

Rotationally specific rates of vibration–vibration energy exchange in collisions of NO($X^2\Pi_{1/2}, v=3$) with NO($X^2\Pi, v=0$)

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Infrared ultraviolet double resonance (IRUVDR) experiments have been performed to investigate the rotational specificity of the vibrational–vibrational ($V-V$) exchange process, $\text{NO}(X^2\Pi_{1/2}, v=3, J_i) + \text{NO}(v=0) \rightarrow \text{NO}(X^2\Pi_{1/2}, v=2, J_f) + \text{NO}(v=1)$, for which the vibrational energy discrepancy corresponds to 55.9 cm^{-1} . Radiation from an optical parametric oscillator was used to excite NO molecules into a specific rotational level (J_i) in the $X^2\Pi, \Omega=\frac{1}{2}, v=3$ state. Laser-induced fluorescence (LIF) spectra of the (0,2) band of the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system were then recorded at delays corresponding to a fraction of a collision. From the relative line intensities, rate coefficients were determined for transfer of the excited NO molecule from the level $X^2\Pi_{1/2}, v=3, J_i$ to different final rotational levels (J_f) in the $X^2\Pi_{1/2}, v=2$ state. Results are reported for $J_i=3.5, 4.5, 7.5, 10.5$, and 15.5 . The data show a significant, though not strong, propensity for J to decrease by one; i.e., for $\Delta J = J_f - J_i = -1$, especially for the higher J_i levels. This result is interpreted as arising from a combination of (a) the tendency to minimize the energy that has to be accommodated in the relative translation of the collision partners, and (b) the favoring of $\Delta J = \pm 1$ changes when $V-V$ intermolecular exchange occurs under the influence of dipole–dipole interactions. © 1999 American Institute of Physics. [S0021-9606(99)00644-3]

I. INTRODUCTION

The vibrational relaxation of diatomic and small polyatomic molecules has been extensively studied and is, in many respects, very well understood.¹ Much of this information was gathered between the late 1960s and the early 1970s by the application of the technique of laser-induced vibrational fluorescence.¹ In this method, a pulsed infrared laser is used to excite molecules to a low-lying vibrational level in their electronic ground state and the time evolution of the spontaneous infrared emission from the excited molecules is observed from mixtures in which the composition is systematically varied. However, although the initial excitation is generally to a specific rotational level in the excited vibrational state, no information is obtained in such experiments about whether the rate of vibrational relaxation depends on the rotational level of the initially excited molecule or about the rotational states which are populated in the collision which brings about vibrational relaxation. In part, this absence of information about rotational specificity arises because the detection sensitivity for the emitted infrared radiation is too low to allow it to be spectrally resolved. Furthermore, the time scales associated with vibrational and rotational relaxation are usually very different. Rotational relaxation occurs on approximately every collision, whatever the collision partner, whereas vibrational relaxation may be several orders-of-magnitude slower. For example, the rate coefficients for relaxation from specific rotational levels of NO($X^2\Pi$) in collisions with Ar at 298 K are

$\approx 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1, 2-6}$ whereas the rate coefficient for vibrational relaxation of NO($X^2\Pi, v=1$) by Ar at the same temperature is $\leq 1.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1, 7}$.

The development of time-resolved optical double resonance methods has provided both rotational state selectivity in the *excitation* of molecules and rotational state specificity in their *detection*. However, the problems associated with the normally very different rates of vibrational and rotational redistribution remain. Thus to examine the initial rotational state populations following vibrational relaxation, it is necessary to observe these populations at a delay which corresponds to a small fraction of the *rotational* relaxation time. In general, this requirement means that only a *very small* fraction of the initially excited molecules will have been transferred from the initially excited vibrational state at the time that the rovibrational level populations are probed. Moreover, one has to observe these molecules in a vibrational level which is neither significantly populated thermally nor is populated in collisions from the vibrational ground state if a self-relaxation process is being studied.

The last few years have seen the emergence of some data for rotationally specific vibrational relaxation in small polyatomic molecules, for the process which is often referred to as *intramolecular* vibrational–vibrational ($V-V$) energy transfer. The polyatomic character increases the chance of rapid transfer between vibrational states, especially when they are strongly mixed by Fermi or Coriolis resonances.⁸ In such cases, the vibrational transfer process can occur at a rate competitive with rotational relaxation. On the other hand, the molecules must not be too large or one loses rotational selectivity in preparation and rotational specificity in observation. Two molecules for which rotational specificity in in-

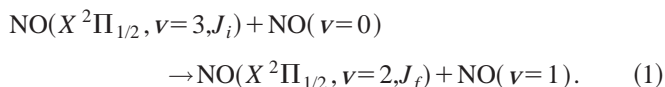
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tramolecular $V-V$ energy transfer has been studied are D_2CO (Ref. 9) and C_2H_2 ,¹⁰⁻¹³ and the information obtained has been reviewed by Orr.¹⁴ In both cases, transfer between the vibrational states that were involved required fewer than 10 collisions, so that it was not too difficult to work at delays corresponding to a small fraction of the rotational relaxation time.

With diatomic molecules, much greater sensitivity would be required to carry out similar rotationally specific measurements on vibrational-rotational, translational ($V-R,T$) energy transfer, for example, in collisions with noble gas atoms. Qualitative evidence for the importance of energy transfer from the molecular vibration of a diatomic species to rotation came in experiments, carried out 20 years ago, in which chemical lasers operating on rotational transitions of OH (Ref. 15) and HF (Ref. 16) demonstrated the importance of near-resonant vibrational-rotational ($V-R$) energy exchange. However, although Taatjes and Leone¹⁷ used collisional transfer from low-lying rotational levels in HF ($v=1$) to ($v=0, J=13$) to measure rotational relaxation rates from this high rotational level in HF, they were unable to quantify the rate of the $V-R$ process.

On the other hand, *intermolecular* vibrational-vibrational ($V-V$) energy exchange often occurs with a collision probability of $\approx 10^{-2}$, increasing the chance of successful experiments at the rotationally resolved level. The results of rotationally resolved experiments on intermolecular $V-V$ energy exchange are interesting from a number of standpoints. In particular, they should cast light on the mechanism for energy exchange, especially whether it is the short-range repulsive^{1,18,19} or long-range attractive^{1,20,21} part of the intermolecular potential which causes vibrational energy to be exchanged.

In the experiments that are described in the present paper, we have examined the rotational specificity of the process,



Because of vibrational anharmonicity, this self-relaxation process is 55.9 cm^{-1} endothermic. At 298 K, it is known to proceed with a rate coefficient of $3.2 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.^{3(a),22,23} Pulses of tunable IR radiation from an optical parametric oscillator prepared a subset of NO molecules in a selected rotational level (J_i) in the $v=3$ level of the $X^2\Pi_{1/2}$ electronic ground state. After a delay corresponding to $\approx 20\%$ of the rotational relaxation time, we recorded a laser-induced fluorescence (LIF) spectrum of the (0,2) band of the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system. The intensities of the lines in this spectrum reflect the numbers of molecules that had been transferred at this short time delay to individual rotational levels (J_f) in $X^2\Pi_{1/2}, v=2$ by the $V-V$ process represented by Eq. (1).

In assessing the results of these experiments, it is important to appreciate that relaxation occurs by collision of the excited molecules with a thermal ensemble of NO molecules, which are therefore distributed, according to the Boltzmann

laws, over rotational levels in $v=0$. Consequently, we believe that little was to be gained by observing the other product of the $V-V$ process, i.e., $NO(v=1)$.

II. EXPERIMENT

The IRUVDR technique used in the present experiments was similar to that employed in earlier studies of vibrational and rotational relaxation in NO from our laboratory.^{3-6,24} Pulses of tunable IR radiation were generated by a $LiNbO_3$ optical parametric oscillator (OPO) which was pumped with the fundamental $1.064\text{ }\mu\text{m}$ output of a Nd:YAG laser (Spectron, SL 803). To excite molecules to ($v=3, \Omega=\frac{1}{2}, J_i$) the frequency of this pump laser was tuned into resonance with a selected line in the R branch of the ($\Omega=\frac{1}{2} \leftarrow \frac{1}{2}$) subband of the (3, 0) second vibrational overtone band of NO at $\approx 1.80\text{ }\mu\text{m}$. The pulse energy of the IR radiation was generally in the range 1.5–2.0 mJ and the bandwidth of the laser output was $\approx 0.2\text{ cm}^{-1}$. The frequency of the IR laser was tuned to the appropriate transition with the aid of a spectrophone containing 50 Torr of NO.

Tunable UV probe radiation, with a bandwidth of $\approx 0.4\text{ cm}^{-1}$, was produced by frequency doubling the output of an excimer-pumped dye laser (Lambda-Physik, FL2002). LIF spectra were recorded by scanning this UV probe radiation through an appropriate part of the (0,2) band of the NO $A^2\Sigma^+ - X^2\Pi_{1/2}$ system between ≈ 246.5 and 247 nm.

The beams from the IR and UV lasers counterpropagated along the axis of a cylindrical Pyrex cell with a CaF_2 window mounted on each end. 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 photomultiplier tube (EMI9781B), through a quartz window and an interference filter (Corion, FWHM 10 nm) centered at 228 nm, which isolated the fluorescence in the (0,0) band of the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system at $\approx 226\text{ nm}$. The equipment for controlling the firing of the lasers and for recording, accumulating and analyzing the LIF signals was the same as that described by Frost and Smith.²⁵

The LIF signal was normalized with respect to the pulse energy from the OPO. This was done by passing the reflection of the OPO beam from the entrance window of the main cell into the spectrophone. The spectrophone signal was then used to normalize the double resonance LIF signal. The latter signal was not normalized with respect to the output from the probe laser since the pulse energy was $\approx 0.5\text{ mJ}$ and was therefore ample to saturate the UV rovibronic transitions in NO.

The time delay between the pump and probe laser pulses was selected with a delay generator (Stanford DG535) and the resulting LIF signal was recorded as the frequency of the probe laser was scanned. The step size between successive points on the spectrum corresponded to $\approx 0.1\text{ cm}^{-1}$ and the intensity at each point was the result of taking the average signal from 30 sets of laser shots. Most experiments were performed with a pressure of 200 mTorr of NO in the cell and a delay between the excitation and probe pulses of $\approx 100\text{ ns}$. At this NO pressure, a delay time of 100 ns corresponds

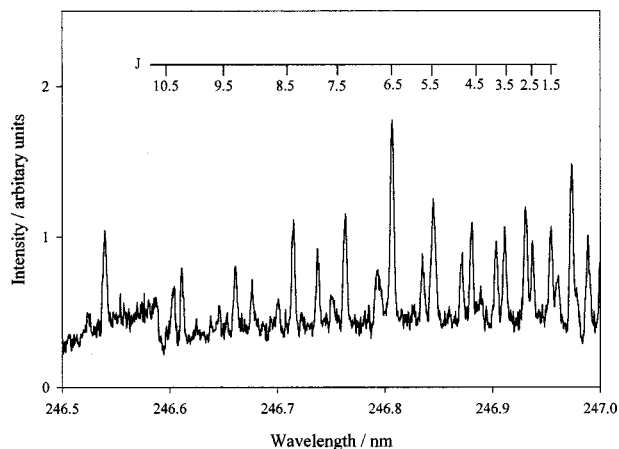


FIG. 1. LIF spectrum of part of the (0,2) band of the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system of NO recorded, from a sample of 187 mTorr NO, ≈ 40 ns after excitation of the $J_i=7.5$ rotational level in the $X^2\Pi_{1/2}$, $v=3$ state. The lines marked belong to the R_{11} branch of the band and the numbers given are the rotational quantum numbers in the lower rovibronic state.

to ≈ 0.2 of the rotational relaxation time and 1.4×10^{-3} of the vibrational self-relaxation time.

III. RESULTS

Figure 1 shows a LIF spectrum of part of the (0,2) band of the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system recorded from a sample of 187 mTorr of NO with a delay of ≈ 40 ns between the excitation pulse, which excited the rotational level $J_i=7.5$ in $\text{NO}(X^2\Pi_{1/2}, v=3)$, and the probe pulse from the dye laser. The signal to noise is typical of the spectra from which the results reported in the present paper have been derived. It can be clearly seen that, although a wide range of rotational levels in the $v=2$ vibrational state are populated by the $V-V$ process represented by Eq. (1), the intensity of the line from $\text{NO}(X^2\Pi_{1/2}, v=2, J_f=6.5)$ is anomalously high, suggesting preferential population of the level accessed by a $\Delta v=-1$, $\Delta J=-1$ transition. In the several spectra which we have recorded following the excitation of NO to $v=3$, $J_i=7.5$, the intensity of the line from $v=2$, $J_f=6.5$ was found to be enhanced.

The quantitative interpretation of the recorded spectra proceeded in two stages. First, *relative* populations in individual rotational levels ($v=2$, J_f) were derived from LIF spectra recorded at different fixed delays, the longest allowing ample time for complete *rotational* relaxation but corresponding to only a small fraction of the *vibrational* relaxation time. As the rotational and vibrational relaxation times differ by a factor of >100 (see earlier) this was not difficult. In each case, the populations N_J in individual rotational levels J were expressed relative to the population in $J=7.5$, which is the most populated rotational level in a thermalized rotational distribution at room temperature. These fractional populations f_J were calculated from the measured line intensities Int_J and the line strength factors S_J for the measured lines, relative to the same quantities for the transition from $J=7.5$, according to the equation

$$f_J = f_{J=7.5} \{ \text{Int}_J / \text{Int}_{J=7.5} \} (S_{J=7.5} / S_J). \quad (2)$$

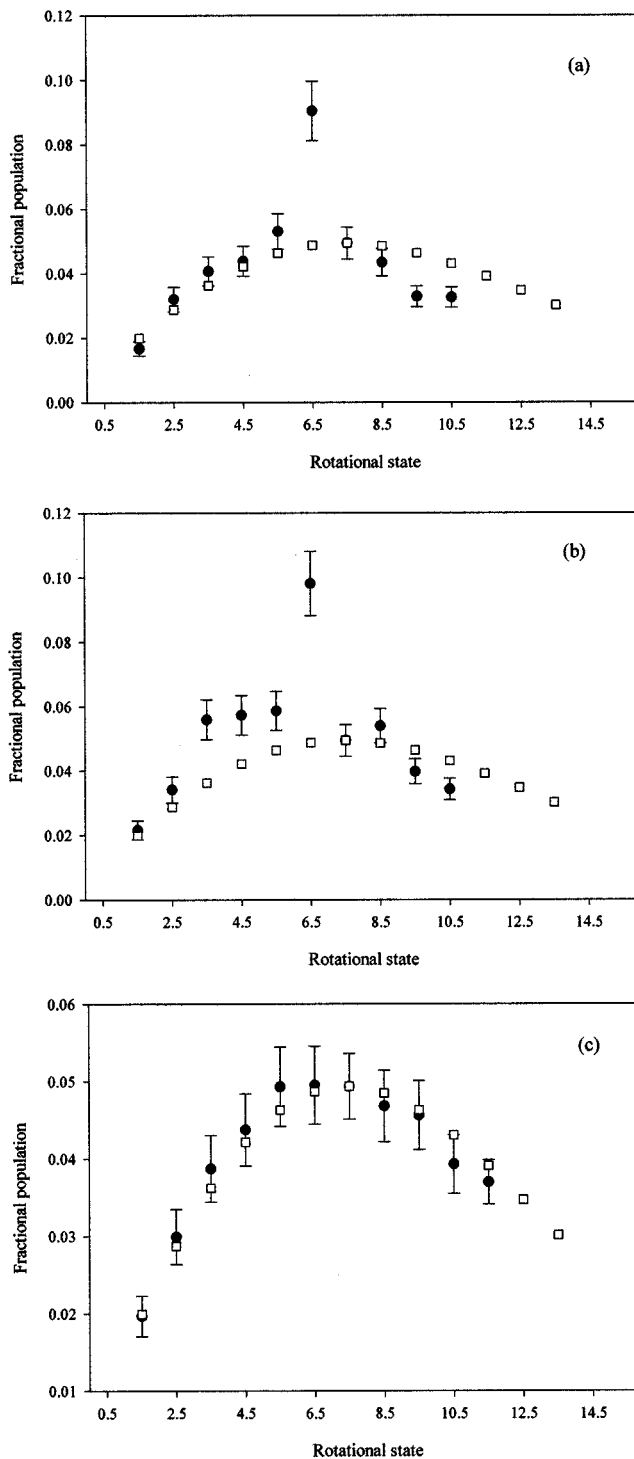


FIG. 2. Relative rotational level populations in NO ($X^2\Pi_{1/2}$, $v=2$, J_f) at different delay times after excitation of the $J_i=7.5$ rotational level in the $X^2\Pi_{1/2}$, $v=3$ state. The pressure of NO was 200 mTorr and the delay times are (a) 40 ns, (b) 120 ns, and (c) 3 μs , corresponding to the rotational relaxation time multiplied by factors of (a) 0.1, (b) 0.25, and (c) 6. The experimental data (\bullet) are compared with a rotational Boltzmann distribution (\square) calculated for 298 K.

Because the pulse energy from the probe laser was sufficient to ensure saturation of the transitions in the $\text{NO } A^2\Sigma^+ - X^2\Pi_{1/2}$ (2,0) band, each line strength factor was taken to be the ratio of the degeneracies in the upper and lower rotational levels of the transition.

In Fig. 2, we compare fractional populations calculated in this way to the Boltzmann rotational distribution for three different time delays following the excitation of NO to ($v=3, J=7.5$). The experimentally derived distribution in Fig. 2(c), at a delay corresponding to about 6 gas kinetic collisions, agrees within experimental error with the calculated Boltzmann distribution confirming that rotational relaxation is essentially complete at this delay. On the other hand the distributions shown at the shorter delays are clearly non-Boltzmann.

Figure 3 shows population distributions derived from spectra recorded at the shortest delays following initial excitation of NO to different initial rotational levels, $J_i=3.5, 4.5, 10.5$, and 15.5 , in $v=3$. The data for $J_i=7.5, 10.5$, and 15.5 all show a clear preference for initial population of the level J_f in NO($v=2$) for which ΔJ (i.e., $J_f - J_i$) = -1 . The position with respect to spectra recorded with $J_i=3.5$ and 4.5 is less clear cut. For $J_i=3.5$, there again appears to be a preference for $\Delta J = -1$ but, for $J_i=4.5$, both $\Delta J = -1$ and $\Delta J = +1$ transitions appear to be favored. It seems unlikely that this difference in behavior for these two neighboring rotational levels is real and it may reflect experimental uncertainty in the relative J_f populations. The errors indicated on the diagrams in Figs. 2 and 3 are $\approx 10\%$ for the highest populations and are estimated from errors in measuring the heights of the individual lines with a small allowance made for the time jitter between the pulses from the pump and probe lasers.

The second stage in the analysis was to derive state-to-state rate coefficients from the LIF spectra taken at the shortest time delay (δt). To do this, it is generally necessary to relate the concentration, $N_{J_f}(\delta t)$, in a given rovibrational level ($v=2, J_f$) at this delay to the concentration, $N_{J_i}^0$, initially excited to the rovibrational level ($v=3, J_i$). Then one can use the equation^{4,5,24}

$$N_{J_f}(\delta t) = k_{J_f J_i} N_{J_i}^0 [\text{NO}] \delta t \quad (3)$$

to determine the rate coefficient $k_{J_f J_i}$ for transfer from J_i to J_f in the collisions between NO($v=3, J_i$) and NO($v=0$) in which V-V energy exchange takes place.

In previous studies,^{4,5,24} in which rate coefficients were determined for transfer between specific rotational levels within the same vibrational state with collider M , we have compared the spectrum taken at a short delay with that taken at delays where rotational relaxation was complete but vibrational relaxation was insignificant. Under these circumstances,

$$\{N_{J_f}(\delta t)/N_{J_i}^0\} = \{\text{Int}_{J_f}(\delta t)/(\text{Int}_{J_f}^\infty/f_{J_f})\}, \quad (4)$$

where $\text{Int}_{J_f}(\delta t)$ is the intensity of a line from J_f in the LIF spectrum taken at the short delay δt , $\text{Int}_{J_f}^\infty$ is the intensity of the same line recorded under completely relaxed conditions, and f_{J_f} is the fraction of molecules in level J_f when rotational relaxation is complete. Hence

$$k_{J_f J_i} = \{\text{Int}_{J_f}(\delta t)/(\text{Int}_{J_f}^\infty/f_{J_f})\}/[M] \delta t. \quad (5)$$

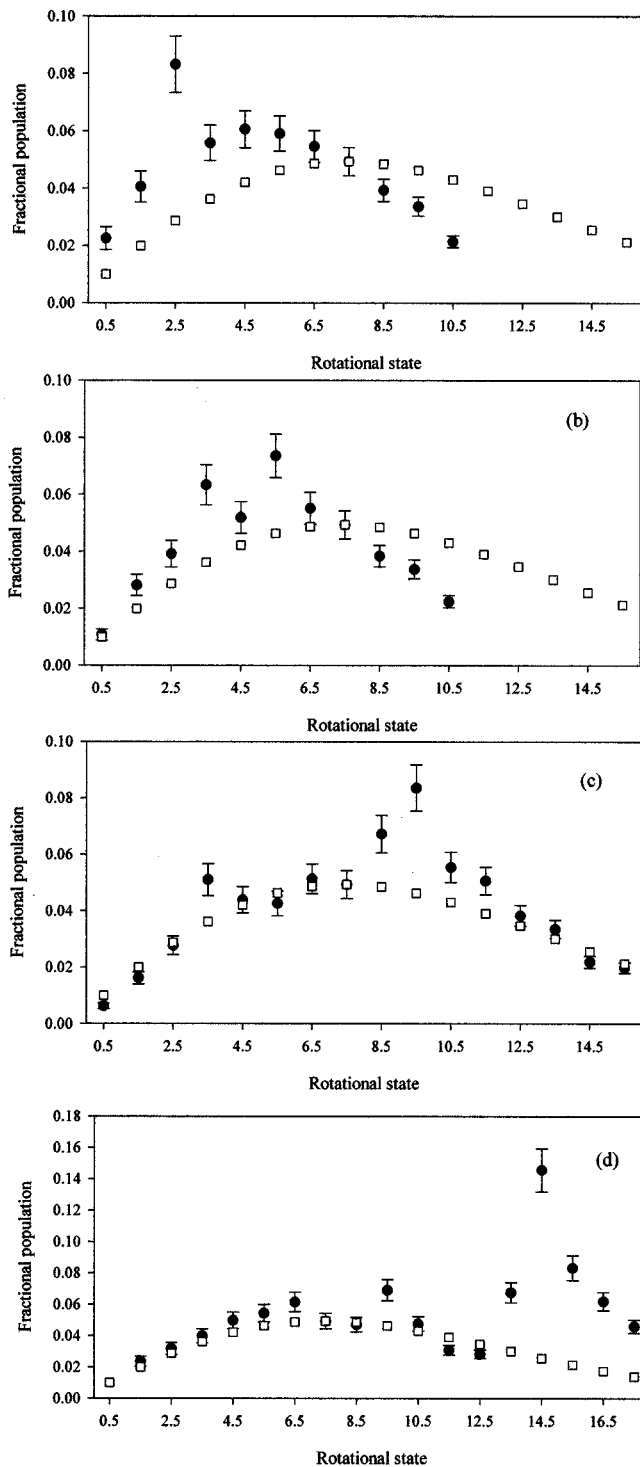


FIG. 3. Relative rotational level populations in NO ($X^2\Pi_{1/2}$, $v=2, J_f$) at short delay times after excitation of different rotational levels in the $X^2\Pi_{1/2}$, $v=3$ state; (a) $J_i=3.5$, (b) $J_i=4.5$, (c) $J_i=10.5$, and (d) $J_i=15.5$. The experimental data (●) are compared with a rotational Boltzmann distribution (□) calculated for 298 K.

In the present experiments, the intensities $\text{Int}_{J_f}^\infty$ could not be measured directly from spectra taken at very long delays, partly because of vibrational “cascading” (i.e., the fact that the excited NO molecules will relax into and then from $v=2$), and also because of experimental problems associated with the very different strength of the LIF signals at

TABLE I. State-to-state rate coefficients ($k/10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer of NO from rovibronic levels ($v=3$, $\Omega=\frac{1}{2}$; J_i) to ($v=2$, $\Omega=\frac{1}{2}$; J_f) in collisions with a thermal ensemble of NO molecules at 298 K.

J_f	$J_i=3.5$	$J_i=4.5$	$J_i=7.5$	$J_i=10.5$	$J_i=15.5$
0.5	1.0	0.5		0.3	
1.5	1.9	1.3	0.8	0.9	0.9
2.5	3.9	1.8	1.5	1.2	1.2
3.5	2.6	3.0	1.9	2.2	1.5
4.5	2.8	2.4	2.0	1.9	1.8
5.5	2.7	3.4	2.4	1.9	2.0
6.5	2.5	2.6	4.2	2.2	2.2
7.5	2.3	2.3	2.3	2.2	1.8
8.5	1.8	1.8	2.0	3.0	1.7
9.5	1.6	1.6	1.5	3.7	2.5
10.5	1.0	1.0	1.5	2.4	1.7
11.5				2.2	1.1
12.5				1.7	1.0
13.5				1.5	2.5
14.5				1.0	5.3
15.5				0.9	3.0
16.5				0.6	2.3
17.5					1.7
$\Sigma k_{J_f, J_i}$	24	22	20	30	34

short and very long delays. (Recall that only about one NO molecule in 10^3 has been relaxed to $v=2$ when the spectra at shortest delays were recorded.) Therefore, to estimate the ratio $\{N_{J_f}(\delta t)/N_{J_i}^0\}$ the usual procedure had to be modified to allow for the incomplete vibrational relaxation of NO molecules from $v=3$ to $v=2$ when the reference spectrum was recorded.

The strategy adopted was to estimate $N_{J_i}^0$ from spectra, like that used to obtain the fractional populations shown in Fig. 2(c), which were recorded at a time $\delta t'$ which was appreciably longer than the rotational relaxation time but only a fraction of the vibrational relaxation time. Under these conditions, the population observed in a given rotational level J_f in $v=2$ is given by

$$N_{J_f}(\delta t') = (f_{J_f} k_{V-V}) N_{J_i}^0 [\text{NO}] \delta t', \quad (6)$$

where k_{V-V} is the rate coefficient for vibrational self-relaxation of NO($v=3$). Then, combining Eqs. (4), (5), and (6) and replacing concentrations (N_J) by intensities (Int_J), one obtains

$$k_{J_f, J_i} = k_{V-V} \{ \text{Int}_{J_f}(\delta t) / \delta t \} / \{ \text{Int}_{J_f}(\delta t') / \delta t' f_{J_f} \}. \quad (7)$$

In using this equation to determine values of k_{J_f, J_i} , we took the value of k_{V-V} to be $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{3(a),22,23} The calculated state-to-state rate coefficients are listed in Table I.

There are two principal assumptions in the treatment used to derive the state-to-state rate coefficients given in Table I. The first assumption is that of complete relaxation over the rotational and spin-orbit levels of $v=2$ in spectra recorded at a time delay corresponding to about six gas kinetic collisions. Previous measurements²⁴ in this laboratory on rotational energy transfer in NO-NO collisions demonstrate no significant preference for spin-orbit conserving

transfers over spin-orbit changing transfers. Consequently, we conclude that the experiments at the longest delays allow ample time for complete relaxation over rotational levels in both spin-orbit states and that this assumption introduces no significant error in the state-to-state rate coefficients.

The second assumption is that the rate constant for $V-V$ energy exchange is independent of the initial rotational level J_i and has a value of $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{3(a),22,23} Obviously any uncertainty in this rate constant, and direct experiments have yielded reported values from $2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,^{3(a),22,23} contributes to the error in the *absolute* values of the rate coefficients derived in the present work. The effect of different values of k_{V-V} for different initial rotational levels J_i would have a subtler effect, since then k_{V-V} would change with time as rotational relaxation of NO occurred in $v=3$. In the last row of Table I, we list rate constants obtained by summing the state-to-state rate coefficients determined for each J_i . Of course, these sums represent lower limits to the true sums, since they do not include the small contributions to the total rates from transfer to levels which gave rise to spectral lines which, at the short time delay, were too weak to measure accurately. These lines fall into two categories; (a) those arising from relatively large changes in J in the observed NO molecule, and (b) those arising from the other spin-orbit component of NO($v=2$), i.e., $\Omega=\frac{3}{2}$. Lines from NO($v=2, \Omega=\frac{3}{2}$) could be identified but with too poor a signal to noise to measure with any accuracy. The fact that the sum of the measured state-to-state rate coefficients for $J_i=15.5$ exceeds the assumed value of k_{V-V} may mean that there is very little transfer to other, unobserved, J_f levels including those in the $\Omega=\frac{3}{2}$ spin-orbit component, or it could be that k_{V-V} for this initial rotational level is somewhat higher than the thermally averaged value.

IV. DISCUSSION

We know of no specific results, either experimental or theoretical, which can be compared directly with the data obtained in the present work. To our knowledge, there have been no previous measurements of $V-V$ exchange between diatomic molecules at a fully or partially resolved rovibrational state to rovibrational state resolved level, nor have there been any "full-scale" quantum scattering calculations performed on *ab initio* potential energy surfaces for such processes.

At a simpler theoretical level, $V-V$ intermolecular energy exchange is generally considered¹ as occurring either under the influence of the short-range repulsion between the collision partners, for example in an extension¹⁸ of the Schwartz, Slawsky, and Herzfeld (SSH) theory for $V-T$ energy transfer,¹⁹ or as a result of interaction via the long-range attraction arising from the nonsymmetric charge distributions on the two molecules. This latter idea, first put forward by Mahan²⁰ for $V-V$ energy exchange between dipolar diatomic molecules, was subsequently developed by Sharma and Brau²¹ into a useful, if still approximate, theory. They included higher-order coupling terms in the attractive potential, from dipole-quadrupole, quadrupole-quadrupole, etc.,

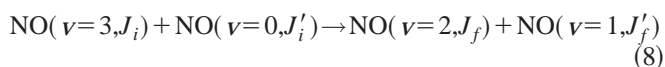
interactions. In general, however, it is found that the term which arises from interaction of the lowest order multipoles appears to exert the dominant influence.

There is now abundant experimental evidence supporting the basic postulate of the Sharma–Brau theory. Particularly persuasive are the data on V – V energy exchange between CO (Ref. 26) and O_2 (Ref. 27) in a range of excited vibrational levels and a variety of diatomic and small polyatomic collision partners. In each case, the collisional probability of energy transfer is related to three factors; (i) the discrepancy between the transition energies in the two molecules, (ii) the dipole transition moment in the collision partner accepting energy from CO(ν) or O_2 (ν), and (iii) the vibrational quantum number ν in the vibrationally excited molecule.

Any realistic treatment of V – V intermolecular energy exchange must consider the changes in the rotational states of the collision partners that can accompany their changes in vibrational state. In some cases, such changes in the rotational levels can reduce the energy discrepancy and hence the energy that must be converted to or from relative translation which might increase the probability of such a transition taking place. Within the first-order Born approximation,¹ these rotational level changes are subject to strict selection rules if V – V energy exchange occurs because of interaction between the electric multipoles on the collision partners. For example, if the dipole–dipole term is predominant, then both molecules must undergo transitions for which ΔJ is either +1 or –1. Calculations to higher orders of perturbation theory have shown²⁸ that changes in J larger than $\Delta J = \pm 1$ then become possible. In addition, of course, such rotational transitions may arise, even within the first-order Born approximation, under the influence of higher-order terms in the intermolecular potential.

Based on the theoretical considerations described in the two previous paragraphs, we believe that the preference which we observe for $\Delta J = -1$ transitions in the NO molecule undergoing transfer from $\nu = 3$ to $\nu = 2$ has its origin in two features of the V – V exchange process (1). First, whatever the transition undergone by the collision partner as it is transferred from $\nu = 0$ to $\nu = 1$, decrease of rotational energy in the initially excited molecule will serve to reduce the energy discrepancy of the overall exchange process. Second, it appears that there must be some preference for small, rather than large, changes in ΔJ . In the case of NO–NO collisions, the largest term in the attractive interaction would arise from the dipole–dipole term and, in the first-order Born approximation, the rotational transitions which accompany the exchange of vibrational energy would be limited to $\Delta J = \pm 1$. These two factors will combine to favor $\Delta J = -1$ transitions, especially for high J_i where the spacings between neighboring rotational levels become large.

In order to examine further the propensities for rotational transitions in the V – V exchange process between NO($\nu = 3$) and NO($\nu = 0$) we have carried out a series of calculations based on the premise that the rate coefficient for the fully state-selected process defined by the equation



is proportional to the product of four factors, $F_{|\Delta E|}$, $F_{|\Delta J|}$, $F_{|\Delta J'|}$, and $F_{\text{exo/endo}}$. The first factor, $F_{|\Delta E|}$, depends on the absolute magnitude of the energy discrepancy of the overall process, that is on $|\Delta E| = |E(\nu=2, J_f) + E(\nu=1, J'_f) - \{E(\nu=3, J_i) + E(\nu=0, J'_i)\}|$. The second and third factors depend on the magnitude of the changes in the rotational quantum numbers of the two NO molecules; i.e., $|\Delta J| = |J_f - J_i|$ and $|\Delta J'| = |J'_f - J'_i|$. The final factor, $F_{\text{exo/endo}}$, is set to 1 if the process represented by Eq. (2) is exothermic and to $\exp(-\Delta E/k_B T)$ for an endothermic process.

In order to estimate state-to-state rate coefficients for comparison with the experimental data according to such a model, it was necessary to allow for the fact that, in the experiments, NO($\nu=3, J_i$) molecules collided with NO molecules thermally distributed over rotational levels in $\nu=0$. In other words, the experimental rate constants are for processes represented by Eq. (1), not Eq. (8). Consequently, the relative values of state-to-state rate coefficients were estimated by first calculating the product

$$F(f, f' \leftarrow i, i') = F_{|\Delta E|} F_{|\Delta J|} F_{|\Delta J'|} F_{\text{exo/endo}} \quad (9)$$

for a wide range of values of J_i and J_f , and then taking a weighted sum of the results according to

$$F(f \leftarrow i) = \sum_{f'} \sum_{i'} w(i') F(f', f \leftarrow i', i), \quad (10)$$

where $w(i')$ is the fraction of NO($\nu=0$) molecules in state $J_{i'}$ in a Boltzmann distribution at room temperature.

Calculations have been carried out with two functions chosen to represent $F_{|\Delta E|}$ and two functions chosen to represent $F_{|\Delta J|}$ and $F_{|\Delta J'|}$. These were combined in all possible ways to yield results for four sets of calculations in all. It is well-established that the probability of intermolecular V – V exchange decreases with an increase in the energy discrepancy and a number of correlations of $\log P_{V-V}$ with ΔE have been suggested^{1,29,26} for exothermic transfers. We have used two functions; (i) $F_{|\Delta E|} = \exp(-\alpha|\Delta E|/hc)$, where α was chosen to be $0.015 \text{ (cm}^{-1}\text{)}^{-1}$, a value which is consistent that suggested for V – V exchange by Callear²⁹ and adopted, among others, by Hancock and Smith,²⁶ and (ii) $F_{|\Delta E|} = 1$ for $|\Delta E/hc| \leq 50 \text{ cm}^{-1}$ and $\exp(-\alpha[|\Delta E/hc| - 50 \text{ cm}^{-1}])$ for larger energy discrepancies. This second form is suggested by the observation of Sharma and Brau²¹ that probabilities of energy exchange under the influence of long-range attractive forces are approximately constant out to some value of the energy discrepancy but then fall quite steeply. For $F_{|\Delta J|}$ and $F_{|\Delta J'|}$, two functions were chosen. In one case, $F_{|\Delta J|}$ and $F_{|\Delta J'|}$ were set equal to $\exp(-\beta|\Delta J|)$ with β set equal to 0.4, a value suggested by our analysis of state-to-state rotational energy transfer in NO–NO collisions.²⁴ In the second case, both $|\Delta J|$ and $|\Delta J'|$ were restricted to ± 1 .

The results did not depend strongly on which function was chosen for $F_{|\Delta E|}$. In the case where all $|\Delta J|$ and $|\Delta J'|$ were allowed, albeit with a decreasing probability for increasing $|\Delta J|$ and $|\Delta J'|$, the distributions over J_f were broad, with a preference for $J_f < J_i$ and small $|\Delta J|$, but no

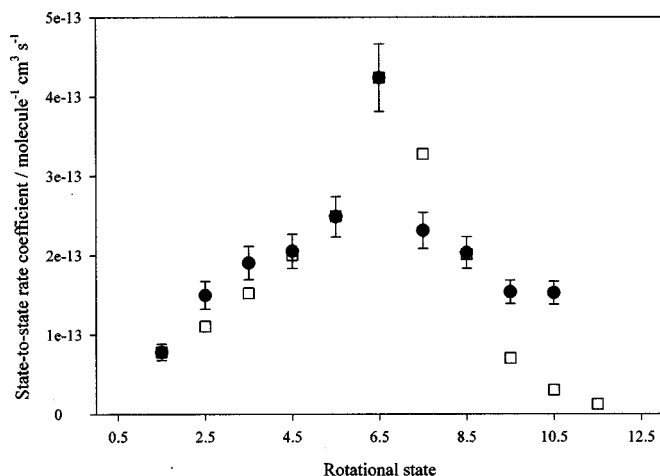


FIG. 4. Fractional nascent rotational populations in $v=2$ following excitation of the $J_i=7.5$ rotational level in the $X^2\Pi_{1/2}$, $v=3$ state (●) compared with the results of model calculations described in the text (□).

distinct propensity was found for $\Delta J = -1$. With $|\Delta J|$ and $|\Delta J'|$ limited to ± 1 , a rather strong preference for $\Delta J = -1$ over $\Delta J = +1$ was found, especially for higher J_i . A reasonable match to the experimentally observed distributions over J_f could be found by taking an appropriate sum of the distribution found with unrestricted changes in the rotational quantum numbers with that obtained when changes were limited to ± 1 . An example of such a comparison with $J_i=7.5$ is shown in Fig. 4. In this case, the normalized distribution over J_f obtained with $F_{|\Delta E|} = \exp(-0.015|\Delta E|/hc)$ and $F_{|\Delta J|} = F_{|\Delta J'|} = \exp(-0.4|\Delta J|)$ was added to one-tenth of the normalized distribution obtained with $F_{|\Delta E|} = \exp(-0.015|\Delta E|/hc)$ and only $\Delta J = \pm 1$ transfers allowed. As shown by Fig. 4, when the experimental and calculated distributions are matched at $J_f = J_i - 1$, the agreement between the experimental distribution over values of J_f and that yielded by the model is fairly good. It could undoubtedly be improved by adjusting the values of α , β and the mixing between the two calculated distributions. However, given the approximate and rather arbitrary nature of the calculations, there seemed little to be gained by refining them.

To summarize: Our experimental results on $V-V$ energy exchange between $\text{NO}(X^2\Pi_{1/2}, v=3)$ molecules in selected rotational levels J_i and NO molecules in the ground vibronic state show some propensity for the excited molecule to be transferred to $(X^2\Pi_{1/2}, v=2, J_i-1)$, especially for higher values of J_i . This finding can be matched by calculations in which some restriction on the changes in the rotational quantum numbers of both molecules to ± 1 was imposed. It is at least plausible that this propensity reflects the fact that intermolecular $V-V$ energy exchange occurs under the influence

of long-range dipole-dipole forces acting between the two NO molecules.

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