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Resonance multiphoton ionization study of the $B\,^1\Sigma^+$ state of CO

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We report measurements of $(4+2)$ resonantly enhanced multiphoton ionization (REMPI) of CO. The excitation route is first to the $\nu=0$ level of the CO $B\,^1\Sigma^+$ state followed by the absorption of additional two photons to reach the ionization continua. Measurements of the CO$^+$ and C$^+$ ion intensities as a function of the wavelength were made, yielding no rotational structure of any intermediate resonant state in contrast to the $(2+1)$ REMPI experiment. In a second measurement, the laser frequency was set at the $\upsilon=0$ band head of the $B\,^1\Sigma^+$ and the kinetic-energy spectrum of the ejected electrons was measured. The observed photoelectron spectrum is assigned to the multiphoton ionization of CO via the resonant $X\,^1\Sigma^+$ to $B\,^1\Sigma^+$ excitation.

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I. INTRODUCTION

The carbon monoxide molecule has been the subject of numerous spectroscopic investigation. The importance of CO molecule to atmospheric processes, combustion chemistry, and astrophysical phenomena has kept the spectroscopy and reaction dynamics of this important molecule a current topic in research. The $B\,^1\Sigma^+(\upsilon=0)\rightarrow X\,^1\Sigma^+(\upsilon=0)$ band of ^{12}C ^{16}O was first observed in absorption by the Copernicus satellite [1]. Rotationally resolved spectra of the $X\,^1\Sigma^+\rightarrow B\,^1\Sigma^+$ band were recorded by Sheffer *et al.* [2]. Large discrepancies in the literature values of the photoabsorption oscillator strengths of the CO (B-X) transitions have hampered the interpretation of these astronomical observations. The B state has four known vibrational levels [3–5].

X-B transitions are strong and have received attention both, experimentally and theoretically. Three experimental approaches have been used in the determination of the B-X band f values, optical-absorption measurements [6,7], radiative lifetime measurements [8,9], and inelastic electron-scattering measurements [10–13]. *Ab initio* calculations of the B-X electronic transitions moment and oscillator strengths have been reported by Kirby and Cooper [14], Chantranupong *et al.* [15], and Rocha *et al.* [16]. Tchang-Brille [4] used a semiempirical close coupling model of the (BD) Rydberg valence interaction to calculate the $B\,^1\Sigma(\upsilon=0)$-$X\,^1\Sigma(\upsilon=0)$ f values ratio. There is little agreement among the previously published results, although it is apparent that the theoretical calculations produce $B(\upsilon=1)\rightarrow X(\upsilon=0)$ f band values that are lower than almost all of the experimentally determined f values. The electronic states of CO have been observed up to excitation energies close to the lowest ionization energy using VUV and XUV absorption and emission techniques [7,17,18]. More recently the application of the multiphoton excitation techniques in the study of the excited states of CO has proved to be of importance. Examples are found in studies of the $A\,^1\Pi$ [19–21], $B\,^1\Sigma$ [22,23], and $E\,^1\Pi$ states [24–26]. The importance of multiphoton excitation is found in the selection rules on $\Delta\Lambda$ and ΔJ, which enables a larger number of transitions to be studied than the one-photon transitions. On the other hand, the signal strength is dependent on the polarization of the excitation light in the case of multiphoton excitation processes while it is independent of polarization in the case of one-photon excitation. An n-photon transition from state g to state f can be regarded as proceeding along an excitation route consisting of n consecutive one-photon transitions via $(n-1)$ virtual intermediate states i. In each of these one-photon transitions, Λ may change by 0 or 1 depending on whether the transition takes place via the z component of the transition dipole moment in the molecule fixed frame (parallel transition) or via the $(x+iy)$ component (perpendicular transition). An excitation route in an n-photon transition may thus be characterized by the number of parallel and the number of perpendicular transitions that occur [27–30].

Data concerning the $B\,^1\Sigma^+-X\,^1\Sigma^+$ transitions have been obtained [3]. Analysis of these data points to the presence of predissociation in particular to the $B\,^1\Sigma^+$, the first member of the Rydberg series $ns\sigma$. The positions of the rovibrational levels in the B state are shifted down to a considerable extent, compared with the corresponding levels of the ground state ion CO$^+$, which must be a consequence of a strong interaction with another electronic state. A possible candidate [31] for the above interaction, within the $^1\Sigma$ manifold, is the $D\,^1\Sigma^+$. It was predicted by Cooper and Langhoff [32] to be in the above energy range and was observed by Wolk and Rich [34]. According to these authors, the interaction between the $D\,^1\Sigma^+$ and the nearby electronic states may be extensive. Eidelsberg [3] suggested that this interaction is responsible for the predissociation observed in the B state. The *ab initio* calculations by Cooper and Kirby [33] confirmed this suggestion showing that the B Rydberg state should correlate adiabatically with the $D\,^1\Sigma^+$. Similar, but weaker predissociation features are observed for the $3p\sigma C\,^1\Sigma^+$ state [18]. In higher states of the Rydberg series $ns\sigma$ and $np\sigma$, predissociation is also present through various features. Therefore, a strong perturbation by the $D\,^1\Sigma^+$

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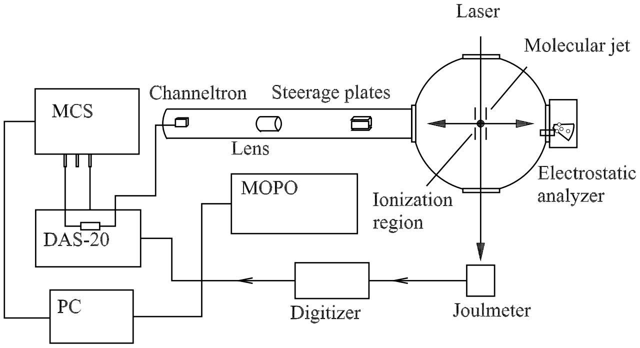

FIG. 1. Schematic diagram of the TOF spectrometer.

valence state seems to be a reasonable hypothesis that needs to be verified taking into account the possibility of accidental resonance.

In the $(2+1)$ photon process, the two-photon excitation takes place to resonant state that is followed with a third-photon absorption resulting in an ion-photoelectron pair. Either the time-of-flight (TOF) spectrum of the ions or the photoelectron energy spectrum can provide information regarding the rovibrational state of the intermediate excited state. It is our objective to investigate the case where the intermediate excited state may be followed by one-photon excitation leading to possible accidental resonant state that is predissociative or to states that are followed by one more photon excitation leading to ionization as well as to obtain some semiquantitative information on how such a process would influence the detection of the rovibrational levels of the resonant state.

II. EXPERIMENTAL APPARATUS

The experimental apparatus shown in Fig. 1 consists of Nd:YAG (yttrium aluminum garnet) pump laser and a Master Oscillator–Power Oscillator (MOPO), a TOF mass spectrometer, and hemispherical electron analyzer.

The 355-nm third harmonic of the Nd:YAG laser is used to pump the MOPO resulting in tunable output in the 440–700 nm wavelength range, 10 Hz frequency, 10 ns duration and wavelength resolution of 10^{-3} cm^{-1} resulting in effective resolution of 4×10^{-3} cm^{-1} for the four photon absorption processes. The laser beam of 97% linearly polarized light in the horizontal plane was focused into the collision volume by a 150-mm quartz convex lens. The measured diameter of the focused laser beam at the center of the ionization region was found to be about 60 μm producing a maximum power of 10^{11} W/cm^2 at 460 nm wave length. At this point, it intersects at right angles a molecular beam produced by a free molecular jet expansion of CO gas of commercial grade. This expansion was generated by a General Valve Iota One System. The TOF mass spectrometer consists of the jet chamber with a pulsed nozzle, a drift chamber with steerage plates, lens, and a channeltron detector. The supersonic beam is perpendicular to both the laser beam and the TOF axis. The laser beam is focused 31 mm away from the 100 μm diameter nozzle. The TOF spectrometer has sufficient resolution to separate the isotope components of Xe and therefore lower mass ions. The signal from the detector was passed into ORTEC VT 120 fast preamplifier and into a multichannel scaler (MCS) Turbo for the registration of the TOF spectrum using a mini computer. The laser pulse initiates the start of the MCS. Since the gas from the molecular jet requires about 3 μs to travel the 31 mm distance, the laser pulse was delayed by 3 μs with respect to the molecular jet pulse in order to maximize the ion signal. The CO gas from the commercial steel cylinder passed through a liquid nitrogen trap to remove $\mathrm{Fe(CO)_5}$ impurities that would otherwise give severely broadened Fe I lines in or near the region of interest. The photoelectrons from the photoionization region were extracted with a small field typically of 1 V/cm and focused into the entrance of the hemispherical electron analyzer (COMSTOCK901B). The analyzer was operated in a constant transmission mode with a resolution of 40 meV and the electron signal was detected using a channel electron multiplier and a standard pulse counting techniques. For the calibration of laser wavelength and electron energy analyzer we measured the photoelectron spectrum resulting from the multiphoton ionization of Xe $^2P_{3/2}$ and $^2P_{1/2}$ previously measured by Compton *et al.* [30] at 440.8 nm. Our photoelectron spectrum was found to agree well with the that of Compton *et al.* [30] yielding a resolution of 50 meV and an excellent peak shape with no indication of tailing.

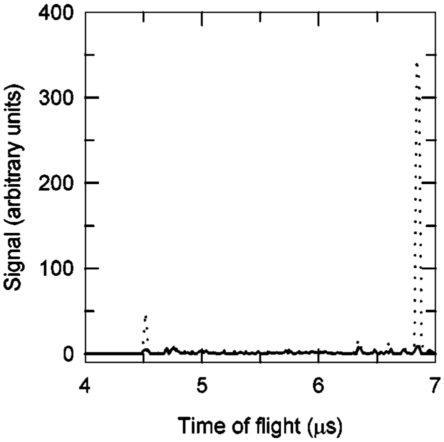

FIG. 2. Resonant (dotted line) and nonresonant (solid line) C^+ and CO^+ TOF spectra recorded at 460.05 and 460.2 nm laser wavelengths. The two peaks of C^+ and CO^+ appear at 4.52 μs and 6.85 μs, respectively.

III. RESULTS AND DISCUSSION

The $B\,^1\Sigma^+$ state is the first member of the ns Rydberg series converging to the electronic ground state of the carbon monoxide ion. Eidelsberg *et al.* [18] have concluded that the $B\,^1\Sigma^+$ state is perturbed by another nearby lying state which causes the upper rotational and vibrational levels of this state to predissociate implying that only the lower rotational levels of the $B\,^1\Sigma^+(v=0)$ may be populated.

The CO^+ and C^+ were measured at laser wavelength of 460.05 nm corresponding to four photon resonant excitations to the $B\,^1\Sigma^+(v=0)$ and at 460.2 nm. The results are shown in Fig. 2. It is apparent that the resonant process vanishes

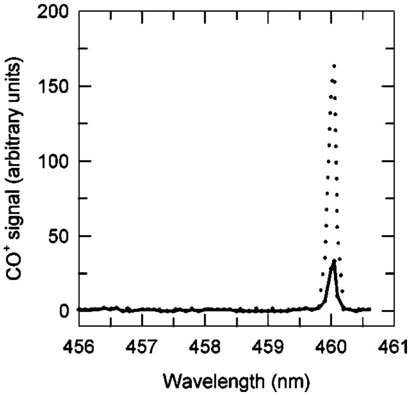

FIG. 3. CO$^+$ (dotted line) and C$^+$ signals (solid line) as a function of wavelength of the laser light.

when the laser wavelength is changed to 460.2 nm. Lowering laser-pulse energy improved the width of the CO$^+$ signal while the C$^+$ signal almost vanished. Higher laser-pulse energies did not yield any O$^+$ signal.

Although the resonance signal was mainly that of CO$^+$ and C$^+$ ions, however the time-of-flight spectrum was obtained for each wavelength and for a defined number of laser pulses. The area under the CO$^+$ and C$^+$ ion peaks was determined from each spectrum, corrected for laser intensity differences and plotted as a function of wavelength in Fig. 3. A strong signal dependence on wavelength is evident. Measurements were made down to 450.43 nm (not shown in Fig. 3).

The full width at half maximum (FWHM) of the CO$^+$ signal is a consequence of the laser-pulse energy as well as the contribution of the very low *J* levels of the $B\,^1\Sigma^+(v=0)$ which are not easily resolved with our experimental resolution. Equally the fact that the potential of the $B\,^1\Sigma^+$ state is similar to that of the ground state, means that the difference in the rotational constants is very small. The consequence of that, the *Q* branch, at least for low *J*, cannot be resolved with a normal pulsed laser. This would explain the unresolved rotational contribution to the CO$^+$ spectrum. Although the O and S transitions can be resolved, however their intensity is two to three orders of magnitude lower and may be observed employing very high power lasers. Wavelengths down to 450.43 nm show absence of any rotational structure in contrast to the $(2+1)$ photon experiment.

In order to investigate the reasons for the absence of any rotational structure pertaining to the $B\,^1\Sigma^+(v=0)$ state, the potential-energy curves for the $B\,^1\Sigma^+$ state as well as upper lying states are needed. Figure 4 shows the positions of the observed vibrational levels in the *B* and *C* Rydberg states [3,18] as well those of the $D\,^1\Sigma$ valance state [34]. Also shown are the observed levels in the $4s$, $5s$, and $6s\,^1\Sigma^+$ Rydberg states [4].

The $B\,^1\Sigma^+(v=0)$ state, shown in Fig. 4, is populated by four-photon excitation (10.78 eV total energy) of the $X\,^1\Sigma^+(v=0)$ at 460.05 nm wavelength. The fifth photon may then excite the CO $B\,^1\Sigma^+(v=0)$ according to the following possibilities: (1) excitation to $\mathrm{C}\,^1\Sigma^+(v\geqslant 7)$; (2) excitation to $4s\sigma$ Rydberg state $(2\leqslant v\leqslant 3)$; (3) excitation to $5s\sigma$ Rydberg state $(v=0)$.

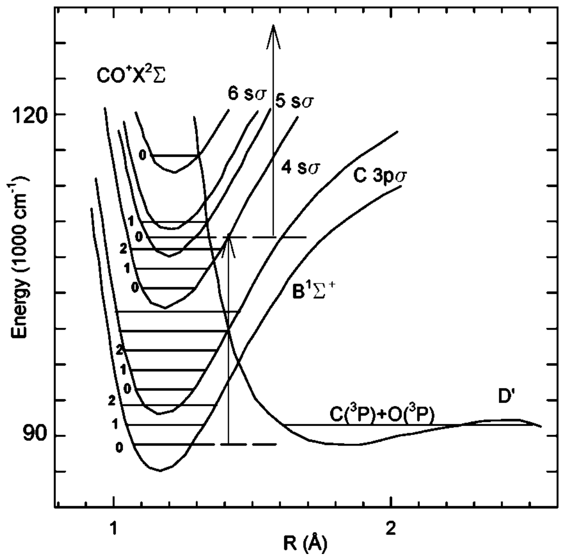

FIG. 4. Schematic $^1\Sigma^+$ diabatic potentials and observed levels in CO with the origin of the energies chosen to be the minimum of the ground-state potential. Arrows indicate the fifth- and sixth-photon excitation.

For the first possibility, the $D\,^1\Sigma$ valance state crosses the $\mathrm{C}\,^1\Sigma^+$ state at $v=3$. This would imply reduced ionization to be observed through the predissociation of the $\mathrm{C}\,^1\Sigma^+(v\geqslant 7)$.

Similarly for the second excitation route, $D\,^1\Sigma$ valance state crosses the $B\,^1\Sigma^+$ ($4s\sigma$ Rydberg state) at $1\leqslant v\leqslant 2$. Therefore the $4s\sigma$ Rydberg state $(v\geqslant 2)$ is expected to predissociate and contribute as well to the reduced ionization.

However for the third excitation possibility, the D^1 valance state crosses the $B\,^1\Sigma^+$ ($5s\sigma$ Rydberg state) just above $v=1$, therefore the population of the $B\,^1\Sigma^+$ [$5s\sigma$ Rydberg state $(v=0)$] at a total energy of 13.48 eV is expected to be enhanced since it corresponds to the energy supplied by the fifth photon (total of five photons excitation). The enhanced population of the $B\,^1\Sigma^+$ [$5s\sigma$ Rydberg state $(v=0)$] may be followed by the absorption of one more photon leading to ionization. Take into account the total excitation energy of six photons to be 16.17 eV and the ionization potential of CO to be 14.01 eV, with the CO atoms populating the $B\,^1\Sigma^+$ [$5s\sigma$ Rydberg state $(v=0)$] needing only about 0.53 eV to reach the ionization continuum with the remaining energy of the sixth photon (2.165 eV) carried away by the liberated photoelectron as kinetic energy. This is confirmed by the measured photoelectron spectrum shown in Fig. 5.

The above discussion strongly suggests that reduced ionization through predissociation do indeed contribute to the absence of any rotational structure pertaining to the $B\,^1\Sigma^+(v=0)$.

The C$^+$ spectrum displays striking similarity to the CO$^+$ spectrum; since the spectral features occur at the same wavelengths, it is obvious that both are being produced by ionization of molecules prepared in the $B\,^1\Sigma^+$ state. The adiabatic energy of the $\mathrm{C}^+(2P)+\mathrm{O}(3P)$ production of 22.35 eV is

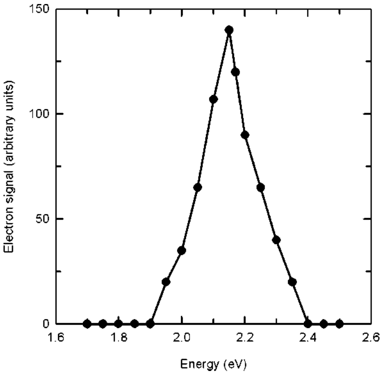

FIG. 5. Photoelectron spectrum of CO determined at the wavelength of the five-photon resonant excitation to the $B\,^1\Sigma^+[5s\sigma(\upsilon=0)]$.

almost exactly resonant with $4+2+3$ photon absorption through the $B\,^1\Sigma^+$ state of CO, therefore ionization of the CO through the population of the $B\,^1\Sigma^+$ may be followed by three-photon absorption into the $C^+(2P)+O(3P)$ dissociation limit. On the other hand if we assume that $B\,^1\Sigma^+(\upsilon=0)$ may predissociate for J values larger than 17, the result is $(C+O)$. It is unlikely that the fragment C will be ionized since that would require five more photons. To verify the process dependence on the number of photons involved, we employed a variable iris in the laser beam path. The iris diameter was decreased gradually, therefore reducing the laser beam intensity in the interaction region. The resulting TOF spectra were recorded for 460.05 nm wavelength. Our results showed that the C^+ signal does indeed vanish while that of CO^+ is still apparent at laser intensities down to 0.2×10^{11} W/cm^2.

IV. CONCLUSION

We have investigated the $(4+2)$ resonantly enhanced multiphoton ionization of CO. The excitation to the $B\,^1\Sigma^+$ was found to involve the $\upsilon=0$ vibrational level only. The recorded photoelectron spectrum confirms that the excitation was that to the $\upsilon=0$ of the $B\,^1\Sigma^+$. The fifth photon excitation to the upper Rydberg states (accidental resonance) that is followed by predissociation through the D^1 state which results in reduced ionization can be considered as the reason for the lack of any rotational structure that has been observed in the $(2+1)$ resonantly enhanced multiphoton ionization experiment.

The C^+ signal we measured may be the result of the CO^+ resultant ions absorbing three more photons leading into dissociation through the $C^+(2P)+O(3P)$ at a total excitation energy of energy 22.35 eV. The disappearance of the C^+ signal at lower laser power intensities confirms this prediction.

Accidental resonance at the five-photon level coupled with the possibility of predissociation almost certainly play an important role in the reduced ionization and the observation of the rotational structure of the intermediate resonant state. It is most likely that such possibility also influences the ionization signal at the $B\,^1\Sigma^+(\upsilon=0)$. Multicolor laser probes can do much to eliminate ambiguities by improving the specificity of the process.

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