

Photofragment angular momentum polarization in the photolysis of symmetric top molecules: Production, detection, and rotational depolarization

Peter S. Shternin^a, Arthur G. Suits^b, Oleg S. Vasyutinskii^{a,*}

^a Ioffe Physical-Technical Institute, Russian Academy of Sciences, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia

^b Department of Chemistry, Wayne State University, 5101 Cass Ave, Detroit, MI 48202, USA

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ABSTRACT

We present the fully quantum mechanical distribution of the photofragment angular momentum polarization in the photolysis of an isotropic ensemble of symmetric top molecules. The distribution is written in terms of the recently established anisotropy transforming coefficients $c_{k_d q_k}^K$ (P.S. Shternin, O.S. Vasyutinskii, Chem. Phys. 128 (2008) 194314) which contain all dynamical information on the photolysis dynamics and can be either determined from experiment, or calculated from theory. Explicit expressions for the coefficients $c_{k_d q_k}^K$ for the case of photolysis of symmetric top molecules were obtained within the full quantum mechanical approach and then simplified using the quasiclassical approximation in the high- J limit. The role of the photofragment angular momentum depolarization due to molecular rotation was analyzed for three important particular cases: photolysis of diatomic molecules, photolysis of symmetric top molecules when the angular momentum polarization of atomic photofragments are detected, photolysis of symmetric top molecules when the angular momentum polarization of molecular photofragments are detected. The obtained rotation factors were compared with the results of previous studies. The paper also presents a compact spherical tensor expression for the 2 + 1 REMPI absorption signal which can be used for direct determination of the coefficients $c_{k_d q_k}^K$ from experiment. A comparison was made between the anisotropy transforming coefficients $c_{k_d q_k}^K$ and the polarization parameters A_q^K introduced very recently by (T.P. Rakitzis, A.J. Alexander, J. Chem. Phys. 132 (2010) 224310) for description of the photofragment polarization in photolysis of polyatomic molecules. This comparison shows that these two sets of parameters are equivalent to each other as they just proportional to each other in pairs.

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1. Introduction

Angular momentum polarization of the products of photolysis of diatomic and polyatomic molecules attracts wide attention for decades [1–10]. The importance of vector properties in photodissociation dynamics is a consequence of the fact that practically all interactions within a reaction complex are intrinsically anisotropic and this fact often results in electronic, or rotational anisotropy in the produced photofragments.

The form and degree of this anisotropy is often a function of the photofragment recoil direction and provides correlation between the direction of the recoil vector and the direction of the photofragment electronic or rotational angular momentum. The complete quantum mechanical treatment of the photofragmentation process is in general required for description of the full range of interference effects and nonadiabatic interactions.

Using the axial recoil approximation, Siebbeles et al. [11] presented a quantum mechanical treatment of the angular momentum distribution of the photofragments based on the spherical tensor formalism for the case of unpolarized parent molecules. This approach allows for separation of the kinematical and dynamical parts of the angular momentum distribution and was later used by Picheyev et al. [12] and by Rakitzis and Zare [13] for introducing two alternative sets of anisotropy (polarization) parameters which contain all information about the photodissociation dynamics and can be either calculated from theory, or determined from experiment. The spherical tensor expression presented in Ref. [11] has been extended to the case of two open shell photofragments by Bracker et al. [14] and by Balint-Kurti et al. [15] who developed a critical link from theoretical description to the experimental observations.

Recently, Shternin and Vasyutinskii [16] have generalized the approach of Siebbeles et al. [11] to the case of photodissociation beyond the axial recoil approximation. Assuming that only one of the two photofragments (the photofragment A) is detected

* Corresponding author.

E-mail address: osv@pms.ioffe.ru (O.S. Vasyutinskii).

Shternin and Vasyutinskii [16] reported a spherical tensor expression for the photodissociation polarization cross section (photo-fragment state multipole moment) for the photolysis reaction



which is valid for any photolysis reaction in diatomic, or polyatomic molecules, irrespectively of the reaction mechanism.

The expression for the photodissociation polarization cross section [16] was presented in terms of the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ which are scalar values containing all information on the photodissociation dynamics.

In general, the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ contain the terms describing the optical excitation of the parent molecule and the following dynamical evolution including nonadiabatic interactions, coherent effects, and rotation of the molecular axis during photodissociation. The explicit expressions for these coefficients for photodissociation of diatomic (linear) parent molecules were presented in Ref. [16,17] for the case of direct photodissociation and slow predissociation.

The generalization of this approach to the case of polarized parent molecules has recently been reported by Krasilnikov et al. [18].

The aim of this paper is to present and analyze an expression for the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ for the case of photolysis of a symmetric top polyatomic molecule, where two moments of inertia are equal to each other $I_x = I_y \equiv I_\perp$ and differ from the third one $I_z \equiv I_\parallel$ [19]. In general, this expression can be written in the full quantum mechanical form for arbitrary value of the molecular total angular momentum J , however in this paper we restrict ourselves to the quasiclassical approximation in the high- J limit, $J \gg 1$.

In particular, we analyze the obtained expression for the anisotropy transforming coefficients and point out main differences between the polyatomic and diatomic photodissociation. Then, the 2 + 1 REMPI detection scheme which can be used for determining of the anisotropy transforming coefficients from experiment is analyzed and a compact spherical tensor expression for the 2 + 1 signal intensity is presented.

The 2 + 1 signal intensity expression is used for comparison between the set of the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ by Shternin and Vasyutinskii [16], the set of the polarization parameters A_v^K very recently suggested by Rakitzis and Alexander [20] and Rakitzis [21] on the basis of the density matrix approach using classical arguments, and the set of the anisotropy parameters suggested earlier of Picheyev et al. [12]. It is shown that all three sets of parameters are equivalent to each other being simply proportional to each other in pairs. Therefore, each set can be used for the description of photofragment polarization from photolysis of arbitrary polyatomic molecules.

As shown, the anisotropy transforming coefficient expression in the high- J limit contains the *rotational factors* which describe the depolarization of the photofragment angular momentum due to the molecular rotation. The rotation factor expression is analyzed for three particular cases of the photolysis reactions. They are: (i) photolysis of diatomic molecules; (ii) photolysis of symmetric top molecules when the angular momentum polarization of atomic photofragments is detected; (iii) photolysis of symmetric top molecules when the angular momentum polarization of molecular photofragments is detected. As shown, the depolarization mechanism for each of the three cases differs from others.

In case (i) total angular momenta of photofragments A and B (j_A and j_B , respectively) are small, $j_A, j_B \ll J$, and the molecular angular momentum \mathbf{J} is mainly perpendicular to the parent molecule symmetry axis. The obtained rotational factor expressions are the same as those reported earlier by Kuznetsov and Vasyutinskii [22,23].

In case (ii) $j_A \ll j_B$, J and the molecular angular momentum \mathbf{J} can have any angle of declination β_j with respect to the parent

molecule symmetry axis. Integration over the angle of declination β_j results in rotational factors which in general differ from those for the case (i). In particular, in the photolysis of spherical top molecules where all three inertia moments are the same, $I_\perp = I_\parallel = I$, the obtained rotation factors are equivalent to those reported very recently by Bougas and Rakitzis [24].

A simple vector model illustrating the depolarization mechanisms related to different anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ in terms of two possible types of free rotation of a symmetric top molecule is presented.

In case (iii) $j_A, J \gg j_B$ and the obtained rotational factors in general differ either from the case (i), or from the case (ii). The main peculiar features of this case are that each Ω -state in the parent symmetric top molecule (where Ω is the projection of the total angular momentum onto the molecular axis) refers to a certain value of the molecular photofragment angular momentum j_A and that a rotational factor is in general a function of Ω and j_A . Therefore, the calculation of the rotation factors become more complicated and the expression for the experimental signal depends in general on the detection procedure.

The obtained results can be used by experimentalist for extracting the dynamical information from vector correlation photodissociation experiment and for analysis of the angular momentum depolarization in symmetric top molecules.

2. Photodissociation polarization cross section

As shown by Shternin and Vasyutinskii [16] using the standard quantum mechanical approach which apply for photodissociation of diatomics as well as polyatomic molecules into two fragments [25–27], the general spherical tensor expression describing the photofragment A angular momentum polarization can be presented in a double expansion form:

$$\sigma_{KQ}^{(j_A)}(\mathbf{k}, \mathbf{e}) = \frac{\sigma_0}{4\pi} \sum_{k_d, q_d, q} \mathbf{c}_{k_d q_k}^K D_{Qq_k}^{K*}(\phi, \theta, 0) D_{q_d q_k}^{k_d}(\phi, \theta, 0) E_{k_d q_d}(\mathbf{e}), \quad (2)$$

where $D_{q_d q_k}^{k_d}(\phi, \theta, 0)$ is a Wigner D -function [28], ϕ and θ are polar angles specifying the photofragment recoil direction \mathbf{k} , and $\sigma_0 = \langle \sigma_{00}^{(j_A)} \rangle$ is the total photodissociation cross section.

The irreducible differential cross section $\sigma_{KQ}^{(j_A)}(\mathbf{k}, \mathbf{e})$ in the left part of Eq. (2) describes the polarization of a photofragment with angular momentum j_A flying apart in the recoil direction \mathbf{k} . The rank K and laboratory frame projection Q describe the orientation and alignment of the photofragment A angular momentum: $K = 0 \dots 2j_A$ and $Q = -K \dots K$.

The term $E_{k_d q_d}(\mathbf{e})$ in Eq. (2), where \mathbf{e} is the photolysis light polarization vector, is the light polarization matrix [19] with rank $k_d = 0, 1, 2$ and laboratory frame spherical projection $q_d = -k_d \dots k_d$.

The spherical tensor $\sigma_{KQ}^{(j_A)}(\mathbf{k}, \mathbf{e})$ describes the photofragment angular momentum polarization in the laboratory frame. In the body frame referred to the recoil direction \mathbf{k} the differential cross section in Eq. (2) can be written in a compact form [16]:

$$\sigma_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k) = \frac{\sigma_0}{4\pi} \sum_{k_d} \mathbf{c}_{k_d q_k}^K E_{k_d q_k}(\vartheta_k, \varphi_k), \quad (3)$$

where both spherical tensors $\sigma_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k)$ and $E_{k_d q_k}(\vartheta_k, \varphi_k)$ are quantized onto the recoil direction \mathbf{k} and the polar angles (ϑ_k, φ_k) specify the direction of the light polarization vector \mathbf{e} in the recoil frame $X_k Y_k Z_k$.

The laboratory and body frame expressions for the differential cross section in Eqs. (2) and (3) have been derived for the case of one photon photoexcitation in the low light intensity (dipole) approximation. It was also assumed that only one of the two photofragments (A) is detected and the averaging over the

quantum numbers of the other, nondetected photofragment was performed.

Under these conditions, Eqs. (2) and (3) are valid for any photodissociation reaction in diatomic, or polyatomic molecules irrespectively on the reaction mechanism.

The scalar expansion coefficients $c_{k_d q_k}^K$ in Eqs. (2) and (3) are anisotropy transforming coefficients which contain all information about the photodissociation dynamics and can be either determined from experiment, or calculated from theory. They depend on three quantum numbers K , k_d , and q_k , where K is the photofragment rank, k_d is the light polarization rank, and q_k is the coherent quantum number [17] which is the projection of the ranks K and k_d onto the recoil axis \mathbf{k} . The coefficient c_{00}^0 is a normalization constant fixed to $c_{00}^0 = -\sqrt{3}$. Although the anisotropy transforming coefficients are in general complex values, all measurable variables, like intensity of the probe light absorption are always real, because they contain only real, or imaginary parts of the coefficients. As can be seen from Eq. (3), the projection q_k onto the recoil axis \mathbf{k} is preserved in the photochemical reaction, which is an important conservation law underlying many vector correlation effects of photochemical reactions. As can be shown, this conservation law is in general based on the conservation of the projection of the total angular momentum of the system photon+molecule onto the recoil axis. The physical meaning of the projection q_k is very clear. It is equal to

$$q_k = \mu - \mu' = \Omega_A - \Omega'_A, \quad (4)$$

where $\mu = 0, \pm 1$ and $\Omega_A = -j_A \dots j_A$ are the projections of the photolysis light polarization vector \mathbf{e} and of the photofragment A total angular momentum \mathbf{j}_A , respectively, onto the asymptotic recoil direction \mathbf{k} .

The values $\mu - \mu'$ and $\Omega_A - \Omega'_A$ in Eq. (4) relate to the coherence in the light polarization matrix and in the photofragment angular momentum system, respectively. Therefore, the conservation of the projection q_k in photochemical reactions is equivalent to the conservation of the corresponding coherences.

In the particular case $K = 0$, $Q = 0$, using the explicit expression of the polarization matrix $E_{k_d q_k}$ [19] Eq. (3) can be readily transformed to the well known expression describing the angular distribution of photofragments [1]:

$$\sigma_{00} = \frac{\sigma_0}{4\pi} [1 + \beta P_2(\cos \vartheta_k)], \quad (5)$$

where $P_2(\cos \vartheta_k)$ is the Legendre polynomial of the second order and the parameter β is equal to $\beta = \sqrt{2/3} c_{20}^0$.

If $K \neq 0$, Eqs. (2) and (3) describe the angular momentum polarization of the photofragment A as function of the recoil angles.

In this paper we derive and analyze the quantum mechanical expressions for the polarization cross section describing the photolysis of a symmetric top molecule resulting in two photofragments, one of them is a symmetric top molecule and another is an atom. The parent symmetric top molecule is considered to behave during dissociation like a rigid rotator, which means that possible vibration effects are neglected.

We start from the expression for the generalized photofragmentation cross section $\sigma(\mathbf{k}, E; j m', j m)$ which can be written in the form [15,25,26]:

$$\begin{aligned} \sigma(\mathbf{k}, E; j m', j m) &= \frac{C}{(2j_i + 1)} \sum_{J_i, M_i, \Omega_i} \langle \Psi^{-(\mathbf{k}, j m')}(\mathbf{R}, \mathbf{r}, E) | \hat{\mathbf{d}} \cdot \mathbf{e} | \Psi_{J_i, M_i, \Omega_i} \rangle \\ &\times \langle \Psi^{-(\mathbf{k}, j m)}(\mathbf{R}, \mathbf{r}, E) | \hat{\mathbf{d}} \cdot \mathbf{e} | \Psi_{J_i, M_i, \Omega_i} \rangle^* N(J_i, \Omega_i), \end{aligned} \quad (6)$$

where j and m are the total photofragment angular momentum, $\mathbf{j} = \mathbf{j}_A + \mathbf{j}_B$ and its laboratory frame projection, respectively, $\hat{\mathbf{d}}$ is a dipole moment operator, \mathbf{R} is the vector connecting the centers of

mass of the fragments, while \mathbf{r} denotes collectively all the internal coordinates of fragments.

Note, that in this paper we denote the molecular frame projection of a symmetric top angular momentum J by the letter Ω , not by the frequently used letter K (see, e.g., Ref. [19]) in order to avoid a confusion, because the letter K is used throughout paper for labelling spherical tensor ranks.

The coefficient C in Eq. (6) is given by $C = 2\pi^2 v / c \epsilon_0$, where v is the frequency of the photolysis light. The term $\Psi_{J_i, M_i, \Omega_i}$ is the wave function of the parent molecule initial state, where J_i , M_i , and Ω_i are the total initial state angular momentum and its projections onto the laboratory axis \mathbf{Z} , and onto the molecular axis \mathbf{R} , respectively. The initial molecular state is assumed to be unpolarized, the term $N(J_i, \Omega_i)$ denotes the population of the corresponding rotational energy sublevels.

The term $\Psi^{-(\mathbf{k}, j m)}(\mathbf{R}, \mathbf{r}, E)$ is the dissociative wave function describing two photofragments flying apart with total energy E in a direction specified by the vector \mathbf{k} . At large internuclear distance R the dissociative wave function obeys usual boundary condition corresponding to an outgoing plane wave with specific internal states and incoming spherical waves in all other channels: [27,30]

$$\Psi^{-(\mathbf{k}, j m)}(\mathbf{R}, \mathbf{r}, E) \stackrel{R \rightarrow \infty}{\sim} e^{i\mathbf{k}\mathbf{R}} |j m\rangle + \sum_{\bar{j} m} f_{j m, \bar{j} m}(\mathbf{R}, \mathbf{k}) \frac{e^{-i\mathbf{k}\bar{j}\mathbf{R}}}{R} |\bar{j} m\rangle. \quad (7)$$

Let the letter A denote the molecular fragment and B denote the atomic fragment. At large internuclear distance R the total photofragment wave function $|j m\rangle$ in Eq. (7) can be expressed in terms of the free fragment wave functions:

$$|j m\rangle \equiv \psi_{j m} = \sum_{m_A, m_B} C_{j_A m_A, j_B m_B}^{j m} \sqrt{\frac{2j_A + 1}{8\pi^2}} D_{m_A, \Lambda_A}^{j_A}(\Phi, \Theta, \Xi) |n_A\rangle |j_B m_B\rangle, \quad (8)$$

where the first term in the right side is a Clebsch–Gordan coefficient and the Euler angles (Φ, Θ, Ξ) describe the position of the molecular fragment axis with respect to the laboratory frame XYZ .

The Wigner D -function $D_{m_A, \Lambda_A}^{j_A}(\Phi, \Theta, \Xi)$ in Eq. (8) is the rotational wave function of the molecular fragment A with angular momentum j_A , laboratory frame projection m_A , and the projection on the fragment axis Λ_A . The terms $|n_A\rangle$ and $|j_B m_B\rangle$ are electronic wave functions of the free fragments A and B, respectively.

At any internuclear distances R the dissociation wave function $\Psi^{-(\mathbf{k}, j m)}(\mathbf{R}, \mathbf{r}, E)$ and the wave function of the initial molecular state $\Psi_{J_i, M_i, \Omega_i}$ in Eq. (6) can be expanded over the orthogonal set of the Wigner D -functions and the internal fragment wave functions [22,25,26]. In this paper for simplicity we use the *adiabatic* basis set, in contrast to the *diabatic* basis set usually used for the diatomic molecules [22]. Within the diabatic basis set the photofragment wavefunctions are taken in the asymptotic form (8) which depends on all electronic coordinates and the angles Φ, Θ, Ξ , but does not depend on R . The expansion coefficients $\mathcal{Y}_{j_i, \Omega_i; j, \Omega_k}^{j_i, \Omega_i}(R)$ (the scattering functions) which are the function of R are the subject of the set of closed-coupled equations [25,26]. These functions depend on the total molecular angular momentum J , on the initial and final quantum numbers \bar{j}, j , and on the helicities Ω_R, Ω_k .

Using the standard transformations of the quantum theory of angular momentum [11,16,22,25,26,29], the fully quantum mechanical expression for the anisotropy transforming coefficients was derived. This expression was simplified using the quasiclassical approximation in the high- J ($J, j \gg 1$) limit. According to the quasiclassical approximation the regions of the internuclear distance R where the dissociation dynamics is mostly adiabatic are assumed to be isolated from the relatively narrow regions where the nonadiabatic interactions occur [27]. Within this approximation

the quantum mechanical scattering matrix $S_{j\Omega_R;j\Omega_k}^J(R)$ (see Ref. [22]) can be presented as a product:

$$S_{j\Omega_R;j\Omega_k}^J(R) \approx \eta_{j\Omega_R;j\Omega_k}^J(R) e^{-2i\delta_{j\Omega_k}^J}, \quad (9)$$

where $\delta_{j\Omega_k}^J$ is the elastic scattering phase which is assumed to be large and results in fast oscillations of the exponent with J , while the term $\eta_{j\Omega_R;j\Omega_k}^J(R)$ weakly depends on J and is responsible for non-adiabatic interactions.

The quantum numbers Ω_R and $\Omega_k = \Omega_A + \Omega_B$ in Eq. (9) are the projections (helicities) of the total angular momentum onto the molecular axis \mathbf{R} and onto the recoil direction \mathbf{k} , respectively.

Using a known asymptotic expression for the elastic scattering wave function

$$\chi^J \approx \sin\left(kR - \frac{\pi J}{2} + \delta_{j\Omega}^J\right) \quad (10)$$

and Eq. (9), the scattering functions $\chi_{j\Omega_R;j\Omega_k}^J$ can be presented in the form:

$$\chi_{j\Omega_R;j\Omega_k}^J(R) \approx e^{-i\delta_{j\Omega_k}^J} \tilde{\chi}_{j\Omega_R;j\Omega_k}^J(R) \quad (11)$$

where the term $\tilde{\chi}_{j\Omega_R;j\Omega_k}^J(R)$ only weakly depends on J and Ω . This allows to take out the phase factors $e^{-i\delta_{j\Omega_k}^J}$ from the dipole transition matrix element in Eq. (6) while the rest part of the matrix element can be calculated at $J = J_i$ (Q branch). This procedure leads to appearance of a phase factor difference in Eq. (6) which can be approximately presented in the form:

$$d\left(\frac{\pi}{2}J - \delta_{j\Omega_k}^J\right) \approx \gamma_{pr}(J)dJ + \gamma_s(J, \Omega)d\Omega, \quad (12)$$

where $\Omega \approx \Omega_R \approx \Omega_k \approx \Omega_i$.

In the quasiclassical limit the quantities $\gamma_{pr}(J)$ and $\gamma_s(J, \Omega)$ in Eq. (12) relate to two classical rotation angles of the symmetric top molecule, see Fig. 6. In particular, $\gamma_{pr}(J)$ is the angle of precession [19] of the molecular axis around the total angular momentum \mathbf{J} during the dissociation time τ :

$$\gamma_{pr}(J) = \frac{J}{I_{\perp}} \tau, \quad (13)$$

where I_{\perp} is the “perpendicular” symmetric top inertia moment.

The value $\gamma_s(J, \Omega)$ in Eq. (12) is the angle of self-rotation [19] of the symmetric top molecule around its symmetry axis during dissociation:

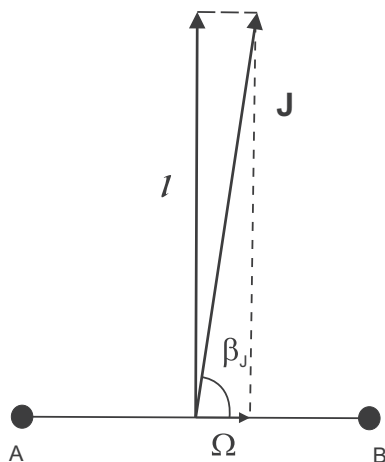


Fig. 1. The vector scheme of the molecular angular momenta coupling in case of a diatomic molecule.

$$\gamma_s(J, \Omega) = \Omega \tau \left(\frac{1}{I_{\parallel}} - \frac{1}{I_{\perp}} \right) = (J + 1/2) \cos \beta_J \tau \left(\frac{1}{I_{\parallel}} - \frac{1}{I_{\perp}} \right) \equiv \gamma_s^0(J) \cos \beta_J, \quad (14)$$

where I_{\parallel} is the “parallel” symmetric top inertia moment and the angle β_J is the declination angle of the angular momentum \mathbf{J} with respect to the molecular axis (see Figs. 1 and 2) which is defined as:

$$\cos \beta_J = \Omega_k / (J + 1/2) \approx \Omega_i / (J_i + 1/2). \quad (15)$$

The angle $\gamma_s^0(J) \equiv \gamma_s^0$ in Eq. (14) is the Ω -independent part of γ_s which is equal to the self-rotation angle at $\beta_J = 0$.

Transforming Eq. (6) to the form of Eq. (2) we obtain the expression for the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ in the following form:

$$\mathbf{c}_{k_d q_k}^K = 3(2K + 1)^{1/2} \mathcal{N}^{-1} \sum_{q, q'} (-1)^{k_d + q'} C_{1q' - q}^{k_d(q - q')} \sum_{J_i, \Omega_k} \sum_{\Delta} \exp\{i[\gamma_{pr}(J_i)\Delta + \gamma_s(J_i, \Omega_k)q_k]\} d_{(q - q')\Delta}^{k_d}(\beta_J) d_{q_k \Delta}^{k_d}(\beta_J) f_K(q, q', q_k) \quad (16)$$

where $d_{q_k \Delta}^{k_d}(\beta_J)$ in the second line is the Wigner d -function [28] and $\Delta = J - J'$.

As will be shown in detail later the sum over Δ in Eq. (16) is responsible for the angular momentum depolarization due to rotation.

The term $f_K(q, q', q_k)$ in the Eq. (16) is the dynamical function [11,18]

$$f_K(q, q', q_k) = \sum_x C_{j_A \Omega_A' K q_k}^{j_A \Omega_A} C_{j_A \Omega_A' j \Omega_k}^{j \Omega_k} C_{j_A \Omega_A' j \Omega_k}^{j \Omega_k} N(J_i, \Omega_i) \times \langle \psi_{j \Omega_k} \tilde{\chi}_{j \Omega_R' j \Omega_k}^J(R) | \hat{d}_{q'} | \psi_{j \Omega_i} \chi_i(R) \rangle \times \langle \psi_{j \Omega_R} \tilde{\chi}_{j \Omega_R' j \Omega_k}^J(R) | \hat{d}_q | \psi_{j \Omega_i} \chi_i(R) \rangle^*, \quad (17)$$

where two terms in the last line are the matrix elements of the dipole moment component \hat{d}_q , where $q, q' = 0, \pm 1$, denote the polar projection of the molecular dipole moment \mathbf{d} onto the body frame \mathbf{R} axis. These matrix elements are responsible for the optical excitation of the parent molecule in the Frank–Condon area and for the following evolution of the electronic and rotational molecular wave function.

The matrix elements contain integration over all “internal” coordinates and over the inter-fragment distance R . The index of summation x in Eq. (16) is an aggregate of the quantum numbers $\Omega_A, \Omega_A', \Omega_B, \Omega_R, \Omega_R', \Omega_i, j, j', j, j_i$. Note that the coherence quantum number $q_k = \Omega_A - \Omega_A'$ in Eqs. (4) and (17) is equal to $\Omega_k - \Omega_k'$ because the B fragment helicities are fixed to $\Omega_B = \Omega_B'$ due to the averaging mentioned above.

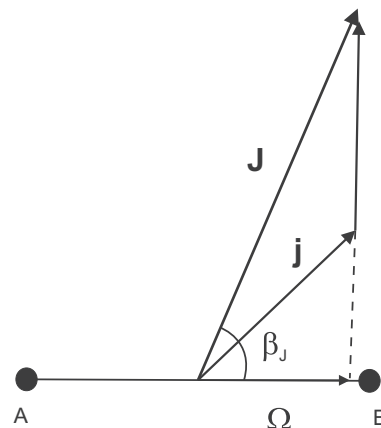


Fig. 2. The vector scheme of the molecular angular momenta coupling in case of a symmetric top molecule.

The wave functions $\psi_{j\Omega_R}$ and $\psi_{j_i\Omega_i}$ in Eq. (17) are the total excited state and initial state photofragment wave functions (8), respectively, transformed to the body frame:

$$\psi_{j\Omega_R} = \sum_m \psi_{jm} D_{m\Omega_R}^j(\phi_R, \theta_R, \chi_R), \quad (18)$$

where the Euler angles ϕ_R, θ_R, χ_R specify the direction of the body frame $X_R Y_R Z_R$ with respect to the laboratory frame XYZ .

Note that the dynamical function does depend on the coherence quantum number $q_k = \Omega_k - \Omega'_k$, however it can only weakly depend on each of the projections Ω_k, Ω'_k because the main Ω_k -dependence is already included in the phase factor in Eq. (16).

The normalization constant \mathcal{N} in Eq. (16) is given by:

$$\mathcal{N} = 2 \sum_{J_i, \Omega_i} \sum_{j, q} \sum_{\Omega_R, \Omega_k} N(J_i, \Omega_i) \left| \langle \psi_{j\Omega_R} \tilde{\chi}_{j\Omega_R, j\Omega_k}^{J_i} | \hat{d}_q | \psi_{j_i\Omega_i} \chi_i(R) \rangle \right|^2 \quad (19)$$

Eq. (16) is one of the main results of this paper. It is written in a form where each of the letters A and B can label either the molecular, or the atomic fragment, however the *detected* fragment is always labelled by the letter A . Therefore, Eq. (16) can be used for description of the angular momentum polarization of either molecular, or atomic fragments produced in the photolysis of a symmetric top molecule.

In the high- J limit the angular momentum of the molecular photofragment is assumed to be large and approximately equal to the total fragment angular momentum, while the angular momentum of the atomic fragment is small.

Comparing Eqs. (2) and (16) with the corresponding high- J limit expressions (18) and (C1) in Ref. [22] which describe the photodissociation of a diatomic molecule, one can see the following main differences between these two expressions:

1. The argument of the d -functions in Eq. (16) is the angle $\beta_j = \arccos[\Omega_k/(J_i + 1/2)]$, unlike $\beta_j = \pi/2$ in Ref. [22]. This feature reflects a well known fact that the total angular momentum J in a diatomic molecule is nearly perpendicular to the molecular axis, while in a symmetric top molecule the angular momentum can have any declination with respect to the molecular axis.
2. The Clebsch–Gordan coefficients are used in Eq. (16) instead of the asymptotic expansion coefficients $T_{j_A \Omega_A, j_B \Omega_B}^{n\Omega_k}$ [22] because of the diabatic representation of fragment wavefunctions used for derivation of Eq. (16).
3. The transition dipole moments in the last line in Eq. (16) are different from those used for diatomic molecules because the atom–diatom fragment wave functions $|j\Omega_R\rangle$ in Eq. (16) differ from the diatomic fragment wave functions.
4. The phase factor in Eq. (16) contains two angles, $\gamma_{pr}(J_i)$ and $\gamma_s(J_i, \Omega_k)$ describing the rotation of a symmetric top molecules, while the phase factor in Eq. (C1) in Ref. [22] contains one angle $\gamma(J)$ describing the rotation of the axis of a diatomic molecule.

3. Detection of polarized photofragments

A method for extracting orientation and alignment information from measurements which use two-photon excitation as a probe of diatomic photofragments has been developed by Kummel et al. [31,32]. This approach have been adapted for atoms by Bracker et al. [14]. Both methods can be used for any probe light polarization, however the obtained expressions are rather cumbersome.

In this section we present a simplified, but very compact tensor expression describing the intensity of the polarized probe light absorbed by the photofragments via two-photon excitation. The expression is valid only in case if the probe light is fully linearly, or circularly polarized, which is suitable for most of the applications. It is convenient to transform from the dissociation polarization cross section $\sigma_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k)$ in Eq. (3) to the photofragment state multiple moment $\rho_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k)$ using the expression:

$$\rho_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k) = \frac{\sigma_{Kq_k}^{(j_A)}(\vartheta_k, \varphi_k)}{(2j_A + 1)^{1/2} \sigma_0}. \quad (20)$$

As shown by Chichinin et al. [33] in case if the light is fully linearly, or circularly polarized the intensity of the two-photon transition in atoms, or molecules for arbitrary direction of the light polarization can be presented in the form:

$$I = I_0 \sum_K (C_K(\mathbf{n}_{pr}) \cdot \rho_K) P_K, \quad (21)$$

where the factor in the parentheses is a scalar product of the modified spherical harmonics $C_{KQ}(\mathbf{n}_{pr})$ [19] and the fragment state multipole ρ_K .

The unit vector \mathbf{n}_{pr} in Eq. (21) is parallel to the probe light polarization vector \mathbf{e}_{pr} if the light is linearly polarized and is parallel to the light propagation direction if the light is circularly polarized. The term P_K in Eq. (21) is the line strength factor introduced by Mo and Suzuki [34].

Under the same conditions the photolysis light polarization matrix $E_{k_d q_k}(\mathbf{e})$ in Eq. (3) can be presented in terms of modified spherical harmonics [33]:

$$E_{k_d q_d}(\mathbf{e}) = (-1)^{k_d+s} C_{1s1-s}^{k_d 0} C_{k_d q_d}(\vartheta, \varphi). \quad (22)$$

If the light is linearly polarized, $s = 0$ and the angles (ϑ, φ) describe the direction of the photolysis light polarization vector \mathbf{e} . If the light is right/left hand circularly polarized, $s = +1/-1$, respectively, and the angles (ϑ, φ) describe the direction of the photolysis light propagation.

Substituting Eqs. (3), (20), and (22) into Eq. (21), the intensity of the two-photon absorption of the probe light by polarized photofragments can be presented in the following spherical tensor form:

$$I = \frac{I_0}{4\pi(2j_A + 1)^{1/2}} \sum_{K, k_d, q_k} (-1)^{k_d+q_k+s} C_{K-q_k}(\mathbf{n}_{pr}) C_{k_d q_k}(\vartheta, \varphi) \mathbf{c}_{k_d q_k}^K \mathbf{c}_{1s1-s}^{k_d 0} P_K, \quad (23)$$

where both photolysis and the probe laser beam polarizations are defined in the recoil frame X_k, Y_k, Z_k .

The corresponding two-photon absorption laboratory frame expression can be readily obtained by substituting Eqs. (2), (20), and (22) into Eq. (21).

Eq. (23) can be used in practice for determination of the anisotropy transforming coefficients $\mathbf{c}_{k_d q_k}^K$ from experiment for any experimental geometry in case if both photolysis and the probe laser beams are fully linearly, or circularly polarized.

Very recently Rakitzis and Alexander [20,21] have reported the expression for the signal intensity in terms of the set of A_{kq} polarization parameters based on the density matrix treatment using classical arguments which allow for the description of the photofragment polarization from polyatomic molecule photodissociation. It is important to compare the A_{kq} polarization parameter nomenclature by Rakitzis and Alexander with the $\mathbf{c}_{k_d q_k}^K$ anisotropy transforming coefficient nomenclature introduced earlier by Shternin and Vasyutinskii [16] on the basis of the full quantum treatment. This comparison can be readily done by close inspection of Eq. (23) and intensity signal expression Eq. (6) from Ref. [21].

The results of the comparison are presented in Table 1. For completeness, in the second column we also added the corresponding anisotropy parameter $\alpha_K, \gamma_K, \eta_K, s_K$ expressions by Pichayev et al. [12]. The constant $V_2(j_A)$ in the second column of Table 1 is defined as: $V_2(j_A) = 5[j_A(j_A + 1)/((2j_A + 3)(2j_A - 1))]^{1/2}$. The constants s_1 and s_2 in the third column are given in Ref. [20]. It should be pointed out that the constant s_2 (the detection sensitivity factor) in the third column in Table 1 should be distinguished from the anisotropy parameter s_2 in the second column.

Table 1
Relationship between the anisotropy transforming coefficients $c_{k_d q_k}^K$ [16], anisotropy parameters [12], and the polarization parameters A_q^K [20,21] of the ranks $K = 0, 1, 2$.

$c_{k_d q_k}^K$	Anisotropy parameter expression	A_q^K polarization parameter expression
c_{00}^0	$-\sqrt{3}$	–
c_{10}^0	0	–
c_{20}^0	$\sqrt{\frac{3}{2}}\beta$	$\sqrt{\frac{3}{2}}\beta$
c_{00}^1	0	–
c_{10}^1	$3\sqrt{6}\alpha_1$	$\frac{\sqrt{2}}{P_1} s_1 A_0^1$
c_{11}^1	$3\sqrt{\frac{3}{2}}\gamma_1$	$-\frac{1}{\sqrt{2}P_1} s_1 \text{Re}[A_1^1]$
c_{20}^1	0	–
c_{21}^1	$-3i\sqrt{\frac{3}{2}}\gamma_1'$	$-\frac{i\sqrt{3}}{2\sqrt{2}P_1} s_1 \text{Im}[A_1^1]$
c_{00}^2	$-\sqrt{15}V_2(j_A)s_2$	$-\frac{\sqrt{3}}{P_2} s_2 A_0^2(\text{iso})$
c_{10}^2	0	–
c_{11}^2	$\sqrt{\frac{15}{2}}iV_2(j_A)\gamma_2'$	$-\frac{i}{\sqrt{2}P_2} s_2 \text{Im}[A_1^2]$
c_{20}^2	$-\sqrt{30}V_2(j_A)\alpha_2$	$\frac{\sqrt{3}}{\sqrt{2}P_2} s_2 A_0^2(\text{aniso})$
c_{21}^2	$-\sqrt{\frac{15}{2}}V_2(j_A)\gamma_2$	$-\frac{\sqrt{3}}{2\sqrt{2}P_2} s_2 \text{Re}[A_1^2]$
c_{22}^2	$-\sqrt{\frac{15}{2}}V_2(j_A)\eta_2$	$\frac{\sqrt{3}}{2\sqrt{2}P_2} s_2 \text{Re}[A_2^2]$

Note, that the indices q_k and q (as well as the index K) in the first and the third columns in Table 1 have the same physical meaning. As clearly seen from Table 1 all three sets of parameters describing photofragment polarization from polyatomic molecule photodissociation are equivalent to each other as they are simply proportional to each other in pairs. Eqs. (23) is equivalent to the intensity signal expression Eq. (6) in Ref. [21], however it is written in more compact tensor form. Therefore, each of the three sets of parameters in Table 1 can in principle be used for extracting the dynamical data from experiment in polyatomic, or diatomic molecule photodissociation.

One can also conclude that the anisotropy transforming coefficients in the first column in Table 1 provides more physical insight into the photolysis mechanism than two other nomenclatures, because of the additional quantum number k_d (the rank of the light polarization matrix). In particular, the coefficients with $k_d = 0$ refer to the isotropic part of the photolysis light. These coefficients describe the photofragment angular momentum polarization which can exist only in the molecular frame and vanishes after averaging over all recoil directions. The coefficients with $k_d = 1$ refer to the orientation (helicity) of the photon spin and can be produced only by circularly polarized light. The coefficients with $k_d = 2$ refer to the alignment of the photon polarization vector \mathbf{e} and can be produced either with linearly polarized light, or with circularly polarized light, or even with unpolarized light.

4. Investigation of the rotation factors

Neglecting the dependence of the dynamical function $f_k(q, q', q_k)$ in the second line in Eq. (16) on the projection Ω_k , the rotation factor which is responsible for the depolarization of the photofragment angular momentum due to molecular rotation is written as:

$$\mathcal{D}_{k_d q_k (q-q')}(\gamma_{pr}, \gamma_s) = \sum_{\Delta, \Omega_k} \exp\{i[\gamma_{pr}(J_i)\Delta + \gamma_s(\Omega_i)q_k]\} d_{(q-q')\Delta}^{k_d}(\beta_J) d_{q_k\Delta}^{k_d}(\beta_J). \quad (24)$$

As shown in Eq. (24), the rotation factor is a function of two classical angles of rotation of a symmetric top molecule (γ_{pr}, γ_s) defined in Eqs. (13) and (14). In general, the rotation factor depends on the rank of the matrix of the photolysis light polarization k_d and on its projections onto the recoil axis q_k and onto the molecular axis $(q - q')$.

For obtaining a compact form of the rotational factor $\mathcal{D}_{k_d q_k (q-q')}(\gamma_{pr}, \gamma_s)$ summation over the indices $\Delta = J - J'$ and Ω_k should be proceeded. The summation cannot be done in general because the summation procedure depends strongly on the details of the molecular structure and on the relationship between the values of the angular momentum of the detected photofragment A , the total molecular angular momentum $J \approx J_i$, and the projection of J_i onto the molecular axis Ω_i . However, the expression for the rotational factor $\mathcal{D}_{k_d q_k (q-q')}(\gamma_{pr}, \gamma_s)$ can be simplified under certain assumptions for several important particular cases.

4.1. Photolysis of a diatomic molecule under the Hund's a, or c cases

In this case the symmetric top parent molecule is reduced to a linear rotator, where $\gamma_{pr} = \gamma$ is the classical angle of rotation of the molecular axis during photodissociation and the angle γ_s in Eq. (24) can be held equal to zero. In this case the photofragment angular momentum J_A is pure electronic and in the high- J limit the following inequality is valid: $J_i \gg J_A, \Omega_i$. The vector scheme of the molecular angular momenta coupling is shown in Fig. 1, where \mathbf{I} is the molecular rotation orbital momentum which is always perpendicular to the molecular axis. As can be seen from Fig. 1 the total molecular angular momentum J is practically perpendicular to the molecular axis, therefore $\Omega_i/J_i \approx 0$ and the angle β_J in Eq. (16) can be set equal to $\beta_J \approx \pi/2$.

As shown by Kuznetsov and Vasyutinskii [22], in this case the right hand part of Eq. (12) contains only the first term. Under the above conditions summation over the index Δ in Eq. (24) gives:

$$\begin{aligned} \mathcal{D}_{k_d q_k (q-q')}(\gamma) &= \sum_{\Delta} e^{i\gamma\Delta} d_{(q-q')\Delta}^{k_d}(\pi/2) d_{q_k\Delta}^{k_d}(\pi/2) \\ &= D_{q_k q-q'}^{k_d}(\pi/2, \gamma, -\pi/2), \end{aligned} \quad (25)$$

where $D_{q_k q-q'}^{k_d}(\pi/2, \gamma, -\pi/2)$ is a Wigner D -matrix [28].

The term in Eq. (25) is the rotation factor for photodissociation of diatomic molecule from a single Ω_i and J_i -state. In general, if several initial states are involved in the photolysis, summation over them should be proceeded in Eq. (16) having in mind that the angle γ depends on J_i , according to Eq. (13).

If the Coriolis interactions during the photolysis can be neglected, $\Omega_R = \Omega_k$ and $\Omega'_R = \Omega'_k$. In this case the indices $q_k = \Omega_k - \Omega'_k = q - q' = \Omega_R - \Omega'_R$ in Eq. (25) and the rotational factors are given by diagonal d -matrices:

$$\mathcal{D}_{k_d q_k q_k}(\gamma) = d_{q_k q_k}^{k_d}(\gamma). \quad (26)$$

Therefore, the rotation depolarization factors depend on the photolysis rank k_d and on its projection q_k . In the long-lifetime limit and under the condition of the broad-band excitation the rotational factors can be obtained simply by averaging of the functions $d_{q_k q_k}^{k_d}(\gamma)$ over the angle γ [23].

The particular values of the rotational factors $d_{q_k q_k}^{k_d}(\gamma)$ for all possible anisotropy parameters in the second column in Table 1 for direct dissociation and predissociation have been tabulated by Kuznetsov and Vasyutinskii [22,23].

4.2. Photolysis of symmetric top molecules: detection of atomic photofragments

In this case in the high- J limit the total angular momentum J_i is much larger than the angular momentum of the detected photofragment: $J_i \gg j_A$, where the photofragment angular momentum j_A is assumed to be pure electronic. However the total photofragment angular momentum $\mathbf{j} = \mathbf{j}_A + \mathbf{j}_B$ has mainly the rotational origin and is assumed to be large, $j \approx j_B \gg 1$. The vector scheme of the molecular angular momenta coupling is shown in Fig. 2 where the vectors \mathbf{J} and \mathbf{j} have the same projection Ω onto the molecular

axis, the rotation orbital momentum \mathbf{l} is perpendicular to the molecular axis, and $\mathbf{J} = \mathbf{l} + \mathbf{j}$. In case of photodissociation of a symmetric top molecule all Ω_i states from $\Omega_i = 0$ to $\Omega_i = J_i$ are populated (in contrast to the diatomic case) and summation over the projection Ω_k should be proceeded in Eq. (16).

Proceeding the summation we assumed that the initial Ω_i states of the parent molecule are equally populated and that the molecule behaves as the rigid rotor thus neglecting molecular vibrations during dissociation. Under the latter condition the helicity is preserved during the reaction: $\Omega_k = \Omega_R$, $q_k = (q - q')$ and the rotational factor in Eq. (24) is labelled with two indices k_d and q_k instead of three.

In the high- J limit the summation over Ω_k in Eq. (24) can be replaced by integration over the angle β_j and the exponent can be presented as an expansion over the Legendre polynomials $P_n(\cos\beta_j)$. Proceeding in Eq. (24) summing over Δ and integrating over β_j the rotation factor can be presented in the following form:

$$\mathcal{D}_{k_d q_k}(\gamma_{pr}, \gamma_s^0) = \frac{1}{2k_d + 1} \sum_L (2L + 1) C_{k_d q_k, L}^{k_d q_k} j_L(\gamma_s^0 q_k) \chi_L^{k_d}(\gamma_{pr}), \quad (27)$$

where the summation index L ranges from $L = 0$ to $L = 2k_d$.

The term $j_L(\gamma_s^0 q_k)$ in Eq. (27) is the spherical Bessel function of the rank L and the term $\chi_L^{k_d}(\gamma_{pr})$ is the generalized character of the rotational group [28]. The explicit expressions of the function $\chi_L^{k_d}(\gamma_{pr})$ of the rank $k_d = 1, 2$ are given in Table 2 ($\gamma_s^0 = 1$) and the explicit expressions of the spherical Bessel functions of the ranks $L = 0 \dots 4$ are given in Table 3.

Eq. (27) presents a compact analytical expression for the rotation factor of a symmetric top molecule. It is clear from Eq. (27) that the rotation factor in general depends on the indices k_d , q_k and on two angles of rotation: γ_{pr} in Eq. (13) and γ_s^0 in Eq. (14). However, this dependence is qualitatively different for the incoherent ($q_k = 0$) and for the coherent ($q_k \neq 0$) anisotropy-transforming coefficients $C_{k_d q_k}^{k_d q_k}$.

If $q_k = 0$, the corresponding incoherent anisotropy-transforming coefficients depend only on the rank k_d and on the precession angle γ_{pr} , but not on the self-rotation angle γ_s because the spherical Bessel function in Eq. (14) is equal to $j_L(0) = \delta_{L,0}$. In this case Eq. (27) is reduced to:

$$\mathcal{D}_{k_d 0}(\gamma_{pr}) = \frac{1}{2k_d + 1} \chi_0^{k_d}(\gamma_{pr}) = \begin{cases} 1, & \text{if } k_d = 0 \\ \frac{1}{3}(1 + 2 \cos \gamma_{pr}), & \text{if } k_d = 1 \\ \frac{1}{5}(1 + 2 \cos \gamma_{pr} + 2 \cos 2\gamma_{pr}), & \text{if } k_d = 2 \end{cases} \quad (28)$$

As can be seen in Eq. (28), the $k_d = 0$ anisotropy transforming coefficients (see Table 1) demonstrate no depolarization due to molecular rotation.

As can be shown from Eq. (27), if the angle γ_s^0 is equal to zero, than the rotational factors $\mathcal{D}_{k_d q_k}(\gamma_{pr}, 0)$ do not depend on the index q_k . The plots of the rotation factors $\mathcal{D}_{10}(\gamma_{pr}) = \mathcal{D}_{11}(\gamma_{pr}, 0)$ and $\mathcal{D}_{20}(\gamma_{pr}) = \mathcal{D}_{21}(\gamma_{pr}, 0)$ in Eq. (28) as function of the precession angle

Table 2
Explicit expressions for the generalized characters $\chi_L^{k_d}(\gamma_{pr})$ [28].

χ_0^1	$1 + 2 \cos \gamma_{pr}$
χ_1^1	$\sqrt{2} \sin \gamma_{pr}$
χ_2^1	$\sqrt{2/5}(1 - \cos \gamma_{pr})$
χ_0^2	$1 + 2 \cos \gamma_{pr} + 2 \cos 2\gamma_{pr}$
χ_1^2	$\sqrt{2/3} \sin \gamma_{pr} (1 + \cos \gamma_{pr})$
χ_2^2	$\sqrt{2/7}(3 + \cos \gamma_{pr} - 4 \cos^2 \gamma_{pr})$
χ_3^2	$2\sqrt{2/7} \sin \gamma_{pr} (1 - \cos \gamma_{pr})$
χ_4^2	$\frac{2}{3} \sqrt{2/7} (1 - \cos \gamma_{pr})$

γ_{pr} are presented by solid lines in the left panels of Figs. 3 and 4, respectively.

If $q_k \neq 0$, the corresponding coherent anisotropy-transforming coefficients depend on the rank k_d , on its projection q_k , and on both the precession angle γ_{pr} and the self-rotation angle γ_s^0 . The explicit analytical expressions for the rotation factors in case $q_k \neq 0$ can be easily obtained from Eq. (27) using Tables 2 and 3. We do not present these expressions here as they are rather cumbersome. Instead, we plot the rotational factors \mathcal{D}_{11} , \mathcal{D}_{21} , and \mathcal{D}_{22} in Figs. 3–5, respectively. In each figure the left panel shows the rotational factor as function of the precession angle γ_{pr} for different values of the angle γ_s^0 and the right panel shows the rotational factor as function of the angle γ_s^0 for different γ_{pr} values. Note, that the rotation factor is a periodic function of γ_{pr} but not of γ_s^0 .

The difference between the incoherent ($q_k = 0$) and coherent ($q_k \neq 0$) angular momentum depolarization mechanisms can be understood by examining the picture of classical rotation of a symmetric top molecule shown in Fig. 6. For definiteness, the case of the prolate symmetric top is shown in this figure, however the explanation is the same for the oblate top.

Rotation of a free symmetric top molecule can be presented as true rolling of the body cone centered on the molecular symmetry axis \mathbf{z} over the space-fixed cone centered on the total angular momentum vector \mathbf{J} [19]. The angular velocity vector $\boldsymbol{\omega}$ is at any time directed along the line belonging to both cones. The rotation of the molecular axis \mathbf{z} about the total angular momentum \mathbf{J} shown in Fig. 6 is the free precession referring to the rotation angle γ_{pr} , while the rotation of the body-fixed cone is the self-rotation referring to the rotation angle γ_s .

As known [10,19,35] the $q_k = 0$ components of the body-frame photofragment spherical tensor cross section (state multipole) $\sigma_{Kq_k}^{(j_A)}(\mathbf{e})$ in Eq. (3) are proportional to the mean value of the $(j_z)^K$ -components of the fragment angular momentum \mathbf{j} which are axially symmetric with respect to the molecular axis \mathbf{z} . As shown in Fig. 6 these components refer to the angular momentum distribution which is not affected by the rotation about this axis and therefore the corresponding depolarization rotation factors depend on the precession angle γ_{pr} only.

The $q_k \neq 0$ components of the body-frame photofragment spherical tensor cross section in Eq. (3) are proportional to the mean value of the $(j_x, j_y)^K$ projections [10,19,35] which are perpendicular to the molecular axis \mathbf{z} . As clear from Fig. 6, these components are effectively depolarized by rotation about the molecular axis \mathbf{z} and about the total angular momentum \mathbf{J} . Therefore, the corresponding rotation factors depend on both the precession angle γ_{pr} and the self-rotation angle γ_s .

In the long-lifetime limit the rotational factor in Eq. (27) approaches the asymptotic value

$$\mathcal{D}_{k_d q_k}(\gamma_{pr}, \gamma_s^0) \rightarrow \frac{1}{2k_d + 1} \quad (29)$$

for $q_k = 0$ and

$$\mathcal{D}_{k_d q_k}(\gamma_{pr}, \gamma_s^0) \rightarrow 0 \quad (30)$$

for $q_k \neq 0$.

Table 3
Explicit expressions for the spherical Bessel functions $j_L(z)$.

$j_0(z)$	$\frac{\sin z}{z}$
$j_1(z)$	$\frac{\sin z - z \cos z}{z^2}$
$j_2(z)$	$\frac{(3 - z^2) \sin z - z \cos z}{z^3}$
$j_3(z)$	$\frac{-3(2z^2 - 5) \sin z + z(z^2 - 15) \cos z}{z^4}$
$j_4(z)$	$\frac{(105 - 45z^2 + z^4) \sin z + 5z(2z^2 - 21) \cos z}{z^5}$

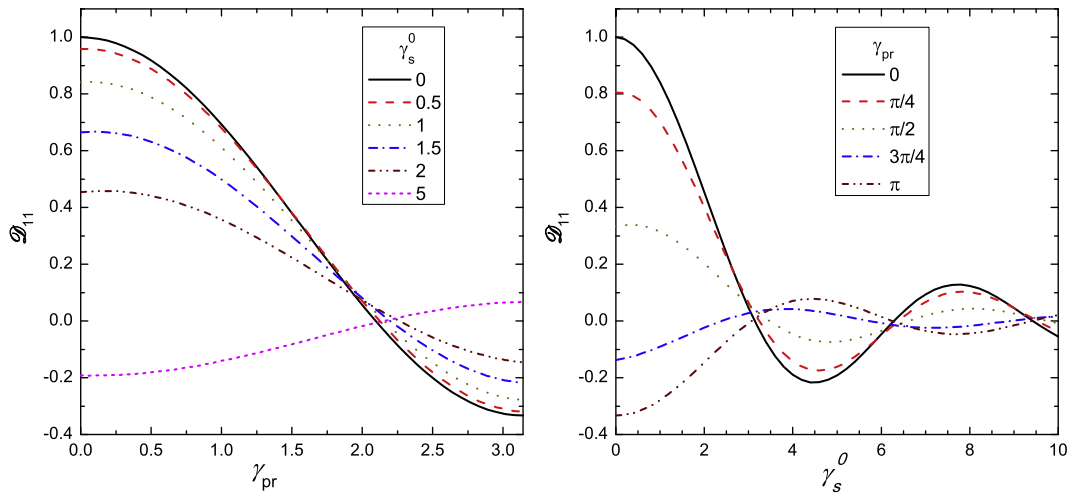


Fig. 3. The rotational factor $\mathcal{D}_{11}(\gamma_{pr}, \gamma_s^0)$ as function of γ_{pr} (left panel) and γ_s^0 (right panel).

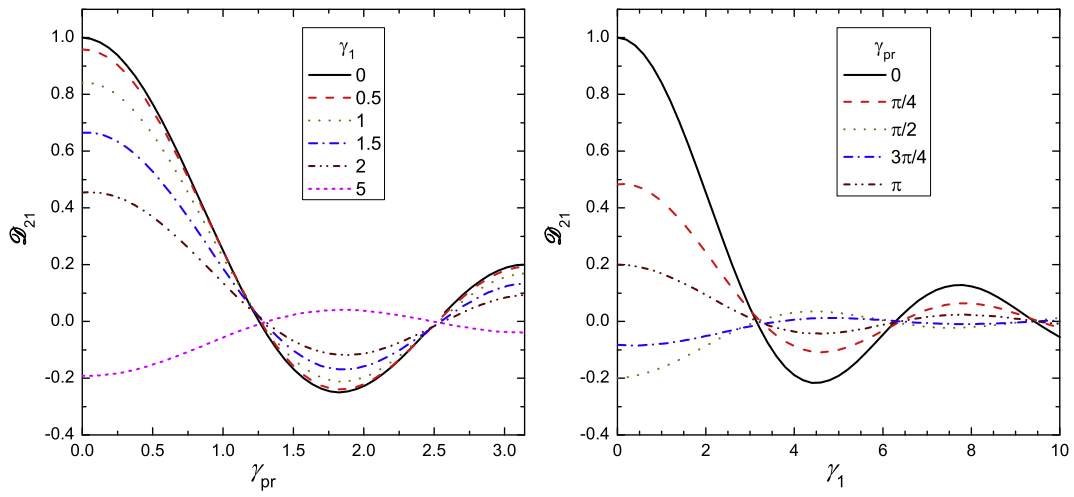


Fig. 4. The rotational factor $\mathcal{D}_{21}(\gamma_{pr}, \gamma_s^0)$ as function of γ_{pr} (left panel) and γ_s^0 (right panel).

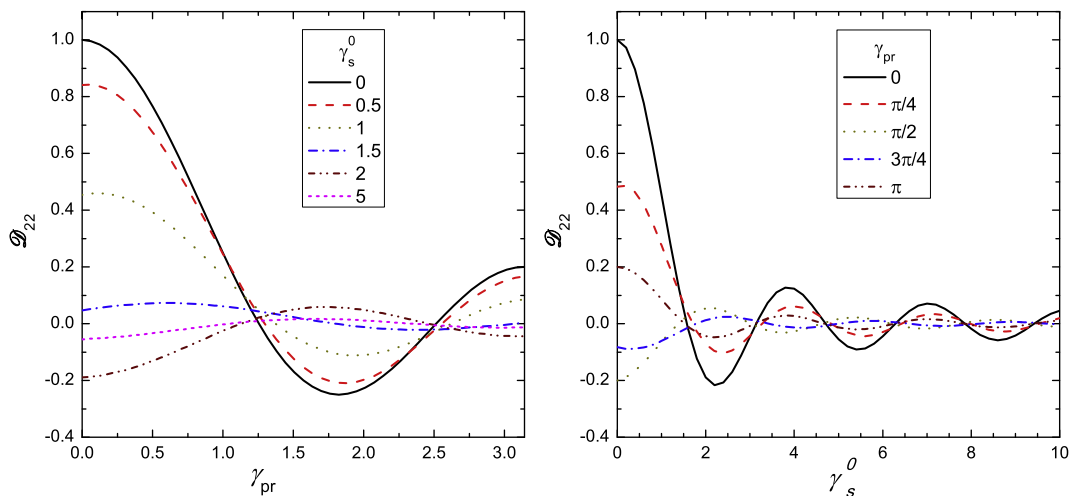


Fig. 5. The rotational factor $\mathcal{D}_{22}(\gamma_{pr}, \gamma_s^0)$ as function of γ_{pr} (left panel) and γ_s^0 (right panel).

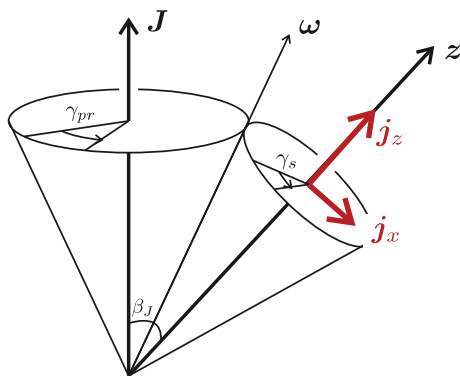


Fig. 6. The scheme of the classical rotation motion of the prolate symmetric top molecule. The total angular momentum \mathbf{J} , molecular symmetry axis \mathbf{z} and instant angular velocity vector $\boldsymbol{\omega}$ are shown as well as the projections of the fragment angular momentum onto the z and x body-frame axes. See text for details.

Eq. (30) shows that the anisotropy-transforming coefficients with $q_k \neq 0$ vanish in the long-lifetime limit.

An important particular case of Eq. (27) is a spherical top molecule where $I_{\parallel} = I_{\perp}$. In this case, $\gamma_s^0 = 0$ in Eq. (27) and the rotation factor is given by Eqs. (28) and (29) irrespectively of the value of the projection q_k . This result has recently been obtained by Bougas and Rakitzis [24] on the basis of classical arguments.

4.3. Photolysis of symmetric top molecules: detection of molecular photofragments

Here we assume that the photofragment A angular momentum is large and has mainly the rotational origin while the photofragment B angular momentum is small: $j_A \approx j \gg j_B \approx 1$. As shown in the vector scheme in Fig. 2, the angular momenta J and j have the same projection value Ω onto the molecular axis. In this case the projection Ω_A can be large and is approximately equal to the projection Ω_k , while the projection Ω_B is always small. Therefore, summation over Ω_k in Eq. (16) cannot be proceeded as above because it should involve also the Clebsch–Gordan coefficient $C_{j_A \Omega_A K q_k}^{j_A \Omega_A}$.

A peculiar feature of the considered case is that different values of the projection Ω in the dissociating parent molecule refer to different values of the photofragment angular momentum $j_A \approx j$. This statement can be proved by determining the photofragment angular momentum j from the set of three following equations:

$$\frac{J^2}{2I_{\perp}} + \Omega^2 \left(\frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) \approx \frac{l^2}{2I_{\perp}} + \frac{j^2}{2I_A} \quad (31)$$

$$J_{\parallel} = j_{\parallel} = \Omega \quad (32)$$

$$J_{\perp} = j_{\perp} + l, \quad (33)$$

where Eq. (31) represents two alternative expressions for the molecular rotation energy calculated at the distance R_b where the chemical bond breaks, while Eqs. (32) and (33) represent the conservation laws for the angular momentum projections parallel (\parallel) and perpendicular (\perp) to the molecular axis, respectively, see Fig. 2.

The terms I_{\perp} and I_{\parallel} in Eqs. (31)–(33) are two inertia moments of the dissociating parent molecule calculated at the distance R_b and the term I_A is the fragment A inertia moment which is assumed to be approximately the same along the directions of all three main fragment inertia axes. The set of Eqs. (31)–(33) can be easily solved under assumption $I_A \approx I_{\parallel}$ giving the following expression for the photofragment angular momentum:

$$j \approx \frac{2J}{(1 + I_{\perp}/I_{\parallel})} \left[1 + \frac{\Omega^2}{4J^2} [(1 + I_{\perp}/I_{\parallel})^2 - 4] \right]^{1/2}. \quad (34)$$

It is clear from Eq. (34) that the fragment angular momentum j is a function of the projection Ω . In particular, if $\Omega = 0$, then $j \approx \frac{2J}{(1 + I_{\perp}/I_{\parallel})}$, while if $\Omega = \pm J$, then $j \approx J$.

Therefore the description of the angular momentum polarization of a single j_A photofragment state in general does not need summation over the projections Ω_k in Eq. (16). The rotation factors in this case depend on the projection $\Omega_k \approx \Omega_i$ (or, equivalent, on the declination angle β_j in Eq. (15)). The parent molecule quantum states Ω_i can be isolated by orientation, or alignment of the parent molecule angular momenta in the body frame.

However in practice pump-and-probe experiment in molecular photofragment angular momentum polarization usually involves simultaneous generation and detection of many j_A fragment states by short laser pulses [36–38]. Therefore summation over the quantum numbers Ω_k and J_i is needed for correct interpretation of the experimental data. The description of these effects is out of the scope of this paper.

5. Conclusion

The fully quantum mechanical expression is presented for the photofragment angular momentum polarization in the photolysis of symmetric top molecules. The angular distribution is written in terms of the anisotropy transforming coefficients \mathbf{c}_{k,q_k}^K which contain all dynamical information on the photolysis dynamics and can be either determined from experiment, or calculated from theory. Explicit expressions for the coefficients \mathbf{c}_{k,q_k}^K are presented in the quasiclassical approximation in the high- j limit. As shown, the coefficients contain important information on photo-excitation of the parent molecule and on the following dynamical processes including possible nonadiabatic interactions, interference effects, long-range interaction between the photofragments, and rotation of the molecular axis during photodissociation.

The role of the photofragment angular momentum depolarization due to molecular rotation is analyzed. The depolarization effect is described by a number of the rotation factors that depend on the rank of the incident-photon polarization matrix and on two classical angles of rotation: the free precession angle γ_{pr} and the self-rotation angle γ_s . Three important particular cases are discussed: photolysis of diatomic molecules, photolysis of symmetric top molecules when the angular momentum polarization of atomic photofragments are detected, photolysis of symmetric top molecules when the angular momentum polarization of molecular photofragments are detected. In the two first cases the explicit expressions for the rotational factors are derived.

A compact spherical tensor expression is presented for the $2 + 1$ REMPI absorption signal which can be used for direct determination of the anisotropy transforming coefficients \mathbf{c}_{k,q_k}^K from experiment. A comparison between the anisotropy transforming coefficients \mathbf{c}_{k,q_k}^K and the polarization parameters A_q^K introduced very recently by Rakitzis and Alexander has shown that these two sets of coefficients are equivalent to each other as they just proportional to each other in pairs.

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