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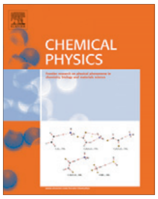

Photofragment angular momentum polarization in the photolysis of symmetric top molecules: Production, detection, and rotational depolarization

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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 $\mathbf{c}^K_{k_d q_k}$ (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 $\mathbf{c}^K_{k_d q_k}$ 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 $\mathbf{c}^K_{k_d q_k}$ from experiment. A comparison was made between the anisotropy transforming coefficients $\mathbf{c}^K_{k_d q_k}$ and the polarization parameters A^K_q 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.

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

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

$$AB(J_i) + h\nu \rightarrow A(j_A) + B(j_B) \tag{1}$$

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 $\mathbf{c}^K_{k_d q_k}$ which are scalar values containing all information on the photodissociation dynamics.

In general, the anisotropy transforming coefficients $\mathbf{c}^K_{k_d q_k}$ 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 $\mathbf{c}^K_{k_d q_k}$ 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 $\mathbf{c}^K_{k_d q_k}$ by Shternin and Vasyutinskii [16], the set of the polarization parameters A^K_q 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 $\mathbf{c}^K_{k_d q_k}$ 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:

$$\sigma^{(j_A)}_{KQ}(\mathbf{k},\mathbf{e}) = \frac{\sigma_0}{4\pi} \sum_{k_d,q_d,q} \mathbf{c}^K_{k_d q_k} D^{K^*}_{Q q_k}(\phi,\theta,0) D^{k_d}_{q_d q_k}(\phi,\theta,0) E_{k_d q_d}(\mathbf{e}), \tag{2}$$

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

The irreducible differential cross section $\sigma^{(j_A)}_{KQ}(\mathbf{k},\mathbf{e})$ 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: $K = 0 \cdots 2j_A$ and $Q = -K \cdots K$.

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 $q_d = -k_d \cdots k_d$.

The spherical tensor $\sigma^{(j_A)}_{KQ}(\mathbf{k},\mathbf{e})$ 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]:

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

where both spherical tensors $\sigma^{(j_A)}_{Kq_k}(\vartheta_k,\varphi_k)$ 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