

Time-of-Flight Measurements of Metastable State Lifetimes*

David E. Kaslow[†] and Jens C. Zorn

Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48104

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A time-of-flight method for measurement of the lifetime of metastable molecules is described. The method is applicable to a molecular beam that has molecules in several different metastable excited states. As compared to methods used previously, the method has the advantages that it does not require selective excitation or quenching of the different states; moreover, it does not require a determination of the relative populations or velocity distributions of molecules in the excited states. The feasibility of the method is demonstrated with a measurement of the lifetime of the $a^1\pi_g$ state of N_2 .

I. INTRODUCTION

Excited states of atoms or molecules are said to be metastable if their lifetimes are long compared to those states whose radiative decay is permitted by electric dipole selection rules. Measurements of metastable state lifetimes are of interest for testing theories of higher order (e.g., magnetic dipole, electric quadrupole, two photon) radiative processes in aeronomy, laser physics, and other applications.

In this paper we discuss the use of a molecular beam technique for the measurement of metastable state lifetimes. We emphasize the time-of-flight (TOF) method because it works well even with low beam intensities. The TOF method described here is applicable to a molecular beam that has molecules in both a long-lived and a short-lived state. The method differs from ones used previously in that it does not require selective excitation or quenching of the different states, and it does not require a determination of the relative populations or the initial velocity distributions of molecules in the metastable states. This technique was tested by a TOF experiment in which we measured the lifetime of the $a^1\pi_g$ metastable state of molecular nitrogen.

II. LIFETIME MEASUREMENTS FROM TIME-OF-FLIGHT DATA

A. General Approach

The apparatus for TOF measurements is shown schematically in Fig. 1 and described in detail elsewhere.¹ A collimated beam of thermal-velocity molecules passes through an electron gun that is pulsed ($\sim 10 \mu\text{sec}$) at a rate of approximately 1000/sec. A small fraction ($\sim 10^{-7}$) of the beam molecules are excited by electron impact to metastable states. These metastable molecules, which suffer only a small change in velocity from the electron impact,² proceed to a distant, windowless electron multiplier where they are rapidly and efficiently detected.³

The detector pulses are encoded as to their time of occurrence with a time-to-height converter so that they can be stored and displayed with a multichannel pulse height analyzer. A representative TOF spectrum is shown in the lower part of Fig. 1. The first, narrow peak in the spectrum is due to photons that arise from the decay of short-lived ($\sim 10^{-8}$ sec) states that have been excited by electron impact; this first peak in the spectrum is convenient for establishing the zero of the time scale. The later, broad peak in the TOF spectrum is from the arrival of metastable molecules.

If it were known that the beam contained molecules in only one metastable state that had lifetime τ , then that lifetime could be determined by relating the TOF distribution at two different source-detector distances with the multiplicative factor $\exp(t/\tau)$.

It is frequently the case, however, that the beam contains molecules in two metastable states, with one state having a lifetime that is considerably longer than the other. If one of these states can be quenched, then the lifetimes can be determined by measuring the TOF spectra at two different source-detector distances with and without the quenching applied. This method is exemplified by the work of Van Dyck *et al.*⁴ in which helium resonance radiation was used for selective quenching in a measurement of the lifetime of $\text{He}(2^1S)$. If quenching is not feasible, then the lifetime of the short-lived state may be determined by a TOF measurement at a single source-detector distance if one can find the velocity distribution of molecules in the long-lived state and if one then assumes that the initial velocity distribution of molecules in the short-lived state is the same. This method is exemplified by the lifetime measurement of $N_2(a^1\pi_g)$ by Borst and Zipf⁵ in which the TOF spectrum of $N_2(A^3\Sigma_u^+)$, as excited by electrons below the threshold for production of $N_2(a^1\pi_g)$ was used as a measure of the initial velocity distribution of molecules in both metastable states when excited by electrons above the $N_2(a^1\pi_g)$ threshold.

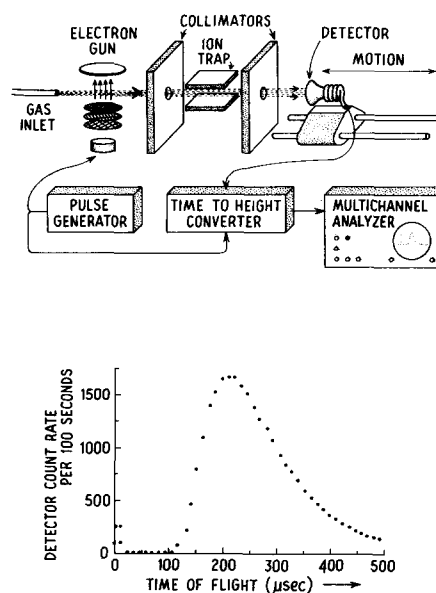


FIG. 1. Schematic of apparatus for lifetime measurements and typical TOF spectrum.

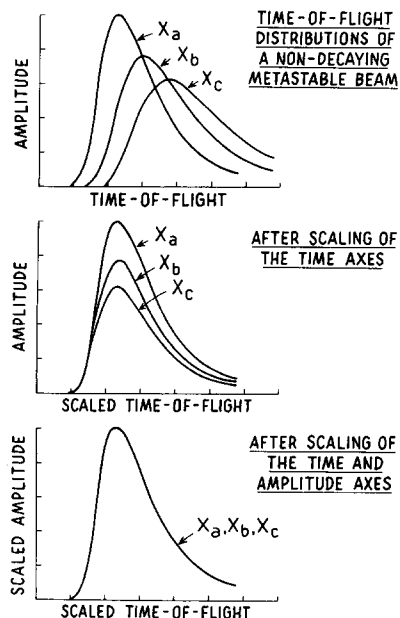


FIG. 2. Idealized TOF spectra of a nondecaying beam of metastable molecules as taken at three different source-detector distances. The scaling of the time and amplitude axes facilitates the comparison of the spectra.

The above conditions may be too restrictive since a molecular beam excited by electron impact often contains molecules in several different metastable states that cannot be quenched. Moreover, it has been shown² that the velocity distribution of metastable molecules excited by electron impact (particularly if the ground state molecules are in a collimated beam) depends on the energy of the bombarding electrons, on the excitation energy of the metastable states, and on the geometry of the incoming and outgoing molecular beam. Thus it is desirable to have a method for lifetime measurement that can be applied to a beam that contains molecules in more than one metastable state without explicit reliance on selective excitation, on quenching, on assumptions about initial state populations, or on knowledge of molecular velocity distributions.

B. Present Method

In this paper we describe a method for the measurement of the lifetime of the short-lived state in a molecular beam that contains molecules in two metastable states. We consider the case where the longer-lived state in a two-component beam has a lifetime that is long compared to the time of flight of molecules through the apparatus; however the method may be extended,¹ albeit with less generality, to situations where the beam has more than two metastable components.

The method presented here requires the acquisition of TOF spectra taken at three different electron gun-detector distances.

It is first necessary to scale the time and amplitude so that these TOF spectra taken at different distances can be displayed on a common set of axes. Consider TOF spectra taken at distances X_a and at $X_b > X_a$. A group of metastable molecules that travels the distance X_a in a time T_a will travel the distance X_b in a time $T_b = (T_a)(X_b/X_a)$. Thus the time axis of the second spectrum must be multiplied by X_a/X_b if the two spectra are to be displayed on a common

time axis. However, because the metastable molecules in this group have a range of velocities, it is necessary to scale the amplitude. After traveling a distance X_a , the molecules have a spread ΔT_a in times of arrival and, after a distance X_b , the time spread is $\Delta T_b = (\Delta T_a)(X_b/X_a)$. Since the time spread increases from X_a to X_b , the amplitude of the TOF spectrum (number of metastable molecules per unit time) must decrease at X_b . Thus the amplitude of the second spectrum must be multiplied by X_b/X_a if the two spectra are to be displayed on a common amplitude axis. These scalings are illustrated in Fig. 2.

Now it is assumed that the metastable beam consists of molecules in two states (a two-component beam), with one state having a lifetime that is long when compared to the time of flight in the apparatus. It is not necessary to make any assumptions about the initial velocity distribution of molecules in these two states; nor does it matter if the detector's efficiency is different for molecules in the two different states. The velocity distributions of molecules in the two states, as registered by the detector, are simply written as $n_1(V)$ and $n_2(V)$, where 1 and 2 refer to the short-lived and long-lived state, respectively. The lifetime of the short-lived state is τ . Since there are three unknowns, $n_1(V)$, $n_2(V)$, and τ , three equations are needed before a solution can be found. These three equations may be derived from TOF spectra taken at three different distances.

Figure 3(a) shows idealized TOF spectra for a two-component metastable beam at the distances X_a , X_b , and X_c , where,

$$X_b = X_a + \Delta X \quad \text{and} \quad X_c = X_a + 2\Delta X. \quad (1)$$

Figure 3(b) shows the same spectra after time and amplitude scaling. The lifetime of the short-lived state can be found as follows. Construct a perpendicular line at T' on the scaled time axis [dotted line in Fig. 3(b)]. This line intersects the three TOF spectra at coordinates (F'_a, T') , (F'_b, T') , and (F'_c, T') . F'_a , F'_b , and F'_c represent scaled amplitudes, at distances X_a , X_b , and X_c , respectively, of a group of mole-

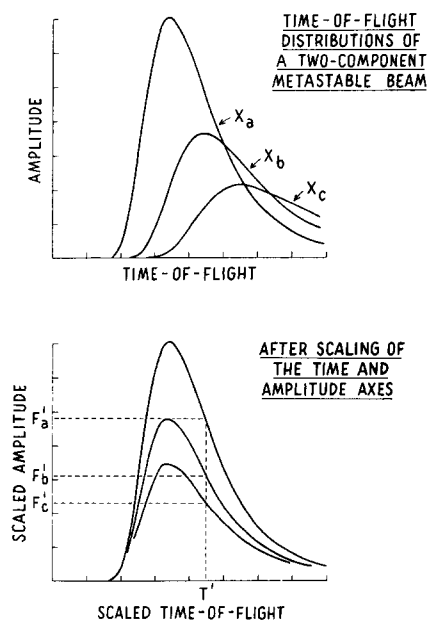


FIG. 3. Idealized TOF spectrum of a beam of molecules that are in two metastable states, one of which has a short lifetime. The effects of the decay of the short-lived state are clearly seen after scaling of the time and amplitude axes (compare Fig. 2), and the lifetime of the short-lived state is found from the scaled amplitudes F'_a , F'_b , and F'_c at the scaled time T' .

cules having a velocity $V = X_a/T'$. These amplitudes can be written as

$$F_a' = n_1(V) \exp[-X_a/(V\tau)] + n_2(V), \quad (2)$$

$$F_b' = n_1(V) \exp[-X_b/(V\tau)] + n_2(V), \quad (3)$$

$$F_c' = n_1(V) \exp[-X_c/(V\tau)] + n_2(V), \quad (4)$$

where the lifetime of state 2 is so long that the exponential associated with the decay of n_2 is taken to be unity. Using Eq. (1), Eqs. (2)–(4) can be solved for the lifetime of the short-lived state,

$$\tau = \frac{T'[(X_b/X_a) - 1]}{\ln\{[F_a'(T') - F_b'(T')]/[F_b'(T') - F_c'(T')]\}}. \quad (5)$$

Note that neither the initial velocity distributions nor the population ratios of the metastable states appears in the expression for the lifetime.

Given the one assumption of a two-component beam, we now have a method for measuring lifetimes from TOF data as follows: (i) take TOF spectra at three distances X_a , $X_b = X_a + \Delta X$, and $X_c = X_a + 2\Delta X$; (ii) scale these spectra for time and amplitude comparison; (iii) pick a scaled time T' and find the corresponding amplitudes F_a' , F_b' , and F_c' ; and (iv) calculate the lifetime of the short-lived component from Eq. (5). This series of steps, carried out for various T' , generates a series of values for the lifetime that can be averaged to get a final result.

III. MEASUREMENT OF THE $N_2^*(a^1\pi_g)$ LIFETIME

It has been assumed that the metastable portion of the molecular beam consists of two components, with one component having a very long lifetime. A beam of N_2 excited by electrons of about 10 eV energy satisfies this assumption since the $a^1\pi_g$ and the $A^3\Sigma_u^+$ states have excitation thresholds of 6.2 and 8.7 eV, and lifetimes on the order of 10^{-4} and 1 sec, respectively.⁶ Therefore, a measurement of the lifetime of the $a^1\pi_g$ state of N_2 was done to demonstrate the feasibility of the technique described above.

To insure that the metastable beam has only two components, the electrons used to bombard the ground state N_2 beam must not excite the metastable $E^3\Sigma_g^+$ state that has an excitation threshold^{5,7} of 11.9 eV. To calibrate the electron gun in this experiment, excitation functions for metastable helium and argon were taken; for the $N_2(a^1\pi_g)$ lifetime measurements the electron energy was maintained about 2 eV below the 11.7 eV threshold for excitation of metastable argon.

It is possible for distance-dependent systematic effects in the TOF spectra to be interpreted as a decay of a metastable state. Some of the likely effects are from molecules scattered by the residual gas and from the detector efficiency depending on stray magnetic fields within the apparatus. One can test for systematic effects by taking TOF spectra for molecules that have very long-lived metastable states; the spectra taken at different distances should overlap after time and amplitude scaling. Argon was selected as a test since the 3P_0 and 3P_2 metastable states are known⁸ to have very long lifetimes; it was found that the TOF spectra taken

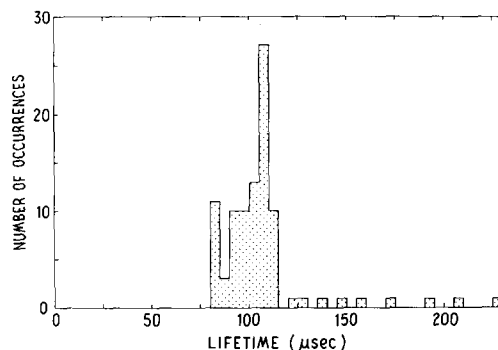


FIG. 4. Histogram displaying values of the lifetime of the $a^1\pi_g$ state of N_2 as determined from TOF data (electrons of 10 eV energy used to excite the molecules).

at different distances did overlap after scaling. Thus we conclude that distance-dependent systematic effects are not a serious source of error in this experiment.

After N_2 TOF spectra are taken at various distances, the data are fed to a computer where they are time and amplitude scaled, and where each spectrum is fitted with a least-squares curve. The scaled amplitudes F' are taken from these curves. For each set of three spectra the scaled time T' is varied from 200 to 350 μsec in steps of 5 μsec , and individual values of the lifetime are calculated with Eq. (5) for each value of T' . Data outside of the 200–350 μsec scale time interval are not used because of the small amplitude differences at shorter times and because of the poor signal-to-noise ratio at longer times.

The histogram of Fig. 4 shows the lifetime values that result from the analysis of seven TOF spectra taken at distances between 13 and 23 cm with electrons of 10 ± 1 eV energy used to excite the molecules. The isolated values in the tail of the histogram result from data near the extremes of the 200–350 μsec scale time interval, regions where the least-squares fit is subject to the most uncertainty. The values of the lifetime shown in the histogram of Fig. 4 average to 106 μsec . The estimated error, ± 35 μsec , arises from the finite length of the excitation and detection regions (1.0 and 0.2 cm, respectively), the 10 μsec width of the electron gun pulse, the 10 μsec interval between adjacent channels of the pulse height analyzer, and the statistical uncertainties in the detector counting rate. No significant portion of the error appears to arise from the method of data analysis. The lifetime of 106 ± 35 μsec for the $a^1\pi_g$ state of N_2 measured in this experiment is in good agreement with the 115 ± 20 μsec lifetime reported by Borst and Zipf,^{5,9} but is somewhat less than the 170 ± 30 μsec value obtained in 1957 by Lichten.¹⁰

It is important to note the reliance on an assumption that excited molecules decay directly to the ground state. Freund, in questioning this assumption, has suggested⁹ that cascading between the $a^1\pi_g$, $a'^1\Sigma_u^+$, and $w^1\Delta_u$ states of N_2 may lead to a nonexponential decay of the $a^1\pi_g$ state and to significant population of the metastable $a'^1\Sigma_u^+$ state. Thus the molecular beam experiments might yield an apparent lifetime for $N_2(a^1\pi_g)$ longer than the one derived from the oscillator strength for the $a^1\pi_g \rightarrow X^1\Sigma_g^+$ transition.⁶ Unfortunately neither the molecular beam experiments nor the

oscillator strength measurements done to date are accurate enough to provide evidence for the occurrence of these cascades between excited states of molecular nitrogen.

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[†]Present address: Physics Department, Lehigh University, Bethlehem, Pennsylvania 18015.

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presents a spatial decay method for measuring lifetimes, and generalizes the methods of Sec. II to a beam containing more than two components.

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