Formation of long-lived CO^{2+} via photoionization of CO^+

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The formation of long-lived CO^{2+} from CO^+ via photoionization in the energy range 25 to 45 eV was studied experimentally at high spectral resolution. All five allowed components of a Rydberg series with an electronically excited $^3\Sigma^+(\nu=0)$ core are identified. Four components of a second Rydberg series with a vibrationally excited $^3\Sigma^+(\nu=1)$ core and structure due to the initial vibrational state of the ion beam are also discernible. The total photoionization cross section was measured with a vibrationally relaxed CO^+ ion beam. Franck-Condon factors from ground state CO^+ to the relevant CO^{2+} states were calculated.


I. INTRODUCTION

There has been a growing interest in understanding the structure and dynamics of multicharged molecular species [1–7]. In particular, long-lived doubly charged carbon monoxide has been used as a benchmark for experiments and theoretical calculations [2–10]. However, high-resolution experimental data remain scarce. The photoionization of molecular ions is also an important fundamental question in molecular physics and other fields [1].

In the present work, the absolute photoionization cross section has been measured for the process

$$CO^+ + h\nu \rightarrow CO^{2+} + e^- \tag{1}$$
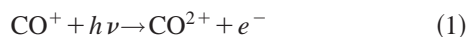
over the photon energy range from 25 to 45 eV with 30 meV resolution, and from 26.5 to 33.5 eV with 15 meV resolution, where the CO^{2+} product is formed in a state that is metastable against dissociation.

II. EXPERIMENT

The experiment was performed at the Advanced Light Source (ALS), using a merged-beams apparatus based on the photoion yield technique [11]. A schematic of the apparatus is shown in Fig. 1. The major difference from experiments reported recently [11,12] is the production of a molecular ion beam.

The CO^+ ion beam was produced by admitting high-purity carbon monoxide into a hot-filament discharge ion source. A 6 kV acceleration potential extracted the ions, and the desired ion beam was selected by a $60°$ analyzing magnet. Typically, the CO^+ beam current was 250 nA.

The photon beam was provided by an undulator at the ALS [13]. The CO^+ beam was merged with the photon beam along a collinear trajectory. The photoionized molecular product ions formed within an electrically biased (typically at $+2$ kV) interaction region 29 cm in length were selected by a demerging magnet and counted with a multichannel plate (MCP) detector. The CO^{2+} photoion yield was recorded as a function of the photon energy and normalized to the ion and photon currents. The photon flux was measured with a calibrated silicon photodiode. The contribution to the CO^{2+} ion count rate due to stripping collisions with the residual gas was subtracted by chopping the photon beam at a frequency of 1 Hz. The operating pressure in the interaction region was constant at approximately 10^{-7} Pa. Relevant to the present experiment is the flight time of a CO^{2+} product ion from the interaction region to the detector, which was typically 7.5 μs.

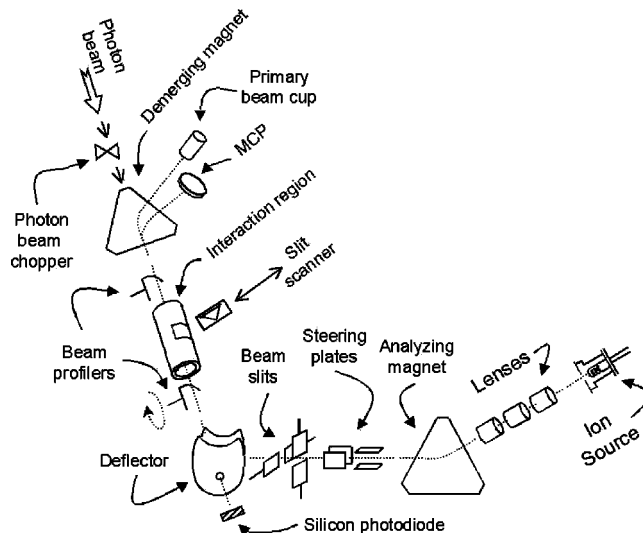Steps in the product ion yield at the known photoioniza-

FIG. 1. Schematic of the experimental apparatus. Some electrostatic elements have been omitted for clarity. For a full description see [15].

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tion thresholds [14] from $O^+(^4S)$ to $O^{2+}(^3P)$ and from $C^+(^2P)$ to $C^{2+}(^1S)$ were measured during the experiment, and used to calibrate the photon energy scale with an uncertainty of ± 7 meV. Depending on the experimental conditions, a Doppler shift varying from $+14$ meV to $+25$ meV was taken into account. The pressure in the ion source was maintained near the upper end of the operating range $(10^{-2}$ Pa) in order to produce a vibrationally relaxed ion beam. Resonant collisions of CO^+ with CO parent gas in the region close to the extraction aperture of the ion source are known to be very efficient in quenching the population of vibrationally excited states through energy transfer [16]. This characteristic of the present ion source has been used to produce other molecular ion beams with significant vibrational relaxation [17].

Two wire scanners located at the ends of the interaction region and a translating slit scanner in the center measured the two-dimensional spatial profiles of the beams and monitored the quality of their overlap. The absolute total photoionization cross section and the photoion yield spectra were measured in different experimental modes. In the spectroscopic mode, the ion yield was optimized, while in the cross-section mode the overlap of the beams was carefully controlled and measured. The absolute cross section was measured at selected photon energies where the spectrum is relatively structureless. Finally, the spectra were normalized to the absolute cross-section measurements. The overall systematic uncertainty of the cross-section measurements is estimated to be $\pm 20\%$. The individual contributions to the total uncertainty are discussed elsewhere [11].

III. RESULTS

Photoionization cross-section measurements taken with 30 meV photon energy resolution are presented in Fig. 2. A first inspection of the spectrum reveals a number of resonances from the threshold near 27.5 eV to about 30 eV, while in the energy range 35 to 45 eV the spectrum is essentially featureless. The spectrum with an expanded energy scale in the near-threshold region is shown in Fig. 2. The first three groupings of structures contain at least three main resonance features, and many small, incompletely resolved features.

The present results are similar to those reported recently by Andersen *et al.* [2] that were also taken with an energy resolution of 30 meV. They attributed the main features to a Rydberg series with a CO^{2+} core in the electronically excited $^3\Sigma^+$ state. They identified four of a total of five allowed components of this Rydberg series. In Table I a comparison of the background cross sections is presented. Differences in the nonresonant (background) cross section cannot be attributed to the experimental uncertainties, and will be discussed below.

The energies of the Rydberg series are given by

$$E_n = L - \frac{R_y Z^2}{(n-\delta)^2} \qquad (2)$$

where R_y is Rydberg's constant, Z is the charge state of the
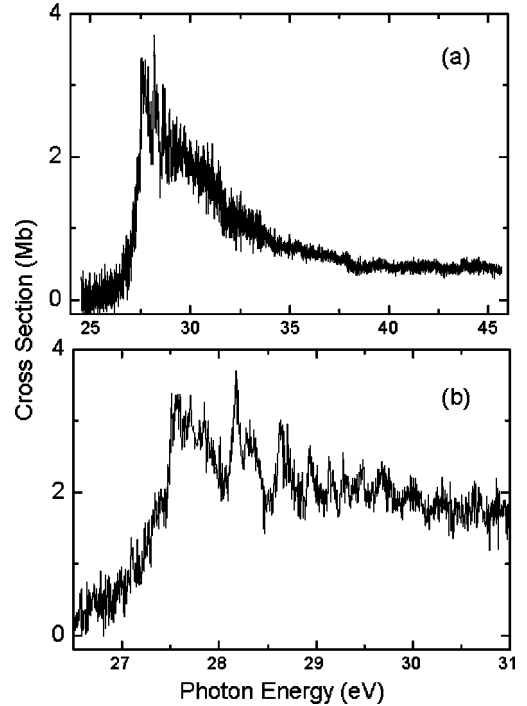

FIG. 2. (a) The cross section for photoionization of CO^+ measured with 30 meV photon energy resolution. (b) An expanded view of the energy interval that contains most of the features discernible with this resolution.

core ion, n is the principal quantum number, L is the ionization limit, and δ is the quantum defect.

To better resolve the structure, a higher-resolution ($\Delta E = 15$ meV) experiment was conducted, and the result is presented in Figs. 3 and 4. Figure 3 indicates the five components of the series with their associated quantum defects. The series starts from $n=5$, and is clearly discernible up to $n=7$. The positions of the resonances were estimated from Gaussian fits. The quantum defects δ shown in Fig. 3 and in Table II correspond to an ionization limit L of 29.79 ± 0.08 eV, which is in excellent agreement with published values [3–6,10].

The larger resonances for $n=5$ and $n=6$ appear double peaked, suggesting additional structure. However, since the apparent energy separation is comparable to the resolution of the experiment (15 meV), planned measurements at higher resolution will be necessary to fully resolve this structure.

Further inspection reveals additional features in the spec-

TABLE I. Background cross section (in Mb) for comparison.

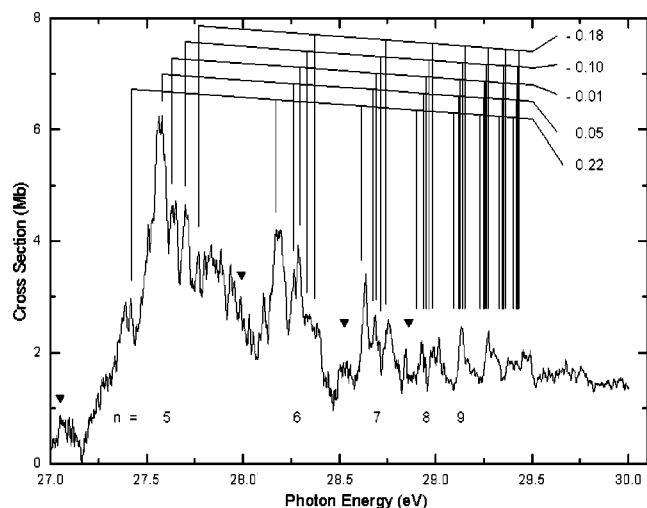| Energy (eV)	Present work	Reference [2]
30	1.83	1.94
31	1.70	1.84
32	1.13	1.68
33	0.96	1.62
35	0.75	1.42
37.5	0.54	1.27
40	0.46	1.14

FIG. 3. The CO$^+$ photoionization cross section measured with 15 meV photon energy resolution. The first Rydberg series and the corresponding quantum defects are identified (shown at the top right). The principal quantum numbers n are shown in the bottom. Inverted triangles indicate contribution from initially vibrationally excited CO$^+$. Only these Rydberg series conform to the upper grouping of Fig. 4.

TABLE II. Quantum defects for the two identified Rydberg series.

Core $^3\Sigma^+(\nu=0)$	Values from Ref. [2]	Core $^3\Sigma^+(\nu=1)$
0.215	0.30	0.075
0.045	0.10	0.040
-0.010	-0.05	-0.015
-0.097	-0.20	-0.07
-0.172		

trum. Four components of a second Rydberg series are resolved (lower grouping of Fig. 4). The associated limit L appears shifted approximately $+250$ meV from the first Rydberg series. Such an energy shift suggests that the core of these products is vibrationally excited, and that this series is associated with the $^3\Sigma^+$ state with $\nu=1$. For this series the features are not sufficiently resolved, especially for $n=6$, where there is additional structure due to initially vibrationally excited CO$^+$, as noted above. For the lower grouping in Fig. 4, a series limit L of 30.05 eV was determined.

The quantum defects for the second Rydberg series are presented in Table II. The fifth component for this core is
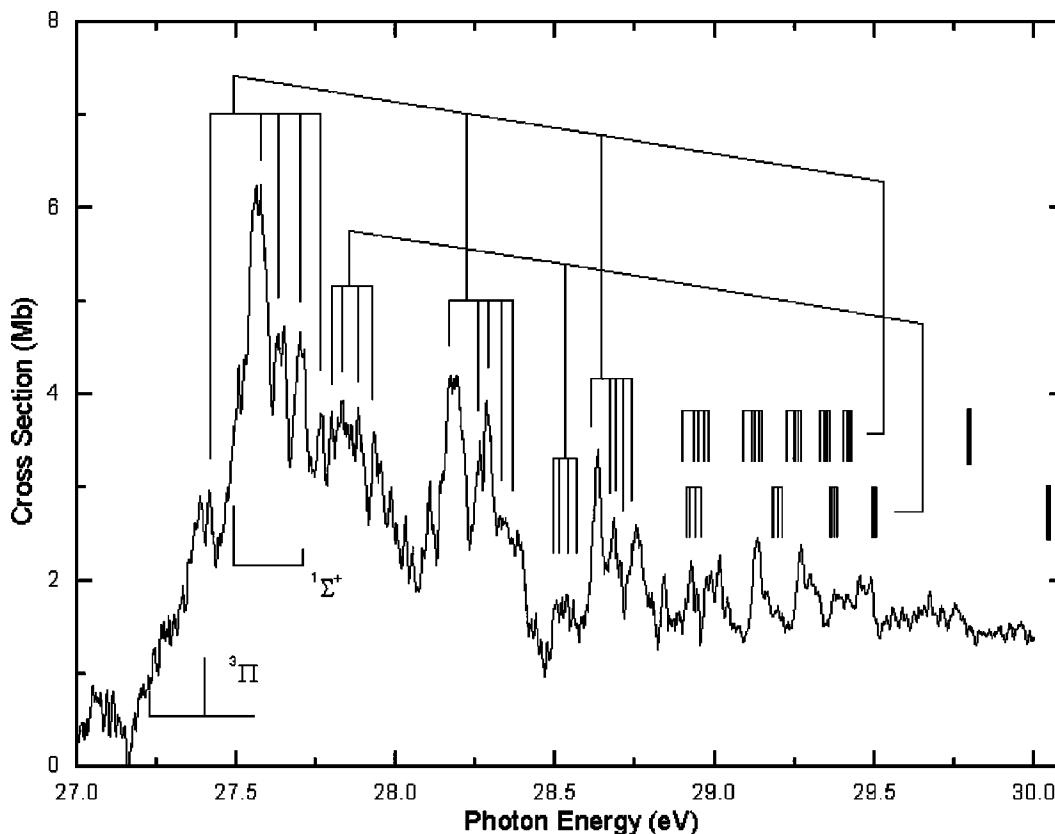

FIG. 4. Cross section for photoionization of CO$^+$ measured with 15 meV photon energy resolution. The first Rydberg series is indicated by the upper grouping, and a second Rydberg series with four components is indicated by the lower grouping. The series limits are indicated by thick vertical lines. Partial vibrational series of the metastable CO^{2+} product are shown at the bottom left of the spectrum, for which the lengths of the vertical lines are proportional to the Franck-Condon factors.

also allowed, but is not resolved. The upper and lower Rydberg series become intermingled from $n=7$ and $n=8$, respectively, making them difficult to distinguish.

Differences between the quantum defects of the present Rydberg series with $^3\Sigma^+[\nu=0]$ core series and those of Ref. [2] are attributed to the higher resolution and photon density (10^{13} s^{-1}) of the present experiment, which allows better localization of the features. On the other hand, there is a good agreement in terms of the signs of the quantum defects, indicating two low angular momentum states (positive δ).

In a recent theoretical paper [8], Veseth presents a comparison with the measurements of Andersen *et al.* [2], finding good agreement if the internuclear separation R_e for the $^3\Pi$ state is assumed to be 2.34 a.u. As indicated in Table I, the present cross-section measurements are lower than those of Andersen *et al.* at higher photon energies. The agreement between the present measurements and theory is better when R_e is assumed to be 2.38 a.u. for the $^3\Pi$ state. Veseth concluded that the $^1\Sigma^+[\nu=0]$ is short lived, so that it would not be expected to contribute to the present measurements.

The peaks indicated by inverted triangles in Fig. 3 have a lower energy threshold shifted about -330 meV from the first Rydberg series. Their positions were calculated using Eq. (2) with $L=29.85$ eV, $\delta=0.593$, and from $n=5$. Their lower excitation energy and intensity indicate that they originate from a small population of vibrationally excited CO$^+[^2\Sigma^+(\nu=1)]$ in the parent ion beam. The components of this Rydberg series are not resolved and hence the values given here for L and δ are approximate.

As in the case of the ground state, the cross section for initially vibrationally excited CO$^+$ is expected to rise at threshold and to decay with increasing energy. A high population of excited CO$^+$ would have resulted in a nonzero cross section at photon energies below the ground state CO$^+$ threshold near 27.5 eV. The superposition of all the nonzero cross sections originating from CO$^+[^2\Sigma^+(\nu>0)]$ would yield a larger cross section at higher photon energies. A comparison of the background cross sections with those of Andersen *et al.* [2] is shown in Table I. Differences are attributed to the unknown populations of initially excited CO$^+$ in both experiments. The faster decay with photon energy of the present measurement may be due to a vanishing contribution from the initially excited CO$^+$ component at the higher energies. A detailed discussion of the origin of the background cross section is presented in Refs. [8,18].

The observed doubly charged states [7,9,19] that have sufficient lifetimes to contribute substantively to the present measurement are the $^3\Pi(\nu=0,1)$ and $^1\Sigma^+(\nu=0)$ states. Their relative contributions to the total cross section cannot be evaluated from this experiment. However, since these are known to be the dominant metastable states of CO^{2+}, the present measurement can be used to estimate the total ionization cross section.

On the other hand, the observation of vibrational structures due to the metastable states of CO^{2+} is feasible. For a complete identification, Franck-Condon (FC) transition factors from ground state CO$^+$ to possible vibrational states of metastable CO^{2+} are needed. The FC transition factors from CO$^+[^2\Sigma^+(\nu=0)]$ to the $^3\Pi$ and $^1\Sigma^+$ states of CO^{2+} were

TABLE III. Franck-Condon transition factors from CO$^+[^2\Sigma(\nu=0)]$ vibrational states of CO^{2+}. Only the $^1\Sigma^+[\nu=0]$ and $^3\Pi[\nu=0,1]$ can be observed in the experiment.

ν	$^3\Pi$	$^1\Sigma^+$	$^1\Pi$
0	0.050	0.736	0.046
1	0.121	0.216	0.118
2	0.164	0.039	0.168
3	0.166	0.007	0.176
4	0.142	0.002	0.153
5	0.109	0	0.116

calculated and are shown in Table III. The potential energy curves have been calculated using *ab initio* methods. An extensive $[5s4p3d2f]$ atomic natural obitals (ANO) basis set [20] was employed and multireference configuration interaction (MRCI) and multireference averaged coupled pair functional (MRACPF) calculations were performed, using the MOLCAS suite of programs [21]. The results are of similar quality to those obtained by Larsson *et al.* [6]. In particular, it is important to point out the correct ordering (from lower to higher) of the electronic states $^3\Pi, ^1\Sigma^+, ^1\Pi$, which are in agreement with the experimental data of Lundqvist *et al.* [4].

To obtain the vibrational energy levels and FC factors, the radial Schrödinger equation was solved using accurate numerical methods with the LEVEL program [22]. The results of the calculations are presented in Table III and indicated graphically in Fig. 4. To assist the identification of these vibrational series, the vertical lines in Fig. 4 were drawn proportionally to the strengths of the calculated FC transition factors for the lowest vibrational states. A definite identification of the vibrational series in the spectrum is difficult to establish, since there are unresolved peaks close to $^1\Sigma^+[\nu=0]$ and $^3\Pi[\nu=1]$ resonances.

IV. SUMMARY AND CONCLUSIONS

The total photoionization cross section has been measured with an initially vibrationally relaxed CO$^+$ ion beam. All five allowed components of a Rydberg series with a $^3\Sigma^+[\nu=0]$ core have been identified, as have four components of a second Rydberg series with a vibrationally excited $^3\Sigma^+[\nu=1]$ core. Within the scope of the present experiment, a conclusion about the main processes involved in the formation of metastable long-lived CO^{2+} can be drawn. An underlying cross section of 2.5 Mb at threshold, falling off at the higher energies covered by this experiment, indicates that direct (nonresonant) photoionization of CO$^+$ to CO^{2+} occurs. Also, the formation of CO^{2+} is through highly excited states of CO$^+$, i.e., Rydberg states with an underlying electronically excited, doubly charged ion core. This observation is consistent with the two-step mechanism discussed by Dawber *et al.* [23] for the production of CO^{2+} from neutral CO. The presence of vibrational structure in the photoionization cross section cannot be clearly resolved in the present experiment.

ACKNOWLEDGMENTS

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