

# State-to-state rate coefficients for transfer from the rotational levels $J = 7.5, 20.5, 31.5$ and $40.5$ in $\text{NO}(X^2\Pi_{1/2}, v = 2)$ in collisions with He, Ar and $\text{N}_2$ and for $J = 7.5, 20.5$ and $31.5$ in collisions with NO: comparisons between experiment and theory

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Using the infrared–ultraviolet double resonance (IRUVDR) technique, state-to-state rate coefficients have been measured for the transfer of NO from the initial rovibronic levels ( $X^2\Pi_{1/2}, v = 2, J_i = 7.5, 20.5$  and  $31.5$ ) in collisions with He, Ar,  $\text{N}_2$  and NO itself. For relaxation by He, Ar and  $\text{N}_2$  from the rotational level  $J_i = 40.5$ , rate coefficients were measured by a new method in which IRUVDR was implemented instantly on NO molecules formed by photodissociation of  $\text{NO}_2$  at 355 nm. As  $J_i$  is increased the distribution of states ( $J_f$ ) was found to change in two ways: (a) the distribution of  $\Delta J (= J_f - J_i)$  values becomes narrower, and (b) negative values of  $\Delta J$  are increasingly favoured over positive values. Thus > 80% of the transfer from  $J_i = 40.5$  is to  $J_f = 39.5$ . As with the earlier experimental results for total transfer, the present results for NO–He and NO–Ar collisions are shown to agree quite well with those from coupled states quantum scattering calculations on *ab initio* potential energy surfaces, although the agreement becomes poorer at high  $J_i$ . Possible reasons for this discrepancy are discussed.

## Introduction

The application of modern experimental techniques, which usually employ lasers, molecular beams or both together, is providing ever more detailed information about intramolecular and intermolecular energy transfer. The intermolecular transfer of rotational energy in collisions involving  $\text{NO}(X^2\Pi_\Omega)$  has been the subject of a large number of previous experimental studies,<sup>1–17</sup> including several from our laboratory in Birmingham.<sup>4–7,10,11</sup> In part, this emphasis on NO is a result of its favourable spectroscopic properties (for a brief discussion, see the introductions to refs. 10 and 11). In addition,  $\text{NO}(X^2\Pi_\Omega)$  is a convenient species for investigating inelastic collisions involving species with open electronic shells.

The increase in the quality and range of experimental information on rotational energy transfer in NO has been paralleled by progress in theory.<sup>18–25</sup> The description of collisions involving  $\text{NO}(X^2\Pi_\Omega)$ , particularly those with the rare gas atoms He and Ar, where accurate *ab initio* potential surfaces are available,<sup>19,24</sup> is an interesting theoretical challenge and serves as a prototype for encounters involving molecular radicals in  $^2\Pi_\Omega$  states. In several recent pieces of work,<sup>10,11</sup> we have sought to determine the level of agreement between the results of completely *ab initio* scattering calculations and experimental data obtained under a variety of conditions.

Experiments on rotational energy transfer in  $\text{NO}(X^2\Pi_\Omega)$  have been of two main kinds which provide complementary information. On the one hand, optical–optical double resonance (DR) techniques have been deployed in ‘bulb’ experi-

ments.<sup>1–11</sup> For example, our work in Birmingham<sup>4–7,10,11</sup> has employed the infrared–ultraviolet double resonance (IRUVDR) method to examine rotational energy transfer in collisions of  $\text{NO}(X^2\Pi_\Omega)$ . In these experiments, a pulsed, tunable, infrared ‘pump’ laser is used to excite NO molecules to a specific rotational level in either the  $v = 2$  or  $v = 3$  vibrational level of the  $X^2\Pi_\Omega$  electronic ground state. A tunable dye laser then excites laser induced fluorescence (LIF) from the rovibrationally excited molecules *via* transitions in the  $A^2\Sigma^+ - X^2\Pi$  system. Rate coefficients for *total* relaxation from a selected initial level can be determined by tuning the frequency of the ‘probe’ laser to a UV transition from the rovibrational level directly populated by IR absorption, and observing the variation of the LIF signal intensity, as the time delay between the pulses from the pump and probe lasers is varied. Alternatively, the delay between the two laser pulses can be fixed to correspond to a small fraction of the time between collisions and the frequency of the probe laser scanned to record a LIF spectrum. The line intensities in this spectrum reflect the concentrations in levels populated in single collisions of the NO molecules in the level originally excited and hence *state-to-state* rate coefficients can be determined. The measurements reported in the present paper are of this second kind. In both instances, additional information, and tests of theory, can be provided by measuring the rate coefficients at different temperatures and by exciting NO to different initial ( $\Omega, v, J$ ) rovibronic levels.

In the second general type of experiment, crossed supersonic molecular beams are used, one of which contains NO.<sup>12–17</sup> The NO is so strongly cooled in the supersonic expansion that significant populations are found in only a few of its lowest rotational levels. Relative values of the integral

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and differential cross-sections for energy transfer from these levels can then be inferred by observing the inelastically scattered molecules using either LIF<sup>12,13a,13b,16</sup> or resonance enhanced multiphoton ionisation (REMPI)<sup>13c,14,15,17</sup> detection. Although such experiments are capable of providing exquisitely detailed information, they do have some serious limitations compared with gas-cell double resonance experiments. Most significantly, it is not possible to determine the *absolute* values of the cross-sections and hence one is deprived of one important comparison with the results of theoretical calculations.

Furthermore, in the beam experiments initial state selection is severely constrained; the initial states are necessarily those low levels which are populated, as a result of the high degree of cooling in the supersonic expansion. To an extent, this limitation is shared by gas-cell double resonance experiments. Because molecules are promoted by an optically allowed transition from a selected rotational level in the  $v = 0$  vibrational level, the excited states that can be initially accessed are limited by the thermal populations of rotational levels in  $\text{NO}(X^2\Pi_\Omega, v = 0)$  and the optical selection rules for the IR transitions. This restriction is particularly apparent in the extensive measurements that have been made on rotational energy transfer at temperatures down to 7 K.<sup>7,10</sup>

Recently we have devised a method to circumvent this restriction to relatively low values of the initial rotational level ( $J_i$ ) and hence to extend the information on rotational energy transfer to higher initial levels, in the case of  $\text{NO}(X^2\Pi_\Omega)$  up to  $J_i = 40.5$ . This has been achieved by performing IRUVDR experiments on NO immediately after its formation in the photodissociation of  $\text{NO}_2$  at 355 nm, which creates  $\text{NO}(X^2\Pi_\Omega)$  in rotational levels in  $v = 0$  and  $v = 1$  up to the energetically accessible limits.<sup>26–29</sup> In our experiments, IR pulses from a difference-frequency laser source have excited molecules from  $v = 0, J = 30.5$  and  $v = 0, J = 39.5$  to  $v = 2, J = 31.5$  and  $v = 2, J = 40.5$ , and kinetic experiments have been performed to measure rate coefficients for removal from these levels in collisions with He, Ar and  $\text{N}_2$ .<sup>11</sup> These results were compared with new, conventional IRUVDR measurements on the rotational relaxation of NO from levels  $J = 7.5, 20.5$  and  $31.5$  and with the results of quantum scattering calculations performed on *ab initio* potential energy surfaces.

From the rate coefficients for *total* transfer of  $\text{NO}(X^2\Pi_{1/2}, v = 2)$  from the initial rotational levels  $J_i = 7.5, 20.5, 31.5$  and  $40.5$ , it was found that the thermally averaged cross-sections for transfer in collisions with He, Ar and  $\text{N}_2$  all decreased slightly but significantly with increasing  $J_i$ , the decrease being least marked in NO–He collisions. The results for NO–He and NO–Ar collisions were shown to agree very well with those from quantum scattering calculations on *ab initio* potential energy surfaces. Further indirect evidence for the dependence of the total rates of rotational relaxation on the initial rotational state comes from line broadening measurements on transitions in the (2, 0) overtone band in the ground state of NO.<sup>30,31</sup> With increasing rotational quantum number, a slight decrease is observed in the parameter which quantifies line broadening and which can often be correlated with the rate coefficients for rotational relaxation.

In the present paper, we report the results of experiments designed to measure the state-to-state rate coefficients for rotational energy transfer from the rotational levels  $J_i = 7.5, 20.5, 31.5$  and  $40.5$ . Again the experimental results are compared with those from *ab initio* theoretical calculations. As well as fundamental interest, in particular the investigation of whether the theoretical results continue to match experiment for high values of  $J$ , where the spacing between neighbouring rotational levels approaches  $k_B T$ , the investigation of rotational energy transfer at high  $J$  is important in respect of various aspects of atmospheric chemistry. Some evidence for a decrease in the total rate for rotational relaxation with

increasing rotational quantum number comes from the observation of emission from high rotational levels of NO in the thermosphere.<sup>32,33</sup> The absence of a thermalised distribution over rotational levels points to the possibility of a decrease in the rate of rotational relaxation with increasing rotational quantum number.

## Experimental method

The experiments were performed using the IRUVDR technique.<sup>4–7,10,11</sup> In the present experiments, pulses of tunable IR radiation were generated by difference-frequency mixing the output of a Nd : YAG pumped dye laser with the fundamental wavelength of the pump laser (Continuum ND8010/6000) in a  $\text{LiNbO}_3$  crystal. The frequency of this IR pump laser was tuned into resonance with a line in the R branch of the ( $\Omega = \frac{1}{2} \leftarrow \frac{1}{2}$ ) sub-band of the (2, 0) first vibrational overtone band at *ca.* 2.6  $\mu\text{m}$ . The pulse energy was in the range 1.5–2.0 mJ and the bandwidth was *ca.* 0.1  $\text{cm}^{-1}$ . The frequency of the IR laser was fine-tuned to the appropriate transition with the aid of a spectrophone containing 50 Torr of NO. Tunable UV probe radiation, with a bandwidth of *ca.* 0.4  $\text{cm}^{-1}$ , was produced by frequency doubling the output of an excimer-pumped dye laser (Lambda-Physik, FL2002). LIF spectra of part of the (0, 2) band of the  $\text{NO A } ^2\Sigma^+ - X^2\Pi$  system at *ca.* 247 nm were recorded with a selected time delay set between the pulses from the IR pump and UV probe lasers. Conventional IRUVDR experiments<sup>4–7,10</sup> were carried out to measure the state-to-state rates of rotational relaxation from  $\text{NO}(X^2\Pi_{1/2}, v = 2, J_i = 7.5, 20.5$  and  $31.5)$  in collisions with He, Ar,  $\text{N}_2$  and NO. Experiments were carried out on samples of either pure NO or mixtures containing <10% NO diluted in He, Ar or  $\text{N}_2$ .

Experiments on the highest rotational level ( $J_i = 40.5$ ) required the initial photolysis of  $\text{NO}_2$  to generate rotationally ‘hot’ NO molecules in the ground vibrational state. For this purpose, laser radiation was generated at 355 nm by mixing the fundamental and doubled output of a Nd : YAG laser (Spectron, SL 803). Typical pulse energies of *ca.* 20 mJ and a bandwidth of 0.1  $\text{cm}^{-1}$  were obtained. Measurements of state-to-state rate coefficients were performed on gas samples at a total pressure of *ca.* 400–450 mTorr containing 5–6%  $\text{NO}_2$  diluted in He, Ar or  $\text{N}_2$ . We estimate that *ca.* 15% of the  $\text{NO}_2$  was photodissociated by the laser pulse at 355 nm. In interpreting the results of these experiments, we assumed that collisions of the excited NO molecules with undissociated  $\text{NO}_2$  or with other NO molecules formed by photolysis were unimportant. The method used to ensure that the IR laser was properly tuned to the selected IR transition was described in our earlier paper.<sup>11</sup>

The beams from the IR and UV lasers counterpropagated along the axis of a cylindrical Pyrex cell with a  $\text{CaF}_2$  window mounted on each end. In all experiments, the time delay between the pump and probe laser pulses was selected with a delay generator (Stanford DG535) and the resulting LIF signals were recorded as the frequency of the UV probe laser was scanned. The typical time delay of 40 ns corresponded to approximately one-fifth of the time for total removal from the initially populated level by rotational relaxation. The photomultiplier, interference filter and a collecting lens were mounted in a central housing which was clamped to this cell. To discriminate against scattered light from the probe laser, the fluorescence was observed using a solar blind photomultiplier tube (Hamamatsu R801), through a quartz window. An interference filter (Corion, FWHM 10 nm) centred at 228 nm isolated the fluorescence in the (0, 0) band of the  $\text{A } ^2\Sigma^+ - X^2\Pi$  system at *ca.* 226 nm.

The equipment for controlling the firing of the lasers and for recording, accumulating and analysing the LIF signals was the same as that described by Frost and Smith.<sup>34</sup> All the

experiments for which data are reported were carried out at room temperature,  $(295 \pm 5)$  K.

## Analysis of experimental data

In the present experiments, LIF spectra of part of the  $A^2\Sigma^+ - X^2\Pi(0, 2)$  band of NO were recorded with a delay time set between the pulse from the pump laser which excited NO molecules to a selected rotational level  $J_i$  in  $(X^2\Pi_{1/2}, v = 2)$  and the pulse from the probe laser whose frequency was scanned to obtain a spectrum. In order to interpret these experiments, it was necessary to transform the observed line intensities into relative populations in individual rotational levels and to deduce state-to-state rate coefficients for transfer from  $J_i$  to neighbouring rotational levels  $J_f$  from the relative populations at delays corresponding to a fraction of a collision.

A method that can be used for any levels that contain a significant population once equilibrium has been established over rotational levels has been described previously.<sup>6,10</sup> Briefly, the rate coefficient  $k_{J_i J_f}$  for transfer from  $J_i$  to  $J_f$  is obtained from the equation:

$$\delta N_{J_f} = k_{J_i J_f} N_{J_i}^0 [M] \delta t \quad (1)$$

where  $\delta N_{J_f}$  is the (small) population in level  $J_f$  at a short delay  $\delta t$ ,  $N_{J_i}^0$  is the population initially excited to level  $J_i$ , and  $[M]$  is the concentration of the collider gas. The ratio  $\delta N_{J_f}/N_{J_i}^0$  is determined by measurements on the same line from the level  $J_f$  at a short delay and at a delay long enough for rotational equilibration to be complete but negligible vibrational relaxation to have occurred. Then  $N_{J_i}^0 = (N_{J_f}^\infty / f_{J_f}^\infty)$  where  $N_{J_f}^\infty$  is the population in level  $J_f$  at the long time delay and  $f_{J_f}^\infty$  is the equilibrium fraction present in this rotational level, rotational relaxation being complete. Consequently,  $k_{J_i J_f}$  can be determined from the equation:

$$k_{J_i J_f} = \{ \text{Int}_{J_f}(\delta t) / \text{Int}_{J_f}(\infty) \} (f_{J_f}^\infty / [M] \delta t) \quad (2)$$

where  $\text{Int}_{J_f}(\delta t)$  and  $\text{Int}_{J_f}(\infty)$  are the intensities of the lines from level  $J_f$  at short and long delays.

The procedure described in the previous paragraph can be applied when the level  $J_f$  retains significant population once rotational relaxation has occurred; for example, in the conventional IRUVDR measurements on relaxation from  $J_i = 7.5, 20.5$  and  $31.5$  in the present work. In practice, however, the intensity of a single line at long time delay was generally used to establish  $N_{J_f}^0$ , due account being taken of line strength factors in converting the intensity of the measured line to relative populations in different rotational levels. Because the pulse energy from the probe laser was sufficient to ensure saturation of the transitions in the NO  $A^2\Sigma^+ - X^2\Pi_{1/2}(0, 2)$  band, each line strength factor was taken to be the ratio of the degeneracies in the upper and lower rotational levels of the transition.

For measurements on the relaxation from  $J_i = 31.5$  and  $40.5$ , generated following the photolysis of  $\text{NO}_2$ , a different procedure had to be used for two reasons. First, the thermalised populations in these and the neighbouring rotational levels were too low to produce acceptably strong signals at long delays. Second, some NO was produced directly in  $v = 2$  via the two-photon photolysis of the  $\text{NO}_2$  (see below) and it contributed significantly to the thermalised populations.

Therefore to deduce relative populations and hence state-to-state rate coefficients from these experiments, pairs of LIF spectra in the region of the line from level  $J_i$  were recorded, at time delays corresponding (a) to about 20% of the rotational relaxation time and (b) to approximately the rotational relaxation time. The latter spectrum was used to estimate  $\text{Int}_{J_i}(0)$ ; that is, the intensity that the line from the initially excited level had at zero time. This indirect procedure was adopted in order to reduce the intensity of the line from level  $J_i$  to a

similar strength to that recorded at short delay from the neighbouring levels  $J_f$  and, in addition, to avoid any effects due to saturation of the detection system. The populations in these neighbouring levels, *i.e.*  $N_{J_f}$ , relative to  $N_{J_i}^0$  could then be calculated from the ratio of intensities  $\{ \text{Int}_{J_f}(\delta t) / \text{Int}_{J_i}(0) \}$ , making due allowance for the small difference in line strength factors. Finally, the state-to-state rate coefficients were determined using:

$$k_{J_i J_f} = \{ \text{Int}_{J_f}(\delta t) / \text{Int}_{J_i}(0) \} / [M] \delta t \quad (3)$$

## Theoretical calculations

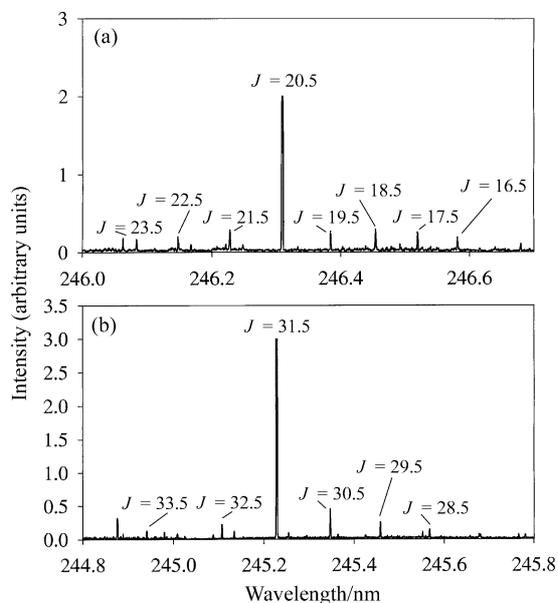
The scattering calculations follow the formalism which has been presented in detail before,<sup>10,11,18–20</sup> in particular, the determination of rate constants for total relaxation from a given initial rotational state.<sup>11</sup> To avoid repetition only a brief description of the method will be given here.

We have used our earlier coupled electron pair approximation (CEPA)<sup>35–37</sup> calculations<sup>24,25</sup> of the two potential energy surfaces (PESs),  $V_{A'}$  and  $V_{A''}$ , which arise when a noble gas atom interacts with an NO molecule in its  $^2\Pi$  ground state.<sup>19</sup> The total wavefunction of the NO–noble gas system is expanded as a sum of products of the molecular electronic–rotational wavefunctions, multiplied by functions which describe the orbital motion of the noble gas collision partner with respect to the diatomic molecule. Collision-induced transitions between any pair of levels, at least one of which is described in this intermediate coupling regime, will be induced by both the average and the difference of the  $V_{A'}$  and  $V_{A''}$  potentials.<sup>18,20,38</sup> The relative contribution of these two potentials will be governed by the degree of mixing of the pure Hund's case (a) rotational basis states of the NO molecule.<sup>20,24,25,38</sup>

To calculate rotationally inelastic cross-sections based on these PESs we used the HIBRIDON 4 package.<sup>39</sup> In the present calculations, the coupled states (CS) approximation was used.<sup>18</sup> It has been shown previously<sup>24,25</sup> to be accurate for collisions of NO( $X^2\Pi$ ) in low rotational levels with both He and Ar. As before, the NO molecule was assumed to be a rigid rotor with a bond distance equal to the average value in the  $v = 2$  vibrational state. Scattering calculations were carried out on a fixed grid of approximately 50 total energies, where the total energy is the sum of the energy of the initial internal state and the collision energy. Subtraction of the internal energy then transformed these results to cross-sections as a function of collision energy.<sup>10</sup> Finally, thermal state-to-state rate coefficients were obtained from the inelastic integral cross-sections by multiplication of the cross-sections by the relative velocity and subsequent integration over a Maxwellian velocity distribution at 300 K.

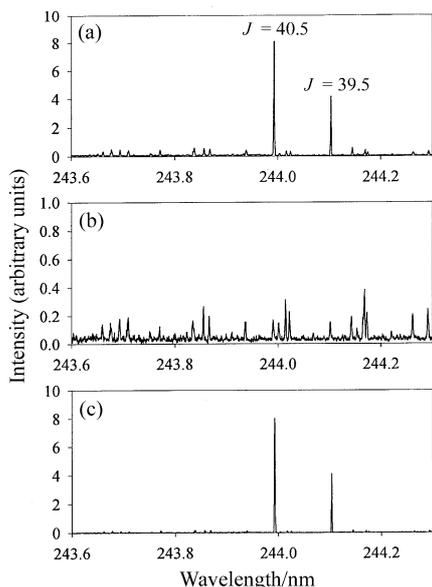
## Results and discussion

Fig. 1 displays two double resonance spectra typical of those recorded at short time delays in the present experiments and from which state-to-state rate coefficients were derived for transfer from the initially excited rotational levels  $J_i = 7.5, 20.5$  and  $31.5$  in NO( $X^2\Pi_{1/2}, v = 2$ ). These spectra are the results of standard IRUVDR experiments; that is, a pulse from the IR pump laser was used to excite NO molecules in a thermal sample in the appropriate R-branch transition of the (2, 0) first vibrational overtone band. The fact that such IRUVDR spectra could be recorded with acceptable signal-to-noise for levels as high as  $J_i = 31.5$ , despite the fact that the fraction of NO molecules in  $v = 0$ ,  $J_i = 30.5$  at room temperature is only  $1.2 \times 10^{-4}$ , is a reflection of the quality of the IR pump laser used in the present experiments, compared with the optical parametric oscillator employed in some earlier experiments of this kind in our laboratory.<sup>6</sup>



**Fig. 1** LIF spectra of part of the NO  $A^2\Sigma^+ - X^2\Pi$  (0,2) band recorded in standard IRUVDR experiments: (a) at a delay time of 40 ns following excitation of  $J_i = 20.5$  in a mixture containing 7.8% NO in He at a total pressure of 445 mTorr; and (b) at a delay time of 40 ns following excitation of  $J_i = 31.5$  in a mixture containing 8.5% NO in He at a total pressure of 452 mTorr.

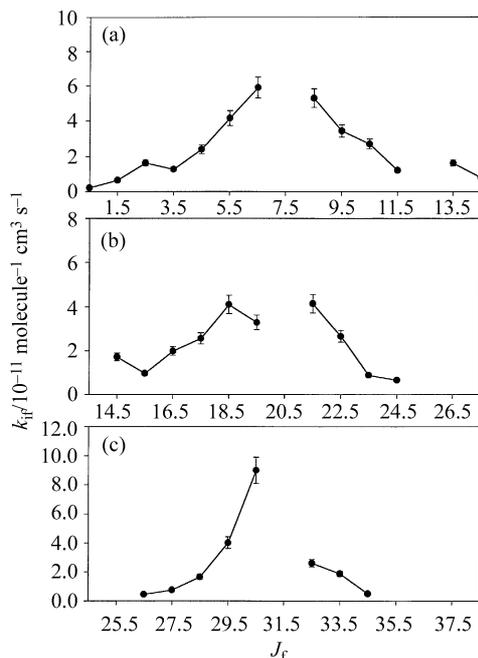
The LIF spectrum shown in Fig. 2(a) was obtained using the photolysis of  $\text{NO}_2$  to generate NO, and then the IRUVDR method to excite NO from  $v = 0, J = 39.5$  to  $v = 2, J = 40.5$ . Clearly, only two lines in the LIF spectrum, that from  $J_i = 40.5$  and that from  $J_f = 39.5$ , have substantial intensity. Some other weak lines are apparent. However, Fig. 2(b) shows that a number of such lines were present even in the absence of the IR pump laser. They apparently arose from the two-photon photolysis of  $\text{NO}_2$  or, just possibly, from the photolysis of  $\text{NO}_2$  in excited vibrational levels. In order to allow for these features, spectra like that in Fig. 2(b) were subtracted from the spectra, like that in Fig. 2(a), recorded with all three lasers operating. Fig. 2(c) provides an example of the result of this procedure, showing the decrease in the intensity of the



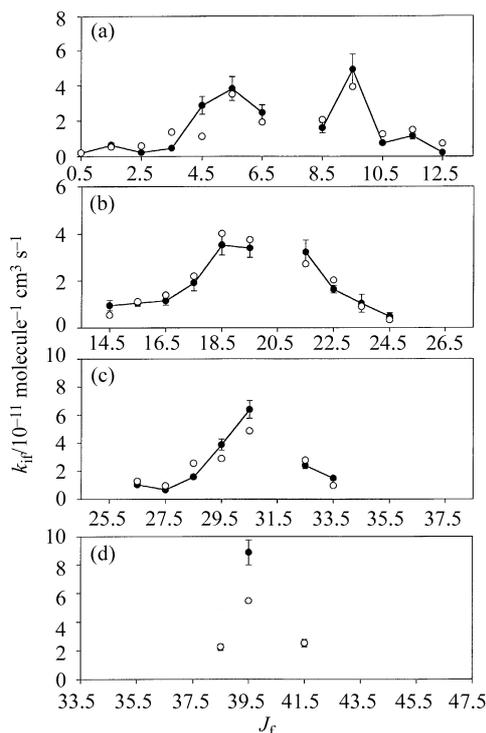
**Fig. 2** (a) LIF spectrum of part of the NO  $A^2\Sigma^+ - X^2\Pi$  (0,2) band recorded at a delay of 40 ns following the excitation of NO, formed in the photolysis of 450 mTorr of a 5% mixture of  $\text{NO}_2$  in He, to  $J_i = 40.5$ ; (b) similar spectrum recorded in the absence of the infrared pump laser; and (c) the spectrum obtained by subtracting (b) from (a).

weaker lines when the subtraction is performed. Relative populations, and ultimately state-to-state rate coefficients for transfer from  $J_i = 40.5$ , were calculated from spectra of this kind.

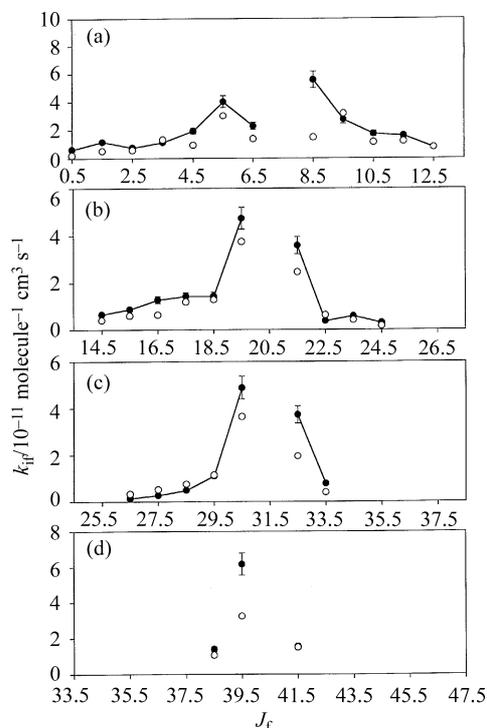
The experimental results of the present work are listed in Table 1 and are displayed in Fig. 2–6. It should be noted that here we report experimental rate coefficients only for transfers



**Fig. 3** State-to-state rate coefficients for transfer between rotational levels within the  $X^2\Pi_{1/2}, v = 2$  state in NO–NO collisions plotted against  $J_f$ : (a) for  $J_i = 7.5$ , (b)  $J_i = 20.5$  and (c)  $J_i = 31.5$ .

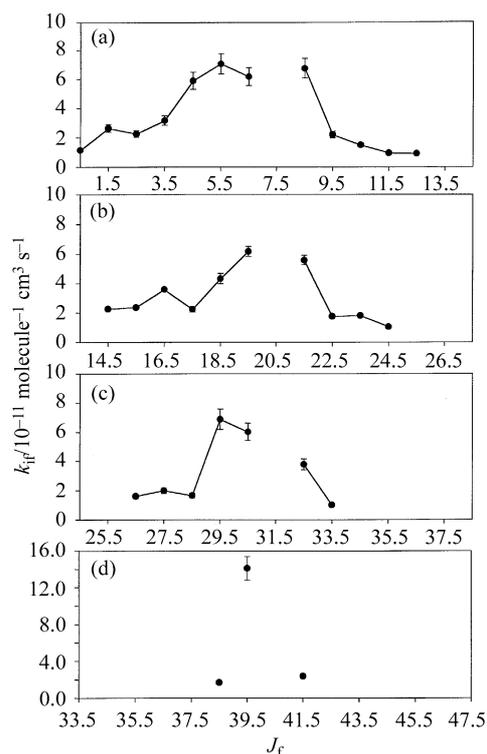


**Fig. 4** State-to-state rate coefficients for transfer between rotational levels within the  $X^2\Pi_{1/2}, v = 2$  state in NO–He collisions plotted against  $J_f$ : (a) for  $J_i = 7.5$ , (b)  $J_i = 20.5$ , (c)  $J_i = 31.5$  and (d)  $J_i = 40.5$ . The filled symbols are the experimental results, the open symbols the theoretical data.



**Fig. 5** State-to-state rate coefficients for transfer between rotational levels within the  $X^2\Pi_{1/2}$ ,  $v=2$  state in NO–Ar collisions plotted against  $J_f$ : (a) for  $J_i = 7.5$ , (b)  $J_i = 20.5$ , (c)  $J_i = 31.5$  and (d)  $J_i = 40.5$ . The filled symbols are the experimental results, the open symbols the theoretical data.

within the rotational manifold of the  $\Omega = 12$  spin–orbit component. Attempts were made to study spin–orbit changing transfers for NO–He collisions with  $J_i = 31.5$ . The spectra suggested that such transfers amounted to no more than *ca.* 20% of the total and they were too weak to allow accurate



**Fig. 6** State-to-state rate coefficients for transfer between rotational levels within the  $X^2\Pi_{1/2}$ ,  $v=2$  state in NO– $N_2$  collisions plotted against  $J_f$ : (a) for  $J_i = 7.5$ , (b)  $J_i = 20.5$ , (c)  $J_i = 31.5$  and (d)  $J_i = 40.5$ .

**Table 1** Experimental state-to-state rate coefficients ( $k/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for transitions between specified rotational levels of  $\text{NO}(X^2\Pi_{1/2}, v=2)$  in collisions with NO, He, Ar and  $N_2$ . The numbers in italics for  $M = \text{He}$  and  $M = \text{Ar}$  are the theoretical rate coefficients in the same units for the same spin–orbit conserving transitions

	M = NO	M = He	M = Ar	M = $N_2$		
(i) $J_i = 7.5$						
$J_f = 0.5$	0.22	0.20	0.20	0.62	0.21	1.2
1.5	0.66	0.64	0.53	1.1	0.51	2.6
2.5	1.6	0.22	0.59	0.74	0.57	2.3
3.5	1.3	0.47	1.36	1.1	1.30	3.2
4.5	2.4	2.9	1.11	1.9	0.91	5.9
5.5	4.2	3.8	3.51	4.0	3.00	7.1
6.5	5.9	2.5	1.92	2.3	1.35	6.2
7.5						
8.5	5.3	1.6	2.06	5.6	1.46	6.8
9.5	3.5	5.0	3.93	2.7	3.17	2.2
10.5	2.7	0.76	1.25	1.7	1.12	1.5
11.5	1.2	1.2	1.50	1.6	1.19	0.96
12.5		0.22	0.73	0.77	0.77	0.93
13.5	1.7		0.67		0.57	
14.5	0.8		0.41		0.45	
sum( $\Omega = \frac{1}{2}$ ) <sup>a</sup>	31	20	20.43	17.8	17.60	38
sum( $\Omega = \frac{3}{2}$ ) <sup>b</sup>			4.37		8.07	
total <sup>c</sup>	42 ± 5	30 ± 3	24.8	34 ± 2	25.67	46 ± 5
(ii) $J_i = 20.5$						
$J_f = 14.5$	1.7	0.95	0.55	0.66	0.41	2.3
15.5	1.0	1.1	1.12	0.87	0.60	2.4
16.5	2.0	1.2	1.40	1.3	0.63	3.6
17.5	2.6	1.9	2.19	1.4	1.19	2.2
18.5	4.1	3.5	4.01	1.4	1.28	4.3
19.5	3.3	3.4	3.75	4.7	3.75	6.2
20.5						
21.5	4.2	3.2	2.71	3.6	2.46	5.6
22.5	2.7	1.6	2.02	0.38	0.62	1.8
23.5	0.88	1.0	0.90	0.58	0.40	1.8
24.5	0.66	0.49	0.34	0.30	0.16	1.1
sum( $\Omega = \frac{1}{2}$ ) <sup>a</sup>	23	18.4	20.52	14.4	13.71	31
sum( $\Omega = \frac{3}{2}$ ) <sup>b</sup>			7.19		8.76	
total <sup>c</sup>	44 ± 3	24.5 ± 5	27.7	28 ± 3	22.5	44 ± 5
(iii) $J_i = 31.5$						
$J_f = 25.5$ <sup>d</sup>			0.44		0.26	
26.5	0.46	1.0	1.28	0.14	0.32	1.6
27.5	0.75	0.67	0.95	0.26	0.50	2.0
28.5	1.7	1.6	2.54	0.48	0.75	1.7
29.5	4.0	3.9	2.88	1.1	1.14	6.9
30.5	9.0	6.4	4.84	4.9	3.64	6.0
31.5						
32.5	2.6	2.4	2.76	3.7	1.95	3.8
33.5	1.9	1.5	0.95	0.77	0.40	1.0
34.5	0.5		0.55		0.15	
sum( $\Omega = \frac{1}{2}$ ) <sup>a</sup>	21	17.4	19.00	11	10.21	23
sum( $\Omega = \frac{3}{2}$ ) <sup>b</sup>			5.29		5.77	
total <sup>c</sup>	35 ± 4	21 ± 3	24.3	19 ± 3	15.98	35 ± 4
(iv) $J_i = 40.5$						
$J_f = 36.5$ <sup>d</sup>			0.73		0.37	
37.5 <sup>d</sup>			2.59		0.53	
38.5		2.2	2.25	1.4	1.06	1.7
39.5		8.9	5.47	6.2	3.24	14
40.5						
41.5		2.5	2.52	1.5	1.50	2.4
42.5 <sup>d</sup>			0.55		0.27	
sum( $\Omega = \frac{1}{2}$ ) <sup>a</sup>		13.6	17.41	9.1	7.94	18
sum( $\Omega = \frac{3}{2}$ ) <sup>b</sup>			3.78		4.35	
total <sup>c</sup>		22 ± 3	21.2	13 ± 2	12.3	25 ± 3

<sup>a</sup> Sum of the experimental or theoretical state-to-state rate coefficients for transitions within the  $\Omega = \frac{1}{2}$  spin–orbit manifold. The theoretical values result from a sum over all final states; the experimental values only from the sum over final states giving rise to lines of significant intensity. <sup>b</sup> Sum of the theoretical state-to-state rate coefficients for transitions from the initial state (with  $\Omega = \frac{1}{2}$ ) to all final rotational levels in the  $\Omega = \frac{3}{2}$  spin–orbit manifold. <sup>c</sup> In the case the theoretical values include the contribution of spin–orbit changing (*i.e.*  $\Omega = \frac{1}{2} \rightarrow \frac{3}{2}$  transfers). The experimental values are taken from ref. 11 and were obtained by observing the decay in population from the initially excited level  $J_i$ . <sup>d</sup> Rate coefficient not measured experimentally for this transition.

estimates of the individual state-to-state rate coefficients for the processes in which the spin-orbit state of the excited NO molecule was changed. Calculations on these spin-orbit changing processes have been carried out and the results are reported below.

Two general features of the variation of the state-to-state rate coefficients with  $J_f$  and  $J_i$  can be distinguished which are essentially independent of collision partner. First, the distribution with respect to  $J_f$  becomes narrower as the value of  $J_i$  increases. Second, as  $J_i$  increases, there is an increasing tendency to favour downward transfers, *i.e.*  $J_f < J_i$ , over upward transfers, *i.e.*  $J_f > J_i$ . This latter observation is similar to that found by James *et al.*<sup>10</sup> in their studies of the rotational relaxation of NO at low temperatures and is unsurprising. At the highest value of  $J_i$  (40.5) in the present experiments, transfer to the next highest level (41.5) is endothermic by an amount ( $\Delta E \equiv 141 \text{ cm}^{-1} \equiv 203 \text{ K}$ ) which is comparable with  $k_B T$  at room temperature.

The results from the present experiments can be compared with three other sets of data: (a) the state-to-state rate coefficients for low initial rotational levels obtained in previous studies,<sup>6</sup> (b) the results of the theoretical calculations which form part of the present work, and (c) the rate coefficients for total removal<sup>11</sup> from the initial rotational levels accessed in the present work. Islam *et al.*<sup>6</sup> reported state-to-state rate coefficients for transfer from rotational levels  $J_i \leq 6.5$  in  $\text{NO}(X^2\Pi_{1/2}, v=2)$  induced by the collision partners  $M = \text{NO}, \text{He}$  and  $\text{Ar}$ . The earlier results for NO-NO collisions and  $J_i = 6.5$  are in good agreement with those obtained here for NO-NO and  $J_i = 7.5$ , in respect of both the absolute values of the state-to-state rate coefficients and their variation with  $\Delta J = J_f - J_i$ . Because of the lower pulse energy and poorer stability of their infrared pump laser, Islam *et al.*<sup>6</sup> needed to use 20% mixtures of NO in He or Ar to examine the rates of rotational energy transfer with these noble gases, so their results for collisions with noble gases are not directly comparable with ours. If our state-to-state rate coefficients are used to calculate rate coefficients for 20% mixtures of NO in He or Ar, the results are in fair agreement with the measurements of Islam *et al.*

In Table 1 and in Figs. 4 and 5, we compare the values of the observed state-to-state rate coefficients for each  $J_i$  and  $M = \text{He}$  and  $\text{Ar}$ , with the state-to-state rate coefficients from the theoretical calculations. On the whole the agreement is excellent. On careful examination, two discrepancies emerge. First, as  $J_i$  increases, the spread of the distribution with  $\Delta J$  of theoretical rate coefficients becomes wider than that found experimentally. This is seen most clearly for  $J_i = 40.5$ . Whereas the experiments show that *ca.* 80% of the transfer is into  $J_f = 39.5$ , *i.e.*  $\Delta J = -1$  is strongly favoured, according to the scattering calculations only 41% of the transfer within the  $\Omega = \frac{1}{2}$  spin-orbit rotational manifold occurs *via* this channel. We return to this point later.

The second discrepancy concerns the relative size of the rate coefficients for the transitions with  $\Delta J = +1$  as compared to those for transitions with  $\Delta J = +2$ . For low values of  $J_i$ , our earlier investigation<sup>10</sup> showed that the most probable upward transition was  $\Delta J = +2$ , particularly for  $J_i = 3.5$  and  $6.5$ . This propensity is also predicted by the theoretical calculations reported in ref. 10, and can be attributed to the near homonuclear character of the NO-Ar and NO-He potentials. In the present comparison, this same propensity is confirmed in the theoretical calculations at  $J_i = 7.5$  for both Ar and He as collision partner. However, experiment reveals that for collisions with Ar, the most probable upward transition is  $\Delta J = +1$ .

Finally, we compare the total rate coefficients estimated by summing the state-to-state rate coefficients with the same quantities from the calculations and with the directly measured rate coefficients for removal from the specified initial

rotational level. There are two parts to this comparison. First, we can compare the sum of the state-to-state rate coefficients, which relate only to transfers in which the spin-orbit state is conserved, with the sum of theoretical state-to-state rate coefficients for spin-orbit conserving transfers. In the latter case, all the significant calculated rate coefficients were included in the sum, not just those listed in Table 1. However, in summing the experimental state-to-state rate coefficients, we could only include those values which led to a significant line intensity in the LIF spectrum. Consequently, the sum of experimental results should give a lower limit to the rate coefficient for all spin-orbit conserving transfers. Bearing this difference in mind, the comparison shown in the lines of Table 1 labelled 'sum' is very satisfactory.

For completeness, we also include in Table 1, in the lines labelled 'total', a comparison of the rate coefficients for total transfer out of a given initial rotational level  $J_i$  with the same quantity calculated theoretically.<sup>11</sup> The differences between numbers in the rows labelled 'sum' and 'total' and in the same column should correspond to the rate coefficients for all spin-orbit changing transitions.

Experimental evidence is neither extensive nor accurate enough to indicate how the ratio of the rates of spin-orbit conserving to spin-orbit changing transfers depends on  $J_i$ . The theoretical calculations can provide information on this for both He and Ar as the collision partner. Table 1 also lists the sum of the theoretically calculated rate coefficients for transfer to, separately, all rotational levels in the  $\Omega = \frac{1}{2}$  and  $\Omega = \frac{3}{2}$  spin-orbit manifolds. The ratio of total spin-orbit changing to spin-orbit conserving transfer is, for collisions with Ar, 0.46, 0.64, 0.57 and 0.55 for  $J_i = 7.5, 20.5, 31.5$  and  $40.5$ , respectively. For collisions with He, the comparable ratios are 0.21, 0.35, 0.38 and 0.22. According to our calculations, the relative efficiency of spin-orbit changing transfer first increases and then slightly decreases as  $J_i$  increases. As discussed in earlier papers,<sup>24,40</sup> the relative efficiency of spin-orbit changing *vs.* spin-orbit conserving transitions is a sensitive function of both the difference between the  $V_{A'}$  and  $V_{A''}$  PESs, as well as the degree of transition toward intermediate Hund's case coupling in the NO molecule, which increases with increasing  $J_i$ . However, earlier comparisons<sup>24</sup> with the results of molecular beam experiments suggest that, if anything, theoretical calculations based on the CEPA PESs that are used in the present calculations underestimate the efficiency of spin-orbit changing transitions. Therefore, future experiments should focus on establishing the rate coefficients for these spin-orbit changing processes in order to assess the accuracy of theoretical estimates of these rate coefficients.

Finally, we return to the discrepancy between experiment and theory in respect of the width of the  $J_f$  distribution at high  $J_i$ . A possible explanation for this difference is that approximations made in the theoretical calculations are no longer valid at high  $J_i$ . The most likely candidate is the coupled states ( $J_z$ -conserving) approximation. Although this is known to be accurate at low  $J_i$  where the results can be compared with those from exact close-coupling calculations,<sup>24</sup> this comparison is no longer possible at high  $J_i$  because of the exceedingly large number of channels that would have to be included in the close-coupling calculations. One remaining possible source of the discrepancy with experiment at high  $J_i$  is the assumption that the NO molecule can be treated as a rigid rotor. A better treatment would be to determine the dependence of the PESs on the NO bond distance,  $r_{\text{NO}}$ , and then to average the results of scattering calculations performed with different  $r_{\text{NO}}$  over the range of internuclear distances accessible to  $\text{NO}(v=2)$ .

However, it is worth pointing out that recently Yang *et al.*<sup>41</sup> have determined rate constants for relaxation out of the  $J = 60.5$  rotational level of the  $\text{CN}(A^2\Pi)$  state in collisions with Ar. The rotational constant and spin-orbit splitting of

CN(A  $^2\Pi$ ) are quite similar to those of NO(X  $^2\Pi$ ). Comparison with theoretical rate constants, determined from coupled states calculations of the kind described here and on potential energy surfaces of similar quality, showed excellent agreement. This suggests that the rate constants for NO relaxation from coupled states calculations should be equally accurate for the values of  $J_i$  considered here.

Some of the discrepancy might be attributable to errors in the potential energy surfaces. As  $J_i$  increases, the value of the total energy corresponding to a given collision energy increases, so that collisions access regions higher on the repulsive wall of the potential energy surfaces. Although the earlier potential energy surface calculations<sup>24,25</sup> did examine the energies up to such values, it is possible that the relative error in the potential energy surfaces becomes larger in the repulsive region. Recently, one of us<sup>42</sup> has reported new *ab initio* NO–Ar potential energy surfaces of very high accuracy. New calculations, similar to that reported here but using these new surfaces, may be necessary to assess more definitively the accuracy of calculated rate constants for relaxation of NO from  $J_i = 40.5$ .

## Summary and conclusions

This paper reports a new experimental technique for measuring state-to-state rate coefficients for rotational energy transfer from high initial rotational levels which should be generally applicable. The method depends on producing the species to be excited in a non-Boltzmann distribution over rotational levels by pulsed laser photolysis of a suitable precursor and then instantly applying the IRUVDR technique to these molecules. The method has been applied to NO generated by photolysis of NO<sub>2</sub> at 355 nm and state-to-state rate coefficients have been determined for transfer from NO(X  $^2\Pi_{1/2}$ ,  $v = 2$ ,  $J_i = 40.5$ ) in collisions with NO, He, Ar and N<sub>2</sub>. These data have been compared with the corresponding results for NO(X  $^2\Pi_{1/2}$ ,  $v = 2$ ,  $J_i = 7.5$ , 20.5 and 31.5). As  $J_i$  increases, the distribution of state-to-state rate coefficients with  $J_f$  is found to become narrower and increasingly to favour transfers with  $J_f < J_i$ . The results are compared with the results of quantum scattering calculations on *ab initio* surfaces. The agreement is generally very good. However, the calculations overestimate the spread of the state-to-state rate coefficients with  $J_f$  for the highest initial value of  $J_i$ . The origin of this discrepancy between experiment and theory is most likely attributable to residual errors in the NO–Ar and NO–He potential energy surfaces used in the calculations. New calculations based on new, more accurate, potential energy surfaces<sup>41</sup> for NO–Ar may resolve this single disagreement with experiment.

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