Predissociation of the Rydberg states of CO : State specific predissociation to the triplet channel

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Predissociation of the Rydberg states of CO: State specific predissociation to the triplet channel

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Photofragment yield spectra of the $3d\pi L'\ ^1\Pi(v=1)$ and $4p\pi L\ ^1\Pi(v=0)$ Rydberg states have been observed by monitoring the fragment atoms generated by the predissociation. The Rydberg states of CO were prepared by two-color double resonant excitation through the $3s\sigma B\ ^1\Sigma^+$ state, and both C(^3P and ^1D) and O(^3P) atom fragments were observed by two-photon resonant three photon (2+1) ionization. In particular, it has been found that the C(^1D) fragmentation takes place in these Rydberg states, which is the first evidence of the predissociation to the triplet channel. Predissociation rates to the triplet channel were estimated, indicating that the rates are comparable to those to the singlet channel. © *1998 American Institute of Physics.* [S0021-9606(98)03805-7]

I. INTRODUCTION

Rydberg states of CO has been extensively studied both experimentally[1–12] and theoretically.[13–17] Letzelter *et al.*[1] observed the absorption spectrum in the region of 90–115 nm and obtained the photoabsorption and photodissociation cross sections. They concluded that the photodissociation of CO takes place after the absorption to the discrete states, most of which are considered to be Rydberg states. Eidelsberg and co-workers[2,3] extensively investigated the one-photon absorption spectrum of the Rydberg states and reported the molecular constants of these states. Ubachs and co-workers[4–6] and Drabbels *et al.*[7] reported the predissociation rates of the Rydberg states ($n=3-6$) by measuring linewidths with a narrow bandwidth laser. Ebata and co-workers[8–11] also reported a spectroscopic study of the Rydberg states ($n=4-7$ for $v'=0$, $n=4-10$ for $v'=1$) of CO by using the ion-dip method with triple resonant excitation, and determined the potential curve of the repulsive $D'\ ^1\Sigma^+$ state. Very recently, Mellinger *et al.*[18,19] investigated the triplet Rydberg states, and analyzed the rotational structure by using laser-reduced fluorescence spectroscopy.

Contrary to the extensive spectroscopic studies of the Rydberg states of CO, very few experiments have been done on the measurement of the photofragment atoms produced by the predissociation process. Forch and Merrow[20,21] observed the atomic oxygen generated after the two-photon absorption of CO at 193 nm. Hill *et al.*[22] detected an emission of the atomic carbon produced by the multiphoton dissociation of CO. However, none of those studies have specified the states from which the predissociation takes place. It is fundamentally important to select the initial state to investigate the state-to-state dynamics of the predissociation, and to determine the potential curves of the repulsive states. In our previous work, we reported the photofragment yield spectra by monitoring the C(^3P) atom and directly confirmed that the dissociation occurs from the Rydberg states.[12] In the present study, we concentrated our study on the detection of the fragments generated by the predissociation of the $3d\pi L'\ ^1\Pi(v=1)$ and $4p\pi L\ ^1\Pi(v=0)$ states at $\sim$103 220 cm^{-1}. Though the two states are separated by only 60 cm^{-1}, they show quite different behavior in the predissociation rate. According to the rotational linewidth measurements by Drabbels *et al.*[7] and Ubachs *et al.*,[4–6] the linewidth of the $3d\pi L'\ ^1\Pi(v=1)$ state is 1.22 cm^{-1} independent of J, while that of the $4p\pi L\ ^1\Pi(v=0)$ state depends not only J but also the parity of the rotational level. In addition, two dissociation channels are energetically possible for the $3d\pi L'\ ^1\Pi(v=1)$ and $4p\pi L\ ^1\Pi(v=0)$ states; a singlet channel leading to C(^3P)+O(^3P) and a triplet channel to C(^1D)+O(^3P). The detection of the C(^3P) and C(^1D) fragments is essential to investigate the potential crossings between the Rydberg and the corresponding manifold of the repulsive states of CO. In the present work, the generation of the C(^1D) fragments was directly confirmed and it was found that the predissociation to the triplet states are comparable to that to the singlet states.

II. EXPERIMENT

Figure 1 shows the excitation scheme and experimental setup of the photofragment yield measurement. Jet-cooled CO was excited to the $3s\sigma B\ ^1\Sigma^+(v=0)$ state by two-photon absorption of ν_1 and further excited to the specific Rydberg state by successive excitation with second laser ν_2. The fragment atoms generated by the predissociation of the Rydberg state were monitored by two-photon resonant three photon ionization (2+1) REMPI with ν_3. The transitions used for the detection of the atomic states were $^3D_{J'}\leftarrow{}^3P_{J''}$ for C(^3P), $^1P_1\leftarrow{}^1D_2$ for C(^1D) and $^3P_{J'}\leftarrow{}^3P_{J''}$ for O(^3P).

Two dye lasers (Lambda Physik FL3002 and Molectron DL14) were simultaneously pumped by a XeCl excimer laser (Lambda Physik LPX 100iMC). A frequency doubled output of FL3002 and a fundamental output of DL14 were used as ν_1 and ν_2, respectively. The laser beams of ν_1 and ν_2 were introduced into a vacuum chamber in a mutually counter-propagated geometry, being focused by lenses ($f=250$ mm). For ν_3 a second harmonic of Nd:YAG laser-pumped dye laser (Quanta-Ray GCR-230-10/Continuum ND6000) was used, which was coaxially introduced with ν_2 by using a beam combiner. All the laser beams were linearly polarized. The delay time between ν_1 (or ν_2) and ν_3 was set to 20 ns by

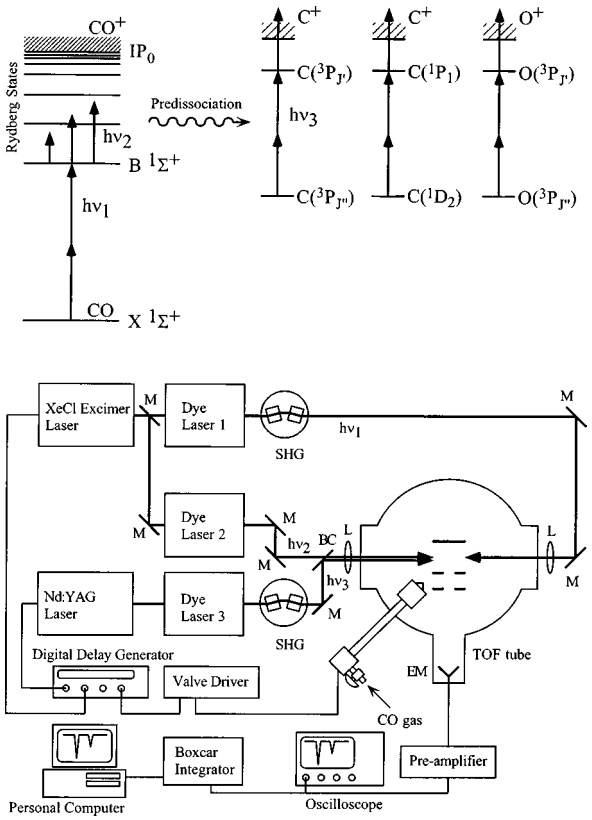

FIG. 1. (Upper) Energy levels and the diagram of the excitation of CO and the detection of the $C(^3P)$, $C(^1D)$, and $O(^3P)$ fragments. (Lower) Schematic diagram of the experimental setup.

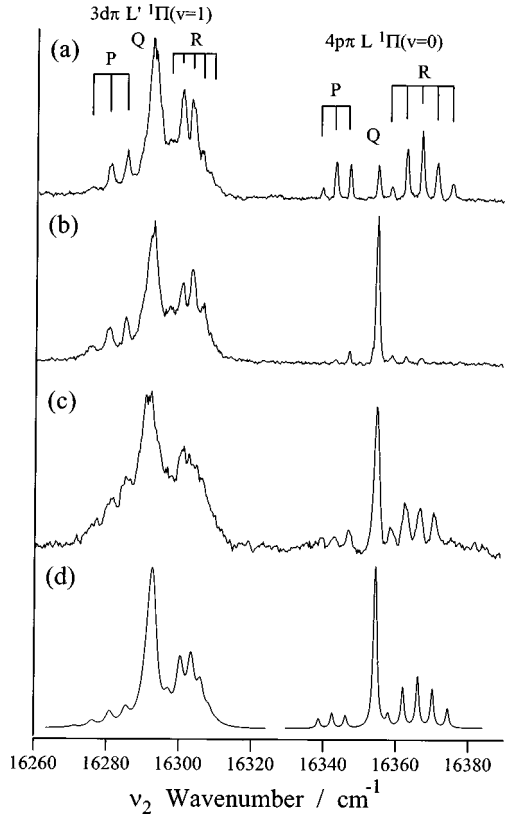

FIG. 2. Photofragment yield spectra of the $3d\pi L'\ ^1\Pi(v=1)$ and the $4p\pi L\ ^1\Pi(v=0)$ states observed by monitoring (a) $C(^3P)$, (b) $C(^1D)$, and $O(^3P)$ fragments. (d) Simulated $L'\ ^1\Pi(v=1)$, $L\ ^1\Pi(v=0) \leftarrow 3s\sigma B\ ^1\Sigma^+(v=0)$ absorption spectra by assuming $T_{\rm rot}=15$ K.

using the digital delay generator (SRS Model DG535). Pure CO was expanded into a vacuum chamber through a pulsed nozzle having an orifice of 400 μm and the three laser beams crossed at 15 mm downstream of the nozzle. The ions were separated by a time-of-flight (TOF) tube and were detected by an electron multiplier (Murata Ceratron). The signal was amplified by an amplifier (NF Model BX-31) and was integrated by a boxcar integrator (PAR Model 4420) connected with a personal computer.

III. RESULTS AND DISCUSSION

In the $3s\sigma B\ ^1\Sigma^+(v=0) \leftarrow X\ ^1\Sigma^+(v=0)$ two-photon transition by using the linearly polarized ν_1, only an intense bandhead of the Q branch was observed, indicating several rotational transitions are overlapped. This is because the rotational constants of both states are similar and the Q branch has strong intensity with the linearly polarized light. Thus ν_1 pumps CO to several rotational levels of the $3s\sigma B\ ^1\Sigma^+(v=0)$ state with the rotational distribution similar to that of the $X\ ^1\Sigma^+(v=0)$ state in the jet. Figures 2(a), 2(b), and 2(c) show the photofragment yield spectrum of the $3d\pi L'\ ^1\Pi(v=1)$ and $4p\pi L\ ^1\Pi(v=0) \leftarrow 3s\sigma B\ ^1\Sigma^+(v=0)$ transitions obtained by monitoring (a) $C(^3P)$, (b) $C(^1D)$, and (c) $O(^3P)$ atoms, respectively. Figure 2(d) shows simulated $3d\pi L'\ ^1\Pi(v=1)$ and $4p\pi L\ ^1\Pi(v=0) \leftarrow 3s\sigma B\ ^1\Sigma^+(v=0)$ spectra by using the rotational constants and the rotational linewidths reported by Drabbels *et al.*[7] and the group of Ubachs.[4–6] In this simulation, we assumed the Boltzmann rotational distribution for the $3s\sigma B\ ^1\Sigma^+(v=0)$ state to be $T_{\rm rot}=15$ K, which is thought to be equal to the rotational temperature of the jet.

First of all, it should be noted that the present work has presented the first state-specific observation of the $C(^1D)$ fragment generated by the predissociation of the Rydberg states of CO. The result is the direct evidence for predissociation involving the triplet channel. As seen in the figures, all the photofragment yield spectra of the $3d\pi L'\ ^1\Pi(v=1)$ state are similar with each other and are in good agreement with the simulated spectrum (d). On the other hand, the photofragment yield spectra of the $4p\pi L\ ^1\Pi(v=0)$ are quite different from each other, and do not fit with the simulated spectrum (d) except for (c). As seen in the figures, the Q branch is weak compared with the P and R branches when the $C(^3P)$ atom is monitored [Fig. 2(a)], while the Q branch is much stronger than the P and R branches and the intensities of the R and P branches monotonously decrease with J when the $C(^1D)$ atom is monitored [Fig. 2(b)]. Since the $O(^3P)$ atom is the common product for the singlet and triplet dissociation channels, the $O(^3P)$ yield spectrum agrees very well with the simulated spectrum [Fig. 2(c)]. Among the photofragment yield spectra, the $O(^3P)$ yield spectrum is broadened due to saturation of ν_2. This is because the $O(^3P)$ ion signal was weaker than those of $C(^3P)$ and $C(^1D)$, and higher ν_2 power (200 μJ) was necessary to obtain the spec-

trum in good signal-to-noise ratio. For other fragment measurements, the ν_2 power was reduced to 50 μJ.

According to the linewidth measurements of the $4p\pi L\ ^1\Pi(v=0)\leftarrow 3s\sigma B\ ^1\Sigma^+(v=0)$ transition reported by Drabbels *et al.*[7] and by the group of Ubachs,[4–6] the linewidth of the Q branch (f-symmetry component) is independent of J, while those of the P and R branches (e-symmetry component) increase proportionally with $J(J+1)$. The J dependence suggests that the e-symmetry component of the $4p\pi L\ ^1\Pi(v=0)$ state predissociates to the repulsive $^1\Sigma^+$ potential surface, that is, $D'\,^1\Sigma^+$ state, and that the predissociation of the f-symmetry component of the $4p\pi L\ ^1\Pi(v=0)$ state dissociates to the repulsive $^1\Pi$ state, that is the $2\ ^1\Pi$ state.[13,17] By assuming that the radiative decay rates of the Rydberg states are much smaller than the predissociation rates, the total quantum yield to the singlet and triplet dissociation channels is considered to be unity. As a consequence, the change of the predissociation rate to the singlet channel leads to the change in the quantum yield of the triplet channel product, that is C(^1D). Thus the observed dependence for the C(^3P) and C(^1D) products for the $4p\pi L\ ^1\Pi(v=0)$ state can be explained by that the predissociation processes to the singlet and triplet channels are competing with the similar rate and the rotational dependence is due to that of the predissociation rate to the singlet channel.

We estimated the predissociation rates to the singlet and triplet channels from the observed photofragment yield spectra and from the reported total decay rate, k, of each rotational levels obtained from the linewidth measurement. Here the total decay rates are the sum of the singlet (k_s) and triplet (k_T) dissociation rates. For the e-symmetry component, the predissociation rate to the singlet manifold is expressed as the sum of the J independent and dependent terms,

$$k_S^e = k_0 + k_J J(J+1). \tag{1}$$

For the f-symmetry component, on the other hand, the rate includes only J independent term,

$$k_S^f = k_0. \tag{2}$$

For the triplet channel, we assumed that k_T is independent of J, since the spin–orbit coupling does not include J. Though this assumption is rather crude, the simulated photofragment yield spectrum well reproduced the observed spectra. The observed signal intensities are given by

$$I(^1D) = S_{J'J''} \times \frac{k_T}{k_S + k_T}, \tag{3}$$

$$I(^3P) = S_{J'J''} \times \frac{k_S}{k_S + k_T}, \tag{4}$$

where $S_{J'J''}$ is the $4p\pi L\ ^1\Pi(v'=0,J')\leftarrow B\ ^1\Sigma^+(v''=0,J'')$ transition intensity. From the linewidth measurements by Drabbels *et al.*,[7] $k_J = 1.2\times 10^9\ \mathrm{s}^{-1}$, and $k_0 + k_T = 1.9\times 10^9\ \mathrm{s}^{-1}$. By changing the value of k_T, we found the simulated spectra well reproduce the observed ones for $k_T = 1.4\times 10^9\ \mathrm{s}^{-1}$, as shown in Fig. 3. From these results, it is concluded that the predissociation of the $4p\pi L\ ^1\Pi(v=0)$ state to the triplet channel competes with that to the singlet channel with comparable rate.

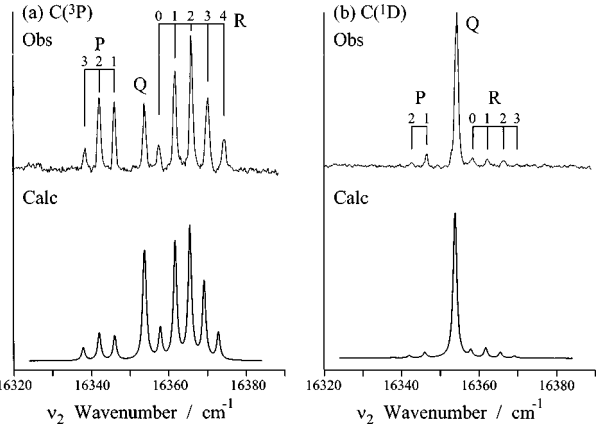

FIG. 3. Photofragment yield and simulated spectra of $4p\pi L\ ^1\Pi(v=0)\leftarrow 3s\sigma B\ ^1\Sigma^+(v=0)$ transition of CO. (a) C(^3P) and (b) C(^1D) fragment monitored spectra.

Furthermore, it is suggested that the predissociation rate of the $3d\pi L'\ ^1\Pi(v=1)$ to the triplet channel is also comparable to that to the singlet channel because the C(^1D) signal intensity of $3d\pi L'\ ^1\Pi(v=1)$ is similar to that of $4p\pi L\ ^1\Pi(v=0)$. Estimated predissociation rate of the $3d\pi L'\ ^1\Pi(v=1)$ state to the triplet channel is $k_T \sim 10^{11}\ \mathrm{s}^{-1}$.

Shafer III *et al.* calculated several valence states for the triplet repulsive states to which the Rydberg states predissociate. According to their calculation, $^3\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$ states are known to cross the potential curves of the Rydberg states at relatively low energy region. At this stage, we can not predict which state is mainly responsible for the predissociation. More detailed analysis is in progress, which includes the rotational and vibrational dependencies of the predissociation rates.

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