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L.J. Medhurst, P.A. Heimann, M.R.F. Siggel, D.A. Shirley, C.T. Chen,
Y. Ma, S. Modesti, and F. Sette

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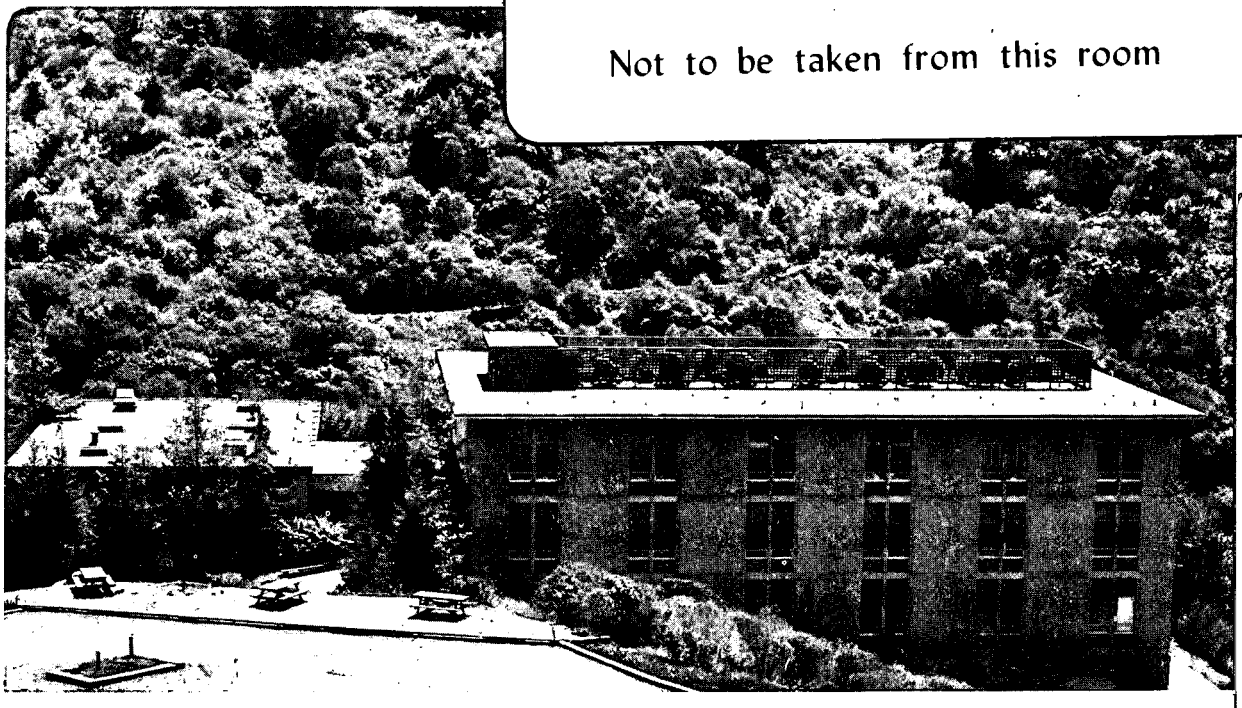

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L. J. Medhurst, P. A. Heimann, M. R. F. Siggel, D. A. Shirley
Department of Chemistry, University of California
and Chemical Sciences Division
MS 2-300, Lawrence Berkeley Laboratory
1 Cyclotron Rd.
Berkeley, California 94720

C. T. Chen, Y. Ma, S. Modesti, and F. Sette
A T & T Bell Laboratories
Murray Hill, New Jersey 07974

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Department of Chemistry, University of California
and Chemical Sciences Division
MS 2-300, Lawrence Berkeley Laboratory
1 Cyclotron Rd.
Berkeley, California 94720

C. T. Chen, Y. Ma, S. Modesti, and F. Sette
A T & T Bell Laboratories
Murray Hill, New Jersey 07974

Abstract

Zero-Kinetic-Energy Photoelectron Spectroscopy (ZKE-PES) was used to measure the Franck-Condon factors for the carbon and nitrogen K-shell ionized states in N_2 and CO. Corresponding features in the two spectra showed nearly identical energy spacings, both below and above the ionization threshold, as predicted by the equivalent-core model. The equilibrium bond length, R_e, for the CO C-$1s^{-1}$ state was determined to be 1.077 ± 0.005 Å, and R_e for the N_2 N-$1s^{-1}$ state was found to be 1.077 ± 0.010 Å, changes of -0.051 Å for CO and -0.020 Å for N_2 from their ground-state equilibrium bond lengths. The two-electron states corresponding to $1s^{-1}$ $val^{-1}\pi^*$ were examined in the binding energy region predicted by Green's function calculations. Two-electron states absent in the X-ray photoemission spectrum are present in both molecules and show evidence of vibrational structure.

Introduction

Core-level photoabsorption spectroscopy accesses highly excited states of the neutral molecule, photoelectron spectroscopy reveals the states of the ion, and the study of emitted electron intensities as a function of incident photon energy gives insight into the dynamics of the photoionization process. Recently, high-resolution monochromators have made it possible to study the photoabsorption of small molecules at the carbon and nitrogen $1s^{-1}$ electron energies with vibrational resolution.[1,2] However, photoelectron spectroscopy usually requires higher incident photon intensity. Since the entire solid angle is collected in ZKE-PES,[3] this technique may be used to obtain vibrationally resolved information about the states of the ion near their thresholds. The near threshold region of the spectrum is also the most dynamically interesting, because this is the energy region where discrete states can interact with the continuum. In this letter we present ZKE-

PES spectra near the C-1s edge in CO and the N-1s edge in N_2. The ionic states are shown to be closely related to the equivalent-core states, which are the ground state and the excited states of NO^+.

Experiment

These experiments were performed using Bell Laboratories high resolution soft X-ray beamline located at the National Synchrotron Light Source, Brookhaven National Laboratory.[4] The experimental vacuum chamber was separated from the beamline by a thin (1200Å) Ti window. The storage ring operated in single-bunch mode. The pulsed photons intersected an effusive gas beam between two biased grids, which extract electrons. The electron detector is described in detail elsewhere.[3] It was oriented at 90° to the polarization vector of the synchrotron radiation. The electrons' kinetic energies were determined by their time-of-flight. The intensity of 0-20 meV kinetic energy electrons versus photon energy form the ZKE-PES spectra. The total instrumental resolution was ~140 meV for CO and ~200 meV for N_2.

Mainlines

Figure 1 shows the ZKE-PES spectra of CO across the carbon K-edge and N_2 across the nitrogen K-edge, with their respective absorption spectra.[1,2] Each spectrum of these isoelectronic molecules contains a strong $1s \rightarrow \pi^*$ transition followed by weaker Rydberg structure leading up to the 1s ionization threshold. In both cases, the ZKE and absorption spectra are quite similar below the ionization threshold. At these photon energies core-excited states generally decay via Auger-like autoionization. Since the core-excitation energy is far above the energy required for double ionization (40.8 eV for CO, 42.68 eV for N_2), it is possible for these states to decay by emitting two electron simultaneously. Previous work[5] on atomic systems has suggested that the kinetic energy distribution of two simultaneously emitted electrons is peaked with one electron having low kinetic energy and the other having correspondingly high kinetic energy. Therefore, ZKE-PES is very sensitive to this two-electron process and all the features in a photoabsorption spectrum can be found in a ZKE spectrum for a core level. This makes possible a more direct comparison of the energies of the neutral and the ion. The relative intensities for these transitions, however, are different in ZKE-PES and absorption.[6] In general, as the electron is excited to higher-lying orbitals the tendency to decay by emitting two electrons simultaneously increases. However, within a single electronic state the relative intensities of the different vibrational levels appear to be the same in ZKE-PES and absorption, as is expected in the Born-Oppenheimer approximation.

The 1s ionization threshold (mainline) appears in the ZKE spectra as an intense peak with vibrational structure. At higher photon energies there is additional structure corresponding to two-electron transitions in the neutral. These peaks are more prominent in the photoabsorption spectra.

They can be considered Rydberg states leading to the excited states of the ion (satellites). As with the mainline state these satellites appear as peaks in the ZKE spectra and steps in the absorption spectra. It is apparent in fig.1 that not only the below threshold features, but also those above the threshold are aligned for these two molecules, in confirmation of the equivalent-core model, discussed below.

Figure 2 shows the mainline peaks and their vibrational structure. The solid line is a least squares fit to the data, and the dashed lines show the individual vibrational peaks. In contrast to the excited states of the neutral molecule, peaks which correspond to an ionization threshold exhibit Post-Collision Interaction (PCI), which broadens the peaks asymmetrically and shifts the maxima to higher photon energy. This is caused by the interaction of the photoelectron with the Auger electron. The energy values reported in table 1 and indicated on fig. 2 are the thresholds for the different vibrational states. The function of Niehaus[7], convoluted with a Gaussian for instrumental broadening, was used to fit the peaks. At threshold the difference between the Niehaus treatment and the more detailed treatment of Russek and Mehlhorn[8] is less than the experimental uncertainty. The Niehaus function depends upon the lifetime of the core hole and the excess photon energy above the ionization threshold. For CO the C-1s natural linewidth was determined from the lineshape to be 95 ± 5 meV. For N_2 the natural linewidth was determined to be 140 ± 20 meV. However, the convergence of the natural linewidth, the vibrational spacing, and the instrumental linewidth is not strong for overlapping Niehaus functions. The peak positions and Franck-Condon factors determined from the spectrum are presented in table 1. Also in table 1 are the harmonic vibrational frequencies, ω_e, obtained from the spectrum and the equilibrium bond lengths, R_e, determined by calculating the harmonic oscillator Franck-Condon Factor's (FCF's) using the algorithm of Nichols[9]. Gelius[10] previously analyzed the vibrationally broadened lineshapes from photoelectron spectra excited by Al Kα radiation. His FCF's for the CO C-1s mainline are 1.00, 0.97, 0.53 and 0.17, and for the N_2 N-1s mainline they are 1.00 and 0.32. He used a Gaussian lineshape and a separation of 2340 cm^{-1} versus the 2490 ± 140 cm^{-1} we determined for CO and 2400 ± 600 cm^{-1} for N_2. Both the neglect of the natural Lorentzian linewidth and the smaller vibrational separation in the least-squares fit decrease the intensity of the first peak relative to the excited vibrational states, and this may explain why the higher vibrational states appear to be more intense for Gelius. Therefore, the differences between our FCFs and his are probably due to differences of analysis and not from any real differences in the Franck-Condon factors.

The structural parameters for the equivalent-core species for both N_2 and CO, the NO^+ X state, are also listed in table 1 . In the equivalent-core model, the core-ionized states have the same potential and therefore the same force constant as the NO^+ X state. The vibrational frequencies should equal that of the NO^+ X state times the square root of the ratio of the reduced masses:

$$\omega_{CO^+} = (\omega_{NO^+}) \sqrt{(\mu_{NO}/\mu_{CO})} = 2480 \text{ cm}^{-1}$$

$$\text{and } \omega_{N2^+} = (\omega_{NO^+}) \sqrt{(\mu_{NO}/\mu_{N2})} = 2390 \text{ cm}^{-1}$$

Here we have used the harmonic oscillator vibrational frequency for NO^+ for a direct comparison. These values are very close to those determined from the spectra, considering the errors. Because the 1s electron is non-bonding and the bond order does not change, the equilibrium bond length is assumed to decrease in the transition to the core ionized state in both molecules. This probably results from valence electrons contracting around the core hole .

Satellites

The core-level satellites of CO and N_2 were studied previously at high incident photon energy[10] and as functions of photon energy.[11] The earlier work focussed on satellites with the same symmetry as the mainline, $^2\Sigma^+$. In both N_2 and CO, there are two fairly intense $^2\Sigma^+$ states of the configuration $1s^{-1}\pi^{-1}\pi^*$, the lowest binding energy state having the π and π^* electrons triplet paired. Recent ZKE spectra at lower resolution [6] suggested that more than one electronic state was present at low photon energy, and Angonoa et. al. [12] calculated states of other symmetries using a Green's function technique. High resolution (ZKE) spectra of the energy region of the first, $^2\Sigma^+$ satellite for CO and the first two $^2\Sigma^+$ states for N_2 are presented in fig. 3. The relative positions of the states calculated by Angonoa et. al. are also indicated. The calculated peak energies have been adjusted to the experimental scale by setting the calculated energies of the lowest binding energy $^2\Sigma^+$ states of N_2 and CO equal to the experimental values of Gelius. Since all the states in N_2 have doublet, gerade symmetry, they are designated in fig. 3 solely by their angular momenta. In both spectra there is a peak lower in energy than the lowest energy $^2\Sigma^+$ state of Gelius. Therefore the increase of intensity previously attributed solely to the $^2\Sigma^+$ peak near its threshold[11] is partially the result of other electronic states. In the Al Kα spectra there was no evidence for states other than $^2\Sigma^+$ in either N_2 or CO.

Core-level satellite states should possess vibrational structure similar to the mainline peaks. Such structure has been reported for the two-electron excited states, which are the Rydberg series for the satellites of CO.[2] A Franck-Condon analysis of the lowest binding energy satellite state for CO^+ is reported in table 2. The uncertainty in the relative intensities of the other fitted peaks made it impossible to perform a Franck-Condon analysis for any other state of CO^+ or N_2^+. The equilibrium bond length for this satellite should be larger than in the ground state. Promoting a bonding electron into an antibonding orbital increases the bond length more than the contraction of electrons around the core hole decreases it. The bond lengths and vibrational frequencies of the two lowest binding energy electronic states of NO^+ are also listed in table 2. One is a $^3\Pi$, and the other

is a $^3\Sigma$ state. The bond length and vibrational frequency of the satellite are closer to those of the $^3\Pi$ state of NO^+, which results from excitation of a 5σ electron to the π^* orbital. This is the same valence-electron configuration as the lowest binding energy $^2\Pi$ state calculated by Angonoa et. al. The $^3\Sigma^+$ excited state of NO^+ has a much longer bond and much smaller vibrational frequency. Therefore the equivalent-core model supports the assignment of this lowest binding energy satellite as the $^2\Pi$ state. In N_2 there is also intensity at energies lower than the binding energy of the first $^2\Sigma^+$, and it is probably also from the $^2\Pi$ state. However, since the ground-state bond length is shorter for N_2 than for CO, the expected Frank-Condon envelope for the satellite states are broader, and we could not separate the electronic states.

The appearance of satellites of different symmetry (especially high angular momentum states) than the mainline at their thresholds is well documented in atomic systems.[13] It has been attributed to Wannier's description[14] of double ionization, in which the two departing electrons are highly correlated. The angular correlations are very stable, but the radial correlations are highly unstable. This promotes excitation into orbitals of high angular momentum as the double ionization threshold is approached. Another possible influence on the intensities of the satellites in this energy range is the σ^* resonance. Both N_2 and CO have a σ^* resonance (CO at 304 eV, N_2 at 419 eV). Since this resonance is nearly degenerate in energy with the triplet paired satellites, it is possible they are enhanced on resonance as is the case with a satellite of SF_6[15].

Conclusions

In spite of post-collision interaction, it is possible to determine the spectroscopic parameters and equilibrium bond lengths for core-ionized species. These states, like the core-excited states of the neutral molecule, can be interpreted using the equivalent-core model. Even the satellites can be interpreted by invoking this model, if they are well resolved. Apparent enhancement of the lowest binding energy $^2\Sigma^+$ satellite near its threshold in both N_2 and CO is partially caused by the onset near their thresholds of other higher angular momentum satellites.

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References:

1. C. T. Chen, Y. Ma, and F. Sette, Phys. Rev. A **40,** 6737 (1989).

2. M. Domke, C. Xue, A. Puschmann, T. Mandel, E. Hudson, D. A. Shirley, and G. Kaindl, Chem. Phys Letters **173**, 122 (1990):, Erratum **174**, 663 (1990); Y. Ma, C. T. Chen, G. Meigs, K. Randall and F. Sette, in "X-ray and Innershell Processes", edited by T. A. Carlson, M. O. Krause and S. T. Manson, AIP Conference Proceedings No. 215, pg 634 (1990).

3. P. A. Heimann, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, R. Wehlitz, D. W. Lindle T. A. Ferrett, and D. A. Shirley, Phys. Rev. A **34**, 3782 (1986).

4. C. T. Chen and F. Sette, Rev. Sci. Instrum. **60**, 1616 (1989); Physica Scripta **T31**, 119 (1990).

5. P. A. Heimann, D. W. Lindle, T. A. Ferrett, S. H. Liu, L. J. Medhurst, M. N. Piancastelli, D. A. Shirley, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, J. Phys B **20**, 5005 (1987).

6. L. J. Medhurst, T. A. Ferrett, P. A. Heimann, D. W. Lindle, S. H. Liu, and D. A. Shirley, J. Chem. Phys. **89**, 6096 (1988).

7. A. Niehaus, J. Phys. B **10**, 1845 (1977).

8. A. Russek and W. Mehlhorn, J. Phys. B **19**, 911 (1986).

9. R. W. Nicholls, J. Chem. Phys **74**, 6980 (1981).

10. U. Gelius, J. Electron Spectrosc. Relat. Phenom. **5**, 985 (1974).

11. A. Reimer, J. Schirmer, J. Feldhaus, A. M. Bradshaw, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, Phys. Rev. Lett. **57**, 1707 (1986).

12. G. Angonoa, O. Walter, and J. Schirmer, J. Chem. Phys. **87**, 6789 (1987).

13. U. Becker, B. Langer, H. G. Kerkhoff, M. Kupsch , D. Szostak, R. Wehlitz, P. A. Heimann, S,.H. Liu, D. W. Lindle, T. A. Ferrett, and D. A. Shirley, Phys. Rev. Lett. **60**, 1490 (1988).

14. G. H. Wannier, Phys. Rev. **90**, 817 (1953).

15. T. A. Ferrett, D. W. Lindle, P. A. Heimann, M. N. Piancastelli, P. H. Kobrin, H. G. Kerkhoff, U. Becker, W. D. Brewer, and D. A. Shirley, J. Chem. Phys. **89**(8), 4726 (1988).

Table 1 Mainlines

	Transition	Energy	FCF	
CO^{+a}	$1s^{-1}$ v=0	296.13 ± 0.03	1.00 ± 0.14	ω_e = 2490 ± 140 cm^{-1}
	v=1	296.45 ± 0.03	0.63 ± 0.06	R_e = 1.077 ± 0.005 Å
	v=2	296.80 ± 0.03	0.21 ± 0.03	
	v=3	297.07 ± 0.03	0.03 ± 0.02	
N_2^{+a}	$1s^{-1}$ v=0	409.91 ± 0.03	1.00 ± 0.23	ω_e = 2400± 600 cm^{-1}
	v=1	410.21 ± 0.06	0.14 ± 0.05	R_e = 1.077 ± 0.010 Å
CO^b	ground state			ω_e = 2168.1358 cm^{-1}
				$\chi_e\omega_e$ = 13.2883 cm^{-1}
				R_e = 1.128323 Å
N_2^b	ground state			ω_e = 2358.57 cm^{-1}
				$\chi_e\omega_e$ = 14.324 cm^{-1}
				R_e = 1.09768 Å
NO^{+b}	$X\ ^1\Sigma^+$			ω_e = 2379.18 cm^{-1}
				$\chi_e\omega_e$ = 16.262 cm^{-1}
				R_e = 1.063 Å

a. This work.

b. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, Princeton, 1979), Vol 4, and references therein.

Table 2 Satellites

	Transition	Energy	FCF	
CO^{+a}	$1s^{-1}5s^{-1}\pi^*$ v=0	304.02 ± 0.05	1.00 ± 0.22	$\omega_e = 2200 \pm 400\ cm^{-1}$
	v=1	304.29 ± 0.03	0.47 ± 0.10	$R_e = 1.174 \pm 0.013$ Å
	v=2	304.64 ± 0.04	0.16 ± 0.09	
	(5s and π^* singlet paired)			
NO^{+b}	a $^3\Sigma^+$			$\omega_e = 1293\ cm^{-1}$
				$\chi_e\omega_e = 15\ cm^{-1}$
				$R_e = 1.284$ Å
NO^{+b}	b $^3\Pi$			$\omega_e = 1710.8\ cm^{-1}$
				$\chi_e\omega_e = 14.0\ cm^{-1}$
				$R_e = 1.175$ Å

a. This work.

b. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (van Nostrand, Princeton, 1979) Vol 4, and references therein.

Figure Captions:

Figure 1: ZKE spectrum of CO across the C-K edge and N_2 across the N- K edge (data points) and the corresponding absorption spectra[1,2] (solid lines). At photon energies above $1s \rightarrow \pi^*$ resonance, the absorption spectra of CO and N_2 have been enlarged 9 and 10 times, respectively, while the ZKE spectrum of CO has been enlarged 3 times. The double excitation and satellite region of the ZKE spectra of CO and N_2 have been enlarged an additional 2.3 and 3 times respectively.

Figure 2: ZKE spectrum of CO at the C-1s ionization threshold and N_2 at the N-1s ionization threshold. The solid lines are fits to the data points. The individual peaks are shown with the dashed lines. The vertical lines at the top mark the thresholds for the different vibrational states. The maxima of the peaks are shifted from this by PCI.

Figure 3: ZKE spectrum of the satellite regions of CO and N_2,.The solid lines are fits to the data points. The individual peaks are shown with the dashed lines. The calculated energies of Angonoa et. al.[14] are shown at the top of spectrum. These energies are calibrated to the experimental high incident photon energy results of Gelius.[11] As in figure 2, these energies correspond to the peak thresholds not the maxima, because of PCI

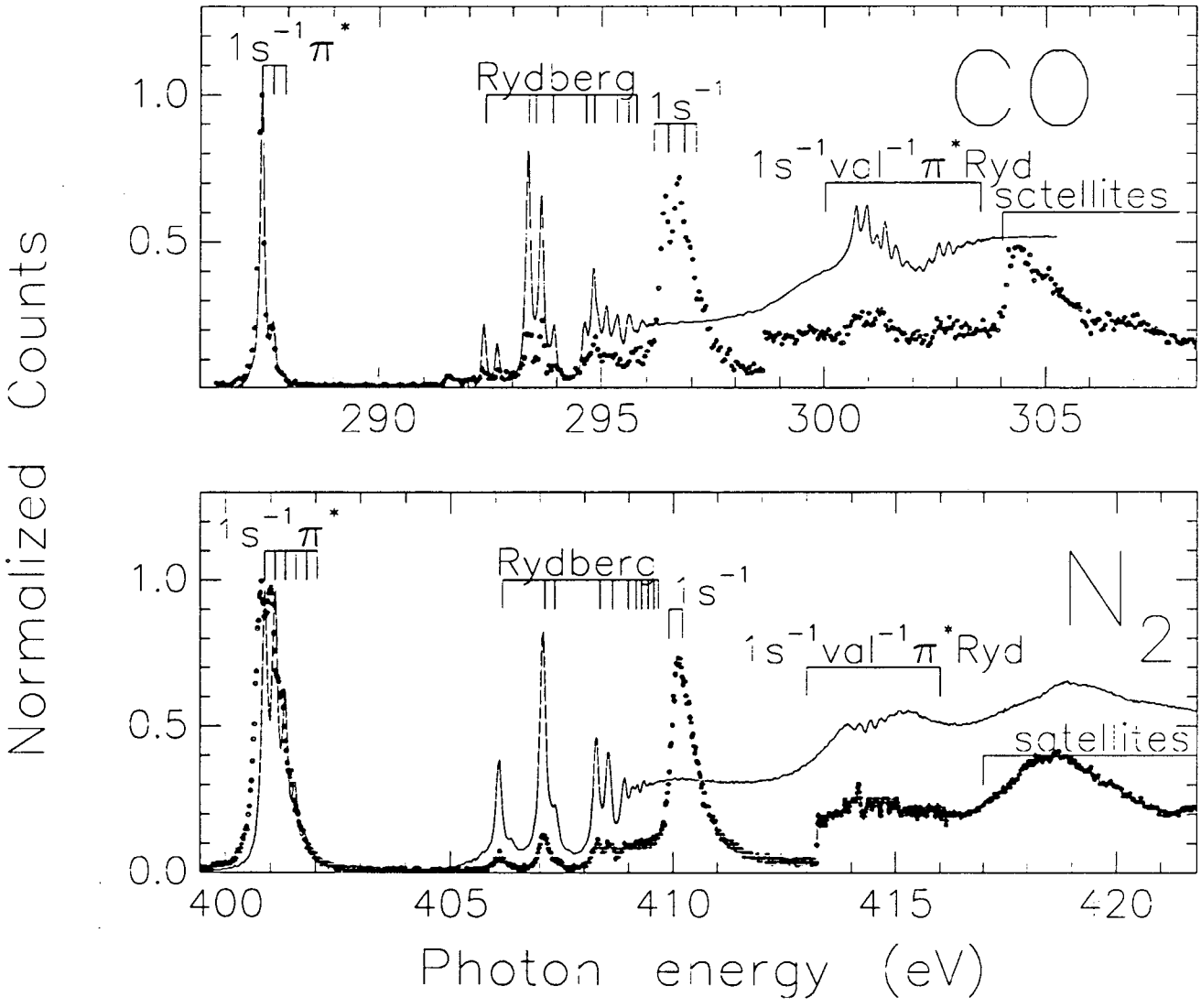

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Figure 1

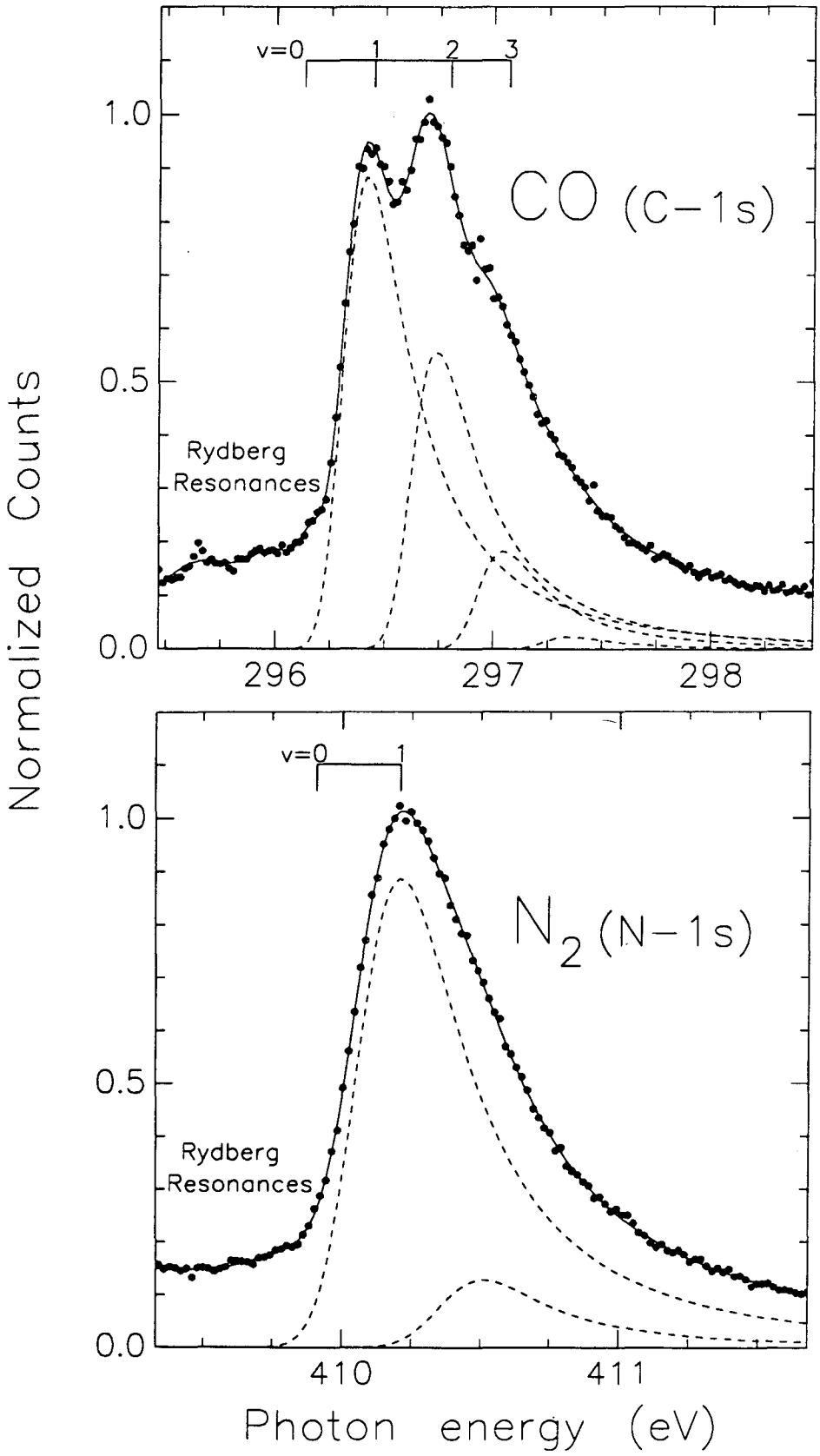

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Figure 2

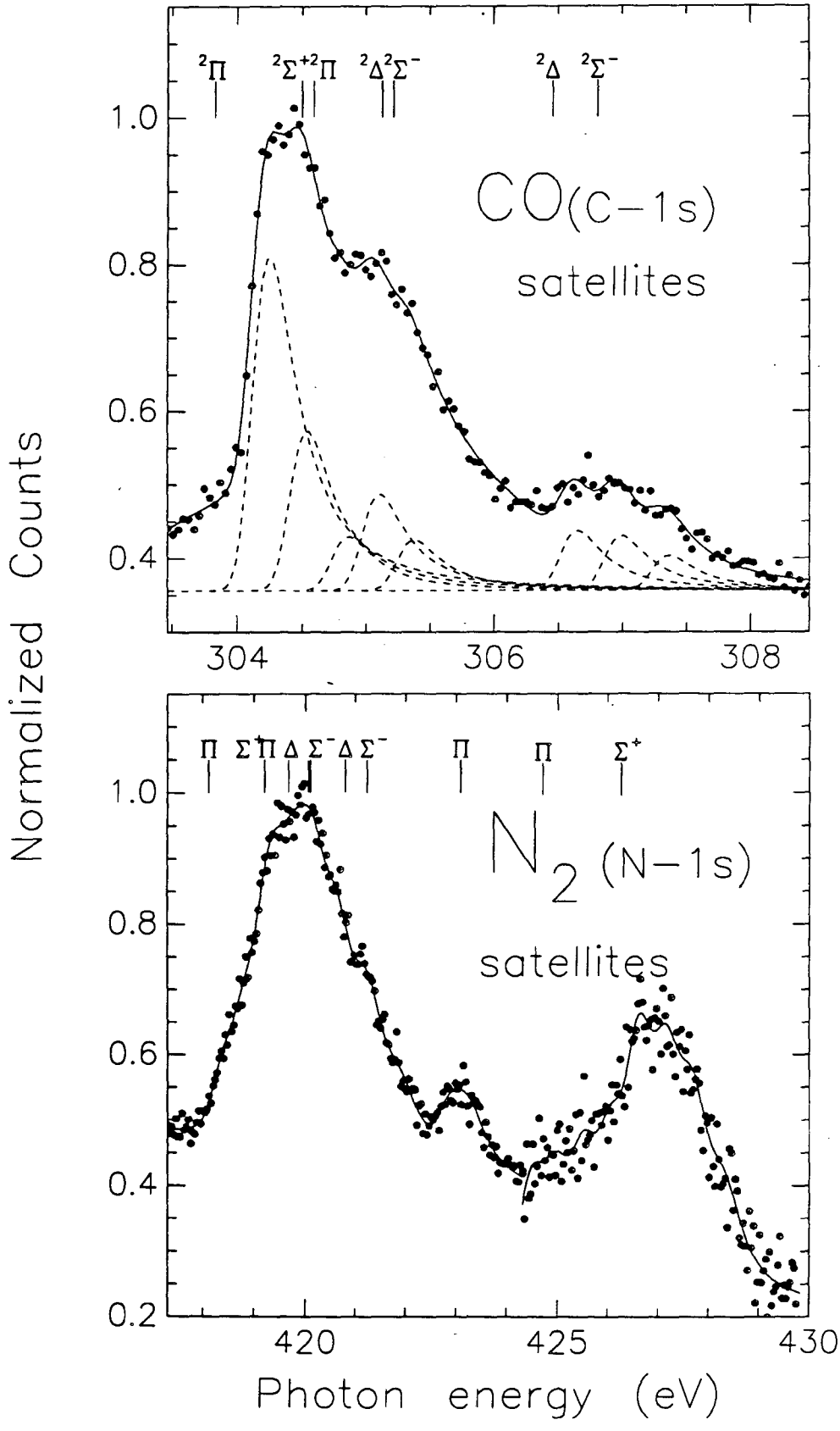

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Figure 3

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