe detuning

(b) Normalized peak ion count vs Red laser power

Figure 25 – (a) Ion count as a function of the probe detuning for different red laser power. (b) Normalized peak ion count as function of the red laser power. A exponential fit was plotted to show the Landau-Zener behavior of the process.

due to the dressing, is only felt when the red laser power is intense.

When route 1 and 3 are compared (Figure 27) one can see that even though no change in the peak height was expected in route 1. When compared to route 3 (Figure 27 b), only a small difference is observed. This decay is also due to the dressing of ground state. Since the absolute difference between the red and the blue detuning is small ($\approx 100 \text{ MHz}$), the effect of the red detuned laser, stimulating the decay of the pair to the ground state, can still be seen.

(a) probe detuning > Red detuning (Route 2)

(b) probe detuning < Red detuning (Route 3)

Figure 26 – Normalized ion count as a function of the probe detuning for two different ionization routes. (a) probe laser absorption occurs before the red laser one. (b) red probe laser absorption occurs after the red laser one. From the two graphs one can see that the red laser is lowering the number of pairs in the ground state, in the region where they internuclear distance is close to the Condon point of the blue laser.

Figure 27 – Normalized ion count as a function of the probe detuning for two different ionization routes. (a) Blue laser absorption occurs before the red laser one. (b) blue laser absorption occurs after the red laser one.

Conclusions

Two-photon cooperative absorption

The two-photon cooperative absorption experiment demonstrated that TPA phenomena can indeed happen in a sample of cold Na atoms. The topic of nonlinearities in colliding cold atoms have potential for many applications, and this first demonstration may stimulate further investigation.

The presented improvement to Rios Leite's model, where we added the attractive behavior of the long-range potential, showed that the peak asymmetry, demonstrated by the experimental data, is due to the effect the excited potential, has an R^{-3} behavior.

Although we did not provide experimental evidence here, this system has a great potential to create entangled atoms, as well as to produce correlated photons with different frequencies.

Photonic Molecule

Using well established ideas we have successfully proposed a model to create a tailorable molecular bound potential. The influence of the changeable parameters, light intensities and frequencies, was deeply studied.

The experimental data shows that the atoms are going to the repulsive state with a 98% efficiency, and to the attractive state with a 99% efficiency. Although this efficiency wouldn't give us a good number of molecules with a reasonable life time, we have shown that the pair is following the route of the bound state.

Since measuring the bound states wasn't possible because of the experimental limitations (another laser was needed), a next step would be to measure these energy

levels and see how they change with the parameters.

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