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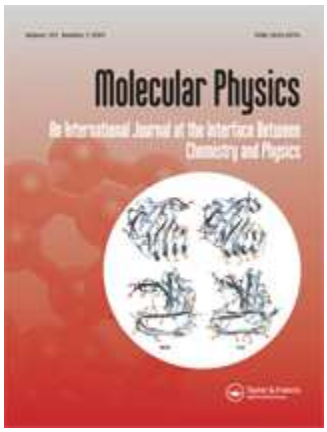

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Photofragment angular momentum distributions from oriented and aligned polyatomic molecules: beyond the axial recoil limit

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A semi-classical theoretical treatment is presented for the description of photofragment polarization in the molecular frame, from the non-axial photodissociation of molecules which are oriented in the laboratory frame. Explicit expressions which quantify the experimental sensitivity to each of the $a_q^k(i)$ polarization parameters, for prompt photodissociation, are given in terms of the non-axial-recoil deflection angles χ, α and $\varphi_{\mu d}$ (which describe the orientation of the dipole and transition dipole moments about the recoil velocity), and the degree of the parent orientation and alignment. The application of this approach for the extraction of important dynamical information in the molecular frame is discussed, including cases where this information cannot be measured for isotropic samples of parent molecules.

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1. Introduction

For several decades, information about the photodissociation process in the molecular frame has been obtained from the measurement of laboratory-frame vector properties. The most well-known example has been the measurement of the angular distribution of photofragments from isotropic parent molecules, with respect to the photolysis laser polarization, introduced by Zare and Herschbach [1]:

$$I(\theta_\varepsilon) = 1 + \beta P_2(\cos\theta_\varepsilon), \quad (1)$$

where θ_ε is the angle between the recoil direction **v** and the polarization of the photodissociating light, and P_2 is the second-order Legendre polynomial (note that this equation is valid only for one-photon photodissociation in the dipole approximation). The parameter β ranges from –1 to +2. For prompt photodissociation in the axial recoil limit, a pure parallel transition produces photofragments with $\beta = +2$, and a pure perpendicular transition produced photofragments with $\beta = -1$. If the photodissociation dynamics of a molecule is known to be prompt and the recoil is axial, then the measurement of the spatial anisotropy β of the photofragments can be used to infer the relative contributions of parallel and perpendicular transitions to the photodissociation process. However, in the general case where axial recoil approximation does not hold, further information is required to unravel the dissociation mechanism.

In recent years, the measurement of photofragment angular momentum polarization has been used as an extremely sensitive probe of photodissociation dynamics, particularly as a unique probe of the interference effects arising from the coherent excitation of multiple dissociative states with different symmetry. In a seminal

paper, Siebbeles *et al.* [2] gave the full quantum mechanical description of photofragment polarization from the prompt dissociation of molecules in the axial recoil limit. In this treatment the photofragment polarization is decomposed into coherent and incoherent contributions from transitions to multiple dissociative states. This formalism, and an equivalent molecular-frame formalism by Rakitzis and Zare [3], was used to successfully describe the photofragment polarization measured from the photodissociation of a number of diatomic molecules (well described by the axial recoil approximation) [4,5,6,7,8,9,10,11,12,13,14,15,16,17,18]. More recently, photofragment polarization has been measured from the photodissociation of polyatomic molecules, for which the axial recoil approximation breaks down [19,20,21,22,23,24,25,26,27,28,29,30,31,32,33]. The polarization measurements can be fit with the same polarization parameter basis functions (as they form a complete basis), however the interpretation of the values of the polarization parameters is no longer straightforward or well-understood.

Recently, Vasyutinskii and coworkers have expanded the Siebbeles formalism beyond the axial recoil approximation, by including the effects of parent-molecule rotation, and by producing general expressions valid for polyatomic systems independent of reaction mechanism [34,35,36,37,38]. However, the theoretical methods for extracting dynamical information from experiments on polyatomic molecule photodissociation have not yet been developed; therefore it is not yet clear that all the dynamical information (such as non-axial recoil deflection angles, in addition to transition amplitudes and phases) can indeed be obtained sensitively, and this will become more clear as these methods are developed. Very recently, Rakitzis and Alexander have extended the $a_q^k(p)$ polarization parameter formalism to allow for the description of photofragment

polarization from polyatomic molecule photodissociation [39], where the transitions to the dissociative states are neither pure parallel nor pure perpendicular transitions.

Direct observation of non-axial recoil dynamics has been achieved by Janssen and coworkers, by observing the angular distribution of photofragments from the photodissociation of hexapole-oriented parent OCS molecules [40,41]. The angular distributions of the photofragments were fit using a theoretical treatment for non-axial recoil dynamics from a single dissociative surface [42,43], and the directional non-axial recoil angle α were determined for each rotational state J of the CO(v=0,J) photofragments [41].

Pipes et al. [44], and Underwood and Powis [45] extended the Siebbeles treatment to the photodissociation of polarized diatomic molecules in the axial recoil limit. However, a treatment of the photodissociation of polarized polyatomic molecules, either within or without the axial recoil limit, is lacking.

The aim of this paper is to provide a framework for the description of photofragment polarization for the photodissociation of polarized polyatomic molecules. We combine the molecular-frame a_q^k polarization-parameter formalism [3] with the semi-classical non-axial recoil dynamics treatment for dissociation of oriented molecules [46,47]. The aim is to allow the experimental decoupling of the measurement of the photofragment polarization and the non-axial recoil dynamics (deflection angles of the photofragment recoil). This will provide a general approach to describe the photofragment polarization from oriented molecules. We emphasize that we decouple the geometrical factors that arise from the fact that the recoil direction **v** results at angles $(\alpha,0)$ to the dipole moment **d** and $(\chi,\varphi_{\mu d})$ to the transition dipole moment $\boldsymbol{\mu}$, *independent*

of the mechanism that produced these angles, and thus represent purely geometrical factors (see Figure 1). The general polarization parameters $a_q^k(i)$ which we use to phenomenologically describe the photofragment polarization (depending on the photodissociation mechanism) may also depend on the angles α,χ, and $\varphi_{\mu d}$.

Here, excitation to only a single excited state is discussed. The goal of future research will be to generalize this approach to describe the coherent excitation of multiple states. The immediate goal of this work is to provide an approach for the fitting of existing $S(^1D)$ photofragment polarization data from the photodissociation of oriented state-selected OCS molecules [48,49], while taking into account the effects of the orientation of the parent molecules. We show that the experimental sensitivity to the $a_q^k(p)$ parameters varies as a function of the degree of the orientation and alignment of the parent molecules, and we quantify this variation in sensitivity. Furthermore, as discussed below, the orientation and alignment of the parent molecules allow the measurement of the photofragment polarization to be sensitive to additional $a_q^k(p)$ parameters (such as those with q>2), which normally would not be the case for the one-photon photodissociation of an isotropic sample of parent molecules.

2. Theory

The calculation presented here of the photofragment angular momentum distribution in the molecular frame from the photodissociation of oriented parent molecules combines the similar methods used for the calculation of photofragment angular momentum distribution of from a sample of *isotropic* parent molecules [3,39], and the *unpolarized* photofragment angular distributions from *oriented* parent molecules

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[42,43]. We will consider here the excitation to only a single excited state of the parent molecule. The incoherent and coherent excitation of multiple states is discussed briefly in the Discussion section.

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2.1 The molecular frame

Figure 1 shows the molecular-frame coordinates of the polarization directions of the photolysis laser **ε**, the probe laser **P**, the Orientation field **O**, and the dynamically significant vectors: the recoil velocity **v**, the transition and the permanent dipole moments **d** and **μ**, respectively. The z axis is parallel to the final recoil direction **v**, and the z-x plane is defined by the Orientation field, **O**. The coordinates of **d** and **μ** are shown, at the time of absorption of the photodissociating photon. We consider the simple case where we assume that the spatial distributions of **d** and **μ** are tightly peaked in the molecular frame, and can be described by polar and azimuthal angles, $\mathbf{d}(\alpha,\xi+\varphi_{O\varepsilon})$ and $\boldsymbol{\mu}(\chi,\varphi_{\mu d}+\xi+\varphi_{O\varepsilon})$, respectively. The angle ξ, which ranges from 0 to 2π, describes the cone of the ensemble of parent-molecule orientations which will yield photofragments with recoil velocities parallel to **v** [50]. The probability of **d** being oriented about **O** is given by the distribution D(cosδ), where **d**·**O**=cosδ [51,52]:

$$D(\cos\delta) = \frac{1}{2} + \sum_{k=1}^{N} c_k P_k(\cos\delta), \qquad (2)$$

where the values of the c_k describe the degree of orientation (for example, for a distribution D(cosδ) proportional to $\cos^2\delta$, c_2=1 and all other c_k are zero). The probability of absorption of a photodissociating photon is given by $|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}|^2$, which can be expressed in terms of the second Legendre polynomial as:

$$|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}|^2 = \frac{1}{3}\left[1+2P_2(\cos\theta_{\mu\varepsilon})\right], \quad (3)$$

where $\theta_{\mu\varepsilon}$ is the angle between $\boldsymbol{\mu}$ and the photolysis polarization direction $\boldsymbol{\varepsilon}$.

Finally, the detection probability of the photofragments in the molecular frame, as a function of the polarization parameters $a_q^k(i)$ [3,39,53,54], is given by $I(a_q^k)$:

$$I(a_q^k) = 1+\sum_{k=1}^{2J} s_k \sum_{q=-k}^{k} a_q^k(i) C_q^k(p,\varphi_{dp}), \quad (4)$$

where $C_q^k(\theta,\varphi)$ is a reduced spherical harmonic [52], p is the angle between the probe polarization direction **P** and **v**, φ_{dp} is the azimuthal angle between **P** and **d** about **v**, given by $\varphi_{dp} = \xi+\varphi_{O\varepsilon}-\varphi_{Op}$ (see Fig. 1), and the index i in $a_q^k(i)$ refers to a particular dissociative excited state, so that the $a_q^k(i)$ describe the photofragment angular momentum polarization of the photofragments produced by excitation to state i.

The molecular frame angular momentum angular distribution is given by the product of three quantities, the parent orientation distribution $D(\cos\delta)$, the photodissociation probability $|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}|^2$, and the angular momentum detection probability $I[a_q^k(i)]$, which is then integrated over the angle ξ to integrate all the molecular geometries that can yield photofragments along **v**:

$$I = \frac{1}{2\pi}\int_0^{2\pi} 6|\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}|^2 D(\cos\delta) I[a_q^k(i)] d\xi, \quad (5)$$

where the numerical factor of 6 is included for the normalization of subsequent equations. Substituting Eqs. (1-3) into Eq. (4), we obtain:

$$I = \frac{1}{2\pi}\int_0^{2\pi}\left[1+2P_2(\cos\theta_{\mu\varepsilon})\right]\times\left[1+2\sum_{k=1}^{N}c_k P_k(\cos\delta)\right]\times\left[1+\sum_{k=1}^{2J}s_k\sum_{q=-k}^{k}\mathrm{a}_q^k(\mathrm{i})\mathrm{C}_q^k(p)e^{iq\varphi_{dp}}\right]d\xi, \quad (6)$$

where $P_2(\cos\theta_{\mu\varepsilon})$ and $P_k(\cos\delta)$ can be expressed in terms of the molecular frame angles χ, γ, ξ, $\varphi_{\mu d}$ and α, δ, ξ, $\varphi_{O\varepsilon}$ respectively, using the spherical harmonic addition theorem, and $\varphi_{dp} = \xi + \varphi_{O\varepsilon} - \varphi_{Op}$:

$$\begin{aligned} I = \frac{1}{2\pi}\int_0^{2\pi}&\left[1+2C_0^2(\chi)C_0^2(\gamma)+4C_1^2(\chi)C_1^2(\gamma)\cos(\xi+\varphi_{\mu d})+4C_2^2(\chi)C_2^2(\gamma)\cos 2(\xi+\varphi_{\mu d})\right] \\ &\times\left[1+\sum_{k=1}^{N}c_k\left(2C_0^2(\alpha)C_0^2(\delta)+4C_1^2(\alpha)C_1^2(\delta)\cos(\xi+\varphi_{O\varepsilon})+4C_2^2(\alpha)C_2^2(\delta)\cos 2(\xi+\varphi_{O\varepsilon})\right)\right] \\ &\times\left[1+\sum_{k=1}^{2J}s_k\sum_{q=-k}^{k}\mathrm{a}_q^k(\mathrm{i})\mathrm{C}_q^k(p)e^{iq(\xi+\varphi_{O\varepsilon}-\varphi_{Op})}\right]d\xi \end{aligned} \quad (7)$$

Evaluation of the integral in Eq. (7) yields the photofragment angular momentum distribution in the molecular frame. We evaluate Eq. (7) for fitting experimental results for the $S(^1D_2)$ photofragment from the photodissociation of OCS oriented in the (JℓM=111) or (JM=10) states. For both of these states, the degree of OCS orientation is described by c_k parameters c_1 and c_2 only, whereas all other c_k vanish. The total angular momentum J of the $S(^1D_2)$ atoms is J=2, so that the a_q^k multipole moment expansion describing the angular momentum distribution is terminated at 2J (i.e. k=4). Furthermore, for linearly polarized probe light, the detection step is only sensitive to a_q^k with even k; therefore the second summation in Eq. (7) includes only k=2 and k=4 terms.

In addition, Eq. (7) can be expressed as purely real by combining the a_q^k terms with +q and –q and expressed in terms of $\mathrm{Re}[a_q^k]$ and $\mathrm{Im}[a_q^k]$, using $a_q^{k*} = (-1)^q a_{-q}^k$ and $C_q^k(p) = (-1)^q C_{-q}^k(p)$ [49,50]:

$$a_q^k C_q^k(p) e^{iq\varphi_{dp}} + a_{-q}^k C_{-q}^k(p) e^{-iq\varphi_{dp}} = 2C_q^k(p)\left(\mathrm{Re}[a_q^k]\cos q\varphi_{dp} + \mathrm{Im}[a_q^k]\sin q\varphi_{dp}\right) \quad (8)$$

Using the constraints described above, Eq. (7) is evaluated and presented below:

$$\begin{aligned}
I = {} & \left[1 + s_2 a_0^2(i) C_0^2(p) + s_4 a_0^4(i) C_0^4(p)\right]\left\{\left[1 + 2C_0^2(\chi)C_0^2(\gamma)\right]\left[1 + 2\sum_k c_k C_0^k(\alpha) C_0^k(\delta)\right]\right. \\
& \left. + \sum_k 8c_k C_1^2(\chi)C_1^2(\gamma)C_1^k(\alpha)C_1^k(\delta)\cos(\varphi_{\mu d} - \varphi_{O\varepsilon}) + \sum_k 8c_k C_2^2(\chi)C_2^2(\gamma)C_2^k(\alpha)C_2^k(\delta)\cos 2(\varphi_{\mu d} - \varphi_{O\varepsilon})\right\} \\
& + \left[s_2\,\mathrm{Re}[a_1^2(i)]C_1^2(p) + s_4\,\mathrm{Re}[a_1^4(i)]C_1^4(p)\right]\left\{\left[1 + 2C_0^2(\chi)C_0^2(\gamma)\right]\sum_k 4c_k C_1^k(\alpha)C_1^k(\delta)\cos(\varphi_{Op})\right. \\
& + 4C_1^2(\chi)C_1^2(\gamma)\cos(\varphi_{p\varepsilon} - \varphi_{\mu d})\left[1 + 2\sum_k c_k C_0^k(\alpha)C_0^k(\delta)\right] + \sum_k 8c_k C_2^2(\chi)C_2^2(\gamma)C_1^k(\alpha)C_1^k(\delta)\cos(2\varphi_{\mu d} - \varphi_{O\varepsilon} - \varphi_{p\varepsilon}) \\
& \left. + \sum_k 8c_k C_1^2(\chi)C_1^2(\gamma)C_2^k(\alpha)C_2^k(\delta)\cos(\varphi_{\mu d} - \varphi_{O\varepsilon} - \varphi_{Op})\right\} \\
& + \left[s_2\,\mathrm{Re}[a_2^2(i)]C_2^2(p) + s_4\,\mathrm{Re}[a_2^4(i)]C_2^4(p)\right]\left\{\left[1 + 2C_0^2(\chi)C_0^2(\gamma)\right]\sum_k 4c_k C_2^k(\alpha)C_2^k(\delta)\cos 2\varphi_{Op}\right. \\
& \left. + 4C_2^2(\chi)C_2^2(\gamma)\cos 2(\varphi_{p\varepsilon} - \varphi_{\mu d})\left[1 + 2\sum_k c_k C_0^k(\alpha)C_0^k(\delta)\right] + \sum_k 8c_k C_1^2(\chi)C_1^2(\gamma)C_1^k(\alpha)C_1^k(\delta)\cos(\varphi_{\mu d} + \varphi_{p\varepsilon} - \varphi_{Op})\right\} \\
& + s_4\,\mathrm{Re}[a_3^4(i)]C_3^4(p)\left\{\sum_k 8c_k C_2^2(\chi)C_2^2(\gamma)C_1^k(\alpha)C_1^k(\delta)\cos(\varphi_{\mu d} + \varphi_{Op} + 2\varphi_{p\varepsilon})\right. \\
& \left. + \sum_k 8c_k C_1^2(\chi)C_1^2(\gamma)C_2^k(\alpha)C_2^k(\delta)\cos(2\varphi_{\mu d} + 2\varphi_{Op} + \varphi_{p\varepsilon})\right\} \\
& + s_4\,\mathrm{Re}[a_4^4(i)]C_4^4(p)\left\{\sum_k 8c_k C_2^2(\chi)C_2^2(\gamma)C_2^k(\alpha)C_2^k(\delta)\cos 2(\varphi_{\mu d} + \varphi_{Op} + \varphi_{p\varepsilon})\right\}
\end{aligned} \quad (9)$$

Notice, for convenience, that the angle $\varphi_{p\varepsilon} = \varphi_{Op} - \varphi_{O\varepsilon}$ is used for the azimuthal angle of **P** and **ε** about **v**.

Inspecting Equation (9), we can compare the molecular-frame detection probability for photofragments from the one-photon photodissociation of *oriented* parent molecules and for *isotropic* parent molecules. In the latter case, it is well-known that (for the one-photon photodissociation in the dipole approximation) experimental signals are sensitive to the $a_q^k(i)$ with $|q| \le 2$. In Eq. (9) we see terms for oriented and aligned parent molecules (which are proportional to the degree of parent orientation c_k) which have q = 3 and q = 4.

When χ=0 and α=0, then we have axial recoil dynamics, and the state i has been accessed via a pure parallel transition; in this case, we expect the photofragment polarization to be described by the $a_0^k(\|)$ parameters only [3]. As expected, we see that the terms with q > 0 vanish, and that the molecular frame expression becomes equal to the product of the parent bond polarization multiplied by the detection expression for photofragments from a parallel transition only. Similarly, when χ=90° and α=0, then again we have axial recoil dynamics, but now the state i has been accessed via a perpendicular transition, and we expect the photofragment polarization to be described by the $a_0^k(\perp)$ and $a_2^k(\perp)$ parameters only [3]. As expected, we see that the terms with q=1 and q > 2 vanish, and that the molecular frame expression becomes equal to the product of the parent bond polarization multiplied by the detection expression for photofragments from a perpendicular transition only, with, however one exception: the q = 2 parameters are reduced by a factor of $\frac{1}{2}\cos 2\varphi_{\mu d}$. This reduction arises from the fact that, for a polyatomic molecule with a transition dipole moment $\boldsymbol{\mu}_i$ with coordinates (χ=90°,$\varphi_{\mu d}$), $\boldsymbol{\mu}_i$

is not fixed in the molecular frame (whereas for a diatomic $\boldsymbol{\mu}_\perp$ is always in the plane defined by **v** and the photolysis polarization **ε**).

Below, we evaluate, quantitatively, the sensitivity to all the $a_q^k(i)$ in the laboratory frame.

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2.2 The laboratory frame

Figure 2 shows the laboratory-frame coordinates of the recoil velocity **v**, with respect to **ε**, **P**, and **O**. The Z axis is parallel to the detection axis (e.g. the time-of-flight axis of a mass spectrometer), and the Z-X plane is defined by **O**. The expressions for the polar angles in the molecular frame, γ, δ, and p, in terms of the laboratory-frame angles are given by:

$$\cos\gamma = \cos\Omega\cos\Gamma + \sin\Omega\sin\Gamma\cos(\Theta - \Phi_{O\varepsilon}), \tag{10a}$$

$$\cos\delta = \cos\Omega\cos\Delta + \sin\Omega\sin\Delta\cos\Theta, \tag{10b}$$

$$\cos p = \cos\Omega\cos P + \sin\Omega\sin P\cos(\Theta - \Phi_{OP}), \tag{10c}$$

The expressions for trigonometric functions of the molecular-frame azimuthal angles, $\varphi_{O\varepsilon}$, φ_{Op}, and $\varphi_{p\varepsilon}$, in terms of the laboratory-frame angles (calculated using Eqs. (22-24) from reference [3]) are given by:

$$\begin{aligned}\cos\varphi_{O\varepsilon} = \{&\sin^2\Omega\cos\Gamma\cos\Delta + \sin\Gamma\sin\Delta\cos\Phi_{O\varepsilon} \\ &- \sin\Omega\cos\Omega[\sin\Delta\cos\Gamma\cos(\Phi_{O\varepsilon} - \Theta) + \sin\Gamma\cos\Delta\cos\Theta] \\ &- \sin^2\Omega\sin\Gamma\sin\Delta\cos(\Phi_{O\varepsilon} - \Theta)\cos\Theta\} / (\sin\gamma\sin\delta),\end{aligned} \tag{11a}$$

$$\sin\varphi_{O\varepsilon} = \{c\cos\Omega\sin\Gamma\sin\Delta\sin\Phi_{O\varepsilon} - \sin\Omega[\sin\Delta\cos\Gamma\sin(\Phi_{O\varepsilon}-\Theta)+\sin\Gamma\cos\Delta\sin\Theta]\}/(\sin\gamma\sin\delta), \quad (11b)$$

$$\cos\varphi_{Op} = \{\sin^2\Omega\cos P\cos\Delta+\sin P\sin\Delta\cos\Phi_{Op} - \sin\Omega\cos\Omega[\sin\Delta\cos P\cos(\Phi_{Op}-\Theta)+\sin P\cos\Delta\cos\Theta] - \sin^2\Omega\sin P\sin\Delta\cos(\Phi_{Op}-\Theta)\cos\Theta\}/(\sin p\sin\delta), \quad (11c)$$

$$\sin\varphi_{Op} = \{c\cos\Omega\sin P\sin\Delta\sin\Phi_{Op} - \sin\Omega[\sin\Delta\cos P\sin(\Phi_{Op}-\Theta)+\sin P\cos\Delta\sin\Theta]\}/(\sin p\sin\delta), \quad (11d)$$

$$\cos\varphi_{p\varepsilon} = \{\sin^2\Omega\cos\Gamma\cos P+\sin\Gamma\sin P\cos(\Phi_{Op}-\Phi_{O\varepsilon}) - \sin\Omega\cos\Omega[\sin P\cos\Gamma\cos(\Phi_{Op}-\Theta)+\sin\Gamma\cos P\cos(\Phi_{O\varepsilon}-\Theta)] - \sin^2\Omega\sin\Gamma\sin P\cos(\Phi_{Op}-\Theta)\cos(\Phi_{O\varepsilon}-\Theta)\}/(\sin\gamma\sin p), \quad (11e)$$

$$\sin\varphi_{p\varepsilon} = \{c\cos\Omega\sin\Gamma\sin P\sin(\Phi_{Op}-\Phi_{O\varepsilon}) - \sin\Omega[\sin P\cos\Gamma\sin(\Phi_{Op}-\Theta)+\sin\Gamma\cos P\sin(\Theta-\Phi_{O\varepsilon})]\}/(\sin\gamma\sin p). \quad (11f)$$

Note that $\Phi_{p\varepsilon} = \Phi_{Op} - \Phi_{O\varepsilon}$. Inserting Eqs. (10) and (11) into (9), we obtain the full three-dimensional (3-D) detection probability. Methods for collapsing this expression to explain signals from 1-D or 2-D experiments are given in Sections 3.1 and 3.2 of reference [40]. Here, we consider slice imaging detection [40], for which we set $\Omega=\pi/2$, and then the photofragment angular distribution is a function of the angle Θ only. The resulting laboratory-frame slice-imaging angular distribution, $I_s(\Theta)$, can be expressed as an expansion of Legendre polynomials, for experimental geometries where the angles Δ and Γ are either 0 or $\pi/2$ (for other angles, the expansion requires more terms which have different symmetry from the $P_n(\cos\Theta)$):

$$I_s(\Theta) = \sum_{n=0}^{8} b_n P_n(\cos\Theta). \tag{12}$$

Notice that the expansion is terminated at n=8; the degrees of spatial anisotropy contributed by the orientation, photodissociation, and angular momentum detection steps are 2 for the orientation (as we considered orientation parameters c_1 and c_2 only), 2 for the photolysis step (for a one-photon photodissociation), and 4 for the angular momentum detection step (given by 2J, where J=2 for S(^{1}D$_2$) atoms). Note that a similar expansion of an isotropic sample of parent molecules would be terminated at n=6 [55].

The coefficients b_n are expressed in terms of a constant k_n, and the 8 possible a_q^k polarization parameters with k = 2 (for which there are k+1 = 3 parameters) and k = 4 (for which there are k+1 = 5 parameters) as follows:

$$b_n = k_n + \sum_{even\,k} \sum_{q=0}^{2} s_k w_q^k(n)\,\mathrm{Re}[a_q^k(\mathrm{i})], \tag{13}$$

where the $w_q^k(n)$ quantify the experimental sensitivity to each particular a_q^k parameter. We consider first the experimental geometry with **O** perpendicular to the imaging plane (Δ=0), which has been used in several of the authors experimental studies [26, 38, 39, 46, 47]. The sensitivity factors $w_q^k(n)$ are calculated for three degrees of orientation, the (JℓM=111) state with c_1 = 3/4 and c_2 = 1/4, the (JM=10) state with c_1 = 0 and c_2 = 1, and an isotropic sample of parent molecules with c_1 = 0 and c_2 = 0; in addition the molecular frame angles are chosen to be $\chi = \pi/6$, $\alpha = \pi/4$, and $\varphi_{\mu d} = 0$. The $w_q^k(n)$ factors are calculated for the geometry A (Δ=0, $\Gamma = \pi/2$, and $P = \pi/2$) are presented in Table I. For

this geometry, we note that there is no experimental sensitivity to the parent orientation (c_1). We see that the sensitivity factors $w_q^k(n)$ do not change too strongly (about 10%) between those from an isotropic sample or from a modestly aligned sample of OCS molecules in the (JℓM=111) state (with the exception of the q=2 parameters), whereas the deviations become more significant (about 30% or larger) for strongly aligned OCS molecules in the (JM=10) state.

Next, we consider the geometry B ($\Delta=\pi/2$, $\Gamma = \pi/2$, and $P = \pi/2$). When the molecules are isotropic ($c_1=c_2=0$), then the results are the same as for isotropic molecules in geometry A (as the only difference is the geometry of the orientation field **O**, which is not yet being utilized). We consider somewhat different dissociation dynamics, by choosing the molecular frame angles to be $\chi = \pi/6$, $\alpha = \pi/4$, $|\varphi_{\mu d}| = \pi/2$. As OCS molecules have planar symmetry, the distribution of the angle $\varphi_{\mu d}$ is an even function, therefore we can set $\langle \sin q\varphi_{\mu d} \rangle = 0$. The sensitivity factors $w_q^k(n)$ are calculated and shown in Table II. Notice that the sensitivity to the q=1 parameters, for the choice of this special case of $|\varphi_{\mu d}| = \pi/2$, now vanishes (as their sensitivity is proportional to $\cos\varphi_{\mu d}$); also the sensitivity to the q=2 parameters changes sign (as their sensitivity is proportional to $\cos 2\varphi_{\mu d}$). However, when the molecules are aligned ($c_2=1$), we see that the sensitivity to the q=1 parameters, from zero, now becomes large, due to the anisotropy of the aligned parent molecules. This is an example of how polarizing parent molecules allows sensitivity to molecular-frame dynamical information, which was not available in experiments with isotropic samples of molecules.

Rakitzis and Alexander [39], in the general case of polyatomic photodissociation, show that both single surface (classical) and multiple-surface interference (quantum mechanical) contributions to the q=1 parameters are allowed. However, they also show that, for isotropic parent molecules, these two contributions cannot be distinguished from the photofragment angular distributions alone, at a single photolysis wavelength. Future work will involve showing, using the methods described in this paper, how to distinguish the single and multiple-surface contributions to the photofragment angular momentum distributions, using polarized parent molecules. Finally, these methods may be useful in combination with emerging techniques for orienting polyatomic molecules [56,57].

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Table I: The sensitivity coefficients $w_q^k(n)$ of the $a_q^k(i)$ parameters calculated for the geometry ($\Delta = 0$, $\Gamma = \pi/2$, and $P = \pi/2$), and for parent molecular alignment of an isotropic sample ($c_2 = 0$), the ($J\ell M=111$) state ($c_2 = 1/4$), and the ($JM=10$) state ($c_2 = 1$, i.e. maximal alignment). For the chosen laboratory slice geometry there is no sensitivity to c_1 (see text). The dynamical angles describing the mutual orientation of permanent dipole moment, transition dipole moment and recoil velocity are chosen to be $\chi = \pi/6$, $\alpha = \pi/4$, and $\varphi_{\mu d} = 0$.

	n =	0	2	4	6
k_n	$c_2 = 0$	1	1.25	0	0
	$c_2 = 1/4$	0.914	1.195	0	0
	$c_2 = 1$	0.656	1.031	0	0
$w_0^2(n)$	0	0.25	1.357	0.643	0
	1/4	0.239	1.256	0.615	0
	1	0.206	0.951	0.530	0
$w_1^2(n)$	0	0.424	0.303	-0.727	0
	1/4	0.438	0.313	-0.750	0
	1	0.477	0.341	-0.818	0
$w_2^2(n)$	0	0.122	-0.175	0.052	0
	1/4	0.057	-0.156	0.098	0
	1	-0.138	-0.098	0.236	0
$w_0^4(n)$	0	0	0.357	1.325	0.568
	1/4	0	0.342	1.224	0.543
	1	0	0.295	0.924	0.469
$w_1^4(n)$	0	0	0.553	0.151	-0.704
	1/4	0	0.571	0.156	-0.726
	1	0	0.622	0.170	-0.792
$w_2^4(n)$	0	0	0.113	-0.185	0.072
	1/4	-0.044	-0.011	-0.080	0.135
	1	-0.178	-0.381	0.236	0.323
$w_3^4(n)$	0	0	0	0	0
	1/4	0.027	0	0.052	-0.025
	1	-0.110	0	0.210	-0.100
$w_4^4(n)$	0	0	0	0	0
	1/4	-0.008	0.014	-0.007	0.001
	1	-0.034	0.056	-0.028	0.005

Table II: The sensitivity coefficients $w_q^k(n)$ of the $a_q^k(i)$ parameters calculated for the geometry ($\Delta = \pi/2$, $\Gamma = \pi/2$, and $P = \pi/2$), and for parent molecular alignment of an isotropic sample ($c_2 = 0$) and the (JM=10) state ($c_2 = 1$). The dynamical angles describing the mutual orientation of permanent dipole moment, transition dipole moment and recoil velocity are chosen to be $\chi = \pi/6$, $\alpha = \pi/4$, and $|\varphi_{\mu d}| = \pi/2$.

	n =	0	2	4	6	8
k_n	$c_2 = 0$	1	1.25	0	0	0
	$c_2 = 1$	1.05	2.036	0.289	0	0
$w_0^2(n)$	0	0.25	1.357	0.643	0	0
	1	0.407	1.714	1.122	0.131	0
$w_1^2(n)$	0	0	0	0	0	0
	1	0.525	0.787	-0.787	-0.525	0
$w_2^2(n)$	0	-0.122	0.175	-0.052	0	0
	1	0.052	0	-0.100	0.048	0
$w_0^4(n)$	0	0	0.357	1.325	0.568	0
	1	0.032	0.623	1.626	0.984	0.110
$w_1^4(n)$	0	0	0	0	0	0
	1	0.176	0.878	0.315	-0.887	-0.481
$w_2^4(n)$	0	0	-0.113	0.185	-0.072	0
	1	0.045	0.072	-0.119	-0.060	0.062
$w_3^4(n)$	0	0	0	0	0	0
	1	-0.073	0.033	0.124	-0.113	0.029
$w_4^4(n)$	0	0	0	0	0	0
	1	-0.030	0.054	-0.034	0.011	-0.001

Figure Captions

Fig. 1: Polar coordinates of the dynamical vectors (**v**, **μ**, and **d**), the photolysis (**ε**) and probe (**P**) polarization directions, and the orientation field (**O**), in the molecular frame.

Fig. 2: Polar coordinates of the dynamical vectors (**v**, **μ**, and **d**), the photolysis (**ε**) and probe (**P**) polarization directions, and the orientation field (**O**), in the laboratory frame.

Figures

Figure 1:

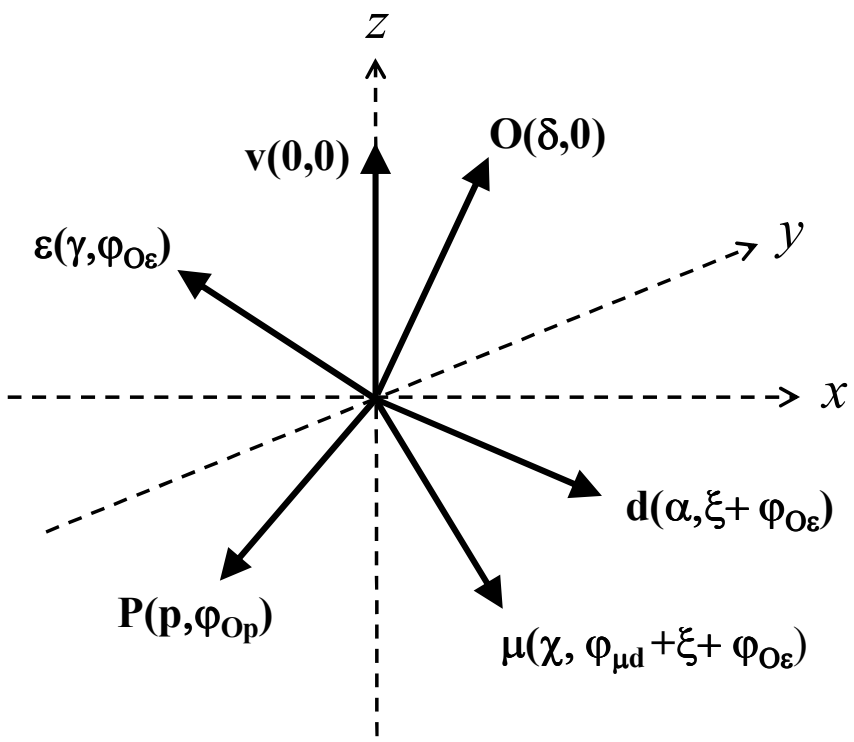
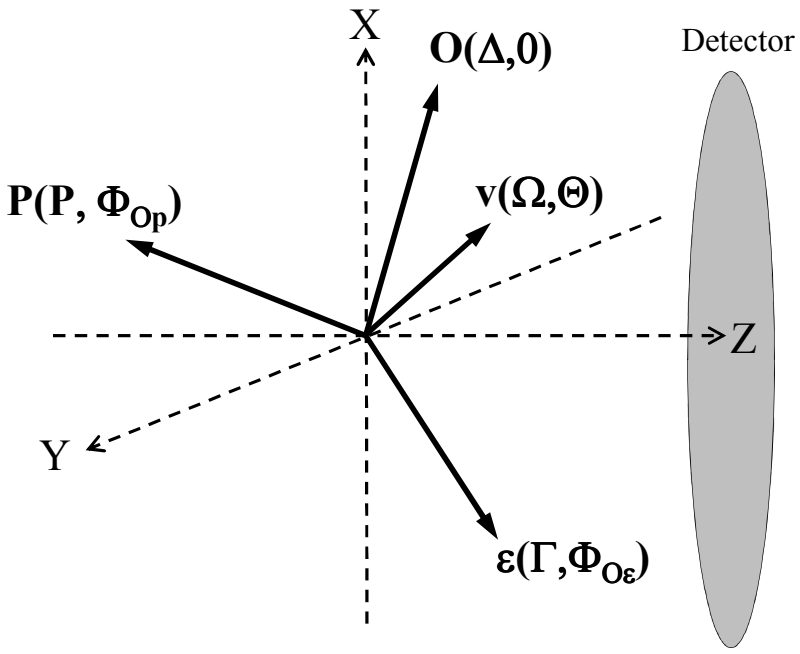


Figure 2:



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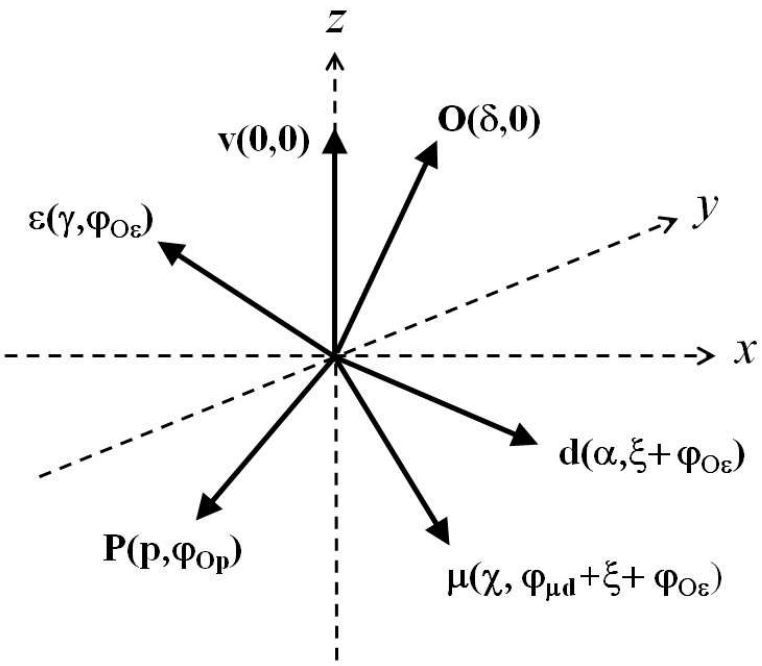

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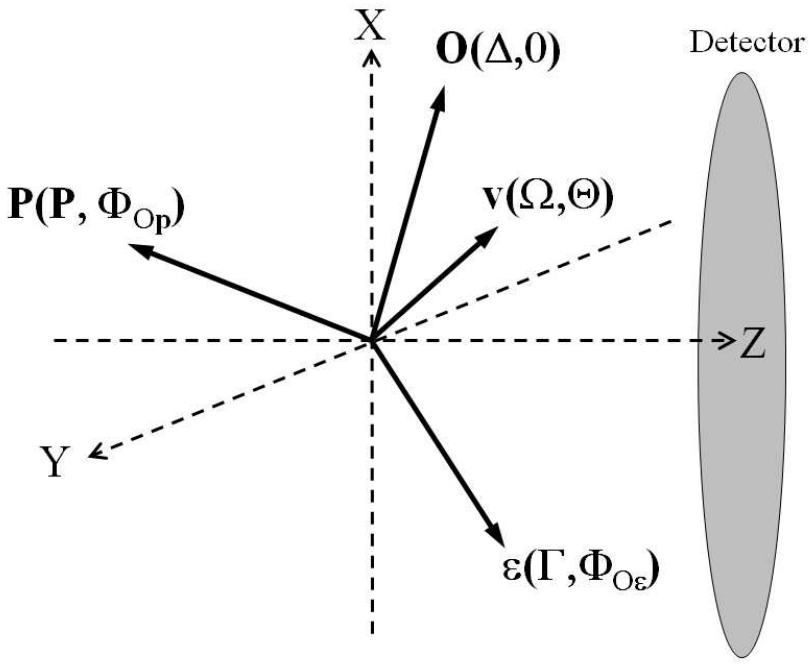

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