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Flash photolysis/temperature jump study of the vibrational relaxation of $N_2O(010)$ by $O(^3P)$ and NO

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Abstract

The rate constants for quenching of $N_2O(010)$ by $O(^3P)$ and NO were determined by monitoring the population of a single rotational level of $N_2O(010)$ during the flash photolysis of mixtures of N_2O, NO_2, NO and Ar. Values of 2.8×10^{-13} and 2.2×10^{-14} cm^3 molecule^{-1} s^{-1} (uncertainty, ±20%) were found for the quenching by O and NO respectively. Comparison with a previous value for the quenching of $CO_2(010)$ by $O(^3P)$ suggests that the rate constant for CO_2 is enhanced, relative to that for N_2O, by the possibility of the formation of a weakly bound triplet state of CO_3.

Keywords: Atomic oxygen; Flash photolysis; Nikitin mechanism; Nitrous oxide; $N_2O(010)$; Temperature jump; Vibrational relaxation; Vibrational relaxation by atoms

1. Introduction

The transfer of vibrational energy during a collision between a molecule and an atomic species, such as $O(^3P)$, can occur either by an impulsive Landau–Teller mechanism [1], which becomes efficient only at high temperatures, or by Nikitin's curve-crossing mechanism [2], which is relatively independent of temperature and thus can be quite efficient at room temperature. With both mechanisms, the rate of energy transfer may be enhanced by the existence of an attractive interaction potential between the molecule and the atom [3]. In a previous study [4], we reported room-temperature measurements of the rate of relaxation of $CO_2(010)$ by $O(^3P)$, together with quasi-classical trajectory calculations, which showed that a Landau–Teller mechanism could account for the high-temperature shock tube results of Center [5] for this system; however, the Nikitin mechanism was required to account for the high efficiency of relaxation at room temperature (measured rate constant for the deactivation of $CO_2(010)$, $(1.2\pm0.2)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}). The experimental method involved monitoring the concentration of one rotational level of $CO_2(010)$ with an IR diode laser while photolysing a mixture of ozone, CO_2 and argon in a conventional flash photolysis system. The photolysis flash served both to dissociate all of the ozone, so producing a known concentration of (eventually) ground state oxygen atoms, and to raise the temperature of the gas mixture by about 20 K so that the desired rate constant could be obtained from the measured rate of relaxation of the $CO_2(010)$ population to its new equilibrium value. With this system, we also made preliminary measurements of the rate of relaxation of $N_2O(010)$ by $O(^3P)$, with a view to determining whether the possibility of formation of a bound CO_3 species would cause the rate constant to be significantly larger for CO_2 than for N_2O. Such a measurement could not, of course, prove this to be the case, but might disprove it. The preliminary measurements appeared to indicate that the rate constant for N_2O was of a similar magnitude to that for CO_2. However, the measurements were affected by the presence of $O(^1D)$ from the photolysis of ozone at short wavelengths, and the experiment clearly needed repeating with a system which did not contain $O(^1D)$. In this paper, we report the results of measurements with $N_2O(010)$ in which the photolysis of NO_2 was the source of $O(^3P)$. The new results show that the quenching of $N_2O(010)$ by ground state oxygen atoms is significantly slower than the quenching of $CO_2(010)$ and, perhaps surprisingly, that the quenching of

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$N_2O(010)$ by the other product of NO_2 photolysis, NO, is even slower, by an order of magnitude.

2. Experimental details

The experimental system, comprising an Applied Photophysics model KF-20 flash photolysis apparatus, a Laser Analytics IR diode laser system, EG&G/Judson HgCdTe IR detectors and a LeCroy transient digitizer, was essentially the same as that described previously [4]. As before, the flash system was located several metres away from the diode laser and detection electronics to reduce electronic interference. A minor improvement was the insertion of a calcium fluoride prism into the IR beam path just before the detector in order to discriminate against stray light from the flash lamps. The population of $N_2O(010)$ was monitored using the F component of the P26 absorption line of the (110)–(010) band at 2185.4756 cm^{-1} [6]. From the published absorption coefficients [7], we concluded that NO_2 should be completely photolysed in our system at somewhat higher partial pressures than the upper limit of around 5 Torr found for ozone [4]. However, our attempts to demonstrate that this was the case, by observing the loss of absorption at 365 nm when samples of NO_2 were flash photolysed, were unsuccessful because essentially all of the NO_2 was re-formed on a timescale shorter than that of the absorption measurement. This observation had a fortunate outcome in that it implied that a series of experiments could be performed with the same gas mixture without serious degradation; it can be understood by noting that, under the conditions of our experiments, the reaction

$$NO + O + M \rightarrow NO_2 + M \qquad (1)$$

for which $k \sim 9 \times 10^{-32}$ cm^6 $molecule^{-2}$ s^{-1} [7], is a far more important channel for the removal of O atoms than

$$O + NO_2 \rightarrow NO + O_2 \qquad (2)$$

for which $k = 6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [7]. Initial gas mixture compositions were in the ranges: N_2O, 0.05–1 Torr; NO_2, 0.4–8.4 Torr; NO, 12–45 Torr (or zero, in experiments without added NO); Ar, 2–40 Torr; higher pressures being generally favoured because the resulting pressure broadening of the N_2O absorption line made it easier to tune the diode laser to the top of the absorption peak. As in the previous study [4], reagent gases were purified by trap-to-trap distillation (NO, NO_2, N_2O) or by passage through a silica gel trap at dry ice temperature (research grade argon).

3. Results

A plot of the transmitted intensity vs. time from a typical experiment is shown in Fig. 1. A decrease in the IR signal corresponds to an increase in the population of $N_2O(010)$. The strong positive excursion in Fig. 1 is produced mainly by residual stray light from the flash, whose duration is seen to be about 15 μs. The differing signal levels before and after the positive excursion correspond to a temperature jump of about 50 °C. For this experiment, which showed a relatively fast decay rate, the rate of exponential decay of the signal towards the final value was measured during the period from 20 μs to 35 μs after the initial trigger. In practice, it made very little difference to the calculated decay rate where, on the tail of the positive excursion, this measurement was begun. This suggests that some depletion of the population of the monitored energy level occurred during the flash and that this depletion contributed to the positive excursion.

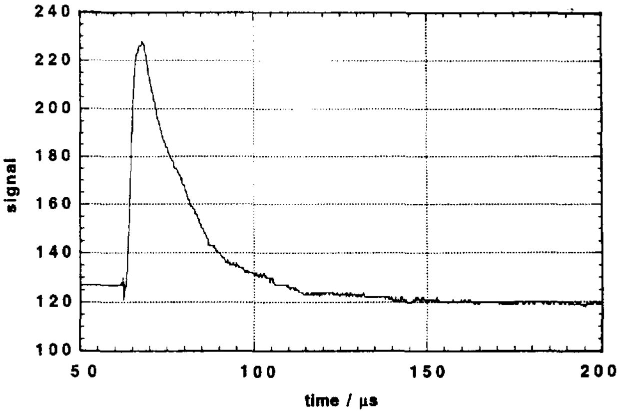

Fig. 1. Typical plot of transmitted intensity vs. time for $N_2O(010)$.

Measured relaxation rates obtained with mixtures of argon, N_2O and NO_2 are plotted against the initial NO_2 concentration in Fig. 2. Each of the data points represents an average of several (up to five; normally three or four) measurements with the same gas mixture. The slope of the line, assuming that the O atom concentration during the decay process is equal to the initial NO_2 concentration, is expected to be the sum of the pseudo-first-order rate constants for the forward and reverse processes in Eq. (3)

$$O + N_2O(010) \leftrightarrow O + N_2O(000) \qquad (3)$$

together with an unknown but probably smaller contribution from relaxation by the other product of NO_2 photolysis, according to

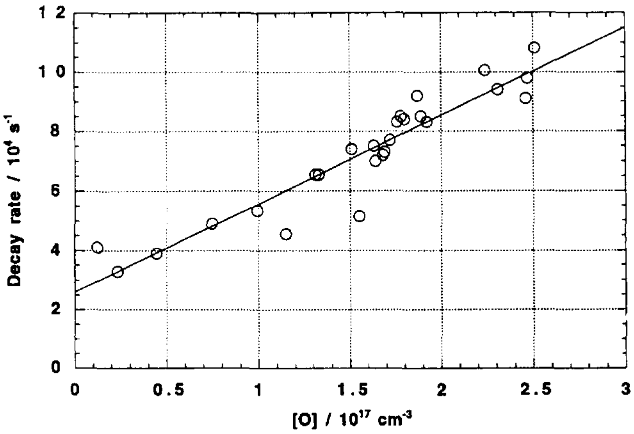

Fig. 2. Variation of the measured relaxation rate with O atom concentration in experiments without added NO.

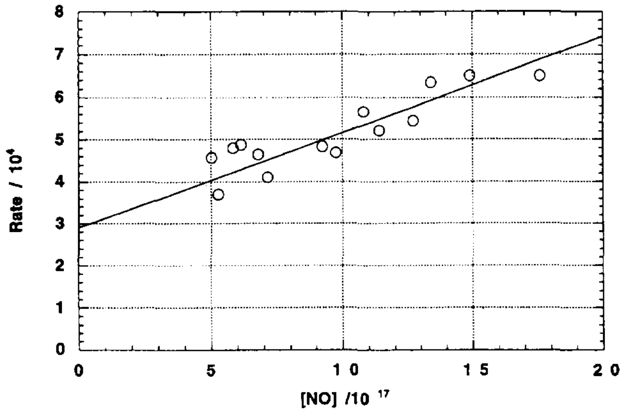

Fig. 3. Variation of the measured relaxation rate with the concentration of added NO.

$$NO + N_2O(010) \leftrightarrow NO + N_2O(000) \quad (4)$$

To determine the effect of the process in Eq. (4), a series of experiments was carried out with sufficient added NO in the photolysis mixture to remove most of the O atoms by the reaction in Eq. (1) during the 5–15 μs delay between the end of the photolysis flash and the beginning of the decay measurement. The resulting decay rates are plotted against the sum of the initial NO and NO_2 concentrations in Fig. 3. The slope of this line, after correcting for relaxation by the few remaining O atoms and assuming that the relaxation rates for NO_2 and NO are approximately equal (this should not lead to significant error because the concentration of NO is an order of magnitude greater than that of NO_2), leads to a value of 2.2×10^{-14} cm^3 molecule^{-1} s^{-1} for the sum of the forward and reverse rate constants of Eq. (4), with an estimated error of $\pm 20\%$ which derives mainly from the uncertainty of the slope of the line in Fig. 3. For the level with $J = 26$, the rate constant of the excitation process is only 0.03 times the rate constant for the quenching process, so that this value is also the rate constant for quenching of $N_2O(010)$ by NO.

To obtain the corresponding rate constants for relaxation by O atoms, it is necessary to correct the results in Fig. 2 for both relaxation by NO resulting from the photolysis of NO_2 and for the loss of O atoms by the reaction in Eq. (1). This was performed by model calculations, using the published rate constants [7] and ignoring the dependence of the rate constant for the reaction in Eq. (1) on the identity of the third body M. The correction for the removal of O atoms by the process in Eq. (1) was sometimes quite large, i.e. up to 30% of the initial NO_2 concentration. The final value obtained for the rate constant for quenching of $N_2O(010)$ by $O(^3P)$ is 2.8×10^{-13} cm^3 molecule^{-1} s^{-1}, again with an estimated uncertainty of about $\pm 20\%$.

The non-zero intercept of the plots in Fig. 2 and Fig. 3 is not solely due to quenching of $N_2O(010)$ by the argon diluent, because variation of the diluent concentration by a factor of 20 did not produce a corresponding change in the decay rate; it is tentatively attributed to relaxation by both argon and ground state N_2O.

4. Discussion

The experiments with NO_2 as the source of O atoms have proven to be easier to carry out and to interpret than the previous experiments with ozone, and our results suggest that this variant of the temperature jump method may be applicable to a wide range of problems. The present experimental system is capable of considerable improvement. For example, the relatively poor shot-to-shot reproducibility of the flash photolysis system may be improved using a system designed specifically for the purpose.

The measurements reported here show that the rate constant for quenching of $N_2O(010)$ by $O(^3P)$ is smaller, by a factor of four, than the corresponding rate constant for quenching of $CO_2(010)$. This suggests that the possibility of formation of a bound triplet CO_3 species may well assist the energy transfer process, although the CO_3 triplet is likely to be only very weakly bound [4]. Accurate quantum chemical calculations for this species would be of considerable interest. The rate constants are sufficiently large for all three quenching processes measured, $CO_2(010)$ quenched by O and $N_2O(010)$ quenched by O and NO, to make it necessary to invoke Nikitin's curve-crossing mechanism. However, two parameters are required in order to model these processes by trajectory calculations: one is the squared matrix element involved in the Landau–Zener formula for the curve-crossing probability and the other is the intermolecular separation at which curve crossing occurs. Both cannot be determined from a measurement at a single temperature. The previous trajectory calculations suggest that these parameters should be able to be obtained separately from measurements of the quenching rate constant over a range of temperatures, especially below room temperature. Work in this direction is planned.

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