

Chapter 6

Theory of photoassociation lineshapes

Photoassociation (PA) spectroscopy has played a significant role in understanding cold collisions. In Chapter 1, photoassociation was described as the process by which an excited molecular bound state is resonantly formed through photoexcitation during the collision of two atoms. Generally, experiments are conducted with the atoms initially in their atomic ground state so that an analysis of the photoassociation lineshapes provides information, via the Franck-Condon overlap, on the colliding ground state wave function. In addition, transitions to the so called “long-range” molecular states[128, 129] that typically have **inner** turning points in the range $\sim 30 - 70$ Bohr, provide information on the ground state wave function at large R . In this way, the s -wave scattering lengths can be determined accurately. In fact, most of the alkali scattering lengths have been determined (at least initially) from an analysis of PA spectroscopy.

Photoassociation spectroscopy was first proposed by Thorsheim, Weiner and Julienne[19]. In that work, the authors developed the theoretical framework needed to analyze a PA spectrum. However, they were mostly concerned with experiments at the comparatively “warm” cloud temperatures of tens of mK. Photoassociation theory has since been extended[130] to include threshold effects of atoms colliding at magneto-optical trap (MOT) temperatures of hundreds of μ K (see also Refs.[131, 132, 133] for a discussion of photoabsorption line shapes). In addition, a further development[134, 135] of the theory now includes the effect of a second laser. An extension of the one-color formulation of Ref.[130] to include multichannel scattering along the lines of Ref.[136] is presented in this chapter. This theoretical framework is then applied in Chapter 7 to analyze the measured rovibrational spectrum of the $^{39}\text{K } 0_g^-$ state, and to extract the s -wave scattering lengths.

This chapter is organized as follows: in Section 6.1, the basic lineshape formula is derived. The main component of this formula is a dipole matrix element that provides the radiative coupling between the ground state and the excited state. It is important to construct molecular wave functions that have the proper symmetries in order to evaluate the radiative coupling matrix element. Symmetry rules for diatomic wave functions in a Hund’s case (a) representation[137] are presented in Section 6.2. The excited state Hamiltonian and ground state Hamiltonian

are constructed in Section 6.3. Here, the “ground state Hamiltonian” describes the interaction of two ground state atoms (S), while the “excited state Hamiltonian” describes the interaction of one ground state atom (S) and one excited state atom (P). Finally, the dipole matrix element that connects these states is evaluated in Section 6.4.

6.1 One color lineshape formula

The centerpiece of photoassociation theory is an expression for the thermal averaged rate constant K_p that describes the rate at which molecular bound states are resonantly formed during the collision of two atoms. The general approach for evaluating K_p is to treat the photoassociation problem as an inelastic scattering process. The inelastic rate constant K_p for the formation of molecules (i.e., coefficient of squared density in the rate equation) is then proportional to

$$K_p = \left\langle \sum_l (2l + 1) \frac{\sigma_l v}{1 + \delta} \right\rangle \quad (6.1)$$

where the brackets denote a thermal average over a distribution of incident velocities v , σ_l is the total inelastic cross section for scattering from an incident continuum channel of partial wave l into a molecular bound state channel, and $\delta = 1$ if the initial pair of atoms are identical and in indistinguishable spin states, or $\delta = 0$ otherwise (see Section 2.1.2). Photoassociation experiments are usually conducted with dilute atom clouds at temperatures of a few hundred μK . Therefore, the thermal averaging procedure can be treated by the classical method presented in Appendix C. This expression for the rate constant assumes that the atom density n can be factored out of the thermal average as will be the case for most atom traps. The result of thermal averaging, after writing the cross section in terms of a scattering matrix element $\sigma/(1 + \delta) = \frac{\pi v}{k^2} |S_p|^2$, is [130]

$$K_p = \frac{1}{hQ_T} \sum_l (2l + 1) \int_0^\infty |S_p|^2 e^{-E/k_B T} dE, \quad (6.2)$$

where k_B is the Boltzmann constant, T represents the cloud temperature, and $Q_T = (2\pi\mu k_B T/h^2)^{3/2}$ is the translational partition function. Perturbative expressions for the scattering matrix element $|S_p|^2$, valid for the low laser intensities generally used in these experiments, have been derived in Refs. [130, 135]. The general result can be written as

$$|S_p(E, l, \omega)|^2 = \frac{\gamma_0 \gamma_s(E, l)}{(E + h\nu_1 - E_b)^2 + (\gamma/2)^2} \quad (6.3)$$

where ν_1 is the laser frequency, E_b is the bound state energy, γ is the total width (in energy units) of the bound state, and γ_0/\hbar represents the rate at which observable products are produced (i.e., atoms lost from the trap by spontaneous emission or atoms (molecules) ionized by a second laser). The main component of equation 6.3 is the radiative width, which can be expressed in terms of a coupling matrix element as

$$\gamma_s(E, l) = 2\pi |\langle \Psi_b(R) | V_{\text{rad}}(R) | \Psi_l^E(R) \rangle|^2 . \quad (6.4)$$

Here, $\Psi_b(R)$ represents a unit normalized bound state wave function, $\Psi_l^E(R)$ is the energy-normalized continuum wave function in the incident channel, and $V_{\text{rad}}(R) = (2\pi I/c)^{1/2} d(\vec{R})$ represents the radiative coupling that is proportional to the square root of the laser intensity I and the molecular dipole operator $d(\vec{R})$. (The molecular dipole operator is described in Section 6.4.)

The last step is to substitute expressions 6.3 and 6.4 into the rate constant equation (6.2) and generalize the result for multichannel scattering. The final result for K_p is given by[136]

$$K_p(v', J', \omega, T) = \frac{4\pi^2 I}{hcQ_T} \sum_{\beta' p' f l p \alpha} n_f (2l + 1) \int_0^\infty dE \frac{e^{-E/k_B T} \gamma_0 |\langle \Psi_{p' \beta'}^{v' J'}(R) | d_{f l p \alpha}^{J' p' \beta'}(R) | \Psi_{f l p \alpha}^E(R) \rangle|^2}{(E + h\nu_1 - E_{v' J'})^2 + (\gamma/2)^2} . \quad (6.5)$$

This expression (6.5) is used for the analysis presented in Chapter 7. It includes a sum over all unresolved final states, an average over all initial states and a thermal average over incident energy. In this multichannel context, the bound molecular wave function Ψ_b is labeled by its vibrational quantum number v' , rotational quantum number J' , parity p' , and a set of additional quantum numbers β' required to define the wave function uniquely. For example β' includes the nuclear spin degrees of freedom. The continuum wave function Ψ^E is energy-normalized and satisfies outgoing-wave boundary conditions. It is labeled by the total spin f of the colliding atoms, the partial wave l , parity p , and α includes all other quantum numbers required to define the initial quantum state uniquely. Also present is a constant n_f representing a weighting factor for the population of atoms in the f entrance channel. For a randomly polarized gas of identical particles, this weight is given by $n_f = \frac{(2f+1)}{N_{\{f_a, f_b\}}}$ where $N_{\{f_a, f_b\}} = (2f_a + 1)(2f_b + 1 + \delta_{f_a, f_b}) / (1 + \delta_{f_a, f_b})$ is the total number of distinct symmetrized spin channels. It should be noted that averaging the dipole matrix elements over initial states cancels both the $(2f + 1)$ factor above and the $(2l + 1)$ term in Eq. 6.5.

6.2 Symmetry rules for diatomic Hund's case (a) wave functions

The field-free diatomic Hamiltonian possesses a number of discrete symmetries beyond the translational and rotational dynamical symmetries. The Hamiltonian commutes with the electron permutation operator \hat{P}_e , the parity operator $\hat{\pi}$, and for homonuclear molecules, the nuclear permutation operator \hat{P}_n . In the Born-Oppenheimer limit[31], the electronic part of the factored wave function possesses additional symmetries. These include reflection of the electronic wave function through a plane containing the internuclear axis, whose operator is denoted $\hat{\sigma}_v$; and for nuclei of equal charge, inversion of the electronic wave function through the center of mass in the molecular frame, whose operator is denoted \hat{i} .

We can construct an eigenfunction of the molecular Hamiltonian in the Born-Oppenheimer limit from a set of Hund's case (a) basis functions. These basis functions have the following form:

$$\Phi(J, M_J, \Omega, \Lambda, S, \Sigma, I, M_I, R, w) = \sqrt{\frac{2J+1}{4\pi}} D_{M_J, \Omega}^{J*}(\alpha, \beta, \gamma) \phi(\Lambda, w) |(s_a s_b) S \Sigma \rangle |i_a i_b\rangle I M_I \rangle F_{J, \Lambda}(R). \quad (6.6)$$

Here, $D_{M_J, \Omega}^J$ is a matrix element of the $(2J+1) \times (2J+1)$ unitary rotation matrix[57]. It is a function of the Euler angles (α, β, γ) which define the relationship of the space-fixed lab frame with that of the body-fixed molecule frame. Zare's[57] definition for the Euler angles, which agrees with that of other standard angular momentum texts (for example, Brink and Satchler[138]; see also Larsson[139] for a discussion of the different conventions) is adopted here. The normalization factor implies that $\gamma = 0$, which is a standard convention for linear molecules[57]. The quantum numbers of the D -function consist of $\vec{J} = \vec{L} + \vec{S} + \vec{l}$, the total angular momentum (neglecting nuclear spin), M_J is the projection of \vec{J} on the space-fixed z axis; and $\Omega = \Lambda + \Sigma$, the projection of J on the body-frame z' axis (taken to be the internuclear axis). The electronic spatial wave function is represented by ϕ , which depends on the projection of the total electronic angular momentum \vec{L} onto the internuclear axis Λ and on the the body-fixed inversion quantum number w that distinguishes gerade (g) and ungerade (u) states. The complete expression for ϕ is worked out later. The total electronic spin and its projection onto the internuclear axis is represented by $|S \Sigma \rangle$. Since, the 0_g^- experiment did not resolve hyperfine structure our analysis is simplified by quantizing the nuclear spin $|I M_I \rangle$ in the lab frame. Finally, $F_{J, \Lambda}(R)$ represents the radial wave function.

First, the electronic orbitals that comprise ϕ must be constructed such that ϕ is an eigenfunction of both \hat{P}_e and \hat{i} . We are primarily interested in the molecular wave function at large R , where there is negligible overlap of the electronic charge distributions. There, ϕ can be expressed in terms of properly symmetrized linear

combinations of atomic orbitals U_{L_c} [140]:

$$\begin{aligned} \phi(\Lambda, w) = N \{ & [U_{L_c}^a(\vec{r}_1)U_{L_d}^b(\vec{r}_2)]_\Lambda + (-1)^n [U_{L_c}^a(\vec{r}_2)U_{L_d}^b(\vec{r}_1)]_\Lambda + \\ & (-1)^{n'} [U_{L_d}^a(\vec{r}_1)U_{L_c}^b(\vec{r}_2)]_\Lambda + (-1)^{n''} [U_{L_d}^a(\vec{r}_2)U_{L_c}^b(\vec{r}_1)]_\Lambda \} . \end{aligned} \quad (6.7)$$

Here, N is a normalization constant and the phase factors n, n', n'' are to be determined. The notation $[U_{L_c}^a(\vec{r}_1)U_{L_d}^b(\vec{r}_2)]_\Lambda$ indicates an atomic orbital with quantum numbers $L_c(L_d)$ centered on atom $a(b)$ that is a function of electron 1(2)'s coordinates and Λ denotes the total projection of $\vec{L} = \vec{L}_c + \vec{L}_d$ onto the internuclear axis. Each atomic orbital has an associated spherical harmonic to represent its angular degrees of freedom, $Y_{L_i\lambda}(\theta_e, \chi_e)$, where the angles θ_e, χ_e are defined relative to the body-fixed coordinate system defined by the Euler angles α, β, γ , with the origin translated to coincide with the atomic center. The inversion of the electronic wave function through the center-of-mass of the body-fixed frame does two things: first it switches the orbitals, then it inverts each orbital about the new atomic center. This is equivalent to letting $\theta_e \rightarrow \pi - \theta_e$ and $\chi_e \rightarrow \pi + \chi_e$, which amounts to adding an additional phase factor to the spherical harmonic, $\hat{i}Y_{L_i\lambda}(\theta_e, \chi_e) = (-1)^{L_i}Y_{L_i\lambda}(\theta_e, \chi_e)$. Therefore, the effect of \hat{i} on each component of ϕ (Eq. 6.7) can be determined from the following:

$$\hat{i}[U_{L_c}^a(\vec{r}_1)U_{L_d}^b(\vec{r}_2)]_\Lambda = (-1)^{L_c+L_d}[U_{L_d}^a(\vec{r}_1)U_{L_c}^b(\vec{r}_2)]_\Lambda . \quad (6.8)$$

We can make ϕ in Eq. 6.7 an eigenfunction of \hat{i} by simply attaching $(-1)^{L_c+L_d+w}$ phase factors to the third and fourth components. The eigenvalue of \hat{i} is $(-1)^w$, where $w = 0$ defines a gerade (g) symmetry and $w = 1$ defines an ungerade (u) symmetry.

The electronic spin degrees of freedom must be included to antisymmetrize the electronic wave function with respect to electron exchange \hat{P}_e . The result when applied to a single component of ϕ (Eq. 6.7) is

$$\begin{aligned} \hat{P}_e [U_{L_c}^a(\vec{r}_1)U_{L_d}^b(\vec{r}_2)]_\Lambda |(s_a s_b)S\Sigma\rangle = & (-1)^{s_a+s_b-S} [U_{L_c}^a(\vec{r}_2)U_{L_d}^b(\vec{r}_1)]_\Lambda \\ & |(s_a s_b)S\Sigma\rangle , \end{aligned} \quad (6.9)$$

where the phase factor arises from the properties of Clebsch-Gordan coefficients. The electronic wave function must be odd under the permutation of two electrons, i.e.

$$\hat{P}_e \phi(\Lambda, w) |(s_a s_b)S\Sigma\rangle = -\phi(\Lambda, w) |(s_a s_b)S\Sigma\rangle . \quad (6.10)$$

In the case of two alkali atoms $s_a = s_b = 1/2$, this equality requires an additional $(-1)^S$ phase factor to be included in the second and fourth components of Eq. 6.7. The final result for the electronic orbital angular momentum wave function, which

is now an eigenfunction of both \hat{i} and \hat{P}_e , is

$$\begin{aligned} \phi(\Lambda, w) = & N \{ [U_{L_c}^a(\vec{r}_1)U_{L_d}^b(\vec{r}_2)]_\Lambda + (-1)^S [U_{L_c}^a(\vec{r}_2)U_{L_d}^b(\vec{r}_1)]_\Lambda + \\ & (-1)^{L_c+L_d+w} [U_{L_d}^a(\vec{r}_1)U_{L_c}^b(\vec{r}_2)]_\Lambda + \\ & (-1)^{L_c+L_d+w+S} [U_{L_d}^a(\vec{r}_2)U_{L_c}^b(\vec{r}_1)]_\Lambda \} . \end{aligned} \quad (6.11)$$

With the complete basis function defined, we now turn to the effect of the parity operator. Hougen[141] has shown that the parity operator acting on the total wave function is equivalent to $\hat{\pi}\Phi = \hat{\sigma}_v\Phi$, provided that $\hat{\sigma}_v$ acts on **all** degrees of freedom of the wave function. There is more than one plane that can be chosen to define the reflection operator $\hat{\sigma}_v$. We adopt Hougen's convention of reflecting through the $x'z'$ plane (see Ref.[139] for a discussion of the different approaches for this symmetry operation). First, the symmetry rules for the action of $\hat{\sigma}_{x',z'}$ on each component of Φ are provided and then a brief outline of their derivations is given. (The separation of the electronic orbital and spin degrees of freedom, as done here, is strictly valid only in one- and two-electron molecules[142]). The symmetry rules for the reflection operator are as follows:

$$\begin{aligned} \hat{\sigma}_{x',z'} D_{M\Omega}^{J*}(\alpha, \beta, \gamma) &= (-1)^{J-\Omega} D_{M-\Omega}^{J*}(\alpha, \beta, \gamma) \\ \hat{\sigma}_{x',z'} \phi(\Lambda, w) &= (-1)^\Lambda \phi(-\Lambda, w) \\ \hat{\sigma}_{x',z'} |S\Sigma\rangle &= (-1)^{S-\Sigma} |S-\Sigma\rangle \\ \hat{\sigma}_{x',z'} |IM_I\rangle &= |IM_I\rangle . \end{aligned} \quad (6.12)$$

There is an additional (-1) phase factor in the relationship for ϕ , if ϕ is a Σ^- electronic state. However, these states are ignored here because they do not factor into our analysis of the 0_g^- spectrum. The parity of a single basis function (Eq. 6.6) is found from these rules (Eq. 6.12) to be $(-1)^{J+S}$ for alkali atoms. A wave function with definite parity $(-1)^p$, which is also an eigenfunction of the symmetry operators \hat{i} and \hat{P}_e , is constructed with the following linear combination of basis functions:

$$\begin{aligned} \Psi_{\text{mol}} = & \sqrt{\frac{2J+1}{4\pi(2-\delta_{\Sigma,0}\delta_{\Lambda,0})}} [D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \phi(\Lambda, w) |S\Sigma\rangle + \\ & (1-\delta_{\Sigma,0}\delta_{\Lambda,0})(-1)^{J+S+p} D_{M-\Omega}^{J*}(\alpha, \beta, \gamma) \phi(-\Lambda, w) |S-\Sigma\rangle] \\ & |IM_I\rangle F_{J,\Lambda}(R) , \end{aligned} \quad (6.13)$$

provided ϕ is constructed according to Eq. 6.11.

The effect of the reflection operator $\sigma_{x',z'}$, which is a sense-reversing symmetry operation, on the rotational degrees of freedom is nontrivial. Hougen discusses the problem at length and eventually adopts the following scheme: $\sigma_{x',z'} D_{M\Omega}^{J*} = C_2(y') D_{M\Omega}^J$. Here, $C_2(y')$ defines a π radians rotation about the y' axis. The outcome of this convention is that $\hat{\sigma}_{x',z'}\Phi$ is equivalent to a π rotation of the molecule-

fixed coordinate system about an axis perpendicular to the internuclear axis (y'), followed by the reflection of all other wave function coordinates through the plane defined by (x', z') . The π rotation about y' amounts to changing the Euler angles by $\alpha \rightarrow \pi + \alpha$, $\beta \rightarrow \pi - \beta$, and $\gamma \rightarrow \pi - \gamma$. Standard identities[57] for the D -functions can be used to determine the symmetry rule for the rotational piece of the factored wave function,

$$D_{M\Omega}^{J*}(\pi + \alpha, \pi - \beta, \pi - \gamma) = (-1)^{(J-\Omega)} D_{M-\Omega}^{J*}(\alpha, \beta, \gamma). \quad (6.14)$$

To assess the effects of $\hat{\sigma}_{x',z'}$ on $\phi(\Lambda, w)$, note that reflection of electronic orbital angular momentum through the x', z' is equivalent to changing the angle $\chi_e \rightarrow -\chi_e$. Each spherical harmonic then transforms as $Y_{L\lambda}(\theta_e, -\chi_e) = Y_{L\lambda}^*(\theta_e, \chi_e) = (-1)^\lambda Y_{L-\lambda}(\theta_e, \chi_e)$. The total wave function acquires the phase factor $(-1)^{(\lambda+\lambda')} = (-1)^\lambda$. Finally, the action of $\hat{\sigma}_{x',z'}$ on the electronic spin would have no effect if it was quantized in the lab frame (as is the case with $|I, M_I\rangle$). Rotating the electronic spin wave function into the space-fixed frame,

$$|SM_S\rangle = \sum_{\Sigma} D_{M_S, \Sigma}^{S*}(\alpha, \beta, \gamma) |S\Sigma\rangle, \quad (6.15)$$

the reflection $\hat{\sigma}_{x',z'}$ of the spin wave function becomes

$$\begin{aligned} \hat{\sigma}_{x',z'} |S, M_S\rangle &= \sum_{\Sigma} [\hat{\sigma}_{x',z'} D_{M_S, \Sigma}^{S*}(\alpha, \beta, \gamma)] [\hat{\sigma}_{x',z'} |S\Sigma\rangle] \\ &= \sum_{\Sigma} (-1)^{S-\Sigma} D_{M_S-\Sigma}^{S*}(\alpha, \beta, \gamma) [\hat{\sigma}_{x',z'} |S\Sigma\rangle]. \end{aligned} \quad (6.16)$$

Thus the lab frame spin wave function will remain invariant only if $\hat{\sigma}_{x',z'} |S\Sigma\rangle = (-1)^{S-\Sigma} |S-\Sigma\rangle$.

The nuclear permutation operator acting on the total wave function provides nuclear selection rules. Hougen has shown[141] that this operation is equivalent to $\hat{P}_n \Psi = \hat{i} \hat{\pi} \hat{P}_I \Psi$, where \hat{P}_I only permutes the nuclear spins. We have already evaluated $\hat{\pi} \hat{\Phi}$, as well as $\hat{i} \hat{\Phi}$, which acts only on the electronic orbital. Therefore, applying \hat{P}_n to the wave function in Eq. 6.13, gives:

$$\hat{P}_n \Psi_{\text{mol}} = (-1)^{p+w+I-i_a-i_b} \Psi_{\text{mol}}. \quad (6.17)$$

For the bosonic alkali atoms, which have half-integer nuclear spins, the wave function must be odd under permutation of the nuclei and therefore the equality $(-1)^{p+w+I} = 1$ must be satisfied. It is necessary to include an additional $[1 + (-1)^{p+w+I}]/2$ term in the wave function (Eq. 6.13) to ensure that it is also an eigenfunction of \hat{P}_n . The final expression for the wave function, which has definite parity, and is an eigen-

function of \hat{i} , \hat{P}_e , and \hat{P}_n is then

$$\begin{aligned} \Psi_{\text{mol}} = & \sqrt{\frac{2J+1}{4\pi(2-\delta_{\Sigma,0}\delta_{\Lambda,0})}} \left(\frac{1+(-1)^{p+w+I}}{2} \right) |IM_I\rangle F_{J,\Lambda}(R) \quad (6.18) \\ & [D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \phi(\Lambda, w) |S\Sigma\rangle + \\ & (1-\delta_{\Sigma,0}\delta_{\Lambda,0})(-1)^{J+S+p} D_{M-\Omega}^{J*}(\alpha, \beta, \gamma) \phi(-\Lambda, w) |S-\Sigma\rangle] . \end{aligned}$$

We are primarily interested in the consequences of these symmetry relationships for the $^{39}\text{K } 0_g^-$ electronic state, i.e. $\Omega = 0$. The rotational levels of an $\Omega = 0$ state have a definite parity and therefore have definite nuclear spin selection rules. This is simply because one way to construct an $\Omega = 0$ wave function is with a single basis function (note the $\delta_{\Sigma,0}\delta_{\Lambda,0}$ function in Eq. 6.18). These individual basis functions (Eq. 6.6) have parity $(-1)^{J+S}$ and the bosonic nuclear permutation symmetry requires $(-1)^{J+S+w+I} = 1$. In the next section, it will be shown that the 0_g^- electronic state is a triplet ($S = 1$) spin state. Therefore, the odd J rotational energy levels have positive parity and the even J rotational energy levels have negative parity. In addition, the nuclear permutation symmetry requires $(-1)^{J+I} = -1$, which limits the nuclear spin states that can contribute to each rotational level. These selection rules play a large role in the analysis of the measured 0_g^- spectra.

6.3 Excited and ground state Hamiltonians

This section is divided into two parts, the bulk of which is presented in 6.3.1. Here, the interactions and general matrix structure for the excited state Hamiltonian are presented. First, the general excited state molecular Hamiltonian is developed and the approximations employed in the analysis of the 0_g^- state are detailed. Next for completeness, the ground state Hamiltonian needed for the analysis presented in Chapter 7 is provided in Section 6.3.2.

6.3.1 $S + P$ Hamiltonian

The interactions that comprise the $S + P$ Hamiltonian include those listed in Section 2.2 and the atomic spin-orbit interaction H^{so} . The zero-field total Hamiltonian is thus composed of the following components:

$$H = H^{\text{BO}} + H^{\text{so}} + H^l + H^{\text{ss}} + H^{\text{hf}} \quad (6.19)$$

where H^{BO} includes the Born-Oppenheimer potentials, H^l is the rotational Hamiltonian, H^{ss} represents the magnetic dipole-dipole interaction, and H^{hf} is the hyperfine interaction. The Hamiltonian is constructed in a Hund's case (a) molecular representation, which will be a convenient representation for evaluating the dipole matrix element. The Born-Oppenheimer potentials that correlate asymptotically with the S

+ P threshold depend on the total spin \vec{S} , the projection of the electronic angular momentum on the internuclear axis Λ , and also the inversion symmetry of the electronic wave function in the molecular frame, labeled g (even) or u (odd). There are thus eight unique Born-Oppenheimer potentials for the alkali atoms, labeled $^{2S+1}\Lambda_{g/u}$, and H^{BO} is an 8×8 diagonal matrix in the Hund's case (a) representation.

The good quantum numbers in the Hund's case (c)[137] angular momentum coupling scheme (neglecting nuclear spin) are the total angular momentum $\vec{J} = \vec{L} + \vec{S} + \vec{l}$ and its projection onto the internuclear axis $\Omega = \Lambda + \Sigma$. The nuclear rotation (or partial wave) \vec{l} is oriented at right angles to the internuclear axis. The Hund's case (c) labels become appropriate when the strength of the spin-orbit interaction H^{so} becomes at least comparable to the energy splittings between the Born-Oppenheimer potentials H^{BO} . Spin-orbit matrix elements in a Hund's case (a) representation have been evaluated in Ref.[143] and are reproduced here (Δ is the atomic spin-orbit splitting):

$$\begin{aligned}
\langle {}^3\Lambda_w, \Sigma | H^{\text{so}} | {}^3\Lambda'_{w'}, \Sigma' \rangle &= \frac{\Delta}{3} \delta_{w,w'} [\Lambda \Sigma \delta_{\Lambda, \Lambda'} \delta_{\Sigma, \Sigma'} + \delta_{\Lambda, \Lambda'-1} \delta_{\Sigma, \Sigma'+1} \\
&\quad + \delta_{\Lambda, \Lambda'+1} \delta_{\Sigma, \Sigma'-1}] \\
\langle {}^1\Lambda_w, \Sigma | H^{\text{so}} | {}^3\Lambda'_{w'}, \Sigma' \rangle &= -\frac{\Delta}{3} \delta_{w,w'} [\Lambda \delta_{\Lambda, \Lambda'} \delta_{\Sigma, 0} - \delta_{\Lambda, \Lambda'-1} \delta_{\Sigma, -1} \\
&\quad + \delta_{\Lambda, \Lambda'+1} \delta_{\Sigma, +1}] \\
\langle {}^1\Lambda_w, \Sigma | H^{\text{so}} | {}^1\Lambda'_{w'}, \Sigma' \rangle &= 0.
\end{aligned} \tag{6.20}$$

The atomic spin-orbit interaction H^{so} breaks the electronic spin projection degeneracy, resulting in 24 Hund's case (c) electronic states. These 24 states can be broken down into four different six-channel blocks which correspond to a definite parity and definite g/u symmetry. In addition, the Hamiltonian $H = H^{\text{BO}} + H^{\text{so}}$ is block diagonal with respect to the value of Ω . Nonvanishing contributions of $H^{\text{BO}} + H^{\text{so}}$ are illustrated in figures 6.1 and 6.2 for opposite parity states.

Evaluation of the rotational Hamiltonian $H^l = \frac{1}{2\mu R^2} \vec{l}^2$ in a Hund's case (a) representation is simplified by first decomposing the nuclear rotation angular momentum vector $\vec{l} = \vec{J} - \vec{L} - \vec{S}$, and then using the commutation properties of each Cartesian component of these operators, i.e. $[J_i, S_i] = 0$. The final expression for H^l , written in terms of the angular momentum operators J, L, S , is[53]

$$\begin{aligned}
H^l &= \frac{1}{2\mu R^2} [(J^2 - J_{z'}^2) + (L^2 - L_{z'}^2) + (S^2 - S_{z'}^2) \\
&\quad + (L_+ S_- + L_- S_+) - (J_+ L_- + J_- L_+) - (J_+ S_- + J_- S_+)] \tag{6.21}
\end{aligned}$$

where $J_{\pm} = J_{x'} \pm iJ_{y'}$ represents standard raising and lowering operators defined in the body-fixed coordinate system, (L_{\pm} and S_{\pm} are defined similarly). There are two difficulties with this expression. First, Hund's case (a) wave functions are not

$0^-_{g/u}$ parity

	${}^3\Pi_{g/u}(\Omega=0)$	${}^3\Sigma^+_{g/u}(\Omega=0)$	${}^3\Pi_{g/u}(\Omega=1)$	${}^3\Sigma^+_{g/u}(\Omega=1)$	${}^1\Pi_{g/u}(\Omega=1)$	${}^3\Pi_{g/u}(\Omega=2)$
${}^3\Pi_{g/u}(\Omega=0)$	$H^{\text{BO}}+H^{\text{so}}+H^l$	$H^{\text{so}}+H^l$	H^l	H^l	0	0
${}^3\Sigma^+_{g/u}(\Omega=0)$	$H^{\text{so}}+H^l$	$H^{\text{BO}}+H^l$	H^l	H^l	0	0
${}^3\Pi_{g/u}(\Omega=1)$	H^l	H^l	$H^{\text{BO}}+H^l$	$H^{\text{so}}+H^l$	H^{so}	H^l
${}^3\Sigma^+_{g/u}(\Omega=1)$	H^l	H^l	$H^{\text{so}}+H^l$	$H^{\text{BO}}+H^l$	H^{so}	H^l
${}^1\Pi_{g/u}(\Omega=1)$	0	0	H^{so}	H^{so}	$H^{\text{BO}}+H^l$	0
${}^3\Pi_{g/u}(\Omega=2)$	0	0	H^l	H^l	0	$H^{\text{BO}}+H^{\text{so}}+H^l$

Figure 6.1: Block Structure of the 6×6 $S + P$ Hamiltonian. The parity $(-1)^p = (-1)^{J+1}$ of the eigenfunctions composing the matrix elements is determined by the symmetry rules for the $0^-_{g/u}$ electronic state. The structure of this matrix is the same for both g and u symmetries. The origin of the nonzero matrix elements are indicated by $H^{\text{BO}} \equiv$ Born-Oppenheimer potentials, $H^{\text{so}} \equiv$ spin-orbit interaction, and $H^l \equiv$ the rotational Hamiltonian.

$0^+_{g/u}$ parity

	$^3\Pi_{g/u}(\Omega=0)$	$^1\Sigma^+_{g/u}(\Omega=0)$	$^3\Pi_{g/u}(\Omega=1)$	$^3\Sigma^+_{g/u}(\Omega=1)$	$^1\Pi_{g/u}(\Omega=1)$	$^3\Pi_{g/u}(\Omega=2)$
$^3\Pi_{g/u}(\Omega=0)$	$H^{BO} + H^{so} + H^I$	H^I	H^I	H^I	0	0
$^1\Sigma^+_{g/u}(\Omega=0)$	H^I	$H^{BO} + H^I$	H^I	H^I	0	0
$^3\Pi_{g/u}(\Omega=1)$	H^I	H^I	$H^{BO} + H^I$	$H^{so} + H^I$	H^{so}	H^I
$^3\Sigma^+_{g/u}(\Omega=1)$	H^I	H^I	$H^{so} + H^I$	$H^{BO} + H^I$	H^{so}	H^I
$^1\Pi_{g/u}(\Omega=1)$	0	0	H^{so}	H^{so}	$H^{BO} + H^I$	0
$^3\Pi_{g/u}(\Omega=2)$	0	0	H^I	H^I	0	$H^{BO} + H^{so} + H^I$

Figure 6.2: Opposite parity block as that shown in Fig. 6.1 (with same notation for nonzero matrix elements). The eigenfunctions composing these matrix elements have a $(-1)^p = (-1)^J$ parity which can be derived from the symmetry rules for a $0^+_{g/u}$ electronic state. In the absence of rotation, the \pm parity eigenstates are degenerate for $\Omega = 1$ and 2

eigenfunctions of \vec{L}^2 . However, electronic orbitals constructed in the separated atom limit, as in Section 6.2, can be treated as approximate eigenfunctions of \vec{L}^2 . The second difficulty is that the total angular momentum J in the body-fixed frame obeys anomalous commutation rules[57], i.e. $[J_{x'}, J_{y'}] = -iJ_{z'}$. A standard approach[57] for resolving the anomalous commutation problem is to redefine the raising and lowering operators such that $J_{\pm} \rightarrow J_{\mp}$. Matrix elements for H^l in a Hund's case (a) representation have been evaluated in Ref.[141].

The matrix structure of H^l in the Hund's case (a) representation can be determined from the operators comprising the Hamiltonian (Eq. 6.21). The first three terms in Eq. 6.21 are diagonal in the Hund's case (a) representation. The fourth term ($\propto L_+ S_-$) gives rise to rotational coupling within a constant Ω block of the Hamiltonian. The last two terms are responsible for electronic-rotational couplings and are often denoted as Coriolis couplings. The rotational Hamiltonian preserves the g/u symmetry of the electronic wave function and therefore preserves the block diagonal matrix structure of H . This is illustrated in figures 6.1 and 6.2. Finally the matrix values of H^{ss} , which are diagonal in a Hund's case (a) representation, were given in Section 2.2.3. These matrix elements are relatively small in the excited state (roughly 10^{-5} the value of the Born-Oppenheimer potentials at large R) and are neglected. In addition, H^{hf} is neglected in the analysis presented in Chapter 7. In Ref.[21], it was shown that the bound state energies of the lowest few vibrational levels of the 0_g^- state were essentially independent of the hyperfine interaction.

In practice, 0_g^- potentials that accurately describe the lowest few vibrational levels are obtained by considering only $H^{BO} + H^{so}$, along with the diagonal elements of the rotational Hamiltonian H^l (the $\Omega=0$ off-diagonal rotational coupling elements for ^{39}K are of the order $\sim 1/\mu$ times smaller than the spin-orbit coupling). This results in the following 2×2 matrix in the representation (${}^3\Pi_g, {}^3\Sigma_g^+$):

$$\underline{H} = \begin{pmatrix} V_{\Pi} + V_{\Pi}^l - \frac{\Delta}{3} & \frac{\sqrt{2}}{3} \Delta \\ \frac{\sqrt{2}}{3} \Delta & V_{\Sigma} + V_{\Sigma}^l \end{pmatrix} \quad (6.22)$$

where $\Delta = 57.706 \text{ cm}^{-1}$ represents the atomic spin-orbit splitting. The Born-Oppenheimer potentials at large R are well-approximated by a multipole expansion,

$$V_{\Lambda'} = -f^{\Pi/\Sigma} \frac{C_3^{\Pi/\Sigma}}{R^3} - \frac{C_6^{\Pi/\Sigma}}{R^6} - \frac{C_8^{\Pi/\Sigma}}{R^8}, \quad (6.23)$$

and the ^{39}K dispersion coefficients were taken from Ref.[144]. Retardation effects are also incorporated in $f^{\Pi/\Sigma}$. These have the form[145]

$$\begin{aligned} f^{\Pi} &= \cos(R/\lambda) + (R/\lambda) \sin(R/\lambda) - (R/\lambda)^2 \cos(R/\lambda) \\ f^{\Sigma} &= \cos(R/\lambda) + (R/\lambda) \sin(R/\lambda). \end{aligned} \quad (6.24)$$

Here, $\lambda = \lambda_{4S \rightarrow 4P} / 2\pi$ is the transition wavelength. The rotational matrix elements $V_{\Lambda'}^l$ incorporate only the first three terms from Eq. 6.21 and are given explicitly by

$$\begin{aligned} V_{\Pi}^l &= \frac{\hbar^2}{2\mu R^2} [J'(J' + 1) + 2] \\ V_{\Sigma}^l &= \frac{\hbar^2}{2\mu R^2} [J'(J' + 1) + 4] . \end{aligned} \quad (6.25)$$

The J' -dependent 0_g^- potentials, $V^{J'}$, are determined by first diagonalizing Eq. 6.22 and then incorporating non-adiabatic diagonal corrections[78]. Bound state energies $E_{v', J'}$ and single channel wave functions $\chi_{v', J'}(R)$ are now easily obtained for the potentials $V^{J'}$. The radial part of the excited state wave function Ψ_b is then conveniently written as an R -dependent linear combination of the two Hund's case (a) basis functions

$$F_b(R) = \sum_{\Lambda'} b_{J', \Lambda'}(R) \chi_{v', J'}(R) \quad (6.26)$$

where $b_{J'}(R)$ is the eigenvector obtained from the diagonalization of Eq. 6.22 that correlates with the potential whose asymptote is $S_{1/2} + P_{3/2}$. This form (6.26) facilitates the evaluation of the dipole matrix element.

6.3.2 $S + S$ Hamiltonian

The ground state Hamiltonian has already been described in detail in Section 2.2. Here, I briefly outline the pertinent details needed for the analysis presented in Chapter 7. The ^{39}K photoassociation experiment[146] was conducted with unpolarized $f_a = f_b=1$ ground state atoms trapped in a dark-spot MOT with cloud temperatures of $\sim 400 \mu\text{K}$. The experiment resolved $J'=0-4$ rotational peaks for a number of vibrational levels. Since no rotational lines were observed with $J' > 4$, it was only necessary to include partial waves up to $l=2$ in the analysis ($\vec{J} = \vec{l} + \vec{L} + \vec{S}$, $L=1$, $S=1$). Neglecting the magnetic dipole interaction, the Hamiltonian for collisions among $f_a=1$ atoms can be separated into five pieces (see Table 5.1). These include $f=0,2$ s -wave and d -wave components, and an $f = 1$ p -wave component. The analysis required thermal averaged radial wave functions for each Hamiltonian. However, the nonzero radial overlap of the ground state wave function and the 0_g^- excited state wave function occurs at $R > 40$ a.u.. Therefore, the MQDT method outlined in Chapter 4 provides an extremely efficient method for generating these wave functions. A single $\underline{K}^{\text{sr}}$ matrix calculated at $E = 0$ for each Hamiltonian (which are functions of the singlet and triplet scattering length and the C_6 coefficient) proved sufficient to obtain accurate radial overlaps over the entire energy range $E = 0-3$ mK required for the thermal average. A comparison of the integrated radial overlaps using MQDT-generated ground state wave functions and FEM R-

matrix generated wave functions is shown in Fig. 6.3.

6.4 Dipole matrix element

The molecular dipole matrix element needed to evaluate the rate constant K_p (Eq. 6.5) is constructed in this section. This derivation provides “nuts and bolts” intermediate steps. The reader more interested in the photoassociation analysis can skip ahead to the next chapter without loss of continuity. The approach detailed here is to first evaluate the molecular dipole matrix in a Hund’s case (a) molecular representation and then to project the ground state molecular wave function onto coupled hyperfine states.

The excited Ψ'_{mol} and ground state Ψ_{mol} molecular wave functions are assumed to have the form given in Eq. 6.18. The radial piece of the wave function will be neglected in the intermediate steps since it has no bearing on the angular momentum algebra. The electronic orbital angular momentum ϕ piece of the factored wave function can be constructed from Eq. 6.11. The excited state orbital is given by:

$$\begin{aligned} \phi(\Lambda', w') = \frac{1}{2} \left\{ [S^a(r_1)P^b(r_2)]_{\Lambda'} + (-1)^{S'} [S^a(r_2)P^b(r_1)]_{\Lambda'} + \right. \\ \left. (-1)^{w'+1} [S^b(r_1)P^a(r_2)]_{\Lambda'} + (-1)^{S'+w'+1} [S^b(r_2)P^a(r_1)]_{\Lambda'} \right\}, \end{aligned} \quad (6.27)$$

and the ground state orbital is given by the expression:

$$\phi(0, w = S) = \frac{1}{\sqrt{2}} \left\{ [S^a(r_1)S^b(r_2)] + (-1)^S [S^a(r_2)S^b(r_1)] \right\}. \quad (6.28)$$

Here, the orbitals are designated by the L_i quantum numbers, i.e. S^a represents an atomic S -orbital on atom a . Primed and unprimed quantities are used to denote excited state and ground state quantum numbers, respectively. The molecular dipole operator $d(\vec{R})$ is approximated as the sum of two atomic dipole operators, which can be rotated into the body-fixed frame as follows:

$$d(\vec{R}) = \sum_q D_{mq}^{1*} [d_q(r_1) + d_q(r_2)]. \quad (6.29)$$

Here, $d_q(r_i)$ is an atomic dipole operator that acts only on electron i . This ensures that only one electron absorbs a photon at a time. The quantum numbers q and m refer to the projection of the dipole operator onto the body-fixed and space-fixed frames, respectively. The dipole matrix element for an $S \rightarrow P$ transition in the

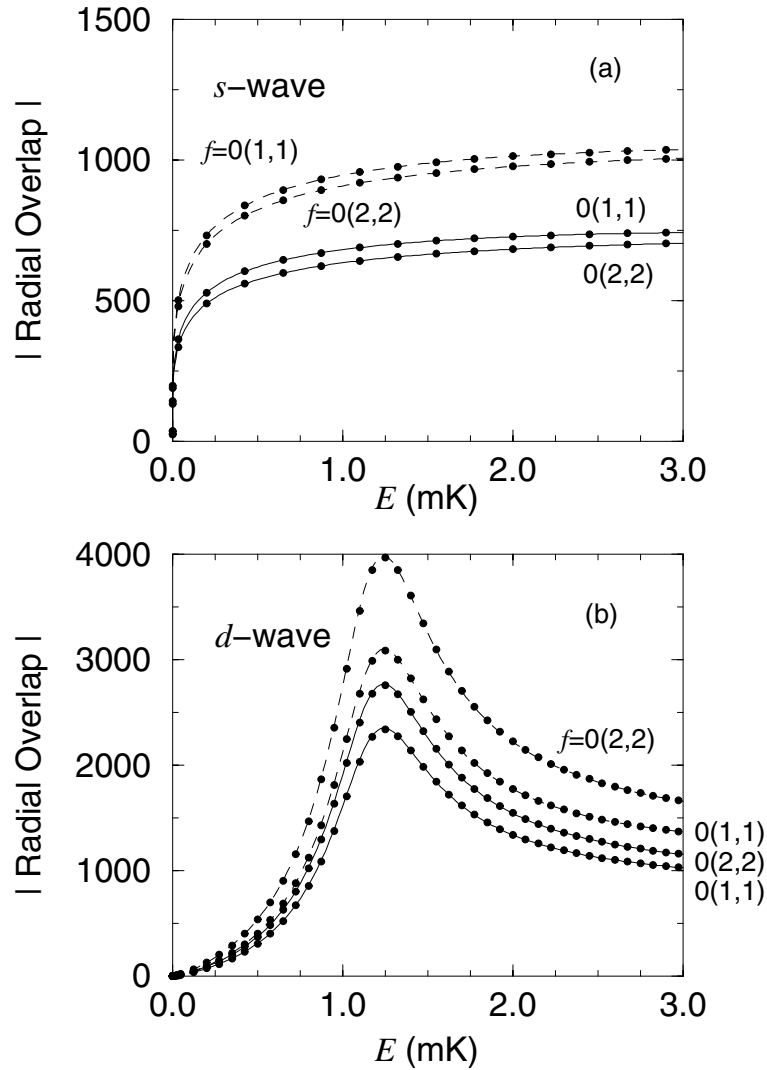


Figure 6.3: ^{39}K Franck-Condon overlaps of the $v'=0$, $J'=2$, 0_g^- rovibrational level with a $f = 0$ s -wave state (a) and a $f = 0$ d -wave state (b) are compared using two different methods to calculate the ground state wave functions. These were: 1) MQDT approach (Eq. 4.35) using a constant $\underline{K}^{\text{sr}}$ calculated at $E=0$, denoted by the solid and dashed lines and a 2) FEM \underline{R} -matrix approach. The FEM \underline{R} -matrix calculations are denoted by the closed circles. Each graph shows the absolute value of the four components that comprise the total overlap. Each component depends on the f_a, f_b ground state quantum numbers and the excited state Λ' quantum number. The $f(f_a, f_b)$ quantum numbers are labeled on the graph. A solid line represents the $\Lambda' = 0$ state, and a dashed line is used for the $\Lambda' = 1$ state. The presence of a $f = 0$ d -wave shape resonance near 1.2 mK is evident from the radial overlaps in (b).

Hund's case (a) representation is given by the following expression:

$$\begin{aligned}
\langle \Psi'_{\text{mol}} | d(\vec{R}) | \Psi_{\text{mol}} \rangle &= \delta_{I',I} \delta_{M'_I, M_I} \delta_{S',S} \delta_{\Sigma',\Sigma} \sqrt{\frac{1}{(2 - \delta_{\Lambda',0} \delta_{\Sigma',0})(2 - \delta_{\Sigma,0})}} \times \\
&\left(\frac{1 + (-1)^{p'+I'+w'}}{2} \right) \left(\frac{1 + (-1)^{p+I+w}}{2} \right) \times \quad (6.30) \\
&\sqrt{\frac{(2J'+1)(2J+1)}{16\pi^2}} \times \\
&\sum_q \left[\langle \phi(\Lambda', w') | d(\vec{R}) | \phi(0, w) \rangle \int d\Omega D_{M'_J \Omega'}^{J'} D_{mq}^{1*} D_{M_J \Omega}^J \right. \\
&+ (-1)^{p'+p+J'+J} (1 - \delta_{\Lambda',0} \delta_{\Sigma',0}) (1 - \delta_{\Sigma,0}) \times \\
&\left. \langle \phi(-\Lambda', w') | d(\vec{R}) | \phi(0, w) \rangle \int d\Omega D_{M'_J -\Omega'}^{J'} D_{mq}^{1*} D_{M_J -\Omega}^J \right]
\end{aligned}$$

First, the electronic dipole piece of this expression is evaluated:

$$\langle \phi(\Lambda', w') | d(\vec{R}) | \phi(0, w) \rangle = \frac{d \delta_{\Lambda',q}}{\sqrt{2}} \left[1 + (-1)^{S+1+w'} \right]. \quad (6.31)$$

Evaluating the second dipole term in Eq. 6.30 leads to the same result after replacing $\delta_{\Lambda',q} \rightarrow \delta_{-\Lambda',q}$. The constant d represents the atomic dipole matrix element. Next, the integrals over the rotational functions are evaluated:

$$\begin{aligned}
\sqrt{\frac{(2J'+1)(2J+1)}{16\pi^2}} \int d\Omega D_{M'_J \Omega'}^{J'} D_{mq}^{1*} D_{M_J \Omega}^J &= \quad (6.32) \\
\sqrt{\frac{(2J+1)}{(2J'+1)}} \langle JM_J, 1m | J'M'_J \rangle \langle J\Omega, 1q | J'\Omega' \rangle
\end{aligned}$$

The same result is obtained for the second integral in Eq. 6.30 except $\Omega \rightarrow -\Omega$ and $\Omega' \rightarrow -\Omega'$. The final expression for the Hund's case (a) dipole matrix element is

given by:

$$\begin{aligned}
\langle \Psi'_{\text{mol}} | d(\vec{R}) | \Psi_{\text{mol}} \rangle &= \frac{d}{\sqrt{2}} \delta_{I',I} \delta_{M'_I, M_I} \delta_{S',S} \delta_{\Sigma',\Sigma} \left(\frac{1 + (-1)^{p'+I'+w'}}{2} \right) \times \\
&\quad \left(\frac{1 + (-1)^{p+I+w}}{2} \right) \left(1 + (-1)^{S+1+w'} \right) \times \\
&\quad \left[1 + (-1)^{p'+p+1} (1 - \delta_{\Lambda',0} \delta_{\Sigma',0}) (1 - \delta_{\Sigma,0}) \right] \times \\
&\quad \sqrt{\frac{1}{(2 - \delta_{\Lambda',0} \delta_{\Sigma',0}) (2 - \delta_{\Sigma,0})}} \sqrt{\frac{(2J+1)}{(2J'+1)}} \times \\
&\quad \langle JM_J, 1m | J' M'_J \rangle \langle J\Omega, 1\Lambda' | J'\Omega' \rangle. \tag{6.33}
\end{aligned}$$

The first two factors in parentheses enforce the nuclear permutation symmetry rules for the excited state and ground state, respectively. The third factor in parentheses guarantees the $g \leftrightarrow u$ dipole selection rule is obeyed. This can be seen from the $(-1)^{S+1+w'}$ phase factor and recalling that $(-1)^S$ determines the ground state g/u symmetry. The fourth factor in parentheses ensures that only terms of opposite parity are coupled. The first Clebsch-Gordan coefficient guarantees that the dipole selection rules $m + M_J = M'_J$ and $J' = J, J \pm 1$ (excluding $J' = J = 0$ transitions) are satisfied.

Next, the transformation from the Hund's case (a) basis into the coupled hyperfine representation is needed for the ground state wave function. Each component (f_a, f_b) of the multichannel wave function in the coupled hyperfine representation has the form

$$\begin{aligned}
\Psi_{\text{hf}} &= \left(\frac{1 + (-1)^{f+l}}{2} \right) \frac{1}{\sqrt{2 - \delta_{f_a, f_b}}} F_{(f_b f_a) f l}^E(R) \times \\
&\quad [|(f_a f_b) f m_f, l m_l \rangle + (-1)^{f+l-f_a-f_b} (1 - \delta_{f_a, f_b}) |(f_b f_a) f m_f, l m_l \rangle], \tag{6.34}
\end{aligned}$$

where $F_{(f_b f_a) f l}^E(R)$ represents a component of the energy-normalized radial wave function. The transformation matrix element that connects the ground state molecular wave function $\Psi_{\text{mol}}(J, M_J, \Omega, S, \Sigma, I, M_I, p, w)$ with the ground state coupled

hyperfine wave function $\Psi_{\text{hf}}((f_a f_b) f m_f, l m_l)$ is given by:

$$\begin{aligned}
 \langle \Psi_{\text{mol}} | \Psi_{\text{hf}} \rangle &= \sqrt{\frac{(2f_a + 1)(2f_b + 1)(2S + 1)(2I + 1)(2l + 1)}{(2J + 1)(2 - \delta_{\Sigma,0})(2 - \delta_{f_a, f_b})}} \times \quad (6.35) \\
 &[1 + (1 - \delta_{\Sigma,0}) + (-1)^{l+S+I}(1 - \delta_{f_a, f_b}) \\
 &+ (-1)^{l+S+I}(1 - \delta_{\Sigma,0})(1 - \delta_{f_a, f_b})] \langle S\Sigma, l0 | J\Omega \rangle \times \\
 &\begin{pmatrix} s_a & i_a & f_a \\ s_b & i_b & f_b \\ S & I & f \end{pmatrix} \sum_{M_S} \langle SM_S, IM_I | f m_f \rangle \langle SM_S, l m_l | JM_J \rangle .
 \end{aligned}$$

The final result for the dipole matrix element that couples the excited state wave function $\Psi'_{\text{mol}}(J', M'_J, \Omega', \Lambda', S'\Sigma', p', w')$ with the ground state hyper-

fine wave function Ψ_{hf} is obtained from equations 6.33 and 6.35:

$$\begin{aligned}
\langle \Psi'_{\text{mol}} | d(\vec{R}) | \Psi_{\text{hf}} \rangle &= \sum_{J, M_J, \Omega, S, \Sigma} \langle \Psi'_{\text{mol}} | d(\vec{R}) | \Psi_{\text{mol}} \rangle \langle \Psi_{\text{mol}} | \Psi_{\text{hf}} \rangle \quad (6.36) \\
&= \frac{d}{\sqrt{2}} \sum_J \left(\frac{1 + (-1)^{p'+I'+w'}}{2} \right) \left(\frac{1 + (-1)^{l+I'+S'}}{2} \right) \\
&\quad \left(\frac{1 + (-1)^{f+l}}{2} \right) \left(1 + (-1)^{S'+w'+1} \right) \times \\
&\quad \left[1 + (-1)^{J'+p'+J+l} (1 - \delta_{\Lambda',0} \delta_{\Sigma',0}) (1 - \delta_{\Sigma',0}) \right] \times \\
&\quad \left[1 + (1 - \delta_{\Sigma',0}) + (-1)^{l+S'+I'} (1 - \delta_{f_a, f_b}) \right. \\
&\quad \left. + (-1)^{l+S'+I'} (1 - \delta_{\Sigma',0}) (1 - \delta_{f_a, f_b}) \right] \times \\
&\quad \langle J M'_J - m, 1m | J' M'_J \rangle \langle J \Omega' - \Lambda', 1\Lambda' | J' \Omega' \rangle \times \\
&\quad \langle S' M_f - M'_I, I' M'_I | f m_f \rangle \langle S' M_f - M'_I, l M_l | J M'_J - m \rangle \times \\
&\quad \begin{pmatrix} s_a & i_a & f_a \\ s_b & i_b & f_b \\ S & I & f \end{pmatrix} \langle S' \Sigma', l 0 | J \Omega' - \Lambda' \rangle \times \\
&\quad \int dR b_{J', \Lambda'}(R) \chi_{J'}(R) F_{(f_a, f_b) f l}^E(R).
\end{aligned}$$

Here, the excited state radial wave function has been written in terms of an adiabatic eigenvector, $F'_{J', \Lambda'}(R) = b_{J', \Lambda'}(R) \chi_{J'}(R)$ (see Eq. 6.26). The complete mod-squared dipole matrix element that is needed for the rate constant equation (Eq. 6.5) is given by a coherent sum of the dipole matrix elements in Eq. 6.36 over the internal quantum numbers of the excited and ground state wave functions, an incoherent average over all initial states, and an incoherent sum over all unresolved final states. For the particular experiment presented in Chapter 7, this expression is:

$$\begin{aligned}
\sum_{\beta' p' f l p \alpha} n_f (2l + 1) |\langle \Psi_{\beta' p' \beta'}^{v' J'}(R) | d_{f l p \alpha}^{J' p' \beta'}(R) | \Psi_{f l p \alpha}^E(R) \rangle|^2 &= \quad (6.37) \\
\frac{1}{N_{\{f_a, f_b\}}} \sum_{M'_J, I', M'_I} \sum_{f, M_f, l, M_l} \left| \sum_{\Lambda', f_a, f_b} \langle \Psi'_{\text{mol}} | d(\vec{R}) | \Psi_{\text{hf}} \rangle \right|^2 &\cdot
\end{aligned}$$

As a final test of this formulation, we have checked that all dipole selection rules are obeyed and that the lifetime of each rotational level (J', M'_j) of the 0_g^- state is equal to one half the atomic lifetime[128]. In addition, to ensure that all pieces of the theory were integrated properly, we have reproduced the Na 0_g^- spectra illustrated in Ref.[136].