

ENERGY TRANSFER FROM ELECTRON-BEAM EXCITED ARGON TO NITROGEN AND POPOP DYE VAPOR

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Excitation transfer processes have been studied in electron-beam pumped binary Ar-POPOP and ternary Ar-N₂-POPOP mixtures. Fluorescence measurements have shown that the major POPOP dye vapor excitation source is the ionic species Ar₂⁺. A previously unreported quenching reaction by N₂ in the Ar-N₂ system has been discovered.

1. Introduction

Since the first observation of electron-beam excited superradiant emission from the organic dye POPOP in the vapor phase buffered by high-pressure pure argon [1], there has been considerable interest in developing this system into an efficient and powerful UV-visible tunable laser [2,3]. In order to establish optimum electron-beam excitation conditions for the organic dye vapor-buffer gas mixture, an understanding of possible energy-transfer processes is necessary. In the present work the energy-transfer processes of Ar-POPOP have been studied and compared to the well-known formation kinetics scheme of Ar-N₂ [4,5]. The species responsible for channeling electron-beam energy into the upper singlet levels of POPOP has been identified, and a number of pertinent reaction rate constants for various energy-transfer processes have been estimated. In addition, a hitherto unreported quenching mechanism in the Ar-N₂ system has been identified.

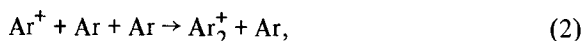
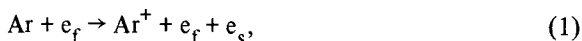
2. Experimental

The apparatus and procedures used in these experiments are essentially the same as those described in ref. [6]. Transverse electron-beam excitation of the gas mixture is obtained with an electron-beam pulse of 1 MeV electrons with a total input energy of 100 J. This energy is coupled into a high-pressure, high-temperature reaction cell through a 0.002 inch thick titanium window of 10 cm² cross-sectional area. The beam-current density behind the foil is 0.7 kA/cm². Faraday cup measurements show that the temporal behavior of the beam current can be well represented by the equation $I = I_0 t \exp(-t/\tau)$, with $\tau \approx 5$ ns. The fluorescence behavior is monitored using either a vacuum photodiode-transient digitizer combination or a grating monochromator to obtain wavelength-integrated POPOP and N₂ fluorescence characteristics. The overall time resolution is better than 1 ns. All experiments using mixtures containing POPOP are performed at 300°C. Such high temperatures are

necessary in order to produce a sufficiently high POPOP vapor pressure.

3. Energy transfer in Ar-N₂ mixtures

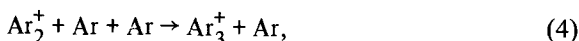
The energy transfer scheme for the excitation of N₂(C³Π_u) in Ar-N₂ mixtures has been discussed in detail by Lorents [7]. All of the experiments reported in this paper were performed using mixtures containing 99% Ar and less than 1% N₂, at total pressures of 1 to 5 atm. Fluorescence was monitored for only 120 ns following electron beam initiation. Under these conditions, the major mechanism leading to excitation of N₂(C³Π_u) is:



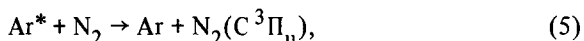
$$k_2 = 2.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1} [4];$$



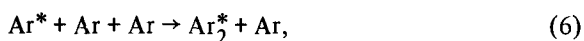
$$k_3 = 3.5 T_e^{-0.67} \times 10^{-5} \text{ s}^{-1} [4];$$



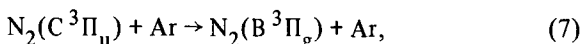
$$k_4 \approx 10^{-31} \text{ cm}^6 \text{ s}^{-1} [8];$$



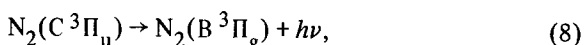
$$k_5 = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} [4];$$



$$k_6 = 10^{-32} \text{ cm}^6 \text{ s}^{-1} [4];$$



$$k_7 = 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} [4];$$



$$k_8 = 2.5 \times 10^7 \text{ s}^{-1} [4].$$

In this mechanism the symbol e_f is used to represent electrons with energies of approximately 1 MeV. These electrons lose a small fraction of their energy in collisions [9], to form argon ions, secondary electrons (e_s), with an average energy of ≈ 6.9 eV [7],

and excited argon atoms [10]. The initial ion and secondary electron density is roughly a linear function of the argon pressure. Approximately 20% of the excitation is funneled directly into excited states of neutral argon [7].

The initial product of reaction (3) is probably the highly energetic state, Ar(3p⁵4p) [7]. This state is rapidly quenched by argon atoms and electrons to Ar(3p⁵4s). Four states have this electron configuration: two metastables, ³P₂ and ³P₀, which are designated Ar* in the above mechanism, the resonance state ¹P₁, and the short-lived ³P₁ state.

Kinetic modeling of the temporal behavior of Ar-N₂ mixtures containing a fixed constant pressure of 0.076 Torr N₂ and various pressures of argon was performed using the above mechanism, and excellent agreement with experiment is obtained when literature rate constants are used [4], and when Ar* is assumed to be formed instantly by the electron beam. This latter assumption allows the model to be solved analytically to yield:

$$[\text{N}_2(\text{C}^3\Pi_u)] = [ck_5(\text{N}_2)(\text{Ar})/(b-a)](e^{-at} - e^{-bt}),$$

where $a = k_5(\text{N}_2) + k_6(\text{Ar})^2$, $b = k_7(\text{Ar}) + k_8$, and c is a constant. The level of agreement between experiment and the predictions of the model is illustrated in fig. 1. As can be seen, N₂ fluorescence is most intense for the mixture containing 2 atm argon.

Some understanding of the various factors that affect the fluorescence pulse shape was obtained as a result of the modeling study. The approach of the N₂ fluorescence to its maximum value depends principally on the rate of the reactions removing N₂(C³Π_u). In contrast, the fluorescence decay is most strongly affected by the rate of removal of the atomic argon metastables Ar*(3p⁵4s¹). The fluorescence peak maximizes at an argon pressure of approximately 2 atm, because at this pressure a rough balance is reached between the formation of Ar*, a process that is linear in argon concentration, and its removal by reaction (6), the rate of which depends on the square of the argon concentration.

A number of experiments were performed at constant argon pressure, in which the N₂ partial pressure was varied from 1 to 15 Torr. Over this range the peak fluorescent intensity, extracted from intensity/time curves, is predicted by the above mechanism to be proportional to the partial pressure of N₂. However,

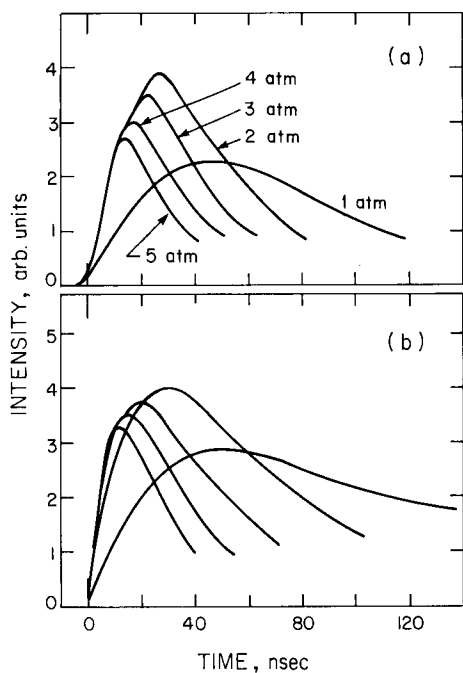


Fig. 1. The intensity of N_2 fluorescence [$C(^3\Pi_u) - B(^3\Pi_g)$] as a function of time for a number of Ar- N_2 mixtures containing a fixed pressure of nitrogen (0.8 Torr) and various pressures of argon. The upper curves (a) are measured; the lower curves (b) are calculated from the model described in the text.

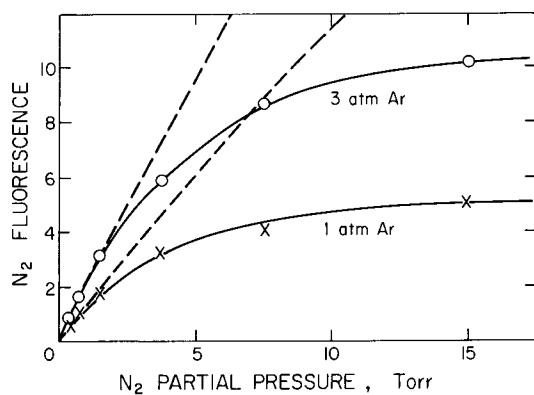


Fig. 2. The maximum intensity of N_2 fluorescence (taken from intensity-time curves) plotted as a function of N_2 partial pressure for two fixed argon pressures (1 and 3 atm). The solid lines are drawn through experimental measurements. The dashed lines represent predictions of the model set forth in the text.

the actual variation of the intensity with N_2 partial pressure was not as predicted, but was found to be as shown in fig. 2. At N_2 pressures in excess of 1.5 Torr, the fluorescence ceased to be linear in N_2 , but instead asymptotically approached a maximum value. Further experiments showed that the peak intensity changed little as the nitrogen partial pressure was increased from 15 to 150 Torr. This behavior can be explained most easily by assuming that a precursor of Ar^* is quenched by N_2 . Further support for such a quenching mechanism was obtained from the study of Ar- N_2 -POPOP ternary mixtures described in section 5.

4. Studies of Ar-POPOP mixtures

Total fluorescence was monitored as a function of reaction time for several mixtures containing 1 Torr POPOP and varying pressures of argon, ranging from 1 to 5 atm. The shape of the fluorescence pulse was found to be identical for all mixtures studied. The pulse rose to a maximum value at approximately 6 ns, and then decayed in an exponential fashion. Its half-width was measured as 11–12 ns. The peak fluorescence intensity varied from mixture to mixture as the argon pressure was changed, rising to a maximum value for mixtures containing 4 atm, then decreasing by 10% as the pressure was further raised to 5 atm.

Since the spontaneous decay time of POPOP ($\tau \approx 1$ ns) [2] is much shorter than the pulse width of the observed fluorescence, the pulse shape must mirror that of the precursor species that transfers energy to POPOP. Now POPOP fluorescence occurs on a timescale that is much shorter than that of the N_2 fluorescence described in section 3. In fact, its pulse shape is very similar to that of the e-beam excitation pulse. Thus the metastable neutrals, $Ar^*(3p^5 4s^3 P_{2,0})$ and Ar_2^* , cannot possibly be excitation sources for POPOP since these metastables have lifetimes of as much as 50–100 ns in mixtures containing 1–2 atm argon.

Other possible excitation sources of POPOP can be divided into two classes: (a) the charged species, among which are Ar^+ , Ar_2^+ and hot secondary electrons, and (b) the short-lived neutrals. In this latter class are the highly energetic atoms, $Ar(3p^5 4p)$, and the argon resonance state, $Ar(3p^5 4s^1 P_1)$. A distinc-

tion between the two classes of excitation source was made by adding small amounts of SF₆ (0.6 Torr) to mixtures containing 1 Torr POPOP and 2 atm argon. SF₆ is known to be a very efficient scavenger of thermal electrons [11]. Therefore, its presence retards the progress of the dissociative recombination reaction, Ar₂⁺ + e → Ar* + Ar, which is the major source of excited neutrals under the conditions of the experiments reported in this paper. This effect of SF₆ has been demonstrated previously by LeCalvé and Bourene [12] who have shown that the intensity of fluorescence from N₂(C³Π_u) in e-beam excited Ar–N₂ mixtures is significantly reduced by the addition of 0.01% SF₆.

In our experiments the addition of 0.6 Torr SF₆ to Ar–POPOP mixtures increased the peak intensity of POPOP fluorescence by 20–30%. In addition, the fluorescence pulse width was slightly lengthened. By comparison, the addition of a similar amount of SF₆ to a mixture containing 1 Torr N₂ and 2 atm argon, at 300°C, decreased the N₂(C³Π_u) fluorescence to one-third of its original value. These experiments conclusively show that POPOP is not excited by the short-lived neutrals formed as a result of dissociative recombination, but instead is excited by one of the electrically charged species.

The slight enhancement of POPOP fluorescence in the presence of SF₆ suggests that the most likely excitation source is Ar₂⁺. In the presence of SF₆, three-body ion–ion recombination with SF₆ will replace reaction (3) as the major loss mechanism for Ar₂⁺. The rate of this reaction has not been measured, but a rough estimate of it can be made, based on a recent calculation for the reaction, Ar₂⁺ + F' + Ar → Ar₂F* + Ar. At room temperature the rate of this latter reaction has been determined as (1–3) × 10⁻⁶ cm³ s⁻¹ [13]. Since the appropriate theory predicts that the rate of three-body ion–ion recombination should have a temperature dependence on the order of T^{-5/2} to T^{-7/2}, and should decrease with increasing mass of the ionic collision partners [14], the rate constant for the reaction with SF₆, at 300°C, can be estimated as (1–3) × 10⁻⁷ cm³ s⁻¹. Therefore, the rate of this reaction is probably somewhat slower than the rate of the reaction of Ar₂⁺ with those "thermal" electrons that are captured by SF₆. If this is true, then the concentration of Ar₂⁺ would be increased by the addition of SF₆. It is difficult to

imagine how the concentration of Ar⁺ or of hot secondary electrons could be anything but decreased in the presence of SF₆.

The hypothesis that POPOP is excited by Ar₂⁺ is supported by the observation that POPOP fluorescence maximizes in mixtures containing 4 atm argon. Computation performed using the mechanism and rate constants given in section 3 showed that the peak concentration of Ar₂⁺ maximizes in mixtures containing 4 atm argon if the initial concentration of secondary electrons is taken to be 2.5 × 10¹⁵ (Ar) cm⁻³ atm⁻¹, and the electron temperature is such that k₃ ≈ 10⁻⁷ s⁻¹. Both are reasonable values for this type of e-beam experiment. By contrast, the peak concentration of Ar⁺ steadily decreased from mixture to mixture as the total argon pressure increased from 1 to 5 atm. Unfortunately, the behavior of the hot secondary electrons is somewhat uncertain, since the reaction of such electrons with Ar₃⁺ has not been studied, and the precise influence of argon on the electron temperature is unknown.

From the above discussion, it is clear that POPOP is not excited by Ar⁺, short-lived argon neutrals, Ar* or Ar₂^{*}. Its most likely excitation source is Ar₂⁺, although excitation by hot secondary electrons cannot be entirely ruled out.

5. Ternary Ar–N₂–POPOP mixtures

The fluorescence observed when a mixture containing 1 Torr POPOP, 0.5 Torr N₂ and 4 atm argon was excited by the electron beam, is shown in fig. 3. Two time-resolved peaks were identified. Independent spectral measurements showed that these were separately produced by the two minority components: The first peak was produced by POPOP, the second by N₂. Since the POPOP fluorescence occurred before that from N₂, optical excitation of POPOP via radiative pumping by N₂ could not have taken place.

In ternary mixtures the dependence of the N₂ fluorescence on the partial pressures of N₂ and Ar was found to be identical to that observed, at 300°C, for binary Ar–N₂ mixtures[‡]. However, the addition

[‡] At 300°C, the N₂ fluorescence pulse width was somewhat larger than that observed at room temperature. The reason for this change is that the third-order rate constant k₆ decreases as the temperature is raised.

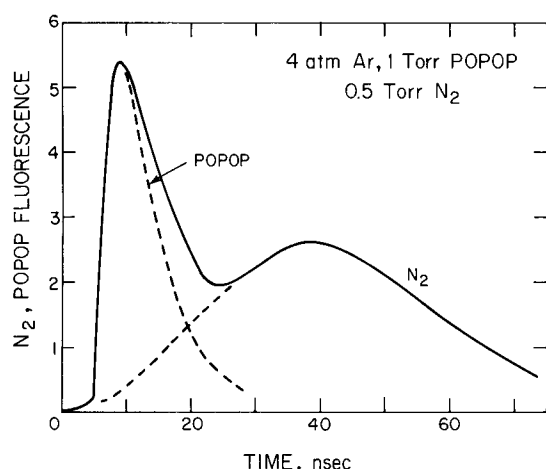


Fig. 3. Temporal fluorescence characteristics of an Ar-N₂-POPOP mixture.

of 1 Torr POPOP reduced the overall intensity of N₂ fluorescence by a factor of two. POPOP fluorescence behaved in a complementary manner. Its pulse shape and the dependence of its intensity on argon pressure were unaltered by the presence of N₂, but its overall intensity was decreased by a factor of two when 1–3 Torr of N₂ was added to Ar-POPOP mixtures.

These observations can be readily interpreted if N₂ reduces the intensity of POPOP fluorescence by reacting with either its excitation source Ar₂⁺, or with a precursor of it, to produce a species that does not transfer energy to the dye. Since only 1–3 Torr of N₂ are required to significantly reduce POPOP fluorescence, the quenching reaction must have a rate constant of $(1-3) \times 10^{-9} \text{ cm}^{-3}$. It should be noted that a quenching reaction of this speed would account quantitatively for the saturation behavior displayed in fig. 2. Therefore, the observation that N₂ quenches POPOP fluorescence, reinforces the finding that N₂ reacts with a precursor of Ar* in Ar-N₂ mixtures.

Significant quenching cannot occur as a result of the reaction of N₂ with Ar⁺ since this reaction is known to be very slow [15]. It possibly occurs as a result of the reaction, $\text{Ar}_2^+ + \text{N}_2 \rightarrow \text{ArN}_2^+ + \text{Ar}$. The ion ArN₂⁺ has been observed previously in Ar-N₂ systems [16]. In such systems its appearance potential has been shown to be identical to that of Ar₂⁺, and its concentration, relative to that of Ar₂⁺, has been shown to be linearly dependent on the partial pres-

sure of N₂ [16]. In addition, Ar₂⁺ is known to react rapidly with many molecules. Rate constants of $\approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ have been measured for reactions with CO₂ [17] and with H₂O [18].

Acknowledgement

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References

- [1] G. Marowsky, R. Cordray, F.K. Tittel and W.L. Wilson, *Appl. Phys. Letters* 32 (1978) 561.
- [2] P.W. Smith, *Opt. Acta* 23 (1976) 901.
- [3] G. Marowsky, R. Cordray, F.K. Tittel, W.L. Wilson and C.B. Collins, *Appl. Phys. Letters* 33 (1978) 59.
- [4] R.M. Hill, R.H. Gutcheck, D.L. Huestis, D. Mukherjee and D.C. Lorents, Stanford Research Institute Report No. MP74-39 (1974).
- [5] V. Puech, F. Collier and Pl. Cottin, *J. Chem. Phys.* 67 (1977) 2887.
- [6] G. Marowsky, R. Cordray, F.K. Tittel and W. Wilson, *Appl. Opt.* (Nov. 1978) 17.
- [7] D.C. Lorents, *Physica* 82C (1976) 19.
- [8] D.K. Bohme, D.B. Dunkin, F.C. Fehsenfeld and E.E. Ferguson, *J. Chem. Phys.* 51 (1969) 863.
- [9] M.J. Berger and S.M. Seltzer, Tables of Energy Losses and Ranges of Electrons and Positrons, Report N65-1206, NASA, Washington, D.C.
- [10] L.R. Peterson and J.E. Allen, *J. Chem. Phys.* 56 (1972) 6068.
- [11] L.G. Christophorou, D.L. McCorkle and J.G. Carter, *J. Chem. Phys.* 54 (1971) 253; R.K. Curran, *J. Chem. Phys.* 38 (1973) 1446.
- [12] J. Le Calvé and M. Bourene, *J. Chem. Phys.* 58 (1973) 1446.
- [13] M.R. Flannery and T.P. Yang, *Appl. Phys. Letters* 32 (1978) 326, 356.
- [14] J.B. Hasted, *Physics of atomic collisions* (Butterworths, London, 1964) p. 274; G.L. Natason, *Zh. Tekh. Fiz.* 29 (1959) 1373.
- [15] F. Howorka, *J. Chem. Phys.* 68 (1978) 804; N.G. Adams, D.K. Bohme and E.E. Ferguson, *J. Chem. Phys.* 52 (1970) 5101.
- [16] M.S.B. Munsen, F.H. Field and J.L. Franklin, *J. Chem. Phys.* 37 (1962) 1790.
- [17] D.K. Bohme, N.G. Adams, M. Mosesman, D.B. Dunkin and E.E. Ferguson, *J. Chem. Phys.* 52 (1970) 5094.
- [18] R.C. Bolden and N.D. Twiddy, *Faraday Discussions Chem. Soc.* 53 (1972) 192.