Characterization of a Supersonic N_2O Beam by Using a 2m-Electric Hexapole Field

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Characterization of supersonic N_2O beam seeded in Ar was carried out by using a 2m-electric hexapole field. The rotational, translational and vibrational distributions were determined by the analysis of the focusing curves at various stagnation temperature. Inversion of the temperature between the rotation (5K) and the translation (9K) was revealed. Regardless of the stagnation temperature, the vibrational temperatures were found to be lower than the stagnation temperatures by ~70K, indicating the constant energy release in the bending mode of N_2O.

For lower frequency vibrational modes, such as bending mode, molecule can be significantly excited even at room temperature. It is important to recognize the collisional cooling of low frequency vibrational mode, because even a small change in temperature could affect the reactivity. Especially, as for a van der Waals molecule, such vibrational modes should be responsible for an internal motion of the constituent molecule, because the higher frequency vibrational modes should be quenched by the vibrational exchange with the lower frequency vibrational modes.[1] The present study directly probed the relaxation of the bending vibrational mode with the rotation and translation of N_2O during the supersonic expansion, by using a 2m-electric hexapole field. The bending motion of N_2O generates an angular momentum labeled as l. Although the mixing of $\pm l$ is the main rotational coupling effect (the l-type doubling), Stark splitting in strong electric hexapole field decouples this mixing completely based on the Stark energy of $[l M/J(J+1)]\mu_0 E$.[2] As a result, N_2O molecule vibrationally excited in the bending mode can be state-selected and oriented by an electric hexapole field.

The experimental apparatus has been described elsewhere.[3] A N_2O beam was generated by a supersonic expansion of the 30% N_2O pre-seeded in Ar with total stagnation pressure of 300 Torr at a pulsed nozzle (0.5 mmϕ in diameter). The stagnation temperature was changed from 20 ℃ to 85 ℃ by a heating block attached to the nozzle. The N_2O beam was skimmed and collimated and introduced into a 2m-electric hexapole field. Since the collisions in the beam can be neglected after the skimmer, the beam characteristic of the free jet expansion at the skimmer 35mm downstream from the nozzle can be probed by the 2m-electric hexapole field as the $|J,l,M>$ state-selection. The $|J,l,M>$ state-selected N_2O beam was focused onto an inlet pinhole (1mmϕ in diameter) of a quadrupole mass spectrometer mounted at 2909 mm downstream from the nozzle. The beam intensity was measured by the quadrupole mass spectrometer as a function of the voltage applied to the hexapole rods, to obtain "focusing curve". The focusing curve was measured at several stagnation temperatures.

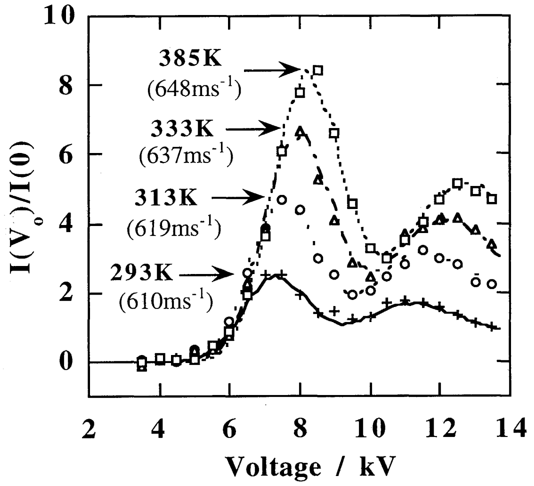

Figure 1. Focusing curves of N_2O beam seeded in Ar at the total stagnation pressure of 300 Torr and N_2O fraction of 30 % under the four stagnation temperature conditions. The simulated curves using Monte Carlo simulations were shown by the lines.

Figure 1 shows the focusing curves with several stagnation temperatures. They are normalized by the intensity of direct beam which is the beam intensity at the hexapole voltage is zero and without beam stop. The focusing curves show clearly resolved the two peaks whose heights increase with the increase of the stagnation temperature. It was found that these peaks shift toward the higher voltage by the nozzle heating. This indicates acceleration in the beam velocity. The focusing curve was analyzed by means of a Monte Carlo trajectory simulation.[4] The simulated stream velocities are shown in the parenthesis in Figure 1. The simulated focusing curves are plotted by the lines. The Monte Carlo trajectory simulation tells that the first peak is identified as $|J,l,M>= |1,1,1>$ peak, and the second peak consists of two rotational states of $|2,1,2>$ and $|3,1,3>$ states. The simulated rotational distributions were found to be approximated nicely as a Boltzmann distribution with 5K regardless of the stagnation temperature.

In order to examine the seeding effect, the mixing fraction of N_2O was varied from 20% to 100% at the fixed total stagnation pressure of 300 Torr and the nozzle temperature of 358K. The results are summarized in Figure 2. The beam intensity enhancement of the $|1,1,1>$ state was almost constant at the N_2O fraction up to 40%, indicating the critical cooling of the rotation. But at the fraction higher than 40%, it begins to decrease perhaps due to insufficient cooling and/or the cluster formation. As for the total stagnation pressure higher than 500 Torr , the decrease of the beam intensity was recognized. Therefore, the experiment were carried out at the N_2O fraction of 30% and the stagnation pressure of 300 Torr.

The velocity distributions of the beam were determined by two parameters assuming a Gaussian-type distribution, and the results are plotted in Figure 3. Although the stream velocities, v_s, were increased with the increase of the stagnation temperature (see Figure 1), the translational temperatures appeared to be

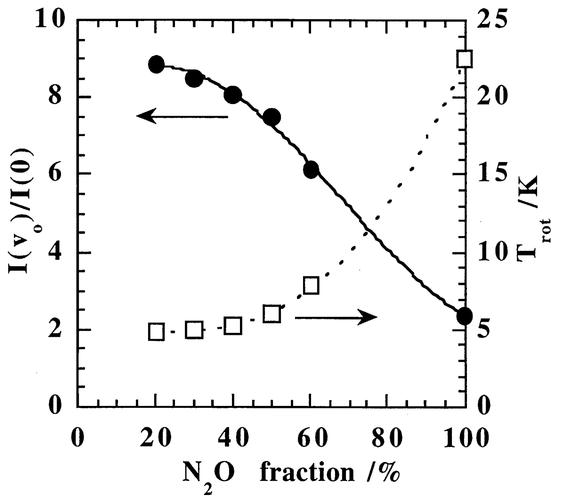

Figure 2. Dependence of the beam intensity enhancement of |111> state upon the N_2O fraction at the total stagnation pressure of 300 Torr and nozzle temperature of 358 K, and the simulated rotational temperature.

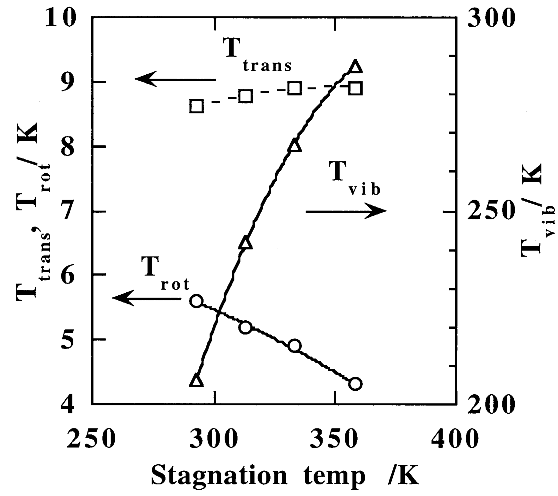

Figure 3. The translational, rotational and vibrational temperatures, of the N_2O beam seeded in Ar, as a function of the stagnation temperature.

almost constant (9K). The velocity distributions of the beam were also determined by time-of-flight (TOF) method. Two methods determined the same N_2O velocity distribution. Our result suggests that the number of collisions is sufficient to maintain the critical cooling for translation during the supersonic expansion. In general, the cooling of the rotational mode is accomplished by collisional energy transfer process from rotation to translation (R→T transfer). Therefore, the rotational temperature T_{rot} is expected to converge asymptotically to a translational temperature T_{trans}. However, the present result shows the inversion of the temperature between the T_{rot} (5K) and the T_{trans} (9K) within the experimental error. The velocity slip between the seeded gas and the carrier gas would be a cause of this inversion. Additional TOF measurement for Ar revealed a significant velocity slip (N_2O is faster than Ar by $\sim 50 mS^{-1}$). Furthermore, different T_{trans} were recognized for N_2O (9K) and Ar (4K). Since T_{rot} (5K) of N_2O seems to converge to T_{trans} (4K) of the carrier gas, our result might indicate that R→T transfer is more efficient than T→T transfer for the collisional energy transfer from the N_2O to Ar.

The vibrational distribution was estimated by the beam intensity enhancement value of the |1,1,1> state as compared with the intensity of direct beam. It is expressed as follows.

$$\frac{I_F}{I_0}=\frac{f_v(l=1)f_R(J=1,M=1)T(J=1,M=1,l=1)}{\Omega}$$

where $f_v(l=1)$ is the fraction of $l=1$ state among the beam ensemble characterized by the vibrational temperature, $f_R(J=1, M=1)$ the fraction of the rotational state having J=1 and M=1, $T(J=1, M=1, l=1)$ is the transmittance of N_2O beam in the |1,1,1> though the electric hexapole field which can be calculated by the Monte Carlo trajectory simulation, Ω is the relative solid angle from nozzle to the pin-hole of the detector divided by the one restricted by the collimator aperture at the front of the hexapole field. According to the experimental value of I_f/I_0 and the rotational distribution of 5 K, the $f_v(l=1)$ was determined as a function of the stagnation temperature. The vibrational temperature of T_v is easily calculated from the experimental value of $f_v(l=1)$. They are plotted in Figure 3. The vibrational temperatures were found to have the lower values than the stagnation one by a constant temperature of 70 K. In general, V →T transfer is known to be less efficient than R→T and T→T transfer.[5] The V→T relaxation times of the bending mode in collisions of N_2O with N_2O and Ar have been reported to be 0.87, 6.8 μS reduced to one atmosphere, respectively.[6] Based on these values, the cooling for the bending mode would be determined by the collision with N_2O around the region of a few mm downstream from the nozzle, and the inefficiency of the energy transfer cause the constant release of the vibrational energy to translation.The velocity slip and higher T_{trans} (9K) of N_2O might be partly responsible for favorable V→T energy transfer by N_2O compared with Ar.

In any event, the cooling of the vibrational bending mode was found to be less efficient and the variation of the stagnation temperature is very useful to control the excitation of the vibrational bending mode.

References and Notes

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