COMMUNICATIONS

Relationship between bipolar moments and molecule-frame polarization parameters in Doppler photofragment spectroscopy

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In terms of the molecular-frame polarization parameters $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$, an equation is derived that describes the shape of a photofragment Doppler profile as a function of the three angles Γ, Δ, and Φ that specify the photolysis and probe laser polarizations about the detection axis. This expression is specialized to linearly polarized photolysis and probe laser beams. For the particular value of the angle between the probe laser polarization and the detection axis, $\Delta=\pi/2$, this equation can be reduced to the form of well-known laboratory-frame expressions that use the bipolar moment formalism introduced by Dixon. Comparison of these forms shows the equivalence of the two formalisms and gives the relationships between the bipolar moments $\beta_Q^K(k_1k_2)$ and the molecule-frame $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$ parameters. We show that linear combinations of the bipolar moments completely describe photofragment polarization in the molecular frame and possess distinct quantum mechanical significance. In particular, it is shown that the coherent contribution to the photofragment alignment is proportional to the linear combination $(1/5)\beta_0^2(02)-(1/7)\beta_0^2(22)-(12/35)\beta_0^2(42)$. © *1999 American Institute of Physics.* [S0021-9606(99)01543-3]

Photofragment angular momentum vector correlations can be highly sensitive to the dynamics of molecular photodissociation. Since Dixon's[1] seminal work in 1986, most investigations of photofragment vector correlations have used Dixon's bipolar moment formalism. The derivation of the formalism is general and follows directly from the treatment by Fano and Macek[2] of the interaction of light with arbitrarily aligned and oriented ensembles. As such, the bipolar harmonics provide a complete phenomenological description of the detectable vector correlations. Dixon provided a semiclassical interpretation of the bipolar moments $\beta_Q^K(k_1k_2)$ that is useful for transitions connecting two states of well-defined symmetry but can be ambiguous for a photodissociation process involving states of mixed symmetry. In particular, the semiclassical interpretation does not consider the contribution of interferences from multiple dissociative states. This interpretation has limited validity for low-*J* photofragments and for systems in which interference effects are expected. For example, the rotational orientation of CN fragments from ICN photodissociation has been attributed to interference between parallel and perpendicular components of the absorption.[3]

Full quantum mechanical treatments of the vector properties of photofragments in the axial recoil limit have been presented by Balint-Kurti and Shapiro[4] and more recently by Siebbeles *et al.*[5] In the latter, the photofragment angular momentum distribution is expressed in terms of the dynamical functions $f_K(q,q')$, which may be related to the transition dipole moment matrix elements. A relation between a set of bipolar moments $b_Q^K(k_2,k_1)$ and $f_K(q,q')$ was presented [Eq. (B6)], although the reference frame for the translational and rotational functions differs from that used by Dixon. Vasyutinskii and co-workers[6] subsequently proposed a set of reduced parameters (s_2, α_2, γ_2, and η_2) selected to isolate dynamically distinct, coherent and incoherent contributions to the measurable photofragment alignment. They have tabulated equivalent bipolar harmonic forms in the high-*J* limit.

More recently, Rakitzis and Zare[7] used simple symmetry arguments to describe the photofragment angular momentum distributions with the molecule-frame $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$ polarization parameters, and they presented methods to measure these parameters. The $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$ formalism is also equivalent to the treatment of Siebbeles *et al.*, and corrected relationships between the $f_K(q,q')$ and the $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$ are given below. As Rakitzis and Zare have emphasized, each $\mathbf{a}_{\mathbf{q}}^{(\mathbf{k})}(p)$ parameter possesses a distinct physical significance (quantum mechanical interpretation) in the axial recoil limit.

The aim of this paper is to give general expressions for

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the experimental Doppler profiles as functions of the directions of the photolysis and probe laser polarizations, and hence to relate the bipolar moments $\beta_Q^K(k_1k_2)$ to the $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$ parameters and vice versa. These relationships allow us to give quantum mechanical interpretations to the widely used bipolar moments when the semiclassical interpretations are inappropriate.

The photofragment detection probability in the molecule frame is given by Eq. (16) in Rakitzis and Zare[7] (for $k \leqslant 2$). This equation is expressed in terms of three angles θ_ϵ, θ, and ϕ, which describe the orientation of the photofragment recoil direction with respect to the photolysis and probe laser polarizations and in terms of the molecule-frame $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$ parameters. Here θ_ϵ is the angle between the photolysis polarization and the recoil direction, and θ and ϕ are the spherical polar angles describing the probe polarization with respect to the recoil direction. This intensity expression gives the detection probability at a specific scattering angle θ_ϵ compared to unpolarized fragments with the same angular distribution, appropriate for the Monte Carlo simulation of experimental signals.[7] To describe the θ_ϵ dependence of the observed signal analytically, the normalization needs to be relative to unpolarized fragments with an isotropic scattering angle distribution. Renormalizing Eq. (16) of Rakitzis and Zare by a factor of $[1+\beta P_2(\cos\theta_\epsilon)]$ and specializing to the case of linearly polarized photolysis and probe lasers, the $k=1$ term is dropped, giving

$$\begin{aligned}
I_{\mathrm{mol}}&[\theta,\phi,\theta_\epsilon,\beta,\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)]\\
&=1+\beta P_2(\cos\theta_\epsilon)+s_2[(1+\beta)\cos^2\theta_\epsilon\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\parallel)P_2(\cos\theta)\\
&\quad+(1-\beta/2)\sin^2\theta_\epsilon\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\perp)P_2(\cos\theta)\\
&\quad+\sin\theta_\epsilon\cos\theta_\epsilon\,\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(\mathbf{2})}(\parallel,\perp)]\sqrt{3/2}\sin 2\theta\cos\phi\\
&\quad+(1-\beta/2)\sin^2\theta_\epsilon\mathbf{a}_\mathbf{2}^{(\mathbf{2})}(\perp)\sqrt{3/2}\sin^2\theta\cos 2\phi].
\end{aligned} \tag{1}$$

In this equation, s_2 is the detection sensitivity for alignment moments of $k=2$, as defined by Rakitzis, Kandel and Zare,[8] not to be confused with the s_2 alignment parameter of Vasyutinskii.[6] The integration of this expression over all photofragments that share the same projections of their velocities along the detection axis yields the laboratory-frame description of the photofragment Doppler-broadened profiles. The molecule-frame angles θ_ϵ, θ, and ϕ can be used to describe the detection probability. Our goal in the present work is to describe the experimental Doppler profiles in terms of the laboratory angles Γ, Δ, and Φ. The angle between the linear photolysis polarization and the detection axis is Γ, the angle between the probe polarization and the detection axis is Δ, and Φ is the azimuthal angle between the projections of the photolysis and probe polarizations in the plane perpendicular to the detection axis. The molecule-frame angles θ_ϵ, θ, and ϕ can be related to the laboratory-frame angles Γ, Δ, and Φ by

$$\cos\theta_\epsilon=\cos\gamma\cos\Gamma+\sin\gamma\sin\Gamma\cos\chi, \tag{2a}$$

$$\cos\theta=\cos\gamma\cos\Delta+\sin\gamma\sin\Delta\cos(\Phi-\chi), \tag{2b}$$

and

$$\begin{aligned}
\cos\phi=\{&\sin^2\gamma\cos\Gamma\cos\Delta+\sin\Gamma\sin\Delta\cos\Phi\\
&-\sin\gamma\cos\gamma[\sin\Delta\cos\Gamma\cos(\Phi-\chi)\\
&+\sin\Gamma\cos\Delta\cos\chi]-\sin^2\gamma\sin\Gamma\sin\Delta\\
&\times\cos(\Phi-\chi)\cos\chi\}/(\sin\theta_\epsilon\sin\theta).
\end{aligned} \tag{2c}$$

Here χ is the azimuthal angle ranging from 0 to 2π that describes all photofragments that share the same Doppler shift, and γ is the angle between the photofragment velocity and the detection axis. Thus $\cos\gamma$ is proportional to the Doppler shift or the time-of-flight shift. The laboratory-frame Doppler expression is obtained by substitution of Eqs. (2a)–(2c) into Eq. (1) and integration over χ,

$$I_{\mathrm{lab}}[\Gamma,\Delta,\Phi,\beta,\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)]=\frac{1}{2\pi}\int_0^{2\pi}I[\theta_\epsilon,\theta,\phi,\beta,\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)]d\chi. \tag{3}$$

Integration of this expression yields:

$$\begin{aligned}
I_{\mathrm{lab}}[\Gamma,\Delta,\Phi,\beta,\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)]=1&+\beta P_2(\cos\Gamma)P_2(\cos\gamma)+s_2\tfrac{1}{3}[(1+\beta)\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\parallel)+2(1-\beta/2)\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\perp)]P_2(\cos\Delta)P_2(\cos\gamma)\\
&+\tfrac{2}{3}[(1+\beta)\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\parallel)-(1-\beta/2)\mathbf{a}_\mathbf{0}^{(\mathbf{2})}(\perp)]\{P_2(\cos\Gamma)P_2(\cos\Delta)[\tfrac{18}{35}P_4(\cos\gamma)+\tfrac{2}{7}P_2(\cos\gamma)+\tfrac{1}{5}]\\
&+\sin\Gamma\cos\Gamma\sin\Delta\cos\Delta\cos\Phi[-\tfrac{36}{35}P_4(\cos\gamma)+\tfrac{3}{7}P_2(\cos\gamma)+\tfrac{3}{5}]\\
&+\sin^2\Gamma\sin^2\Delta\cos 2\Phi[\tfrac{9}{140}P_4(\cos\gamma)-\tfrac{3}{14}P_2(\cos\gamma)+\tfrac{3}{20}]\}+\sqrt{6}\,\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(\mathbf{2})}(\parallel,\perp)]\\
&\times\{P_2(\cos\Gamma)P_2(\cos\Delta)[-\tfrac{8}{35}P_4(\cos\gamma)+\tfrac{2}{21}P_2(\cos\gamma)+\tfrac{2}{15}]\\
&+\sin\Gamma\cos\Gamma\sin\Delta\cos\Delta\cos\Phi[\tfrac{8}{35}P_4(\cos\gamma)+\tfrac{19}{21}P_2(\cos\gamma)-\tfrac{2}{15}]+\sin^2\Gamma\sin^2\Delta\cos 2\Phi\\
&\times[-\tfrac{1}{35}P_4(\cos\gamma)-\tfrac{1}{14}P_2(\cos\gamma)+\tfrac{1}{10}]\}+\sqrt{3/2}(1-\beta/2)\mathbf{a}_\mathbf{2}^{(\mathbf{2})}(\perp)\{P_2(\cos\Gamma)P_2(\cos\Delta)\\
&\times[\tfrac{8}{35}P_4(\cos\gamma)-\tfrac{16}{21}P_2(\cos\gamma)+\tfrac{8}{15}]+\sin\Gamma\cos\Gamma\sin\Delta\cos\Delta\cos\Phi[-\tfrac{16}{35}P_4(\cos\gamma)+\tfrac{8}{7}P_2(\cos\gamma)\\
&+\tfrac{8}{5}]+\sin^2\Gamma\sin^2\Delta\cos 2\Phi[\tfrac{1}{35}P_4(\cos\gamma)+\tfrac{4}{7}P_2(\cos\gamma)+\tfrac{2}{5}]\}\}.
\end{aligned} \tag{4}$$

Equation (4) describes one-dimensional profiles (either Doppler or time-of-flight profiles) of experiments with arbitrary directions of the linear photolysis and probe polarizations. The limitation to terms with $k \leqslant 2$ in this expression reflects the maximum detectable information with only one photon in the resonant step, such as $1+1$ resonantly enhanced multiphoton ionization or one-photon absorption spectroscopy. This provides a complete description of the alignment of fragments having $J \leqslant 3/2$.

The analogous bipolar moment expression of Dixon,[1] specialized for one-photon absorption, as given by Hall and Wu[9] is

$$D(x_D;\theta_a,\chi_a)=1+h^{(2)}\beta_0^2(02)[\tfrac{3}{5}\sin^2\theta_a\cos 2\chi_a-\tfrac{2}{5}P_2(\cos\theta_a)]+P_2(x_D)\{2P_2(\cos\theta_a)\beta_0^2(20)-h^{(2)}\beta_0^0(22)+h^{(2)}\beta_0^2(22)\times[\tfrac{6}{7}\sin^2\theta_a\cos 2\chi_a+\tfrac{4}{7}P_2(\cos\theta_a)]\}+P_4(x_D)\{h^2\beta_0^2(42)[\tfrac{9}{35}\sin^2\theta_a\cos 2\chi_a-\tfrac{36}{35}P_2(\cos\theta_a)]\}. \tag{5}$$

In Doppler probing, the velocity resolution is necessarily along a direction perpendicular to the probe polarization, i.e., $\Delta=\pi/2$. The probe angles θ_a and χ_a defined by Fano[2] in this case are the same as Γ and Φ in the notation of Eq. (4), the normalized Doppler shift x_D is the same as $\cos\gamma$, and for one-photon linearly polarized probing, $h^{(2)}=s_2$. When $\Delta=\pi/2$ is substituted into Eq. (4), the result can be rearranged into the form of Eq. (5). Comparing terms, we find the bipolar moments can be expressed in terms of the $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$ by

$$\beta_0^2(20)=\tfrac{1}{2}\beta, \tag{6a}$$

$$\beta_0^0(22)=\tfrac{1}{6}[(1+\beta)\mathbf{a}_\mathbf{0}^{(2)}(\parallel)+2(1-\beta/2)\mathbf{a}_\mathbf{0}^{(2)}(\perp)], \tag{6b}$$

$$\beta_0^2(02)=\tfrac{1}{6}[(1+\beta)\mathbf{a}_\mathbf{0}^{(2)}(\parallel)-(1-\beta/2)\mathbf{a}_\mathbf{0}^{(2)}(\perp)] +\frac{\sqrt{6}}{6}\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(2)}(\parallel,\perp)]+\frac{\sqrt{6}}{3}(1-\beta/2)\mathbf{a}_\mathbf{2}^{(2)}(\perp), \tag{6c}$$

$$\beta_0^2(22)=-\tfrac{1}{6}[(1+\beta)\mathbf{a}_\mathbf{0}^{(2)}(\parallel)-(1-\beta/2)\mathbf{a}_\mathbf{0}^{(2)}(\perp)] -\frac{\sqrt{6}}{12}\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(2)}(\parallel,\perp)]+\frac{\sqrt{6}}{3}(1-\beta/2)\mathbf{a}_\mathbf{2}^{(2)}(\perp), \tag{6d}$$

$$\beta_0^2(42)=\tfrac{1}{6}[(1+\beta)\mathbf{a}_\mathbf{0}^{(2)}(\parallel)-(1-\beta/2)\mathbf{a}_\mathbf{0}^{(2)}(\perp)] -\frac{\sqrt{6}}{9}\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(2)}(\parallel,\perp)]+\frac{\sqrt{6}}{18}(1-\beta/2)\mathbf{a}_\mathbf{2}^{(2)}(\perp). \tag{6e}$$

Equations (6a)–(6e) can be inverted to express the $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$ in terms of the bipolar moments:

$$\beta=2\beta_0^2(20), \tag{7a}$$

$$\mathbf{a}_\mathbf{0}^{(2)}(\parallel)=\frac{4}{(1+\beta)}[\tfrac{1}{5}\beta_0^2(02)-\tfrac{2}{7}\beta_0^2(22)+\tfrac{18}{35}\beta_0^2(42) +\tfrac{1}{2}\beta_0^0(22)], \tag{7b}$$

$$\mathbf{a}_\mathbf{0}^{(2)}(\perp)=\frac{2}{(1-\beta/2)}[-\tfrac{1}{5}\beta_0^2(02)+\tfrac{2}{7}\beta_0^2(22)-\tfrac{18}{35}\beta_0^2(42) +\beta_0^0(22)], \tag{7c}$$

$$\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(2)}(\parallel,\perp)]=2\sqrt{6}\left[\tfrac{1}{5}\beta_0^2(02)-\frac{1}{7}\beta_0^2(22)-\tfrac{12}{35}\beta_0^2(42)\right], \tag{7d}$$

$$\mathbf{a}_\mathbf{2}^{(2)}(\perp)=\frac{\sqrt{6}}{(1-\beta/2)}\left[\frac{1}{5}\beta_0^2(02)+\frac{2}{7}\beta_0^2(22)+\frac{3}{35}\beta_0^2(42)\right]. \tag{7e}$$

Equations (4), (6a)–(6e), and (7a)–(7e) are the central results of this paper. Equations (7a)–(7e) give quantum mechanical interpretations to linear combinations of bipolar moments [see Rakitzis and Zare for interpretations of the $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$]. In particular, the entire contribution to photofragment alignment from the interference of multiple dissociative states is carried in the $\mathrm{Re}[\mathbf{a}_\mathbf{1}^{(2)}(\parallel,\perp)]$ term, proportional to γ_2 in the notation of Vasyutinskii.[6]

In the high-J limit, this coherent contribution to the photofragment alignment vanishes. Siebbeles *et al.* have previously made the equivalent observation that $f_2(1,0)=0$ in the semiclassical limit.[5] Very recent frequency modulated Doppler measurements on the CN photofragments from ICN photodissociation have confirmed that the same high-J fragments exhibiting coherent orientation display negligible coherent alignment.[10] For low-J photofragments where coherent alignment is possible, the bipolar moments still provide a complete phenomenological set of experimental fitting parameters, although their semiclassical interpretation in the body-fixed frame of the transition moment must be abandoned. The normal ''physical'' limits on the $k_2=2$ bipolar moments[1] may, but need not be exceeded in this case. Equation (7d) provides an experimental means of assessing the coherent contribution to the alignment, proportional to the linear combination $\tfrac{1}{5}\beta_0^2(02)-\tfrac{1}{7}\beta_0^2(22)-\tfrac{12}{35}\beta_0^2(42)$.

The treatment of Siebbeles *et al.* considers the description of the photodissociation of molecules AB to give fragments A and B with angular momenta $\mathbf{j}_A=0$ and $\mathbf{j}_B$. The description of the polarization of $\mathbf{j}_B$ is given by the dynamical functions $f_K(q,q')$. For this special case of $\mathbf{j}_A=0$, the relationship between the $f_K(q,q')$ and the $\mathbf{a}_\mathbf{q}^{(2)}(p)$ is given by

$$f_2(0,0)/[f_0(0,0)+2f_0(1,1)]=\frac{(1+\beta)}{6}\mathbf{a}_\mathbf{0}^{(2)}(\parallel), \tag{8a}$$

$$f_2(1,1)/[f_0(0,0)+2f_0(1,1)]=\frac{(1-\beta/2)}{6}\mathbf{a}_\mathbf{0}^{(2)}(\perp), \tag{8b}$$

$$f_2(1,0)/[f_0(0,0)+2\,f_0(1,1)] = -\frac{\sqrt{2}}{12}\mathbf{a}_1^{(2)}(\parallel,\perp), \tag{8c}$$

$$f_2(1,-1)/[f_0(0,0)+2\,f_0(1,1)] = -\frac{(1-\beta/2)}{3}\mathbf{a}_2^{(2)}(\perp). \tag{8d}$$

Note that similar expressions relating the $\mathbf{a}_\mathbf{q}^{(\mathbf{k})}(p)$ and $f_K(q,q')$ given in the Appendix of Rakitzis and Zare[7] have incorrect normalization constants. For this special case of $\mathbf{j}_A=0$ the relationships between the bipolar moments and the $f_K(q,q')$ can be determined by substituting Eqs. (8a)–(8d) into Eqs. (6b)–(6e) and Eqs. (7b)–(7e).

Experiments using circularly polarized probe and photolysis polarizations will be discussed in future work.[11] As mentioned above, several formalisms have been presented to describe photofragment polarization. This paper connects these formalisms, so that photofragment polarization can be discussed in a common language.

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[11] The treatment of circularly polarized photolysis in Appendix B of Ref. 7 is incorrect and a revision is in preparation.