Vibrational branching ratios in photoionization of CO and N$_2$

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We report results of experimental and theoretical studies of the vibrational branching ratios for CO $4\sigma^{-1}$ photoionization from 20 to 185 eV. Comparison with results for the $2\sigma_u^{-1}$ channel of the isoelectronic N$_2$ molecule shows the branching ratios for these two systems to be qualitatively different due to the underlying scattering dynamics: CO has a shape resonance at low energy but lacks a Cooper minimum at higher energies whereas the situation is reversed for N$_2$. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1631818]

I. INTRODUCTION

In studies of molecular photoionization and vacuum ultraviolet (VUV) spectroscopy, comparisons of similar chemical systems serve to highlight subtle aspects of the photoelectron scattering. In particular, comparisons of isoelectronic systems can illuminate microscopic aspects of photoelectron dynamics in anisotropic molecular potentials.[1–3] In studies of N$_2^+(B\,^2\Sigma_u^+)$ and CO$^+(B\,^2\Sigma^+)$ photoion rotational distributions,[1,2] we found the energy dependences of the rotational populations to be different, even far from threshold. This behavior is surprising since molecular photoelectron scattering phenomena are not expected to extend far into the continuum, where atomic effects are normally assumed to dominate. The current study focuses on *vibrational* branching ratios for these systems where differences in vibrational behavior are also seen to extend far into their respective ionization continua. This study—in conjunction with previous rotational[1,2] and polarization studies[3,4]—demonstrate that molecular aspects of ionization dynamics emerge even far from threshold, and that different molecular motions probe different aspects of the photoionization process.

The previous investigations[1,2] demonstrated that the contrasting rotational distributions emerged largely as a result of the inversion symmetry of N$_2$. For CO, an $l=3$ shape resonance in the $4\sigma \rightarrow k\sigma$ channel resulted in large ΔN transitions, even at low energies. Because higher partial waves become more significant at higher energies, the rotational distributions are relatively constant as a function of energy. For nitrogen, symmetry precludes odd partial waves, so there is no corresponding resonance. Also for N$_2$, Cooper minima in high angular momentum components suppressed large ΔN transitions until much higher energies. The rotational distri-

butions for N$_2$ hence exhibit a pronounced inflection at $h\nu \approx 120$ eV, and the populations of the higher rotational levels begin to increase dramatically at higher energies. It was subsequently determined that the Cooper minima in N$_2$ were strongly R dependent.[5] As a result, these Cooper minima led to a wide-ranging Franck–Condon breakdown, i.e., the vibrational branching ratios for the N$_2^+(B\,^2\Sigma_u^+)$ state depended on energy, even 200 eV above the ionization threshold.[6] However, there has not been a comparable vibrationally resolved investigation into CO. One expects that the energy dependence of the vibrational branching ratios for CO$^+(B\,^2\Sigma^+)$ would differ significantly from those of N$_2$, as the Cooper minima responsible for the higher energy excursions in N$_2$ are absent in CO. The current investigation addresses this issue by determining CO$^+(B\,^2\Sigma^+)v^+=1/v^+=0$ vibrational branching ratios over a wide energy range for comparison with those of N$_2^+(B\,^2\Sigma_u^+)$.

While there has been enormous effort expended in understanding the VUV spectroscopy and photoionization dynamics of CO,[7–23] none has dealt with vibrationally resolved measurements over a wide range of energy (i.e., >100 eV). Previous work,[1,2,4,6] in conjunction with results from the current study, demonstrate that molecular aspects of the ionization dynamics emerge far from threshold.

II. METHODS

Dispersed fluorescence is an ideal method for generating vibrationally resolved data over a broad spectral range since the detection bandwidth is decoupled from the excitation bandwidth, and high resolution data on the ion are accessible even when the excitation bandwidth is comparatively broad.[24–27] Vibrational branching ratios for the CO$^+(B\,^2\Sigma^+)$ state were determined by measuring dispersed fluorescence from the excited state ion[2,24,25,28] from threshold to 185 eV. The monochromatized synchrotron radiation intersected molecules emerging from an unskimmed supersonic beam, and the ionic fluorescence was collected, dispersed, and detected. We used synchrotron radiation from the 6 m plane grating monochromator beamline[29] at CAMD (the Center for Ad-

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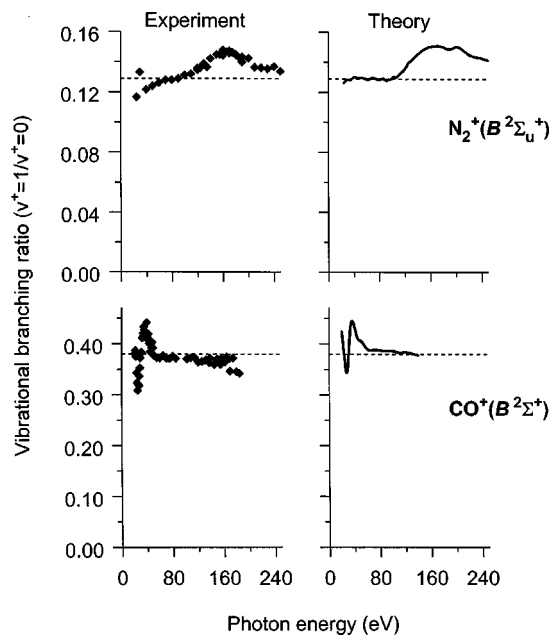
FIG. 1. Comparison of the energy dependence of vibrational branching ratios for CO $4\sigma^{-1}$ and N_2 $2\sigma_u^{-1}$ photoionization. The differences are clear and wide-ranging, and are due to the underlying photoionization dynamics.

vanced Microstructures and Devices at Louisiana State University) with an excitation bandwidth of ~0.2 eV. The CO gas was introduced to the interaction region from a gas jet with a 50 μm orifice. The stagnation pressure was adjusted until the background chamber pressure was 5×10^{-4} Torr. Results were checked at lower pressures to ensure that the data are free of artifacts due to secondary processes. The fluorescence radiation was dispersed by an optical monochromator (SPEX 500M) and detected by a charge coupled device optical multichannel analyzer (Princeton Instruments No. LN/CCD-1024-EUV). The emission monochromator was operated at a resolution of 1 nm. The fluorescence spectra compared well with those obtained previously over a more limited range.[23]

The theoretical methods employed in these studies have been discussed previously[5,6] and only a brief discussion is given here. The photoelectron orbitals are obtained using a procedure based on the Schwinger variational principle. Calculations are performed at the Hartree–Fock level, which is sufficient to account for the key dynamics. The ground state wave function of CO is obtained at the self-consistent-field (SCF) level and the Gaussian basis functions used are the same as in Ref. 1. For the final state, we assume a frozen-core Hartree–Fock model in which the ion orbitals are taken to be that of the ground state of CO and the photoelectron orbital is obtained as a solution of a one-electron Schrodinger equation.

III. RESULTS AND DISCUSSION

The results are shown in Fig. 1. The bottom frames show the $v^+=1/v^+=0$ vibrational branching ratio data for CO and the top frames show the results for N_2.[6] The calculated results are in excellent agreement with experiment for both molecules. There are obvious qualitative differences between

N_2 and CO. The N_2 curves show strong deviations from Franck–Condon behavior over a broad range at high energies while the CO results do not. In contrast, the CO results show strong deviations at lower energy,[22,23] while the N_2 curves are relatively flat in this region.

The striking differences between the N_2 and CO vibrational data can be related to the photoelectron partial wave dipole amplitudes that have been reported previously.[1–3,5] The excursion in the CO vibrational branching ratio curve at $h\nu\approx35$ eV results from the $l=3$ shape resonance in the $4\sigma \rightarrow k\sigma$ channel.[2,4] The higher energy regime is featureless because there is no shape resonance at higher energies, and the Cooper minima are relatively weak.[30] For N_2, the vibrational branching ratios vary from 100 to 200 eV, while at the lower energy the results are comparatively constant. The high energy behavior results from the strong dependence of the Cooper minima on bond length.[5,6] The low energy region is featureless because there is no shape resonance corresponding to the one observed in CO. This stems from symmetry, i.e., the $l=3$ partial wave is forbidden in the case of N_2 because the final electronic wave function is of gerade symmetry and therefore contains only even partial waves. In fact, it would seem that the CO shape resonance redistributes the oscillator strength sufficiently to result in all of the major differences between CO and N_2.

Finally, we note that the specific motions probed via state-resolved measurements (i.e., rotation, vibration, etc.) are revealing different aspects of the underlying continua. For example, the rotational distributions for CO were relatively flat in the lower energy region[1,2,30] (i.e., $20\leqslant h\nu \leqslant50$ eV) while the vibrational distributions vary significantly in this same region. Similarly, polarization data for CO[3,4] in the high energy region demonstrated that the photoelectron is ejected preferentially along the molecular axis, while the vibrational and rotational data were insensitive to this aspect of the photoelectron ejection. These observations underscore the point that measurements which emphasize molecular aspects elucidate details of the photoelectron scattering dynamics that would be otherwise inaccessible.

IV. CONCLUSIONS

Vibrationally resolved $CO^+(B\,^2\Sigma^+)\rightarrow CO^+(X\,^2\Sigma^+)$ dispersed fluorescence measurements are used to generate vibrational branching ratios for the $CO^+(B\,^2\Sigma^+)$ state photoion over a broad range of excitation energies, $20\leqslant h\nu \leqslant185$ eV. The results are compared to similar measurements on N_2 and are found to be qualitatively different. Theoretical predictions are generated, and compared to experiment, and the agreement is excellent. The differences between the N_2 and CO results are attributable to the photoelectron scattering dynamics, which differ because a shape resonance present for CO is symmetry-forbidden in the case of N_2.

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780   J. Chem. Phys., Vol. 120, No. 2, 8 January 2004

Rathbone *et al.*

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