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# Electronic Energy Transfer between Metastable Argon Atoms and Ground-state Oxygen Atoms

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We have measured the rate constants for excitation of the $3p\ ^3P$ and $3s\ ^3S$ states of atomic oxygen by metastable $Ar(^3P_{2,0})$ to be $(7.6 \pm 2.6)$ and $(8.2 \pm 2.5) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. Using a vacuum ultraviolet absorption technique we have also determined a translational energy of *ca* 0.4 eV for $O(3s\ ^3S)$. The coincidence of the two rate-constant measurements and the results of the translational-energy measurement shows that the electronic energy-transfer reaction between $Ar^*(^3P_{0,2})$ and $O(2p^4\ ^3P)$ excites primarily $O(3p\ ^3P)$ and that >90% of the $O(3s\ ^3S)$ excitation is by radiative cascade.

Studies on the transfer of electronic energy from metastable argon atoms to various atomic quenchers have produced some interesting results. Energy transfer to other rare-gas atoms (Kr, Xe)[1–3] is a near resonant process, the bulk of the excitation appearing in states of the acceptor atom which are energetically close to the metastable argon energy (11.548 eV for the $^3P_2$ state and 11.723 eV for the $^3P_0$ state). For these two atoms, quenching is negligible into states with energy defects >0.1 eV. In contrast, the excitation of N,[4] O,[3,5] Cl[3,6] and H[7,8] atoms by energy transfer from metastable argon occurs with large excitation rate constants into acceptor levels with large energy defects, being >1 eV in the case of N, Cl and H.

We had observed previously[5] that the Ar* + O interaction excited the $O(3p\ ^3P)$ state directly (see fig. 1) and estimated the rate constant for the excitation process by comparison with the excitation of atomic krypton by metastable argon[1,2,9] in the same reactor. Our more recent experience, however, indicates that the atomic-oxygen number density in that study was probably overestimated by as much as a factor of three or four.[10]

In the present study we have redetermined the rate constant for $O(3p\ ^3P)$ excitation by metastable argon, with an accurate determination of the atomic oxygen number density this time; we have measured the rate constant for excitation of the $3s\ ^3S$ state to see if that state is produced solely by radiative cascade from the $3p\ ^3P$ state or if there is some direct excitation; and we have determined the translational energy in the $O(3s\ ^3S)$ state using an absorption technique we developed previously.[11] The three sets of measurements are consistent with our earlier speculations that primarily $O(3p\ ^3P)$ is excited by energy transfer from metastable argon to atomic oxygen, but indicate that the rate constant for the process is three and a half times that reported previously.

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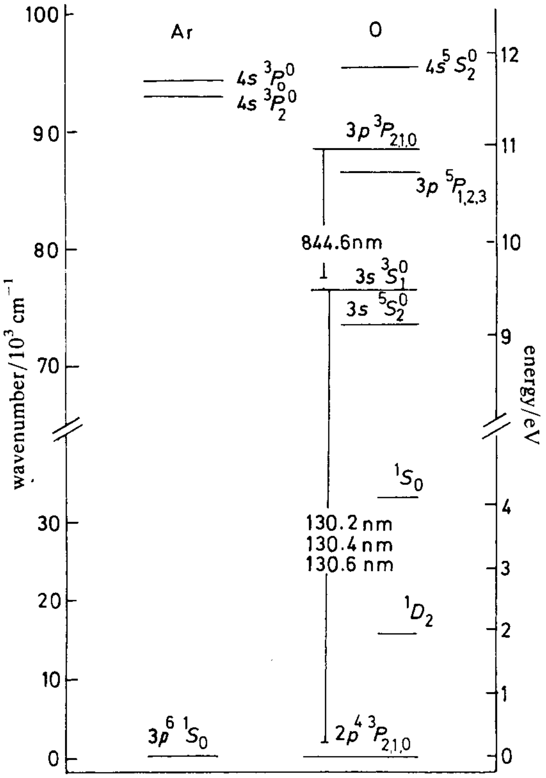

FIG. 1—Energy-level diagram of atomic oxygen showing the levels and transitions important to understanding the transfer of electronic energy from metastable Ar($^3P_{2,0}$) to O($^3P$).

## EXPERIMENTAL

Fig. 2 shows the discharge–flow apparatus used for the vacuum ultraviolet measurements.[12] Argon carrier gas, previously purified by flowing through a molecular sieve trap (Linde 5A) at liquid-nitrogen temperature, flows through a cold, hollow-cathode discharge (*ca.* 200 V d.c., *ca.* 5 mA) which converts a small fraction of the argon to metastables. A 90° bend in the discharge tube and a Wood's horn light-trap eliminate resonance states of argon and v.u.v. resonance emission. The reagent flow (Ar, $N_2$, $O_2$ and $Cl_2$ in various combinations; *ca.* 70 μmol $s^{-1}$ in all) enters the flow tube coaxially with the metastables, and the reactants mix diffusively. A microwave discharge through a flow of argon containing small amounts ($\leqslant 1\%$ of total flow) of molecular oxygen or nitrogen produces the atomic reagents. In some instances the residual $O_2$ impurity in the tank argon gave sufficiently large atomic oxygen number densities (*ca.* $5 \times 10^{11}$ atom cm$^{-3}$) that additional $O_2$ was unnecessary. When oxygen had to be known quantitatively, atomic nitrogen was titrated with nitric oxide, and the resulting atomic-oxygen flow was assumed to be equal to the nitric oxide flow. Relatively large amounts of argon flowed through the reagent side arm to shorten the residence time and thereby ensure negligible atomic oxygen recombination on the side-arm walls.

A v.u.v. monochromator observed light produced in the energy-transfer reaction normal to the gas flow. For the 130 nm linewidth studies, ground-state atomic oxygen flowing through a second flowtube which separated the metastable flow tube and the monochromator by LiF windows absorbed a fraction of the emitted resonance radiation. Quantitative titration of an excess of N (made in a microwave discharge through a flow of argon and nitrogen) with NO produced the absorbing oxygen atoms in the second flow tube. We observed no

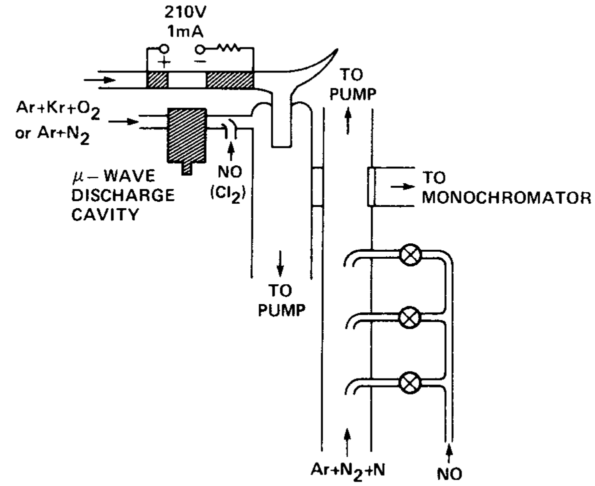

FIG. 2—Diagram of discharge–flow apparatus used in the v.u.v. measurements.

systematic variations in absorbance when the N + NO mixing times were varied at fixed flows of N and NO. Thus the N + NO reaction was essentially complete, and O-atom losses from wall recombination were negligible.

Atomic-oxygen number densities in the Ar* + O mixing zone less than or equal to $10^{12}$ atom cm$^{-3}$ ensured that complications from self-reversal did not mar the absorption measurements. Flows of added $O_2$ through the discharge were sufficiently small that the atomic-oxygen number densities were $<10^{12}$ atoms cm$^{-3}$ even in the event of 100% dissociation of the molecular oxygen. In general, we have found that effective dissociations as measured in similar flow tubes are more nearly $35 \pm 15\%$.[10] As an additional check, the oxygen resonance triplet was scanned before each experiment. The ratio of the intensities of the three lines (130.2, 130.5 and 130.6 nm) was 4.6:2.9:1, which is close enough to the ideal 5:3:1 to preclude significant self-reversal. The observed triplet ratio implies an atomic-oxygen optical depth in the Ar* + O region of 0.15[13] ($[O] \approx 6 \times 10^{11}$ atom cm$^{-3}$). This low source optical depth will affect the experimental results by no more than 5%.

The experiments on the excitation of the $3p\ ^3P$ state of atomic oxygen were done on a different discharge–flow reactor which Piper *et al.*[14,15] have described in detail. A hollow-cathode discharge produces the metastable argon atoms which then flow past a light trap and into a 2 in.† diameter quartz flow tube. The reagent atomic oxygen and krypton are added through a polyethylene loop injector downstream of the metastable discharge. A 0.5 m monochromator equipped with a thermoelectrically cooled EMI 9558 QA photomultiplier and SSR photon-counting rate meter observed the light in the reactor normal to the flow of the reagent gases. The monochromator is mounted on rails which are parallel to the flow tube, so that observations can be made as a function of mixing time.

A microwave discharge through a flow of helium containing traces of oxygen and krypton produced the atomic oxygen for these measurements. The atomic-oxygen number densities were determined in the reactor using the air-afterglow method[16,17] using procedures one of us[14,18] has described in detail.

The atomic-oxygen emission observed in these experiments is at 844.6 nm, which is at the long-wavelength sensitivity limit of the photomultiplier that was available. To make matters even worse, the available grating of the monochromator was blazed at 250 nm. Thus the major experimental problem in this series of measurements was to determine a reliable spectral-response calibration curve for the monochromator at wavelengths > 800 nm. In general, we do not trust standard lamps or the air afterglow[19-22] to be reliable in this

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† 1 in. ≡ $2.54 \times 10^{-2}$ m.

region of the spectrum because both will produce scattered light which cannot be discriminated against adequately, even with the use of short-wavelength cut-off filters (unless an inordinate supply of them is available). We therefore used a branching ratio technique to calibrate the relative response of the monochromator in this region.

We scanned the spectrum of Kr and Ar pen lamps and used the branching ratios for transitions from a common upper state to various lower states as published by Chang *et al.*[23,24] to establish the fall-off in system spectral response at longer wavelengths. The branching-ratio measurements were tied to a spectral response curve determined from measurements on a quartz halogen lamp at wavelengths <650 nm, and agreed with the quartz halogen measurements out to 750 nm. At longer wavelengths, the quartz halogen measurements were subject to problems with scattered light, and indicated a greater system sensitivity than was indicated by the branching-ratio measurements. The system spectral response falls by two and a half orders of magnitude between 750 and 850 nm. Despite these problems, we think that our response calibration should be accurate to better than 25%.

## RESULTS

### RATE CONSTANT FOR EXCITITION OF $O(3s\ ^3S)$ IN THE $Ar^* + O(^3P)$ REACTION

The rate constant for the excitation of the $3s\ ^3S$ state of atomic oxygen by metastable argon was determined by comparison of the intensities of the 130.5 and 130.6 nm lines from oxygen with the 138 nm line of atomic chlorine excited in the interaction between metastable argon and molecular chlorine. The intensity determinations were run simultaneously so that the metastable-argon number density was the same for both measurements. This technique has been discussed exhaustively.[1,2,4,5,9] The desired rate constant is obtained from eqn (1):

$$k_\lambda = k_{138} I_\lambda q_\lambda [Cl_2]/(I_{138} q_{138} [O]) \quad (1)$$

where $I_\lambda$ represents the line intensity, $q_\lambda$ the monochromator response correction factor and $k_\lambda$ the rate constant for excitation of the subscripted wavelength. We have shown recently[4] that, after making some minor corrections to earlier results, $k_{138}$ is $6.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Fig. 3 and 4 show the variation in intensity of the 130.5 and 130.6 nm lines as a function of O-atom number density, the atomic oxygen having been produced by the addition of NO to excess N. A 10% correction was applied to the 130.5 nm results to account for self-reversal. Five runs on the 130.5 nm line and six on the 130.6 nm line gave excitation rate constants of $(8.0 \pm 0.7) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(8.4 \pm 1.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. The error limits quoted are two standard deviations from the mean of the runs. Averaging the data from all runs gives a rate constant of $(8.2 \pm 1.2) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The overall uncertainty (r.m.s.) in the measurements of $k_{130}$ is 30% because of additional uncertainties in the relative monochromator response function (10%) and in $k_{138}$ (25%).

### RATE CONSTANT FOR EXCITATION OF $O(3p\ ^3P)$ IN THE $Ar^* + O$ REACTION

The rate constant for the excitation of the $3p\ ^3P$ state of atomic oxygen by metastable argon was measured by comparing the intensities of the 844.6 nm multiplet of atomic oxygen with the 760.2 nm line of krypton, both of which were excited by metastable argon under identical conditions. Ratios of the two line intensities were measured for six different values of metastable-argon number

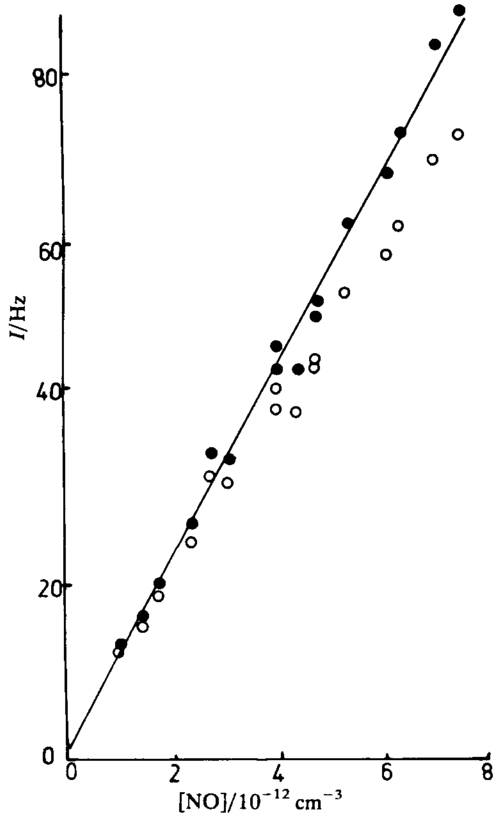

FIG 3.—Variation in intensity of the 130.5 nm transition of OI ($2s^22p^33s\ ^3S$–$2s^22p^4\ ^3P_1$) excited in the interaction between metastable argon and atomic oxygen. The open circles are the raw data and the filled circles show the results corrected for self reversal.

density for each of two atomic-oxygen number densities which differed by an order of magnitude. The metastable-argon number density was varied by making the measurements at different reaction times in the flow tube. The data were analysed by an equation similar to eqn (1) and are corrected for the ratio of 760.2 nm excitation to all excitation in the Ar* + Kr reaction (0.685).[1] The measurements at the two different oxygen number densities gave a rate constant of $7.6 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The overall uncertainty in this value (r.m.s.) is 35%, due primarily to the uncertainty in the relative monochromator response calibration at 845 nm (25%), but also includes contributions from the statistical scatter in the intensity ratio measurements (10%), uncertainty in the atomic-oxygen number density (12%), and the uncertainty in the rate constant for excitation of the 760.2 nm line of krypton by metastable argon (15%).

## TRANSLATIONAL ENERGY IN O($3s\ ^3S$) EXCITED IN THE Ar* + O REACTION

We have described in detail the technique we use to determine translational energies of species excited in energy-transfer reactions.[11] The resonance emission from these excited species serves as the radiation source for absorption experiments using known number densities of 300 K absorbers. The absorption data are then

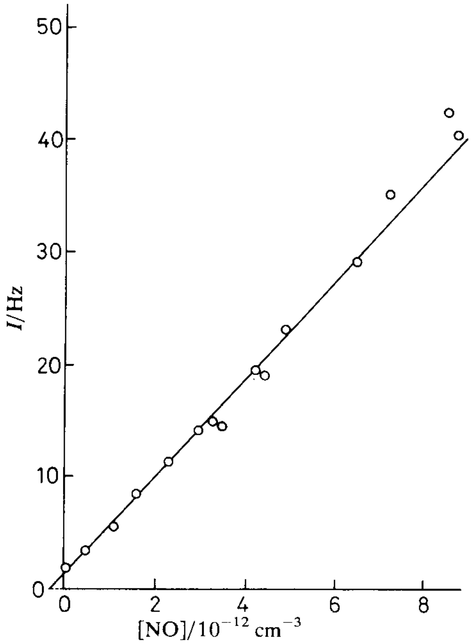

FIG 4.—Variation in intensity of the 130.6 nm transition of OI ($2s^22p^33s\ ^3S$–$2s^22p^4\ ^3P_0$) excited in the interaction between metastable argon and atomic oxygen.

analysed according to a defined line profile. Because the experiments are performed at low pressures and with low number densities of atomic oxygen, the only significant line-broadening mechanism is Doppler broadening, which is a function of the translational-energy distribution of the emitters and absorbers.[13] The translational-energy distribution of the absorbers is clearly a Maxwell–Boltzmann distribution at 300 K.

In fitting our data, we have used two different translational-energy distributions for the emitters. In one case, the emitting species are assumed to be in a Maxwell–Boltzmann translational-energy distribution but with an effective translational temperature different from that of the absorbers. The important parameter in this absorption model is $\alpha$, the ratio of the square root of the tanslational temperature of the emitters to that of the absorbers. The data are fitted to the model expression[11] with the Doppler width of the emission line as the variable parameter and using the well established oscillator strength of the O($3s\ ^3S$–$2p\ ^3P$) transition[13] (see for example fig. 5).

The other model assumes a monoenergetic velocity for the excited oxygen atom, the key parameter here being $E_{\text{diss}}$, which is the effective dissociation energy of the Ar* + O molecular complex formed in the collision process. The width of the spectral line then is governed by $E_{\text{diss}}$.

Measurements at 1.6 Torr† give a value of $\alpha$ of $3.37 \pm 0.15$ ($2\sigma$), from which we may calculate an effective O-atom translational temperature of $3400 \pm 300$ K or an average kinetic energy in the O-atoms of $0.44 \pm 0.04$ eV ($\frac{3}{2}\ kT$) (see table 1). The same data analysed with the monoenergetic translational-energy distribution

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† 1 Torr ≡ 133.3 Pa.

TABLE 1.—RESULTS FROM $Ar^* + O$ STUDY

| process | rate constant[a] | cross-section[b] |
|---|---|---|
| $Ar^* + O(2p^4\ {}^3P) \rightarrow O^*(3p\ {}^3P) + Ar$ | $7.6 \pm 2.6$ | $10.2 \pm 3.5$ |
| $Ar^* + O(2p^4\ {}^3P) \rightarrow O^*(3s\ {}^3S) + Ar$ | $8.2 \pm 2.5$ | $11.0 \pm 3.4$ |

| | translational energy measurements | | |
|---|---|---|---|
| | $O^*(3p\ {}^3P)$ exit channel | $O^*(3s\ {}^3S)$ exit channel | experiment |
| $T_{source}/K$ | 3096 | 11 220 | $3400 \pm 300$ |
| $\frac{3}{2}kT_{source}/eV$ | 0.40 | 1.45 | $0.44 \pm 0.04$ |

[a] Units $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$; [b] units $Å^2$.

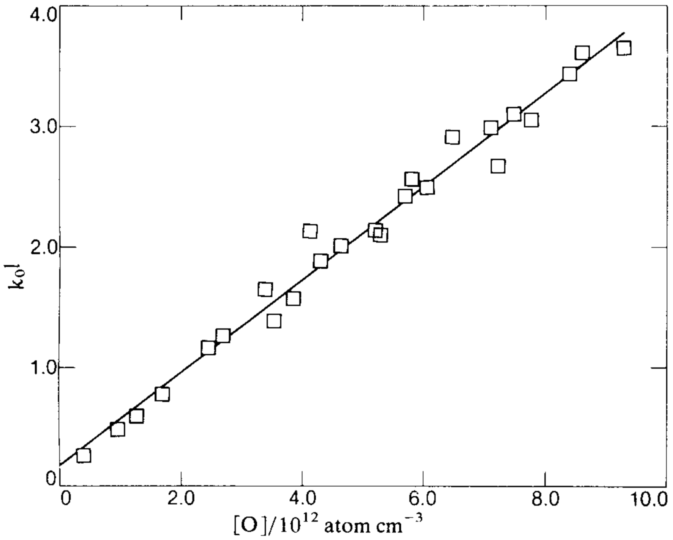

FIG. 5—Variation in optical depth ($k_O l$) with number density of oxygen-atom absorbers for OI 130.2 nm transition excited in the interaction between metastable argon and atomic oxygen, $\alpha = 3.31$, source pressure = 1.65 Torr.

give a value of $E_{diss}$ of $0.44 \pm 0.04$ eV or an average translational energy in the excited oxygen atoms of $0.31 \pm 0.03$ eV. A few measurements at other pressures in the $Ar^* + O$ flow tube indicated that there might be an increase in emitter translational energy with decreasing pressure. The pressure dependence of the linewidths was not investigated in detail, however.

## DISCUSSION

Piper[5] showed that a primary excitation channel was the $3p\ {}^3P$ state at 10.99 eV above the ground state of atomic oxygen. This state radiates in the infrared at

844.6 nm to populate the $3p\ ^3P$ state, which is observed in emission at 130.4 nm in the present study. Piper's estimate of the rate constant for excitation of the $3p\ ^3P$ state by comparison with the excitation of Kr by metastable argon[1] was $2.3 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. This value is a factor of three to four too low, because Piper overestimated his atomic-oxygen number density. He proposed that the quenching could proceed *via* an ionic-intermediate, curve-crossing mechanism,[25] and calculated an excitation rate constant of $9.6 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ with this model.[5] This value agrees well with the present experimental value.

King *et al.*[3] redetermined the $3p\ ^3P$ excitation rate constant using an indirect measurement of the atomic-oxygen number density performed in a separate experiment. Their indirect measurement indicated *ca.* 50% dissociation and led to a rate constant of $4.1 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Our results indicate that they overestimated their atomic-oxygen number density by a factor of two. King *et al.* suggested that direct excitation of the $3s\ ^3S$ state also was possible, in addition to the ionic-intermediate, curve-crossing mechanism, since several excited Ar–O potential curves are sufficiently bound to overcome the 2 eV difference in energy between the Ar ($^3P_2$) and O($3s\ ^3S$) states.

The absorption measurements indicate an average kinetic energy of O($3s\ ^3S$) of $0.44 \pm 0.04$ eV using the Maxwell–Boltzmann model or $0.31 \pm 0.03$ eV using the monoenergetic model. If the only excitation channel were to the $3p\ ^3P$ state, the expected exoergicity would be 0.56 eV, with 0.40 eV ending up as kinetic energy in the oxygen atom. The Maxwell–Boltzmann model gives a value *ca.* 10% higher than the theoretical exoergicity, whereas the monoenergetic model indicates a kinetic energy in the oxygen atom *ca.* 25% less than the theoretical exoergicity. In the limit of zero pressure, where the excited oxygen atoms radiated before experiencing collisions, we would expect the monoenergetic emission-line profile to be correct. If the excited atoms experience a number of collisions prior to radiation, the emission-line profile will become narrower. At 1.6 Torr most of the excited oxygen atoms will have experienced at least one collision with an argon atom prior to radiation ($\tau_{rad} = 35.7$ ns).[26] Thus a lower energy than expected is not surprising. Taking the collision diameter of Ar–O* to be similar to that for Ar–Na,[27] 3.65 Å, we calculate the hard-sphere collision rate at 1.6 Torr to be $5.2 \times 10^7$ $s^{-1}$ for oxygen atoms initially traveling with 0.40 eV of kinetic energy. Because the $3p\ ^3P$ radiative rate is $2.8 \times 10^7$ $s^{-1}$,[26] *ca.* 65% of the excited oxygen atoms will suffer at least one collision prior to radiation. One collision will reduce the average kinetic energy of the translationally hot atoms by *ca.* 17%[28] to 0.33 eV in accord with our observations. This value should be a reasonable approximation to the average kinetic energy of the translationally hot atoms, given that 35% radiate without experiencing any collisions and while only 25% experience more than two collisions.

Direct excitation of O($3s\ ^3S$) would result in an excited-oxygen-atom kinetic energy of 1.45 eV or an effective kinetic temperature of 11 222 K corresponding to $\alpha = 6.1$. For this kinetic temperature and assuming an Ar–O* collision diameter as above we calculate a hard-sphere collision rate of $1 \times 10^8$ $s^{-1}$. Because the radiative rate for O($3s\ ^3S$) is $5.6 \times 10^8$ $s^{-1}$,[13] only 15% of the excited oxygen atoms would experience any collisions prior to radiation. Thus if the $3s\ ^3S$ state were excited directly our measurements at 1.6 Torr would reflect accurately the initial kinetic-energy distribution. If the O($3s\ ^3S$) emission line profile were a composite of lines corresponding to the two kinetic-energy distributions associated with $3p\ ^3P$ and direct $3s\ ^3S$ excitation our measurements would reflect an average kinetic energy midway between the two distributions. Without making careful measurements as a function of pressure in order to assess more accurately the degree of collisional moderation of the initially excited $3p\ ^3P$ atoms, it is impossible to assess accurately the fraction of direct $3s\ ^3S$ excitation. However, even if the average energy loss per collision of the $3p\ ^3P$ atoms is double what we estimated, our measurements are incompatible with any more than 10% direct $3s\ ^3S$ excitation.

Thermalization of $O(3s\ ^3S)$ by electronic-energy exchange with cold, ground-state oxygen atoms would require ridiculously large cross-sections ($> 10^6$ Å$^2$) in order to be significant. Quenching of the $3s\ ^3S$ to $3s\ ^5S$ in collisions with argon does not appear to be a significant effect ($\leqslant 2\%$), since we did not observe emission at 135.6 nm.

Two rough measurements[29,30] of the linewidth of the 844.6 nm transition produced in an $Ar + O_2$ discharge give linewidth values consistent with those given here for the 130.2 transition. Bennett *et al.*[29] report a linewidth value for the 844.6 nm transition of *ca.* 3 GHz. This corresponds to a linewidth which is roughly three times the Doppler width at room temperature, in accord with our measurements on the 130.2 nm line. Tunitskii and Cherkasov[30] measured the linewidths of the 844.6 nm lines using an interferometer. The results quoted in their paper vary between 0.12 and 2.2 $cm^{-1}$ ($\alpha$ values of 3.2–5.4), also in accord with the results of the present investigations.

Our rate constants for excitation of the $3p\ ^3P$ and $3s\ ^3S$ states of atomic oxygen in the $Ar^* + O$ interaction are the same within experimental error. We take this as evidence that the major product of the energy transfer is $O(3p\ ^3P)$ and that $O(3s\ ^3S)$ is formed primarily by radiative cascade at 844.6 nm. This evidence is not conclusive, however, because the experimental error is sufficiently large that as much as half of the $O(3s\ ^3S)$ excitation could be direct: $k_{[O(3s\ ^3S)]}/k_{[O(3p\ ^3P)]} = 1.1^{+1.0}_{-0.1}$. Our linewidth studies, on the other hand, are not consistent with a major direct channel for $3s\ ^3S$ excitation.

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