Photofragment angular momentum distribution beyond the axial-recoil approximation

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Abstract

The paper reviews recent advantages in the theory of the rapidly growing field of the angular momentum orientation and alignment in photolysis of small molecules. Particular emphasis is put on the photofragment orbital orientation and alignment in molecular photolysis beyond the axial-recoil approximation. One of the most important recent achievements is derivation of a universal expression for the recoil-angle dependence of the polarization cross section in terms of the anisotropy parameters (anisotropy transforming coefficients), which is valid for one photon photolysis reaction of any diatomic or polyatomic molecule irrespective of the reaction mechanism. The anisotropy parameters contain all information about the reaction dynamics in the frame of the quantum scattering theory, they can be either determined from experiment or calculated from *ab initio* theory. Expressions for the anisotropy parameters for the photolysis of rotating diatomic/linear molecules are analyzed, which contain information on radial and Coriolis nonadiabatic interactions as well as on the full range of interference effects. In the case of direct photodissociation, the molecular rotation is taken into consideration in the quasi-classical approximation by introducing the set of rotation factors, which depend on the molecular axis rotation angle γ and on the quantum numbers of the photon polarization matrix. In the case of slow predissociation, the molecular rotation is taken into consideration by introducing the set of reduction factors. As shown, in most cases molecular rotation decreases the angular momentum polarization of the photofragments.

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1. Introduction

The photolysis of small molecules has attracted much attention of research all over the world for decades because it plays an important role in physics and chemistry of atmospheres of planets as well as in many combustion and industrial processes [1, 2]. The most informative up-to-date method for studying the photolysis processes is investigation of the recoil-angle distributions of photofragments produced in a definite quantum state characterized by the full set of their quantum numbers including the photofragment total angular momentum j and its laboratory frame projection m [3–7]. This approach is equivalent to the investigation of the photofragment angular momentum polarization in terms of the state multipole moments [8, 9].

Experimentally, these studies are now mainly based on two methods both combining selectivity to the photofragment recoil-angle distribution and to their angular momentum polarization: polarization Doppler technique [10, 11] and ion imaging [7, 12, 13].

A complete quantum mechanical treatment is required in order to describe the full range of interference effects and nonadiabatic interactions in molecular photolysis. Several theoretical approaches have been developed for a number of years for understanding in this area [14–24]. Most of them have been built upon the foundation established by Siebbeles *et al* [3] based on the expression for the recoil-angle dependence of the fragment state multipole moments using the axial-recoil approximation where the dissociation time

τ_{diss} is much shorter than the molecular rotation period T_{rot}. The important advantage of these approaches is that they allow for the complete separation of the kinematical part and the so named dynamical functions from each other and can in many cases be used for analysis of the dynamical processes in photodissociation and for interpretation of the experimental data without actual solving of the set of closed coupling equations.

However, the importance of taking the molecular rotation into account is obvious, because it underlies many important effects and nonadiabatic processes in diatomic and polyatomic molecules. Although fully quantum expressions for the differential state-to-state photodissociation polarization cross sections that rely only on the assumption of the electric dipole transition were reported relatively long ago by Balint-Kurti and Shapiro [25, 26], Freed and co-workers [27, 28], Roncero *et al* [29] and Mo and Suzuki [19], all these expressions do not provide separation of the kinematical and dynamical parts of the expression from each other which makes the analysis complicated.

The generalization of the Siebbeles *et al* theory [3] to the case of rotating molecules has recently been developed in a series of our papers [30–33] using quasi-classical approximation. This achievement allowed to treat the fast dissociation of rotating molecules, the predissociation, and to take into consideration possible Coriolis nonadiabatic interactions. The theory provides the isolation of different photodissociation mechanisms from each other, it also provides a critical link from theoretical description to the experimental observations based on a set of the anisotropy parameters, which contain all information about the dissociation dynamics and can be either determined from experiment or computed from theory. Moreover, the angle-recoil dependence of the state multipoles of one of the photofragments for an arbitrary one-photon photolysis reaction has been derived under the condition that the average over the quantum numbers of another (undetected) photofragment is performed. It was shown that the polarization of atomic or molecular photofragments in the photolysis of a diatomic or a polyatomic molecule can be described in terms of the anisotropy parameters irrespective of the photodissociation mechanism.

This paper reviews recent achievements of the theory of the photofragment angular momentum polarization in molecular photodissociation. The paper is organized as follows.

Section 2 presents the main features of the general recoil-angle distribution of the photofragment state multipoles moments produced in the photodissociation of rotating molecules. The particular case of direct photodissociation is considered in section 3 and the particular case of slow predissociation is considered in section 4. The perspectives of further development of the theory are discussed in conclusions (section 5).

2. General expressions

All theoretical treatments of the angle-recoil distribution of the photofragment state multipole moments produced in the photolysis reaction $AB + \hbar\omega \rightarrow A + B$ are based on the expression for the generalized photodissociation differential

cross section $\sigma(\mathbf{k}, E, j'm', jm)$. Here $\mathbf{k} = \mathbf{k}(\theta, \phi)$ is the recoil vector, E is the photofragment total energy, and j, m are the product total angular momentum and its projection onto the laboratory Z-axis. If both photofragments are open shell atoms/molecules, $\mathbf{j} = \mathbf{j_A} + \mathbf{j_B}$ and $m = m_A + m_B$, where j_A, m_A, j_B and m_B are the fragment angular momenta and their Z-projections. The cross sections $\sigma(\mathbf{k}, E, j'm', jm)$ with $j = j'$, $m = m'$ describe the diagonal components of the photofragment density matrix and the cross sections with $j \neq j'$ and/or $m \neq m'$ describe the off-diagonal components of the photofragment density matrix [8]. In the case that the parent molecules are randomly oriented in space, the generalized photodissociation differential cross section in the first-order of the time-dependent perturbation theory can be presented in the form [34, 35]:

$$\sigma(\mathbf{k}, E, j'm', jm) = C \sum_{M_i} \langle \Psi^{-(\mathbf{k}, j'm')}(\mathbf{R}, \mathbf{r}, E)|\hat{\mathbf{d}} \cdot \mathbf{e}|\Psi_{J_i M_i}\rangle$$
$$\times \langle \Psi^{-(\mathbf{k}, jm)}(\mathbf{R}, \mathbf{r}, E)|\hat{\mathbf{d}} \cdot \mathbf{e}|\Psi_{J_i M_i}\rangle^*, \tag{1}$$

where $\mathbf{e}$ is a photolysis light polarization vector, $\hat{\mathbf{d}}$ is a molecular dipole moment, $\mathbf{R}$ is the vector connecting the centers of mass of the fragments, $\mathbf{r}$ denotes all internal coordinates of the fragments, $E = E_i + \hbar\omega$ is the total photofragment energy, ω is the photolysis light frequency, and C is a constant: $C = \pi\omega/[c\varepsilon_0(2J_i + 1)]$ [31].

The term $\Psi_{J_i M_i}$ in equation (1) is the wavefunction of the initial molecular state, where J_i and M_i are the molecular total angular momentum and its laboratory frame projection, respectively.

The term $\Psi^{-(\mathbf{k}, jm)}(\mathbf{R}, \mathbf{r}, E)$ in equation (1) is the excited state wavefunction. It is the solution of time-independent Schrödinger equation for the molecular excited state of the molecule at all possible interfragment distances $0 < R < \infty$, this wavefunction coincides with a Ψ^- scattering function of the collision theory [36]. In the case of photodissociation, this function obeys the usual boundary condition at infinity corresponding to an outgoing plane wave in the channel with a specific internal state and incoming spherical waves in all other possible open channels [26].

In the entire range of the internuclear distance R the wavefunction $\Psi^{-(\mathbf{k}, jm)}(\mathbf{R}, \mathbf{r}, E)$ can be expanded over the partial waves in the total angular momentum J representation [36, 37]. A convenient form of the expansion using the Wigner D-functions can be written as [30]:

$$\Psi^{-(\mathbf{k}, jm)}(\mathbf{R}, \mathbf{r}, E) = \frac{1}{R} \sum_{JM} \sum_{\bar{n}n} \sum_{\Omega_R \Omega_k} \frac{2J+1}{4\pi} (-1)^{\mathrm{i}(\pi/2)J}$$
$$\times \langle n\Omega_k|j\Omega_k\rangle D^{j\,*}_{m\Omega_k}(\phi, \theta, 0)$$
$$\times D^{J}_{M\Omega_k}(\phi, \theta, 0) D^{J}_{M\Omega_R}(\phi_R, \theta_R, 0)$$
$$\times |\bar{n}\Omega_R\rangle \chi^{J}_{\bar{n}\Omega_R;\, n\Omega_k}(R), \tag{2}$$

where (θ_R, ϕ_R) are spherical angles specifying the direction of the vector $\mathbf{R}$.

The indices Ω_k and Ω_R in equation (2) are the projections of the total angular momentum $\mathbf{J}$ onto the recoil direction

k and onto the interfragment direction **R**, respectively (helicity quantum numbers) and M is the projection of the angular momentum J onto the laboratory frame Z-axis. The term $|j\Omega_R\rangle$ in equation (2) is a body frame electronic wavefunction of free photofragments and the term $|\bar{n}\Omega_R\rangle \equiv \Psi^{el}_{\bar{n}\Omega_R}(\mathbf{r}, R)$ is an adiabatic body frame molecular electronic wavefunction, where the index $\bar{n}$ counts the electronic states with the same Ω_R. It is an eigenfunction of the full electronic Hamiltonian $H_{el} = H_0(\mathbf{r}) + V(\mathbf{r}, R)$ at fixed nuclei, where $H_0(\mathbf{r})$ is the Hamiltonian of free fragments and $V(\mathbf{r}, R)$ is the interaction.

The terms $\langle n\Omega_k | j\Omega_k \rangle$ are the expansion coefficients of the adiabatic molecular electronic wavefunction $|n\Omega_k\rangle$ over functions of free fragments $|j\Omega_k\rangle$ in the asymptotic region $R \to \infty$ [30, 31]. The advantage of the expansion in equation (2) is that the quantum numbers $\bar{n}$, Ω_R in the case of linear molecules are preserved during dissociation in the absence of nonadiabatic interactions. The functions $\chi^J_{\bar{n}\Omega_R; n\Omega_k}(R)$ in equation (2) are the scattering functions. They can be found as a result of the solution of the molecular frame coupled scattering equations [30, 37].

The expansion in equation (2) is written in a form that does not take into account the parity of the molecular states. The expansion that takes into account the molecular parity has been presented in our paper [32]. The advantage of the parity-adapted presentation of the molecular wavefunction is that it allows for separation of the set of close-coupled equations of scattering theory into two blocks corresponding each to the positive or negative total parity of the molecule μ that can greatly simplify the solution of scattering equations. However, as shown in [31, 32] the final expression for the photofragment state multipole moments is the same in both approaches.

The general expression for the irreducible polarization cross section $\sigma_{KQ}(\theta, \phi)$ describing the angle-recoil distribution of the fragment A angular momentum polarization can be presented in the following universal form [32]:

$$\sigma^{(j_A)}_{KQ}(\theta, \phi) = \frac{\sigma_0}{4\pi} \sum_{k_d, q_d} \sum_{q_k} \mathbf{c}^K_{k_d q_k} D^{K}_{Q q_k}{}^*(\phi, \theta, 0)$$

$$\times D^{k_d}_{q_d q_k}(\phi, \theta, 0) E_{k_d q_d}(\mathbf{e}), \qquad (3)$$

where σ_0 is the total reaction cross section, $E_{k_d q_d}(\mathbf{e})$ is the photon polarization matrix [9] and $\mathbf{c}^K_{k_d q_k}$ are the *anisotropy transforming coefficients* describing photodissociation dynamics and $\mathbf{c}^0_{00} = -\sqrt{3}$. The polarization rank K and its projection Q are integer and limited to the values: $0 \leqslant K \leqslant 2j_A$ and $-K \leqslant Q \leqslant K$.

In case $K = Q = 0$ and if the photolysis light is linearly polarized along the Z-axis, equation (3) is equivalent to the conventional differential reaction cross section:

$$\sigma^{(j_A)}_{00}(\theta, \phi) = \frac{\sigma_0}{4\pi} [1 + \beta P_2(\cos\theta)], \qquad (4)$$

where $\beta = (2/3)^{1/2} \mathbf{c}^0_{20}$, while the terms with $K > 0$ describe the photofragment angular momentum polarization (orientation and alignment [9]).

As shown in [32], equation (3) is general and can be used for the description of any one-photon photolysis reaction including photodissociation of diatomic and polyatomic molecules in the frame of the first-order time-dependent perturbation theory under the condition that the average over the quantum numbers of the undetected photofragment B is performed. The anisotropy transforming coefficients $\mathbf{c}^K_{k_d q_k}$ are proportional to the known anisotropy parameters β, s_K, α_K, γ_K, γ'_K, η_K [7] in pairs. The relationship between these two sets of parameters is tabulated in [32]. In general, the coefficients $\mathbf{c}^K_{k_d q_k}$ depend on the photofragment polarization rank K, on the photon rank k_d, and on their projection onto the recoil axis q_k.

As shown in [32, 33], the 'coherent' quantum number q_k is preserved in any photochemical reaction due to the symmetry of rotation of the body-frame state multipole $\sigma^{(j_A)}_{Kq_k}$ about the recoil axis **k**. This quantum number is equal to $q_k = \lambda - \lambda' = \Omega_k - \Omega'_k$ where λ and Ω_k are the photon helicity and the photofragment helicity onto the recoil axis, respectively. Therefore, the physical meaning of preservation of the quantum number q_k is that the coherence of the photolysis photons $\lambda - \lambda'$, which is introduced to the parent molecule, is preserved in the reaction and transferred into the coherence of the produced photofragments $\Omega_k - \Omega'_k$, when both coherences are defined in the same recoil frame.

The anisotropy transforming coefficients $\mathbf{c}^K_{k_d q_k}$ are scalar values which contain all information about the photodissociation dynamics and can be either calculated theoretically or determined from experiment. It is clear that the particular values of the coefficients $\mathbf{c}^K_{k_d q_k}$ depend on the parent molecule and on the photolysis mechanism. In the case of dissociation of diatomic molecules, the explicit expression for the coefficients $\mathbf{c}^K_{k_d q_k}$ in terms of the quantum mechanical scattering matrix $S^J_{\bar{n}\Omega_R; n\Omega_k}$ describing the dynamics of the molecular excited state are presented in [33].

3. The role of molecular rotation in direct photodissociation

The influence of rotation of molecular axis on the angular momentum polarization of the photofragments produced in the direct photodissociation has been theoretically treated in [30, 32] in the frame of the quasi-classical approximation in the high-J limit. Within the quasi-classical approximation the entire internuclear distance area can be divided into wide regions where the dissociation dynamics is mostly adiabatic and relatively narrow regions where the nonadiabatic interactions occur [37]. Within this approximation the quantum mechanical scattering matrix $S^J_{\bar{n}\Omega_R; n\Omega_k}$ can be factorized as

$$S^J_{\bar{n}\Omega_R; n\Omega_k} \approx \eta^J_{\bar{n}\Omega_R; n\Omega_k} e^{-2i\,\delta^J_{n\Omega_k}}, \qquad (5)$$

where the phase $\delta^J_{n\Omega_k}$ is close to the elastic scattering phase which is assumed to be large and leads to the fast oscillations of the exponent as a function of J, while the term $\eta^J_{\bar{n}\Omega_R; n\Omega_k}$ describes nonadiabatic interactions and weakly depends on J in the region $J_i \pm 1$.

Equation (5) allows us to introduce the classical angle of rotation of the molecular axis γ and to derive analytical

Table 1. Anisotropy parameters describing the fragment angular momentum polarization in fast photodissociation of rotating molecules in the high-J limit [30]. Only the radial nonadiabatic interactions are taken into account. The superscript index (0) labels the anisotropy parameters calculated for photodissociation of nonrotating molecules in the axial-recoil approximation.

K	1	2	3	4
α_K	$\alpha_1^{(0)}\cos\gamma$	$\alpha_2^{(0)}P_2(\cos\gamma)$	$\alpha_3^{(0)}\cos\gamma$	$\alpha_4^{(0)}P_2(\cos\gamma)$
s_K	$\dots$	$s_2^{(0)}$	$\dots$	$s_4^{(0)}$
γ_K	$\gamma_1^{(0)}\dfrac{1+\cos\gamma}{2}$	$\gamma_2^{(0)}\dfrac{2\cos^2\gamma+\cos\gamma-1}{2}$	$\gamma_3^{(0)}\dfrac{1+\cos\gamma}{2}$	$\gamma_4^{(0)}\dfrac{2\cos^2\gamma+\cos\gamma-1}{2}$
γ_K'	$\gamma_1'^{(0)}\dfrac{2\cos^2\gamma+\cos\gamma-1}{2}$	$\gamma_2'^{(0)}\dfrac{1+\cos\gamma}{2}$	$\gamma_3'^{(0)}\dfrac{2\cos^2\gamma+\cos\gamma-1}{2}$	$\gamma_4'^{(0)}\dfrac{1+\cos\gamma}{2}$
η_K	$\dots$	$\eta_2^{(0)}\dfrac{(1+\cos\gamma)^2}{4}$	$\eta_3^{(0)}\dfrac{(1+\cos\gamma)^2}{4}$	$\eta_4^{(0)}\dfrac{(1+\cos\gamma)^2}{4}$

expressions for the anisotropy parameters/anisotropy transforming coefficients in equation (3) for the case of direct photodissociation where the dissociation time τ_{diss} is smaller than the molecular rotation period T_{rot}. These expressions take into account radial and Coriolis nonadiabatic interactions as well as the full range of interference effects. The influence of molecular rotation on the photofragment angular momentum polarization is described in these expressions by a set of the *rotational factors* $D_{q_k q_R}^{k_d}(\frac{\pi}{2}, \gamma, -\frac{\pi}{2})$, where $k_d = 0, 1, 2$ is the photon rank, see equation (3), whereas q_k and q_R are the photon rank spherical projections [9] onto the directions **k** and **R**, respectively.

If the Coriolis nonadiabatic interactions can be neglected, $q_k = q_R$ and each anisotropy parameter β, s_K, α_K, γ_K, γ_K', η_K can be presented as a product of the corresponding 'axial recoil' anisotropy parameter $\beta^{(0)}$, $s_K^{(0)}$, $\alpha_K^{(0)}$, $\gamma_K^{(0)}$, $\gamma_K^{(0)'}$, $\eta_K^{(0)}$ and a rotational factor, where the 'axial recoil' anisotropy parameters describe the photofragment angular momentum polarization in nonrotating molecules [7].

The expressions for anisotropy parameters of the rank $K = 1, 2, 3, 4$ as a function of the angle γ are collected in table 1. As is clear from the table, the rotation of the molecular axis in most cases decreases the values of the anisotropy parameters, thus decreasing the fragment angular momentum anisotropy.

For the zeroth rank anisotropy parameter β the theory gives the expression

$$\beta = P_2(\cos\gamma)\beta^{(0)}, \tag{6}$$

which is in perfect agreement with previously reported results obtained by different classical and quantum mechanical methods [38–41].

If both radial and Coriolis nonadiabatic interactions are taken into account, the expression for the anisotropy parameters β, s_K, α_K, γ_K, γ_K' and η_K are more complicated and can be presented as a sum of terms each related to a certain photodissociation mechanism [32]. In this case, the anisotropy parameters cannot be characterized by the symmetry of optical excitation (parallel, perpendicular, etc) because in general many types of optical excitation can be involved in each parameter. For example, the parameter β can

be presented in the form [32]:

$$\begin{aligned}
\beta ={}& 2\,d_{00}^2(\gamma)\frac{[f_0(0,0,0,0) - f_0(1,1,1,1)]}{\mathcal{N}} + 2\,d_{00}^2(\gamma) \\
&\times \frac{[2f_0(0,0,1,1) - f_0(1,1,0,0) - f_0(1,1,2,2)]}{\mathcal{N}} \\
&- 4\sqrt{3}\,d_{01}^2(\gamma)\frac{\mathrm{Im}[f_0(1,0,1,1) + f_0(1,0,0,0)]}{\mathcal{N}} \\
&+ 2\sqrt{6}\,d_{02}^2(\gamma)\frac{f_0(1,-1,0,0)}{\mathcal{N}},
\end{aligned} \tag{7}$$

where the normalization factor $\mathcal{N}$ is given by

$$\begin{aligned}
\mathcal{N} ={}& f_0(0,0,0,0) + 2f_0(1,1,1,1) + 2f_0(0,0,1,1) \\
&+ 2f_0(1,1,0,0) + 2f_0(1,1,2,2),
\end{aligned} \tag{8}$$

where $d_{q_k q_R}^K(\gamma)$ are the Wigner d-functions [42].

The terms $f_K(q, q', \tilde{q}, \tilde{q}')$ in equations (7) and (8) are generalized dynamical functions [30], which contain all information on the photodissociation dynamics. They depend on the photofragment rank K and on the indices q, q', $\tilde{q}$, $\tilde{q}'$. The indices $q = \Omega_R - \Omega_i = 0, \pm 1$, $q' = \Omega_R' - \Omega_i = 0, \pm 1$ and $\tilde{q} = \Omega_k - \Omega_i = 0, \pm 1, \pm 2$, $\tilde{q}' = \Omega_k' - \Omega_i = 0, \pm 1, \pm 2$ describe the symmetry of the optical and nonadiabatic transitions, respectively, in such a way that for the parallel optical transitions $q = 0$, for the perpendicular optical transitions $q = \pm 1$, for the radial nonadiabatic transitions $\tilde{q} = q$ and for the Coriolis nonadiabatic transitions $\tilde{q} = q \pm 1$. The first line in equation (7) relates to the adiabatic photodissociation or to the pure radial nonadiabatic transitions during the photodissociation. Two other lines describe different contributions from the Coriolis nonadiabatic transitions.

As shown in [32], the Coriolis nonadiabatic interactions can result in new dissociation mechanisms. For example, due to the Coriolis interaction the photodissociation via a pure parallel transition can produce the orientation ($K = 1$) of the photofragment angular momenta. Explicit expressions for the anisotropy parameters of the ranks $K = 0, 1, 2$ and detailed discussion of all photolysis mechanisms that are possible in the presence of the Coriolis interactions can be found in [32].

4. Slow predissociation

The case of slow predissociation when the excited state life time is much larger than the rotation period, $\tau_{\mathrm{diss}} \gg T_{\mathrm{rot}}$ has been theoretically treated in [31, 33]. In this case, the J and J' coherent terms in the general expression for the anisotropy parameters can be neglected resulting in noticeable simplification of the obtained formulae. In particular, in case $K = 0$, $Q = 0$ the general expression for the parameter β can be written in the relatively simple form which is valid to any integer and half-integer J values and takes into account all possible radial and Coriolis nonadiabatic transitions [33]:

$$\beta = \sqrt{30}(-1)^{J+J_i}\sqrt{2J+1}\begin{Bmatrix} J & J & 2 \\ 1 & 1 & J_i \end{Bmatrix} C^{J\Omega_k}_{J\Omega_k 20}, \quad (9)$$

where $C^{J\Omega_k}_{J\Omega_k 20}$ is the Clebsch–Gordan coefficient, and the term in the curly brackets is a $6j$-symbol [42].

As shown in equation (9), the parameter β depends on the final projection Ω_k of the total angular momentum J, but not on initial projection Ω_i and the intermediate one Ω_R. If only the radial nonadiabatic interactions are important, $\Omega_k = \Omega_R$.

Equation (9) is the generalization of the previous results reported by Zare [43] and by Liyanage and Gordon [44], who did not take into account the Coriolis coupling. In the high-J limit, $J_i \gg 1$, the parameter β for the P, Q and R rotational branches is given by: $\beta(\mathrm{Q}) = -1$, $\beta(\mathrm{P, R}) = 1/2$ in agreement with the previous results [43, 44].

The expressions for recoil-angle dependences of the photofragment anisotropy parameters of the rank $K \geqslant 0$ in the high-J limit have been reported for the case of the broad-band optical excitation when all rotational branches are excited simultaneously [31, 32] and for the case when each of the rotational branches is excited separately [31, 33]. As shown, the expressions for the broad-band excitation can be formally obtained from the expressions for direct photodissociation by averaging the rotation factors $D^{k_d}_{q_k q_R}(\frac{\pi}{2}, \gamma, -\frac{\pi}{2})$ over the angle γ. The obtained terms which can be called the *reduction factors* describe the reduction of the corresponding photolysis mechanism in the limit of infinitely long molecular rotation.

For example, the rotational factor $P_2(\cos\gamma)$ in equation (6) in the case of slow predissociation should be replaced by $\langle P_2(\cos\gamma)\rangle = 1/4$ which is in agreement with the semiclassical result reported earlier by Jonah [39] and with the quantum mechanical result reported by Mukamel and Jortner [45]. The anisotropy parameters of the rank $K = 1$–4 for the case of slow predissociation calculated in the absence of the Coriolis interactions are presented in table 2 and the corresponding expressions calculated in presence of the Coriolis interactions are discussed in [32]. Some of the rotation factors after averaging of the angle γ have zero value [31, 33], therefore the number of possible photodissociation mechanisms resulting in the photofragment angular momentum polarization in the case of slow predissociation is in general smaller than the number of photodissociation mechanisms in the case of direct photodissociation. The obtained results for the radial and for the Coriolis interactions differ from each other dramatically.

Particularly, in the absence of the Coriolis interactions the photofragment orientation ($K = 1$) can be produced only via the coherent $\Delta\Omega_R = \pm 1$ optical excitation of the $\Omega_R = \pm 1/2$

Table 2. Anisotropy parameters describing the fragment angular momentum polarization in the case of slow predissociation in the high-J limit [31]. Only the radial nonadiabatic interactions are taken into account. The superscript index (0) labels the anisotropy parameters calculated for photodissociation of nonrotating molecules in the axial-recoil approximation.

K	1	2	3	4
α_K	0	$\frac{1}{4}\alpha_2^{(0)}$	0	$\frac{1}{4}\alpha_4^{(0)}$
s_K	$\ldots$	$s_2^{(0)}$	$\ldots$	$s_4^{(0)}$
γ_K	$\frac{1}{2}\gamma_1^{(0)}$	0	$\frac{1}{2}\gamma_3^{(0)}$	0
γ_K'	0	$\frac{1}{2}\gamma_2'^{(0)}$	0	$\frac{1}{2}\gamma_4'^{(0)}$
η_K	$\ldots$	$\frac{3}{8}\eta_2^{(0)}$	$\frac{3}{8}\eta_3^{(0)}$	$\frac{3}{8}\eta_4^{(0)}$

electronic states on the $|\Omega_i| = 1/2 \to |\Omega_R| = 1/2$ transition where either the initial or the final electronic state must be a mixture of the $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states [31]. However, when the Coriolis interaction is involved, several other predissociation mechanisms are possible which begin with the incoherent optical excitation from the ground electronic state $^1\Sigma$ to a single predissociative state and then continue with simultaneous radial and Coriolis nonadiabatic transitions [33].

In the cases of slow predissociation and intensive Coriolis nonadiabatic interactions, the expression for the anisotropy parameters β, s_K, α_K, γ_K, γ_K' and η_K can be presented as sums of the terms each related to a certain photodissociation mechanism [32]. In this case, as in the case of direct photodissociation, the anisotropy parameters cannot be characterized by the parallel or perpendicular optical excitation because in general many types of optical excitation can be involved.

5. Conclusion

As shown above, the recoil-angle distribution of the photofragment state multipole moments can be presented in a universal form in terms of the anisotropy transforming coefficients irrespective of the photolysis mechanism. The explicit expressions for the anisotropy transforming coefficients (anisotropy parameters) in the case of photolysis of a diatomic molecules are now well understood. These expressions contain contributions from the radial and Coriolis nonadiabatic interactions, possible coherent effects, long-range interactions, and can also take into account the effect of molecular rotation (at least in the high-J limit). Therefore, the anisotropy transforming coefficients can be directly obtained from the experiment and used for determination of important information on the photodissociation dynamics. This is the information on: the excited state symmetry and the photolysis reaction channels, possible interference effects, symmetry, amplitudes and phases of possible nonadiabatic transitions, rotation of the molecular axis during dissociation [4, 7]. These expressions also allow for calculation of the corresponding parameters from *ab initio* theory (at least in principle), thus making possible the complete experiment in the field of molecular photolysis [7].

The next important step of the research in the field seems to be the transformation of the ideas and methods,

which are well established now for diatomic molecules, to the photolysis of triatomic and small polyatomic molecules, which play an important role in photochemical reactions in the atmosphere and in industrial apparatus. Determination of the corresponding anisotropy parameters from experiment is straightforward, because it is based on the same universal recoil-angle distribution for the polarization cross section in equation (3). In fact, for the moment there have already been performed a series of remarkable experimental studies on spin and orbital momentum orientation and alignment in photolysis of triatomic and polyatomic molecules in many world laboratories, see the review papers [3–7]. However, the interpretation of these experimental results is so far rather poor, because the theoretical methods for extracting the dynamical information from the experimental data are not developed enough. To our mind, these theoretical methods can be developed based on the results presented in this review paper.

Acknowledgment

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