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Lifetime of the  $\alpha$   $^3\Pi$  Metastable State of Carbon Monoxide \*

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ABSTRACT

The rotational dependence of the lifetime of the  $\alpha$   $^3\Pi$  metastable state of CO has been investigated using a time-of-flight technique. The velocity distribution of metastable molecules is sampled and detected at two positions, 1.9 m and 6.7 m from the pulsed electron gun used to excite the ground state molecules effusing from a cooled source slit. The initial population distribution among rotational levels is changed by varying the temperature of the source. A comparison of the number of metastables within given velocity intervals at the two detectors determines the number which decay in flight and yields an experimental plot of the number which decay versus time of flight. A theoretical decay plot is also obtained using the  $\alpha$   $^3\Pi$  metastable state lifetimes calculated by James, who predicts rotational level lifetimes ranging from three msec to several hundred msec. For

two different source temperatures, the experimental and theoretical decay plots are in good agreement.

## I. INTRODUCTION

Discovery of carbon monoxide and strong uv emission from its  $\alpha^3\Pi - X^1\Sigma$  Cameron band in the Martian upper atmosphere by the Mariner missions<sup>1</sup> appears to have stimulated considerable interest in this forbidden transition. The  $\alpha^3\Pi$  state is metastable and decays to the  $X^1\Sigma$  ground state through spin-orbit mixing with the  $A^1\Pi$  state; see Fig. 1.<sup>2</sup> Both the intensity of the transition and the lifetimes of various rotational levels of the  $\alpha^3\Pi$  state have been calculated by James.<sup>3</sup> Although earlier experimental values for the  $\alpha^3\Pi$  state varied tremendously, ranging from 10  $\mu$ sec to 60 msec, two recent experiments<sup>4,5</sup> report average values for the lifetime in reasonable agreement with James' calculations. However, both experiments confine CO in a suitable "bulb" and neither experiment is able to measure the  $\alpha^3\Pi$  lifetime unperturbed by collision effects. The results, after suitable extrapolation to zero pressure, are therefore only average lifetimes and do not supply any information about the rotational dependence of the  $\alpha^3\Pi$  lifetime. Another recent experiment,<sup>6</sup> which compares the time-of-flight distribution for the  $\alpha^3\Pi$  state of CO with that of the  $A^3\Sigma_u^+$  state of  $N_2$  and attributes any difference to decay of the  $\alpha^3\Pi$  state, reports an average lifetime of 1 msec; this result is probably somewhat too short for the lower vibrational-rotational levels of the  $\alpha^3\Pi$  state.

The time-of-flight technique<sup>7</sup> we previously used to successfully measure the lifetime of the  $2^1S_0$  metastable state of helium has been used to observe the decay of the  $\alpha^3\Pi$  metastable state of CO. The rotational dependence of the lifetime has been considered when comparing our experimentally measured decay with theoretical predictions. The experiment is first outlined, and then the analysis appropriate for the  $\alpha^3\Pi$  state of CO is explained. Finally our results are discussed and compared with James' theoretical calculations.

## II. EXPERIMENT

A complete description of our apparatus and data-collection scheme has been reported previously.<sup>7</sup> The present investigation of the  $\alpha^3\Pi$  metastable state of CO does not use a quenching lamp as did our earlier experiment on the  $2^1S_0$  metastable state of He. The only other change was the substitution of heated tantalum targets for the original copper targets. The improved efficiency of the tantalum targets, when heated to several hundred degrees centigrade by ohmic heating, increased our counting rate of metastable CO molecules by almost a factor of 100.<sup>8</sup> A brief summary is now given of those aspects of the experiment which are pertinent to understanding the present investigation.

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-meter path between two fixed detectors; this assumption demands a very low pressure ( $< 10^{-7}$  Torr)

in the drift region to minimize scattering losses. The neutral, ground-state beam effuses from a cooled source slit; the molecules are immediately excited to metastable states by a pulse of antiparallel, magnetically focused electrons. The metastable beam is then collimated while passing through three buffer chambers and finally detected at both ends of the 5-m drift region. The first detector consists of a 60% transmitting tantalum mesh target. The secondary electrons which are ejected from the heated tantalum surface by the metastable molecules are collected by an EMI electron multiplier. The second detector is a solid tantalum target and intercepts the transmitted metastable molecules which survive the flight between the two detectors.

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. 2, and represents about 500 000 separate collection sweeps during a total collection time of 12 hours. 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. All channel widths are equal to 200  $\mu$ sec. The time-of-flight distribution at detector 2 has been integrated over a partition width which corresponds to the channel width at detector 1 for metastable molecules with the same velocity. The amount of background subtraction, usually about 0.1% of the peak, is obtained from the long tail of the detector 1 time-of-flight distribution, and from the beginning few channels of the detector 2 distribution.

### III. ANALYSIS

The time-of-flight technique is ideally suited for a lifetime measurement only when the beam consists of a single metastable state. Even though the initial excitation of the beam may simultaneously yield several metastable states, a metastable beam containing a single state can sometimes be obtained by using state-selecting techniques such as resonance quenching<sup>7</sup> or molecular-beam resonance.<sup>9</sup> The excitation of a molecule, however, generally produces a large number of vibrational-rotational metastable states and makes state selection very impractical. It is then usually necessary to interpret the experimentally measured decay as an "average" lifetime of the metastable states in the beam. Our present experiment is able to avoid this interpretation; we compare our experimental plot of the number of metastable molecules which decay versus time of flight with a theoretical plot calculated using the rotational dependence of the  $a^3\Pi$  metastable state lifetimes predicted by James.<sup>3</sup>

#### A. Experimental Decay Plot

The experimental plot of the number of metastable molecules which decay versus time of flight is obtained from the distributions shown in Fig. 2. The correct partitioning of the detector 2 distribution assures that each point for both detectors corresponds to metastable molecules with the same velocity. Then the ratio of detector 2 to detector 1 data is taken; the natural logarithm of this ratio versus time of flight  $t$  is our decay plot.



If only one component were present, as in our previous discussion<sup>7</sup> of the time-of-flight technique,  $\ln R$  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 we expect several rotational levels of the  $a^3\Pi$  state to be metastable and to have different radiative lifetimes, we must now explicitly consider this possibility.

### B. Theoretical Decay Plot

The number of molecules in a particular metastable state  $k$  with initial velocity distribution  $n_0(v, k)$ , which arrives at detector  $i$  at time  $t_i$ , is  $n_0(v, k)e^{-t_i/\tau_k}$ ; the exponential factor allows for the possibility of radiative decay with mean life  $\tau_k$ . The probability of detecting a particular metastable molecule depends upon the surface efficiency  $\epsilon_i(k)$  of detector  $i$ . Although this efficiency should be velocity-independent for the thermal velocity range of this experiment, it is not necessarily true that the efficiency is independent of position on the detector surface. The total number  $N_i(v)$  of metastable molecules with velocity  $v$  that are counted at detector  $i$  is therefore obtained not only by summing over the different metastable states  $k$ , but also by integrating over the surface of the detector:

$$N_i(v) = \sum_k \int_{\text{surface}} \epsilon_i(k) n_0(v, k) e^{-t_i/\tau_k} dS . \quad (1)$$

Dependence on the details of the detector surface is eliminated by insuring that the initial velocity distribution  $n_0(v, k)$  is uniform

across the beam so that each position on the detector surface sees the same velocity distribution. The number of metastable molecules counted is then

$$N_i(v) = \sum_k C_i(k) n_o(v, k) e^{-t_i/\tau_k}, \quad (2)$$

where  $C_i(k) = \int_S \epsilon_i(k) dS$  is a constant efficiency factor of the  $i^{\text{th}}$  detector. The ratio of the number of metastable molecules in the same velocity interval at two spatially separated detectors yields the desired decay plot, since, with the reasonable assumption that the efficiency factor  $C_i(k)$  is the same for all states  $k$ , the ratio

$$R = \frac{N_2(v)}{N_1(v)} = C \frac{\sum_k n_o(v, k) e^{-t_2/\tau_k}}{\sum_k n_o(v, k) e^{-t_1/\tau_k}} \quad (3)$$

is independent of the two detector efficiencies except for an overall normalization constant  $C$ .

The electron bombardment excitation of the  $\alpha$   $^3\Pi$  metastable state occurs in a time which is short compared to the rotational period of the ground state; therefore, for a particular vibrational excitation, the relative initial populations of the metastable rotational levels are essentially the same as that of the ground state.<sup>10</sup> The relative population distribution at a temperature  $T$  among the rotational levels of the metastable state is then<sup>10</sup>

$$n_o(N, T) = (2N + 1) \frac{hcB}{kT} e^{-BN(N + 1)hc/kT} \quad (4)$$

where  $B$  is the rotational constant of the ground state and  $N$  is the

rotational quantum number. Figure 3 shows the relative rotational populations versus  $N$  for several temperatures.

The relative population of the  $a^3\Pi$  vibrational levels produced by electron bombardment several volts above threshold has been observed to agree with the calculated Franck-Condon factors.<sup>11</sup> The radiative lifetime, however, is expected to vary slowly as a function of vibrational level<sup>12</sup>; therefore, to a good approximation, we can consider the metastable lifetime to depend only upon the rotational quantum number. Thus, using the theoretically predicted lifetimes listed in Table I where  $J = N + \Omega$  is the total angular momentum, Eqs. (3) and (4) allow calculation of the expected theoretical decay plot. We shall treat the temperature  $T$  and a factor uniformly multiplying all the lifetimes of Table I as variable parameters when comparing the theoretical and experimental decay plots.

#### IV. RESULTS

Immediately apparent in Fig. 4 is the curvature of the decay plots, as expected for the decay of a multicomponent metastable beam. The higher temperature plot is for data taken with the source at room temperature while the lower temperature plot represents data taken with liquid nitrogen cooling. The change in slope and curvature of the decay plot with change in source temperature arises from the modification of the relative populations of the rotational levels; see Fig. 3. The slopes at the beginning and the end of the experimental decay plot indicate that metastable states with lifetimes ranging from 10 msec to

60 msec are present in our beam.

Although the source was operated both at room temperature and with liquid-nitrogen cooling, the close proximity of the source slit to the hot filament of the electron gun limited the actual source temperature to a value somewhat higher. Therefore, since the effective temperature of the CO ground-state beam effusing from the source slit is not well known, we shall, as the first step in comparing the experimental and theoretical decay plots, vary the effective temperature; see Eq. (4). Figure 4(a) indicates that, for the lifetimes of Table I, the two effective temperatures giving the best agreement are  $200^\circ$  and  $350^\circ$ . Although not shown, the same two temperatures ( $\pm 25^\circ$ ) are also obtained when the lifetimes of Table I are uniformly multiplied by both a factor of 1.25 as well as by 0.75. Thus, the same effective temperatures give good agreement between the experimental and theoretical decay plots over a range of lifetimes from  $0.75 \tau$  to  $1.25 \tau$ , where  $\tau$  refers collectively to the predicted lifetimes listed in Table I.

Now that the effective temperature has been determined, we can compare our experimental results with theoretical predictions, as in Fig. 4(b). The agreement between theory and experiment is remarkably good; we conclude that James' calculation<sup>3</sup> of the rotational dependence of the  $\alpha^3 \Pi$  metastable state lifetimes is correct, and that his predicted rotational level lifetimes taken as a group are accurate to better than 25%.

Finally, we mention that, except for the expected dependence on source temperature, our results are independent of various experi-

mental parameters such as electron gun voltage, channel width, beam flow rate, and drift region pressure. The failure to observe any dependence on electron gun voltage from just-above threshold to over one hundred volts above threshold lends strong support to our conclusion that the  $\alpha^3\Pi$  metastable state lifetime varies slowly as a function of vibrational level.

#### ACKNOWLEDGMENTS

We would like to express our appreciation to Dr. Richard H. Gammon for his continued interest in our experiment and for providing us, through numerous discussions, with the benefits of his earlier work on the radio-frequency spectrum of the  $\alpha^3\Pi$  state of CO; we especially thank him for the suggestion to replace our copper targets with the heated tantalum targets. Also, we would like to thank Dr. Tom James for making available to us his theoretical results prior to their publication.

Table I. Lifetimes in msec of the rotational levels of the  $\alpha^3\Pi$  metastable state.  $J = N + \Omega$  is the total angular momentum and  $N$  the rotational angular momentum. The lifetimes are those calculated by James.

J	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$
0	99999.00	-	-
1	451.00	2.93	-
2	154.00	3.03	160.00
3	79.00	3.18	60.00
4	50.00	3.37	38.30
5	35.30	3.58	28.00
6	26.80	3.85	22.00
7	21.70	4.15	18.00
8	18.10	4.50	15.20
9	15.50	4.90	13.20
10	13.80	5.41	11.70
11	12.50	5.80	10.70
12	11.50	6.40	9.95
13	10.70	7.00	9.35
14	10.00	7.60	8.90
15	9.44	8.37	8.49
16	9.03	9.10	8.23
17	8.70	9.90	8.00
18	8.40	10.70	7.77
19	8.10	11.60	7.53
20	7.90	12.50	7.34
21	7.70	13.60	7.20
22	7.50	14.70	7.03
23	7.35	15.80	6.90
24	7.20	16.90	6.78
25	7.10	18.10	6.68
26	7.00	19.40	6.60

## References

- \* Work supported in part by United States Atomic Energy Commission.
- † Present address: Department of Physics, University of Washington, Seattle, Washington 98105.
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  - <sup>8</sup> This improvement was not observed for either the  $2^1S_0$  metastable state of He or the  $c^3\Pi$  metastable state of  $H_2$ .
  - <sup>9</sup> W. Lichten, *Bull. Am. Phys. Soc.* 7, 43 (1962).
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  - <sup>11</sup> R. C. Stern, R. H. Gammon, M. E. Lesk, R. S. Freund, and W. A. Klemperer, *J. Chem. Phys.* 52, 3467 (1970).
  - <sup>12</sup> Dr. T. C. James, Ames Research Center, private communication.

Figure Captions

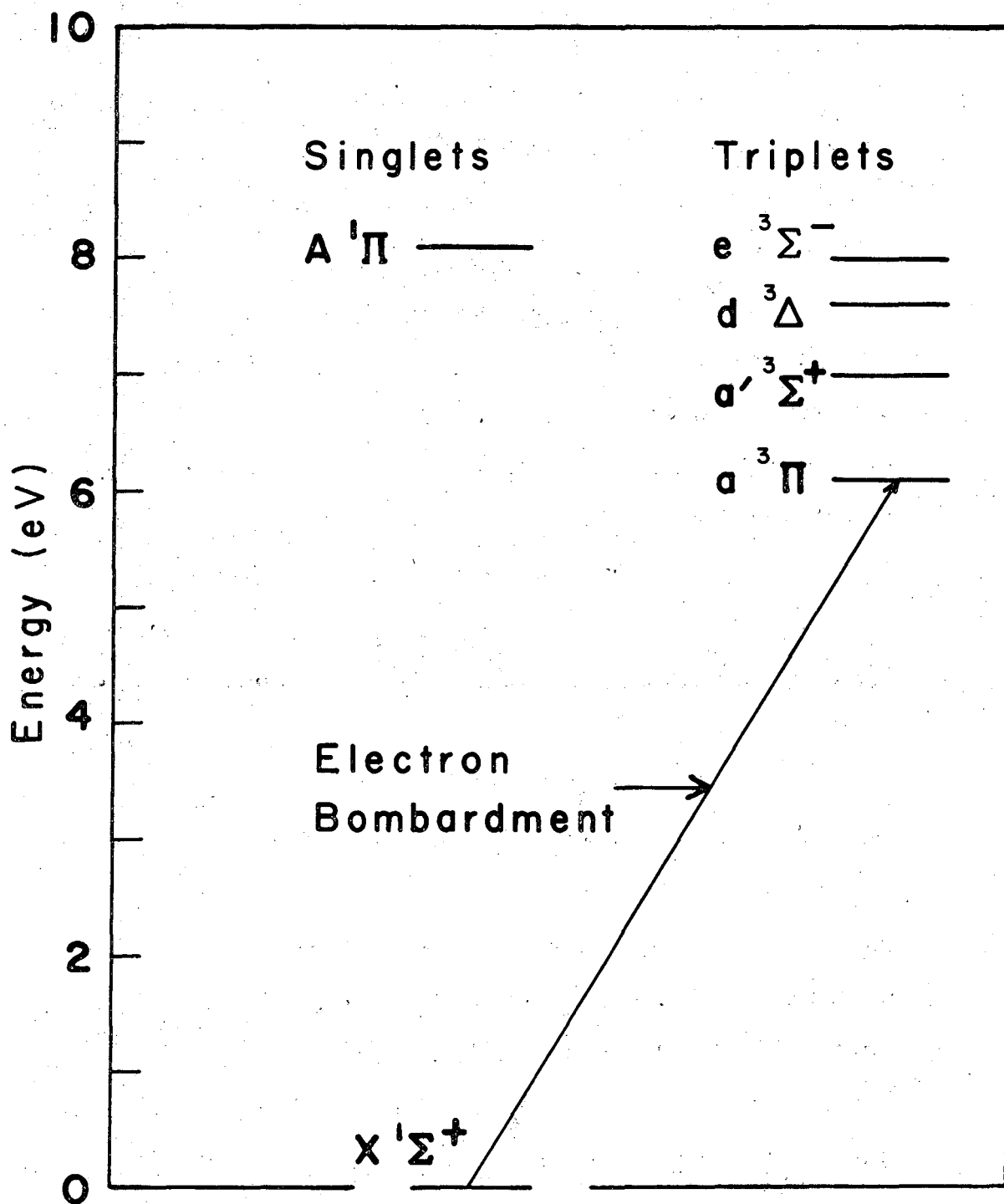
Fig. 1. CO energy-level diagram showing the lowest-lying levels. The  $a^3\Pi$  metastable state is produced by electron bombardment. Its decay to the ground state occurs through spin-orbit mixing with the  $A^1\Pi$  state.

Fig. 2. Time-of-flight distributions, representing about 500 000 separate collection sweeps. The channel numbers are for detector 1; the data for detector 2 has been partitioned and averaged over velocity intervals whose width is determined by the channel width at detector 1.

Fig. 3. The relative population of the rotational levels of the ground state of CO is plotted versus rotational quantum number  $N$ . The change of relative population with temperature produces the corresponding change in the decay plots of Fig. 4.

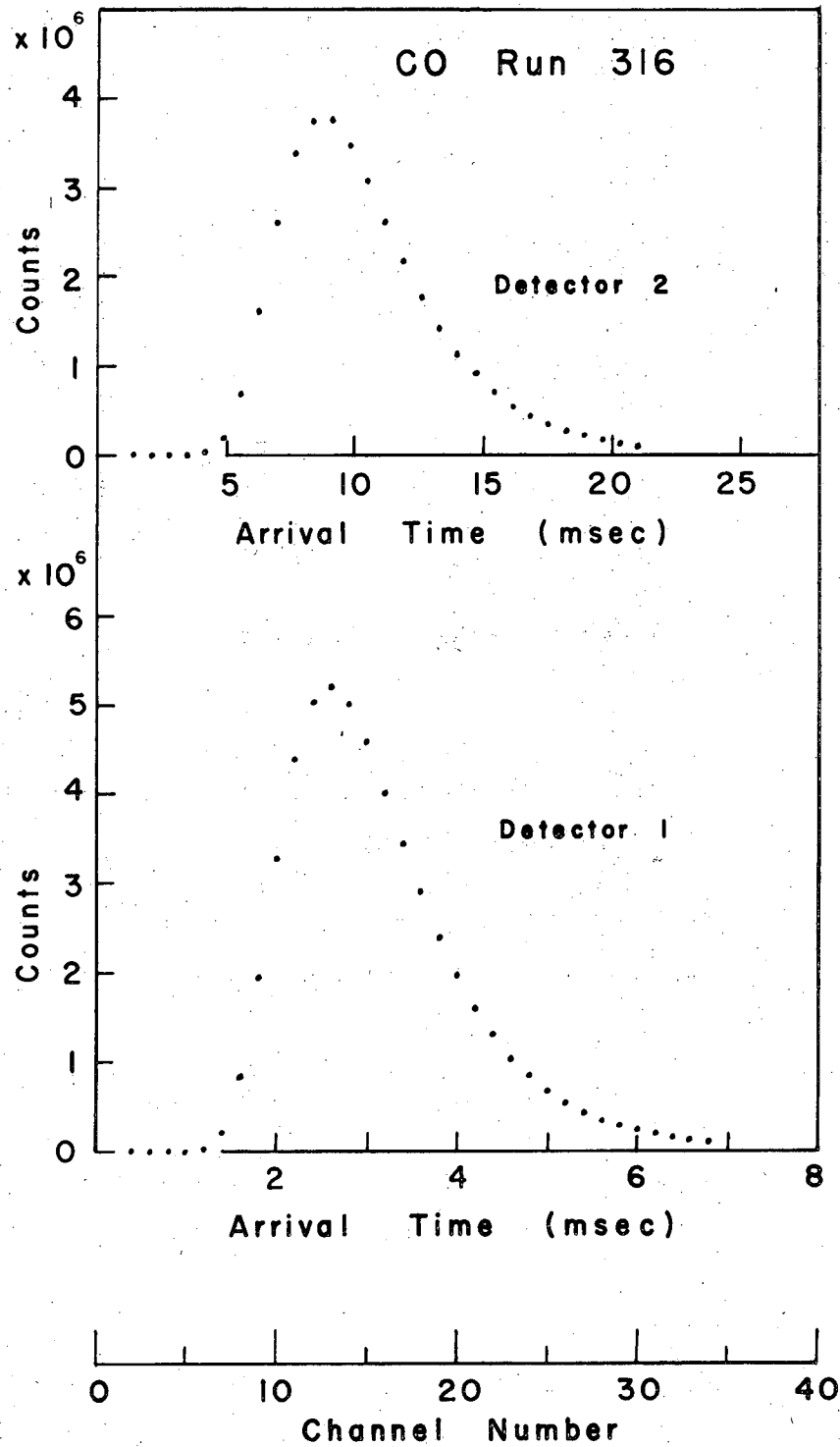
Fig. 4. Decay plots. The ratio of detector 2 to detector 1 metastable atom distributions versus time of flight between detectors is plotted on a logarithmic plot. Part (a) compares the experimentally measured decay for data taken at two different source temperatures with the theoretical decay calculated for several effective temperatures using Eqs. (3) and (4) and the lifetimes of Table I. Part (b), using temperatures of  $200^\circ$  and  $350^\circ$ , compares the experimental decay with the theoretical decay for the lifetimes  $\tau$  of Table I as well as for the lifetimes uniformly multiplied by factors of 1.25 and 0.75.





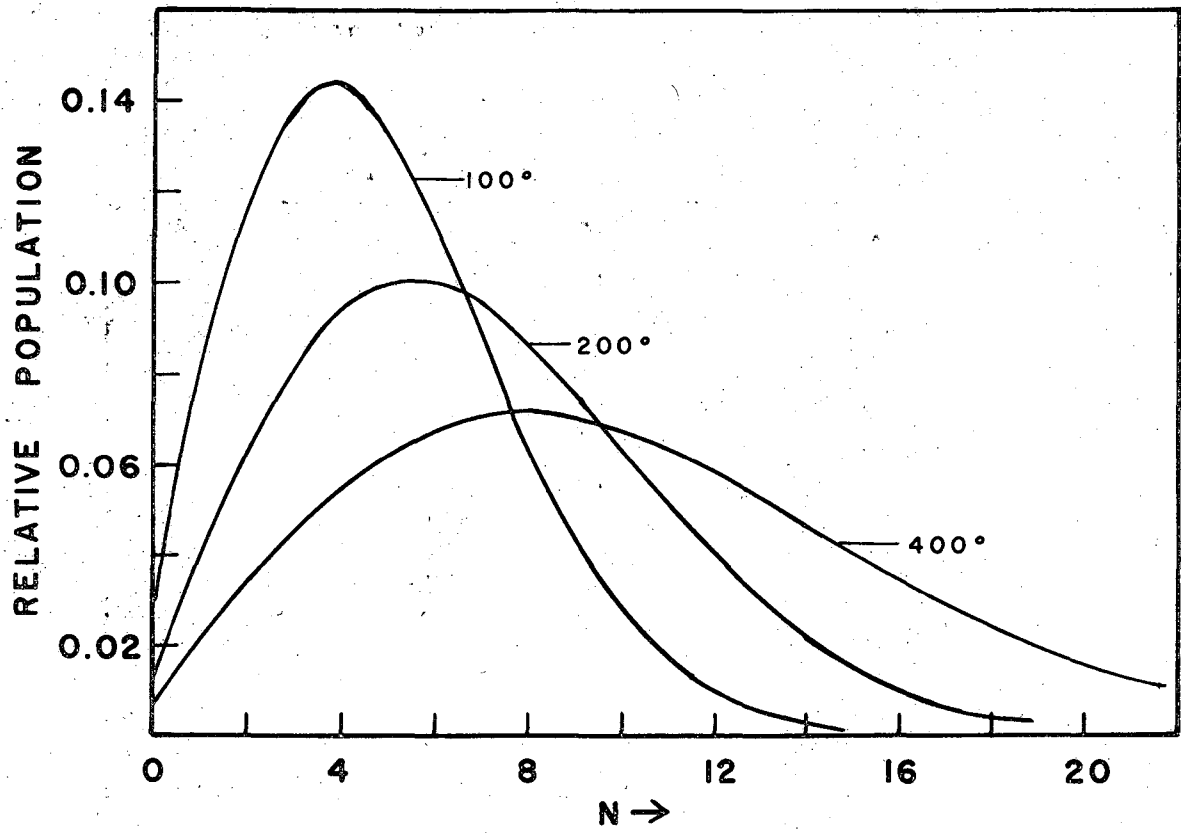
XBL 717-1183

Fig. 1



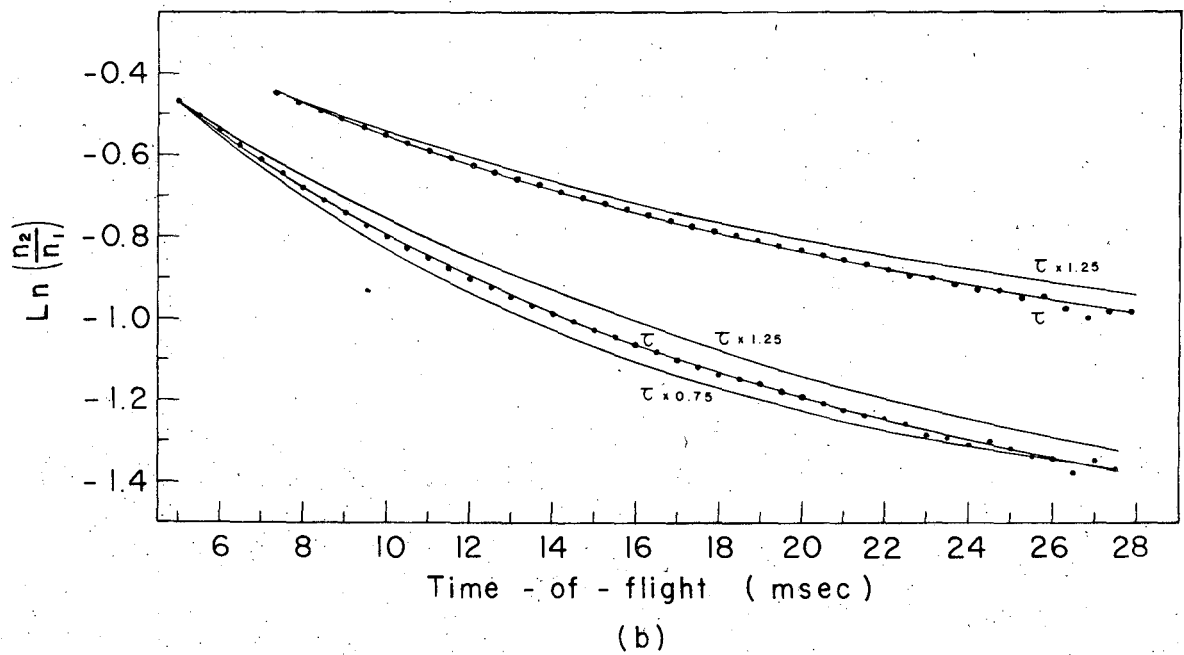
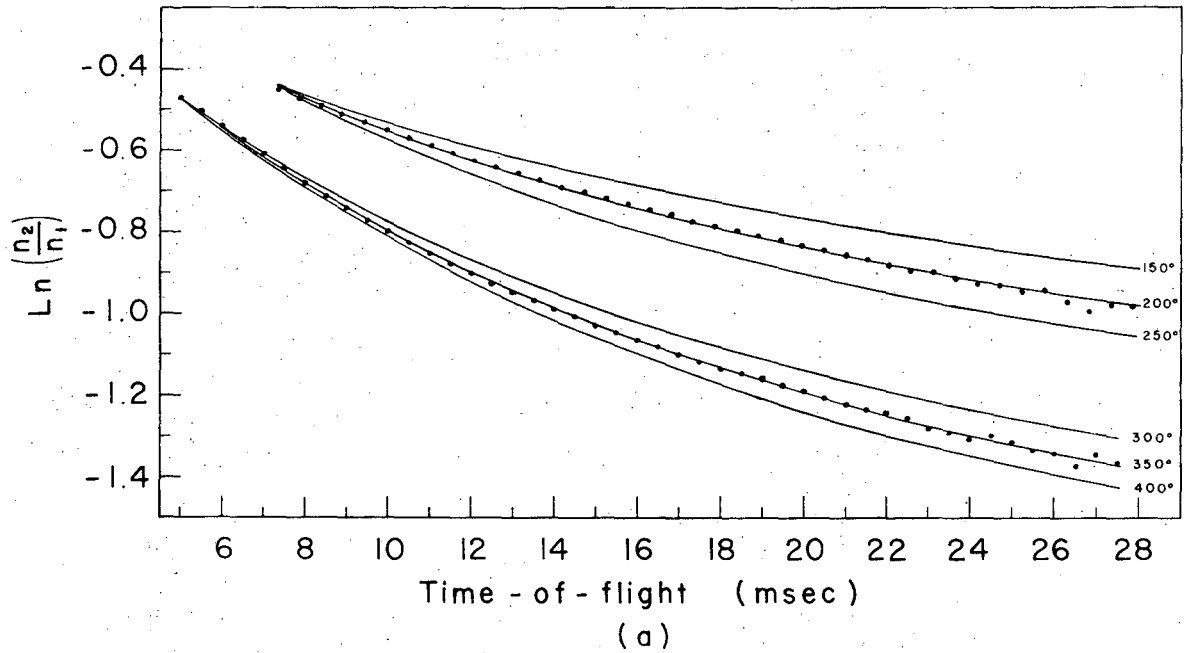
XBL 718-1182

Fig. 2



XBL 717-1185

Fig. 3



XBL 717-1187

Fig. 4

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