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Unimolecular Reaction Rates of Rotationally Selected NO₂

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ABSTRACT

Unimolecular reaction rates have been measured for NO₂ molecules whose rotational angular momenta (N') are well characterized ($N-1 \leq N' \leq N+1$). Odd N in the range 1-15 were examined separately by using a double resonance approach that combines the picosecond-resolution pump-probe technique and state resolved preselection using a 0.02 cm⁻¹ linewidth IR parametric oscillator. The rotational energy of the tagged molecules was varied over a range of 100 cm⁻¹ ($1 \leq N \leq 15$; $K=0$), with all other experimental parameters held constant. The measured rates were found to be independent of parent rotational level over the full range examined, providing a benchmark for detailed theories of unimolecular reactions.

1. Introduction

Calculating rates of chemical reactions from quantum mechanical first principles is as realistic as space travel, that is, it is only possible in the simplest of cases and with an outrageous amount of effort. This makes statistical rate theories attractive, particularly when reliable estimates are needed and theoretical justifications are of secondary importance. That such theories do in fact work has been verified repeatedly. *Why* they work is a question of some depth.

Being approximate, statistical rate theories require experimental verification. However, most of the experimental work in this area has dealt with fixed-temperature samples, making it difficult to distinguish between a range of input parameters and fundamental problems of the approximate theories. Recently, the combined use of laser methods and supersonically-cooled samples has dramatically increased experimental selectivity and has allowed more detailed comparisons to be made with statistical theories. For example, time resolved measurements of unimolecular decomposition rates¹⁻³ have confirmed the predictive power of methods like variational RRKM.⁴

In statistical theories, the energy (E) and angular momentum (J) characterize the decomposing molecule. Effects of vibrational excitation on unimolecular decomposition have been studied more often than effects of rotational excitation; in fact, to the best of our knowledge there is only one experimental work that addresses this issue⁵ despite significant theoretical interest.⁶ Two obvious reasons for this dearth are: (i) in most practical situations vibrational excitation has a larger effect and (ii) rotational effects are more difficult to study experimentally.

In the experiments reported herein, unimolecular reaction rates of rotationally selected NO₂ were measured in real time. NO₂ was chosen because of the immense amount of data available on its spectroscopy⁷ and photoinitiated reaction dynamics.^{3,8,9} Its three low-lying excited electronic states are ²A₂, ²B₁ and ²B₂, with ²B₂ responsible for most of the

absorption in the vicinity of D_0 ($25,130.6 \text{ cm}^{-1}$). Conical intersection of the 2A_1 ground electronic state with 2B_2 results in thorough ${}^2A_1/{}^2B_2$ mixing and vibronic chaos above $16,000 \text{ cm}^{-1}$.⁷

Reasonable accord with statistical theory was found in our previous study of NO_2 decomposition.³ Rates were obtained for rotationally cold as well as room temperature samples for excess energies up to $\sim 1000 \text{ cm}^{-1}$. The data indicated that rotational energy is on average one third as efficient in promoting reaction as vibrational energy. A detailed analysis of rotational effects was impossible because the results were averaged over the room temperature rotational state distribution. Clearly, it is most desirable to prepare decomposing molecules having specified values of rotational angular momentum.

2. Results

Though harder to implement than one-photon excitation, double resonance is ideal for establishing the rotational character of the reactant. In the present experiments, NO_2 is excited to the (1,0,1) vibrational level ($\nu_0 = 2906 \text{ cm}^{-1}$)¹⁰ by using a 0.02 cm^{-1} linewidth IR parametric oscillator. Odd N values in the range 1-15 (having $K = 0$) are selected. These tagged molecules are then promoted to reactive levels by using a picosecond visible pulse (center frequency = $22,240 \text{ cm}^{-1}$, 30 cm^{-1} FWHM). The double-resonance nature of the experiment ensures that only molecules which have absorbed both IR and visible photons have sufficient energy to react. Thus, $N-1 \leq N' \leq N+1$, where N' denotes the rotational angular momentum of the decomposing molecule. Note that the sum of the (1,0,1) vibrational energy and the $22,240 \text{ cm}^{-1}$ center frequency lies 15 cm^{-1} above D_0 . Following the visible pulse, NO product is detected via LIF by using a second picosecond pulse. Varying the delay between the two picosecond pulses yields NO buildup times, from which NO_2 decomposition rates are extracted.

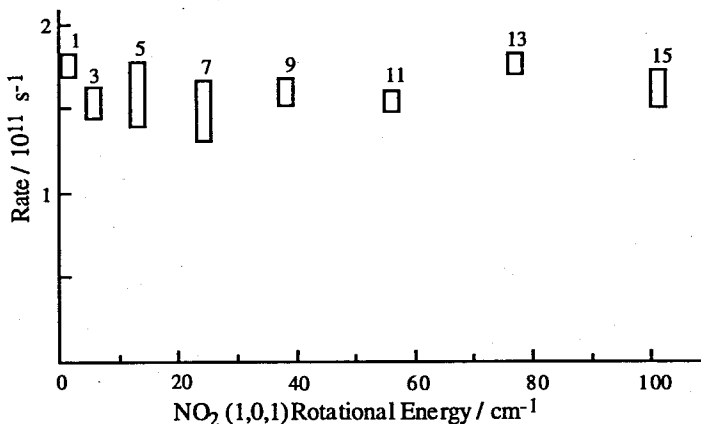


Fig. 1. Reaction rate versus (1,0,1) rotational energy: numbers indicate N values ($K = 0$); photolysis center frequency = $22,240 \text{ cm}^{-1}$; $\Delta\nu = 30 \text{ cm}^{-1}$ FWHM. Vertical distances indicate 70% confidence.

Figure 1 shows the measured rate versus the rotational energy in the intermediate excitation step with the photolysis center frequency fixed at $22,240\text{ cm}^{-1}$. The rate shows no variation with (1,0,1) rotational level. This was somewhat unexpected, since it had been found previously that for room temperature samples the rate was higher than for expansion-cooled samples excited at the same photolysis wavelength.³

3. Discussion

The present experiments show that, to within the uncertainty of the measurements, the addition of up to 100 cm^{-1} of rotational energy leaves the reaction rate unaffected. Since the data are quite new, the implications of this result have not yet been determined. Specifically, it will be instructive to see which statistical models can be used to fit the data.

Within the framework of transition state theory, barrierless reactions pose two main conceptual challenges. First, there is no intuitive transition state region, rather, the transition state is viewed as a dynamical bottleneck, with variational approaches deemed most suitable for computational studies. Second, complications arise when calculating reaction rates for rotating molecules. For stable molecules, it is common to first take overall rotation and internal motions as separable, and then include interactions such as Coriolis and centrifugal as perturbations. However, due to the large amplitude motions and the small anisotropic forces constraining the geometry of the barrierless transition state, Coriolis forces are large and a separation of rotation and vibrations may be improper. One alternative is to consider such a floppy transition state as a hindered rotor whose orbital angular momentum is coupled strongly to the total angular momentum, as is done in flexible transition state theories.⁶ Superiority of one or the other of these approximations will depend on parameters such as the PES, energy above D_0 , and the angular momentum.

For energies just above the thresholds of barrierless reactions, transition states are believed to lie at large separations, thus making the hindered-rotor transition state model more applicable. Phase space theory (PST) is a simple implementation of the flexible transition state theory with two additional assumptions: (i) the anisotropy of the potential is neglected, and (ii) the transition state is taken as the top of the centrifugal barrier. Thus, according to PST, transition state channels in NO_2 decomposition have the same energy spacings as the NO rotational levels, at least below the product spin-orbit energies. Behavior consistent with this simple model was reported for NO_2 just above D_0 , namely, for the first two open channels (i.e., NO with $J = 0.5$ and 1.5).⁸

This fact stimulated us to carry out PST calculations that incorporate all relevant experimental conditions. This work is in progress. A very important instrumental parameter is the spectral content of the photolysis radiation. In the present experiments, the linewidth is $\sim 30\text{ cm}^{-1}$ FWHM. This large energy spread can have a marked effect on the measured rates. For example, for photolysis photon energies near $D_0 - 2906\text{ cm}^{-1}$ (i.e., threshold for non-rotating molecules), PST predicts that the rate increases as roughly the square root of the rotational energy. On the other hand, if the photolysis photon energies are increased by just 20 cm^{-1} , the rate first decreases and then increases with rotational energy. Thus, the spectral content of the photolyzing radiation must be taken carefully into account when modeling the experiments.

No matter how well a PST estimate reproduces the data — and preliminary estimates show that it may come close — this approximation becomes progressively less accurate with increasing energy. As the excess energy increases, the anisotropy becomes essential

for the dynamics. This may be most easily seen for the case of a non-rotating molecule. The location of the transition state in a barrierless reaction has to be determined variationally, which is straightforward if adiabatic hindered rotation-bend curves are known. Specifically, the transition states are at the maxima of the curves, and the number of open channels equals the number of curves below the excess energy in the transition state. When the anisotropy of the potential is unimportant (as in PST), the adiabatic curves do not exhibit maxima larger than the centrifugal barrier. However, the calculations of Katagiri and Kato indicate that the fourth adiabat shows a 80 cm^{-1} maximum at 3 \AA separation.¹¹ This suggests that the anisotropy of the PES becomes dynamically important at energies in excess of a few NO rotational quanta. Thus, a more sophisticated model than PST is required.

An important question about this experiment is whether the parameters of the molecule that are not conserved in the spectroscopic sense just below D_0 are approximately conserved on the time scale of the reaction and, therefore, are important for the dynamics. For example, as is known from the spectroscopy of NO_2 ,⁷ Coriolis and spin-rotation interaction are known to mix levels with different K quantum numbers (K , which is the projection of the rotational angular momentum on the a -axis, is not a rigorously conserved quantity because of the slight inertial asymmetry of NO_2). However, since the dipole selection rule for the perpendicular transition is $\Delta K = 0$ and the intermediate level has $K = 0$, the wave packet initially prepared above D_0 has $K = 0$, which then dephases. If the dephasing is slow on the time scale of the reaction, one is allowed to speak of approximate K conservation throughout the course of the reaction. Thus, the $K = 0$ condition imposed on the intermediate level may become important for the dynamics and, therefore, needs further experimental investigation. Intuitively, K mixing is not expected to be large, since the dissociating molecules undergo at most a few rotations.

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