

Determination of Molecular Symmetry Axis (\hat{z}) Orientation via Photoelectron Angular Distribution Measurements

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The molecular symmetry axis (\hat{z}) orientation of an ensemble of symmetric-top molecules causes the energy-resolved photoelectron angular distributions (PADs) following two-photon ($1 + 1'$) ionization to have a form characterized by odd multipole moments ($Y_{LM}(\theta, \phi), L = \text{odd}$). Selection rules are derived for the photoionization process. Expressions are developed that relate the form of the PAD to the degree of \hat{z} orientation.

Introduction

A number of chemical processes produce oriented molecules. Examples include the desorption and scattering of molecules from a surface,¹⁻⁵ the photodissociation of polyatomics with polarized light,^{6,7} and the study of chemical reactions in directed beams.⁸⁻¹¹ The determination of the orientation of an ensemble of molecules can provide valuable information about dynamical interactions. Although laboratory-frame angular momentum orientation can be relatively easily measured by optical methods,^{10,12-14} the measurement of molecular symmetry axis (\hat{z}) orientation in the laboratory is not straightforward. Experimental measurements of such orientation have so far been made by Bernstein and co-workers¹⁵ and by Novakoski and McClelland.³ Bernstein and co-workers observed the photofragment up-down asymmetry from the photodissociation of oriented alkyl halides. Novakoski and McClelland used a static electric hexapole field as a means of detecting orientation of CF_3H desorbed from $\text{Ag}(111)$. Kohl and Shipsey¹⁶ have proposed a method to measure orientation by electron scattering but, to our knowledge, this has not been experimentally realized. In this paper we propose a method to determine \hat{z} orientation from the measurement of energy- and angle-resolved photoelectron distributions.

"Polarization" and "orientation" have many meanings. In this work, "polarization" describes collectively the alignment and orientation of the angular momentum distribution of a molecular ensemble. Orientation refers to "up-down asymmetry" with respect to some axis. It is important to clarify the subtle distinctions

between various types of angular momentum orientation of a symmetric-top molecule. We use the term " \hat{z} orientation" to refer to the orientation of the symmetry axis of a symmetric-top molecule. We distinguish this from (a) laboratory-frame orientation of the rotational angular momentum vector N (" M -state orientation") and (b) molecular-frame orientation of N (" K -state orientation"). Unqualified use of the word "orientation" can refer to any of these three types of orientation.

Angular distributions of photofragments carry with them the signature of the polarization of the precursor molecule. This idea has already been exploited by Bernstein and co-workers¹⁵ in the photodissociation of \hat{z} -oriented symmetric-top alkyl halide molecules. Greene and Zare¹⁷ have discussed the relationship between the polarization of photodissociated molecules and the resulting photofragment angular distributions. Because photoionization is another form of photofragmentation, similar relationships hold for photoelectron angular distributions. For example, Dubs et al.¹⁸ have developed a theory for the determination of alignment from circular dichroism in photoelectron angular distributions (CDAD). Circular dichroism refers to the change in the photoelectron signal at a fixed detection angle when the helicity of the polarization of the ionizing photon is varied. This paper addresses a related phenomenon: a \hat{z} -oriented ensemble of symmetric-top molecules yields oriented photoelectron angular distributions (PADs) following photoionization. The presence of up-down asymmetry in PADs has been observed experimentally by Kaesdorf, Schönhense, and Heinzmann,¹⁹ who studied the photoionization of oriented CH_3I in a non-quantum-state-specific manner.

In what follows, we relate the polarization (i.e., alignment or any form of orientation) of a molecular ensemble to the photoionization dynamics of the molecules and the form of the PADs. We explain how this relationship can be exploited to deduce the polarization of an ensemble of symmetric-top molecules through the observation of energy-resolved PADs. We present selection rules based on group theoretical arguments for the photoionization of symmetric-top molecules in which the initial, intermediate, and final states are vibronically nondegenerate. As an illustration, we calculate PADs following ($1 + 1'$) resonance-enhanced multiphoton ionization (REMPI) of a \hat{z} -oriented ensemble of generic symmetric-top molecules.

Theory

Consider a photoionization process in which a symmetric-top molecule in the state ($N_i, |K_i|$) yields ions in the states ($N^+, |K^+|$). Here, N is the rotational quantum number and K the quantized projection of N on the molecular figure axis \hat{z} (see Table I for nomenclature). Although spectroscopists use K to refer to the absolute value of this projection, for our purposes we choose to

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make K a signed quantity. For each photoionization channel ($N_i, |K_i|$) \rightarrow ($N^+, |K^+|$), the photoelectron angular distribution has the general form²⁰

$$I(\theta, \phi) = \sum_{LM} \beta_{LM} Y_{LM}(\theta, \phi) \quad (1)$$

where (θ, ϕ) are the polar angles measured in the laboratory frame, the $Y_{LM}(\theta, \phi)$ are spherical harmonics, and the β_{LM} are coefficients of this expansion. In eq 1, the sum over L and M is restricted so that M ranges from $-L$ to L in unit steps and L depends on the overall polarization of the photoionization process. For an unpolarized target molecule, L is restricted to even values and ranges from 0 to $2n$ for an n -photon ionization process. For a polarized target molecule, it is possible for L to be odd; this cannot occur for a purely aligned target or for a target having only M -state orientation, but can occur for a molecule with \hat{z} orientation. Because, as we will show below, PAD orientation is directly related to \hat{z} orientation, analysis of PADs corresponding to each photoionization channel allows the deduction of detailed information about the orientation of an ensemble of molecules.

One-photon ionization does not permit in general the selection of a single ($N_i, |K_i|$) level from an ensemble of thermally populated ($N_g, |K_g|$) levels, and thus is of limited use for quantitative measurements of polarization. Resonance-enhanced multiphoton ionization (REMPI), on the other hand, makes this state selection possible. With REMPI, a single ($N_g, |K_g|$) level of an ensemble can be optically selected by a bound-bound transition to an electronically excited intermediate ($N_i, |K_i|$) level; this single ($N_i, |K_i|$) level is then ionized by another photon. Because a single intermediate rotational level is selected, only a few rotational levels of the ion are formed, and the resulting photoelectron kinetic energy spectrum is greatly simplified. Given sufficient photoelectron energy resolution,^{21,22} PADs corresponding to individual rotational levels ($N^+, |K^+|$) of the ion can be observed. In what follows, we present expressions for the rotationally resolved photoelectron intensities $I(\theta, \phi)$ appropriate for two-photon ($1 + 1'$) REMPI of vibronically nondegenerate symmetric-top molecules.

Because the selection rules governing the photoionization of vibronically nondegenerate levels of symmetric-top molecules are quite simple (as shown below), we limit our discussion to the consideration of REMPI process involving only such levels. In addition, nondegenerate vibronic states have, by definition, no electronic or vibrational angular momenta; thus, the treatment of the angular momenta of the molecule is relatively straightforward. Although it is not difficult to extend our treatment to degenerate levels, such an extension is beyond the scope of this paper. As it stands, our treatment can be applied directly to, for example, NH_3 and PH_3 ; it can be extended to include asymmetric-top molecules such as H_2O . In addition, our treatment can be applied directly to all vibrationally nondegenerate linear molecules; indeed, for these we relax the requirement of electronic nondegeneracy, because the projection of the total angular momentum on the internuclear axis is purely electronic.

The ground-state polarization of the rotational angular momentum can be described in terms of statistical tensors, the expectation values of which are called state multipole moments $\rho_{Q_i}^{N_i, K_i}$ (N_g, K_g).^{23,24} These moments are related to the density matrix elements, $\rho_{M_g, M'_g}(N_g, K_g)$, by

$$\rho_{Q_i}^{N_i, K_i} = \sum_{M_g, M'_g} (-1)^{N_g - M'_g} (2\mathcal{H}_g + 1)^{1/2} \times \begin{pmatrix} N_g & N_g & \mathcal{H}_g \\ M_g & -M'_g & -Q_g \end{pmatrix} \rho_{M_g, M'_g}(N_g, K_g) \quad (2)$$

Here, \mathcal{H}_g is the rank and Q_g the component of the multipole. Following the absorption of one photon, the polarization of the intermediate level ($N_i, |K_i|$) is described by $\rho_{Q_i}^{N_i, K_i}$ where the values of N_i and K_i are constrained by the well-known electric-dipole selection rules. We relate $\rho_{Q_i}^{N_i, K_i}$ to $\rho_{Q_g}^{N_g, K_g}$ by

$$\rho_{Q_i}^{N_i, K_i} = \sum_{\mathcal{H}_i, Q_i} B(\mathcal{H}_i, Q_i, \mathcal{H}_g, Q_g) \rho_{Q_g}^{N_g, K_g} \quad (3)$$

where the expression for the $B(\mathcal{H}_i, Q_i, \mathcal{H}_g, Q_g)$ coefficients is worked out in Appendix A. Note that the M -state orientation is described by terms with $\mathcal{H} = \text{odd}$, and angular momentum alignment by terms with $\mathcal{H} = \text{even}$. K -state orientation arises when $\rho_0^0(N, K) \neq \rho_0^0(N, -K)$. Finally, \hat{z} orientation arises when $\rho_0^{\mathcal{H}}(N, K) \neq \rho_0^{\mathcal{H}}(N, -K)$ with $\mathcal{H} = \text{odd}$; we note that $K = 0$ states (or $\Lambda = 0$ states for linear molecules) are not \hat{z} orientable.

We now consider how to quantify the \hat{z} orientation of an ensemble of symmetric-top molecules. As Kramer and Bernstein²⁵ noted, the orientation of a symmetric-top molecule in the state $|NKM\rangle$ can be expressed by the following relationship:

$$\langle \hat{z} \cdot \hat{Z} \rangle = \frac{KM}{N(N+1)} \quad (4)$$

where \hat{Z} is a unit vector directed along the laboratory-fixed Z axis. To determine the \hat{z} orientation of the level ($N, |K|$) when an ensemble of angular momentum sublevels are populated, eq 4 must be summed over the distribution of the sublevels $K (= \pm|K|)$ and M . In terms of the state multipole moments, the ensemble-averaged \hat{z} orientation is

$$\langle \hat{z} \cdot \hat{Z} \rangle = |K| \frac{\sum_{\mathcal{H}} D(\mathcal{H}, N) [\rho_0^{\mathcal{H}}(N, K) - \rho_0^{\mathcal{H}}(N, -K)]}{[\rho_0^0(N, K) + \rho_0^0(N, -K)]} \quad (5)$$

where

$$D(\mathcal{H}, N) = \frac{(2\mathcal{H} + 1)^{1/2}}{N(N+1)(2N+1)^{1/2}} \times \sum_M (-1)^{N+M} \begin{pmatrix} N & N & \mathcal{H} \\ M & -M & 0 \end{pmatrix} \quad (6)$$

The coefficients $D(\mathcal{H}, N)$ will be nonzero only when \mathcal{H} is odd.

Having quantified the polarization of the intermediate state, we now calculate the β_{LM} coefficients describing the form of the PADs (see eq 1). The treatment presented previously for the one-photon ionization of diatomic molecules^{26,27} is readily generalized to the one-photon ionization of polarized, rotationally state-selected symmetric-top molecules. Our formalism applies directly only to those nondegenerate vibronic states for which spin functions can be separated from the rovibronic wave functions. The β_{LM} coefficients can be expressed as

$$\beta_{LM} = \sum_{K_i = \pm|K_i|} \sum_{\mathcal{H}_i, Q_i} \sum_{l, l'} \sum_{k, k'} \sum_{\mu, \mu'} A_{LM\alpha} r(l, k_i, \mu_k) r(l', k'_i, \mu'_k) \times \cos[\eta(l, k_i, \mu_k) - \eta(l', k'_i, \mu'_k)] \rho_{Q_i}^{N_i, K_i} \quad (7)$$

where the real quantities $r(l, k_i, \mu_k)$ and $\eta(l, k_i, \mu_k)$ represent the magnitude and phase, respectively, of the electric dipole matrix element that connects the intermediate electronic state to the (l, k_i) partial waves, and the coefficients $A_{LM\alpha}$ are defined in Appendix B. The α subscript of A is an index that stands for the values of N^+ , $|K^+|$, μ_0 , \mathcal{H}_i , Q_i , l , k_i , μ_k , l' , k'_i , and μ'_k ; l is the orbital angular momentum quantum number of the photoelectron partial wave, k_i is the projection of l on the molecular figure axis \hat{z} , and μ_k is the projection of the angular momentum of the ionizing photon on the molecular figure axis and is fixed by the relation $\mu_k = K^+ - K_i + k_i$. All quantum numbers are defined in Table I.

Equation 7 shows that the β_{LM} coefficients depend on three factors: the coefficients $A_{LM\alpha}$, the dynamical parameters $r(l, k_i, \mu_k)$ and $\eta(l, k_i, \mu_k)$, and the multipole moments $\rho_{Q_i}^{N_i, K_i}$ describing the polarization of the intermediate level (N_i, K_i). The $L = \text{odd}$

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TABLE I: Quantum Numbers Used in the Text^a

angular momentum quantum no.	lab-fixed projection	molecule-fixed projection	description of angular momentum
J			total angular momentum (excluding nuclear spin)
S			electronic spin angular momentum
N_x	M_x	K_x	total angular momentum excluding spin ($N = J - S$)
l	m_l	k_l	photoelectron orbital angular momentum
l	μ_0	μ_k	photon angular momentum rank and component of the N_x spherical tensor
\mathcal{K}_x	\mathcal{Q}_x		

^aHere, x may be subscript g or i, or superscript +, denoting ground, intermediate, and ion state, respectively. It may also stand for the subscript t, which denotes transferred angular momentum. The use of any quantity with a prime indicates a value coherently prepared with the unprimed value.

terms of eqs 1 and 7 can arise only when the sum of l and l' is odd; they cause up-down asymmetry in the PAD. This interference between even and odd l partial waves can only occur when \hat{z} orientation is present.

We consider the selection rules governing the photoionization process for symmetric-top molecules, including diatomic molecules. The vibronic symmetries (and resulting selection rules) depend on the point group of the molecule in question. As mentioned above, we limit our discussion to nondegenerate vibronic levels (i.e., irreducible representations of A or B symmetry) for the states of the neutral and ionic molecules. We recall that the change in the K quantum number (ΔK) for bound-bound transitions of symmetric-top molecules is limited to $\Delta K = 0$ for parallel transitions, and to $\Delta K = \pm 1$ for perpendicular transitions.^{28,29} The same rule is true for photoionization, except that the photoelectron and the molecular ion must be considered as a single superexcited entity. We deduce which ionic states can be formed from the resulting decomposition of this superexcited state. Symmetry relationships and selection rules are illustrated in Figure 1 for two classes of point groups and for partial waves with $l = 0$ and 1. From this figure we conclude that $K^+ - K_i = 0$ for both parallel and perpendicular ionizing transitions.³⁰ We also note that for molecules of the higher symmetry class (namely, those belonging to point groups that contain the i and/or the σ_h symmetry operators; see part b of Figure 1) only odd l waves are produced for the transitions from neutral vibronic state to ion vibronic state $A'(A_g) \rightarrow A'(A_g)$ and $A''(A_u) \rightarrow A''(A_u)$, and only even l waves for the transitions $A'(A_g) \leftrightarrow A''(A_u)$. These selection rules eliminate the possibility of interference between even and odd l waves. Hence no PAD orientation can arise for molecules having these higher symmetries. This result is consistent with the fact that these molecules cannot exhibit \hat{z} orientation; for example, the nondegenerate vibronic state of a planar molecule cannot point "up", as opposed to "down".

The coefficients $A_{LM\alpha}$ of eq 7 can be easily calculated (see Appendix B), given a program that generates the values of Wigner 3- j symbols.²⁴ A more complicated problem is the determination of the dynamical parameters $r(l, k_l, \mu_k)$ and $\eta(l, k_l, \mu_k)$. We consider three possibilities: (a) all these parameters are known, (b) all the parameters except the relative phase between even and odd partial waves are known, and (c) none of the parameters are known.

In option (a), the molecular multipole moments $\rho_{Q_i}^{X_i}(N_i, K_i)$ can be determined directly from eq 7 by performing a nonlinear least-squares fit to experimental data.^{21,22} Equation 3 can then be inverted to yield the ground-state multipole moments

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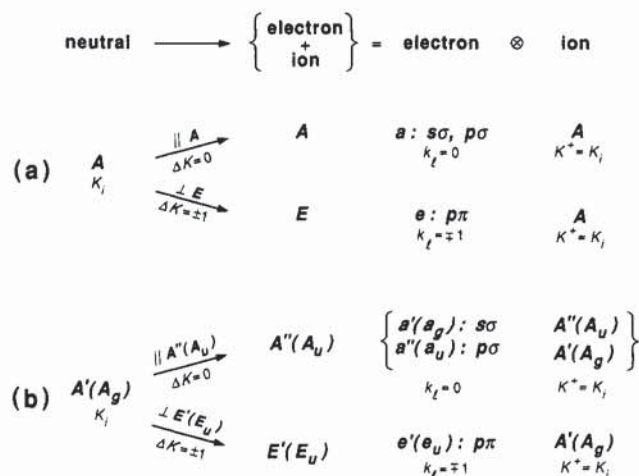


Figure 1. Diagram to illustrate the selection rules controlling the photoionization step for symmetric-top molecules of (a) symmetry C_n and C_∞ and of (b) symmetry C_{nh} , D_{nd} , and D_{nh} where $n \geq 3$ (including $n = \infty$). The neutral and ionic wave functions are chosen to be nondegenerate.

$\rho_{Q_i}^{X_i}(N_i, K_i)$ for each K_i , and hence the \hat{z} orientation, which we quantify by $\langle \hat{z} \cdot \hat{Z} \rangle$ (see eq 5). The dynamical parameters can be calculated by ab initio methods, as demonstrated by McKoy and co-workers,³¹ but their experimental determination is problematic. This difficulty arises both from the need to have sufficient photoelectron energy resolution to separate the rotational states of molecular ions and from the requirement that the ensemble of molecules be prepared with a known orientation. This second requirement arises from the need to determine the relative phases between even and odd l partial waves. These relative phases are critical parameters for the quantitative application of our method because they control the magnitude and direction of orientation in PADs. Consequently, option (a) will only rarely be realized experimentally.

In option (b), all the dynamical parameters except these relative phases have been determined experimentally. In recent work, Allendorf et al.²¹ and Leahy et al.²² have shown that the observation of energy-resolved PADs following REMPI of a thermal distribution of ground-state molecules provides enough information to deduce the dynamical parameters controlling molecular photoionization. However, in this case only the relative phases between even and other even partial waves or between odd and other odd partial waves can be determined. With this knowledge, it would be possible to gain information on the polarization by fitting the experimental data to parameters that control the degree of polarization and the relative phase between the odd and even partial waves.

Option (c) is probably the most practical application of the ideas presented in this paper. Even with no knowledge of the dynamical parameters it would be possible to establish the presence or absence of orientation by observing the PADs: oriented PADs can only arise when a molecular ensemble with \hat{z} orientation is photoionized.

The method of observing the orientation of the photoelectron angular distribution as a measure of the \hat{z} orientation of an ensemble of symmetric-top molecules is readily implemented under conditions where no external field perturbs the flight path of the photoelectron to the detector. However, we note that some important methods of preparing oriented molecules³²⁻³⁵ require the

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TABLE II: Branching Ratios (β_{00}) of the Ion Rotational Levels following Photoionization with Linearly Polarized Light of a Generic Symmetric-Top Molecule in the Rotational Level $|111\rangle$ Using the Radial Dipole Matrix Elements Listed in Eqs 8a–8d^a

N^+	$K^+ = +1$		
	$\mu_0 = 0$	$\mu_0 = +1$	$\mu_0 = -1$
1	$\equiv 100$	56.9	92.3
2	25.3	42.1	11.2
3	2.69	5.39	0.90

^aThe values are normalized such that $\beta_{00} \equiv 100$ for $N^+ = 1, K^+ = 1$.

presence of strong electric fields, which may render the application of this method impractical.

Illustration

As an example of the effect of \hat{z} orientation on PADs, we have chosen arbitrary values for the dynamical parameters (namely, the magnitudes $r(l, k_l, \mu_k)$ and phases $\eta(l, k_l, \mu_k)$ of the electric dipole matrix elements) that describe the photoionization of a generic symmetric-top molecule. We have calculated the PADs resulting from the photoionization of the $|N_i = 1, K_i \times M_i = +1\rangle$ (i.e., $|111\rangle$ or $|1-1-1\rangle$) rotational level. This constitutes an $N_i = 1$ level having complete \hat{z} orientation ($\langle \hat{z} \cdot \hat{Z} \rangle = 0.5$). The calculations were performed for all values of N^+ that are consistent with total angular momentum conservation ($|N^+ - N_i| \leq l_{\max} + 1$). Because in our example (involving transitions between nondegenerate levels with $l = 0$ or 1) k_l is constrained by symmetry to be equal to μ_k , we omit the μ_k label of the dynamical parameters. In an experimental situation, usually both the states $+|K_i|$ and $-|K_i|$ would have some population and the \hat{z} orientation would be related to the population difference. For simplicity, we have truncated the partial wave expansion at $l = 1$ (p wave). The dynamical parameters used were as follows:

$$r(l=0; k_l=0) = 1.0 \quad (8a)$$

$$r(l=1; k_l=0) = 1.0 \quad (8b)$$

$$r(l=1; k_l=\pm 1) = 0.5 \quad (8c)$$

$$\eta(l=0,1; k_l=0,\pm 1) = 0.0 \quad (8d)$$

Although these values maximize the effect of orientation on PADs, this effect will generally be sizable whenever the photoionization process yields even and odd l waves that can interfere and that have similar cross sections.

We have chosen the electric vector of the ionizing radiation to lie along the laboratory-frame orientation axis of the ensemble of symmetric tops, in direct analogy with the photodissociation studies of Bernstein and co-workers.¹⁵ In our example, cylindrical symmetry is preserved in the photoionization process; thus, only β_{LM} coefficients with $M = 0$ are nonzero. The expansion in L terminates at $L = 2$ because this is the maximum degree of anisotropy that can be attained by an $l = 1$ wave. Because orientation is characterized by $L = \text{odd}$, the PAD orientation is completely described by the β_{10} term. No orientation is exhibited in the $|\Delta N = N^+ - N_i| = 2$ PADs because the influence of the s wave is confined by the selection rule $|\Delta N| \leq 1$.

In Figure 2a, we present the predicted rotationally resolved PADs following ionization of the level $|N_i = 1, K_i \times M_i = \pm 1\rangle$ with linearly polarized light. All PADs are normalized to portray equal angle-integrated cross sections ($\beta_{00} = 1$) of the rotational levels (the true relative cross sections for Figure 2a are listed in Table II). Figure 2a also shows the PAD for unresolved N^+ (for $K^+ = 1$). In the event that ions with more than one value of $|K^+|$ are formed, the $|K^+|$ -splitting could be resolved in a high-resolution angle-resolved time-of-flight experiment for a highly prolate symmetric-top molecule. The required photoelectron energy resolution would be $\sim 2A(2K^+ - 1)$, or about $20 \times K^+ \text{ cm}^{-1}$ for a methyl halide molecule. The best angle-resolved photoelectron energy resolution so far reported^{21,22} is $< 20 \text{ cm}^{-1}$, which would be sufficient for this purpose. In practice, rotational resolution would be desirable for extracting \hat{z} -orientation information;

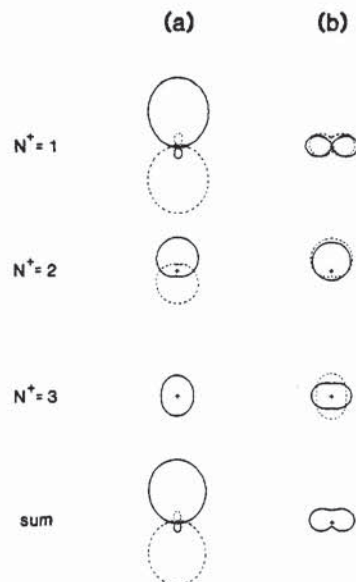


Figure 2. Predicted photoelectron angular distributions (PADs) following photoionization of the level $|1, |K_i \times M_i| = 1\rangle$ to produce the ion state $|K^+| = 1$ using the dynamical parameters listed in eqs 8a–d. The laboratory Z axis lies along the vertical and $\Delta N = N^+ - N_i$. The lowest angular distribution in each column represents the weighted sum of the N^+ -specific PADs. In (a) $\mu_0 = 0$; the solid line corresponds to ionization of the level $|1, K_i \times M_i = 1\rangle$ and the dashed line corresponds to ionization of the level $|1, K_i \times M_i = -1\rangle$. The dashed line also represents the PAD resulting from the photoionization of $|1, K_i \times M_i = +1\rangle$, when the phase $\eta(l = 0; k_l = 0)$ is changed to π radians (with the other parameters as before). In (b) the ionized level is $|1, K_i \times M_i = +1\rangle$; the solid line shows the result for $\mu_0 = +1$ and the dashed line shows the result for $\mu_0 = -1$.

however, in the absence of rotational resolution, the example presented here would yield a highly oriented PAD.

The solid line of Figure 2a represents the PADs following the photoionization of the level $|1, K_i \times M_i = +1\rangle$, while the dashed lines represent the PADs resulting from the photoionization of the level $|1, K_i \times M_i = -1\rangle$, i.e., the “upside down” molecule. The forms of the PADs are unchanged, but the sense of orientation is inverted. This simple demonstration conveys the power of this method to determine the sense of the state-specific molecular-frame orientation of an ensemble of molecules. It is clear that the detection of \hat{z} orientation does not require the measurement of a complete angular distribution. The simplest method involves the simultaneous observation of photoelectron flux at axially opposed detectors. In our example, detectors placed at $+\hat{Z}$ and $-\hat{Z}$ would record a significant difference in flux.

The dashed lines in Figure 2a also result when the $s\sigma$ phase is changed from 0° to 180° . This shows that the direction of the orientation of the PADs is quite sensitive to the relative phase between the even and odd l waves. The interference between even and odd l waves (s and p in this case) does not affect photoionization cross sections but does create orientation in the PADs.

In Figure 2b, the solid and dashed lines show the PADs resulting from photoionization with left- and right-handed circularly polarized light ($\mu_0 = +1$ and -1), respectively. Again, the axis of quantization of the radiation is chosen to coincide with that of the laboratory-fixed frame of the oriented ensemble; thus the PAD is cylindrically symmetric. Note that this choice of quantization axes, given a fixed \hat{z} orientation, would require a different light beam geometry from that used for linear polarization because circularly polarized light has its projection quantized along the propagation direction of the light. The important role of polarization in the shaping of the PADs is evident.

Conclusions

The ability to determine \hat{z} orientation is of great use in a wide array of dynamical stereochemistry studies. Examples are gas-phase reactions, photodissociation, and surface desorption and scattering. Direct observation of \hat{z} orientation has already been achieved through photodissociation studies¹⁵ and by use of a

hexapole field.³ The measurement of oriented PADs provides an alternative method of determining the existence of \hat{z} orientation. Moreover, with this method, \hat{z} orientation can be determined as a function of quantum state.

We have presented a calculation of the oriented PADs that result from the photoionization of an ensemble of symmetric-top molecules with $\langle \hat{z} \cdot \hat{Z} \rangle = 0.5$. The up-down asymmetry in the PADs may be substantial; the forms of the PADs are sensitive to the \hat{z} orientation of the neutral molecule as well as to the photoionization dynamics, the change in molecular rotation, and the polarization of the ionizing light. If photoionization dynamics are known (for example, by ab initio methods), then it is possible to determine the orientation of an ensemble of symmetric-top molecules, rotational level by rotational level. Even in the case where the photoionization dynamics are not well characterized, the presence of \hat{z} orientation can be established in a rotationally state-specific manner.

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Appendix A

The coefficients of eq 3 are derived simply from the relationship between density matrix elements $\rho_{MM'}(N, K)$ and angular momentum multipole moments $\rho_{Q_i}^{\mathcal{H}_i}(N, K)$, which is given in eq 2, and the relationship between the density matrices for the ground state and the excited state, which is given by

$$\rho_{M_i M'_i}(N_i, K_i) \propto S(N_g, N_i) \sum_{M_g, M'_g} (-1)^{M_i + M'_i} \times \begin{pmatrix} N_i & 1 & N_g \\ -M_i & \mu_0 & M_g \end{pmatrix} \begin{pmatrix} N_i & 1 & N_g \\ -M'_i & \mu_0 & M'_g \end{pmatrix} \rho_{M_g M'_g}(N_g, K_g) \quad (\text{A1})$$

In eq A1 $S(N_g, N_i)$ is the line-strength factor for the $N_g \rightarrow N_i$ transition and the polarization vector of the exciting radiation is assumed to lie along the orientation axis of the ground-state molecular ensemble. Combining eqs 2 and A1 we obtain

$$\rho_{Q_i}^{\mathcal{H}_i}(N_i, K_i) = \sum_{M_i, M'_i} (-1)^{\mu_0 + Q_i} (2\mathcal{H}_i + 1)^{1/2} \times \begin{pmatrix} N_i & N_i & \mathcal{H}_i \\ -M_i & M'_i & -Q_i \end{pmatrix} \begin{pmatrix} N_i & 1 & N_g \\ -M_i & \mu_0 & M_i - \mu_0 \end{pmatrix} \times \begin{pmatrix} N_i & 1 & N_g \\ -M'_i & \mu_0 & M'_i - \mu_0 \end{pmatrix} \sum_{\mathcal{H}_g, Q_g} (2\mathcal{H}_g + 1)^{1/2} \times \begin{pmatrix} N_g & N_g & \mathcal{H}_g \\ -M_i + \mu_0 & M'_i - \mu_0 & -Q_g \end{pmatrix} \rho_{Q_g}^{\mathcal{H}_g}(N_g, K_g) \quad (\text{A2})$$

from which it follows that

$$B(\mathcal{H}_i, Q_i, \mathcal{H}_g, Q_g) = \sum_{M_i, M'_i} (-1)^{\mu_0 + Q_i} (2\mathcal{H}_g + 1)^{1/2} (2\mathcal{H}_i + 1)^{1/2} \times \begin{pmatrix} N_i & 1 & N_g \\ -M_i & \mu_0 & M_i - \mu_0 \end{pmatrix} \begin{pmatrix} N_i & 1 & N_g \\ -M'_i & \mu_0 & M'_i - \mu_0 \end{pmatrix} \times \begin{pmatrix} N_g & N_g & \mathcal{H}_g \\ -M_i + \mu_0 & M'_i - \mu_0 & -Q_g \end{pmatrix} \begin{pmatrix} N_i & N_i & \mathcal{H}_i \\ -M_i & M'_i & -Q_i \end{pmatrix} \quad (\text{A3})$$

The value of $B(\mathcal{H}_i, Q_i, \mathcal{H}_g, Q_g)$ depends strongly on the values of μ_0 and $\Delta N = N_i - N_g$. We may also need to determine the ground-state polarization $\rho_{Q_g}^{\mathcal{H}_g}(N_g, K_g)$ from the intermediate-state polarization $\rho_{Q_i}^{\mathcal{H}_i}(N_i, K_i)$. To do this, we need to invert the system of equations (eq 3).

Appendix B

The $A_{LM\alpha}$ coefficients in eq 7 are derived in a similar manner to that presented recently for a diatomic molecule.²⁷ Here, we write the projection of the rotational angular momentum, N , on the molecular axis as K rather than Λ . (Although, in these equations, we have included a sum over degenerate ion states $+K^+$ and $-K^+$, we applied the selection rule³⁰ $K^+ - K_i = 0$ in the calculation of the $A_{LM\alpha}$ coefficients in the illustration.) We find that

$$A_{LM\alpha} = [(2N_i + 1)(2N^+ + 1)(2\mathcal{H}_i + 1)(2L + 1)]^{1/2} \times \sum_{K^+ = \pm|K^+|} \sum_{M^+} \sum_{M_i, M'_i} \sum_{m, m'} \sum_{N_i, N'_i} (-1)^{N_i - M_i + M - m_i} \times \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ m_i & -m'_i & M \end{pmatrix} \begin{pmatrix} N_i & N_i & \mathcal{H}_i \\ M_i & -M'_i & Q_i \end{pmatrix} \times C(l, k, m_i, N_i, M_i, \mu_k) C(l', k', m'_i, N'_i, M'_i, \mu'_k) \quad (\text{B1})$$

where

$$C(l, k, m_i, N_i, M_i, \mu_k) = (-1)^{K^+ + M^+ + \mu_k} (2N_i + 1)(2l + 1)^{1/2} \times \begin{pmatrix} N_i & 1 & l \\ M_i & \mu_0 & -m_i \end{pmatrix} \begin{pmatrix} N^+ & N_i & N_i \\ -K^+ & K_i & K_i \end{pmatrix} \times \begin{pmatrix} N_i & 1 & l \\ -K_i & \mu_k & -k_i \end{pmatrix} \begin{pmatrix} N^+ & N_i & N_i \\ -M^+ & M_i & M_i \end{pmatrix} \quad (\text{B2})$$

The values of the $A_{LM\alpha}$ coefficients are seen to be independent of the dynamical parameters $r(l, k, \mu_k)$ and $\eta(l, k, \mu_k)$ and the angular momentum polarization $\rho_{Q_i}^{\mathcal{H}_i}(N, K)$.