

Kinetics of the phase relaxation of N_2 vibrations in a supersonic jet

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Direct measurements have been carried out on the decay kinetics of the optical polarization on a vibrational-rotational transition of N_2 molecules cooling in a supersonic jet. The measurements were made by time-dependent picosecond coherent active Raman spectroscopy. Quantum beats were detected for the first time in certain vibrational-rotational components of the inhomogeneously broadened spectrum. These beats were used to determine the distribution of the rotational temperature in the jet. The cross section for phase-relaxing collisions increases as the temperature is reduced to 20 K.

1. This letter reports some experiments by picosecond active Raman spectroscopy which constitute the first study of the phase-relaxation kinetics of inhomogeneously broadened vibrational-rotational transitions of molecules cooling in a supersonic jet. Specifically, a new technique¹ developed in our laboratory for picosecond active spectroscopy of molecules in the gas phase was used to study the phase relaxation of vibrations of N_2 molecules cooling in a supersonic jet (transitions in the Q band). The results show that under these conditions the decay of the free polarization, which is of the nature of damped beats ("quantum beats") of various vibrational-rotational components, can be interpreted quantitatively. This quantitative analysis of the beat pattern reveals the rotational temperature of the molecules and the phase-relaxation time of an individual vibrational-rotational component. The results show that the cross section for phase-relaxing collisions increases significantly as the temperature is lowered from room temperature to $T = 20$ K.

2. The jet is produced as nitrogen flows from a high-pressure tank ($P_0 = 28$ atm) into a cell with a residual pressure of 2 Torr through a cylindrical channel with a diameter $D = 100$ μm . Figure 1 shows a diagram of the jet, along with the pulse sequence and a diagram of the levels and transitions to illustrate the excitation and probing of the molecular vibrations. For the excitation we use single picosecond pulses from a YAG:Nd³⁺ laser ($\lambda_1 = 1.06$ μm , $\tau_p = 40$ ps) and a parametric light source ($\lambda_2 = 1.4$ μm , $\tau_p = 20$ ps, $\Delta\tilde{\nu} = 30$ cm^{-1}). The coherent vibrations are probed with second-harmonic pulses ($\lambda_3 = 0.53$ μm , $\tau_p = 30$ ps). A noncollinear arrangement (Fig. 1) is used to improve the localization of the excitation and the probing, to eliminate the parasitic signal from atmospheric nitrogen, and to perform a spatial filtering of the optical signals. The energy of the anti-Stokes scattering pulse, W_a , is measured as a function of the delay (τ) of the probing pulse with respect to the exciting pulses (the coherent pulsed response). Each value of $W_a(\tau)$ is found by taking the average over 60 laser shots. The accuracy of the measurements is checked by measuring the phase

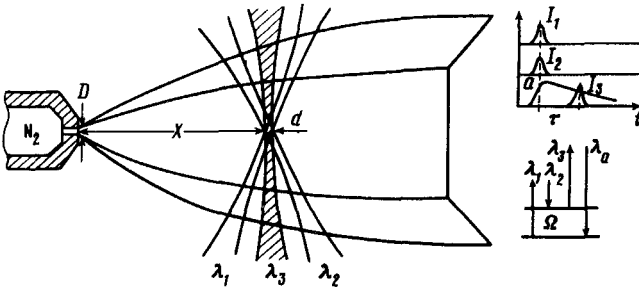


FIG. 1. Excitation and probing of the molecules in the supersonic jet. The Q band of the N_2 molecule ($\tilde{\nu} = 2330 \text{ cm}^{-1}$) is excited by biharmonic picosecond pumping ($\lambda_1 = 1.06 \text{ }\mu\text{m}$, $\lambda_2 = 1.4 \text{ }\mu\text{m}$) and probed by delayed picosecond pulses with $\lambda_3 = 0.53 \text{ }\mu\text{m}$. Here $D = 100 \text{ }\mu\text{m}$ and $d = 50 \text{ }\mu\text{m}$. The insets show the level scheme and pulse sequence of the exciting and probing pulses.

relaxation of the solitary vibrational resonance of hydrogen $Q_{01}(1)$ (Fig. 2). The response is seen to be strictly exponential, and the measured phase-relaxation time agrees with the generally accepted value.²

The pulsed response in the supersonic nitrogen jet is measured at various distances (X) from the end of the channel at the axis of the jet. The points in Fig. 3 are the experimental values of $W_a(\tau)$ found at $X = 0.4$ and 3.5 mm . The response takes the form of beats.

3. Serious difficulties are known to arise in attempts to quantitatively interpret the signals from time-dependent active spectroscopy for an inhomogeneously broadened transition. It is for this reason that studies of molecules in the liquid phase are usually restricted to obtaining data on the frequency difference between the various components of an inhomogeneously broadened line.³ The difficulties are of a fundamental nature for broadened, structureless bands. The response frequently incorporates information on only the length of the exciting pulses.⁴ Supersonic jets present a much more promising experimental situation.

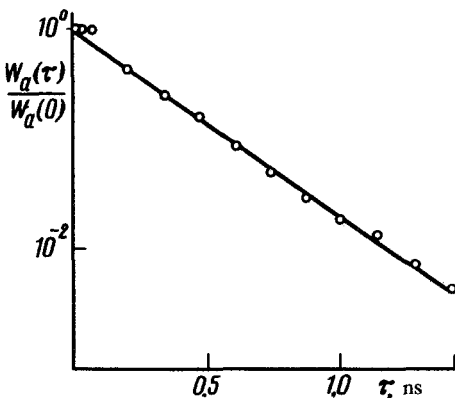


FIG. 2. Phase relaxation of the $Q_{01}(1)$ hydrogen line at 13.6 atm and $T = 300 \text{ K}$ (an isolated Lorentzian line).

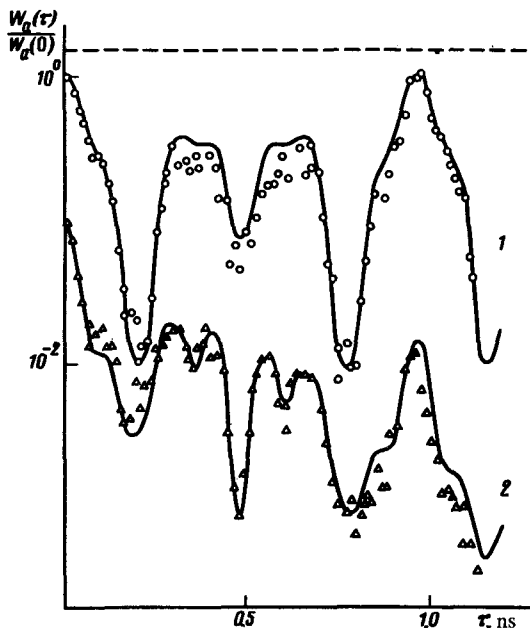


FIG. 3. Kinetics of the phase relaxation of the Q band of the N_2 molecules at the axis of the jet at various distances (X) from the end of the cylindrical channel. Points—experimental results on $W_a(\tau)$; solid curves—calculated from expression (1). 1) $X = 3.5$ mm, $T_{\text{rot}} = 20$ K, $T_2 > 10$ ns. 2) $X = 0.4$ mm, $T_{\text{rot}} = 35$ K, $T_2 = 1$ ns. Dashed curve—Doppler phase relaxation at $T = 100$ K and the dashed curve are shifted along the ordinate axis.

Since the width (Q) of the nitrogen line is less than $1/c\tau_p$ at low temperatures, the experimental results can be interpreted quantitatively with the help of a simple model for calculating the response of a set of identically excited rotational components. In this case we find the following result for $W_a(\tau)$:

$$W_a(\tau) = Q_0^2 |\Phi(\tau)|^2 \int_{-\infty}^{+\infty} \left| \sum_j N_j e^{-i\Delta\Omega_j t'} E_3(t' - \tau) \right|^2 dt'. \quad (1)$$

Here Q_0 is the amplitude of the molecular vibrations (the same for all j), and $\Delta\Omega_j = \bar{\Omega} - \Omega_j$ is the difference from the central frequency of the Q band. The integral in (1) describes beats of the excited components of the Q branch; these beats are averaged over the length of the probing pulse. The quantity $|\Phi(\tau)|^2$ describes the phase relaxation of an individual component. We are assuming that $\Phi(\tau)$ is independent of j . All the rest of the notation is standard.

It can be seen from the dashed line in Fig. 3 that at $\tau = 1.5$ ns the Doppler phase relaxation can be ignored even at 100 K. We can thus describe $\Phi(\tau)$ by $\Phi(\tau) = e^{-\tau/T_2}$, corresponding to a collisional phase-relaxation mechanism.¹⁾

We can use (1) to simulate the experimental situation by working from the known dependence of the distribution of molecules in rotational level, N_j , on T_{rot} . The solid

TABLE I.

X/D	T^{theo} , K	$T_{\text{rot}}^{\text{expt}}$, K	T_2^{expt} , ns	$\pi\sigma_\phi^2$, Å ²
4	41	35 ± 5	1.0 ± 0.1	86 ± 20
7	25	27 ± 5	2.5 ± 0.2	152 ± 40
10	18	25 ± 2	2.8 ± 0.3	350 ± 90
15	13	25 ± 2	8.0 ± 2.0	400 ± 150
—	300	—	0.14 ± 0.01	43 ± 4

curves in Fig. 3 are theoretical curves of $W_a(\tau)$ for those values of T_2 and T_{rot} which lead to the best fit of the experimental points.

This technique can thus be used for the thermometry of a deeply cooled molecular gas and to measure the phase relaxation times T_2 .

4. From the measured phase relaxation times T_2 we can determine the cross section for phase-relaxing collisions: $\pi\sigma_\phi^2 = (n\bar{u}T_2)^{-1}$, where $n = n_0(T/T_0)^{1/(\gamma-1)}$ is the density of molecules ($\gamma = 1.4$ for nitrogen), and $\bar{u} = (16kT/m\pi)^{0.5}$.

Table I lists values of $\pi\sigma_\phi^2$ calculated from this expression. For $T = 300$ K, we found $\pi\sigma_\phi^2$ from the measured values of T_2 in a cell holding nitrogen at atmospheric pressure. As the temperature is lowered to 20 K, $\pi\sigma_\phi^2$ increases by a factor of about six. The translational temperatures T shown in Table I (from which $\pi\sigma_\phi^2$ were calculated) were determined from the expressions of Ref. 5 (see also Refs. 6 and 7). The calculated values of T agree with the experimental values of T_{rot} .

5. These results demonstrate the extensive possibilities of picosecond active spectroscopy of molecules in supersonic jets. A natural next step would be to study more complex molecules. Estimates^{8,9} show that the use of intense spectrally limited picosecond pulses would make it possible to achieve substantial changes in the populations of Raman-active modes, opening up new opportunities for studying vibrational resonances and in laser photochemistry.

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¹The absence of an average decay at the point $X = 3.5$ mm (curve 1 in Fig. 3) implies that the average decay detected at lower values of X cannot be attributed to either instrumental errors or transit-time effects. Over the time $\tau = 1.5$ ns, the molecules in the jet are displaced a distance $u\tau = (8 \times 10^4) \times (1.5 \times 10^{-9}) = 1.2 \times 10^{-4}$ cm, which is much shorter than the dimension of the probing region along the axis of the jet, 50×10^{-4} cm.

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