

NASR  
121714

~~NASA CR 121614~~

SPACE RESEARCH COORDINATION CENTER



CASE FILE  
COPY

PRODUCTION OF  $\text{CO}(A^3\Pi)$  AND OTHER  
METASTABLE FRAGMENTS BY ELECTRON  
IMPACT DISSOCIATION OF  $\text{CO}_2^*$

BY

W. C. WELLS, W. L. BORST AND E. C. ZIPF

SRCC REPORT NO. 155

UNIVERSITY OF PITTSBURGH  
PITTSBURGH, PENNSYLVANIA

JULY 1971

The Space Research Coordination Center, established in May, 1963, has the following functions: (1) it administers predoctoral and postdoctoral fellowships in space-related science and engineering programs; (2) it makes available, on application and after review, allocations to assist new faculty members in the Division of the Natural Sciences and the School of Engineering to initiate research programs or to permit established faculty members to do preliminary; work on research ideas of a novel character; (3) in the Division of the Natural Sciences it makes an annual allocation of funds to the interdisciplinary Laboratory for Atmospheric and Space Sciences; (4) in the School of Engineering it makes a similar allocation of funds to the Department of Metallurgical and Materials Engineering and to the program in Engineering Systems Management of the Department of Industrial Engineering; and (5) in concert with the University's Knowledge Availability Systems Center, it seeks to assist in the orderly transfer of new space-generated knowledge in industrial application. The Center also issues periodic reports of space-oriented research and a comprehensive annual report.

The Center is supported by an Institutional Grant (NsG-416) from the National Aeronautics and Space Administration, strongly supplemented by grants from the A. W. Mellon Educational and Charitable Trust, the Maurice Falk Medical Fund, the Richard King Mellon Foundation and the Sarah Mellon Scaife Foundation. Much of the work described in SRCC reports is financed by other grants, made to individual faculty members.

PRODUCTION OF CO( $a^3\Pi$ ) AND OTHER METASTABLE FRAGMENTS BY ELECTRON  
IMPACT DISSOCIATION OF CO<sub>2</sub>\*

(Submitted to the Journal of Geophysical Research)

W. C. Wells, W. L. Borst<sup>†</sup> and E. C. Zipf

Department of Physics

University of Pittsburgh

Pittsburgh, Pennsylvania 15213

February 1971

Production of  $\text{CO}(a^3\Pi)$  and Other Metastable Fragments By Electron  
Impact Dissociation of  $\text{CO}_2^*$

W. C. Wells, W. L. Borst<sup>†</sup> and E. C. Zipf

Abstract

The dissociative excitation of  $\text{CO}(a^3\Pi)$  and other metastable fragments such as  $\text{O}(^5S^0)$  produced by electron impact on  $\text{CO}_2$  has been investigated from threshold to 50 eV. The observed threshold for  $\text{CO}(a^3\Pi)$  production at  $(11.9 \pm 0.5)$  eV was near the minimum required energy of 11.5 eV. Assuming an isotropic distribution of  $\text{CO}(a^3\Pi)$  fragments after dissociation, and cross section for dissociative excitation of  $\text{CO}(a^3\Pi)$  from  $\text{CO}_2$  was found to be about  $3.6 \times 10^{-17} \text{cm}^2$  at 20 eV which is 3 times smaller than the maximum cross section for the direct excitation of  $\text{CO}(a^3\Pi)$  from CO. We also used our time of flight data to infer a value for the  $\text{CO}(a^3\Pi)$  dissociative excitation cross section from Ajello's relative cross section measurements (1971 A) and we obtained a slightly lower value of  $1.6 \times 10^{-17} \text{cm}^2$  at 20 eV. These experiments imply a maximum cross section value of  $(4.1 \pm 3.0) \times 10^{-17} \text{cm}^2$  at 27 eV. The differential cross section for the dissociative excitation of  $\text{CO}(a^3\Pi)$  at right angles to the electron beam was found to be  $d\sigma/d\Omega = (3.0 \pm 2.2) \times 10^{-18} \text{cm}^2/\text{sterad}$  at an energy of 20 eV.

## INTRODUCTION

Recent observations of the intense CO Cameron band emission in the upper Martian atmosphere by Mariner 6 and 7 (Barth et al., 1969; Barth et al., 1971) has generated a renewed interest in the dissociative excitation of  $\text{CO}_2$  by both electron impact and photodissociation. In order to determine the role played by these processes, it is necessary to know the absolute collision and absorption cross sections. To this end we have studied the production of metastable fragments by electron impact on  $\text{CO}_2$  in an attempt to arrive at an absolute cross section for the production of the  $\text{CO}(a^3\Pi)$  state.

## APPARATUS

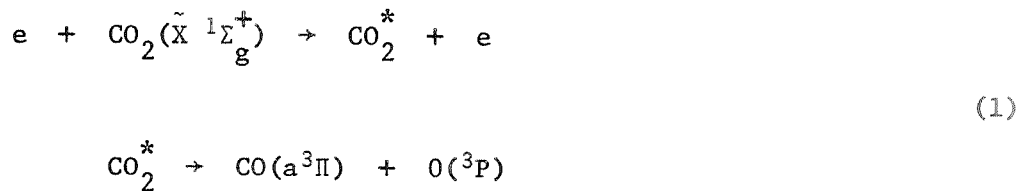
The pulsed electron beam time of flight apparatus used in this experiment and its modes of operation have been described in detail elsewhere [Borst and Zipf, 1971 A; 1971 B]. Two major modifications have been carried out. Firstly, voltage programming the electron energy to sweep concurrently with the multiscaler has permitted signal averaging of excitation functions and has significantly improved the signal to noise ratio in the primary data.

Secondly the metastable detector was rearranged so that several different metal surfaces could be used as Auger detectors. Electrons which were ejected from a metal surface by incident metastable fragments were accelerated toward an electron multiplier. The metal surface was positioned at an angle of  $45^\circ$  with respect to the incoming metastables, and was at an effective distance of 20.0 cm from the center of the collision

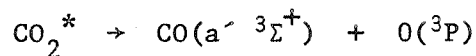
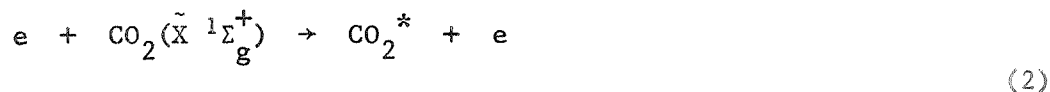
chamber. The metals used in this experiment were tungsten and magnesium. The solid angle subtended by the detector surface at the center of the collision chamber was 0.007 sterad at an angle of 90° with respect to the electron beam. The electron beam pulse was typically 10  $\mu$ sec wide with a repetition rate of  $2 \times 10^2$ /sec.

## RESULTS AND DISCUSSION

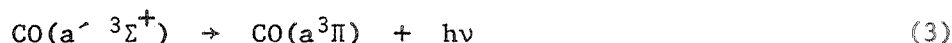
As in previous studies [Freund and Klemperer, 1967, and Clampitt and Newton, 1969] metastable CO<sub>2</sub> molecules were not observed in this experiment. The excitation function [Fig. 2] for the production of the relatively slow metastable fragments [Structure A, Fig. 1] exhibited an appearance potential of  $11.9 \pm 0.5$  eV [Fig. 2]. This threshold is to be compared to Freund and Klemperer's [1967] value of 12 - 15 eV and Clampitt and Newton's [1969] value of  $11.0 \pm 0.6$  eV. Our threshold value is in agreement with the observations of Freund and Klemperer. The threshold reported by Clampitt and Newton probably corresponds to the detection of O(<sup>1</sup>S) atoms as was pointed out by McConnell and McElroy [1970]. Our detector, like that of Freund's, was not sensitive to O(<sup>1</sup>S) atoms. Accurate determination of the threshold in our experiment was made difficult by such effects as the slight non-instrumental curvature of the excitation function at threshold and poor signal to noise ratio at threshold. Freund and Klemperer [1967] showed that the metastable fragment is polar and hence probably is CO(a<sup>3</sup> $\Pi$ ). The excitation process that we are observing is most likely,



which has a threshold of 11.5 eV. Our threshold determination does not completely rule out a cascade process where



and



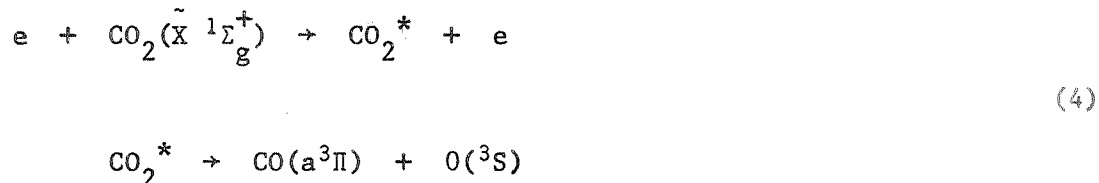
The end result in either case is the production of  $\text{CO}(a^3\Pi)$ .

The mean energy of the  $\text{CO}(a^3\Pi)$  molecules near threshold was observed to be about 0.08 eV which corresponded to a total fragment mean kinetic energy of about 0.2 eV. This is in general agreement with the observations of Freund and Klemperer [1967] but in disagreement with the work of Clampitt and Newton [1969] who observed a total fragment mean kinetic energy of 0.7 eV. Again this discrepancy could be due to the fact that Clampitt and Newton were detecting a small percentage of very energetic  $\text{O}(^1\text{S})$  along with the  $\text{CO}(a^3\Pi)$ ; this was not possible in our experiment. The low velocity tail [Structure A. Fig. 1] corresponds to the production of some  $\text{CO}(a^3\Pi)$  molecules with virtually no excess kinetic energy.

#### Other Sources of $\text{CO}(a^3\Pi)$

As we went to higher electron impact energies we produced  $\text{CO}(a^3\Pi)$  molecules from processes other than those mentioned previously. It is possible that cascade processes similar to (3) and (4) involving higher lying triplet levels of the CO molecule contributed to the production of  $\text{CO}(a^3\Pi)$

molecules. Another excitation process may have been



which has a minimum threshold of 21.0 eV.

A detailed study of high resolution time of flight curves revealed the development of a new structure which manifested itself as a high velocity tail on structure A [Fig. 1] at about 22 eV. This new source of  $\text{CO}(a^3\Pi)$  is evident in Fig. 2 in both excitation functions A and B since the TOF spectra for process (4) falls into both the slow and fast portions of the TOF spectrum which the excitation functions represent. The  $\text{CO}(a^3\Pi)$  molecules from process (4) are visible as additional structure to excitation function A at  $21.6 \pm 1$  eV and as a threshold in excitation function B at  $22.1 \pm 1$  eV. These energy thresholds are in agreement with the minimum threshold of 21.0 eV for process (4) and furthermore are consistent with the thresholds for  $\text{O}(^3\text{S})$  production of  $21.0 \pm 2$  eV and 23 eV observed by Ajello [1971 B] and Mumma [1970], respectively.

To determine if all the metastable fragments in structure A [Fig. 1] were  $\text{CO}(a^3\Pi)$  molecules, the excitation function A [Fig. 2] was observed using four different detector surfaces. The efficiency  $\gamma_m$  for Auger ejection of electrons by  $\text{CO}(a^3\Pi)$  from these different surfaces varied by as much as a factor of 5. The four surfaces were a Cu-Be nude dynode, two contaminated tungsten surfaces for which  $\gamma_m$  differed by a factor of 2 and a contaminated magnesium surface. It is known [Clampitt and Newton, 1968] that the apparent



excitation function due to an incident metastable flux consisting of a mixture of different metastable states has a different shape when detected with surfaces having different work functions. Indeed  $\gamma_m$  is a sensitive function of the difference between the work function of the surface and the metastable energy level. All the surfaces used in this experiment yielded quite similar excitation functions leading us to conclude that excitation function A represents the production of  $\text{CO}(a^3\Pi)$  from electron impact on  $\text{CO}_2$ .

#### Determination of $\text{CO}(a^3\Pi)$ Differential Cross Section

To determine the differential cross section for the dissociative excitation of  $\text{CO}(a^3\Pi)$ , we also observed the excitation function [Borst and Zipf, 1971 B] on the same TOF apparatus for the direct process



Using Ajello's [1971 A] peak cross section for this process [ $1.1 \times 10^{-16} \text{cm}^2$  at 10.4 eV] and our knowledge of the relative peak production rates of  $\text{CO}(a^3\Pi)$  from CO and  $\text{CO}_2$  we arrived at a differential cross section of

$$\left( \frac{d\sigma}{d\Omega} \right)_{90^\circ} = 3 \times 10^{-18} \text{cm}^2/\text{sterad} \quad (6)$$

at 20 eV. A lifetime of 1 msec [Borst and Zipf, 1971 B] was used to correct the cross section measurement for the radiative decay of the  $\text{CO}(a^3\Pi)$  in flight. This correction is relatively insensitive to the specific lifetime value used. Choosing a longer lifetime would result in at most a 10% change in the relative signal of  $\text{CO}(a^3\Pi)$  from CO and  $\text{CO}_2$ . At the same time it should

be noted that the absolute magnitude of this dissociative excitation cross section does depend linearly on Ajello's [1971 A] direct excitation cross section and that Ajello's cross section in turn depends linearly on the lifetime of the  $\text{CO}(a^3\Pi)$  state. Ajello used a value of 1 msec [Borst and Zipf, 1971 B].

There has been a great deal of discussion of the  $\text{CO}(a^3\Pi)$  lifetime in the literature recently. Borst and Zipf [1971 B] have discussed the early lifetime work on this state at length. More recently Lawrence [1971] has reported a lifetime of 7.5 msec for this state while Slanger and Black [1971] found a value of 5 msec. It must be said at the outset in a discussion of the  $\text{CO}(a^3\Pi)$  radiative lifetime that it is misleading to assume that a complex electronic band system such as the  $a^3\Pi \leftrightarrow X^1\Sigma^+$  transition has a single-valued lifetime. As a matter of fact there is an entire manifold of different radiative lifetimes, one for each rotational sublevel [Shemansky, 1969]. Recently Fairbairn [1971] discussed this lifetime variation with J and spin substate  $\Sigma$  in connection with an absorption measurement. James [1971] has also dealt with this problem in a theoretical calculation of the f values and lifetimes. Although it is convenient experimentally to measure some "average" lifetime for this system, it must not be forgotten that the end result obtained depends on just how the rotational and spin states are populated.

At low rotational levels ( $J < 16$ ) the  $^3\Pi_1$  levels exhibit shorter radiative lifetimes and larger line strengths than the corresponding  $^3\Pi_0$  and  $^3\Pi_2$  levels [Hexter, 1967; Fairbairn, 1970]. In electron impact experiments such as those of Ajello [1971 A] and Borst and Zipf [1971 B] where CO at room temperature (300°K) is excited, the  $^3\Pi_1$  levels will be preferentially excited. In experiments involving high pressures where the  $\text{CO}(a^3\Pi)$  molecule

undergoes several collisions before radiating we would expect the populations of the spin states to equilibrate resulting in a longer observed lifetime; quenching, of course, further complicates the analysis of these afterglow experiments. The fact that the result of Borst and Zipf [1971 B] ( $\tau = 1$  msec) measured in a low pressure environment falls on the low side of the recent lifetime measurements made in high pressure environments (Slanger and Black [1971] (5 msec) and Lawrence [1971] (7.5 msec)) suggests that this is indeed the case.

These considerations argue that Ajello used the appropriate lifetime in normalizing his results [Ajello, 1971 A]. Choosing a lifetime of 7 msec would have resulted in a cross section for process (5) of  $7.7 \times 10^{-16} \text{cm}^2$  and the differential cross section (6) would have become  $2.1 \times 10^{-17} \text{cm}^2/\text{sterad}$ . These would be remarkably large values.

It has been assumed in arriving at this differential cross section that the effective Auger efficiency for detecting the  $\text{CO}(a^3\Pi)$  has been the same for direct and dissociative excitation. This is equivalent to assuming that the mean energy carried in vibrational energy is the same for both processes provided that the variation of  $\gamma_m$  with metastable energy is quasi-linear over this narrow range. This is not an unreasonable assumption despite the fact that Barth et al. [1971] reported that the vibrational population distribution of dissociative excited  $\text{CO}(a^3\Pi)$  is different from that of directly excited  $\text{CO}(a^3\Pi)$ . As a matter of fact the mean vibrational energy calculated based on the populations Barth reports and the mean energy calculated based on the Franck Condon factors of Nicholls [1962] are the same to within 0.05 eV. Differences in rotational distributions should have an unnoticeable effect on the effective  $\gamma_m$  for detecting  $\text{CO}(a^3\Pi)$  because of the small energies involved.

The uncertainty in our value for the cross section arising from experimental errors in the actual relative intensity measurements are deemed to be less than 30%. In view of this we feel that the uncertainty in our absolute cross section for dissociative excitation of  $\text{CO}(a^3\Pi)$  is determined primarily by the uncertainty in Ajello's [1971 A] cross section for process (5) which is a factor of 2.

#### Determination of $\text{CO}(a^3\Pi)$ Total Cross Section

Examination of Ajello's [1971 B] excitation function for the dissociative excitation of the Cameron bands by electron impact on  $\text{CO}_2$  reveals a steadily increasing curve with a broad maximum centered about 90 eV. This is to be compared to the relatively flat behavior of excitation function A [Fig. 2] above 20 eV with the maximum at 27 eV. Ajello's excitation function is 30% larger at its peak than at 27 eV. If we assume that at 20 eV we have isotropic scattering, we are in a position to renormalize Ajello's excitation function at low energies.

At 20 eV Ajello's [1971 B] emission cross section is  $6.1 \times 10^{-18} \text{cm}^2$  where he assumed a thermal velocity distribution of the  $\text{CO}(a^3\Pi)$  fragment. The slow metastable CO molecules [Structure A, Fig. 1] have a mean velocity 2.7 times a thermal mean velocity. This yields an absolute emission cross section for the slow fragments of

$$\sigma \approx 1.6 \times 10^{-17} \text{cm}^2 \quad (7)$$

at 20 eV. This can be compared to the differential cross section (6) derived earlier. Assuming isotropic scattering with respect to the scattering angle

results in an excitation cross section of

$$\sigma \approx 3.6 \times 10^{-17} \text{cm}^2 \quad (8)$$

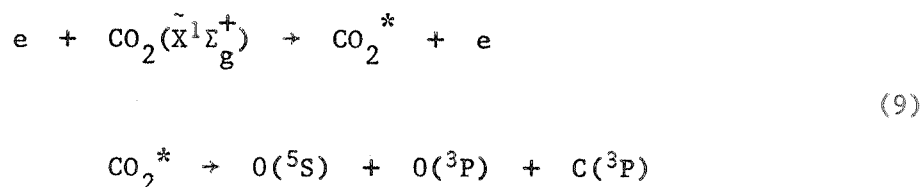
at 20 eV. In arriving at the cross section values (7) and (8) we assumed isotropic scattering. Strictly speaking we only assumed that the velocity distribution of  $\text{CO}(a^3\Pi)$  was unaltered in arriving at cross section (7). One might expect as we go to higher energies that the strong angular dependencies in the differential cross section would disappear since more repulsive states in  $\text{CO}_2$  are being excited. But the discrepancy in shape between our excitation and that of Ajello's discussed above would argue that at high energies the scattering is not isotropic. It is difficult to assess precisely the uncertainty in our total cross sections which would result from anisotropy since the angular distribution has not been examined yet. We estimate here a factor of two uncertainty due to the assumption of isotropy.

In arriving at cross section (7) we used Ajello's [1971 B] cross section which he arrived at using a lifetime of 1 msec [Borst and Zipf, 1971 B] to account for those  $\text{CO}(a^3\Pi)$  molecules which left his field of view before radiating. As has been discussed previously the "average" lifetime for the  $\text{CO}(a^3\Pi)$  depends dramatically on the rotational level population and spin state populations. There is no reason to expect these populations to be the same for directly excited  $\text{CO}(a^3\Pi)$  and dissociatively excited  $\text{CO}(a^3\Pi)$ . Indeed Mumma et al. [1971] have observed non-thermal rotational distribution in  $\text{CO}(A^1\Pi)$  produced by dissociative excitation of  $\text{CO}_2$  by electron impact. If the spin states are more or less equally populated and the rotational distribution is skewed toward higher rotational numbers the net effect would be a longer  $\text{CO}(a^3\Pi)$

lifetime. This would result in a corresponding increase in cross section (7) bringing it into closer agreement with cross section (8). The cross sections (7) and (8) are to be compared with an order of magnitude estimate of the maximum cross section of  $2 \times 10^{-16} \text{cm}^2$  at 40 eV by Freund and Klemperer [1967]. The reason for the large disagreement is not understood. McConnell and McElroy [1970] arrived at a maximum cross section of  $8 \times 10^{-17} \text{cm}^2$  for the production of  $\text{CO}(a^3\Pi)$  based on a theoretical paper by Strickland and Green [1969].

#### $\text{O}(^5\text{S})$ Cross Section

We observed that as the detector surface was changed the peak height of structure B [Fig. 1] remained relatively unchanged while that of structure A changed dramatically. This implied that structure B was composed in part of higher lying metastable states and possibly Rydberg states of C, O, and CO. The change in slope in excitation function A [Fig. 2] around  $29 \pm 2$  eV probably corresponds to the dissociative process



which has a minimum threshold of 25.7 eV. Dissociative production of  $\text{O}(^5\text{S}^0)$  has been observed by Ajello [1971 B] with a threshold of  $27 \pm 2$  eV. Assuming that excited oxygen atoms are being observed, then structure B [Fig. 1] corresponds to atomic fragments with a sum total kinetic energy of at least 3 eV. Ajello [1971 B] observed a cross section for the production of  $\text{O}(^5\text{S}^0)$

atoms approximately 0.95 times the  $O(^3S)$  cross section [ $7.6 \times 10^{-19} \text{cm}^2$  at 100 eV] assuming a thermal velocity distribution. If we assume that structure B [Fig. 1] is largely due to the excitation of  $O(^5S)$  atoms then our measurements imply a mean velocity for these oxygen atoms 9 times the mean thermal velocity. Multiplying Ajello's cross section by 9 to compensate for excited atoms which left his field of view before radiating yields an emission cross section

$$\sigma \approx 6.8 \times 10^{-18} \text{cm}^2 \quad (10)$$

at 100 eV for the production of  $O(^5S^0)$  atoms.

#### SUMMARY

We have excited the  $\text{CO}(a^3\Pi)$  Cameron band system with high efficiency by electron impact dissociation of  $\text{CO}_2$  near the minimum possible threshold of 11.5 eV and up to 50 eV. We have further studied energy spectra of the resulting  $\text{CO}(a^3\Pi)$  and other metastable fragments. We obtained a cross section of about  $3.6 \times 10^{-17} \text{cm}^2$  for the dissociative excitation of  $\text{CO}(a^3\Pi)$  at 20 eV assuming an isotropic angular distribution of metastables after dissociation; this result is probably accurate to within a factor of 2. A maximum cross section occurring at higher energies was not observed in contrast to Ajello's measurements. However, interpretation of the high energy domain was rendered difficult because of the presence of metastable fragments other than  $\text{CO}(a^3\Pi)$ , e.g.  $O(^5S)$ . The above cross section was deduced by comparing  $\text{CO}(a^3\Pi)$  signals obtained in dissociative excitation with those for direct excitation using Ajello's cross section for direct excitation of  $\text{CO}(a^3\Pi)$  from  $\text{CO}(X^1\Sigma^+)$ . We further applied our time-of-flight measurements

of non-thermal CO( $a^3\Pi$ ) fragments to Ajello's optical measurements of Cameron bands produced in dissociative excitation from CO<sub>2</sub> and inferred a cross section of  $1.6 \times 10^{-17} \text{cm}^2$  at an energy of 20 eV. The two values of  $3.6 \times 10^{-17} \text{cm}^2$  and  $1.6 \times 10^{-17} \text{cm}^2$  thus obtained agree well within the limits of error.

We can conclude that the cross section for the dissociative excitation of CO( $a^3\Pi$ ) by electron impact on CO<sub>2</sub> is large. However, the probable errors in these measurements are also large so that some care should be exercised in applying these results to the analysis of planetary atmospheres. This suggests that it is premature to conclude that electron impact dissociative excitation is the primary source of the Cameron bands in the Martian dayglow.



## References

- \* This work was supported by the NASA (NGL 39-011-030) and by the Advanced Research Projects Agency, The Department of Defense, and was monitored by U. S. Army Research Office-Durham, under Contract No. DA-31-124-ARO-D-440).
- † Present Address: Department of Physics, Southern Illinois University, Carbondale, Illinois 62901.
- Ajello, J. M., Emission Cross Sections of CO by Electron Impact in the Interval of 1260Å - 5000Å: Part I, J. Chem. Phys., 00, 0000, 1971 A.
- Ajello, J. M., Emission Cross Sections of CO<sub>2</sub> by Electron Impact in the Interval of 1260Å - 5000Å: Part II, J. Chem. Phys., 00, 0000, 1971 B.
- Barth, C. A., W. G. Fastie, C. W. Hard, J. B. Pearce, K. K. Kelly, A. I. Stewart, G. E. Thomas, G. P. Anderson, O. F. Raper, Mariner 6: Ultraviolet Spectrum of Mars Upper Atmosphere, Science 165, 1004, 1969.
- Barth, C. A., C. W. Hard, J. B. Pearce, K. K. Kelly, G. P. Anderson, A. I. Stewart, Mariner 6 and 7: Ultraviolet Spectrometer Experiment: Upper Atmosphere Data, J. Geophys. Res., 76, 2213, 1971.
- Borst, W. L. and E. C. Zipf, Energy Spectra of Metastable Oxygen Atoms Produced by Electron Impact Dissociation of O<sub>2</sub>, Phys. Rev. 00, 0000, 1971 A.
- Borst, W. L. and E. C. Zipf, Lifetimes of Metastable CO and N<sub>2</sub> Molecules, Phys. Rev. A, 3, 979, 1971 B.
- Clampitt, R. and Amos. S. Newton, Metastable Species Produced by Electron Impact of N<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>, J. Chem. Phys., 50, 1997, 1969.
- Clampitt, R. and Amos. S. Newton, Surface Effects in the Ejection of Electrons by Electronically Excited Molecules, Surface Science, 12, 92, 1968.
- Fairbairn, A. R., Band Strengths in Forbidden Transitions: The Cameron Bands of CO, J. Quant. Spectros. Radiat. Transfer, 10, 1321, 1970.
- Freund, R. S. and William Klemperer, Molecular Beam Time-of-Flight Measurements for the Study of Metastable and Repulsive Electronic States, J. Chem. Phys. 47, 2897, 1967.

- Hexter, R. M., Forbidden Transitions in Molecular Crystals: The Cameron System of Solid  $\alpha$  - CO, J. Chem. Phys. 46, 2300, 1967.
- James, T. C., Transition Moments, Franck-Condon Factors, and Lifetimes of Forbidden Transitions. Calculation of the Intensity of the Cameron System of CO, to be published, 1971.
- Lawrence, G. M., Quenching and Radiation Rates of CO( $a^3\Pi$ ), Chem. Phys. Letters, 1971, to be published.
- McConnell, John C. and Michael B. McElroy, Excitation Processes for Martian Dayglow, J. Geophys. Res., 75, 7290, 1970.
- Mumma, M. J., E. J. Stone and E. C. Zipf, Non-thermal Rotational Population of the CO( $A^1\Pi$ ) State Produced by Dissociative Excitation of CO<sub>2</sub> by Electron Impact, Abstracts of Papers, Seventh ICPEAC, Amsterdam, 1971.
- Mumma, M. J., Dissociative Excitation of Atmospheric Gases, Ph.D. Thesis, University of Pittsburgh, 1970.
- Nicholls, R. W., Laboratory Astrophysics, J. Quant. Spectrosc. Radiat. Transfer, 2, 433, 1962.
- Shemansky, D. E., N<sub>2</sub> Vegard-Kaplan System in Absorption, J. Chem. Phys., 51, 689, 1969.
- Slanger, T. G. and G. Black, CO( $a^3\Pi$ ), Its Production, Detection, Deactivation, and Radiative Lifetime, J. Chem. Phys., 00, 0000, 1971.
- Strickland, D. C. and A. E. S. Green, Electron Impact Cross Sections for CO<sub>2</sub>, J. Geophys. Res., 74, 6515, 1969.

## Figure Captions

**Figure 1** Multi-channel analyzer plot of the time-of-flight distribution of metastable fragments resulting from the dissociation of  $\text{CO}_2$  by 38.5 eV electrons. The channel width was 10  $\mu\text{sec}$ . Peak heights of A and B depended on the detector surface used.

**Figure 2** Excitation functions for the dissociative excitation of metastable fragments. Curves A and B correspond to the excitation of structures A and B in Fig. 1, respectively. In an attempt to separate the partially resolved structures, the following counting windows were used: curve A, 145 to 1000  $\mu\text{sec}$  with a 50  $\mu\text{sec}$  gun pulse and curve B, 25 to 55  $\mu\text{sec}$  with a 10  $\mu\text{sec}$  pulse. At an energy of 50 eV with a tungsten surface, the ratio of curve A to curve B was 2.74. Curve A corresponds mainly to  $\text{CO}(a^3\Pi)$  where as curve B was caused mainly by  $\text{O}(^5\text{S})$ .

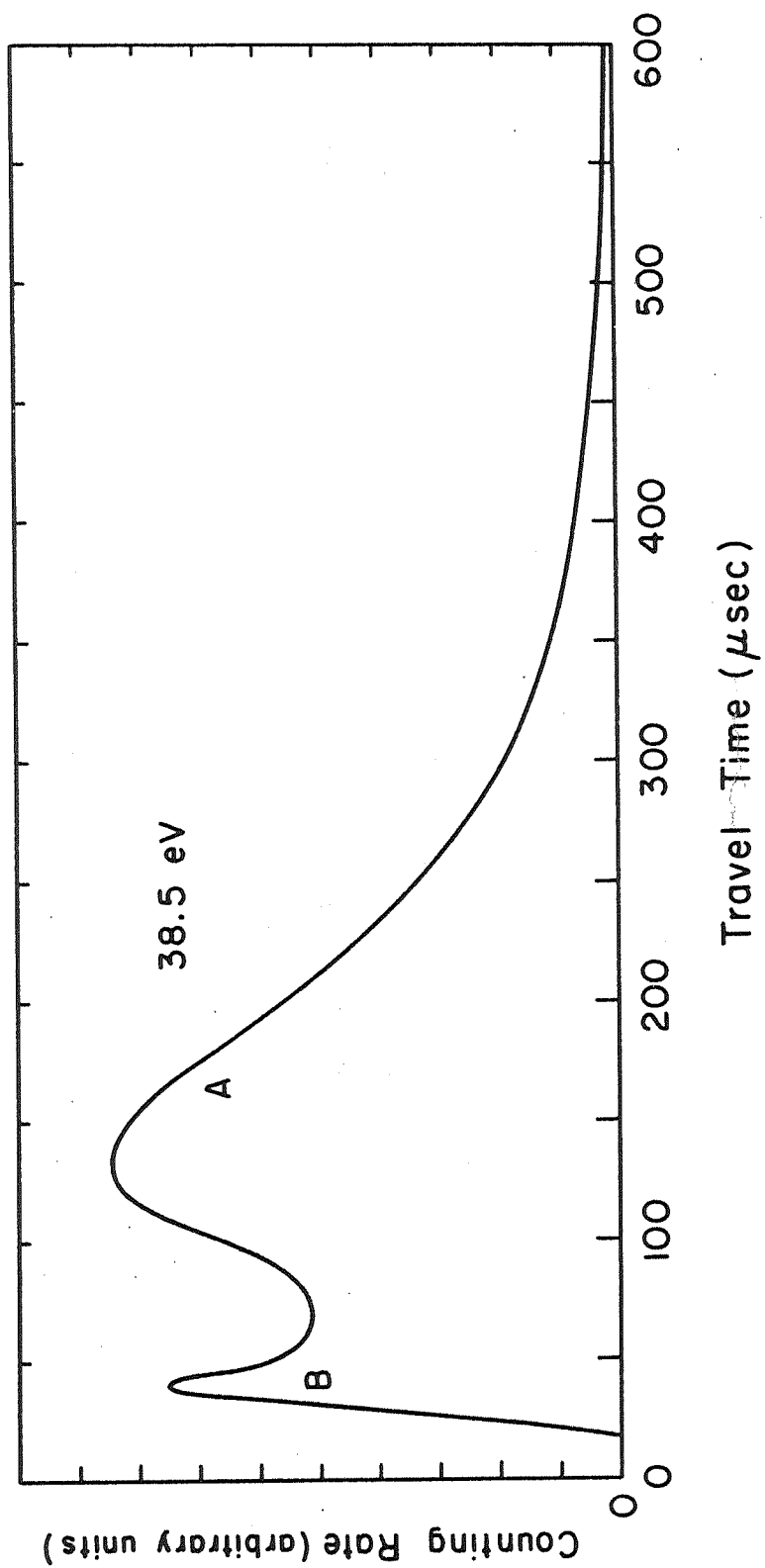


Figure 1

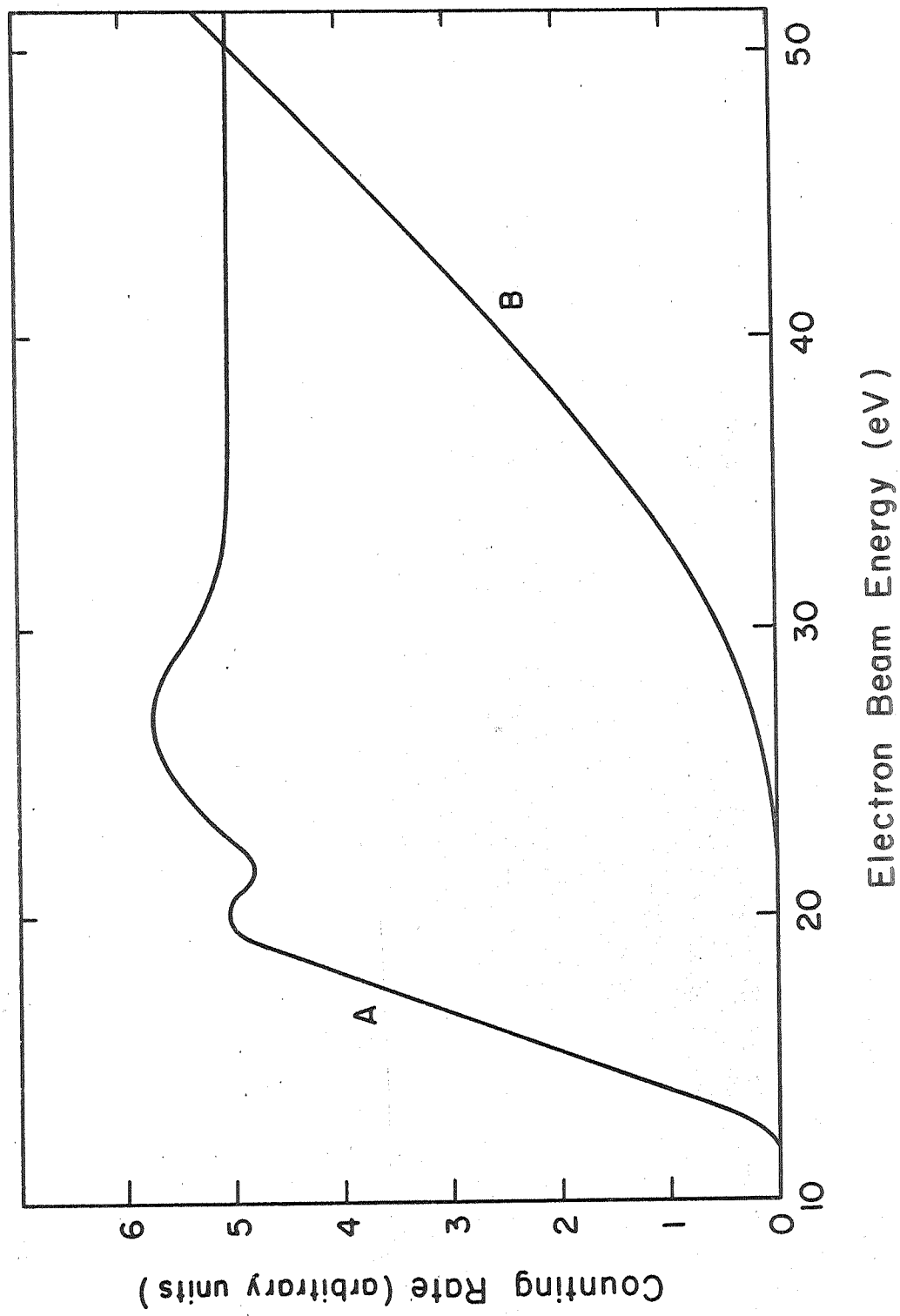


Figure 2