

Infrared–ultraviolet double resonance measurements on the temperature dependence of rotational and vibrational self-relaxation of $\text{NO}(X^2\Pi, v = 2, j)$

MICHAEL J. FROST,¹ MEEZANUL ISLAM, AND IAN W.M. SMITH²

School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

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This paper is dedicated to Professor John C. Polanyi on the occasion of his 65th birthday

MICHAEL J. FROST, MEEZANUL ISLAM, and IAN W.M. SMITH. *Can. J. Chem.* **72**, 606 (1994).

Infrared–ultraviolet double resonance experiments have been performed to measure the rates of rotational and vibrational self-relaxation in NO at three temperatures: 295 K, 200 K, and 77 K. Pulses of tunable infrared radiation from an optical parametric oscillator have been used to excite molecules into selected rotational levels ($j = 0.5, 6.5, \text{ or } 15.5$) in the $|v = 2; \Omega = 1/2\rangle$ vibronic component of the $X^2\Pi$ electronic ground state of NO. Loss of population from the initially excited level was observed by making time-resolved laser-induced fluorescence measurements on appropriate lines in the $A^2\Sigma^+ - X^2\Pi(2,2)$ band. The rate constants for removal of population from specific rovibronic levels are essentially independent of j and at 295 K agree well with previous direct measurements on a range of v, j levels. The rotationally thermalized population in $v = 2$ relaxes by vibration–vibration (V–V) energy exchange, $\text{NO}(v = 2) + \text{NO}(v = 0) \rightarrow 2 \text{NO}(v = 1)$, at a rate which is almost independent of temperature and which seems to be uninfluenced by the presence of spin-orbit degeneracy in, and attractive forces between, the NO collision partners.

MICHAEL J. FROST, MEEZANUL ISLAM et IAN W.M. SMITH. *Can. J. Chem.* **72**, 606 (1994).

Dans le but de mesurer les vitesses d'autorelaxation rotationnelle et vibrationnelle du NO, on a réalisé des expériences de double résonance infrarouge–ultraviolet à trois températures, 295 K, 200 K et 77 K. On a utilisé des pulsations d'une radiation infrarouge ajustable, obtenues à l'aide d'un oscillateur optique paramétrique, pour exciter les molécules vers des niveaux rotationnels choisis ($j = 0,5, 6,5 \text{ ou } 15,5$) du $|v = 2; \Omega = 1/2\rangle$ composante vibronique de l'état électronique fondamental $X^2\Pi$ du NO. On a observé la perte de population de l'état excité initial en effectuant, sur les raies appropriées de la bande $A^2\Sigma^+ - X^2\Pi(2,2)$, des mesures de fluorescence induites au laser et résolues dans le temps. Les constantes de vitesse pour les pertes de population à partir de niveaux rovibroniques donnés sont essentiellement indépendantes de j et, à 295 K, elles sont en bon accord avec les mesures directes effectuées antérieurement sur un ensemble de niveaux v, j . La relaxation de la population thermalisée par rotation dans $v = 2$ se fait par un échange d'énergie vibration–vibration (V–V), $\text{NO}(v = 2) + \text{NO}(v = 0) \rightarrow 2\text{NO}(v = 1)$, à une vitesse qui est pratiquement indépendante de la température et qui ne semble pas être influencé par la présence d'une dégénérescence spin-orbite dans ou par les forces d'attraction entre les partenaires de collision du NO.

[Traduit par la rédaction]

1. Introduction

The capacity of double resonance techniques to reveal the state-resolved details of energy transfer processes has been appreciated for some time. In experiments of this kind, the Boltzmann distribution of molecules over rovibronic levels is perturbed by pumping a particular spectroscopic transition using a powerful monochromatic source, usually a laser, and then the rates and pathways of the relaxation processes which reestablish equilibrium are examined using spectroscopic techniques. When the pump and probe sources are both pulsed tunable lasers, two types of measurement can be performed. In the first, the frequency of the probe laser is fixed to correspond to the frequency of a discrete transition in the molecule under investigation, and the time delay between excitation and probe lasers is scanned to yield kinetic information about how the population in the selected level evolves in time. Alternatively, the time delay between the two laser pulses is fixed and the frequency of the probe laser is scanned. The spectrum that is obtained contains information about the relative populations in different molecular states at the instant the second laser is fired. If the chosen delay is much shorter than the average time between collisions in the gas sample, then the populations in levels other than that directly accessed in the pump process directly reflect the state-to-state rate coefficients for transfer from the initially populated level into neighbouring levels.

Experiments in which laser-induced fluorescence is used to probe the kinetic behaviour of populations in excited rovibrational levels of electronic ground states have been pioneered by Orr and co-workers, in a series of elegant experiments, initially on D_2CO and HDCO (1) and more recently on C_2H_2 and C_2D_2 (2). In addition, Crim and co-workers (3), Zacharias and co-workers (4), and Frost and Smith (5) have all performed recent double resonance experiments on different states of C_2H_2 . Earlier in our laboratory, Smith and Warr (6) had performed preliminary measurements on the vibrational relaxation pathways in HCN using the double resonance technique. In the present work, as in the experiments of Frost and Smith (5) and Smith and Warr (6), a LiNbO_3 based optical parametric oscillator (OPO) is used as the “pump” source to prepare an initial population in a selected rovibronic level of the molecule under investigation.

The present paper reports infrared–ultraviolet double resonance measurements on the temperature dependence of collisional energy transfer processes in NO. Radiation from the OPO has been used to prepare molecules in either the $j = 0.5, 6.5, \text{ or } 15.5$ rotational level in the $\Omega = 1/2$ lower spin-orbit component of the $X^2\Pi, v = 2$ vibronic level. In this paper, we report rate coefficients for *total* removal of population (i.e., to all final states) with NO itself as the collision partner for several initial rotational states, as well as rate coefficients for vibrational self-relaxation from $v = 2$. The temperature dependences of these processes have been investigated by carrying out experiments at 295 K, 200 K, and 77 K.

The rates of collisional rotational and vibrational energy

¹Present address: JILA, University of Colorado, Boulder, CO 80309-0440, U.S.A.

²Author to whom correspondence may be addressed.

transfer provide a probe of the intermolecular potential acting between the collision partners. In this respect, double resonance experiments on NO are especially interesting, as well as being relatively easy to perform, because the electronic ground state of NO is $^2\Pi$. NO is known to form a dimer with a dissociation energy (D_0) equivalent to ca. 800 cm^{-1} (7) and to undergo unusually rapid vibrational-translational (V-T) relaxation (8), probably as a result of an electronically non-adiabatic mechanism (9). In this context, it is particularly interesting to examine relaxation processes at low temperature, where the dissociation energy of $(\text{NO})_2$ becomes appreciably greater than kT .

Our experiments and the results that we have obtained on rotational energy transfer are closely related to those of Sudbo and Loy (10), reported in 1982. They excited specific (j, Ω) levels in $\text{NO}(v=2)$ using the output from a pulsed F-centre laser pumped by a Nd:YAG laser. Populations in specific $(v=2, j, \Omega)$ levels were then detected using a tunable ultraviolet laser to ionize molecules via levels in the $A^2\Sigma^+(v=2)$ vibronic level in a $(1+1)$ resonance-enhanced multiphoton ionization process. As well as obtaining total relaxation rates out of particular (j, Ω) levels, they obtained state-to-state rate coefficients by fixing the frequency of the probe laser and scanning that of the excitation laser with the delay between the two laser pulses set at a fraction of the average time between NO-NO collisions. However, their measurements were all performed at room temperature and they could only derive an upper limit to the rate constant for vibrational relaxation of $\text{NO}(v=2)$.

More recently, Wodtke and co-workers obtained rotational (11, 12) and vibrational (11, 13) relaxation rates within and for high vibrational levels of NO ($8 \leq v \leq 24$). Theirs might be described as a *triple* resonance method. Levels in the $X^2\Pi$ ground state are populated by stimulated emission pumping (SEP), two tunable dye lasers being deployed to "pump-and-dump" molecules into selected rovibronic levels with high v . A third tunable laser is then used to observe how the excited population that has been created evolves as collisions cause relaxation.

2. Experimental

The apparatus and experimental procedures used in the present work were very similar to those described previously by Frost and Smith (5), so only essential details of the experiments, and ways in which they differ from the earlier ones, are described here. A schematic diagram of the experimental arrangement is given as Fig. 1 in the paper by Frost (5b).

In the present experiments, NO was excited to single selected rovibronic levels using pulses of tunable radiation at ca. $2.7\text{ }\mu\text{m}$ from a LiNbO₃ OPO that was pumped by the fundamental output from a Nd:YAG laser. The pulse energy in the idler beam of the OPO at the required wavelength was in the range 0.1–1.0 mJ, its fluence at the observation region was $0.5\text{--}5.0\text{ mJ cm}^{-2}$, and its bandwidth was ca. 0.3 cm^{-1} . This output was tuned into resonance with lines in the P-branch of the $(v=2 \leftarrow 0; \Omega=1/2 \leftarrow 1/2)$ sub-band using a monochromator and a spectrophone containing 20 Torr of NO and 20 Torr of argon (1 Torr = 133.3 Pa).

The probe radiation was provided by a dye laser (Lambda Physik, FL2000) pumped by an excimer laser (Lumonics, series 400) operating on XeCl. The fundamental output from the dye laser was frequency-doubled in a BBO crystal to provide radiation at 222 nm, in order to excite NO in the (2,2) band of the $A^2\Sigma^+ - X^2\Pi$ band system. The probe radiation contained $<10\text{ }\mu\text{J}$ per pulse, had a bandwidth of ca. 0.2 cm^{-1} , and irradiated a region ca. 2 mm in diameter in the centre of the cylindrical volume illuminated by the output from the OPO. To discriminate against scattered radiation from the probe laser, the fluorescence was observed, using a photomultiplier tube (EMI, model

9781B), through a UG11 broad-band filter, which effectively cuts out radiation below ca. 250 nm. In some experiments (see below), NO in $v=1$ was observed. In these the probe radiation was tuned to lines in the (1,1) band; the arrangements for observing fluorescence remained the same.

The cell used for the present experiments was different from that employed by Frost and Smith (5). However, it was very similar to that used recently (14) in experiments to determine the rate constants for reactions of OH radicals at low temperatures. It is constructed from three concentric Pyrex tubes, so that the inner tube, in which the gas sample of pure NO or NO diluted in argon is placed, is surrounded by a double jacket. The outer jacket is permanently evacuated and refrigerant is placed in, or circulated through, the inner jacket, which is 30 cm long. To achieve low temperatures in the present experiments, either liquid N₂ was placed in the inner jacket or methanol that had been cooled in Dry Ice was flowed slowly through it. The vapour pressure of NO at 77 K is only 81 mTorr ($= 1.02 \times 10^{16}\text{ molecule cm}^{-3}$), but this was quite adequate for all the experiments that were carried out in the present series. Statistical mechanical calculations based on the spectroscopic properties of the $(\text{NO})_2$ dimer (7, 15) show that the mole fraction of $(\text{NO})_2$ under these conditions is less than 10^{-4} . We assume here that the static gas in the observation region is at the temperature of the walls. This is consistent with spectroscopic observations made on NO that had rotationally been completely relaxed. We also note that the rates of the processes under investigation in the present work show very little dependence on temperature.

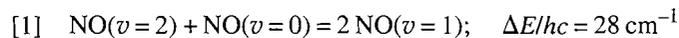
CaF₂ windows were mounted at each end of the central tube in which NO was placed. The two laser beams counterpropagated along the central axis of this cell. To view the LIF from electronically excited NO, the cell had to be fitted with quartz windows. One window is attached to a short sidearm, which is joined to the central tube at its midpoint and passes through the inner jacket. The second window is mounted on the outer wall of the evacuated jacket. The photomultiplier tube, the filter, and a collecting lens are mounted in a housing that is clamped to the jacketed cell so that fluorescence, which passes through the quartz windows, is collected and directed onto the photomultiplier tube. Pressures in the cell are measured directly, using a 0–10 Torr capacitance manometer (MKS Baratron, model 222BA).

The equipment for controlling the firing of the two lasers and for recording, accumulating, and analysing the LIF signals has been described by Frost and Smith (5) and the description is not repeated here.

NO (Electrochem Ltd., 99.99%) was admitted to the vacuum line via a liquid N₂ trap and was purified by trap-to-trap distillations until it condensed in liquid N₂ as a pure white solid. Ar (BOC, zero grade, 99.998%) was used without further purification.

3. Results and discussion

In the present experiments the fraction of NO excited by the OPO laser pulse in the region probed by the ultraviolet laser was estimated. This was done by using the intensities of lines in the (1,1) band of the $A^2\Sigma^+ - X^2\Pi$ system excited in a room temperature sample for calibration. The intensities of these lines could then be compared either with those excited in the (2,2) band, making due allowance for differences in Franck-Condon factors and dye laser intensities, or by comparing the (1,1) spectrum from a thermal sample with that recorded following the excitation of NO to $v=2$, with a delay time chosen to be sufficiently long to allow complete rotational relaxation and for the vibration-to-vibration (V-V) energy exchange process:



to have gone to completion, but short enough for insignificant V-T relaxation to have occurred. These comparisons indicated that, for excitation to $v=2, j=6.5$ at room temperature, the concentration of NO excited by the pulse from the OPO was ca. 10^{-3} times the total concentration of NO present.

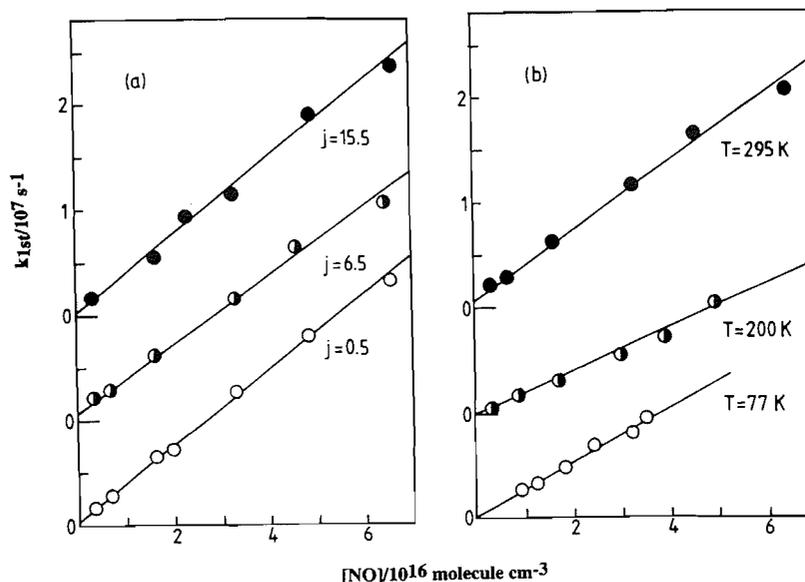


FIG. 1. First-order rate constants for the decay of LIF signals from initially populated rovibronic state $|v = 2, j, \Omega = 1/2\rangle$ plotted against concentration of NO: (a) for $j = 0.5$ (○), 6.5 (●), and 15.5 (●) at 295 K; (b) for $j = 6.5$ at 295 K (●), 200 K (●), and 77 K (○). The values of k_{1st} and $[NO]$ for the data at 77 K are both one third for the values indicated on the axes, and the plots are displaced vertically for clarity.

(a) Rotational self-relaxation of NO ($v = 2; j = 0.5, 6.5, 15.5;$
 $\Omega = 1/2$)

Experiments on rotational self-relaxation were carried out on samples of undiluted NO. Measurements were performed using NO concentrations in the range $(0.3 - 6.0) \times 10^{16}$ molecule cm^{-3} . The intensities of the LIF signals, which were recorded at different delay times, always accurately fitted a single exponential decay yielding a first-order rate constant (k_{1st}) for relaxation of population in the initially excited level for the chosen temperature and concentration of NO. For the range of NO concentrations used, mean relaxation lifetimes varied between ca. 1 μs and 50 ns.

The values of k_{1st} determined in a given series of experiments and at a particular temperature were then plotted against the corresponding concentrations, $[NO]$, yielding a second-order rate constant for self-relaxation of the initially excited $|v, j, \Omega\rangle$ state in NO-NO collisions at that particular temperature. This rate constant corresponds to that for overall relaxation from the initial rovibronic level. It may contain contributions from transfers to j levels in both Ω components. Several plots of k_{1st} versus $[NO]$ are showing in Fig. 1. Panel (a) compares data for relaxation from different rotational levels at room temperature, 295 K. Panel (b) shows results for relaxation from the state, $|v = 2, j = 6.5, \Omega = 1/2\rangle$, at the three temperatures of our experiments: 295 K, 200 K, and 77 K. The second-order rate constants for rotational self-relaxation resulting from all our experiments are summarized in Table 1. Each value quoted is the average of at least two series of experiments on a particular rovibronic level and at a given temperature. It can be seen that, at room temperature, the overall rotational relaxation rates are independent of j , in the range of j, Ω covered in our experiments.

The rate constants derived in the way just described are clearly not obtained under single collision conditions, and they characterize the rate at which the initial population ($N_{i,0}$) in the selected state i relaxes to the population ($N_{i,e}$) in the same state once complete rotational (and spin-orbit) relaxation has occurred. The equation describing the rate of change of population $N_{i,t}$ is

TABLE 1. Rate constants ($k/10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$) for relaxation and for total transfer from specific rovibronic levels, $|v = 2, j, \Omega = 1/2\rangle$, together with collisional probabilities for total transfer, in collisions with NO at different temperatures

T/K	$j = 0.5$	$j = 6.5$	$j = 15.5$
295	3.60 ± 0.24	3.08 ± 0.16	3.50 ± 0.12
	3.56	2.93	3.43
	1.22	1.00	1.16
200	1.85 ± 0.10	2.08 ± 0.18	1.76 ± 0.28
	1.82	1.95	1.74
	0.66	0.75	0.63
77	1.80 ± 0.16	2.43 ± 0.16	2.67 ± 0.23
	1.70	2.22	2.67
	0.63	0.83	1.00

*Obtained by dividing the observed rate constant by $Z_{1,1}^2$, the second-order rate constant for all collisions assuming a Lennard-Jones potential between the NO collision partners.

$$dN_{i,t}/dt = -\sum k_{i \rightarrow j}[NO]N_{i,t} + \sum k_{i \leftarrow j}[NO]N_{j,t}$$

where $k_{i \rightarrow j}$ and $k_{i \leftarrow j}$ are state-to-state rate constants for transfer from and to the observed state, $N_{j,t}$ are populations in all other rotational and spin-orbit states in $v = 2$ at time t , and both summations are over j . The first term on the right-hand side of this rate equation can clearly be written as $-k_{i \rightarrow}[NO]N_{i,t}$, where $k_{i \rightarrow} = \sum k_{i \rightarrow j}$ is the rate constant for total removal of population from the prepared state i .

To estimate values of $k_{i \rightarrow}$, we assume that the second term on the right-hand side of the rate equation can be written as $k_{i \leftarrow}[NO]\sum N_{j,t}$. Within this approximation, the observed relaxation rate constant is equal to $(k_{i \rightarrow} + k_{i \leftarrow})$ and, since at long times $dN_i/dt = 0$, the ratio of the rate constants is given by $k_{i \leftarrow}/k_{i \rightarrow} = N_{j,t \rightarrow \infty}/\sum N_{j,t \rightarrow \infty}$ and can be calculated using statistical mechanics. The rate coefficients $k_{i \rightarrow}$ for total removal of population from specific rovibronic levels are listed as the second entry in each element of Table 1. The values decrease slightly as

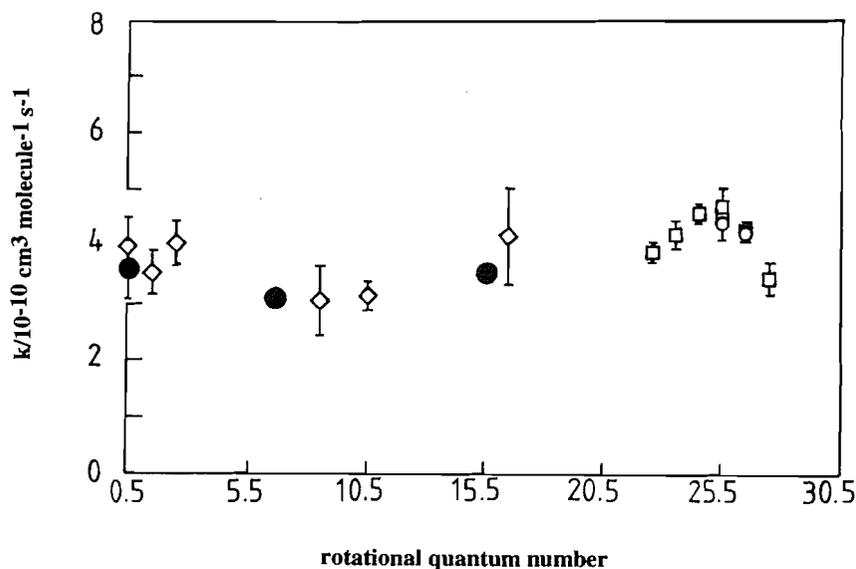


FIG. 2. Second-order rate constants for removal from specific rotational levels $j = 0.5, 6.5,$ and 15.5 in $|v = 2, \Omega = 1/2\rangle$ (●) compared with similar data for levels in $v = 2$ (◇) (10) and in $v = 8$ (○) and 19 (□) (13).

the temperature is lowered and this effect appears to be greatest for the lowest rotational state investigated.

Table 1 also lists the collisional probabilities for removal from specific levels. These numbers are derived by dividing the observed second-order rate constants for *total* removal by the rate constants calculated for all collisions assuming that a Lennard-Jones potential acts between two NO molecules. The collisional probabilities are all within a factor of two of unity, confirming again the efficiency of rotational energy transfer. The reduced collision rate goes some way to explaining the reduction in relaxation rate coefficients that is observed below room temperature, but the probabilities do seem somewhat reduced at lower temperatures. This could reflect a reduction in the endothermic state-to-state rate coefficients (e.g., those for transfer to levels in the higher Ω component) as the temperature is lowered.

Our results at room temperature can be compared most directly with those of Sudbo and Loy (10) and of Yang and Wodtke (12). To facilitate these comparisons, Fig. 2 displays the rate constant for total decay from selected rovibronic levels obtained for different v, j levels in these three sets of measurements. It can be seen that the rate coefficients are essentially independent of both rotational and vibrational level over quite wide ranges of v and j , within the accuracy of the experimental results. A similar conclusion has been reached for rotational energy transfer in C_2H_2 , as a result of a number of recent measurements (2-5).

Rate constants for total removal of population from a given rovibronic level can also be compared with line-broadening data for spectroscopic transitions terminating on the same state. For states in the electronic ground states of N_2 (16) and C_2H_2 (5a), for example, it appears that rate constants derived from the two kinds of measurements correlate well, indicating that energy transfer, rather than elastic m_j -changing collisions, are predominantly responsible for collision broadening in rovibrational transitions in these $^1\Sigma_g^+$ molecules. A large number of studies have been carried out on the pressure broadening of infrared transitions of NO. One of the most recent and thorough is that carried out by Pine et al. (17) on lines in the (2,0) first

overtone band. The collision-broadening coefficients, which they determined at room temperature, are slightly higher for lines between $^2\Pi_{3/2}$ components than for lines in the $^2\Pi_{1/2} - ^2\Pi_{1/2}$ sub-band. The self-broadening coefficients for the R(0.5), R(6.5), and R(15.5) lines in the latter sub-band translate into rate coefficients varying from 5.5×10^{-10} to 4.8×10^{-10} to 4.5×10^{-10} cm^3 molecule⁻¹ s⁻¹, there being a slight decrease in the broadening coefficients as the rotational energy levels involved in the transition increase. These rate coefficients are about 50% higher than those observed in the direct studies of population transfer made by Sudbo and Loy (10), Yang and Wodtke (12), and ourselves.

The reason for this difference is not obvious. Sudbo and Loy's analysis indicates that, in the case of self-relaxation, the transfer of molecules between Ω components makes a significant contribution to population transfer, as well as j -changing transitions within the same Ω component, but that this is not true when the collision partner is other than NO. In any case, there seems to be no reason why this effect should destroy the correlation between rate coefficients derived from collision-broadening data and those determined directly in relaxation experiments. However, calculations by Orlikowski and Alexander (18) suggest that NO-NO collisions may be unusual in another respect: namely, in that the usual propensity for m_j -preserving collisions is relaxed in this case due to the $^2\Pi$ electronic nature of both collision partners. It therefore seems possible that m_j -changing collisions make some contribution to pressure broadening in pure NO. It will be interesting to check whether the difference between rotational energy transfer rates for NO measured directly and inferred from line-broadening measurements extends to collision partners other than NO itself.

(b) Vibrational self-relaxation of NO ($v = 2$)

Experiments on vibrational self-relaxation of NO ($v = 2$) were carried out on samples of NO diluted to 10 Torr in argon. The argon diluent helps to cause rapid equilibration of the excited population over rotational levels, and decreases the rate at which the excited state population diffuses out of the region

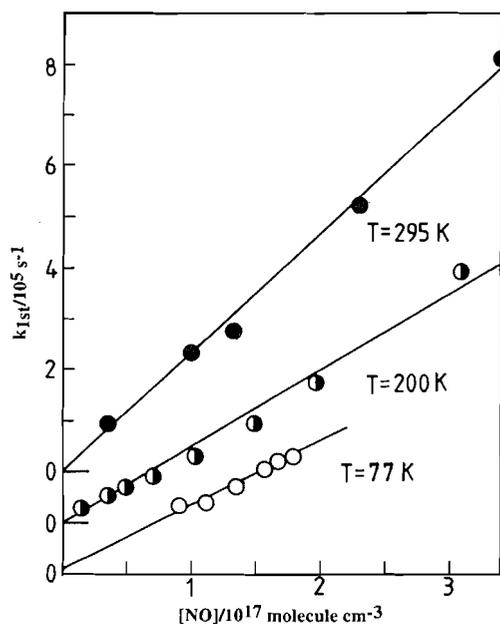


FIG. 3. First-order rate constants for the decay of LIF signals from $\text{NO}(v=2)$, in which the rotational and spin-orbit populations have become thermalised, plotted against concentration of NO. The values of k_{1st} and $[\text{NO}]$ for the data at 77 K are one fifth and one tenth respectively, of the values indicated on the axes, and the plots are displaced vertically for clarity.

illuminated by the probe laser. Its effect on the rate of vibrational relaxation was negligible (8). Vibrational relaxation of $\text{NO}(v=2)$ is approximately two orders of magnitude slower than rotational relaxation. Therefore, in these measurements, the concentrations of NO used were in the range $(3-30) \times 10^{16}$ molecule cm^{-3} . As before the LIF signals always accurately fitted single exponential decays yielding first-order rate constants for transfer of population from $|v=2\rangle$ with a thermal distribution of molecules over the rotational levels of both spin-orbit components.

Examples of the plots of k_{1st} against $[\text{NO}]$ are shown in Fig. 3. The gradients of the lines yield the second-order constants (k_e) for vibrational relaxation from $\text{NO}(v=2)$, which undoubtedly occurs by the slightly endothermic V-V exchange process represented by eq. [1]. These rate constants, those (k_e) for the reverse exothermic process calculated by applying the principle of detailed balance, and collisional probabilities for both processes are listed in Table 2.

The rate constants and probabilities for V-V energy transfer obtained in the present experiments at 295 K are compared with previous values for the same process determined at room temperature. Neither the measurements of Macdonald and Sopchshyn (19) nor those of Horiguchi and Tsuchiya (20) can be described as direct, since in neither case was the mode of vibrational excitation state-specific. Stephenson's measurements (8) were made by exciting $\text{NO}(v=1)$ with a frequency-doubled CO_2 laser and observing the time-dependent behaviour of the (2,1) band emission as the vibrational level populations came into equilibrium, using a cold gas filter to discriminate against (1,0) emission. Our result at 295 K is in reasonable agreement with that of Stephenson (8).

Yang, Kim, and Wodtke (13) measured room temperature rate constants for the deactivation of $\text{NO}(v \geq 8)$ by NO. Their conclusion is that up to ca $v=8$ the removal of NO molecules

TABLE 2. Rate constants (10^{-12} cm^3 molecule $^{-1}$ s $^{-1}$) and collisional probabilities for V-V energy exchange in the endothermic (k_e) and exothermic (k_e) directions in NO-NO and CO-CO collisions

T/K	k_e (NO-NO) ^a	k_e (NO-NO) ^b	k_e (CO-CO) ^c
295	2.44 ± 0.3	2.80 ± 0.3	—
		0.0096	
		3.8 ± 0.9 (8a)	3.46 ± 0.1 (24)
200	1.60 ± 0.3	2.3 ± 0.2 (19)	—
		1.6 ± 1.1 (18)	—
		0.0072	4.25 (24) ^d
77	2.10 ± 0.2	3.5 ± 0.3	—
		0.0130	

^aRate constant for $\text{NO}(v=2) + \text{NO}(v=0) \rightarrow 2\text{NO}(v=1)$.

^bRate constant for $2\text{NO}(v=1) \rightarrow \text{NO}(v=2) + \text{NO}(v=0)$.

^cRate constant for $2\text{CO}(v=1) \rightarrow \text{CO}(v=2) + \text{CO}(v=0)$.

^dInterpolated from Stephenson's results (24) obtained at temperatures between 105 K and 300 K.

from excited vibrational levels in collisions with unexcited NO is dominated by V-V energy exchange. At higher levels of excitation, other mechanisms involving chemical forces appear to come into play. Using their data, one can compare the value of k_e/v for $\text{NO}(v-1) + \text{NO}(v=1) \rightarrow \text{NO}(v) + \text{NO}(v=0)$ and $v=8$, with our value of the same quantity for $v=2$. The resultant "reduced rate constants" are 2.25×10^{-13} and 1.3×10^{-12} cm^3 molecule $^{-1}$ s $^{-1}$, respectively. The decrease in the reduced rate constant that is observed with the increase in energy discrepancy from $\Delta E/hc = 28$ cm^{-1} to 223.5 cm^{-1} is in sensible agreement with both theoretical expectation (13, 21, 22) and from extensive work on vibrational relaxation in CO (23).

We are unaware of any measurements of V-V energy exchange in NO-NO collisions at temperatures below room temperature. However, Stephenson and Mosburg (24) studied this process in CO at temperatures between 100 K and 300 K. Values of k_e for $2\text{CO}(v=1) \rightarrow \text{CO}(v=2) + \text{CO}(v=0)$ are given for comparison in Table 2. A comparison of both the absolute values of the rate constants for V-V exchange and their variation with temperature suggests that the $2^2\Pi$ electronic character of the ground state of NO exerts no significant influence on the rate of V-V energy exchange in contrast to its role in facilitating V-T energy transfer (8, 9). The similarity of the rate constants for V-V energy exchange in NO-NO and CO-CO collisions and their insensitivity to temperature suggest that, in both cases, energy transfer occurs under the influence of long-range attractive forces, arising from the electrostatic charge distributions in the molecules and their modulation by the molecular vibrations, in accord with the long-established theory of Sharma and Brau (25).

4. Summary and conclusions

A double resonance method, using tunable laser sources of infrared and ultraviolet radiation, has been employed to determine rate constants for rotational energy transfer in collisions between $\text{NO}(v=2, j, \Omega=1/2)$ and other NO molecules, for three different j levels and at three different temperatures. The rate constants are insensitive to the initial rotational level but decrease slightly as the temperature is lowered. The reasons for this change will be explored in future measurements of state-to-state rate coefficients and their dependence on temper-

ature, and the generality of this finding will be examined by investigating the effect of collision partners other than NO.

By performing similar experiments on NO samples diluted in argon and over longer pulse-probe time-scales, rate constants have also been measured for the self-relaxation of NO($v=2$) by V-V energy transfer. The rate constants and their relative insensitivity to temperature indicate that in NO, at least for low vibrational levels, as for CO, V-V energy exchange occurs under the influence of long-range, attractive forces and the existence of spin-orbit degeneracy in NO is unimportant.

Acknowledgements

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1. (a) J.G. Haub and B.J. Orr. *Chem. Phys. Lett.* **107**, 162 (1984); (b) *J. Chem. Phys.* **86**, 3380 (1987); (c) C.P. Bewick and B.J. Orr. *J. Chem. Phys.* **93**, 8634 (1990).
2. (b) B.L. Chadwick and B.J. Orr. *J. Chem. Phys.* **95**, 5476 (1991); (b) *J. Chem. Phys.* **97**, 3007 (1992).
3. (a) E. Carrasquillo, A.L. Utz, and F.F. Crim. *J. Chem. Phys.* **88**, 5976 (1988); (b) A.L. Utz, J.D. Tobiason, E. Carrasquillo, M.D. Fritz, and F.F. Crim. *J. Chem. Phys.* **97**, 389 (1992); (c) J.D. Tobiason, A.L. Utz and F.F. Crim. *J. Chem. Phys.* **97**, 7437 (1992).
4. (a) R. Dopheide, W.B. Gao, and H. Zacharias. *Chem. Phys. Lett.* **182**, 21 (1991); (b) R. Dopheide and H. Zacharias. *J. Chem. Phys.* **99**, 4864 (1993).
5. (a) M.J. Frost and I.W.M. Smith. *Chem. Phys. Lett.* **191**, 574 (1992); (b) M.J. Frost. *J. Chem. Phys.* **98**, 8572 (1993).
6. I.W.M. Smith and J.F. Warr. *J. Chem. Soc. Faraday Trans.* **87**, 205 (1991).
7. M.P. Casassa, J.C. Stephenson, and D.S. King. *J. Chem. Phys.* **89**, 1966 (1988).
8. (a) J.C. Stephenson. *J. Chem. Phys.* **59**, 1523 (1973); (b) *J. Chem. Phys.* **60**, 4289 (1974).
9. (a) E.E. Nikitin. *Opt. Spectrosc.* **9**, 8 (1960); E.E. Nikitin and S. Ya. Umanski. *Faraday Discuss. Chem. Soc.* **53**, 1 (1972).
10. (a) Aa.S. Sudbo and M.M.T. Loy. *Chem. Phys. Lett.* **82**, 135 (1981); (b) *J. Chem. Phys.* **76**, 3646 (1982).
11. X. Yang, J.M. Price, J.A. Mack, C.G. Morgan, C.A. Rogaski, D. McGuire, E.H. Kim, and A.M. Wodtke, *J. Phys. Chem.* **97**, 3944 (1993).
12. X. Yang and A.M. Wodtke. *J. Chem. Phys.* **96**, 5123 (1992).
13. (a) X. Yang, E.H. Kim, and A.M. Wodtke. *J. Chem. Phys.* **93**, 4483 (1990); (b) *J. Chem. Phys.* **96**, 5111 (1992).
14. P. Sharkey and I.W.M. Smith. *J. Chem. Soc. Faraday Trans.* **89**, 631 (1993).
15. C.M. Western, P.R.R. Langridge-Smith, and B.J. Howard. *Mol. Phys.* **44**, 145 (1981).
16. G.O. Sitz and R.L. Farrow. *J. Chem. Phys.* **93**, 7883 (1990).
17. A.S. Pine, A.G. Maki, and N.-Y. Chou. *J. Mol. Spectrosc.* **114**, 132 (1985).
18. T. Orlikowski and M.H. Alexander. *J. Chem. Phys.* **80**, 4133 (1984).
19. R.G. MacDonald and F.C. Sopchyshyn. *Chem. Phys.* **94**, 455 (1985).
20. H. Horiguchi and S. Tsuchuja. *Jpn. J. Appl. Phys.* **18**, 1207 (1979).
21. (a) R.N. Schwartz, Z.I. Slawsky, and K.F. Herzfeld. *J. Chem. Phys.* **20**, 591 (1952); (b) R.N. Schwartz and K.F. Herzfeld. *J. Chem. Phys.* **22**, 767 (1954).
22. (a) D. Rapp and P. Englander-Golden. *J. Chem. Phys.* **40**, 573 (1964); *J. Chem. Phys.* **43**, 316 (1965).
23. G. Hancock and I.W.M. Smith. *Appl. Opt.* **10**, 1827 (1971).
24. J.C. Stephenson and E.R. Mosburg, Jr. *J. Chem. Phys.* **60**, 3562 (1974).
25. (a) R.D. Sharma and C.A. Brau. *J. Chem. Phys.* **50**, 924 (1969); (b) R.D. Sharma. *Phys. Rev.* **177**, 102 (1969).