# A KINETIC STUDY OF VIBRATIONALLY EXCITED $O_2(a^1\Delta_g, v = 1)$ BY TIME-RESOLVED ABSORPTION SPECTROSCOPY IN THE VACUUM ULTRA-VIOLET

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## SUMMARY

A kinetic study of vibrationally excited $O_2(a^1\Delta_g, v = 1)$ has been carried out by absorption spectroscopy in the vacuum ultra-violet following the pulsed irradiation of ozone. The species $O_2(a^1\Delta_g, v = 0$ and $1)$, $O_2(X^3\Sigma^-_g, v'' = 0$ and $1)$ and $O_3$ were monitored by plate photometry in the Schumann region following photolysis in the presence of different gases. Within the restrictions imposed by this method, it is concluded that vibrational equilibrium is maintained between $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ in the presence of the gases He and $CF_4$, over a wide pressure range, and that a breakdown in this equilibrium takes place at higher pressures. Rate data for the vibrational relaxation of $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ on collision with He, $CF_4$, $SF_6$, Ar and $N_2$ are reported. Further, the efficiency of the electronic-to-vibration energy transfer process:

$$O(2^1D_2) + CO(v'' = 0) \rightarrow O(2^3P_J) + CO(v'' = 1)$$
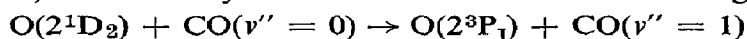
has been estimated and found to be $9.4 \pm 1.4\%$ and $6.0 \pm 1.0\%$ in the presence of the gases He and Ar, respectively.

## INTRODUCTION

Electronically excited molecular oxygen in its lowest lying singlet state, $O_2(a^1\Delta_g)$, 0.98 eV above the $O_2(X^3\Sigma^-_g)$ ground state[1], has been amenable to study by a number of experimental methods both because it is optically metastable[2,3] and because of the low deactivation efficiencies exhibited by many collision partners[4-6]. Recently[7,8], we have described a highly sensitive method for the kinetic study of $O_2(a^1\Delta_g)$, generated by the pulsed irradiation of ozone and monitored by means of strong Rydberg transitions[8,9] using time-resolved absorption spectroscopy in the vacuum ultra-violet. This previous investigation[8], whilst confined to a study of the vacuum ultra-violet spectrum of this molecule and the kinetics for the vibrational level $v = 0$, also resulted in the observation of vibrational excitation in this elec-

tronic state with up to $v = 5$. The present paper is concerned with a detailed kinetic investigation in the vacuum ultra-violet of $O_2(a^1\Delta_g, v = 1)$ to which the higher vibrationally energized molecules rapidly relax[8].

Kinetic investigations of $O_2(a^1\Delta_g)$, generated either from the photolysis of ozone[10-12] or by energy transfer from photochemically generated triplet benzene[13-15], and which have employed detection of the infra-red atmospheric bands $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma^-_g) + h\nu$, have been limited to the study of the $v = 0$ level by observation of the (0,0) transition at 1270 nm. This restriction has arisen as a result of the weak emission from the (1,0) band, whose relative intensity to that of the (0,0) band is 2.2 : 100[2,4,16] for this highly forbidden electronic transition ($A = 2.58 \times 10^{-4}$ sec$^{-1}$)[2]. Vibrationally excited $O_2(a^1\Delta_g)$ has been detected in a flow discharge by observation of the 580 nm "dimol" emission band from $O_4(^1\Delta_{v=1}, {}^1\Delta_{v=0})$[17]. In general, kinetic studies of $O_2(a^1\Delta_g)$ generated in flow discharges and which have employed the infra-red atmospheric system have been restricted to measurements on the (0,0) band[18-25]. It is hoped that the present study on the level $v = 1$ will assist in the interpretation of data derived from flow systems containing this molecular state, whether generated photochemically or by means of a discharge.

EXPERIMENTAL

The details of the general experimental arrangement have been given hitherto[8]. $O_2(a^1\Delta_g)$ was generated by the pulsed irradiation of ozone, primarily in the Hartley band continuum[26], and this with other transient species, as well as stable molecules, were monitored photographically by kinetic absorption spectroscopy in the vacuum ultra-violet. The system employed a 1 m concave grating vacuum spectrograph (Jarrell Ash Grating, 1180 grooves/mm, blaze wavelength = 110 nm) and absorption spectra, taken by means of a Garton–Wheaton spectroscopic flash lamp (Chelsea Instruments) through lithium fluoride optical materials ($\lambda > 105$ nm), were recorded on film (Ilford HP4, sodium salicylate sensitized[27]). Plate intensities were measured by means of a Joyce–Loebl double beam recording microdensitometer (Mark III). A standard electronic delay circuit was employed to set the chosen times between the onset of the photolytic pulse, initiated by means of an Ignitron high voltage switch system[8], and the spectroscopic source, triggered photoelectrically from scattered light derived from the high energy photolytic source. Pressures of ozone employed for kinetic measurements ($p_{O_3} = 33.3$ N m$^{-2}$) were higher than used hitherto[8], and a high photolytic energy ($E = 1650$ J, $C = 33\ \mu$F, $V = 10$ kV, $\tau_{1/2} = \sim 15\ \mu$s) was used principally to cause close to complete decomposition ($\sim 90\%$) of $O_3$, which has a continuous absorption spectrum[28] in the region of the transitions monitored.

The following are the principal species monitored spectroscopically in this investigation with the appropriate transitions:

$O_2(a^1\Delta_g, v = 1)$:  $g_1{}^1\Delta_u(v = 0) \leftarrow a^1\Delta_g(v = 1)$, $\lambda = 151.98$ nm[8]

$O_2(a^1\Delta_g, v = 0)$:  $h_1{}^1\Pi_u(v = 0) \leftarrow a^1\Delta_g(v = 0)$, $\lambda = 145.50$ nm[8]
$(\varepsilon = 164 \pm 28$ atm.$^{-1}$ cm$^{-1})$[29]

$O_2(X^3\Sigma^-_g, v'' = 1)$:  $? \leftarrow X^3\Sigma^-_g(v'' = 1)$, $\lambda = 126.86$ nm[30]

$O_2(X^3\Sigma^-_g, v'' = 0)$:  $B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$, Schumann–Runge continuum, $\lambda = \sim 147$ nm $(\varepsilon \cong 370$ atm.$^{-1}$ cm$^{-1})$[30]

$O_3$:  continuum, $\lambda = 122$ nm $(\varepsilon \cong 650$ atm.$^{-1}$ cm$^{-1})$[28]

The electronically unassigned band at $\lambda = 126.86$ nm employed for monitoring $O_2(X^3\Sigma^-_g, v'' = 1)$ lies 1560 cm$^{-1}$ $(O_2, \omega_e - 2\omega_e x_e = 1556$ cm$^{-1})$[1] to the long wavelength side of the band arising from $v'' = 0$ at $\lambda = 124.4$ nm[30]. Further, Boltzmann populations of $O_2(v'' = 1)$ have been observed *via* the band at $\lambda = 126.86$ nm[30].

Absolute concentrations of $O_2(a^1\Delta_g, v = 0)$ and $O_2(X^3\Sigma^-_g, v'' = 0)$ may clearly be obtained by employing the appropriate absolute extinction coefficients at $\lambda = 145.50$ and 147 nm, respectively[29,30]. Relative concentrations of $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ were derived from measurements of the plate intensities at $\lambda = 151.98$[8] and 126.86 nm[30] using the modified Beer–Lambert law[31]:

$$I_{tr} = I_0\exp(-\varepsilon(cl)^\gamma) \tag{i}$$

where the symbols have their usual significance[31]. Equation (i) was combined with standard "two path" experiments[32], the results of which are shown in Fig. 1. A linear plot comparing microdensitometer peak heights (O.D.) for the full and half vessels[32] is a line of slope $2^\gamma$ which yields, in this instance, values of $\gamma = 0.66 \pm 0.1$ and $0.83 \pm 0.1$ for the transitions at $\lambda = 151.98$ and 126.86 nm, respectively. Thus $(1/\gamma) . \ln [\ln(I_0/I_{tr})]$ or $(1/\gamma) . \ln$ (optical density) is a logarithmic measure of the concentrations of the species in the vibrational levels $v = 1$.
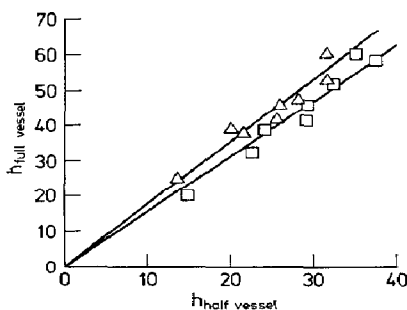


Fig. 1. Results of "two path" experiments for the transitions at $\lambda = 126.86$ nm $(X^3\Sigma^-_g, v'' = 1, \triangle)$ and $\lambda = 151.98$ nm $(g_1{}^1\Delta_u \leftarrow a^1\Delta_g, (0,1), \square)$. Upper line $O_2(X^3\Sigma^-_g)$; lower line $O_2(a^1\Delta_g)$.

*Materials*

$O_3$ prepared by the method of Clough and Thrush[33], was purified and employed as hitherto[8]. Similarly, the source and purification of the gases He, Ar, Kr (for the photolysis lamp), Xe, $H_2$, $N_2$ and CO have been described previously[8]. $CF_4$ and $SF_6$ (cylinder, Matheson Co.) were thoroughly degassed and fractionally distilled from an isopentane slush ($-160°C$) to liquid nitrogen temperature ($-196°C$).
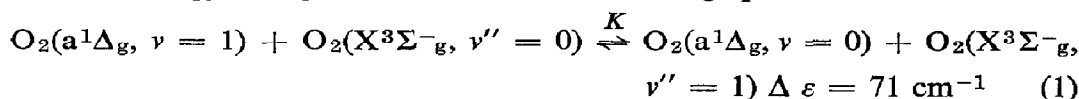
Experimental factors severely restrict the choice of collision partners. The added gas must be characterized by a vibrational relaxation efficiency causing, on addition, a modification to the lifetime of $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ significant compared with the error in the measurement. The spectrum of the gas must clearly not obscure the vacuum ultra-violet transitions of $O_2$ to be monitored. Further, the chemical reactivity of $O(2^1D_2)$, generated on the photolysis of $O_3$, prevents the use of molecules containing hydrogen atoms.
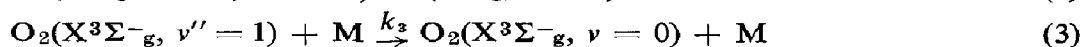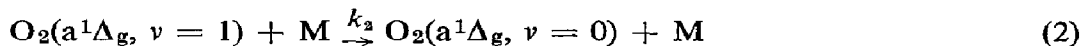
RESULTS AND DISCUSSION

*Vibrational equilibrium between $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma^-_g)$*

Time-resolved absorption spectra in the vacuum ultra-violet following the pulsed irradiation of ozone in the presence of excess helium buffer gas to maintain isothermal conditions have been given hitherto[8]. These indicate the production of $O_2(a^1\Delta_g)$ with up to $v = 5$, readily observed *via* the system $g_1(v = 0$ progression) $\leftarrow$ $O_2(a^1\Delta_g, v = 0$ to $5)$[8]. The highly vibrationally excited $O_2(a^1\Delta_g)$ is rapidly relaxed to the level $v = 1$, whose lifetime lies approximately in the range 200–300 $\mu s$, and it is the modification to this lifetime by added gases that is the principal experimental parameter in this kinetic investigation. In the present type of experimental system, $O_2(a^1\Delta_g, v = 0)$ is very long lived, with a lifetime measured in seconds[8], and thus the removal of this electronically excited metastable species may be neglected in the time scales employed here to study vibrational energy removal.

Following relaxation to $O_2(a^1\Delta_g, v = 1)$, the oxygen system may be regarded essentially as a mixture of $O_2(a^1\Delta_g, v = 0$ and $1)$ and $O_2(X^3\Sigma^-_g, v'' = 0$ and $1)$, with small traces of undissociated $O_3$, *all of these species being monitored directly in these experiments*. The fundamental vibration frequencies of $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma^-_g)$ are close in magnitude $[\omega_e(^1\Delta) = 1509$ cm$^{-1}$; $\omega_e(^3\Sigma^-_g) = 1580$ cm$^{-1})$[1] and hence the energy change for the vibrational exchange processes:

$$O_2(a^1\Delta_g, v = 1) + O_2(X^3\Sigma^-_g, v'' = 0) \overset{K}{\rightleftharpoons} O_2(a^1\Delta_g, v = 0) + O_2(X^3\Sigma^-_g,$$
$$v'' = 1) \; \Delta\varepsilon = 71 \text{ cm}^{-1} \qquad (1)$$

is small (where $\varepsilon_{0-1} = \omega_e - 2\omega_e x_e$). We employ and test the initial assumption that this near resonance exchange is rapid[34-36] and that process (1) is continually in equilibrium. We further include the energy transfer processes involving relaxation by other gases:

$$O_2(a^1\Delta_g, v = 1) + M \xrightarrow{k_2} O_2(a^1\Delta_g, v = 0) + M \tag{2}$$

$$O_2(X^3\Sigma^-_g, v'' = 1) + M \xrightarrow{k_3} O_2(X^3\Sigma^-_g, v = 0) + M \tag{3}$$

Writing $O_2(a^1\Delta_g, v = 1$ and $0)$ as $\Delta_1$ and $\Delta_0$, respectively, and $O_2(X^3\Sigma^-_g, v'' = 1$ and $0)$ as $\Sigma_1$ and $\Sigma_0$, respectively, then eqns. (1), (2) and (3) yield:

$$\frac{-d(\ln[\Delta_1])}{dt} = \frac{-d(\ln[\Sigma_1])}{dt} = \frac{\left(k_2 + \dfrac{k_3 K[\Sigma_0]}{[\Delta_0]}\right)}{\left(1 + \dfrac{K[\Sigma_0]}{[\Delta_0]}\right)}[M] \tag{ii}$$
$$= k'$$

Hence the overall first-order decay coefficients, $k'$, for $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ should be equal for a given reaction mixture. Further, measurement of $k'$, $[\Sigma_0]$ and $[\Delta_0]$, coupled with the magnitude of $K (= 0.71$ at 300 K) and existing rate data for the collisional relaxation of $O_2(X^3\Sigma^-_g, v'' = 1)$ $(k_3)$ should, in principle, yield rate data for the collisional relaxation of $O_2(a^1\Delta_g, v = 1)$ for which there are no previous data, by added gases (M), by substitution in eqn. (ii). The procedures for measuring the concentrations of $\Delta_1$, $\Delta_0$, $\Sigma_1$ and $\Sigma_0$ are given in the experimental section.

## RESULTS

Figure 2 shows typical first-order plots for the decay of $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ in the presence of helium. The slopes of these plots $(-\gamma k')$ may thus be converted into overall first-order decay coefficients $(k')$ using the experimentally determined values of $\gamma$. Figure 3 indicates the variation of $k'$ for these two vibrationally excited states with the pressure of helium, and a similar plot for $CF_4$ is given in Fig. 4. Unfortunately, the spectrum of $SF_6$ obscured most of the region of present interest in the vacuum ultra-violet and permitted measurements of only $O_2(a^1\Delta_g, v = 1)$ at $\lambda = 151.98$ nm, the results of which are shown in Fig. 5.
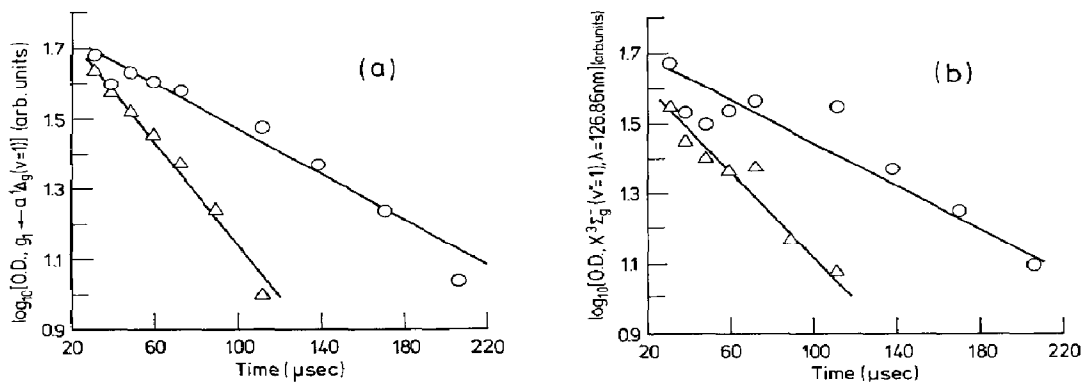


Fig. 2. Typical first-order plots for the decay of $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ in the presence of helium. (a) $O_2(a^1\Delta_g, v = 1)$. (b) $O_2(X^3\Sigma^-_g, v'' = 1)$. $p_{He}(kN\ m^{-2})$: $\bigcirc$, 13.3; $\triangle$, 66.5.
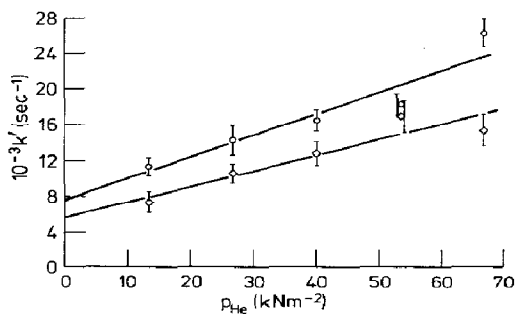
Fig. 3. Variation of the overall first-order coefficients ($k'$, $\gamma$-corrected) for the decay of $O_2(a^1\Delta_g$, $v = 1$) and $O_2(X^3\Sigma^-_g$, $v'' = 1$) in the presence of helium. $p_{O_2} = 33.3$ N m$^{-2}$; $E = 1650$ J. O, $O_2(a^1\Delta_g$, $v = 1$), upper line; $\diamond$, $O_2(X^3\Sigma^-_g$, $v'' = 1$), lower line.
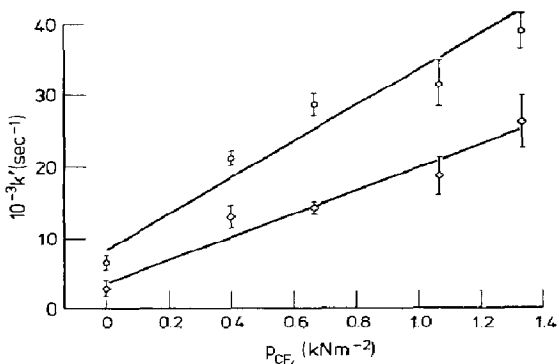
Fig. 4. Variation of the overall first-order coefficients ($k'$, $\gamma$-corrected) for the decay of $O_2(a^1\Delta_g$, $v = 1$) and $O_2(X^3\Sigma^-_g$, $v'' = 1$) in the presence of $CF_4$. $p_{O_2} = 33.3$ N m$^{-2}$, $p_{total}$ with Ar $= 6.65$ kN m$^{-2}$; $E = 1650$ J. O, $O_2(a^1\Delta_g$, $v = 1$), upper line; $\diamond$, $O_2(X^3\Sigma^-_g$, $v'' = 1$), lower line.

The test of eqn. (ii) is limited here to the data for He and $CF_4$ for reasons discussed in the experimental section. Figure 6 shows the data of Figs. 3 and 4 presented as a comparison of the overall decay coefficients in a given experiment for the first vibrational levels of the two states of oxygen. The slope ($S$) of the resulting plot is obtained by taking the mean of the slopes derived from taking a weighted least squares regression of the ordinate on the abscissa and *vice versa*. This yields $S = 0.63 \pm 0.15$, the intercept, as would be expected, being zero within experimental error ($0.2 \pm 2.2$). This departure from the unity required by eqn. (ii) may arise, in part, from the difference in the $\gamma$ values for the transitions at $\lambda = 126.86$ and $151.98$ nm, derived from Fig. 1. The scatter in Fig. 1, which is inevitable when employing plate photometry in the vacuum ultra-violet for "two-path" experiments,
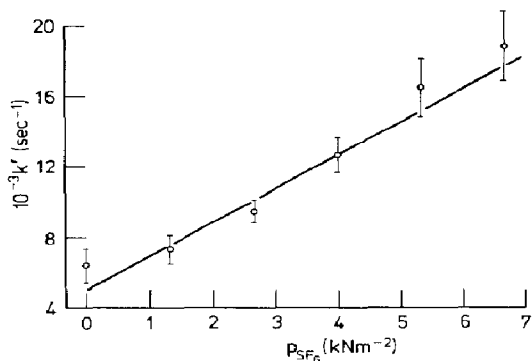


Fig. 5. Variation of the overall first-order coefficient ($k'$, $\gamma$-corrected) for the decay of $O_2(a^1\Delta_g$, $v = 1$) in the presence of $SF_6$. $p_{O_2} = 33.3$ N m$^{-2}$, $p_{total}$ with Ar $= 6.65$ kN m$^{-2}$; $E = 1650$ J.
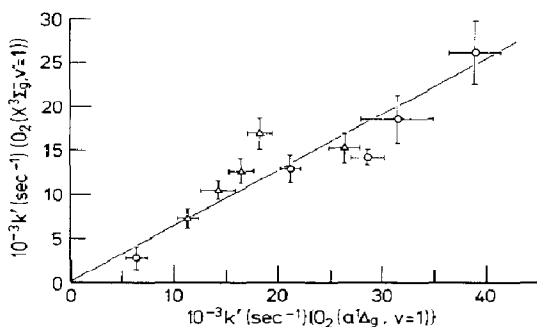
Fig. 6. Comparison of overall first-order coefficients ($k'$) for the decay of $O_2(a^1\Delta_g$, $v = 1$) and $O_2(X^3\Sigma^-_g$, $v'' = 1$). $\triangle$, He; O, $CF_4$.

indicates that a mean value of $\gamma$ for both transitions could be employed, yielding $S = 0.79 \pm 0.19$. Within the limitations and accuracy of plate photometric measurements in the vacuum ultra-violet, photoelectric measurements not being feasible in this system in the absence of a suitable resonance source for $O_2(a^1\Delta_g)$,[8] it would appear that vibrational equilibrium is maintained between the two electronic states.

There is some evidence in these experiments at higher pressures of $CF_4$ ($\sim 2.0$ kN m$^{-2}$) of significant departures from the equality of $k'$ for the two states and of the breakdown of the equilibrium. Even the near resonance exchange (1) would be expected to require $\sim 100$ collisions[34-36] and, at sufficiently high pressures, processes (2) and (3) would become too fast to permit the maintenance of this equilibrium. Unfortunately, these effects take place at fast rates which lie within the "tail" of the photoflash discharge and could not be investigated here in detail with the required accuracy. The use of a shorter photolysis pulse of lower energy could not be employed as a large energy discharge must be used here to dissociate $O_3$ near to completion in order to penetrate the vacuum ultra-violet continuum of this molecule. At the low pressures of flow systems generally containing an inert buffer gas, the assumption of equilibrium between $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ should be justified.

We cannot elucidate in these experiments the effect of very rapid *electronic* energy exchange between $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma^-_g)$ observed by Jones and Bayes[37] which may also provide an efficient route for the maintenance of the vibrational equilibrium between these two states. The present experiments further permit an estimate of a limit for the rate of the electronic quenching of $O_2(a^1\Delta_g)$ by $CF_4$, namely, $k(300 \text{ K}) < 2 \times 10^{-19}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, which may now be included with other data obtained by this method[8].

Unfortunately, rearrangement of eqn. (ii) to yield $k_2$:

$$k_2 = \frac{k'}{[M]}(1 + K[\Sigma_0]/[\Delta_0]) - k_3 K[\Sigma_0]/[\Delta_0] \tag{iii}$$

gives rise to two terms which, in these experiments, will always be of comparable magnitude and whose difference will be small compared with the error in the measurement. This arises because $k'$ increases linearly with $[M]$ (Figs. 3–5) and presumably because of the close magnitudes of $k_2$ and $k_3$ for these similar vibration frequencies. The measured ratios of $[\Sigma_0]/[\Delta_0]$ generally lay in the range 2–3 and hence $k_2$ could not be separated out with the required accuracy. As an approximation, we employ $k_2 = k_3$ in eqn. (ii) and report rate constants for $k_2$ and $k_3$ from measurements of the individual decay plots for the two levels $v = 1$. The results are given in Table 1 and compared with other data on $O_2(X^3\Sigma^-_g, v'' = 1)$, generally following Borell's analysis[38] on previous work reported in the literature. As indicated earlier, the values for $k_2$ and $k_3$ for He and $CF_4$ would be closer employing equal $\gamma$ values for the appropriate transitions.

In general, it is clear that $O_2(a^1\Delta_g, v = 1)$ and $O_2(X^3\Sigma^-_g, v'' = 1)$ are coupled. Thus any experimental method for the detailed kinetic study of vibrational energy transfer out of one of these electronic states, especially when these are generated following excitation by radiation or by an electrical discharge, should contain the capacity for monitoring both states simultaneously. Apart from developing the sophisticated technique of time-resolved laser Raman experiments for the present system, the method described here, limited by the normal constraints of plate photometry in the vacuum ultra-violet, provides the only procedure available for this type of investigation. It is doubtful whether the application of photoelectric methods to this system could result in an accuracy sufficient to separate the terms

TABLE 1

RATE DATA FOR THE VIBRATIONAL RELAXATION OF $O_2(a^1\Delta_g, v = 1)$ AND $O_2(X^3\Sigma^-_g, v'' = 1)$ ON COLLISION ($k$, CM$^3$ MOLECULE$^{-1}$ SEC$^{-1}$, 300 K)

| Collision partner | $O_2(a^1\Delta_g, v = 1)$ | $O_2(X^3\Sigma^-_g, v'' = 1)$ | $O_2(X^3\Sigma^-_g, v'' = 1)$ (previous work) |
|---|---|---|---|
| He | $9.8 \pm 2.0 \times 10^{-16}$ | $7.2 \pm 1.4 \times 10^{-16}$ | $9.1 - 9.5 \times 10^{-16}$ (refs. 38, 39) |
| $CF_4$ | $1.1 \pm 0.2 \times 10^{-13}$ | $6.7 \pm 1.0 \times 10^{-14}$ | — |
| $SF_6$ | $7.9 \pm 1.1 \times 10^{-15}$ | — | — |
| Ar | $<2 \times 10^{-16}$ | $<3 \times 10^{-17}$ | $9.0 \times 10^{-20}$ (ref. 38) |
| $N_2$ | $<3 \times 10^{-16}$ | $<2 \times 10^{-16}$ | $1.8 \times 10^{-18}$ (ref. 40) |

in eqn. (iii), especially in the absence of resonance sources for both states. Thus, whilst either a photoelectric or plate photometric method may give rise to overall coefficients of suitable accuracy for a single decay, the requirement of an accuracy for considering absolute small differences in these coefficients is considerably more severe. The present study, constituting the first kinetic investigation of vibrationally excited $O_2(a^1\Delta_g)$, has indicated the importance of energy coupling with the ground state, has given rise to kinetic data that can sensibly be compared with previous work on the vibrationally excited ground state molecule within reasonable approximations, and indicated the stringent kinetic requirements that any technique must provide in the future for studies on this aeronomically important system.

*Efficiency of the process*

$$O(2^1D_2) + CO(v'' = 0) \rightarrow O(2^3P_J) + CO(v'' = 1) \tag{4}$$
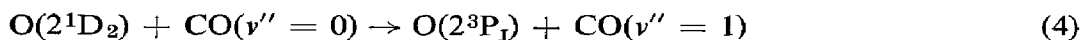
During experiments designed to measure the vibrational relaxation of oxygen on collision with carbon monoxide, concentrations of $CO(v'' = 1)$ were observed at effectively zero time delay, too large to arise from vibrational energy transfer. The results permitted an estimate to be made of the electronic-to-vibration trans-

fer process (4). Initially we calibrate the plate intensity at $\lambda = 159.74$ nm for the (0,1) transition of the fourth positive system of $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ using the Boltzmann fraction in $CO(v'' = 1)$ at 300 K $(3.43 \times 10^{-5})$.

Table 2 summarizes the yields at short delay of $CO(v'' = 1)$ and $O_2(^1\Delta_g)$ in He and Ar (i) for $O_3/CO/He$, Ar mixtures, (ii) with added xenon and (iii) with $p_{O_2} = 0$. Measurement of the absolute concentration of $O_2(a^1\Delta_g)$ employed the extinction coefficient for this molecule at $\lambda = 144.20$ nm ($\varepsilon = 1548$ atm.$^{-1}$ cm$^{-1}$) given by Ogawa[29]. The results in column 3 of Table 2 give the yield of $CO(v'' = 1)$ following quenching of $CO(a^3\Pi)$, optically excited by the photoflash *via* the Cameron bands, $CO(a^3\Pi \leftarrow X^1\Sigma^+)$, reported hitherto by Donovan and Husain[41]. The addition of $p_{Xe} = 665$ N m$^{-2}$ reduces the yield of $CO(v'' = 1)$ from that of an

TABLE 2

CO $(v'' = 1)$ GENERATED ON THE PHOTOLYSIS OF $O_3/CO$ MIXTURES

$M = \{p_{O_2} = 6.7$ N m$^{-2}$, $p_{CO} = 67$ N m$^{-2}$, $p_{total} = 6.7$ kN m$^{-2}$ with Ar or 13.3 kN m$^{-2}$ with He $\}$ $E = 1650$ J, $t = \sim 50\,\mu$s

| | (1) M | (2) M + $p_{Xe}$ = 665 N m$^{-2}$ | (3) $p_{O_2}$ = 0 |
|---|---|---|---|
| **Ar** | | | |
| $p_{CO}(v'' = 1)$ (N m$^{-2}$) | 0.25 ± 0.03 | 0.085 ± 0.02 | 0.055 ± 0.01 |
| $p_{O_2}(a^1\Delta_g)$ (N m$^{-2}$) | 0.44 ± 0.04 | 0.42 ± 0.04 | — |
| **He** | | | |
| $p_{CO}(v'' = 1)$ (N m$^{-2}$) | 0.51 ± 0.06 | 0.14 ± 0.03 | 0.055 ± 0.01 |
| $p_{O_2}(a^1\Delta_g)$ (N m$^{-2}$) | 0.65 ± 0.05 | 0.56 ± 0.05 | — |

$O_3/CO$ mixture (i), to effectively that for CO alone (iii). Xenon quenches $O(2^1D_2)$ with very high efficiency, approximately one in two collisions[42], whereas quenching by He and Ar[42,43] may be neglected here. Similarly, we may neglect the effect of quenching of $CO(v'' = 1)$[41] and $O_2(a^1\Delta_g)$[8] by noble gases. We employ the assumption that, following the photolysis of $O_3$ in this system, $[O_2(a^1\Delta_g)\ (t = 0)] = [O(2^1D_2)\ (t = 0)]$[44,45]. Hence we may attribute the difference in the yields of $CO(v'' = 1)$ in columns 1 and 2, and 1 and 3 to process (4). From the energies of $O(2^1D_2)$ (16030 cm$^{-1}$)[46] and $CO(v'' = 1)$ (2143 cm$^{-1}$)[1], we estimate the efficiencies ($\varepsilon$) for process (4) in He and Ar, namely:

$$\varepsilon \text{ (He)} = 9.4 \pm 1.4\% \text{ and } \varepsilon \text{ (Ar)} = 6.0 \pm 1.0\%$$

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