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# LIFETIME OF CO($\underline{a}\,^3\Pi$) FOLLOWING ELECTRON IMPACT DISSOCIATION OF $CO_2$

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## DISCLAIMER

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# Lifetime of $CO(\underline{a}^3\Pi)$ Following Electron Impact Dissociation of $CO_2$ †

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The same time-of-flight technique previously employed to measure the lifetime[1] of the $\underline{a}^3\Pi$ metastable state of CO produced by electron bombardment of a molecular beam of ground state CO has been used to investigate, for several electron bombardment energies, the lifetime of $CO(\underline{a}^3\Pi)$ following electron impact dissociation[2,3] of $CO_2$. Knowledge of the lifetime and velocity distribution of $CO(\underline{a}^3\Pi)$ following its dissociative excitation is of interest not only because of the observation[4] of CO Cameron band emission in the Martian upper atmosphere by Mariner 6 and 7, but also in connection with measurement[5] of the dissociative excitation cross section for production of $CO(\underline{a}^3\Pi)$ by electron impact on $CO_2$.

A complete description of our apparatus, data-collection scheme, data analysis, and time-of-flight theory has been given previously.[6]

The experiment is based on the time-of-flight technique where an atom or molecule is assumed to leave the metastable state only by radiative decay as it drifts over a 5-m path between two fixed detectors. Neutral, ground-state $CO_2$ molecules effuse from a source slit and are immediately excited by a pulse of magnetically focused electrons. The metastable $CO(\underline{a}\,^3\Pi)$ molecules resulting from the dissociation[2,3] of the excited $CO_2$ molecules are then collimated while passing through three buffer chambers and finally detected at both ends of the 5-m drift region.

The data-taking and timing aspects of the experiment are controlled by an on-line PDP-8 computer. An example of the data collected is shown in Fig. 1. The electron gun is pulsed on only during channel 0 and counts are then collected simultaneously at both detectors into 199 channels, not all of which are shown. The 20-V distribution, representing 48 hr of data collection, contains about 3000 counts at the peak, while in contrast the 200-V distribution has about 27 000 peak counts and was collected in only 4 hr.

Taking the ratio R of detector-2 counts to detector-1 counts for metastable CO molecules of the same velocity gives a decay plot of $\ell n R$ vs time of flight t, as shown in Fig. 2. If only one component were present, as in our previous discussion[6] of the time-of-flight technique, $\ell n R$ vs t would be a straight line, and the lifetime $\tau$ of the metastable state would be obtained from the slope = $-1/\tau$ of this straight line. But since several vibrational and rotational levels of $CO(\underline{a}\,^3\Pi)$ are metastable and have different radiative lifetimes,[1,7] the decay plots of Fig. 2 have curvature, as expected for the decay of a multicomponent metastable beam. Only an average lifetime $\bar{\tau}$ of CO($\underline{a}^3\Pi$) can be obtained from the "average" slope of the decay plot for each electron bombardment voltage, since, unlike our earlier lifetime measurement[1] of CO($\underline{a}^3\Pi$) produced by direct electron excitation of CO, the relative populations of the various CO($\underline{a}^3\Pi$) rotational levels are unknown for dissociative excitation of $CO_2$. In fact, the change in average lifetime at about 35 V apparent in Fig. 2 implies a corresponding change in the relative populations of the CO($\underline{a}^3\Pi$) levels.

The author would like to thank Dr. W. C. Wells for suggesting these measurements.

## References

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1. C. E. Johnson and R. S. Van Dyck, Jr., J. Chem. Phys. 56, 1506 (1972).
2. W. C. Wells, W. L. Borst, and E. C. Zipf, J. Geophys. Res. 77, 69 (1972).
3. R. S. Freund, J. Chem. Phys. 55, 3569 (1971).
4. C. A. Barth, C. W. Hard, J. B. Pearce, K. K. Kelly, G. P. Anderson, and A. I. Stewart, J. Geophys. Res. 76, 2213 (1971).
5. J. M. Ajello, J. Chem. Phys. 55, 3169 (1971).
6. R. S. Van Dyck, Jr., C. E. Johnson, and H. A. Shugart, Phys. Rev. A 4, 1327 (1971).
7. T. C. James, J. Chem. Phys. 55, 4118 (1971).

## Figure Captions

Fig. 1. $CO(\underline{a}\,^3\Pi)$ time-of-flight distributions taken at detector 2, 6.62 m from the electron gun used to bombard the $CO_2$ molecular beam. The shoulder on the distribution for an electron bombardment energy of 200 eV first appears at about 120 eV and is a new feature not reported in refs. 2 or 3.

Fig. 2. Decay plots. The ratio of detector-2 to detector-1 metastable CO distributions versus time of flight between detectors is plotted on a logarithmic plot for several electron bombardment voltages. The average lifetime $\bar{\tau}$ of $CO(\underline{a}\,^3\Pi)$ at each voltage represents -1/average slope of the decay plot; the solid curves are only for comparison purposes.

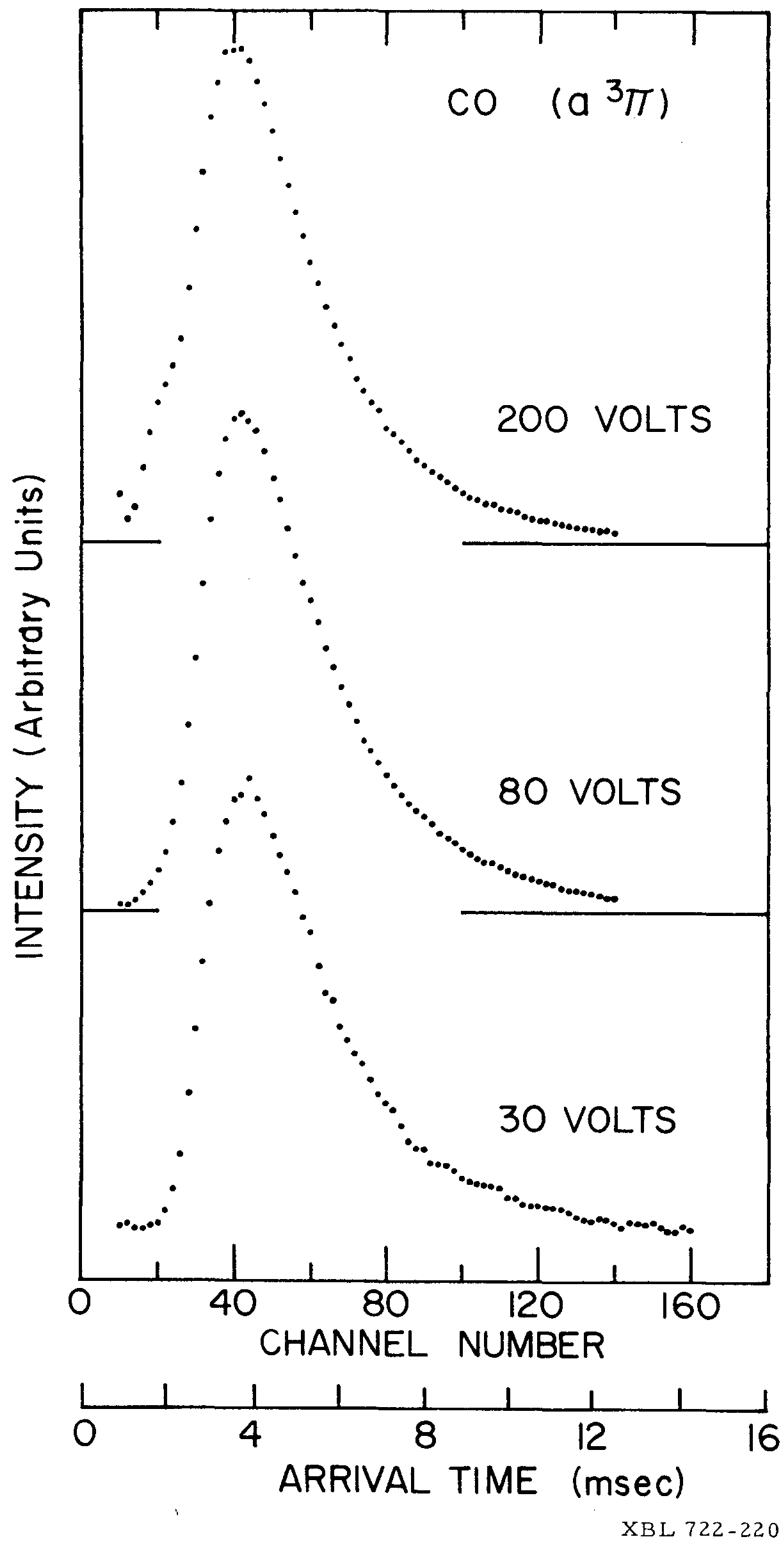
CO (a $^3\Pi$)
200 VOLTS
80 VOLTS
30 VOLTS
INTENSITY (Arbitrary Units)
0
40
80
120
160
CHANNEL NUMBER
0
4
8
12
16
ARRIVAL TIME (msec)
XBL 722-220

Fig. 1

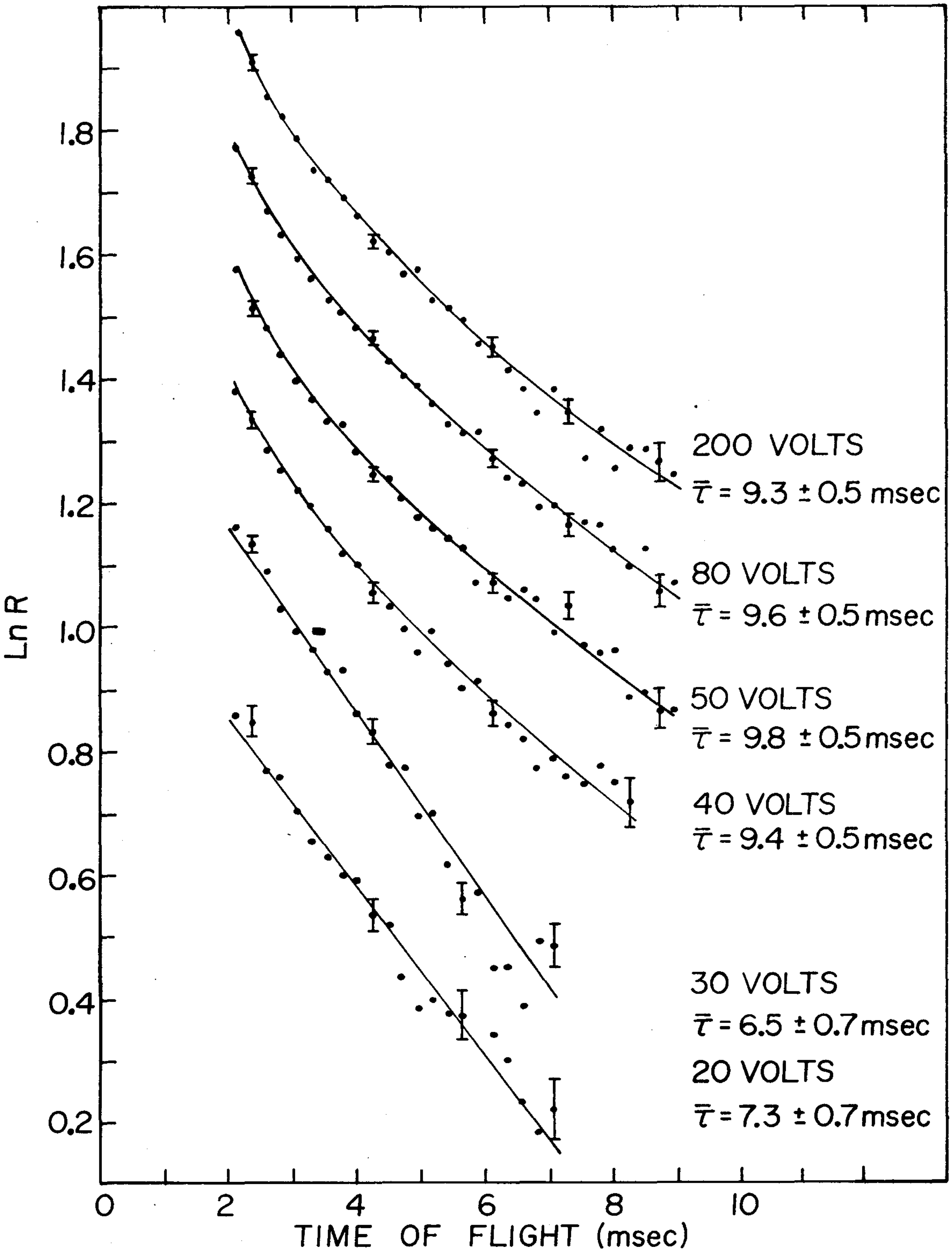


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Fig. 2

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