Rotational-resolved pulsed field ionization photoelectron study of $NO^+(A'^1\Sigma^-, v^+ = 0\text{-}17)$ in the energy range of 17.70-20.10 eV

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INTRODUCTION

We have obtained rotationally resolved pulsed field ionization-photoelectron (PFI-PE) spectra of NO in the energy range of 17.79-20.04 eV, covering ionization transitions of $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17, J^+) \leftarrow NO\ (X^2\Pi_{3/2,1/2}, v''=0, J'')$. The PFI-PE bands for $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17)$ obtained here represent the first rotationally resolved spectroscopic data for these states. As in previous studies, the PFI-PE bands are simulated using the Buckingham-Orr-Sichel model as an empirical scheme to derive reliable spectroscopic constants. The simulation also allows the identification of local intensity enhancements of rotational transitions for several vibrational bands, which can be attributed to the perturbation of nearby autoionizing Rydberg states. Based on the simulation, accurate spectroscopic constants for $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17)$ are obtained, including ionization energies, vibrational constants and rotational constants. In general, the total angular momentum transfer values $\Delta J = \pm1/2, \pm3/2, \pm5/2, \pm7/2$ and $+9/2$ are found in all the PFI-PE vibrational bands for $NO^+(A'^1\Sigma^-)$, indicating that continuum photoelectron states with orbital angular momenta l =0, 1, 2, 3, 4 and 5 are produced in the threshold photoionization of NO ($X^2\Pi_{3/2,1/2}$) to form $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17)$.

EXPERIMENT

The beamline consists of a 10 cm period undulator, a gas harmonic filter, a 6.65m off-plane Eagle monochromator, and a photoion-photoelectron apparatus, all of which has been discussed in detail previously. In the present experiment, He is used in the harmonic gas filter to suppress the higher undulator harmonics. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by either a 2400 lines/mm (dispersion = 0.32 Å/mm) before entering the experimental apparatus.

The NO sample was introduced as an effusive beam through a metal orifice with a diameter of 0.5 mm at room temperature and a distance of 0.5 cm from the photoionization/photoexcitation (PI/PEX) region. We estimate that the NO density in the PI/PEX region is $\approx 10^{-3}$ Torr and that the rotational temperature for the NO sample is 298 K.

The synchrotron based PFI-PE measurements were achieved by employing the electron TOF scheme and have been described in detail previously.[1] In the present experiment, a nominally zero electrostatic dc field was maintained across the PI/PEX region prior to the application of a pulsed electric field (height = 1.2 V/cm, width = 40 ns) to the repeller plate on the electron spectrometer side of the PI/PEX region. The pulsed electric field was applied with a period identical to the synchrotron ring period of 656 ns (or frequency of 1.53 MHz) and a delay corresponding to 20 ns after the beginning of the 80-ns dark gap. Then a 10 ns collection gate opens for the PFI-PE detection. Spectra were flux normalized using the photon signal obtained at a tungsten detector positioned behind the PI/PEX region intercepting the monochromatized VUV beam. The absolute photon energy scale was calibrated using the $Ar^+(^2P_{3/2})$, and $Ne^+(^2P_{3/2})$ PFI-PE bands recorded under the same experimental conditions before and after each scan. On the basis of previous experiments, the accuracy of the energy calibration is believed to be within ±0.5 meV.

RESULTS AND DISCUSSION

The ground NO ($X^2\Pi$) state has the main electronic configuration $(1\sigma)^2(2\sigma^*)^2(3\sigma)^2(4\sigma^*)(1\pi)^4(5\sigma)^2(2\pi^*)^1$, with an unpaired electron residing in the anti-bonding $2\pi^*$ orbital. Including the spin-orbit interaction, the ground NO state becomes the $X^2\Pi_{1/2}$ state. The excited $^2\Pi_{3/2}$ spin-orbit state is known to locate 123.35 cm^{-1} above the ground $X^2\Pi_{1/2}$ state. The removal of one electron from the 1π bonding orbital results in the formation of either $a^3\Sigma^+$ or $A'^1\Sigma^-$ state, depending on the spin of the remaining electron in the 1π orbital.

A. Relative PFI-PE vibrational band intensities for $NO^+(A'^1\Sigma^-, v^+ = 0\text{-}17)$

Figures 1(a) and 1(b) shows the relative intensities of the PFI-PE bands for $NO^+(A'^1\Sigma^-, v^+ = 0\text{-}17)$ in the energy ranges of 17.70-18.80 and 18.58-20.10 eV, respectively. The positions of the $NO^+(A'^1\Sigma^-, v^+=0\text{-}17)$ vibrational bands are marked in the figures, along with the positions of vibrational bands for the $NO^+(b^3\Pi, w^3\Delta, b'^3\Sigma^-, W^1\Delta$ and $A^1\Pi)$ electronic states. As can be seen from Fig. 1, $NO^+(A'^1\Sigma^-, v^+=0\text{-}17)$ coexists with many vibronic states for this entire energy range. Extensive overlaps among two or more vibrational bands that belong to different electronic states are a dominant feature in the energy range of 15.6 - 20.1 eV for the PFI-PE spectra of NO.

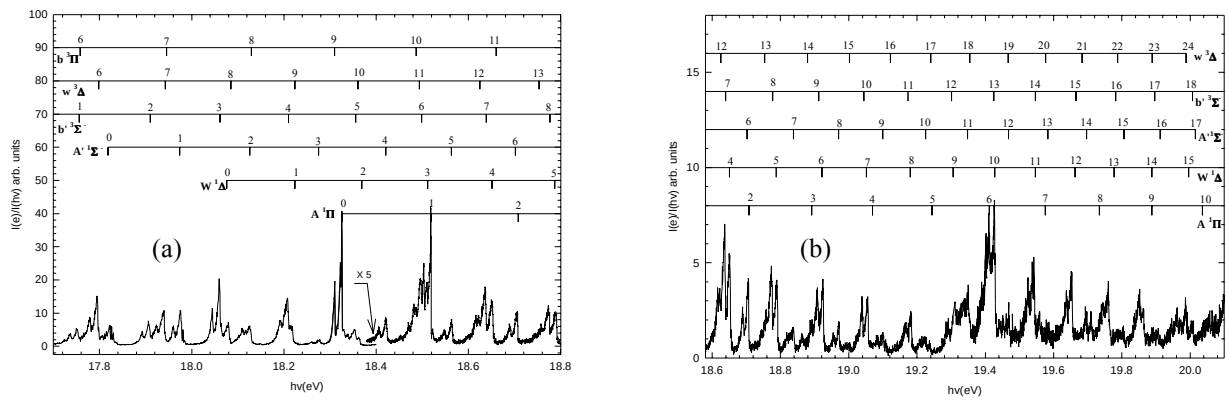

Figure 1. PFI-PE spectrum of NO in the range (a) 17.75–18.80 and (b) 18.58-20.10 eV showing the relative intensities for the $NO^+(A'^1\Sigma^-, v^+=0\text{-}17)$ states. Also marked in the figure are vibrational states for the $NO^+(b^3\Pi, w^3\Delta, b'^3\Sigma^-, W^1\Delta$ and $A^1\Pi$) electronic states.

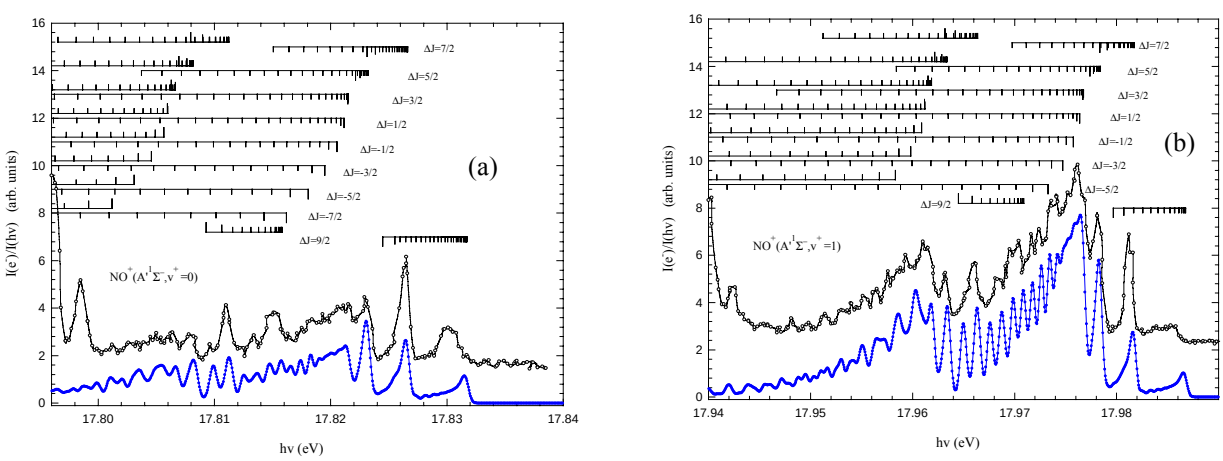

Figure 2. Comparison of experimental (○) and simulated (●) PFI-PE spectra for $NO^+(A'^1\Sigma^-)$: (a) $v^+ = 0$ and (b) $v^+=1$. All spectra were measured at a nominal wavelength resolution of 0.035 Å (FWHM). The positions of the rotational transitions for $NO(X^2\Pi_{1/2}) \rightarrow NO^+(A'^1\Sigma^-)$and $NO(X\ ^2\Pi_{3/2}) \rightarrow NO^+(A'^1\Sigma^-)$ are also shown as up-pointing and down-pointing lines, respectively. In each ΔJ case shown, the positions of the first and second transitions (e.g. $J^+ = 0 - J'' = 1/2$ and $J^+ = 1 - J'' = 3/2$ for $\Delta J = -1/2$) are indicated by progressively shorter lines.

B. Spectral simulation of rotational transition intensities

The relative intensities for rotational structures observed in individual vibrational bands for $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17)$ were simulated using the BOS model, which was described in detail previously. The simulated spectra (lower spectra, solid circles) are selectively depicted along with the experimental PFI-PE bands (upper spectra, open circles) for $NO^+(A'\ ^1\Sigma^-, v^+ = 0$ and 1) in Figs. 2(a) and 2(b), respectively. The rotational temperature used for NO in the simulated spectra was 298 K. The positions of the rotational transitions for ionization transitions $NO^+(A'\ ^1\Sigma^-, v^+, J^+) \leftarrow NO\ (X^2\Pi_{1/2}, v''=0, J'')$ and $NO^+(A'\ ^1\Sigma^-, v^+, J^+) \leftarrow NO\ (X^2\Pi_{3/2}, v''=0, J'')$ are marked as up-pointing and down-pointing lines, respectively, in these figures.

The rotational structures observed in the v^+=0-17 PFI-PE bands can be accounted for by BOS coefficients C_λ (λ=1-4), indicating that the angular momentum states for the photoelectron can be l =0, 1, 2, 3, 4 and 5 and the rotational branches contributed to the spectra are $\Delta J = \pm 1/2$, $\pm 3/2$, $\pm 5/2$, $\pm 7/2$, $\pm 9/2$ and $\pm 11/2$. The total angular transfer values $\Delta J = \pm 11/2$ contribute to the overall simulations negligibly and the intensity for ΔJ = -9/2 branch is significantly weaker than that of its counterpart ΔJ = 9/2 for all the simulations. In our previous PFI-PE studies of $NO^+(X^1\Sigma^+)$ and $NO^+(a^3\Sigma^+)$,[2,3] an increase in the angular momentum exchanged between the photoelectron and the ion core was observed as v^+ increases. The observed intensity increases for higher ΔJ values as a function of v^+ may reflect the increase in inelastic cross sections for higher angular momentum transfers in electron-molecular ion core collisions resulting from the greater bond distances of NO^+ in higher v^+ states. However, the consistent observation of ΔJ = +9/2 branch in all vibrational bands for $NO^+(A'\ ^1\Sigma^-)$ indicates that there is a less sensitive correlation between the maximum ΔJ values and the v^+ values or the internuclear distances. This different behavior might arise from the fact that the $NO^+(X^1\Sigma^+)$ and $NO^+(a^3\Sigma^+)$ states converge to the first dissociation limit of $N(^4S^0)+O^+(^4S^0)$, while the $NO^+(A'\ ^1\Sigma^-)$ correlates to the second dissociation limit of $N^+(^4P)+O(^3P)$.

Generally, excellent agreements between the simulated and experimental data are obtained for the $NO^+(A'^1\Sigma^-, v^+$=0-17) PFI-PE bands. However, for the $NO^+(A'^1\Sigma^-, v^+$=0 and 1) PFI-PE bands [Fig. 2(a) and (b)], a large perturbation is observed at 17.826 eV and 17.981 eV respectively. These perturbations are most likely caused by the presence of low-n Rydberg interloper states.

C. Ionization energies and rotational constants

Based on BOS simulation, accurate ionization energies and rotational constants for $NO^+(A'\ ^1\Sigma^-, v^+ = 0\text{-}17)$ are directly determined for the first time. Dunham expansion on these values gives vibrational constants (ω_e=1272.03±1.45 cm^{-1}, $\omega_e\chi_e$=11.924± 0.188 cm^{-1}, and $\omega_e y_e$=-0.059±0.007 cm^{-1}) and rotational constants [B_e=1.3562±0.0024 cm^{-1}, α_e = 0.01780±0.00061 cm^{-1}, and γ_e = -(1.574 ±0.328) x10^{-4} cm^{-1}].

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