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Author
Southworth, S.

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PHOTOIONIZATION CROSS SECTIONS AND PHOTOELECTRON ASYMMETRIES OF THE VALENCE ORBITALS OF NO

S. Southworth, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, W. D. Brewer,* and D. A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, CA 94720

ABSTRACT

Partial photoionization cross sections and photoelectron asymmetry parameters were measured for the valence orbitals of NO over the photon energy range 16-31 eV by photoelectron spectroscopy, using synchrotron radiation. The results are compared with previous measurements and with theoretical curves based on the multiple-scattering model. Maxima observed in the partial cross sections of the 2π, 5σ, and 4σ orbitals are attributed to continuum shape resonances. The multiple-scattering model calculations predict the observed photoelectron asymmetries of the 5σ and 1π orbitals very well, but the calculated asymmetry curves are shifted strongly from the measured asymmetries produced by the 2π and 4σ orbitals. The π molecular orbitals are observed to produce qualitatively different photoelectron asymmetry curves than do the σ orbitals. We discuss the double-angle time-of-flight method for the measurement of photoelectron angular distributions. This technique offers the advantages of increased electron collection efficiency and the elimination of certain systematic errors.

*Permanent address: Institut für Atom-und Festkörperphysik, Freie Universität Berlin, 1000 Berlin 33, West Germany
I. INTRODUCTION

Experimental measurements of the energies, intensities, and angular distributions of photoelectrons, when combined with theoretical calculations, can provide a sensitive probe of atomic and molecular electronic structure and dynamics.1 The full power of photoelectron spectroscopy is only realized when measurements are made over a range of incident photon energy, as the spectral variation of cross sections and angular distributions characterizes the electronic structure and photoionization dynamics. Wavelength-dependent photoelectron spectroscopy has become established in the past decade through use of the tunable VUV continuum provided by synchrotron radiation.2,3

For any particular channel, photoionization can be characterized by an energy-dependent cross section and a product angular distribution. The form of the angular distribution of photoelectrons, or any photofragment, is restricted by angular momentum and parity conservation.5 For a linearly polarized photon beam producing electric dipole excitation of randomly oriented target molecules, the differential cross section is given by

$$\frac{d\sigma(\theta, \varepsilon)}{d\Omega} = \frac{\sigma(\varepsilon)}{4\pi} [1 + \beta(\varepsilon) P_2(\cos\theta)] . \quad (1)$$

Here $\sigma(\varepsilon)$ is the angle-integrated partial cross section, $P_2$ is the second Legendre polynomial, equal to $(1/2)(3\cos^2\theta - 1)$, $\theta$ is the photoelectron ejection angle with respect to the photon polarization vector, $\varepsilon$ is the photoelectron kinetic energy, and $\beta(\varepsilon)$ is the
asymmetry parameter. This parameter completely characterizes the angular distribution. It is restricted to values in the range 

\[-1 \leq \varepsilon(\varepsilon) \leq 2.\]

We have used synchrotron radiation to measure partial photoionization cross sections \(\sigma(\varepsilon)\) and photoelectron asymmetries \(\varepsilon(\varepsilon)\) for the valence molecular orbitals of NO over the photon energy range \(\hbar \nu = 16-31\) eV. Features were observed which are attributed to a continuum shape resonance, as predicted by the multiple-scattering model (MSM) calculations.\(^6,7\) Analogous shape resonance features have been observed in the related first-row diatomic molecules \(\text{N}_2,\ CO,\ \text{and} \ \text{O}_2\) (see, for example, Refs. 8-15). The MSM\(^{16}\) shows that this shape resonance occurs in the \(\varepsilon\sigma\) ionization channel and is produced predominantly by the \(f\)-partial wave (\(\ell = 3\)). An alternative characterization of the shape resonance is provided by the method of improved virtual molecular orbitals (IVO).\(^{18}\) In the IVO calculations, centrifugal barriers in the molecular ionic potential for high \(\ell\)-wave components cause resonant trapping of the photoelectron into \(\sigma^*\) valencelike orbitals. For the \(2\pi\) orbital of NO, a second, stronger resonance feature was also observed which is attributed to the \(\varepsilon\pi\) and \(\varepsilon\phi\) ionization channels.

The experimental method and data analysis are described in Section II. Results are presented in Section III and compared with theory and previous measurements. Conclusions are given in Section IV.
II. EXPERIMENTAL

The asymmetry parameter $\beta(\varepsilon)$ is usually determined by measuring photoelectron intensities at several ejection angles and fitting the results to the form of Eq. (1) (for example, as in Refs. 10 and 19). From this equation, however, it is clear that $\beta(\varepsilon)$ can be determined by measuring photoelectron intensities at only two angles. In our apparatus the time structure (0.3 nsec pulse width and 780 nsec repetition period) of the synchrotron radiation at the Stanford Synchrotron Radiation Laboratory (SSRL) is used to record time-of-flight (TOF) photoelectron spectra. As shown schematically in Fig. 1, two TOF detectors are operated simultaneously. One detector is positioned to accept electrons ejected at 0° with respect to the polarization vector, for which $P_2(\cos \varepsilon)$ is unity, and the other at 54.7°, the "magic angle," where $P_2(\cos \varepsilon)$ vanishes. In the TOF method, ejected electrons of all energies are recorded simultaneously, which greatly increases the collection efficiency and signal-to-noise ratio in comparison with single-channel electrostatic analyzers. These are important advantages in our experiments, because beam time at SSRL is limited and the incident photon beam is two orders of magnitude less intense than that from a typical He(I) line discharge lamp. More fundamentally, by recording all of the photoelectron peaks simultaneously at both angles, we avoid the need to correct peak areas for variations in sample density or photon beam intensity, thereby reducing systematic error.
Because the two TOF detectors have different collection efficiencies and detect electrons from somewhat different portions of the interaction volume, it is necessary to calibrate the apparatus as a function of electron kinetic energy by recording photoelectron lines having known $\beta(\epsilon)$ values. For this purpose we record spectra of the rare gases at photon energies where accurate $\beta(\epsilon)$ values have been measured using resonance lines$^{21}$ or synchrotron radiation.$^{22}$ From Eq. (1), the differential cross sections observed by the two detectors are

$$\frac{d\sigma(0^\circ, \epsilon)}{d\Omega} = \frac{\sigma(\epsilon)}{4\pi} [1 + \beta(\epsilon)]$$  \hspace{1cm} (2)

$$\frac{d\sigma(54^\circ, \epsilon)}{d\Omega} = \frac{\sigma(\epsilon)}{4\pi}$$  \hspace{1cm} (3)

Assuming, initially, the ideal conditions of a point source of photoelectrons, point detectors, 100 percent linearly polarized light, and perfect geometrical alignment of detectors and photon beam, the two detectors would record photoelectron signals $N(\theta, \epsilon)$ whose relative strengths depend only on the detector collection efficiencies $T(\theta, \epsilon)$ and differential cross sections,

$$N(\theta, \epsilon) \propto T(\theta, \epsilon)\frac{d\sigma(\theta, \epsilon)}{d\Omega}$$  \hspace{1cm} (4)

Calibration with a known $\beta(\epsilon)$ yields the relative collection efficiency $f_0(\epsilon)$ at a particular kinetic energy,
The subscript \( c \) in Eq. (5) represents the calibration photoelectron line. Unknown \( \beta(\varepsilon) \) values are then determined from the observed ratio of photoelectron intensities upon inversion of Eq. (5).

\[
f_0(\varepsilon) \equiv \frac{T(0^\circ, \varepsilon)}{T(54^\circ, \varepsilon)}
\]

\[
= \frac{N_c(0^\circ, \varepsilon)/N_c(54^\circ, \varepsilon)}{1 + B_c(\varepsilon)}
\]  \quad (5)

The efficiency calibration curve \( f_0(\varepsilon) \) determined in the present experiments is plotted in Fig. 2.

The subscript \( 0 \) is given to \( f_0(\varepsilon) \) and \( \beta_0(\varepsilon) \), because Eqs. (5) and (6) are zero-order expressions which neglect effects on the measured signal ratios due to having less than 100 percent linearly polarized light and to having a finite source region and finite collection solid angles. To account for these effects we have numerically computed the angular distribution produced by partially polarized light\(^{23} \) and integrated over the solid angles of the detectors observing a photoelectron source region of finite volume. This calculation requires knowledge of both the geometrical parameters of the spectrometer\(^{20} \) and the degree of linear polarization of the photon beam. A lower limit of 97 percent linear polarization is estimated for the VUV beam line at SSRL.\(^{24} \) The \( \beta(\varepsilon) \) values reported here are those of Eq. (6) after correction for these effects. Table I shows the corrected \( \beta \) values.
values that would be obtained from various uncorrected $\beta_0$ values for the typical case of a calibration value $\beta_C = 1.5$. The very small corrections needed indicate that the experimental system closely approaches the ideal case of point source, point detectors, and 100 percent polarization.

We estimate residual systematic error as $\pm 0.10$ or less $\beta$ unit due to uncertainty in the light polarization, geometrical parameters, and alignment of the detectors and photon beam. Deviations from the idealized experimental conditions are largely accounted for by being folded into the calibration function $f_0(\epsilon)$, Eq. (5). The magnitude of the $\beta$ correction generally increases with increasing difference between the $\beta_C$ value used for calibration and the $\beta$ value being determined.

In the limit that the unknown $\beta$ value is identical to the calibration $\beta_C$ value, there is no correction to Eq. (6). This result is obtained no matter how great the deviation of the actual experimental conditions from the idealized experiment. This is illustrated in Table II where deviations from the corrected $\beta$ values of Table I are listed for a large range of partially polarized photon beams. The deviations are small except for $\beta$ values in the range $\beta_0 = -0.5$ to $-1.0$, which are far removed from the calibration value $\beta_C = 1.5$. Thus, if the polarization were uncertain by 20–30 percent it would be necessary to use calibration $\beta_C$ values near to those being measured. The calibration procedure also accounts for the loss of experimental photoelectron asymmetry due to elastic scattering, an effect discussed by Kibel et al. 19 Thus, even if such experimental systematic errors occur, the
observed asymmetries are scaled to the accurately known $\beta(\varepsilon)$ values of the calibration lines.

As stated in Eqs. (3) and (4), the photoelectron signals observed by the TOF detector at the magic angle are proportional to the angle-integrated partial cross sections, independent of $\beta(\varepsilon)$. Energy-dependent, relative partial cross sections were determined by

$$
\sigma(\varepsilon) \propto \frac{N(54^\circ,\varepsilon)}{T(54^\circ,\varepsilon) n t \tilde{I}} \quad (7)
$$

where $N(54^\circ,\varepsilon)$ is the number of photoelectron counts recorded at the magic angle detector, $T(54^\circ,\varepsilon)$ is the collection efficiency (relative transmission) of the detector at electron energy $\varepsilon$, $n$ is the sample gas density, $t$ is the spectrum collection time, and $\tilde{I}$ is the intensity of the photon beam. A sodium salicylate scintillator, optical phototube, and picoammeter were used to monitor the photon beam intensity. For each gas, the sample density in the interaction region was assumed proportional to the pressure backing the gas inlet, as measured by a capacitance manometer. The picoammeter and manometer signals were integrated over the collection time to account for variations. Collection times were typically 1000 sec. The magic angle detector transmission function was determined from photoelectron spectra of the rare gases, for which reliable cross sections have been tabulated.

The partial cross sections of Eq. (7) were corrected slightly for the effects of incomplete linear polarization of the photon beam and angle-averaging over the finite source volume and detector solid angle.
As for the \( \beta \) measurements, there is no correction to the measured cross section if the \( \beta \) value of the gas being measured is identical to the \( \beta \) value of the transmission calibration gas. In the present experiment the corrected partial cross sections differed by 2 percent or less from the values given by Eq. (7).

The electron spectrometer was separated from the ultrahigh vacuum of the monochromator and beam line by an ultrathin Al window.\(^{20}\) The transmission of the window and the high energy cut-off of the beam line optics limited the photon energy range to about 16-31 eV. All spectra were recorded with the monochromator operated at a fixed bandpass of 2.7\( \AA \) FWHM.

III. RESULTS

Synchrotron radiation measurements of \( \beta(\varepsilon) \) for the valence orbitals of \( \text{N}_2 \) have been reported previously.\(^{9,10,27}\) As a check on our experimental method we present \( \beta(\varepsilon) \) measurements for the \( 3\sigma_g \) molecular orbital, i.e., for the ground ionic state \( \text{N}_2^+ X^2\Sigma^+_g \). The results\(^{28}\) are plotted in Fig. 3 along with the measurements of Marr and co-workers\(^{9,10}\) and those of Carlson et al.\(^{27}\) Structure observed in the \( \beta(\varepsilon) \) measurements between 16-23 eV is due to autoionization.\(^{30}\) Agreement among the three sets of measurements is good, with an average deviation of about 0.05 \( \beta \) unit.

The relative partial cross section determined for \( \text{N}_2^+ X^2\Sigma^+_g \) from the magic angle TOF spectra reproduced the previously measured\(^8\) 40 percent rise over \( h\nu = 20-28 \text{ eV} \) due to the \( 3\sigma_g \rightarrow \varepsilon\sigma_u \) shape resonance.\(^{18}\) Good agreement of the TOF results with previous measurements for \( \text{N}_2^+ X^2\Sigma^+_g \)
serve to confirm the calibration and data analysis procedures applied in these experiments.

The ground configuration of the open-shell molecule NO is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1, \chi^2 \Pi$$

The antibonding $2\pi$ electron ($\pi^2 2p$) is bound by 9.3 eV, giving a $^1\Sigma^+$ ground ionic state in NO$^+$ that is easily resolved from the second band which starts at 15.7 eV in the photoelectron spectrum (see Fig. 4). However, due to alternative couplings of spin and orbital angular momenta in the final ionic states, ionization from the $1\pi$ and $5\sigma$ orbitals gives a series of seven overlapping photoelectron bands between 15.7 eV and 20.0 eV binding energy. These final states have been assigned, having been resolved in high resolution photoelectron spectra.$^{31,32}$ Unfortunately, the lower resolution ($\Delta E/E = 0.03$) attained in the present TOF spectra precludes an accurate deconvolution. However, ionization of a $5\sigma$ electron gives a predominantly $v' = 0, b^3\Pi$ photoelectron peak at 16.6 eV which is sufficiently strong to allow a reliable deconvolution of its intensity.

The band at 21.7 eV binding energy results from ionization of the $4\sigma$ orbital; however, assignment of the final state(s) remains controversial. Edqvist et al.$^{32}$ regard this band as the overlapped $c^3\Pi$ and $B^1\Pi$ final states derived from the $4\sigma$ orbital. However, Rydberg series recorded in absorption spectra$^{33}$ indicate that a single ionic state, the $c^3\Pi$, is formed at 21.7 eV. Theoretical calculations$^{34}$
support the assignment of \(c^3\Pi\) for the 21.7 eV band. These calculations indicate that the \(B^1\Pi\) \((4\sigma)^{-1}\) ionic state is strongly modified by configuration interaction and suggest that this state be assigned to a broad, weak band at 22.7 eV binding energy (not shown in Fig. 4; see Ref. 32). We adopt these assignments; i.e., the \(c^3\Pi\) band at 21.7 eV and \(B^1\Pi\) at 22.7 eV. Unfortunately, the 22.7 eV band was recorded in only a few of the present TOF spectra and with low counting statistics, so \(\beta(\varepsilon)\) measurements are not reported.

The present TOF measurements for NO\(^+\) \(X^1\Sigma^+\), \(b^3\Pi\), and \(c^3\Pi\) were also quoted in Ref. 6, where the relative partial cross sections were scaled to absolute units (Mb) by normalizing the \(X^1\Sigma^+\) partial cross section to 3.25 Mb at 21.2 eV photon energy. That normalization was determined from the photoionization yield measurements of Watanabe et al.,\(^{35}\) the photoelectron branching ratio data of Bahr et al.,\(^{36}\) and the total photoabsorption cross section tabulated by Berkowitz.\(^{37}\) However, we prefer to adopt the more self-consistent normalization procedures used by Brion and Tan\(^4\) and by Gustafsson and Levinson\(^38\) for their partial cross section measurements of NO. Thus, the partial photoionization cross sections reported here have been scaled to units of Mb by apportioning the total photoabsorption cross section\(^37\) according to the photoelectron branching ratios measured over \(h\nu = 29-31\) eV by the magic angle TOF detector. It is assumed that the photoionization yield\(^35\) is unity at those energies. This normalization procedure increased the absolute partial cross sections reported here by 13 percent relative to the original normalization reported in Ref. 6. The branching ratios over 29-31 eV photon
energies are listed in Table III along with those measured at 28 eV and 30 eV by dipole \((e, 2e)\); the agreement is very good.

Present results for the photoionization cross sections and photo-electron asymmetry parameters are listed in Tables IV and V, respectively. The results are plotted in Figs. 5-8 along with previous measurements\(^4,38,40\) and theoretical curves from the MSM calculation.\(^6,7\)

Three distinct resonant features are apparent in the partial cross section for \(\text{NO}^+ X^1\Sigma^+\) in which the antibonding \(2\pi (\pi^*2p)\) electron has been photoejected (see Fig. 5(a)). The strong, sharp resonance at 17.00 eV photon energy we attribute to autoionization of the Rydberg excitation \(5\sigma \rightarrow 4p\pi\). This is the third member of the \(\gamma(0,0)\) Rydberg series,\(^41\) having as series limit the \(A^1\Pi\) state of \(\text{NO}^+\) at 18.32 eV binding energy. A maximum in the experimental cross section at \(h\nu = 19\) eV agrees well with the energy position of the small \(2\pi \rightarrow \epsilon\sigma\) shape resonance predicted by the MSM. The strong, broad resonance centered at \(h\nu = 29\) eV in the TOF and \((e, 2e)\)\(^4\) data is not reproduced by the MSM calculation. However, IVO calculations\(^42\) for the corresponding \(\pi^*2p\) orbital in \(O_2\) (the \(1\pi_g\) orbital) predict a weak resonance near threshold in the \(1\pi_g \rightarrow \epsilon\pi_u\) channel and strong resonances in the \(\epsilon\pi_u\) and \(\epsilon\delta_u\) channels near 16 eV kinetic energy. Experimental cross section measurements\(^14,15\) are in good agreement with the IVO theory. It appears likely, therefore, that the strong shape resonance in \(\text{NO}^+ X^1\Sigma^+\) is produced in the \(\pi\) and \(\delta\) ionization channels.
The photoelectron asymmetry measurements for the $2\pi$ orbital are plotted in Fig. 5(b) and agree well with line source measurements. Oscillations in the measurements below 20 eV we attribute to the auto-ionization and $\varepsilon\sigma$ resonances observed in the partial cross section. The MSM correctly predicts the rise of $\beta(\varepsilon)$ with increasing energy, but the calculated values are too high by about 0.6 $\sigma$ unit.

Results for NO$^+$ $b^3\Pi$ are plotted in Fig. 6. The cross section measurements show a broad resonant feature centered near the energy position of the $5\sigma \rightarrow \varepsilon\sigma$ resonance predicted by the MSM. The calculated feature is somewhat more narrow and intense than experiment. Very good agreement was obtained among the present $\beta(\varepsilon)$ measurements, line source measurements, and the calculated $\beta(\varepsilon)$ curve. Structure in the measurements at low energies likely results from autoionization of the Rydberg-excited $4\sigma$ electron.

Partial cross section measurements for NO$^+$ $c^3\Pi$ are plotted in Fig. 7(a). The present results are in conflict with previous measurements based on synchrotron radiation for the energy position and intensity of the $4\sigma \rightarrow \varepsilon\sigma$ shape resonance. The measurements of Ref. 38 place the resonance maximum near 29 eV, while the maximum was observed near 27 eV in the present measurements and with an absolute intensity 40 percent smaller. The (e,2e) data and MSM calculation also indicate the resonance maximum lies at higher energy than we report here. The present results were obtained over a more limited energy range, and we note an indication of two maxima in the data of Ref. 38, as was observed above for the $2\pi$ orbital. Thus, perhaps the first
maximum was observed here. The difference in the magnitudes of the measured cross sections indicates a discrepancy in the measured photo-electron branching ratios. Table III shows that the present branching ratio measurements are in good agreement with the (e,2e) results. Note that the (e,2e) cross sections plotted in Fig. 7(a) are for the combined $c^3\Pi$ and $B^1\Pi$ ionic states,\textsuperscript{39} which could not be resolved in the (e,2e) spectra. As shown in Table III and in Ref. 38, the $B^1\Pi$ band accounts for 30 percent of the total $c^3\Pi + B^1\Pi$ intensity. Hence, the (e,2e) data are in good agreement with the present measurements for cross section magnitude, and the cross sections reported in Ref. 38 appear too large. The $\beta(e)$ measurements plotted in Fig. 7(b) exhibit the resonance minimum predicted by the MSM; however, the observed minimum lies 3 eV lower in energy and the calculated values are too high by 0.6 $\beta$ unit.

Photoejection from the $1\pi$ and $5\sigma$ orbitals produces a series of seven overlapping bands in the photoelectron spectrum between 15.7 eV and 20.0 eV binding energy (see Fig. 4 and Refs. 31 and 32). It was not possible, in the present experiment, to isolate a single ionic state derived from the $1\pi$ orbital. However, at low energies it was possible to approximately deconvolute the intensities of the two $5\sigma$-derived final states $b^3\Pi$ and $A^1\Pi$. The remaining intensity was due to the five final states, $a^3\Sigma^+$, $w^3\Delta$, $b^3\Sigma^-$, $A^1\Sigma^-$, and $w^1\Delta$, derived from the $1\pi$ orbital. Figure 8 shows $\beta(e)$ measurements pertaining to the average over these five $(1\pi)^{-1}$ ionic states.\textsuperscript{43} The results are in very good agreement with fixed-nuclei MSM calculations\textsuperscript{7} for the $1\pi$ orbital.
The present measurements and MSM calculations for NO and previous results\textsuperscript{9-12} for \( N_2 \), \( CO \), and \( O_2 \) show that \( \pi \) molecular orbitals produce qualitatively different \( \beta(\varepsilon) \) curves near threshold than do \( \sigma \) orbitals. For \( \pi \) orbitals, \( \beta \) is \( \leq 0 \) near threshold, and it increases with energy to positive values. For the \( \sigma \) orbitals, \( \beta \) is generally large and positive at threshold, decreases somewhat (particularly through a shape resonance), then remains large and positive to high energy. This observation is consistent with Chang's analysis\textsuperscript{44} of molecular photoionization transitions in terms of parity favoredness.\textsuperscript{45} More simply, however, the \( \beta(\varepsilon) \) values produced near threshold likely reflect the orbital angular momentum composition of the molecular orbitals. Single-center expansions of \( \sigma \) molecular orbitals generally contain large components of \( \ell = 0 \) (s atomic orbital) angular momentum. Thus, the large \( \beta(\varepsilon) \) values for \( \sigma \) orbitals near threshold likely reflect large \( ns \to \varepsilon p \) components, which have\textsuperscript{46} \( \beta_{ns} = 2 \). However, the \( \pi \) molecular orbitals contain \( \ell > 1 \) components, which produce smaller \( \beta \) values. For example,\textsuperscript{46} \( \beta(np \to \varepsilon s) = 0 \) and \( \beta(np \to \varepsilon d) = 1 \).
IV. CONCLUSIONS

The partial photoionization cross sections measured for the 2π, 5σ, and 4σ orbitals of NO exhibit shape resonance features attributed to the σ continuum in qualitative agreement with MSM calculations. A strong shape resonance in the (2π)⁻¹ cross section is attributed to the π and σ continua and was not reproduced by the MSM theory. MSM calculations of photoelectron asymmetries for the 1π and 5σ orbitals are in very good agreement with the measured θ(ε) values, but strong deviations between theory and experiment were obtained for the 2π and 4σ orbitals.

Shape resonances now appear to be prevalent, characteristic features in molecular photoionization spectra. The MSM has generally predicted these features and has clarified their dynamical nature. However, the MSM is a semi-quantitative, one-electron model calculation, roughly equivalent to the Hartree-Slater (central field) model of atomic photoionization. More accurate theories of molecular photoionization in small molecules, on the level of Hartree-Fock accuracy, are highly desirable, so that one-electron processes are treated quantitatively, and the importance of many-electron and electronic-nuclear interactions can be assessed systematically. The IV0 method provides such a theoretical framework for the accurate calculation of partial photoionization cross sections. However, the present measurements on NO demonstrate that the photoelectron asymmetry θ(ε) also is very sensitive to the accuracy of the theoretical calculation. Calculations of θ(ε) for small molecules on the level of Hartree-Fock theory are currently in progress, and the first results are highly promising.
ACKNOWLEDGEMENTS

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REFERENCES

3. Energy-dependent total and partial cross sections for several small molecules have also been measured by the dipole (e,2e) pseudophoton technique. See Ref. 4 and references therein.


28. The present $\beta(\varepsilon)$ measurements are for the average over vibrations of the final state $N_2^+ X^2 \Sigma^+$. The measurements of Refs. 9 and 10 are also for the average over vibrations in the photon energy range 23-32 eV, but are for $v' = 0$ only in the range 16-23 eV. The measurements taken from Ref. 27 and plotted in Fig. 3 are for $v' = 0$. The predominant $v' = 0$ transition accounts for about 90 percent of the intensity (see Ref. 29), so that $\beta$ for $v' = 0$ differs from $\beta$ averaged over vibrations by less than 0.10 $\beta$ unit.


37. Reference 1, p. 113.


39. In Ref. 4 the photoelectron band at 21.7 eV is assigned as the combined states $c^3\Pi + B^1\Sigma^+$, and the band at 22.7 eV is assigned $B^1\Sigma^+$. Regardless of the assignments, the $(e,2e)$ measurement is for the sum of the bands at 21.7 eV and 22.7 eV.


43. An approximate band center of 17.5 eV binding energy was chosen for this sum of the five \(1\pi\)-derived ionic states.


47. See, for example, S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968); S. T. Manson, J. Electron Spectrosc. Relat. Phenom. 1, 413 (1973).


Table I. Corrected $\beta$ values vs $\beta_0$ values given by Eq. (6).\textsuperscript{a}

<table>
<thead>
<tr>
<th>$\beta_0$</th>
<th>$\beta$ (corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.97</td>
</tr>
<tr>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>0.50</td>
<td>0.53</td>
</tr>
<tr>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>-0.50</td>
<td>-0.49</td>
</tr>
<tr>
<td>-1.00</td>
<td>-1.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The corrections assume 97 percent linearly polarized light and a calibration $\beta_c = 1.50$. 
Table II. Deviations of corrected $\beta$ values from those of Table I for a range of partially (%) linearly polarized photon beams.$^a$

<table>
<thead>
<tr>
<th>$\beta_0$</th>
<th>100%</th>
<th>90%</th>
<th>80%</th>
<th>70%</th>
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<tr>
<td>2.00</td>
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<td>-0.02</td>
<td>-0.04</td>
<td>-0.06</td>
</tr>
<tr>
<td>1.50</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>0.50</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>0.00</td>
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<td>-0.01</td>
<td>-0.02</td>
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</tr>
<tr>
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<td>-1.00</td>
<td>0.02</td>
<td>-0.06</td>
<td>-0.16</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

$^a$A calibration $\beta_c = 1.50$ is assumed.
Table III. Photoelectron branching ratios (%) for NO⁺.

<table>
<thead>
<tr>
<th>State</th>
<th>Binding energy (eV)</th>
<th>Present results</th>
<th>(e,2e)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>29 eV</td>
<td>30 eV</td>
</tr>
<tr>
<td>X¹Σ⁺</td>
<td>9.3</td>
<td>26(2)</td>
<td>26(2)</td>
</tr>
<tr>
<td>(1π+5σ)ᵃ</td>
<td>15.7-20.0</td>
<td>63(5)</td>
<td>62(5)</td>
</tr>
<tr>
<td>c³Π</td>
<td>21.7</td>
<td>8.8(7)</td>
<td>8.5(8)</td>
</tr>
<tr>
<td>B¹Π</td>
<td>22.7</td>
<td>1.5(3)</td>
<td>3.1(5)</td>
</tr>
</tbody>
</table>

ᵃFor the combined states a³Σ⁺, b³Π, w³Δ, b'³Σ⁻, A'¹Σ⁻, A¹Π, and W¹Δ derived from the 1π and 5σ orbitals.

ᵇDipole (e,2e) results, Ref. 4.

cFor the combined states c³Π and B¹Π (see note 39).
Table IV. Partial photoionization cross sections (Mb) for NO⁺.

<table>
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<tr>
<th>hv(eV)</th>
<th>$\chi_{1\Sigma}^+$</th>
<th>$b_{3\Pi}$</th>
<th>$c_{3\Pi}$</th>
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<td>16.5</td>
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<td>…</td>
</tr>
<tr>
<td>17.0</td>
<td>8.4(10)</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>17.3</td>
<td>4.5(6)</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>17.5</td>
<td>4.1(5)</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>18.0</td>
<td>4.4(5)</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>18.6</td>
<td>4.5(6)</td>
<td>6.6(8)</td>
<td>…</td>
</tr>
<tr>
<td>19.1</td>
<td>4.4(6)</td>
<td>7.5(8)</td>
<td>…</td>
</tr>
<tr>
<td>19.6</td>
<td>4.0(5)</td>
<td>6.7(8)</td>
<td>…</td>
</tr>
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<td>20.0</td>
<td>3.2(3)</td>
<td>6.0(7)</td>
<td>…</td>
</tr>
<tr>
<td>20.5</td>
<td>3.2(2)</td>
<td>6.7(8)</td>
<td>…</td>
</tr>
<tr>
<td>21.2</td>
<td>3.7(3)</td>
<td>6.6(8)</td>
<td>…</td>
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<td>21.6</td>
<td>4.0(3)</td>
<td>6.8(8)</td>
<td>…</td>
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<td>22.0</td>
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<td>6.9(8)</td>
<td>…</td>
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<td>7.2(8)</td>
<td>…</td>
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<td>7.3(6)</td>
<td>…</td>
</tr>
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<td>7.2(6)</td>
<td>1.1(1)</td>
</tr>
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<td>7.6(6)</td>
<td>1.4(2)</td>
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<td>7.4(6)</td>
<td>1.6(2)</td>
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<td>1.6(2)</td>
</tr>
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<td>1.9(2)</td>
</tr>
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<tr>
<td>31.0</td>
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<td>1.6(1)</td>
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Table V. Photoelectron asymmetry parameters $\beta$ for NO$^+$. 

<table>
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<tr>
<th>$\nu$(eV)</th>
<th>$^1\Sigma^+$</th>
<th>$^3\Pi$</th>
<th>$(1\pi)^a$</th>
<th>$^3\Pi$</th>
</tr>
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<td>16.5</td>
<td>0.16(10)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>17.0</td>
<td>-0.02(5)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
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<td>17.3</td>
<td>0.20(7)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>17.5</td>
<td>0.34(6)</td>
<td>1.11(9)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>18.0</td>
<td>0.31(6)</td>
<td>0.84(6)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>18.6</td>
<td>0.19(5)</td>
<td>0.59(5)</td>
<td>-0.24(5)</td>
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<tr>
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<td>0.44(4)</td>
<td>-0.20(4)</td>
<td>...</td>
</tr>
<tr>
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<td>0.61(5)</td>
<td>-0.02(4)</td>
<td>...</td>
</tr>
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<td>0.72(5)</td>
<td>-0.06(7)</td>
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<td>0.53(4)</td>
<td>0.08(4)</td>
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<td>0.19(5)</td>
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</tr>
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<td>0.43(5)</td>
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<td>0.40(5)</td>
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<td>0.43(7)</td>
<td>0.65(6)</td>
<td>0.38(7)</td>
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<tr>
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<td>0.43(6)</td>
<td>...</td>
<td>0.09(5)</td>
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<td>0.40(6)</td>
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<td>0.39(7)</td>
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<td>0.54(9)</td>
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<td>0.61(15)</td>
<td>0.47(9)</td>
<td>...</td>
<td>0.73(12)</td>
</tr>
</tbody>
</table>

$^a$For the average over the five final states $a^3\Sigma^+$, $w^3\Delta$, $b^3\Sigma^-$, $A^1\Sigma^-$, and $W^1\Delta$ derived from the $1\pi$ orbital (see note 43).
FIGURE CAPTIONS

Fig. 1. Schematic diagram of the double-angle-TOF experiment for the measurement of photoelectron angular distributions. The time structure of the synchrotron radiation is used to record time-of-flight (TOF) photoelectron spectra. Two TOF detectors are operated simultaneously, one positioned at 0° and the other at 54.7° with respect to the polarization vector of the photon beam.

Fig. 2. Relative collection efficiency (Eq. (5)) of the two TOF detectors vs electron kinetic energy. The curved line is a least-squares polynomial fit to the calibration data.

Fig. 3. Photoelectron asymmetries for N₂ X ²Σ⁺⁺ measured using synchrotron radiation. ●, Present results; □, Ref. 27; solid line, Refs. 9 and 10 (see note 28).

Fig. 4. Energy-converted TOF spectra of NO recorded at 0° and 54.7° with respect to the photon polarization, and at 24.3 eV photon energy.

Fig. 5. Partial photoionization cross section (a) and photoelectron asymmetry (b) for NO⁺ X ¹Σ⁺ (2π)-¹. Experimental: ●, present results; ○, Ref. 4; X, Ref. 40. The solid line is the MSM theoretical calculation, Ref. 6.

Fig. 6. Partial photoionization cross section (a) and photoelectron asymmetry (b) for NO⁺ b ³Π (5σ)-¹. Experimental: ●, present results; X, Ref. 40. The solid line is the MSM theoretical calculation for the average over nuclear motion, Ref. 6.
Fig. 7. Partial photoionization cross section (a) and photoelectron asymmetry (b) for NO$^+$ $c^3\Pi (4\sigma)^{-1}$. Experimental: ●, present results; ■, Ref. 38; ○, Ref. 4 (see note 39 and discussion in the text). The solid line is the MSM theoretical calculation for the triplet fraction of (4\sigma)^{-1} only, Ref. 6.

Fig. 8. Photoelectron asymmetry for the average over the states $a^3\Sigma^+, b^3\Delta, b^1\Sigma^-, A^1\Sigma^-$, and $w^1\Delta$ derived from the $1\pi$ orbital (see note 43). The solid line is the MSM theoretical curve, Ref. 7.
Figure 4

NO⁺

\[ h\nu = 24.3 \text{ eV} \]

54.7 deg

\( (1\pi)^{-1} + (5\sigma)^{-1} \)

\( c^{3}\Pi, A^{1}\Pi, b^{3}\Pi, X^{1}\Sigma^{+} \)

Counts

binding energy (eV)
Figure 5

(a) $\text{NO}^+ \; \chi^1\Sigma^+ \; (2\pi)^{-1}$

(b) 

Cross section (Mb)

Photon energy (eV)
Figure 6

(a) NO$^+$ b$^3\Pi$ (5σ)$^{-1}$

(b) β versus photon energy (eV)

Cross section (Mb)

Photon energy (eV)
Figure 7
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