FORMATION AND ANALYSIS OF ULTRACOLD POLAR MOLECULES

Elizabeth Ann Juarros, Ph.D.

University of Connecticut, 2007

Alkali hydride molecules are polar, exhibiting large ground-state dipole moments. As ultracold sources of alkali atoms, as well as hydrogen, have been created in the laboratory, we explore theoretically the feasibility of forming such molecules from a mixture of the ultracold atomic gases, employing various photoassociation schemes. In this work we use lithium and sodium hydride as benchmark systems to calculate molecule formation rates through stimulated onephoton radiative association directly from the continuum as well as two-photon stimulated radiative association (Raman transfer) and excitation to bound levels of an excited state followed by spontaneous emission to the ground state. Using accurate molecular potential energy curves and dipole transition moments and with laser intensities and MOT densities that are easily attainable experimentally, we have found that substantial molecule formation rates can be realized even after the effect of back-stimulation has been accounted for. We examine the spontaneous emission cascade which takes place from the upper vibrational levels of the singlet ground state on a time scale of milliseconds. Because photon emission in the cascade process does not contribute to trap loss, a sizable population of molecules in the lowest vibrational level can be achieved. The triplet ground electronic state is of particular interest for experimental efforts since, although it has never been observed experimentally, molecular structure calculations of the $a^{3}\Sigma^{+}$ state for LiH and NaH predict a a small van der Waals attraction, with a potential energy well so shallow that it can support only one bound rotationalvibrational level. Any molecule formed in the triplet ground state would then be immediately in the lowest and most stable level of that state and would be quite long-lived, unlike molecules in high vibrational levels which have significantly shorter lifetimes. As an analysis of our method of calculating molecule formation rates, we investigate more thoroughly the two-photon stimulated photoassociation process by employing the exact treatment of Dalgarno & Lewis to solve the Raman scattering problem.

FORMATION AND ANALYSIS OF ULTRACOLD POLAR

MOLECULES

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Doctor of Philosophy Dissertation

FORMATION AND ANALYSIS OF ULTRACOLD POLAR

MOLECULES

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Introduction

The coldest place in the known universe is right here on Earth. In some physics laboratories, small clouds of atoms and molecules have been cooled to temperatures as close to absolute zero as ever realized. Understanding the interactions between light and matter enables us to conceive of environments where quantum effects can be observed on relatively large scales. It is in this ultracold regime that we propose to analyze schemes of formation of polar molecules.

Over the past two decades, with the advent of laser cooling and trapping techniques, [1–7] atomic and molecular interactions in the ultracold regime have become a subject of intense interest. It is generally accepted that *cold* is designated for atoms and molecules with translational temperatures between 1 and 1000 mK and *ultracold* for translational temperatures that are less than 1 mK. [8] Ultracold collisions between atoms provide a way to explore "subtle forces and rare internal states hardly ever seen in the everyday world. Trapped in cages of light and magnetic fields and cooled to almost absolute zero, these atoms can form fragile molecules far larger and more tenuously bound than could survive in our room-temperature world." [9] At low temperatures, atoms move much slower than they do at room temperature and thus it is possible to probe the details of atomic collisions on a scale unheard of before. Also at ultracold temperatures, the quantal nature of matter plays a profound role in the manner that atoms interact. They behave more like waves and interact at extremely large distances. By implementing various cooling techniques, researchers have been able to manipulate cold bosonic atoms into a unique form of matter called a Bose-Einstein Condensate (BEC), which typically occurs in the range of tens to hundreds of nanoKelvin (roughly nine to ten orders of magnitude lower than room temperature). The initial motivation which led to actual observed BEC's may have been to compare with the theory proposed much earlier by Bose and Einstein and simply to explore the unknown. Once achieved, BEC's have become the grounds for many new discoveries. Physicists have rotated their small clouds of atoms and observed vortices. They have brought BEC clouds together in order to observe interference between them. In the quest to explore the unknown, a natural next step is to achieve similar results with molecules, which are more complicated, and hence could be considered more interesting, than atoms.

"Cooling molecules is more difficult than cooling atoms. The complex molecular internal level structure precludes a simple extension of laser cooling to molecules." [8] It was stated in the special edition on Ultracold Polar Molecules in the European Physical Journal D in 2004 that "there are now at least nine different techniques used to produce cold molecules, a number that increased from zero over the past eight years." [8] One such technique involves making ultracold molecules from a gas of ultracold atoms. In this scheme, the difficulties of cooling molecules directly can be circumvented by first cooling atoms and then forming diatomic molecules in selected rotational-vibrational (ro-vibrational) states by photoassociation [6,7] of atom pairs with laser light. Depending on the particular atomic species used, photoassociation can yield either homonuclear molecules, where the molecule is comprised of two like atoms, or heteronuclear molecules, where the molecule is comprised of two different atoms. Heteronuclear molecules can have a body-fixed electric dipole moment that is not available with atoms alone, and are referred to as polar molecules; the larger the electric dipole moment of a molecule, the more polar it is.

An immediate motivation to study ultracold polar molecules is the production of dense samples in which to control chemical reactions, [8] as well as the possible realization of a quantum computation scheme. [10] Beyond chemistry and molecular physics, ultracold polar molecules may enable us, with high resolution spectroscopy, to test fundamental symmetries in nature that go beyond the Standard Model, such as the violation of time-reversal symmetry that may be revealed by measuring the electron electric dipole moment. [11]

The subject of this work is to consider the formation of alkali hydride molecules via photoassociation. Alkali hydride molecules have significant dipole moments in their electronic ground state, as well as large dipole transition moments between ground and excited electronic states. The large slope of their dipole moment functions and the anharmonicities in their ground state potential energy curves make the alkali hydrides benchmark systems with which to explore stimulation of transitions to ground electronic states from a dual species atomic cloud. For alkali hydride systems, the molecular potential energy curves, the dipole functions and transition moment functions as a function of atomic
separation are relatively well known. BEC's have already been obtained for the component atoms: H, ⁷Li, ²³Na, ⁴¹K, ⁸⁵Rb, ⁸⁷Rb, and ¹³³Cs. It is therefore possible to obtain ultracold samples of the atomic systems, thus it may be feasible to produce ultracold alkali hydride molecules by implementing photoassociation schemes for prepared atomic systems.

1

General Theory

The purpose of this chapter is to introduce the theoretical considerations involved in the photoassociation process. Certain aspects of the theory of light– matter and matter–matter interactions that are relevant to the description of collisions in the presence of a light field in the ultracold regime will be presented. The non-relativistic motion of diatomic molecules will be addressed and the potential energy curves that describe their interactions will be examined. Then, the effect of relativistic contributions to the molecular motion will be added to the analysis. The formulation of a line shape expression that describes molecular formation rates for both one and two-photon processes will be illustrated. Lastly, the two-photon process will be revisited by consideration of an exact treatment of the Raman scattering process.

1.1 Photoassociation: General Picture

When a gas of atoms is illuminated with light of frequency equal to the energy difference between colliding pairs of free atoms and bound molecular states, two colliding atoms can emit a photon and photoassociate to form a bound, electronically excited molecule described by [12]

$$A + B + \gamma \longrightarrow (AB)^*, \tag{1}$$

or, if the atoms are heteronuclear, it may be possible for two colliding atoms to emit a photon and *photoassociate* to form a bound, ground electronic molecule directly:

$$A + B + \gamma \longrightarrow AB. \tag{2}$$

As shown in Figure 1 this is a resonant process: the sum of the initial kinetic energy of the atoms together with the energy of the absorbed photon must be equal to the energy of the bound molecular state when viewed in the center-ofmass frame. [12] When the atoms are coupled to an electronically excited state, the excited molecule spontaneously decays by emitting a photon. This process typically takes place on the order of tens of nanoseconds. Depending on the energy of the decay photon γ_d , the final product can be either two free atoms or a bound, ground electronic state molecule,

$$(AB)^* \longrightarrow \begin{cases} A + B + \gamma_d \\ \\ AB + \gamma_d \end{cases}$$
(3)



internuclear separation R

Fig. 1: A schematic of the photoassociation (PA) process $A+B+\gamma \rightarrow (AB)^*$. The electronic ground and excited potential energy curves are shown as a function of internuclear separation of the two atoms with horizontal lines representing some of the bound vibrational molecular states within each potential curve. The solid upward arrow (labeled PA) represents the photoassociation transition and the dashed downward arrow (labeled decay) symbolizes the spontaneous radiative decay from the excited molecular state with binding energy E_{bound} . The collision energy E_{thermal} is greatly exaggerated for clarity, and the separation between the asymptotic limits of the ground (A + B) and excited $(A^* + B)$ molecular states is defined as E_{atomic} .

Typically, the free atoms produced by the first process have more kinetic energy than the initial colliding pair, which leads to losses in the trapped gas. [13] Furthermore when two photons of different frequency are present, a two-photon stimulated radiative association – Raman transfer of the colliding atoms can take place.

It is possible to observe photoassociation (hereafter PA) at a wide range of atomic collision temperatures, but this observation becomes very crisp, with high spectral resolution, for lower temperatures. [12] The development of laser cooling techniques [1–3] has made it possible to achieve samples of ultracold (1 mK or less) atoms. "For these very cold samples, the spread of the initial kinetic energy of the colliding atoms is small and thus the spread in photon frequencies needed to drive the resonant PA process is small. In fact, this spread in frequencies can be comparable to, or smaller than, the natural linewidth of the electronically excited molecular state" [12], set by the spontaneous emission process of Eq. (3).

In the ultracold regime, the PA scheme begins with a pair of ultracold atoms approaching one another with relative kinetic (or thermal) energy E_{thermal} . The atoms interact via the potential energy of the molecular electronic state characterized by two ground state atoms A + B. The atom pair can absorb a photon from the laser and would then be promoted to a bound state of energy E_{bound} in the excited molecular state potential for $A^* + B$ (or demoted into the ground state if the atoms are heteronuclear). This laser is tuned to an angular frequency which is detuned by some amount Δ from the bound state. In addition, the laser's intensity I gives rise to a radiative coupling $\sim D(R)$, where D(R)represents a molecular dipole matrix element that varies with the internuclear separation of the atoms. [14]

The observed line shape is given by the thermally averaged product of the relative speed of the atoms and the photoassociation cross section,

$$\mathsf{K}(T, I, \Delta) = \langle v_{rel} \, \sigma_{\mathrm{PA}} \rangle \,, \tag{4}$$

where $\mathsf{K}(T, I, \Delta)$ will be referred to as the photoassociation rate coefficient. The cross section σ_{PA} contains the probability amplitude for the atom pair to encounter each other with energy E_{thermal} and interact under the influence of the laser light. The task at hand is to relate these probability amplitudes to the various parameters of the laser, as well as to the stimulated rates arising from the coupling due to the laser light, and the spontaneous rates due to natural decay. The major subject of this work is to examine the feasibility of forming ultracold heteronuclear (alkali hydride) molecules using a variety of PA molecule formation schemes for this system. This involves understanding the wavefunctions associated with the various *initial* and *final* states. The wavefunctions can only be determined if the potential energy curves are understood (see § 1.2 and 1.3).

1.2 The Molecular Wavefunction

The PA process is the coupling of state of two colliding atoms (also called a scattering or continuum state) to a bound state, and can be treated by resonant scattering theory. [15,16] The strength of the optical coupling between the bound state (for now, simply called $|b\rangle$) and the collisional state $|\varepsilon, \ell\rangle$ at relative energy $E_{\text{thermal}} \equiv \varepsilon$ with partial wave ℓ is given, in CGS units, by the matrix element [17]

$$D_b(\varepsilon, \ell) = \sqrt{\frac{2\pi I}{c}} \langle b | \mathbf{d} \cdot \mathbf{e} | \varepsilon, \ell \rangle , \qquad (5)$$

where **d** is the *R*-dependent molecular electric dipole or transition moment. The incident light that is the source of this coupling is described by polarization vector **e**, intensity *I* and frequency ω . The partial wave component of the scattering state defines the type of collision and is given the following names: *s*-wave for $\ell = 0$, *p*-wave for $\ell = 1$, *d*-wave for $\ell = 2$ and *f*-wave for $\ell = 3$, for example.

In order to proceed with analyzing the PA process, it is necessary to explore the shape of the potential energy curves governed by the atomic interactions both when the atoms are close together and far apart, as well as some of the elements of scattering theory that pertain to obtaining the wavefunctions needed for this calculation.

The Born-Oppenheimer approximation is essentially the adiabatic approximation applied to a molecular system. An *adiabatic* process is characterized by a gradual change in the external conditions of a system. This technique of solving the equations of motion for a molecule involves calculating the electronic wavefunctions, assuming at first that the nuclei are at rest, and then using these wavefunctions to obtain information about the positions and the relatively sluggish motion of the nuclei. The change in the Hamiltonian describing the molecule is not restricted to *small* changes (as in perturbation theory), but can be very large with the requirement that this change happens *slowly*. [18]

To begin, it is helpful to consider a molecule as formed from two *nonrel-ativistic* atoms, ignoring spin-orbit interactions and hyperfine interactions and ignoring, for the time being, rotation of the molecule so that the interatomic axis is fixed in space. The problem is then reduced to solving the *time inde-pendent* Schrödinger equation, using the *Born-Oppenheimer approximation*, for a stationary state system.

1.2.1 The Born-Oppenheimer approximation

A postulate of quantum mechanics specifies the time development of the wavefunction $\Psi(\mathbf{s}, t)$: the wavefunction for a system develops in time according to the *time-dependent Schrödinger equation* [19]

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{s}, t) = \mathbf{H} \Psi(\mathbf{s}, t),$$
 (6)

where \mathbf{H} is the Hamiltonian operator of the system and \mathbf{s} denotes all positions associated with the system.



Fig. 2: Schematic for Born-Oppenheimer Hamiltonian for a diatomic molecule.

For any diatomic molecule (see Figure 2), the non-relativistic Hamiltonian, excluding spin, is given by

$$\mathbf{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I} \frac{\nabla_I^2}{M_I} + \sum_{i>j} \frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R_{AB}} - \sum_{I,i} \frac{Z_I e^2}{r_{Ii}}, \qquad (7)$$

where m_e represents the mass of an electron, and M_I and Z_I describe each nucleus. The first two terms are the kinetic energy operators for the electrons and the nuclei. The third term is the electron-electron interaction, the fourth is the potential energy of the electrons in the field of the ions and finally, the last term is the potential energy between the nuclei.

Notice that this Hamiltonian is *time-independent*, so that the time dependence of the wavefunction may be directly separated out and Eq. (6) admits particular solutions of the form

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{r}, \mathbf{R}) e^{-iE_{tot}t/\hbar} \,. \tag{8}$$

Here **R** and **r** stand for nuclear and electronic coordinates, respectively. The timeindependent wavefunction $\Phi(\mathbf{r}, \mathbf{R})$ satisfies the time-independent Schrödinger equation

$$\mathbf{H}\Phi(\mathbf{r},\mathbf{R}) = E_{tot}\Phi(\mathbf{r},\mathbf{R}).$$
(9)

For the case where $M_I \gg m_e$, the solution can be approximated as

$$\Phi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}, \mathbf{R})\phi(\mathbf{R}), \qquad (10)$$

where $\phi(\mathbf{R})$ accounts for the rotation and vibration of the nuclei.

Let us consider a diatomic molecules, as in Figure 2. The Born-Oppeneimer approximation involves first solving for the electronic motion, at internuclear separation $R_{AB} = R$, with the assumption that the nuclei are at rest

$$\left[-\frac{\hbar^2}{2m_e}\sum_{i}\nabla_i^2 + \sum_{i>j}\frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R} - \sum_{I,i}\frac{Z_I e^2}{r_{Ii}}\right]\psi(\{\mathbf{r}_i\}, R) = E_e(R)\psi(\{\mathbf{r}_i\}, R).$$
(11)

The result is an approximate electronic wavefunction and energy for every value of R.

The next step involves solving for the slower nuclear motion, using $E_e(R)$ as an effective potential in which the nuclei move according to the following equation

$$\left[-\frac{\hbar^2}{2}\sum_I \frac{\nabla_I^2}{M_I} + E_e(R)\right]\phi(R) = E\phi(R)\,,\tag{12}$$

where $E = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$. Note that in this expression the angular momentum is assumed to be zero, and if not, it must be refined to incorporate the projection of the angular momentum along the internuclear axis.

This process provides a method to solve for the approximate motion of the nuclei by obtaining time-independent stationary wavefunctions for the nuclei, while the electrons follow adiabatically the motion of the nuclei.

1.2.2 Stationary Wavefunction

With the goal being to understand the general form of diatomic molecular wavefunctions, consider a non-relativistic collision between two particles A and B. The particles have mass M_A and M_B respectively and coordinates \mathbf{R}_A and \mathbf{R}_B measured from some fixed origin \mathcal{O} . The Born-Oppenheimer approximation states that these particles interact through a real potential V(R) which depends only upon the relative coordinate $R = |\mathbf{R}_A - \mathbf{R}_B|$. [20]

The Hamiltonian for the two nuclei is simply

$$\mathbf{H} = -\frac{\hbar^2}{2M_A} \nabla_{R_A}^2 - \frac{\hbar^2}{2M_B} \nabla_{R_B}^2 + V(R) \,, \tag{13}$$

and the Schrödinger equation to solve is $\mathbf{H}\Phi(\mathbf{R}_A, \mathbf{R}_B) = E_{tot}\Phi(\mathbf{R}_A, \mathbf{R}_B)$. This problem can be simplified using the center of mass coordinates and introducing the following vectors

$$\mathbf{r} \equiv \mathbf{R}_A - \mathbf{R}_B, \qquad (14)$$

$$\mathbf{R} \equiv \frac{M_A \mathbf{R}_A + M_B \mathbf{R}_B}{M_A + M_B}, \qquad (15)$$

where \mathbf{r} is called the relative coordinate and \mathbf{R} is the center of mass coordinate. The Schrödinger equation of Eq. (13) can be written in terms of the new coordinates (\mathbf{r}, \mathbf{R}) as

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(\mathbf{r})\right]\Phi(\mathbf{r},\mathbf{R}) = E_{tot}\Phi(\mathbf{r},\mathbf{R}),\qquad(16)$$

where the total mass M and the reduced mass μ of the system are defined by

$$M = M_A + M_B, \qquad (17)$$

$$\mu = \frac{M_A M_B}{M_A + M_B}.$$
 (18)

Since the potential only depends on \mathbf{r} , $\Phi(\mathbf{r}, \mathbf{R})$ can be separated into a product of functions of relative coordinates and center of mass coordinates (*i.e.*, $\Phi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{R})\psi(\mathbf{r})$). The functions $\phi(\mathbf{R})$ and $\psi(\mathbf{r})$ satisfy the eigenvalue equations

$$-\frac{\hbar^2}{2M}\nabla_R^2\phi(\mathbf{R}) = E_{CM}\phi(\mathbf{R}), \qquad (19)$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla_R^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}), \qquad (20)$$

$$E_{tot} = E_{CM} + E. (21)$$

Working in the center of mass coordinate system eliminates the need to consider the motion of the center of mass. "The problem of the scattering of two particles interacting through potential $V(\mathbf{r})$ which depends only on their relative coordinate \mathbf{r} is therefore entirely equivalent, in the center of mass system, to the scattering of a particle of reduced mass μ by the potential $V(\mathbf{r})$." [20]

If *E* is the energy of the *reduced mass particle*, then when $V(\mathbf{r})$ goes to zero asymptotically, it must hold that $E = \frac{p^2}{2\mu} = \frac{\hbar^2 k^2}{2\mu}$, where the initial momentum \mathbf{p} and wavenumber \mathbf{k} are given by $\mathbf{p} = \hbar \mathbf{k}$. Also if the *reduced potential*

$$U(\mathbf{r}) = \frac{2\mu}{\hbar^2} V(\mathbf{r}) \tag{22}$$

is introduced, it follows that the Schrödinger equation to solve becomes

$$\left[\nabla_r^2 + k^2 - U(\mathbf{r})\right]\psi(\mathbf{r}) = 0.$$
(23)

The potential $V(\mathbf{r})$ tends to zero faster than $\frac{1}{r}$ as $r \to \infty$ since diatomic molecular potentials are not Coulombic (see § 1.3). A particular solution of Eq. (23) can be found which is typically called the stationary scattering wavefunction and denoted by $\psi_{\vec{k}}^+(\mathbf{r})$. This function satisfies the asymptotic boundary condition

$$\psi_{\vec{k}}^{+}(\mathbf{r}) \longrightarrow A(k) \left\{ e^{i\mathbf{k}\cdot\mathbf{r}} + f(k,\theta,\phi) \frac{e^{ikr}}{r} \right\} .$$
(24)

The amplitude A does not depend on \mathbf{r} , and θ and ϕ are the usual spherical polar angles given the orientation of the incident wave vector \mathbf{k} along the z-axis.

1.3 Molecular Potential Energy Curves

A molecular potential energy curve as a function of internuclear separation typically has three defining regions. In Figure 3, a representative potential energy curve is plotted. Region I is called the inner wall and signifies the repulsive nature of the system at very small separation. In this region, chemical bonding is important and atomic electronic clouds are strongly distorted. [12] Region II is the well that supports molecular binding. The various molecular binding energy levels depend on the rotational and vibrational degrees of freedom for a particular diatomic molecule. For low levels of vibrational excitation, the vibrating molecule looks quite similar to a quantum harmonic oscillator. But for highly excited



Fig. 3: Schematic of a diatomic potential energy curve with respect to internuclear separation.

vibrational levels, since the potential curve is highly anharmonic, the effective interatomic "spring" is very flexible and thus the molecule spends most of its time near the classical outer turning point of the system. [12] The molecular binding portion of the curve is frequently constructed using ab initio data as well as RKR spectral data. [22–24] Finally, Region III is called the tail of the potential energy curve. The tail is comprised of two forms: the long-range portion, where the atoms are far apart and the atomic clouds remain undistorted, [12] and the exchange energy.

1.3.1 Long-Range Dispersion Forces

The long-range region of the potential energy curve can begin anywhere from $11 a_o$ to $65 a_o$ [6], as soon as the overlap of the charge distributions is negligible. The long-range behavior of diatomic molecules can be derived from the separated atom picture. [6] This is accomplished by applying perturbation theory to the properties of the separate atoms at large distances in order to attain the potential energy of the system. In general, the asymptotic potential energy can be expressed as a power series in 1/R:

$$V(R) = -\sum_{k} \frac{C_k}{R^k},$$
(25)

where $V(\infty) = 0$ "and the leading exponent depends on the states of the two atoms. For example, k = 6 for the van der Waals interactions of an ns + nsatomic asymptote, k = 3 for the resonant dipole-dipole interaction of an ns + npatomic asymptote, and k = 5 for the quadrupole-quadrupole interaction of an ns + nd atomic asymptote, respectively." [6]

At these large internuclear distances, a high vibrational level spends most of its time near its classical outer turning point in the attractive $C_n R^{-n}$ long-range region. So, the properties of these levels are largely determined by the longrange portion of the molecular well. [12] Since PA transitions tend to favor high vibrational levels, the correct long-range form of the potential becomes extremely important in determining PA rates. Using second-order perturbation theory, the long-range part of interaction between two atoms a and b in their ground states can be expanded in terms of a series of inverse powers of the separation R [25]

$$V_{ab} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \qquad (26)$$

where the coefficients C_6 , C_8 , and C_{10} are

$$C_6 = \frac{3}{\pi} G_{ab}(1,1), \qquad (27)$$

$$C_8 = \frac{15}{2\pi} G_{ab}(1,2) + \frac{15}{2\pi} G_{ab}(2,1), \qquad (28)$$

$$C_{10} = \frac{14}{\pi} G_{ab}(1,3) + \frac{14}{\pi} G_{ab}(3,1) + \frac{35}{\pi} G_{ab}(2,2), \qquad (29)$$

where

$$G_{ab}(l_a, l_b) = \int_0^\infty \alpha_{l_a}^a(i\omega) \alpha_{l_b}^b(i\omega) d\omega \,. \tag{30}$$

In Eq. (30), $\alpha_{l_a}^a(i\omega)$ is the dynamic 2^{l_a} polarizability for atom a at imaginary frequency $i\omega$. The dynamic polarizability can be expressed in terms of a sum over all intermediate states, including the continuum, as shown in [25].

"It should also be noted that the properties of diatomic vibrational levels with outer classical turning points in the attractive C_n/R^n long-range region are approximately determined by C_n , the coefficient of the long-range potential, and by n, the inverse power of R. These properties include binding energy, vibrational spacing, kinetic energy, potential energy, oscillator strength, density of states, classical vibrational period, outer classical turning point, powers of R, rotational constant, and centrifugal distortion constant." [6]

1.3.2 Exchange Energy

The Smirnov and Chibisov [26] form of the exchange energy is written as

$$V_E(R) = -\alpha e^{-\beta R} R^{\gamma} \,. \tag{31}$$

The parameters β and γ are determined from the atomic ionization energies I_X , where X denotes A (an alkali atom; Li or Na) or H (a hydrogen atom). For a heteronuclear interaction [27], these parameters are given by

$$\rho_X = \sqrt{2I_X} \,, \tag{32}$$

$$\beta = \rho_{Li} + \rho_H, \text{ and}$$
(33)

$$\gamma = \frac{2}{\rho_{Li}} + \frac{2}{\rho_H} - \frac{1}{(\rho_{Li} + \rho_H)} - 1.$$
(34)

For some types of potentials the parameter α depends on R and is given by the expansion

$$\overline{\alpha}(R) = \sum_{i=0}^{N} J_i(\rho_A, \rho_H) R^i (\rho_A - \rho_H)^i / i! \,. \tag{35}$$

The parameters $J_i(\rho_A, \rho_H)$ are calculated using the formula [27]

$$J_i(\rho_A, \rho_H) = (\mathcal{A}_X \mathcal{A}_Y)^2 \mathcal{C}_{X,Y} \left[\mathcal{J}_i(\rho_X, \rho_Y) + (-1)^i \mathcal{J}_i(\rho_Y, \rho_X) \right]$$
(36)

The parameters $J_i(\rho_A, \rho_H)$ are calculated using the formula [27]

$$J_i(\rho_A, \rho_H) = (\mathcal{A}_X \mathcal{A}_Y)^2 \mathcal{C}_{X,Y} \left[\mathcal{J}_i(\rho_X, \rho_Y) + (-1)^i \mathcal{J}_i(\rho_Y, \rho_X) \right], \qquad (37)$$

where

$$\mathcal{J}_i(\rho_X, \rho_Y) = \left(\frac{2\rho_X}{\beta}\right)^{1/\rho_Y} \left(\frac{2\rho_Y}{\beta}\right)^{1/\rho_X} \left(\frac{\rho_X}{\rho_Y}\right)^{1/\beta} e^{\left[\frac{1}{2}\left(\frac{1}{\rho_X} - \frac{1}{\rho_Y}\right)\right]}$$

$$\times \int_{0}^{1} dz \, z^{i} \, e^{\frac{z}{\beta}} (1+z)^{2/\rho_{X}-2/\rho_{Y}+1/\beta} (1-z)^{2/\rho_{Y}-1/\beta} \\ \times \left[1 - \left(\frac{\rho_{X}-\rho_{Y}}{\beta}z\right) \right]^{-2-1/\beta},$$
(38)

$$\mathcal{C}_{X,Y} = 2\Gamma\left(\frac{1}{\beta}\right)(2\beta)^{-2-1/\beta}\left(\frac{2\rho_X}{\beta}\right)^{1/\beta-1/\rho_Y}\left(\frac{2\rho_Y}{\beta}\right)^{1/\beta-1/\rho_X} \times e^{\left[-\frac{1}{2}\left(\frac{1}{\rho_X}+\frac{1}{\rho_Y}\right)\right]},$$
(39)

and \mathcal{A}_X are the asymptotic caefficients for the normalized wave functions of atom X.

1.4 Spin-Orbit & Hyperfine Interactions

The description of a diatomic molecule thus far has involved only a nonrelativistic picture of the constituent atoms. This treatment determines the largest energy scales in atoms and molecules. "Weaker relativistic interactions, such as spin-orbit and hyperfine interactions, are, nonetheless, still vastly larger then the kinetic energy of the colliding atoms and the typical spectroscopic accuracy obtainable in PA spectroscopy." [12] Spin-orbit structure in spectra arises from the interaction between the total electron spin and the total electron orbital angular momentum. It is the largest relativistic interaction.

The spin-orbit interaction for an atom is typically introduced in the form of an effective Hamiltonian

$$\dot{H}_{\rm eff}^{\rm so} = A_{\rm so} \,\ell \cdot \mathbf{s}\,,\tag{40}$$

where A_{so} is called the spin-orbit constant. Since ℓ and s are good quantum numbers for light atoms, the total angular momentum for a particular atom is found from $\mathbf{j} = \ell + \mathbf{s}$. In general the spin-orbit interaction in a molecule requires a more complex effective Hamiltonian that describes the dependence of the interaction on internuclear separation. [28] However, frequently it is possible to estimate the molecular spin orbit interaction by summing the atomic spin orbit interactions. "Regardless of the detailed form of the spin-orbit interaction, the molecular wavefunctions have certain symmetry properties. Since a dimer is cylindrically symmetric, Ω , the absolute value of the projection of $\mathbf{j} = \mathbf{j}_{\mathbf{a}} + \mathbf{j}_{\mathbf{b}} =$ $\mathbf{L} + \mathbf{S}$ along the internuclear axis, is conserved. Here the subscripts indicate atom a and b and \mathbf{j} is the total electron angular momentum. In general \mathbf{j} is not conserved." [12] Note that since the total electron spin S is zero for a singlet molecule, there is no spin-orbit interaction for a molecule in any ${}^{1}\Sigma$ state.

"The resolution of PA spectroscopy is sufficiently high that it is possible to include hyperfine interactions in the description of the molecule. For the initial scattering state used in PA spectroscopy, the thermal energy is typically orders of magnitude smaller than the atomic hyperfine splittings." [12] Explaining the hyperfine structure involves assuming that the atomic nucleus, as well as the electrons, posess an intrinsic angular momentum (nuclear spin) i. [29] The coupling between the nuclear spin and the electronic spin gives rise to small energy differences, causing small splittings of spectral lines, known as hyperfine splittings. For an atom, the hyperfine interaction is introduced as an effective Hamiltonian

$$\hat{H}_{\text{eff}}^{\text{hf}} = a_{\text{hf}} \mathbf{s} \cdot \mathbf{i} \,, \tag{41}$$

where a_{hf} is the hyperfine constant and, similar to the spin-orbit interaction, the hyperfine interaction for a molecule can often be approximated by the sum of the atomic hyperfine interactions. These interactions can couple the adiabatic Born-Oppenheimer potentials with different symmetry and different total electron spin.

If the constituent atoms of a dimer are sufficiently far apart, potentials are labeled by atomic hyperfine quantum numbers f_a and f_b , where $\mathbf{f}_a = \mathbf{s}_a + \mathbf{i}_a$ and $\mathbf{f}_b = \mathbf{s}_b + \mathbf{i}_b$. For the case when the atoms are in close proximity, the effective hyperfine interaction is $a_{\text{eff}} \mathbf{S} \cdot \mathbf{I}$, where $\mathbf{S} = \mathbf{s}_a + \mathbf{s}_b$ and $\mathbf{I} = \mathbf{i}_a + \mathbf{i}_b$.

1.5 Hund's Cases

"The Hund's cases classify the relative strengths of the Born-Opperheimer interactions, the spin-orbit interaction, and rotation. In other words, they describe the way in which the angular momenta in the moleucle are coupled together." [12]

The following discussion of Hund's cases is taken from Herzberg's section on *Coupling of Rotation and Electronic Motion* [29]. The various angular momenta in a molecule, namely the electron spin, the electronic orbital angular momentum, and the angular momentum of the nuclear rotation form a resultant **J** designated as the total angular momentum, disregarding nuclear spin. For the case when the electronic spin **S** and orbital angular momentum Λ of the electrons are zero (that is a ${}^{1}\Sigma$ state) the angular momentum of nuclear rotation is the same as the total angular momentum **J** and the problem can be analyzed like the case of a simple rotor. In all other cases, it is necessary to distinguish between different modes of coupling of the angular momenta. There are several coupling schemes, but only the first two (Hund's case(a) and Hund's case (b)) will be reviewed here since they generally best describe the systems considered in this work, although Hund's case (c) is usually used in PA.

Hund's case (a). It is assumed that the interaction of the nuclear rotation and the electronic motion (including both orbital motion and spin) is very weak and that the electronic motion itself is coupled very strongly to the internuclear axis. In this case, the good quantum numbers Ω , the projection of the electronic angular momentum on the internuclear axis, and N, the nuclear rotational angular momentum, form the resultant J, where $\mathbf{J} = \Omega + \mathbf{N}$. Ω and N rotate about J (nutation). L and S precess about the internuclear axis as shown in Figure 4. In Hund's case (a), the precession is much faster than the nutation.

Hund's case (b). When $\Lambda = 0$ and $S \neq 0$, the spin vector **S** is not coupled to the internuclear axis. Therefore, Ω is not defined and Hund's case (a) cannot apply. Also, it can happen that for light molecules, even if $\Lambda \neq 0$, S may be only very weakly coupled to the internuclear axis. These situations are characteristic of Hund's case (b). In this case, the angular momentum Λ



Fig. 4: Schematic of Hund's case (a).



Fig. 5: Schematic of Hund's case (b).

(when different from zero) and N form a resultant which is here designated as K. $\mathbf{K} = \mathbf{\Omega} + \mathbf{N}$ is the total angular momentum apart from spin and $\mathbf{J} = \mathbf{K} + \mathbf{S}$ as shown in Figure 5. The precession of K and S about J is very slow with respect to the nuclear rotation.

1.6 General Scattering Theory: Method of Partial Waves

In order to give some insight into the form of scattering wavefunctions and how they relate to the angular momentum of a system, consider the case when a system is interacting in a *central* potential (one that depends only on r). The Schrödinger equation may be separated in spherical coordinates and a simple connection between radial solutions and the asymptotic form of the stationary scattering wavefunction may be found.

Consider a spinless particle of mass m in the presence of a real central potential V(r). It is most convenient to work in a spherical coordinate system with the z-axis along the incident direction, while the origin coincides with the origin of the vector \mathbf{r} . The Hamiltonian operator $H = -(\hbar^2/2m)\nabla_{\mathbf{r}}^2 + V(r)$, in spherical coordinates, becomes

$$H = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial^2 \phi} \right] + V(r) \,. \tag{42}$$

The orbital angular momentum operator is written as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. It is important to note that \mathbf{L} is designated here as associated with the nuclear motion, not the electronic motion as in the last section. The linear momentum of the particle is written as $\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}$ so that

$$L^{2} = L_{x}^{2} + L_{y}^{2} + L_{z}^{2} = -\hbar^{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2}}{\partial^{2} \phi} \right], \quad (43)$$

with

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y \tag{44}$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0.$$
(45)

The eigenfunctions that are common to the operator L^2 and the z-component of **L** are given by the spherical harmonics $Y_{lm}(\theta, \phi)$;

$$L^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta, \phi), \qquad (46)$$

$$L_z Y_{\ell m}(\theta, \phi) = m \hbar Y_{\ell m}(\theta, \phi), \qquad (47)$$

where ℓ is the orbital angular momentum quantum number and $m_{\ell} \equiv m$ is the *projection* of the angular momentum on the z-axis, also called the *magnetic* quantum number.

Writing the Hamiltonian in a simpler way

$$H = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{\hbar^2 r^2} \right] + V(r)$$
(48)

yields the commutation relations: $[H, L^2] = [H, L_z] = 0$. Then, expanding the wavefunction $\psi_{\vec{k}}^+$ in *partial waves* corresponding to ℓ and m,

$$\psi_{\vec{k}}^{+}(k,\mathbf{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell m} R_{\ell m}(k,\mathbf{r}) Y_{\ell m}(\theta,\phi) , \qquad (49)$$

leads to the determination that for every radial wavefunction $R_{\ell}(k, r)$,

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{\ell(\ell+1)}{r^2} \right] R_\ell(k,r) + V(r) R_\ell(k,r) = E R_\ell(k,r) \,. \tag{50}$$

Notice that this equation does not depend on m_{ℓ} .

It is convenient to define a new radial function $u_{\ell}(k,r) = rR_{\ell}(k,r)$, so that the radial equation becomes

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2} - U(r)\right] u_\ell(k,r) = 0, \qquad (51)$$

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and

where the wavenumber and the potential are written as $k = \sqrt{2mE/\hbar^2}$ and $U = 2mV/\hbar^2$, respectively. The solution to this equation for a free particle contains Bessel $[j_\ell(kr)]$ and Neumann $[n_\ell(kr)]$ functions. In addition, for a particle in a potential U(r) such that $\lim_{r\to\infty} |U(r)| < \frac{M}{r^{\ell+\epsilon}}$, where M is some constant and ϵ is greater than zero, the solution to Eq. (51) also contains Bessel and Neumann functions. For large distances,

$$\begin{cases} j_{\ell}(x) \to \frac{1}{x} \sin(x - \frac{1}{2}\ell\pi) \\ n_{\ell}(x) \to -\frac{1}{x} \cos(x - \frac{1}{2}\ell\pi) \end{cases} . \tag{52}$$

Recall Eq. (24): the asymptotic form of the scattering wavefunction $\psi_{\vec{k}}^{+}(k, \mathbf{r})$,

$$\psi_{\vec{k}}^{+}(\mathbf{r}) \longrightarrow A(k) \left\{ e^{i\mathbf{k}\cdot\mathbf{r}} + f(k,\theta,\phi)\frac{e^{ikr}}{r} \right\}$$
 (53)

The partial wave expansion of the plane wave is given by

$$e^{i\mathbf{k}\cdot\mathbf{r}} \equiv e^{ikz} = \sum_{\ell=0}^{\infty} (2\ell+1)i^{\ell} j_{\ell}(kr) P_{\ell}(\cos\theta), \qquad (54)$$

where $P_{\ell}(\cos \theta)$ are the Legendre polynomials

$$P_{\ell}(\cos\theta) = \sqrt{\frac{4\pi}{2\ell+1}} Y_{\ell,0}(\theta,\phi) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell,m}^{*}(\hat{\mathbf{k}}) Y_{\ell,m}(\hat{\mathbf{k}}) .$$
(55)

Using the asymptotic expression for $j_{\ell}(kr)$ and matching both forms of the wavefunction [20], the scattering amplitude can be written as

$$f(k,\theta) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} \left[e^{2i\delta_{\ell}(k)} - 1 \right] P_{\ell}(\cos\theta)$$
$$= \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1)a_{\ell}(k)P_{\ell}(\cos\theta), \qquad (56)$$

where the partial amplitude $a_{\ell}(k)$ is given by $a_{\ell}(k) = e^{i\delta_{\ell}(k)} \sin \delta_{\ell}$. The amplitude A(k) is found by requiring the wavefunction to be energy normalized. In later sections, the wavefunction $\psi_{\vec{k}}^{+}(\mathbf{r})$ will be referred to as $|\varepsilon, \ell\rangle$ for continuum states corresponding to collision energy ε and partial wave ℓ .

1.7 Singlet or Triplet Projection

As described in § 1.4, diatomic molecules can be described by different quantum numbers depending on the separation of the atoms. In the *atomic basis* (or *hyperfine basis*) the angular momentum of each atom is defined separately so that the molecular state is $|F, M_F\rangle = |f_1, m_1\rangle \otimes |f_2, m_2\rangle$. When the atoms are sufficiently close together, the electrons interact with each other so that in the *molecular basis* the angular momentum of all the electrons must be defined separately from the total nuclear spin state, which can be written as $|S, m_S\rangle \otimes$ $|I, m_I\rangle$, where $|S, m_S\rangle$ represents the electronic spin state and $|I, m_I\rangle$ represents the nuclear spin state. These angular momentum quantities are defined as

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2, \qquad (57)$$

$$\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2; \tag{58}$$

$$\mathbf{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2 = 0, \qquad (59)$$

since $\ell_i = 0$ for alkali atoms in their ground state (e.g. Li(3s), Na(3s), etc.). Also,

$$\mathbf{f}_1 \equiv \mathbf{i}_1 + \mathbf{s}_1 + \ell_1 = \mathbf{i}_1 + \mathbf{s}_1,$$
 (60)

$$\mathbf{f}_2 \equiv \mathbf{i}_2 + \mathbf{s}_2 + \boldsymbol{\ell}_2 = \mathbf{i}_2 + \mathbf{s}_2,$$
 (61)

$$\mathbf{F} \equiv \mathbf{f}_1 + \mathbf{f}_2 = \mathbf{S} + \mathbf{I} \,. \tag{62}$$

The projection of the atomic basis on the molecular one is

$$|f_1, m_1; f_2, m_2\rangle = \sum_{S, m_S, I, m_I} \langle S, m_S; I, m_I | f_1, m_1; f_2, m_2 \rangle | S, m_S; I, m_I \rangle.$$
(63)

For simplicity of the notation, we write the Clebsch-Gordan coefficients below as $\langle S, m_S; I, m_I | f_1, m_1; f_2, m_2 \rangle \equiv a_{S,m_S,I,m_I}.$

For instance, the projection of the atomic basis onto the singlet molecular manifold (defined by S = 0 with $m_S = 0$), for any *I*, is written

$$P_S = \sum_{I,m_I} |a_{S=0,m_S=0,I,m_I}|^2 \tag{64}$$

and the projection onto the triplet molecular manifold (defined by S = 1 with $m_S = -1, 0, +1$), for any I, is

$$P_T = \sum_{I,m_I,m_S} |a_{S=1,m_S,I,m_I}|^2 \,. \tag{65}$$

And it must hold that $P_S + P_T = 1$.

Projecting between the atomic and molecular basis involves the coupling of four angular momenta. In order to go from $|f_1, m_1; f_2, m_2\rangle \longrightarrow |S, m_S; I, m_I\rangle$, it is necessary to transform the basis in three steps. Firstly,

$$|f_1, m_1; f_2, m_2\rangle \longrightarrow |f_1, f_2; F, m_F\rangle, \qquad (66)$$

then next,

$$|f_1, f_2; F, m_F\rangle \longrightarrow |I, S; F, m_F\rangle,$$
(67)

and finally,

$$|I, S; F, m_F\rangle \longrightarrow |S, m_S; I, m_I\rangle.$$
 (68)

These bases are connected by Clebsch-Gordan coefficients, as collected into various j-symbols. The particular transformations are

$$|f_{1}, m_{1}; f_{2}, m_{2}\rangle = \sum_{F, m_{F}} (-1)^{f_{2} - f_{1} - m_{F}} \sqrt{2F + 1} \begin{pmatrix} f_{1} & f_{2} & F \\ m_{1} & m_{2} & -m_{F} \end{pmatrix} \times |f_{1}, f_{2}; F, m_{F}\rangle, \qquad (69)$$

$$|f_{1}, f_{2}; F, m_{F}\rangle = \sum_{I,S} |I, S; F, m_{F}\rangle (f_{1}, f_{2}; F, m_{F}|I, S; F, m_{F})$$

$$= \sum_{I,S} \sqrt{(2f_{1}+1)(2f_{2}+1)(2I+1)(2S+1)}$$

$$\times \begin{cases} i_{1} \quad s_{1} \quad f_{1} \\ i_{1} \quad s_{1} \quad f_{1} \\ I \quad S \quad F \end{cases} |I, S; F, m_{F}\rangle, \text{ and} \qquad (70)$$

$$|I, S; F, m_{F}\rangle = (-1)^{S-I-m_{F}} \sum_{m_{I}, m_{S}} \sqrt{2F+1} \begin{pmatrix} I \quad S \quad F \\ m_{I} \quad m_{S} \quad -m_{F} \end{pmatrix}$$

$$\times |S, m_S; I, m_I\rangle. \tag{71}$$

Here (\cdots) represents a 3j symbol and $\{\cdots\}$ represents a 9j symbol. Thus in order to change basis $|f_1, m_1; f_2, m_2\rangle \longrightarrow |I, m_I; S, m_S\rangle$, it is necessary to evaluate the following expression

$$|f_1, m_1; f_2, m_2\rangle = \sum_{\substack{F, m_F, I, m_I, S, m_S \\ \times \sqrt{(2f_1 + 1)(2f_2 + 1)(2I + 1)(2S + 1)}}} (-1)^{f_2 - f_1 - m_F + S - I - m_F} (2F + 1)$$

$$\times \begin{pmatrix} f_{1} & f_{2} & F \\ m_{1} & m_{2} & -m_{F} \end{pmatrix} \begin{pmatrix} I & S & F \\ m_{I} & m_{S} & -m_{F} \end{pmatrix} \begin{cases} i_{1} & s_{1} & f_{1} \\ i_{2} & s_{2} & f_{2} \\ I & S & F \\ I & S & F \\ \end{cases} \\ \times |I, m_{I}; S, m_{S} \rangle.$$
(72)

The fraction of singlet molecules is found by using Eq. (64) with

$$a_{S=0,m_S=0,I,m_I} = \sum_{F,m_F,I,m_I} (-1)^{f_2 - f_1 - m_F - I - m_F} (2F + 1) \sqrt{(2f_1 + 1)(2f_2 + 1)(2I + 1)} \\ \times \begin{pmatrix} f_1 & f_2 & F \\ m_1 & m_2 & -m_F \end{pmatrix} \begin{pmatrix} I & 0 & F \\ m_I & 0 & -m_F \end{pmatrix} \begin{cases} i_1 & s_1 & f_1 \\ i_2 & s_2 & f_2 \\ I & 0 & F \end{cases} .$$
(73)

For instance, when the hyperfine values for the low-field seeking atomic hyperfine states $(f_1 = 1, m_1 = -1)$ in ⁷Li and $(f_2 = 1, m_2 = 1)$ in H are used to calculated $a_{0,0,I,m_I}$ in Eq. (73), the result for the fraction of singlet molecules from Eq. (64) 1/8. See Tables 1 and 2 for the results for all hyperfine states of ^{6,7}Li and H and D.

		⁷ Li							
Η	(2,2)	(2,1)	(2,0)	(2, -1)	(2, -2)	(1, -1)	(1,0)	(1,1)	
(1,1)	0	1/8	1/4	3/8	1/2	1/8	1/4	3/8	
$(1,\!0)$	1/4	1/4	1/4	1/4	1/4 .	1/4	1/4	1/4	
(1, -1)	1/2	3/8	1/4	1/8	0	3/8	1/4	1/8	
(0,0)	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	

Table 1: Fraction χ_S for combinations of various hyperfine states (F, m_F) of ⁷Li and H. The triplet fraction is obtained from $\chi_T = 1 - \chi_S$.

	⁶ Li								
Н	$\left(\frac{3}{2},\frac{3}{2}\right)$	$\left(\frac{3}{2},\frac{1}{2}\right)$	$\left(rac{3}{2},-rac{1}{2} ight)$	$\left(\frac{3}{2},-\frac{3}{2}\right)$	$\left(\frac{1}{2},-\frac{1}{2}\right)$	$\left(\frac{1}{2},\frac{1}{2}\right)$			
(1,1)	0	1/6	1/3	1/2	1/6	1/3			
(1,0)	1/4	1/4	1/4	1/4	1/4	1/4			
(1, -1)	1/2	1/3	1/6	0	1/3	1/6			
(0,0)	1/4	1/4	1/4	1/4	1/4	1/4			

Table 2: Same as Table 1, except for ⁶Li and H.

	7 T. j							
$^{2}\mathrm{H}$	(2,2)	(2,1)	(2,0)	(2, -1)	(2,-2)	(1, -1)	(1,0)	(1,1)
$(\frac{3}{2},\frac{3}{2})$	0	1/8	1/4	3/8	1/2	1/8	1/4	3/8
$\left(rac{3}{2},rac{1}{2} ight)$	1/6	2/10	1/4	3/10	1/3	2/10	1/4	3/10
$(\frac{3}{2}, -\frac{1}{2})$	1/3	3/10	1/4	2/10	1/6	3/10	1/4	2/10
$(\frac{5}{2}, -\frac{5}{2})$	1/2	3/8	1/4	1/8	0	3/8	1/4	1/8
$(\frac{1}{2}, -\frac{1}{2})$	1/6	2/10	1/4	3/10	1/3	2/10	1/4	3/10
$(\frac{1}{2}, \frac{1}{2})$	1/3	3/10	1/4	2/10	1/6	3/10	1/4	2/10

Table 3: Same as Table 1, except for 7 Li and 2 H.

1.8 Photoassociation in a Mixed Species Gas: One-Photon Photoassociation

Now that the components necessary to approach the theoretical considerations of the photoassociation process have been presented, we can address our goal, which is to find the number of molecules formed per second in a specific state for a particular pair of atomic species. Of the various PA processes discussed in § 1.1, let us begin by investigating the unique PA process of Eq. (2) that is only achievable in a heteronuclear system; one-photon PA. The lack of a

	⁶ Li								
$^{2}\mathrm{H}$	$\left(\frac{3}{2},\frac{3}{2}\right)$	$\left(\frac{3}{2},\frac{1}{2}\right)$	$\left(\frac{3}{2},-\frac{1}{2}\right)$	$(\frac{3}{2}, -\frac{3}{2})$	$(\frac{1}{2}, -\frac{1}{2})$	$\left(\frac{1}{2},\frac{1}{2}\right)$			
$-\frac{3}{\left(\frac{3}{2},\frac{3}{2}\right)}$	0	1/6	1/3	1/2	1/6	1/3			
$(\frac{3}{2},\frac{1}{2})$	1/6	2/9	5/18	1/3	2/9	5/18			
$(\frac{3}{2}, -\frac{1}{2})$	1/3	5/18	2/9	1/6	5/18	2/9			
$(\frac{3}{2}, -\frac{3}{2})$	1/2	1/3	1/6	0	1/3	1/6			
$\left(\frac{\overline{1}}{2},-\frac{\overline{1}}{2}\right)$	1/6	2/9	5/18	1/3	2/9	5/18			
$(\frac{1}{2}, \frac{1}{2})$	1/3	5/18	2/9	1/6	5/18	2/9			

Table 4: Same as Table 1, except for ${}^{6}Li$ and ${}^{2}H$.

permanent dipole moment in homonuclear systems leaves no possibility for transitions within a given electronic state, in the dipole approximation. However, in a heteronuclear system that has a non-zero dipole moment which varies with internuclear distance it is viable to form diatomic molecules from a mixture of the ultracold gases via a one-photon stimulated radiative association process directly from the continuum to bound vibration-rotation levels of the ground electronic state, as shown in Figure 6.

1.8.1 Line Shape Expression

For a pair of atoms approaching each other along the molecular ground state potential energy curve with a given asymptotic relative kinetic energy ε , a laser of intensity I, detuned by the quantity Δ from the molecular bound level v, one can induce a transition into that level v (see Figure 6). The rate coefficient for the photoassociation (PA) process is given by [13,30]

$$\mathsf{K}_{v}(T, I, \Delta) = \left\langle \frac{\pi v_{\mathrm{rel}}}{\kappa^{2}} \sum_{\ell=0}^{\infty} (2\ell + 1) |S_{\ell, v}(\varepsilon, I, \Delta)|^{2} \right\rangle , \qquad (74)$$



Fig. 6: Schematics of one-photon stimulated molecule formation and the electronic ground state dipole moment as a function of internuclear separation.

where $\varepsilon = \hbar^2 \kappa^2 / 2\mu = \mu v_{\rm rel}^2 / 2$, μ is the reduced mass, and $v_{\rm rel}$ is the relative velocity of the colliding pair. The sum is over all partial waves ℓ , and $S_{\ell,v}$ represents the scattering matrix element for producing the final state v from the initial continuum state. Averaging over relative velocities is implied by $\langle \cdots \rangle$. The thermal average of $K_v(T, I, \Delta)$ can be written as an integral over scattering energies as shown in the following discussion.

For a system characterized by temperature T and a Maxwell-Boltzmann velocity distribution, the thermal average of some arbitrary function $\mathcal{F}(v)$ is

$$\langle \mathcal{F}(v) \rangle = \int_0^\infty dv f(v) \,\mathcal{F}(v) \,,$$
(75)

where k_B is the Boltzmann constant and $f(v) = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{\mu v^2}{2k_B T}}$ is the velocity distribution for a Maxwell-Boltzmann distribution of particles. Then,

$$\langle \mathcal{F}(v) \rangle = 4\pi \int_0^\infty dv \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{\mu v^2}{2k_B T}} \mathcal{F}(v) \,. \tag{76}$$

It is assumed that a Maxwell-Boltzmann distribution is representative of a mixed species ultracold gas. If the system relatively light, like LiH for instance, then it is characterized by temperatures less than 1 mK so that only *s*-wave ($\ell = 0$) scattering is relevant. Then, keeping only the $\ell = 0$ contribution, $K_v(T, I, \Delta)$ at ultralow temperatures becomes

$$\mathbf{K}_{v}(T, I, \Delta) = \frac{\pi \hbar^{2}}{\mu^{2}} \left\langle \frac{|S_{\ell, v}(\varepsilon, I, \Delta)|^{2}}{v} \right\rangle$$

$$= \frac{\hbar^{2}}{\mu^{1/2}} \left(\frac{1}{2\pi k_{B}T} \right)^{3/2} \int_{0}^{\infty} dv \, v \, e^{\frac{-\mu v^{2}}{2k_{B}T}} |S_{\ell=0, v}(\varepsilon, I, \Delta)|^{2}. \quad (77)$$

Writing this expression in terms of the energy $\varepsilon = \mu v^2/2$, so that $d\varepsilon = \mu v dv$,

$$\mathsf{K}_{v}(T,I,\Delta) = h^{2} \left(\frac{1}{2\pi\mu k_{B}T}\right)^{3/2} \int_{0}^{\infty} d\varepsilon \, e^{-\varepsilon/k_{B}T} |S_{\ell=0,v}(\varepsilon,I,\Delta)|^{2} \,. \tag{78}$$

Define the translational partition function $Q_T = (2\pi\mu k_B T/h^2)^{3/2}$; then finally the thermal average can be written as an integral over collision energies:

$$\mathsf{K}_{v}(T, I, \Delta) = \frac{1}{hQ_{T}} \int_{o}^{\infty} d\varepsilon \, e^{-\varepsilon/k_{B}T} \left| S_{\ell=0,v}(\varepsilon, I, \Delta) \right|^{2}.$$
(79)

Bohn and Julienne [14] carried out full quantum close-coupling calculations and found that a simple resonant scattering expression for an isolated resonance v, J is an excellent approximation at MOT temperatures. The scattering matrix

is well approximated by

$$|S_{J,v}(\varepsilon, I, \Delta)|^2 = \frac{\gamma_v \gamma_s(\varepsilon, J)}{\left[(\varepsilon - \Delta)^2 + (\gamma/2)^2\right]},$$
(80)

where $\gamma = \gamma_v + \gamma_s$. Here γ_v is the width of the bound level v and γ_s is the stimulated width from the continuum initial state $|\varepsilon, \ell = 0\rangle \equiv |\varepsilon\rangle$ to the state $|v, J = 1\rangle \equiv |v\rangle$. The only problem with this approximation exists at the level (v = 0, J = 0) in the ground state potential (where $\gamma_v = 0$).

At low laser intensities, the stimulated width can be written as

$$\gamma_s(I,\varepsilon,v) \simeq 4\pi^2 \frac{I}{c} |D_v(\varepsilon)|^2 = 2\pi\hbar^2 \Omega_{\varepsilon v}^2 , \qquad (81)$$

where $|D_v(\varepsilon)|^2 = |\langle v|D(R)|\varepsilon, J\rangle|^2$ is the square of the dipole matrix element, D(R) is the permanent molecular dipole moment within the ground state and $\Omega_{\varepsilon v}$ is the Rabi frequency between the continuum and bound states. The Rabi frequency is defined as $\Omega \equiv E_{max}d/2\hbar$, where $d = \langle f|D(R)|i\rangle$ is the dipole moment matrix element between the initial energy-normalized wavefunction $|i\rangle$ and the final bound state wavefunction $|f\rangle$ and E_{max} is the amplitude of the oscillating electric field. From the definition of intensity $I = \frac{1}{2}\epsilon_0 c E_{max}^2$, where ϵ_0 is the vacuum permittivity. In CGS units (using $4\pi\epsilon_0 = 1$), $\hbar\Omega = d\sqrt{I/2\epsilon_0 c} = d\sqrt{2\pi I/c}$, and hence Eq. (81). Note that the units of $\hbar\Omega_{\varepsilon v}$ are Joules^{1/2}, due to the energy normalized continuum wavefunction appearing in d.

The scattering matrix defined in Eq. (80) has the general form of a Lorentzian

$$\frac{\lambda}{x^2 + \lambda^2} \,. \tag{82}$$

As $\lambda \to 0$, the peak of the Lorentzian becomes sharper and higher and tends to a delta function $\lim_{\lambda\to 0} \left\{ \frac{\lambda}{x^2+\lambda^2} \right\} = c \,\delta(x).$

The delta function may be approximated by a sequence of functions, one in particular is written [21]

$$\delta_n(x) = \left(\frac{n}{\pi}\right) \frac{1}{1+n^2 x^2} \,. \tag{83}$$

The scattering matrix element of Eq. (80) can be written in the form of Eq. (83)

$$|S_{J,v}(\varepsilon, I, \Delta)|^2 = \frac{\gamma_v \gamma_s(\varepsilon, J)}{[(\varepsilon - \Delta)^2 + (\gamma/2)^2]}$$

= $\pi \gamma_s (\gamma_v / \pi) \frac{1}{[(\varepsilon - \Delta)^2 + (\gamma_v / 2)^2]}$, (84)

since the intensity of the laser light is assumed to be low and since $\gamma_s \propto I$, $\gamma_v + \gamma_s \approx \gamma_v$. Setting $x \equiv \varepsilon - \Delta$ and $n \equiv \gamma_v / \pi$,

$$|S|^{2} = \pi \gamma_{s} \left(\frac{\gamma_{v}}{\pi}\right) \frac{4}{\gamma_{v}^{2}} \left[\frac{1}{1+\frac{4}{\gamma_{v}^{2}}x^{2}}\right]$$
$$= \pi \gamma_{s} \left(\frac{2}{n\pi}\right) n^{2} \left[\frac{1}{1+n^{2}x^{2}}\right]$$
$$= 2\pi \gamma_{s} \left[\left(\frac{n}{\pi}\right) \frac{1}{1+n^{2}x^{2}}\right]$$
$$\approx 2\pi \gamma_{s} \delta(x) . \tag{85}$$

Then for the case of low intensity and if $\gamma_v/2\varepsilon \ll 1$ and $\gamma_s/\gamma_v \ll 1$, then $|S_{\ell=0,v}|^2$ can be approximated by

$$|S_{\ell=0,v}(\varepsilon, I, \Delta)|^2 \simeq 2\pi\gamma_s(\varepsilon, J)\delta(\varepsilon - \Delta) , \qquad (86)$$

and Eq. (79) takes the simple form

$$\mathsf{K}_{v} = \frac{2\pi}{hQ_{T}} e^{-\Delta/k_{B}T} \gamma_{s}(I, \Delta, v) .$$
(87)

In order to investigate the validity of the delta function approximation for the scattering matrix elements, consider the ratio of the rate coefficient expression with $|S|^2$ taken to be the full Lorentzian of Eq. (80) to the rate coefficient with $|S|^2$ taken to be the delta function of Eq. (86):

$$\Phi \equiv \frac{\int_{o}^{\infty} d\varepsilon \, e^{-\varepsilon/k_{B}T} \left\{ \frac{\gamma_{v} \gamma_{s}(\varepsilon, J)}{\left[(\varepsilon - \Delta)^{2} + (\frac{\gamma_{v} + \gamma_{s}}{2})^{2}\right]} \right\}}{\int_{o}^{\infty} d\varepsilon \, e^{-\varepsilon/k_{B}T} \left\{ 2\pi \gamma_{s}(\varepsilon, J)\delta(\varepsilon - \Delta) \right\}}.$$
(88)

Taking $\gamma_s = \frac{\pi}{\varepsilon_0 c} I |D(\varepsilon)|^2$ (in SI units), where the dipole matrix elements are written as $|D(\varepsilon)|^2 = C_v \sqrt{\varepsilon}$, and assuming a detuning $\Delta = k_B T/2$ and the upper bound of integration over energies $\varepsilon_{max} = 10 k_B T$, the ratio is reduced to

$$\Phi = \frac{\gamma_v \, e^{1/2}}{2\pi \sqrt{\frac{k_B T}{2}}} \int_0^{\varepsilon_{max}} d\varepsilon \frac{\sqrt{\varepsilon} \, e^{-\varepsilon/k_B T}}{(\varepsilon - \frac{k_B T}{2})^2 + \frac{\left[\gamma_v + \frac{\pi}{\varepsilon_0 c} I \, C_v \sqrt{\varepsilon}\right]^2}{4}}.$$
(89)

The ratio Φ is shown in Figure 7 for the case when T = 1 mK for typical ground and excited state levels which are described by their natural width γ_v and the strength of the optical coupling for that level C_v . At low intensities, the delta function expression of Eq. (86) best approximates the Lorentzian form of the scattering matrix elements and the ratio Φ goes to one. As shown in Figure 7, Φ remains reasonably close to one for intensities up to kilowatts per square centimeter for both ground and excited levels when the temperature is 1 mK.

Figure 7 implies that the effect of the intensity is more important for an excited state level than for a ground state level. This is not always the case. The ratio γ_v/γ_s , i.e., the sharpness of the natural width of the level along with the
size of the dipole matrix elements determine whether the ground or excited level depends more strongly on intensity.

Figure 8 and Figure 9 show the temperature dependence of the ratio Φ_{ground} and Φ_{excited} versus I for typical ground and excited state levels, respectively. For a ground state level, the delta function expression better approximates the Lorenztian as the temperature decreases. However for temperatures below 10 μ K, this approximation begins to fail. As the temperature decreases, the peak of the Lorentzian moves closer to zero energy and its contribution is cut. For an excited state level, the approximation begins to fail for higher temperatures (typically below 1 mK), which is due largely in part to the fact that the width of excited state levels is broader than for the ground state levels and therefore the contribution from the Lorentzian is more pronouncedly cut.

We conclude that the approximation of $|S_{J,v}|^2$ by a delta-function is valid for I of the order of 1 kW/cm² or less, and collision energy ε/k_B larger than 10 μ K.

It is confirmed that $\gamma_s/\gamma_v \ll 1$ and $\gamma_v/2\varepsilon \ll 1$ for the systems considered in this work, the details of which are shown in Chapters 3, 4, 5, and 6.

To determine the value of the detuning Δ using K_v , we find its extremum with $K_v \propto e^{-\Delta/k_B T} \sqrt{\Delta}$,

$$\frac{d}{d\Delta} \left(e^{-\Delta/k_B T} \sqrt{\Delta} \right) = 0$$
$$\frac{e^{-\Delta/k_B T}}{\sqrt{\Delta}} \left(\frac{1}{2} - \frac{\Delta}{k_B T} \right) = 0$$



Fig. 7: The ratio Φ from Eq. (89) plotted as a function of intensity I for a typical ground state level and a typical excited state level which are described by a natural width γ_v and optical coupling C_v . Both curves are calculated assuming temperature T = 1 mK. For a typical ground state level, the natural width γ_v is taken to be approximately 5×10^{-8} cm⁻¹ and the optical coupling C_v is taken to be approximately 1×10^3 a.u. For a typical excited state level, it is assumed that $\gamma_v \sim 5 \times 10^{-5}$ cm⁻¹ and $C_v \sim 1 \times 10^7$ a.u. These same parameters were used in the calculation of the curves shown in Figures 8 and 9.



Fig. 8: The ratio Φ from Eq. (89) plotted as a function of intensity I for a typical ground state level at temperatures T = 10 mK, 1 mK, 100 μ K, and 10 μ K.



Fig. 9: The ratio Φ from Eq. (89) plotted as a function of intensity I for a typical excited state level at temperatures T = 10 mK, 1 mK, 100 μ K, and 10 μ K.



Fig. 10: Plotted here are a wavefunction for an upper vibrational level $\psi_{v,J}(R)$ and a dipole transition moment function $D_{XY}(R)$. Notice that in the vicinity of the last lobe of the wavefunction (between R_1 and R_2), the transition moment is essentially constant, where R_1 and R_2 define the location of the last lobe.

$$\Rightarrow \Delta = \frac{k_B T}{2}$$

Using the delta-function approximation for $|S|^2$ and recalling that $\gamma_s \simeq 4\pi^2 \frac{I}{c} |D_v(\varepsilon)|^2$ the maximum rate coefficient K_v is obtained at $\Delta = k_B T/2$, and is simply given by

$$\mathsf{K}_{v}(T,I) = \frac{8\pi^{3}}{h^{2}} \frac{I}{c} \frac{e^{-1/2}}{Q_{T}} |D_{v}(k_{B}T/2)|^{2} , \qquad (90)$$

where $|D_v(k_BT/2)|^2 = |\langle v, J|D(R)|\varepsilon = k_BT/2, \ell \rangle|^2$. $|\varepsilon = k_BT/2, \ell \rangle$ represents the wavefunction of the initial continuum state, $|v, J\rangle$ represents the wavefunction of the final bound state, and D(R) is the molecular dipole moment function.

Let us take a moment to examine the dipole matrix element integrals. For simplicity of notation take the particular case, $|D_v(\varepsilon)|^2 = |D_{v,\varepsilon}^{J=1,\ell=0}|^2$.

$$D_{v}(\varepsilon) = \langle v, J | D_{XY}(R) | \varepsilon, \ell \rangle$$

=
$$\int_{0}^{\infty} dR \, \psi_{v,J}^{X}(R) \, D_{XY}^{i}(R) \, \psi_{\varepsilon,\ell}^{Y}(R) \,, \qquad (91)$$

where $\psi_{v,J}^X(R)$ and $\psi_{\varepsilon,\ell}^Y(R)$ denote the *R*-dependent bound and continuum wavefunctions for electronic states *X* and *Y* respectively, and $D_{XY}(R)$ is the dipole transition moment function. For highly excited vibrational levels, where $\psi_{v,J}(R)$ extends to larger distances (see Figure 10), most of the contribution to the integral comes from the overlap of the last lobe with the continuum wavefunction and the dipole moment. At large *R*, we have a constant limit, $D_{XY}(R) \to D_0$, so that

$$|D_{v}(\varepsilon)|^{2} = \left| \int_{0}^{\infty} dR \, \psi_{v,J}^{X}(R) \, D_{XY}(R) \, \psi_{\varepsilon,\ell}^{Y}(R) \right|^{2} \simeq |D_{0}|^{2} \left| \int_{R_{1}}^{R_{2}} dR \, \psi_{v,J}^{X}(R) \, \psi_{\varepsilon,\ell}^{Y}(R) \right|^{2}, \qquad (92)$$

where R_1 and R_2 are defined by the location of the last lobe. Since ultracold corresponds to $\varepsilon \to 0$, then in the vicinity of the lobe the continuum wavefunction takes its asymptotic form [20]

$$\psi_{\varepsilon,\ell}^{Y}(R) \simeq \sqrt{\frac{2\mu}{\pi\hbar^{2}k}} \sin \delta_{\ell}(k) \frac{\sin \left[kR - \ell\pi/2 + \delta_{\ell}(k)\right]}{\sin \delta_{\ell}(k)}$$
$$\simeq \sqrt{\frac{2\mu}{\pi\hbar^{2}k}} \left(1 - \frac{r}{a}\right) \sin \delta_{\ell}(k) , \qquad (93)$$

where a is the scattering length. The dipole matrix element integral can then be written as

$$|D_{v}(\varepsilon)|^{2} \simeq |D_{0}|^{2} \frac{2\mu}{\pi\hbar^{2}k} \sin^{2}\delta_{\ell}(k) \left| \int_{R_{1}}^{R_{2}} dR \left(1 - \frac{r}{a} \right) \psi_{v,J}^{X}(R) \right|^{2}$$

$$\simeq |D_{0}|^{2} \frac{2\mu}{\pi\hbar^{2}k} \left(1 - \frac{r}{a} \right)^{2} L^{2} \left| \psi_{v,J}^{X}(r) \right|^{2} \sin^{2}\delta_{\ell}(k) , \qquad (94)$$

where r is the position of the center of the lobe and L is its size in k. Knowing that $\delta_{\ell}(k) \to 0$ as $k \to 0$, in addition with using the effective range expansion [20] for $\ell = 0$:

$$\sin^2 \delta_0(k) = \frac{k^2}{k^2 + k^2 \cot^2 \delta_0(k)}$$
(95)

$$\simeq a^2 k^2 \left[1 + a k^2 (r - a) \right] + \mathcal{O}(k^5)$$
(96)

which is valid for energies up to $10^{-9} - 10^{-8}$ au for $\ell = 0$. [20] With this,

$$|D_{v}(\varepsilon)|^{2} = |D_{0}|^{2} \frac{2\mu}{\pi\hbar^{2}k} \left(1 - \frac{r}{a}\right)^{2} L^{2} \left|\psi_{v,J}^{X}(r)\right|^{2} \sin^{2}\delta_{\ell}(k)$$

$$\simeq |D_{0}|^{2} \frac{2\mu}{\pi\hbar^{2}k} \left(1 - \frac{r}{a}\right)^{2} L^{2} \left|\psi_{v,J}^{X}(r)\right|^{2} \left\{a^{2}k^{2} + a^{3}k^{4}(r - a) + \mathcal{O}(k^{5})\right\}$$

$$= |D_{0}|^{2} \frac{2\mu k}{\pi\hbar^{2}} L^{2} \left|\psi_{v,J}^{X}(r)\right|^{2} (a - r)^{2} + \mathcal{O}(k^{3}).$$
(97)

Then finally, with $k = \sqrt{2\mu\varepsilon}$,

$$|D_v(\varepsilon)|^2 \propto \sqrt{\varepsilon}, \quad [\ell=0].$$
 (98)

This is one instance of Wigner's threshold law [31]., which in general states that $|D_v(\varepsilon)|^2 \propto \varepsilon^{(2\ell+1)/2}$.

In the ultralow energy limit, $|D_v|^2 = C_v \sqrt{\varepsilon}$, so that $\gamma_s \propto \sqrt{\varepsilon}$, in accordance with Wigner's threshold law [31]. Under these conditions, the rate coefficient can be written finally as

$$\mathsf{K}_{v}(T,I) = \frac{8\pi^{3}}{h} \frac{I}{c} \frac{e^{-1/2}}{Q_{T}} C_{v} \sqrt{k_{B}T/2} \,. \tag{99}$$

Note that the light polarization has not been accounted for in the above expression, which would introduce a factor of three in the denominator.

1.9 Photoassociation via an excited state

Another route to ground state molecule formation is photoassociation via an excited state. This process can take place either by two-photon stimulated radiative association or by excitation to bound levels of an excited state followed by spontaneous emission to bound levels of the ground state. Both of these schemes start with the same initial photoassociation transition from the vibrational continuum of the ground state to some intermediate electronically excited state (detuned by an amount Δ), followed by either stimulated (detuned by an amount δ) or spontaneous transitions back to the ground state, as illustrated in Figure 11.

1.9.1 Initial photoassociation step

The theoretical treatment of the initial photoassociation step is equivalent to one-photon direct stimulation from continuum, except the continuum state is coupled to v', J' levels of an excited state with the dipole transition moment function $D_{XY}(R)$, rather than to v, J levels of the ground state. The rate coefficient



Fig. 11: Schematics of two-photon stimulated Raman molecule formation. The arrows represent PA transitions with $A^1\Sigma^+$ as the intermediate state.

for populating the v' levels of an excited state holds with the same assumptions and approximations as § 1.8, so that

$$\mathsf{K}_{v'}^{(1)}(T, I_1) = \frac{8\pi^3}{h} \frac{I_1}{c} \frac{e^{-1/2}}{Q_T} C_{v'} \sqrt{k_B T/2} \ . \tag{100}$$

1.9.2 Two-photon stimulated photoassociation

A two-photon stimulated Raman photoassociation process is described by the rate coefficient $K^{(2)}$. Let us consider the two-photon interaction to be essentially a second order perturbation from the one-photon scheme and assume it is possible to write $K^{(2)}$ in terms of the one-photon rate coefficient $K^{(1)}$. The Rabi frequency between an initial state $|i\rangle$ coupled by an electric field via an intermediate state $|n\rangle$ to a final state $|f\rangle$ is defined to first order as

$$\Omega_{fi} = \langle f | \mathbf{e} \cdot \mathbf{r} | i \rangle = 0, \qquad (101)$$

if $|i\rangle$ and $|f\rangle$ have the same parity. To second order,

$$\Omega_{fi} = \sum_{n \neq f,i} \frac{\langle f | \mathbf{e} \cdot \mathbf{r} | n \rangle \langle n | \mathbf{e} \cdot \mathbf{r} | i \rangle}{E_n - (E_f - E_i)} \,. \tag{102}$$

The detuning from an intermediate level Δ is $E_n - (E_f - E_i)$. Define $\Omega_{fn} \equiv \langle f | \mathbf{e} \cdot \mathbf{r} | n \rangle$ and $\Omega_{ni} \equiv \langle n | \mathbf{e} \cdot \mathbf{r} | i \rangle$, so that for the case where the initial state is the scattering state $|\varepsilon, \ell\rangle$, the intermediate state is the excited bound level $|v', J'\rangle$ and the final state is the ground bound level $|v, J\rangle$, the Rabi frequency coupling the initial and final states Ω_{if} can be written as an effective Rabi frequency

$$\Omega_{\rm eff} \equiv \frac{\Omega_{v'v}\Omega_{v'\varepsilon}}{\Delta} \,. \tag{103}$$

With a two-photon interaction assumed to be an *effective* one-photon interaction (shown schematically in Figure 12), then the rate coefficient $\mathsf{K}^{(2)}$ depends on the detuning δ , the effective Rabi frequency from Eq. (103) Ω_{eff} , and the temperture T. Recall that $\mathsf{K}^{(1)} \propto e^{-\Delta/k_B T} \gamma_s$ and $\gamma_s = 2\pi \hbar^2 \Omega_{v'\varepsilon}^2$, so that $\mathsf{K}^{(1)} = \frac{\hbar}{Q_T} e^{-\Delta/k_B T} \Omega_{v'\varepsilon}^2$. Then,

$$\mathbf{K}^{(2)}(\delta, \Omega_{\text{eff}}, T) = \frac{h}{Q_T} e^{-\Delta/k_B T} \Omega_{\text{eff}}^2
= \frac{h}{Q_T} e^{-\Delta/k_B T} \Omega_{v'v}^2 \left(\frac{\Omega_{v'\varepsilon}}{\Delta}\right)^2
= \mathbf{K}^{(1)} \left(\frac{\Omega_{v'\varepsilon}}{\Delta}\right)^2.$$
(104)

So that, in general, if the value of Δ is large when compared to the natural



Fig. 12: Schematics of a two-photon process (shown on the left) and of the equivalent effective one-photon process (shown on the right). For the two-photon process, the relevant transitions between the two electronic states are indicated by arrows, and the laser intensities and frequencies for the two photons are shown as $I_1 I_2$, and ω_1 and ω_2 . The effective one-photon process is described by a coupling between the states ($\varepsilon, \ell = 0$) and (v, J) that is defined by Ω_{eff} , which is given by Eq. (103).

width $\gamma_{v'}$ of the intermediate level v', we can use an effective Rabi frequency formulation [7] and write the two-photon Raman rate coefficient $\mathsf{K}^{(2)}$ in terms of the one-photon photoassociation rate $\mathsf{K}^{(1)}$ to v' and the ratio of the bound-bound Rabi frequency $\Omega_{vv'}$ and the detuning Δ

$$\mathsf{K}_{vv'}^{(2)}(T, \{L\}) = \mathsf{K}_{v'}^{(1)}(T, I_1, \delta) \left(\frac{\Omega_{vv'}}{\Delta}\right)^2 \,. \tag{105}$$

Here, $\{L\} \equiv \{L_1, L_2\}$ stands for the various laser parameters. Note that $\mathsf{K}^{(1)}$ is computed using the two-photon detuning δ (see Figure 11). This approximation clearly fails when $\Delta \to 0$; if it so happens that $\Delta \ll \gamma_{v'}$. The detuning Δ must be large enough so that hyperfine structure effects may safely be ignored. If the ratio of the detuning to the spontaneous decay width of level v', is not large enough, Autler-Townes splittings and large spontaneous decays would need to be taken into account [30].

Writing $\hbar^2 \Omega_{v'v}^2 = (2\pi I_2/c) |D_{v'v}|^2$, and using the result of Eq.(100) for $\mathsf{K}^{(1)}$, Eq.(105) becomes

$$\mathsf{K}_{vv'}^{(2)}(T, \{L\}) = \frac{64\pi^6}{h^3} \frac{I_1 I_2}{c^2} \frac{e^{-1/2}}{Q_T} \sqrt{\frac{k_B T}{2}} C_{v'} \frac{|D_{v'v}|^2}{\Delta^2} \,. \tag{106}$$

Again note that the light polarization has not been accounted for in the above expression.

1.9.3 Spontaneous radiative decay

The excited rovibrational levels (v', J') can decay spontaneously into other excited rovibrational levels with lower energy or into bound ground state (or other lower electronic state) rovibrational levels. The allowed paths of decay take place under strict selection rules governed by angular momentum algebra in quantum mechanics. For each set of allowed transitions, the Hönl-London factors (or rotational line strength factors), which govern the relative weight for each decay path, must be calculated. The allowed decay paths (or *branches*) for transitions within particular electronic states, as well as the calculation of the respective Hönl-London factors, are shown in the subsequent chapters.

In general, the transition probabilities for spontaneous decay from a level (v', J') in an excited state are given by

$$A_{v'}^{\text{tot}} = A_{v'}(\text{EX}_1) + A_{v'}(\text{EX}_2) + A_{v'}(G) , \qquad (107)$$

where the three components correspond to the allowed decays within one excited state (EX₁), into one or more different lower energy excited states (EX₂), and into the ground state (G), respectively. Each component $A_{v'}(Y)$ is the sum of the allowed R, Q, and P-branches into the electronic state Y

$$A_{v'}(Y) = A_{v'}^R(Y) + A_{v'}^Q(Y) + A_{v'}^P(Y) , \qquad (108)$$

where each branch α includes the contribution from discrete-discrete and discretecontinuum transitions as appropriate:

$$A^{\alpha}_{v'}(Y) = \sum_{v} A^{\alpha}_{v'v}(Y) + \int d\varepsilon A^{\alpha}_{v'}(Y,\varepsilon) . \qquad (109)$$

Here, the allowed transitions from the initial upper state $|v', J'\rangle$ to lower discrete states $|v, J\rangle$ or continuum states $|\varepsilon, \ell\rangle$ are given by

$$A^{\alpha}_{v'v}(Y) = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega^{\alpha}_{v'v}}{c}\right)^3 W^{\alpha}_{J'} |\langle vJ|D_{\mathrm{EX},Y}|v',J'\rangle|^2$$
(110)

$$A_{v'}^{\alpha}(Y,\varepsilon) = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega_{v'}^{\alpha}(\varepsilon)}{c}\right)^3 W_{J'}^{\alpha} |\langle \varepsilon \ell | D_{\mathrm{EX},\mathrm{Y}} | v', J' \rangle|^2, \qquad (111)$$

where $W_{J'}^{\alpha}$ are the Hönl-London (or rotational line strength) factors corresponding to each branch. The frequencies are defined as $\hbar \omega_{v'v}^{\alpha} = E_{v',J'} - E_{vJ}$ and $\hbar \omega_{v'}^{\alpha}(\varepsilon) = E_{v',J'} - E_{\varepsilon \ell}$, respectively. Also, the function $D_{\text{EX},Y}(R)$ stands for the dipole moment of the excited state (if $Y = \text{EX}_1$), or the dipole transition moment between one excited state and another (if $Y = \text{EX}_2$) or the ground state (if Y = G).

The lifetime of a given level (v', J' = 1) is simply given by

$$\tau_{v'} = \frac{1}{A_{v'}^{\text{tot}}} \,. \tag{112}$$

Finally, the branching ratio for radiative decay from an initial (v', J' = 1)into a bound level (v, J) of the electronic ground state $X^1\Sigma^+$ is simply given by

$$r_{vJ}^{v',J'}(\alpha) \equiv \frac{A_{v'v}^{\alpha}(G)}{A_{v'}^{\text{tot}}}.$$
(113)

1.10 Molecule Formation Rates

We write the rate coefficient $K_v(T, I)$ in terms of the various experimental parameters in the form

$$\mathsf{K}_{v}(T,I) = A \, \frac{C_{v}I}{T} \, \mathrm{cm}^{3}/\mathrm{s}\,, \tag{114}$$

where A contains all other constants and factors (e.g., the reduced mass). As an example, if C_v is in a.u., I in W/cm², and T in Kelvin, we have

$$\mathsf{K}_{v}(T,I) = \begin{cases} 9.0 \times 10^{-24} \frac{C_{v}I}{T} \, \mathrm{cm}^{3}/\mathrm{s} \,, & \text{for } {}^{7}\mathrm{LiH} \\ \\ 8.0 \times 10^{-24} \frac{C_{v}I}{T} \, \mathrm{cm}^{3}/\mathrm{s} \,, & \text{for } {}^{23}\mathrm{NaH} \end{cases}$$
(115)

As mentioned in § 1.4, the hyperfine states of the trapped ultracold atoms can lead to scattering wavefunctions containing both singlet and triplet components. The singlet and triplet fractions, χ_S and $\chi_T = 1 - \chi_S$, depend on the atomic hyperfine states (F, m_F) populated in a particular experiment.

A rate R of molecules formed per second is obtained by multiplying the rate coefficient by the density of the alkali atom n_A , by the density of atomic hydrogen n_H , and by the volume V illuminated by the laser beam(s) by the rate coefficient. For one and two-photon processes,

$$\mathsf{K}_{v} = \begin{cases} \mathsf{K}_{v'}^{(1)}(T, I) & \text{one-photon direct} \\ \\ r_{vJ}^{v',J'}(\alpha) \, \mathsf{K}_{v'}^{(1)}(T, I_{1}) & \text{one-photon} \\ \\ \\ \mathsf{K}_{vv'}^{(2)}(T, \{L\}) & \text{two-photon} \end{cases}$$
(116)

where only α denotes the particular decay branch. In addition, because the hyperfine states of the trapped ultracold atoms can lead to scattering wavefunctions containing both singlet and triplet components, the rate coefficient must also be multiplied by the fraction χ_S or χ_T (see § 1.7). Thus the formation rate of singlet

molecules can be written as

$$\mathsf{R}_v = \chi_S n_{Li} n_H \mathsf{K}_v V \,, \tag{117}$$

and for triplet molecules as

$$\mathsf{R}_v = \chi_T n_{Li} n_H \mathsf{K}_v V \,, \tag{118}$$

where χ_S and χ_T are given in § 1.4. Note that population of any level other than the ground level (v = 0, J = 0) will lead to further radiative cascade that will populate a distribution of rotational levels in the singlet ground state ($X^1\Sigma^+$).

1.11 Back-stimulation

The PA process is not "directional", and free atoms can form bound molecules with the absorption of a photon just as a bound molecule can emit a photon and dissociate to free atoms. For any stimulated process, *back-stimulation* must be considered in the calculation of rates of molecules formed per second. This effect becomes relevant when the time associated with the stimulated photoassociation process becomes comparable to or smaller than the radiative lifetime of the target state. Then, large fractions of the molecules produced are dissociated before they can radiatively decay into a lower level that is not resonant with the laser frequency or be removed from the interaction region by some other means.

For the one-photon process and for the case when spontaneous decay of the molecule is possible, the stimulated width is given by Eq. (81): $\gamma_s(I, \varepsilon, v) \simeq$ $4\pi^2 \frac{I}{c} |D_v(\varepsilon)|^2 = 2\pi\hbar^2 \Omega_{\varepsilon v}^2$. The time scale of the stimulated process (call it the back-stimulation time τ_s) is then

$$\tau_s = \hbar / \gamma_s \,. \tag{119}$$

If this time scale is much longer than the lifetime of the ro-vibrational level τ_v or $\tau_{v'}$, then the molecules would undergo spontaneous decay before they can be dissociated. To that effect, if $\tau_s \gg \tau_v$ then the calculated formation rates are acceptable.

For the two-photon process, we can estimate the back-stimulation time $\tilde{\tau}_s = \hbar/\tilde{\gamma}_s$ using the expression for γ_s in Eq. (81), but with the effective Rabi frequency $\Omega_{\text{eff}} = \Omega_{\varepsilon v'} \Omega_{v'v} / \Delta$

$$\tilde{\gamma_s} = 2\pi\hbar^2 \Omega_{\text{eff}}^2 = \gamma_s \left(\frac{\Omega_{v'v}}{\Delta}\right)^2 \,. \tag{120}$$

Again, if $\tilde{\tau}_s \gg \tau_v$ then the calculated two-photon formation rates are acceptable.

The back-stimulation time will depend on the particular traits of the system and which PA route is taken to achieve molecule formation. For the processes considered in this work, the issue of back-stimulation is discussed in § 3.1.4 and 5.5.

1.12 Comparison to the Line Shape Expression of Pillet *et al.*

Pillet *et al.* [7] develop a quantum mechanical approach to describe the photoassociation phenomenon in a sample of cold atoms initially at thermal equilibrium. In their work, the rate of formation of diatomic homonuclear molecules is calculated in the weak field regime using a perturbative approach. They also present analytical expressions for the overlap between initial and final molecular wavefunctions and show that these analytical expressions are in agreement with numerical calculations.

The Hamiltonian for a system of N atoms interacting by two-body interactions in the Born-Oppenheimer approximation is given by

$$H_N = \sum_{a=1}^{N} \left(\frac{p_a^2}{2m} + H_a^{el} \right) + \sum_{a,b=1;a>b}^{N} V(R_{ab}); \qquad (121)$$

 $p_a^2/2m$ is the atomic kinetic energy, H_a^{el} is the electronic Hamiltonian and $V(R_{ab})$, with $R_{ab} = |\mathbf{r_a} - \mathbf{r_b}|$, is the interatomic potential energy. The picture is developed further restricted to the model of a given pair of atoms under the dipole approximation. The characteristic features of the photoassociation process are dependent upon the initial continuum state $|\alpha\rangle$ and the excited molecular wavefunction $|n\rangle$, which is essentially determined by the strength and shape of the coupling matrix element function $w_n(\alpha)$ defined by

$$\langle n|W(t)|\alpha\rangle = w_n(\alpha)\cos(\omega_L t - k_L \mathcal{Z}),$$
 (122)

where it is assumed that the laser field is monochromatic (laser frequency ω_L , with wave vector \mathbf{k}_L parallel to the laboratory fixed z-axis) and linearly polarized (unit vector ϵ_L) and $W(t) = -\sum_{a=1,2} (\mathbf{E}(\mathbf{z}, t) \cdot \mathbf{D}_a)$. Note that they have replaced extended the dipole approximation by replacing \mathbf{z} with the barycentric coordinate \mathcal{Z} . Also $w_n(\alpha)$ contains the matrix element of the molecular transition dipole

moment, d:

$$\langle n | \mathbf{d} \cdot \epsilon_{\mathbf{L}} | \alpha \rangle = \sum_{q,q'=0,\pm 1} (\epsilon_L)_{-q} \mathcal{M}_{qq'} \int_0^\infty F_n(R) d_{q'}(R) F_\alpha(R) dR , \qquad (123)$$

where the sum is over the components of the molecular frame; \mathcal{M} is an angular factor and $d_{q'}(R)$ is the matrix element of a component of the molecular dipole moment between the initial and final electronic molecular states, which is proportional to the atomic dipole moment for the $s \to p$ transition, D:

$$d_q = c_q(\Lambda, \Omega; R)D.$$
(124)

For very loosely bound vibrational states $|n\rangle$ considered here, the radial integral is determined by the asymptotic region and the internuclear variation of the electric dipole moment is neglected. The coupling matrix element is then written as

$$w_n(\alpha) = 2\hbar K \mathcal{A}(\Lambda, \Omega, J_n^t, M_n^t, J^t, M^t, \epsilon_{\mathbf{L}}) \mathcal{S}_n(\alpha) , \qquad (125)$$

where $2K = E_0 D/\hbar$ is the atomic Rabi frequency, E_0 is the amplitude of the electromagnetic field, $\mathcal{A}(\Lambda, \Omega, J_n^t, M_n^t, J^t, M^t, \epsilon_{\mathbf{L}})$ is purely angular and contains both the *c* factors of Eq. (124) and the Höln-London factor, and $\mathcal{S}_n(\alpha)$ is the overlap integral between initial and final radial wavefunctions

$$S_n(\alpha) = \int_0^\infty F_n(R) F_\alpha(R) dR \,. \tag{126}$$

This overlap integral is dependent upon the nature of the continuum and bound wavefunctions, $F_n(R)$ and $F_{\alpha}(R)$, where (for J = 0)

$$F_{\alpha}(R) \approx \left(\frac{2\mu}{\pi^2 \hbar E}\right)^{1/4} \sin[k(R - A(k))]$$
 (127)

$$F_n(R) \approx \frac{\sqrt{\pi}}{(aR_0^n)^{1/4}} \operatorname{Airy}\left(\frac{\mathbf{R} - \mathbf{R}_0^n}{\mathbf{a}}\right); \quad \mathbf{a} = \left(\frac{\hbar \mathbf{R}_0^n}{6\mu\Delta_n}\right)^{1/3}.$$
 (128)

The detuning from a particular rovibrational level is Δ_n and in the vicinity of R_0^n , the asymptotic molecular potential may be linearized according to

 $V(R) = -\hbar\Delta_n + \frac{3C_3}{(R_0^n)^4}(R - R_0^n)$, where $R_0^n = \left(\frac{C_3}{\hbar\Delta_n}\right)^{1/3}$. Note that the continuum wavefunction $F_{\alpha}(R)$ is energy normalized. Then the analytical form of the overlap integral is found to be

$$S_{n}(\alpha) = (3E\hbar\Delta_{n})^{-1/4} \sin\left[k(R_{0}^{n} - A(k)) - \frac{(ka)^{3}}{3}\right]$$

$$\approx (3\hbar\omega_{m}\hbar\Delta_{n})^{-1/4} \frac{\sin[k(R_{0}^{n} - A(k))]}{\sqrt{k(R_{0}^{n} - A(k))}}, \qquad (129)$$

with

$$\hbar\omega_m = \frac{\hbar^2}{2\mu (R_0^n - A(k))^2} \,. \tag{130}$$

A perturbative approach is then applied [7] in order to obtain an expression for the photoassociation rate \mathcal{R}_n (of the number of molecules formed in state $|n\rangle$ per unit time divided by the total number of atoms N). Since perturbative regime is assumed, $\mathcal{N}(t)$, the number of molecules formed in state $|n\rangle$, is taken to be small compared to the total number of atoms so that $\mathcal{N}(t) \ll \frac{N(N-1)}{2} \approx \frac{N^2}{2}$. Using the formulation and approximations of Pillet *et al*, the formation rate of molecules in a $J_n = 0$ level (that is for the case when the total angular momentum, excluding spin, for a particular state is zero) is

$$\mathcal{R}_{n}(E_{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{h}{2} \frac{N}{\mathcal{V}} \lambda_{th}^{3} e^{-\beta E_{r}} K^{2} \frac{\sin^{2}[k_{r}(R_{0}^{n} - A(k))]}{\sqrt{3E_{r}\hbar\Delta_{n}}}, \qquad (131)$$

where $\lambda_{th} = h\sqrt{\beta/3\mu}$ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, N is the total number of atoms, \mathcal{V} is the MOT volume, $E_r = \hbar(\omega_n - \omega_L)$ is the resonant energy, and Δ_n is the laser detuning for a particular level.

In order to compare this expression with the rate expression developed in § 1.8, let us write Eq. (131) in similar terms. With $N/\mathcal{V} = n$ (atomic density) and $\lambda_{th} = \left(\frac{2\pi}{3}\right)^{3/2} \frac{1}{Q_T}$, the rate reduces to

$$\mathcal{R}_{n}(E_{r}) = \frac{h}{2} \frac{n}{Q_{T}} e^{-E_{r}/k_{B}T} K^{2} \frac{\sin^{2}[k_{r}(R_{0}^{n} - A(k))]}{\sqrt{3E_{r}\hbar\Delta_{n}}}.$$
(132)

Since the square of the Rabi frequency $K^2 = \frac{1}{4\hbar^2} E_0^2 D^2$ and the laser intensity $I = \varepsilon_0 c E_0^2 / 2 = 8\pi I / c$ in C.G.S. units,

$$K^{2} = \frac{2\pi}{\hbar^{2}} \frac{I}{c} D^{2} \,. \tag{133}$$

The last portion of Eq. (132) is comparable to the dipole matrix elements term $|D_{v'}(\varepsilon)|^2$ in Eq. (101) and can be written as

$$K^2 \frac{\sin^2[k_r(R_0^n - A(k))]}{\sqrt{3E_r \hbar \Delta_n}} \sim \frac{4\pi}{\hbar^2} \frac{I}{c} |\langle v', J' | D(R) | \varepsilon, J \rangle|^2, \qquad (134)$$

where the extra factor of 2 comes from the differing definitions of the Rabi frequency. The Pillet *et al.* rate expression can then be written in terms of the rate expression discussed in § 1.10 as

$$\frac{\mathcal{R}_{v'}}{N} = 8\pi^3 \frac{I}{c} \frac{n}{hQ_T} e^{-\varepsilon/k_B T} |D_{v'}(\varepsilon)|^2, \qquad (135)$$

which is essentially equivalent to the rate expression derived from the rate coefficient of Bohn/Julienne [14]

$$\mathsf{R}_{v'} = 8\pi^3 \frac{I}{c} \frac{n_A n_H}{h Q_T} V e^{-\varepsilon/k_B T} |D_{v'}(\varepsilon)|^2.$$
(136)

Keep in mind that Eq. (135) has been derived for a homonuclear system of atomic density n, whereas Eq. (136) is for a heteronuclear system with atomic densities n_A and n_H , and notice that $n_A n_H V \sim n^2 V = nN$.

1.13 Radiative Cascade

Once an upper vibrational level is populated, it will decay by spontaneous emission into lower levels, ultimately cascading down to v = 0. Due to the selection rule $\Delta J = \pm 1$ for such transitions, this cascade process will result in a distribution of J states in the v = 0 manifold. We obtained these distributions by calculating the one-photon emission branching ratios $r_{v_2J_2}^{v_1J_1}$, between a starting state (v_1, J_1) and an ending state (v_2, J_2) , which we define as

$$r_{v_2 J_2}^{v_1 J_1} \equiv \frac{A_{v_2 J_2}^{v_1 J_1}}{A_{\text{Tot}}^{v_1 J_1}} = A_{v_2 J_2}^{v_1 J_1} \tau_{v_1 J_1} , \qquad (137)$$

where $A_{\text{Tot}}^{vJ} = \sum_{v',J'} A_{v',J'}^{vJ} = 1/\tau_{vJ}$. The cascade from an initial (v_i, J_i) state to a final $(v = 0, J_f)$ state can take several paths, denoted by α , with the probability

$$p_{\alpha}(v=0,J_f) \equiv r_{v_1J_1}^{v_iJ_i} \cdot r_{v_2J_2}^{v_1J_1} \cdots r_{v=0,J_f}^{v_n,J_n} , \qquad (138)$$

where (v_n, J_n) is the state reached just before cascading to the final state $(v = 0, J_f)$, as shown schematically in Figure 13. The final *J*-distribution is obtained by summing over all possible paths starting from the initial state (v_i, J_i) and ending in the final state $(v = 0, J_f)$

$$p(J_f) = \sum_{\alpha} p_{\alpha}(v = 0, J_f)$$
 (139)

We restricted the paths so that no decays take place within the last v = 0manifold. That is, transitions from $(v = 0, J) \rightarrow (v = 0, J - 1) \rightarrow (v = 0, J - 2) \cdots \rightarrow (v = 0, J = 0)$ are neglected as, for the lower rotational levels, these



Fig. 13: Schematic for the cascade process, that is one-photon spontaneous radiative decay from a rovibrational level (v_n, J_n) to $(v_{n-1}, J_{n\pm 1}), (v_{n-2}, J_{n\pm 1\pm 1}), \cdots,$ (v_0, J_{v_n+1}) . For ${}^{1}\Sigma - {}^{1}\Sigma$ transitions, selection rules for the rotational quantum number require that $\Delta J \pm 1$. Selected decay paths are shown as arrows. The arrow labeled $A_{v_1,J_3}^{v_2,J_2}$ represents the A-Einstein coefficient for spontaneous decay from rovibrational level (v = 2, J = 2) to level (v = 1, J = 3), with $\Delta v = -1$ and $\Delta J = +1$. Similarly, the arrow labeled $A_{v_2,J_0}^{v_2,J_0}$ represents the A-Einstein coefficient for spontaneous decay from rovibrational level (v = 2, J = 1) to level (v = 2, J = 0), with $\Delta v = -21$ and $\Delta J = -1$.

transitions are several orders of magnitude slower than those in the vibrational cascade. Finally, clearly, we must have $\sum_{J_f} p(J_f) = 1$.

Potential Energy Curves & Dipole and Transition Moment Functions: Lithium and Sodium Hydride

 $\mathbf{2}$

2.1 Potential Energy Curves

The interaction of ground state alkali-hydrogen pairs of atoms, such as Li or Na(²S) and H(²S), gives rise to two molecular electronic states, $X^{1}\Sigma^{+}$ and $a^{3}\Sigma^{+}$. The singlet state is the ground state in all alkali hydride systems, with a binding energy of 2.52 eV for LiH [32] and 1.92 eV for NaH [33]. Molecular structure calculations of the $a^{3}\Sigma^{+}$ state for LiH [34,35] and NaH [36] predict a small van der Waals attraction, with a well so shallow that it can support only one bound rovibrational level (v = 0, J = 0), although the triplet state has never been observed experimentally. The singlet and triplet potential energy curves for LiH and the singlet curve for NaH are plotted as a function of internuclear separation and are shown in Figure 14. There are four molecular states correlating to the excited state asymptotes, Li (²P) and H(²S), namely $A^{1}\Sigma^{+}$, $B^{1}\Pi$, $b^{3}\Pi$, and $c^{3}\Sigma^{+}$ (the last of which is purely repulsive for both LiH [32] and NaH [33,37]). The three bound curves are shown in Figure 14.

We have used the X¹ Σ^+ state potentials from [34] and [36] for LiH and NaH, respectively. The correct long range form is incorporated in these potentials. The C_6 and C_8 coefficients for each potential curve are taken from Geum *et al.* [36] and are listed in Table 5. We have used $a^3\Sigma^+$ and $b^3\Pi$ state potential energy curves from Gadea and Dickinson [35] for LiH. For the $A^1\Sigma^+$ potential curve of LiH, we have used the curve of [38] (see their Table 1): however, the value of the potential ar $R = 17.5 a_0$ was corrected from its published value of -7.891443_{16} a.u. to -7.891458_{16} a.u. [39]. These data were joined smoothly to the long range form $-C_6/R^6 - C_8/R^8$, with coefficients from [40], listed in Table 5. For the B¹\Pi potential energy curve of LiH, we used the *ab initio* data from Partridge *et al.* [41], again joined smoothly to the correct long range form, with coefficients from [40], also listed in Table 5.

2.2 Dipole & Transition Moment Functions

Dipole and transition moments as a function of the internuclear separation for each electronic state were taken from previously published data. The calculated points were fitted using a cubic spline and joined smoothly to the form



Fig. 14: Potential energy curves plotted as a function of internuclear separation for the ground state (correlating to the $\text{Li}(^2\text{S}) + \text{H}(^2\text{S})$ asymptote) and the first excited state (correlating to the $\text{Li}(^2\text{P}) + \text{H}(^2\text{S})$ asymptote) of LiH. Also shown is $X^1\Sigma^+$ state of NaH.

	$\overline{C_6(a.u.)}$	$C_{8}(a.u.)$
LiH: $X^1\Sigma^+$	66.544	3265.0
$\mathrm{a}^{3}\Sigma^{+}$	66.544	3265.0
$A^{1}\Sigma^{+}$	147.9	20700
$\mathrm{B}^{1}\Pi$	84.327	14794.02
${ m b}^3\Pi$	84.327	14794.02
NaH: $X^1\Sigma^+$	73.83	4059

Table 5: Values for C_6 and C_8 coefficients for the ground and excited electronic states of LiH and the ground singlet state of NaH.

 be^{-cR} at large separations. These fitting parameters, along with the values of separation (R_1 and R_2) at which the curves were fit, for each dipole and transition moment are listed in Table 6. The dipole moment functions for the ground and excited states of LiH and for the singlet ground state of NaH are shown in Figure 15. Note that the dipole moment for the X¹ Σ^+ state of LiH is very large in the molecular binding region (2.35 ea_0 at the equilibrium separation R_e), reflecting the dominant influence of the ion pair state (Li⁺H⁻) in the X state (the same is true for NaH).

The dipole moments $D_X(R)$ for the X¹ Σ^+ state of LiH and NaH were taken from the calculations of Docken and Hinze [42] and from Sachs and Hinze [43], respectively. For the A¹ Σ^+ state, the dipole moment function $D_A(R)$ was taken from the calculations of Partridge *et al.* [41]. For the B¹ Π state, the dipole moment function $D_B(R)$ was taken from the calculations of Partridge *et al.* [41] (neglecting the data at R = 10 a.u. and 11 a.u.).



Fig. 15: Dipole moment functions for the ground and excited states of LiH and the singlet ground state of NaH.



Fig. 16: Dipole transition moment functions for LiH.

The dipole transition moments for LiH: $D_{XA}(R)$ between $X^1\Sigma^+$ and $A^1\Sigma^+$, $D_{XB}(R)$ between $X^1\Sigma^+$ and $B^1\Pi$, $D_{AB}(R)$ between $A^1\Sigma^+$ and $B^1\Pi$, and $D_{ab}(R)$ between $a^3\Sigma^+$ and $b^3\Pi$, were taken from [41]. The constructed curves for the various transition moments are shown in Figure 16.

	b	С	$R_1(a_0)$	$R_2(a_0)$
LiH: D_X	1651.7	0.959	10.0	12.0
D_a	-31.0	0.69	7.5	12.0
D_A	11294.6	0.755	20.0	22.5
D_B	0.49478	0.3133	13.5	15.0
D_{XA}	2.3493	0	R > 20.0	
D_{XB}	2.3335	0	R > 15.0	
D_{AB}	249245.4	1.24272	13.5	15.0
D_{ab}	3.3589	0	R > 12.0	
NaH: D_X	23.426	0.618	15.0	20.0

.

Table 6: The fitting parameters (be^{-cR} at points R_1 and R_2) for the dipole and transition moment functions for the ground and excited states of LiH and the dipole moment function for the singlet ground state of NaH.

3

One-Photon Process for LiH and NaH

We begin examination of the various photoassociation schemes by considering a mixture of two different species of ultracold atoms in a gaseous state. As stated in § 1.8, only heteronuclear mixtures furnish the possibility of forming a molecule via a dipole-allowed one-photon stimulated radiative association process directly from the continuum because of the non-zero dipole moment which varies with internuclear distance. A schematic of this process is shown in Figure 17. In this work we use lithium and sodium hydride [44] as benchmark systems to calculate molecule formation rates by this method.

Needed for the rate calculations are the potential energy curves and dipole moment functions for the ground electronic molecular state. We use accurate data that has been previously published [34,36,41,42]; see Chapter 2. We note that only *s*-waves contribute to the process and hence, only (v, J = 1) ro-vibrational states in the X¹ Σ ⁺ electronic state of LiH and NaH can be populated. We first



Fig. 17: Schematics of one-photon stimulated molecular formation (a) and the dipole moment (b). In (a), we show only the LiH $X^{1}\Sigma^{+}$ state, and in (b), its dipole moment. The $X^{1}\Sigma^{+}$ potential energy curve and dipole moment of NaH are similar and shown in Figures 14 and 15, respectively.

consider the feasibility of forming singlet molecules in this one-photon direct scheme.

3.1 Singlet Dipole Matrix Elements

Colliding atoms in the presence of laser light are radiatively coupled. The strength of the coupling depends directly on the intensity of the laser as well as the molecular dipole moment function, D(R). We write the dipole matrix element squared as $|D_v(\varepsilon)|^2 = |\langle v, J|D(R)|\varepsilon, \ell = 0\rangle|^2$, where $|\varepsilon, \ell = 0\rangle$ represents the wavefunction of the *s*-wave continuum state, and $|v, J\rangle$ represents the wave function of the bound state for a particular vibrational level in the potential curve. These, and all other, wavefunctions were calculated by solving the radial Schrödinger equation of Eq. (23) using the three point Numerov method.For this case, the potential energy curves (see Figure 14) and the molecular dipole moment functions (see Figure 15) described in Chapter 2 were used.

We calculated the integral $\langle v, J | D(R) | \varepsilon, \ell \rangle$ over a range of energies, from $\varepsilon = 10^{-12}$ a.u. to 10^{-1} a.u. The result for each value of energy depends on the overlap of the continuum wavefunction, the bound molecular wavefunction and the molecular dipole moment function. Consider the function D(R) written in a Taylor series expansion: $D(R) = D_0 + R \frac{dD}{dR} + \mathcal{O}(R^2)$. Then, the integral

$$\langle v, J | D(R) | \varepsilon, \ell \rangle = \left\langle v, J \left| D_0 + R \frac{dD}{dR} + \mathcal{O}(R^2) \right| \varepsilon, \ell \right\rangle$$
 (140)

$$= \langle v, J | D_0 | \varepsilon, \ell \rangle + \left\langle v, J \left| R \frac{dD}{dR} \right| \varepsilon, \ell \right\rangle +$$
(141)

+
$$\langle v, J | \mathcal{O}(R^2) | \varepsilon, \ell \rangle$$
.

The first term in Eq. (142) becomes $D_0 \langle v, J | \varepsilon, \ell \rangle = 0$, since D_0 is a constant and $\langle v, J | \varepsilon, \ell \rangle = 0$, since $|v, J \rangle$ and $|\varepsilon, \ell \rangle$ are orthogonal wavefunctions belonging to the same electronic manifold. The next leading term depends on the slope of the dipole moment function dD/dR. We can then conclude that even if a dipole is large, but constant, or varying only slightly, then the dipole matrix element integral would be small. A steep slope of the dipole moment function is necessary in order for there to be a chance of large dipole matrix elements. The results for $|D_v(\varepsilon)|^2$ are similar for both systems and are plotted in Figures 18, 19, 21, 23, 25, and 27 for ⁷LiH and Figures 20, 22, 24, and 26 for ²³NaH.

Notice that for energies lower than $\varepsilon/k_B \sim 10$ mK ($\varepsilon \simeq 1 \times 10^{-7}$ a.u.), the dipole matrix elements do indeed fit the form $|D_v(\varepsilon)|^2 = C_v \sqrt{\varepsilon}$, in accordance with the Wigner threshold law. The C_v coefficients are listed in Tables 7 and 8. At higher energies, the matrix elements take on a more complicated structure mapping out the nodal structure of the wavefunctions. Typically, the matrix elements increase with increasing vibrational level, ranging from values near 10^{-12} a.u. to near 1000 a.u. The matrix elements do not follow this increasing trend strictly though since a particular wavefunction, with its unique nodal structure, may overlap more or less than the next nearest v level with the continuum wavefunction.



Dipole Matrix Elements: LiH Singlet Transitions

Fig. 18: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for $^7\mathrm{LiH}.$


Fig. 19: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ⁷LiH for levels v = 0 - 4, J = 1.



Fig. 20: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ²³NaH for levels v = 0 - 5, J = 1.



Fig. 21: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ⁷LiH for levels v = 5 - 9, J = 1.



Fig. 22: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ²³NaH for levels v = 6 - 11, J = 1.



Fig. 23: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ⁷LiH for levels v = 10 - 14, J = 1.



Fig. 24: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ²³NaH for levels v = 12 - 17, J = 1.



Fig. 25: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ⁷LiH for levels v = 15 - 19, J = 1.



Fig. 26: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ²³NaH for levels v = 18 - 21, J = 1.



Fig. 27: Dipole matrix elements (energy normalized) for singlet one-photon direct transitions for ⁷LiH for levels v = 20 - 23, J = 1.

3.1.1 Singlet Molecule Formation Rates

Under the approximations and assumptions discussed in § 1.8, the maximum rate coefficients are

$$\mathsf{K}_{v}(T,I) = \begin{cases} 9.0 \times 10^{-24} \frac{C_{v}I}{T} \, \mathrm{cm}^{3}/\mathrm{s} & \text{[for } {}^{7}\mathrm{LiH}\text{]} \\ \\ 8.0 \times 10^{-24} \frac{C_{v}I}{T} \, \mathrm{cm}^{3}/\mathrm{s} & \text{[for } {}^{23}\mathrm{NaH}\text{]} \end{cases}$$
(142)

with C_v in a.u., I in W/cm², and T in Kelvin. In Tables 7 and 8 the rate coefficients are listed for the various target levels v assuming conservative experimental conditions (T = 1 mK and I = 1000 W/cm²). Also listed are the corresponding photon wavelengths needed to induce the transitions and the lifetimes for J = 1 of each v level. Notice that for both LiH and NaH, K_v is very small for the deepest levels, but reaches $\sim 10^{-13}$ cm³/s for the upper levels above v = 17 or so.

A rate of molecules formed per second is found from Eq. (117) or (118). The singlet fraction χ_S depends on the hyperfine states (F, m_F) (see § 1.7). If, for example, the low-field seeking atomic hyperfine states $(f_1 = 1, m_1 = -1)$ in ⁷Li and $(f_2 = 1, m_2 = 1)$ in H are populated in a particular experiment, then $\chi_S =$ 1/8. Using this and typical experimental values in Eq. (117) $(n_A = n_H = 10^{12}$ cm⁻³ for the density of each atomic sample and $V = 10^{-6}$ cm³ for the volume illuminated by the laser light), a few tens of thousand singlet molecules per second can be formed in these upper levels. For instance, in LiH, the molecule formation rate for populating v = 19, J = 1 with a laser of wavelength 9.75 μ m, close to the CO₂ laser, is 9.9×10^3 molecules/sec. For NaH, PA into v = 17, J = 1 can

Level	$ au_v$	C_v	K _v	λ
v	(ms)	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(nm)
<u></u>		·····		
0	84491	2.25 [-5]	$2.03 \ [-22]$	520
1	22.14	2.23 [-5]	2.01 [-22]	558
2	11.75	1.40 [-4]	1.26 [-21]	602
3	8.36	4.78 [-5]	4.30 [-22]	651
4	6.72	9.11 [-7]	8.20 [-24]	707
5	5.77	7.48 [-5]	6.73 [-22]	772
6	5.17	1.42 [-3]	1.28 $[-20]$	846
7	4.77	9.61 [-3]	8.65 [-20]	932
8	4.48	1.95 [-2]	1.76 [-19]	1034
9	4.28	2.82 [-2]	2.54 [-19]	1155
10	4.12	4.12 [-2]	3.71 [-19]	1301
11	3.97	1.00 [-1]	9.00 [-19]	1481
12	3.82	3.73 [-1]	3.36 [-18]	1705
13	3.63	1.74 [-1]	1.57 [-18]	1993
14	3.43	4.39[-1]	3.95 [-18]	2372
15	3.21	3.68~[0]	3.31 [-17]	2887
16	3.02	5.41 [+1]	4.87 [-16]	3621
17	2.89	1.56 [+3]	1.40 [-14]	4725
18	2.88	1.36 [+4]	1.22 [-13]	6515
19	3.06	1.77 [+4]	1.59 [-13]	9744
20	3.58	1.40 [+4]	1.26 [-13]	16595
21	4.82	3.13 [+5]	2.82 [-12]	35846
22	8.91	5.19 [+5]	4.67 [-12]	136682
23	130.95	4.93 [+4]	4.44 [-13]	24511907

Table 7: For LiH, rate coefficients K_v , lifetimes τ_v for J = 1, coefficients C_v and wavelengths λ for photoassociation from the continuum (assuming T = 1 mK and $I = 1000 \text{ W/cm}^2$) into vibrational levels v, J = 1. Numbers in bracket indicate powers of ten.

Level	τ_v	C_v	K _v	λ
v	(ms)	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(nm)
0	233700	2.05 [-6]	1.64 [-23]	653
1	28.32	$1.40 \ [-5]$	$1.12 \ [-22]$	705
2	15.02	1.78 [-4]	1.42 [-21]	765
3	10.69	3.77 [-3]	3.02 [-20]	832
4	8.58	2.87 [-2]	2.30 [-19]	909
5	7.33	7.19 [-2]	5.75 [-19]	998
6	6.50	2.46 [-2]	$1.97 \ [-19]$	1103
7	5.93	1.17 [-2]	9.36 [-20]	1226
8	5.49	2.06 [-1]	$1.65 \ [-18]$	1374
9	5.12	6.61 [-1]	5.29 [-18]	1553
10	4.77	9.71 [-1]	7.77 [-18]	1776
11	4.42	$3.21 \ [0]$	2.57 [-17]	2058
12	4.06	3.68 [+1]	2.94 [-16]	2422
13	3.72	9.60 [+1]	7.68 [-16]	2909
14	3.45	1.73 [+2]	1.38 [-15]	3585
15	3.27	2.01 [+3]	$1.61 \ [-14]$	4567
16	3.21	2.02 [+4]	1.62 [-13]	6088
17	3.31	5.79 [+4]	4.63 $[-13]$	8655
18	3.68	2.78 [+3]	2.22 [-14]	13561
19	4.55	3.51 [+5]	2.81 [-12]	24998
20	6.74	1.43 [+6]	1.14 [-11]	63627
21	17.05	1.13 [+6]	9.04 [-12]	418095

Table 8: Same as Table 7 for NaH.

be achieved with a 8.66 μ m laser at a rate of 2.9×10^4 molecules/sec. Much larger rates are attainable with less conservative experimental parameters. It is important to note that taking into account the issue of back-stimulation, which has been presented in § 1.11, can greatly effect the values of R_v given here. The details of the effect of back-stimulation on the rates for this particular process are discussed in § 3.1.4.

3.1.2 Lifetimes of $X^1\Sigma^+$ Rotation-Vibration Levels

The lifetime τ_v of each rovibrational level is given by the inverse of its linewidth ($\tau_v = \frac{1}{\gamma_v}$). The width γ_v is obtained by including all possible decay paths from a given *v*-level, taking into account the specific Hönl-London factors for each decay branch. Since the selection rule for ${}^{1}\Sigma - {}^{1}\Sigma$ transitions requires that $\Delta J = \pm 1$, the width for J = 1 can be written as

$$\gamma_{v,J=1} = W_J^R \sum_{v_f=0}^{v} A_{v,J=1}^{v_f,J_f=0} + W_J^P \sum_{v_f=0}^{v-1} A_{v,J=1}^{v_f,J_f=2}, \qquad (143)$$

where

$$W_J^R = \left(\frac{J_f}{2J_f + 1}\right), \quad W_J^P = \left(\frac{J_f + 1}{2J_f + 1}\right).$$
 (144)

We have computed τ_v of the (v, J = 1) rovibrational states for LiH and NaH and the results are given in Tables 7 and 8, respectively. The lifetime depends on J as well as on v, but to a lesser extent. We show the lifetimes for the vibrational levels of ⁷LiH for J = 0, 1, and 2 in Table 9. Our computed values of τ_v are in good agreement with previously published data. [58] For most rovibrational states, the lifetime is of the order of a few milliseconds. Compared to other mixed alkali dimers, for example KRb, for which $\tau_v \sim 10^3$ sec. [45], this lifetime is relatively short and can be attributed mainly to the proportionality of the Einstein A coefficient to ω^3 and secondly to the large and varying dipole moment in the ground state. A small reduced mass leads to large spacings between the energy levels, so that, since $\tau \propto 1/\omega^3 |D|^2$, the factor of ω^3 contributes significantly.

3.1.3 Radiative Cascade Results: Rotational Distribution for Population in Initial State ($v_{\text{start}}, J = 1$)

Once an upper vibrational level of the $X^1\Sigma^+$ state is populated, it will decay by spontaneous emission into lower levels of $X^1\Sigma^+$, ultimately cascading down to v = 0. Due to the selection rule $\Delta J = \pm 1$ for such transitions, this cascade process will result in a distribution of J states in the v = 0 manifold. The details of the process of this calculation are shown in § 1.13.

In order to explore the distribution of population among the rotational levels associated with v = 0, we have restricted the paths so that no decays take place within the last v = 0 manifold. That is, transitions from $(v = 0, J) \rightarrow (v =$ $0, J - 1) \rightarrow (v = 0, J - 2) \cdots \rightarrow (v = 0, J = 0)$ are omitted as these transitions are several orders of magnitude slower than the vibrational cascade for the lowest rotational levels in the v = 0 manifold. For the higher rotational levels within the v = 0 manifold, the lifetimes are only longer than those of the uppermost vibrational levels by a factor of three or so.

Level	$\tau_v \text{ (msec.)}$		
v	J = 0	J = 1	J=2
0	∞	84.49[+3]	8.816[+3]
1	22.10	22.14	22.22
2	11.73	11.75	11.80
3	8.345	8.361	8.392
4	6.708	6.721	6.747
5	5.762	5.773	5.795
6	5.159	5.169	5.189
. 7	4.756	4.765	4.784
8	4.474	4.483	4.500
9	4.269	4.277	4.293
10	4.108	4.115	4.129
11	3.963	3.969	3.982
12	3.810	3.815	3.825
13	3.631	3.635	3.641
14	3.426	3.429	3.432
15	3.211	3.213	3.213
16	3.018	3.020	3.017
17	2.889	2.891	2.886
18	2.876	2.878	2.873
19	3.056	3.060	3.055
20	3.568	3.576	3.574
21	4.797	4.818	4.831
22	8.811	8.913	9.063
23	98.75	130.9	

Table 9: Lifetimes for the vibrational levels in the $X^{1}\Sigma^{+}$ state of ⁷LiH for J = 0, 1, and 2. The numbers in brackets indicate powers of ten.

We have computed this J-distribution, $p(J_f)$, for a range of initial levels v, and found that the distribution peaks near the low J-values (see Figure 28). For the lower vibrational levels the cascade is dominated by $\Delta v = 1$ transitions, but for the vibrational levels near the top of the potential well, transitions with $\Delta v = 4$, 3 or 2 contribute more. We also examined the most probable paths to reach v = 0. For LiH, we found that although J = 15 is the state reached by the most probable path (in roughly 40 μ sec), several hundreds of paths slightly less probable reach $J \sim 5$ (in roughly 4 msec), hence the large population is centered around $J \sim 5$ (the same is true for NaH). Thus, it takes roughly 4 - 5 msec to reach the $J \sim 5$ level from the starting v = 19, J = 1 level of LiH. Note that for high v_{start} , these distributions are very similar to the expected binomial distributions of a random walk, except for the "reflection" near J = 0 (since J < 0 is not possible).

Because the momentum direction of the emitted photon is random for each step of the decay process, the kinetic energy of the molecule is increased at most by the single largest such momentum kick. If one estimates the momentum kick imparted to the molecule by the emission of a photon, the largest energy $\Delta v = 1$ kick is between v = 1 and 0, which corresponds to a kinetic energy of about 20 nK for the molecule. So, at worst, a $\Delta v = 4$ transition would heat up the sample by less than 80 nK.

The cascade process allows for the production of large quantities of v = 0LiH and NaH singlet molecules starting with photoassociation to a high-lying



Fig. 28: Distribution into the J states of the v = 0 manifold starting from each of the initial vibrational levels (v = 0 - 23) for LiH. The initial J value is 1 in each case. Notice that the vertical scale is larger for v = 7 - 11 and larger still for v = 1 - 6. Also, the distributions for v = 12 - 23 are quite similar. For starting level v = 12, the maximum population is in J = 4 with 0.15%, whereas for starting level v = 23, the maximum population is in J = 5 with 0.12%. Since we are neglecting decay within the v = 0 manifold in this calculation, there is no distribution for populations starting in the v = 0 level.



Fig. 29: Distribution into the J states of the v = 0 manifold starting from (a) v = 17 and 23, J = 1 for LiH and (b) v = 15 and 21, J = 1 for NaH. In both cases, we observe that the maximum population is achieved around $J \sim 5$.

vibrational level. In addition, because this decay process removes molecules from the initial v level selected by the laser, one can use CW lasers and neglect the stimulation back from v to the continuum. However, it is imperative to carefully consider the timescales for molecule formation compared to spontaneous decay in order to realize the conditions for which it is possible to overcome backstimulation into the continuum. The comparison of these time scales is discussed in § 3.1.4. This irreversible process insures the robust production of large quantities of ground state molecules. Note that if the molecule density becomes large enough, one would be limited by vibrational quenching due to atom-molecule or molecule-molecule collisions, in which the atom/molecule system could gain considerable kinetic energy, normally larger than the trap depth.

In Figure 30, we show the decay time to cascade from a given J state into the allowed J - 1 state starting from the $v = 0, J_f$ manifold populated in the vibrational cascade depicted in Figure 29. We find that the time it takes to reach the ground state v = 0, J = 0 is basically governed by the last few steps which are on the order of one hundred seconds. Therefore, it might require a few minutes to cascade down to the absolute ground state.

In the v = 0 manifold, because the energy difference between $v = 0, J \neq 0$ and v = 0, J = 0 is large (due to the small mass of hydrides; e.g. $E/k_B =$ 21.64K, 323.5 K, and 2525.2 K for J = 1, 5, and 15 respectively), any direct quenching from collision with surrounding atoms/molecules would result in trap loss of the molecule. Assuming a vibrational quenching rate due to collisions



Fig. 30: Decay time from $J \to J - 1$ in the v = 0 manifold for both LiH and NaH.

with atoms/molecules of the order 10^{-11} cm³/s [46], molecules could radiatively cascade down to v = 0 (many *J* levels) in less than 0.01 seconds and build up a large population as long as their density is smaller than about 10^8 cm⁻³, corresponding to a collisional lifetime of about 0.1 seconds).

3.1.4 Back-stimulation

As discussed in § 1.11, back-stimulation from a target level (v, J = 1) into the continuum needs to be considered along with the rate of molecules formed per second. The time scale given in Eq. (119) must be smaller than the width of the target level in order not to loose the majority of molecules to dissociation. The back-stimulation time is $\tau_s = \hbar/\gamma_s$, where $\gamma_s = 4\pi^2 I/c |D_v(\varepsilon)|^2$. The worst case; level (v = 22, J = 1), with I = 1000 W/cm² and T = 100 μ K, $\gamma_s = 1.28 \times 10^{-30}$ J corresponds to a stimulated lifetime of $\tau_s = 82 \ \mu s$. Since the lifetime of this level is 8.9 ms, it does not hold that $\tau_s \gg \tau_v$. We need then to increase τ_s by at least three orders of magnitude, which can be achieved by reducing the laser intensity to $I = 1 \text{ W/cm}^2$. If so, we obtain a stimulated lifetime of 82 ms and then τ_s is large enough compared to τ_v to argue that back-stimulation should not be a major problem. The other levels have even larger values for τ_{s} , so the conditions that avoid the back-stimulation issue for v = 22 readily avoid it for the rest of the levels. It is important to note though that reducing the laser intensity likewise reduces the values of K_v in Tables 7 and 8 by a factor of 10^3 ; however lowering the temperature from T = 1 mK to 100 μ K increases K_v by a factor of 10. Ultimately, with the consideration of back-stimulation into the continuum, the rate coefficients for the one-photon direct stimulation process are then reduced by a factor of 100.

3.2 Triplet Molecule Formation

The triplet ground electronic state of LiH and NaH are of particular interest for experimental efforts since it supports only one bound vibrational level, as discussed in § 2.1. Any molecule formed in the lowest triplet state would then be immediately in the lowest and most stable level of that state. If the photoassociation rate is favorable then the molecules formed would be quite long-lived, unlike molecules in high vibrational levels which have significantly shorter lifetimes.

Because we are considering molecule formation at temperatures for which only s-wave scattering is relevant, one-photon formation of the triplet state is not possible ($\ell = 0 \rightarrow J = 0$). Formation rates of triplet molecules can be calculated by considering $\ell = 1 \rightarrow J = 0$ or $\ell = 0 \rightarrow J = 1$ (for deuterides) one-photon transitions or, as discussed later in Chapter 6, by considering a twophoton process.

The dipole matrix element that represents the coupling between the atomic and molecular states in the presence of a light field is relatively small for the case of one-photon direct stimulation from the continuum to the one bound rovibrational level in the lowest triplet potential. The matrix element $|D(\varepsilon)|^2 = |\langle v =$ $0, J = 0|D(R)|\varepsilon, \ell = 1\rangle|^2$ is plotted as a function of energy in Figure 31. The Wigner threshold law, in general for any initial scattering state $|\varepsilon, \ell\rangle$, is given by $|D_v|^2 = C_v \varepsilon^{(2\ell+1)/2}$. For this case it holds that $|D(\varepsilon)|^2 = C_{v=0} \varepsilon^{3/2}$ for energies below $\varepsilon/k_B \sim 10$ mK ($\varepsilon \simeq 1 \times 10^{-7}$ a.u.), where $C_{v=0} = 7.2 \times 10^7$ a.u.

The only bound level of the $a^{3}\Sigma^{+}$ state is relatively loosely bound, therefore the radiation wavelength that drives transitions from the ultracold continuum to this level is large ($\lambda \sim 5$ cm) compared to transitions within the singlet state. The molecular production rate is directly proportional to the square of the dipole matrix element and, for the case of *p*-wave scattering, the rate does not depend on



Fig. 31: Dipole matrix elements for $|\varepsilon, \ell = 1\rangle$, $|v = 0, J = 0\rangle$ transitions within the triplet manifold.

the temperature of the ultracold atomic gases. Without the possibility of applying the PA process to atomic systems with lower temperatures, the small value for the dipole matrix element leads to small molecule accumulation. Since there is only one bound level in the triplet state, back stimulation into the continuum becomes a serious issue, (see § 1.11). However, this being the lowest level implies there would be no spontaneous decay and hence no resulting cascade process would take place (except for deuterides where $v = 0, J = 1 \longrightarrow v = 0, J = 0$ decay can occur).

4

Formation of LiH in the $X^1\Sigma^+$ state via the $A^1\Sigma^+$ State

In the previous chapter, we explored the formation of ultracold LiH and NaH by one-photon stimulated radiative association, involving transitions directly from the continuum to specific rovibrational levels in the ground electronic state. [44] We turn our attention now to the formation of lithium hydride molecules in the electronic ground state $X^1\Sigma^+$ via an excited electronic state, namely $A^1\Sigma^+$. [47] We start with mixtures of the ultracold gases, Li and H, at temperatures of 1 mK or below. Because of the large dipole transition moments, LiH can serve as a favorable benchmark system with which to explore the feasibility of forming ultracold polar molecules using an excited electronic state. The focus in this chapter will be on formation of singlet ground state LiH molecules



Fig. 32: Schematic of two-photon stimulated Raman molecule formation. The relevant transitions between the two electronic states of LiH are indicated by double arrows, and the laser frequencies and intensities for the two photons are shown as ν_1 , ν_2 , and I_1 and I_2 respectively.

only. Such molecules might be produced in a magneto-optical trap (MOT) or in an all-optical trap.

We will explore molecule formation rates for two different schemes: firstly, by two-photon stimulated radiative association – Raman excitation (this process is illustrated schematically in Figure 32) and secondly, through excitation to bound levels of the $A^1\Sigma^+$ state, followed by spontaneous emission to the $X^1\Sigma^+$ state.

4.1 Dipole Matrix Elements: $A^{1}\Sigma^{+} - X^{1}\Sigma^{+}$ Transitions

We consider ultracold temperatures, so that only s-wave scattering occurs. Thus, only (v', J' = 1) rovibrational levels of the intermediate state $A^1\Sigma^+$ are relevant, and final (v, J = 0) or (v, J = 2) rovibrational states of the $X^1\Sigma^+$ state can be populated according to selection rules for ${}^1\Sigma - {}^1\Sigma$ transitions. The results for the continuum to bound transitions are presented in § 4.1.1 and the bound to bound transitions are presented in § 4.1.2. We focus our discussion on the $(v', J' = 1 \longrightarrow v, J = 0)$ branch, noting that the results for the $(v', J' = 1 \longrightarrow v, J = 2)$ branch are of comparable magnitude.

4.1.1 $X^{1}\Sigma^{+}$ Continuum to $A^{1}\Sigma^{+}$ Bound Levels

The dipole matrix elements $|D_{v'}(\varepsilon)|^2 = |\langle v', J' = 1|D_{XA}(R)|\varepsilon, \ell = 0\rangle|^2$ associated with the continuum-ground to bound-excited transitions are shown in Figures 33, 34, 35, and 36, where $|v', J' = 1\rangle$ is the bound state wavefunction for a particular vibrational level in the $A^1\Sigma^+$ state and $|\varepsilon, \ell = 0\rangle$ is the continuum wavefunction in the $X^1\Sigma^+$ state. Since $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ describes the curves well for $\varepsilon/k_B \sim 10$ mK, the values of $C_{v'}$ were determined by a fit and are listed in Table 10. C_v depends on the continuum-bound dipole transition matrix element which generally, although not strictly, grows from small values at low v' (where the ground state continuum and excited bound state wavefunctions overlap poorly) to larger values as the overlap becomes better. Overall, the continuum-bound



Fig. 33: Continuum-bound dipole transition matrix elements for $A^1\Sigma^+$ to $X^1\Sigma^+$ transitions for ⁷LiH for levels v' = 0 - 6, J' = 1.

matrix elements $|D_{v'}(\varepsilon)|^2$ are similar to the matrix elements for the one-photon continuum-bound transitions in Chapter 3.

4.1.2 A¹ Σ^+ Bound Levels to X¹ Σ^+ Bound Levels

We also computed all dipole transition matrix elements for the boundbound transitions $|D_{v'v}|^2$ for all combinations of intermediate and target vibrational levels (v', J' = 1 and v, J = 0). The results are similar for J = 0 and 2 since the ground state wavefunctions differ only slightly for each case. For each target level v (from 0 to 23), $|D_{v'v}|^2$ is plotted as a function of the intermediate level v' (from 0 to 26) in Figure 37.



Fig. 34: Continuum-bound dipole transition matrix elements for $A^1\Sigma^+$ to $X^1\Sigma^+$ transitions for ⁷LiH for levels v' = 7 - 13, J' = 1.



Fig. 35: Continuum-bound dipole transition matrix elements for $A^1\Sigma^+$ to $X^1\Sigma^+$ transitions for ⁷LiH for levels v' = 14 - 20, J' = 1.



Fig. 36: Continuum-bound dipole transition matrix elements for $A^1\Sigma^+$ to $X^1\Sigma^+$ transitions for ⁷LiH for levels v' = 21 - 26, J' = 1.

$\overline{v'}$	C'_v (a.u.)	τ'_v (nsec)	τ'_v (nsec) [41]	τ'_v (nsec) [40]
0	1.853[-3]	28.78	27.4	28.9
1	3.70[-1]	29.95	28.4	29.5
2	6.42[0]	30.78	29.2	30.2
3	1.87[1]	31.57	29.8	30.8
4	4.45[1]	32.17	30.4	31.5
5	3.17[3]	32.84	31.0	32.0
6	1.81[4]	33.48	31.6	32.6
7	8.64[3]	34.05	32.1	33.1
8	8.05[4]	34.57	32.6	33.6
9	6.62[5]	35.05	33.0	34.2
10	4.98[5]	35.55	33.3	34.6
11	1.37[5]	36.03	33.7	35.5
12	1.49[6]	36.32	34.0	35.7
13	7.68[5]	36.68	33.8	35.8
14	2.81[5]	37.00	33.6	35.6
15	7.29[5]	37.21	32.9	35.4
16	2.267[5]	37.36	32.3	34.9
17	5.121[4]	37.35	32.1	34.5
18	3.34[4]	37.25	31.3	33.7
19	4.58[5]	37.04	29.9	32.6
20	1.67[6]	36.59	28.7	31.5
21	1.89[6]	35.97	27.1	30.4
22	4.62[6]	35.03	26.2	29.3
23	6.73[6]	33.76	25.6	28.3
24	1.09[7]	32.07	24.7	27.5
25	1.93[7]	29.91	24.0	27.1
26	8.93[6]	28.10	23.5	27.1

Table 10: Coefficient $C_{v'}$ of the dipole matrix element $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ for transitions from the continuum of $X^1\Sigma^+$ ($\ell = 0$) to bound levels of $A^1\Sigma^+$ (J' = 1) of ⁷LiH, and lifetimes of the intermediate levels v'. Powers of ten are given in square brackets.



Dipole Matrix Elements: A-X Bound-Bound Transitions

Fig. 37: Dipole matrix elements $|D_{v'v}|^2$ for ⁷LiH X¹ Σ^+ – A¹ Σ^+ transitions.

As v increases from 0 to 4, $|D_{v'v}|^2$ roughly mirrors the nodal structure of the associated wavefunctions; only one maximum for v = 0 located at v' = 7(where the Franck-Condon factor is maximal), then two peaks for v = 1 with the largest value at v' = 4, then three peaks for v = 2 with the largest value at v' = 2, and so on. This structure is more clearly visible in Figures 38, 39, 40, and 41. The value of the largest peak increases slowly from 0.12 a.u. for v = 0 to 0.25 a.u. for v = 4. For larger v's, the nodal structure is still apparent in $|D_{v'v}|^2$, although the more rapidly oscillatory nature of the wavefunction prevents the previous simple mapping; the number of oscillations in $|D_{v'v}|^2$ saturates roughly between 5 and 8. Our results match reasonably well with previously published data. [49]

In order to find the largest two-photon rate, we need to identify the most favorable combination of X-A free-bound and A-X bound-bound transitions.

4.2 $A^{1}\Sigma^{+} - X^{1}\Sigma^{+}$: Raman Excitation

By taking the results for the free-bound and the bound-bound dipole transition matrix elements, we can select the best combinations of states to achieve a particular target level v in the X¹ Σ^+ ground state. From Eq. (106), the largest two-photon rate-coefficient K⁽²⁾, for given experimental parameters (I_1, I_2, T, Δ) , is obtained when $C_{v'}|D_{v'v}|^2$ is maximal. In Figures 38, 39, 40, and 41, we plot this product as a function of the intermediate level v' for a given target state v: the level v' for which the maximal value occurs is also listed in Table 11. For each target level v, there are often several intermediate levels v' that give a large product $C_{v'}|D_{v'v}|^2$, and those levels could be used, although with less efficiency. For example, for v = 0, the largest product arises from v' = 9, but v' = 12 is just slightly smaller. For v = 1, v' = 12 clearly gives the largest value, followed by v' = 15, and then v' = 10, 20 - 25: these last levels have similar values (roughly 20% of v' = 12). Although in Table 11 we give the numbers for v' with the largest value, other intermediate levels might be more advantageous for certain experimental setups (e.g., laser frequencies available in a given experiment). As seen from Table 11, the maximum value of $C_{v'}|Dv'v|^2$ varies roughly between 10^5 a.u. and 10^7 a.u.

If we express the photoassociation rates $\mathsf{K}^{(1)}$ and $\mathsf{K}^{(2)}$ in terms of the same experimental parameters as in § 3.1.1, with T in Kelvin, I_1 and I_2 in W/cm², $C_{v'}$ and $|D_{v'v}|^2$ in atomic units, and Δ in MHz, we find the molecule formation rates. For the maximum values of $C_{v'}|D_{v'v}|^2$ in Table 11, we give the rates for typical conservative experimental parameters; we assume $I_1 = I_2 = 1000 \text{ W/cm}^2$, T = 1 mK, and $\Delta = 500 \text{ MHz}$ (so that $\Delta \gg \gamma_{v'}$ for all v'). The rate coefficient $\mathsf{K}^{(1)}$ for the best intermediate level combinations range from 4.7×10^{-12} to $1.7 \times 10^{-10} \text{ cm}^3/\text{s}$, while $\mathsf{K}^{(2)}$ varies between 2.8×10^{-11} and $8.4 \times 10^{-10} \text{ cm}^3/\text{s}$, except for the last level, v = 23, for which $\mathsf{K}^{(2)} = 1.0 \times 10^{-8} \text{ cm}^3/\text{s}$.

As discussed in § 1.8, in order for Eq. (86) to be valid, it is necessary that $\gamma_s/\gamma_{v'} \ll 1$. Using lifetimes of the $A^1\Sigma^+$ state as listed in Table 10, we have verified that for the largest $C_{v'}$ (10⁷) and $T \sim 1$ mK, this relationship is satisfied



Fig. 38: Squares of the bound-bound dipole transition matrix elements, $|D_{v'v}|^2$, are plotted with open circles following the left-hand side vertical scale, for values of the final X-state v = 0 to 5, as a function of the intermediate A state vibrational level v'. The quantities $C_{v'}|D_{v'v}|^2$ are plotted similarly using filled circles on the right-hand side vertical scale.



Fig. 39: Same as Figure 38 for v = 6 to 11 of the X state.



Fig. 40: Same as Figure 38 for v = 12 to 17 of the X state.



Fig. 41: Same as Figure 38 for v = 18 to 23 of the X state.

v	v'	$C_{v'} D_{v'v} ^2$	$K_{v'}^{(1)}$	$K^{(2)}_{vv'}$	R_v
		(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec.)
0	9	6.4 [4]	6.0 [-12]	2.8 [-11]	3.5[6]
1	12	9.1 [4]	1.3 [-11]	4.0 [-11]	5.0[6]
2	24	9.2[4]	1.0 [-10]	4.0 [-11]	5.0[6]
3	25	2.1 [5]	1.7 [-10]	9.0 [-11]	1.1 [7]
4	25	1.2 [5]	1.7 [-10]	5.5 [-11]	6.8[6]
5	12	9.2[4]	1.3 [-11]	4.1 [-11]	5.1[6]
6	24	1.7[5]	1.0 [-10]	7.7 [-11]	9.6[6]
7	12	9.1 [4]	1.3[-11]	4.0 [-11]	5.0[6]
8	22	1.2[5]	4.3 [-11]	5.4 [-11]	6.7[6]
9	25	2.1[5]	1.7 [-10]	9.1 [-11]	1.1 [7]
10	12	8.9[4]	1.3 [-11]	3.9 [-11]	4.9[6]
11	24	2.3 [5]	1.0 [-10]	1.0 [-10]	1.2 [7]
12	12	1.5 [5]	1.3 [-11]	6.5 [-11]	$8.1 \ [6]$
13	22	1.8[5]	4.3 [-11]	8.0 [-11]	1.0[7]
14	25	2.9[5]	1.7 [-10]	1.2 [-10]	1.5[7]
15	22	1.2[5]	4.3 [-11]	5.2 [-11]	6.5[6]
16	24	2.5 [5]	1.0 [-10]	1.1 [-10]	1.4[7]
17	25	2.9[5]	1.7 [-10]	1.2 [-10]	1.5[7]
18	9	2.1 [5]	6.0 [-12]	9.0 [-11]	$1.1 \ [7]$
19	12	3.0[5]	1.3 [-11]	1.3 [-10]	1.6[7]
20	9	1.9[6]	6.0 [-12]	8.4 [-10]	1.1 [8]
21	10	1.0[6]	4.7 [-12]	4.7 [-10]	5.9[7]
22	12	7.8[5]	1.3 [-11]	3.4 [-10]	4.25 [7]
_23	25	2.4 [7]	1.7 [-10]	1.0 [-8]	1.25 [9]

Table 11: One-photon $\mathsf{K}^{(1)}$ and two-photon $\mathsf{K}^{(2)}$ rate coefficients (assuming $I_1 = I_2 = 1000 \text{ W/cm}^2$, T = 1 mK and $\Delta = 500 \text{ MHz}$), and the total formation rate R_v (assuming $\chi_S = 1/8$, $n_{\mathrm{Li}} = n_{\mathrm{H}} = 10^{12} \text{ cm}^{-3}$ and $V = 10^{-6} \text{ cm}^3$) for a given target state v of the $X^1\Sigma^+$ state of ⁷LiH via the intermediate v' level of $A^1\Sigma^+$ with the largest value for $C_{v'}|D_{v'v}|^2$. Powers of ten are given in square brackets.
for $I \sim 1 \text{kW/cm}^2$. Furthermore, to approximate S by a delta function, it is necessary that $\varepsilon/\gamma_{v'} \gg 1$, again satisfied for $T \sim 1$ mK or more.

4.3 Spontaneous Emission Rates from $A^1\Sigma^+$ to Bound Levels of the $X^1\Sigma^+$ state and Lifetimes of $A^1\Sigma^+$ Rovibrational Levels

Once the $A^1\Sigma^+$ state is populated, the rovibrational levels can decay by spontaneous emission into lower levels in the same electronic state and to continuum or discrete levels in the $X^1\Sigma^+$ state. We have computed lifetimes $\tau_{v'}$ of the vibrational levels of $A^1\Sigma^+$ for J'=1, which are listed in Table 10. Note that in the lifetime calculation, we do not take into account quenching to lower levels due to collisions. We calculated lifetimes of the order of tens of nanoseconds, ranging from 28.10 ns to 37.36 ns. This former value is very close to the Li(2p)atomic lifetime of 27.102 ns, [50] as expected because the $A^{1}\Sigma^{+}$ state correlates asymptotically to H(1s) + Li(2p). The widths $\gamma_{v'}$ behave as the reciprocal of $\tau_{v'}$. In Table 10 we also list the lifetimes of Partridge and Langhoff (1981) [41] and Zemke, Crooks and Stwalley (1978) [51] and notice that the three sets of values are comparable for v' = 0 - 9. Differences arise as v' increases, because of the increasing importance of the continuum levels of the X state in the decay of the higher v' states. We calculated this contribution explicitly, integrating over the full range of continuum energies, whereas both of the other references used an approximate treatment involving a sum over the discrete levels to estimate the decay into the continuum.

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Branching ratios $r_{vJ}^{v'J'}$ for decay from the A state levels (v', J' = 1) to lower levels (v, J) of the X state were computed and are shown in Figures 42, 43, and 44 for the R-branch $(v', J' = 1 \longrightarrow v, J = 0)$, as well as listed in Table 12. The nodal structure of the wavefunctions is quite clear for the lower intermediate levels (v' = 0 - 9) in Figure 42. Then, for higher v' levels, the nodal structure washes out. For the uppermost v' levels, the population predominantly decays to the uppermost v level in the X state, with $\sim 24\%$ of the population going to v = 23 from v' = 25 and $\sim 38\%$ going to v = 23 from v' = 26. This is due essentially to the fact that the uppermost vibrational wavefunctions have large lobes at relatively large internuclear separation that hardly overlap at all with the most deeply bound levels. Our results (see Figure 44) confirm the results of Zemke and Stwalley [49] which showed very selective, directed emission from v' = 26 to v = 23.

4.4 Radiative Cascade

Each target level v in the ground state, except for v = 0, will radiatively cascade to lower lying vibrational levels of the $X^1\Sigma^+$ state within τ_v , as given in Table 9. Because of the large dipole moment in the X state, the lifetimes are relatively short (~4 ms), and therefore (at low density) most molecules will radiatively decay to v = 0, even though higher levels may originally be populated in this process. The molecules populate vibrational levels of $X^1\Sigma^+$ with J = 0or 2. Because of the $\Delta J = \pm 1$ selection rule, a distribution of rotational levels,



Fig. 42: Branching ratios $r_{vJ}^{v'J'}(R)$ for decay from an initial (v', J' = 1) level of the $A^1\Sigma^+$ state to a lower (v, J = 0) level of the $X^1\Sigma^+$ state for the R branch.



Fig. 43: Branching ratios $r_{vJ}^{v'J'}(R)$ to decay from an initial (v', J' = 1) level of the $A^1\Sigma^+$ state to a lower (v, J = 0) level of the $X^1\Sigma^+$ state for the R branch.



Fig. 44: Branching ratios $r_{vJ}^{v'J'}(R)$ to decay from an initial (v', J' = 1) level of the $A^1\Sigma^+$ state to a lower (v, J = 0) level of the $X^1\Sigma^+$ state for the R branch. Notice that the scale of the uppermost v' = 25, 26 levels is different from the rest. The percentage of decay from v' = 25 in the A-state to v = 23 in the X-state is 24.0% and from v' = 26 in the A-state to v = 23 in the X-state is 37.8%.

${v}$	$r_{vJ}^{v'J'}$	R_v
	(%)	(mol./sec.)
0	5.37 [-3]	1.14 [3]
1	1.34 [-1]	2.85[4]
2	8.41 [-1]	1.79[5]
3	1.77[0]	3.75 [5]
4	9.45 [-1]	2.00[5]
5	2.39[-2]	5.00[3]
6	1.03 [0]	2.17 [5]
7	3.93[-1]	8.34 [4]
8	2.65 [-1]	5.62 [4]
9	8.41 [-1]	1.78[5]
10	6.61 [-3]	1.40 [3]
11	6.56 [-1]	1.39[5]
12	3.24 [-1]	6.89[4]
13	1.58 [-1]	$3.34 \ [4]$
14	6.28 [-1]	1.33~[5]
15	4.08 [-2]	8.67[3]
16	3.13 [-1]	6.64 [4]
17	4.39[-1]	9.32[4]
18	2.55 [-2]	5.42[3]
19	1.33 [-1]	2.82 [4]
20	2.95 [-1]	6.26 [4]
21	1.88 [-1]	3.98 [4]
22	2.44 [-4]	5.10 [1]
	2.40 [+1]	5.10 [6]

Table 12: Branching ratios $r_{vJ}^{v'J'}$ for the R-branch and total formation rates R_v for the target states v, J = 0 of $X^1\Sigma^+$ state of ⁷LiH via the intermediate level v' = 25, J' = 1 of $A^1\Sigma^+$ (assuming $I_1 = 1000 \text{ W/cm}^2$, T = 1 mK, $n_{Li} = n_H = 10^{12} \text{ cm}^{-3}$, $V = 10^{-6} \text{ cm}^3$ and $\chi_S = 1/8$). Powers of ten are given in square brackets.

for v = 0, will result from the radiative cascade. The rotational distributions for populations of molecules starting in J = 0 or 2 is discussed fully in § 5.4.

4.5 Back-Stimulation

Since the lifetime of excited rovibrational levels of the $A^1\Sigma^+$ state and the $B^1\Pi$ state are about the same (see § 5.3), the analysis of the issue of backstimulation presented in § 1.11 from a target level, (v', J' = 1) for the one-photon process and (v, J = 0 or 2) for the two-photon process is equivalent. The details of this discussion are given in § 5.5.

 $\mathbf{5}$

Formation of LiH in the $X^1\Sigma^+$ State via the $B^1\Pi$ State

In the previous chapter, we explored the possibility of producing polar molecules in the electronic ground state via a two-photon Raman transition scheme, as well as a one-photon stimulated absorption followed by spontaneous emission scheme . We concentrated our efforts on the singlet transition through the intermediate excited electronic state $A^{1}\Sigma^{+}$, and found that sizable steady rates can be achieved for almost all target (v, J = 0) levels of the $X^{1}\Sigma^{+}$ state, using standard experimental parameters and choosing the appropriate intermediate level v'. As we will show in this chapter, it turns out that the B¹ Π excited electronic state of LiH as an intermediate step in this process produces even larger rates, as some of its bound vibrational levels overlap more favorably with continuum levels of the X state. [52] In order to compute the molecule formation rates using the expressions for the one- and two-photon rate coefficients, it was necessary to obtain rovibrational wavefunctions for the bound levels of the B¹II state and the bound and continuum levels of the X¹ Σ^+ state. Again, we solved the radial Schrödinger equation using the molecular potentials for the X and B states described in Chapter 2. The wavefunctions were used together with the X-B transition moment to obtain the matrix elements $D_{v'}(\varepsilon)$ and $D_{v'v}$. For comparison purposes, we used the same parameters as in Chapters 3 and 4, notably laser intensities of 1000 W/cm², detuning $\Delta = 500$ MHz (so that $\Delta \gg \gamma_{v'}$ for all v') and a temperature of 1 mK. We note that larger rate coefficients can be obtained by lowering the temperature, since K⁽¹⁾, and thus K⁽²⁾, are inversely proportional to T (see Eqs.(100) and (105)).

As mentioned before, only s-wave $(\ell = 0)$ scattering contributes. As it is required that $J' \ge \Lambda'$ [29,48], only J' = 1 of B¹II (with $\Lambda' = 1$) can be excited by a first laser L_1 with intensity I_1 , frequency ν_1 , and detuning Δ associated with the transition $|\varepsilon, \ell = 0\rangle \rightarrow |v', J' = 1\rangle$. In this case only the negative parity state (Π^-) for J' = 1 is populated because the initial state has positive parity $(J = 0, X^1\Sigma^+)$. The second stage of both schemes can populate J = 0 and J = 2 of the $X^1\Sigma^+$ state by spontaneous emission, or by emission stimulated by a laser L_2 with intensity I_2 , frequency ν_2 , and detuning δ associated with the transitions $|v', J' = 1\rangle \rightarrow |v, J\rangle$. No J = 1 level in the X state can be directly populated from the B state via a Q-branch transition because of parity considerations. Although (v, J) with J = 0 and 2 can be populated in the $X^1\Sigma^+$



Fig. 45: Schematics of two-photon stimulated Raman molecule formation. The relevant transitions between the two electronic states of LiH are indicated by the double arrows, and the laser intensities and frequencies for the two photons are shown as I_1 I_2 , and ν_1 and ν_2 . The energy values of the B¹ Π potential curve (defined with respect to the H(1s)+Li(2p) asymptote) have been multiplied by 30 to enhance the visibility of the potential well.

state via the B¹II state using the appropriate laser frequencies, we will focus our attention on the formation rate for (v, J = 0) rovibrational states; the rates for (v, J = 2) are of comparable magnitude.

5.1 Dipole Matrix Elements: $B^{1}\Pi - X^{1}\Sigma^{+}$ Transitions

Presented in the following two sections are the structure of the dipole matrix elements versus collision energy for continuum-bound transitions when the $B^1\Pi$ state is taken as the intermediate level, as well as the dipole matrix elements describing the various bound-bound transitions.



Fig. 46: Continuum-bound dipole transition matrix elements for $B^1\Pi$ to $X^1\Sigma^+$ transitions.

5.1.1 $X^{1}\Sigma^{+}$ Continuum to $B^{1}\Pi$ Bound Levels

The dipole matrix elements between continuum X and bound B states are very similar to those previously discussed in Chapters 3 and 4. There are fewer bound rovibrational levels in the B¹II state compared to the A¹ Σ^+ state, but the magnitude of the matrix elements for the uppermost v level is even larger than for the comparable level in the A state. Notice, in Figure 46, that each $|D_{v'}(\varepsilon)|^2$ covers many orders of magnitude; for v' = 2, the values range from below 10⁻¹⁰ a.u. to almost 10 000 a.u. They each follow Wigner's law at low energy, $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$: we give $C_{v'}$ for the various levels in Table 14.



Fig. 47: Bound–bound dipole transition matrix elements for $B^1\Pi$ to $X^1\Sigma^+$ transitions.

5.1.2 $B^{1}\Pi$ Bound Levels to $X^{1}\Sigma^{+}$ Bound Levels

Plotted in Figure 47 are the dipole transition matrix elements for coupling between the X and B states. The nodal structure of the bound wavefunctions is evident in these results. Notice that $|D_{v'v}|^2$ is relatively large for v' = 0 for the mid to lower v target levels. However, the largest value of $|D_{v'v}|^2$, by almost two orders of magnitude, is for the coupling between the uppermost bound levels for both electronic states (v' = 2 and v = 23), as previously noted for $A^1\Sigma^+ - X^1\Sigma^+$ transitions. But these results must be combined with the continuum-bound results in order to determine the most favorable paths overall.



Fig. 48: Coefficients $C_{v'}|D_{v',v}|^2$ for the Raman process from the continuum through the intermediate level v', J' = 1 of B¹II to the target level v, J = 0 of $X^1\Sigma^+$.

5.2 $B^{1}\Pi - X^{1}\Sigma^{+}$: Two-Photon Molecule Formation Rates

The factors $C_{v'}|D_{v',v}|^2$ appearing in Eq. (106) describing the excitation from the continuum to the intermediate levels v' of the B¹II state and then to the target level v of the X¹ Σ^+ state of LiH have been computed and are shown in Figure 48. There are only three bound vibrational levels in the B state. It is clear that the largest rate coefficients, by several orders of magnitude, will be obtained by exciting through the v' = 2, J' = 1 level (except for v = 19 with v' = 1).

Table 13 shows the two-photon rate coefficients $\mathsf{K}_{vv'}^{(2)}$ for populating selected $X^1\Sigma^+$ levels, v, J = 0, through v' = 2, J' = 1 of the B state. The largest rate coefficients are associated with populating the highest lying vibrational levels of

the ground state. Also listed in Table 13 are the rates for molecule formation computed using Eq. (117) and $n_{Li} = n_H = 10^{12} \text{ cm}^{-3}$, $V = 10^{-6} \text{ cm}^3$, and $\chi_S = 1/8$ for the the case when the low-field seeking atomic hyperfine states $(f_1 = 1, m_1 = -1)$ in ⁷Li and $(f_2 = 1, m_2 = 1)$ in H are populated. The rates for v = 5 and up are all well over 10^6 molecules/sec, and population of the lowest v = 0 level is a respectable 3.25×10^5 molecules/sec. These values are comparable to those obtained using $A^1\Sigma^+$ as the intermediate state for the twophoton process: $K_{vvv'}^{(2)}$ is of the same order of magnitude [47] (except for v = 0which is about ten times larger using $A^1\Sigma^+$). Note that both values of $K_{vv'}^{(2)}$ to reach v = 0 are much larger than the rate coefficient $K_v^{(1)} = 2.03 \times 10^{-22} \text{ cm}^3/\text{s}$ to form the molecule directly to v = 0 from the continuum with one-photon stimulation [44]. The higher molecule formation rates for v > 0 are offset by the resultant cascade which takes place and reduces the control over the *J*-level population in v = 0, as discussed in Section 5.4.

We note here that the back-stimulation from the target level in the X state into the continuum needs to be considered (see Section 5.5).

5.3 Spontaneous Emission Rates from $B^{1}\Pi$ to Bound Levels of the $X^{1}\Sigma^{+}$ State and Lifetimes of $B^{1}\Pi$ Rovibrational Levels

The excited vibrational levels (v', J' = 1) of the B¹ Π state can decay into lower levels in the B¹ Π , A¹ Σ^+ , or X¹ Σ^+ electronic states. Following Kovacs [48], the Hönl-London factors for ¹ Π – ¹ Σ transitions (with the convention that

v	$\overline{C_{v'} D_{v'v} ^2}$	$K^{(2)}_{vv'}$	R_v
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec)
0	6.0 [3]	2.6 [-12]	3.25 [5]
5	1.0[5]	4.4 [-11]	5.50[6]
10	5.9[4]	2.6 [-11]	3.25[6]
15	3.7 [5]	1.6 [-10]	2.00[7]
20	4.4 [5]	1.9 [-10]	2.38[7]
23	8.0 [7]	3.5 [-08]	4.38 [9]

Table 13: Two-photon rate coefficients $\mathsf{K}^{(2)}$ and total formation rate R for selected target states v, J = 0 of the $X^1\Sigma^+$ state of ⁷LiH via the intermediate level v', J' =1 of the B¹II state with the largest value for $C_{v'}|D_{v'v}|^2$. Parameters used are: $I_1 = I_2 = 1000 \text{ W/cm}^2$, T = 1 mK, $\Delta = 500 \text{ MHz}$, $n_{Li} = n_H = 10^{12} \text{ cm}^{-3}$, $V = 10^{-6} \text{ cm}^3$ and $\chi_S = 1/8$. Powers of ten are given in square brackets.

 $\Delta \Lambda = \Lambda' - \Lambda \equiv +1$) and with $J' = \Lambda' = 1$ for the *R*-branch (J = 0), *Q*-branch (J = 1), and *P*-branch (J = 2), are in general given by

$$W_{J'}^R = \frac{(J' + \Lambda')(J' - 1 + \Lambda')}{2J'(2J' + 1)} = \frac{1}{3}, \qquad (145)$$

$$W_{J'}^Q = \frac{(J' + \Lambda')(J' + 1 - \Lambda')(2J' + 1)}{2J'(J' + 1)(2J' + 1)} = \frac{1}{2}, \qquad (146)$$

$$W_{J'}^P = \frac{(J'+1-\Lambda')(J'+2-\Lambda')}{2(J'+1)(2J'+1)} = \frac{1}{6}.$$
 (147)

However in our case, because we populate only the odd parity $\Pi^- J = 1$ state starting from the $\ell = 0$ partial wave in the continuum, there can be no Q-branch decay populating J = 1 in the X state due to parity restrictions. Transitions can occur only through the R-branch and P-branch, for which the weights are doubled due to the lack of a Q-branch, $W_{J'}^R = \frac{2}{3}$ and $W_{J'}^P = \frac{1}{3}$.

For the first transition from $J' = \Lambda' = 1$ within the B¹ Π state ($\Delta \Lambda = 0$), the Hönl-London factors are non-zero only for the Q-branch (J = 1) and P-branch (J = 2) transitions, as no J = 0 level (hence no *R*-branch transition) is allowed:

$$W_{J'}^R = \frac{(J' + \Lambda')(J' - \Lambda')}{J'(2J' + 1)} = 0 , \qquad (148)$$

$$W_{J'}^Q = \frac{\Lambda'^2}{J'(J'+1)} = \frac{1}{2} , \qquad (149)$$

$$W_{J'}^P = \frac{(J'+1+\Lambda')(J'+1-\Lambda')}{(J'+1)(2J'+1)} = \frac{1}{2}.$$
 (150)

The transition probabilities for spontaneous decay from a level (v', J') in the B¹ Π state are given by

$$A_{v'}^{\text{tot}} = A_{v'}(\mathbf{B}^{1}\Pi) + A_{v'}(\mathbf{A}^{1}\Sigma^{+}) + A_{v'}(\mathbf{X}^{1}\Sigma^{+}) , \qquad (151)$$

where the three components correspond to the allowed decays within the B¹ Π state, into the A¹ Σ^+ state, and into the X¹ Σ^+ state, respectively. Each component $A_{v'}(Y)$ is the sum of the allowed R, Q, and P-branches into the electronic state Y

$$A_{v'}(Y) = A_{v'}^R(Y) + A_{v'}^Q(Y) + A_{v'}^P(Y) , \qquad (152)$$

where each branch α includes the contribution from discrete-discrete and discretecontinuum transitions as appropriate:

$$A_{v'}^{\alpha}(Y) = \sum_{v} A_{v'v}^{\alpha}(Y) + \int d\varepsilon \ A_{v'}^{\alpha}(Y,\varepsilon) \ . \tag{153}$$

Here, the allowed transitions from the initial upper state $|v', J'\rangle$ to lower discrete states $|v, J\rangle$ or continuum states $|\varepsilon, \ell\rangle$ are given by

$$A^{\alpha}_{v'v}(Y) = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega^{\alpha}_{v'v}}{c}\right)^3 W^{\alpha}_{J'} |\langle vJ|D_{BY}|v'J'\rangle|^2, \qquad (154)$$

$$A^{\alpha}_{\nu'}(Y,\varepsilon) = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega^{\alpha}_{\nu'}(\varepsilon)}{c}\right)^3 W^{\alpha}_{J'} |\langle \varepsilon \ell | D_{BY} | v' J' \rangle|^2, \qquad (155)$$

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where the frequencies are defined as $\hbar \omega_{v'v}^{\alpha} = E_{v'J'} - E_{vJ}$ and $\hbar \omega_{v'}^{\alpha}(\varepsilon) = E_{v'J'} - \varepsilon$, respectively. Also, the function $D_{BY}(R)$ stands for the dipole moment of the B¹II state (if Y = B), or the dipole transition moment between the B¹II and the A¹\Sigma⁺ state (if Y = A) or the X¹Σ⁺ state (if Y = X).

The lifetime of a given level (v', J' = 1) is simply given by

$$\tau_{v'} = \frac{1}{A_{v'}^{\text{tot}}} \,. \tag{156}$$

Finally, the branching ratio for radiative decay from an initial level (v', J' = 1) into a bound level (v, J) of the electronic ground state $X^1\Sigma^+$ is simply given by

$$r_{vJ}^{v'J'}(\alpha) \equiv \frac{A_{v'v}^{\alpha}(X^{1}\Sigma^{+})}{A_{v'}^{\text{tot}}}.$$
(157)

Again, for very low energies, we have $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ for X–B transitions. The coefficients $C_{v'}$ together with the one-photon rate coefficient $K_{v'}^{(1)}$ to the three vibrational levels of the B state, assuming T = 1 mK and $I_1 = 1000$ W/cm², have been calculated and are presented in Table 14. Due to its large $C_{v'}$, it is clear that population of v' = 2 leads to a much higher rate coefficient than population of either v' = 0 or 1.

Once the B¹ Π state is populated, the rovibrational levels can decay by spontaneous emission into lower levels in the same electronic state, to discrete levels of the A¹ Σ^+ state with lower energy, or into continuum or discrete levels of the X¹ Σ^+ ground state. We have computed the transition probabilities, $A_{v'}$, associated with each of these possible branches, and the total lifetime for the

Level	$\overline{C_{v'}}$	$K_{v'}^{(1)}$	
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	
0	1.8 [0]	1.6 [-17]	
1	9.8[4]	8.8 [-13]	
2	1.9 [7]	1.7 [-10]	

Table 14: Coefficient $C_{v'}$ of the dipole matrix element $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ for transitions from the continuum of the X¹ Σ^+ state (J = 0) to bound levels of the B¹ Π state (J' = 1) of ⁷LiH, and the one-photon rate coefficient $\mathsf{K}_{v'}^{(1)}$ to those levels v', assuming T = 1 mK and $I_1 = 1000$ W/cm². Powers of ten are given in square brackets.

three v' levels in the B¹II state. These are listed in Table 15. We calculated lifetimes of the order of tens of nanoseconds, ranging from 11.6 nsec for v' = 0 to 29.9 nsec for v' = 2. The values of $\tau_{v'}$ increase with v', reaching a value slightly larger than the lithium atomic lifetime of 27.102 nsec [50] for the uppermost level v' = 2, as expected since the B¹II state correlates asymptotically to H(1s)+Li(2p). The widths $\gamma_{v'}$ behave as the reciprocal of $\tau_{v'}$. We compare our results with other published values in Table 15, and find that the lifetimes are comparable for v' = 0and 1, but that for v' = 2, our value is larger, reflecting the importance of the decay back to the continuum; unlike Ref. [53], we did not approximate the decay into the continuum from the decay into the discrete levels of the X¹ Σ^+ state, but instead integrated the continuum contribution using the calculated square of the dipole transition matrix element $|D_{v'}(\varepsilon)|^2$.

Branching ratios $r_{vJ}^{v'J'}$ for decay from B state levels (v', J' = 1) to lower levels (v, J) of the X state were computed and are shown in Figure 49. Even

Level	contribution to $A_{v'}^{\text{tot}}$ (sec ⁻¹)				$ au_{v'}$ (n	usec)	
v'	$(B \rightarrow B)$	$(B \rightarrow A)$	$(B \rightarrow X)$	$(B \rightarrow free)$	$A_{v'}^{\mathrm{tot}}$	this work	Ref. [53]
0	0.00	2.96 [6]	8.31 [7]	2.42	8.61 [7]	11.6	11.3
1	1.45 [-2]	1.14[6]	5.44[7]	4.80[4]	5.56[7]	18.0	17.0
2	1.60[-3]	8.85[4]	3.31[7]	2.67[5]	3.34[7]	29.9	24.0

Table 15: Lifetimes of the levels v' for J' = 1. Also listed are the various contributions to $A_{v'}^{\text{tot}} = 1/\tau_{v'}$. The *Q*-branch contributions are included in order to compare with the previously published values of Stwalley, Zemke and Way [75]. Powers of ten are given in square brackets.

though the branching ratios to low-lying vibrational levels in the X state are largest for v' = 0, it must be remembered that the rate coefficient for populating this level by laser excitation from the continuum is seven orders of magnitude smaller than for populating v' = 2, since its $C_{v'}$ is seven orders of magnitude smaller than for v' = 2. The v' = 2 level predominantly decays to v = 23 of the X state.

The molecule formation rates due to direct spontaneous emission into rovibrational levels in the X state (without radiative cascade) have been computed using Eq. (116) and (117), assuming population of the intermediate level v' = 2, J' = 1 of the B¹II state. The temperature, densities and laser parameters are the same as were used in the two-photon case. The rates are listed in Table 15 for six different rovibrational levels. For forming molecules in v = 0 by one-photon excitation to the intermediate B state, followed by spontaneous emission, the rate is approximately 13,000 molecules/sec, about 25 times slower than found for populating v = 0, J = 0 using the two-photon stimulated Raman mechanism



Fig. 49: Branching ratios $r_{vJ}^{v'J'}(\alpha)$ to decay from an initial (v', J' = 1) level of the B¹ Π state to a lower (v, J) level of the X¹ Σ^+ state. The last three levels v = 21, 22, and 23 for v' = 2 are off-scale. Note that there is no *P*-branch for v = 23 bdue to the abscence of a J = 2 bound level.

i	R-bi	ranch	P-b	P-branch		
v	$r_{vJ}^{v'J'}$	R_v	$r_{vJ}^{v'J'}$	R_v		
	(%)	(mol./sec)	(%)	(mol./sec)		
0	5.98 [-2]	1.27 [4]	3.03 [-2]	6.43 [3]		
5	5.36 [-1]	1.14~[5]	2.66 [-1]	5.66 [4]		
10	1.68 [-1]	3.57 [4]	8.55 [-2]	1.82 [4]		
15	5.65 [-1]	1.20[5]	2.81 [-1]	5.97 [4]		
20	4.09 [-3]	8.69 [4]	2.17[-1]	4.61 [4]		
23	6.61 [+1]	1.40[7]				

Table 16: Branching ratios $r_{vJ}^{v'J'}$ and total formation rates R_v for each branch for the target states v, J of the $X^1\Sigma^+$ state of ⁷LiH via the intermediate level v' = 2, J' = 1 of the B¹II state (assuming $I_1 = 1000 \text{ W/cm}^2$, T = 1 mK, $n_{Li} = n_H = 10^{12} \text{ cm}^{-3}$, $V = 10^{-6} \text{ cm}^3$ and $\chi_S = 1/8$). Powers of ten are given in square brackets.

(325,000 molecules/second in Table 13). Spontaneous radiative decay from v' = 2 overwhelmingly populates v = 23, J = 0, at a rate of 1.4×10^7 molecules/sec. This is competitive with the rate of molecule formation via the two-photon process to mid-level rovibrational states of the $X^1\Sigma^+$ state, $5 \le v \le 15$. In both cases, significant radiative cascade then takes place as will be discussed in the following section.

5.4 Radiative Cascade Results: Rotational Distribution for Population in Initial States (v_{start} , J = 0 and 2)

As has been shown above, the rate coefficients for directly populating the v = 0 level of the X state by either the one-photon or the two-photon process are extremely small. Significant molecule formation rates can therefore only be achieved through populating higher vibrational levels of the X state. Because the

ground state of LiH has a large dipole moment, which varies with the internuclear separation R, once an upper vibrational level (v, J) of $X^1\Sigma^+$ is populated, it will decay by spontaneous emission into lower rovibrational levels, ultimately cascading down to v = 0. Due to the selection rule $\Delta J = \pm 1$ for such transitions, this cascade process will result in a distribution of J states in the v = 0 manifold. As described in the previous chapter, we obtain these distributions by calculating the branching ratios $r_{v_2J_2}^{v_1J_1}$, between a starting level (v_1, J_1) and an ending level (v_2, J_2) in the X state. As we noted, the cascade from an initial (v_i, J_i) level to a final level $(v = 0, J_f)$ can take any number of different paths, mostly through $\Delta v = 1, 2, 3, \text{ or } 4$ transitions. We do not consider radiative decay within the v = 0manifold (via $\Delta J = -1$ transitions) because the lifetime for such transitions is so much longer than in the vibrational cascade.

We have computed the lifetimes, τ_v , of the rovibrational levels (v, J = 0, 1, 2) of the X state. They are listed in Table 9. Here we include J = 1, as these levels can be populated in the cascade through the X¹ Σ^+ state. The values of τ_v initially decrease starting at about 22.2 msec for v = 1 down to about 2.88 msec for v = 18, before increasing rapidly to reach about 8.9 msec for v = 22 and finally 99 msec (J = 0) or 131 msec (J = 1) for the last vibrational level v = 23, although this (23,1) level can never be populated without radiative cascade starting from a pure s-wave continuum state. This last very large value reflects the poor overlap of the wavefunction of v = 23 with all other levels in

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regions where the variation of the dipole moment is appreciable, as well as the exponentially decaying magnitude of the dipole moment.

Using the calculated lifetimes for a range of (v, J) levels in the X state, and computing the branching ratios for spontaneous radiative cascade decay, we have obtained the rotational distributions of LiH molecules in v = 0 starting from various initial vibrational levels of the X state (and $J_{\text{initial}} = 0, 2$). These distributions are shown in Figure 50. As is to be expected, the rotational distribution becomes broader with increasing v_{initial} . The most probable final J-value is around J = 5 for v > 10.

The momentum direction of the emitted photon is random for each step of the decay process. Thus, the kinetic energy of the molecule is increased at most by the largest single jump in energy, in this case for $\Delta v = 4$. At worst, a $\Delta v = 4$ transition would heat up the trapped molecule by less than 80 nK, see § 3.1.3.

5.5 Back-stimulation

The analysis of the issue of back-stimulation presented in § 1.11 from a target level, (v', J' = 1) in an excited state for the one-photon process and (v, J = 0 or 2) in the ground state for the two-photon process is equivalent for PA schemes involving the $A^1\Sigma^+$ or $B^1\Pi$ states as the intermediate states, since the lifetimes of the electronically excited rovibrational levels are approximately the same.

Here we assume a lower temperature of 100 μ K (attainable for both Li and H samples), so that the rate coefficients listed in Tables 11, 13 and 14 are



Rotational Distributions

Fig. 50: Distribution of final J into the v = 0 manifold due to radiative cascade from an initial level ($v_{\text{start}}, J = 0$ and 2) in the $X^1\Sigma^+$ state, for various v_{start} .

increased by a factor of ten. For the one-photon process with $I_1 = 1000 \text{ W/cm}^2$ and $T = 100 \ \mu\text{K}$, the stimulated width $\gamma_s = 2\pi\hbar^2\Omega_{sv'}^2$ for the upper level of $B^1\Pi$ (v' = 2, J' = 1) is 4.7×10^{-29} Joules, leading to a stimulated lifetime $\tau_s = \hbar/\gamma_s = 2.34 \ \mu\text{sec.}$ Since the spontaneous radiative lifetime of that level is about 30 nsec (see Tables 10 and 15), the condition that $\tau_s \gg \tau_{v'}$ is readily satisfied. The other levels of both states have much smaller γ_s or longer τ_s (because of their smaller value of $C_{v'}$, see Table 10 and 14), and thus the same is true for these levels as well. We conclude that back-stimulation is not an issue for the one-photon process into any excited state.

For the two-photon process, the back stimulation time is found by $\tilde{\tau}_s = \hbar/\tilde{\gamma}_s$, where $\tilde{\gamma}_s$ is given in Eq. (120). Using $I_1 = I_2 = 1000 \text{ W/cm}^2$, $T = 100 \mu \text{K}$, and, for example, the intermediate level v' = 2 of the B¹II state, we obtain for target levels around v = 15 or so (with $C_{v'}|D_{v'v}|^2 \sim 4 \times 10^5$ a.u.), $\tilde{\gamma}_s \simeq 4.8 \times 10^{-29}$ Joules (or $\tilde{\tau} \simeq 2.2 \ \mu$ s). With $\tau_v \sim 4$ msec, we need to increase $\tilde{\tau}$ by at least four orders of magnitude, which can be done be reducing the laser intensities, say to $I_1 = I_2 = 10 \text{ W/cm}^2$; in this case, we obtain $\tilde{\tau} \sim 22$ msec, and the back-stimulation should not contribute to significantly decreasing the calculated molecule formation rates. Note, though, that the value of K⁽²⁾ will also be reduced by 10⁴. However, by lowering the temperature to $T = 100 \ \mu$ K, we increase the values for K⁽²⁾ in Table 13 by a factor of 10, and a subsequent reduction by 10⁴ in the laser power still results in rate coefficients for v = 15 of about 10⁻¹³ cm³/s, leading to rates of 10⁴ molecules/sec using the densities and volume listed in

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Table 13. Finally, the laser intensities do not need to be equal, and one could use $I_1 = 1000 \text{ W/cm}^2$ while $I_2 = 0.1 \text{ W/cm}^2$ to obtain the same effect. With the $A^1\Sigma^+$ state as the intermediate state, the time scales are essentially the same for the intermediate level v' = 12 and target level v = 22.

Another possibility to mitigating back-stimulation would be to use short duration laser pulses with a repetition rate that would allow radiative cascade to remove the molecules formed from the frequency range resonant with the lasers. This also allows the use of more intense lasers. For example, using both $I_1 = I_2 = 1000 \text{ W/cm}^2$ (with $T = 100 \ \mu\text{K}$), the two-photon stimulated time is $\tilde{\tau}_s = 2.2 \ \mu\text{s}$, and a pulse duration τ_{pulse} of 200 ns would be short enough to minimize back-stimulation. The number of molecules formed during a pulse is thus simply $N_{\text{mol}} = \tau_{\text{pulse}} R = 40$ molecules/pulse (assuming $R \sim 2 \times 10^8$ mol/sec for v = 15). Because one has to wait about 4 ms (decay time of most v levels) before sending another pulse, the number of pulses, N_{pulse} , per second is 250, so that the total "pulsed formation rate" $R_{\text{pulse}} = N_{\text{pulse}}N_{\text{mol}}$ is about 10^4 mol./sec , *i.e.*, of the same order as before.

Note that other approaches which can also give large rates, such as the use of chirped pulses [54], could be explored. Finally, for the direct two-photon formation of (v = 0, J = 0 or 2) molecules, one cannot mitigate back-stimulation using the same methods described above since the J = 0 state does not decay to any other state, while the lifetime of J = 2 is extremely long (over 2 hours, see Table 9). A possible solution is to remove the molecules from the interaction

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region with the laser beams. This could be realized experimentally by allowing the molecules to fall under the influence of gravity, or through their extraction by using far-detuned optical or electrostatic fields.

6

Formation of LiH in the $a^3\Sigma^+$ State via the $b^3\Pi$ State

As discussed in § 3.2, $a^3\Sigma^+$ molecules can be formed by direct stimulation from the continuum only at temperatures that are high enough to allow *p*-wave scattering. However, the rates are small enough to make this method impractical. Photoassociation using a triplet excited state turns out to be much more productive.

6.1 Dipole Matrix Elements: $b^3\Pi - a^3\Sigma^+$ Transitions

As shown in Figure 51, the well that supports the one bound rovibrational level in $a^3\Sigma^+$ is considerably further out in internuclear separation than other molecular wells. For this reason, when the $a^3\Sigma^+$ state is radiatively coupled to



Fig. 51: Schematic of the two-photon stimulated Raman molecule formation process. The relevant transitions between the two electronic states of LiH are indicated by the double arrows, and the laser intensities and frequencies of the two photons are shown as I_1 , I_2 , and ν_1 and ν_2 . The energy values of the b³ Π potential curve (defined with respect to the Li(2p) + H(1s) asymptote) have been divided by 100 to enhance to visibility of the shallow a³ Σ^+ potential well.



Fig. 52: Energy normalized dipole matrix elements $|D_{v'}(\varepsilon)|^2$ for $a^3\Sigma^+$ ($\ell = 0$) – $b^3\Pi$ (v', J' = 1) transitions as a function of collision energy ε .

an excited state, the features of the overlap of the wavefunctions are different than they are for the singlet states.

The integral $\langle v', J'|D_{ab}(R)|\varepsilon, \ell = 0 \rangle$ was calculated for energies between 10^{-12} a.u. to 10^{-1} a.u. The results for $|D_{v'}(\varepsilon)|^2$ are plotted in Figure 52. As usual for ultralow energies, $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$. The values for $C_{v'}$ were determined from a fit for all isotopes of LiH and are listed, along with the one-photon rate coefficients (calculated using Eq. (99)), in Tables 17, 18, 19 and 20. There is a difference between the structure of $|D_{v'}(\varepsilon)|^2$ versus ε for triplet transitions and

the structure of $|D_{v'}(\varepsilon)|^2$ versus ε for singlet transitions, specifically: for the lower intermediate levels (v' = 0 - 4), the matrix elements increase at energies above $\varepsilon/k_B \sim 1$ mK rather than decrease. $|D_{v'}(\varepsilon)|^2$ peaks at energies ranging from about 10^{-4} a.u. to 10^{-2} a.u. This increase is accounted for by examining the relationship between the bound and continuum wavefunctions for a range of collision energies. The energy normalized continuum wavefunction changes dramatically as the energy of the colliding pair increases; the first peak decreases in amplitude and moves in towards the inner wall and the extended part of the wavefunction oscillates more rapidly, as shown in Figure 53. As can be deciphered by examining the circled region of Figure 53, the energy normalized continuum wavefunction hardly overlaps at all with the bound (v' = 0, J' = 1) wavefunction when the collision energy is $\varepsilon = 10^{-8}$ a.u. For higher collision energies ($\varepsilon = 10^{-2}$ a.u.), the first peak of the continuum wavefunction is smaller and located at a smaller internuclear separation R that happens to overlap better with the bound wavefunction.

The bound-bound matrix elements $|D_{v'v}|^2 = |\langle v', J'|D_{ab}(R)|v = 0, J = 0\rangle|^2$ have also been calculated and are shown for ⁷LiH in Figure 55. The results reflect the poor overlap between the loosely bound $a^3\Sigma^+$ (v = 0, J = 0) state and the lower vibrational levels of $b^3\Pi$ as well as the excellent overlap of the a-state with the two uppermost levels of $b^3\Pi$, as shown in Figure 55.

Since (v = 0, J = 0) is the only bound level in the $a^3\Sigma^+$ state, there is no radiative cascade once molecules are formed there; hence back-stimulation can



Fig. 53: Illustration of the overlap of the bound rovibrational wavefunction for v = 0, J = 0 of the b³II state with the a³ Σ^+ continuum wavefunction for collisional energies of $\varepsilon = 10^{-8}$ a.u. (which is off the scale due to the energy normalization factor) and $\varepsilon = 10^{-2}$ a.u. Notice that the circled area of the figure draws attention to the main region of contribution to the overlap integral.



Fig. 54: The bound wavefunctions of the various rovibrational levels of the $a^3\Sigma^+$ state and the $b^3\Pi$ state, as well as the continuum wavefunction for the particular case when the collision energy is $\varepsilon = 10^8$ a.u. for ⁷LiH. The inset graph shows the overlap of the only bound level (v = 0, J = 0) of the $a^3\Sigma^+$ state and the two upper most vibrational levels (v = 5 and 6, J = 1) of the $b^3\Pi$ state.



Fig. 55: Dipole matrix elements $|D_{v'v}|^2$ for ⁷LiH a³ Σ^+ (v = 0, J = 0) – b³ Π (v', J' = 1) transitions.

become an overwhelming problem for two-photon stimulated PA which tends to significantly decrease the two-photon rates presented in § 6.2. Triplet molecules formed by excitation to bound levels of the b³II state followed by spontaneous emission to (v = 0, J = 0) in the a³ Σ ⁺ state, as discussed in § 6.3, are not effected by back-stimulation since back-stimulation is not an issue for the short-lived (on the order of tens of nanoseconds) excited rovibrational levels (see § 5.5).

From the triplet scattering state $|\varepsilon, \ell = 0\rangle$ for ultracold temperatures, transitions to odd parity components of J' = 0, 1 and 2 of $b^3\Pi_0$ are possible. The levels of $b^3\Pi_1$ and $b^3\Pi_2$ cannot be populated since the transition lines are weak for molecules characterized by Hund's case (b) (LiH in this case – see § 1.5). Here, we focus our attention on population of the J' = 1 vibrational levels of $b^3\Pi_0$ in the initial PA step. Then, the second stage of the scheme involves transitions only from $J' = 1 \rightarrow K = 0$ (J = 1) of $a^3\Sigma^+$ since parity considerations restrict $J' = 1 \rightarrow K = 1$ (J = 0, 1 or 2) transitions and $J' = 1 \rightarrow K = 2$ (J = 1 or 2) are weak for Hund's case (b).

6.2 $b^{3}\Pi - a^{3}\Sigma^{+}$: Two-Photon Molecule Formation Rates

The factors $C_{v'}|D_{v'v}|^2$ appearing in Eq. (106) describing excitation from the continuum to the target level (v = 0, J = 0) of the $a^3\Sigma^+$ state via the intermediate levels v' of the $b^3\Pi$ state have been computed and are listed for all isotopes of LiH in Tables 21, 22, 23 and 24. Also listed in these tables are the two-photon rate coefficients $K_{v'v}^{(2)}$ for populating the (v = 0, J = 0) level in $a^3\Sigma^+$ through each

Level	$C_{v'}$	$K_{v'}^{(1)}$	E_b	E_b
\mathbf{v}	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(Hartree)	(cm^{-1})
0	4.30 [-5]	3.87 [-22]	8.04 [-3]	1.76 [3]
1	7.40 [-1]	6.66 [-18]	5.54 [-3]	1.22 [3]
2	8.70 [1]	7.83 [-16]	3.48[-3]	7.64 [2]
3	9.40[3]	8.46 [-14]	1.89 [-3]	4.15 [2]
4	1.00[6]	9.00 [-12]	7.91 [-4]	1.74 [2]
5	1.07[8]	9.63 [-10]	1.79 [-4]	3.93[1]
6	6.70[9]	6.03 [-8]	1.45 [-6]	3.18[-1]

Table 17: Coefficient $C_{v'}$ of the dipole matrix element $|D_{v'}(\varepsilon)|^2 = C_{v'}\sqrt{\varepsilon}$ for transitions from the continuum of the $a^3\Sigma^+$ state $(\ell = 0)$ to bound levels of the $b^3\Pi$ state (J' = 1) of ⁷LiH, and the one-photon rate coefficient $K_{v'}^{(1)}$ to those levels v', assuming T = 1 mK and $I_1 = 1000$ W/cm². Also shown are the binding energies in atomic units and cm⁻¹ for each vibrational level v', J' = 1 of the $b^3\Pi$ state. Powers of ten are given in square brackets.

excited level in $b^3\Pi$. It is clear that the largest rate coefficients, by several orders of magnitude, will be obtained by exciting through the uppermost rovibrational level.

The rates of molecule formation were computed using Eq. (118) and the following parameters: $n_{Li} = n_H = 10^{12} \text{ cm}^{-3}$, $V = 10^{-6} \text{ cm}^3$ and $\chi_T = 1$. $\chi_T = 1 - \chi_S = 1$ corresponds to the fully stretched state, when the hyperfine values for the atomic hyperfine states are $(f_1 = 2, m_1 = 2)$ in ⁷Li and $(f_2 = 1, m_2 = 1)$ in H (see § 1.7). The rates are extremely small for molecules excited through the lowest v' levels, from 6×10^{-14} molecules/sec for v' = 0to 3.5 molec./s for v' = 3. Excitation through the mid v' levels yields larger rates (between 4×10^5 and 4.6×10^9 molecules/sec), which are comparable to singlet molecule formation through high vibrational levels through the $B^1\Pi$ state
Level	$C_{v'}$	$K_{v'}^{(1)}$	E_b	$\overline{E_b}$
v'	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(Hartree)	(cm^{-1})
0	4.70 [-3]	4.36 [-20]	8.02 [-3]	1.76 [3]
1	8.50 [-1]	7.89 [-18]	5.50 [-3]	1.21 [3]
$^{\circ}2$	1.03[2]	9.56 [-16]	3.44 [-3]	7.55 [2]
3	1.15[4]	1.07 [-13]	1.84 [-3]	4.04 [2]
4	1.28[6]	1.19[-11]	7.51 [-4]	1.65[2]
5	1.41 [8]	1.31 [-9]	1.58 [-4]	3.47[1]
6	5.35[7]	4.97 [-10]	1.39 [-7]	3.05 [-2]

Table 18: Same as Table 17, except for ⁶LiH.

Level	$C_{v'}$	$K_{v'}^{(1)}$	E_b	E_b
v'	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(Hartree)	(cm^{-1})
0	2.20 [-7]	8.37 [-25]	8.40 [-3]	1.84 [3]
1	4.30 [-5]	1.64 [-22]	6.44 [-3]	1.41 [3]
2	5.40 [-3]	2.05 [-20]	4.73 [-3]	1.04[3]
3	5.60 [-1]	2.13 [-18]	3.27 [-3]	7.18 [2]
4	5.30[1]	2.02 [-16]	2.08[-3]	4.57 [2]
5	4.70[3]	1.79 [-14]	1.15 [-3]	2.52 [2]
6	3.90[5]	1.48 [-12]	5.11 [-4]	1.12 [2]
7	2.50[7]	9.51 [-11]	1.40 [-4]	3.07[1]
8	3.10 [8]	1.18 [-9]	8.36 [-6]	1.83 [0]

Table 19: Same as Table 17, except for ⁷LiD.

(see § 5.2). Excitation through the uppermost $b^3\Pi$ level yields extremely large rates, larger by about three orders of magnitude than singlet rates via the $B^1\Pi$ state. Nevertheless, these results are not realistic without evaluating the consequences of back-stimulation.

Level	$\overline{C_{v'}}$	K ⁽¹⁾	E_b	E_b
v'	(a.u.)	$(\mathrm{cm}^{3}/\mathrm{s})$	(Hartree)	(cm^{-1})
0	4.00 [-7]	1.61 [-24]	8.39 [-3]	1.84 [3]
1	7.80 [-5]	3.13 [-22]	6.39 [-3]	1.40[3]
2	9.80 [-3]	3.94 [-20]	4.66 [-3]	1.02[3]
3	$1.01 \ [0]$	4.06 [-18]	3.19 [-3]	7.00 [2]
4	9.70[1]	3.90 [-16]	1.99 [-3]	4.37 [2]
5	8.70 [3]	3.50 [-14]	1.08[-3]	2.37[2]
6	7.20 [5]	2.89 [-12]	4.52 [-4]	9.92 [1]
7	4.40 [7]	1.77 [-10]	1.09 [-4]	2.39 [2]
8	1.07 [8]	4.30 [-10]	3.27 [-6]	7.18 [-1]

Table 20: Same as Table 17, except for ⁶LiD.

6.2.1 Back-stimulation

Back-stimulation from a target level, (v', J' = 1) for the one-photon process and (v = 0, J = 0) for the two-photon process, into the continuum needs to be taken into account. Since the lifetimes of the excited (v', J' = 1) levels are tens of nanoseconds, similar to the singlet excited lifetimes, we can conclude that backstimulation does not significantly affect molecules formed in the b³II levels. (See § 5.5.)

The crucial problem with back-stimulation in triplet molecule formation comes from back-stimulation from the $a^{3}\Sigma^{+}$ bound level, due to the fact that this level has essentially no natural width for lithium hydride (the v = 0, J = 1level in the deuterides would have a long lifetime and a narrow width). For this reason, it is necessary to consider a pulse sequence in which molecules could be formed and then physically removed from the interaction region (with lasers or

v'	$C_{v'} D_{v'v} ^2$	$K^{(2)}_{vv'}$	R'_v
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec.)
0	1.50 [-16]	6.61 [-32]	6.61 [-14]
1	4.62 [-10]	2.03 [-25]	2.03 [-7]
2	6.61 [-6]	2.91 [-21]	2.91 [-3]
3	7.89 [-2]	3.47 [-17]	3.47[1]
4	9.27[2]	4.08 [-13]	4.08[5]
5	1.08[7]	4.77 [-9]	4.77 [9]
6	5.64 [10]	2.48 [-5]	2.48 [13]

Table 21: Two-photon rate coefficients $K^{(2)}$ and the total formation rate R for the target state v = 0, J = 0 of the $a^3\Sigma^+$ state of ⁷LiH via intermediate levels v', J' = 1 of the $b^3\Pi$ state. Powers of ten are given in square brackets.

$\overline{v'}$	$\overline{C_{v'} D_{v'v} ^2}$	$K^{(2)}_{vv'}$	R'_v
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec.)
0	1.96 [-14]	8.91 [-30]	8.91 [-12]
1	6.33 [-10]	2.87 [-25]	2.87 [-7]
2	9.34 [-6]	4.24 [-21]	4.24 [-3]
3	1.16 [-1]	5.26 [-17]	5.26 [1]
4	1.44[3]	6.53 [-13]	6.53[5]
5	1.76[7]	7.97 [-9]	7.97 [9]
6	5.76 [8]	2.61 [-7]	2.61 [11]

Table 22: Same as Table 21, except for ⁶LiH.

gravity) before they are dissociated and lost. If the experimental parameters are adjusted so that $I_1 = I_2 = 10 \text{ W/cm}^2$ and $T = 100 \ \mu\text{K}$, then for the case when $C_{v'}|D_{v'v}|^2 \simeq 3 \times 10^9$ a.u. (which corresponds to a rate of $R \sim 5 \times 10^{11}$ molecules/sec), we obtain an interaction (or stimulated) time of $\tau_s \simeq 3 \ \mu\text{s}$. If the laser pulse duration is sufficiently smaller than τ_s and taken to be 100 ns, then the number of molecules formed would be $N_{\text{mol}} = \tau_{\text{pulse}} R \approx 50\,000$ molecules/pulse. The time between pulses would have to be arranged so that the sample of $a^3\Sigma^+$

$\overline{v'}$	$\overline{C_{v'} D_{v'v} ^2}$	$K^{(2)}_{vv'}$	R'_v
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec.)
0	6.14 [-22]	1.14 [-37]	1.14 [-19]
1	2.45 [-17]	4.55 [-33]	4.55 [-15]
2	3.89 [-13]	7.23 [-29]	7.23 [-11]
3	4.19 [-9]	7.79 [-25]	7.79 [-7]
4	3.77 [-5]	7.01 [-21]	7.01 [-3]
5	3.01 [-1]	5.60 [-17]	5.60[1]
6	2.08[3]	3.86 [-13]	3.86[5]
7	8.71 [6]	1.62 [-9]	1.62 [9]
8	2.62 [9]	4.87 [-7]	4.87 [11]

Table 23: Same as Table 21, except for 7 LiD.

molecules could be removed from the interaction region before the next pulse is applied.

6.3 Spontaneous Emission Rates from $b^3\Pi$ to Bound Levels of the $a^3\Sigma^+$ State and Lifetimes of $b^3\Pi$ Rovibrational Levels

Once the b³ Π state is populated, the rovibrational levels can decay by spontaneous emission into lower levels in the same electronic state and to discrete and continuum levels of the a³ Σ^+ state. Since the Q-branch ($J' = 1 \rightarrow K = 0$ (J = 1)) is the only decay path for this relatively light system with ³ Π – ³ Σ transitions, [29] the rotational line strength factor for this transition must be 1.

The transition probabilities for spontaneous decay from a level (v', J') in the b³ Π state are given by the A-Einstein coefficient for spontaneous decay,

$$A_{v'}^{\text{tot}} = A_{v'}(b^3\Pi) + A_{v'}(a^3\Sigma^+) .$$
(158)

$\overline{v'}$	$C_{v'} D_{v'v} ^2$	$K^{(2)}_{vv'}$	R'_v
	(a.u.)	$(\mathrm{cm}^3/\mathrm{s})$	(mol./sec.)
0	1.94 [-21]	3.81 [-37]	3.81 [-19]
1	7.65 [-17]	1.50 [-32]	1.50 [-14]
2	$1.21 \ [-12]$	2.37 [-28]	2.37 [-10]
3	1.29 [-8]	2.54 [-24]	2.54 [-6]
4	1.19 [-4]	2.33 [-20]	2.33 [-2]
5	9.63 [-1]	1.89 [-16]	1.89 [2]
6	6.64[3]	1.30 [-12]	1.30 [6]
7	2.57[7]	5.05 [-9]	5.05[9]
8	1.09 [9]	2.15 [-7]	2.15 [11]

Table 24: Same as Table 21, except for ⁶LiD.

The probability for transitions within the $b^3\Pi$ state is very small and therefore their contribution is neglectged in the lifetime calculation. Since the Q-branch is the only allowed decay path, $A_{v'}$ includes the contribution from discretecontinuum transitions and is given by

$$A_{v'} = \sum_{v} A_{v'v} + \int d\varepsilon A_{v'}(\varepsilon) . \qquad (159)$$

Here, the allowed transitions from the initial upper state $|v', J' = 1\rangle$ to lower bound state $|v = 0, J = 0\rangle$ or continuum states $|\varepsilon, \ell\rangle$ are given by

$$A_{v'v} = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega_{v'v}}{c}\right)^3 |\langle vJ|D_{ab}|v'J'\rangle|^2$$
(160)

$$A_{\nu'}(\varepsilon) = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\omega_{\nu'}(\varepsilon)}{c} \right)^3 |\langle \varepsilon \ell | D_{ba} | \nu' J' \rangle|^2, \qquad (161)$$

where the frequencies are defined as $\hbar \omega_{v'v} = E_{v'J'} - E_{vJ}$ and $\hbar \omega_{v'}(\varepsilon) = E_{v'J'} - \varepsilon$, respectively. Also, the function $D_{ba}(R)$ stands for the dipole transition moment between the b³II state and the a³ Σ^+ state.

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The lifetime of a given level (v', J' = 1) is simply given by

$$\tau_{v'} = \frac{1}{A_{v'}^{\text{tot}}} \,. \tag{162}$$

Finally, the branching ratio for radiative decay from an initial (v', J' = 1)into the bound level (v = 0, J = 0) of the electronic ground state $a^3\Sigma^+$ is simply given by

$$r_{vJ}^{v'J'} \equiv \frac{A_{v'v}(\mathbf{a}^3\Sigma^+)}{A_{v'}^{\text{tot}}}.$$
(163)

We have computed the transition probabilities, $A_{v'}$, associated with each of these possible decay paths, and the total lifetime for the v' levels in the b³II state. The lifetimes of the v' levels for J' = 1 for each isotope of LiH are listed in Tables 25, 26, 27 and 28. We calculated lifetimes of the order of tens of nanoseconds, ranging from 111 ns for v' = 0 of ⁷LiD to about 27 ns for the uppermost v' level of all isotopes. The larger lifetimes for the lowest v' levels are explained by the poor overlap of the bound lower and excited state wavefunctions, which is described below.

The ratio $r_{vJ}^{v'J'}$ of molecules that spontaneously decay to the the bound level (v = 0, J = 0) of the $a^3\Sigma^+$ state versus the continuum of the $a^3\Sigma^+$ state were computed for all isotopes and are shown in Figure 56. Notice that for the uppermost levels v' = 6 or 8, the percentage of molecules that spontaneously decay to the bound level rather than into the continuum is very large (73% for ⁷LiH, 96% for ⁶LiH, 76% for ⁷LiD and 92% for ⁶LiD). This is explained by the fact that the wavefunctions of these uppermost v' excited levels are so loosely

Level	Contrib	$\tau_{v'}$ (nsec)		
v'	(bound-bound)	(bound-free)	$A_{v'}^{\text{tot}} (\text{sec}^{-1})$	-
0	8.02 [-6]	9.34 [6]	9.34 [6]	107
1	1.62 [-3]	1.22 [7]	1.22 [7]	82.0
2	2.18 [-1]	1.59[7]	1.59[7]	62.8
3	2.59[1]	2.07[7]	2.07[7]	48.3
4	3.00[3]	2.64[7]	2.64[7]	37.8
5	3.37 [5]	3.23 [7]	3.27[7]	30.6
6	2.82[7]	1.04[7]	3.86[7]	25.9

Table 25: Lifetimes of the levels v' for the b³ Π state for ⁷LiH. Also listed are the various contributions to $A_{v'}^{\text{tot}} = 1/\tau_{v'}$. Powers of ten are given in square brackets.

Level	Contrib	$\tau_{v'}$ (nsec)		
v'	(bound-bound)	(bound-free)	$A_{v'}^{\text{tot}} (\text{sec}^{-1})$	
0	9.61 [-6]	9.36 [6]	9.36 [6]	107
1	1.94 [-3]	1.23[7]	1.23[7]	81.5
2	2.60 [-1]	1.61 [7]	1.61 [7]	62.2
3	3.11 [1]	2.09[7]	2.09[7]	47.8
4	3.65[3]	2.68[7]	2.68[7]	37.4
5	4.15 [5]	3.26[7]	3.30[7]	30.3
6	3.61 [7]	1.67[6]	3.78 [7]	26.5

Table 26: Same as Table 25, except for ⁶LiH.

bound that the last lobe extends far out in internuclear separation, which is precisely the case for the very loosely bound a-state so that there is large overlap between these levels. The lowest v' levels overlap poorly with the bound lower level and therefore the decay from these levels takes place almost entirely into the continuum.

The molecule formation rates due to spontaneous emission into rovibrational levels in the lower state have been computed using Eqs.(116) and (118).



Fig. 56: Branching ratios $r_{vJ}^{v'J'}$ to decay from an initial (v', J' = 1) level of the b³II state to the bound level of a³ Σ^+ (v = 0, J = 0) state for each isotope of LiH, namely: ⁶LiH, ⁷LiH, ⁶LiD and ⁷LiD. For the uppermost levels v' = 6 or 8, the percentage of molecules that spontaneously decay to the bound level rather than into the continuum is very large (73% for LiH and 96% for LiD).

Level	Contrib	$\tau_{v'}$ (nsec)		
v'	(bound-bound)	(bound-free)	$A_{v'}^{\mathrm{tot}} \; (\mathrm{sec}^{-1})$	
0	4.37 [-9]	9.02 [6]	9.02 [6]	111
1	1.08 [-6]	1.10[6]	1.10[6]	90.7
2	1.61 [-4]	1.35[7]	1.35[7]	74.1
3	1.91 [-2]	1.65[7]	1.65[7]	60.6
4	2.01 [0]	2.00[7]	2.00[7]	50.1
5	1.96 [2]	2.41 [7]	2.41 [7]	41.4
6	1.72 [4]	2.88[7]	2.88[7]	34.7
7	1.16[6]	3.23[7]	3.35[7]	29.9
8	2.83 [7]	8.81 [6]	3,71 [7]	26.9

Table 27: Same as Table 25, except for ⁷LiD.

The temperature, densities and laser parameters are the same as in the twophoton case. The rates are listed in Tables 29, 30, 31 and 32. For forming molecules in the a-state (v = 0, J = 0) of ⁷LiH by one-photon excitation to the intermediate b state, followed by spontaneous emission, the rate is approximately 4×10^{10} molecules/sec, only about 2×10^3 times slower than found for populating v = 0 using the two-photon stimulated Raman mechanism. However, these rates happen to be large and since there is no problem with back-stimulation in the one-photon process, this method may also be an effective way to produce triplet molecules.

Level	cont	$\tau_{v'}$ (nsec)		
v'	(bound-bound)	(bound-free)	$A_{v'}^{\text{tot}} (\text{sec}^{-1})$	
0	1.10 [-8]	9.04 [6]	9.04 [6]	111
1	2.44 [-6]	$1.11 \ [7]$	1.11 [7]	90.1
2	3.34 [-4]	1.36[7]	1.36[7]	73.4
3	3.72 [-2]	1.67[7]	1.67[7]	59.8
4	3.75~[0]	2.03[7]	2.03[7]	49.2
5	3.54[2]	2.46[7]	2.46[7]	40.7
6	3.03 [4]	2.93[7]	2.94[7]	34.1
7	1.95[6]	3.21[7]	3.41[7]	29.4
8	3.43[7]	3.17[6]	3.74[7]	26.7

Table	28:	Same	as	Table	25,	\mathbf{except}	for	⁶ LiD.
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v'	$r_{vJ}^{v'J'}(Q)$	R_v
	(%)	(mol./sec.)
0	8.59 [-11]	3.32 [-16]
1	1.33 [-8]	8.86 [-10]
2	1.37 [-6]	1.07 [-5]
3	1.25 [-4]	1.06 [-1]
4	1.13 [-2]	1.02[3]
5	1.03[0]	9.93 [6]
6	7.31 [+1]	4.41 [10]

Table 29: Branching ratio $r_{vJ}^{v'J'}(Q)$ (J = J') and the total formation rate R for populating the bound level of the $a^3\Sigma^+$ state of ⁷LiH via the various intermediate levels v', J' = 1 of the $b^3\Pi$ state. Powers of ten are given in square brackets.

v'	$r_{vJ}^{v'J'}(Q)$	R_v
	(%)	(mol./sec.)
0	1.03 [-10]	4.48 [-14]
1	1.58 [-8]	1.25 [-9]
2	1.62 [-6]	1.55 [-5]
3	1.49 [-4]	1.59 [-1]
4	1.36 [-2]	1.62[3]
5	1.26[0]	1.65[7]
6	9.56 [+1]	4.75 [8]
$\overline{\mathbf{n}}$		

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						-		

	1.27	
v'	$r_{vJ}^{v'J'}(Q)$	$R_v$
	(%)	(mol./sec.)
0	7.98 [-14]	6.67 [-22]
1	1.39[-11]	2.28 [-17]
2	1.51 [-9]	3.10 [-13]
3	1.34 [-7]	2.86 [-9]
4	1.10 [-5]	2.22 [-5]
5	8.49 [-4]	1.52 [-1]
6	6.06 [-2]	9.00 [2]
7	3.47[0]	3.30 [6]
8	7.63 [+1]	8.99 [8]

Table 31: Same as Table 29, except for ⁷LiD.

/	$r^{v'J'(O)}$	P
v	$V_{vJ}(Q)$	Nv
	(%)	(mol./sec.)
0	1.21 [-13]	1.95 [-21]
1	2.20 [-11]	6.90 [-17]
2	2.45 [-9]	9.66 [-13]
3	2.22 [-7]	9.02 [-9]
4	1.85 [-5]	7.19 [-5]
5	1.44 [-3]	5.03 [-1]
6	1.03 [-1]	2.99[3]
7	5.72 [0]	1.01 [7]
8	9.15 [+1]	3.93 [8]

_	0 01.		0.00 [0]	
Table 32:	Same	as Table	29, except	for ⁶ LiD.

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## Conclusions

We have explored the possibility of forming LiH and NaH molecules in their electronic ground state. We have shown that it should be possible to produce these ultracold molecules in the v = 0 level of the singlet ground electronic state through one-photon laser-assisted radiative association. By populating high-lying vibrational levels through stimulated emission, using laser wavelengths in the vicinity of 10  $\mu$ m, more than 10⁴ molecules per second can be formed. But, backstimulation of molecules into the continuum becomes a problem for the laser intensities that we have assumed in calculating the rates. So, lowering both the intensity of the laser and the temperature to the point where the time scale of the stimulated process is much longer than the natural width of the level yields smaller rates (about 10² molecules per second).

We have likewise shown that it should be possible to produce LiH molecules in their electronic ground state via both a two-photon Raman transition scheme and through spontaneous radiative decay utilizing the  $A^1\Sigma^+$  or the  $B^1\Pi$  states as the intermediate state. Assuming laser intensities and atomic densities that are attainable experimentally, we found that significant quantities of molecules can be formed in various v, J levels of the electronic ground state. With the same parameters, the molecule formation rate obtained with the two-photon process is two to three orders of magnitude larger than the one-photon process followed by spontaneous emission. However, when we take into account back-stimulation into the continuum, that advantage vanishes. At that point, the one-photon rate is 10-100 times larger, depending on the target level populated in the ground state. Although the two-photon process gives better selectivity, the one-photon process may be easier to implement experimentally.

In any case for singlet states, the vibrationally hot molecules undergo spontaneous emission and cascade ultimately to v = 0 and end up spread out in a distribution of final rotational levels within the v = 0 manifold. We have shown this rotational distribution for populations of molecules starting in high-lying vibrational levels looks generally like a binomial distribution of a random walk and tends to peak at about J = 4 - 5.

Through examination of triplet transitions, we have shown that spontaneous emission into the one bound level of the  $a^3\Sigma^+$  state via the uppermost bound level of the  $b^3\Pi$  state is more likely than decay into the continuum. Using the same experimental parameters as in the singlet calculations, we found that very large quantities of molecules (on the order of  $10^8$  molecules per second) can be formed in this  $a^{3}\Sigma^{+}$  state. Triplet molecule formation using a two-photon process also yields large rates, but since there is essentially no width to the (v = 0, J = 0) level of the a-state, back-stimulation from this level into the continuum cannot be mitigated by simply reducing the laser intensity. Rather, a pulse sequence allowing for periods removal of molecules between periods of formation becomes necessary.

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