Observation of Coherent and Incoherent Dissociation Mechanisms in the Angular Distribution of Atomic Photofragment Alignment

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(Received 3 July 1997)

We have analyzed the recoil angle dependence of chlorine atom angular momentum alignment for the dissociation of chlorine molecules at 355 nm. This angular distribution was isolated from ion image measurements, which map a three-dimensional velocity vector distribution of state-selectively-ionized photofragments into a two-dimensional spatial distribution. Using a general quantum mechanical method to simulate the alignment angular distribution, we show that there are clear contributions to alignment from both incoherent and coherent components of a perpendicular optical transition in the molecule. [S0031-9007(97)05242-3]

PACS numbers: 33.80.Gj, 34.50.Gb, 34.50.Lf

Photofragment angular momentum polarization (orientation and alignment) is a detailed signature of molecular photodissociation dynamics. For atomic photofragments, this polarization provides information on the electronic rearrangement which occurs during optical excitation and dissociation of the parent molecule. Several factors contribute to this polarization [1-5]. For the idealized case of a diatomic system which dissociates on a single adiabatic potential energy curve, only the electronic state symmetry and the associated Coulomb interaction at large interatomic distance will govern the polarization. However, in general, multiple molecular electronic states are involved, both in the initial excitation and during the course of dissociation. They are individually expected to yield different atomic polarizations, and coherent excitation of two or more states can lead to strong interference effects. Finally, nonadiabatic transitions between electronic states will mix the contributions of individual states.

Measurements of photofragment angular momentum polarization as a function of recoil angle (**v**-**j** correlation) provide the most detailed information on the dissociation dynamics. While this property has been studied for rotating diatomic photofragments for over a decade, the atomic **v**-**j** correlation has been observed only recently [6,7]. However, none of the recent reports have used theoretically rigorous methods for analyzing the experimental data. It is particularly important to account for coherence effects, since they directly affect the shape of the polarization angular distribution, and their identification can give crucial information about the dissociation mechanism.

For the high angular momenta which are typical of diatomic photofragments, the polarization angular distribution may be described semiclassically as an expansion of bipolar harmonics [8]. Although this widely used method can be adapted for low rotational states, there now exists a fully quantum mechanical treatment which uses parameters with explicit dynamical significance [9]. This approach is especially useful for the low values of the electronic angular momentum quantum numbers encountered in investigations of polarized atomic photofragments. In this Letter, we have used this general theory to identify contributions of the excited state symmetry and coherence effects to an ion imaging measurement of the alignment angular distribution.

In studying the polarization angular distribution, one must measure both the recoil velocity vector and the correlated angular momentum polarization. The velocity vector distribution is easily resolved with twodimensional photofragment ion imaging [10], while laserbased spectroscopic probes, such as resonance-enhanced multiphoton ionization (REMPI), are sensitive to angular momentum polarization. Figure 1 shows a schematic of our imaging experiment. An initial laser pulse (355 nm) dissociates chlorine molecules in a supersonic expansion, and a second pulse (234.336 nm) state-selectively ionizes the chlorine atom photofragments with 2 + 1REMPI $[Cl^+ \leftarrow Cl(4p^2D_{3/2}^\circ) \leftarrow Cl(3p^2P_{3/2}^\circ)].$ The ion packet expands as it travels down a flight tube, then strikes a gated microchannel plate. Electrons emerging from the back of the microchannel plate impinge on a phosphor screen. The resulting images are collected and signal averaged with a video camera. To further improve the signal-to-noise ratio, we used an image processor to combine the raw data images with their horizontal and vertical reflections.

In order to obtain complete information about the velocity and alignment anisotropy, we used four different combinations of the dissociation and probe light polarization vectors. The dissociation laser polarization was either parallel or perpendicular to the ion flight axis (*Z* axis), which we refer to as geometries I and II, respectively. The probe laser polarization was either parallel or perpendicular to the dissociation laser polarization. The four corresponding images are presented in Fig. 2.



FIG. 1. Schematic of experimental apparatus. The Cartesian axis definition in this figure is used throughout the paper.

Ion images are projections onto the detector plane of a three-dimensional distribution of ions. The dominant contribution to the shape of this distribution is the wellknown photofragment velocity anisotropy, described by the expression $P(\theta) \propto 1 + \beta P_2(\cos \theta)$, where θ is the polar recoil angle with respect to the dissociation laser polarization. At 355 nm, the perpendicular optical transition ${}^1\Pi_{1_u} \leftarrow {}^1\Sigma_{0_s^+}$ contributes more than 90% of the light absorption [11], so the anisotropy parameter β is close to its limiting value of -1. The coarse image shapes for geometries I and II represent two different projections of $P(\theta)$.

The smaller modulations in the images are of greater significance for this Letter. Since these modulations depend on the probe laser polarization, they are most easily seen by contrasting the images in Fig. 2 (top vs bottom), or by viewing the weighted differences shown in Fig. 4 (top). This variation of the two-photon detection sensitivity with laser polarization is a direct result of angular momentum alignment.

Another manifestation of photofragment angular momentum alignment is that the total signal intensity depends on the relative polarizations of the dissociation and probe lasers. It can be shown that the total photofragment alignment parameter A_{20} is proportional to the ratio $(\langle I_Z \rangle - \langle I_Y \rangle)/(\langle I_Z \rangle + 2\langle I_Y \rangle)$ [12], where Z and Y refer to the linear polarization axis of the probe laser, and the angle brackets indicate averaging over all recoil directions. In our experiment, the value of this ratio was -0.032 ± 0.012 . Both incoherent and coherent processes



FIG. 2. Chlorine photofragment ion images. Geometries I and II correspond to the dissociation laser polarization along the Z and Y axes, respectively. The probe laser polarization was also along either the Z or Y axis.

contribute to the total alignment parameter A_{20} [3–5], but only measurements of the alignment (or orientation) angular distribution permit them to be independently isolated.

Angular momentum polarization can be conveniently described in terms of irreducible density matrix components (state multipoles) [12,13]. For molecular dissociation, the photofragment state multipoles are a function of recoil angles, i.e., $\rho_{kq} = \rho_{kq}(\theta, \phi)$. The $\rho_{00}(\theta, \phi)$ term represents the angular distribution of photofragment density, while terms with rank k > 0 describe angular momentum polarization. As shown in a recent theoretical analysis [9], state multipoles with all combinations of the indices kand q (i.e., k = 0, ..., 2i; q = -k, ..., k) can be nonzero. Even for linearly polarized dissociation light, it is possible to produce angle-dependent multipoles with odd k (orientation). However, a linearly polarized two-photon optical probe is capable of detecting only alignment moments with k = 0, 2, and 4. Given these considerations, for this Letter only rank k = 0 (photofragment density) and k = 2(quadrupolar alignment) multipoles are important.

In this Letter, we are interested in the angular distribution of alignment rather than photofragment density. We isolate the relatively small modulation in signal intensity, which results from alignment, by choosing linear combinations of images for which the $\rho_{00}(\theta, \phi)$ term disappears. By combining three orthogonal probe polarization geometries, we can also obtain the alignment-independent part of the signal. For a two-photon probe, the general expressions for these combinations are

$$I_{X,Y} - I_Z = \frac{C}{\sqrt{2}} R_2 \{ \rho_{20}(\theta, \phi) \\ \mp \sqrt{\frac{2}{3}} \operatorname{Re}[\rho_{22}(\theta, \phi)] \}, \quad (1a)$$

$$I_Y - I_X = \frac{2C}{\sqrt{3}} R_2 \operatorname{Re}[\rho_{22}(\theta, \phi)],$$
 (1b)

$$I_X + I_Y + I_Z = CR_0\rho_{00}(\theta, \phi),$$
 (1c)

where the signs - and + in Eq. (1a) refer to I_X and I_Y , respectively, and *C* is a constant. The coefficients R_k in Eq. (1) are similar to the line strength moments P_q^k of Ref. [14], except that the laser polarization dependence has been factored out and evaluated. In principle, all three measurable alignment multipoles may be isolated by an appropriate combination of images, although in practice it may be difficult to obtain images for certain geometries, due to limitations in the experimental apparatus.

In order to project the three-dimensional intensity distribution onto two dimensions, we used the transformation

$$M(\varrho,\phi) = 2 \int_{\varrho}^{\infty} \frac{f(\arcsin(\varrho/r),\phi)g(r)}{\sqrt{1-\varrho^2/r^2}} dr, \quad (2)$$

where $M(\varrho, \phi)$ is the image, (ϱ, ϕ) are polar coordinates, and *r* is the length of the photofragment radius vector. The function $f(\arcsin(\varrho/r), \phi) \equiv f(\theta, \phi)$ in Eq. (2) describes the angular dependence of the intensity distribution and can be substituted with one of the intensity differences in Eq. (1). The function g(r) describes the radial

dependence of the three-dimensional distribution, which is a delta function for this work, since the chlorine atom photofragments are monoenergetic. Equation (2) assumes reflection symmetry of the function $f(\arcsin(\varrho/r), \phi)$ in the X-Y plane. Unlike the Abel transform, Eq. (2) cannot be directly inverted to reconstruct the three-dimensional ion distribution from image data. Although the inverse-Abel transform is widely used for this purpose [15], it requires as input the projections of cylindrically symmetric distributions with the symmetry axis parallel to the detector plane. These geometric restrictions are often violated in experiments designed to measure a **v**-**j** correlation.

The integral in Eq. (2) can be evaluated analytically for $g(r) = \delta(r - r_0)$, where $r_0 = v_0 \tau$, v_0 is the photofragment velocity, and τ is the flight time of the ions. We show explicit results only for the I_Z - I_Y case used in our experiments. For dissociation polarization geometries I and II, using Eq. (1a) for f in Eq. (2) yields

$$M_{YZ}^{I}(t,\phi) \propto \frac{2}{\sqrt{1-t^{2}}} \{ [s_{2} - 2\alpha_{2} + 3\alpha_{2}t^{2}] [1 - t^{2}(1 + \sin^{2}\phi)] - 2\gamma_{2}t^{2}(1 - t^{2})(1 + \sin^{2}\phi) - \frac{\eta_{2}}{4}t^{2}[t^{2} + (2 - t^{2})\cos(2\phi)] \},$$
(3a)

and

$$M_{YZ}^{II}(t,\phi) \propto \frac{2}{\sqrt{1-t^2}} \bigg\{ [s_2 + \alpha_2(1-3t^2\sin^2\phi)] [1-t^2(1+\sin^2\phi)] + 2\gamma_2 t^2 \sin^2\phi [2-t^2(1+\sin^2\phi)] \bigg\}$$

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$$+ \frac{\eta_2}{2} \left[t^2 (2 - t^2) \cos(2\phi) + 1 - t^2 + t^4 \left(1 - \frac{\sin^2(2\phi)}{4} \right) \right] \right].$$
(3b)

The variable *t* is the radial coordinate normalized to the maximum possible radius, i.e., $t = \rho/r_0$. Note that for a δ -function energy (radial) distribution, there is a one-to-one mapping between the three-dimensional distribution and its two-dimensional projection. In this sense, the difference images presented below are an explicit depiction of the alignment angular distribution.

The anisotropy parameters s_2 , α_2 , γ_2 , and η_2 in Eq. (3), which characterize the alignment angular distribution, are a subset of the polarization anisotropy parameters defined in Ref. [16]. They are normalized combinations of the theoretically derived "dynamical functions" $f_k(q, q')$ [5,9]. (General expressions for the angle-dependent state multipoles in terms of $f_k(q, q')$ can be found in Ref. [9].) These new anisotropy parameters have a clear physical interpretation as contributions to the total photofragment orientation and alignment parameters A_{10} and A_{20} from incoherent and coherent excitation mechanisms.

Equations (3a) and (3b) provide a powerful means for interpreting the alignment contribution to photofragment ion image data, since each of four alignment mechanisms is associated with a unique radial and angular dependence in the images. This important fact is emphasized in Fig. 3, where each spatial dependence is shown in isolation. The calculated images of Fig. 3(a) show the contribution of a pure perpendicular optical transition $(|\Omega - \Omega_0| = 1)$, where Ω_0 and Ω are projections of the total angular momentum onto the internuclear axis for ground and excited states, respectively). Figure 3(a) was obtained by setting $s_2 = 2\alpha_2$ and the other parameters to zero. Figure 3(b) corresponds to a pure parallel transition $(\Omega - \Omega_0 = 0)$ and was obtained by setting $s_2 = -\alpha_2$ and the other parameters to zero. The above relationships between s_2 and α_2 are apparent from their definitions in terms of dynamical functions [16]. Parameter η_2 corresponds to coherent perpendicular excitation ($\Omega = \pm 1$) [Fig. 3(c)], while

 γ_2 corresponds to coherent excitation via both parallel and perpendicular transitions [Fig. 3(d)].

The data images in Fig. 2 were subtracted as prescribed by Eq. (1a). These differences are shown together with



FIG. 3(color). Plots of $M_{YZ}(t, \phi)$ [Eq. (3)] for dissociation polarization geometries I and II. Cases (a)–(d) correspond to four mechanistic limits as follows: (a) incoherent perpendicular excitation, (b) incoherent parallel excitation, (c) coherent perpendicular excitation, and (d) coherent parallel and perpendicular excitation. Blue, red, and white correspond to positive, negative, and zero values, respectively.

simulations in Fig. 4. In order to adequately simulate the measured differences, we included both perpendicular incoherent and coherent contributions, such that the ratio of alignment anisotropy parameters α_2/η_2 was -1.5. Since we are concerned here with qualitative identification of the dominant mechanisms, only the angular dependence of Eq. (1a) was relevant, but not its absolute scaling. For this reason, it was not necessary to calculate the twophoton line strength factors R_2 and R_0 . Eventually, these factors will be needed to obtain quantitative values of the alignment anisotropy parameters (rather than just a ratio), as well as the absolute degree of $Cl({}^2P_{3/2}^{\circ})$ alignment.

Our observation of a contribution from incoherent perpendicular excitation agrees with earlier investigations of chlorine dissociation [11], although in all previous studies, this dominant mechanism was deduced from the velocity anisotropy or spin-orbit branching ratio rather than from the alignment angular distribution. For the first time, we have also identified a coherence contribution to the alignment angular distribution. Previous evidence of coherence has been observed for calcium dimer photodissociation from measurements of total atomic alignment [3]. However, such measurements provide only the sum $\alpha_2 + \gamma_2 + \eta_2$, in which coherent and incoherent terms are mixed, whereas measurement of the alignment angular distribution makes it possible to determine each of the alignment anisotropy parameters individually. Future measurements of atomic polarization in chlorine dissociation will help to clarify the role of the parallel excitation process discussed in previous work [11]. New studies should include quantitative alignment measurements for the ground state atom, such as those reported in this paper, as well as measurement of orientation for the excited $({}^{2}P_{1/2}^{\circ})$ chlorine atom.

In summary, we have shown that the angular distribution of atomic photofragment alignment explicitly reveals electronic state symmetries and coherence effects. Evidence for the latter cannot be directly obtained from measurements of velocity anisotropy or spin-orbit branching ratios, nor can it be isolated in measurements of total photofrag-



FIG. 4(color). Contribution of photofragment alignment to data signal (top row) and qualitative simulation (bottom row) based on Eq. (3). Only contributions from perpendicular transitions [Figs. 3(a) and 3(c)] were included.

ment alignment. We have derived general expressions for the alignment contribution to photofragment ion images. These expressions provide a direct connection between experimental observables and important theoretical quantities. Measurements of orientation and alignment at higher image spatial resolution, combined with quantitative analysis using two-photon line strength factors, should permit an even more detailed assignment of the electronic states and nonadiabatic transitions involved in photodissociation.

The authors thank Dr. T. P. Rakitzis and Dr. R. N. Zare for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by a Cooperative Grant from the Civilian Research and Development Foundation, CRDF Award No. RP1-223.

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