

Ar(3P_2)-N $_2$ ($C^3\Pi_u$) excitation transfer cross section and radiative lifetimes of the nitrogen-molecular-laser transitions

W. R. Bennett, Jr. and John Flint

Dunham Laboratory, Yale University, New Haven, Connecticut 06520

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The total deactivation cross section for Ar(3P_2) metastables in Ar-N $_2$ collisions was measured to be (9.4 ± 1) Å 2 at 663°K in an experiment using pulsed threshold excitation of the Ar(3P_2) metastables in an electron gun and monitoring the transient decay of (second positive) bands from the N $_2$ ($C^3\Pi_u$) electronic state. It is concluded that the measured total velocity-averaged cross section is associated primarily with excitation transfer to the $C^3\Pi_u$ ($v' = 0,1$) vibrational levels of N $_2$. Comparison with other measurements implies a substantial increase of the cross section with gas temperature. The following values for radiative lifetimes of molecular nitrogen levels were also determined: (37.6 ± 1) nsec for the N $_2$ ($C^3\Pi_u$, $v' = 0$) level; (40 ± 1) nsec for the N $_2$ ($C^3\Pi_u$, $v' = 1$) level, and (37.9 ± 1.8) nsec for the $B^2\Sigma_u^+$ ($v' = 0$) level of N $_2^+$.

Excitation transfer in two-body collisions from the argon atomic metastable levels to the $C^3\Pi_u$ levels of molecular nitrogen (second positive system of N $_2$ with strongest bandhead at 3371 Å) was first reported by one of the present authors (W.R.B.) some time ago.^{1,2} Interest in the problem at that time was twofold: (i) to get rid of the effect by removing nitrogen impurities in the noble gas samples to the point where spectra and excitation transfer processes could be studied in pure argon at high pressures (the excitation process was found to be so sensitive that trace amounts of nitrogen in "spectroscopically pure" gas samples dominated the entire ultraviolet spectrum at pressures in the order of one atmosphere); and (ii) to utilize the Ar-N $_2$ (and other) excitation transfer process as the basis of efficient gas scintillation counters for measuring the energy of radioactive charged particles stopping in the gas mixture. After the initial report of pulsed laser oscillation on the second positive bands in pure nitrogen by Heard,³ it was also suggested by Bennett that quasiresonant collisions with argon metastables could be used to enhance the operation of the uv nitrogen laser.⁴ The recent observations of enhanced oscillation on the uv nitrogen laser transitions through use of electron beam-pumped Ar-N $_2$ mixtures⁵⁻⁹ have renewed interest in cross section measurement for this resonant excitation transfer process. Quite a number of papers have now appeared reporting measurements of transfer cross sections between Ar(3P_2) metastables and the N $_2$ ($C^3\Pi_u$) vibrational levels.⁹⁻²² If taken at face value, there appear to be very substantial discrepancies among the different measurements of these transfer cross sections. In some instances the methods of analysis are of very dubious accuracy and depend on drastic oversimplification of the

actual experimental conditions.

Most precise studies of metastable deactivation cross sections have been based on the early methods of Biondi²³ and Phelps.²⁴ Typical experiments have involved monitoring the time dependence of the absorption of resonance radiation terminating on the metastable level in the afterglow of pulsed discharges containing gas mixtures. There are a number of serious practical limitations in this type of experiment: (i) One is forced to monitor small changes on a large background of resonance radiation and consequently, noise levels are inherently high and extreme sensitivity is not obtained. (ii) The transmitted radiation is sensitive to relative changes in source and absorber line shape. Hence, elaborate corrections to the data are required which are not always of certain reliability. (iii) Relatively large densities of charged particles and metastable states are produced in these discharges. These particles have relatively slow relaxation times under discharge conditions and typically limit the processes that may be studied to ones having time constants in excess of ≈ 10 μ sec. Hence, highly probable transfer reactions can only be studied at low partial pressures for the second gas component and the experiments are very sensitive to the effects of impurity contamination. Hence, although the pulsed discharge experiments have been useful in determining metastable diffusion coefficients, three-body destructive collision processes, and in identifying a number of excitation transfer processes, measurements of excitation transfer cross sections made in different experiments of this type have not all been consistent. Attempts to improve on these limitations by the adoption of flowing mixture experiments have resulted in analogous problems.¹⁸ The limits of error in such flow experi-

ments are frequently hard even to estimate. For example, the measurements in Ref. 18 are based on an approximate model of the flow problem, as well as the Mitchell and Zemansky approximate method for treating resonance absorption. In addition, the data were only obtained for variations in absorption over a relatively slight range and at only a few discrete points. More recently, crossed molecular beams studies have been reported of metastable deexcitation cross sections by Winicur and Fraites.²⁰ Although the beams experiments probably represent the cleanest experiments from an atomic physics point of view, they too have substantial practical limitations. Such experiments tend to be limited to moderately high relative particle velocities for the determination of thermal collision cross sections. In addition, the differential scattering cross sections are the directly measured quantities and must be integrated to obtain the total cross sections of interest in most laser systems. The net errors in total cross sections determined in that manner have typically been $\approx 30\%$ and, hence, much larger than those obtainable in principle from pulsed decay experiments of the type described in the present paper. Because interesting aspects of atomic physics might lie behind the apparent discrepancies among the different cross section measurements, it seemed desirable to repeat the $\text{Ar}(^3P_2)\text{-N}_2$ deactivation cross section measurement with a different, reasonably clean approach. It is our conclusion that many of the different cross section measurements are in reasonably good agreement if there is a substantial, but smooth, variation of the velocity-averaged cross section with gas temperature.

I. PRESENT METHOD

The present experimental method represents a modification of an earlier approach developed by Bennett²⁵ for the determination of radiative lifetimes and collision transfer cross sections to the first helium-neon laser (see Fig. 1). The primary differences from the earlier technique consist of the fact that the entire experiment is controlled by an on-line minicomputer for data acquisition and analysis and that time-interval measurements are made using a counter capable of responding directly at 500 MHz. A pulse generator applies periodic pulses to an electron gun with amplitude matched closely to the threshold energy of the initial state to be excited. The pulse amplitude is modulated slightly (≈ 0.2 eV) about the threshold value and data are stored in an add-subtract fashion so as to further minimize the detection of events gen-

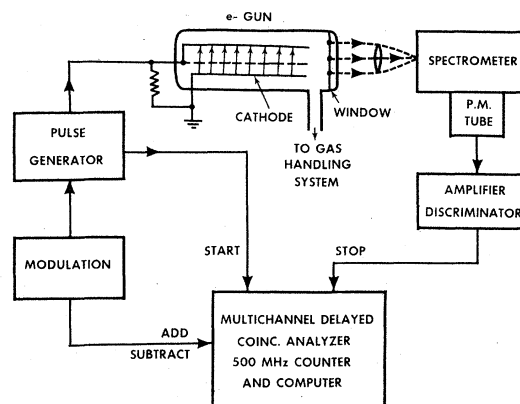


FIG. 1. Schematic diagram of the apparatus used for the measurement of excitation transfer cross sections and radiative lifetimes.

erated by levels falling significantly above threshold for the state under concern. The sharp decay (< 1 nsec) of the excitation pulse marks the start of a delayed multichannel coincidence interval. The end of the interval is defined by the occurrence of a photomultiplier tube pulse at the output of a high-resolution spectrometer tuned to a transition of interest. Reduction of the data to appropriate functional forms is accomplished with a Hewlett-Packard 2100 series minicomputer using the method of weighted least squares.²⁶

The main features of the experiment are illustrated schematically in the two-level model shown in Fig. 2. The level densities n_1 and n_2 are coupled through the equations

$$\begin{aligned} \dot{n}_1 &= -(\Gamma_1 + a_1)n_1 + a_{21}n_2, \\ \dot{n}_2 &= -(A_2 + a_2)n_2 + a_{12}n_1, \end{aligned} \quad (1)$$

after the short pulse of electron excitation is turned off. Here, the quantities are defined as stated in the caption to Fig. 2 with the addition that a_1 and a_2 represent the sums of all two-body

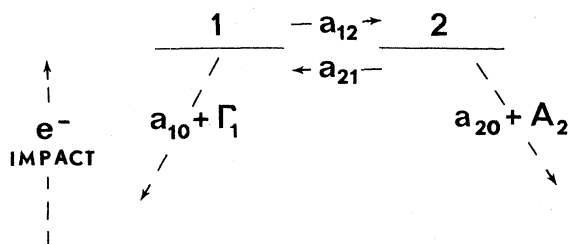


FIG. 2. Two-level collision transfer model used to analyze the present experiments. The metastable level (1) is excited by threshold energy electron impact. The process is detected by the total decay rate from level 2 using radiative decay at rate A_2 . Γ_1 is the diffusion rate of the metastable and a_1 , a_2 are collision destruction rates for levels 1 and 2.

collision destruction channels including the primary transfer rates of interest (a_{12} and its inverse a_{21}). The solutions for n_1 and n_2 are given by the sum of two exponential terms with decay rates

$$R_1 = \frac{1}{2}(\Gamma_1 + A_2 + a_1 + a_2) + \frac{1}{2}(\Gamma_1 - A_2) \times \left(1 + \frac{2(a_1 - a_2)}{(\Gamma_1 - A_2)} + \frac{(a_1 - a_2)^2 + 4a_{12}a_{21}}{(\Gamma_1 - A_2)^2}\right)^{1/2} \quad (2)$$

and

$$R_2 = \frac{1}{2}(A_2 + \Gamma_1 + a_2 + a_1) + \frac{1}{2}(A_2 - \Gamma_1) \times \left(1 + \frac{2(a_2 - a_1)}{(A_2 - \Gamma_1)} + \frac{(a_2 - a_1)^2 + 4a_{21}a_{12}}{(A_2 - \Gamma_1)^2}\right)^{1/2}$$

Expanding the exact solutions in Eqs. (2) through second-order terms in the pressure,

$$R_1 = \Gamma_1 + a_1 - \frac{3(a_1 - a_2)^2 + 16a_{12}a_{21}}{4(A_2 - \Gamma_1)} + O(a^3) \quad (\text{Slow}) \quad (3)$$

and

$$R_2 = A_2 + a_2 + \frac{3(a_1 - a_2)^2 + 16a_{12}a_{21}}{4(A_2 - \Gamma_1)} + O(a^3) \quad (\text{Fast})$$

Thus the decay of the radiating second component is described by the sum of a slow and a fast exponential component, and so long as A_2 is not at all comparable to Γ_1 , a linear pressure dependence of the slow decay rate at low pressures occurs which permits a precise determination of the collision transfer cross section. The coefficients $a_1 = a_{10} + a_{12}$ involve the appropriate ground-state densities, relative velocities, and velocity averaged cross sections. Specifically,

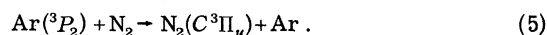
$$a_{12} = 0.81 \times 10^6 P_2 \sigma_{12} \left[\left(\frac{300}{T} \right) \left(\frac{M_1 + M_2}{M_1 M_2} \right) \right]^{1/2} \text{sec}^{-1}, \quad (4)$$

where P_2 is the partial pressure of the second component in Torr, σ_{12} is the cross section for rate a_{12} expressed in units of 10^{-16} cm 2 , M_1 and M_2 are the masses of the two gas components expressed in amu, and T is the absolute temperature. In some instances, "level 2" must be regarded as any group of electronic levels of the second gas component which is in close (for example, ≈ 0.5 eV) energetic coincidence for energy transfer from level 1. Under these circumstances σ_{12} represents a total transfer cross section to the group of levels involved. However, it then becomes especially important to take data at low enough pressures to insure the absence of quadratic pressure dependent terms in the excited state decay rates. (Most data previously reported in the literature of such two-component gas systems have been extracted in a manner which totally ignores these fundamental requirements on

pressure, not to mention equally important requirements on selective excitation of the initial state.) Except in the case of Penning ionization, the destructive collision rate through non-resonant channels (i.e., the rate a_{10}) tends to be negligible at low pressures.

II. RESULTS FOR Ar-N $_2$ MIXTURES

As an example of the method, consider the excitation of the second positive (uv laser) bands of N $_2$ by collision with argon metastables in argon-nitrogen mixtures. The primary excitation reaction is



Representative data for this reaction taken with our apparatus are shown in Fig. 3 where the time-dependent decay of the $C^3\Pi_u$ ($v' = 0$) level of N $_2$ is shown when excited by Ar(3P_2) metastables in an Ar-N $_2$ mixture. As is readily seen from the data, the level decay is clearly characterized by two widely different decay rates after the electron pulse is turned off. The slow component decay rates were extracted using a least-squares fit to a functional form consisting of the sum of two exponential decaying terms plus a background constant. Values for the decay rates of the slow component are shown in Fig. 4 as a function of nitrogen partial pressure, for constant argon pressure (1.66 Torr) and temperature (663°K). From Eq. (4) we then extract values of the excitation trans-

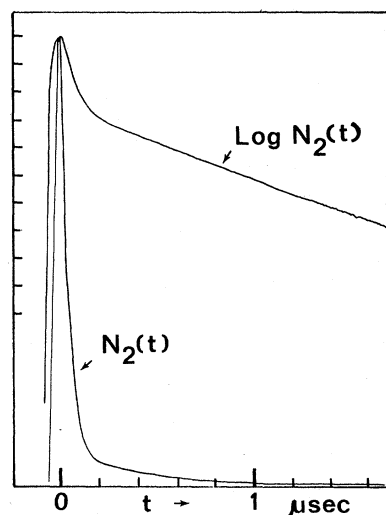


FIG. 3. N $_2$ ($C^3\Pi_u$) ($v' = 0$) as a function of time (from 3371 Å) after threshold energy electron pulse for Ar(3P_2) metastable is turned off in Ar-N $_2$ mixture. (Ar at 1.2 Torr and N $_2$ at 1.4 Torr at 663°K.) Both the signal and log of the signal are shown plotted against time. (The fiducial marks on the vertical axis represent $1/e$ points for the log plot.)

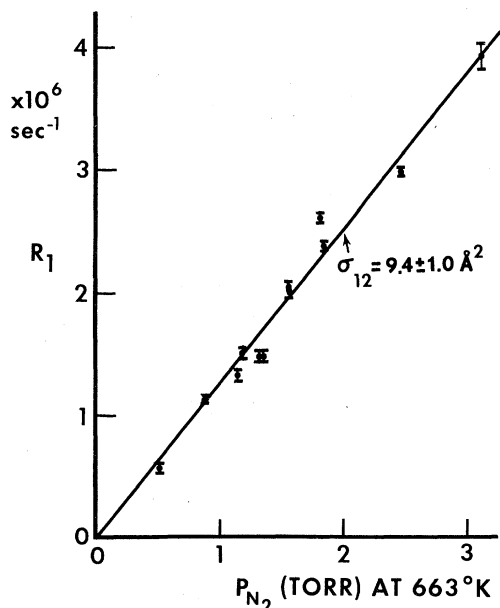


FIG. 4. Variation of the decay rate of the slow exponential component extracted from data such as that in Fig. 3, shown as a function of nitrogen partial pressure. The straight line corresponds to an excitation transfer cross section from the Ar metastables of $9.4 \pm 1.0 \text{ \AA}^2$. (Error bars are standard deviations in least-squares fit and the cross-section error quoted represents 2σ in a fit of all the data points to a straight line.)

fer cross section from the argon metastables. The results imply a cross section of $9.4 \pm 1.0 \text{ \AA}^2$ for the transfer reaction. We believe that this is the most accurately determined value for this cross section to date.

A few words are in order regarding the identity of the initial and final levels of the two-level transfer model as applied to the present experiment. The electron energy spread in our electron gun ($\approx 0.2 \text{ eV}$) is only marginally capable of resolving the Ar(3P_2) metastable from the other argon levels in the same configuration. However, recent high-resolution electron energy-loss spectroscopy has shown that even at energies significantly above the threshold for exciting all four levels in this configuration, the cross section for the Ar(3P_2) is substantially larger than those for the Ar(3P_1 , 3P_0 , or 1P_1).²⁷ Hence the identity of the initially excited state as the Ar(3P_2) metastable is fairly well established. Strictly speaking, the results for the present cross-section measurement should be regarded as a total deactivation cross section for the Ar(3P_2) in Ar- N_2 collisions. However, under the present conditions of low pressure and electron density, essentially nothing other than transfer to the $N_2(C^3\Pi_u)$ vibrational levels can occur with signifi-

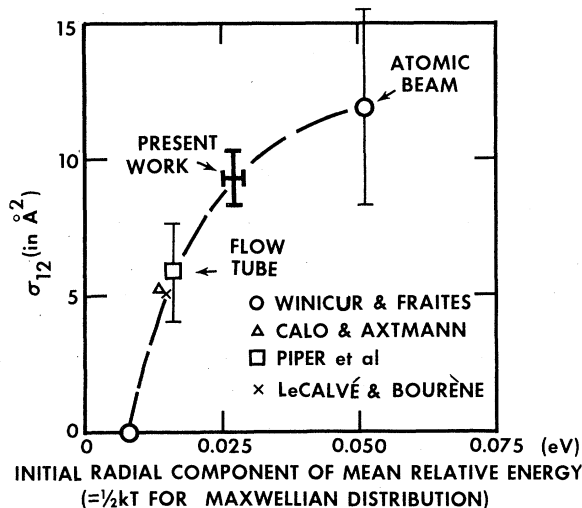


FIG. 5. Excitation transfer cross section for Ar(3P_2)- N_2 collisions as a function of energy. References quoted are Winicur and Fraites (Ref. 20), Piper *et al.* (Ref. 18), Calo and Axtmann (Ref. 15), and LeCalvé and Bourène (Ref. 19).

cant probability (see the more extended discussion in Ref. 2). Hence we are substantially certain that the cross section measured in Fig. 4 does indeed represent the total cross section for reaction (5). However, the excitation transfer is spread over the rotational and (to a lesser extent) the vibrational levels of $N_2(C^3\Pi_u)$ electronic state in the reaction. Our results indicate that the transfer is roughly governed by a Frank-Condon factor for $v'=0$ and 1 (see Ref. 2). However, the production of vibrational levels for $v > 1$ was not carefully monitored.

A comparison with other measured values for the transfer cross section is given in Fig. 5. The different measurements imply a large variation of the cross section with mean relative initial energy, hence gas temperature. The results for the cross section are expressed in Å^2 and are shown plotted as a function of the mean relative energy of the radial component of the motion as seen initially in the center of mass system. This relative kinetic energy is simply $\frac{1}{2}kT$ when both gas components have Maxwellian velocity distributions at the same temperature. This method of expressing the data was needed to permit comparison with the cross section obtained from the crossed atomic beam experiment and is done in the same manner as portrayed in Ref. 20. It is tempting to speculate that the large increase in effective cross section with temperature implied by the results in Fig. 5 occurs due to a potential bump in the surface representing the electronic energy between the colliding particles. For ex-

ample, if there were a potential bump of magnitude E_0 , a simple classical analysis would imply that only some fraction f of colliding molecules would have enough energy to overcome the bump, where

$$f \approx \exp(-E_0/\frac{1}{2}kT)$$

and T is the gas temperature. Depending on the size of the bump, order of magnitude increases in effective excitation transfer rate could be obtained simply by heating the gas. This sort of interpretation was used previously to explain observed changes in magnitude of the excitation transfer cross section pertinent to the helium-neon laser by Jones *et al.*²⁸ Indeed, the presence of such bumps could lead in some instances to the use of barrier tunneling as an efficient pump for exciplex laser systems.²⁹ However, there are reasonably well-established cases in which large increases in transfer rate coefficients occur with temperature and in which no maxima in the pertinent potential energy curves are believed to exist.³⁰⁻³²

III. RADIATIVE LIFETIMES OF MOLECULAR NITROGEN LEVELS

The zero-pressure intercept of the fast decay component in Eq. (3) should correspond to the radiative lifetime of the particular nitrogen level if the transfer model is correct. In order to have an accurate basis for comparison, the radiative lifetimes of several N₂ molecular levels were directly measured in pure nitrogen samples at pressures ranging from about 0.05 to 5 Torr.

TABLE I. Radiative lifetimes for several N₂ molecular levels.

State	Lifetime (nsec)	Monitoring transition
C ³ Π _u (v'=0)	37.6±1	3371 Å
C ³ Π _u (v'=1)	40 ±1	3159 Å
B ² Σ _u ⁺ (v'=0)	37.9±1.8	3914 Å

Values were again measured at threshold energy for the state and the lifetimes were determined from the zero pressure intercepts of the decay rates. The results obtained for several N₂ states are summarized in Table I. (Included in Table I is the radiative lifetime for the upper level of the N₂⁺ laser at 3914 Å, which incidentally is excited strongly by various metastable carriers of energy in helium-nitrogen mixtures.^{1,2}) Substantial differences occur between the values in Table I and previously reported measurements which we attribute to systematic errors from radiative and collision cascade in the earlier work.³³ The zero-pressure intercepts of the fast decay component in our Ar-N₂ measurements agreed with the corresponding values in Table I within the errors of the two-component reduction.

ACKNOWLEDGMENT

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