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Polar and azimuthal dependence of the molecular frame photoelectron angular distributions of spatially oriented linear molecules

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The general form of the molecular frame photoelectron angular distributions (MFPADs) for linear ground-state molecules ionized by linearly polarized light ($\hat{n}$) is reported. A comparison between computed and measured MFPADs as a function of the polar and azimuthal emission angles is presented for photoionization of NO leading to the $c\ ^3\Pi$ state of NO$^+$. The importance of the azimuthal dependence of the MFPADs for the determination of the symmetry of the states involved in the excitation and of the underlying photoionization dipole matrix elements is demonstrated.

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Probing molecular-frame photoelectron angular distributions (MFPADs) provides detailed dynamical information on photoionization processes through the determination of the dipole matrix elements [1]. Taking advantage of dissociative ionization, where the molecular orientation can be determined from the recoil direction of the fragment ion, significant steps have been achieved recently towards complete experiments by measuring the $I(\theta)$ photoelectron angular distribution for inner-shell excitation of molecules aligned parallel or perpendicular to the linear polarization of the exciting light [2–4], where θ is the angle between the molecular axis and the emission direction of the photoelectron. Recent results have also been obtained for the polar dependence of the MFPAD for valence shell ionization of oriented molecules [5–7].

The general expression for the MFPAD was first given by Dill [1], with the case of linear molecules later being discussed by Cherepkov and Raseev [8], where the arbitrary orientation between the photon and molecular frames was considered. In particular, investigation of the azimuthal dependence of the MFPAD brings new information each time the axial symmetry of the problem is broken. The effectiveness of the azimuthal analysis in the description of a photoionization process has been illustrated by the study of rotationally resolved angular distributions of electrons emitted from molecules aligned by optical pumping [9]. The theoretical description of the MFPAD has also been given for Auger emission from fixed-in-space molecules [10] or photoionization of molecules adsorbed on surfaces [11].

In this paper, we report a theoretical and experimental determination of the complete angular distribution $I(\theta_n,\theta_k,\phi_k)$ for photoionization of a ground-state diatomic molecule induced by linearly polarized light, where (θ_k,ϕ_k) are the polar and azimuthal angles which characterize the direction of emission of the photoelectron, $\hat{k}$, in the molecular frame, and θ_n is the polar angle of the molecular axis with respect to the polarization axis. A comparison of the computed and measured angular distributions $I(\theta_n,\theta_k,\phi_k)$ is presented for the photoionization of NO leading to the $c\ ^3\Pi$ state of NO$^+$ for a photon energy of about 24 eV, for which we have reported partial experimental results previously [12].

In the context of the present experimental approach, the MFPAD can take a simpler form than the one derived by Cherepkov and Raseev [8]. Namely, we choose the molecular frame coordinate system with the z axis oriented along the molecular axis $\hat{m}$, pointed towards the N atom. The x axis lies in the plane defined by the molecular ($\hat{m}$) and polarization ($\hat{n}$) directions, oriented in the direction of $\hat{n}-\hat{m}(\hat{n}\cdot\hat{m})$. Deriving the MFPAD in this frame leads to the remarkably simple functional form

$$\begin{aligned}I(\theta_n,\theta_k,\phi_k)=&F_{00}(\theta_k)+F_{20}(\theta_k)P_2^0(\cos\theta_n)\\&+F_{21}(\theta_k)P_2^1(\cos\theta_n)\cos(\phi_k)\\&+F_{22}(\theta_k)P_2^2(\cos\theta_n)\cos(2\phi_k).\end{aligned}\tag{1}$$

The F_{LN} functions are partial-wave expanded in terms of the dipole matrix elements $T_{lm\mu}^{M_iM_f}$ [the definition used here contains an additional phase factor of $(-1)^\mu$ relative to that found in Ref. [13]] as follows:

$$F_{LN}(\theta_k)=\sum_{L'} C_{L'LN}P_{L'}^N(\cos\theta_k),\tag{2}$$

with

$$C_{L'LN}=\frac{2\pi E}{cg_i(1+\delta_{N,0})}\sum_{M_iM_f}(-1)^{M_i-M_f}\sum_{\substack{l,m,\mu\\ l',m',\mu'}}T^{M_iM_f}_{lm\mu}(T^{M_iM_f}_{l'm'\mu'})^*\times\left[\frac{(2l+1)(2l'+1)(L-N)!(L'-N)!}{(L+N)!(L'+N)!}\right]^{1/2}\times\langle ll'00|L'0\rangle\langle ll'(-m)m'|L'N\rangle\langle 1100|L0\rangle\langle 11(-\mu)\mu'|L(-N)\rangle, \tag{3}$$

where M_i and M_f are the total orbital angular momentum about the *z* axis of the initial (unionized) and final (ionized) target states, *m* and μ are the corresponding projected momenta of the electron and the photon, g_i is the degeneracy of the initial state, *c* is the speed of light, and *E* is the photon energy. $\mu=0$ and $|\mu|=1$ correspond to the parallel and perpendicular transitions. Thus $I(\theta_n,\theta_k,\phi_k)$ is fully described by the four functions $F_{LN}(\theta_k)$, whose determination requires in general an analysis in the azimuthal angle. One interesting feature of the MFPAD form in Eq. (1) is the simple dependence on the angle ϕ_k. By averaging over θ_k, one can emphasize the ϕ_k dependence for a particular value of θ_n:

$$I^{(\theta_n)}(\phi_k)=\frac{\sigma^{(\theta_n)}}{2\pi}\{1+D_1^{(\theta_n)}\cos(\phi_k)+D_2^{(\theta_n)}\cos(2\phi_k)\}. \tag{4}$$

Photoionization of a linear molecule aligned parallel to the polarization axis ($\theta_n=0$) restores the axial symmetry ($D_1=D_2=0$). On the other hand, analyzing the $\cos(2\phi_k)$ dependence of the MFPAD for the perpendicular geometry ($\theta_n=\pi/2$), where $D_1=0$, provides direct insight into the symmetry of the initial and final molecular states involved. If these states both have Σ^+ or Σ^- symmetry, the dipole matrix elements of opposite *m* and μ values are equal, $T^{M_iM_f}_{lm\mu}=T^{M_iM_f}_{l,-m,-\mu}$, leading to the reduced form [13]: $I(\phi_k)=(\sigma/\pi)\cos^2(\phi_k)$. If either the initial or final target states has Σ^+ symmetry and the other has Σ^- symmetry, then $T^{M_iM_f}_{lm\mu}=-T^{M_iM_f}_{l,-m,-\mu}$ leading to $I(\phi_k)=\sigma/\pi\sin^2(\phi_k)$. In general, when one or both of the initial and final target states do not have Σ symmetry, there are no simple values for the *D*'s. Finally, analyzing the $\cos(\phi_k)$ dependence of the MFPAD for any geometry where the molecular axis is neither parallel nor perpendicular to the polarization gives access to η, the relative phase between the $\mu=0$ and $|\mu|=1$ matrix elements. Possibilities to obtain this type of information were discussed recently in the study of inner-shell excitation of CO [14]. Here, we define this phase as $\eta=\arg(T_{2,0,0}/T_{2,-1,1})$, and we use the magic angle geometry ($\theta_n=0.304\pi$) to represent the case in which θ_n is different from 0 and $\pi/2$.

We now consider the possibility of a ‘‘complete'' experiment allowing for the determination of the $T_{lm\mu}$, apart from an overall phase. The limits imposed by the use of linearly polarized light, however, prevent one from determining the overall sign of the relative phases that will be achieved if circularly polarized light is used [9]. A close examination of the number of independent parameters leads to the following statements. For a Σ to Σ photoionization transition, the F_{00} and F_{20} distributions contain enough information to determine all the $T_{lm\mu}$ except for the η phase. The F_{00} and F_{20} functions can be obtained by measuring the MFPADs for the $\theta_n=0$ and $\pi/2$ geometries, and η by measuring the $\theta_n=0.304\pi$ MFPAD. If only one of the initial and the final target states is a Σ state, then a complete experiment is performed if one measures the $\theta_n=0$, $\theta_n=0.304\pi$, and $\theta_n=\pi/2$ MFPADs including the ϕ_k dependence, yielding F_{00}, F_{20}, F_{21}, and F_{22}. Finally, if neither the initial nor the final target states are Σ states, measuring the four F_{LN} functions does not provide in general enough parameters to determine the $T_{lm\mu}$ elements.

We present here the computed and measured MFPADs for photoionization of NO($X\ ^2\Pi[4\sigma^25\sigma^21\pi^42\pi^1]$) leading to NO$^+$($c\ ^3\Pi[4\sigma^15\sigma^21\pi^42\pi^1]$), labeled as process I. The photoionization amplitudes are computed using the multichannel Schwinger configuration interaction (MCSCI) method [15,16]. The details of the calculation are the same as in Ref. [16], except that we have used 17 channels compared to the 5 channel used previously. The 17 states of NO$^+$ include the 12 states listed in Table I of Ref. [16] and 5 higher-energy states that lead to the inclusion of important correlation terms.

The $I(\theta_n,\theta_k,\phi_k)$ angular distribution for process I has been determined experimentally using the $(\vec{v}_{A+},\vec{v}_e,\hat{n})$ vector correlation method developed for the investigation of dissociative photoionization of diatomic molecules by linearly polarized light [12]. Briefly, it consists here in measuring the $\vec{v}_{\mathrm{N}}{}^+$ and $\vec{v}_e$ velocity vectors of the N$^+$ fragment and the photoelectron emitted from the same event involving predissociation of the $c\ ^3\Pi$ state:

$$\mathrm{NO}+h\nu(\hat{n})\rightarrow\mathrm{NO}^+(c\ ^3\Pi)+e\rightarrow\mathrm{N}^+(^3P)+O(^3P)+e. \tag{5}$$

The experiment was performed at the synchrotron radiation facility Super ACO (LURE, Orsay) in the 22–25 eV photon energy range. The velocity spectrometer [12,17] combines the ion and electron time-of-flight resolved coincidence technique with position-sensitive detection yielding a 4π collection of ions and electrons [18,19]. The $(\mathrm{N}^+,e)_{\mathrm{I}}$ coincident events are selected using the ion-electron kinetic-energy correlation [12]. Within the recoil axial approximation [20], the set of angles determined experimentally $(\chi_{\mathrm{N}^+},\theta_e,\phi_e)$ [12], χ_{N^+} being the N$^+$ emission angle with respect to the polarization and (θ_e,ϕ_e) the polar and azimuthal electron emission angles with respect to the $\vec{v}_{\mathrm{N}^+}$ vector, identifies with the

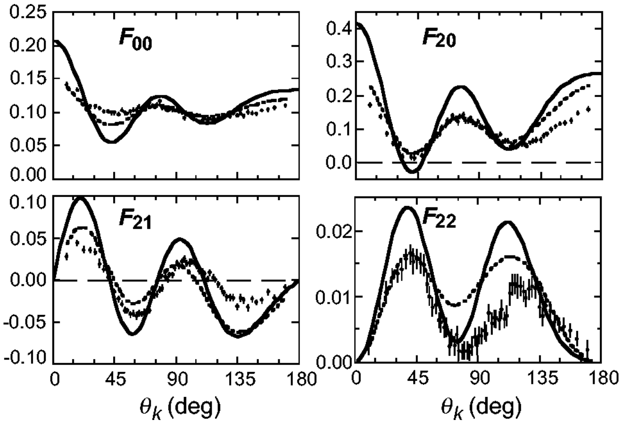

FIG. 1. The F_{LN} (θ_k) functions for process I (in Mb). Full line: 17-channel MCSCI calculation at $h\nu=25.0$ eV; dots: experiment at $h\nu=23.64$ eV; dashed line: calculations convoluted with the apparatus function. Theory and experiment are normalized such that the total photoionization cross sections are identical.

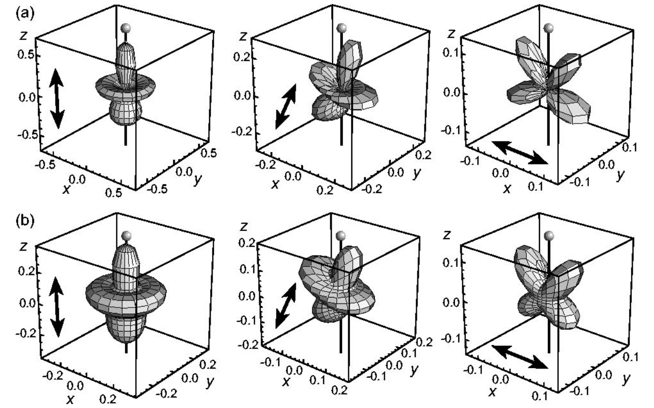

FIG. 2. The MFPADs for process I corresponding to the F_{LN} given in Fig. 1. The arrows indicate the direction of the polarization ($\hat{n}$). The computed (a) and experimental (b) parallel, magic angle, and perpendicular MFPADs are shown.

three angles (θ_n,θ_k,ϕ_k). Here we report the $I(\theta_n,\theta_k,\phi_k)$ angular distribution for process I in the form of the four $F_{LN}(\theta_k)$ functions defined by Eq. (1). These are extracted from the Fourier analysis in ϕ_k as a function of θ_k of the $(\theta_k,\phi_k)_{\theta_n}$ angular correlation histograms of the $(\mathrm{N}^+,e)_\mathrm{I}$ events, defined for specific θ_n selections of the molecular axis orientations. Here we derived the four $F_{LN}(\theta_k)$ functions using the following relationships, after integration over the θ_n intervals indicated:

$$I_{0-180}(\theta_k,\phi_k)=2F_{00}(\theta_k)+4F_{22}(\theta_k)\cos(2\phi_k),$$

$$I_{0-90/90-180}(\theta_k,\phi_k)=F_{00}(\theta_k)\pm F_{21}(\theta_k)\cos(\phi_k)+2F_{22}(\theta_k)\cos(2\phi_k),$$

$$I_{60-120}(\theta_k)=F_{00}(\theta_k)-0.375F_{20}(\theta_k)+2.75F_{22}(\theta_k)\cos(2\phi_k). \tag{6}$$

In this study, we compare the experiments performed at a photon energy of 23.64 eV, with the 25 eV calculations, which represent a comparable excitation energy above the vertical ionization potential of the $B'\ {}^1\Sigma^+$ state, estimated at 23.2 eV experimentally [21] and at 24.5 eV in this calculation. The measured $F_{LN}(\theta_k)$ compared with the computed values, as well as with the theoretical results convoluted with the apparatus function, taking into account the instrumental widths [17], are presented in Fig. 1. The main oscillatory structures observed experimentally are very well predicted by the calculations, although some quantitative disagreement persists between the experiment and the convoluted theory. These may be attributed to an imperfect description of the apparatus function, or to the sensitivity of the calculation to the photon energy and the channels included in the wave function. The corresponding three-dimensional representations of the measured and calculated MFPADs for the parallel, the magic angle, and the perpendicular geometries are presented in Fig. 2. They illustrate the strong evolution of the MFPAD with the polarization direction in the molecular frame. For the parallel transition, the dominant shape of the angular distribution is that of a $d\sigma$ wave, whereas the perpendicular transition exhibits an angular distribution characteristic of a $d\pi$ wave, where only the lobes in the $(\hat{m},\hat{n})$ plane are populated. The strong anisotropies observed support *a posteriori* the assumption of a fast predissociation of the $\mathrm{NO}^+(c)$ state and the axial recoil approximation. The shape of the MFPAD at the magic angle lies in between, and the significant backward-forward asymmetry in the $(\hat{m},\hat{n})$ plane carries the information about the η phase. The very good agreement between experiment and theory for the dominant features of the MFPADs was only achieved with the larger 17-channel calculation. In particular, the MFPAD for the perpendicular geometry is very sensitive to the correlation included in the wave function. Such a relatively weak ionization channel is indeed more sensitive to interference effects with amplitude coming from other channels, and thus to the correlation that induces the coupling between channels [22].

The remarkable azimuthal dependence of the MFPAD for the perpendicular geometry is close to a $\cos^2\phi_k$ distribution. A pure $\cos^2\phi_k$ behavior would be expected if the π_{+1} scattering continuum had exactly the same interaction with the target as the π_{-1} continuum and if the cross section for exciting the Π_{-1} ion state from the Π_{+1} initial state were zero. These conditions are indeed nearly satisfied. This result indicates that process I, for which the initial and the final target states are Π states, behaves like a Σ^+ to Σ^+ transition, consistent with the creation of the $4\sigma^{-1}$ hole in the excited $c\ {}^3\Pi$ state while the 2π electron acts essentially as a spectator. This enables us to extract the $T_{lm\mu}^{M_iM_f}$ dipole matrix elements from the measured F_{00}, F_{20}, F_{22}, and F_{21} functions assuming that the only nonzero dipole matrix elements are those with $M_i=M_f$ and $T_{lm\mu}^{M_iM_f}=T_{l,-m,-\mu}^{M_iM_f}$. The magnitudes and phases of the $T_{lm\mu}$ obtained by fitting the sets of the $C_{L'LN}$ coefficients using the assumed Σ^+ to Σ^+ symmetry are displayed in Fig. 3. The difference between the computed $T_{lm\mu}$ and those obtained by fitting the truncated sets of the $C_{L'LN}$ is fairly small. The $T_{lm\mu}$ obtained from fitting the

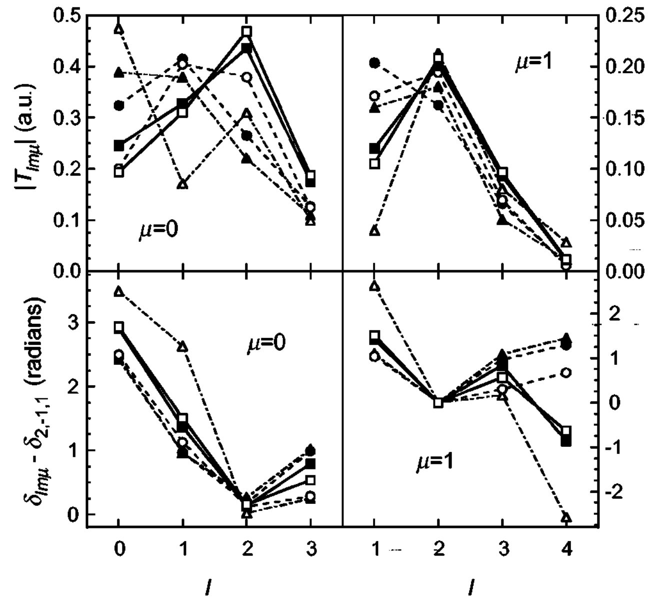

FIG. 3. The magnitudes and phases of the $T_{lm\mu}$ matrix elements: computed (open squares) and obtained by fitting the $C_{L'LN}$ parameters including terms up to $L'=7$ and 6 for $N>0$ and $N=0$, respectively, derived from (i) the calculation (filled squares), (ii) the calculation convoluted with the apparatus function (open circles: RMS=3.51, filled circles: RMS=3.50), and (iii) the experiment (open triangles: RMS=11.41, filled triangles: RMS=10.36). The phases are given after subtraction of the Coulomb phase shifts [13] and are relative to the phase of $T_{2,-1,1}$.

calculations convoluted with the apparatus function are seen to be rather close to the computed values of $T_{lm\mu}$ for the $\mu=1$ matrix elements. The phases of the $\mu=0$ elements are also in good agreement with only fair agreement in the magnitudes. We note that the magnitudes of the matrix elements of the lowest partial waves are more affected by the instrumental convolution. Finally, the $T_{lm\mu}$ values derived from the experimental F_{LN} functions show a pattern of agreement with the computed $T_{lm\mu}$ similar to that obtained from the convoluted theory. This figure gives the two best fits for the experimentally determined $C_{L'LN}$ that are characterized by the root mean square (RMS) of the deviation from the experimental values divided by the experimental uncertainties. Finally, we note that the η phase is computed to be 0.16, in good agreement with the experimental value of 0.26 from the RMS=10.36 fit.

In this paper, we have reported a theoretical and experimental determination of the complete angular distribution $I(\theta_n,\theta_k,\phi_k)$ for photoionization of a diatomic molecule induced by linearly polarized light, and we emphasized the new insight gained into the photoionization process by the determination of the azimuthal dependence of the MFPADs. The $\cos(\phi_k)$ dependence gives access to the relative phase between parallel and perpendicular transition matrix elements, whereas the $\cos(2\phi_k)$ dependence characterizes the initial- and final-state symmetries. For photoionization of NO to the $c\ ^3\Pi$ state of NO^+, the good agreement achieved between the computed and measured MFPADs, for any orientation of the molecule with respect to the polarization axis, emphasizes the important role of the electronic correlation. The azimuthal dependence of the MFPAD shows that the π electron is a spectator resulting in a Σ^+ to Σ^+ type transition. With this assumed symmetry, a complete experiment is performed in the sense that all the moduli and phases of the dipole matrix elements are determined.

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