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ELECTRON IMPACT EXCITATION FUNCTIONS OF RADIATING AND
METASTABLE STATES OF CARBON MONOXIDE*

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Excitation functions near threshold have been measured for the production of photons and for the production of long-lived metastable molecules from carbon monoxide. An interesting peaked feature exists at the threshold for photon production.

- - -

One technique for obtaining electron impact excitation functions for long-lived metastable states of atoms and molecules is the crossed electron and neutral beam technique. The metastables produced by electron impact are detected via their ability to eject an electron from a metal surface placed downstream from the collision region in the path of the neutral beam [1]. Photons higher in energy than the work function of the metal detector can also be measured. By pulsing the electron beam and by using time-of-flight (TOF) techniques, the two signals can be measured independently [2]. A TOF technique using a diffuse, rather than a directed gas source has recently been used by Borst and Zipf to measure excitation efficiency curves for metastable production and to deduce lifetimes of metastable states in CO and N₂ [3].

The molecular beam apparatus and the electron gun used in this study have been described previously by Clampitt and Newton [2]. The only significant

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change in the apparatus was that an EMI 9603 Be-Cu electron multiplier was used as the detector. This multiplier had an effective photoelectric work function of 5.1 eV, measured using a deuterium light source and a monochromator. The distance between the electron gun and the detector was 10.7 cm. The data-gathering system has been described by Thomas and Vogelsberg [4]. It is possible to operate the electron gun in this instrument as a high resolution electron source using the RPD technique. However, the photon signal from CO was very weak, and it was not possible to obtain an adequate signal-to-noise ratio in the RPD mode. Therefore, in this work, the two-cycle RPD operation of the gun was eliminated and only the first cycle of the pulsing scheme previously described [4] was used. The electron beam pulse width was 10 μ sec, and the electron current during the pulse was $\sim 10^{-6}$ A. To record the photon curve, the data count gate was opened only during the electron pulse. For the metastable curve, the count gate was delayed for 60 μ sec and was then opened to intercept the majority of the TOF distribution of the CO metastables. The time between electron pulses was 1 msec. The CO gas used was CP grade obtained from the Matheson Company. Its purity was $> 99.5\%$. Impurities other than N_2 were $< 0.1\%$ each.

The electron energy scale was calibrated by running the appropriate CO curve and then, while still scanning, adding a small impurity of argon to the beam source. The data count gate was simultaneously opened to count argon metastables. The signal strength from the added argon was so high compared to that from the CO that a sharp Ar^* threshold could be superimposed on the CO curve within 30 sec of adding the argon to the beam. It was necessary to assume that potential drifts did not occur in this short time. The Ar^* threshold was taken to be 11.62 eV [5]. It is estimated that the energy scale established in this fashion was accurate to ± 0.2 eV.

Figure 1 shows the excitation function for metastable states produced by electron impact on CO. The excitation threshold was found to be 5.9 eV as compared to the spectroscopic value of 6.01 eV. All curves recorded in this study showed the same steady rise to a plateau at approximately 10 eV. A reproducible feature was the small increase in signal near 13 eV. The shape of the curve agrees quite well with the initial portion of a metastable CO curve recently published by Borst and Zipf [3]. It is, however, quite different from the curve measured by Olmsted, Newton, and Street [6]. Referring to Krupenie's compilation of spectroscopic data on CO [7], the only known state which could contribute to the metastable signal in the region immediately above 6 eV is the a $^3\Pi$ state. Thus the present observations reinforce the conclusion of Borst and Zipf that the lifetime of the a $^3\Pi$ state is considerably longer than 10 μ sec suggested earlier by Hansche [8]. It is possible that the Ag-Mg multiplier used in the study of Olmsted, Newton, and Street scarcely responded to the a $^3\Pi$ metastables. The signal observed by these authors above 10.5 eV [6] must then be ascribed to a second metastable state. Freund [9] has pointed out the low conversion efficiency of a Be-Cu surface for the CO a $^3\Pi$ metastables, and the extremely low efficiency for this state on the Ag-Mg surface used by Olmsted, Newton, and Street.

Figure 2 shows the excitation function obtained for the production of prompt radiation of energy greater than 5.1 eV from CO. An unusual feature of this curve is the sharp peak observed at threshold. The onset of the curve is at 7.4 eV and the peak occurs at 8.3 eV. The width at half height of the peak is 0.9 eV, including the broadening caused by the energy spread of the electrons from the thoriated iridium filament. There is a second strong emission threshold

at ~ 11 eV. It is also apparent that there is weak emission below 11 eV which is probably not connected with the peaked feature, but the threshold of this emission is obscured. It is not possible in the present instrument to measure the wavelength distribution of the emitted light.

The strong emission above 11 eV can have several sources. Duffendack and Fox [10] observed radiation from the "3A" system of CO ($c\ ^3\Sigma^+ \rightarrow a\ ^3\Pi$). The upper state of this system has an excitation potential of 11.1 eV [10]. At least a portion of this band system is sufficiently energetic to be detected here. Other triplet levels in this energy range might decay in a similar fashion. Another possible source of the radiation is from the series of high-lying $^1\Sigma^+$ states listed by Krupenie [7]. These states (the B $^1\Sigma^+$, E₀ $^1\Sigma^+$ and C $^1\Sigma^+$) can decay either via allowed transitions to the A $^1\Pi$ state, which in turn can decay to the X $^1\Sigma^+$ ground state or via a direct transition to the ground state. Moore and Robinson [11] have indicated that the latter transition has a higher probability in the case of the B state. The trapped electron spectrum of Brongersma and Oosterhoff [12] indicates that at least some of the states in this energy region are excited by electron impact at threshold. Definite conclusions regarding the source(s) of the light cannot be drawn without knowledge of the wavelength distribution.

The sharp peak at 8.3 eV in the photon excitation efficiency curve is somewhat difficult to explain. The only known states of CO accessible to Franck-Condon transition below 8 eV are the a $^3\Pi$ and the a' $^3\Sigma^+$ [ref. 7]. The a $^3\Pi$ state can be eliminated from consideration on the basis of its long radiative lifetime [3]. Its excitation function should resemble that of CO in fig. 1. Furthermore, this state becomes inaccessible to a Franck-Condon transition from

the ground state above 7 eV and no new phenomena preceded by direct excitation of this state should occur above this energy.

To interpret the peaked feature as arising from a direct transition to the $a' \ ^3\Sigma^+$ state followed by the decay of this a' state to the ground state is also difficult. Figure 3 compares the peak observed here with the optical absorption envelope for the transition $a' \ ^3\Sigma^+ \leftarrow X \ ^1\Sigma^+$ observed by Herzberg and Hugo [13]. The ordinates of the two curves have been normalized at the peak values. It is clear the a' state passes through the Franck-Condon region in the appropriate energy range. However, the width of the electron impact peak compared to the optical envelope is suspicious. It would be expected that the electron impact peak would be broadened if direct excitation were involved. The electron impact excitation functions for the individual vibronic levels are not expected to be extremely sharp for direct excitation, even in the case of a triplet level. Secondly, the electron impact data must be inherently broadened by the energy spread of the exciting electrons.

An alternative that is consistent with the present data is that selected vibrational levels of the a' state are being populated via a resonant state. This could certainly account for the narrow width of the excitation function. Sanche and Schulz [14] have recently searched for resonances in CO in an electron transmission experiment. A resonant state which may be responsible for populating the $b \ ^3\Sigma^+$ state of CO was found near 10.4 eV. It would be necessary to postulate a similar resonant state (undetected in the experiment of Sanche and Schulz) for populating the a' state. If it is assumed that the a' state is indeed the source of the light, some rough conclusions could be drawn regarding its lifetime and modes of de-excitation. This state can radiate to the metastable $a \ ^3\Pi$ via a dipole-allowed transition (the Asundi System). No radiations

directly to the $X^1\Sigma^+$ ground state have been observed. The present observations would demand that the branching ratio for depopulation of the a' state by direct radiation to the ground state be an appreciable fraction of the total population. The lifetime of the a' state must be less than or of the same order of magnitude as the 10 μ sec observation time used here.

An improbable source of the light is by direct excitation to the $A^1\Pi$ state which radiates to the ground state (Fourth Positive bands). The threshold for this state is at 8.03 eV, well above the observed threshold of 7.4 eV. This difference is well outside the experimental error in establishing the energy scale. Further there is no precedent in which the electron impact excitation of an allowed state exhibits resonance behavior. Excitation functions for various members of the Fourth Positive band system in CO were determined by Mumma, Stone, and Zipf [15]. While the authors do not show detailed threshold behavior, their curves indicate a gradual rise from threshold to a maximum intensity at ~ 25 eV. Excitation of the $A^1\Pi$ state could account for the low intensity light in the 9-11 eV region of Fig. 2.

If the $a'^3\Sigma^+$ state populated via a resonant state is not the source of the radiation, it seems necessary either to postulate an unknown [7] and unpredicted [16] state of CO in the appropriate energy range, or to consider the possibility of photon emission proceeding via a long-lived CO^- state at the observed energy and the unstable $^2\Pi$ ground state of CO^- . This is the dielectronic attachment process [17]. The ground state of CO^- has been observed in electron scattering experiments [18] and its potential energy curve has been estimated by Boness, Hasted, and Larkin [19]. Chantry [20] has shown that there are excited states of CO^- which have dissociation limits of 9.62 eV ($C(^3P) + O^-(^2P)$)

and 10.88 eV ($C(^1D) + O^-(^2P)$), and Stamatovic and Schultz [21] have shown still a third state with the dissociation limit of 9.84 eV ($C^-(^4S) + O(^3P)$). Both the states leading to $O^-(^2P)$ have their maximum yield near the threshold with the kinetic energy of O^- equal to zero [20]. One can therefore assume that these are not repulsive states and that there are bound levels of these states below the dissociation limit which lie within the Franck-Condon region. The fate of these levels is not known.

In order to clarify the nature of the peaked feature observed here it would be useful to measure the wavelength distribution of the emitted light. A second useful experiment might be to search for a resonance in CO in the energy range between 7 and 8 eV. This resonance might be manifested in the inelastic cross section of the a' state or in the cross section for vibrational excitation of the ground state if the dielectronic attachment process is taking place.

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Figure Captions

Fig. 1. Excitation function for production of long-lived metastable states of CO.

Fig. 2. Excitation function for the production of prompt photons of energy
> 5.1 eV from CO.

Fig. 3. Excitation function for the production of prompt photons from CO
(dashed curve) compared to photon absorption intensities for the forbidden
 $a' \ ^3\Sigma^+ \leftarrow X \ ^1\Sigma^+$ transition (points from Ref. 13).

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Fig. 1

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Fig. 2

XBL 716-1161

Fig. 3

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