

# Total and state-to-state rate coefficients for rotational energy transfer in collisions between NO( $X^2\Pi$ ) and He at temperatures down to 15 K

Philip L. James, Ian R. Sims, Ian W.M. Smith

*School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

Received 2 April 1997; in final form 8 May 1997

---

## Abstract

Infrared–ultraviolet double resonance (IRUVDR) experiments have been implemented in the ultra-cold environment provided by a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. This has enabled us to measure rate coefficients for rotational energy transfer in collisions between NO and He of two kinds: those relating to total removal from a specific rovibrational state of NO( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $v = 3$ ;  $J = 0.5, 3.5$  or  $6.5$ ) and also state-to-state rate coefficients for transfer from these levels. Using different Laval nozzles, results have been obtained at four different temperatures: 149, 63, 27 and 15 K, and are also reported for 295 K. © 1997 Elsevier Science B.V.

## 1. Introduction

Over the past four years, as the result of a collaboration between our group and that of Rowe at the University of Rennes, rate constants have been measured for a number of elementary reactions between neutral species at temperatures down to 13 K [1,2]. In these experiments, pulsed laser photolysis (PLP) is used to generate free radicals and laser-induced fluorescence (LIF) is used to observe their kinetic decay. This PLP–LIF method is implemented in gas mixtures which have been cooled drastically by expansion through a Laval nozzle in the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus at the University of Rennes. The expansion creates a supersonic flow of relatively dense gas in which there are frequent collisions so that thermal equilibrium is maintained. So far rate constants have been measured for over 20 reactions

of the radicals CN, OH and CH, [2] as well as for the vibrational relaxation of CH( $v = 1$ ) by CO, N<sub>2</sub> and H<sub>2</sub> [3,4].

Recently a CRESU apparatus, which is only the second of its kind world-wide, has been established at the University of Birmingham. Here we report the first application of this apparatus, to the measurement of rates of rotational energy transfer in collisions between NO and He. Measurements on NO have become a major testing ground for models and theoretical treatments of rotational energy transfer. Previous measurements fall into two main categories: (i) infrared–ultraviolet double resonance experiments performed under thermally equilibrated conditions [5–8], like those reported in the present paper and (ii) crossed molecular beam experiments which provided cross-sections for energy transfer, generally out of the lowest rovibrational level, at a defined collision energy [9–12]. Alexander and co-

workers [13,14] have been particularly active in performing high quality quantum scattering calculations on ab initio potential energy surfaces, especially for NO–He collisions.

The present experiments are the first direct measurements on the rates of rotational energy transfer that have been carried out at temperatures below 80 K, the temperature achieved by Islam et al. [7,8] in cryogenically cooled cells. Of course, rate constants for rotational energy transfer are closely related to those for collisional broadening and, using a “collisional cooling” technique, Willey et al. have measured line-broadening for spectroscopic transitions in a number of gases, including NO diluted in He [15], at temperatures down to 1.7 K.

There are at least two reasons for interest in the rates of rotational energy transfer at ultra-low temperatures. First, such measurements will provide particularly demanding tests of theory at collision energies less than the typical well-depth in the intermolecular potential between closed shell species and comparable to the spacing between neighbouring rotational levels even at low levels of excitation. Second, such rates are required for the interpretation of astrophysical observations. In particular, the temperatures in interstellar clouds are inferred from the intensities of lines in the rotational spectra of observed molecules and a proper analysis must include the rates of collisional transfer between specific rotational levels at the very low temperatures in these regions of the interstellar medium [16].

## 2. Experimental method

The method employed in our experiments is similar in principle, but different in detail, to that employed by Islam et al. [7,8]. Pulses of tuneable infrared radiation at ca. 1.8  $\mu\text{m}$  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 LiNbO<sub>3</sub> crystal mounted within an autotracking unit (Con-

tinuum), to give the difference frequency radiation at ca. 1.8  $\mu\text{m}$ . Typically, pulse energies of 5 mJ and spectral bandwidths of 0.1  $\text{cm}^{-1}$  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. As in the previous experiments in Rennes, 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.

Full specifications of the Birmingham CRESU apparatus will be given in a future publication. It 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 [1]. The four nozzles used in the present work were characterised by impact-pressure measurements which yielded temperatures of 149, 63, 27 and 15 K. These temperatures were confirmed by recording LIF spectra of NO of three kinds: (i) NO was introduced into the gas flow and a LIF spectrum of the ( $A^2\Sigma^+ - X^2\Pi$ ) (0,0) band was recorded by scanning the UV-probe laser; (ii) the LIF spectrum of the ( $A^2\Sigma^+ - X^2\Pi$ ) (0,3) band was recorded, with the frequency from the IR-pump laser fixed to a line in the (3,0) second overtone band in  $X^2\Pi$  and the delay between the laser pulses being sufficient to allow time for complete rotational relaxation or (iii) a spectrum of the (3,0) overtone band in  $X^2\Pi$  was recorded by fixing the frequency of the UV-probe laser and scanning the IR-pump laser, again sufficient time being allowed for complete rotational relaxation. Fig. 1 shows a spectrum of type (iii) taken at 15 K.

Two kinds of experiments were performed on collisional energy transfer. In the first, *total* rates of relaxation from a particular selected level were measured by fixing the UV-probe laser to a line from the

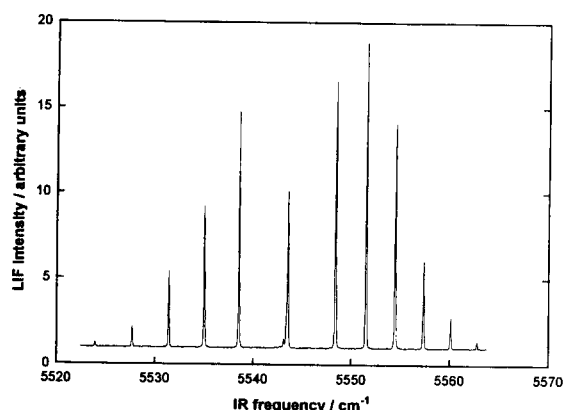


Fig. 1. IRUVDR spectrum of the NO  $X^2\Pi_{1/2}$  ( $\nu' = 3; J'$ )  $\leftarrow$   $X^2\Pi_{1/2}$  ( $\nu'' = 0; J''$ ) second overtone transition at 15 K in the CRESU apparatus, obtained by scanning the frequency of the IR laser with the UV laser set to detect a single rotational state in the ( $\nu = 3$ ) manifold, at a delay time (5  $\mu$ s) sufficient for complete rotational relaxation.

level ( $\nu = 3$ ,  $\Omega = 1/2$ ,  $J$ ), which was being directly populated by the IR-pump laser and the time delay between the two laser pulses was varied systematically as the LIF intensity was recorded. In the second series of experiments, the time delay between the lasers was fixed at 30 ns, corresponding to a short fraction of the time between collisions and the frequency of the UV-probe laser was scanned. These

experiments yield LIF spectra from which relative populations in individual states can be calculated and hence *state-to-state* rate coefficients deduced. Because the fraction of NO in the gas flow was always less than 2%, and because rotational energy transfer in NO–He collisions is virtually as rapid as in NO–NO collisions [6–8], all the rate coefficients which we have obtained are for energy transfer in collisions between NO and He. Furthermore, because a different Laval nozzle is needed for every combination of temperature and total gas density, the rate coefficients for total relaxation which we report for particular temperatures are based on measurements using a single Laval nozzle, rather than on a series of measurements in which the density of the relaxant gas is varied [7,8].

### 3. Results and discussion

The rate constants for the relaxation of NO by He from selected rotational levels in the  $X^2\Pi_{1/2}$ ,  $\nu = 3$  vibronic level are summarised in Table 1. The values denoted by  $k_{1st}$  are the first-order rate constants derived by fitting the decays of LIF signals from a

Table 1

Rate coefficients for the relaxation of NO( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $\nu = 3$ ;  $J = 0.5, 3.5$  or  $6.5$ ) in collisions with He at 15, 27, 63, 149 and 295 K

$T/K$	[He] ( $10^{16} \text{ cm}^{-3}$ )	$J$	$k_{1st}$ ( $\mu\text{s}^{-1}$ )	$1 - f_{j,e}$	$k_{1st,f}$ ( $\mu\text{s}^{-1}$ )	$k_{2nd}$ ( $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ )	$\langle \sigma \rangle$ ( $\text{\AA}^2$ )
15	5.01	0.5	$4.17 \pm 0.55^a$	0.727	$3.03 \pm 0.40$	$0.60 \pm 0.08$	$20.3 \pm 2.7$
		3.5	$3.84 \pm 0.35$	0.894	$3.43 \pm 0.31$	$0.68 \pm 0.06$	$23.0 \pm 2.1$
		6.5	$4.50 \pm 0.21$	0.999	$4.49 \pm 0.21$	$0.90 \pm 0.04$	$30.1 \pm 1.4$
27	4.68	0.5	$4.99 \pm 0.32$	0.839	$4.19 \pm 0.27$	$0.89 \pm 0.06$	$22.3 \pm 1.4$
		3.5	$4.38 \pm 0.43$	0.824	$3.61 \pm 0.35$	$0.77 \pm 0.08$	$19.2 \pm 1.9$
		6.5	$4.54 \pm 0.32$	0.982	$4.46 \pm 0.31$	$0.95 \pm 0.07$	$23.7 \pm 1.7$
63	2.08	0.5	$3.36 \pm 0.17$	0.929	$3.12 \pm 0.16$	$1.50 \pm 0.08$	$24.3 \pm 1.2$
		3.5	$3.11 \pm 0.21$	0.835	$2.59 \pm 0.18$	$1.25 \pm 0.09$	$20.2 \pm 1.4$
		6.5	$3.29 \pm 0.22$	0.915	$3.01 \pm 0.20$	$1.45 \pm 0.10$	$23.5 \pm 1.6$
149	1.45	0.5	$3.69 \pm 0.15$	0.969	$3.58 \pm 0.15$	$2.47 \pm 0.10$	$26.1 \pm 1.1$
		3.5	$3.46 \pm 0.26$	0.903	$3.12 \pm 0.23$	$2.15 \pm 0.16$	$22.8 \pm 1.7$
		6.5	$3.75 \pm 0.18$	0.898	$3.37 \pm 0.16$	$2.32 \pm 0.11$	$24.6 \pm 1.2$
295	2.03	0.5	$7.13 \pm 0.24$	0.984	$7.01 \pm 0.24$	$3.45 \pm 0.12$	$25.9 \pm 0.9$
		3.5	$6.57 \pm 0.20$	0.944	$6.20 \pm 0.19$	$2.90 \pm 0.09$	$21.8 \pm 0.7$
		6.5	$7.26 \pm 0.25$	0.925	$6.71 \pm 0.23$	$3.16 \pm 0.11$	$23.7 \pm 0.8$

<sup>a</sup> Errors are quoted as  $\pm 2\sigma$  statistical error only.

particular level as the time delay between pulses from the pump and probe lasers was varied. Because the population relaxes not to zero but to the equilibrium concentration in that vibronic level at the temperature of the experiment, the observed rate constants correspond to the sum of the rate constants into and out of the observed level. To obtain the rate constants for transfer out of the level  $J$  ( $k_{1st, f}$ ) from the observed value of  $k_{1st}$ , we assume that the rate constant for transfer into  $J$  ( $k_{1st, r}$ ) is, at all times during the relaxation, the same as it would be from an equilibrium distribution [8]. The ratio ( $k_{1st, f}/k_{1st, r}$ ) is then the ratio of the population in level  $J$  at equilibrium to the sum of the populations in all other levels. It is then straightforward to show that the values of  $k_{1st}$  need to be multiplied by  $(1 - f_{J, e})$ , where  $f_{J, e}$  is the fraction of molecules in level  $J$  when rotational equilibrium has been established, to yield values of  $k_{1st, f}$ .

The second-order rate constants for relaxation from selected rotational levels,  $k_{2nd}$ , are obtained by dividing the corrected first-order rate constants,  $k_{1st, f}$ , by  $[\text{He}]$ , the density of He in the gas flow. Finally we list values of the thermally averaged cross-sections by dividing the values of  $k_{2nd}$  by the mean relative speed in NO–He collisions. As with the results obtained between 80 and 295 K [8], the thermally averaged cross-sections show no systematic variation with either the value of  $J$ , within the fairly limited range covered in the present experiments, or the temperature. The cross-sections derived from the present work are compared in Fig. 2 with those measured for rotational energy transfer by Islam et al. [7,8], and in Fig. 3 with the values at temperatures below 5 K derived by Willey et al. [15] from pressure-broadening parameters for lines from the  $X^2\Pi_{1/2}$ ,  $v=0$ ,  $J=0.5$  state. The agreement with the data of Islam et al. is good and the results demonstrate the invariance in the thermally averaged cross-sections for relaxation from specific rotational levels of NO( $X^2\Pi$ ) in collisions with He down to 15 K. Our results are also similar to those deduced by Willey et al. [18] at the higher end of the temperature range covered in their experiments (1.8–4.2 K).

On the naive basis in which rotational energy transfer occurs as a result of impulsive collisions between “hard” species, it is surprising that the total cross-section for energy transfer does not decrease at

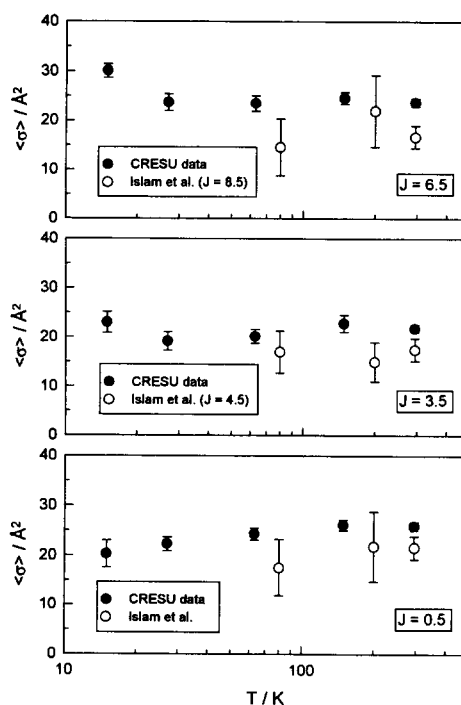


Fig. 2. Cross sections for relaxation of NO ( $X^2\Pi$ ;  $\Omega=1/2$ ;  $v=3$ ;  $J=0.5, 3.5$  or  $6.5$ ) in collisions with He at 15, 27, 63, 149 and 295 K, measured in the CRESU apparatus (●). The data of Islam et al. [7,8] for  $J=0.5, 4.5$  and  $8.5$  are indicated for comparison (○).

low temperatures. As the temperature is lowered, the decrease in (average) collision energy should reduce the torques on the molecule during “hard” collisions. Hence, in an increasing fraction of collisions,

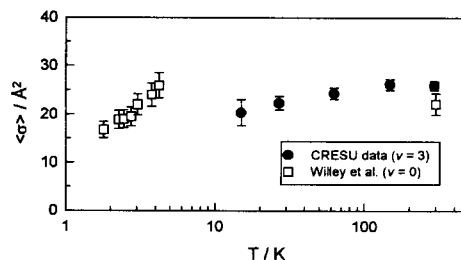


Fig. 3. Comparison of cross sections for overall relaxation of NO ( $X^2\Pi$ ;  $\Omega=1/2$ ;  $v=3$ ;  $J=0.5$ ) in collisions with He, measured in the CRESU apparatus (●), with those of Willey et al. [15] for NO ( $X^2\Pi$ ;  $\Omega=1/2$ ;  $v=0$ ;  $J=0.5$ ) measured in their collisional cooling apparatus (□).

the torque might be insufficient to change the rotational state of the molecule, resulting in a decrease in the effective cross section for  $J$ -changing collisions. Two effects, both connected to the existence of an attractive well on the intermolecular potential might counteract this effect at very low temperatures and hence explain the lack of any reduction in the cross-section for overall rotational energy transfer, at least until the lowest temperatures of the experiments of Willey et al. [15]. First, the long-range intermolecular attraction could increase the rate of “capture” and hence the cross-section for collisions with the repulsive “core”. If this is so, the “extra” collisions will have large impact parameters and be especially effective in transferring rotational energy. Second, rotational energy transfer may be facilitated through the effects of long-lived resonances.

The effect of long-lived resonances is thought [17] to be responsible for the observed *increase* in collision-broadening by He of the CO ( $J = 1 \leftarrow J = 0$ ) transition as the temperature is lowered below 5 K [17]. For the NO ( $J = 3/2 \leftarrow J = 1/2$ ) transition, the trend is in the opposite direction. A full theoretical explanation for all these findings requires quantum scattering calculations. For our part, we shall perform similar experiments to those reported here, using Ar and N<sub>2</sub> as collision partners. In both cases, the collisional cooling technique cannot be applied since the bath gas would condense, but the existence of deeper wells in the intermolecular potentials for NO–Ar and NO–N<sub>2</sub>, compared with NO–He, means that even at ca. 100 K the mean collision energy is comparable to the van der Waals well-depth, so that quantum mechanical effects on the rotational energy transfer rates may become more apparent.

As well as the rate constants for total relaxation from specific rotational levels, we have measured state-to-state rate coefficients for transfer from  $J = 0.5, 3.5$  and  $6.5$  at 149, 63, 27 and 15 K. In these experiments, pairs of LIF spectra were recorded with delays of 30 ns and 5  $\mu$ s set between the IR-pump and UV-probe laser pulses. The shorter delay corresponds to a collisional probability of  $\leq 0.1$  at each temperature, whilst the longer delay allows for complete rotational and spin–orbit equilibration. The intensities of individual lines of the (0, 3) band in the ( $A^2\Sigma^+ - X^2\Pi_{1/2}$ ) sub-band were compared at these two delays.

Estimates of state-to-state ( $J' \leftarrow J$ ) rate coefficients ( $k_{J',J}$ ) were based on the rate equation:

$$dN_{J'}/dt = k_{J',J}N_J[\text{He}]$$

where  $N_J$  and  $N_{J'}$  are the concentrations of NO in the initial ( $J$ ) and final ( $J'$ ) states. This equation was re-cast in the approximate form:

$$k_{J',J} = (\delta N_{J'}/N_J^0)/(\delta t[\text{He}])$$

where  $\delta t$  is the time delay (30 ns) in the short delay experiments and  $N_J^0$  is the concentration of NO molecules initially excited by the IR-pump laser to level  $J$ . For a given  $J'$ ,  $(\delta N_{J'}/N_J^0)$  was estimated from the relative intensities of a particular line in the LIF spectrum from level  $J'$  recorded at 30 ns ( $I_{J'}^{\delta t}$ ) and 5  $\mu$ s ( $I_{J'}^{\infty}$ ). Since rotational and spin–orbit relaxation was complete at 5  $\mu$ s, the intensity which the selected line would have had if *all* the initially excited molecules had been transferred to the level  $J'$  could be estimated by dividing  $I_{J'}^{\infty}$  by  $f_{J',e}$ , the

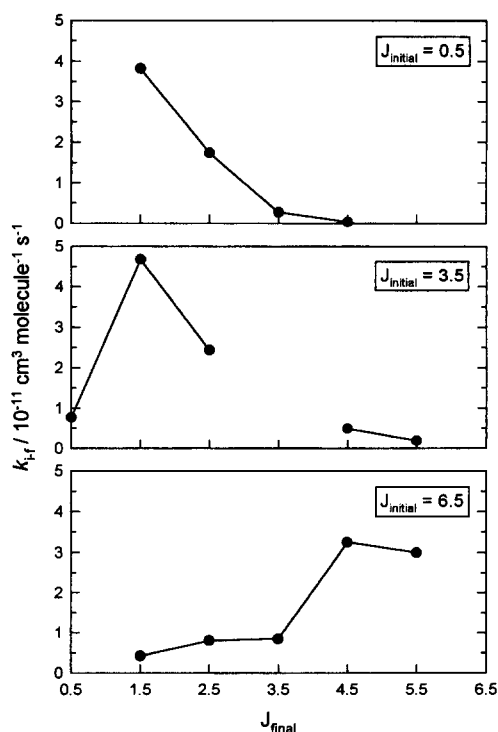


Fig. 4. State-to-state rate coefficients for transfer of NO ( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $\nu = 3$ ;  $J = 0.5, 3.5$  or  $6.5$ ) to ( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $\nu = 3$ ;  $J_{\text{final}}$ ) in collisions with He at 15 K, measured in the CRESU apparatus.

fraction of molecules in the level  $J'$  at thermal equilibrium. Consequently,  $(\delta N_{J'}/N_J^0)$  is given by  $I_{J'}^{\delta f}/(I_J^{\infty}/f_{J',e})$ . This method of calculation meant that, in contrast to other procedures, no allowance had to be made for differing line strength factors or laser intensities.

The state-to-state rate coefficients obtained by this analysis of experiments at 15 and 63 K for  $J = 0.5, 3.5$  and  $6.5$  are displayed in Figs. 4 and 5. The variation of  $k_{J',J}$  with  $|\Delta J|$  shows the familiar form in which the rate coefficients decrease with increasing  $|\Delta J|$  with a steeper fall-off for positive  $\Delta J$  ( $= J' - J$ ) than negative  $\Delta J$  on account of the endothermicity of the former processes. This effect is more marked the higher the value of  $J$  as the energy gaps between successive rotational levels increase. In addition, we note that the rate coefficients fall-off more steeply with  $\Delta J$  the lower the temperature. Although the cross-section for total removal from an

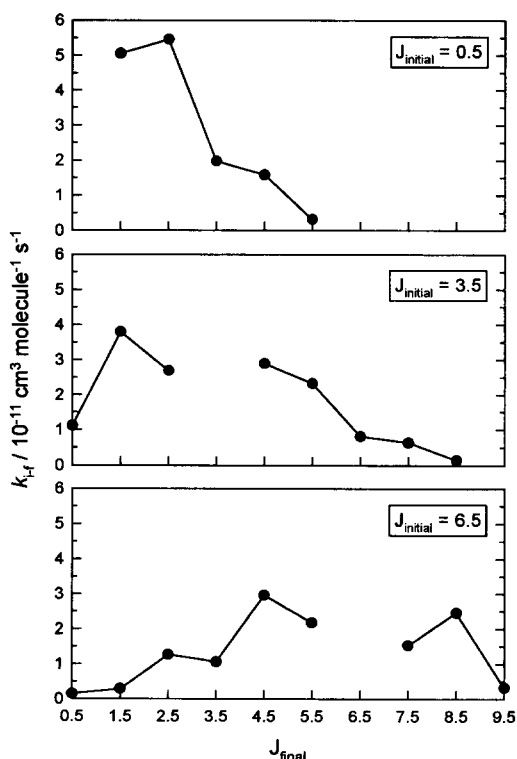


Fig. 5. State-to-state rate coefficients for transfer of NO ( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $v = 3$ ;  $J = 0.5, 3.5$  or  $6.5$ ) to ( $X^2\Pi$ ;  $\Omega = 1/2$ ;  $v = 3$ ;  $J_{\text{final}}$ ) in collisions with He at 63 K, measured in the CRESU apparatus.

initially prepared state is invariant with temperature, the state-to-state cross-sections change with temperature, those for lower  $\Delta J$  increasing as the temperature is lowered whilst those for higher  $\Delta J$  decrease.

Finally, we note that, in our results, there is a clear preference for *even*  $\Delta J$  transfers over *odd*  $\Delta J$  transfers, as has been observed in the results of experiments at defined collision energy [9–12]. This propensity in the state-to-state rate coefficients is predicted by theory whenever the diatomic molecule in which energy transfer is being observed is “nearly homonuclear”. Using semi-classical scattering theory, McCurdy and Miller [19] ascribed this effect to interferences which arise between trajectories scattered from similar parts of the two “ends” of the intermolecular potential. Yang and Alexander [14] have calculated state-to-state integral and differential cross-sections using full close coupling and coupled states methods and potential energy surfaces computed by the coupled electron pair approximation. They point out that the “even” terms in the intermolecular potential, which would be the only ones present for a homonuclear molecule, couple *e/f* conserving transitions with even  $\Delta J$  and *e/f* changing transitions with odd  $\Delta J$ , whilst the reverse is true for the additional “odd” terms which are present in the intermolecular potential in the case of a heteronuclear molecule. The preference for even  $J$  is then equivalent to a preference for *e/f* conservation.

Further details of the results on state-to-state rotational energy transfer will be given in a future publication which will include the results of experiments on energy transfer induced by collisions with partners other than helium. The extension of the quantum scattering calculations to the regime of collision energies appropriate to our low temperature experiments is desirable.

## Acknowledgements

We are grateful to EPSRC for a substantial research grant to construct the CRESU apparatus and a studentship to one of us (PLJ). The Continuum laser system providing the IR-pump beam was obtained on loan from the EPSRC Laser Loan Pool at the Rutherford–Appleton laboratory, for which we express our thanks. We are also very grateful to Dr

Bertrand Rowe and his colleagues at Rennes for valuable advice and discussion and to Stuart Arkless, Mark Cheshire and Steve West for their skilled technical work.

## References

- [1] (a) I.R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, B.R. Rowe and I.W.M. Smith, *J. Chem. Phys.* 97 (1992) 8798; (b) I.R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe and I.W.M. Smith, *J. Chem. Phys.* 100 (1994) 4229.
- [2] I.R. Sims, I.W.M. Smith, *Annu. Rev. Phys. Chem.* 46 (1995) 109.
- [3] L.B. Herbert, I.R. Sims, I.W.M. Smith, D.W.A. Stewart, A.C. Symonds, A. Canosa, B.R. Rowe, *J. Phys. Chem.* 100 (1996) 14928.
- [4] R.A. Brownsword, A. Canosa, B.R. Rowe, I.R. Sims, I.W.M. Smith, D.W.A. Stewart, A.C. Symonds and D. Travers, *J. Chem. Phys.* (1997) in press.
- [5] P. Esherick, R.J.M. Anderson, *Chem. Phys. Lett.* 70 (1980) 621.
- [6] (a) Aa.S. Sudbo and M.M.T. Loy, *Chem. Phys. Lett.* 82 (1981) 135; (b) Aa.S. Sudbo and M.M.T. Loy, *J. Chem. Phys.* 76 (1982) 3646.
- [7] (a) M.J. Frost, M. Islam and I.W.M. Smith, *Can. J. Chem.* 72 (1994) 606; (b) M. Islam, I.W.M. Smith and J.W. Wiebrecht, *J. Phys. Chem.* 98 (1994) 9285.
- [8] M. Islam, I.W.M. Smith, J.W. Wiebrecht, *J. Chem. Phys.* 103 (1995) 9676.
- [9] (a) P. Andresen, H. Joswig, H. Pauly and R. Schinke, *J. Chem. Phys.* 77 (1982) 2204; (b) H. Joswig, P. Andresen and R. Schinke, *J. Chem. Phys.* 85 (1986) 1904.
- [10] S.D. Jons, J.E. Shirley, M.T. Vonk, C.F. Giese, W.R. Gentry, *J. Chem. Phys.* 97 (1992) 7831.
- [11] L.S. Bontuyan, A.G. Suits, P.L. Houston, B.J. Whitaker, *J. Phys. Chem.* 97 (1993) 6342.
- [12] H. Meyer, *J. Chem. Phys.* 102 (1995) 3151.
- [13] (a) T. Orlikowski and M.H. Alexander, *J. Chem. Phys.* 79 (1983) 6006; (b) T. Orlikowski and M.H. Alexander, *J. Chem. Phys.* 80 (1984) 4133; (c) M.H. Alexander, *J. Chem. Phys.* 99 (1993) 7725.
- [14] M. Yang, M.H. Alexander, *J. Chem. Phys.* 103 (1995) 6973.
- [15] D.R. Willey, D.N. Bittner, F.C. De Lucia, *Mol. Phys.* 67 (1989) 455.
- [16] E. Roueff in *Molecular Astrophysics — A Volume Honouring Alexander Dalgarno*, ed. T.W. Hartquist (Cambridge University Press, Cambridge, 1990) 232 pp.
- [17] S. Green, L.D. Thomas, *J. Chem. Phys.* 73 (1980) 5391.
- [18] D.R. Willey, R.L. Crownover, D.N. Bittner, F.C. De Lucia, *J. Chem. Phys.* 89 (1988) 1923.
- [19] C.W. McCurdy, W.H. Miller, *J. Chem. Phys.* 67 (1977) 463.