

HIGH RESOLUTION LASER SPECTROSCOPY IN COLD SUPERSONIC MOLECULAR BEAMS COOLING, REDUCTION OF DOPPLER WIDTH AND APPLICATION

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Abstract

The cooling of molecules during the adiabatic expansion of supersonic seeded molecular beams is reviewed and illustrated by the example of NO₂-molecules. The reduction of the Doppler width by collimation of the beam and the cooling to low rotational temperatures brings a significant simplification of the complex NO₂-absorption spectrum and allows its assignment. The measured rotational temperature is $T_{\text{rot}} = 10^{\circ}\text{K}$. Some examples from our work illustrate this promising technique of high resolution laser spectroscopy in cold beams.

Introduction

One of the major contributions to the spectral line width in gases at low pressure is the Doppler width which is due to thermal motion of the absorbing or emitting (atoms) molecules. Therefore, the spectral resolution of many spectroscopic methods is in principle limited by the Doppler width of (atomic) molecular absorption or emission line spectra [1]. The density of electronic states even of diatomic molecules is much larger than that of the corresponding atoms, because each combination of two atoms $A(n_a, L_a, S_a)$ and $B(n_b, L_b, S_b)$ in states with principle quantum number, n , orbital angular momentum quantum number, L , and spin quantum number, S , given rise to several electronic states of the molecule AB [2]. In addition, the manifold of vibrational and rotational levels in each electronic state adds to the level density. Molecular spectra are therefore generally by far more complex than those of atoms and often many lines may overlap within their Doppler width. In such cases the conventional spectroscopic techniques, which have extensively contributed to our knowledge about atomic and molecular spectra, are not suitable for a detailed investigation of these molecules since the spectral resolution of these

techniques is in principle limited by the Doppler width but in practice limited by the resolving power of the wavelength dispersing instrument.

Fortunately, there exist several new experimental methods to over-come these difficulties. The first group is based on the **increase** of spectral resolution by using Doppler-free techniques. The second group relies on the **decrease** of line densities by working at very low temperatures, where the number of populated molecular levels is drastically reduced. Examples of this latter are: Matrix isolation spectroscopy and spectroscopy in cold supersonic beams.

Spectroscopy in collimated cold supersonic beams can achieve both advantages simultaneously, i.e. sub-Doppler resolution at very low temperatures.

Adiabatic cooling in molecular beams

Molecular beams are formed by selecting molecules which happen to leave a reservoir which is filled with a gas or vapor at pressure p_0 and extended through a small nozzle A into the vacuum with background pressure p . The gas starts from a state (p_0, T_0) at thermal equilibrium in the reservoir and accelerates with an imposed pressure $p_0 - p$ through the source exit. If the molecular mean free

Key words: Doppler width, laser Spectroscopy

path λ is large compared to the dimensions of the exit channel A, many collisions occur during the flow through the nozzle A and the process of beam formation has to be described as supersonic expansion into the vacuum. During this expansion the random thermal motion is converted into directed mass flow with mean flow velocity u . The translational temperature T (defined in terms of the width of the Maxwellian velocity distribution) decreases while the flow velocity u increases. Conservation energy in this adiabatic process requires that

$$h_0 = h + 1/2 u^2 \tag{1}$$

where h is the enthalpy per unit mass at any particular point in the expansion and h_0 is the enthalpy per unit mass prior to the expansion [3]. In order to calculate the temperature in the expanding gas, for an ideal gas, we can write

$$h_0 - h = c_p(T_0 - T) = [\gamma / (\gamma - 1)] r(T_0 - T) \tag{2}$$

where we have made use of the relation $c_p - c_v = r$, $c_p / c_v = \gamma$. Here c_p is the heat capacity at constant pressure per unit mass and r is the gas constant per unit mass. For an ideal gas the speed of sound is given by

$$v_s = (\gamma rT)^{1/2} \tag{3}$$

and therefore substitution of eqs. (3) and (2) into eq. (1) gives

$$\frac{T}{T_0} = \left[1 + \frac{\gamma - 1}{2} M^2 \right]^{-1} \tag{4}$$

in which M is the Mach number equal to the ratio between gas flow speed u and the local speed of sound v_s . For $M \leq 1$ one talks of effusive or sonic beams while molecular beams with $M > 1$ are called supersonic beams. An extreme cooling as low as 0.006 K has been obtained in helium molecular beams [4]. In this example the Mach number is very large, i.e. the gas is supersonic, not because the mass flow is large, but because the local speed of sound ($\propto T^{1/2}$) is very low. The velocity distribution on this example corresponds to Mach number of ~ 350 .

Reduction of Doppler width in molecular beams

In a gas, the atoms or molecules undergo random motions. When such a moving molecule interacts with radiation, the apparent frequency of the incident wave is different from the frequency seen by a stationary atom. This is called "Doppler effect". Equivalently, one may say that the resonance frequency of the atom is shifted due to the motion.

Consider a molecule moving with a velocity

$v = (v_x, v_y, v_z)$ relative to the rest frame of the observer across a plane electromagnetic wave, $E = E_0 \exp [i(\omega t - \vec{k} \cdot \vec{r})]$. The wave frequency in the rest frame, ω , is Doppler shifted in the frame of the moving molecules to

$$\omega' = \omega - \vec{k} \cdot \vec{v} = \omega - kv_z \tag{5}$$

The probability that a molecule of mass m in a gas at temperature T has a velocity component between v and $v+dv$ is given by the Maxwellian velocity distribution. The number of molecules $n_i(v_z)dv_z$ in the energy level E_i per unit volume with a velocity component between v_z and v_z+dv_z is therefore

$$n_i(v_z) dv_z = \frac{N_i}{v_p \sqrt{\pi}} e^{-(v_z/v_p)^2} dv_z \tag{6}$$

where $N_i = \int n_i(v_z) dv_z$ is the density of molecules in the level E_i , $v_p = (2k_B T/m)^{1/2}$ is the most probable velocity and k_B is the Boltzmann constant.

Since the absorbed or emitted radiation power $p(\omega) d\omega$ is proportional to the density $n_i(\omega) d\omega$, the intensity profile of a Doppler broadened spectral line becomes;

$$I(\omega) = I_0 \exp \left\{ - \left[\frac{c(\omega - \omega_0)}{v_p \omega_0} \right]^2 \right\} \tag{7}$$

which is a Gaussian profile. Its full width at half maximum (FWHM) is

$$\delta \omega_D = \frac{\omega_0}{c} (8k_B T \ln 2/m)^{1/2} \tag{8}$$

This quantity is called Doppler-line width. For example if we consider the 6328 Å transition of Ne in the He-Ne laser at room temperature, the Doppler width, using eq. (8), is $\cong 1700$ MHz.

How is the Doppler width reduced in a collimated molecular beam? We will now consider molecules effusing into the vacuum through a small hole A from a reservoir. The molecular density N behind A and the background pressure in the vacuum should be so small that the mean free path of the molecules is large compared to the distance between A and the observation region. In fact in a small region near the nozzle, about ten nozzle diameters long, the gas is accelerated to a velocity very close to its final value. After this region the streamlines have become straight lines originating from a point source at the orifice A. In this free expansion region the molecular density decreases as $1/r^2$, when r is the distance from the nozzle. The number of molecules per unit volume is then given by [5].

$$n_i(v, r) dv = c_i \frac{\cos \theta}{r^2} N_i v^2 \exp \{ -(v/v_p)^2 \} dv \tag{9}$$

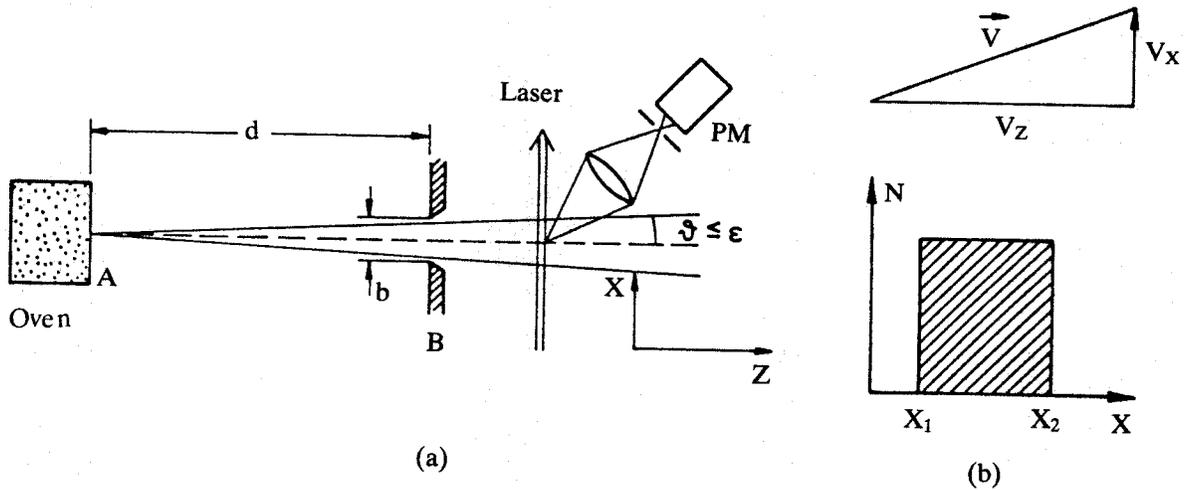


Fig. 1:
(a) Schematic diagram of sub-Doppler excitation spectroscopy in a collimated molecular beam.

(b) Velocity diagram and spatial density profile [from Ref. 1 used with permission].

where the normalization factor $c_1 = \frac{4}{\sqrt{\pi}} v_p^{-3}$ assures that the total density of the molecules is $N_i = \int n_i(v) dv$ and v_p has the same meaning as in eq. (6)

At a distance d from the point source A a slit B, with width b , is located parallel to the y -axis which selects molecules moving within a small angular interval $-\epsilon \leq v \leq \epsilon$ in the x -direction around $v = 0$ (see Fig. 1). The molecules passing through the slit B from a molecular beam in the z -direction which is collimated with respect to the x -direction. Now we define the maximum divergence of the molecular beam as the collimation ratio, namely,

$$\tan \epsilon = \frac{b/2}{d} = \frac{v_{xm}}{v_z} \quad (10)$$

where $v_{xm} = v \sin \epsilon$ and $v = |v|$ is the absolute value of velocity $v = (v_x, v_y, v_z)$ of a molecule in the beam. If the orifice diameter is small compared with slit width b and if $b \ll d$, the flux density behind the slit B is approximately constant across the beam diameter since $\cos \vartheta \cong 1$ for $v \ll 1$ (see fig. 1b).

Let a narrow laser beam of frequency ω and negligible cross section $\Delta y, \Delta z \ll z_0^2$ pass through the molecular beam at $y=0$ and $z=z_0$ in the x -direction from x_1 to x_2 . The laser power P_0 absorbed due to absorption by the molecules along the absorption pass $\Delta x = x_2 - x_1$ is given by

$$\Delta P(\omega) = P_0 \int_{x_1}^{x_2} \alpha(\omega, x) dx \quad (11)$$

After some calculations [6] one arrives at

$$\Delta P(\omega) = c_2 \int_{-\infty}^{+\infty} \frac{e^{-(\omega_0 - \omega)^2 / (\Delta \omega_D \sin \epsilon)^2}}{[(\omega_0 - \omega)^2 - (\Delta \omega_0^2) + (\gamma/2)^2]} d(\Delta \omega_0) \quad (12)$$

where $c_2 = c_1 v_p^2 P_0 N_i \sigma_0 \frac{\gamma^2}{4} (\frac{C}{\omega_0})^3$ and $\Delta \omega_D = \omega_0/c (8 k_B T (\ln 2/m)^{1/2})$ is the full Doppler line width of the gas which previously was calculated.

Equation (12) represents a Voigt profile which represents the reduced velocity distribution $n(v_x)$ with a residual Doppler width of

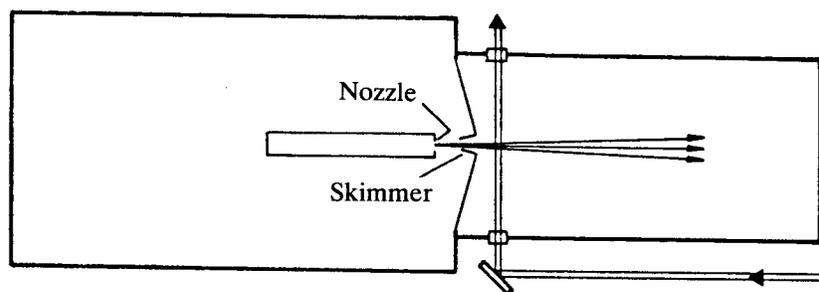
$$\Delta \omega_{red} = \sin \epsilon \cdot \Delta \omega_D \quad (13)$$

A comparison of eq. (13) with eq. (8) shows that the Doppler width is reduced by a factor $\sin \epsilon$ which is equal to collimation ratio of the beam. With slit width $b=1\text{mm}$ and $d=50\text{mm}$ we obtain $\sin \epsilon = 0.01$. This illustrates that the Doppler width of typical 1 GHz in the visible region of spectrum can be reduced to 10 MHz and becomes comparable to the natural line width. For example, the upper state lifetime of Na-D lines at $\lambda=590\text{nm}$ is 16 ns which results in a natural line width of $\sim 10\text{MHz}$.

Application of laser spectroscopy in supersonic molecular beams to the analysis of the NO₂ spectrum

The congested visible absorption spectrum respon-

Top View:



Side View:

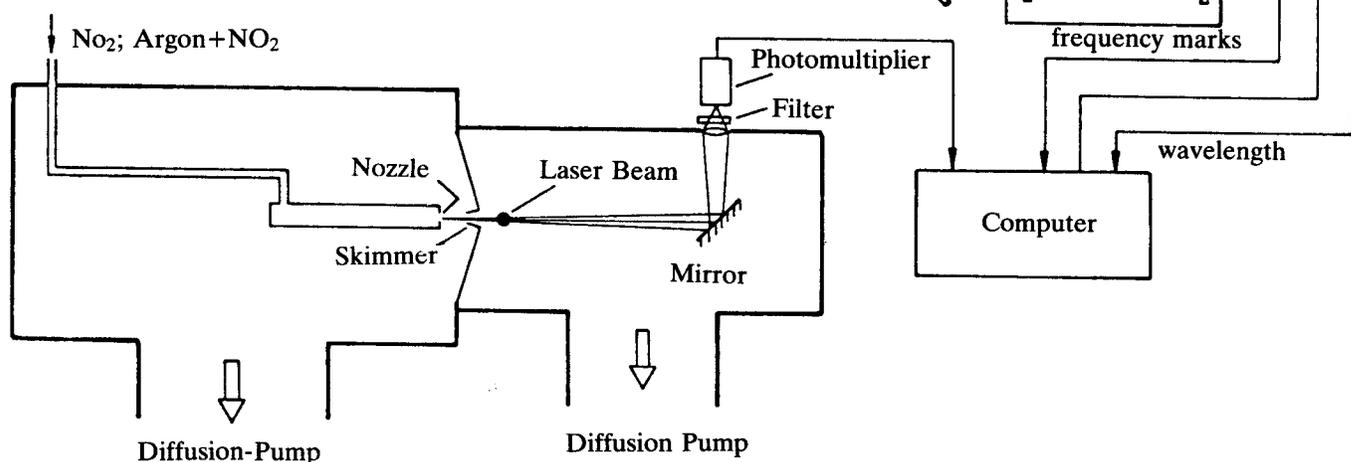


Fig. 2:

Experimental arrangement of sub-Doppler laser spectroscopy in molecular beams. The laser wavelength is measured with a wave-meter, frequency marks are generated by a long Fabry-Perot

interferometer and a computer controls the laser and stores spectra, frequency marks, and wavelength readings.

sible for the orange-brown color of nitrogen dioxide has been a challenge to spectroscopists for many decades [7,8]. Two fundamental problems have prevented analysis of the bulk of the NO_2 visible absorption spectrum. The first is that there are too many lines. The spectrum extends from about 800 nm to beyond the dissociation limit near 400 nm and this entire 400 nm region contains a very high density of lines. The second is that the spectrum shows no obvious regularities or periodicity. This complexity is due to vibronic coupling between levels of electronically excited states with a dense manifold of high lying vibrational levels of the electronic ground state, which causes the level density and therefore the density of absorption lines within the visible range to be very high [9].

Here we describe an experiment using a supersonic molecular beam seeded in argon which provides a great reduction in rotational structure of the congested spectrum without completely removing it [10] and which allows high resolution studies of free molecules unperturbed even by gas phase collisions. The experimental set up is shown in Fig. 2. The focused beam of a tunable, stabilized, and single mode cw ring dye laser was crossed perpendicularly with the supersonic beam of 5% NO_2 seeded in Argon. The supersonic NO_2 beam was realized by expansion of seeded NO_2 beam (at a total pressure up to 700 mbar of the NO_2 argon mixture in a reservoir at room temperature) through a nozzle of 50 μm diameter into the vacuum chamber. The collimation ratio of 10^{-2} was obtained by a skimmer

Fig.3

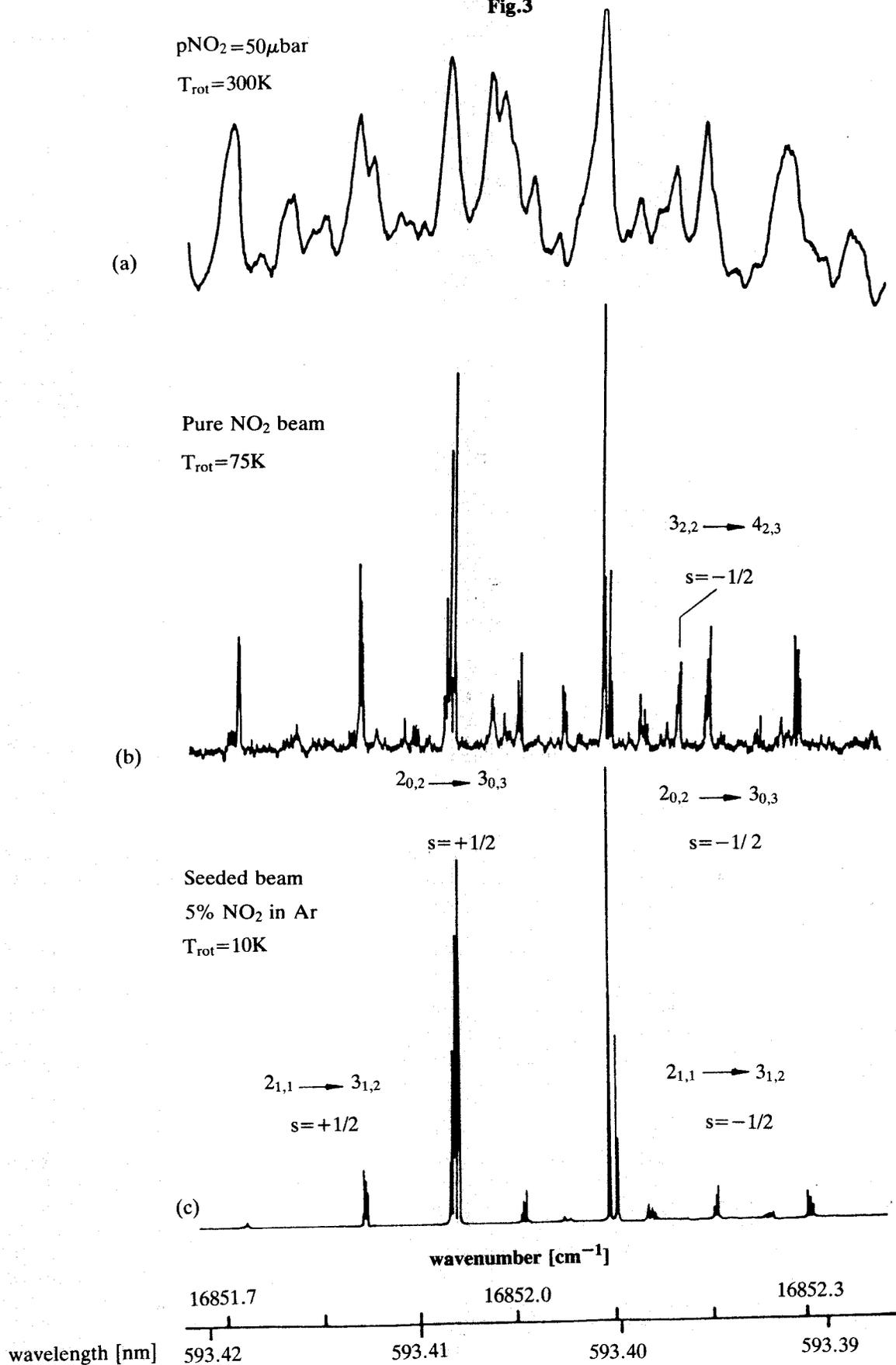


Fig. 3:

A section of fluorescence excitation spectrum of NO₂ obtained (a) a conventional room temperature absorption cell of pure NO₂ at 50 μbar pressure, (b) in a supersonic beam of pure NO₂ and (c) in a supersonic beam of 5% NO₂ seeded in Ar. All spectra were taken with a cw dye laser of 1.2×10⁻³ nm bandwidth (for details see text).

(slit B in Fig. 1) located 50 mm downstreams with a slit width of 1 mm which reduced the Doppler width of NO₂ from 900 MHz to ~ 10 MHz. The total undispersed NO₂ fluorescence is observed in the direction of the molecular beam as a function of laser wavelength. Because the mean lifetime of the excited NO₂ molecules range from 1 μs to ≅ 100 μs [11] the molecules in the beam may travel several centimeters from the point of excitation before they radiate. It is therefore more efficient to collect the fluorescence in the direction of the molecular beam rather than perpendicular to it. For wavelength measurements of NO₂ absorption lines the laser is stabilized onto the centre of a selected line in the excitation spectrum and its wavelength is measured with a specially designed computer controlled Michelson interferometer [12].

Figure 3a–c shows a section of the excitation spectrum of NO₂ obtained for a conventional experimental sample of NO₂ gas at ~ 50 μ bar at room temperature (a) and in pure NO₂ supersonic beam with medium cooling ($T_{rot} \approx 75^\circ\text{K}$) (b) and in a beam of argon seeded with 5% of NO₂ (c). Due to many collisions between the cold argon atoms and the NO₂ molecules during the expansion the rotational temperature drops to about 10°K (see below).

The absorption lines of NO₂ in a conventional absorption cell (Fig. 3) are Doppler broadened and many lines overlap within their Doppler width. The reduction of the Doppler width in the molecular beam (eq. 13) and the simplification of the spectrum due to rotational cooling is illustrated in Fig. 3b–c. The intensities of the absorption lines are proportional to the product of two factors: a) the population densities N_i of the absorbing vibrational-rotational level and b) the transition probability $B_{ik}S_L$ for a transition from the absorbing level $|i\rangle$ to the upper level $|k\rangle$ at a laser spectral radiation density S_L .

From the measured ratios of line intensities for transitions starting from two different lower levels ($v, J'' = J' - 1$) and ($v, J'' = J' + 1$) but ending at the

same upper level (v', J'), the rotational temperature T_{rot} can be obtained, (see next section).

The rotational cooling of molecules compresses the population into the lowest rotational levels and therefore reduces the number of absorption lines. In this simplified spectrum the hyperfine component of the R (2) transition in the vibronic band No. 99 [7] can be clearly recognized (Fig. 3c). The assignment can be achieved from known microwave data of the ground state [13].

Measurement of rotational temperature

During the adiabatic expansion of the supersonic molecular beam, the molecules can transfer part of their internal energy (rotational and vibrational energy) through collisions with the noble gas atoms into translational motion. If thermal equilibrium could be reached, all degrees of freedom (translational, rotational and vibrational) would reach the same low temperature. However, collision can only occur within a short region behind the nozzle where the density of molecule is sufficiently high. The effectiveness of energy transfer depends on the number of collisions and on the deactivation cross section σ_{rot} for rotational-translational transfer and σ_{vib} for vibrational-translational transfer. Since the cross section for elastic collision σ_{elas} is much larger than that of collision-induced rotational transitions which are still larger than those for vibrational transition, i.e. $\sigma_{vib} \ll \sigma_{rot} \ll \sigma_{elas}$ vibrational cooling is much less effective than rotational cooling which are still much less effective than translational cooling and we obtain $T_{trans} < T_{rot} < T_{vib}$ [14].

The rotational-vibrational temperatures can be obtained by comparing the intensities of absorption lines which start from different lower levels. Assuming thermodynamic equilibrium at a temperature T the population density $N_i(v_i, J_i, K_i)$ of a rotational-vibrational level (K is the projection of rotational quantum number J onto the symmetry axis) follows Maxwell-Boltzmann distribution

$$N_i(v_i, J_i, K_i) = \frac{N}{G} g(v) (2J+1) (2K+1) \exp(-(E_{vib} + E_{rot})/k_B T) \quad (14)$$

where N represents the total molecular density. The partition function $G = 1/N \sum N_i(v_i, J_i, K_i)$ acts as a normalization factor to ensure $N = \sum N_i(v_i, J_i, K_i)$ and $g(v)$ is the statistical weight of the vibrational level, where $v = (v_1, v_2, v_3)$ represents the 3 quantum numbers of the normal vibrations.

During the adiabatic expansion of supersonic beams generally no complete thermal equilibrium

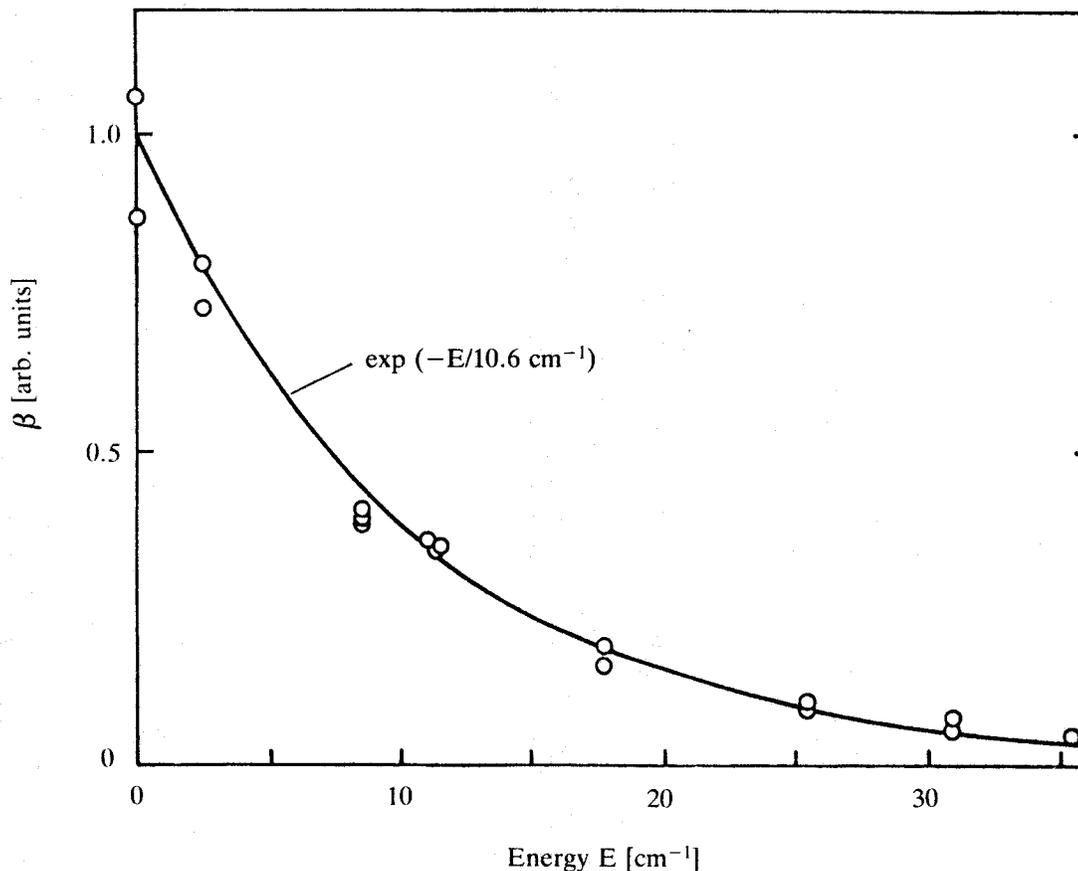


Fig. 4: Theoretical (solid line) and experimental values (circles) of population density of NO₂ rotational

levels ($v = 0, K = 0, J_i$) versus the rotational energy.

among all degrees of freedom is reached [15]. If the rotational-rotational transfer rates are sufficiently large, the actual population $N(J,K)$ of rotational levels within a vibrational state can still be approximated by a Boltzmann distribution.

$$N(J,K) \propto (2J+1) \cdot (2K+1) e^{-E_{rot}/k_B T_{rot}} \quad (15)$$

A convenient way of determining the population distribution $N(J,K)$ is based on the measurement of relative intensities of rotational lines within a vibrational band:

$$\beta = \frac{I(v''_i, J''_i \rightarrow v'_k, J'_k)}{I(v''_i, J''_m \rightarrow v'_k, J'_k)} = \frac{(2J_i+1)(2K_i+1)}{(2J_m+1)(2K_m+1)} \cdot e^{-\frac{\Delta E_{rot}}{k_B T_{rot}}} \quad (16)$$

Former experiments have shown that the rota-

tional temperature of a pure NO₂ molecular beam at 200 mbar reservoir pressure turns out to be about 75°K [16]. Figure 4 shows a plot of measured values of β for the NO₂ band No. 99 [17]. The results prove very well that the measured population distribution $N(v=0, J_i)$ fits a Boltzmann distribution. This implies that for this case a rotational temperature T_{rot} is well defined.

Conclusion

The example of high resolution spectra of the NO₂ molecule, measured in a collimated cold molecular beam, demonstrate the capability of the combination of laser spectroscopy with molecular beam techniques.

In order to fully exploit the many possibilities of this technique (including nonlinear spectroscopy [17] and optical-optical double resonance spectroscopy)

further work is necessary which will be continued in the near future.

Acknowledgements

The experimental part of this work was performed at the Fachbereich Physik, Universität Kaiserslautern, W. Germany. I am grateful to Prof. Dr. W. Demtröder for valuable discussions. I also thank Dr. F. Bylicki for his help in the experiment and fruitful discussions.

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