

Complete Description of Molecular Photoionization from Circular Dichroism of Rotationally Resolved Photoelectron Angular Distributions

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The photoionization process $\text{NO } A^2\Sigma^+(v=0, N=22) \rightarrow \text{NO}^+ X^1\Sigma^+(v^+=0, N^+)+e^-$ is studied with sufficient energy resolution that the photoelectron angular distributions associated with individual rotational levels N^+ of the ion are determined. By ionizing with left and right circularly polarized light and observing the change in the rotationally resolved photoelectron angular distributions, we can deduce all dynamical information, including the *signs* of the relative phase shifts of the photoelectron partial waves. This information constitutes the first complete description of the photoionization of a molecule.

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A complete description of a photoionization process enables us to predict all aspects of the system's state after photoionization [1]. This description requires that the complex transition matrix elements associated with each outgoing partial wave be determined. Consider the photoionization of an atom in the state $|nl\rangle$: spherical symmetry and the dipole approximation limit the photoelectron angular momentum l to the two values $l'-1$ and $l'+1$. In this case, the cross sections $\sigma_{l'+1}$ and $\sigma_{l'-1}$ for the accessible partial waves and the relative phase shift δ between these partial waves are sufficient to represent completeness [1]. These quantities can be extracted from the absolute photoionization cross section, photoelectron angular distribution, and photoelectron spin polarization. A complete description must include the sign of the relative phase shift, which can be determined only when the experimental geometry imposes a handedness on the observations. In this Letter, we report the first truly complete description of a molecular photoionization process. Our chosen system of study is $\text{NO } A^2\Sigma^+(v=0, N) \rightarrow \text{NO}^+ X^1\Sigma^+(v^+=0, N^+)+e^-(l,\lambda)$; here, v and N are the vibrational and rotational quantum numbers, and λ denotes the projection of l on the internuclear axis of the diatomic molecule.

Many complete experiments have been performed on atomic systems [2]. Complications arise for those atomic systems in which electron correlation and relativistic effects are important [3]. Molecules present additional difficulties associated with the large number of accessible partial waves, as well as with the rovibrational degrees of freedom of the molecular ion. In our previous experiments [4,5] linearly polarized light effected the photoionization, and photoelectron angular distributions (PADs) were recorded for rotationally resolved ion levels. From these, we extracted the cross sections and relative phase shifts for all the partial waves contributing to the photoionization process [6,7]. We present here new studies in which the photoionization is performed with circularly polarized light. The helicity of this light allows us to observe the *handedness* associated with the photoionization. Analysis of the resulting PADs permits us to extract the

signs of the phase shifts between partial waves [8]. With this additional information, our experiment can be said to be truly complete.

The experiment we have performed is known as circular dichroism in angular distributions (CDAD) [9,10]. CDAD is the difference observed in the photoelectron angular distributions that result from ionization with left and right circularly polarized light [11]. The size and shape of the CDAD signal are related to the detailed photoionization dynamics and to the degree of angular momentum alignment of the atomic or molecular ensemble. The method was proposed by Dubs, Dixit, and McKoy [12] to be used as a probe of alignment, complementary to optical methods [13], and has found limited experimental application [14-16]. In the present study, the alignment was created by a one-photon excitation to the $\text{NO } A^2\Sigma^+$ electronic state using linearly polarized light. This alignment is a known quantity; the detailed photoionization dynamics are what interest us.

We can write the PAD associated with the N^+ rotational level of the ion as an expansion in spherical harmonics $Y_{LM}(\theta,\phi)$:

$$I(N^+, \mu_0, \theta, \phi) = \sum_{LM} \beta_{LM} Y_{LM}(\theta, \phi). \quad (1)$$

Because only two photons are involved in our excitation-ionization process, this expansion can be terminated at $L=4$. We have chosen to express our distributions in the frame of the ionization laser: The quantization axis (Z axis) is defined to lie along the propagation direction of the circularly polarized light beam, and μ_0 is the projection of the ionizing photon angular momentum on that axis. This choice is different from that adopted by Dubs, Dixit, and McKoy [12]. In our frame of reference, the X axis coincides with the electric vector of the linearly polarized excitation laser. The polar angles (θ, ϕ) denote the direction of photoelectron ejection in this right-handed XYZ coordinate frame. The PAD measurements are taken in the X - Y plane, where θ is fixed at 90° ; we observe the azimuthal dependence of the photoelectron flux $I(\phi)$. When the spherical harmonics are evaluated at

$\theta=90^\circ$, an angular distribution of the form

$$I(N^+, \mu_0, \theta=90^\circ, \phi) = \frac{1}{\sqrt{2\pi}} \beta_{00} - \left(\frac{5}{16\pi} \right)^{1/2} \beta_{20} + \left(\frac{15}{32\pi} \right)^{1/2} (e^{-2i\phi} \beta_{2-2} + e^{2i\phi} \beta_{22}) \\ + \frac{9}{16\sqrt{\pi}} \beta_{40} - \frac{3\sqrt{5}}{8\sqrt{2\pi}} (e^{-2i\phi} \beta_{4-2} + e^{2i\phi} \beta_{42}) \quad (2)$$

arises for each ion rotational level N^+ . Note that the excitation process has broken cylindrical symmetry [7]. The explicit ϕ dependence of Eq. (2) can be expressed as

$$I(N^+, \mu_0, \theta=90^\circ, \phi) = a + b \cos 2\phi + c \sin 2\phi, \quad (3)$$

where a , b , and c can be easily deduced from Eq. (2). In particular,

$$c = (15/32\pi)^{1/2} \text{Im}(\beta_{2-2} - \beta_{22}). \quad (4)$$

The first and second terms of Eq. (3) do not depend on the handedness of the light; i.e., they are unchanged if the helicity of the ionizing light is reversed. The third term is nonzero only when elliptically or circularly polarized light is used. The size of the c coefficient, which is defined in Eq. (4), depends on the degree of helicity of the ionizing light and reaches a maximum in the case of pure circularly polarized light. In addition, the c coefficient *changes sign* when the *handedness* of the helicity of the light is reversed. This relationship is the source of the CDAD spectrum.

We may express the β_{LM} coefficients in terms of dynamical parameters, in a manner analogous to Eq. (6) of Ref. [7]:

$$\beta_{LM} = \sum_{l\lambda} \xi_{\alpha l\lambda} r_{l\lambda} r_{l'\lambda} [\cos(\eta_{l\lambda} - \eta_{l'\lambda}) + i \sin(\eta_{l\lambda} - \eta_{l'\lambda})]. \quad (5)$$

Here, $r_{l\lambda}$ is the magnitude and $\eta_{l\lambda}$ is the phase of the radial dipole matrix element connecting the intermediate state to a given $l\lambda$ partial wave [17], and the $\xi_{\alpha l\lambda}$ coefficients result from coupling angular momenta, including a frame rotation through the Euler angles (0° , 90° , 0°) that relate the excitation and ionization frames (for derivation, see Ref. [7]). The subscript α is an index that represents the values of N^+ , L , M , and μ_0 . If the ionizing laser is linearly polarized ($\mu_0=0$), there is no net imaginary contribution in Eq. (5); in this case, Eq. (5) becomes equivalent to Eq. (6) of Ref. [7]. On the other hand, when circularly polarized light ($\mu_0=\pm 1$) is used for ionization, the $\beta_{2\pm 2}$ terms include an imaginary component that contains a factor of $\sin(\eta_{l\lambda} - \eta_{l'\lambda})$. As in Ref. [10], the CDAD spectrum is defined to be

$$I_{\text{CDAD}}(\phi) \equiv I(\text{left-handed light}) - I(\text{right-handed light}) \\ = I(N^+, \mu_0 = +1, \theta=90^\circ, \phi) \\ - I(N^+, \mu_0 = -1, \theta=90^\circ, \phi). \quad (6)$$

Making use of Eqs. (3)–(5), we find

$$I_{\text{CDAD}} = 2c \sin 2\phi, \quad (7)$$

where

$$c = \left(\frac{15}{8\pi} \right)^{1/2} \sum_{l\lambda} \xi_{\alpha l\lambda} r_{l\lambda} r_{l'\lambda} \sin(\eta_{l\lambda} - \eta_{l'\lambda}). \quad (8)$$

In Eq. (8), the α index was chosen to refer specifically to $L=2$, $M=+2$, and $\mu_0=+1$.

We choose the transition $\text{NO } X^2\Pi(v_g=0, J_g=22.5) \rightarrow \text{NO } A^2\Sigma^+(v=0, N=22) \rightarrow \text{NO}^+ X^1\Sigma^+(v^+=0, N^+)$ and observe energy-resolved photoelectrons as a function of the angle ϕ between their ejection direction and the direction of the polarization vector of the linearly polarized excitation light. The angular distribution measurement is performed by rotating this polarization vector. The energy resolution is sufficient to resolve individual rotational levels of the resulting ion.

The photoelectron spectrometer has been described in Ref. [5]. Briefly, it is a field-free time-of-flight spectrometer with a magnetically shielded 50-cm drift region. Our photoelectron energy resolution of 20 cm^{-1} is more than sufficient to resolve the $> 80 \text{ cm}^{-1}$ spacing of the NO^+ rotational levels with $N^+ \approx 22$. (See Ref. [5] for a typical time-of-flight spectrum.) A skimmed molecular beam (neat nitric oxide, 1.3 atom stagnation pressure) is crossed at right angles by the counterpropagating excitation and ionization light beams. The photoelectron time-of-flight axis is mutually perpendicular to the molecular and laser beam directions.

Both light beams are generated by frequency doubling the output of tunable, Nd:YAG-pumped dye lasers. Both were unfocused and passed through $\sim 1 \text{ mm}$ apertures prior to entering the apparatus. The excitation laser power was held at 500 nJ per pulse and the ionizing laser delivered 100 μJ per pulse. A power dependence study revealed that under these conditions there was no saturation of either transition. The excitation laser was tuned to 225 nm to be in resonance with the $Q_{11} + P_{21}(22.5)$ line of the $\text{NO } X^2\Pi(v_g=0) \rightarrow \text{NO } A^2\Sigma^+(v=0)$ transition. This laser was passed through a zero-order quartz half wave plate centered at 225.6 nm; the wave plate was rotated by a computer-controlled stepper motor to vary the angle ϕ . A multichannel plate detector measured the time-resolved photoelectron flux as a function of the wave-plate position.

The ionization wavelength was set to 313.5 nm to reach the same region of the continuum as that studied by Al-lendorf *et al.* [4]. The linearly polarized output of the doubling crystal was passed through a zero-order quarter wave plate cut for 314 nm. Note that the orientation of

the fast optic axis of the wave plate with respect to the plane of polarization of the input beam controls whether left or right circularly polarized light is generated. The handedness of the resulting light was analyzed with a single Fresnel rhomb; a complete discussion of this analysis (on which the sign of the CDAD signal rests) will be presented in a subsequent paper [18].

Figure 1 displays polar plots of our experimental data. The relative intensities β_{00} are listed alongside the PADs. Only data corresponding to the transitions $\Delta N (\equiv N^+ - N^-) = -2, -1, \text{ and } 0$ are presented here. The rotationally resolved angular distributions show a marked dependence on the rotational transition: The $\Delta N = 0$ signal has a positive c parameter [see Eq. (3)] for left circularly polarized light and $c < 0$ for right circularly polarized light; $\Delta N = -1$ has the opposite behavior; and the $\Delta N = -2$ PADs show almost no CDAD signal. Because the rotationally summed signal is dominated by the large $\Delta N = 0$ transition, much additional information is obtained through the rotational resolution. Although the magnitude of our rotationally summed CDAD signal is similar to that observed by White and co-workers [14], the sign of the signal cannot be compared because the handedness was not assigned in Ref. [14].

To extract values for the dynamical parameters r_{λ} and η_{λ} , we have performed a nonlinear least-squares fit [5] of the experimental angular distributions with equations of the form of Eq. (3). In the fit, we consider simultaneously our CDAD data along with those PADs measured for ($v=0, N=25$) in Ref. [4]. In Table I, we present the results of this fit along with those calculated from *ab initio* methods by Rudolph and McKoy [19]. In this table, we express the relative phases over the interval $[-180^\circ, 180^\circ]$, as opposed to the more conventional interval $[0^\circ, 360^\circ]$, to emphasize that the signs of the phases are determined from the data. The results of the fit are not

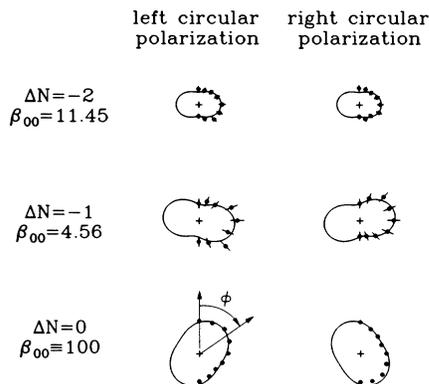


FIG. 1. Polar plots of the experimental data together with the fit by the model [Eq. (1)]. The error bars represent 2σ uncertainties. The solid curves show the predicted angular distributions calculated from the parameters extracted from a least-squares fit (see Table I). The relative angle-integrated cross sections β_{00} [see Eqs. (1) and (5)] are also listed.

TABLE I. Parameters resulting from the fit of experimental data for photoionization of NO via the $A^2\Sigma^+(v=0)$ state. The relative phases are defined as follows: $\delta_{\lambda-l\lambda'} = \eta_{\lambda} - \eta_{l\lambda'}$. Also shown are the results of the *ab initio* calculation of Rudolph and McKoy [19]. The r_{λ} values are normalized so that their squares sum to unity. The total ionization cross section ($\sigma = 7.0 \times 10^{-19} \text{ cm}^2$) has been measured by Zacharias, Schmiedl, and Welge [20]. The values in parentheses represent 1σ uncertainties.

Parameter	Fit	<i>Ab initio</i>
$r_{s\sigma}$	0.205(2)	0.158
$r_{p\sigma}$	0.511(11)	0.278
$r_{p\pi}$	0.459(6)	0.537
$r_{d\sigma}$	0.177(37)	0.221
$r_{d\pi}$	0.073(18)	0.020
$r_{f\sigma}$	0.334(25)	0.358
$r_{f\pi}$	0.247(12)	0.268
$\delta_{p\pi-p\sigma}$	+11.4°(1.5)	+9.9°
$\delta_{d\pi-d\sigma}$	-71°(15)	-92.8°
$\delta_{f\pi-f\sigma}$	-2°(17)	-1.6°
$\delta_{d\sigma-s\sigma}^a$	-150°(10)	+173.7°
$\delta_{f\sigma-p\sigma}^a$	-59°(13)	-76.3°

^aUnlike in our previous work [5], we have excluded the factor $(-i)^{l-l'}$ from these phases.

significantly different from those presented before [5,6], except that the overall signs of the relative phases are no longer arbitrary, and the uncertainties of the fit have been reduced considerably. We report remarkably good agreement between the values and signs of our extracted relative phases and those published by Rudolph and McKoy. As in our earlier work, no attempt has been made to deduce the absolute total photoionization cross section in our experiment; instead we adopt the result of Zacharias, Schmiedl, and Welge [20]. Using the values determined in our fit we have calculated angular distributions that are displayed along with the data in Fig. 1.

Some aspects of the dynamical interpretation of the parameters listed in Table I have been discussed before [5]. The p partial wave dominates the photoionization process, indicating that the Rydberg orbital of the NO $A^2\Sigma^+$ state behaves much like an atomic s orbital. On the other hand, the amount of f partial wave observed in the photoionization suggests the presence of a significant quadrupolar moment in the ion core potential. The new information that has been obtained from the CDAD spectra is the observation of contributions from terms that are proportional to $\sin \delta_{\lambda-l\lambda'}$ [see Eq. (5)]. These results allow us to obtain signed values for the relative phase shifts $\delta_{\lambda-l\lambda'}$, which are related to the relative attractiveness of the potential for the outgoing partial waves $|\lambda\rangle$ and $|\lambda'\rangle$. In our earlier work, we determined only the magnitude of the relative phase shift. As an example, consider our observation that the phase of the $p\pi(\lambda = \pm 1)$ partial wave is advanced by $+12^\circ$ with respect to that of the $p\sigma(\lambda = 0)$ partial wave; the sign of this phase demon-

strates that the $p\pi$ partial wave is more attracted by the ion core potential than the $p\sigma$ partial wave.

The results presented in Table I constitute a complete description of the photoionization of the $A^2\Sigma^+$ state of NO. "Completeness" must always be qualified to some degree by the underlying assumptions of the model. As is usual, we neglect contributions of higher-order interactions than electric dipole. We truncate the photoelectron partial wave expansion at $l=3$ because we do not observe sizable peaks corresponding to $|\Delta N| > 2$. We make the assumptions that the photoionization dynamics are independent of the molecular rotational level and that the photoionization dynamical parameters are constant over the range of photoelectron kinetic energies involved in our experiment (136–203 meV). The influence of nuclear and electronic spins in our system of study is very weak, although nonzero. Therefore we expect the emitted photoelectron to have no spin polarization so we have not attempted to measure this quantity. Finally, in this photoionization process (but not in all cases; e.g., see Ref. [21]), the relative phase shifts between even and odd l waves are not observable because parity conservation dictates that these waves cannot interfere [22]. These phase shifts are therefore not shown in Table I.

In conclusion, we report here the first rotationally resolved CDAD spectra. These spectra show a strong dependence on the rotational transition of the ionization step. We have performed a fit to the photoelectron angular distributions resulting from photoionization with left and right circularly polarized light to extract dynamical parameters. These parameters constitute the first complete molecular photoionization experiment. A full paper will discuss further the meaning of these results in terms of the molecular photoionization dynamics [18].

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