

ELECTRONIC ENERGY TRANSFER BETWEEN METASTABLE ARGON ATOMS AND GROUND-STATE OXYGEN ATOMS

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The transfer of electronic energy between metastable argon and ground-state oxygen atoms has been studied in a discharge-flow apparatus. The excitation energy of the argon metastables is transferred to the $3p\ ^3P$ state of atomic oxygen with a cross section of $3\ \text{\AA}^2$. The energy transfer is discussed in terms of an ionic-intermediate, curve-crossing mechanism for which the calculated cross section is $13\ \text{\AA}^2$.

1. Introduction

Recent studies on electronic energy transfer indicate that a variety of mechanisms govern the energy transfer process; and therefore that each system needs to be examined individually before an appropriate mechanism may be proposed [1–3]. We wish to relate an experimental and theoretical study on the rate of transfer of electronic energy from metastable argon atoms (3P_2 , 11.55 eV) to ground-state oxygen atoms (3P_j). Not only do our results contribute to energy-transfer studies by supplying a reasonable theory to correlate our experimental observations, but also they elucidate the excitation mechanism of the Ar–O₂ laser [4], and confirm that energy transfer in an Ar/O₂, microwave-discharge, resonance lamp contributes to the anomalous absorption behavior of OI ($2\ ^3P_{2,1,0} - 3s\ ^3S_1$) [5, 6].

2. Experimental

Our apparatus was a discharge-flow reactor similar to others used in this laboratory [7, 8]. A flow of argon was passed through a hollow-cathode dc discharge

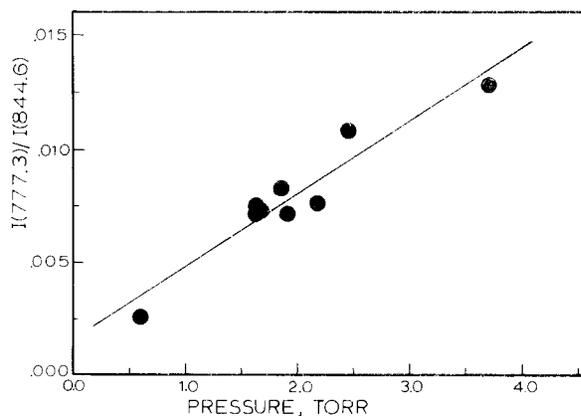


Fig. 1. Variation of the O($3p\ ^5P - 3s\ ^5S$)/O($3p\ ^3P - 3s\ ^3S$) intensity ratio versus argon pressure. The line shown is the least square fit to the points.

which converted some of the argon into 3P metastables. A microwave discharge in a flow of less than 1% O₂ in Ar produced ground-state O atoms. The reactant flows entered the observation region of the flow tube coaxially and were mixed by diffusion. Spectral observations (200–900 nm) were made normal to the gas flow with a 0.75 m Jarrell–Ash, Czerny–Turner scanning monochromator which was equipped with an EMI 9558QA photomultiplier and SSR photon-counting rate meter.

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Table 1
Rate constants for formation and quenching of $O(3p^3P_J)$

Process ^{a,b)}	Rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Cross section ^{c)} (\AA^2)
$\text{Ar}^*(^3P_2) + O(2p^4\ ^3P_J) \rightarrow O^*(3p^3P_J) + \text{Ar}(^1S_0)$	$(2.3 \pm 0.6) \times 10^{-11}$	3.1
$O^*(3p^3P_J) + \text{Ar}(^1S_0) \rightarrow O^*(3p^5P_J) + \text{Ar}(^1S_0) + \Delta E$	$(2.8 \pm 0.4) \times 10^{-12}$	0.37

a) All measurements, as well as calculations for the cross section are for a temperature of 295 K.

b) No distinction is made between multiplet levels for any of the $O(^3P)$ states, i.e., the rate constant refers to the sum of all multiplet levels.

c) Derived by dividing the measured rate constant by the mean relative velocity of the reactants.

3. Results

3.1. Experiment

Only two transitions of atomic oxygen were observed, the $3p^3P_J - 3s^3S_1$ multiplet at 844.6 nm and the $3p^5P_J - 3s^5S_2$ multiplet at 777.3 nm. Because emission intensities from the multiplets were weak, individual lines within them were not resolved. The ratio of emission intensity from the 5P states to that from the 3P states was pressure dependent (fig. 1) and had an intercept which did not differ significantly from zero. Thus the 5P levels of oxygen were populated by quenching of $O^*(3p^3P)$ by ground-state argon rather than by a primary excitation of ground-state oxygen atoms by argon metastables. A steady-state kinetic analysis gives

$$\frac{I(O^* 3p^5P)}{I(O^* 3p^3P)} = \tau_1 k_a [\text{Ar}], \quad (1)$$

where τ_1 is the lifetime of the $O^*(3p^3P)$ level (35.7 ns) [9] and k_a is the rate constant for the deactivation of $O^*(3p^3P)$ by Ar. The experimental data indicate that $k_a = (2.8 \pm 0.4^\dagger) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (table 1).

The rate constant for the quenching of metastable argon by atomic oxygen was measured by comparing the relative O^* and Kr^* emission intensities when a small amount of krypton was added to the argon-oxygen mixture. We have assumed that the quenching of $\text{Ar}^*(^3P_2)$ by Kr, which proceeds with a rate constant of $6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [1], results only in emission of krypton (from the $5p(1\frac{1}{2})_{1,2}$ levels [10]).

[†] Standard deviation of slope.

A steady-state kinetic analysis gives

$$k_Q(O) = \frac{I(O^* 3p^3P)}{I(\text{Kr}^*)} \frac{[\text{Kr}]}{[\text{O}]} k_Q(\text{Kr}). \quad (2)$$

The main uncertainty in the experimental parameters lies in the determination of the oxygen-atom concentration. This quantity was inferred from a reasonable estimate of the degree of dissociation of molecular oxygen produced by the microwave discharge. Elias et al. [11] determined that the extent of dissociation in a microwave discharge of an O_2/Ar mixture increases as the molecular-oxygen concentration in the mixture decreases, up to 85% dissociation for very low concentrations of oxygen in argon. Consequently, we have assumed 85% dissociation to calculate the atomic-oxygen concentration in the reaction zone. Two mixtures containing different ratios of oxygen to krypton gave $k_Q(O) = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Uncertainties in the parameters in eq. (2), principally the oxygen-atom concentration (15%), and the rate constant for quenching $\text{Ar}^*(^3P_2)$ by Kr (20%) [1], require error limits of $\pm 25\%$ to be placed upon $k_Q(O)$.

3.2. Calculation

We have calculated cross sections for the quenching of metastable argon by ground-state oxygen atoms using the ionic-intermediate, curve-crossing mechanism as developed by Fisher and co-workers [3]. This mechanism proposes that the reactant and product channels are coupled via charge-transfer reactions on to and off an ionic curve (fig. 2). The probability of crossing at each intersection of potential curves is calculated from Landau-Zener theory using the Hasted-Chong correlation [12] to approximate the matrix

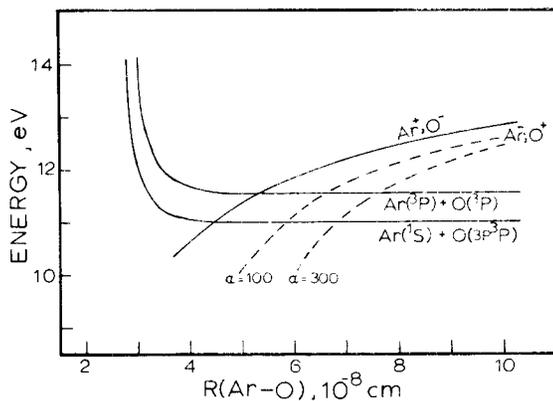


Fig. 2. Potential energy diagram for the interaction of $\text{Ar}(^3\text{P}_2)$ with $\text{O}(^3\text{P})$. The Ar^+-O^- and Ar^--O^+ limits are 14.3 and 14.1 eV, respectively. The dotted lines are the coulomb curves for Ar^--O^+ with the two values of the polarizabilities (\AA^3) of Ar^- as shown. The Lennard-Jones parameters were $C_6 = 138 \times 10^{-60}$ erg cm^6 and $\sigma = 5.05$ \AA for Ar^--O and $C_6 = 132 \times 10^{-60}$ erg cm^6 and $\sigma = 4.55$ \AA for $\text{Ar}-\text{O}^+$. The crossing points were 5.32 and 4.44 \AA for Ar^--O and O^--Ar , respectively, by Ar^+-O^- and 6.60 and 5.81 \AA for crossing by Ar^--O^+ with $\alpha = 100 \text{\AA}^3$ and 7.62 and 6.83 \AA for crossing by Ar^--O^+ with $\alpha = 300 \text{\AA}^3$.

element for the interaction between the two curves at the crossing point. Modification of the Landau-Zener probability of crossing onto the ionic curve from the entrance channel is required because only a limited fraction of input configurations ($\approx 22\%$ for an Ar^+O^- intermediary and $\approx 7.5\%$ for an intermediary of Ar^-O^+) will have the proper molecular symmetry to undergo adiabatic behavior at both crossing points. The total quenching probability in the two crossing-point case can be calculated analytically [3].

An obvious choice for the ionic-coupling curve is not apparent because an Ar^-O^+ curve involves the unstable species Ar^- , whereas the Ar^+O^- curve couples with the exit channel through a two-electron process. Recent work on the Penning ionization of Cd, Hg and Ba by metastable helium [13-15], shows that formal two-electron processes do occur, although with reduced cross sections. Configuration interaction between the 2p and 3p levels of oxygen may make the Ar^+O^- pathway viable. We have calculated cross sections for both intermediate curves.

The potential energy functions for the neutral curves are the Lennard-Jones 12-6 potentials in

which C_6 was calculated from the Slater-Kirkwood approximation and σ values were estimated as outlined in Hirschfelder and Eliason [16], but reduced by 30% [1]. Unknown polarizabilities were calculated by the method of Slater as outlined in Hirschfelder et al. [17]. This method gives polarizability for Ar^- of 300\AA^3 which seems unusually large. We have made calculations with this value as well as some with a smaller value of 100\AA^3 . The ionic curves include only the coulombic and ion-induced-dipole terms. The electron affinity of metastable argon is unknown, but has been estimated [18] to be 0.5 eV less than the excitation energy of metastable argon.

Our calculations give cross sections of 13\AA^2 for quenching via the Ar^+O^- intermediary, 0.003\AA^2 for quenching via Ar^-O^+ with $\alpha = 300 \text{\AA}^3$, and 0.25\AA^2 for the latter intermediary but with a polarizability of 100\AA^3 . Since a formal two-electron process is expected to occur with a reduced cross section relative to what would be expected using Hasted-Chong values for the interaction matrix element, our experimental value of 3\AA^2 is in reasonable accord with the value of 13\AA^2 calculated for the Ar^+O^- intermediary. The other intermediary leads to unrealistic values regardless of the polarizability assumed for Ar^- . Excitation of the $3p \ ^5\text{P}_j$ states of oxygen is spin forbidden along the Ar^+O^- intermediary, and it is gratifying that primary excitation of these levels was not observed.

The quenching of $\text{O}^*(3p \ ^3\text{P})$ by ground-state argon to give $\text{O}^*(3p \ ^5\text{P})$ is not amenable to a simple curve-crossing treatment because of spin restrictions on the transition probabilities. Presumably some kind of curve crossing mechanism will explain this process; however, the nature of the interaction remains to be discovered.

4. Discussion

An rf discharge through a resonant cavity containing a mixture of argon and oxygen results in laser oscillation at 844.6 nm [4], corresponding to the $3p \ ^3\text{P}-3s \ ^3\text{S}$ transition in atomic oxygen. Bennett et al. [4] showed that the excitation of atomic oxygen to the $3p \ ^3\text{P}$ level occurred by a two-step process, and they suggested that argon in one of its 4s excited states ($^3\text{P}_{2,1,0}, \ ^1\text{P}_1$) interacted with molecular oxygen to

bring about dissociation into $O(2^3P)$ and either $O(2^1S)$ or $O(2^1D)$, and that dissociation was followed by excitation of $O(2^3P)$ by electron impact to the $3p^3P$ level. Breckenridge and Miller [19] have shown that metastable argon atoms ($3P_2$) do indeed cause dissociation of molecular oxygen, and we previously [1] have reported the cross section for quenching $Ar^*(3P_2)$ by O_2 which is 35 \AA^2 . Since we have shown here that metastable argon atoms excite atomic oxygen to the $3p^3P$ level, the laser must be excited, in part at least, by two collisional-excitation processes involving excited argon atoms.

Determination of f -values for the 130.2–130.6 nm resonance transitions ($3s^3S_1 - 2p^4^3P_J$) of atomic oxygen by absorption of radiation emanating from a microwave-excited Ar/O_2 mixture has led to erroneously low results [5]. Our data indicate that an important mechanism for production of the resonance radiation will be the transfer of electronic energy from metastable argon atoms to atomic oxygen, exciting its $3p^3P_J$ levels, followed by radiative cascade to oxygen's $3s^3S$ resonance state. Because the energy transfer is accompanied by the release of 0.56 eV of translational energy, the assumption of a Doppler-broadened emission line at the prevailing plasma temperature, cannot be considered valid. Our results thus confirm the speculation [6] that excitation by energy transfer is important in undermining the analysis in the oscillator-strength studies [5].

5. Conclusions

The ionic-intermediate, curve-crossing mechanism is useful in providing insight into some quenching processes for metastable, rare-gas atoms. In particular, it will be important for reagents with large electron affinities and for cases in which entrance and exit channels differ significantly in energy. The quenching of $Ar^*(3P_2)$ by oxygen atoms provides an example.

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