

Rotationally Resolved Pulsed Field Ionization Photoelectron Spectroscopy Study of $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$ and $\text{O}_2^+(\text{X}^2\Pi_g, v^+=0-38)$

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INTRODUCTION

Using third generation multi-bunch undulator synchrotron radiation at the Chemical Dynamics Beamline of ALS, we have obtained rotationally resolved pulsed field ionization photoelectron (PFI-PE) spectra of $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$ and $\text{O}_2^+(\text{X}^2\Pi_g, v^+=0-38)$ in the vacuum ultraviolet region. For the first time, higher energy levels [$\text{NO}^+(\text{X}^1\Sigma^+, v^+>6)$, $\text{CO}^+(\text{X}^1\Sigma^+, v^+>1)$, and $\text{O}_2^+(\text{X}^2\Pi_g, v^+>24)$] were rotationally resolved. This allowed the accurate determination of high-order spectroscopic constants for these molecular states. Such PFI-PE experiments make possible the detailed investigation of molecular photoionization dynamics and chemical reaction mechanisms near the dissociation limit.

EXPERIMENT

The Chemical Dynamics Beamline consists of a 10 cm period undulator, a gas harmonic filter, a 6.65 m off-plane Eagle monochromator, and a photoion-photoelectron apparatus, all of which has been discussed in detail previously.^{1,2} In the present experiment, Ar, Ne, and He were used in the harmonic gas filter to suppress higher undulator harmonics with photon energies greater than 15.76, 21.56 and 24.59 eV, respectively. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by either a 2400 lines/mm (dispersion = 0.64 Å/mm) or a 4800 lines/mm grating (dispersion = 0.32 Å/mm) before entering the experimental apparatus.

The ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns. Each electron bucket emits a light pulse of 50 ps with a time separation of 2 ns between successive bunches. In each storage ring periods, a dark gap (16-80 ns) consisting of 8-40 consecutive unfilled buckets exists for the ejection of cations from the orbit.

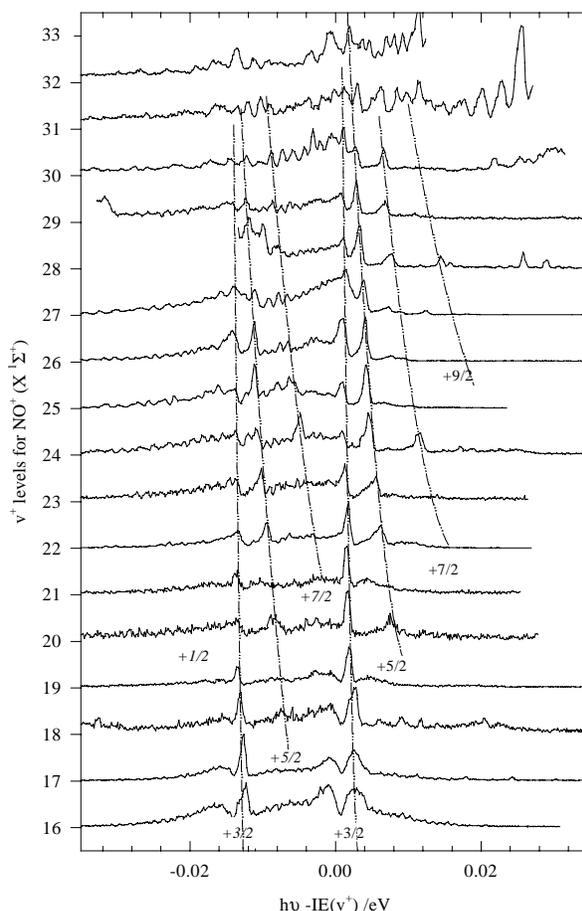


Figure 1. PFI-PE spectra for $\text{NO}^+(\text{X}^1\Sigma^+, v^+ = 16-32)$. The branch heads for rotational branches $\Delta J = \pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2$, and $+9/2$ of the $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$ PFI-PE bands are linked by dotted lines.

The NO and CO samples were introduced as effusive beams through a metal orifice at room temperature, while a continuous molecular beam of pure O₂ was produced by supersonic expansion through a stainless steel nozzle at a stagnation pressure of 760 Torr and a nozzle temperature of 298 K. The molecular beam was skimmed by a conical skimmer before intersecting the monochromatized VUV light beam. The rotational temperatures used in the simulations of the PFI-PE spectra were 298 K (NO and CO), 220 K (O₂), and 20 K (O₂). The procedures for performing PFI-PE measurements using the photoion-photoelectron apparatus have been described in detail previously.²

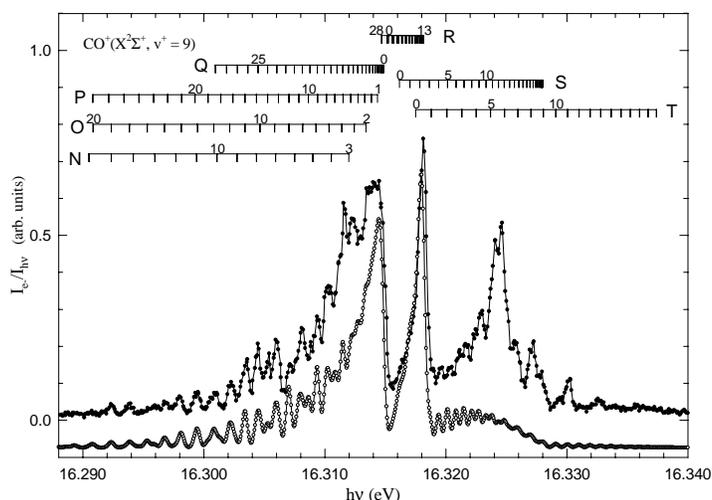


Figure 2. Comparison of the experimental (●) and simulated (○) PFI-PE spectra for CO⁺(X²Σ⁺, v⁺=9). Positions for individual rotational transitions are marked in the figure according to the level of origin (N^{''}) for each observed rotational band (N, O, P, Q, R, S, & T).

The absolute photon energy scale was calibrated using the Xe⁺(²P_{3/2}), Kr⁺(²P_{3/2}), Ar⁺(²P_{3/2}), and Ne⁺(²P_{3/2}) PFI-PE bands recorded under the same experimental conditions before and after each scan. This calibration procedure assumes that the Stark shift for ionization thresholds of target gases and the rare gases are identical. On the basis of previous experiments, the accuracy of the energy calibration is ± 0.5 meV.

RESULTS

A. NO⁺(X¹Σ⁺, v⁺=0-32)

The main point of note for the NO⁺ spectra was that the maximum ΔJ values and intensities for high ΔJ rotational branches are found to generally increase as v⁺ increases (see Figure 1).³ This observation is attributed to an increase in the inelastic cross-section for collisions between the outgoing photoelectron and the non-spherical molecular ion core as bond distance for NO⁺ is increased. This provides strong support for the electron-molecular-ion-core scattering model for angular momentum and energy exchanges in the threshold photoionization of NO.

B. CO⁺(X²Σ⁺, v⁺=0-42)

We have obtained rotationally resolved pulsed field ionization photoelectron (PFI-PE) spectra of CO in the energy range of 13.98-21.92 eV, covering the ionization transitions CO⁺(X²Σ⁺, v⁺ = 0-42, N⁺) ← CO(X¹Σ⁺, v^{''} = 0, N^{''}).⁴ The PFI-PE bands for CO⁺(X²Σ⁺, v⁺ = 8-42) obtained here represent the first rotationally resolved spectroscopic data for these states. The high-resolution features observed in the PFI-PE spectra allow the identification of vibrational bands for the CO⁺(X²Σ⁺, v⁺=10, 13, 14, 15, 18, 21, 25, and 30) states, which were not observed previously due to overlap with prominent vibrational bands of the CO⁺(A²Π_{3/2,1/2}, B²Σ⁺) states. The PFI-PE bands for CO⁺(X²Σ⁺, v⁺ = 0-42) were simulated using the Buckingham-Orr-Sichel (BOS) model⁵ derived for prediction of rotational line strengths in the single-photon ionization of diatomic molecules. Generally good agreement is observed between the experimental and simulated spectra, indicating that the one-electron BOS model adequately describes the single-photon

threshold ionization of CO. This simulation provides accurate molecular constants for $\text{CO}^+(\text{X}^2\Sigma^+, v^+ = 0-42)$, including ionization energies, vibrational constants ($\omega_e^+ = 2218.8 \pm 3.5 \text{ cm}^{-1}$, $\omega_e^+\chi_e^+ = 16.20 \pm 0.32 \text{ cm}^{-1}$, $\omega_e^+\gamma_e^+ = 0.074 \pm 0.011 \text{ cm}^{-1}$, and $\omega_e^+z_e^+ = -0.00183 \pm 0.00013 \text{ cm}^{-1}$), and rotational constants ($B_e^+ = 1.9755 \pm 0.056 \text{ cm}^{-1}$, $\alpha_e^+ = 0.0184 \pm 0.0011 \text{ cm}^{-1}$, $\gamma_e^+ = -7.6 \times 10^{-6} \pm 61 \times 10^{-6} \text{ cm}^{-1}$, $z_e^+ = -2.8 \times 10^{-6} \pm 0.9 \times 10^{-6} \text{ cm}^{-1}$). Enhancement of $\Delta N < 0$ branches was observed for each vibrational level where rotational structure was clearly resolved. The $\Delta N < 0$ enhancements were attributed to field-induced rotational autoionization. Significant local enhancements due to near-resonance autoionization were observed for $\text{CO}^+(\text{X}^2\Sigma^+, v^+ = 5-9)$, the region of which has a high density of autoionizing interloper Rydberg states (see Figure 2). The observation of a long vibrational progression in the Franck-Condon gap region where no strong autoionization states are present suggests that high- n Rydberg states converging to these highly excited vibrational levels are populated via excitation to a dissociative state. The relatively constant PFI-PE intensities found for these highly vibrationally excited levels are also consistent with the direct excitation model.

C. $\text{O}_2^+(\text{X}^2\Pi_g, v^+=0-38)$

It is well known that extensive overlaps exist between vibrational bands for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g})$ and $\text{O}_2^+(\text{a}^4\Pi_u, v^+)$ [and/or $\text{O}_2^+(\text{A}^2\Pi_u)$] at energies above 16.4 eV. However, we were able to make unambiguous identifications of individual vibrational bands for these states by spectral simulations of the PFI-PE bands obtained at 20 and 220 K.⁶ Figure 3 shows the cold PFI-PE spectrum (20K) for O_2^+ in the region of 17.01~17.06 eV where the most serious overlap involving vibrational bands of the $\text{O}_2^+(\text{X}^2\Pi_g, \text{a}^4\Pi_u, \text{and } \text{A}^2\Pi_u)$ states occurs. An excellent simulation was obtained [middle curve of Fig. 2(b)] which also constitutes a very minor contribution from $\text{O}_2^+(\text{A}^2\Pi_u, v^+=0)$.

As was observed in previous studies, we found that C_1 and C_2 were the dominant BOS coefficients for most vibrational bands, indicating that the p - and d -partial waves of the ground electron wave function are the major contributors in the ionizing transitions. Based on the simulations, we were able to obtain accurate vibrational, rotational, and spin-orbit coupling constants. Accurate ionization energies for states up to $v^+=38$ were also determined. This covers 90% of the potential well depth.

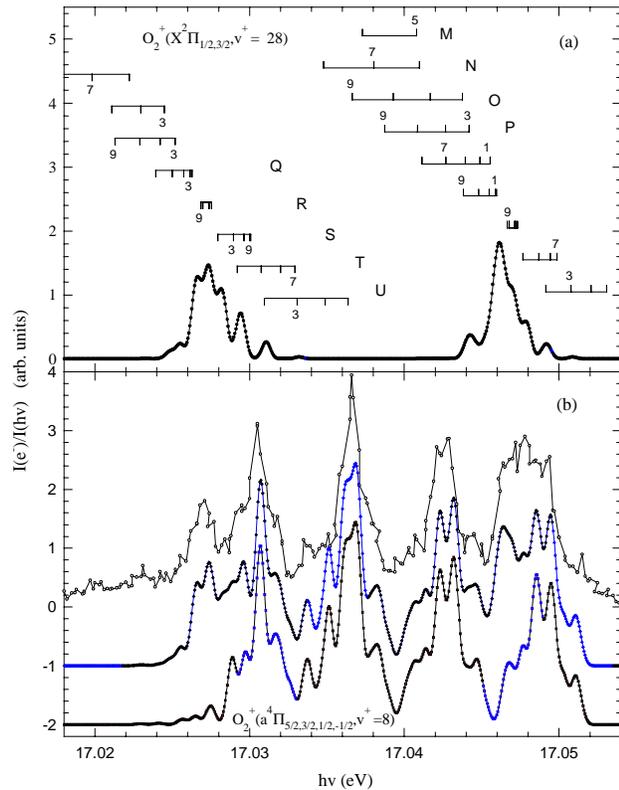


Figure 3. Deconvoluted (or simulated) PFI-PE band for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+=28)$. The rotational transitions for the $\text{O}_2^+(\text{X}^2\Pi_{1/2g})$ and $\text{O}_2^+(\text{a}^4\Pi_{3/2g})$ are marked using downward pointing and upward pointing sticks, respectively. (b) The upper spectrum is the experimental PFI-PE spectrum for O_2 in the region of 17.01-17.06 eV obtained using an O_2 sample with a rotational temperature of 20 K; The deconvoluted (or simulated) PFI-PE band for $\text{O}_2^+(\text{a}^4\Pi_u, v^+=8)$ is shown as the bottom spectra; and the middle spectrum represents the sum of the deconvoluted (simulated) bands for $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+=28)$ and $\text{O}_2^+(\text{a}^4\Pi_u, v^+=8)$.

To interpret local enhancements observed in the PFI-PE spectra for $v^+ < 14$, we concluded that these rotational lines are perturbed by nearby autoionizing Rydberg states. For the $v^+ \geq 14$ bands, we believe that direct excitation to a neutral dissociative state and subsequent coupling to high- n Rydberg states which were then pulsed field ionized would be a possible model for the photoionization mechanism.

SUMMARY

Using the broadly tunable high-resolution undulator synchrotron source at the Chemical Dynamics Beamline of the Advanced Light Source, we have obtained rotationally resolved photoelectron bands for $\text{NO}^+(\text{X}^1\Sigma^+, v^+=0-32)$, $\text{CO}^+(\text{X}^2\Sigma^+, v^+=0-42)$, and $\text{O}_2^+(\text{X}^2\Pi_{1/2,3/2g}, v^+=0-38)$. Highly accurate spectroscopic constants for these molecular states were obtained from the simulation of the experimental data using the BOS model. Possible photoionization mechanisms were discussed in detail. With the improvements made to our current instrumentation, obtaining high-quality PFI-PE spectra has become a routine yet exciting process.

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