DETERMINATION OF THE TRANSLATIONAL ENERGY OF O(3s ^{3}S) EXCITED IN THE DISSOCIATIVE EXCITATION OF O$_2$ AND NO BY He*(2 ^{3}S)

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The translational energy in O(3s ^{3}S) excited in the dissociative excitation of NO and O$_2$ by metastable helium (2 ^{3}S) has been determined using a resonance absorption technique in the vacuum UV. The absorption data are analyzed using two different emission line profiles: a gaussian profile from a high temperature Maxwell–Boltzmann source, and a trapezoidal profile from a monoenergetic source. The analysis using the gaussian profile indicates an average translational energy of the excited O-atom of ≥ 0.60 eV from the He* + O$_2$ source and ≥ 0.23 eV from the He* + NO source. The analysis using the monoenergetic profile gives excited O-atom translational energies of ≥ 0.30 eV from He* + O$_2$ and ≥ 0.15 eV from He* + NO. There is a marked reduction in effective O-atom translational energy with increased total pressure for both the He* + O$_2$ and He* + NO cases.

1. Introduction

A number of papers have appeared in recent years describing the disposal of electronic and vibrational energy in various chemical or energy-transfer reactions. Much less has been done in determining translational-energy disposal, although this information is required for complete specification of the reacting system. Translational-energy disposal in a chemical reaction or energy-transfer process can be determined most easily either by resolving the emission-line profiles of radiating species, or by probing absorption-line shapes of resonance transitions for ground-state or metastable products. For example, Biondi and co-workers [1–4] used an interferometer to resolve emission-line profiles of electronically excited Ar and Ne atoms produced in the dissociative recombination of Ar$_2^+$ or Ne$_2^+$. Dye lasers with very narrow frequency distributions can be scanned across absorption lines of product species to gain information on the translational energy contained in them [5]. These two techniques are limited to species with transitions in the visible or infrared. We developed a technique which, although not so precise as line scanning with an interferometer or frequency-narrowed laser, will give information on species with transitions in the vacuum ultraviolet. The technique has been applied to several cases in which electronically excited atoms have been produced in energy-transfer or dissociative-excitation reactions involving metastable argon atoms with Kr [6], O [7], Cl [8], and Br$_2$ [9], and metastable helium with O$_2$ and NO. In each reaction, electronically excited atoms with emissions in the vacuum ultraviolet region of the electromagnetic spectrum were produced. By absorbing this product atomic-resonance emission with known concentrations of thermal ground-state atoms, and by comparing the resultant curve-of-growth with various

models, it has been possible to obtain information on the translational energy in the emitting atoms.

In the present paper, we discuss results on the translational energy contained in O($3s\ ^3S$) excited in collisions between metastable He($2\ ^3S$) with O_2 and NO.

2. Experimental

The apparatus used in these studies is similar to the one pictured by Clyne and Smith [9]. The electronically excited oxygen atoms are produced in collisions between He($2\ ^3S$) and O_2 and NO which take place in a standard metastable flow tube [10–12]. Helium gas is purified by passage through a molecular sieve trap (Linde 5A) at liquid nitrogen temperature. A small fraction of the carrier gas then is converted to metastables in a cold, hollow-cathode discharge operated at about 350 V dc in He. Helium vacuum UV resonance emission is eliminated by a 90° bend in the discharge tube and a Wood's horn-type light trap. The reagent flow enters coaxially with the flow of metastables in the main flow tube, and the reactants are mixed by diffusion.

Light produced in the energy-transfer reactions is observed normal to the flow with a 1-meter vacuum ultraviolet monochromator (Hilger and Watts E 760). The resonance radiation is absorbed by ground-state oxygen atoms flowing in a second flow tube which is between the metastable flow tube and the mono-chromator and separated from them by LiF windows. Nitrogen atoms are produced upstream in this second flow tube in a micro-wave discharge through nitrogen. Oxygen atoms then are made quantitatively by titrating the N, which is in excess, with NO,

$$N + NO \rightarrow O + N_2. \qquad (1)$$

In order to check for completeness of the reaction and for losses in O due to recombination on the flow-tube walls, absorbances were checked periodically for several N/NO mixing times but with fixed flows of N and NO. No sys-tematic variations in absorbance were observed.

In these studies, self-reversal of the resonance emission excited in the metastable cell is negligible, because even in the case of complete dissociation, the O-atom concentration can be no larger than the initial metastable helium concentration. Previous work with similar reaction cells has indicated metastable concentrations on the order of 10^{11} atoms cm^{-3} or less [11]. A concentration of O atoms on this order produces negligible attenuation of the resonance light in the 1.5 cm distance from the center of the metastable flame region to the flow tube window [13].

3. Results

The experiment involves measurements of the fractional absorbance of the resonance radiation by known concentrations of ground-state, ther-mal-energy absorbers. The expression relating the absorbance, A, to the intensity of the emission line, and the absorption coefficient of the absorption line, both of which are functions of frequency, is [14]

$$A = (I_0 - I_{trans})/I_0 = \frac{\int_{-\infty}^{\infty} I(\nu)\,(1 - e^{-k_\nu l})\,d\nu}{\int_{-\infty}^{\infty} I(\nu)\,d\nu}, \qquad (2)$$

where $I(\nu)$ is the function describing the intensity distribution of the emission line and k_ν is the frequency-dependent absorption coefficient. Under the conditions of the present experiments, all sources of line broadening other than Doppler broadening may be neglec-ted [13]. Since the absorbers are oxygen atoms at 300 K, the functional form of the absorption coefficient is well established,

$$k_\nu = k_0\,e^{-\omega^2}, \qquad (3)$$

where k_0 is the absorption coefficient at the line center and the reduced frequency, ω, is

$$\omega = [2(\nu - \nu_0)/\Delta\nu_D]\,(\ln 2)^{1/2}, \qquad (4)$$

ν_0 being the position of the line center, and $\Delta\nu_D$ the full width at half maximum of the absorption line as determined by Doppler broadening.

The absorption coefficient k_0 is a function of the number density of absorbers, N, and their oscillator strength, f,

$$k_0 \, (\text{cm}^{-1}) = \frac{2}{\Delta \nu_D} \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\pi e^2}{m_e c} Nf, \tag{5}$$

where m_e and e are the electron mass and charge (esu), respectively, and c is the speed of light. The Doppler full width at half maximum of the absorbers, $\Delta \nu_D$, is given by

$$\Delta \nu_D \, (\text{s}^{-1}) = (2/\lambda_0)(2RT \ln 2/M)^{1/2}, \tag{6}$$

R being the gas constant, T the temperature, M the molecular weight and λ_0 the central wavelength of the transition. The absorption oscillator strength of this transition has been established by a number of experiments in the past ten years to be 0.048 ± 0.004 (95% confidence level [13]). Thus, it remains only to model the frequency distribution of the emission line in order to interpret the experimental data.

We have chosen two different models for the emission-line profile, and feel that the true profile will probably lie somewhere between the two extremes. The first model is a high temperature Maxwell–Boltzmann (gaussian) profile. This profile differs from the ambient Doppler line shape by the parameter α which is the square root of the ratio of the effective temperature of the emission source to the temperature of the absorbers (300 K). Thus,

$$I(\nu) = I_0 \, e^{-(\omega/\alpha)^2} \tag{7}$$

and the integral expression for A becomes

$$A = (I_0 - I_{\text{trans}})/I_0$$
$$= \frac{\int_{-\infty}^{\infty} [1 - \exp(-k_0 l \, e^{-\omega^2})] \exp[-(\omega/\alpha)^2] \, d\omega}{\int_{-\infty}^{\infty} \exp[-(\omega/\alpha)^2] \, d\omega}. \tag{8}$$

The other model for the emission line we have used was originally developed by Biondi and co-workers in their work on dissociative electron–ion recombination involving Ar_2^+ and Ne_2^+ [1–4]. In that model, the two atoms dissociated with essentially a monoenergetic kinetic energy distribution. This fixed dissociation energy when coupled with the initial thermal energy in the dissociating complex led to an emission profile which was essentially trapezoidal in shape. The width of the line is governed by the dissociation energy of the complex. Expressed mathematically, the emission-line profile from this model is

$$I(\omega) = (a/4b) \{ \text{erf}(a\omega + b) - \text{erf}(a\omega - b) \}, \tag{9}$$

where

$$a = (1 + M_2/M_1)^{1/2},$$

M_1 being the mass of the emitting atom, M_2 that of the other atom in the dissociating complex, and

$$b = [(E_{\text{diss}}/RT)M_2/M_1]^{1/2},$$

where E_{diss} is the kinetic energy of dissociation of the excited complex. An expression similar to eq. (8) gives the measured absorbance when eq. (9) is used in place of eq. (7) to describe the emission-line profile.

Eq. (8) lends itself readily to numerical integration by gaussian quadrature whether the emission-line profile, and feel that the true (9). The data, therefore, were analyzed rapidly by use of a computer. A program was written which would compute a table of values of A versus N for a given input set of atomic masses, oscillator strength, absorption path length, and either α or E_{diss}. The program then went through an interpolation sub-routine to convert the experimental A to $k_0 l$ using the above derived table, and would use those $k_0 l$ values to compute the slope of the line relating k_0 to N [eq. (5)] for the given set of conditions. Values of α or E_{diss} were varied until the computed experimental slope of k_0 versus N was the same as the theoretical slope computed from the correct value of the absorption oscillator strength, f [13]. The input conditions which reproduced the correct oscillator strength were taken to measure the effective line width of the emitters in the experiments. Several representative plots are shown in figs. 1–3. The finite intercepts in figs. 1–3 result from some residual atomic
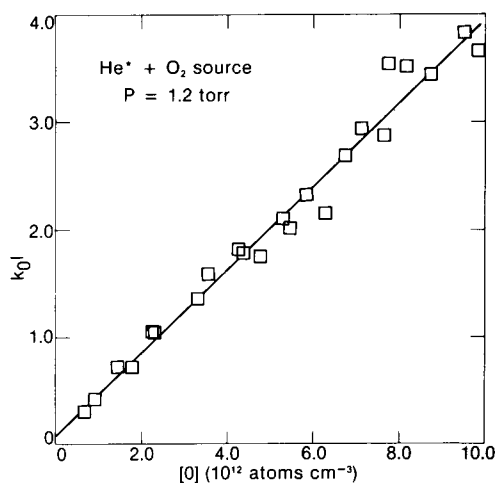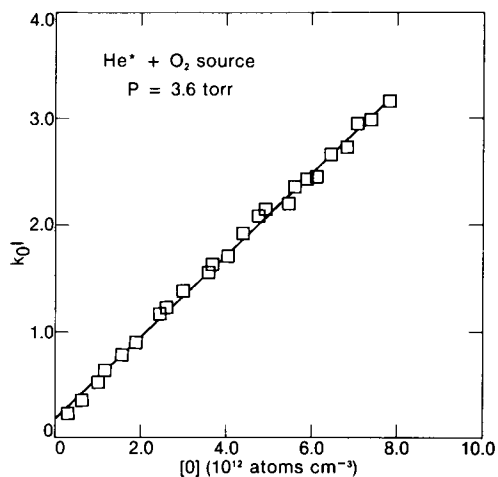
Fig. 1. Variation in optical depth with number density of O-atom absorbers for the OI 130.2 nm transition excited in the interaction between metastable helium and molecular oxygen. $\alpha = 3.73$, source pressure = 1.18 Torr.

oxygen ($\approx 5 \times 10^{11}$ atoms cm^{-3}) in the nitrogen-atom flow prior to titration with NO. The fits are quite sensitive to changes in α or E_{diss}. For example, changes in α of about 5% result in changes in the slopes of the $k_0 l$ versus N plots of about 15%. The standard deviations of the slopes of the $k_0 l$ plots are only a few percent.

Fig. 2. Variation in optical depth with number density of O-atom absorbers for the OI 130.2 nm transition excited in the interaction between metastable helium and molecular oxygen. $\alpha = 2.78$, source pressure = 3.6 Torr.
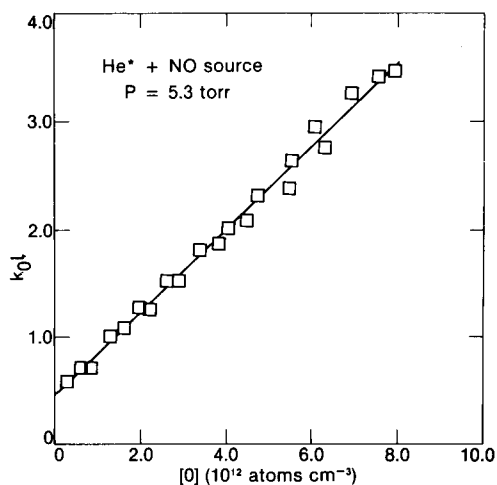

Fig. 3. Variation in optical depth with number density of O-atom absorbers for the OI 130.2 nm transition excited in the interaction between metastable helium and nitric oxide. $\alpha = 1.99$, source pressure = 5.3 Torr.

Thus the α or E_{diss} values determined by this technique are quite precise.

Fig. 4 shows that there is a strong variation in the O emission line width from the He*+O$_2$ source and a smaller but significant variation from the He*+NO source. The effective translational energy in the excited atoms will be reduced by collisions with the bath gas, providing there is a significant probability of collision before emission. Under no circumstances would there be much probability of collision if the
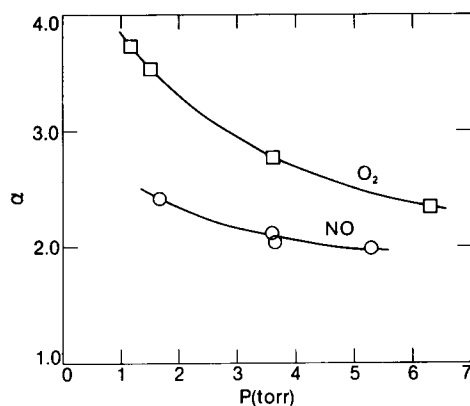

Fig. 4. Variation in α with source pressure for He*+NO source $\bigcirc$, and He*+O$_2$ source $\square$.

O(3s ^{3}S) state were excited directly since it has a radiative lifetime of less than 2 ns [13]. Thus, a significant fraction of the 3s ^{3}S excitation is via radiative cascade from higher lying states which are excited directly and which are sufficiently long lived to experience collisions at a few Torr pressure.

The actual line shapes will be a composite of several components each having widths determined by the exoergicity of the various accessible exit channels, and a 300 K gaussian core for the excited atoms which have become thermalized. In the present experiments, the effective line widths reflect the average translational energy of the excited oxygen atoms at the pressure of the measurements. At sufficiently low pressures, the line widths should reflect the average amount of reaction exoergicity which appears in translation. The pressures in the present experiments were probably not low enough to avoid some thermalization of the excited oxygen atoms. We summarize our results in table 1 therefore by giving only lower limits to the average O(3s ^{3}S) translational energy.

4. Discussion

While the direct transfer of energy to an atom is straightforward to interpret, the three-body nature of the dissociative-excitation processes observed here makes the interpretation of the translational-energy disposal much more difficult. We can think of two limiting cases for the dissociative-excitation process, and presumably the true interaction lies somewhere in between. In the first case, one could think of the whole of the electronic energy in the metastable helium being transferred to a superexcited state of molecular O_2 or NO, with none of the internal energy of the metastable helium being retained by the helium in the form of kinetic energy after the transfer. In this case, the metastable acts essentially as a photon; then, the kinetic energy in the dissociating atoms can be computed easily from the exoergicity of the reaction.

The second limiting case can be considered as essentially two separate two-body interactions. The metastable helium collides with the molecule creating an excited He–O_2 or He–NO molecular state which is sufficiently long-lived that the He* energy is distributed throughout the complex. The complex dissociates to He and an excited molecule which subsequently dissociates. In this second case, a large fraction of the exoergicity of the reaction can be carried away by the departing helium atom. For dissociative excitation of O_2 and NO by metastable helium, as much as 90% of the exoergicity of the reaction can be carried off by the helium, the actual amount depending upon the internal energy in the super-excited molecule.

Chang et al. [15] have recorded the emission between 140 and 800 nm which is excited in the interaction between metastable helium and NO and O_2. In the He* + NO reactions, they observed excitation of only the 3s ^{3,5}S and 3p ^{3,5}P states, with the quintet states being heavily

Table 1
Translational energy in O($2s^2 2p^2 3s$ ^{3}S) excited in rare gas metastable reactions[a]

Reaction	Maxwell–Boltzmann		Monoenergetic profile	
	α	$[\frac{3}{2}]kT$(eV)	E_{diss}(eV)	E_{0^*}(eV)
He*(2 ^{3}S) + NO → O($2s^2 2p^2 3s$ ^{3}S) + N(^{4}S) + He(^{1}S)	$\geqslant 2.42$	$\geqslant 0.23$	$\geqslant 0.32$	$\geqslant 0.15$
He*(2 ^{3}S) + O_2 → O($2s^2 2p^2 3s$ ^{3}S) + O(^{3}P) + He(^{1}S)	$\geqslant 3.7$	$\geqslant 0.54$	$\geqslant 0.60$	$\geqslant 0.30$

[a] The values given are the values observed at the lowest pressures studied, 1.67 Torr for the He* + NO study and 1.18 Torr for the He* + O_2 study.

favored over the triplet states, and with the majority of the excitation being to the lower-lying 3s states. The triplet manifold excitation is divided about equally between the 3s ³S and 3p ³P states for which the exoergicities of excitation are 3.7 and 2.2 eV, respectively. For the case of no kinetic energy carried off by the helium atom after the collision, the excited oxygen atoms would have 1.7 or 1.0 eV of translational energy for dissociation into the ³S and ³P states, respectively. Were the helium to recede with the maximum possible kinetic energy, the translational energy in the O atoms would be 0.2 and 0.12 eV, respectively. These values are to be compared to the experimentally observed energy of 0.23 eV at the lowest pressures studied. Clearly, much of the exoergicity in the reaction must have been carried off by the quenched helium atom.

In the interaction between metastable helium and molecular oxygen, Chang et al. observed excitation of both triplet and quintet states with 3s, 3p, 4p, and 4d excited electrons, and, in addition, the quintet states associated with 5s, 6s, 3d, and 5d excited electrons. The majority of the triplet excitation observed by them was into the 3p and 3s states. The populations of these states, which have exoergicities of 3.6 to 5.1 eV, respectively, were about equal. The expected translational energy in the excited oxygen atoms is 2.65 and 1.8 eV for the 3s ³S and ³P excitation, respectively, for the case of no translational energy carried away by the helium, and 0.28 and 0.20 eV, respectively, for the case in which helium carries away the maximum allowed translational energy. Our experimental measurements indicate that the excited oxygen atoms have a mean translational energy of ≥0.6 eV at low pressure.

Rawlins and Kaufman [17] investigated the linewidths of the oxygen resonance transition from both microwave and rf excited resonance lamps containing mixtures of helium and oxygen and using techniques similar to those used here. They found emission-line profiles which indicated the translational energies of the emitters were much in excess of the ambient temperatures which they had determined in their

lamps from rotational temperatures of minor molecular emitters in the lamps. The non-ambient character of the emission lines was most pronounced for the rf-excited lamps, and, in addition, showed a strong inverse pressure dependence as in the case of the present experiments. The magnitude of the thermal broadening observed by Rawlins and Kaufman at a given pressure was less than that observed here, presumably because in the rf-excited lamps electron-impact excitation of O atoms, which would be expected to give ambient distributions, is occurring in addition to the dissociative excitation of O_2 by metastable helium. Over the range of pressures common to both experiments our effective translational temperatures are a factor of two larger than those deduced by Rawlins and Kaufman. If this effect holds to even lower pressures, then the 4300 K effective Doppler temperature observed by Rawlins and Kaufman at 0.2 Torr would imply an effective Doppler temperature of 8600 K from the dissociative-excitation channel, or a translational energy of 1.1 eV.

5. Summary and conclusions

We have presented a technique for studying the translational energy in excited species following electronic-energy-transfer or dissociative-excitation processes, and have used this technique to study the translational energy in O(3s ³S) excited by the dissociative-excitation reactions of metastable helium with O_2 and NO.

The experimental results indicate that substantial amounts of the reaction exoergicity are carried away by the helium atom after the quenching collision. The details of the interaction cannot be fully specified in the present study since the emission-line profiles have been substantially modified by collisions with the bath gas as indicated by the strong inverse dependence between emission line width and pressure. In addition, the true emission line is undoubtedly a composite of a number of different lines with different widths correspond-

ing to the different exit channel exoergicities of the reaction.

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