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Excitation of Higher-Lying Metastable States in Carbon Monoxide by Electron Impact: Cross-Section and Lifetime Measurements*

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The electron-impact cross section and radiative lifetime of the 10-eV metastable state in CO has been investigated from threshold (9.5 ± 0.4 eV) to 45 eV using a time-of-flight apparatus. The absolute cross section at the peak of the excitation function (15.5 eV) was estimated to be 3×10^{-18} cm^2 to within a factor of 3. The radiative lifetime at 15 eV was found to be 97 ± 15 μsec. Measurements at 45 eV resulted in a smaller lifetime, suggesting the existence of more than one state. The assignment of the state as $b\,^3\Sigma^+$ is rejected based on cross section and lifetime arguments, and the $D\,^1\Delta$ and $I\,^1\Sigma^-$ states are suggested as alternate candidtates based on threshold considerations.

I. INTRODUCTION

A 10-eV metastable state in CO has been observed by several investigators in electron-impact experiments. Olmsted *et al.*,[1] using a surface detector, observed a rising cross section with an onset of 10.5 eV on top of the $a\,^3\Pi$ cross section. They estimated the lifetime of this 10-eV state to be of the order of 100 μsec and suggested that it might be $b\,^3\Sigma^+$. Cermák,[2] using Penning-ionization detection, established the existence of two metastable states, one with an energy in the range 9.2–10.2 eV and the other with an energy ≥ 10.2 eV. Cermák[2] suggested that the latter state is identical with the one Olmsted *et al.*[1] associated with the $b\,^3\Sigma^+$ state. Borst and Zipf,[3] in an experiment similar to the one of Olmsted *et al.*,[1] derived the excitation function of this metastable state by subtracting the electron-impact cross section for the $a\,^3\Pi$ state, observed optically by Ajello[4] from the total metastable excitation function. They estimated a lifetime of the order of 150 μsec for this state and pointed out that it is probably not the $b\,^3\Sigma^+$ state owing to its much shorter lifetime. In this paper, we report a more thorough study of this unidentified metastable state in CO. Using the same apparatus as Borst and Zipf,[3] we employed different experimental and analytical techniques to deduce the cross section and lifetime of this state.[5]

II. EXPERIMENTAL

The experimental time-of-flight (TOF) apparatus has been described in detail elsewhere.[3,6-8] The basic TOF apparatus is shown in Fig. 1. A pulsed magnetically collimated electron beam was incident on CO in the collision chamber. Beam pulses were 2 μsec wide with repetition rates of 1 KHz, resulting in an integrated beam current of 10^{-7} A. The collision chamber with the CO gas at a uniform pressure ($\sim 10^{-4}$ Torr) acted as a diffuse gas source. The metastable CO gas molecules produced by electron impact were detected at right angles to the electron beam at a distance of 6.4 cm with a nude Cu-Be electron multiplier. The incoming pulses from the multiplier were amplified and deposited in a multichannel scaler (MCS), which was being triggered synchronously with the beam pulse. The time-to-amplitude converter and the pulse-height analyzer used for fast arrival times were not necessary in this experiment for the study of slow thermal CO^m molecules. The dwell time of the MCS was 10 μsec/channel. To obtain good TOF spectra (see Fig. 3) with a typical counting rate of 100 counts/sec it was necessary to run the MCS for about 2 h. The data were transferred for processing from the MCS to a high-speed digital computer via paper tape and a time-sharing terminal (not shown in Fig. 1).

A schematic diagram of the excitation-function apparatus is shown in Fig. 2. Excitation functions were made of various portions of the TOF spectra by employing a delayed coincidence window of variable width and position such that only those counts falling within the window were passed onto the MCS for storage. The MCS was swept synchronously with the electron-beam energy employing a dwell time of 0.5 sec/channel. A typical run would involve 200 sweeps and would last 7 h. At the beginning and end of a run, the beam energy and the beam current were recorded as a function of channel number by monitoring the respective

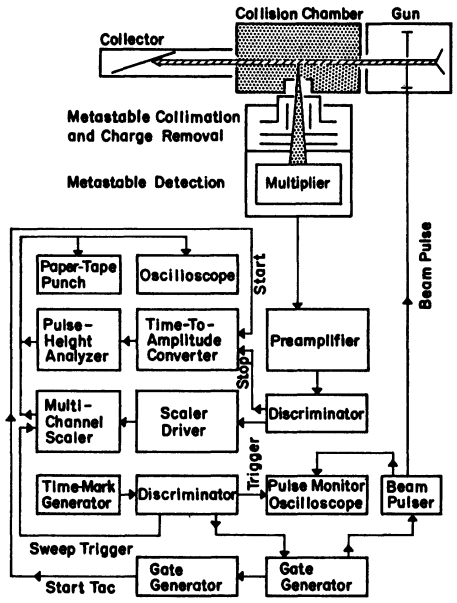

FIG. 1. Experimental TOF apparatus.

voltages with an analog-to-digital converter (ADC) and recording the digital signal on the MCS in one sweep. This approach facilitated current normalization of the excitation function and corrected for any slight nonlinearities in the electron-beam sweep.

III. RESULTS

For electron-impact excitation of a gas, the TOF spectra is given by

$$S_E(t) = K'H(t) \sum_i \sigma_i(E)\gamma_i e^{-t/\tau_i}, \quad (1)$$

where K' is a constant, $H(t)$ is the Maxwell-Boltzmann distribution, $\sigma_i(E), \gamma_i$, and τ_i are the absolute electron-impact cross section, the metastable detection efficiency, and the radiative lifetime, respectively, of the ith electronic state; the sum is over all electronic states.

The time dependence of the Maxwell-Boltzmann distribution can be written as

$$H(t) = Ct^{-4} e^{-\beta t^{-2}}, \quad (2)$$

where C is a normalization constant and $\beta = ml^2/2kT$. The mass of the molecules is given by m, l is the distance between the collision chamber and detector ($l = 6.4$ cm), and T is the temperature of the gas in the collision chamber ($T \simeq 293$ °K).

If $\sigma_i(E)\gamma_i e^{-t/\tau_i}$ vanishes for all but two states, A and B, for the times and energies of interest and $\tau_B \gg \tau_A$, then Eq. (1) can be rewritten

$$S_E(t) = KH(t)(1 + R_E e^{-t/\tau_A}), \quad (3)$$

where K is a constant and

$$R_E = \frac{\sigma_A(E)\gamma_A}{\sigma_B(E)\gamma_B}. \quad (4)$$

Similarly, if $\sigma_i(E)\gamma_i e^{-t/\tau_i}$ vanishes for all but one state, then

$$S_E(t) \simeq KH(t)\sigma(E)\gamma e^{-t/\tau}. \quad (5)$$

A. Lifetime Determination

To determine the lifetime of the unidentified metastable state in CO, two techniques were used to unfold the contribution of the CO($a^3\Pi$) state. The first technique involved fitting Eq. (3) to the TOF spectrum at 15 eV, where the maximum in the cross section for the unidentified state occurs. $H(t)$ was first determined empirically by fitting Eq. (5) to the TOF spectrum at 7 eV, where only CO($a^3\Pi$) molecules were observed. The best fit was made by varying β in Eq. (2). A lifetime of 7 msec [9-11] was used as an effective mean lifetime for the Cameron band system. This lifetime was not a critical parameter in this experiment be-

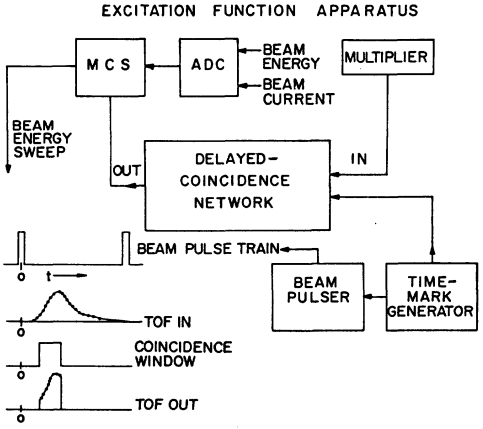

FIG. 2. Excitation function apparatus.

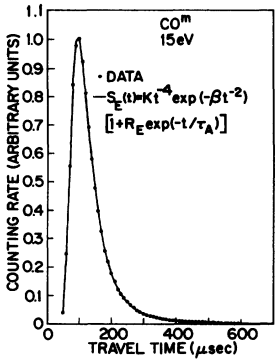

FIG. 3. Fitted TOF spectrum to experimental points at $E = 15$ eV (see text).

cause it was much longer than the times of interest. A typical example of the nonlinear least-squares fit to the data is shown in Fig. 3, where R_E and τ_A were varied for a best fit.

The second technique used to ascertain the lifetime was slightly different and has been employed previously with good success to measure metastable lifetimes in N_2[3]. It involved dividing the TOF spectrum at 15 eV by that at 7 eV. This is equivalent to dividing Eq. (3) by Eq. (5), which yields

$$F = S_{15}/S_7 = K_1 + K_2 e^{-t/\tau_A}. \tag{6}$$

This result is plotted in Fig. 4(a) on a semilog plot. The asymptotic value of F yields K_1. Then plotting $(F-K_1)$ on a semilog plot [Fig. 4(b)] yields a straight line, the slope of which is minus the reciprocal lifetime. Using these two techniques, we arrived at lifetime values, all in good agreement. The average result was $\tau = 97 \pm 5$ μsec. Including systematic errors, the result was $\tau = 97 \pm 15$ μsec. The result for the mixture parameter was $R_{15} = 4.1$.

B. Cross Section

To deduce the relative cross section of this state, two excitation functions were made with windows on both leading and trailing edges of the TOF spectrum. The relative abundance of short-lived CO^m to $CO(a\,^3\Pi)$ was larger within the 50–70-μsec window than within the 200–350-μsec window. This is shown dramatically in Fig. 5 by the different shapes of the excitation functions. The excitation function of the short-lived state was obtained by normalizing and then subtracting the 200–350-μsec-window excitation function from that taken at 50–70 μsec. The result is shown by curve C (Fig. 5). Mathematically, this subtraction process can be written as

$$G(E) = C\sigma(E)\Big[\int_{50}^{70} H(t)(1+R_E e^{-t/\tau})dt - K\int_{200}^{350} H(t)(1+R_E e^{-t/\tau})dt\Big], \tag{7}$$

where K is chosen such that $G(E) = 0$ for $E < 9$ eV, C is a constant, and $\sigma(E)$ is the electron-impact cross section for the production of $CO(a\,^3\Pi)$. Our result indicates the threshold is at 9.5 ± 0.4 eV with a peak at 15.5 eV.

It is possible to make an estimate of the absolute cross section when one considers that the observed counting rate due to one state is given by

$$S = \left(\frac{I}{e}\right) nx \left(\frac{d\sigma}{d\Omega}\right)_{90°} \Delta\Omega \gamma_m \Gamma, \tag{8}$$

where S is the counting rate, I is the current, e is the charge of an electron, n is the number density of scatterers, x is the scattering path length, $(d\sigma/d\Omega)_{90°}$ is the differential cross section at 90°, $\Delta\Omega$ is the solid angle subtended by the detector, γ_m is the metastable detection efficiency, and Γ is the attenuation of the signal due to in-flight radiative decay. The cross section can then be calculated since the other quantities in Eq. (7) are either known or measured in the experiment. The value of γ_m was taken from Borst[12] for a

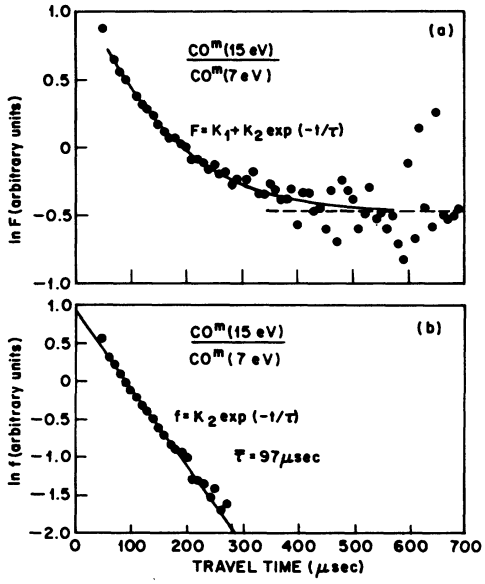

FIG. 4. Semilog plots of exponential decay functions.

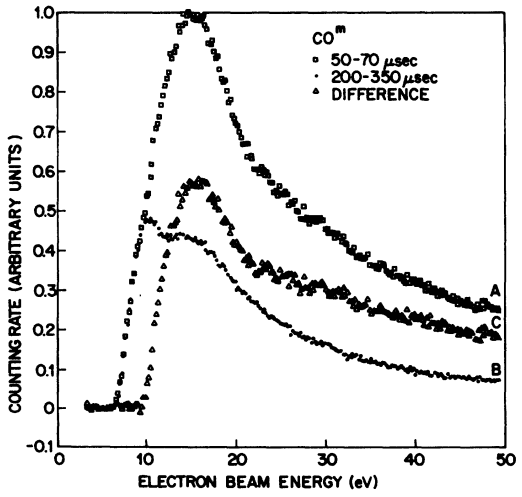

FIG. 5. Excitation functions of CO^m for two different windows with slopes normalized in the 6–9-eV region. Curve C is the difference between A and B and represents the non-$CO(a\,^3\Pi)$ contribution to CO^m.

10-eV metastable. The cross section is then given by

$$\sigma = 4\pi\left(\frac{d\sigma}{d\Omega}\right)_{90^\circ}. \quad (9)$$

Since the lifetime was determined along with the mixing coefficient, it was possible to ascertain what part of the observed signal was due to the short-lived metastable. Using Eqs. (7) and (8), we find a peak cross section at 15.5 eV of $\sigma = 3 \times 10^{-18}$ cm^2. Owing to the uncertainties in γ_m, we think this result is only good to a factor of 3.

IV. DISCUSSION

We have observed a distinct 10-eV metastable state rather than cascade contributions to the $a\,^3\Pi$ state. The measured lifetime is shorter by an order of magnitude than the shortest lifetime attributed to the various levels of the $a\,^3\Pi$ states.[10,11] Furthermore, changing the detection surface from CuBeO to tantalum resulted in more than an order of-magnitude change in the relative fractions of the signals from the $a\,^3\Pi$ and 10-eV states. This was due to a change in the relative metastable detection efficiencies[12] and corresponds to what we would expect for a 6- and a 10-eV state. The observed change in metastable detection efficiencies is not consistent with a mixture of CO($a\,^3\Pi$) molecules having two different vibrational distributions. Lastly, the optical excitation function[4] did not indicate the presence of any cascade contribution of the same order of magnitude as the direct-excitation process.

It is interesting to compare our excitation function with those of Cermák.[2] We see in Fig. 6 that there is very good qualitative agreement between our result and Cermák's lower-lying metastable excitation function (curve D_1). There is little doubt that we are observing the same state. Cermák indicates that this state has an energy

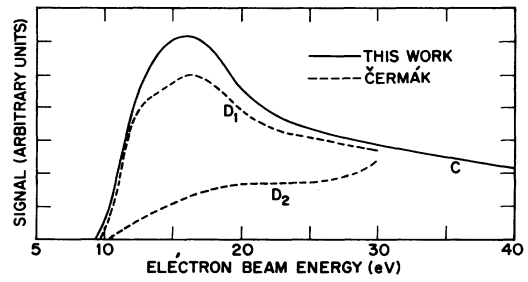

FIG. 6. Curve C from Fig. 5 is plotted for comparison with Cermák's results which are both on arbitrary scales. Curve D_1 represents the excitation function of CO^m with $9.24 < E < 10.2$ eV and curve D_2 corresponds to a state with $E \geq 10.2$ eV.

$9.2 < E < 10.2$ eV, based on its inability to Penning-ionize cyclo-C_3H_6, in agreement with our observations. The fact that Cermák saw a different excitation function for the CO^m capable of ionizing cyclo-C_3H_6 (curve D_2, Fig. 6) implies the existence of still another 10-eV metastable state, this time with $E \geq 10.2$ eV. It is difficult to estimate the relative cross sections of these two states, since Cermák's detection efficiencies were not known. But if one were to extrapolate curves D_1 and D_2 to higher energies, it would appear then the higher-lying state, represented by D_2, becomes more significant. This is particularly interesting in light of a lifetime measurement we carried out at 45 eV. A typical fit is shown in Fig. 7 with the resultant lifetime of $\tau = 65 \pm 20$ μsec and a mixture coefficient of $R_{45} = 6.1$. The fact that this result disagrees with the lifetime we obtained at 15 eV suggests that we may be observing yet another metastable state. To resolve this question, a series of lifetime measurements should be carried out as a function of energy, as was done for metastable nitrogen molecules.[3]

The identity of the 10-eV metastable state under study is still uncertain, but we can probably exclude the $b\,^3\Sigma^+$ state. Since the observations of Cermák[2] and Olmsted *et al.*,[1] there have been many measurements[13] of the radiative lifetimes of the $v' = 0$, 1 levels of the $b\,^3\Sigma^+$ state. The results indicate that the lifetime for this state is about 60 nsec. This is more than three orders of magnitude smaller than the lifetime measured here. It is highly unlikely that the excited molecule in the $b\,^3\Sigma^+$ state could be detected in our

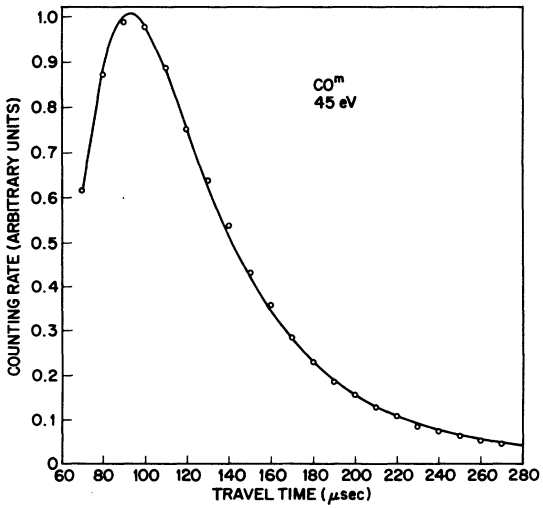

FIG. 7. Fitted TOF spectrum to experimental points at $E = 45$ eV. Spectrum was truncated at short times owing to the presence of nonthermal dissociation fragments.

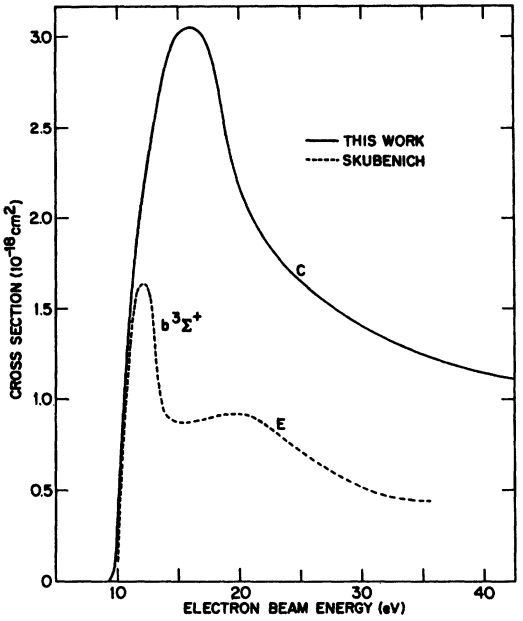

FIG. 8. Absolute electron-impact cross sections for the $b^3\Sigma^+$ state (curve E) and the metastable state discussed in this paper (curve C).

TOF experiment before radiatively decaying. Secondly, when we compare our cross section with one measured optically by Skubenich[14] (Fig. 8), we see marked qualitative differences. In addition, the 10.4-eV threshold for the $b^3\Sigma^+$ state falls above the threshold reported in this paper by 0.9 ± 0.4 eV. For these reasons, the $b^3\Sigma^+$ can be fairly safely excluded from the possible candidates.

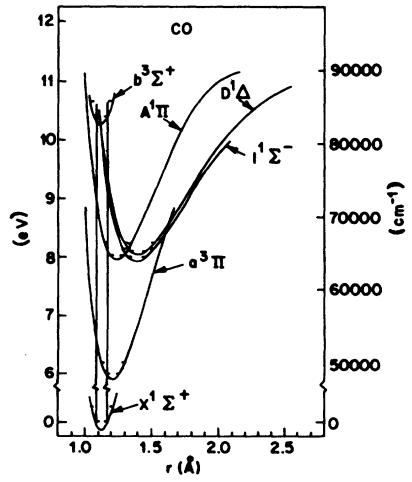

FIG. 9. Potential energy curves for selected states of CO with the Franck-Condon region indicated for excitation from the ground state (after Tilford and Simmons, Ref. 15).

Other possible candidates are the $D^1\Delta$ and $I^1\Sigma^-$ states. The potential energy curves[15] for these and other neighboring states are shown in Fig. 9. Note how the minima for the $D^1\Delta$ and $I^1\Sigma^-$ curves lie in the 8-eV region, yet the Franck-Condon region indicates these states are not accessible from the ground state by electron impact with electron energies less than about 9.5 eV. To pursue this, synthetic electron-impact excitation functions were generated for excitation from the ground state to the $I^1\Sigma^-$ and $D^1\Delta$ states. Triangular excitation functions, which rose to a maximum at 4 eV above threshold, were used for each vibrational level. A superposition of these excitation functions, weighted with the appropriate Franck-Condon factors and modified to include the effects of a 0.3-eV electron-beam spread, resulted in the curves shown in Fig. 10.

The threshold behavior of the deduced metastable excitation function is compared with that of the synthetic excitation functions for the $I^1\Sigma^-$ and $D^1\Delta$ states. The linearly extrapolated threshold for the data was 9.5 ± 0.4 eV, while for the $I^1\Sigma^-$ and $D^1\Delta$ states it was 9.7 eV and 9.8 eV, respectively. The agreement between the curves is excellent, but considering the assumptions made in generating the synthetic excitation functions and the uncertainty in the energy scale of the experimental curve, the agreement must be considered somewhat fortuitous. Nonetheless there is a strong indication that the state we are observing is either the $D^1\Delta$ or the $I^1\Sigma^-$.

Once excited, these states probably decay to the $A^1\Pi$ state emitting photons in the infrared (see Fig. 9). Radiative transitions directly to the ground state are forbidden. The $D^1\Delta - A^1\Pi$ and

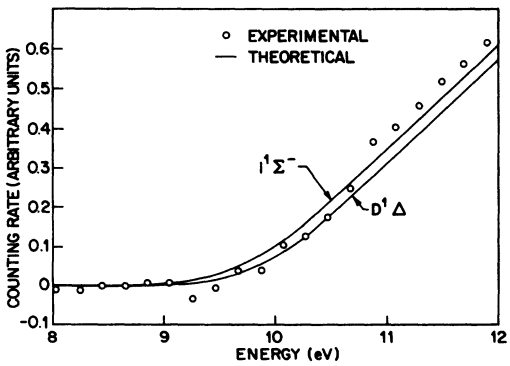

FIG. 10. Threshold behavior of the deduced CO^m excitation function and of synthetic excitation functions for the $I^1\Sigma^-$ and $D^1\Delta$ states. The synthetic excitation functions have been calculated for an electron beam resolution of 0.3 eV. The excitation functions have been normalized at their maxima near 15 eV. The marked curvature at threshold is primarily noninstrumental.

$I^1\Sigma^- - A^1\Pi$ transitions would be electronically allowed, but the small ν^3 factor in the transition-probability expression suggests that the lifetime for these transitions might be of the order of 100 μsec, which would be in agreement with the measured lifetime. At high electron-impact energies, the electron-impact transition probability for the $X^1\Sigma^+ - I^1\Sigma^-$ transition vanishes according to the Born approximation,[16] but at low energies this need not be the case. This would suggest that at higher energies, the signal we see arises from the $D^1\Delta$ state, but at threshold we may be seeing either one or both of the $I^1\Sigma^-$ and $D^1\Delta$ states.

The existence of a 10-eV state in CO has also been inferred in proton energy-loss spectra by Moore.[17] The tentative identification of this state based on predicted energy-loss spectra using Franck-Condon factors is $D^1\Delta$. This would be consistent with our observations.

Lawton and Pichanick[18] have examined the production of photons and metastables in a high-energy-resolution non-TOF experiment in the energy range 6–12 eV. The $B^1\Sigma^+$, $A^1\Pi$, and $b^3\Sigma^+$ states were observed. They found no evidence for the long-lived state reported here. This we feel, is because the metastable signal was swamped by the uv photon signal. Taking radiative decay into account, we would estimate that the metastable signal, which was unrecognized by Lawton *et al.*,[18] was less than 12% of the photon signal at 11.2 eV and would have blended imperceptively into their rising background contribution from the $A^1\Pi$ state.

V. CONCLUSION

We have observed a metastable state in CO excited by electron impact and having a lifetime at 15 eV of $\tau = 97 \pm 15$ μsec. An electron-impact cross section of 3×10^{-18} cm^2 at 15.5 eV was deduced with an uncertainty of a factor of 3. We have argued that the observed state is not the $b^3\Sigma^+$ state, as was thought earlier, and have suggested that it may be either the $D^1\Delta$ or $I^1\Sigma^-$ state or both. Lifetime measurements at 45 eV suggest that there may be more than one metastable state, which is consistent with the results of Cermák.[2] We recommend that more lifetime measurements be made at various energies to explore this possibility.

ACKNOWLEDGMENTS

We would like to thank Dr. J. H. Moore, Jr. for calling the $D^1\Delta$ state to our attention and Dr. D. C. Cartwright for pointing out $D^1\Delta$ and $I^1\Sigma^-$ as equally likely candidates. We are further indebted to Dr. D. C. Cartwright for kindly providing us with the Franck-Condon factors used in our synthetic excitation functions. The assistance of C. Stutzman in the early part of the data analysis is appreciated.

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