First observation of the *v*=3 level of the *B* $^1\Sigma^+$ Rydberg state of CO

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A new diffuse vuv band of $^{12}C^{16}O$ at 92 800 cm^{-1} has been observed in absorption and assigned to the $B-X(3-0)$ transition. The assignment is based on the excellent agreement found between the observed band and a calculated spectrum of the $B-X(3-0)$ transition, where a previously optimized two channel close-coupling model of the B $^1\Sigma^+-D'$ $^1\Sigma^+$ Rydberg–valence predissociation interaction has been used to calculate the $B(v=3)$ state molecular constants, J dependent predissociation widths and the J dependent $B-X(3-0)$ vibronic transition moments. The relative absorption cross-section for this transition has also been calculated. © *1995 American Institute of Physics.*

I. INTRODUCTION

Prior to this study only the first three vibrational levels of the $3s\sigma$ B $^1\Sigma^+$ Rydberg state of CO were known. Fluorescence from the $v=0$ and 1 levels to the A $^1\Pi$ state was first reported by Angstrom and Thalen in 1875,[1] although the actual assignment came later in 1926 from the detailed analysis of the $A-X$ and $B-A$ emission bands by Birge.[2] The $v=2$ level of the B state, which does not fluoresce, has only recently in 1987 been unambiguously assigned by Eidelsberg *et al.*[3] in a rotationally resolved isotopic study of vuv absorption from the X $^1\Sigma^+(v=0)$ ground state. The B state, as is often the case for the first member of a Rydberg series, shows deviations from Rydberg character. This is due to its strong interaction with the shallow bound D' $^1\Sigma^+(1\pi\rightarrow2\pi)$ valence state.[3,4]

The D' state, which has a potential energy minimum at relatively large internuclear distance, was first predicted theoretically[5,6] and later observed experimentally by Wolk and Rich[7] from uv laser induced fluorescence of highly vibrationally excited CO(X $^1\Sigma^+$, $v=20-40$). This state cannot be accessed directly from the lowest-lying vibrational levels of the ground state because of unfavorable Franck–Condon overlap. Cooper and Kirby[8] showed using *ab initio* methods that the B state in fact correlates adiabatically with the D' state, giving rise to a double minimum adiabatic state, which dissociates to the lowest energy atomic pair, C(^3P)+O(^3P). A two-channel close coupling model of the B $^1\Sigma^+-D'$ $^1\Sigma^+$ interaction was constructed by some of us[4] in 1992 which reproduced the available experimental data concerning the $B-X$ transitions such as molecular constants, predissociation linewidths and the $B-X$ relative absorption cross-sections of the $v=0$, 1, 2 levels of the B $^1\Sigma^+$ state.

In the present study we have observed a new absorption band of $^{12}C^{16}O$ at 92 800 cm^{-1}. This new band can be assigned to the $B-X(3-0)$ transition and therefore represents the first observation of the $v=3$ level of the B $^1\Sigma^+$ state. To aid in the assignment of this feature the B $^1\Sigma^+-D'$ $^1\Sigma^+$ close coupled model of Ref. 4 has been employed to calcu-

late the molecular constants, predissociation linewidths and relative $B-X$ absorption cross section for the $v=3$ level of the B $^1\Sigma^+$ state. A calculated spectrum of the $B-X(3-0)$ transition has also been realized for comparison with the experimental spectrum.

II. EXPERIMENT AND RESULTS

The experimental details have been described elsewhere[3,9] and hence only a brief consideration is given here. Photographic absorption spectra of natural CO, recorded on Kodak SWR plates, were obtained at room temperature between 98 000–87 000 cm^{-1} by means of the 10 m Eagle mounting vuv spectrograph of the Meudon observatory. Between threshold and saturation the photographic plates have approximately a logarithmic response to the transmitted light. Natural isotopic composition, 99.997% purity, carbon monoxide gas was introduced into the spectrograph, which constitutes an absorption cell of about 20 m path length. The pressure inside the spectrograph was varied from 0.02 to 1.5 Torr and the exposure time from 30 min to 3 h. Calibration was achieved using known atomic emission lines in a hollow cathode lamp as well as known lines appearing in the actual CO absorption spectra.

Figure 1 shows densitometer recordings of the photographic spectra in the 93 600–92 300 cm^{-1} absorption region of natural CO at three different pressures. Figure 1(a) shows the spectrum at 0.15 Torr where the E $^1\Pi-X$ $^1\Sigma^+$(0–0) band of $^{12}C^{16}O$ can be seen (the low J'' lines of this transition are completely saturated at this pressure). This band is blue degraded and has a P-branch bandhead at $J''\approx46$, 47 at 92840.7±0.2 cm^{-1} as derived from the known molecular constants of the E and X states.[10,11] The apparent anomalous intensity of the $R(30)$ and $P(32)$ lines is caused by a localized perturbation with a predissociated state at $J'=31$ of the E state.[12,13] The rotationally resolved k $^3\Pi-X$ $^1\Sigma^+$(2–0) band of $^{12}C^{16}O$ is also observed in Fig. 1(a). The k $^3\Pi$ valence state has only recently been properly assigned[9,14,15] and is responsible for the local perturbation in the $E(v=0)$ state mentioned above as well as localized perturbations in the $E(v=1)$[9,14] and $B(v=2)$[16] states. At 0.5 Torr, see Fig. 1(b), a broad feature showing no resolved rotational structure can be seen. This band underlies the
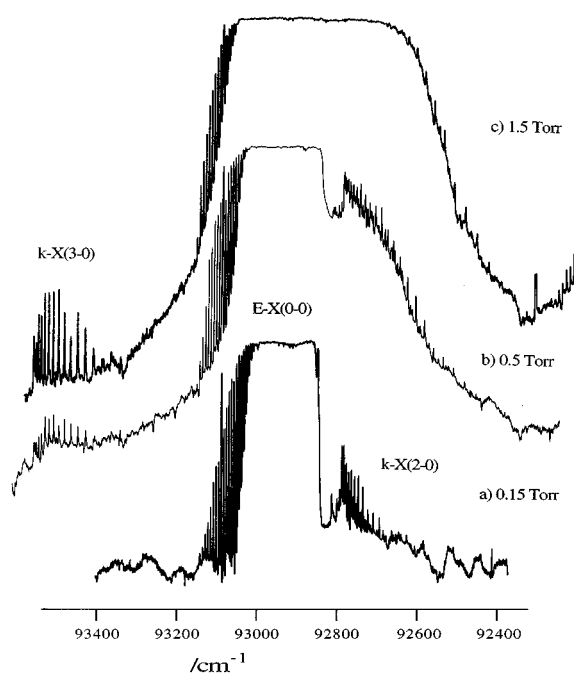
FIG. 1. Absorption spectra of natural CO in the 93 600–92 300 cm^{-1} wave number range at a CO pressure of (a) 0.15 Torr, (b) 0.5 Torr, and (c) 1.5 Torr. The resolution of these recordings is limited by the slit width of the densitometer and the thickness of the pen nib.
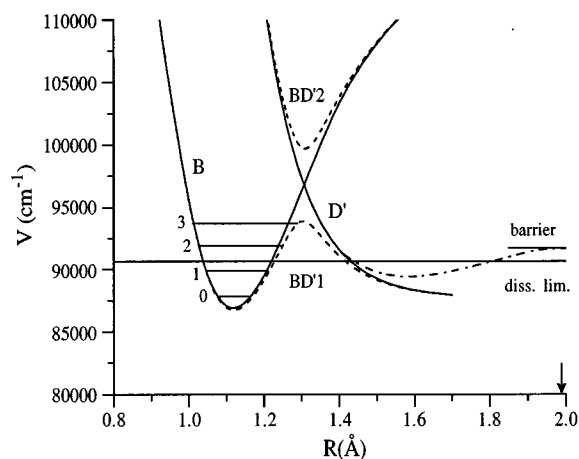

FIG. 2. Model diabatic (solid line) and adiabatic (dashed line) potentials (Ref. 4). The energy is referenced to the minimum of the ground state potential energy curve. The positions of the dissociation limit, the D' state barrier to dissociation and the calculated $J=0$ levels of the B state (for ^{12}C^{16}O) are shown. The deperturbed D' RKR potential is represented by the $\cdots$ line. The arrow indicates the calculated (Ref. 8) position of the barrier maximum.

$k-X(2-0)$ band and is partially overlapped by the $E-X(0-0)$ band at higher transition frequencies. At this pressure allowed transitions arising from ^{13}C^{16}O and to a lesser extent ^{12}C^{18}O appear in absorption since these are present in trace amounts (1% and 0.2%, respectively) in the natural CO sample used for this study. However, the $E-X(0-0)$ bands of these CO isotopomers are also blue degraded with P-branch bandheads both coincidentally (to within the estimated error) at 92 843.2±1.0 cm^{-1} as derived from their molecular constants given in Refs. 11 and 14. Hence, these isotopomeric bands will be totally overlapped by the $E-X(0-0)$ band of ^{12}C^{16}O and will not contribute to that part of the broad feature appearing to the low frequency side of it. Hence, this broad band is a new feature of the ^{12}C^{16}O absorption spectrum. At 1.5 Torr this band becomes completely saturated as is evident in Fig. 1(c).

An estimate of the intensity maximum of this band of $\approx$92 800 cm^{-1} has been made from measurements of the spectra. This should correspond approximately to the band origin. In fact, this band can be seen as an absorption background in Fig. 1 of Ref. 9 which shows the photographic spectrum of the rotationally resolved $k-X(2-0)$ band. As described later this band may be assigned to the $B-X(3-0)$ transition. No other features in the CO absorption spectrum could be positively assigned to higher vibrational levels of the B state.

III. CALCULATIONS

The previous two channel close coupling model of the strong $B-D'$ Rydberg–valence interaction has been employed here. The detailed description of the modeling pro-

cess is given in Ref. 4. We shall give here only its main features. The close coupling method is applied in a diabatic formulation where both states, B and D', are described by diabatic potentials which are allowed to interact. The 2×2 matrix Schrödinger equation is solved for a given energy E and rotational quantum number J. The B state is always a closed channel while the D' state can be either closed or open depending on the energy. When the D' state is open, the photodissociation cross section $\sigma(E)$ is proportional to the square of the matrix element of the electric dipole operator between the ground state and the excited coupled channel state. Near a rovibrational level $v'J'$ of the B state, the resonance line shape $\sigma(E)$ is well represented by an isolated Lorentzian which gives the position and the predissociation width of the $v'J'$ level. The area under the line is proportional to the square of the J dependent (i.e., R dependent) vibronic transition moment. No interference is observed so long as the direct absorption to the D' state is negligible.

This model has been optimized to reproduce all the experimental observations concerning the B state ($v=0$ to 2) when its interaction with the D' state is taken into account. Figure 2 shows the diabatic potential curves used, together with the adiabatic potentials resulting from the diagonalization of the Hamiltonian. The B state diabatic potential is represented by an RKR potential generated from four free parameters with values for ^{12}C^{16}O of;[4] $\omega_e = 2196.24$ cm^{-1}, $\omega_e x_e = 33$ cm^{-1}, $B_e = 1.966\,055$ cm^{-1}, and $\alpha_e = 0.0218$ cm^{-1}, which were allowed to differ slightly from their $X\,^2\Sigma^+\,^{12}$C^{16}O$^+$ ionic core values. The D' potential is described by a purely repulsive potential extrapolated from the left limb of a deperturbed RKR potential and is represented analytically by $V^d_{D'}(R) = Ae^{-bR} + C$, with $A = 1.3939\times10^9$ cm^{-1}, $b = -9.1348$ Å^{-1} and $C = 785$ cm^{-1}. It was shown in Ref. 4 that the calculated vibrational level energy shifts of the B state depended only on the left limb of

the D' RKR potential, i.e., was insensitive to the shape of the D' potential beyond the short-range repulsive part. In addition the barrier to dissociation of the D' potential was found to have little effect on the calculated predissociation widths for levels above it. The coupling operator mixing the two diabatic states was taken as constant $V_0 = 2900$ cm^{-1} for $R < R_c$ and a decaying Gaussian function with half-width $\Delta R = 0.20$ Å for $R > R_c$, where $R_c = 1.307\,11$ Å is the assumed crossing point of the two diabatic potentials. In addition, by normalizing against the experimental $B-X(0-0)$ band oscillator strength,[17] the diabatic transition moments for the $B-X$ and $D'-X$ transitions were found to be 0.031 and 1.56 a.u., respectively, i.e., the $D'-X$ electronic transition moment is about 50 times greater than that for the $B-X$ transition. This is in reasonable agreement with the *ab initio* MCSCF study of Cooper and Kirby,[8,18] where the electronic transition dipole moment from the ground state to the adiabatic $B-D'$ double minimum potential increases by an order of magnitude when the internuclear distance R varies from the B state minimum to the D' state minimum. This is an important feature of the interaction because, by mixing with the D' state, the $B-X$ transition can gain extra intensity, even though the $D'-X$ transition is not observable here (due to poor Franck–Condon overlap).

In the present work, the above model[4] is expected to yield accurate predictions for the $B(v=3)$ state without further modifications. Using the same diabatic potentials, coupling operator and diabatic transition moments, close coupling calculations have been performed in the energy range of the $B(v=3)$ state for selected J' values: $J'=0,5,10,...,50$ in addition to $J'=7$ (where $J''=7$ is the maximum of the ground state rotational distribution at $T=298$ K). All the line shapes obtained are Lorentzian to a good extent (less than 2% difference at five half-widths from the center). From these calculations the $B(v=3)$ state term values, predissociation widths, Γ, and the J dependent $B-X$ vibronic transition moments, μ_{ev}, were determined and then interpolated for the other values of J' by polynomial fits. For simplification these calculations were carried out for $\Delta J = 0$ transitions. Only μ_{ev} shows any non-negligible changes when P and R branches are considered as done later for calculation of the spectrum. The error in $|\mu_{\text{ev}}|^2$ *for a given J'* is $\approx 0.1\%$ for $J'=0$ which increases to $\approx 5\%$ for $J'=50$, with $|\mu_{\text{ev}}(P(J''=J'+1))|^2 > |\mu_{\text{ev}}(Q(J''=J'))|^2 > |\mu_{\text{ev}}(R(J''=J'-1))|^2$. The net intensity of the $Q(J)$ transitions are, of course, zero for the $B-X$ transition due to the conservation of angular momentum.

The term values of the calculated levels of the $B(v=3)$ state of $^{12}C^{16}O$ (referenced to the $X\,^1\Sigma^+(v=0,\,J=0)$ ground state) have been interpolated by fitting to the expression,

$$T(v'=3,J') = T_{30} + B_3 J'(J'+1) - D_3 (J'(J'+1))^2$$
$$+ H_3 (J'(J'+1))^3, \quad (1)$$

where the correlation coefficient of the fit differed from 1 by only 2×10^{-11}. This yields the molecular constants of $^{12}C^{16}O$ given in the second column of Table I. This table also gives G_3, the vibrational energy of the $B(v=3)$ state of $^{12}C^{16}O$ referenced to the minimum of the $BD'1$ adiabatic potential

TABLE I. Calculated results of the close coupling model for the $B(v=3)$ state.[a]

	$^{12}C^{16}O$ $B\,^1\Sigma^+$	$^{12}C^{16}O^+$ $X\,^2\Sigma^{+\,b}$	$^{13}C^{16}O$ $B\,^1\Sigma^+$	$^{13}C^{16}O^+$ $X\,^2\Sigma^{+\,c}$
T_{30}	92 792.04		92 683.27	
G_3	6 946.73	7564.13	6 813.77	7399.50
B_3	1.833 40	1.910 84	1.755 79	1.827 13
D_3 (10^{-6})	9.348 90		9.674 94	
H_3 (10^{-9})	1.224 98		1.116 11	
$\Gamma(J=0)$	90.4^{d}		67.6	

[a]All values are in cm^{-1}.
[b]Experimental values, from Ref. 21.
[c]Experimental values, from Ref. 19.
[d]Based on the same model (Ref. 4), a recent theoretical study of quasibound states using optical potential and discrete variable representation (Ref. 20) applied to the $B-D'$ interaction in CO as example, led to a predissociation width of 90.9 cm^{-1} for the $J=0$ level.

(see Fig. 2). The calculated values of G_3 and B_3 differ from the corresponding experimental values of the $X\,^2\Sigma^+$ $^{12}C^{16}O^+$ ionic core[21] by $\delta G_3 = -617.4$ cm^{-1} and $\delta B_3 = -0.0774$ cm^{-1}, respectively. These large differences indicate the deviation of the B state from Rydberg character. Figure 3 gives a plot of $\delta G_v = G_v(B) - G_v(\text{ion})$ against v, for the B state, and shows that this deviation increases with the vibrational quantum number.

The predissociation widths Γ, of the rotational levels of the $B(v=3)$ state were found to be strongly J dependent, increasing from 90.4 cm^{-1} for $J'=0$ to 357.4 cm^{-1} for $J'=50$. They are plotted as a function of J' in Fig. 4(a). Figure 4(b) shows the variation of $|\mu_{\text{ev}}|^2$ with J' (for $\Delta J=0$), where $|\mu_{\text{ev}}|^2$ has been normalized with respect to its $J'=0$ value. In general for an unperturbed, nonpredissociated excited state one would assume the vibronic transition moment to be independent of J (i.e., independent of R), over a given
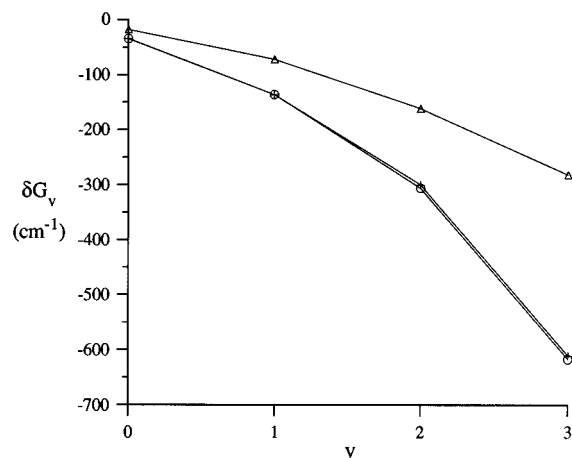

FIG. 3. Shifts of the vibrational levels, v, of the $B\,^1\Sigma^+$ state of $^{12}C^{16}O$ defined as $\delta G_v = G_v(B) - G_v(\text{ion})$, where the $v=0$ to 2 values were taken from Refs. 3 and 4. $+$=experimental values, where the $v=3$ value was obtained by assuming an experimental band origin of 92 800 cm^{-1} for the $B-X(3-0)$ transition; $\bigcirc$=calculated values; $\triangle$=diabatic model shifts (without D' interaction).
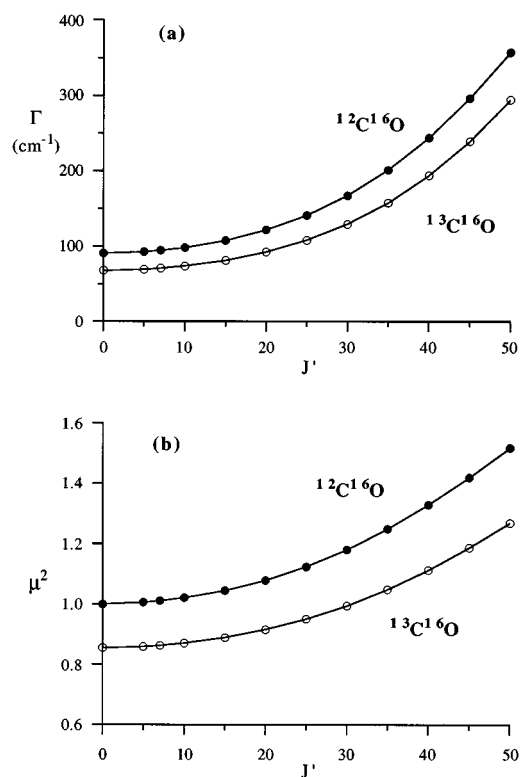
FIG. 4. (a) Variation of the calculated $B(v=3)$ state predissociation widths Γ for $^{12}\mathrm{C}^{16}\mathrm{O}$ (filled circles) and $^{13}\mathrm{C}^{16}\mathrm{O}$ (open circles). (b) Variation of the calculated $B-X(3-0)$ vibronic transition moments squared (for $\Delta J=0$) and normalized with respect to the $J'=0$ transition moment of $^{12}\mathrm{C}^{16}\mathrm{O}$.
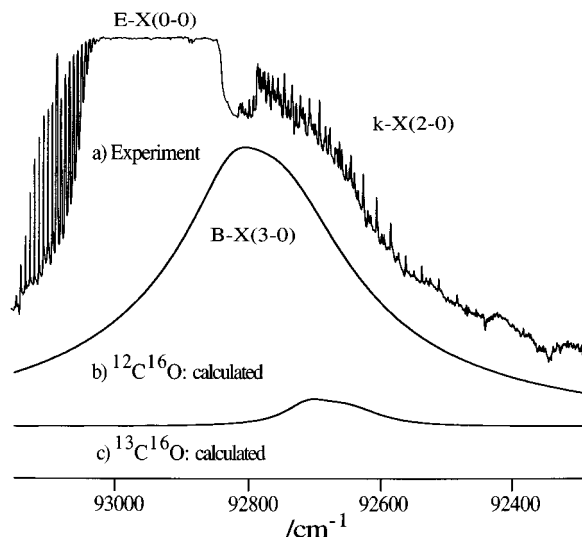

FIG. 5. Experimental and calculated spectra of the $B-X(3-0)$ band in the 93 200–92 300 cm^{-1} range (a) Experimental spectrum at 0.5 Torr. (b) Calculated $B-X(3-0)$ band of $^{12}\mathrm{C}^{16}\mathrm{O}$. (c) Calculated $B-X(3-0)$ band of $^{13}\mathrm{C}^{16}\mathrm{O}$. For the calculations $^{13}\mathrm{C}^{16}\mathrm{O}$ is assumed to be in 1% abundance compared to $^{12}\mathrm{C}^{16}\mathrm{O}$ and the intensity scale is in logarithmic units. See the text for details of the calculations.

vibronic transition from the ground state. However, for the $B-X(3-0)$ transition a relatively large variation is found with J.

The $B-X(3-0)$ spectrum of $^{12}\mathrm{C}^{16}\mathrm{O}$ was finally calculated as follows. The P and R-branch line positions were derived from the calculated $B(v=3)$ state term values by subtracting from them the appropriate ground state rotational energies.[11] The relative intensities of the rotational lines were obtained from the product of the appropriate Hönl–London factor, the Boltzmann factor (assuming $T=298$ K) and the square of the J dependent vibronic transition moment $|\mu_{\mathrm{ev}}|^2$ (here calculated with the correct selection rules $\Delta J=\pm1$). These were then convoluted with a Lorentzian line shape having the J dependent predissociation width, Γ.

Similar calculations to those described above for $^{12}\mathrm{C}^{16}\mathrm{O}$ were also performed for the $^{13}\mathrm{C}^{16}\mathrm{O}$ isotopomer. The calculated molecular constants for the $B(v=3)$ state of $^{13}\mathrm{C}^{16}\mathrm{O}$ are given in the fourth column of Table I and its J dependent predissociation widths are shown in Fig. 4(a). Similar to $^{12}\mathrm{C}^{16}\mathrm{O}$, the $B(v=3)$ state of $^{13}\mathrm{C}^{16}\mathrm{O}$ was found to have very large predissociation widths increasing from 67.6 cm^{-1} at $J'=0$ to 294.8 cm^{-1} at $J'=50$. Figure 4(b) also shows the variation of $|\mu_{\mathrm{ev}}|^2$ with J' for this isotopomer, where $|\mu_{\mathrm{ev}}|^2$ has been normalized with respect to the $J'=0$ value of $^{12}\mathrm{C}^{16}\mathrm{O}$.

IV. DISCUSSION

Figure 5(a) gives the experimental spectrum of natural CO in the range 93 200–92 300 cm^{-1} at 0.5 Torr and shows the newly observed diffuse vuv band of $^{12}\mathrm{C}^{16}\mathrm{O}$. Figure 5(b) gives the calculated $B-X(3-0)$ spectrum of $^{12}\mathrm{C}^{16}\mathrm{O}$ where the intensity has been plotted in arbitrary logarithmic units for comparison with the experimental spectrum. As is evident, there is very good agreement between the experimental and calculated spectra, in terms of absolute position, width, and band shape (although the high frequency side of the diffuse band is overlapped by the more intense $E-X(0-0)$ band). Hence, this new feature can be assigned to the $B-X(3-0)$ transition. The band origin of the calculated spectrum occurs at 92 792 cm^{-1} while the intensity maximum occurs at 92 802 cm^{-1}. This compares well to the experimental band maximum of $\approx$92 800 cm^{-1}.

Figure 5(c) shows the calculated $B-X(3-0)$ spectrum for $^{13}\mathrm{C}^{16}\mathrm{O}$. This band also does not show rotational structure due to the large calculated predissociation widths. The intensity maximum of the calculated band occurs at 92 698 cm^{-1}, i.e., about 100 cm^{-1} to the low frequency side of the corresponding band of $^{12}\mathrm{C}^{16}\mathrm{O}$. There does seem to be a weak shoulder at $\approx$92 650 cm^{-1} in the experimental spectrum [see Fig. 5(a)] on the $B-X(3-0)$ band of $^{12}\mathrm{C}^{16}\mathrm{O}$ which would be consistent with this, although, it is difficult to determine for certain due to the overlapping $k-X(2-0)$ transition. However, the isotopomeric band should make a contribution to the experimental spectrum of Fig. 1(c) obtained at 1.5 Torr, i.e., to the apparent extension of the broad band to lower frequencies, since $^{13}\mathrm{C}^{16}\mathrm{O}$ forms about one percent of the natural CO sample used in this study.

The effect of the D' interaction on the lifetimes of the different B state levels shall now be considered. The $v=0$

and 1 vibrational levels for low J, below the dissociation limit, emit with a radiative lifetime of ≈ 30 ns.[18] A first intensity weakening in emission above $J'=37$ and 17 for $v=0$ and 1, respectively, in $^{12}C^{16}O$ occurs when the levels go energetically above the dissociation limit but these levels are still below the energy barrier of the D' state—see Fig. 2, and so this predissociation is caused by some state other than the D' state. A second intensity weakening in emission from the $v=1$ level above $J'=35$ and 36 for $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively, has also been observed by Eidelsberg et al.[3] Tchang-Brillet et al.[4] considered that this was due to the rotational levels going over the D' state energy barrier and so coupling with the D' dissociation continuum. Partly from this they estimate the D' energy barrier to be 1048 ± 19 cm^{-1} above the dissociation limit. The $v=2$ level, which lies above the D' barrier, has only been seen in absorption and shows rotational line broadening, most notably in $^{12}C^{16}O$ which has experimental linewidths ranging from 0.7 to 2 cm^{-1}.[3,4] This corresponds to lifetimes shorter than 8 ps, which when compared with the expected radiative lifetime of ≈ 30 ns indicates 100% dissociation. It is therefore not surprising that this level does not fluoresce. The close coupling model predicts an even stronger interaction for the $v=3$ level with a predissociation width of 90 cm^{-1} for $J'=0$, corresponding to a lifetime of about 56 fs. This explains why the $B-X(3-0)$ band shows no rotational structure. The $v=3$ level also shows the greatest deviation in its molecular constants, G_v and B_v, when compared to the corresponding quantities of the $X\,^2\Sigma^+$ ground state of CO$^+$ (compare Table I of this study with Table III of Ref. 4). As can be seen in Fig. 3, the deviations, δG_v, due to the $B-D'$ interaction increase with increasing v, which is not surprising considering that the vibrational levels approach closer to the crossing point of the B and D' diabatic states with increasing v—see Fig. 2.

Finally, due to the importance of vuv photodissociation of CO to astrophysical modeling of planetary atmospheres and interstellar clouds, a consideration of the integrated absorption cross-section, $\sigma(v'=3)$ of the $B-X(3-0)$ transition of $^{12}C^{16}O$ shall be made. An order of magnitude estimate of this quantity can be obtained from the densitometer recordings by comparing the intensity of this band to the neighboring absorption bands of natural CO which have known integrated absorption cross sections[17,22,23] and taking into account the response of the photographic plates. This yields an estimate of $\sigma(v'=3)\approx 10^{-20}$ cm^2 nm. The close coupling model gives a $\sigma(v'=3)/\sigma(v'=0)$ cross section ratio of 1.1×10^{-3} which yields $\sigma(v'=3)=5.8\times10^{-21}$ cm^2 nm, when the experimental value of $\sigma(v'=0)=5.29\times10^{-18}$ cm^2 nm is used.[22] Hence, there is reasonable agreement between the theoretical value and the experimental estimate. In the diabatic model the cross section ratio $\sigma(v'=3)/\sigma(v'=0)$, is given by the ratio of the respective Franck–Condon factors which is calculated to be 1.5×10^{-5}. This is much smaller than the ratio obtained using the model. A similar effect is found for $v'=1$ and 2 relative to $v'=0$, for the $B-X(v'-0)$ transition.[4] This indicates that these transitions gain extra intensity via the increased coupling of the B Rydberg state to the D' valence state with increasing v', since as has been

mentioned in the previous section, the electronic transition moment for the $D'-X$ transition is about 50 times greater than that for the $B-X$ transition. The intensity borrowing is strongest near the crossing point of the two diabatic potentials. This explains why the calculated vibronic transition moments [see Fig. 4(b)] of $^{13}C^{16}O$ are smaller than the corresponding values of $^{12}C^{16}O$, since the $B(v=3)$ state of $^{13}C^{16}O$ has a downward isotopic energy shift, away from the crossing point. The increase of the vibronic moment with J can also be explained since the $B(v=3)$ state outer turning point is localized at the internuclear distances where the $BD'1-X$ adiabatic transition moment strongly increases.[4,18] In general one would assume the vibronic transition moment to be constant for a given transition, i.e., independent of J and hence independent of R, however, this assumption is not true in the present case.

V. CONCLUSION

A new feature in the vuv absorption spectrum of $^{12}C^{16}O$ has been observed at 92 800 cm^{-1} and assigned to the $B-X(3-0)$ transition. It is a weak broad band which shows no rotational structure. The $B(v=3)$ state is also found to be shifted to lower energy by about 617 cm^{-1} compared to the corresponding level of the ion. All these features are due to the strong predissociating interaction between the B Rydberg state and the valence D' state which has been described using a two channel close coupling model previously[4] applied successfully in the modeling of the $B(v'=0-2)$ levels. The calculated $B-X(3-0)$ band agrees very well with the experimental spectrum both in absolute position and band shape.

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