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State-specific rate constants for the relaxation of $O_2(X\,^3\Sigma_g^-)$ from vibrational levels $v=8$ to 11 by collisions with NO_2 and O_2

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Abstract

Rate constants are reported for the state-specific vibrational relaxation of $O_2(8 \leqslant v \leqslant 11)$ by NO_2 and O_2 at 295 K. O_2 is formed in vibrational levels up to $v=11$ by the reaction of $O(^3P)$ atoms with NO_2. The oxygen atoms were created by partial photolysis of NO_2 at 355 nm using a frequency-tripled Nd:YAG laser, and the kinetics of O_2 in particular v levels observed by laser-induced fluorescence in the $(0, v)$ bands of the $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ system. The rate constants for relaxation of O_2 by NO_2, in units of 10^{-13} cm^3 molecule^{-1} s^{-1}, are 5.5 ± 1.2, 6.8 ± 1.1, 9.3 ± 1.2, 7.0 ± 0.8 for $v=8, 9, 10, 11$, respectively, and by O_2, in units of 10^{-14} cm^3 molecule^{-1} s^{-1}, are 8.5 ± 1.7, 10.8 ± 1.7, 8.2 ± 1.4, 7.5 ± 0.3 for $v=8, 9, 10, 11$, respectively. The results are compared with those obtained previously for higher vibrational levels of O_2, and their implications for atmospheric chemistry are discussed briefly.

1. Introduction

Interest in the behaviour of molecules in states of high vibrational excitation is long-standing. An ultimate goal is to measure rate constants for the transfer of molecules between all vibrational levels up to the dissociation limit for their ground electronic state, so that dissociation rates can be calculated by application of the appropriate master equations. Although this aim is some way from being achieved, there is a large, and increasing, body of rate constants for energy transfer from high-lying vibrational levels, especially those of diatomic molecules.

A variety of experimental methods have been employed to obtain these data, differing both in the methods used to access the high-lying states and in the techniques employed to observe the kinetic behaviour of the excited molecular population. Ideally, the excitation method should 'cleanly' transfer some of the molecules of interest from levels which are thermally populated to a specific vibrational (or ro-

vibrational) level which has insignificant thermal population. Such specificity can be provided by optical pumping using tunable lasers.

Two principal methods of optical pumping have been developed. In the first, a powerful visible or near-infrared laser pulse promotes molecules to moderately high levels of excitation by direct overtone absorption. Such methods are particularly appropriate for hydrides, for example HF [1] and C_2H_2 [2], since the vibrational quanta and transition moments associated with hydride stretching vibrations are both unusually large. However, even for hydrides, the transition moments decrease by about an order-of-magnitude for each successive overtone, with the result that it is difficult to promote sufficient molecules for detection to levels with more than about five quanta in the hydride stretching mode.

Within the past few years, the technique of stimulated emission pumping (SEP) has been developed [3,4]. Using a combination of 'pump' and 'dump' laser pulses, appreciable concentrations can be trans-

ferred to high vibrational levels in the electronic ground state of a molecule, if a suitable bound excited state exists. Using this technique, Wodtke and co-workers have measured rate constants for state-specific vibrational relaxation of $NO(v=8-25)$ [5] and $O_2(v=19-28)$ [6].

In addition to optical pumping methods, exothermic photochemical and chemical reactions can be used to generate species in excited vibrational states. The disadvantage is that molecules are produced over a range of states, often up to the highest which is accessible energetically, and this distribution relaxes in a step-wise fashion down the manifold of vibrational levels. This cascade of population means that the kinetic behaviour of the populations in individual states becomes increasingly complicated the further a level is below the maximum populated in the pumping process. On the other hand, the photochemical/chemical pumping method is relatively easy to apply and it has provided valuable information on relaxation from high vibrational levels in, for example, steady-state experiments on CO [7] and HF [8], quasi-steady-state experiments on HF [9] and HCl [10], and time-resolved experiments on HF [11] and O_2 [12,13].

An ingenious combination of chemical and optical pumping has been employed by Copeland and co-workers [13,14] to measure relaxation rates from high vibrational states of OH. The reaction between H atoms and O_3 is used to generate OH radicals in levels up to $v=9$ and then high-overtone pumping raises some of these species to levels as high as $v=13$.

Interest in relaxation from high vibrational states of O_2 has intensified recently, following the proposal [15,16] that vibrationally excited O_2 could play an important role in the production of O_3 in the upper atmosphere via an autocatalytic mechanism. The major channel in the photodissociation of O_3 in the Hartley bands between 200 and 300 nm produces $O_2(^1\Delta_g)+O(^1D)$, but $\approx 10\%$ of the products are $O_2(^3\Sigma_g^-)+O(^3P)$ [16], with the O_2 in the electronic ground state being produced over a wide range of vibrational levels up to, at least, $v=25$ [18,19]. This observation has lead to the suggestion that local thermal equilibrium may break down and that photodissociation of vibrationally excited O_2 may be important, leading to net production of 'odd oxygen'. The importance of this mechanism depends crucially on

the relative rates of photodissociation and relaxation of O_2 molecules in high vibrational states. With this problem in mind, Price et al. [6] and Park and Slanger [12,13] have recently investigated the vibrational relaxation of O_2; in the case of Price et al. from $v=19-28$, whereas Park and Slanger report relaxation rates for $v=8$, 14 and 18–22.

In the present Letter, we report state-specific rate constants for the relaxation of O_2 from levels $v=8-11$ in collisions with NO_2 and O_2. We employ the reaction

$$O(^3P)+NO_2 \rightarrow O_2(v \leqslant 11)+NO ,$$
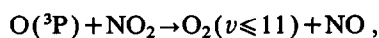
$$\Delta_r H^0 = -193 \text{ kJ mol}^{-1} , \tag{1}$$

as the source of vibrationally excited O_2. As in the experiments of Smith et al. [20], reaction was initiated by pulsed laser photolysis of NO_2 at 355 nm, and the kinetic behaviour of $O_2(v)$ was observed by observing the intensity of laser-induced fluorescence signals excited in $(0, v)$ or $(2, v)$ bands of the Schumann–Runge B $^3\Sigma_u^- - $X $^3\Sigma_g^-$ system. Smith et al. [20] determined the vibrational state distribution of the O_2 formed in reaction (1) for $v=6-11$. The present measurements usefully extend the range of O_2 vibrational levels for which state-specific relaxation rate constants are available. We also note that reaction (1) is important in one of the catalytic cycles which destroy O_3 in the mid-stratosphere [21]. At least in principle, the formation of vibrationally excited O_2 in reaction (1) and the subsequent photolysis of these molecules could reduce the effectiveness of the NO_x cycle in destroying ozone.

2. Experimental

The experimental apparatus and method are similar to those employed by Smith et al. [20]. The reaction cell was constructed from pyrex in the form of a cross. Gas mixtures of NO_2 in argon flowed slowly through the main, 40 mm inner diameter, tube. A small fraction ($<5\%$) of the NO_2 was photolysed by the frequency-tripled output ($\lambda=355$ nm) of a Nd:YAG laser beam. This photolysis laser beam and the probe dye laser beam entered the cell in counterpropagating direction through the two side arms, crossing the gas flow at right angles. These side arms

carried baffles to reduce any scattered laser light and fluorescence from the windows at the end of the side arms. Delays between the two laser pulses were controlled by a delay generator (Stanford Research Systems, DG 535). The method of collecting and processing LIF signals has been described [22].

Flows of the gases were controlled by mass flow controllers. In experiments to determine the rates of relaxation of $O_2(v)$ by NO_2, the flow of NO_2 (SIP, CP grade) was varied to give concentrations in the range 5×10^{14} to 6×10^{15} molecule cm^{-3}. Argon (SIP, zero grade, 99.98%) was used without purification and added to keep the total pressure constant at 50 Torr. In experiments designed to determine the rates of relaxation of $O_2(v)$ by O_2, the NO_2 concentration was kept constant at 3.2×10^{15} molecule cm^{-3} and the concentration of added O_2 (BOC, Industrial Grade, 99.9%) was varied from zero to 6×10^{16} molecule cm^{-3}. All the experiments reported here were performed at room temperature, 295 ± 3 K.

3. Analysis

Each experiment provides a record of how the LIF signal varies with time following initiation of reaction (1) by the pulsed photolytic production of $O(^3P)$ atoms. As rotational energy transfer is extremely rapid under the conditions of our experiments, the signals directly reflect how the concentrations of O_2 in a specific vibrational level vary with time.

In general, the kinetics of these v-specific concentrations depend on:

    (i) the rate at which reaction (1) directly produces $O_2(v)$,

    (ii) the rate at which collisions relax these molecules to lower vibrational levels, and

    (iii) the rate at which collisions relax more highly excited molecules into the level v.

In the case of the highest populated level, $v=11$ in the case of reaction (1) [20], only the first two processes need to be considered, and it is straightforward to show [11] that the concentration varies as the difference between two exponential terms,

$$[O_2(v_{max})] = A[\exp(-\lambda_{slow}t) - \exp(-\lambda_{fast}t)].$$
(2)

For the present system, previous experiments [20]

have shown that reaction (1) is faster than relaxation so that, under pseudo-first-order conditions, λ_{fast} can be equated to $k_1[NO_2]$ and λ_{slow} to $\Sigma_M k_M^v[M]$, where k_M^v is the rate constant for relaxation of $O_2(v)$ by collision with species M, present in concentration [M] in the gas mixture. LIF signals from $O_2(v=11)$ were fitted to a function of the form given on the right-hand-side of Eq. (2) using a non-linear least-squares fitting program, yielding values of λ_{fast} and λ_{slow} for the conditions of that particular experiment. The variation of these pseudo-first-order rate constants with the composition of the gas mixture was then analysed to determine the second-order rate constants for reaction (1) and for relaxation from $v=11$.

For vibrational levels below $v=11$, the analysis has to allow for process (iii), i.e. the cascading of O_2 molecules down the vibrational level manifold. Assuming pseudo-first-order kinetics for reaction and each relaxation process, and relaxation only occurs by steps of $\Delta v=1$, the rate equations for each level population can be solved yielding expressions with an additional exponential for each increase in $v_{max}-v$ (i.e. one for $v=10$, two for $v=9$, etc.). In the case of $v=10$, we fitted our experimental data to the three-exponential analytical expression, using the rate constants for reaction and for relaxation from $v=11$ determined by the method described above, together with the relative reaction rates into $v=11$ and $v=10$ determined by Smith et al. [20]. This procedure gave pseudo-first-order rate constants for relaxation from $v=10$.

For levels below $v=10$ we did not attempt to fit the (complicated) form of the analytical expression. Rather we numerically solved the set of coupled rate equations and fitted the predicted variation of $[O_2(v)]$ versus time to the observed traces of LIF signal. In these simulations, the input included the rate constant for reaction, those for relaxation from higher levels, and the relative reaction rates into levels v and above. The pseudo-first-order rate constant for relaxation from level v and a scaling factor were then adjusted to minimise the deviation between the observed LIF signals and the calculated variation of the concentration $O_2(v)$. The variation of these pseudo-first-order constants with mixture composition was then analysed to yield second-order rate constants for relaxation for levels $v=8$ and 9. Because the relative rates at which reaction (1) popu-

lates the levels $v=8$–11 in O_2 fall monotonically and quite steeply as v increases [20], the problems caused by the stepwise cascade of excited molecules are relatively minor.

4. Results and discussion

4.1. Rate constants for the reaction of $O(^3P)$ atoms with NO_2 and for the relaxation of $O_2(v)$ by NO_2

Measurements of how the LIF signals excited in the $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ (0, 11) band varied with time following the pulsed photolysis of NO_2 were used to determine the rate of reaction (1) and the rate of relaxation of $O_2(v=11)$. A typical set of signals from $O_2(v=11)$ is displayed in the inset to Fig. 1. Although the signals from $O_2(v=11)$ are the simplest in their form, the signal-to-noise on these traces is poorest because of the low fractional yield of $O_2(v=11)$ in the reaction of $O(^3P)$ atoms with NO_2 [20]. As explained above, the signals from $O_2(v=11)$ in a given experiment were fitted to yield values of two first-order rate constants, λ_{fast} and λ_{slow} and this type of experiment was repeated as the concentration of NO_2 was systematically varied. Examples of plots
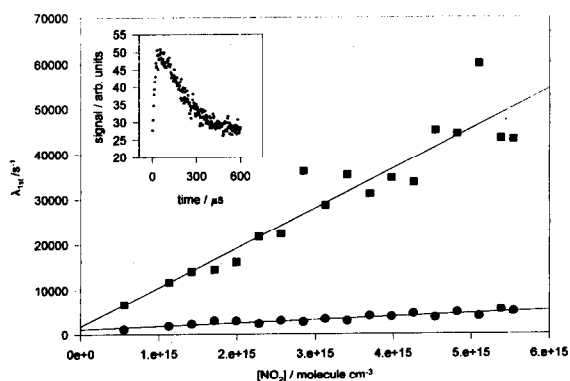

Fig. 1. Pseudo-first-order rate constants, (●) λ_{slow} and (■) λ_{fast}, obtained by fitting LIF signals from $O_2(v=11)$ plotted against the concentration of NO_2, in mixtures containing only NO_2 and argon at a total pressure of 50 Torr ($\equiv 1.62\times10^{18}$ molecule cm^{-3}). The gradients of the lines yield rate constants for the reaction between $O(^3P)$ and NO_2 and for the relaxation of $O_2(v=11)$ by NO_2. The inset shows an example of how the LIF signals from $O_2(v=11)$ vary with time. They are fitted by an analytical expression involving the difference between two exponentials to yield values of λ_{slow} and λ_{fast}.

of λ_{fast} and λ_{slow} versus [NO_2] are shown in Fig. 1. Gradients of several plots of this kind yield the second-order rate constants for reaction (1) between $O(^3P)$ atoms and NO_2, k_1, and for the relaxation of $O_2(v=11)$ by NO_2, $k_{v=11}(NO_2)$. The value obtained for k_1 is $(1.0\pm0.1)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, in excellent agreement with the recommended value of 9.7×10^{-12} cm^3 molecule^{-1} s^{-1} [23]. The value of $k_{v=11}(NO_2)$ is listed in Table 1, along with the rate constants for relaxation of other vibrational levels of O_2 determined in the present work.

The rate constants $k_v(NO_2)$ for $v<11$, which are listed in Table 1, were again obtained by observing how the pseudo-first-order constant for relaxation from a defined vibrational level varied as the concentration of NO_2 in the gas mixture was altered. The analytical procedures used to determine the first-order rate constants for different vibrational levels were described earlier. The errors quoted in Table 1 correspond to a single standard deviation in the gradients of the plots of first-order rate constants against [NO_2] or [O_2]. They include no allowance for systematic error; for example, the errors in derived values of λ_{slow} for levels $v<11$ as a result of uncertainties in the either the distribution of $O_2(v)$ produced in reaction (1) or the rate constants for relaxation from higher levels than that being examined. We have estimated these cumulative errors by examining the effects on the derived rate constants of altering these input data by amounts corresponding to their error.

Table 1
Rate constants and reduced collisional probabilities for the relaxation of $O_2(v=7$–11) by NO_2 and O_2 at 295 K
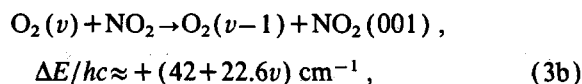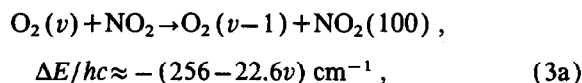
	NO_2	O_2
$v=11$	$(7.0\pm0.8)\times10^{-13}$ 2.4×10^{-4} [a]	$(7.5\pm0.3)\times10^{-14}$ 2.7×10^{-5}
$v=10$	$(9.3\pm0.5)\times10^{-13}$ 3.5×10^{-4}	$(8.2\pm0.7)\times10^{-14}$ 3.3×10^{-5}
$v=9$	$(6.8\pm0.5)\times10^{-13}$ 2.9×10^{-4}	$(10.8\pm0.6)\times10^{-14}$ 4.8×10^{-5}
$v=8$	$(5.5\pm0.4)\times10^{-13}$ 2.6×10^{-4}	$(8.5\pm0.2)\times10^{-14}$ 4.3×10^{-5}

[a] The reduced collisional probability is equal to P/v where $P=k/Z^0$ and Z^0 is the rate constant for collisions between hard-spheres using the collision diameters: $\sigma(O_2+NO_2)=46$ Å^2 and $\sigma(O_2+O_2)=40$ Å^2.

On the basis of these calculations, we derive the errors quoted for each rate constant given in the abstract.

Table 1 also lists 'reduced collisional probabilities'. They are calculated by first dividing the rate constants for relaxation by the rate constant for all bimolecular collisions between the partners treating them as hard-spheres, and then further dividing by v, the quantum number of the vibrationally excited O_2 molecule. This latter factor allows approximately for changes in the matrix elements for different $(v, v-1)$ vibrational transitions [7].

There appears to have been no previous determination of the rate at which NO_2 relaxes vibrationally excited O_2. The magnitude of the observed rate constants and the reduced collisional probabilities are consistent with a vibrational–vibrational (V–V) exchange mechanism. NO_2 has two vibrational modes which might accept energy from vibrationally excited O_2 in near-resonant V–V energy exchange processes: the (100, 000) transition is centred at 1320 cm^{-1} and the (001, 000) transition is at 1618 cm^{-1}. The two possible, near-resonant, V–V processes and the discrepancies in the vibrational transition energies can be expressed as

$$O_2(v) + NO_2 \rightarrow O_2(v-1) + NO_2(100),$$

$$\Delta E/hc \approx -(256 - 22.6v)\ cm^{-1}, \tag{3a}$$

$$O_2(v) + NO_2 \rightarrow O_2(v-1) + NO_2(001),$$

$$\Delta E/hc \approx +(42 + 22.6v)\ cm^{-1}, \tag{3b}$$

where the variations in the energy discrepancies arise from the anharmonicity in the O_2 vibration and the expressions for $\Delta E/hc$ are appropriate for the range of O_2 vibrational levels $(v=8-11)$ of interest in the present work. Although processes (3a) are more resonant than (3b) and are exothermic for $v=8-11$, whereas processes (3b) are endothermic, the (100, 000) band in NO_2 is only weakly infrared active [24,25], in contrast to the (001, 000) band which absorbs strongly [24,26]. There is now ample evidence (see, e.g., Ref. [7]) that there is a correlation between the strengths of radiatively and collisionally induced vibrational transitions, in accord with the theory of Sharma and Brau [27] in which V–V exchange is proposed to occur under the influence of the long-range attractive potential arising from inter-

actions between the multipoles on the two collision partners and the modulations of the interaction by vibrational motions. Consequently, (3a) is likely to be favoured by energetic and resonance considerations, whereas (3b) is likely to be favoured by the magnitude of the matrix element for the vibrational transition in NO_2. It is not possible on the basis of our data to infer whether one or other process is dominant in inducing the relaxation of $O_2(v=8-11)$.

4.2. Rate constants for the relaxation of $O_2(v)$ by O_2

To find rate constants for the relaxation of vibrationally excited O_2 formed in reaction (1) by O_2, series of experiments were performed in which the concentration of O_2 added to a constant NO_2/Ar mixture was systematically varied. The inset to Fig. 2 shows the result of a typical experiment: the LIF signal excited in the B $^3\Sigma_u^- $–X $^3\Sigma_g^-$ (0, 9) band are fitted to a trace obtained by solving the appropriate kinetic equations as described above. The first-order rate constants obtained in one series of experiments on $O_2(v=9)$ are plotted against the concentration of added O_2 in Fig. 2. The gradient yields an estimate of the rate constant, $k_{v=9}(O_2)$, for relaxation of $O_2(v=9)$ by O_2.

Rate constants and reduced collisional probabilities for relaxation of O_2 from levels $v=8-11$ by O_2 are listed in Table 1. Again the values of these param-
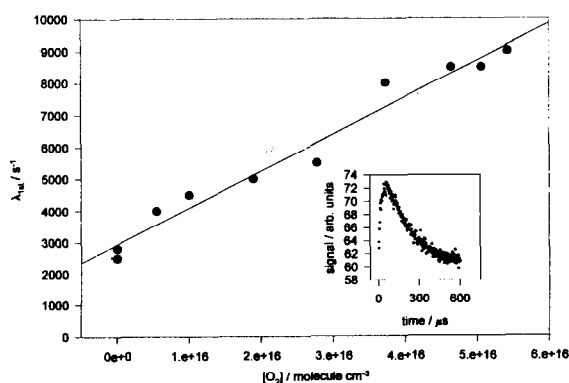

Fig. 2. The pseudo-first-order rate constants for decay of the LIF signals from $O_2(v=9)$ plotted against the concentration of O_2 in mixtures containing NO_2, O_2 and argon, at a total pressure of 50 Torr ($\equiv 1.62 \times 10^{18}$ molecule cm^{-3}). The gradients of the line yields the rate constant for relaxation of $O_2(v=9)$ by O_2. The inset shows an example of how the LIF signals from $O_2(v=9)$ vary with time.

eters are consistent with relaxation by V–V exchange,

$$O_2(v) + O_2(v=0) \rightarrow O_2(v-1) + O_2(v=1),$$
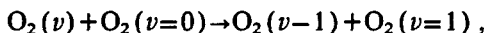
$$\Delta E/hc \approx +22.6v \, cm^{-1}. \tag{4}$$

These processes become less resonant and more endothermic as the level of excitation in the excited molecule increases. The reduction in the reduced collisional probabilities as v increases is therefore expected.

In Fig. 3, we compare our results with those obtained, largely for higher vibrational levels in O_2, by Park and Slanger [12,13] and by Price et al. [6], and with the theoretical calculations of Billing and Kolesnick [28]. Bearing in mind the increasing energy discrepancy and endothermicity of the V–V exchange process as v increases, our results are consistent with those found previously for relaxation from higher vibrational levels. Our rate constants are somewhat larger than those estimated by Billing and Kolesnick, which were in turn much greater than those originally estimated by very approximate methods [29] by Toumi et al. [16].

The implications of faster rates of relaxation of $O_2(v)$ for the atmospheric production of O_3 via the photodissociation of vibrationally excited O_2, as originally hypothesised by Slanger et al. [15], have been discussed by Park and Slanger [12,13]. They conclude that deactivation of $O_2(v)$ appears to be too rapid for the photodissociation mechanism to provide an important source of O_3, although they point out that low temperature measurements should be
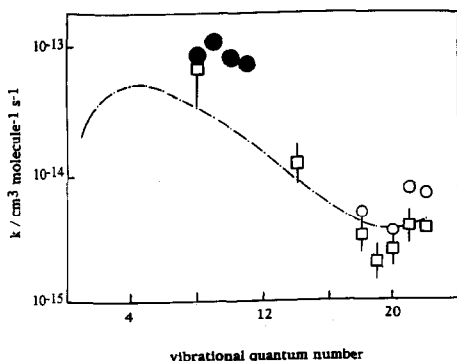
made to confirm this conclusion. Our own results, demonstrating the relatively rapid relaxation of $O_2(v)$ in the range $v=8–11$ further strengthen the conclusions of Park and Slanger [12,13].

Acknowledgement

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Fig. 3. Rate constants for the relaxation of $O_2(v)$ by O_2 plotted against v. The symbols show the results of the present work (●), and the measurements of Park and Slanger (□) [12,13], and of Price et al. (○) [6]. The solid line shows the results of calculations by Billing and Kolesnick [28].

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