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The NO vibrational state distribution in the reaction $O(^1D) + N_2O \rightarrow 2NO$

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Abstract

The vibrational distribution of NO products from the reaction $O(^1D) + N_2O \rightarrow 2NO$ has been measured from $v = 0$ to $v = 12$. The measurement was performed in a molecular beam apparatus, in which the product NO was rotationally but not vibrationally cooled. The measured NO vibrational population is found to be peaked at $v = 7$, with average vibrational energy between 24 000 and 28 000 cm^{-1}, much greater than previously reported. The vibrational distribution presented in this Letter is inconsistent with the dominance of either a stripping or a statistical mechanism producing a substantial fraction of the product NO.

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1. Introduction

The reaction of $O(^1D)$ with N_2O has received considerable experimental and theoretical attention over the last 30 years [1–10]. The reaction has two major product channels:

$$O(^1D) + N_2O \rightarrow N_2 + O_2 , \qquad (1)$$

$$O(^1D) + N_2O \rightarrow NO(v', j') + NO(v'', j'') , \qquad (2)$$

with each channel accounting for ~ 50% of the product yield. Experimental studies have focused on the production of the two NO molecules because NO detection techniques (such as LIF or REMPI) are quite sensitive. Reaction (2) is thought to be the primary source of NO in the upper stratosphere, where the reactant $O(^1D)$ is formed from UV photodissociation of ozone. NO_x species in the stratosphere play a large role in the catalytic destruction of ozone.

The mechanism of reaction (2) is still largely undetermined, although several experimental and theoretical investigations of this reaction have been performed [1–10]. Measurements of the vibrational population of the NO products might be useful in identifying possible reaction mechanisms, especially since the high reaction exothermicity means that a large number of vibrational states are energetically accessible. For example, a bimodal vibrational distribution might be indicative of a ‘stripping’ type mechanism, with one mode of the distribution corresponding to the ‘old’ NO (where the NO is originally a part of the N_2O molecule) and the other mode corresponding to the ‘new’ NO. Early work by the Simons group investigated the rotational and vibrational populations of $v = 0–4$ [11]. They found a

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substantial population in $v=0$ with little rotational excitation. Later work from the same group looked at the translational and angular distribution of highly vibrationally excited NO($v=16,17$; near the energetic limit for the reaction) [3,4]. They concluded from these studies that a substantial fraction of the reaction undergoes a stripping mechanism which produces translationally and rotationally cold ‘old’ NO paired with a vibrationally excited ‘new’ NO.

Some more recent measurements and theoretical calculations have shown that the fraction of reactions that undergo a stripping type reaction to produce NO($v=16,17$) + NO($v=0$) might not be as high as previously assumed [1,6,8,12]. A static cell experiment has measured the vibrational populations of NO from $v=11$ to 17 and showed that the population monotonically decreases over this range, which would be unexpected if a stripping mechanism accounts for a large portion of the reaction products [12]. However, a more recent experiment by the same group has measured the vibrational population of the NO products from this reaction of the lower vibrational quantum states ($v=0$–11). The more recent results indicate a monotonic decrease in vibrational population for $v=0$–11, which is consistent with a stripping mechanism. Results from another experiment using isotopically labeled ‘new’ and ‘old’ NO suggest that, while in general there is more vibrational excitation in the ‘new’ NO than the ‘old’ NO, there is still substantial vibrational excitation in the ‘old’ NO [1]. This observation would indicate that there is some energy transfer in the ONNO reaction complex before it falls apart into two NO molecules. Doppler resolved measurements of NO($v=0$) have shown that the reaction is perhaps as not as strongly forward scattered as once believed [8]. Also, recent measurements of the rotational population of NO($v=0$) ascribe much more rotational excitation to this fragment than was previously reported [8]. Theoretical calculations on the reaction with a three-atom PES have shown that the amount of ‘new’ NO that has $v=16$ or 17 is small even when the ‘old’ NO is treated as an united atom [5].

The vibrational distribution measurements presented in this work represent a departure in some ways from previous measurements in that the $v=0$ is not found to be the state with the highest vibrational population. A possible reason for this departure could be ascribed to the difficulty involved in correcting for background NO from previous reactions. This experiment, which was designed to minimize the contribution of background NO, finds a vibrational distribution that is consistent with a mechanism in which there is some energy exchange between the two NO molecules in ONNO before it breaks apart. The measured vibrational distribution is qualitatively similar to the NO vibrational state distribution obtained from three-body QCT calculations performed recently. However, the three-body QCT calculations only account for the vibrational excitation in one of the NO products, hence the reported distribution is only for one fragment and difficult to compare to the distribution reported here. A full four-body treatment of the reaction, accounting for energy transfer to the ‘old’ NO, might reconcile some of the quantitative differences between the measured vibrational populations and theoretical predictions.

2. Experimental

The experiments were carried out in a previously described apparatus, shown in Fig. 1 [13]. Briefly, a mixture of O_3 (1%) and N_2O (6%) seeded in He was expanded through a pulsed valve [14]. The O(^{1}D) was produced by 266 nm photolysis of O_3 at the exit of a pulsed nozzle. The products from the reaction of O(^{1}D) + N_2O are formed in the high-pressure region of the expansion. As a result of the expansion, the products are rotationally cooled and remain trapped in the molecular flow of the expansion. The expansion is collimated with a 1 mm skimmer before entering the detection chamber.

The NO($^2\Pi$; v, j) products are detected using $1+1'$ REMPI [15,16]. The resonant probe transition (220–238, 270–315 nm) was obtained using the output of a frequency-doubled dye laser, either a excimer (308 nm) pumped FL2002 or a Nd:YAG (532 nm) pumped Scanmate. The 308 nm excimer pulse was split and optically delayed from the resonant transition pulse to produce a 1–3 mJ/pulse ionization pulse. The unfocused probe pulse, the loosely focused (1 m F.L. lens) ionization pulse, and the molecular beam intersect each other in the detection chamber, where the NO($^2\Pi$; v, j) products are

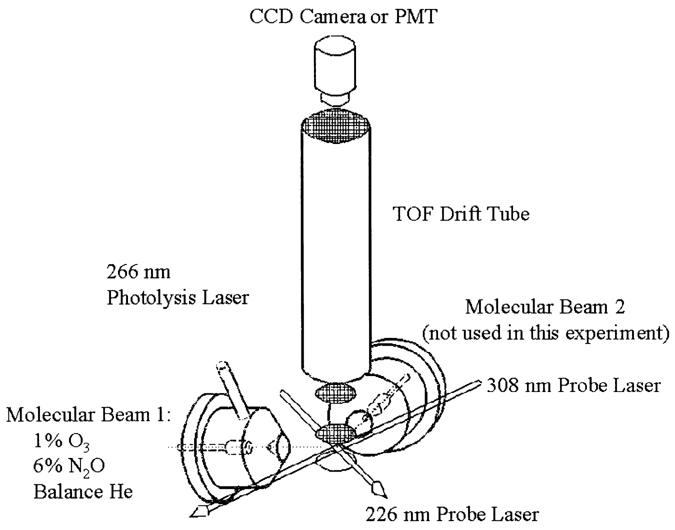

Fig. 1. Schematic of experimental apparatus.

state-selectively ionized. The resulting ions are detected in a time-of-flight mass spectrometer with a MCP-phosphor ion detector (Galileo), which emits light proportional to the ion intensity. The ion intensity was monitored with a PMT (Thorn EMI). The signal from the PMT is measured by a digital oscilloscope and then transferred to a computer, where a boxcar is set to monitor the intensity of NO^+.

The vibrational distribution of the NO products is measured by monitoring the ion intensity as the probe laser is scanned over the rotational structure of several vibronic transitions, several of which are shown in Fig. 2. Each point in each spectrum is collected in two modes to allow for corrections due to any background NO^+ signal: 15 probe laser shots were taken with the ozone photolysis on, followed by 15 probe laser shots with the ozone photolysis off. The detector settings (e.g., MCP voltage) were recorded for each spectrum. The laser power was measured with a Molectron power meter before and after each scan, and no appreciable change in the probe power was observed. The laser power was also monitored by a photodiode during each scan to insure the laser power was truly constant.

The effective gain of the signal is nonlinearly dependent on the detector settings (e.g., MCP voltages), and it is necessary to correct the data for the effective gain of a particular set of detector parameters. The effective gain, C_{det}, was calibrated by measuring the intensity of several rotational peaks as a function of the detector settings.

Vibrational relaxation of the products during the expansion will influence the measured vibrational distribution. The amount of vibrational relaxation occurring was tested by comparing the intensity of two vibronic bands (γ 3–8 and γ 0–4) at different seeding concentrations: $\sim 0.1\%$ O_3/$\sim 0.3\%$ N_2O, 1.6% O_3/7% N_2O and 0.9% O_3/4.4% N_2O. If collisions of NO with another polyatomic species (O_3, O_2, N_2, N_2O, NO) are responsible for vibrational relaxation of the NO products, the intensity ratio of these two vibronic bands will depend upon the seeding concentration. The intensity ratio of $I(\gamma\,3\text{–}8)/I(\gamma\,0\text{–}4)$ was constant within 10%, indicating that NO–polyatomic collisions are not responsible for significant vibrational relaxation in this experiment.

Detection of NO products in this experiment is limited to the NO fragments trapped in the molecular beam. We thus examined whether NO products produced with a large amount of translational energy might possibly not be trapped in the expansion. The measured population of that vibrational state would then be lower than the actual population. If we consider the limit where all available energy is im-

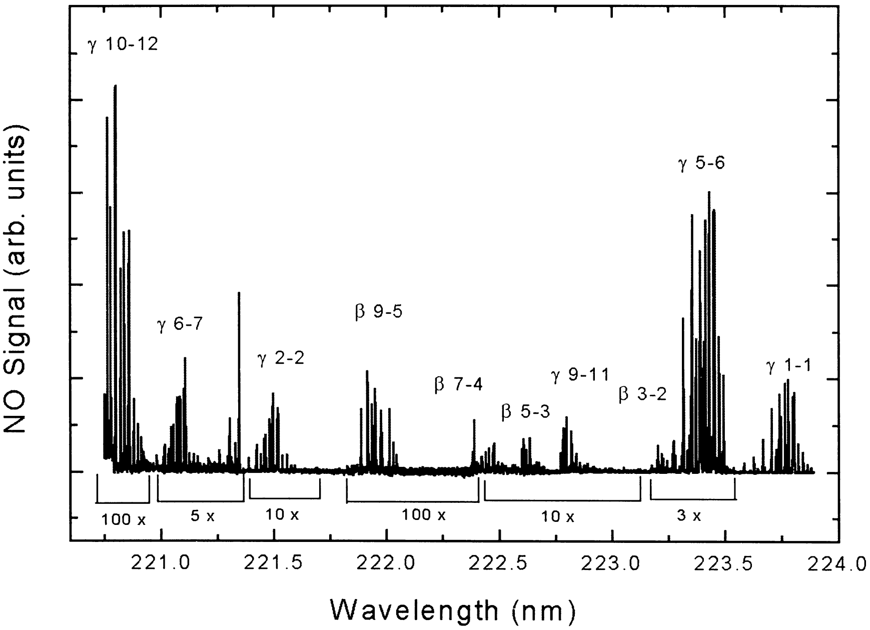

Fig. 2. NO product signal vs. REMPI probe wavelength from 220 to 224 nm. The rotational cooling that occurs as a result of expansion from a pulsed valve allows vibrational transitions to be easily assigned (as shown). Additional spectra were recorded up to 237 nm, as well as from 270 to 315 nm.

parted to translational motion ($E_{rxn} + E_{collision} \approx$ 32 000 cm^{-1}), the NO product velocity would be ~ 4500 m/s. Collisional deactivation studies of S(^{1}D) atoms elastically colliding with argon have shown that after 5–10 elastic collisions the average velocity of the S(^{1}D) atoms has cooled from ~ 1250 m/s to the room-temperature equilibrium of ~ 400 m/s [17]. Given that NO produced at the exit of the pulsed valve experiences ~ 1000 collisions during the molecular beam expansion, it thus seems likely that even the NO produced with the maximum possible translational energy (~ 5000 m/s) is trapped in the molecular beam expansion. Also, a simple experiment was performed to test the trapping of high-velocity products in the molecular beam. O_3, dissociated at 266 nm, forms O(^{3}P) as a minor channel (10%) with high translational energy (~ 4900 m/s) preferentially in the direction of the photolysis polarization [18]. Using the same experimental apparatus described above, the O(^{3}P) was produced at the exit of the pulsed valve from photolysis of O_3 expanded in a carrier gas of helium and then probed in the interaction chamber using 226 nm light. We found that the intensity of O(^{3}P) measured in the interaction chamber is independent of whether the polarization of the photolysis laser is parallel or perpendicular to the molecular beam, indicating that an equal number of O(^{3}P) atoms was entrained under these two conditions. Furthermore, by scanning the delay between the photolysis laser and the probe laser, we obtained an arrival time profile of the O(^{3}P) produced in the beam. The profile, for both polarizations, was a single narrow peak at a time corresponding to translational equilibrium of the O(^{3}P) in the beam expansion. Based on these measurements, it is assumed that high-velocity NO product does not preferentially escape the molecular beam expansion.

3. Results

3.1. Background NO

Signal from vibrationally relaxed NO from earlier reactions was observed in the detection chamber and contributed a background signal to the vibrational population measurements. The background level was only observable for the $\upsilon = 0$ and $\upsilon = 1$ measurements, and was at least a factor of ten lower than the total signal for any vibrational transitions.

3.2. Rotational relaxation

Since the reaction occurs in the high-pressure region of the supersonic expansion, the products are rotationally cooled. The rotationally resolved spectra of each vibronic band were simulated using a rigid rotor Hamiltonian and spectral constants from the literature [19]. The relative rotational population for each probed vibrational state was adequately simulated using a Boltzmann distribution ($T = 10 \pm 5$ K), as shown in Fig. 3.

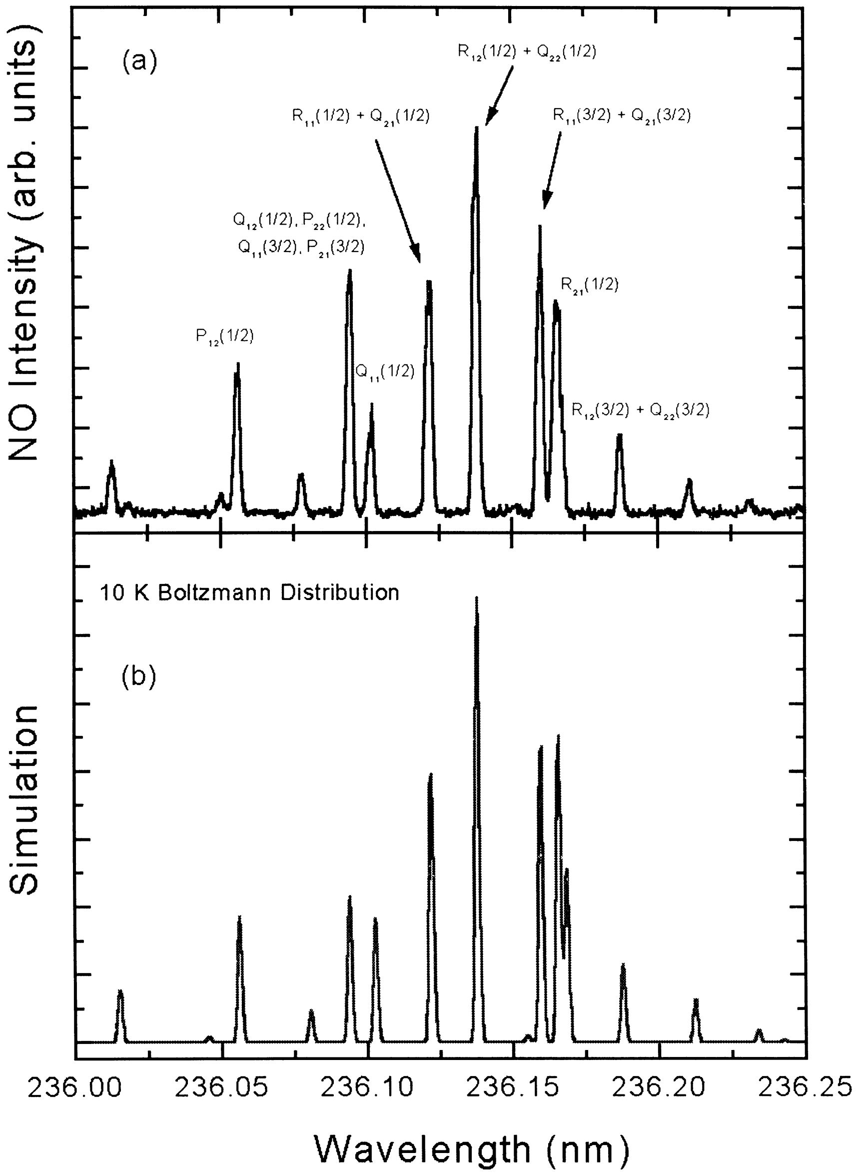

Fig. 3. Example of a single vibrational transition (γ 0–1) and fit. (a) The background subtracted data with labeled rotational transitions. (b) A simulation of the vibrational transition at a Boltzmann temperature of 10 K.

3.3. Vibrational relaxation

Recent work by Wodtke and co-workers has shown that the vibrational relaxation rates for NO–NO collisions are several orders of magnitude faster than NO–X (X = He, Ne, O_2, N_2) vibrational relaxation rates [20–24]. The amount of rotational cooling observed in the products indicates that the products undergo a significant number of collisions (~ 1000) during the expansion process. Since the gas mixtures are fairly dilute, the majority of the NO collisions are with the He carrier gas. Based upon the vibrational relaxation rates of NO colliding with He, we would not expect significant vibrational relaxation to occur for $v = 0–12$. Monitoring several vibrational state populations as a function of reactant concentration and total stagnation pressure indicated that vibrational relaxation does not have a substantial effect over this range of vibrational states.

For $v > 12$, the vibrational relaxation rates are fast enough to have a significant effect upon the total population. For example, a $v = 16$ state of NO has a 1/e lifetime of ~ 29 collisions with another NO molecule [21]. The corresponding 1/e lifetime for collisions with He is not accurately known, but has a lower limit of ~ 600 collisions. The lack of observable population in the highest vibrational states is an indication of either: (1) a very small initial population (some of which will relax), (2) vibrational relaxation rates that are sufficiently fast to depopulate the high vibrational states, or (3) a combination of these explanations. If the population in the high ($v > 12$) vibrational states is large, the vibrational population would likely undergo vibrational relaxation, which would effectively transfer all of the high vibrational state population into $v = 12$. All of the higher vibration state population would be effectively relaxed into $v = 12$ due to the fast vibrational relaxation constants and would stay there due to much slower vibrational relaxation constants for $v \leq 12$. Since we do not observe a peak at $v \approx 12$, we conclude either that the population in $v > 12$ is small and/or that the vibrational relaxation rates are much slower than the upper estimates used here.

3.4. Vibrational distribution

The relative vibrational population was extracted from each rotationally resolved vibronic spectrum by simulating the rotational structure using known line strengths and spectral constants [19,25,26]. The total intensity of the simulated spectrum was optimized to match the measured spectrum, and used as a measure of the vibrational population. The total intensity was normalized to probe laser power, Franck–Condon factor, C_{det}, the effective gain of the detector, and the relative oscillator strength for the γ and β absorption bands [27–30]. Each relative vibrational population in Table 1 is an average of the multiple determinations of several vibronic bands.

Table 1
Vibrational state distribution of the reaction: $O(^1D) + N_2O \rightarrow 2NO$

Vibrational state	Probed transitions	Relative population
0	γ 0–0	0.053 ± 0.018
1	γ 0–1	0.023 ± 0.009
2	γ 2–2	0.050 ± 0.010
3	γ 2–3	0.080 ± 0.009
4	γ 0–4, γ 3–4, β 7–4	0.090 ± 0.027
5	γ 4–5	0.150 ± 0.020
6	γ 0–6, γ 1–6, γ 5–6, β 2–6	0.140 ± 0.060
7	γ 1–7, γ 2–7, γ 6–7	0.205 ± 0.055
8	γ 2–8, γ 3–8, γ 6–8	0.123 ± 0.044
9	γ 3–9, β 14–9	0.110 ± 0.022
10	γ 3–10, γ 4–10, γ 7–10	0.030 ± 0.016
11	γ 4–11, γ 5–11, γ 9–11	0.037 ± 0.003
12	γ 5–12, γ 9–12, γ 10–12	0.013 ± 0.005

4. Discussion

The vibrational state distribution reported here indicates the formation of vibrationally excited NO products is more important than previously measured. Ignoring population in $v > 12$ states, the average vibrational energy per molecule reported here is $\langle E \rangle \approx 12\,000$ cm^{-1}. Assuming the population in states $0 \geq v \geq 4$ uniquely correlates with the population in states $13 \geq v \geq 17$ (e.g., $P_{v=17} = P_{v=0}$), we can calculate the upper limit of the average vibrational energy per molecule of $\langle E \rangle \approx 18\,000$ cm^{-1}. These results indicate the average amount of energy partitioned into vibrational motion is between 24 000 and 36 000 cm^{-1}. Since 36 000 cm^{-1} is greater than the available energy (32 000 cm^{-1}), the upper limit of the average vibrational energy from the reaction is

32 000 cm^{-1}. Previous measurements indicate the NO vibrational state distribution is monotonically decreasing with $\langle E_{vib} \rangle \approx 4000\ cm^{-1}$ and $v = 0$ population being a factor of 10–500 more than the population in $v = 1$–9 [1,3,4,6,8,9,12,31]. The most likely reason for this apparent discrepancy is difficulty in accurately subtracting background NO. Experiments in our laboratory have shown that even in a chamber baked at 100°C for 5 h and pumped out to $\sim 7 \times 10^{-8}$ Torr, it is possible to measure a thermal (300 K) rotational distribution of NO in $v = 0$. Background NO will be thermalized ($> 99\%$ in $v = 0$), making it difficult to distinguish between NO($v = 0$) from a reaction on a single laser shot vs. background NO($v = 0$) from previously occurring reactions. The large difference in the average vibrational energy in our experiment compared to previous experiments is due almost exclusively to differences in the $v = 0$ populations.

The vibrational distribution shown in Fig. 4 does not contain any structure, and, therefore, it is difficult to deduce from it a mechanism for the reaction. However, the peak of the vibrational distribution ($v = 7$) and the large average vibrational energy is indicative of efficient energy transfer between the two departing NO molecules. Efficient energy transfer between the NOs implies that a stripping mechanism is not likely responsible for formation of the moderately excited ($v = 1$–12) NO products. Recent experiments using isotopic labels to label the 'new' and 'old' NO have shown the 'old' NO vibrational distribution is slightly colder than the 'new' NO distribution, but both distributions have significant population over all of the energetically accessible vibrational states [1,12]. These results suggest that an efficient energy transfer mechanism within a short-lived 'complex' is a more adequate description than a stripping mechanism.

Previous measurements from the Simons group have indicated a stripping mechanism is a consistent description for the formation of the highly vibrationally excited NO($v = 16, 17$) [3,4]. These vibrational states are not observed in our experiment due to the combination of a low initial population and the possibility of significant vibrational relaxation. Although these high vibrational states are likely formed via a stripping mechanism, it appears that this channel accounts only for a small percentage of the products formed.

Phase space theory (PST) will predict the vibrational distribution in the limit of a long-lived complex, where the complex survives long enough to

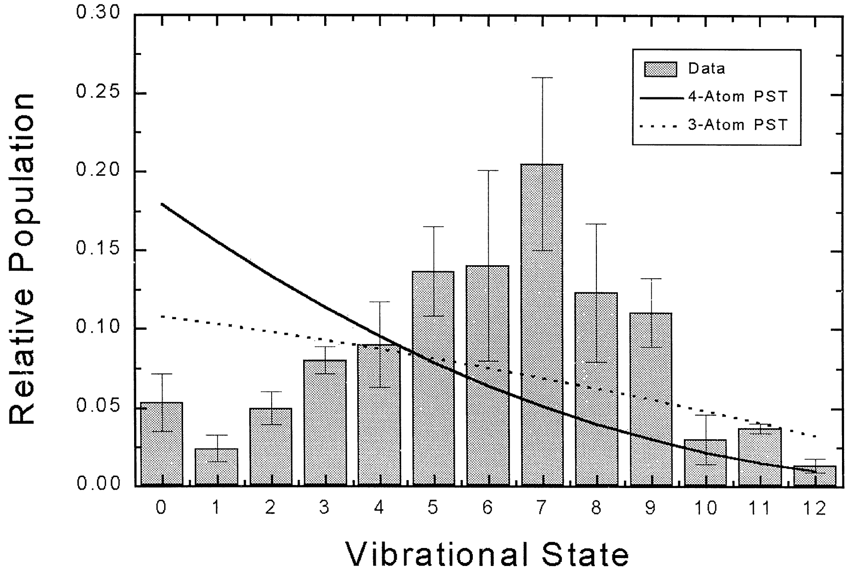

Fig. 4. The measured vibrational distribution of NO products from the reaction of O(^{1}D) with N_2O along with the predictions of three-atom phase space theory (dashed line) and four-atom phase space theory (solid line).

undergo intramolecular vibrational energy redistribution (IVR). Treatment of the reaction as a three- $(A+BC)$ [32,33] vs. four- $(AB+CD)$ [34] body reaction can be done explicitly using PST. The results of the two PST calculations are shown in Fig. 4 and clearly do not match the data. These calculations show that despite energy transfer within ONNO, the energy transfer does not reach the statistical limit. However, the vibrational distribution here does imply that significant energy transfer occurs within ONNO. Energy transfer between the two NO products is likely to be enhanced because of the large state density of ONNO and because both fragments have the same vibrational frequency. These factors will lead to a large IVR rate, but if the lifetime of the complex is short compared to the IVR rate then the complex will not reach complete equilibrium for energy redistribution [1,35].

In summary, the results presented here indicate the NO products are formed with significantly more vibrational excitation than found in previous measurements. The mechanistic origin of this vibrational excitation is unclear, but these results imply that there is efficient energy transfer occurring between the two fragments. Further experiments are ongoing in this lab to investigate this reaction in more detail by state selectively detecting a particular rotational–vibrational state of the NO product from the reaction of $O(^1D)$ and N_2O in crossed molecular beams.

Acknowledgements

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