Control of ultracold photodissociation with magnetic fields: Supplemental material

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This supplement summarizes our extension of the quantum mechanical theory of photodissociation to the situation where the total angular momentum is not a conserved quantum number, as is the case in our ultracold-molecule experiments with applied magnetic fields.

NOTATION

In the following theoretical description of quantum mechanical photodissociation, the notation follows Refs. [1, 2] with slight changes. The main symbols are as follows:

- $\mathbf{R} = (R, \Theta, \Phi)$: vector that connects the pair of atomic fragments. The angles Θ, Φ are defined relative to the molecular axis.
- $\{\mathbf{r}\}$: set of electronic coordinates of the atoms.
- $\mathbf{k} = (k, \theta, \phi)$: scattering wave vector of the photofragments. The angles θ, ϕ are defined relative to the z axis, the quantum axis in the lab frame.
- $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$: combined angular momentum of the atomic fragments.
- $m_j \equiv m$: projection of $\mathbf{j}$ onto the lab z axis.
- $\mathbf{l}$: orbital angular momentum of the atomic fragments about their center of mass.
- m_l: projection of $\mathbf{l}$ onto the lab z axis.
- $\mathbf{J} = \mathbf{j} + \mathbf{l}$: total angular momentum of the photodissociated system.
- $M = m_j + m_l$: projection of $\mathbf{J}$ onto the lab z axis.
- Ω: projection of $\mathbf{J}$ onto the molecular axis.

A novel aspect of this work is that the total angular momentum J is not conserved, while M is the rigorously conserved quantum number. To account for this, we introduce the indexed angular momenta J_R and J_k, where the subscripts R and k denote the "entrance" and "exit" channels for the continuum wave function of the photofragments.

PARAMETRIZATION OF THE PHOTOFRAGMENT ANGULAR DISTRIBUTION

For photodissociation of a diatomic molecule, the photofragment angular distribution (PAD) is given by the intensity function of the polar angle θ and azimuthal angle ϕ as

$$I(\theta, \phi) \propto \beta_0 \left(1 + \sum_{\mu=1}^{\infty} \sum_{\nu=0}^{\mu} \beta_{\mu\nu} P_\mu^\nu(\cos\theta) \cos(\nu\phi) \right), \quad (1)$$

where $P_\mu^\nu(\cos\theta)$ are the associated Legendre polynomials and $\beta_{\mu\nu}$ are anisotropy parameters. For the parallel polarization of light, the PADs are cylindrically symmetric (no ϕ dependence) [3], and we set $\beta_\mu \equiv \beta_{\mu 0}$ while all other $\beta_{\mu\nu}$ vanish.

THEORY OF PHOTODISSOCIATION IN A MAGNETIC FIELD

The photodissociation process is characterized by a differential cross section $\sigma(\hat{k}) = |f|^2$, defined by Fermi's golden rule with the electric-dipole (E1) transition operator. The corresponding scattering amplitude is

$$f \propto \langle \Psi_{\mathbf{k}}^{j m_j p_f}(\{\mathbf{r}\}, \mathbf{R}) | \hat{T}_{\text{E1}}^1 | \Psi_{J_i M_i}^{p_i}(\{\mathbf{r}\}, \mathbf{R}) \rangle, \qquad (2)$$

where $\Psi_{J_i M_i}^{p_i}(\{\mathbf{r}\}, \mathbf{R})$ and $\Psi_{\mathbf{k}}^{j m_j p_f}(\{\mathbf{r}\}, \mathbf{R})$ are the initial (bound-state) and final (continuum) wave functions. This description was first applied in the Born-Oppenheimer approximation in [4]. Furthermore, the treatment of triatomic photodissociation [5, 6] is useful for our diatomic case with additional internal atomic structure. Detailed derivation of photodissociation theory for individual magnetic sublevels is available in literature [1, 2, 7]. However, to the best of our knowledge, the wave functions in the presence of a magnetic field (eigenfunctions of the Zeeman Hamiltonian) have not been previously incorporated into the theory. Photodissociation in a magnetic field was discussed in Ref. [8], but J was assumed to be a good quantum number, which is not the case in our experimental regime even for weak fields.

In this work we consider E1 photodissociation of weakly bound ground-state $^{88}\text{Sr}_2$ molecules into the $0_u^+/1_u$ *ungerade* continuum correlating to the $^1S_0 + {}^3P_1$ atomic threshold. The transition operator connecting the initial and final wave functions is assumed to be constant and proportional to the atomic value. This approximation is valid for weakly bound molecules. It is assumed that the field affects only the excited states, since the ground state (correlating to $^1S_0 + {}^1S_0$) is nearly nonmagnetic.

Bound state wave function

Since the initial (bound-state) wave function is not affected by the magnetic field B, it is given by the standard form using the electronic coordinates $\{\mathbf{r}\}$ and the internuclear vector $\mathbf{R}$,

$$
\begin{aligned}
\Psi^{p_i}_{J_i M_i}(\{\mathbf{r}\}, \mathbf{R}) = & \frac{1}{\sqrt{2}} \sqrt{\frac{2J_i+1}{8\pi^2}} \sum_{\Omega_i=-J_i}^{+J_i} \frac{1}{\sqrt{1+\delta_{\Omega_i 0}}} \\
& \times \left(D^{(J_i)^\star}_{M_i \Omega_i}(\phi, \theta, 0) \psi^{p_i}_{J_i \Omega_i}(\{\mathbf{r}\}, R) + \sigma_i D^{(J_i)^\star}_{M_i -\Omega_i}(\phi, \theta, 0) \psi^{p_i}_{J_i -\Omega_i}(\{\mathbf{r}\}, R) \right),
\end{aligned}
\tag{3}
$$

where σ is the spectroscopic parity defined as $p(-1)^J$, p is the parity with respect to the space-fixed inversion, and $D^J_{M\Omega}$ are the Wigner rotation matrices. In Hund's case (c) the internal wave function $\psi^{p_i}_{J_i \Omega_i}(\{\mathbf{r}\}, R)$ can be represented by the Born-Huang expansion [9, 10],

$$
\psi^{p_i}_{J_i \Omega_i}(\{\mathbf{r}\}, R) = \sum_{n_i} \phi_{n_i \Omega_i}(\{\mathbf{r}\}; R) \chi^{p_i}_{n_i J_i \Omega_i}(R), \tag{4}
$$

where $\phi_{n_i \Omega_i}(\{\mathbf{r}\}; R)$ are the solutions of the electronic Schrödinger equation including spin-orbit coupling, $\chi^{p_i}_{n_i J_i \Omega_i}(R)$ are the rovibrational wave functions, and the index n labels all relativistic electronic channels that are included in the model. The rovibrational wave functions are solutions of a system of coupled differential equations as detailed in Ref. [11].

Continuum state wave function

The correct description of the final (continuum) wave function is crucial to explaining and predicting the outcome of photodissociation in a magnetic field. Zeeman

mixing of rovibrational levels was responsible for observations of forbidden molecular (bound-to-bound) E1 transitions that violate the $\Delta J = 0, \pm 1$ selection rule [12]. Similar effects are expected for bound-to-continuum photodissociation transitions.

In a magnetic field, the only conserved quantities are the projection of the total angular momentum M and the total parity. For dissociation to the *ungerade* continuum ($^1S_0 + {}^3P_1$), the atomic angular-momentum quantum number is $j = 1$. Its magnetic sublevels $m_j = 1, 0, -1$ are split by the field, and therefore the photodissociation cross section calculations have to be performed for each sublevel individually. The 0_u^+ and 1_u states, corresponding to $\Omega = 0$ and $|\Omega| = 1$, are coupled by the nonadiabatic Coriolis interaction, while the Zeeman interaction couples the $\Delta J = 0, \pm 1$ states. For these reasons, two sets of additional numbers are introduced: Ω_R, J_R, n_R correspond to the entrance channels of the multichannel continuum wave function and Ω_k, J_k, n_k correspond to the exit channels. In this work, selection rules set $\Omega_R = 1$.

As a result, the continuum wave function corresponding to the wave vector $\mathbf{k}$ is

$$
\begin{aligned}
\Psi^{pjm_j}_{\mathbf{k}}(\{\mathbf{r}\}, \mathbf{R}) = & \sum_{J_k M J_R} \sum_{\Omega_k \Omega_R} \sum_{lm_l} (-1)^{J_k+\Omega_k} Y^\star_{lm_l}(\hat{k}) \sqrt{\frac{2l+1}{8\pi^2}} \begin{pmatrix} J_k & j & l \\ -M & m_j & m_l \end{pmatrix} \begin{pmatrix} J_k & j & l \\ \Omega_k & -\Omega_k & 0 \end{pmatrix} \\
& \times \frac{\sqrt{2J_k+1}}{\sqrt{1+\delta_{\Omega_k 0}}} \frac{1}{\sqrt{1+\delta_{\Omega_R 0}}} \left(D^{J_R}_{\Omega_R M}(\hat{R}) \psi^{jJ_k\Omega_k p}_{J_R \Omega_R}(\{\mathbf{r}\}, R) + p D^{J_R}_{-\Omega_R M}(\hat{R}) \psi^{jJ_k\Omega_k p}_{J_R -\Omega_R}(\{\mathbf{r}\}, R) \right),
\end{aligned}
\tag{5}
$$

where Y_{lm_l} are spherical harmonics. The detailed derivation of this wave function is found in Refs. [2, 5], but for the simpler case when J is a good quantum number and the J_k, J_R channel numbers are not needed.

The function $\psi^{jJ_k\Omega_k p}_{J_R \Omega_R}(\{\mathbf{r}\}, R)$ can be expressed by the

Born-Huang expansion as

$$
\psi^{jJ_k\Omega_k p}_{J_R \Omega_R}(\{\mathbf{r}\}, R) = \sum_{n_k n_R} \phi_{n_R \Omega_R}(\{\mathbf{r}\}, R) \chi^{jJ_k\Omega_k n_k p}_{J_R \Omega_R n_R}(R),
$$

$$\tag{6}$$

where the wave functions $\phi_{n_R\Omega_R}(\{\mathbf{r}\}, R)$ are the solutions of the electronic Schrödinger equation. The rovibrational wave functions $\chi_{J_R\Omega_R n_R}^{jJ_k\Omega_k n_k p}(R)$ are obtained by solving the nuclear Schrödinger equation with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{\hbar^2\mathbf{l}^2}{2\mu R^2} + V(R), \qquad (7)$$

where $V(R)$ is the potential matrix including the Coriolis and Zeeman couplings, $\hbar$ is the reduced Planck constant, and μ is the reduced atomic mass.

At large interatomic distances in the presence of external fields, the asymptotic value of $V(R)$, or V_{as}, is not diagonal in the basis of the wave functions $\phi_{n_R\Omega_R}(\{\mathbf{r}\}, R)$. It is then necessary to introduce a transformation $\mathbb{C}$ that diagonalises V_{as}. The rovibrational functions $\chi_{J_R\Omega_R n_R}^{jJ_k\Omega_k n_k p}(R)$ form a matrix $\bar{\mathbb{X}}$ that is propagated to large distances and transformed to the basis that diagonalizes the asymptotic potential, $\mathbb{X} = \mathbb{C}^T\bar{\mathbb{X}}\mathbb{C}$. Then the boundary conditions are imposed [13, 14] as

$$\mathbb{X}(R) \rightarrow J(R) + N(R) \cdot K, \qquad (8)$$

where K is the reaction matrix, $J(R)$ and $N(R)$ are the diagonal matrices containing the spherical Bessel functions for the open channels,

$$[J(R)]_{ij} = \delta_{ij}\frac{1}{\sqrt{k_j}}j_l(k_jR), \quad [N(R)]_{ij} = \delta_{ij}\frac{1}{\sqrt{k_j}}n_l(k_jR), \qquad (9)$$

k_j is the wave number of the jth channel, and l is the orbital angular momentum of the jth channel. A more detailed description of the close-coupled equations in a magnetic field can be found in Ref. [15].

Anisotropy parameters

After inserting the wave functions (3) and (5) into Fermi's golden rule (2) and transforming the cross section for photodissociation using the Clebsch-Gordan series and properties of the Wigner $3j$ symbols, we obtain the following expansion for the PAD:

$$I(\theta, \phi) \propto \beta_0\left(1 + \sum_{\mu=1}^{\infty}\sum_{\nu=0}^{\mu}\beta_{\mu\nu}P_{\mu}^{\nu}(\cos\theta)\cos(\nu\phi)\right), \qquad \text{(1 revisited)}$$

where the anisotropy parameters are given by

$$\beta_{\mu\nu} = \frac{1}{\beta_0}\sum_{J_kJ_RJ_k'J_R'}\sum_{ll'MM'}t_{J_R}^{J_k}t_{J_R'}^{J_k'\star}U_{J_RM}^{J_kl}U_{J_R'M'}^{J_k'l'}[\mu]\sqrt{\frac{(\mu-\nu)!}{(\mu+\nu)!}}(2-\delta_{MM'})\begin{pmatrix} l & l' & \mu \\ M-m_j & m_j-M' & \nu \end{pmatrix}\begin{pmatrix} l & l' & \mu \\ 0 & 0 & 0 \end{pmatrix} \qquad (10)$$

and $[A] \equiv 2A + 1$. The symbols $U_{J_RM}^{J_kl}$ in Eq. (10) are

defined as

$$U_{J_RM}^{J_kl} = \sum_{P\Omega_km_l}(-1)^{J_k+\Omega_k-m_j}[l]\frac{\sqrt{[J_k]}}{\sqrt{1+\delta_{\Omega_k0}}}\begin{pmatrix} J_k & j & l \\ -M & m_j & m_l \end{pmatrix}\begin{pmatrix} J_k & j & l \\ \Omega_k & -\Omega_k & 0 \end{pmatrix}\begin{pmatrix} J_R & 1 & J_i \\ -M & P & M_i \end{pmatrix}, \qquad (11)$$

and the symbols $t_{J_R}^{J_k}$ are the scaled matrix elements of the

asymptotic body-fixed E1 transition operator d_{BF} with the initial and final rovibrational wave functions,

$$t_{J_R}^{J_k} = \frac{1}{2\sqrt{2}} \sum_{\Omega_i=-J_i}^{J_i} \sum_{\Omega_R=-J}^{J} \sum_{q=-1}^{1} \sum_{n_k n_R} (-1)^{M-\Omega_R} \frac{\sqrt{[J_i]}}{\sqrt{1+\delta_{\Omega_i 0}}} \frac{\sqrt{[J_R]}}{\sqrt{1+\delta_{\Omega_R 0}}} \tag{12}$$
$$\times \begin{pmatrix} J_R & 1 & J_i \\ -\Omega_R & q & \Omega_i \end{pmatrix} \langle \chi_{J_R \Omega_R n_R}^{j J_k \Omega_k n_k p}(R) | d_{\text{BF}} | \chi_{n_i J_i \Omega_i}^{p_i}(R) \rangle.$$

The normalization factor β_0 is given by

$$\beta_0 = \sum_{lM} \left| \sum_{J_k J_R} t_{J_R}^{J_k} U_{J_R M}^{J_k l} \sqrt{2l+1} (-1)^{J_k} \right|^2. \tag{13}$$

In Eq. (11), the polarization index $P = 0$ if the photodissociation light is polarized along the z axis, while $P = -1, 1$ if the light is polarized perpendicularly to the z axis.

The properties of the $3j$ symbols force the following rules for the μ, ν indices:

- μ is even for homonuclear dimers.
- $\mu_{\max} = 2J_{k,\max} + 2j = 2J_{k,\max} + 2$ for resolved m sublevels. Thus the number of terms in the expansion (1) is limited by the number of channels used to construct the continuum wave function. (When the m sublevels are degenerate and are observed simultaneously, additional symmetry leads to $\mu_{\max} = 2J_{k,\max}$.) If $B = 0$, then $J_{k,\max} = 1$ and $\mu_{\max} = 4$, as can be seen in Fig. 3(d-h) of the manuscript.
- $\nu = M' - M$. Since $M = M' = M_i$ for parallel light polarization, $\nu = 0$ and thus the photodissociation cross section is cylindrically symmetric in this case.

The anisotropy parameters presented in Fig. 3(d-h) of the manuscript are calculated using Eq. (10), but instead of summing over J_k, J_k', the normalized contributions of each combination J_k, J_k' are individually plotted. The curves in Fig. 3(d) illustrate the relative contributions to the photodissociation transition strength; note that all curves in Fig. 3(d) must add to unity if the $(J_k, J_k' \neq J_k)$ contributions are doubled.

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