

# Resonance structure in the vibrationally resolved photoelectron branching ratios and angular distributions of the $2\pi^{-1}$ channel of NO

S. H. Southworth<sup>a)</sup>

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

A. C. Parr and J. E. Hardis

National Bureau of Standards, Gaithersburg, Maryland 20899

J. L. Dehmer

Argonne National Laboratory, Argonne, Illinois 60439

(Received 30 June 1987; accepted 28 July 1987)

We report on vibrationally resolved measurements of photoelectron angular distributions and branching ratios for  $\text{NO}^+(2\pi^{-1})X^1\Sigma^+$  using synchrotron radiation over  $h\nu = 11.5\text{--}26$  eV. Normally weak vibrational levels are strongly enhanced below 18 eV, and the photoelectron asymmetry parameters and branching ratios display a vibrationally dependent, broad spectral structure over  $h\nu \cong 11\text{--}18$  eV. These observations may reflect the presence of the expected  $\sigma$  shape resonance, however, various interchannel coupling mechanisms may also be involved. Resonance structure in the photoelectron asymmetry parameters is also observed in the  $h\nu \cong 19\text{--}22$  eV region. This structure is likely associated with Rydberg excitations from the  $4\sigma$  orbital.

## I. INTRODUCTION

Several theoretical studies of the photoionization cross section and photoelectron angular distribution of the  $2\pi$  orbital of NO have predicted the presence of a shape resonance in the  $\sigma$  continuum channel.<sup>1-5</sup> The  $\sigma$  shape resonance is present in other photoionization channels of  $\text{NO}^{1,2,5-12}$  as well as in certain channels of several other first-row linear molecules.<sup>13-16</sup> Theoretical studies indicate that relatively intense, nonresonant  $\pi$  and  $\delta$  continuum channels may obscure the effects of the resonant  $\sigma$  channel in  $\text{NO } 2\pi^{-1}$  photoionization. In addition, the experimental search for the predicted  $\sigma$  shape resonance may be complicated by the presence of several autoionizing Rydberg series associated with the  $1\pi^{-1}$  and  $5\sigma^{-1}$  ionization thresholds.<sup>5,17-21</sup>

Previous experimental studies of  $\text{NO } 2\pi^{-1}$  photoionization obtained using the dipole ( $e,2e$ ) method<sup>7</sup> and synchrotron radiation<sup>8</sup> do not extend down to the region of  $h\nu \cong 14$  eV where recent theoretical calculations predict the  $\sigma$  shape resonance to be located.<sup>3-5</sup> Also, the previous measurements are vibrationally unresolved. It has been demonstrated in theoretical and experimental studies that a shape resonance can produce significant vibrational dependence in the partial photoionization cross section or branching ratios and in the photoelectron asymmetry parameters  $\beta$ .<sup>12,13,15,16,22</sup> These effects constitute a breakdown of the Franck-Condon approximation.

Removal of the antibonding  $2\pi$  electron from NO results in the  $\text{NO}^+ X^1\Sigma^+$  ionic state having an internuclear separation ( $R_e = 1.063$  Å) smaller than that of the ground state  $\text{NO } X^2\Pi$  ( $R_e = 1.151$  Å).<sup>23</sup> Consequently, several vibrational levels of  $\text{NO}^+ X^1\Sigma^+$  are observed in the photoelectron spectrum (PES), even for the case of nonresonant photoionization.<sup>24</sup> In addition, the  $2\pi^{-1}$  PES is well separated from the higher ionization bands.<sup>20,24</sup> These factors make

the  $\text{NO } 2\pi^{-1}$  PES a favorable system for studies of vibrational effects in resonant photoionization processes.

We have conducted a search for effects of the predicted  $\text{NO } 2\pi \rightarrow \epsilon\sigma$  shape resonance by recording vibrationally and angularly resolved PES over the range  $h\nu = 11.5\text{--}26$  eV. From these PES we have derived the vibrational branching ratios and asymmetry parameters  $\beta$ . As described fully below, we observe a broad, vibrationally dependent spectral structure in the branching ratios and  $\beta$  parameters over  $h\nu \cong 11\text{--}18$  eV. The normally very weak vibrational levels ( $v > 4$ ) are strongly enhanced at photon energies below 18 eV, while above approximately 18 eV we observe essentially Franck-Condon behavior in the vibrational intensities. These observations are suggestive of the presence of the expected  $\sigma$  shape resonance. However, other photoexcitation channels are also likely to affect the  $2\pi^{-1}$  photoelectron dynamics in this spectral region. These possible interchannel interaction mechanisms should also be considered in discussing the experimental results presented below.

Most notable is the presence of several Rydberg excitation series from the  $1\pi$  and  $5\sigma$  orbitals over the range  $h\nu \cong 12\text{--}18$  eV which have been identified in photoabsorption and photoionization spectra<sup>17-21</sup> and in fluorescence<sup>25</sup> and electron energy-loss<sup>26</sup> studies. Thus, the observed broad structure and the enhancement of weak vibrational levels may be due at least in part to unresolved autoionizing Rydberg excitations.

Based on calculated ground state orbital energies<sup>5</sup> we note that the  $4\sigma \rightarrow 2\pi$  valence excitation would also be expected to occur near  $h\nu \cong 14$  eV. This valence-like excited state would be expected to autoionize rapidly, producing a fairly broad spectral structure in the  $2\pi^{-1}$  photoelectron dynamical parameters. Such an autoionizing valence state has been proposed to explain broad, vibrationally dependent spectral structure in the  $\text{C}_2\text{H}_2$   $1\pi_u^{-1}$  photoionization cross section and  $\beta$  parameter.<sup>27-32</sup> Similarly, a proposed<sup>33</sup> doubly excited valence-like autoionizing state has been considered

<sup>a)</sup> Present address: National Bureau of Standards, Gaithersburg, MD 20899.

to produce broad spectral structure observed<sup>34,35</sup> in partial photoionization cross sections and photoelectron asymmetry parameters of N<sub>2</sub>.

Molecular autoionization processes can be further complicated by configuration mixing among the Rydberg and valence excited states having the same total symmetry.<sup>14,16,36</sup>

The actual states are likely to possess both Rydberg and valence character, with the configuration mixing coefficients dependent on internuclear separation. Clear evidence of a strongly mixed Rydberg–valence autoionizing state has been demonstrated in the case of O<sub>2</sub> 3σ<sub>g</sub><sup>-1</sup> photoionization in which broad, vibrationally dependent structure has been measured in the O<sub>2</sub><sup>+</sup> b 4Σ<sub>g</sub><sup>-</sup> partial photoionization cross section.<sup>37</sup> The present case of NO 2π<sup>-1</sup> photoionization may therefore be complicated by the presence of and interaction among at least three types of resonant channels: (1) the 2π → εσ shape resonance, (2) the 4σ → 2π valence excitation, and (3) the 1π and 5σ Rydberg excitations. Theoretical calculations are required to determine the relative importance of the various resonance processes suggested here.

An additional factor that could affect the NO 2π<sup>-1</sup> photoelectron dynamics is an interaction between ionization and neutral dissociation. The observation in N<sub>2</sub>O of an apparent link between the production of low energy photoelectrons and the production of fluorescence from the products of neutral dissociation led Guyon *et al.*<sup>38</sup> to propose a model of interacting ionization and dissociation processes. In this model a dissociative valence state is initially populated via a predissociated Rydberg excitation but leads to ionization either through direct autoionization or by coupling to other Rydberg states which subsequently autoionize. This model appears to explain the photoelectron energy distribution observed at certain wavelengths in N<sub>2</sub>O and has recently been proposed to explain similar observations in CO<sub>2</sub>.<sup>39</sup> The case of neutral dissociation interacting with vibrational autoionization in NO has also been treated theoretically.<sup>40</sup> With regard to the present experiment, we note that the quantum yield of ionization ranges between approximately 40%–90% over  $h\nu = 11$ –18 eV and passes through a broad minimum near 14 eV.<sup>18</sup> Assuming that molecular fluorescence is a negligible decay process, the ionization yield data suggest that neutral dissociation is competitive with ionization in this spectral region. Direct evidence of dissociation processes in this energy range has been given by excitation of fluorescence from atomic fragments.<sup>25</sup> The fluorescence measurements show that the 1π and 5σ Rydberg excitations are predissociated. The presence of both ionization and dissociation continua does not necessarily mean that there is a significant interaction in the present case. We mention it here as one more factor which could play a role in explaining the observations presented below.

In addition to the broad structure observed between 11–18 eV, we also report a broad, vibrationally dependent structure in the NO 2π<sup>-1</sup> β parameters between approximately 19–22 eV. This structure is likely associated with Rydberg excitations from the 4σ orbital which occur in this spectral region.<sup>41–43</sup> We note, though, that neutral dissociation,<sup>25,44</sup> dissociative ionization,<sup>7,45</sup> and ion-pair formation processes<sup>46</sup> also occur in this energy region.

## II. EXPERIMENT

The measurements were made using a high-resolution photoelectron spectrometer<sup>47</sup> on the 2 m normal-incidence beam line<sup>48</sup> at the Synchrotron Ultraviolet Radiation Facility (SURF) at the National Bureau of Standards. A photon beam bandwidth of 2.2 Å was used to record PES of NO 2π<sup>-1</sup> over  $h\nu = 11.5$ –26 eV at intervals of 0.25 eV. With this moderate wavelength resolution and point density, we expected to partially wash out sharp autoionization structure but retain broad structure arising from a shape resonance. The photon beam intensity was monitored using tungsten photodiodes, and the polarization of the photon beam was measured using triple-reflection analyzers to be typically 70%–75%.

Two hemispherical photoelectron analyzers (10.2 cm mean radius) were operated simultaneously at angles of 0° and 90° with respect to the major polarization axis of the photon beam. Branching ratios and asymmetry parameters were derived from the relative intensities of photoelectrons detected at the two angles. We have previously reported detailed descriptions of the photoelectron spectrometer<sup>47</sup> and of the procedures used for spectrometer calibration and data analysis.<sup>49</sup> The spectrometer calibration was based on an extensive set of measurements on the rare gases, for which the photoionization cross sections and photoelectron branching ratios and asymmetry parameters are known fairly well.

Commercially obtained gas cylinders of NO were used without further purification (99% purity quoted). Prior to recording measurements on NO, the spectrometer had been operated for several months using Ne, Ar, Kr, Xe, N<sub>2</sub>, and H<sub>2</sub> sample gases. The spectrometer calibration was stable over this period, based on regular calibration data sets using Ar. However, introduction of NO to the spectrometer caused an increase of approximately 0.26 eV in the observed kinetic energies of the photoelectron peaks. Both electron analyzers were affected in the same way, and the kinetic energy shifts remained when the NO was pumped out and Ar sample gas introduced. The shifts were apparently due to a change in surface potentials caused by absorption of NO in the collision region and/or the electron analyzers. After a day or two of running NO, the energy scale stabilized (to within 0.05 eV) at the shifted position. Shifting of the kinetic energy scale had the effect of slightly modifying the rare-gas-derived calibration functions for the two electron analyzers. The effects were accounted for in the analysis of the NO data. We note that a shifting kinetic energy scale could cause errors in results obtained using the techniques of constant-ionization-state PES or threshold PES.

As described previously,<sup>49</sup> studies were conducted to check for pressure dependent effects which can arise due to photoelectron scattering from the sample gases. Two sets of NO 2π<sup>-1</sup> PES were recorded over a range of photon energies at different sample pressures. The first data set was obtained at lower pressure (1 × 10<sup>-5</sup> Torr background pressure in the spectrometer chamber), and only the  $v = 0$ –4 vibrational levels were recorded. The second data set was obtained at higher sample gas pressure (3 × 10<sup>-5</sup> Torr background pressure), and a wider range of vibrational levels were recorded. The branching ratio and asymmetry parameter results for

the  $v = 0-4$  levels which were derived from the two data sets are in good agreement. This indicates that the results are free of significant pressure effects.

### III. RESULTS AND DISCUSSION

Figures 1 and 2 show the  $0^\circ$  and  $90^\circ$  PES of  $\text{NO } 2\pi^{-1}$  recorded at photon energies of 19.75 and 12.5 eV. The 19.75 eV PES shows the vibrational intensity distribution typically obtained in a nonresonant photoionization process where the vibrational intensities are well described by the Franck–Condon factors. In dramatic contrast, the 12.5 eV PES shows vibrational intensities strongly modified relative to the Franck–Condon picture. The normally weak vibrational levels ( $v > 4$ ) were observed to be strongly enhanced at photon energies below approximately 18 eV. Considerable intensity was observed for vibrational levels up to  $v = 13$ , which we arbitrarily chose as a limit for the accepted binding energy range in our PES. Still higher vibrational levels have been recorded in discrete-line-excitation PES.<sup>50</sup>

The  $0^\circ$  and  $90^\circ$  PES shown in Figs. 1 and 2 have been corrected for the relative collection efficiencies of the electron analyzers, and the curves drawn through the data points are the results of a fitting procedure. The vibrational branching ratios and asymmetry parameters were determined from the areas of the fitted peaks. Our branching ratio results are reported as the ratio of the particular vibrational intensity relative to the total band intensity. Thus, there is some error in the branching ratio results due to excluding

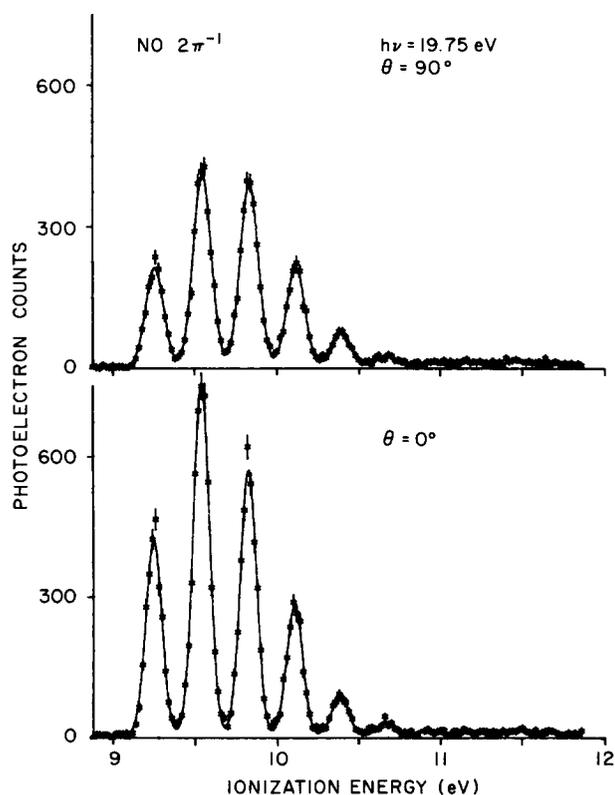


FIG. 1. The  $0^\circ$  and  $90^\circ$  photoelectron spectra of  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$  recorded at 19.75 eV photon energy.

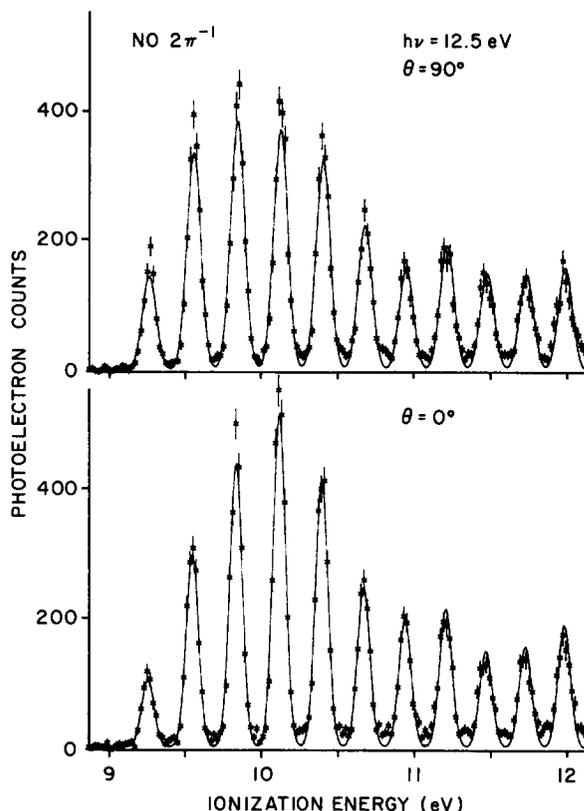


FIG. 2. The  $0^\circ$  and  $90^\circ$  photoelectron spectra of  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$  recorded at 12.5 eV photon energy.

$v > 13$  levels from the total band intensities. In addition, we have excluded vibrational levels recorded in the PES which have kinetic energies below 0.3 eV, because the relative collection efficiencies of the electron analyzers were not determined with sufficient accuracy at very low kinetic energy. We believe that these limitations do not significantly affect the main information derived from the results.

The  $\beta$  parameters and branching ratios for the  $v = 0-5$  levels are plotted in Figs. 3 and 4. Also plotted for reference in Fig. 3 is the fixed-nuclei theoretical curve from Ref. 3, which is more appropriately to be compared with the vibrationally averaged experimental results. The calculated Franck–Condon factors from Ref. 51 are shown with the branching ratio measurements in Fig. 4. The sum of the branching ratios for the  $v = 6-13$  levels is plotted in Fig. 5. And the vibrationally averaged  $\beta$  parameter results are plotted in Fig. 6 along with previous vibrationally unresolved data<sup>8</sup> and three theoretical curves.<sup>1,3,4</sup>

It is seen in Fig. 5 that the  $v > 5$  levels, which have negligible intensity in direct, Franck–Condon ionization, are strongly enhanced below 18 eV. Individual results for levels  $v > 5$  are not shown, however, they appear similar to the results shown for  $v = 5$  in Figs. 3 and 4. In particular, the  $\beta$  parameters for the  $v = 6$  and 7 levels also appear to display broad, deep minima near 21 eV. The  $v = 0-4$  levels also display an increasingly pronounced, broad feature in their  $\beta$  parameters in the 19–22 eV region. Correspondingly pronounced structure in this energy region is not apparent in the branching ratio measurements. This spectral structure is

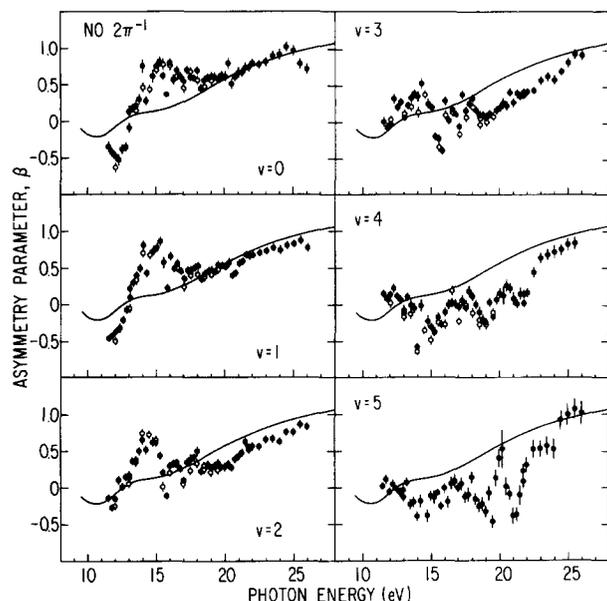


FIG. 3. The photoelectron asymmetry parameters for the  $v = 0-5$  vibrational levels of  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$ . Open circles: present results obtained at lower sample gas pressure; closed circles: present results obtained at higher pressure. The same fixed-nuclei theoretical curve from Ref. 3 is shown for all the levels.

likely associated with Rydberg excitations from the  $4\sigma$  orbital which have been observed in photoabsorption spectra.<sup>41-43</sup> It would be expected that more pronounced resonance features would be observed for the  $v > 4$  levels, because weak final states are more sensitive to interchannel interactions. However, while the  $v = 0$  and 3 levels have comparable intensities, the  $v = 3$  level displays a suppression of  $\beta$  above approximately 19 eV, while the  $v = 0$  level does not. This indicates that the resonance effect depends on internu-

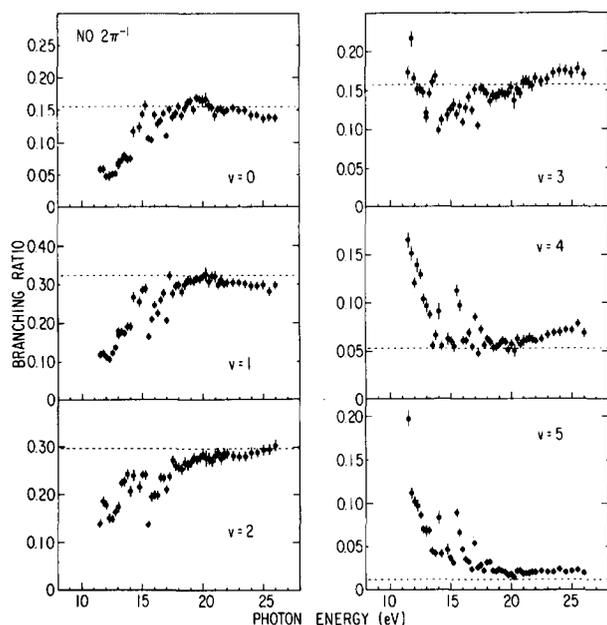


FIG. 4. The vibrational branching ratios for the  $v = 0-5$  levels of  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$ . The dashed lines are the calculated Franck-Condon factors from Ref. 51.

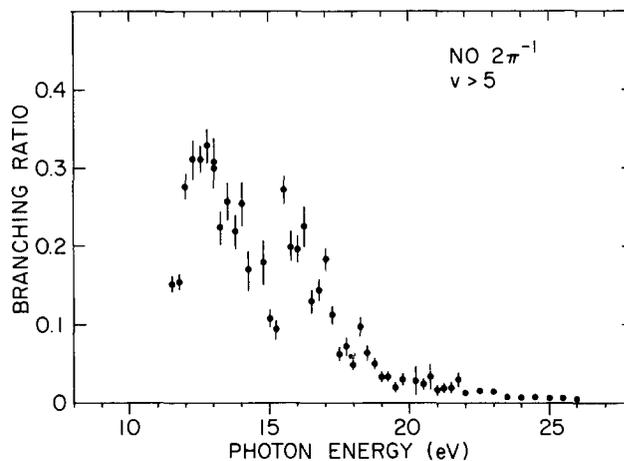


FIG. 5. The summed vibrational branching ratio for the levels  $v = 6-13$  of  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$ .

clear separation. In this regard, we note that the thresholds for the ion fragmentation channels  $\text{N} + \text{O}^+$  (20.124 eV) and  $\text{N}^+ + \text{O}$  (21.04 eV) occur in this energy region.<sup>45</sup> Ion-pair formation  $\text{N}^+ + \text{O}^-$  is also observed.<sup>46</sup> And fluorescence from atomic fragments shows that the  $4\sigma$  Rydberg excitations decay in part by neutral dissociation.<sup>25,44</sup> Therefore, the resonance effects observed in this energy region may be of a complex, multichannel nature which includes various ionization and dissociation pathways which may interact to a significant degree.

Returning to the results for  $h\nu < 18$  eV, it is seen that the  $v = 0-5$  levels display an apparently broad structure in their  $\beta$ s and branching ratios which is  $v$  dependent. With the exception of the features in  $\beta$  over 19–22 eV discussed above, there is essentially Franck-Condon behavior above approximately 18 eV. That is, the branching ratios are close to the Franck-Condon factors and the  $\beta$  values are similar and slowly varying. The vibrationally averaged asymmetry parameter, plotted in Fig. 6, also shows a broad maximum

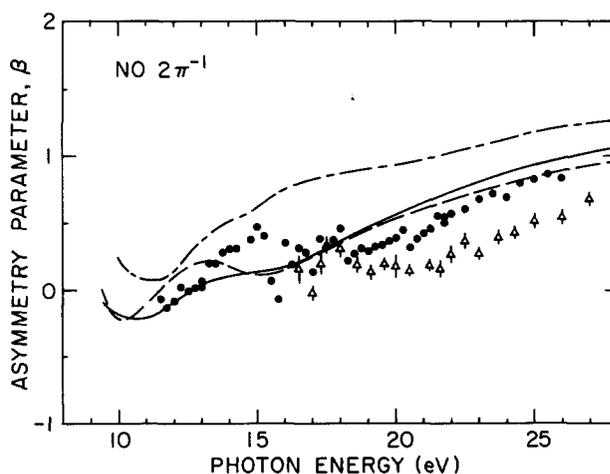


FIG. 6. The photoelectron asymmetry parameter for  $\text{NO}^+ (2\pi^{-1}) X^1\Sigma^+$ . Closed circles: present vibrationally averaged results; open triangles: vibrationally unresolved results from Ref. 8; solid curve: fixed-nuclei calculation from Ref. 3; dashed curve: fixed-nuclei calculation from Ref. 4; chain-dashed curve: vibrationally averaged calculation from Ref. 1.

between 13–17 eV in qualitative agreement with fixed-nuclei theoretical calculations.<sup>3,4</sup> These calculations include the effect of the  $\sigma$  shape resonance but do not include interchannel interactions. We have no explanation for the shift in absolute magnitude between the present results and earlier, vibrationally unresolved  $\beta$  measurements.<sup>8</sup> The present results are in better agreement with recent calculations above 18 eV, the region of apparently nonresonant photoionization.

The broad, vibrationally dependent structure observed below 18 eV is supportive of the presence of the predicted  $\sigma$  shape resonance. As discussed earlier, however, autoionizing Rydberg and valence excitations are likely to also play a role. Some sharp structure is apparent in the data, indicating the presence of Rydberg excitations. No attempt was made in the present measurements to either hit or miss prominent Rydberg excitations which are known from photoabsorption and photoionization studies. Autoionizing Rydberg states excited from valence orbitals generally produce relatively narrow ( $<0.1$  eV) resonance structures, however, several closely spaced or overlapping series of resonances can occur for a given ionization threshold, due to alternative angular momentum and vibrational quantum numbers of the Rydberg levels. An additional complexity arises in the present case where the open-shell structure of NO results in seven electronic ionization thresholds based on the  $1\pi^{-1}$  and  $5\sigma^{-1}$  configurations in the range  $h\nu \cong 15.5$ – $19.5$  eV.<sup>20,24</sup> The presence of these many ionic states with their associated vibrational structure results in several closely spaced or overlapping Rydberg series over the energy range  $h\nu \cong 12$ – $18$  eV.<sup>17–21</sup> These numerous, unresolved Rydberg excitations conceivably could contribute to the apparently broad spectral features observed in the present PES measurements, considering our limited wavelength resolution and point density.

Several early studies of NO  $2\pi^{-1}$  PES obtained using discrete-line-excitation sources also revealed dramatic non-Franck–Condon vibrational intensity distributions.<sup>50,52</sup> These early observations of non-Franck–Condon effects were attributed to electronic autoionization, and theoretical models were developed<sup>53</sup> based on the configuration-interaction formalism.<sup>54</sup> In this model, the partial cross section for producing a particular vibrational level of the ion can, in certain cases, be expressed in terms of Franck–Condon overlap integrals among the neutral ground state, the Rydberg state, and the ionic state.<sup>55</sup> One result of this model was the explanation of multiple maxima appearing in the photoelectron vibrational intensity distributions to be a reflection of the multiple maxima which occur in the probability distribution over internuclear distance  $R$  of vibrationally excited Rydberg states.<sup>50,53</sup> Some of the presently recorded PES do display multiple maxima in the vibrational intensity distributions, thus suggesting a contribution from electronic autoionization. We note in addition, however, that the model calculation of Guyon *et al.*<sup>38</sup> of an autoionizing dissociative state also resulted in multiple maxima in the photoelectron vibrational distribution. In the present case of NO in the  $h\nu \cong 11$ – $18$  eV region, photoionization yield measurements<sup>18</sup> and fluorescence from atomic fragments<sup>25</sup> indicate that dissociation is a prominent decay mode. Thus, the possi-

bility exists of an interaction between dissociation and ionization.

#### IV. CONCLUSIONS

The purpose of the present study was to search for broad structure arising from a shape resonance, and this was apparently observed. However, interchannel interactions involving Rydberg and valence excitations are also likely to play a role and interaction with dissociative channels is also a possible factor. Additional photoelectron measurements made at high spectral resolution may help address these issues. On the theoretical side, it would be useful at this point to compare the vibrationally resolved data of Figs. 3 and 4 with corresponding  $v$ -dependent calculations obtained at the independent electron level to see if the  $\sigma$  shape resonance can account for the observed broad structure. Such calculations are underway.<sup>56,57</sup> Beyond that, theoretical studies would also be required to test the suggestions of more complex resonance phenomena involving interchannel interactions, including dissociative channels. In fact, Lynch *et al.*<sup>57</sup> have calculated the effects of autoionizing valence and Rydberg excitations and have found them to be highly significant.

#### ACKNOWLEDGMENTS

We are grateful to the staff at SURF for their cooperation during the course of this work. We thank T. J. Gil, P. W. Langhoff, M. E. Smith, D. L. Lynch, and V. McKoy for helpful correspondence and discussions. This work was supported in part by the U. S. Department of Energy, Office of Health and Environmental Research, under Contract No. W-31-109-Eng-38.

- <sup>1</sup>S. Wallace, D. Dill, and J. L. Dehmer, *J. Chem. Phys.* **76**, 1217 (1982).
- <sup>2</sup>J. J. Delaney, I. H. Hillier, and V. R. Saunders, *J. Phys.* **B 15**, 1477 (1982).
- <sup>3</sup>M. E. Smith, R. R. Lucchese, and V. McKoy, *J. Chem. Phys.* **79**, 1360 (1983).
- <sup>4</sup>L. A. Collins and B. I. Schneider, *Phys. Rev. A* **29**, 1695 (1984).
- <sup>5</sup>M. R. Hermann, C. W. Bauschlicher, W. M. Huo, S. R. Langhoff, and P. W. Langhoff, *Chem. Phys.* **109**, 1 (1986).
- <sup>6</sup>T. Gustafsson and H. J. Levinson, *Chem. Phys. Lett.* **78**, 28 (1981).
- <sup>7</sup>(a) C. E. Brion and K. H. Tan, *J. Electron Spectrosc. Relat. Phenom.* **23**, 1 (1981); (b) Y. Iida, F. Carnovale, S. Daviel, and C. E. Brion, *Chem. Phys.* **105**, 211 (1986).
- <sup>8</sup>S. Southworth, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, W. D. Brewer, and D. A. Shirley, *J. Chem. Phys.* **76**, 143 (1982).
- <sup>9</sup>M. E. Smith, V. McKoy, and R. R. Lucchese, *J. Chem. Phys.* **82**, 4147 (1985).
- <sup>10</sup>P. Morin, in *Photophysics and Photochemistry above 6 eV*, edited by F. Lahmani (Elsevier, Amsterdam, 1985), p. 1.
- <sup>11</sup>M. R. Hermann, S. R. Langhoff, and P. W. Langhoff, *Chem. Phys. Lett.* **109**, 150 (1984).
- <sup>12</sup>M. R. Hermann, S. R. Langhoff, T. J. Gil, and P. W. Langhoff, *Chem. Phys. Lett.* **125**, 336 (1986).
- <sup>13</sup>V. McKoy, T. A. Carlson, and R. R. Lucchese, *J. Phys. Chem.* **88**, 3188 (1984).
- <sup>14</sup>(a) P. W. Langhoff, T. N. Rescigno, N. Padias, G. Csanak, and B. V. McKoy, *J. Chim. Phys.* **77**, 589 (1980); (b) P. W. Langhoff, in *Resonances in Electron–Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics*, edited by D. G. Truhlar (American Chemical Society, Washington, D.C., 1984), p. 113.
- <sup>15</sup>(a) J. L. Dehmer, D. Dill, and A. C. Parr, in *Photophysics and Photochemistry in the Vacuum Ultraviolet*, edited by S. McGlynn, G. Findley, and R. Huebner (Reidel, Dordrecht, 1985), p. 341; (b) J. L. Dehmer, A. C. Parr,

- and S. H. Southworth, in *Handbook on Synchrotron Radiation*, edited by G. V. Marr (North-Holland, Amsterdam, 1987), Vol. II.
- <sup>16</sup>(a) P. M. Guyon and I. Nenner, *Appl. Opt.* **19**, 4068 (1980); (b) I. Nenner and J. A. Beswick, in *Handbook on Synchrotron Radiation*, edited by G. V. Marr (North-Holland, Amsterdam, 1987), Vol. II.
- <sup>17</sup>R. M. Reese and H. M. Rosenstock, *J. Chem. Phys.* **44**, 2007 (1966).
- <sup>18</sup>K. Watanabe, F. M. Matsunaga, and H. Sakai, *Appl. Opt.* **6**, 391 (1967). The results of Watanabe *et al.* are shown plotted in figures in J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy* (Academic, New York, 1979), pp. 111–115.
- <sup>19</sup>H. Metzger, G. R. Cook, and M. Ogawa, *Can. J. Phys.* **45**, 203 (1967).
- <sup>20</sup>O. Edqvist, E. Lindholm, L. E. Selin, H. Sjögren, and L. Åsbrink, *Ark. Fys.* **40**, 439 (1970).
- <sup>21</sup>(a) S. Takezawa, *J. Mol. Spectrosc.* **66**, 121 (1977).
- <sup>22</sup>J. L. Dehmer, D. Dill, and S. Wallace, *Phys. Rev. Lett.* **43**, 1005 (1979).
- <sup>23</sup>D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, *J. Chem. Phys.* **71**, 3271 (1979).
- <sup>24</sup>(a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, London, 1970); (b) O. Edqvist, L. Åsbrink, and E. Lindholm, *Z. Naturforsch. Teil A* **26**, 1407 (1971).
- <sup>25</sup>H. Schmoranzler and R. Zietz, Abstracts of Papers, 10th International Conference on the Physics of Electronic and Atomic Collisions, 1977, p. 104.
- <sup>26</sup>R. J. Stubbs, T. A. York, and J. Comer, *Chem. Phys.* **106**, 161 (1986).
- <sup>27</sup>R. Unwin, I. Khan, N. V. Richardson, A. M. Bradshaw, L. S. Cederbaum, and W. Domcke, *Chem. Phys. Lett.* **77**, 242 (1981).
- <sup>28</sup>P. W. Langhoff, B. V. McKoy, R. Unwin, and A. M. Bradshaw, *Chem. Phys. Lett.* **83**, 270 (1981).
- <sup>29</sup>P. R. Keller, D. Mehaffy, J. W. Taylor, F. A. Grimm, and T. A. Carlson, *J. Electron Spectrosc. Relat. Phenom.* **27**, 223 (1982).
- <sup>30</sup>A. C. Parr, D. L. Ederer, J. B. West, D. M. P. Holland, and J. L. Dehmer, *J. Chem. Phys.* **76**, 4349 (1982).
- <sup>31</sup>Z. H. Levine and P. Soven, *Phys. Rev. Lett.* **50**, 2074 (1983).
- <sup>32</sup>D. Lynch, M.-T. Lee, R. R. Lucchese, and V. McKoy, *J. Chem. Phys.* **80**, 1907 (1984).
- <sup>33</sup>G. Wendin, *Int. J. Quantum Chem. Symp.* **13**, 659 (1979).
- <sup>34</sup>S. H. Southworth, A. C. Parr, J. E. Hardis, and J. L. Dehmer, *Phys. Rev. A* **33**, 1020 (1986), and references cited therein.
- <sup>35</sup>E. D. Poliakoff, M. H. Ho, G. E. Leroi, and M. G. White, *J. Chem. Phys.* **84**, 4779 (1986).
- <sup>36</sup>R. S. Mulliken, *Acc. Chem. Res.* **9**, 7 (1976).
- <sup>37</sup>P. Morin, I. Nenner, M. Y. Adam, M. J. Hubin-Franskin, J. Delwiche, H. Lefebvre-Brion, and A. Giusti-Suzor, *Chem. Phys. Lett.* **92**, 609 (1982).
- <sup>38</sup>P. M. Guyon, T. Baer, and I. Nenner, *J. Chem. Phys.* **78**, 3665 (1983).
- <sup>39</sup>T. Baer and P. M. Guyon, *J. Chem. Phys.* **85**, 4765 (1986).
- <sup>40</sup>A. Giusti-Suzor and Ch. Jungen, *J. Chem. Phys.* **80**, 986 (1984).
- <sup>41</sup>B. Narayana and W. C. Price, *J. Phys. B* **5**, 1784 (1972).
- <sup>42</sup>A. Gardner, M. Lynch, D. T. Stewart, and W. S. Watson, *J. Phys. B* **6**, L262 (1973).
- <sup>43</sup>M. Sasanuma, Y. Morioka, E. Ishiguro, and M. Nakamura, *J. Chem. Phys.* **60**, 327 (1974).
- <sup>44</sup>H. Hertz, H. W. Jochims, H. Schenk, and W. Sroka, *Chem. Phys. Lett.* **29**, 572 (1974).
- <sup>45</sup>J. A. R. Samson, T. Masuoka, and P. N. Pareek, *J. Chem. Phys.* **83**, 5531 (1985).
- <sup>46</sup>H. Oertel, H. Schenk, and H. Baumgärtel, *Chem. Phys.* **46**, 251 (1980).
- <sup>47</sup>A. C. Parr, S. H. Southworth, J. L. Dehmer, and D. M. P. Holland, *Nucl. Instrum. Methods* **222**, 221 (1984).
- <sup>48</sup>D. L. Ederer, B. E. Cole, and J. B. West, *Nucl. Instrum. Methods* **172**, 185 (1980).
- <sup>49</sup>S. H. Southworth, A. C. Parr, J. E. Hardis, J. L. Dehmer, and D. M. P. Holland, *Nucl. Instrum. Methods A* **246**, 782 (1986).
- <sup>50</sup>(a) P. Natalis, J. Delwiche, J. E. Collin, G. Caprace, and M. T. Praet, *Chem. Phys. Lett.* **49**, 177 (1977); (b) *Phys. Scr.* **16**, 242 (1977).
- <sup>51</sup>M. E. Wacks, *J. Chem. Phys.* **41**, 930 (1964).
- <sup>52</sup>(a) V. I. Kleimenov, Yu. V. Chizhov, and F. I. Vilesov, *Opt. Spectrosc. (USSR)* **32**, 371 (1972); (b) J. L. Gardner and J. A. R. Samson, *J. Electron Spectrosc. Relat. Phenom.* **2**, 153 (1973).
- <sup>53</sup>A. L. Smith, *Philos. Trans. R. Soc. London Ser. A* **268**, 169 (1970).
- <sup>54</sup>U. Fano, *Phys. Rev.* **124**, 1866 (1961).
- <sup>55</sup>For reviews see Refs. 16 and J. H. D. Eland, *J. Chim. Phys.* **77**, 613 (1980).
- <sup>56</sup>T. J. Gil and P. W. Langhoff (unpublished).
- <sup>57</sup>D. L. Lynch, B. I. Schneider, L. A. Collins, B. V. McKoy, and W. Huo (unpublished).