

MOLECULAR BEAM METHODS FOR MEASUREMENT  
OF METASTABLE STATE LIFETIMES

by

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## ABSTRACT

This thesis presents several methods for measuring a lifetime of a metastable state using spatial decay and time-of-flight data. The experimental apparatus consists of a gas source, an electron gun, and a movable detector. Spatial decay data are accumulated by operating the electron gun in a DC mode and translating the detector along the molecular beam. Time-of-flight data are obtained by pulsing the electron gun and leaving the detector stationary.

The spatial decay analysis assumes that i) the metastable beam consists of two components, with one component having a very long lifetime and ii) the velocity distribution can be approximated by  $v^n \exp(-mv^2/2kT)$  where a value for  $n$  is estimated by fitting a non-decaying time-of-flight spectrum ( $n$  is not a critical parameter).

The time-of-flight analysis is the main analytic technique and makes only one assumption: the metastable beam consists of two components, with one component having a very long lifetime. The time-of-flight analysis may be generalized to a beam consisting of more than two components.

The TOF method was developed to overcome difficulties present in other methods for measuring lifetimes: it does not require quenching one of the metastable states, it does not require a knowledge of the metastable velocity distribution, and it does not require the long-lived metastable state to be individually excited.

These techniques were tested on a two-component, computer-simulated metastable beam and on an experiment with molecular nitrogen. The lifetime of the  $a^1\Pi_g$  state was found to be  $(106 \pm 35)$  usec, in good agreement with recent measurements made by other workers using different methods.



## CHAPTER 1

### AN INTRODUCTION TO LIFETIME MEASUREMENTS

#### 1.1 An Introduction

This work began as part of a program to develop a series of satellite-borne experiments to measure molecular nitrogen temperatures and to study the accommodation of molecular nitrogen on surfaces in the space environment. Since it was necessary to develop an analysis of  $N_2$  time-of-flight (TOF) spectra, this experiment was initiated.

$N_2$  has three primary metastable states excited by electron impact (Freund, 1969b): the  $A^3\Sigma_u^+$  state at 6.16 eV, the  $a^1\Pi_g$  state at 8.54 eV, and the  $E^3\Sigma_g^+$  at 11.87 eV. At the time this experiment began, the lifetime of the  $A^3\Sigma$  state was known to be on the order of seconds (see Shemansky, 1969a for a recent measurement and a review of other work) and the lifetime of the  $a^1\Pi$  state had been measured by Lichten (1957) and by Olmsted, Newton, and Street (1965). Lichten found a lifetime of  $(170 \pm 30)$   $\mu\text{sec}$  by measuring the spatial decay of a metastable  $N_2$  beam. Olmsted, Newton, and Street observed the time-of-flight and excitation function of  $N_2$  at two electron gun-detector separations and estimated the lifetime to be  $(120 \pm 50)$   $\mu\text{sec}$ . After this experiment began, additional results were published. Freund (1969a) measured the prompt and delayed emission spectra and TOF spectra of  $N_2$ , estimating

the lifetime of the  $E^3\Sigma$  state to be  $(270 \pm 100)$   $\mu\text{sec}$  (by assuming the lifetime of the  $a^3\Pi$  state of CO to be 60 msec). Borst and Zipf (1971) measured the lifetimes of the  $a^1\Pi$  and  $E^3\Sigma$  states to be  $(115 \pm 20)$   $\mu\text{sec}$  and  $(190 \pm 30)$   $\mu\text{sec}$ , respectively. Borst and Zipf measured these lifetimes by comparing the TOF spectra for the  $a^1\Pi$  and  $E^3\Sigma$  states with a TOF spectrum for just the  $A^3\Sigma$  state (a long-lived state). The lifetime of the  $a^1\Pi$  state has also been found from laboratory analyses of the optical Lyman-Birge-Hopfield transition ( $a^1\Pi_g - X^1\Sigma_g^+$ ) that is of considerable aeronautical importance: Jeunehomme (1967) obtained 10  $\mu\text{sec}$ , Holland (1969) found 80  $\mu\text{sec}$ , and Shemansky (1969b) measured lifetimes ranging from 140  $\mu\text{sec}$  for the first vibrational level to 160  $\mu\text{sec}$  for the eighth vibrational level.

It should be noted that the metastable states of helium (Van Dyck, Johnson, and Shugart, 1970; A. S. Pearl, 1970) and molecular hydrogen (Johnson, 1971) have recently been studied with TOF methods. The lifetime measurements on the  $2^1S$  state of helium performed by Van Dyck, Johnson, and Shugart yield results that agree with the calculations of Drake, Victor and Dalgarno (1969), but sharply disagree with the results of A. S. Pearl. Since helium is one of the few cases where a theoretical calculation can be made, it is seen that a good understanding of TOF lifetime measurements is essential.

We have been speaking of metastable states. By "metastable" we mean that the excited state of an atom or molecule is forbidden to decay to the ground state by the usual

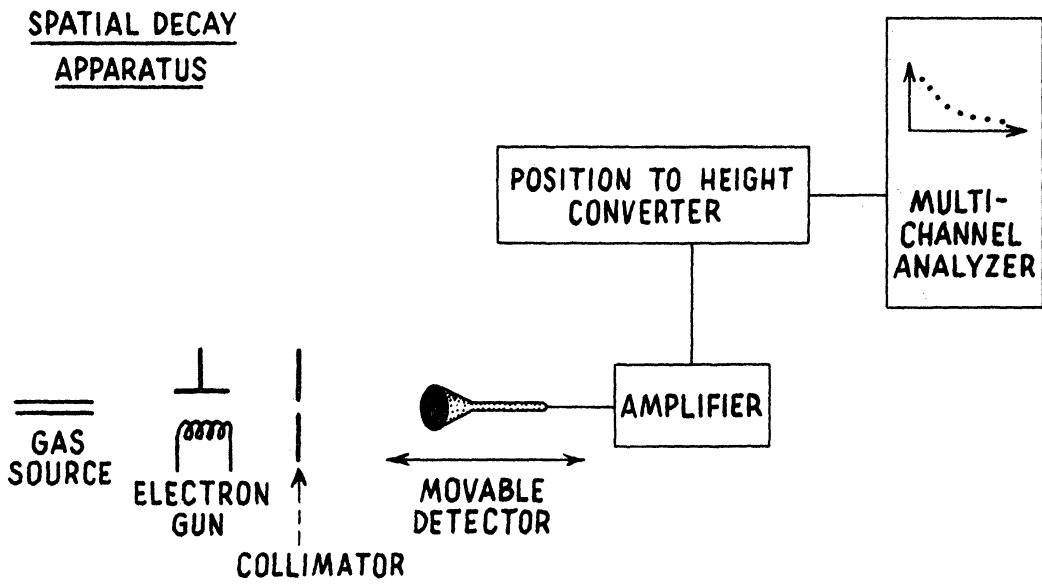
dipole selection rules. However, the state may decay by emitting magnetic dipole or electric quadrupole radiation, resulting in lifetime on the order of  $10^{-4}$  seconds or longer.

This brief presentation of several lifetime measurements in He and  $N_2$  demonstrates that additional measurements using different techniques are needed. This thesis presents several methods for measuring lifetime from spatial decay and TOF data. These methods apply to a two-component metastable beam, with one component having a very long lifetime, and overcomes some of the difficulties of earlier experiments.

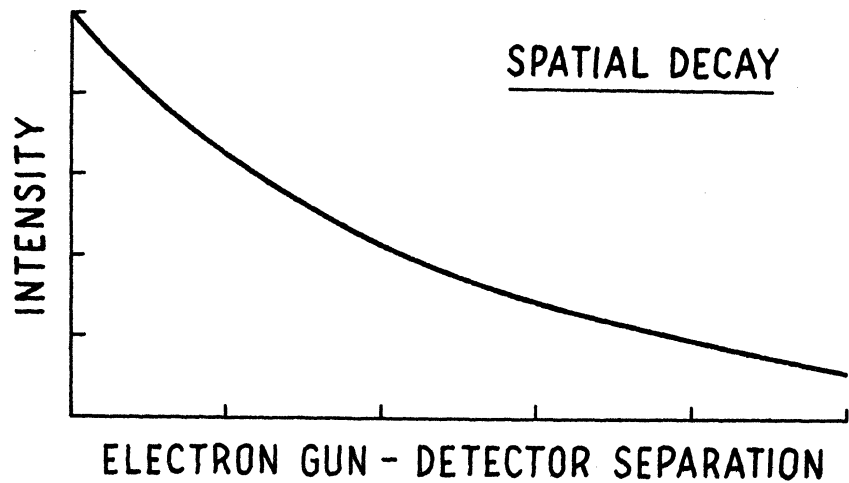
The organization of this thesis is as follows. The analysis of spatial decay and TOF data is introduced (chapter 1) by outlining several basic techniques. However, these introductory methods are very limited and several main techniques are developed. These main techniques are the primary development of this thesis and are tested on a computer simulated metastable beam (chapter 3) and on the  $a^1\Pi$  state of  $N_2$  (chapter 5), with the results being discussed and compared to the results found by other experimenters (chapter 6). The experimental apparatus is described and tested on a non-decaying metastable argon beam in chapter 4. Appendix A contains a generalization of the TOF technique to a beam containing more than two metastable components.

## 1.2 Spatial Decay

One method of measuring lifetimes involves the spatial decay of a metastable beam. Figure 1.1a is a schematic of



(a)



(b)

Figure 1.1

- (a) Apparatus that could be used for taking spatial decay data.
- (b) A typical spatial decay.

the apparatus that might be used to record the spatial decay. Gas effuses from a source into an interaction region where a small fraction of the ground state molecules are excited by electron bombardment. The molecules then pass through collimating slits and strike a detector that translates along the axis of the beam. Because these molecules have a thermal distribution of speeds (approximately  $10^4$  cm/sec) only those molecules in metastable states live long enough to travel the several centimeters to be detected. The detector position is encoded on the detector pulses by the position-to-height converter, and these pulses are sorted and stored according to height by the multichannel analyzer. A typical spatial decay is shown in figure 1.1b. The lifetime of the metastable state may be obtained from these data.

One method of analyzing the spatial decay to obtain lifetimes is to assume a single-component beam and to replace the distribution of velocities by a single velocity. Then the intensity of the beam is written as

$$\frac{I(X_a)}{I(X_b)} = e^{-(X_a - X_b)/v \cdot \tau} ,$$

where  $X$  is the electron gun-detector separation,  $v$  is the velocity, and  $\tau$  is the lifetime. This equation may be solved for

$$\tau = \frac{(X_b - X_a)/v}{\ln \frac{I(X_a)}{I(X_b)}} \quad (1.1)$$

Since all the quantities in the right side of equation 1.1

can be measured, the lifetime can be calculated.

If a Maxwellian velocity distribution is assumed, the intensity of the metastable beam is written as an integral over all velocities:

$$I(x) = N \int_0^{\infty} v^2 e^{-mv^2/2kT} e^{-x/v\tau} dv$$

where  $m$  is the mass of the molecule,  $k$  is Boltzmann's constant, and  $T$  is the temperature. The lifetimes can now be measured in the manner detailed by Lichten (1957).

However, the velocity distribution is generally not Maxwellian and, therefore, a method for measuring lifetimes under more general conditions is needed. Such a method is described in section 2.1.

### 1.3 Time-of-Flight

Another approach to measuring lifetimes involves the TOF distribution of the metastable beam. Figure 1.2a is a schematic of apparatus that might be used to record the TOF spectrum. The electron gun is pulsed and the detector is stationary. Since the metastable molecules have a distribution of speeds, they will have a distribution of times-of-arrival at the detector. The time-of-arrival is encoded on the detector pulses by the time-to-height conversion, and these pulses are sorted and stored according to height by the multichannel analyzer. A typical TOF spectrum is shown in figure 1.2b (solid curve). The first peak in the TOF spectrum is due to the arrival of photons. These photons are from the rapid decay of the non-metastable states and are used to mark zero

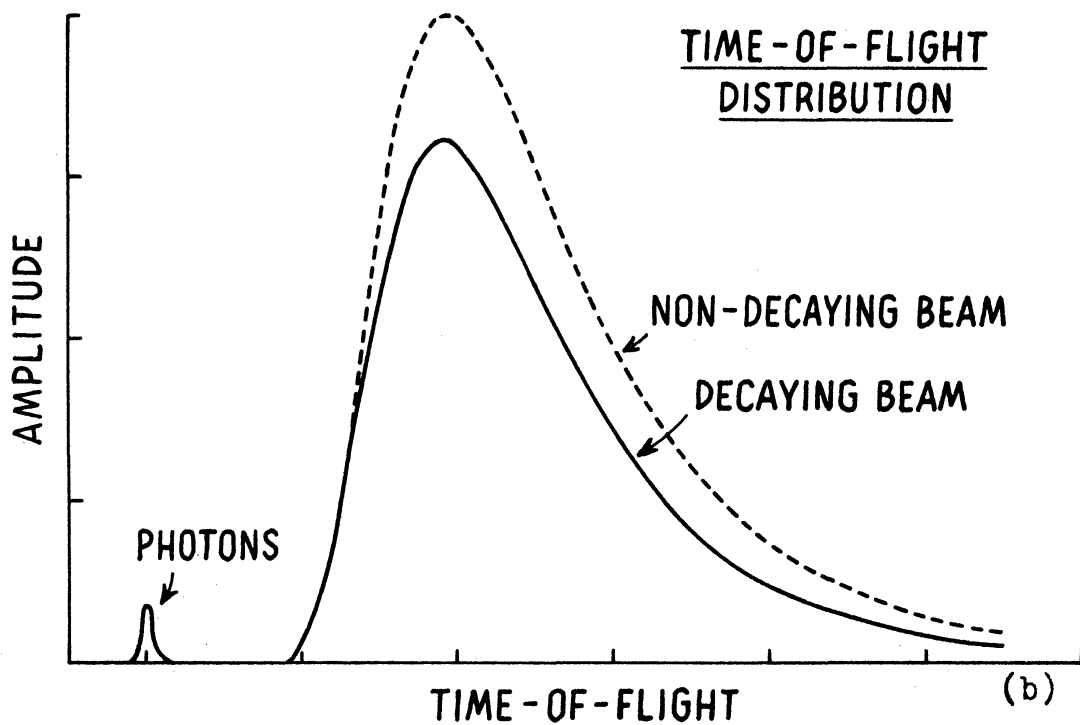
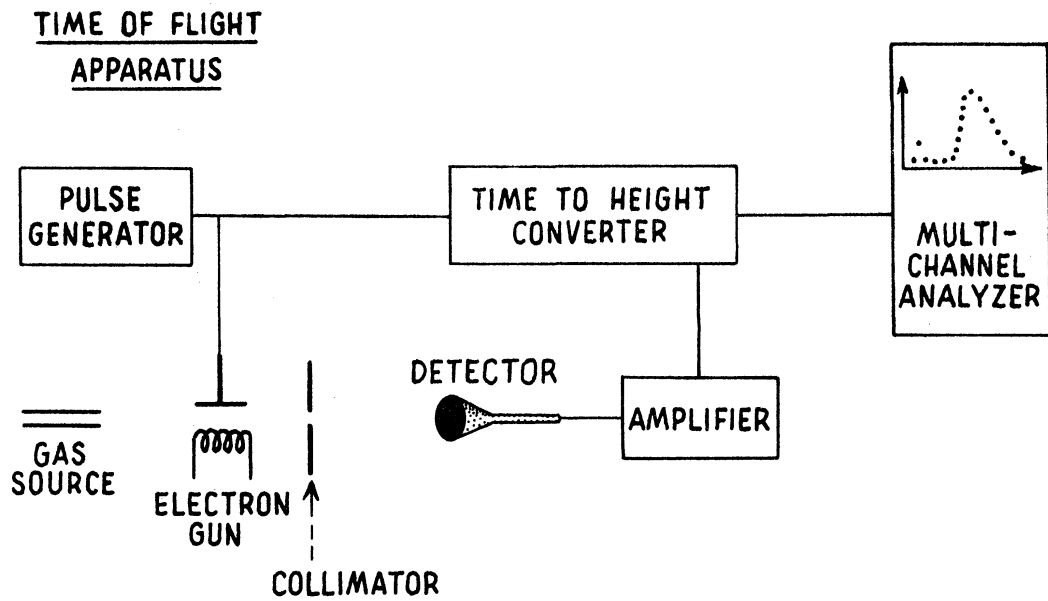


Figure 1.2

- (a) Apparatus that could be used for taking time-of-flight data.
- (b) Typical time-of-flight distributions for a decaying and non-decaying metastable beam. The arrival of the photons from the rapid decay of the non-metastable states is used to mark zero time.

time. The second peak is due to the arrival of the metastable molecules. The lifetime of the metastable state may be measured from these data.

One method of analyzing these TOF data to obtain lifetimes is to assume a single-component beam that has a certain TOF distribution in the absence of any decay (dashed curve in figure 1.2b). By multiplying this initial distribution by  $e^{-t/\tau}$  one gets the solid curve in figure 1.2b. Then the lifetime is found by adjusting  $\tau$  to give a good fit to the experimental data.

The first problem to arise is the determination of the initial velocity distribution. J. C. Pearl (1970) developed a theory to predict the molecular velocity distribution after electron impact. However, his theory requires knowledge of the electron energy and the collimation of the incoming and outgoing molecular beam, and is not easily applied to lifetime measurements.

Another problem often arises from the presence of more than one metastable component. In the case of He, the  $2^1S$  component can be quenched (Fry and Williams, 1969) and this was done in the lifetime measurements performed by A. S. Pearl (1970) and by Van Dyck, Johnson, and Shugart (1970). But these quenching techniques do not apply to  $N_2$ .

A method for measuring lifetimes that does not depend on knowledge of the velocity distributions, and that accounts for the presence of more than one component, is presented in section 2.2.



## CHAPTER 2

### THE THEORY OF A LIFETIME MEASUREMENT

The spatial decay and TOF techniques discussed in sections 1.2 and 1.3 have the drawbacks that they do not consider the proper velocity distribution and they do not apply to a beam including more than one metastable component.

The methods for measuring lifetimes presented below do apply to a beam consisting of more than one component and either use a measured approximation to the velocity distribution (spatial decay method) or do not depend on the velocity distribution at all (TOF method).

#### 2.1 A Lifetime Measurement from Spatial Decay Data

The spatial decay analysis generalizes the approach of Lichten (1957) and assumes the following:

- i) The metastable beam consists of two components: one component has an initial population  $N_1$  and a lifetime  $\tau$ , and the other component has an initial population  $N_2$  with an infinite lifetime. By "infinite lifetime" we mean that the state does not measurable decay from the time of creation to the time of detection.
- ii) The velocity distribution of the molecules after electron impact is described by the

function  $v^n \exp(-mv^2/2kT)$  where a value for  $n$  is assigned by fitting a non-decaying TOF distribution (section 4.4.3).

Figure 2.1a shows the spatial decay for a two-component metastable beam. Since the intensity of the long-lived state is not a function of  $x$ , examine the short-lived state's behavior by taking the derivative of the intensity with respect to  $x$  (figure 2.1b). Take the ratio of the derivatives at two points  $X_a$  and  $X_b$  to give

$$G_{\text{expt}} = \frac{\left. \frac{dI}{dx} \right|_{X_a}}{\left. \frac{dI}{dx} \right|_{X_b}} \quad (2.1)$$

The notation "expt" is to remind us that this is an experimental quantity.

$G_{\text{expt}}$  is used to measure the lifetime as follows. Since it is assumed that the velocity distribution of the two-component beam is known, the intensity of the beam is written as an integral over all velocities:

$$I(x) = C \int_0^{\infty} v^n \cdot e^{-mv^2/2kT} \cdot (N_1 \cdot e^{-x/v\tau} + N_2) dv \quad (2.2)$$

The constant  $C$  with any number of primes is a normalization constant.

It is convenient to express the velocity and

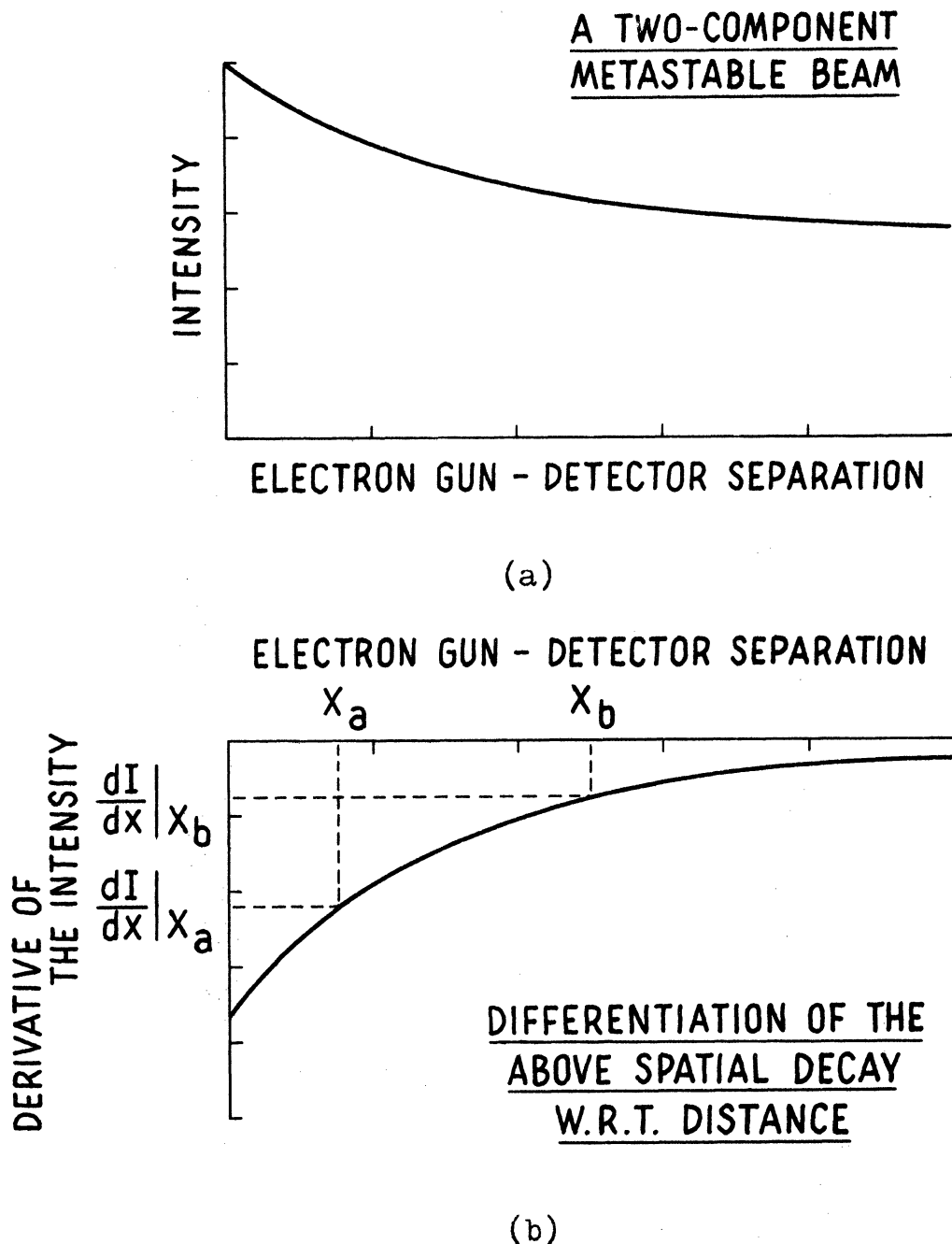


Figure 2.1

- (a) Spatial decay of a two-component metastable beam. One component has a very long lifetime.
- (b) Differentiation of the two-component decay with respect to distance. This differentiation eliminates the long-lived component since its intensity is not a function of distance. The lifetime of the short-lived component is found from the ratio of the derivatives of the intensity at two points  $x_a$  and  $x_b$ .

distance using variables

$$u = v \sqrt{\frac{m}{2kT}} \quad W = \frac{x}{\tau} \sqrt{\frac{m}{2kT}} \quad (2.3)$$

Then equation 2.2 is

$$I(x) = C' \int_0^{\infty} u^n \cdot e^{-u^2} \cdot (N1 \cdot e^{-W/u} + N2) du \quad (2.4)$$

Take the derivative of equation 2.4 with respect to  $x$  to eliminate the long-lived component. Remember that  $W$  is a function of  $x$ .

$$\frac{dI}{dx} = - \frac{C \cdot N1}{\tau} \int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot e^{-W/u} du \quad (2.5)$$

Given an  $n$ , the integral in equation 2.5 is a function of  $W$  and may be evaluated numerically.

Now take the ratio of the derivatives at two points  $X_a$  and  $X_b$ :

$$\frac{\frac{dI}{dx} \Big|_{X_a}}{\frac{dI}{dx} \Big|_{X_b}} = \frac{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot e^{-W(X_a)/u} du}{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot e^{-W(X_b)/u} du} \quad (2.6)$$

But equation 2.3 gives

$$W(X_b) = \frac{X_b}{X_a} W(X_a) \quad . \quad (2.7)$$

Substitution of equation 2.7 into equation 2.6 gives

$$\frac{\frac{dI}{dx}|_{X_a}}{\frac{dI}{dx}|_{X_b}} = \frac{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot \exp[-W(X_a)/u] \, du}{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot \exp\left[-\frac{X_b}{X_a} W(X_a)/u\right] \, du} \quad . \quad (2.8)$$

But the left side of equation 2.8 may be replaced by the left side of equation 2.1:

$$G_{\text{expt}} = \frac{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot \exp[-W(X_a)/u] \, du}{\int_0^{\infty} u^{n-1} \cdot e^{-u^2} \cdot \exp\left[-\frac{X_b}{X_a} W(X_a)/u\right] \, du} \quad . \quad (2.9)$$

The left side of equation 2.9 is an experimental number while the right side is a theoretical expression. Since  $n$ ,  $X_a$ , and  $X_b$  are known, the right side of equation 2.9 can be evaluated for various  $W(X_a)$  until the equality is satisfied. Once  $W(X_a)$  is determined, equation 2.3 gives

$$\tau = \frac{X_a \sqrt{m/2kT}}{W(X_a)} \quad . \quad (2.10)$$

Given the two assumptions at the beginning of this section, we now have a method for measuring lifetimes from spatial decay data. This technique is used as follows:

- i) Estimate  $n$  by fitting a non-decaying TOF spectrum with  $v^n \exp(-mv^2/2kT)$ , where  $n$  is varied to give a best fit.
- ii) Take the ratio of the derivatives of the spatial decay at two points  $X_a$  and  $X_b$ , forming  $G_{\text{expt}}$ .
- iii) Use equation 2.9 to find  $W(X_a)$ . This is done by evaluating the right-hand side for various  $W(X_a)$  until the equality is satisfied.
- iv) Once  $W(X_a)$  is found, the lifetime of the short-lived component is given by equation 2.10.

This series of steps is carried out for various  $X_a$  and  $X_b$ , generating a series of values for the lifetime. Since these numbers should all be the same, an average can be taken.

This method of measuring lifetimes will be applied to a computer-simulated metastable beam (section 3.3) and to an experiment on metastable molecular nitrogen (chapter 5).

## 2.2 A Lifetime Measurement from Time-of-Flight Data

It is first necessary to develop a method of scaling time and amplitude so that TOF spectra can be compared on a common set of axes. The principles of this scaling are

conveniently illustrated by a non-decaying beam (argon for example). Figure 2.2a displays non-decaying TOF spectra at 13, 17, and 21 cm.

### 2.2.1 Scaling of the Time Axes

Consider TOF distributions at distances  $X_a$  and  $X_b$ . A group of metastable molecules having a velocity  $V$ , has an amplitude  $F_a(T_a = X_a/V)$  at the distance  $X_a$ . By "amplitude" we mean the number of particles per unit time. This same group has an amplitude  $F_b(T_b = X_b/V = T_a \cdot X_b/X_a)$  at the distance  $X_b$ . If these two TOF distributions are to be displayed on a common time axes so that  $F_a$  and  $F_b$  have the same time coordinate, then the time scale of the second TOF spectrum must be multiplied by  $X_a/X_b$ . Figure 2.2b shows the results of scaling the time axes of the TOF spectra at 17 and 21 cm by multiplying by 13/17 and 13/21, respectively. The TOF spectra still do not overlap because a scaling of the amplitude axes is necessary.

### 2.2.2 Scaling of the Amplitude Axes

Again consider TOF spectra taken at distances  $X_a$  and  $X_b$  (the time axes are not scaled). Consider a group of molecules at  $X_a$  that has times-of-arrival between  $T_a$  and  $T'_a$ . The time spread is  $\Delta T_a = T'_a - T_a$ . Note that this group has velocities between  $V = X_a/T_a$  and  $V' = X_a/T'_a$ . This same group has times-of-arrival at

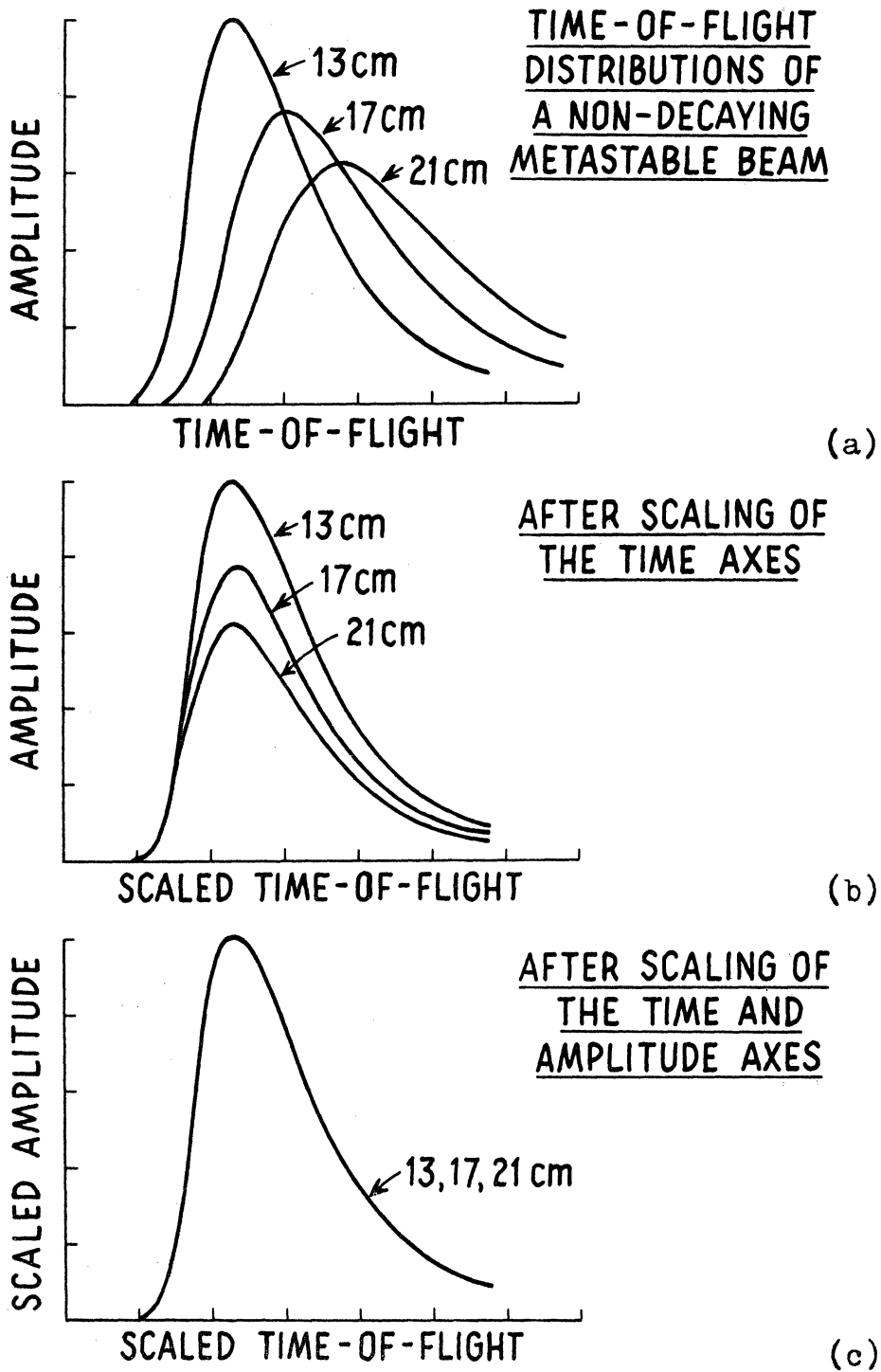


Figure 2.2

Time-of-flight spectra for a non-decaying metastable beam.

- (a) Time-of-flight distributions at three distances.
- (b) The spectra after scaling of the time axes (section 2.2.1).
- (c) The distributions after scaling of the time and amplitude axes (section 2.2.2). The spectra overlap as they should.



$X_b$  of  $T_b = X_b/V = T_a \cdot X_b/X_a$  and  $T'_b = X_b/V' = T'_a \cdot X_b/X_a$ .  
 This group now has a time spread of  $\Delta T_b = T'_b - T_b =$   
 $T'_a \cdot X_b/X_a - T_a \cdot X_b/X_a = \Delta T_a \cdot X_b/X_a$ . Note that the time  
 spreads of this group at the two distances are related  
 as  $\Delta T_a = \Delta T_b \cdot X_a/X_b$ . Since the number of particles  
 does not change from  $X_a$  to  $X_b$  and since the time spread  
 does increase at  $X_b$ , the amplitude (number of particles  
 per unit time) must decrease. It must decrease by the  
 ratio of the distances. If these two TOF spectra are to  
 be displayed on a common amplitude axis so that this  
 spreading of the particles is corrected, the amplitude  
 scale of the second TOF spectrum must be multiplied by  
 $X_b/X_a$ . Figure 2.2c shows the results of scaling the  
 amplitude axes (the time axes are also scaled) of the  
 TOF spectra at 17 and 21 cm by multiplying by 17/13 and  
 21/13, respectively. The three TOF distributions now  
 overlap, as they should.

### 2.2.3 Measurement of the Lifetime

Only one assumption is needed to obtain lifetimes  
 of metastable states from time-of-flight data: the  
 beam consists of only two metastable states, with one  
 state having a very long lifetime.

The description of the two-component metastable  
 beam requires the knowledge of three unknowns: the  
 initial populations of the long-lived state ( $N_2$ ), the  
 initial population of the short-lived state ( $N_1$ ), and

the lifetime of the short-lived state ( $\tau$ ). Since there are three unknowns, three equations are needed if a solution is to be found. These three equations may be derived from three TOF distributions as measured at different electron gun-detector separations (distances).

Figure 2.3a shows TOF spectra for a two-component metastable beam at the distances

$$X_a, X_b = X_a + \Delta X, \text{ and } X_c = X_a + 2 \cdot \Delta X \quad . \quad (2.11)$$

Figure 2.3b shows the same spectra after time and amplitude scaling. How does this change in shape of TOF spectra relate to the decay of the short-lived metastable state?

Construct a perpendicular line on the scaled time axis at  $T'$  (dotted line in figure 2.3b). The intersections of this line with the three TOF distributions gives the amplitudes of a group of molecules having a velocity  $V = X_a/T'$  at the distances  $X_a$ ,  $X_b$ , and  $X_c$ . Label the coordinates of the intersections  $(F'_a, T')$ ,  $(F'_b, T')$ , and  $(F'_c, T')$ . The prime denotes a scaled quantity. Since we assume a two-component beam, the initial populations are designated  $N_1(V)$  and  $N_2(V)$ , with  $N_2$  having the infinite lifetime. This dependence of the initial populations on  $V$  is simply the distribution of velocities. The amplitudes of this group of metastable molecules

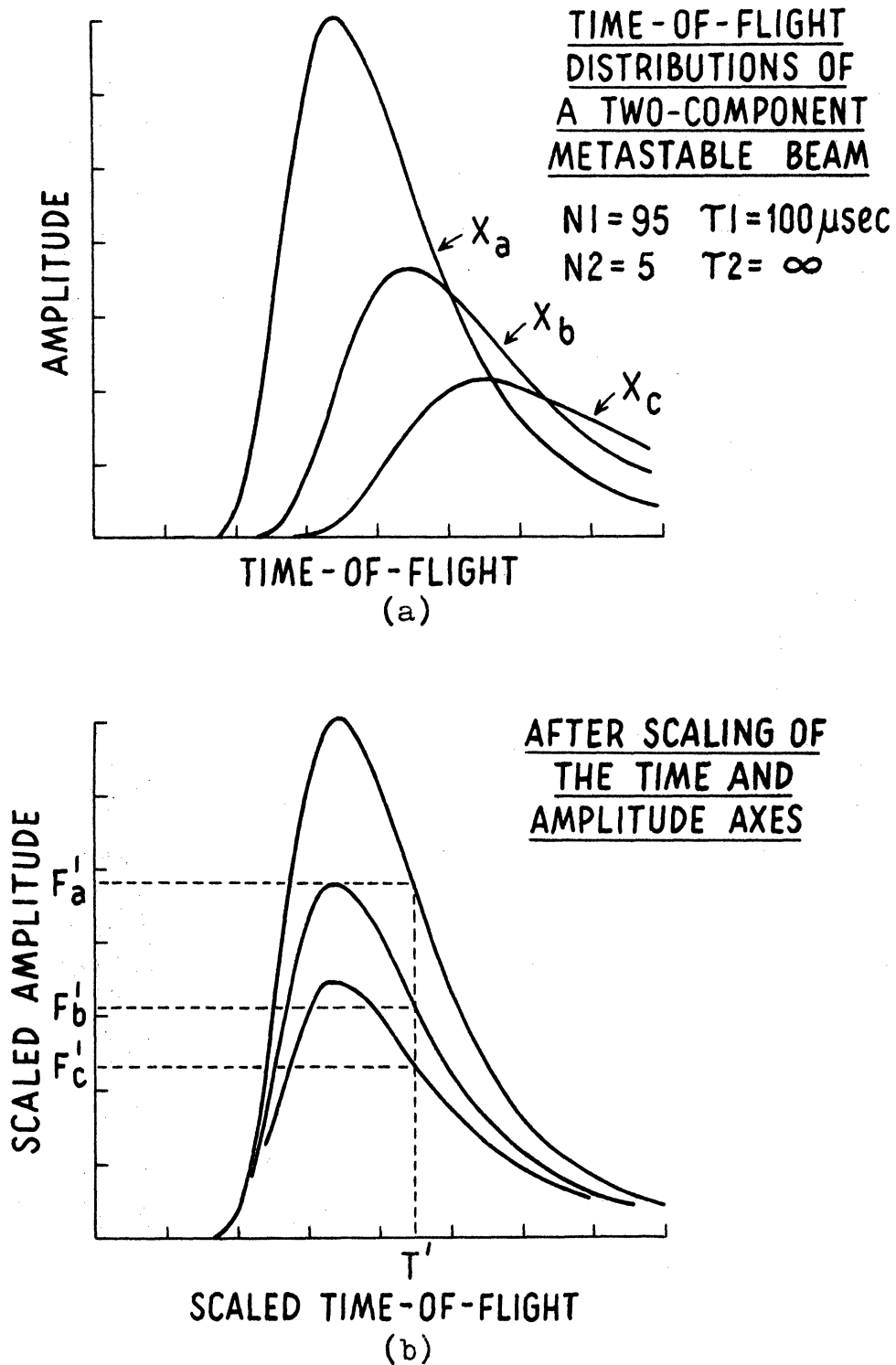


Figure 2.3

Time-of-flight distributions for a two-component metastable beam ( $N_1=95$ ,  $N_2=5$ ,  $\tau_1=100\text{ usec}$ , and  $\tau_2=\infty$ ).

- (a) Time-of-flight spectra at three distances.
- (b) The distributions after scaling of the time and amplitude axes (sections 2.2.1 and 2.2.2). The lifetime of the short-lived state is found from the three amplitudes  $F'_a$ ,  $F'_b$ , and  $F'_c$ , at the time  $T'$ .

at the three points are written as

$$F'_a = N1(V) \cdot e^{-X_a/V \cdot \tau} + N2(V) \quad V = X_a/T' \quad (2.12)$$

$$F'_b = N1(V) \cdot e^{-X_b/V \cdot \tau} + N2(V) \quad (2.13)$$

$$F'_c = N1(V) \cdot e^{-X_c/V \cdot \tau} + N2(V) \quad (2.14)$$

Since this theory should apply directly to experimental data, equations 2.12, 2.13, and 2.14 are written in terms of unscaled time and amplitude as

$$F_a(T_a) = N1 \cdot e^{-T_a/\tau} + N2 \quad T_a = X_a/V \quad (2.15)$$

$$(X_b/X_a) \cdot F_b(T_b) = N1 \cdot e^{-T_b/\tau} + N2 \quad T_b = X_b/V \quad (2.16)$$

$$(X_c/X_a) \cdot F_c(T_c) = N1 \cdot e^{-T_c/\tau} + N2 \quad T_c = X_c/V \quad (2.17)$$

Equation 2.11 implies

$$T_b = T_a + \Delta T, \quad T_c = T_b + \Delta T, \quad \text{and} \quad \Delta T = \Delta X/V \quad (2.18)$$

Subtracting pairs of equations to eliminate N2 and substituting from equation 2.18, equations 2.15, 2.16, and 2.17 become

$$F_a(T_a) - \frac{X_b}{X_a} F_b(T_b) = Nl \cdot e^{-T_a/\tau} \cdot (1 - e^{-\Delta T/\tau}) \quad (2.19)$$

$$\frac{X_b}{X_a} F_b(T_b) - \frac{X_c}{X_a} F_c(T_c) = Nl \cdot e^{-T_b/\tau} \cdot (1 - e^{-\Delta T/\tau}) \quad (2.20)$$

Now divide equation 2.19 by equation 2.20 to eliminate  $Nl$  and solve for the lifetime:

$$\tau = \frac{T_b - T_a}{\ln \left[ \frac{F_a(T_a) - (X_b/X_a) \cdot F_b(T_b)}{(X_b/X_a) \cdot F_b(T_b) - (X_c/X_a) \cdot F_c(T_c)} \right]} \quad (2.21)$$

Equation 2.21 is written in terms of scaled quantities as

$$\tau = \frac{T' \cdot (X_b/X_a - 1)}{\ln \left[ \frac{F'_a(T') - F'_b(T')}{F'_b(T') - F'_c(T')} \right]} \quad (2.22)$$

Given the one assumption at the beginning of this section, we now have a method for measuring lifetimes from TOF data. This technique is used as follows:

- i) Take TOF distributions at three distances  $X_a$ ,  $X_b = X_a + \Delta X$ , and  $X_c = X_a + 2\Delta X$ .
- ii) Time and amplitude scale these spectra.

- iii) Pick a scaled time  $T'$  and find the corresponding amplitudes  $F'_a$ ,  $F'_b$ , and  $F'_c$ .
- iv) Then the lifetime of the short-lived component is given by equation 2.22.

This series of steps is carried out for various  $T'$ , generating a series of values for the lifetime. Since these numbers should all be the same, an average can be taken.

Note that equation 2.22 does not require a knowledge of the initial populations or their velocity distributions.

This method of measuring lifetimes will be applied to a computer-simulated metastable beam (section 3.4) and to an experiment on metastable molecular nitrogen (chapter 5).

### 2.3 An Alternate Method for Measuring a Lifetime from Time-of-Flight Data

The theory of the previous section applies only to a two-component metastable beam. The following theory may be applied to a three-component beam.

Suppose the first component has an initial population  $N_1(V)$  and a lifetime  $\tau_1$ , the second component has an initial population  $N_2(V)$  and a lifetime  $\tau_2$ , and the third component has an initial population  $N_3(V)$  and an infinite lifetime. It is assumed that the initial

populations have the same velocity distributions; the relative populations  $N_1/N_3$  and  $N_2/N_3$  are velocity independent.

If the appearance potentials of the three states are such that just  $N_1$  and  $N_3$  are excited with low voltage electrons then the TOF theory for a two-component beam (section 2.2) gives the lifetime  $\tau_1$ . Now increase the energy of the electrons until all three states are excited. We now have four unknowns:  $N_1$ ,  $N_2$ ,  $N_3$ , and  $\tau_2$  ( $\tau_1$  has just been measured). By using TOF spectra at four distances, the theory of section 2.2 may be generalized to measure  $\tau_2$  (appendix A).

However, the range of detector movement may not permit TOF data to be taken with sufficient separation for the spectra to be distinct and allow unambiguous measurements. Or it may not be possible to separately excite the metastable states. It is, therefore, desirable to have a second method for calculating lifetimes from TOF data.

Suppose TOF spectra are taken at distances  $X_a$  and  $X_b$ , and time and amplitude scaled. It should be possible to use the spectrum at  $X_a$  and calculate the spectrum at  $X_b$ , using assumed population ratios and lifetimes. Then if the experimental and calculated distributions compare favorably, the assumed population ratios and lifetimes are correct.

As in the previous sections, we examine a group of

molecules that has a velocity  $V$ . At the distance  $X_a$ , this group has a time-of-flight  $T_a = X_a/V$  and an amplitude (number of particles per unit time)  $F_a(T_a)$ .

The amplitude is written as

$$F_a(T_a) = N1(V) \cdot e^{-T_a/\tau 1} + N2(V) e^{-T_a/\tau 2} + N3(V). \quad (2.23)$$

Since the relative population ratios are assumed to be known from other considerations, divide equation 2.23 by  $N3(V)$ :

$$\frac{F_a(T_a)}{N3(V)} = \frac{N1(V)}{N3(V)} e^{-T_a/\tau 1} + \frac{N2(V)}{N3(V)} e^{-T_a/\tau 2} + 1. \quad (2.24)$$

Equation 2.24 is solved for

$$N3(V) = \frac{F_a(T_a)}{(N1/N3) \cdot e^{-T_a/\tau 1} + (N2/N3) \cdot e^{-T_a/\tau 2} + 1}; \quad (2.25)$$

The right-hand side of equation 2.25 contains only known quantities:  $F_a(T_a)$  (experimental data),  $N1/N3$ ,  $N2/N3$ ,  $\tau 1$ , and  $\tau 2$ . The left-hand side of equation 2.25 is the initial population of molecules in the long-lived state having a velocity  $V$ . The initial populations of the other two states are found from equation 2.25 and the assumed relative population ratios:



$$N1(V) = (N1/N3) \cdot N3(V) \quad (2.26)$$

$$N2(V) = (N2/N3) \cdot N3(V) \quad (2.27)$$

Equations 2.25, 2.26, and 2.27 give the initial populations of molecules having a velocity V.

At  $X_b$ , this same group of molecules has a time-of-arrival of  $T_b = X_b/V$ . Since the time-of-flight, the initial populations, and the lifetimes are known, the amplitude at  $X_b$  is found from

$$F_b^P(T_b) = N1(V) \cdot e^{-T_b/\tau_1} + N2(V) \cdot e^{-T_b/\tau_2} + N3(V) \cdot (2.28)$$

The superscript p denotes  $F_b(T_b)$  to be a predicted amplitude. The predicted amplitude can be compared with the experimental amplitude, and if the two compare favorably, the assumed population ratios and lifetimes are correct.

As an example,  $\tau_1$  might be known from a previous measurement and  $N1/N3$  and  $N2/N3$  could be estimated from cross-section measurements. Then various values of  $\tau_2$  are assumed and the TOF spectra at  $X_a$  are used to predict the spectra at  $X_b$  (using the above theory). By comparing the predicted and experimental spectra, the best value of  $\tau_2$  is picked.

## CHAPTER 3

### COMPUTER PROGRAMS AND SIMULATED BEAMS

#### 3.1 Generation of the Simulated Beams

The preceding analysis of the spatial decay and TOF data is best performed by a computer. The computer programs and the analysis are tested by generating a set of simulated data (spatial decay and TOF data) with assumed populations and lifetimes. Then this set of simulated data is treated as "real data" and analyzed by the computer. The computer routines should return the assumed lifetimes.

The simulated data are generated with the following assumptions:

- i) The metastable beam has two components. One state has an initial population  $N_1$  and a lifetime  $\tau$ . The other state has an initial population  $N_2$  and an infinite lifetime.
- ii) The velocity distribution of metastable molecules is given by the function  $v^3 \exp(-mv^2/2kT)$ .  $k$  is Boltzmann's constant,  $m$  is the molecular weight of molecular nitrogen, and the temperature  $T$  is taken as 300 K.

The simulated spatial decay [intensity ( $I$ ) versus

distance (x)] and TOF data [amplitude (F) versus time-of-flight (t) at a distance (x)] are generated with the following functions:

$$i) \quad I(x) = \int_0^{\infty} v^3 e^{-mv^2/2kT} (N_1 \cdot e^{-x/v\tau} + N_2) dv \quad .$$

$$ii) \quad F(t) = \frac{x^4}{t^5} e^{-mv^2/2kT} (N_1 \cdot e^{-t/\tau} + N_2) \quad .$$

These functions are calculated as follows:

- i) Assume  $N_1 = 90\%$ ,  $N_2 = 10\%$ , and  $\tau = 100$  usec.
- ii) Evaluate the spatial decay function from  $x = 13$  cm to  $x = 27$  cm in 0.2 cm intervals.
- ii) Evaluate the TOF function from  $t = 50$  usec to  $t = 500$  usec in 10 usec intervals, at the distances  $x = 13, 17,$  and  $21$  cm.

It should now be possible to analyze these computer-simulated metastable beams and retrieve the assumed lifetime of 100 usec.

### 3.2 Computer Programs

All the computer programs contain a subroutine that fits the data with a least squares curve. The fitting technique is detailed in Mathews and Walker (1965) and is based on a computer program written by Mr. George Schofield of this laboratory.

The spatial decay intensity is fitted with the function:

$$c_0 + c_1 \cdot (x-13) + \dots + c_4 \cdot (x-13)^4 \quad (3.1)$$

where 13 cm is the distance of closest approach.

The natural logarithm of the TOF amplitude is fitted with the function:

$$c_0 + c_1 \cdot \ln \frac{X}{t} + c_3 \cdot \frac{X}{t} + c_4 \cdot t \quad [t \text{ is in usec}] \quad (3.2)$$

The coefficients  $c_i$  are computed by the least squares subroutine and the fitted curves are returned to the main program for the lifetime calculation. These two functions are sufficiently general so that they do not bias the data.

The spatial decay program uses the theory of section 2.1. The data are fitted with a least squares curve and the slope is found at distances  $X_a$  and  $X_b (=R \cdot X_a)$ . Then equations 2.1 and 2.9 are used to find  $W(X_a)$ , with equation 2.10 giving the lifetime. A series of lifetime values is calculated by fixing  $X_a$  and incrementing  $R$ , or fixing  $R$  and incrementing  $X_a$ .

The TOF program uses the theory of section 2.2. TOF distributions at three distances are time and amplitude scaled and fitted with a least squares curve. A time  $T'$  is picked and equation 2.22 gives the lifetime.  $T'$  is incremented between two limits, generating a series of values for the lifetime.

### 3.3 Analysis of the Simulated Spatial Decay Data

The data points in figure 3.1a are the spatial decay

SPATIAL DECAY OF  
A TWO-COMPONENT  
METASTABLE BEAM

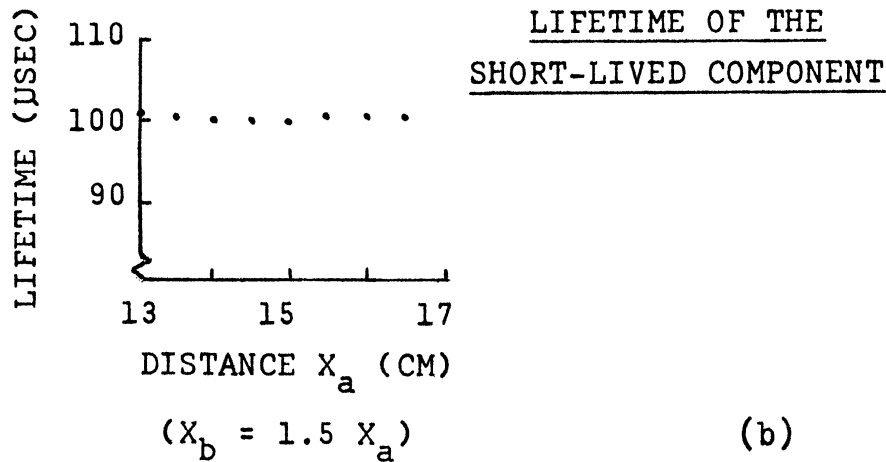
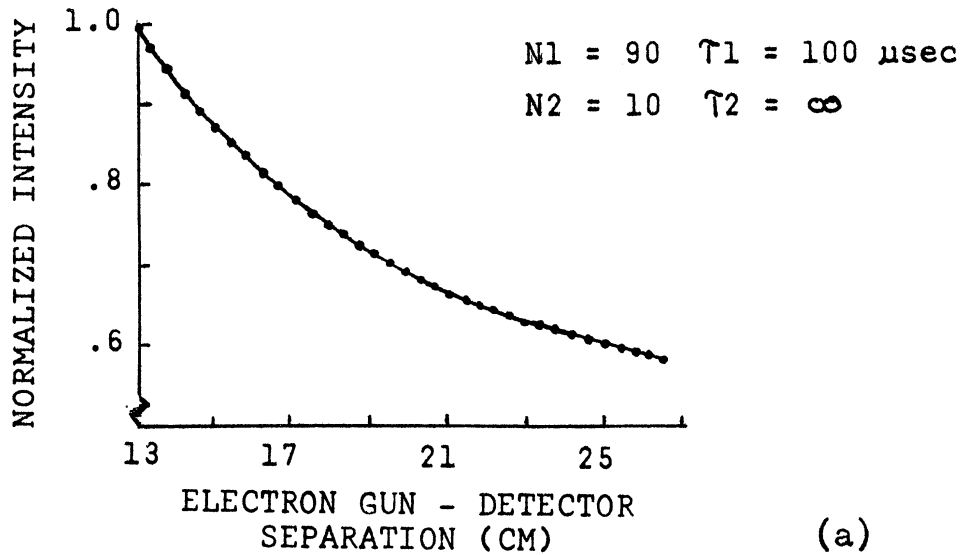


Figure 3.1

Spatial decay for a two-component, computer-simulated metastable beam ( $N_1=90$ ,  $\tau_1=100 \text{ } \mu\text{sec}$ , and  $\tau_2=\infty$ ).

- (a) A least squares fit (solid curve) to the spatial decay (data points).
- (b) The lifetime of the short-lived component as found from the spatial decay. The lifetime is found from the derivative of the intensity at two points  $X_a$  and  $X_b$  ( $=R \cdot X_a$ ).

generated according to section 3.1. The solid curve is the least squares fit using function 3.1. Since the simulated data is assumed to have a velocity distribution  $v^3 \exp(-mv^2/2kT)$ , the data is analyzed with  $n = 3$ . Figure 3.1b shows the results of analyzing this simulated data with the theory of section 2.1. As expected,  $\tau = 100$   $\mu\text{sec}$  with only a small scatter ( $\pm 1$   $\mu\text{sec}$ ) in values.

Since the value of  $n$  in a real experiment is generally not known with any certainty, the simulated spatial decay data are analyzed allowing  $n$  to assume values of 2.50, 2.75, 3.00, 3.25, and 3.50. Figure 3.2 shows that the value used for  $n$  is not very critical: a 17% error in  $n$  results in only a 5% error in the lifetime.

#### 3.4 Analysis of the Simulated Time-of-Flight Data

The data points in figure 3.3a are the three TOF spectra (after time and amplitude scaling) generated according to section 3.1. The solid curve is the least square fit using function 3.2. Figure 3.3b shows the results of analyzing this simulated data with the theory of section 2.2. As expected,  $\tau = 100$   $\mu\text{sec}$ , with only a small scatter ( $\pm 2$   $\mu\text{sec}$ ) in values.

The slight oscillatory behavior of the lifetime values is a result of the least squares fit to the data. If the form of the fitting function is changed, the oscillations change. However, the average lifetime is always  $(100 \pm 2)$   $\mu\text{sec}$ , regardless of the particular form of the fitting function.

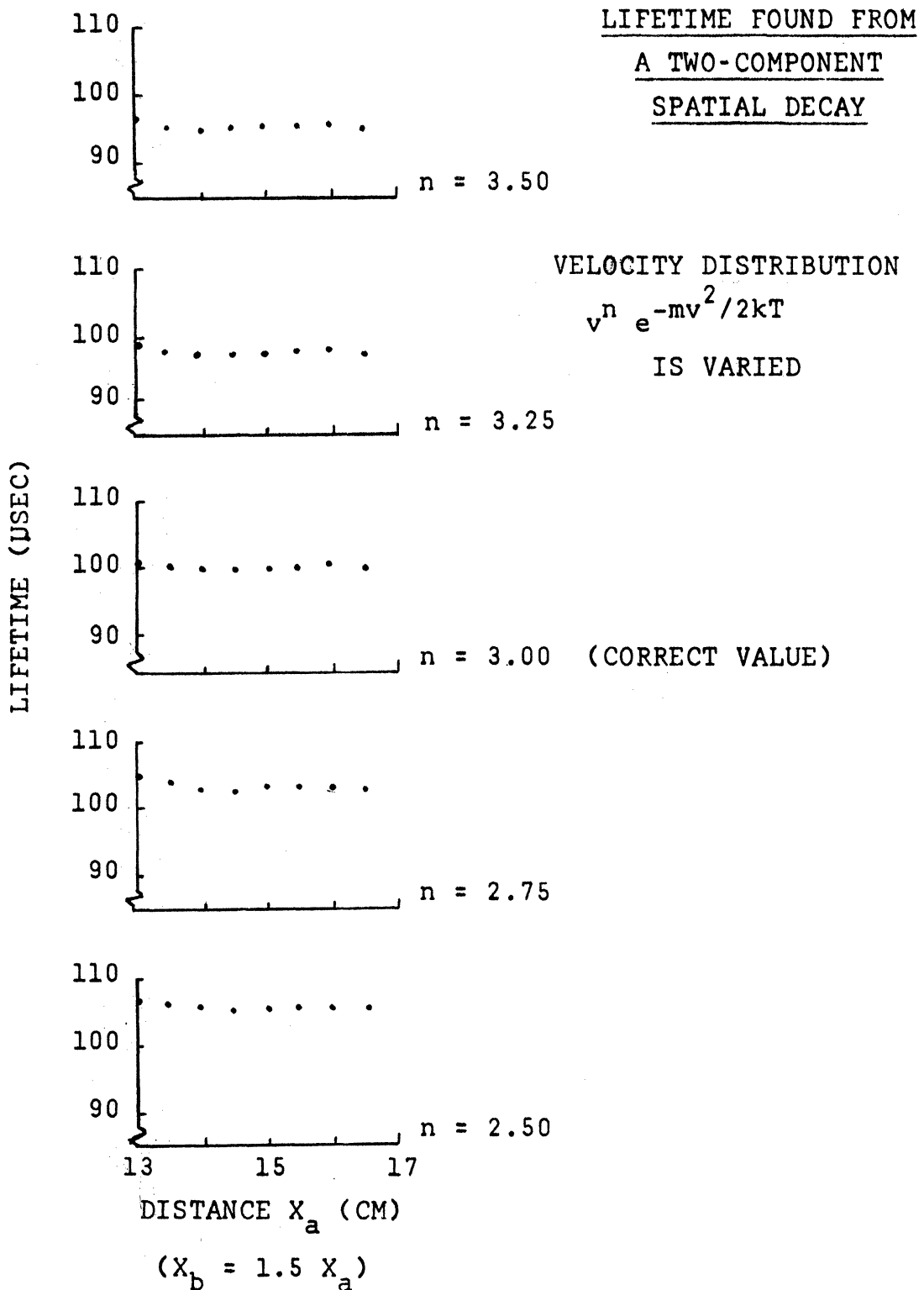


Figure 3.2

Dependence of the spatial decay lifetime calculation on the value of  $n$ , where  $v^n \exp(-mv^2/2kT)$  is the velocity distribution. The correct value of  $n$  is 3.0 for the two component, simulated spatial decay. A 17% error in  $n$  results in only a 5% error in the lifetime.

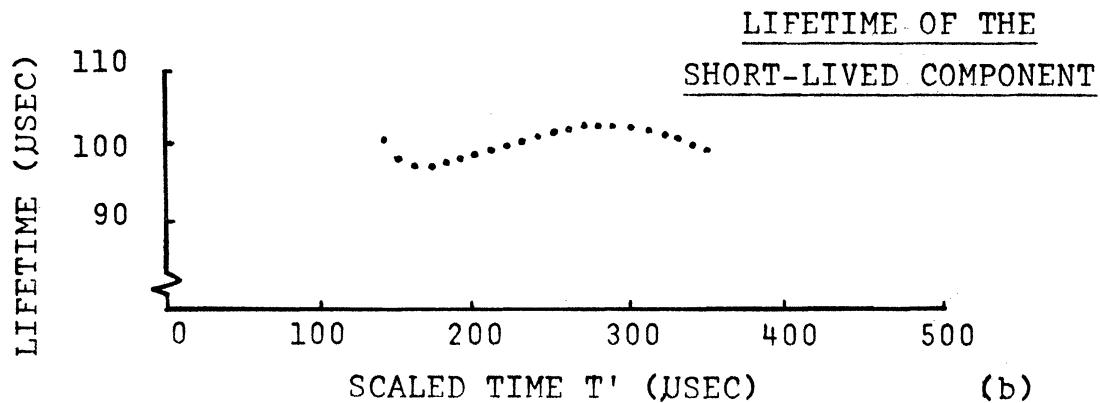
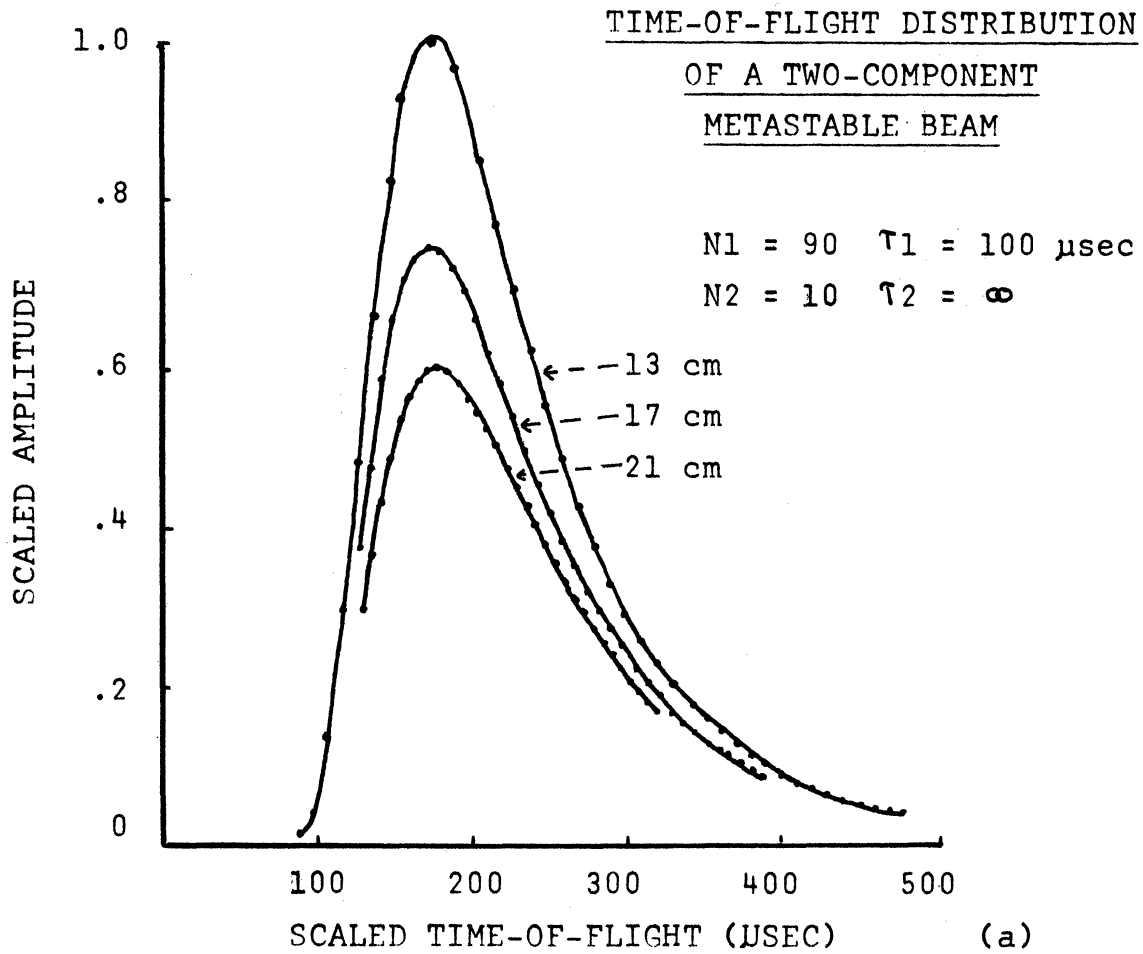


Figure 3.3

Time-of-flight spectra for a two-component, computer-simulated metastable beam ( $N_1=90$ ,  $N_2=10$ ,  $\tau_1=100 \mu\text{sec}$ , and  $\tau_2=\infty$ ).

- (a) A least squares fit (solid curve) to the time and amplitude scaled distributions (data points).
- (b) The lifetime of the short-lived component as found from the above spectra. The lifetime is found at a time  $T'$  from the corresponding amplitudes of the three spectra.



## CHAPTER 4

### EXPERIMENT

#### 4.1 Apparatus

Figure 4.1 is a schematic of the experimental apparatus. The vacuum chamber is divided by a bulkhead into a source chamber and a detector chamber. Each section contains a cold trap and is evacuated by an oil diffusion pump equipped with a baffle to prevent backstreaming of pump oil. The diffusion pumps exhaust into a common foreline that is backed by a rotary forepump. Pressures in each section are monitored by ionization gauges. Base pressures, with liquid nitrogen in the cold traps, are approximately  $1 \times 10^{-7}$  torr. Operating pressures in the source chamber are typically in the  $10^{-6}$  torr range.

The gas to be studied is emitted into the source chamber through a long copper pipe. The gas reservoir is a balloon. The gas flow of about .1 micron-liter/sec is controlled by a Nupro very fine needle valve.

The electron gun has four elements: an indirectly heated cathode, two accelerating grids, and an enclosed anode. At an anode-cathode potential difference of +30 volts, the anode typically draws 100  $\mu$ amps. The electron energy spread is estimated to be (section 4.2)  $\pm 1$  eV.

EXPERIMENTAL  
APPARATUS

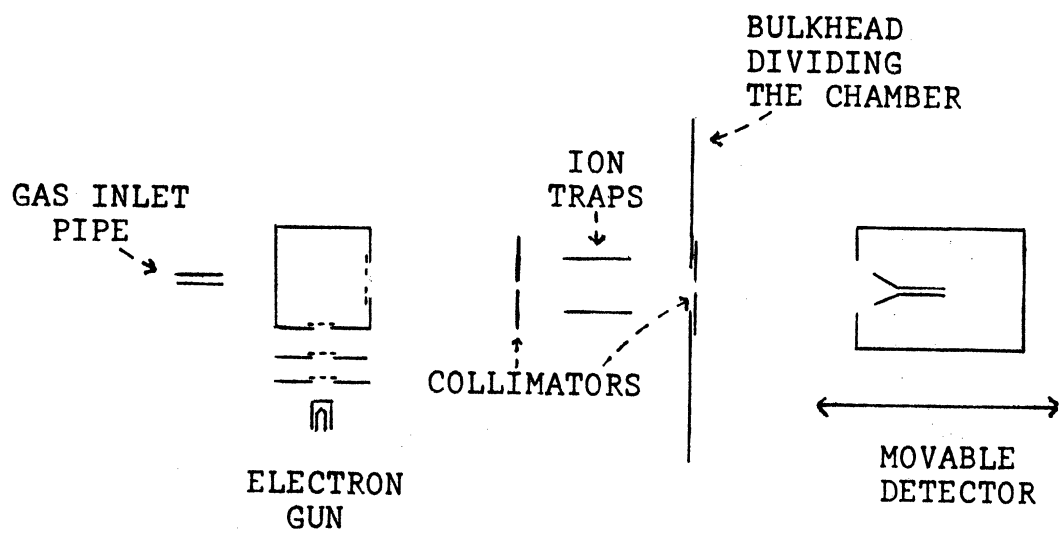


Figure 4.1  
Experimental Apparatus

An electromagnet of approximately 100 gauss is used to focus the electron beam and to confine charged particles to the interaction region.

The collimators are holes approximately 1 mm in diameter, in a .003 inch thick metal plate. The charged particle traps are two metal plates approximately 2 cm apart. These plates are typically biased at  $\pm 100$  volts.

The detector is a Bendix "Channeltron" continuous dynode electron multiplier (Donnelly et al., 1969). Upon striking the detector surface, ultraviolet photons and metastable molecules eject electrons (with an efficiency of a few percent) by the photoelectric and Auger process, respectively. These electrons are cascaded by the continuous dynode structure into a detector pulse. The detector is enclosed in an aluminum box to reduce the background counts, and is mounted on a movable carriage that translates along the beam axis. The detector has a range of movement of approximately 17 cm and has a distance of closest approach to the electron gun of 12.7 cm.

As outlined in chapter 1, this apparatus may be used to observe spatial decay of TOF spectra.

The time-to-height conversion takes place as follows. When the pulse generator supplies a voltage pulse to the anode it also initiates a linear voltage ramp. The detector pulses, generated by the metastable molecules created during the electron gun pulse, are passed through

a preamplifier, an amplifier, and to the input of a linear gate. This linear gate is operated in a coincidence mode with the linear ramp. Thus, the output of the linear gate is a series of pulses, with the height of each pulse being proportional to the transit time of the metastable molecules. These pulses are sorted according to height and stored by the multichannel analyzer.

The distance-to-height conversion follows the same series of steps as the time-to-height conversion, except that the electron gun is in a DC mode and the linear ramp is generated by a battery and a multi-turn potentiometer connected to the detector drive.

#### 4.2 Excitation Functions

The techniques presented in sections 2.2 and 2.3 for measuring lifetimes assume a two-component metastable beam, with one component having a very long lifetime. The  $A^3\Sigma$  and  $a^1\Pi$  states of  $N_2$  satisfy these criteria with the  $A^3\Sigma$  having a lifetime on the order of seconds (Shemansky, 1969a). Before a lifetime measurement can be made, it must be determined that these two states can be excited while the  $E^3\Sigma$  state is excluded. The excitation function measurements described below confirm that the  $E^3\Sigma$  state is not excited if the energy of the electrons is below 12.0 eV.

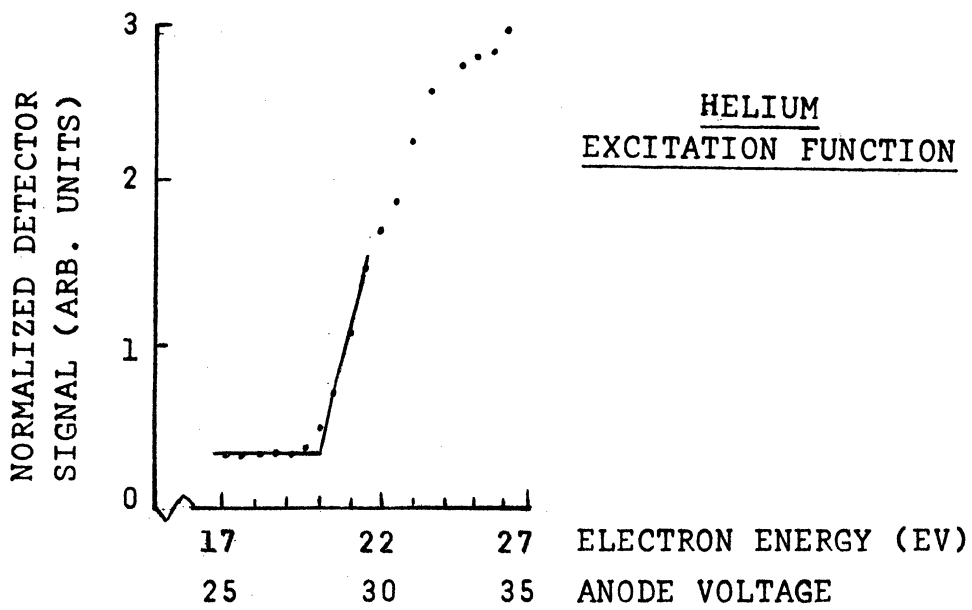
The anode voltage of the electron gun is calibrated using the known appearance potentials for the metastable

states of He and Ar. Figures 4.2a and 4.2b show the plots of normalized detector signal versus anode voltage (the excitation function) for He and Ar (since the anode current increased with the anode voltage, the detector signal is normalized by dividing with the anode current). It is seen from the excitation functions that the initial increase in normalized signal has a portion that is linear with anode voltage. The extrapolation of this linear portion back to the zero or background level gives the appearance potential of the state that is being excited.

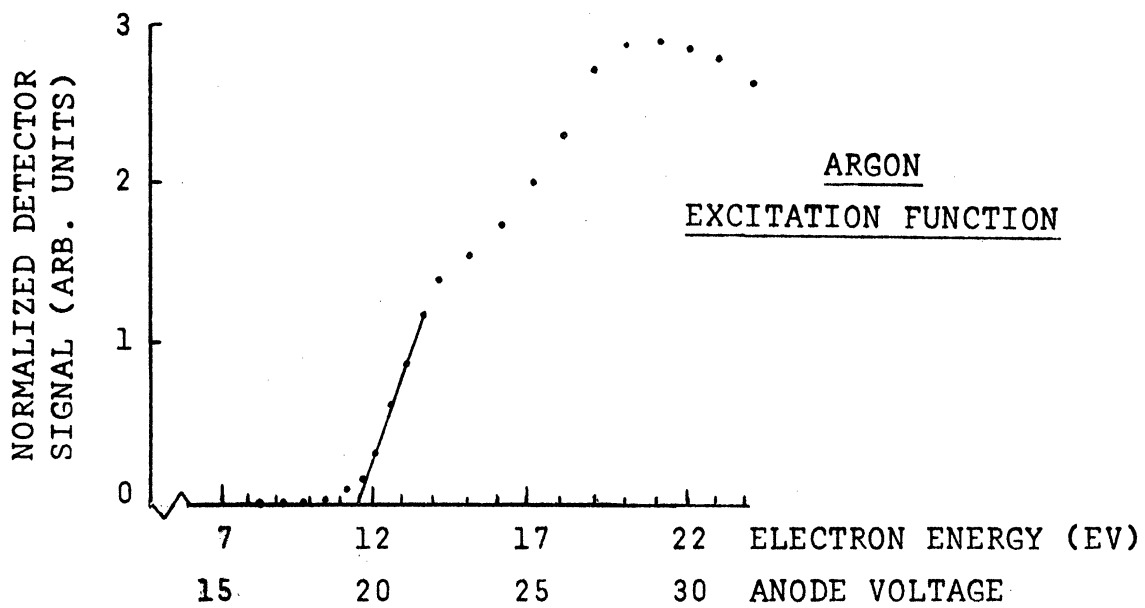
Figure 4.2a and 4.2b show that the He appearance potentials (known to be 19.82 eV) is measured to be 28.0 eV, while the Ar appearance potential (known to be 11.55 eV) is measured to be 19.5 eV. The discrepancy of approximately 8 eV is not fully understood, but it is not unusual when compared to the results of other workers in this laboratory. Since this 8 eV discrepancy was measured on a number of occasions, it is reasonable to assume that the difference between the actual and measured anode voltage is 8 eV for all excitation functions.

The electron energy spread is estimated from the He excitation function (Fox, et al. 1955) to be  $\pm 1$  eV.

Figure 4.3a is an energy level diagram for  $N_2$  showing the lower lying states, and figure 4.3b is the excitation function measured in this experiment. Freund (1969b) reported that the metastable excitation function is mainly due to the  $A^3\Sigma$ ,  $a^1\Pi$ , and  $E^3\Sigma$  states. The small peak at 6 eV



(a)



(b)

Figure 4.2

## Excitation Functions

- (a) Helium
- (b) Argon

LOWER ENERGY LEVELS OF N<sub>2</sub>

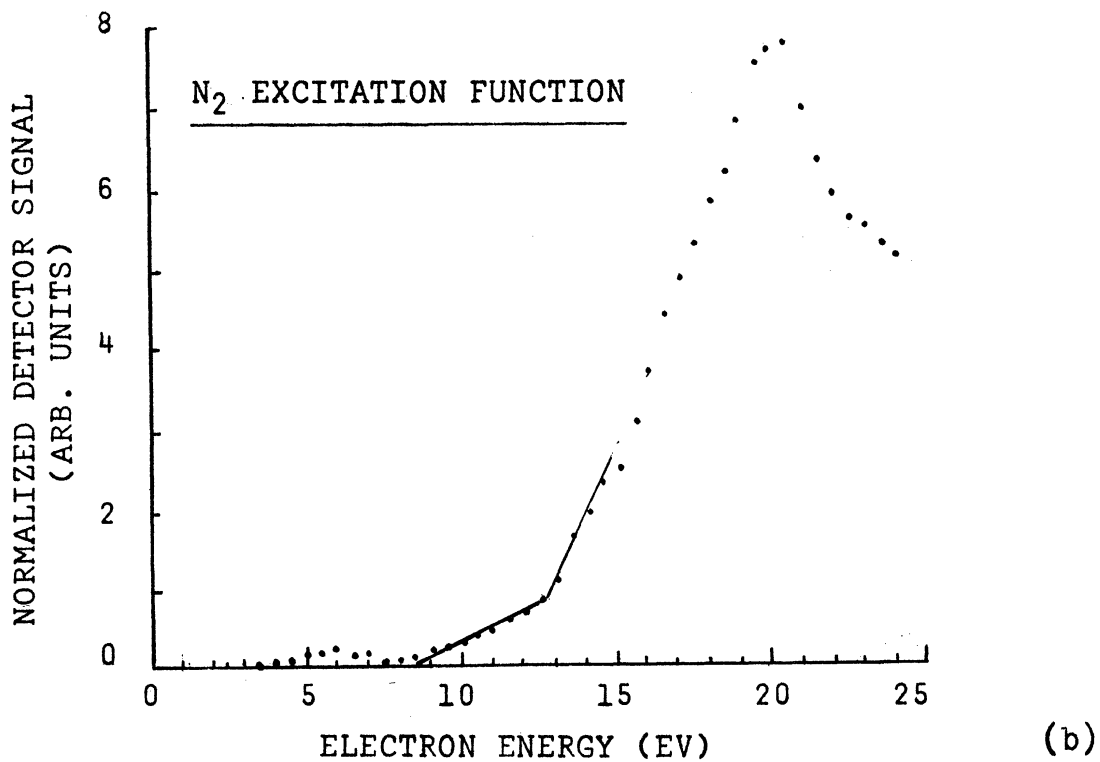
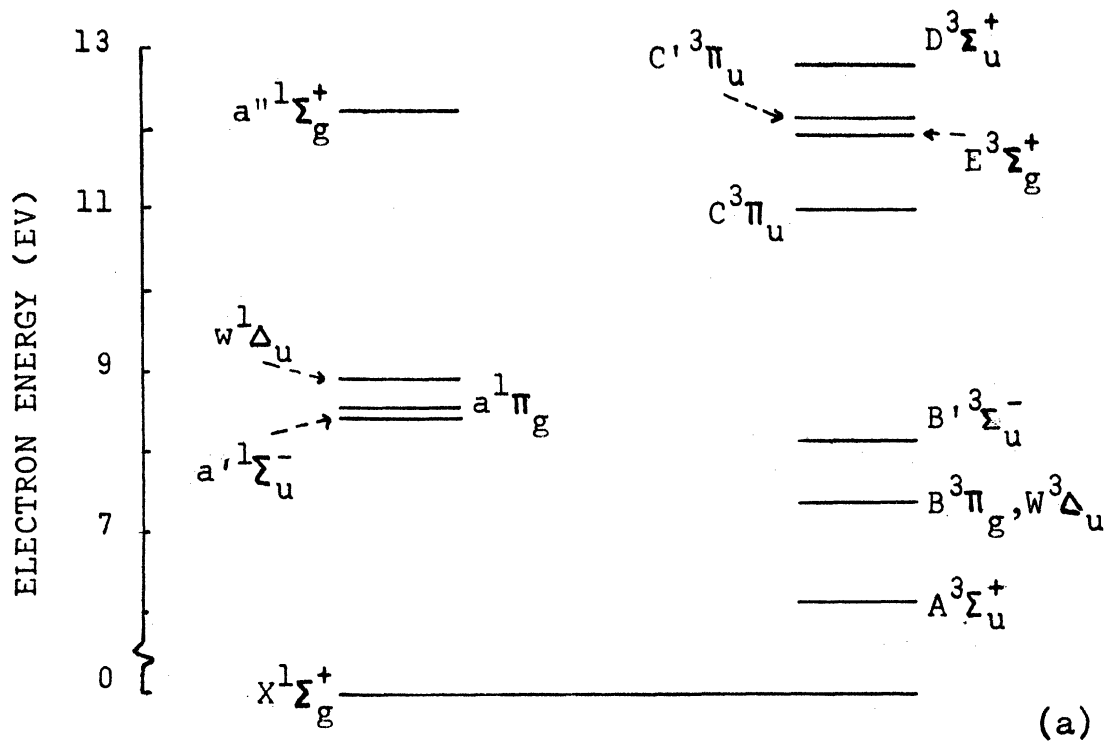


Figure 4.3

- (a) Energy level diagram for N<sub>2</sub> showing lower lying states (after Dressler, 1969).  
 (b) Excitation function for N<sub>2</sub>.

is assigned to the  $A^3\Sigma$  state. The linear rise that gives an 8.5 eV appearance potential is due to the  $a^1\Pi$  state, and the break in the excitation function at 12.5 eV is assigned to the  $E^3\Sigma$  state. Thus, if we are to use a two component beam, the electron energy must be below 12.0 eV.

#### 4.3 Acquisition of Spatial Decay and Time-of-Flight Data

The spatial decay data were taken by connecting the detector drive to a motor and making four passes over the range of interest. The data were checked for drifts of the beam intensity and for binding of the detector drive by requiring that data taken with the same electron energy and source pressure overlapped (when plotted on the same graph).

Ar and  $N_2$  spatial decay data were taken for a variety of voltages and pressures. However, problems with the beam stability and uniformity of the detector drive were severe enough that only 22 eV data were retained for final analysis. Since the superior TOF techniques were developed while the spatial decay measurements were going on, the spatial decay experiment was not carried to completion except for the 22 eV data.

Since the beam intensity should remain constant during a series of TOF measurements, electron gun current and source chamber pressure were monitored. The source pressure always remained constant, but occasionally the electron current would drift. The anode current was not monitored, but the second grid current was recorded at both the beginning and



end of each single TOF distribution acquisition. After a series of these distributions were taken, each spectrum was normalized to correct for any current drift.

As a further check on beam stability, the first and last TOF distributions in a series were taken at the same distance. If these two spectra did not overlap after current normalization, the series was rejected. Only the TOF data taken with 10 and 22 eV electrons survived this test.

The TOF distributions are fitted with a least squares curve before lifetimes are calculated. Figure 4.4 gives examples of fits to data with large and small scatter. These spectra as well as all other spectra used function 3.2 as a fitting function. The remaining TOF distributions are presented only as fitted curves.

#### 4.4 Analysis of the Argon Data

Since the two metastable states of argon ( $^3P_0$  and  $^3P_2$ ) have very long lifetimes (Muschlitz, 1968), they do not decay while travelling from the electron gun to the detector. Thus Ar data is used to i) investigate instrumental effects in spatial decay and TOF data, ii) verify the time and amplitude scaling as outlined in sections 2.2.1 and 2.2.2, and iii) determine the velocity distribution in the absence of any decay.

##### 4.4.1 Spatial Decay

The data in figure 4.5a is Ar spatial decay taken

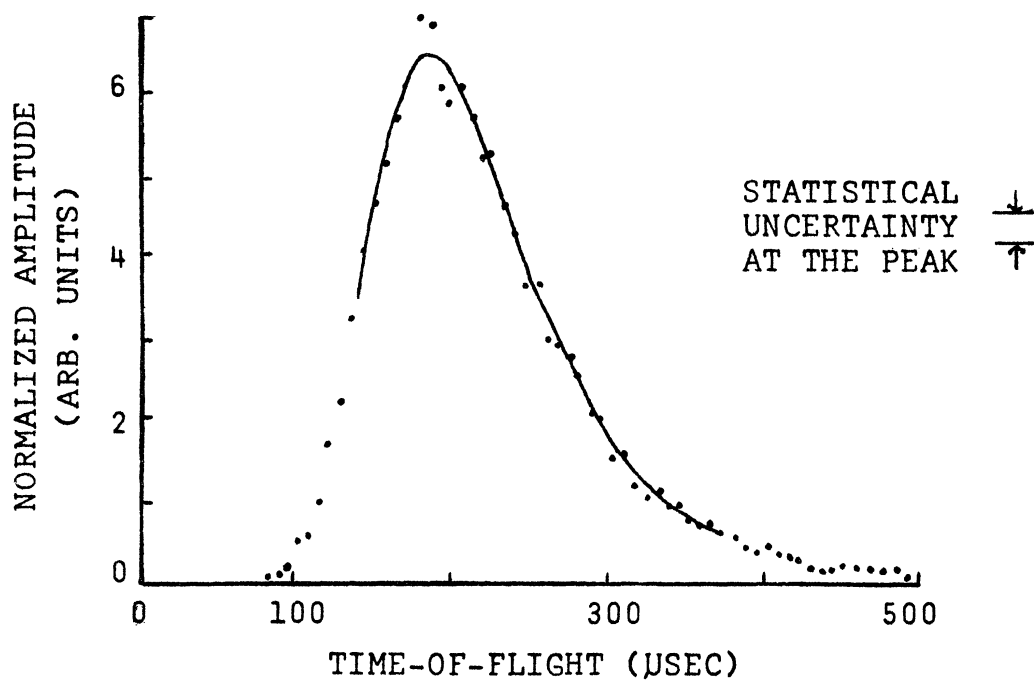
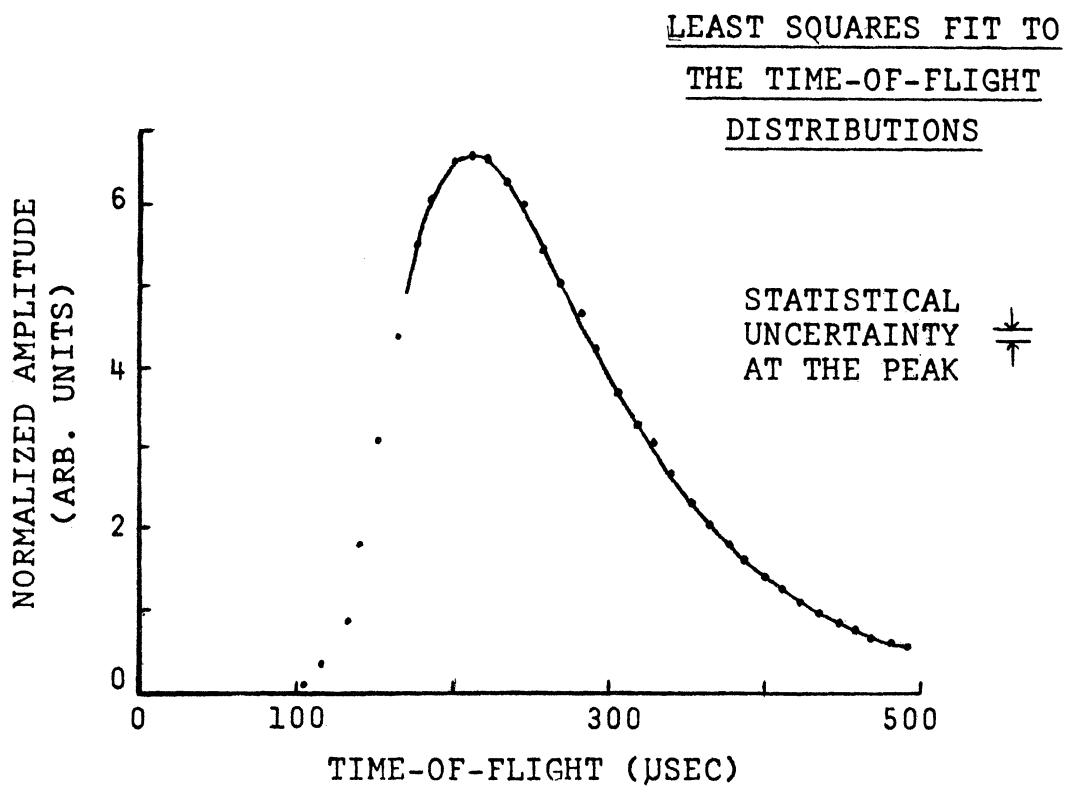


Figure 4.4

Least Squares Fitting to the Time-of-Flight Distributions

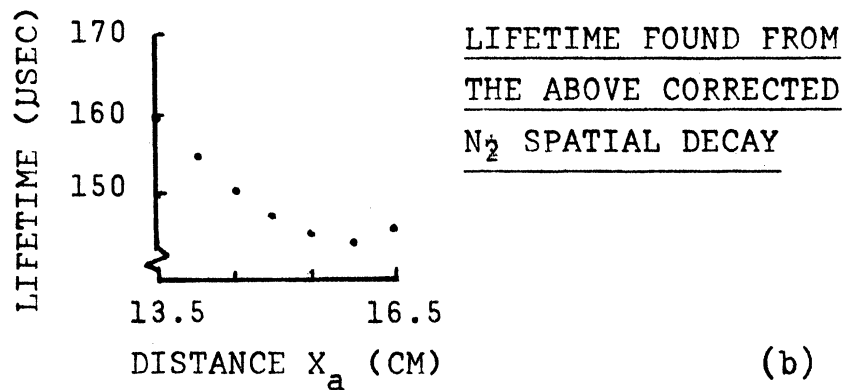
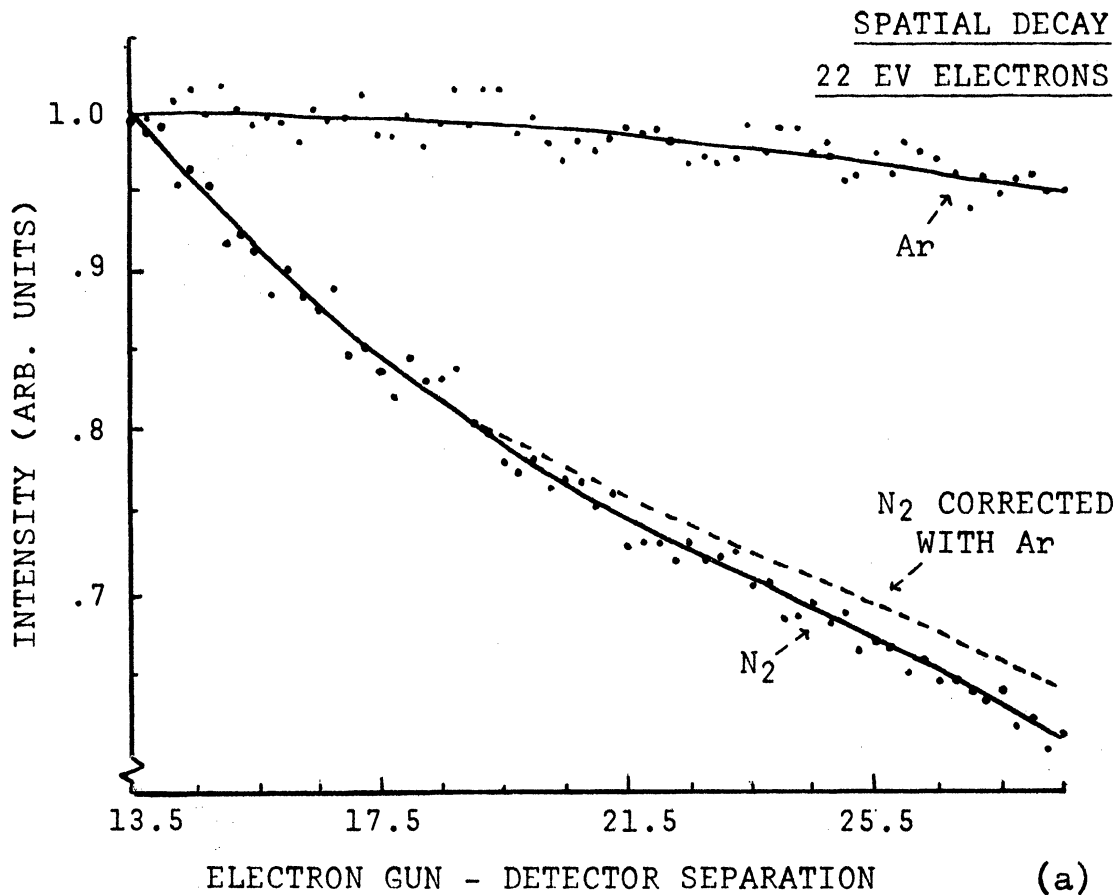


Figure 4.5

Spatial decay taken with 22 eV electrons.

- (a) Ar and N<sub>2</sub> spatial decay (data points) are fitted with a least squares curve (solid line). The Ar fitted curve provides a correction to the N<sub>2</sub> data points (the dashed curve is the least squares fit to the corrected N<sub>2</sub> data).
- (b) The lifetime as calculated (according to technique I) from the corrected N<sub>2</sub> data. The lifetime is found from the derivative of the intensity at two points X<sub>a</sub> and X<sub>b</sub> (=R·X<sub>a</sub>). The lifetime is assigned to a composite of the a<sup>1</sup>π and E<sup>3</sup>Σ states.

with 22 eV electrons. The solid curve is the least squares fit using

$$c_0 + c_1 \cdot (x-13.5) + c_2 \cdot (x-13.5)^2$$

as a fitting function. Only three terms are used so that the scatter in the data is averaged out. Since metastable Ar does not decay, this spatial variation in intensity is due to effects such as atoms scattering out of the beam, geometrical spread of the beam, and spatial dependence of the detector efficiency (due to stray magnetic fields).

The Ar spatial decay provides a correction to the N<sub>2</sub> spatial decay as follows. The Ar data is fitted with the three term fitting function and the percentage change is found at each point along the fitted curve. This percentage change is applied as a correction to the N<sub>2</sub> data. Then the corrected N<sub>2</sub> spatial decay is fitted with a least squares curve. The Ar spatial decay in figure 4.5a is used as the correction for all the N<sub>2</sub> spatial decay data.

Since the electron gun is operated in a DC mode for spatial decay data, this data includes photons as well as metastable molecules. However, these photons contribute only a small percentage to the total signal, and do not present a problem.

#### 4.4.2 Scaling of the Time-of Flight Distributions

Non-decaying TOF distributions taken at different

distances should overlap after time and amplitude scaling. This is found to be true for all the Ar spectra, with the distributions in figure 4.6 being typical. These three TOF spectra overlap to within the statistical uncertainty of the data (defined as plus or minus the square root of the number of counts). Since the Ar spatial decay is fairly constant over the region from 13.5 to 21.5 cm, it is not necessary to provide a correction to the TOF data.

Thus, if  $N_2$  TOF distributions taken at different distances do not overlap after scaling, a decay of the metastable states is observed.

#### 4.4.3 Determination of the Velocity Distribution

The theory of lifetime measurements from spatial decay data (section 2.1) assumes that the metastable velocity distribution is described by

$$f(v) dv = v^n \cdot e^{-mv^2/2kT} dv \quad .$$

This distribution converts to a TOF distribution

$$f(t) dt = \frac{x^{n+1}}{t^{n+2}} e^{-(m/2kT) \cdot x^2/t^2} dt \quad .$$

The parameter  $n$  is found by fitting Ar TOF spectra with the above distribution and varying  $n$  to give a best fit.

The data points in figure 4.7 show an Ar TOF spectrum

TIME AND AMPLITUDE SCALING  
OF ARGON TIME-OF-FLIGHT  
DISTRIBUTIONS

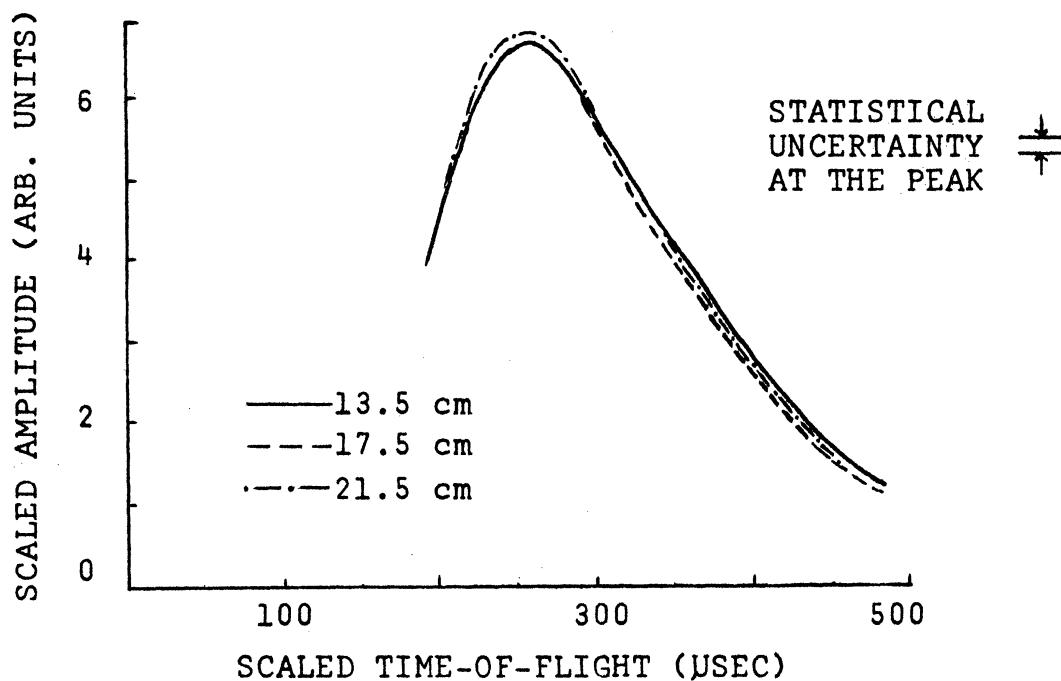


Figure 4.6

Argon time-of-flight distributions at three distances after scaling of the time and amplitude axes.

A FITTING OF ARGON  
DATA TO DETERMINE THE  
VELOCITY DISTRIBUTION

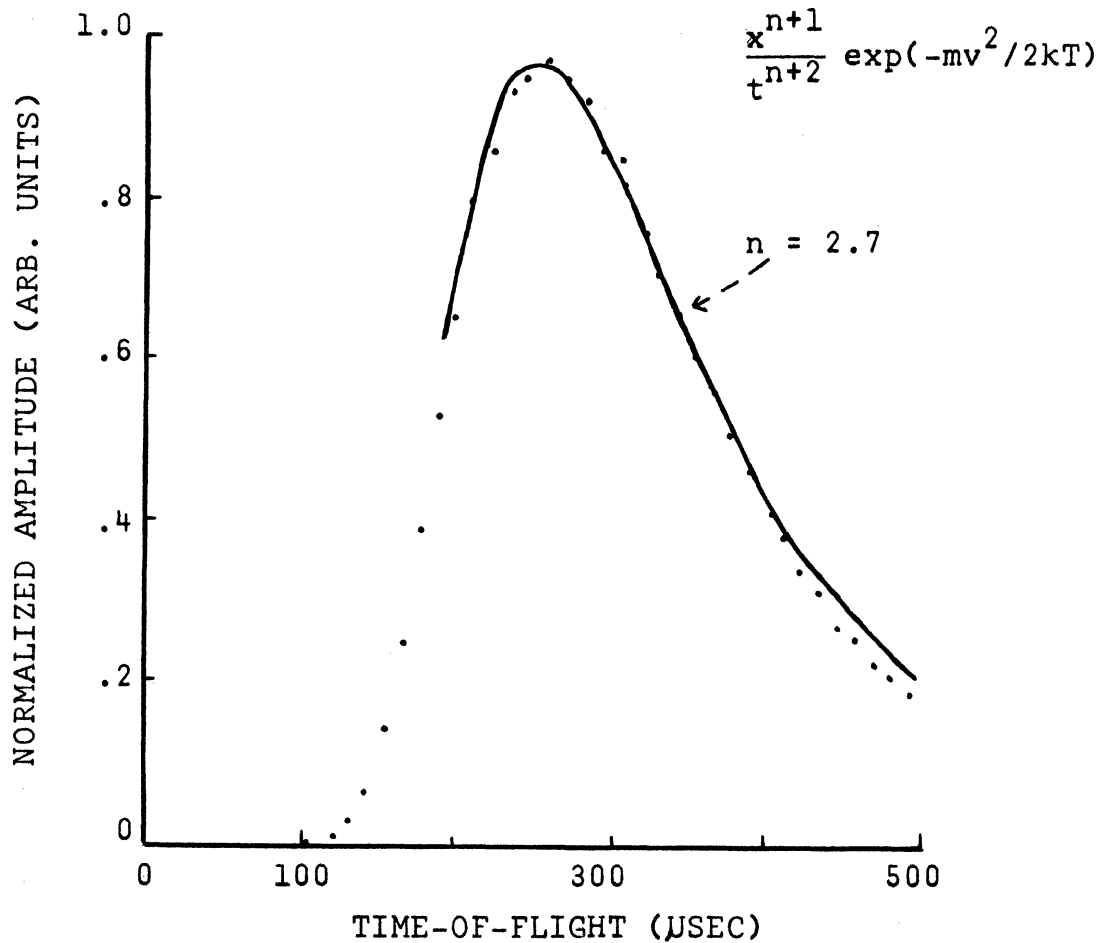


Figure 4.7

Determination of the argon velocity distribution. An argon time-of-flight distribution is fitted with the function  $x^{n+1}/t^{n+2} \exp(-mv^2/2kT)$ .  $n$  is varied to give a best fit. The solid curve is calculated with  $n=2.7$ .

taken with 22 eV electrons at 13.5 cm from the electron gun. The solid curve is the fit using the above distribution with  $n = 2.7$ . This value of  $n$  is consistent with the remaining Ar data and is used in the analysis of all the  $N_2$  spatial decay.

It has been observed that the velocity distribution depends on many parameters, including the source pressure, the electron energy, and the molecular mass. Thus, the velocity distribution that describes Ar might not apply to  $N_2$ . However, it has been shown (section 3.3) that the exact value of  $n$  is not needed for an accurate lifetime measurement.



## CHAPTER 5

### ANALYSIS OF THE NITROGEN DATA

In chapter 4 we described the calibration of the electron gun and showed that the Ar spatial decay and TOF spectra behaved as expected. We may now use the techniques of chapter 2 on  $N_2$  spatial decay and TOF data to obtain a value for the lifetime of the  $a^1\Pi$  state.

#### 5.1 A Summary of Analytic Techniques

We have three methods for analyzing the  $N_2$  data. These techniques and some comments:

I) The first technique (section 2.1) is applied to spatial decay data. It assumes a two-component beam, with one component having a very long lifetime. It also assumes that the  $N_2$  velocity distribution can be approximated by the Ar velocity distribution. This method is limited since it requires some knowledge of the velocity distribution and is not easily generalized to more than a two-component beam. We found that the data were hard to obtain cleanly and reproducibly since this method relies upon the long term beam stability and the uniformity of the detector drive.

II) The second technique (section 2.3) is applied to

TOF spectra. It assumes a two or three-component beam, with one component having a very long lifetime. It also assumes that the relative populations are independent of velocity. This method is limited by the ability to judge the "goodness" of a theoretical fit to experimental data. It is included as a technique for investigation and is not intended as an accurate measurement technique.

III) The third technique (section 2.2) is the main analytic tool to be applied to TOF spectra. It assumes a two-component beam, but does not make any assumption concerning the velocity distribution. TOF distributions are taken at three equally spaced distances and time and amplitude scaled (sections 2.2.1 and 2.2.2). Then a time  $T'$  is picked and equation 2.21 gives the lifetime. Lifetimes are calculated for a series of  $T'$  and an average is taken.

Method III is an accurate technique of handling a two-component beam as seen from the analysis of a computer-simulated metastable beam (section 3.4). This technique can be generalized to the analysis of a more than two-component beam (appendix A).

## 5.2 Data

The data consists of i) spatial decay taken with 22 eV electrons, ii) TOF spectra taken with 22 eV electrons,

and iii) TOF spectra taken with 10 eV electrons. Before this data is analyzed, recall that (section 4.2) if 10 eV electrons are used, the  $A^3\Sigma$  and the  $a^1\Pi$  states are excited. If 22 eV electrons are used, the  $A^3\Sigma$ ,  $a^1\Pi$ , and  $E^3\Sigma$  states are excited.

### 5.2.1 Spatial Decay at 22 eV

Seven sets of data pass the stability tests and are retained for final analysis. Figure 4.5a shows the spatial decay for one of these runs. The solid curve is the least square fit with

$$c_0 + c_1 \cdot (x-13.5) + \dots + c_4 \cdot (x-13.5)^4$$

used as a fitting function. Figure 4.5a also shows the  $N_2$  data after the Ar correction (section 4.4.1) is applied. The slight break in the corrected data in the 23 to 24 cm region occurs in all the  $N_2$  spatial decay. Because this break cannot be explained, calculations are limited to data in the 13.5 to 22.5 cm region.

Technique I is used to calculate the lifetime from corrected and fitted  $N_2$  spatial decay. The derivative of the intensity at points  $X_a$  and  $X_b$ , and the approximate velocity distribution (section 4.4.3) are needed for the calculation.  $R (=X_b/X_a)$  is fixed at 1.26 and  $X_a$  is incremented from 13.5 to 16.5 cm in intervals of 0.5 cm. Figure 4.5b is a display of the lifetime found from the single spatial decay in figure 4.5a. Figure 5.1 is a

histogram displaying the lifetimes found from all seven runs. The apparent lifetime is 154  $\mu\text{sec}$ . Since we are applying a two-component theory to a three-component beam, the 154  $\mu\text{sec}$  refers to a composite lifetime of the  $a^1\pi$  and  $E^3\Sigma$  states.

### 5.2.2 Time-of-Flight at 22 eV

The data from seven runs at distances of 13.5, 17.5, and 21.5 cm pass the stability tests (section 4.3) and are therefore retained for the final calculations. Figure 5.2a shows one set of 22 eV TOF distributions.

Technique III is used to calculate the lifetime from the scaled and fitted spectra. The scaled time  $T'$  is incremented from 200 to 400  $\mu\text{sec}$  in 10  $\mu\text{sec}$  intervals and equation 2.22 is used to calculate the lifetime. Figure 5.2b is a display of the lifetime found from the single set of TOF spectra in figure 5.2a. Figure 5.3a is a histogram displaying the lifetimes found from all the combinations of distances. The apparent lifetime is 161  $\mu\text{sec}$ . Since we have again applied a two-component theory to a three-component beam, the 161  $\mu\text{sec}$  refers to a composite lifetime of the  $a^1\pi$  and  $E^3\Sigma$  states. Note that this lifetime agrees very well with the spatial decay data taken with 22 eV electrons (154  $\mu\text{sec}$ ) where we also analyzed a two-component beam with a three-component theory.

HISTOGRAM OF THE LIFETIMES  
FOUND FROM N<sub>2</sub> SPATIAL DECAY

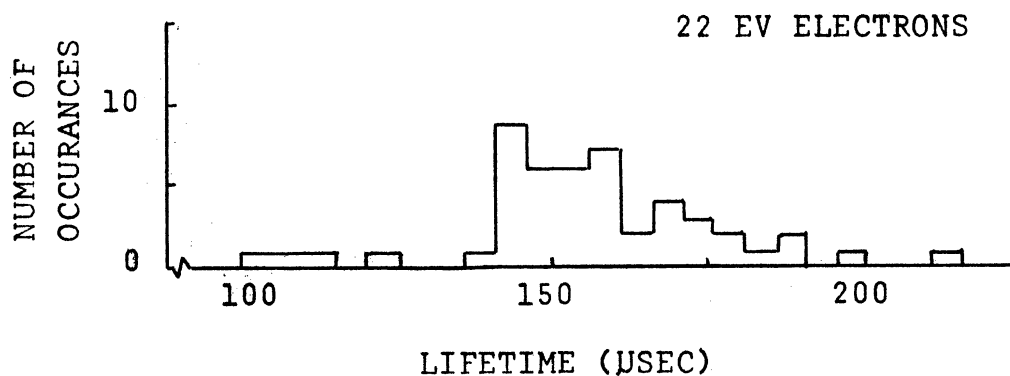


Figure 5.1

A histogram displaying the lifetimes (calculated according to technique I) found from all the N<sub>2</sub> spatial decay taken with 22 eV electrons. Each spatial decay contributes seven points to the histogram. The lifetime (154 usec) is assigned to a composite of the a<sup>1</sup>π and E<sup>3</sup>Σ states.

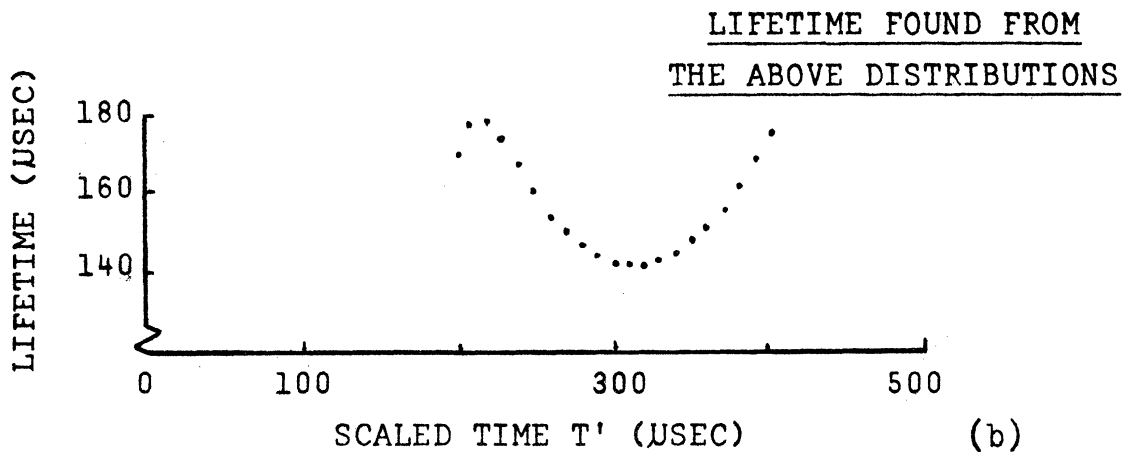
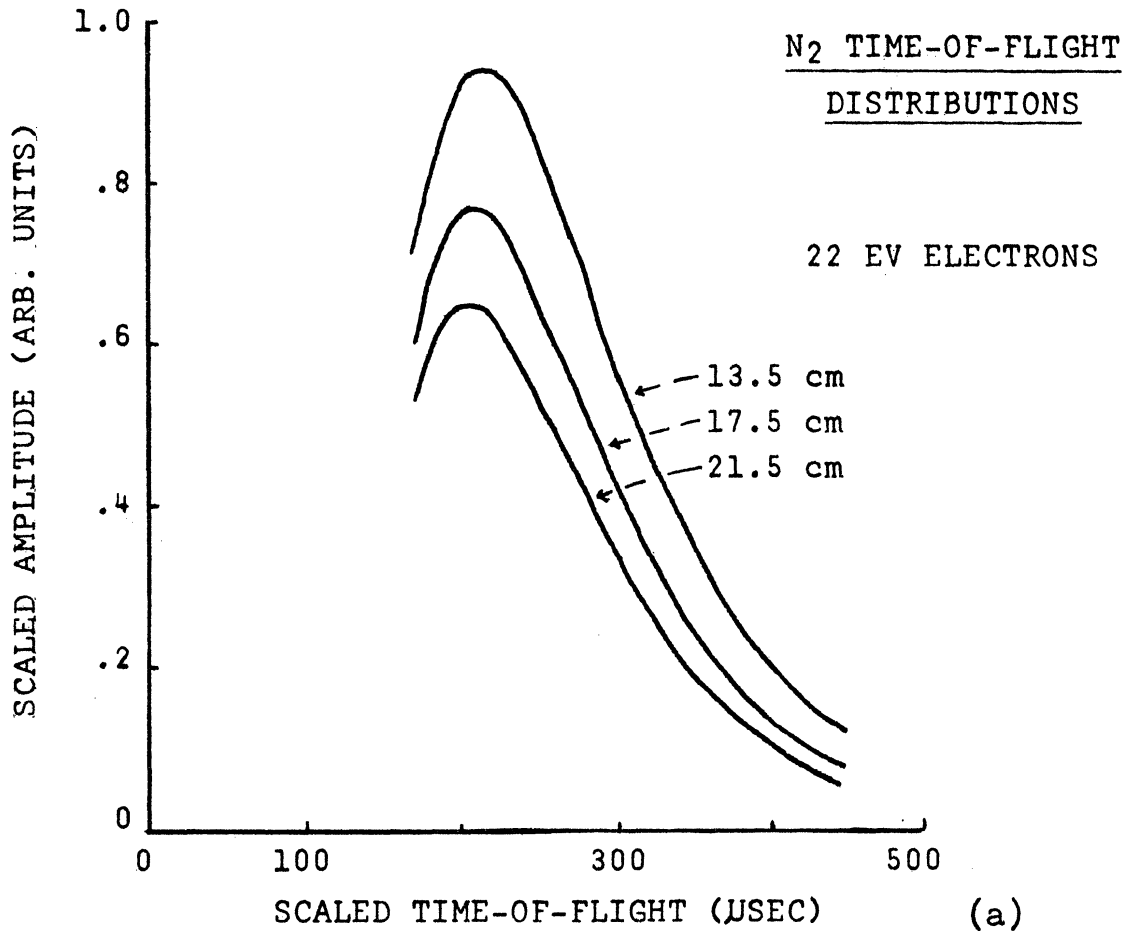


Figure 5.2

N<sub>2</sub> time-of-flight spectra taken with 22 eV electrons.

- (a) A least squares fit of the time and amplitude scaled distributions.
- (b) The lifetime as calculated (according to technique III) from the above spectra. The lifetime is found at a time T', from the corresponding amplitudes of the three spectra. The lifetime is assigned to a composite of the  $a^1\Pi$  and  $E^3\Sigma$  states.

HISTOGRAMS OF THE  
LIFETIMES FOUND FROM  
N<sub>2</sub> TIME-OF-FLIGHT DATA

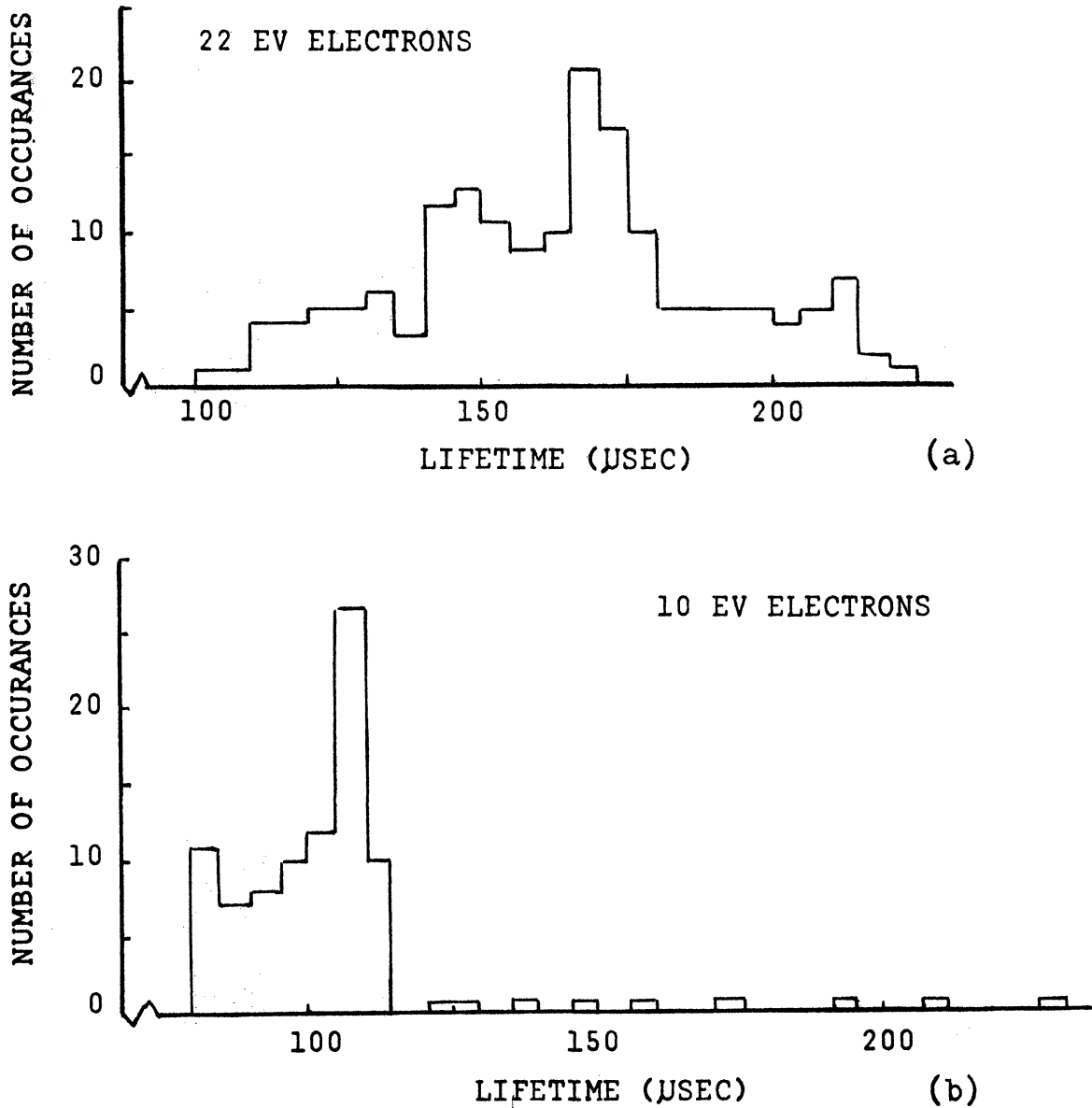


Figure 5.3

Histograms displaying the lifetimes (calculated according to technique III) found from all the N<sub>2</sub> time-of-flight data.

- (a) Lifetimes found from data taken with 22 eV electrons. This lifetime (161 μsec) is assigned to a composite of the  $a^1\Pi$  and  $E^3\Sigma$  states.
- (b) Lifetimes found from data taken with 10 eV electrons. This lifetime (106 μsec) is assigned to the  $a^1\Pi$  state.

Now we will analyze this data as a three-component beam according to technique II. Figures 5.4a, 5.4b and 5.4c show the TOF spectra at 13.5, 17.5, and 21.5 cm. The solid curve in figure 5.4a is a least squares fit using function 3.2. The solid curves in figures 5.4b and 5.4c are the TOF spectra predicted using i) the least squares fit of figure 5.4a, ii) lifetimes of  $\tau_1 = 105$   $\mu$ sec and  $\tau_2 = 210$   $\mu$ sec (section 2.3), and iii) adjusting the populations to give a best fit ( $N_1 = 30$ ,  $N_2 = 70$ , and  $N_3 = 12$  is displayed). Because we have a three-component beam, the 105  $\mu$ sec refers to the  $a^1\Pi$  state and the 210  $\mu$ sec refers to the  $E^3\Sigma$  state.

Altogether, it would be better to work at low enough electron energies so that only two states are excited. This approach is described in the next section.

### 5.2.3 Time-of-Flight at 10 eV

The data from seven runs at distances of 12.9, 14.9, 16.9, 18.9, 20.9, and 22.9 cm pass the stability tests (section 4.3) and are therefore retained for final calculations. Figure 5.5a shows one set of 10 eV TOF distributions.

Technique III is used to find the lifetime from the scaled and fitted spectra. The scaled time  $T'$  is incremented from 200 to 350  $\mu$ sec in 10  $\mu$ sec intervals and equation 2.22 is used to calculate the lifetime. Figure 5.5b is



N<sub>2</sub> TIME-OF-FLIGHT DISTRIBUTIONS

22 EV ELECTRONS

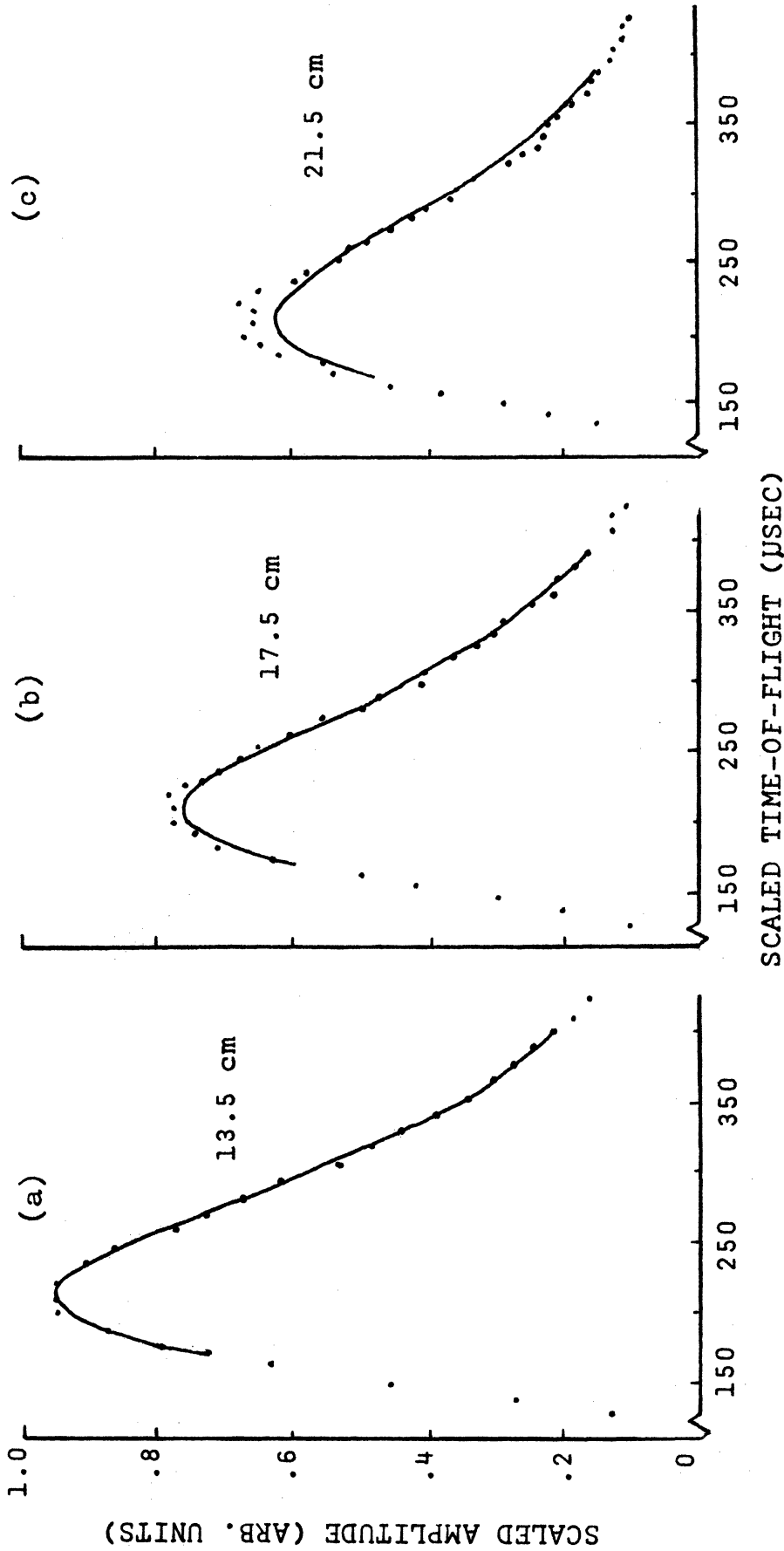


Figure 5.4

N<sub>2</sub> time-of-flight spectra taken with 22 eV electrons.

(a) A least squares fit (solid curve) to the data.

(b) Predicted time-of-flight distributions (solid squares) using the least squares

(c) fit and assumed populations and lifetimes for the metastable beam (section 5.2.2).

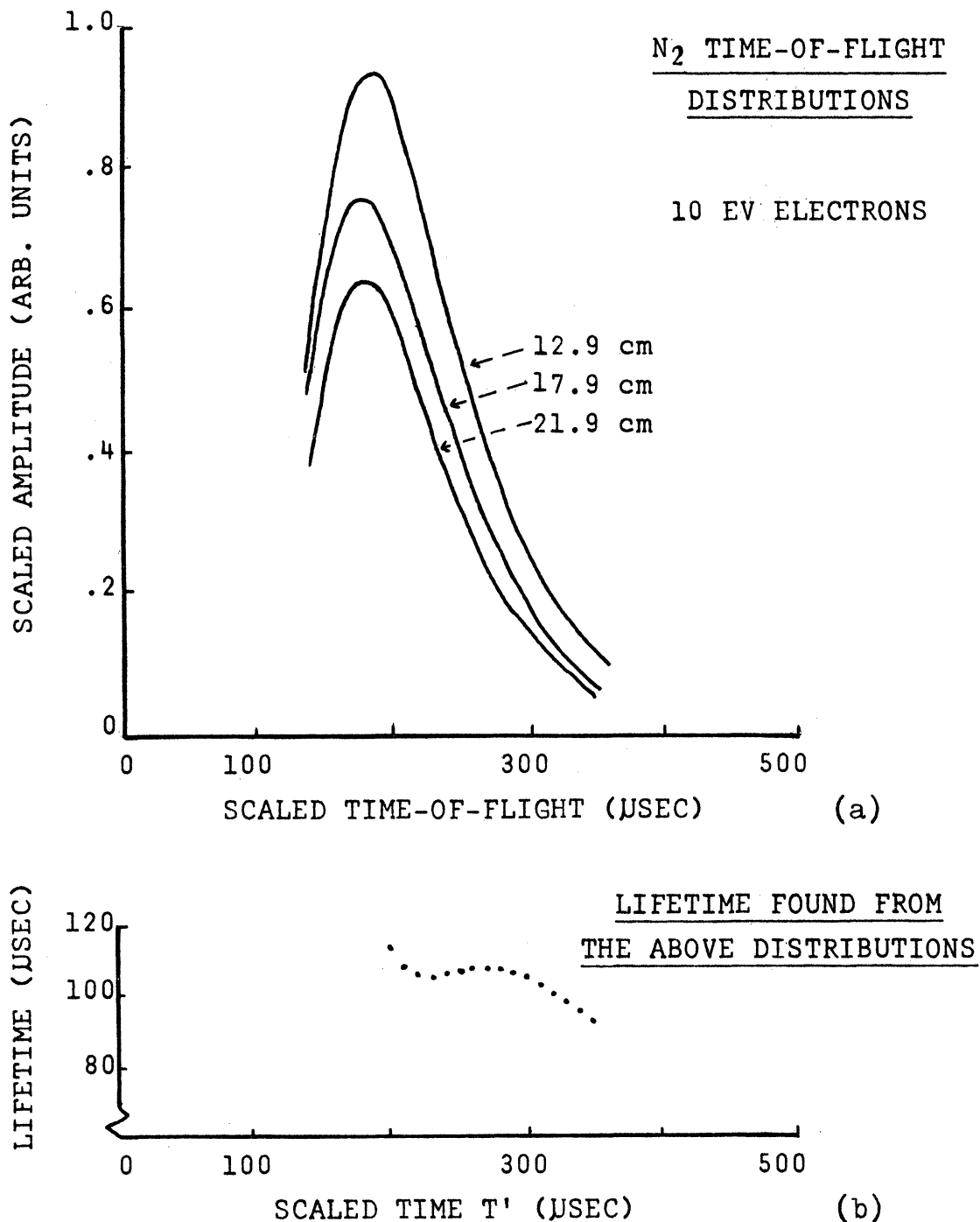


Figure 5.5

N<sub>2</sub> time-of-flight spectra taken with 10 eV electrons.

- (a) A least squares fit of the time and amplitude scaled distributions.
- (b) The lifetime as calculated (according to technique III) from the above spectra. The lifetime is found at a time T', from the corresponding amplitudes of the three spectra. The lifetime is assigned to the  $a^1\pi$  state.

a display of the lifetime found from the single set of TOF spectra in figure 5.5a. Figure 5.3b is a histogram displaying the lifetimes found from all the appropriate combinations of distances. The calculated lifetime is 106  $\mu\text{sec}$ . Since we have applied a two-component theory to a two-component beam, the 106  $\mu\text{sec}$  refers to the  $a^1\Pi$  state.

The stability of the beam is checked by taking the first and last TOF spectra in a series at the same distance (section 4.3). If the two spectra do not overlap, the entire series is rejected. If the beam is stable for six of the spectra and drifts during only the last spectra, the entire series is rejected. Valid data (the first six spectra) could be lost in this manner. To check on this possibility, the rejected data is analyzed according to technique III. In every case except one, the lifetime values have extreme amounts of scatter and are entirely meaningless (the data was properly rejected). In the one case, the lifetime values have only a small amount of scatter with values very close to the 106  $\mu\text{sec}$  found above (we had rejected some data that was partially okay).

One final bit of analysis with technique II substantiates the 106  $\mu\text{sec}$  lifetime of the  $a^1\Pi$  state. Figures 5.6a, 5.6b, and 5.6c show the TOF spectra at 12.9, 16.9, and 20.9 cm. The solid curve in figure 5.6a is a least squares fit using function 3.2. The solid curves in

N<sub>2</sub> TIME-OF-FLIGHT DISTRIBUTIONS

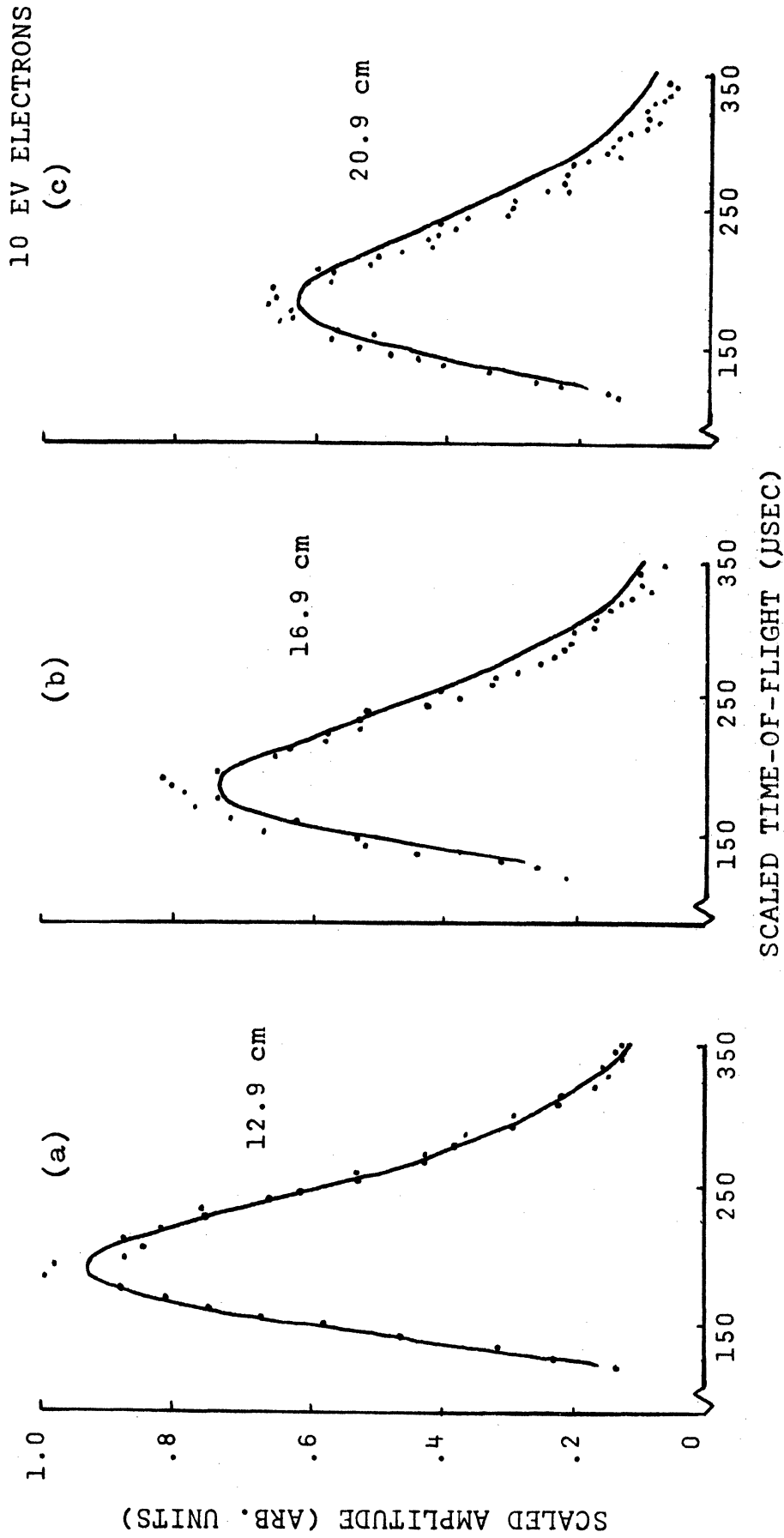


Figure 5.6

N<sub>2</sub> time-of-flight spectra taken with 10 eV electrons.

(a) A least squares fit (solid curve) to the data.

(b) & Predicted time-of-flight distributions (solid curves) using the least squares fit (c) and assumed populations and lifetimes for the metastable beam (section 5.2.2).

figures 5.6b and 5.6c are the TOF spectra predicted using i) the least squares fit of figure 5.6a, ii) a lifetime of  $\tau_1 = 105 \mu\text{sec}$  (section 2.3), and iii) adjusting the populations to give a best fit ( $N_1 = 100$ ,  $N_2 = 0$ , and  $N_3 = 17$  is displayed). Because we have a two-component beam, the  $105 \mu\text{sec}$  refers to the  $a^1\Pi$  state.

## CHAPTER 6

### DISCUSSION OF EXPERIMENTAL RESULTS

#### 6.1 Other Experiments

There are two common methods for measuring the lifetime of the  $a^1\pi$  state of  $N_2$ . One method involves the analysis of the optical transition  $a^1\pi_g - X^1\Sigma_g^+$  and yields values ranging from 10 to 160  $\mu\text{sec}$  (Jeunehomme, 1967; Holland, 1969; Shemansky, 1969b). The second method, which involves either spatial decay or TOF measurements on a beam of excited  $N_2$  molecules, has yielded results with less scatter.

The spatial decay method used by Lichten (1957) gave a lifetime of  $(170 \pm 30)$   $\mu\text{sec}$  for the  $a^1\pi$  state, but it was necessary to assume a Maxwellian velocity distribution. However, the work of J. C. Pearl (1970) demonstrated that the velocity distribution after electron impact is often not Maxwellian. The techniques presented in this thesis overcome this difficulty: the spatial decay method uses a measured velocity distribution and the TOF method does not depend on the velocity distribution at all.

On the basis of the analysis of the  $N_2$  experimental data and of the computer-simulated data, it appears that the TOF method presented here is capable of yielding more accurate results than the method employed by Olmsted, Newton

and Street (1965) in which the lifetime of  $(120 \pm 50)$   $\mu\text{sec}$  was estimated from the excitation function data taken at two distances.

Borst and Zipf (1971) used a TOF method to measure the lifetime of the  $a^1\pi$  state. They recorded two TOF spectra: one spectrum was taken with low energy electrons exciting just the  $a^1\pi$  state, while the other spectrum was taken with higher energy electrons exciting both the  $A^3\Sigma$  and  $a^1\pi$  states. Then by assuming that the kinematics of the electron - molecule collision is the same for each TOF spectrum, they measured a lifetime of  $(115 \pm 20)$   $\mu\text{sec}$  by attributing the difference in shape of the two TOF spectra to the decay of the  $a^1\pi$  state. This assumption of unchanging kinematics is a good one for their particular geometry, but could be a very poor assumption in other experimental situations (see J. C. Pearl, 1970). Furthermore, their method requires that a long-lived state can be excited and the TOF spectrum recorded while the short-lived state remains unexcited, which can be difficult for an electron gun of modest energy resolution (for example, helium has metastable states separated by only .8 eV). The TOF technique presented in this thesis is not limited by the kinematical assumption and does not require that the long-lived state be individually excited.

## 6.2 Present Experiment

### 6.2.1 Data

The analyzed data falls into two categories: i) 10 eV data involving the lifetime of the  $a^1\pi$  state and ii) 22 eV data involving the composite lifetime of the  $a^1\pi$  and the  $E^3\Sigma$  states.

The 22 eV data consists of seven TOF runs and seven spatial decays. The lifetime of approximately 157  $\mu\text{sec}$  as found by techniques I and III is assigned to a composite of the  $a^1\pi$  and the  $E^3\Sigma$  states on the basis of excitation function measurements. This is in good agreement with the work of Borst and Zipf (1971): they found a composite lifetime of 154  $\mu\text{sec}$  when 12.2 eV electrons were used to excite  $\text{N}_2$ . The TOF data is also analyzed by technique II indicating a lifetime for the  $a^1\pi$  state in the region of 105  $\mu\text{sec}$ .

The 10 eV data consists of seven TOF runs retained for final analysis with an additional six runs supplying supportive results. The lifetime of 106  $\mu\text{sec}$  as found by technique III is assigned to the  $a^1\pi$  state on the basis of excitation function measurements. The 106  $\mu\text{sec}$  is also confirmed by analysis with technique II.

### 6.2.2 Errors and Difficulties

There are several experimental uncertainties. The electron gun-detector separation is uncertain ( $\pm 0.5$  cm) because of the finite lengths of the interaction region and detector



cone. The electron gun pulse width (10  $\mu$ sec) and the multi-channel bin width (10  $\mu$ sec) make any time calibration uncertain. In addition to these experimental uncertainties, the histogram displaying the results of the lifetime calculation (figure 5.3b) shows that there is some statistical uncertainty. A calculation of the standard deviation of the mean is very difficult because of problems such as i) weighing the result of each lifetime calculation (a TOF spectrum can be involved in more than one calculation) and ii) assigning the error resulting from the least squares fitting. The standard deviation of the mean was not found, but an estimate for the limit of the error is  $\pm 35$   $\mu$ sec.

The major difficulty in this experiment was the extremely low detector signal when using 10 eV electrons. As can be seen from the excitation function for  $N_2$  (figure 4.3), the detector signal at 10 eV was more than an order of magnitude lower than the signal at 22 eV.

To continue this experiment it would be desirable to have an electron gun with better energy resolution and with improved long-term stability. With better resolution it would be easier to determine which states were being excited, and with improved stability it would be possible to integrate the TOF spectra over long periods of time. Another desirable modification would be to use a detector with a larger sensitive area so that more of the excited molecules in the beam could be counted.

### 6.3 Summary

This thesis has presented spatial decay and TOF techniques for measuring the lifetime of a short-lived metastable state in a two-component beam. The TOF method overcomes difficulties present in other methods for measuring lifetimes: it does not require quenching of one of the metastable components, it does not require a knowledge of the metastable velocity distribution, and it does not require the long-lived metastable state to be individually excited. A generalization of the TOF technique can be used in the analysis of a beam consisting of more than two components. These spatial decay and TOF methods were tested on a two-component, computer-simulated beam and on an experiment with molecular nitrogen. The lifetime of the  $a^1\Pi$  state of  $N_2$  was found to be  $(106 \pm 35)$   $\mu\text{sec}$ , in good agreement with recent measurements made by other workers using different techniques.

## APPENDIX A

### ANALYSIS OF A THREE COMPONENT BEAM

Assume the three-component beam described in section 2.3. The first component has an initial population  $N_1(V)$  and a lifetime  $\tau_1$ , the second component has an initial population  $N_2(V)$  and a lifetime  $\tau_2$ , and the third component has an initial population  $N_3(V)$  and an infinite lifetime. It is assumed that  $\tau_1$  is known from a previous measurement and we wish to measure  $\tau_2$ . Then we have four unknowns  $N_1$ ,  $N_2$ ,  $N_3$ , and  $\tau_2$  and we will need TOF spectra at four distances  $X_a$ ,  $X_b$ ,  $X_c$ , and  $X_d$ , where

$$X_b = X_a + \Delta X, X_c = X_b + \Delta X, \text{ and } X_d = X_c + \Delta X \quad . \quad (\text{A.1})$$

If we are going to measure  $\tau_2$ , assuming  $\tau_1$  to be known, then consider a group of metastable molecules having a velocity  $V$ . At the four distances, this group has amplitudes (number of molecules per unit time) and times-of-arrival

$$F'_a = N_1 \cdot e^{-T_a/\tau_1} + N_2 \cdot e^{-T_a/\tau_2} + N_3 \quad T_a = X_a/V \quad (\text{A.2})$$

$$F'_b = N_1 \cdot e^{-T_b/\tau_1} + N_2 \cdot e^{-T_b/\tau_2} + N_3 \quad T_b = X_b/V \quad (\text{A.3})$$

$$F'_c = N1 e^{-T_c/\tau1} + N2 e^{-T_c/\tau2} + N3 \quad T_c = X_c/V \quad (A.4)$$

$$F'_d = N1 e^{-T_d/\tau1} + N2 e^{-T_d/\tau2} + N3 \quad T_d = X_d/V \quad (A.5)$$

where the prime denotes a scaled amplitude.

Equation A.1 implies

$$T_b = T_a + \Delta T, \quad T_c = T_b + \Delta T, \quad \text{and} \quad T_d = T_c + \Delta T \quad (A.6)$$

where  $\Delta T = \Delta X/V$ . Substituting equation A.6 into equations A.2, A.3, A.4, and A.5, and subtracting pairs of equations to eliminate N3:

$$F'_a - F'_b = N1 \cdot e^{-T_a/\tau1} \cdot (1 - e^{-\Delta T/\tau1}) + \\ N2 \cdot e^{-T_a/\tau2} \cdot (1 - e^{-\Delta T/\tau2}) \quad (A.7)$$

$$F'_b - F'_c = N1 \cdot e^{-T_a/\tau1} \cdot e^{-\Delta T/\tau1} \cdot (1 - e^{-\Delta T/\tau1}) + \\ N2 \cdot e^{-T_a/\tau2} \cdot e^{-\Delta T/\tau2} \cdot (1 - e^{-\Delta T/\tau2}) \quad (A.8)$$

$$F'_c - F'_d = N1 \cdot e^{-T_a/\tau1} \cdot e^{-2 \cdot \Delta T/\tau1} \cdot (1 - e^{-\Delta T/\tau1}) + \\ N2 \cdot e^{-T_a/\tau2} \cdot e^{-2 \cdot \Delta T/\tau2} \cdot (1 - e^{-\Delta T/\tau2}) \quad (A.9)$$

Rearranging equations A.7, A.8, and A.9 and subtracting pairs

of equations to eliminate N1:

$$\begin{aligned} (F'_a - F'_b) - (F'_b - F'_c) \cdot e^{\Delta T/\tau_1} = \\ N2 \cdot e^{-T_a/\tau_2} \cdot (1 - e^{-\Delta T/\tau_2}) \cdot (1 - \exp[-\Delta T/\tau_2 + \Delta T/\tau_1]) \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} (F'_b - F'_c) - (F'_c - F'_d) \cdot e^{\Delta T/\tau_1} = \\ N2 \cdot e^{-T_a/\tau_2} \cdot (1 - e^{-\Delta T/\tau_2}) \cdot e^{-\Delta T/\tau_2} \cdot (1 - \exp[-\Delta T/\tau_2 + \Delta T/\tau_1]) \end{aligned} \quad (\text{A.11})$$

Divide equations A.10 and A.11 to eliminate N2:

$$\frac{(F'_a - F'_b) - (F'_b - F'_c) e^{\Delta T/\tau_1}}{(F'_b - F'_c) - (F'_c - F'_d) e^{\Delta T/\tau_1}} = \frac{1}{e^{-\Delta T/\tau_2}} \quad (\text{A.12})$$

Then equation A.12 can be solved for:

$$\tau_2 = \frac{\Delta T}{\frac{(F'_a - F'_b) - (F'_b - F'_c) e^{\Delta T/\tau_1}}{(F'_b - F'_c) - (F'_c - F'_d) e^{\Delta T/\tau_1}}} \quad (\text{A.13})$$

where  $\Delta T = \Delta X \cdot T_a / X_a$ .

The lifetime of the second component may be found as follows:

- i) Measure the lifetime of the first component in the manner suggested in section 2.3 (by exciting just the first and third component and using the theory of section 2.2).
- ii) Take TOF spectra at distances  $X_a$ ,  $X_b = X_a + \Delta X$ ,  $X_c = X_a + 2 \cdot \Delta X$ , and  $X_d = X_a + 3 \cdot \Delta X$ .
- iii) Amplitude scale these spectra.
- iv) Pick a time  $T_a$ , and find the times  $T_b$ ,  $T_c$ , and  $T_d$  by using equation A.6.
- v) Find the scaled amplitudes  $F'_a$ ,  $F'_b$ ,  $F'_c$ , and  $F'_d$  corresponding to the times in iv.
- vi) Use equation A.13 to find the lifetime  $\tau_2$  (knowing the lifetime  $\tau_1$ ).

This series of steps is carried out for various  $T_a$ , generating a series of values for the lifetime  $\tau_2$ . Since these numbers should all be the same, an average can be taken.

It appears that this method of TOF spectrum analysis can be generalized to a beam that has an arbitrary number of components. It would only be necessary to have at least as many TOF spectra as there are unknowns in the problem.

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