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PHOTOELECTRON SPECTROSCOPY OF NO**

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ABSTRACT

Photoelectron energy and angular distributions of NO following three different high-order multiphoton ionization (MPI) schemes have been measured. The 3+3 resonantly enhanced multiphoton ionization (REMPI) via the $A^2\Sigma^+$ ($v=0$) level yielded a distribution of electron energies corresponding to all accessible vibrational levels ($v^+=0-6$) of the nascent ion. Angular distributions of electrons corresponding to $v^+=0$ and $v^+=3$ were significantly different. The 3+2 REMPI via the $A^2\Sigma^+$ ($v=1$) level produced only one low-energy electron peak ($v^+=1$). Nonresonant MPI at 532 nm yielded a distribution of electron energies corresponding to both four- and five-photon ionization. Prominent peaks in the five-photon photoelectron spectrum (PES) suggest contributions from near-resonant states at the three-photon level.

INTRODUCTION

REMPI-PES has become an established tool for probing the photoionization dynamics of atoms and molecules.¹ In particular, measurements of photoelectron angular distributions (PEAD) in a REMPI process can, in principle, provide information about both the dynamics of the bound-continuum transition and the alignment of an optically-prepared intermediate state.^{2a,b,c} Of the molecular systems studied thus far, NO has received the most attention due to its low ionization potential and well-characterized spectroscopy. For details and references to previous REMPI-PES studies of NO and other systems, the reader is referred to a recent review by Compton and Miller.¹ To date, the $A^2\Sigma^+$ state has been probed by either 2+2 or 1+1 REMPI processes, with few PEAD measurements. In this paper we describe PES and PEAD measurements for 3+3 and 3+2 REMPI via the $A^2\Sigma^+$ ($v=0$) and ($v=1$) levels, respectively. In addition, we have measured the PES for nonresonant MPI of NO at 532 nm. The apparatus has been described in detail elsewhere³ and will not be described here.

RESULTS AND DISCUSSION

The spectra of the 3+3 $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) and 3+2 $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,1) bands were measured by monitoring the mass-selected NO^+ ion intensity as the laser wavelength was scanned. Both spectra lacked resolved rotational structure and appeared as broad, shifted resonances, indicative of a.c. Stark effects due to the high laser power necessary to affect six- and five-photon ionization. As a result, no rotational state selection was possible and PES and PEAD were

measured at arbitrary wavelengths within the resonances where optimum signals were obtained.

Figure 1 shows a representative PES obtained for the 3+3 process at 676.2 nm. Other wavelengths within the resonance produced similar spectra, although peak height ratios varied (especially $v^+=2,4$). Due to the Rydberg character of the $A^2\Sigma^+$ state, the Franck-Condon principle predicts that direct ionization of the $v=0$ level would produce only the $v^+=0$ level of the ion. The appearance of higher v^+ levels thus suggests additional ionization mechanisms, as discussed previously¹ for 2+2 and 1+1 processes. In the present case, possible mixing of states at the fourth- and fifth-photon levels might complicate the dynamics further.

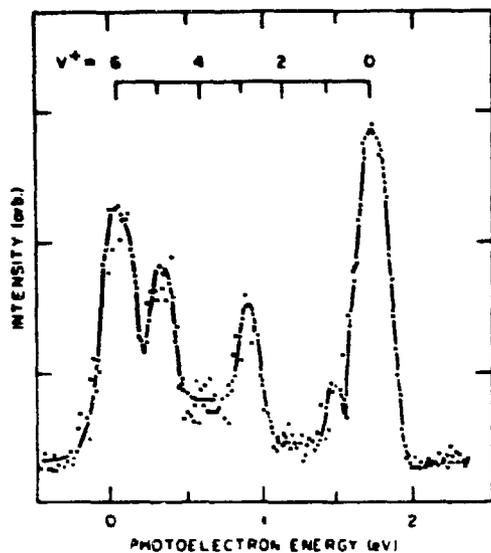


Fig. 1. 3+3 PES

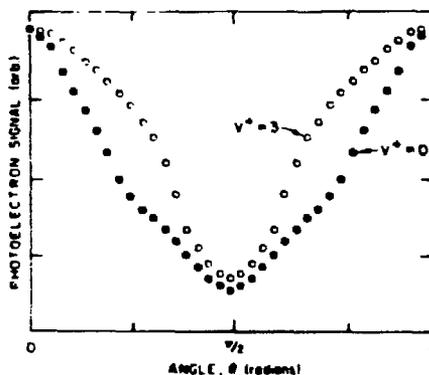


Fig. 2. 3+3 PEAD's

PEAD's measured for electrons corresponding to $v^+=0$ and 3 are shown in Fig. 2. Both distributions were fit, using a least-squares procedure, to a Legendre polynomial expansion^{2a}

$$I(\theta) = \sum_{k=0}^N a_{2k} P_{2k}(\cos\theta),$$

where N is the order of the ionization process. It was found that terms up to $P_5(\cos\theta)$ were necessary to fit the data within experimental error:

$$v^+ = 0 : I(\theta) = 1 + 1.23(1)P_2 + 0.16(2)P_4 + 0.22(2)P_6$$

$$v^+ = 3 : I(\theta) = 1 + 1.07(1)P_2 - 0.34(1)P_4 + 0.13(1)P_6,$$

where uncertainties of the fit are shown in parentheses. This contrasts with recent 1+1 PEAD measurements of the $A^2\Sigma^+$ ($v=0$) level⁴ for which the data were fit by including only the P_2 term. The most dramatic difference between the distributions above is in the sign of the P_4 coefficients. Further theoretical

work is necessary, however, to determine if this difference might lead to better understanding of the ionization mechanisms involved.

The 3+2 REMPI of the $A^2\Sigma^+$ ($v=1$) level at 644.1 nm produced only one electron peak, corresponding to $v^+=1$, indicating direct ionization of this level. In this case, however, the fifth photon energy is only slightly above the $v^+=1$ threshold and channels leading to higher vibrational levels of the ion are not accessible. In order to fit the PEAD, it was necessary to include terms up to P_4 :

$$I(\theta) = 1 + 1.54(2)P_2 + 0.32(2)P_4.$$

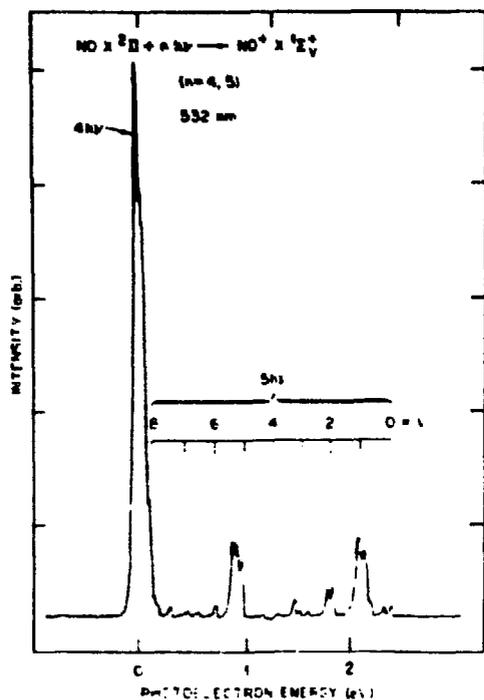


Fig. 3. 532 nm PES

The PES resulting from nonresonant MPI at 532 nm is shown in Fig. 3. Four photons are sufficient to ionize NO at this wavelength (0.06 eV above the $v^+=0$ threshold), and a very intense low energy electron peak is seen in the PES.

In addition, however, several weaker peaks are observed at energies consistent with absorption of five photons, leaving the ion predominantly in the $v^+=1$, 2, and 5 vibrational levels. It is interesting to note that the third photon energy is within $\sim 800 \text{ cm}^{-1}$ of the $A^2\Sigma^+$ ($v=5$), $C^2\Pi$ ($v=2$), and $D^2\Sigma^+$ ($v=1$) levels of NO. The five-photon PES might be reflecting the contributions of these "near-resonant" intermediate states. Experiments are currently in progress to measure the PEAD's of these electrons. More extensive measurements of PEAD's for various $n+1$ REMPI processes are also planned for the future.

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