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Orientation, alignment, and hyperfine effects on dissociation of diatomic molecules to open shell atoms

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We demonstrate how magic angle detection of the circular polarization ratio can be used to probe the orientation of open shell atomic photofragments produced in photodissociation with circularly polarized light. The orientation provides new information concerning the dynamics of photodissociation which supplements that available from the alignment or from angular distribution measurements. The general theory of alignment and orientation is provided for photodissociation of diatomic molecules to open shell atoms and incorporates the asymptotic nonadiabatic interactions. Hyperfine depolarization factors are computed and tabulated for the first excited $^2P_{3/2,1/2}$ states of a number of alkali atoms. They are used to transform between theoretical electronic orientation and alignment and experimentally observed values in the limit where the nuclear spins are unpolarized prior to photodissociation and where hyperfine transitions are not separated in the detection process. Orientation and alignment parameters are calculated for a variety of photodissociations in the high energy axial recoil limit.

I. INTRODUCTION

Recently there has been considerable experimental¹⁻⁵ and theoretical⁵⁻¹⁵ interest in the dissociation of diatomic molecules to open shell atoms because of the nonadiabatic couplings which can contribute in the dissociation, because of the desire to probe open shell atom-open shell atom potential curves, and because of the interest in producing electronically excited atoms and fragment population inversions for new lasers.⁵ Some of the experiments have investigated the measurement of polarization effects, through the emission or laser induced fluorescence of the fragments, in order to gain additional information concerning the dynamics of the photodissociation which cannot be obtained from population measurements. These experiments with linearly polarized exciting light have determined the alignment of the photofragments from the linear polarization ratio measured with a photodetector located normal to the electric vector of the exciting light,

$$P_L = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp}), \quad (1.1)$$

where I_{\parallel} is the intensity of emitted light polarized parallel to the electric vector of the exciting light and I_{\perp} is that with an orthogonal direction. This polarization ratio is directly proportional to the alignment A_0 which is defined by^{15,16}

$$A_0 = \langle j^2 - 3j_z^2 \rangle / j(j+1), \quad (1.2)$$

where the average is over the states of the emitting fragment and j is the total angular momentum for the emitting fragment atom.

Additional information can be provided by measurements of the orientation O_0 which is given by

$$O_0 = \langle j_z \rangle / [j(j+1)]^{1/2}. \quad (1.3)$$

For instance, states with $j = 1/2$ have $A_0 = 0$, but O_0 may be nonzero. No direct measurement of orientation O_0 has, to our knowledge, been made for photodissociation, although experimental evidence has been reported for the presence of nonzero orientation of cesium atoms produced by photodissociation of CsI.^{17,18} One of the main purposes of this paper is to show how O_0 can be directly measured experimentally using circularly polarized light and how it can be calculated theoretically by an extension of our general theory of the photodissociation of diatomic molecules to open shell atoms. Experiments with incident linearly polarized light cannot determine the orientation, so use of circularly polarized light is necessary. Circularly polarized photodissociating light enables the measurement of the circular polarization ratio

$$P_c = (I_r - I_l) / (I_r + I_l), \quad (1.4)$$

with I_r and I_l the emitted right and left circularly polarized light intensity, respectively. However, at arbitrary detection angles P_c depends in a complicated fashion on both the orientation and alignment. In Sec. II we show how the use of magic angle detection makes P_c proportional *only* to the orientation.

Because experimental measurements of orientation and alignment depend on the *total* angular momentum of the emitting atomic fragment, O_0 and A_0 are both affected by the presence of nuclear spins even when hyperfine couplings play no role in the dynamics of the photodissociation. Methods for disentangling the effects of nuclear spins and hyperfine couplings have been provided in contexts other than diatomic dissociations.¹⁶ It is necessary to incorporate such corrections into our general theory of the dissociation of diatomic molecules to open shell atoms in order to predict

orientations and alignments observed in experiments. An equivalent alternative involves applying these corrections to experimental data to extract the *electronic* orientation and alignment which follow from our previous theoretical calculations for the alignment and their extensions in the present paper for orientation. Specific examples are provided here for the alkali atoms to illustrate the use of the theory and to provide a tabulation of the hyperfine depolarization ratios necessary to convert between total angular momentum orientation and alignment and their electronic angular momentum counterparts which are of central dynamical interest. Criteria are also derived under which the hyperfine effects can be described using simple hyperfine depolarization ratios.

Our previous work is concerned only with electronic alignment, not orientation. Here we calculate the electronic orientation in the high energy axial recoil limit where dynamical information concerning photodissociation is not required. In addition, general theoretical prescriptions are given to enable the calculation of the orientation in the low energy region where our previous work predicts the occurrence of nonadiabatic induced resonances in the photodissociation. A future work is planned to be devoted to this low energy region to investigate how the orientation varies near these resonances.

The next section provides general formulas defining the relevant cross sections and polarization intensities. This involves an extension of our previous theory to treat complex polarization vectors (i.e., circular polarization), so that the orientation O_0 can be defined and evaluated. We show how magic angle detection with circularly polarized light enables the separation of the orientation from the alignment. Section III discusses the hyperfine depolarization ratios and how they are used to transform between total and electronic orientation and alignment. Hyperfine depolarization ratios are tabulated for the first excited P states of the alkali atoms ${}^3\text{Li}^7$, ${}^{11}\text{Na}^{23}$, ${}^{19}\text{K}^{39}$, ${}^{19}\text{K}^{41}$, ${}^{37}\text{Rb}^{85}$, and ${}^{37}\text{Rb}^{87}$. Axial recoil limit calculations are presented in Sec. IV for the orientation and alignment for photodissociation with circularly polarized light.

II. CROSS SECTIONS, ORIENTATION, ALIGNMENT, AND POLARIZATION RATIOS

Consider a molecule which is photodissociated by absorption of light with fragments receding from each other in the direction \hat{k} and with emission having polarization vector $\hat{\epsilon}_S$ from one of the fine structure states of the atomic fragments. Both \hat{k} and $\hat{\epsilon}_S$ are defined relative to the z axis of a space fixed coordinate system which is conveniently defined by the photodissociating light. For instance, if this light is linearly polarized, the space fixed z axis is taken along the incident light polarization vector, while for circularly polarized light \hat{z} is taken parallel to the direction of propagation of the incident beam.

Our general theory of the photodissociation of diatomic molecules to open shell atoms provides the means for calculating the double differential cross section

$$\frac{d^2\sigma}{d\Omega_\epsilon d\Omega_k}(\hat{\epsilon}_S, \hat{k}) = \sum_{K_S Q_S K_D Q_D} \tilde{\sigma}_{K_S Q_S K_D Q_D} \times \phi_{K_S Q_S}(\hat{\epsilon}_S) C_{K_D Q_D}(\hat{k}) \quad (2.1)$$

through explicit recipes for evaluating the coefficients $\tilde{\sigma}_{K_S Q_S K_D Q_D}$. Here $C_{K_Q}(\theta, \phi)$ are defined in terms of the usual spherical harmonics $Y_{K_Q}(\theta, \phi)$ by¹⁹

$$C_{K_Q}(\theta, \phi) = [4\pi/(2K+1)]^{1/2} Y_{K_Q}(\theta, \phi) \quad (2.2)$$

and $\phi_{K_S Q_S}(\hat{\epsilon}_S)$ is given by²⁰

$$\phi_{K_S Q_S}(\hat{\epsilon}_S) = \sum_{q\bar{q}} (-1)^{1-\bar{q}} \langle K_S Q_S | 11q_1 - \bar{q}_1 \rangle \epsilon_q^* \epsilon_{\bar{q}}. \quad (2.3)$$

For the special case of linearly polarized light, considered previously,^{6,8,11} Eq. (2.3) reduces to

$$\phi_{K_S Q_S}(\hat{\epsilon}_S) = -\langle K_S 0 | 1100 \rangle C_{K_S Q_S}(\hat{\epsilon}_S) \quad \text{for } \hat{\epsilon}_S = \hat{\epsilon}_S^*, \quad (2.3a)$$

but in order to treat cases with detection of circularly polarized light, the extension (2.3) is required.

The alignment and orientation of the atomic excited states is expressed below in terms of the coefficients $\tilde{\sigma}_{K_S Q_S K_D Q_D}$ as are various polarization ratios. For instance, the polarization ratio (1.1) can be written in terms of the fluorescence anisotropy parameter

$$\tilde{\beta}_S = \tilde{\sigma}_{20,00}/\tilde{\sigma}_{00,00}$$

as described below. Full close coupled quantum calculations for $\tilde{\beta}_S$ and P_L have been made for the dissociation of several diatomic molecules to open shell atoms.^{9,10,12} In addition, calculations have been provided for $\tilde{\beta}_S$ and P_L in the high energy recoil limit approximation^{6,8,9} where dynamical calculations are unnecessary. Tabulated results are provided in our previous papers for $\tilde{\beta}_S$ and P_L when excitation involves a single molecular state and when the initial molecular levels are well approximated by Hund's case (a) or (b) wave functions.^{6,8,9} General techniques are provided for treating molecules with intermediate Hund's coupling and with more than one molecular state participating in the excitation process.⁶ The nonnegligible effects of nuclear spins and hyperfine splittings, however, are not contained in these previous calculations, but they are necessary for comparisons with experiment whenever hyperfine splittings are present in the emitting state even if these splittings are not resolved.

We limit the discussion here to situations in which the directions of the recoiling photofragments are not detected. Then, integrating Eq. (2.1) over all directions \hat{k} reduces it to

$$\frac{d\sigma}{d\Omega}(\hat{\epsilon}_S) = 4\pi \sum_{K_S Q_S} \tilde{\sigma}_{K_S Q_S 00} \phi_{K_S Q_S}(\hat{\epsilon}_S). \quad (2.4)$$

To be definite, we take atom a to emit from a state labeled by indices $c_a j_a$ to state $c'_a j'_a$ while fragment b remains in state $c_b j_b$. (It is straightforward to extend the discussion to cases of detection by laser induced fluorescence, but here we discuss the situation where a fragment emits.^{6,8})

Let the photon detector be located at the Euler angles (ϕ, θ, χ) in the space fixed coordinate system,^{15,16} and let the detector be sensitive to light with polarization angle β within the detector's coordinate system. Thus, the detector fixed

polarization vector is given by the column vector¹⁶

$$\hat{\epsilon}_S^{\text{D.F.}} = (\cos \beta, i \sin \beta, 0)^T, \quad (2.5)$$

where the components of $\hat{\epsilon}_S^{\text{D.F.}}$ in Eq. (2.5) are the Cartesian components of $\hat{\epsilon}_S^{\text{D.F.}}$ in a frame whose z axis is pointing outward from the emitting atom to the detector. Thus, $\beta = 0$ represents linearly polarized light along the detector's x axis, while $\beta = +\pi/4$ ($-\pi/4$) corresponds to right (left) circular polarization. The space fixed polarization vector $\hat{\epsilon}_S$ is obtained through the operation $R(\phi, \theta, \chi)$ of rotation of the detector axes into the space fixed ones¹⁹

$$\hat{\epsilon}_S = R(\phi, \theta, \chi) \hat{\epsilon}_S^{\text{D.F.}}. \quad (2.6a)$$

When the polarization vector is decomposed into spherical polar components, the above relation is explicitly realized as

$$\hat{\epsilon}_{S,q} = \sum_q D_{q,q}^1(\phi, \theta, \chi) \hat{\epsilon}_{S,q}^{\text{D.F.}}, \quad (2.6b)$$

where $D_{q,q}^1$ is a Wigner matrix element. The detected intensity is then written as a function of the angles β, ϕ, θ , and χ through

$$I(\beta, \phi, \theta, \chi) = \frac{d\sigma}{d\Omega}(\hat{\epsilon}_S). \quad (2.7)$$

Consider first P_L of Eq. (1.1), which requires $I_{||}$ with $\hat{\epsilon}_S = (0, 0, 1)$,

$$I_{||} = I(0, 0, \pi/2, 0) = 4\pi[(3)^{-1/2}\tilde{\sigma}_{00,00} - (2/3)^{1/2}\tilde{\sigma}_{20,00}], \hat{\epsilon}_S = (0, 0, 1), \quad (2.8)$$

where the second equality follows from Eqs. (2.4), (2.6), and (2.7). I_{\perp} with $\hat{\epsilon}_S = (0, 1, 0)$ is given by

$$I_{\perp} = I(0, 0, \pi/2, \pi/2) = 4\pi[(3)^{-1/2}\tilde{\sigma}_{00,00} + (6)^{-1/2}\tilde{\sigma}_{20,00} + (1/2)(\tilde{\sigma}_{22,00} + \tilde{\sigma}_{2-2,00})], \hat{\epsilon}_S = (0, 1, 0). \quad (2.9)$$

When the initial molecular distribution and the excitation source are cylindrically symmetric about the space fixed axis, then $\tilde{\sigma}_{K_S Q_S 00} = 0$ for $Q_S \neq 0$, and Eq. (2.9) reduces to

$$I_{\perp} = 4\pi(3)^{-1/2}[\tilde{\sigma}_{00,00} + (1/2)^{1/2}\tilde{\sigma}_{20,00}], \text{ cylindrical symmetry.} \quad (2.10)$$

Hence, the polarization ratio (1.1) is

$$P_L = -\tilde{\sigma}_{20,00}/(2)^{1/2}\tilde{\sigma}_{00,00}. \quad (2.11)$$

Consider now the detection of circularly polarized light with a detector located at an angle θ relative to the z axis, the direction of propagation of the incident light. The right and left circularly polarized light detected is written in terms of the $\tilde{\sigma}_{K_S Q_S 00}$. From Eqs. (2.4), (2.6), and (2.7) they are, respectively,

$$I_r(\theta) = I(\pi/4, 0, \theta, 0) = 4\pi\{(3)^{-1/2}\tilde{\sigma}_{00,00} + (2)^{-1/2}\cos\theta\tilde{\sigma}_{10,00} + (i/2)\sin\theta(\tilde{\sigma}_{11,00} + \tilde{\sigma}_{1-1,00}) - [(1-3\cos^2\theta)/2(6)^{1/2}]\tilde{\sigma}_{20,00} + (i/2)\sin\theta\cos\theta(\tilde{\sigma}_{21,00} + \tilde{\sigma}_{2-1,00}) + [(\cos^2\theta-1)/4](\tilde{\sigma}_{22,00} + \tilde{\sigma}_{2-2,00})\},$$

$$\hat{\epsilon}_S = (2)^{-1/2}(1, i\cos\theta, -i\sin\theta), \quad (2.12)$$

$$I_l(\theta) = I(-\pi/4, 0, \theta, 0) = 4\pi\{(3)^{-1/2}\tilde{\sigma}_{00,00} - (2)^{-1/2}\cos\theta\tilde{\sigma}_{10,00} - (i/2)\sin\theta(\tilde{\sigma}_{11,00} + \tilde{\sigma}_{1-1,00}) - [(1-3\cos^2\theta)/2(6)^{1/2}]\tilde{\sigma}_{20,00} + (i/2)\sin\theta\cos\theta(\tilde{\sigma}_{21,00} + \tilde{\sigma}_{2-1,00}) - [(\cos^2\theta-1)/4](\tilde{\sigma}_{22,00} + \tilde{\sigma}_{2-2,00})\},$$

$$\hat{\epsilon}_S = (2)^{-1/2}(1, -i\cos\theta, i\sin\theta). \quad (2.13)$$

For the usual case of cylindrical symmetry about the space fixed z axis, Eqs. (2.12) and (2.13) simplify to

$$I_r(\theta) = 4\pi\{(3)^{-1/2}\tilde{\sigma}_{00,00} + (2)^{-1/2}\cos\theta\tilde{\sigma}_{10,00} - [(1-3\cos^2\theta)/2(6)^{1/2}]\tilde{\sigma}_{20,00}\}, \quad (2.14)$$

$$I_l(\theta) = 4\pi\{(3)^{-1/2}\tilde{\sigma}_{00,00} - (2)^{-1/2}\cos\theta\tilde{\sigma}_{10,00} - [(1-3\cos^2\theta)/2(6)^{1/2}]\tilde{\sigma}_{20,00}\}. \quad (2.15)$$

The circular polarization ratio P_c of Eq. (1.4) is now a function of the detector angle

$$P_c(\theta) = (3)^{1/2}\cos\theta\tilde{\sigma}_{10,00}/\{(2)^{1/2}\tilde{\sigma}_{00,00} - [(1-3\cos^2\theta)/2]\tilde{\sigma}_{20,00}\}. \quad (2.16)$$

Note that $P_c(\theta)$ depends on $\tilde{\sigma}_{10,00}$ which is nonzero for excitation by circularly polarized light but vanishes by symmetry considerations for linearly polarized excitations. Equation (2.16) shows $P_c(\theta)$ provides additional information to $\tilde{\sigma}_{20,00}/\tilde{\sigma}_{00,00}$ obtained from P_L (or from fluorescence angular distribution measurements). It is convenient to isolate this new information by viewing at the "magic angle" θ_M , given by $\cos^2\theta_M = 1/3$, which reduces Eq. (2.16) to

$$P_c(\theta_M) = \tilde{\sigma}_{10,00}/(2)^{1/2}\tilde{\sigma}_{00,00}. \quad (2.17)$$

Again for the common case of cylindrical symmetry the emission intensity $I(\beta, \phi, \theta, \chi)$ is written in terms of the orientation O_0 and alignment A_0 parameters as¹⁵

$$I(\beta, \phi, \theta, \chi) = (I_0/3)\{1 - h^{(2)}(j_i, j_f)(A_0/2)[P_2(\cos\theta) - (3/2)\sin^2\theta\cos 2\chi\cos 2\beta] + (3/2\cos\theta\sin 2\beta)h^{(1)}(j_i, j_f)O_0\}, \quad (2.18)$$

where P_2 is a Legendre polynomial, $j_i = j_a$ and $j_f = j_a'$ are the initial and final total angular momenta, respectively, of the emitting atom, $h^{(k)}(j_i, j_f)$ are given by

$$h^{(k)}(j_i, j_f) = (-1)^{j_i-j_f}[j_i(j_i+1)]^{-1/2} \times \left\{ \begin{matrix} j_i & j_i & k \\ 1 & 1 & j_f \end{matrix} \right\} / \left\{ \begin{matrix} j_i & j_i & k \\ 1 & 1 & j_i \end{matrix} \right\}, \quad (2.19)$$

and where the curly brackets designate $6j$ symbols.¹⁹ The quantities P_L and $P_c(\theta_M)$ are then simply proportional to A_0 and O_0 , respectively,

$$P_L = (1/2)h^{(2)}(j_i, j_f)A_0, \quad (2.20)$$

$$P_c(\theta_M) = [(3)^{1/2}/2]h^{(1)}(j_i, j_f)O_0. \quad (2.21)$$

Our previous papers⁶⁻¹² employ an alternative representation to Eq. (2.1) which is convenient for cases of photodissociation by linearly polarized light. It is useful to compare Eq. (2.11) with our previous definition:

$$32\pi^2 \frac{d^2\sigma}{d\Omega_e d\Omega_k} = \sum_{K_S Q_S K_D Q_D} \sigma_{K_S Q_S K_D Q_D}$$

$$\times C_{K_S Q_S}(\hat{e}_S) C_{K_D Q_D}(\hat{k}) \quad (2.22)$$

to enable use of methods given by us for the exact and approximate evaluation of the coefficients $\sigma_{K_S Q_S, K_D Q_D}$. Because Eq. (2.22) is written in terms of $C_{K_S Q_S}(\hat{e}_S)$, this representation is convenient for real \hat{e}_S [see Eq. (2.2)] where Eq. (2.3a) implies

$$\sigma_{K_S Q_S, K_D Q_D} = -32\pi^2 \langle K_S 0 | 1100 \rangle \tilde{\sigma}_{K_S Q_S, K_D Q_D} \hat{e}_S \text{ real.} \quad (2.23)$$

Because $\langle 10 | 1100 \rangle = 0$, we have $\sigma_{1 Q_S, K_D Q_D}$ vanishing for \hat{e}_S real. When light is circularly polarized, the representation (2.22) is less convenient than Eq. (2.1) since the meaning of complex $C_{K_S Q_S}(\hat{e}_S)$ is not clear. The relation (2.23) for linear polarization provides the convenient parameter of Refs. 6, 8, and 11:

$$\beta_S = \sigma_{20,00}/\sigma_{00,00} = -(2)^{1/2} \tilde{\sigma}_{20,00}/\tilde{\sigma}_{00,00} \quad (2.24)$$

such that

$$P_L = \beta_S/2. \quad (2.25)$$

III. MODIFICATION OF DIFFERENTIAL CROSS SECTIONS DUE TO UNRESOLVED HYPERFINE STRUCTURE

Both the emitting atomic state of atom a and the final state in this radiative decay are eigenfunctions of the atomic Hamiltonian which, of course, contains hyperfine interactions when both the nuclear spin and the electronic angular momentum are nonzero. These atomic eigenstates are written as $|c_a i_a j_a f_a m_{f_a}\rangle$ with i_a the nuclear spin quantum number, and the properties of the emitted light depend nontriv-

ially on the presence of the additional quantum number i_a .

Many photodissociation experiments involve initial molecular electronic states in which the hyperfine interactions are sufficiently small that the hyperfine levels can be taken to be equally populated. If further the hyperfine splittings in the exciting and emitted light are not resolved, the hyperfine effects on photodissociation are rather easily incorporated because the nuclear spins do not affect the dynamics of the photodissociation apart from their coupling to the other angular momenta having a strong influence on this dynamics. In this case it is only necessary to uncouple the nuclear spins from the other angular momenta and to describe the effects of the nuclear spins on the properties of the emission from the atomic fragments. When, however, the initial molecular state has the nuclear spins polarized or when hyperfine splittings of the absorbed or emitted light are resolved, the treatment of nuclear spin effects of photodissociation becomes very involved and requires a full angular momentum recoupling analysis which is analogous to that used by us to describe recoil limits.^{6,8,11} The former situation can arise in resonant two photon dissociations where hyperfine splittings in the bound-bound transition are resolved, while the latter can occur with heavy atomic fragments. Here we analyze the mathematically simpler case where nuclear spins are unpolarized and where hyperfine splittings are not resolved since this case should pertain to many experiments involving lighter atomic fragments. Those who are uninterested in the mathematical details may skip to the results beginning with Eq. (3.10).

In the absence of nuclear spins our general theory provides the double differential cross section as a product of four Liouville space matrices

$$\frac{d^2\sigma}{d\Omega_\epsilon d\Omega_k}(\hat{e}_S, \mathbf{k}) = \Gamma \sum_{\substack{B_2 B_1 \bar{B}_0 J_1 j_l J_0 \\ B_2 B_1 \bar{B}_0 \bar{J}_1 \bar{j}_l \bar{J}_0}} \mathcal{D}^\dagger[B_2 \beta_2(j_a; j_a)] \mathcal{U}^\dagger[B_2 \beta_2(j_a; j_a) | B_1 \beta_1(J_1 j_l; \bar{J}_1 \bar{j}_l)] \\ \times \mathcal{L}[B_1 \beta_1(J_1 j_l; \bar{J}_1 \bar{j}_l) | B_0 \beta_0(J_0 \eta_0; \bar{J}_0 \bar{\eta}_0)] \rho[B_0 \beta_0(J_0 \eta_0; \bar{J}_0 \bar{\eta}_0)], \quad (3.1)$$

where

$$\rho[B_0 \beta_0(J_0 \eta_0; \bar{J}_0 \bar{\eta}_0)] = (J_0 + 1)^{-1/2} \delta_{J_0 \bar{J}_0} \delta_{\eta_0 \bar{\eta}_0} \delta_{B_0 0} \delta_{\beta_0 0}, \quad (3.2)$$

with η_0 an abbreviation for all electronic and vibrational quantum numbers of the initial molecular state,

$$\mathcal{L}[B_1 \beta_1(J_1 j_l; \bar{J}_1 \bar{j}_l) | B_0 \beta_0(J_0 \eta_0; \bar{J}_0 \bar{\eta}_0)] = \sum_{\substack{m_1 m_0 \\ \bar{m}_1 \bar{m}_0}} (-)^{J_1 - \bar{M}_1} \langle B_1 \beta_1 | J_1 \bar{J}_1 M_1 - \bar{M}_1 \rangle \langle E J_1 M_1 j_l j_a j_b^{(-)} | \hat{\epsilon} \cdot \mathbf{x} | J_0 M_0 \eta_0 \rangle \\ \times \langle \bar{J}_0 \bar{M}_0 \bar{\eta}_0 | \hat{\epsilon} \cdot \mathbf{x} | E \bar{J}_1 \bar{M}_1 \bar{j}_l \bar{j}_a \bar{j}_b^{(-)} \rangle (-)^{J_0 - \bar{M}_0} \langle B_0 \beta_0 | J_0 \bar{J}_0 M_0 - \bar{M}_0 \rangle, \quad (3.3)$$

$$\mathcal{U}^\dagger[B_1 \beta_2(j_a; j_a) | B_1 \beta_1(J_1 j_l; \bar{J}_1 \bar{j}_l)] = \sum_{\substack{m_a m_b \\ \bar{m}_a \bar{m}_b}} (-)^{j_a - \bar{m}_a} \langle B_2 \beta_2 | j_a j_a m_a - \bar{m}_a \rangle \\ \times \left\{ \sum_{m_\mu} \langle J_1 M_1 | j_l m_\mu \rangle \langle j m | j_a j_b m_a m_b \rangle i^{-1} Y_{l\mu}(\hat{k}) \right\} \left\{ \sum_{\bar{m}_\mu} \langle J_1 M_1 | \bar{j}_l \bar{m}_\mu \rangle \langle \bar{j} m | \bar{j}_a \bar{j}_b \bar{m}_a \bar{m}_b \rangle i^1 Y_{l\mu}^*(\hat{k}) \right\} \\ \times (-)^{J_1 - \bar{M}_1} \langle B_1 \beta_1 | J_1 \bar{J}_1 M_1 - \bar{M}_1 \rangle \quad (3.4)$$

and

$$\mathcal{D}^\dagger[B_2 \beta_2(j_a j_a)] = \sum_{m_a \bar{m}_a} (-)^{j_a - \bar{m}_a} \langle B_2 \beta_2 | j_a j_a m_a - \bar{m}_a \rangle \sum_{m'_a} \langle j'_a m'_a | \hat{\epsilon}_S \cdot \mathbf{x} | j_a m_a \rangle \langle j_a \bar{m}_a | \hat{\epsilon}_S \cdot \mathbf{x} | j'_a m'_a \rangle. \quad (3.5)$$

In addition $\hat{\epsilon}$ is the polarization vector of the exciting light, and Γ is a constant prefactor which converts to the proper cross sectional units.

The matrix $\rho_0[B_0\beta_0(J_0\eta_0;\bar{J}_0\bar{\eta}_0)]$ is the density matrix for the initial molecular state (with quantum numbers $J_0\eta_0$) before photon absorption. The matrix $\mathcal{L}[B_1\beta_1(J_1j_l;\bar{J}_1\bar{j}_l)|B_0\beta_0(J_0\eta_0;\bar{J}_0\bar{\eta}_0)]$ is the half-collision operator accounting for all the photodissociation dynamics; it transforms the Liouville space vector $\rho[B_0\beta_0(J_0\eta_0;\bar{J}_0\bar{\eta}_0)]$ of the initial states of the molecule into another vector which describes the coherent superposition of fragment states produced by absorption of the second photon. The remaining adjoint matrices, that make up the differential cross section, \mathcal{U}^\dagger [Eq. (3.4)] and \mathcal{D}^\dagger [Eq. (3.5)] are detection operators. They probe the coherent superposition of fragment states specified by the product of \mathcal{L} and ρ to extract the observables of interest to us. The operator $\mathcal{U}^\dagger[B_2\beta_2(j_a;j_a)|B_1\beta_1(j_l;j_l;\bar{J}_1\bar{j}_l)]$ contains geometrical, not dynamical, information. It transforms a dual space vector from the partial wave basis specified by quantum numbers $Jj_l;\bar{J}\bar{j}_l$, to the plane wave basis, labeled by $\mathbf{k}j_a j_b; \mathbf{k}j_a j_b$. The former is the basis most convenient for dynamical calculations, while the latter corresponds to experimental measurement of fragments receding from each other with wave vector \mathbf{k} . The probability of detecting fluorescence with polarization vector $\hat{\epsilon}_s$ is given by contraction

of the dual space bra vector $\mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)]$ in Eq. (3.5) with the ket vector that describes the superposition of magnetic sublevels m_a produced in the photodissociation.

Given the assumption of initially unpolarized nuclear spins and no separation of hyperfine splittings in the experiments, the only role of the nuclear spins is to modify the matrix elements of the detection matrix $\mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)]$ to include the nuclear spin. The matrices ρ and \mathcal{U}^\dagger are merely multiplied by a unit matrix in nuclear spin. Without hyperfine effects the matrix elements of \mathcal{D}^\dagger are of the form

$$\mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)] = \delta_{B_2K_S}\delta_{\beta_2-Q_S}(j'_a)(-)^{Q_S}\phi_{K_SQ_S}(\hat{\epsilon}_s) \times W(1K_S j'_a j_a; 1j_a | \langle j'_a || x || j_a \rangle)^2, \quad (3.6)$$

with $W(\dots)$ a Racah coefficient. In Eq. (3.6) and subsequent expressions we use the notation (k) , where k is an angular momentum quantum number, to designate the quantity $2k+1$. The proper incorporation of unresolved hyperfine interactions requires the recoupling of j_a with the nuclear spin angular momentum i_a to form the total angular momentum f_a and requires the inclusion of the effects of the temporal phase factors $\exp(iE_{f_a}t)$ associated with the hyperfine level $|i_a j_a f_a\rangle$ with lifetime τ_{j_a} . The necessary analysis has been given previously in other contexts,¹⁶ and in our notation it modifies \mathcal{D}^\dagger to

$$\begin{aligned} \mathcal{D}^\dagger[B_2\beta_2(j'_a;j_a)] &\rightarrow \langle j'_a || \int_0^\infty \frac{dt \exp(-t/\tau_{j_a})}{\tau_{j_a}} \frac{\text{Trace}_{m_i}}{2i_a+1} \{e^{iHt}\mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)]e^{-iHt}\} || j'_a \rangle \\ &= \sum_{f'_a f_a} \frac{(f'_a)(f_a)}{(i_a)} \left\{ \begin{matrix} f'_a & f_a & B_2 \\ j_a & j_a & i_a \end{matrix} \right\}^2 \mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)] \frac{1}{\tau_{j_a}} \int_0^\infty dt \exp[-t/\tau_{j_a} + i(E_{f'_a} - E_{f_a})t] \\ &= \sum_{f'_a f_a} \frac{(f'_a)(f_a)}{(i_a)} \left\{ \begin{matrix} f'_a & f_a & B_2 \\ j_a & j_a & i_a \end{matrix} \right\}^2 \mathcal{D}^\dagger[B_2\beta_2(j_a;j_a)] \frac{1}{1 + (E_{f'_a} - E_{f_a})^2 \tau_{j_a}^2}. \end{aligned} \quad (3.7)$$

The factors

$$\left[\frac{(f'_a)(f_a)}{(i_a)} \left\{ \begin{matrix} f'_a & f_a & B_2 \\ j_a & j_a & i_a \end{matrix} \right\}^2 \right]^{1/2} \quad (3.8)$$

in Eq. (3.7) arise from the recoupling of i_a and j_a to form f_a by means of the orthogonal transformation coefficients¹⁶

$$((i_a j_a) f'_a (i_a j_a) f_a | (i_a i_a) 0 (j_a j_a) B_2)^k = (-1)^{i_a+j_a+f_a k} \left[\frac{(f'_a)(f_a)}{(i_a)} \right]^{1/2} \left\{ \begin{matrix} f'_a & f_a & k \\ j_a & j_a & i'_a \end{matrix} \right\}. \quad (3.9)$$

Combining Eqs. (3.7) and (3.8) with the constraint $B_2 = K_S$ from Eq. (3.6) enables the coefficients $\tilde{\sigma}_{K_S Q_S K_D Q_D}(c_a j_a, c_b j_b)$, calculated without hyperfine considerations, to be modified in the presence of hyperfine structure to the hyperfine corrected

$$\tilde{\sigma}_{K_S Q_S K_D Q_D}(j_a, j_b)^{(\text{HF})} = \tilde{\sigma}_{K_S Q_S K_D Q_D}(j_a, j_b) \sum_{f'_a f_a} \frac{(f'_a)(f_a)}{(i_a)} \left\{ \begin{matrix} f'_a & f_a & K_S \\ j_a & j_a & i_a \end{matrix} \right\} \frac{1}{1 + (E_{f'_a} - E_{f_a})^2 \tau_{j_a}^2}, \quad (3.10)$$

where the photodissociation leads to atoms a and b , respectively, in states j_a and j_b and where the observed emission is from state j_a to state j'_a . Introducing the notation

$$g_{j_a}^{[K_S]} \equiv \sum_{f'_a f_a} \frac{(f'_a)(f_a)}{(i_a)} \left\{ \begin{matrix} f'_a & f_a & K_S \\ j_a & j_a & i_a \end{matrix} \right\} \frac{1}{1 + (E_{f'_a} - E_{f_a})^2 \tau_{j_a}^2} \quad (3.11)$$

for the hyperfine depolarization ratio of the K_S multipole of the j_a fine structure state enables Eq. (3.10) to be simply rewritten as

$$\tilde{\sigma}_{K_S Q_S K_D Q_D}(j_a, j_b)^{[HF]} = g_{j_a}^{[K_S]} \tilde{\sigma}_{K_S Q_S K_D Q_D}(j_a, j_b). \quad (3.10a)$$

The evaluation of $g_{j_a}^{[K_S]}$ is straightforward given the lifetimes τ_{j_a} and the hyperfine energies E_{j_a} . The τ_{j_a} are available for a large number of atomic states,²¹ while the energies E_{j_a} have contributions from magnetic dipole and electric quadrupole contributions to the nuclear-electronic interaction energies²²⁻²⁴

$$E_{f_a i_a j_a} = (1/2)A_{i_a j_a} K_a + (1/4)B_{i_a j_a} [(3/2)K_a(K_a + 1) - 2i_a(i_a + 1)j_a(j_a + 1)]/[i_a(2i_a - 1)j_a(2j_a - 1)], \quad (3.12)$$

where

$$K_a = f_a(f_a + 1) - i_a(i_a + 1) - j_a(j_a + 1), \quad (3.13)$$

and the A and B parameters are proportional to the magnetic dipole and electric quadrupole moment of the nucleus, respectively.

Values of A , B and τ_{j_a} are summarized in Table I for the lowest $^2P_{1/2,3/2}$ states of the alkali atoms along with the calculated depolarization coefficients $g^{[1]}$ and $g^{[2]}$ for these states. Note that the alignment depolarization ratios $g_{3/2}^{[2]}$ for the $^2P_{3/2}$ state can be quite large and that the orientation depolarization ratios $g_{1/2}^{[1]}$ are even larger. The hyperfine corrected polarization ratios $P_L^{H.F.}$ and $P_c(\theta_M)^{H.F.}$ are obtained from the purely electronic polarization ratios, calculated by ignoring nuclear spin, through the relations

$$P_L^{H.F.} = g^{[2]} P_L, \quad (3.14)$$

$$P_c^{H.F.}(\theta_M) = g^{[1]} P_c(\theta_M). \quad (3.15)$$

At arbitrary detection angles equation (2.16) for $P_c(\theta)$ must be analyzed with the more general equation (3.10a) which implies the general case of $\theta \neq \theta_M$ involves both $g^{[1]}$ and $g^{[2]}$.

IV. ORIENTATION AND ALIGNMENT IN THE AXIAL RECOIL APPROXIMATION

At high relative kinetic energies of the recoiling fragments the axis between the atomic fragments barely rotates

on the time scale of the photodissociation. Using this simplified picture the photodissociation can be viewed as occurring in a nonrotating body-fixed frame which is randomly oriented with respect to the polarization vector of the incident light. Moreover, it is possible to further simplify the treatment by ignoring the differences in the kinetic energies of fragments produced in different atomic fine structure states. We present a heuristic derivation of the orientation and alignment parameters in this simplifying axial recoil limit. It can be rigorously justified by examination of the detailed photodissociation amplitudes and by taking the limit that the kinetic energy is much larger than the rotational energy.^{6,8,11}

In the axial recoil approximation the amplitude τ for photodissociation and subsequent fluorescence decay is factored into a product of amplitudes: (a) $\langle \Omega_0 | \epsilon \cdot \mathbf{x} | \Omega_1 \rangle$ for photodissociation from molecular state $|\Omega_0\rangle$ to state $|\Omega_1\rangle$, (b) $\langle \Omega_1 | j_a \Omega_a j_b \Omega_b \rangle$ for production of atomic state $|j_a \Omega_a j_b \Omega_b\rangle$ by dissociation through molecular level $|\Omega_1\rangle$, and (c) $\langle j_a \Omega_a | \hat{\epsilon}_S \cdot \mathbf{x}_a | j'_a \Omega'_a \rangle$ for fluorescence decay from excited atomic level $|j_a \Omega_a\rangle$ to $|j'_a \Omega'_a\rangle$. Hence, in this approximation τ is given by

$$\tau = \langle \Omega_0 | \epsilon \cdot \mathbf{x} | \Omega_1 \rangle \langle \Omega_1 | j_a \Omega_a j_b \Omega_b \rangle \langle j_a \Omega_a | \hat{\epsilon}_S \cdot \mathbf{x} | j'_a \Omega'_a \rangle, \quad (4.1)$$

where Ω is the projection of the electronic angular momentum on the body fixed axis, and the subscripts a and b refer to the fluorescing and nonfluorescing atomic fragments, re-

TABLE I. Alkali hyperfine depolarization ratios and associated isotopic parameters.

Isotope	$i_a^{P_a}$	Abundance (%)	Atomic state	Lifetime (ns)	A (MHz)	B (MHz)	$g_{j_a}^{[1]}$	$g_{j_a}^{[2]}$
^7Li	$\frac{3}{2}^-$	92.6	$2P_{1/2}$	11.3	45.91		0.676	0.0
			$2P_{3/2}$		-3.05	-0.221	0.997	0.912
^{23}Na	$\frac{3}{2}^+$	100	$3P_{1/2}$	15.9	94.45		0.430	0.0
			$3P_{3/2}$		19.06	2.58	0.848	0.652
^{39}K	$\frac{3}{2}^+$	93.1	$4P_{1/2}$	26.2	27.80		0.575	0.0
			$4P_{3/2}$	25.8	6.13	2.72	0.948	0.859
^{41}K	$\frac{3}{2}^+$	6.9	$4P_{1/2}$	26.2	15.19		0.758	0.0
			$4P_{3/2}$	25.8	3.40	3.34	0.981	0.946
^{85}Rb	$\frac{5}{2}^-$	72.2	$5P_{1/2}$	25.5	120.71		0.412	0.0
			$5P_{3/2}$		25.32	24.41	0.820	0.633
^{87}Rb	$\frac{5}{2}^-$	27.8	$5P_{1/2}$	25.5	409.4		0.491	0.0
			$5P_{3/2}$		85.87	11.86	0.911	0.776

spectively. For simplicity, we designate the ground and dissociative molecular electronic states $|\Omega_0\rangle$ and $|\Omega_1\rangle$, respectively, only by their projections of electronic angular momentum on the diatomic axis, and we do not explicitly write other quantum numbers, such as total spin, which do not change upon photon absorption for the cases illustrated below.

The factorized expression (4.1) for the photodissociation amplitude τ describes single photon induced dissociation in the axial recoil limit approximation when absorption to only one dissociative molecular level $|\Omega_1\rangle$ is involved in the fragmentation. The multiplet levels of the initial molecular state [e.g., projections Σ of total electron spin S in Hund's case (a)] are here assumed statistically populated, so we average $|\tau|^2$ over initial and sum over final multiplet levels. The molecular transition amplitude $\langle\Omega_0|\epsilon \cdot \mathbf{x}|\Omega_1\rangle$ is taken to be independent of multiplet states, an excellent approximation for large dissociation energies.

Even though the molecular levels are designated by projections of electronic angular momentum Ω , as would be appropriate for Hund's case (a) or (c) multiplet structure, the axial recoil limit cross sections given below are invariant to the intramultiplet coupling in the dissociating molecule. Under the assumptions stated above the averaging of $|\tau|^2$ over initial multiplet levels removes all dependence on coupling scheme. States with definite projection Ω are therefore only used for convenience. Axial recoil limit cross sections for more complicated situations and less restrictive physical assumptions are given in our previous work,^{6,8,11} and a similar analysis can be applied to the orientation parameter by modification of the analysis below.

The rather lengthy expression for the differential fluorescence cross section obtained by substitution of Eq. (4.2) into

$$\frac{d\sigma}{d\Omega_e}(\hat{\epsilon}_S) \propto |\tau|^2 \quad (4.2)$$

is considerably simplified upon transformation to an irredu-

cible Liouville space basis. Details of this procedure are given elsewhere.^{6,7} The final results are cast as a product of four Liouville space matrices with identical physical interpretation as in Eqs. (3.1)–(3.5),

$$\begin{aligned} \frac{d\sigma}{d\Omega_e}(\hat{\epsilon}_S) = & \Gamma \sum_{\substack{B_0 B_1 B_2 \Omega_0 \Omega_1 \\ \beta_0 \beta_1 \beta_2 \bar{\Omega}_0 \bar{\Omega}_1}} \mathcal{D}^\dagger[B_2 \beta(j_a; j_a)] \\ & \times \tilde{\mathcal{Q}}^\dagger[B_2 \beta_2(j_a; j_a) | B_1 \beta_1(\Omega_1; \bar{\Omega}_1)] \\ & \times \tilde{\mathcal{L}}[B_1 \beta_1(\Omega_1; \bar{\Omega}_1) | B_0 \beta_0(\Omega_0; \bar{\Omega}_0)] \tilde{\rho}_0[B_0 \beta_0(\Omega_0; \bar{\Omega}_0)]. \end{aligned} \quad (4.3)$$

When single photon induced dissociation proceeds through only one dissociative molecular level $|\Omega_1\rangle$, the $\tilde{\mathcal{L}}$ and $\tilde{\mathcal{Q}}^\dagger$ previous given for more general situations in Eqs. (125) and (126), respectively, of Ref. 6 reduce to the expressions which follow below, while \mathcal{D}^\dagger is discussed in Sec. III of this work.

For single photon dissociation $\tilde{\rho}_0[B_0 \beta_0(\Omega_0; \bar{\Omega}_0)]$ is just $\delta_{B_0,0} \delta_{\beta_0,0} \delta_{\Omega_0, \bar{\Omega}_0}$ divided by the degeneracy of the initial multiplet. When B_0 is zero and only one excited molecular level participates in the dissociation, $\tilde{\mathcal{L}}$ is given by

$$\begin{aligned} \tilde{\mathcal{L}}[B_1 \beta_1(\Omega_1; \bar{\Omega}_1) | B_0 = 0(\Omega_0; \bar{\Omega}_0)] \\ = (-)^{1+B_1-\delta} \begin{pmatrix} 1 & 1 & B_1 \\ q & -q' & -\delta \end{pmatrix} \phi_{B_1, \beta_1}(\hat{\epsilon}_S) \\ \times \tau(\Omega_1 | \Omega_0) \tau^*(\bar{\Omega}_1 | \bar{\Omega}_0), \end{aligned} \quad (4.4)$$

where $q' = \Omega_1 - \Omega_0$, $q' = \bar{\Omega}_1 - \Omega_0$, $\phi_{B_1, \beta_1}(\hat{\epsilon}_S)$ is the polarization matrix (2.3) for the incident radiation, and $\tau(\Omega_1 | \Omega_0)$ is the matrix element of the molecular dipole moment function between radial nuclear wave functions for bound and dissociative states. Both $\tau(\Omega_1 | \Omega_0)$ and $\tau^*(\bar{\Omega}_1 | \bar{\Omega}_0)$ appear in Eq. (4.4) because they are part of the bilinear sum in Eq. (4.2).

The geometrical matrix $\tilde{\mathcal{Q}}^\dagger$ is rather complicated in general. We confine the discussion here to photodissociation in which the nonfluorescing fragment is in an S state ($l_b = 0$). In this case $\tilde{\mathcal{Q}}^\dagger$ becomes

$$\begin{aligned} \tilde{\mathcal{Q}}^\dagger[B_2 \beta_2(j_a; j_a) | B_1 \beta_1(\Omega_1; \bar{\Omega}_1)] \\ = \delta_{B_1, B_2} (-)^{B_2 + S + l_a - \bar{\Omega}_1} \sum_{XZ} (X)(Z)(S)(j_a) \begin{pmatrix} l_a & l_a & X \\ \Lambda_a & -\bar{\Lambda}_a & -\delta \end{pmatrix} \begin{pmatrix} B_2 & Z & X \\ \delta & 0 & -\delta \end{pmatrix} \begin{pmatrix} Z & S & S \\ 0 & \Sigma & -\Sigma \end{pmatrix} \\ \times \sum_{FF} (F)(\bar{F})(-)^{j_a + s_b + \bar{F}} \begin{Bmatrix} \bar{F} & \bar{F} & B_2 \\ j_a & j_a & s_b \end{Bmatrix} \begin{Bmatrix} S & F & l_a \\ j_a & s_a & s_b \end{Bmatrix}^2 \begin{Bmatrix} X & B_2 & Z \\ l_a & F & S \\ l_a & \bar{F} & S \end{Bmatrix}. \end{aligned} \quad (4.5)$$

In our other work the operator $\tilde{\mathcal{Q}}^\dagger$ is given for $l_b \neq 0$, and the complications which arise in this general case are described elsewhere.^{6,8,11}

The orientation parameter P_c (2.17) in the axial recoil limit is calculated using Eqs. (4.3)–(4.5). Note that $B_1 = B_2 = K_S$ and $\beta_1 = \beta_2 = Q_S$ appear in Eq. (4.3). This result no longer applies if fragment angular distributions are also resolved or if more than one photon is used to dissociate the molecule. Computations of axial recoil limit orientation and alignment for common transition symmetries and atom-

ic term limits are given in Table II. These examples illustrate several selection rules which hold true in the axial recoil limit, but which may be violated at lower excess dissociation energies.

An important selection rule for the orientation parameter originates in the half-collision operator $\tilde{\mathcal{L}}$ of Eq. (4.4). If $K_S = B_1 = 1$, the operator is zero unless $q' = \bar{q}' = \pm 1$. Therefore, *only perpendicular transitions produce oriented fragments in the axial recoil limit*. The result is originally noted by Vasyutinskii.²⁴ However, the rule breaks down at

TABLE II. Orientation and alignment parameters calculated in the axial recoil approximation. In each case the molecule is dissociated through the absorption of one photon.

Atomic term limit	Molecular transition symmetry	j_a	$\bar{\sigma}_{10}/\bar{\sigma}_{00}$	$\bar{\sigma}_{20}/\bar{\sigma}_{00}$
$^1P + ^1S^a$	$^1\Sigma \rightarrow ^1\Pi$	1	$\frac{3}{2(6)^{1/2}}$	$\frac{7}{10(2)^{1/2}}$
	$^1\Pi \rightarrow ^1\Sigma$	1	0	$\frac{-1}{5(2)^{1/2}}$
$^2P + ^2S^a$	$^1\Sigma \rightarrow ^1\Pi$	1/2	$\frac{1}{(6)^{1/2}}$	0
	$^1\Sigma \rightarrow ^1\Pi$	3/2	$\frac{5}{4(6)^{1/2}}$	$\frac{7}{20(2)^{1/2}}$
	$^1\Pi \rightarrow ^1\Sigma$	1/2	0	0
	$^1\Pi \rightarrow ^1\Sigma$	3/2	0	$\frac{-1}{10(2)^{1/2}}$
	$^3\Sigma_{0,1} \rightarrow ^3\Pi$	1/2	$\frac{1}{(6)^{1/2}}$	0
	$^3\Sigma_{0,1} \rightarrow ^3\Pi$	3/2	$\frac{5}{4(6)^{1/2}}$	$\frac{35}{100(2)^{1/2}}$
	$^3\Pi_0 \rightarrow ^3\Sigma$	1/2	$\frac{1}{(6)^{1/2}}$	0
	$^3\Pi_1 \rightarrow ^3\Sigma$	1/2	0	0
	$^3\Pi_2 \rightarrow ^3\Sigma$	1/2	$\frac{-1}{(6)^{1/2}}$	0
	$^3\Pi \rightarrow ^3\Sigma^b$	1/2	0	0
	$^3\Pi_0 \rightarrow ^3\Sigma$	3/2	$\frac{1}{2(6)^{1/2}}$	$\frac{-1}{10(2)^{1/2}}$
	$^3\Pi_1 \rightarrow ^3\Sigma$	3/2	0	$\frac{-1}{10(2)^{1/2}}$
	$^3\Pi_2 \rightarrow ^3\Sigma$	3/2	$\frac{-1}{2(6)^{1/2}}$	$\frac{-1}{10(2)^{1/2}}$
	$^3\Pi \rightarrow ^3\Sigma^b$	3/2	0	$\frac{-1}{10(2)^{1/2}}$
	$^3\Sigma_{0,1} \rightarrow ^3\Pi$	3/2	$\frac{3}{10(6)^{1/2}}$	$\frac{-1}{5(2)^{1/2}}$
	$^3\Sigma_{0,1} \rightarrow ^3\Pi$	5/2	$\frac{7}{10(6)^{1/2}}$	$\frac{1}{5(2)^{1/2}}$
$^2D + ^2S^c$	$^3\Pi_0 \rightarrow ^3\Sigma$	3/2	$\frac{1}{5(6)^{1/2}}$	$\frac{2}{25(2)^{1/2}}$
	$^3\Pi_1 \rightarrow ^3\Sigma$	3/2	0	$\frac{2}{25(2)^{1/2}}$
	$^3\Pi_2 \rightarrow ^3\Sigma$	3/2	$\frac{-1}{5(6)^{1/2}}$	$\frac{2}{25(2)^{1/2}}$
	$^3\Pi \rightarrow ^3\Sigma^b$	3/2	0	$\frac{2}{25(2)^{1/2}}$
	$^3\Pi_0 \rightarrow ^3\Sigma$	5/2	$\frac{3}{10(6)^{1/2}}$	$\frac{-2}{25(2)^{1/2}}$
	$^3\Pi_1 \rightarrow ^3\Sigma$	5/2	0	$\frac{-2}{25(2)^{1/2}}$
	$^3\Pi_2 \rightarrow ^3\Sigma$	5/2	$\frac{-3}{10(6)^{1/2}}$	$\frac{-2}{25(2)^{1/2}}$
	$^3\Pi \rightarrow ^3\Sigma^b$	5/2	0	$\frac{-2}{25(2)^{1/2}}$

^a Anisotropy parameters for fluorescence decay of the P -state fragment to an S state.

^b Statistical population of initial multiplet levels. Anisotropy parameters are summed over all initial Ω weighted by the strength of each transition.

^c Anisotropy parameter for fluorescence decay of the 2D fragment to $^2P_{3/2}$. The same trends are found for $^2D_{3/2}$ to $^2P_{1/2}$ fluorescence as for $^2P_{3/2}$ to $^2S_{1/2}$ fluorescence.

lower energies where the recoil limit approximation is no longer valid and the orientation parameter may be nonzero for parallel transitions.

Table II only presents the axial recoil limit results for perpendicular transitions because otherwise the orientation parameter is automatically zero. The alignment parameter for the parallel transitions is given in our previous pa-

pers.^{6,8,11} Several features in Table II are worthy of note as follows: Nonzero orientation is predicted for atomic states with total angular momentum $j = 1/2$ even though no alignment can be detected in such states. When the dissociative molecular level is a Σ state ($\Lambda = 0$) and the nonfluorescing atom is produced in an S state, the observation of orientation is severely restricted in the recoil limit. In this case the recoil

limit geometrical matrix $\tilde{\mathcal{Z}}^\dagger$ of Eq. (4.5) vanishes for $K_S = B_2 = 1$ when the molecular spin $S = 0$. If $S \neq 0$ but the initial projections Σ of S are equally populated, the orientation also vanishes. (See the $\Pi \rightarrow \Sigma$ transitions in Table II for illustrations of these features.) This is confirmed by summing $\tilde{\mathcal{Z}}^\dagger$ in Eq. (4.5) over all Σ ; the result is proportional to

$$\begin{pmatrix} I_a & I_a & K_S \\ \Lambda - \bar{\Lambda} & -\delta \end{pmatrix}$$

which is zero if $\Lambda = \bar{\Lambda} = 0$ and $K_S = 1$. However, oriented fragments can be produced by transitions to Σ levels if the initial value of Σ and hence of $\Omega_0 = \Lambda_0 + \Sigma$ can be selected. This is often not possible for single photon induced photodissociation but is quite feasible for two photon experiments where a particular multiplet level is prepared in the initial bound-bound transition.

V. DISCUSSION

Our ability to interpret results of a photodissociation experiment is enhanced when anisotropy parameters are measured along with the total cross section. Of the many anisotropy parameters which may be observed in a photodissociation experiment, it is crucial to understand the orientation and alignment because these parameters are conveniently probed by detecting polarized fluorescence from excited photofragments or by inducing fluorescence from fragments in a laser induced fluorescence (LIF) scheme. Orientation and alignment information is particularly useful in identifying the participating molecular electronic levels and in assessing the importance of electronically nonadiabatic transitions during the fragmentation process. While the total photofragment cross section certainly reflects the properties of excited electronic states, anisotropy parameters like the orientation and alignment yield far more direct information about molecular electronic processes during photodissociation. For instance, when the excess dissociation energy is much larger than the term splittings of the fragments, anisotropy parameters are independent of photon energy and are directly interpretable in terms of the symmetry of the molecular levels coupled by the exciting light. (Tables for this purpose are given in Sec. IV above.) Otherwise, strong energy dependence of the anisotropy parameters indicates that interesting electronically nonadiabatic effects are occurring during the half collision or perhaps that more than one dissociative level is coupled to the radiation field. The total cross section by itself would not point to either of these possibilities in an obvious way.

We have extended our theory for photodissociation of diatomic molecules⁶⁻¹⁴ to facilitate observation and interpretation of anisotropy parameters. For the first time we consider the orientation parameter which may be nonzero even when observation of alignment is forbidden by symmetry. We propose that magic angle detection be used to directly observe the orientation of fragments without the necessity of fitting experimental fluorescence intensity as a function of angle to disentangle the orientation from alignment.

For those cases in which the presence of hyperfine structure in atomic fragments affects measured anisotropy parameters, we apply the results of Fano and Macek,¹⁶ and Greene and Zare¹⁵ to show how to relate observed anisotropy parameters to theoretical predictions in which hyperfine interactions are neglected. It is hoped that these new results will spark more experimental measurement of anisotropy parameters. This will give us greater understanding of molecular electronic processes.

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- ¹E. W. Rothe, U. Krause, and R. Dürer, *Chem. Phys. Lett.* **72**, 100 (1980); *J. Chem. Phys.* **72**, 5145 (1980); E. K. Kraulings and M. L. Yanson, *Opt. Spectrosc.* **46**, 629 (1979); D. M. Feldman and R. N. Zare, *Chem. Phys.* **15**, 415 (1976).
- ²J. Keller and J. Weiner, *Phys. Rev. A* **29**, 2943 (1984).
- ³H. Katô and K. Onomichi, *J. Chem. Phys.* **82**, 1642 (1985).
- ⁴H. J. Vedder, G. K. Chawla, and R. W. Field, *Chem. Phys. Lett.* **111**, 303 (1984).
- ⁵P. P. Sorokin, N. S. Shiren, J. R. Lankard, E. C. Hammond, and T. G. Kazyaka, *Appl. Phys. Lett.* **10**, 44 (1967); J. C. White and D. Henderson, *Opt. Lett.* **7**, 204 (1982).
- ⁶S. J. Singer, K. F. Freed, and Y. B. Band, *Adv. Chem. Phys.* **61**, 1 (1985).
- ⁷S. J. Singer, K. F. Freed, and Y. B. Band, *Laser Chemistry* (Gordon and Breach, New York, 1983).
- ⁸S. J. Singer, K. F. Freed, and Y. B. Band, *J. Chem. Phys.* **81**, 3064 (1984).
- ⁹S. J. Singer, K. F. Freed, and Y. B. Band, *J. Chem. Phys.* **81**, 3091 (1984).
- ¹⁰S. J. Singer, K. F. Freed, and Y. B. Band, *Chem. Phys. Lett.* **105**, 158 (1984).
- ¹¹S. J. Singer, K. F. Freed, and Y. B. Band, *J. Chem. Phys.* **79**, 6060 (1983).
- ¹²S. J. Singer, K. F. Freed, and Y. B. Band, *Chem. Phys. Lett.* **91**, 12 (1982).
- ¹³Y. B. Band, K. F. Freed, and D. J. Kouri, *Chem. Phys. Lett.* **79**, 233 (1981).
- ¹⁴Y. B. Band and K. F. Freed, *Chem. Phys. Lett.* **79**, 238 (1981).
- ¹⁵C. M. Greene and R. N. Zare, *J. Chem. Phys.* **48**, 4304 (1984).
- ¹⁶U. Fano and J. M. Macek, *Rev. Mod. Phys.* **45**, 553 (1973).
- ¹⁷O. S. Vasyutinskii, *JETP Lett.* **31**, 428 (1980).
- ¹⁸O. S. Vasyutinskii, *JETP* **54**, 855 (1981).
- ¹⁹D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Clarendon, Oxford, 1968).
- ²⁰A. Omont, *Prog. Quantum Electron.* **5**, 69 (1977).
- ²¹W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, Natl. Bur. Stand. (U. S. GPO, Washington, D. C.), Vol. I, 1966; Vol. II, 1969.
- ²²E. Arimondo, M. Inguscio, and P. Violino, *Rev. Mod. Phys.* **49**, 31 (1977).
- ²³N. Bendali, H. T. Duong, and J. L. Vialle, *J. Phys. B* **14**, 4231 (1981).
- ²⁴G. H. Fuller, *J. Phys. Chem. Ref. Data* **5**, 835 (1976).