Polarization of Fluorescence Following Molecular Photoionization

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With use of the $B\,^2\Sigma_u^+$ state of N_2^+ as an example, this Letter presents the first measurements demonstrating that fluorescence from molecular ions formed by photoionization is partially polarized. Furthermore, it is shown that the degree of polarization reflects the alignment of the molecular ion and the ratio of the dipole strengths for the degenerate channels producing the ionic state. The wavelength-dependent measurements are compared with both quantum mechanical and classical calculations. Temperature-dependent effects are predicted.

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Molecular photoionization is an inherently anisotropic process since degenerate ionization pathways have different symmetries and, in general, different dipole strengths. This anisotropy will manifest itself by a partial alignment of the residual ion which depends only upon the relative dipole strengths of the alternative photoelectron channels. Because of the energy degeneracy of the photoelectrons, however, the ratio of these strengths cannot be measured directly by photoelectron spectroscopy; moreover, while photoelectron angular distributions do contain this information, it is folded together with the relative phases of the ionization channels, and cannot be extracted without additional information. In this Letter, we show that the alignment of molecular ions can be probed directly by measuring the polarization of their fluorescence, and that this polarization yields the relative strengths for degenerate photoelectron channels. To demonstrate the effect, we report the first such measurement, for the $N_2^+\ B^2\Sigma_u^+$ state produced by photoionization of N_2 in the range $450\ \text{Å} < \lambda < 660\ \text{Å}$, and compare the results with model calculations.

Molecular alignment is an anisotropic distribution of molecules in the laboratory frame arising from an unequal population of $|M_J|$ states.[1a] In a classical analysis, the alignment and resulting degree of fluorescence polarization are determined by the average angle, α, between the absorption and fluorescence transition dipoles. The degree of polarization, P, is given by[1b,2]

$$P = (3\cos^2\alpha - 1)/(\cos^2\alpha + 3)\,. \qquad (1)$$

This is valid in the limit where the fractional change in rotational angular momentum, $\Delta j/j_i$, is small. In photoionization, this condition is approached at high temperature (large j_i) or low electron kinetic energy (negligible angular momentum l removed by the photoelectron). Our analysis also assumes that fluorescence occurs after many rotational periods, a condition usually met. In N_2^+, the B state fluoresces to the ground state ($X^2\Sigma_g^+$), yielding a fluorescence transition dipole parallel to the internuclear axis.[3] Thus, the angle α is the average angle between the photoionization (absorption) dipole and the internuclear axis. Photoionization proceeds as $N_2(X\,^1\Sigma_g^+) \rightarrow N_2^+(B^2\Sigma_u^+) + e^-(\epsilon\sigma_g, \epsilon\pi_g)$, via σ_g (parallel) and π_g (perpendicular) transition dipoles.[3] Hence, for "pure" σ_g photoionization, both the absorption and fluorescence transition dipoles will lie in the plane of molecular rotation. Because molecular rotation is so fast relative to fluorescence, the two transition dipoles are uncorrelated, yielding an average angle, α_σ, of

45° and $P = \frac{1}{7}$.[1b] For "pure" π_g photoionization, the absorption transition dipole remains in the plane of molecular rotation for P and R branch transitions, giving $\alpha_{\pi,P} = \alpha_{\pi,R} = 45°$, but shifts perpendicular to the plane for Q branch transitions, giving $\alpha_{\pi,Q} = 90°$. Weighting each branch by its rotational strength,[4] we obtain the "π_g only" polarization of $-\frac{1}{13}$.[5] The observed polarization should be bracketed by these limits, the precise value of P reflecting the ratio $R \equiv D_\pi{}^2/D_\sigma{}^2$ of photoionization strengths for the σ_g and π_g channels, i.e.,

$$P = (1 - R)/(7 + 13R). \tag{2}$$

For low temperatures or high photoelectron energies, the problem must be treated quantum mechanically. This analysis, to be described in detail elsewhere,[6] yields $P = (\sigma_\parallel - \sigma_\perp)/(\sigma_\parallel + \sigma_\perp)$, where $\sigma_\parallel$ and $\sigma_\perp$ are the cross sections for production of the B state followed by its decay to the X state by fluorescence polarized parallel and perpendicular to the incident ϵ vector, respectively.

These cross sections are given by

$$\sigma_q = \sigma(B \to X) \sum_{j_f j_*} (2j_* + 1)^2 (j_*0, 10 | j_f 0)^2 \sum_{t_\gamma t_i} (2t_i + 1)^{-1} (10, 1q | t_\gamma q)^2 \begin{Bmatrix} 1 & 1 & t_\gamma \\ t_i & j_f & j_* \end{Bmatrix}^2$$
$$\times \sum_{l\mu\mu'} D_{l\mu'\mu'}{}^{-*} D_{l\mu\mu}{}^{-} (1\mu', j_*0 | t_i \mu')(1\mu, j_*0 | t_i \mu)(l\mu', j_i 0 | t_i \mu')(l\mu, j_i 0 | t_i \mu), \tag{3}$$

where q is the projection of the fluorescence dipole interaction in the laboratory frame (parallel for $q = 0$ and perpendicular for $q = \pm 1$). Here, the $D_{l\mu\mu}{}^-$, defined in Eq. (3) of Ref. 7, are photoionization amplitudes for ejection of an electron with asymptotic orbital momentum $\vec{l}$ and with projection μ along the molecular axis of both $\vec{l}$ and the dipole interaction. The quantum numbers, j_i, j_*, and j_f, give the rotational momenta of the initial neutral N_2, the excited $N_2{}^+$, and the final (ground state) $N_2{}^+$. The angular correlation between the ionization and fluorescence dipole interaction can have harmonics $t_\gamma = 0, 1, 2$. The angular momentum transferred from the ionizing dipole interaction to the excited-state molecular rotation is $\vec{t}_i$. Finally, the fluorescence cross section is represented by $\sigma(B \to X)$. This result is for the $\Sigma \to \Sigma \to \Sigma$ transition sequence studied here. The general expression and its fuller discussion will be presented in a subsequent publication.[6]

To illustrate the general behavior of the new theoretical formulation presented in Eq. (3), we will use dipole amplitudes $D_{l\mu\mu}{}^-$ calculated using the multiple scattering model (MSM).[8] We emphasize, however, that Eq. (3) represents a general theoretical framework which can be evaluated using dipole strengths computed from a whole hierarchy of approximations, from the model calculation used here to much more sophisticated calculations incorporating electron correlation, vibrational effects, etc. We see from Eq. (3) that, in the quantum mechanical formulation, the polarization depends both on the dipole strengths $D_\sigma{}^2 \equiv \sum_l |D_{l00}{}^-|^2$ and $D_\pi{}^2 \equiv \sum_l |D_{l\pm1\pm1}{}^-|^2$, and on the interference of the dipole amplitudes for a given l. However, numerical evaluation of Eq. (3) shows that for $j_i \geqslant 5$ the interference terms have negligible effect; i.e., except for very low temperatures, *the polarization depends only on the dipole strength ratio* $D_\pi{}^2/D_\sigma{}^2$ [Fig. 1(a)]. Furthermore, for $j_i \geqslant 5$, the polarization computed from Eq. (3) agrees precisely with that derived from the classical formulation, Eq. (2) [see dashed curve in Fig. 1(b)]. The $j_i = 3$ and 4 curves are not shown in Fig. 1(b), but lie just above the $j_i = 5$ curve. Note that a Boltzmann-

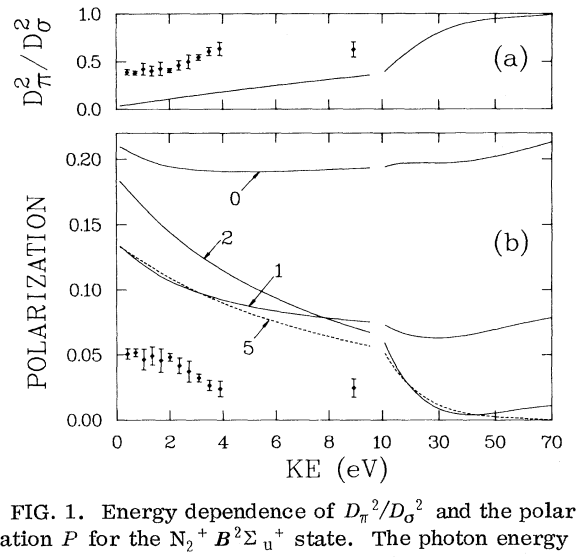

FIG. 1. Energy dependence of $D_\pi{}^2/D_\sigma{}^2$ and the polarization P for the $N_2{}^+ B\,{}^2\Sigma_u{}^+$ state. The photon energy corresponding to the zero of the graph is 18.757 eV (see Ref. 13). Note that the energy scale changes at 10 eV kinetic energy. (a) MSM predictions and experimental determination for $D_\pi{}^2/D_\sigma{}^2$; (b) MSM predictions and experimental determinations for P. The numbers refer to the value of j_i. The $j_i = 5$ curve is dashed and is indistinguishable from the classical result using the MSM dipole strengths.

weighted average is not shown in Fig. 1(b) but is accurately represented by the $j_i = 5$ curve. For low j_i, the quantal rotational motion and the interference terms combine to yield polarizations greater than the classical prediction, especially for $j_i = 0$ for which $P \sim 20\%$ over a very large energy range. This predicted temperature dependence could be experimentally tested by using a supersonically cooled expansion. We are planning such an arrangement for future studies.

The experimental apparatus is shown schematically in Fig. 2. The radiation source for this work was the U. S. National Bureau of Standards Synchrotron Ultraviolet Radiation Facility (SURF-II). A high-flux, 2-m normal incidence monochromator dispersed the radiation,[9] providing typical photon fluxes of 3×10^{10} photons/sec at a bandpass of 0.6 Å. The polarization of the excitation radiation was 0.74. Results presented in Fig. 1 have been corrected for this partial polarization; i.e., they refer to a completely linearly polarized excitation source. An effusive gas jet was employed to ensure that no alignment of the target molecules would be induced by a supersonic expansion.[1a] The gas was thus near ambient laboratory temperature, ~300 K. The fluorescent radiation was collected by a plano-convex lens (half-angle of collection of 18°),[10] and then passed through a sheet polarizer which was rotated into a position either parallel or perpendicular to the major polarization component of the incident radiation. A shutter was placed in front of the photomultiplier tube and was opened and closed to determine background levels in the photomultiplier tube due to thermal noise. The fluorescent radiation was not monochromatized. The vacuum ultraviolet photoionization of N_2 to the $B^2\Sigma_u^+$ state populates principally (~90%) the $v' = 0$ level.[11] Thus, Franck-Condon factors coupling vibrational levels of the X and B states of the ion indicate that the fluorescence will lie mainly around 3900 Å.[12]

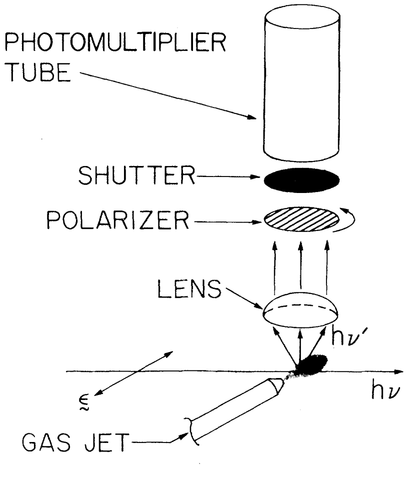

FIG. 2. Schematic of experimental apparatus.

The experimental polarization results are shown in Fig. 1(b).[13,14] There we see that the observed polarization is positive and decreases with increasing photon energy; the highest degree of polarization measured was $P = 0.052 \pm 0.003$ at an energy of 0.7 eV above threshold[13] (18.757 eV). Clearly, all of the experimental points in Fig. 1(b) lie substantially below the predictions ($j_i = 5$) based on the MSM model. This, in turn, implies that the experimentally deduced D_π^2/D_σ^2 ratios will be larger than the theoretical ones, as indicated in Fig. 1(a). On the one hand, the agreement between the MSM-level calculation and experiment is poor, and clearly indicates the need for improved calculations of the dipole amplitudes. On the other hand, the MSM calculation serves to exhibit basic aspects of the theory in Eq. (3) and acts as a point of reference for future improvements, as discussed in the following remarks. *First*, the model calculation properly reflects the positive slope of D_π^2/D_σ^2 at low energies and the approach of this ratio to unity at high energy, where the dynamics are dominated by the spherical environment in the atomic cores. The general increase in D_π^2/D_σ^2 at low energy is caused by the suppression near threshold of the *d*-wave lead term of the π_g continuum wave function by centrifugal forces. *Second*, future improvement in the calculation can be confined to computing better dipole amplitudes, which can then be transformed into the observable polarization by use of Eq. (3). The inaccuracy in the MSM-based amplitudes is, of course, a consequence of the approximations implicit in the MSM model.[8] However, we note that $2\sigma_u$ photoionization in N_2 appears to be a somewhat pathological case; e.g., the photoelectron asymmetry parameters for this channel were by far the worst in a MSM treatment[8] of the valence levels of N_2. This might imply that the problem traces to electron correlation effects or nuclear motion effects. Two possibilities are *inter*channel coupling with states[15] associated with the $C^2\Sigma_u^+$ state of N_2^+ and *intra*channel coupling which would redistribute the π_g oscillator strength distribution whose concentration in the $1\pi_g$ valence state by the centrifugal barrier[8] is probably overemphasized by a one-electron treatment. *Third,* as the temperature-dependent effects derive mainly from geometric considerations, implicit in Eq. (3), the qualitative aspects of the temperature dependence indicated in Fig. 1(b) are valid, although the quantitative aspects are suspect, because of the inaccurate D_π^2/D_σ^2 *ratio* used here.

In conclusion, the measurement of fluorescence polarization following molecular photoionization to excited states yields the ratio of dipole strengths for *degenerate* ionization channels. This experiment is the newest member of a class of experiments which probe the alignment of atomic[16,17] and molecular[7] ions and which, by virtue of not detecting (integrating over) the photoelectron ejection angle, are independent of the relative phases of the ionization channels. Though these techniques have yet to be extensively exploited, they are important complements to the traditional measurements of photoelectron branching ratios and angular distributions, providing the additional information necessary to determine the magnitudes and phases of dipole transition amplitudes *separately.* Combining these complementary probes will therefore lead to a new level of understanding of molecular photoionization dynamics.

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[1a] M. P. Sinha, C. D. Caldwell, and R. N. Zare, J. Chem. Phys. 61, 491 (1974).

[1b] M. McClintock, W. Demtröder, and R. N. Zare, J. Chem. Phys. 51, 5509 (1969).

[2] Except where otherwise noted, the polarization is defined as $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$.

[3] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).

[4] I. Kovacs, *Rotational Structure in the Spectra of Diatomic Molecules* (American Elsevier, New York, 1969).

[5] The prescription for averaging polarizations weighted by line strengths is done by transforming the P index (see Ref. 2) to the r index, defined as $r = (I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$. The r indices are then averaged by the convention $\bar{r} = (\Sigma D_i^2 g_i r_i)/(\Sigma D_i^2 g_i)$, where D_i^2 is the strength of the ith transition (or branch) and g_i is the degeneracy. Finally, $\bar{r}$ is transformed to P.

[6] D. Dill, to be published.

[7] J. L. Dehmer and D. Dill, Phys. Rev. A 18, 164 (1978).

[8] D. Dill and J. L. Dehmer, J. Chem. Phys. 61, 692 (1974); J. L. Dehmer and D. Dill, in *Electron-Molecule and Photon-Molecule Collisions*, edited by T. Rescigno, V. McKoy, and B. Schneider (Plenum, New York, 1979); S. Wallace, D. Dill, and J. L. Dehmer, J. Phys. B 12, L417 (1979); J. L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. 43, 1005 (1979).

[9] D. L. Ederer, B. E. Cole, and J. B. West, Nucl. Instrum. Methods 172, 185 (1980).

[10] Corrections for this solid angle were made, though quite small (< 0.002 changes in P). See P. E. Zinsli, J. Phys. E 11, 17 (1978).

[11] J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. Relat. Phenom. 13, 7 (1978).

[12] A. Loftus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).

[13] The threshold for $B^2\Sigma_u^+$ state production is at 18.757 eV. See G. R. Cook and P. H. Metzger, J. Chem. Phys. 41, 321 (1964).

[14] The region between 4 and 8 eV kinetic energy contains many autoionizing resonances which are discussed in K. Codling, Astrophys. J. 143, 552 (1966). Data taken on a 0.25-Å energy mesh near 554.1-Å resonance revealed no discernible structure in the polarization dependence. In fact, spot checks throughout the whole region indicate a very flat polarization dependence.

[15] See A. L. Roche and J. Tellinghuisen, Mol. Phys. 38, 129 (1979), and references therein.

[16] C. D. Caldwell and R. N. Zare, Phys. Rev. A 16, 255 (1977); H. Klar, J. Phys. B 13, 2037 (1980); W. Mauser and W. Mehlhorn, to be published.

[17] S. Flugge, W. Mehlhorn, and V. Schmidt, Phys. Rev. Lett. 29, 7 (1972).