

Rate coefficients for the vibrational self-relaxation of $\text{NO}(X^2\Pi, v = 3)$ at temperatures down to 7 K

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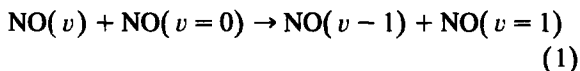
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Abstract

Infrared–ultraviolet double resonance (IRUVDR) experiments have been implemented in the super-cold environment provided by a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. This method has enabled us to measure rate coefficients for the vibrational self-relaxation of $\text{NO}(X^2\Pi; v = 3)$, i.e. $\text{NO}(v = 3) + \text{NO} \rightarrow \text{NO}(v < 3) + \text{NO}$. Using different Laval nozzles, results have been obtained at six different temperatures between 85 and 7 K. The rate coefficients *increase* strongly as the temperature is lowered. The endothermicity of single quantum vibrational–vibrational (V–V) energy exchange ($\Delta E/hc = 55.9 \text{ cm}^{-1}$) means that the rate of this process must *decrease* markedly at the lowest temperatures of our experiments. Therefore, the high relaxation rates which are observed must be due to vibrational–translational (V–T) energy transfer. It is proposed that this process is efficient because of the transient formation of $(\text{NO})_2$ collisional complexes in which intramolecular vibrational energy transfer occurs at rates competitive with re-dissociation of the dimer to $\text{NO}(v = 3)$ and $\text{NO}(v = 0)$. © 1997 Elsevier Science B.V.

1. Introduction

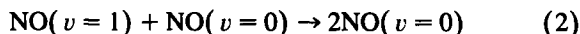
The collisionally-induced relaxation of NO from excited vibrational levels of its $X^2\Pi$ electronic ground state has been a subject of interest for many years. With most *molecular* collision partners, the dominant relaxation mechanism is single quantum vibrational–vibrational (V–V) energy exchange. This is also true for *self-relaxation* of NO vibrational levels above $v = 1$ [1–8], when the V–V process can be represented by the equation:



When relaxation is dominated by V–V energy exchange, NO appears to behave as a “normal”, non-hydride, diatomic molecule; that is, there is no clear

evidence that its rate of relaxation is affected by the fact that the electronic ground state is $^2\Pi$ rather than $^1\Sigma$. Thus the rates of processes represented by Eq. (1) are similar to those for self-relaxation of CO from high vibrational levels [9–11].

The situation is different for self-relaxation of $\text{NO}(v = 1)$ which must occur by vibrational–translational (V–T) energy transfer. At room temperature, this process



is much faster [12–16] than the corresponding processes for $\text{CO}(v = 1)$ [17,18]. At 300 K, the rate constant for Eq. (2) is $k(v = 1) = 7.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [12–16], a result which compares with $k(v = 1) < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the corresponding self-relaxation process in CO [17,18].

Moreover, the temperature dependence of $k(v=1)$ is quite different in the two cases. For CO, the rate constant for self-relaxation above room temperature shows a strong positive dependence on temperature, approximately in accord with the predictions of SSH (Schwartz, Slawsky and Herzfeld) theory [19,20], whereas for NO the variation of $k(v=1)$ shows a shallow minimum at around room temperature [14].

The unusually rapid V–T relaxation of NO($v=1$) has attracted considerable theoretical attention. The early experimental observations led to the proposal by Nikitin [21] that V–T relaxation occurs by an electronically non-adiabatic mechanism. That is, during collisions, the system undergoes a transition between different vibronic states at geometries where the energy splitting between different electronic potential energy surfaces matches the separation of the ($v=1$) and ($v=0$) vibrational levels. An alternative possibility in the case of NO–NO collisions is that relaxation is facilitated by the nature of the lowest potential energy surface. It is known that NO can form (NO)₂ dimers which are held together by a bond that is weak ($D_0 = 8.5 \text{ kJ mol}^{-1} \equiv 710 \text{ cm}^{-1}$ [22–25]), but which is stronger and more directional than van der Waals attraction, and it has been suggested [22–27] that this attraction, like that between species that can form hydrogen bonds, might accelerate energy transfer.

Weak intermolecular attractions are likely to exert their greatest effect on collisional processes at low temperatures, when the average kinetic energy is much less than the well-depth on the intermolecular potential. The lowest temperature at which self-relaxation in NO had been investigated before the present work was 77 K, in the experiments performed in cryogenically cooled cells on the relaxation of NO($v=2$) and NO($v=3$) by Islam et al. [6,7]. Earlier, Stephenson [12,13] had measured the rate of self-relaxation of NO($v=1$) at 100 K. In the present paper, rate constants for vibrational self-relaxation of NO($v=3$) are reported at temperatures down to 7 K. These data have been obtained by implementing the IRUVDR (Infrared–Ultraviolet Double Resonance) technique in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus [28,29]. We have previously reported the results of such experiments yielding total and state-to-state rate coefficients for *rotational* en-

ergy transfer in collisions between NO and He at temperatures down to 15 K [29].

2. Experimental method

Our experiments make use of a CRESU apparatus which has recently been established in Birmingham, and, in other respects, they are similar to those that have been performed previously in our laboratory to measure total and state-to-state rate coefficients for rotational energy transfer in collisions between NO and He [6,7,29]. Pulses of tuneable infrared radiation at ca. 1.8 μm were provided by difference frequency mixing. An injection-seeded Nd:YAG laser (Continuum Powerlite 8010) provided frequency-doubled pump radiation at 532 nm for a dye laser (Continuum ND6000) operating at ca. 670 nm on a mixture of DCM and LD700 dyes (Exciton) in methanol. The dye laser beam was then combined with residual narrow band 1064 nm radiation from the injection-seeded Nd:YAG laser in a LiNbO₃ crystal mounted within an autotracking unit (Continuum), to give the difference frequency radiation at ca. 1.8 μm . Typically, pulse energies of 5 mJ and spectral bandwidths of 0.1 cm^{-1} were achieved, though it is estimated that only ca. 1–2 mJ reached the experiment. The IR frequency was initially chosen by reference to signals from a photoacoustic cell filled with 10 Torr NO, though once the technique had been established, double-resonance LIF was used to tune the IR. The population in the $v=3$ level of the $X^2\Pi_{1/2}$ state was observed by exciting LIF in the (0,3) band of the ($A^2\Sigma^+ - X^2\Pi$) system using the frequency-doubled output of a second dye laser (LAS LDL205) pumped by the frequency-tripled output of another Nd:YAG laser (Spectron SL805), and operating on Coumarin 500 laser dye (Exciton) in methanol. The two laser beams were combined and co-propagated through the gas reservoir and nozzle in the CRESU apparatus and along the axis of the supersonic flow downstream from the nozzle.

The Birmingham CRESU apparatus closely resembles the one in Rennes which has been used to measure rate constants for elementary neutral–neutral reactions and which has been described fully elsewhere [28]. The six nozzles used in the present work were characterised by impact-pressure measurements which yielded temperatures of 85, 52, 45,

27, 15 and 7 K. In some cases, these temperatures were confirmed by recording LIF spectra of NO at a time delay of 5 μs which was long enough to allow complete equilibration of the rotational state distribution but short enough for vibrational relaxation to be prevented. To achieve 7 K, the gas reservoir and the nozzle itself were cooled by liquid N_2 .

The IR-pump laser in our experiments causes initial excitation to a single rotational level in the $v = 3$ vibrational level of the lower spin-orbit component ($\Omega = 1/2$) of the $^2\Pi$ electronic ground state of NO. Our previous experiments [29] and those of Islam et al. [6,7] on rotational energy transfer demonstrated that, as a result of collisions between NO and the carrier gas, rotational and spin-orbit relaxation would be complete within ca. 2 μs in all the gas flows used in the present work. On the other hand, helium, argon and nitrogen are all inefficient at inducing vibrational relaxation [12,13]. Consequently, the rate coefficient for self-relaxation of $\text{NO}(v = 3)$ at each temperature could be determined by performing a series of experiments on gas flows which contained different concentrations of NO. For each gas mixture (the mole fraction of NO was, in all cases, $< 2\%$), the first-order decay of LIF signal from $\text{NO}(v = 3)$ was measured as the time delay between the IR-pump laser and the UV-probe laser was varied systematically. In the case of experiments at 7 K, the amount of NO included in the gas mixture was limited to 0.1% by the requirement not to exceed the vapour pressure of NO at 77 K (81 mTorr) in the liquid N_2 cooled gas reservoir prior to expansion through the Laval nozzle.

3. Results

Typical traces of LIF signal plotted versus the time delay between pulses from the pump and probe lasers are displayed in Fig. 1. It is evident that the signals did not in all cases fully return to their pre-trigger value during the time it took for the supersonic gas flow to travel the distance from the exit of the Laval nozzle to the downstream observation point [28]. The values of the pseudo-first-order decay coefficients that could be obtained were limited (a) by the magnitude of the second-order rate coefficient for self-relaxation and (b) by the amount

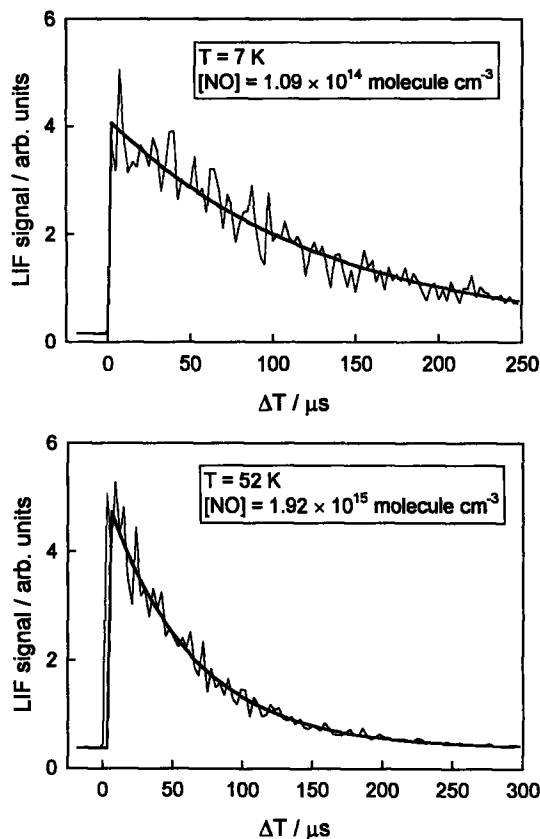


Fig. 1. Traces showing the variation of LIF signal with time delay ΔT between the IR-pump and UV-probe lasers at 7 K and 52 K, with the concentration of NO indicated. The results of non-linear least square fits to a single exponential decay are also shown.

of NO that can be included in the gas flow. In experiments at 7 K, where the gas was pre-cooled by liquid N_2 prior to expansion through the Laval nozzle, the NO concentration was restricted by its vapour pressure at 77 K (see above). In the other experiments, the amount of NO was kept below 2% of the total gas to maintain the integrity and uniformity of the supersonic gas flow.

A non-linear least-squares algorithm was employed to fit each trace of LIF intensity versus time delay to a single exponential decay, yielding pseudo-first-order rate coefficients, k_{1st} , for vibrational relaxation. Fitting was started after a delay of 5 μs to ensure complete rotational and spin-orbit relaxation, and the baseline was fixed using points recorded with “negative” time delays (probe before

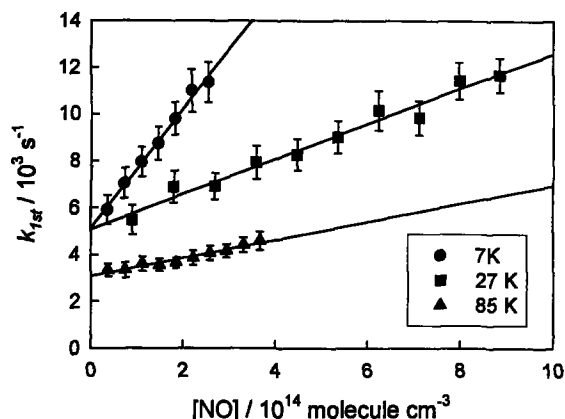


Fig. 2. Variation of first-order rate coefficients, k_{1st} , for self-relaxation of $\text{NO}(v=3)$ with concentration of NO, $[\text{NO}]$, at 7 K, 27 K and 85 K.

pump), necessitated by the restricted scan times arising in some cases from the finite duration of the uniform supersonic flow. The set of first-order rate coefficients obtained at a given temperature was then plotted against the concentration of NO present in the flowing gas mixture as shown in Fig. 2. The gradients of the lines gave the second-order rate coefficients (k) for self-relaxation of $\text{NO}(v=3)$ which are listed in Table 1. The intercepts obtained from these plots were consistent with the rate estimated for diffusion out of the volume illuminated by both the pump and the probe lasers. The linear dependence of k_{1st} versus $[\text{NO}]$ in all cases demonstrates the absence of any stable $(\text{NO})_2$ dimer formation under these conditions. The last column of Table

Table 1

Rate coefficients, k , and thermally-averaged cross-sections, S , for vibrational self-relaxation of $\text{NO}(v=3)$ in the temperature range $T=7\text{--}85$ K. The nature of the carrier gas, M , and its total density are also indicated for each measurement

T (K)	$[M]$ (10^{16} molecule cm^{-3})	M	k (10^{-12} cm^3 molecule $^{-1}$ s^{-1})	$\langle S \rangle$ (\AA^2)
7	19.2	He	25.8 ± 1.8	26.0 ± 0.2^a
15	5.05	He	13.6 ± 0.6	9.35 ± 0.40
27	4.53	He	7.6 ± 0.8	3.87 ± 0.42
45	2.92	Ar	6.4 ± 0.7	2.55 ± 0.26
52	5.36	Ar	6.1 ± 0.6	2.27 ± 0.24
85	1.69	N_2	3.9 ± 0.5	1.12 ± 0.15

^a All errors quoted are $\pm 1\sigma$ statistical error where t is the appropriate value of Student's t -distribution for the 95% point.

1 lists the thermally averaged cross-section for vibrational self-relaxation calculated by dividing the second-order rate coefficient by the mean relative speed in NO–NO collisions at that temperature.

4. Discussion

The rate coefficients for vibrational self-relaxation of $\text{NO}(v=3)$ which have been obtained in the present work at very low temperatures are compared in Fig. 3 with those from previous studies conducted at and above 77 K. Where they overlap with the result of Islam et al [6,7] at 77 K, the present results are ca. 80% higher. The reason for this discrepancy is unknown, although we note that the rate coefficient measured at 295 K by Islam et al. is also somewhat lower than other recently measured values [4,5,8].

Below 77 K, where the present results are quite unique, the rate coefficients for vibrational self-relaxation of $\text{NO}(v=3)$ are large and show a strong negative temperature dependence. The relatively rapid self-relaxation of $\text{NO}(v>1)$ at $T \geq 77$ K has been ascribed to near-resonant V–V energy exchange [4–7]. However, because of vibrational anharmonicity, this process, which is represented by Eq. (1) with $v=3$, is endothermic by 55.9 cm^{-1} , which corresponds to a value of $\Delta E/k_B$ (where k_B is the Boltzmann constant) of 80 K. Consequently,

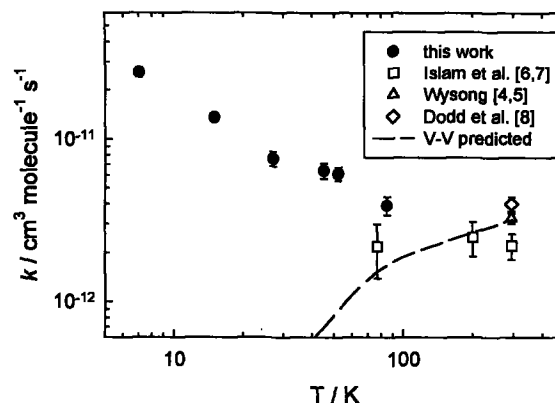


Fig. 3. Variation of rate coefficients for self-relaxation of $\text{NO}(v=3)$ with temperature presented on a log-log plot, showing results from the present work, and for comparison, results from Islam et al. [6,7], Wysong [4,5] and Dodd et al. [8]. The dashed line is a prediction of the rate coefficient based solely on (V–V) exchange, as described in the text.

the rate of V–V energy exchange between $\text{NO}(v=3)$ and $\text{NO}(v=0)$ must decrease sharply through the temperature range covered by our experiments. The dashed line in Fig. 3 is a rough estimate of its rate constant, based on the assumption that the rate constant for the reverse exothermic process, i.e. V–V energy exchange between $\text{NO}(v=2)$ and $\text{NO}(v=1)$, is invariant with temperature and equal to the average of the values determined at room temperature by Wysong [4,5], Islam et al. [6,7] and Dodd et al. [8]. Stephenson [13] finds a value for the rate coefficient for relaxation of $\text{NO}(v=1)$ by NO (which can only occur by V–T transfer) at room temperature which is ca. 40 times less than this average value for $\text{NO}(v=3)$ relaxation by NO. While a small increase in V–T energy transfer rate would be expected in passing from $\text{NO}(v=1)$ to $\text{NO}(v=3)$, most of the relaxation rate for $\text{NO}(v=3)$ at room temperature must therefore be as a result of V–V transfer. However, it is clear from Fig. 3 that V–V energy exchange cannot be responsible for the rapidly accelerating rate of self-relaxation of $\text{NO}(v=3)$ which we observe as the temperature is lowered towards 0 K.

If V–V energy exchange is excluded, then the observed rates of relaxation must correspond to those for V–T energy transfer and it seems certain that the rapidity of this process must be associated with the relatively strong attractive forces which lead to formation of $(\text{NO})_2$ dimers at low temperatures [22–25]. At 7 K, the lowest temperature of our experiments, $D_0/k_B T$ [22–25] is equal to ca. 150, and it seems likely that transient collision complexes can form in collisions between $\text{NO}(v=3)$ and $\text{NO}(v=0)$, with lifetimes with respect to re-dissociation that are long enough for intramolecular vibrational relaxation, and hence vibrational predissociation, to occur. This mechanism for facile, collisionally-induced, vibrational relaxation has previously been invoked [30,31] to explain the rapid rates found for relaxation of one radical species by another (e.g. $\text{NO}(v=1)$ by radical atoms [32,33] and $\text{OH}(v=1)$ by NO and NO_2 [34]). Unfortunately, and contrary to the situation for radical–radical systems [30,31], there have been no measurements of the pressure-dependent rates of association of two NO molecules to form $(\text{NO})_2$. It is therefore impossible to compare the present results with rate coefficients for association to the dimer in the limit of high pressure.

The phenomenon of vibrational predissociation of $(\text{NO})_2$ dimers has been investigated in a series of elegant experiments by Casassa et al. [22–25]. They created dimers in free jet expansions of NO and excited them to various vibrationally excited states using tuneable infrared radiation. The rates of vibrational predissociation were found to depend quite strongly on which vibration was excited. Thus, the dimer with one quantum in the *symmetric* NO stretch mode was found to have a mean lifetime of 880 ps, whereas for the dimer with one quantum in the *anti-symmetric* NO stretch vibration the lifetime with respect to vibrational predissociation is only 39 ps [24]. It is not clear which value provides the better estimate of the rate of intramolecular energy transfer in $(\text{NO})_2$ complexes formed at low temperatures from association of $\text{NO}(v=3)$ with $\text{NO}(v=0)$.

Casassa et al. [24,25] have discussed the mechanism for vibrational predissociation of $(\text{NO})_2$ dimers in some detail. They pointed out that eight electronic potential energy surfaces, four singlets and four triplets, correlate with $\text{NO}(X^2\Pi_{g-}) + \text{NO}(X^2\Pi_{g-})$ and they discussed whether the mechanism for dissociation of a dimer which is excited vibrationally in one or both of the monomer units involves intramolecular vibrational energy transfer within the $^1A'$ electronic ground state or an electronically non-adiabatic mechanism in which the dimer dissociates via an electronically excited state. Unfortunately, although the electronic and geometric structure of the $(\text{NO})_2$ $^1A'$ ground state are well-characterised, little is known about the excited states.

Since the spin–orbit splitting in the electronic ground state of NO is 121 cm^{-1} , corresponding to $(\Delta E_{s-o}/k_B) = 174\text{ K}$, in our experiments at temperatures $\leq 85\text{ K}$ only the lower $\Omega = 1/2$ spin–orbit component is appreciably populated, reducing to two (one singlet and one triplet) the number of surfaces which can be accessed adiabatically. If one assumes that only one quarter of NO + NO collisions occur on the $^1A'$ potential energy surface and that only these collisions cause vibrational relaxation, then our values of k_{relax} correspond to thermally averaged cross-sections for relaxation on this surface of 33 \AA^2 at 15 K and 103 \AA^2 at 7 K.

To examine whether these cross-sections correspond to relaxation in every collision on the $^1A'$ ground electronic surface, we compare them with the

cross-sections, $\langle S \rangle_{\text{L}}$, determined for capture on an orientation-averaged Lennard–Jones potential. Then, according to a simple two-body model, $\langle S \rangle_{\text{L}} = \pi \sigma_{\text{L}}^2 \Omega^{(2,2)*}$, where $\Omega^{(2,2)*}$ is the collision integral [35]. With values of the Lennard–Jones parameters of $\sigma_{\text{L}} = 3.49 \text{ \AA}$ and $\epsilon_{\text{L}}/k_{\text{B}} = 117 \text{ K}$, the values of $\langle S \rangle_{\text{L}}$ are ca. 200 \AA^2 at 15 K and 260 \AA^2 at 7 K. It therefore appears that, even at the lowest temperatures of our experiments, vibrational relaxation may not occur in every collision on the lowest $(\text{NO})_2$ potential in which capture occurs, but that re-dissociation of the complexes to $\text{NO}(v=3) + \text{NO}(v=0)$ prior to vibrational predissociation may occur in a fraction of these collisions.

5. Summary

Implementing an infrared–ultraviolet double resonance technique within the extremely cold environment provided by expansion through a Laval nozzle in a CRESU apparatus, rate coefficients have been measured for the vibrational relaxation of $\text{NO}(v=3)$ in collisions with $\text{NO}(v=0)$ at six temperatures between 85 and 7 K. The rate coefficients show a marked negative dependence on temperature, reaching a value at 7 K which suggests a collisional deactivation efficiency approaching unity. It is pointed out that the observed relaxation must be the result of V–T energy transfer, since V–V energy exchange is too endothermic to occur at the rates which are observed experimentally at the lowest temperatures. It is further proposed that V–T energy transfer is facilitated by the transient formation of $(\text{NO})_2$ complexes which last long enough for vibrational predissociation within the complexes to compete with re-dissociation to $\text{NO}(v=3) + \text{NO}(v=0)$.

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