ROTATIONAL TRANSFER RATES AND PROPENSITY RULE IN NITRIC OXIDE—RARE GAS COLLISIONS *

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In the first application of the technique of multistep ionization to the measurement of rotational transfer rates within an electronically excited molecular state, we have observed a propensity to even ΔJ in NO colliding with rare gases and have measured a number of transfer rates with high accuracy. A propensity to even ΔJ has been predicted but no observation of it has been previously reported.

1. Introduction

Rotational energy transfer in collisions of diatomic molecules with atoms has been the subject of a number of experimental [1–6] and theoretical [7–12] investigations in recent years. In such collisions, homonuclear molecules obey the selection rule ΔJ = even. Molecules that are nearly homonuclear, such as CO or NO, are expected to exhibit a propensity toward ΔJ = even [9] but no observation of the effect has been previously reported. In this paper we present results which verify this propensity in collisions of NO with Ne, Ar, and Kr but not with He. Our measurements also yield accurate absolute rotational energy transfer rates for the A 2Σ+(v = 0) electronic state of NO and demonstrate an exponential variation of these rates with the rotational energy change.

These measurements are performed using a stepwise ionization technique in which lasers are employed to select the excited rovibronic level as well as to monitor the rotational relaxation. A single rotational level of the A 2Σ+(v = 0) state of NO is first populated by one laser (see fig. 1). After a fixed time delay, during which collisional redistribution occurs, a second laser excites the molecules in the A 2Σ+(v = 0) state to the E 2Σ+(v = 0) state. Finally, a third laser ionizes molecules in the E level. By scanning the wavelength of the second laser across the rotational lines of the E ← A transition (see fig. 2a), the rotational population distribution resulting from collisional relaxation with the A level is determined. Our technique is similar to that first demonstrated by Esherick and Anderson [13] and used by Sudbo and Loy [14] in measuring rotational transfer in the ground electronic state of NO. We report the first use of this technique for the determination of rotational relaxation rates in an electronically excited level, and we determine absolute rotational transfer rates for the A 2Σ+(v = 0) state of NO in collisions with Ne, Ar, Kr and He.

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2. Experimental details

The three lasers used in this experiment are dye lasers pumped by the frequency-doubled and -tripled light from a Q-switched Nd: YAG laser. The pump laser is a coumarin 460 dye laser, frequency doubled in an angle-tuned KPB crystal, and provides the 225 nm radiation for exciting a single rotational level in the A 2Σ⁺ state. This pump laser has an energy of \( \approx 5 \mu J \) in a bandwidth of 0.1 cm\(^{-1}\). The probe laser, optically delayed 49 ns relative to the pump laser, scans the E-A transition near 600 nm. It has a linewidth of 1 cm\(^{-1}\) and a pulse energy of 10 \( \mu J \). The narrow linewidth of this laser allows us to excite individual rotational transitions of the E-A manifold and thereby measure the rotational population distribution in the A state. The ionizing laser (\( \lambda = 640 \) nm) has a large bandwidth (\( >2 \) cm\(^{-1}\)) and high energy (3 mJ) and is delayed an additional 7 ns. The three beams (pulse duration \( \approx 5 \) ns) are collinear in the sample cell, each with a diameter of 5 mm. The lasers are linearly polarized, the pump laser being polarized perpendicular to the probe and ionizing lasers.

The 49 ns delay of the probe laser is chosen to be long compared to the laser pulse lengths, so that the collision period is well defined, but short compared with the 200 ns lifetime of the A state. The 7 ns delay between the probe and ionizing lasers maximizes the signal while avoiding power shifts or broadening in the E-A transition.

The NO gas and its collision partner (He, Ne, Ar, Kr) are contained in a small (\( \approx 500 \) cm\(^3\)), room-temperature, static gas cell. Gas pressures are typically 10 mTorr NO and 1 Torr rare gas and are measured with a capacitance manometer to 5% accuracy. A set of parallel plate electrodes, separated by 1 cm and biased to 45 V, collects the electrons and ions. At this bias voltage, the ion signal is found to be linear in the pulse energy of the 225 nm light and thus linear in the number of ions created. With lower bias voltages, the ion signal saturates at high signal levels, possibly due to electron-ion recombination processes. Apart from this saturation, the scans are identical at biases of 4 and 45 V.

A microprocessor-based data acquisition system digitizes and records the data. The ion signal is first processed by a low-noise preamplifier, a gated charge integrator, and an analog to digital converter. The computer is programmed to normalize each ion pulse to the 225 nm pulse energy. Normalization to the other two lasers is unnecessary because the signal is power saturated by the probe laser (second laser) and because the energy of the ionizing laser fluctuates relatively little. Nevertheless, data are accepted only when all laser energies are within 15% of a preset average. A scan such as that in fig. 2a typically consists of 3 pulses averaged at each wavelength setting with 1000 such points comprising a scan.

To locate a particular line in the A 2Σ⁻ → X 2Π spectrum, two-photon ionization is used. The pump laser is focused and the other two lasers are turned off. A small portion of the resulting spectrum is shown in fig. 2b. For example, to excite the \( N = 24 \) level of the A state, the laser is tuned to the unresolved R\(_{11}\) + Q\(_{21}\) transition indicated by the arrow in fig. 2b. Under experimental conditions used to measure rotational transfer, this two-photon-ionization signal is essentially zero.
3. Analysis

It is possible to obtain rotational-transfer rate constants directly from the ratios of daughter rotational peak heights to the initially populated parent peak height if certain experimental conditions are met. First, in order to ensure that secondary processes (those involving more than one $N$-changing collision) are unimportant, the parent population must be much greater than any of the daughter populations. Second, the efficiency of transfer from the A to E state must be independent of the rotational quantum number $N$. This condition is approximated in our experiment by power saturating the $E \leftrightarrow A$ transition so that the populations in the two states are nearly equalized. Our probe laser energy (10 $\mu$J) is several times the saturation energy, with the limit on its energy being imposed by the necessity of keeping power broadening less than the rotational line spacing. This saturation also tends to minimize the effect of the slight variation (7%) in probe laser intensity across the scanned range and the effect of alignment of the molecules induced by the pump laser. Third, the ionization probability must be independent of $N$. With our choice of ionizing laser, we expect this to be the case. Fourth, all rotational levels of the A state must have the same lifetime in the presence of the collision gas. If the above conditions are met, the absolute transfer rates are obtained directly from the ratio of rotational peak heights using the formula

$$k(N \rightarrow N') = R(N' / N)20.4/P \mu s^{-1} \text{Torr}^{-1}, \quad (1)$$

where $R(N' / N)$ is the ratio of daughter to parent peak height and $P$ is the gas pressure in Torr. A more detailed discussion of these points will be presented in a future paper [15].

In the above discussion we have ignored the fact that each $N$ level is actually a spin-split doublet with $J = N + 1/2$ and $J = N - 1/2$. This is justified since the doublet structure is not resolved and the electron spin is expected to be unimportant in the rotation changing collisions. For example, when $N = 24$ is the parent level, it is pumped via the unresolved $R_{11}$ plus $Q_{21}$ transition (see fig. 2b). The $R_{11}$ populates the $F_J(J = N + 1/2)$ component of the $N = 24$ level and has about twice the transition strength of the $Q_{21}$ transition which populates the $F_{2J}(J = N - 1/2)$ component. Thus about two thirds of the $A^2 \Sigma^+ \ N = 24$ population is in the $J = 49/2$ level and one third in the $J = 47/2$ level.

4. Results

Fig. 3 is a plot of the measured peak heights of the rotational levels when $N = 24$ is initially populated and 1.0 Torr of collision gas (He, Ne, Ar, Kr) is added. The vertical positions of the data for the various gases are offset to disentangle the graph. For all gases, the parent peaks are about equal for these data. When the collision gas is absent, there is essentially no rotational transfer on this time scale as demonstrated by the absence of any but the parent peak. Note that the propensity for even $\Delta N$ illustrated in fig. 3 becomes stronger in the Kr to Ar to Ne progression but is absent for He. The overall shape of the He profile also seems quite different, falling rapidly with increasing $\Delta N$.

As indicated in eq. (1), the rotational energy trans-
fer rates can be obtained directly from the ratio of the measured peak heights. The rates determined this way are listed in table 1. However, for the condition of this experiment, 20% of the population in \( N = 12 \) results from relaxation from all rotational level other than the parent, \( N = 24 \). Correction for this effect is not taken into consideration in table 1. This correction decreases as \( \Delta N \) decreases and can be determined to within 5% [15]. We estimate no more than a 10% additional error results from a variation on excitation and ionization by the lasers.

To determine how the rates scale with the magnitude of the rotational energy transfer, we measured rates for \( \Delta N = +2 \) transfer from a number of rotational lines \((N = 5, 11, 22, 25)\) in collisions with Ar. These rates are plotted in fig. 4 as log(relative rate) versus \( N \) or equivalently versus \( \Delta E \) [\( \Delta E = 2.0(4N - 2) \) \( \text{cm}^{-1} \)]. For \( N = 26 \), \( \Delta E \) is equal to \( kT \) (205 \( \text{cm}^{-1} \)). The measured \( \Delta N = +2 \) rates are related to \( \Delta N = -2 \) rates by detailed balance and plotted as \( \Delta N = -2 \) rates at position \( N + 2 \). The exponential dependence of \( k(N \rightarrow N - 2) \) on \( \Delta E \) is evident in fig. 4.

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Fig. 4. Plot of \( \Delta N = -2 \) transfer rates in collisions with Ar for various values of energy gap.

5. Discussion

Using a semiclassical \( S \)-matrix approach, McCurdy and Miller [9] have investigated the influence on the \( \Delta J \) = even propensity rule of terms in the diatom–atom interaction potential which are of even and odd symmetry in exchange of the nuclei. They have shown that the propensity rule is quite sensitive to the relative contributions of the two terms. For large odd anisotropies, the propensity can even become reversed over a range of the \( \Delta J \), favoring \( \Delta J = \text{odd} \). Therefore, we expect that the magnitude of oscillations we measure may provide a sensitive measure of the odd asymmetry term in the NO–rare gas potential. Further measurements, particularly at lower \( N \) values, should help to resolve this issue and will be undertaken in the future.

An alternative collision process which can exhibit the \( \Delta J = \text{even} \) propensity is collisional transfer of molecular alignment or orientation rather than population transfer. For example, McCormack and McCFerrin [2] have observed a \( \Delta J = \text{even} \) propensity in orientation transfer (but not in total rotational transfer) for NaK*–He collisions. Although the strong saturation of the \( E \leftrightarrow A \) transition in our present measurements reduces the effects of alignment, our technique should be easily adapted to look specifically for collisional transfer of alignment or orientation. If such alignment effects do exist, and one wishes to avoid them, they may possibly be eliminated by using “magic angle” [16] polarizations.
6. Summary

Using the technique of step-wise ionization to measure rotational energy transfer rates in an electronically excited state of a molecule, we have demonstrated a propensity for $\Delta J = \text{even}$ (assuming the electron spin is not affected) changes in collisions of NO with Kr, Ar, and Ne and an apparent lack of such a propensity in collisions with He. The reason for the dramatically different behavior of NO–He collisions is not understood. We have also measured transfer rates for $\Delta N = -2$ in collision with Ar and observed the rates to be exponential in energy gap over the range examined.

Note added in proof

Since the completion of this manuscript, a paper [17] has come to our attention which describes the even propensity rule for $\Delta J$-changing collisions, presumably out of the lowest rotational level of the ground electronic ($X^2\Pi$) state of NO.

References


