

# Diode-Laser Study of Rotational Temperature and Absorption Line Shape in Supersonic Free Jets\*

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Z. Naturforsch. **42 a**, 246–252 (1987); received October 9, 1986

Infrared spectra of NNO and OCS have been studied in a supersonic free jet by using a diode-laser spectrometer. The sample gas of the molecules of 1 bar pressure was injected into a vacuum chamber ( $p \approx 10^{-5}$  mbar) through a nozzle with a magnetic valve. The molecular beam was pulsed ( $\approx 82$  Hz) by controlling the magnetic valve. Near the nozzle and for low values of the quantum number  $J$  the rotational temperature was determined to range between 29 and 3 K. For NNO we have observed the unusual line shapes in detail. They are caused by superposition of absorption signals of molecules in the jet and the background.

## Introduction

Molecular spectroscopy of supersonic free jets has been successfully applied for a number of molecules especially in the optical region [1]. Spectroscopy on molecular jets offers several advantages over conventional spectroscopic techniques, because very low temperature can be maintained while the molecules are still in the gas phase. For example, molecular spectra at room temperatures often exhibit very densely populated and complicated rotational structures which can prevent the assignment of the spectra. These complications can partially be removed by observing molecules in supersonic jets. The very low rotational and vibrational temperatures in the jet reduce the intensities of transitions arising from high energy states. Recent advances in highly sensitive infrared laser spectroscopy has allowed to extend this method to the infrared region [2–5]. In the present work we have observed the infrared spectra of molecules in a supersonic free jet by using a diode-laser spectrometer. In this paper we report the instrumental details of the apparatus, we discuss the measured low rotational temperatures, and we propose a model for the observed line profiles.

We have measured the rotational temperature of NNO and OCS with an accuracy of  $\pm 1$  K for various  $J$  values and for different locations in the

jet. Deviations from the Boltzmann distribution were clearly observed.

In addition we have observed anomalous line shapes for NNO transitions. Similar anomalous line shapes have already been found and discussed in [2, 4, 6, 7].

## Experimental

The experiments have been made with the diode-laser spectrometer which has been described earlier [8]. The laser beam was directed through the vacuum chamber, Fig. 1, where the molecular jet was formed by injecting the gas into the chamber through a nozzle placed in front of a modified commercial automobile valve (Bosch GmbH, West Germany) [7]. A home made pin hole of 0.07 mm diameter was fixed on the end of the magnetic valve by epoxy binder. The wall thickness of the pin hole is about 0.1 mm. The nozzle was operated in a pulsed mode by controlling the magnetic valve electrically. For best sensitivity the optimal duty cycle was found for a repetition rate of about 82 Hz.

The sample gas was injected through the nozzle with a pressure of 1 bar. The chamber was evacuated by a diffusion pump (2500 l/s) backed up with a rotary pump (500 l/s); the background pressure in the chamber was approximately  $10^{-5}$  mbar and during operation the pressure increased to about  $10^{-3}$  mbar. A liq.  $N_2$  cold trap was useful to reduce the background pressure by one to two orders of magnitude.

\* This work was supported in part by the Deutsche Forschungsgemeinschaft, SFB-301.

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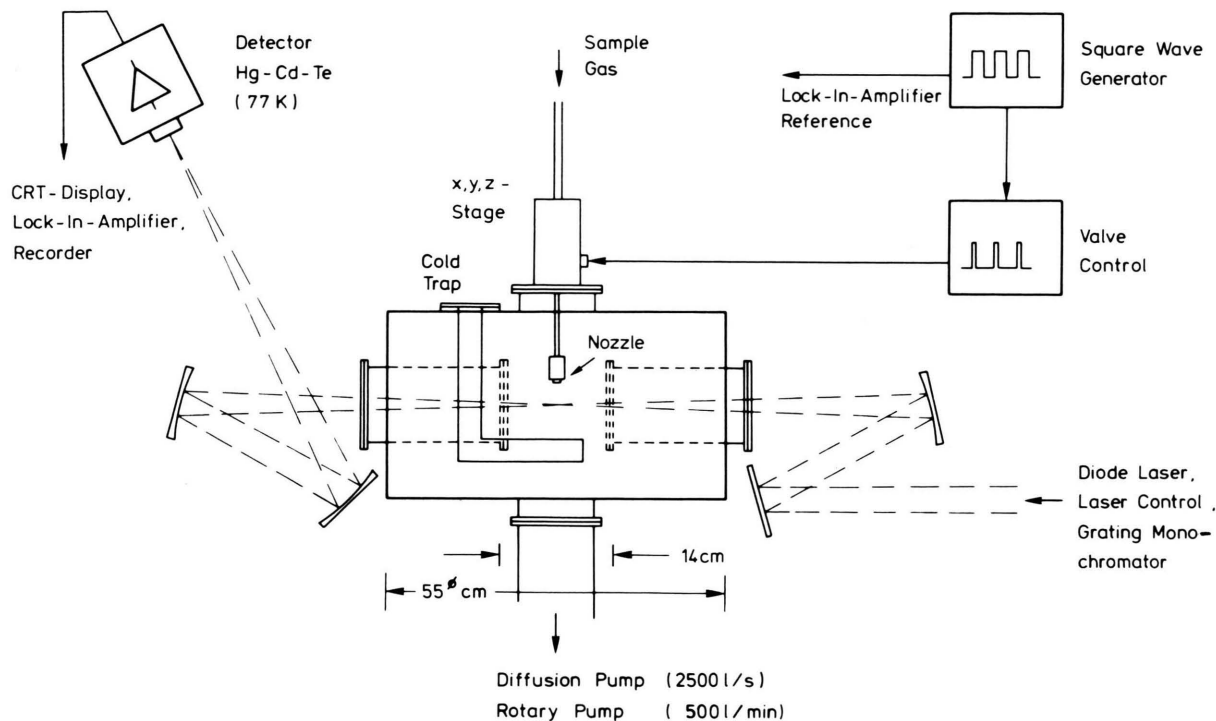


Fig. 1. Experimental apparatus with the vacuum chamber and nozzle. The path of the laser beam is schematically indicated. The nozzle is located near the focus point of the laser beam and can be adjusted by the  $xyz$ -manipulator. The path through the vacuum chamber was either 65 cm or 14 cm.

The position of the nozzle can be adjusted relative to the laser beam by an  $xyz$ -manipulator with an accuracy of about 0.1 mm. The  $z$ -axis was chosen as the nozzle axis, thus the  $z$  value indicates the distance between the pin hole and the laser beam. The  $x$ -axis was determined to run vertically to the laser axis. The incident laser beam of approximately 5 mm diameter is focussed near the nozzle's head, with a beam waist of about 0.8 mm. In the present study two different path lengths – 65 cm and 14 cm – were used to verify background absorption effects. After leaving the chamber the laser beam is focussed onto a detector, whose output signal is demodulated at the frequency of the pulsed nozzle by a lock-in amplifier yielding the absorption spectra.

The spatial distribution of the molecules in the jet is characteristic of the nozzle used. Figure 2 shows the observed intensity distribution of the  $R(4)$  transition of the  $\nu_1$  band of NNO in the molecular jet. Since the absorption intensity depends on the molecular density and on the rotational tempera-

ture, which varies for different locations in the jet, this profile is not a simple function of the density distribution only. However, as will be shown later, at larger distances from the nozzle the rotational temperature was found to be nearly constant, implying that the intensity profile represents the molecular number density with fair accuracy. A slight asymmetry in the column density profile with respect to the nozzle axis suggests a mechanical misalignment of the pin hole. The molecular beam was not completely parallel to the  $z$ -axis.

### Rotational Temperature

The rotational temperature is calculated from the measured absorption intensity. For a weak absorption of linear molecules, the absorbance  $A$  of a rovibrational transition  $J' - J$  is given as

$$A(m) = (I_0 - I)/I_0 = C_0 |m| \exp[-BJ(J+1)/kT], \quad (1)$$

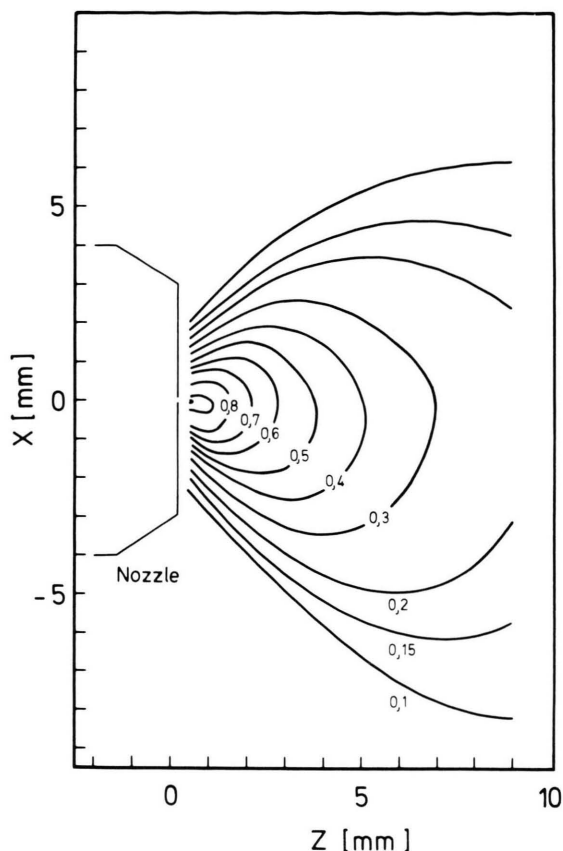


Fig. 2. The intensities of the  $R(4)$  transition of  $\text{NNO } \nu_1$  band observed for various beam locations are summarized here as a contour map. The numbers in the contour map represent the relative intensities. This map shows approximately the distribution of the column density of  $\text{NNO}$  molecules of  $J=4$  state in the jet. The asymmetry of the map is caused by the mechanical misalignment of the nozzle.

where  $I$  is the transmitted laser power,  $I_0$  is the incident laser power,  $B$  is the rotational constant, and  $C_0$  is a constant which depends on the vibrational transition moment, the transition frequency, and the total column density of the molecules. For R-branch transitions  $m = J+1$  and for P-branch transitions  $m = -J$ .

The rotational excitation temperature  $T$  can be deduced from (1) using the absorbance  $A$  of two different rotational transitions. The rotational temperatures of several  $\nu_1$  band transitions of  $\text{NNO}$  relative to  $R(4)$  as determined is shown in Figure 3a. This graph illustrates the dependence of the rotational temperature on (i) the distance from the nozzle and (ii) the quantum number  $J$ .

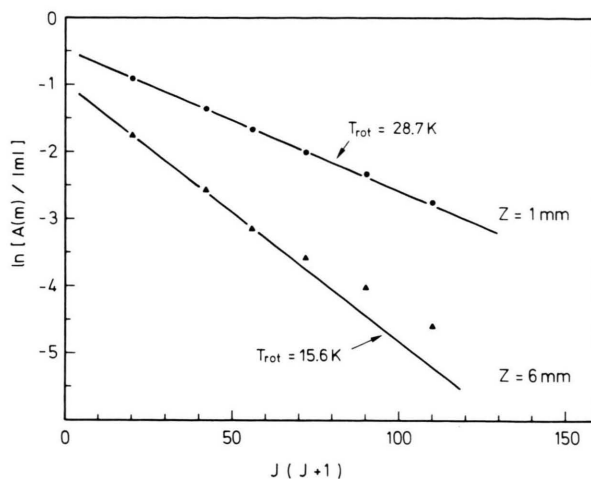


Fig. 4. The  $\ln[A(m)/|m|]$  values for  $\text{NNO } \nu_1$  band are plotted against  $J(J+1)$ . In the case of the Boltzmann distribution this plot results in a straight line, the slope of which is proportional to  $T^{-1}$ . The straight lines drawn are for rotational temperatures of 28.7 K and 15.6 K for  $z = 1$  mm and 6 mm, respectively.

Equation (1) can be rewritten as

$$\ln[A(m)/|m|] = C_1 - BJ(J+1)/kT. \quad (2)$$

The dependence of the experimentally determined left side on  $J(J+1)$  should be linear provided that the molecular distribution for the rotational levels follows Boltzmann.

For example by observing the  $R(4)$  to  $R(10)$  transition of the  $\nu_1$  band of  $\text{NNO}$  we found that the Boltzmann distribution was valid only near the nozzle and only for low  $J$ . The plots of (2) for nozzle distances of 1 mm and 6 mm are given in Figure 4. For a distance of 1 mm from the nozzle the rotational temperature was 28.7 K. For the 6 mm nozzle distance there appears a deviation in the measured values from the straight line as determined from low  $J$  values; the straight line represents a rotational temperature of 15.6 K. The deviation from the Boltzmann distribution becomes apparent for high  $J$  and with larger distances from the nozzle.

By seeding molecules in a rare gas the rotational temperature decreases. Figure 3b shows the rotational temperature in the jet of  $\text{OCS}$  at a partial pressure of 225 mbar diluted by Ar of 1 bar pressure. The partial pressure of  $\text{OCS}$  was kept constant using a trap at dry ice temperature.

In this case we have observed transitions for a wider  $J$  range, between  $J=1$  and 16 (R- and P-branch of the  $\nu_1$  band). Figure 5 illustrates the large

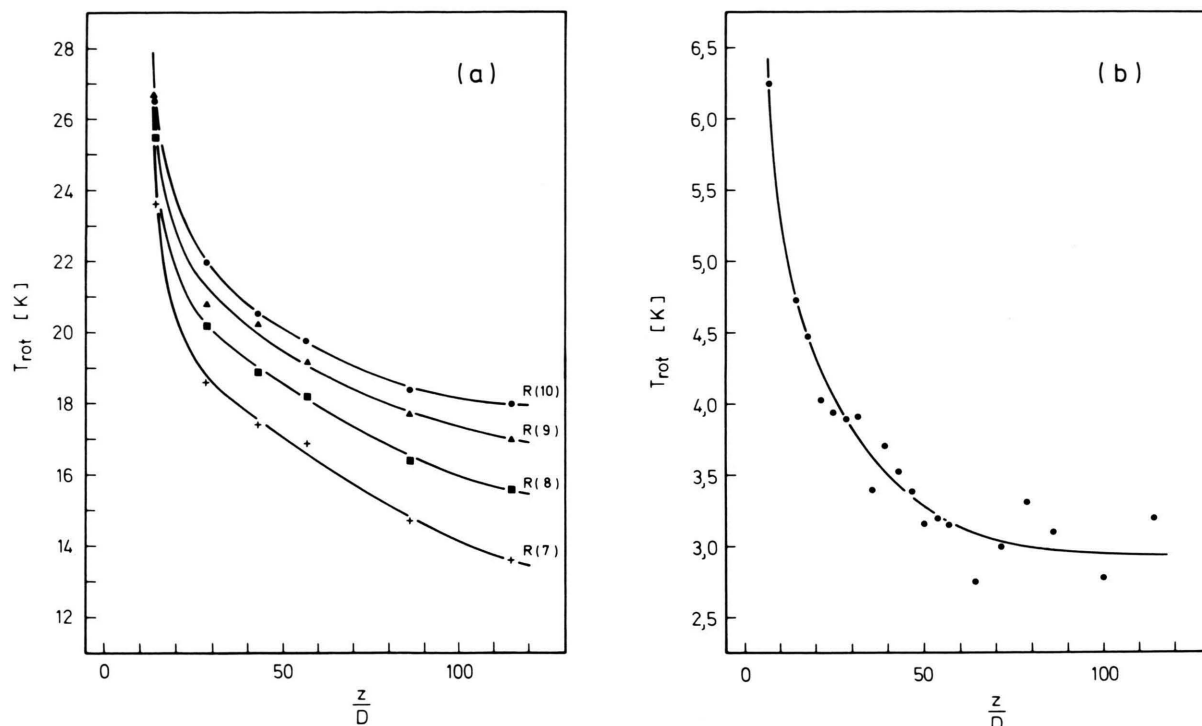


Fig. 3. Variation of the rotational temperature is shown as a function of the nozzle distance in units of the nozzle diameter ( $D = 0.07$  mm). (a): The temperatures were obtained for several transitions of NNO  $v_1$  band using the  $R(4)$  transition as a reference. (b): The rotational temperature of  $P(3)$  transition of the  $v_1$  band of OCS (225 mbar) seeded in Ar (1 bar). The reference line used was  $P(2)$ .

deviation from the Boltzmann distribution for high  $J$  values. The measurements were made for a distance of 6 mm from the nozzle. A linear fit using  $J$  values from 1 to 4 results in a rotational temperature of 4.9 K.

### Anomalous Line Shape

The molecular absorptions observed with NNO in the jet showed remarkable line profiles, which differ strongly from the Gaussian form as shown in Figure 6. For low  $J$  transitions the full width at half maximum (FWHM) is almost constant (216 MHz) and nearly twice as large as the expected Doppler width at room temperature (112 MHz). In addition the line shape is  $J$  dependent. For example, the lines with  $J > 10$  in the  $v_1$  band of NNO were found to be split into two components, which prevented precise measurements of the appropriate line width. The magnitude of the splitting increases with increasing  $J$ . In addition, the observed line shapes were asymmetric.

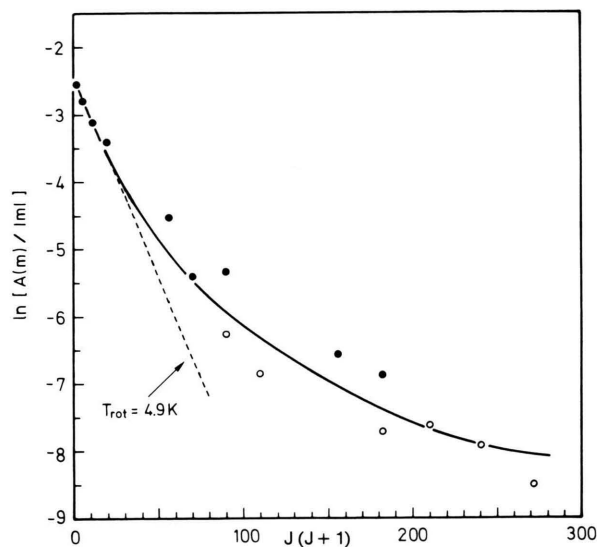


Fig. 5. The  $\ln[A(m)/|m|]$  values for OCS  $v_1$  band are plotted against  $J(J+1)$  for the nozzle distance of 6 mm. The OCS gas of 225 mbar is seeded in 1 bar Ar. Open circles indicate values of P-branch transitions and filled circles those of R-branch transitions. The straight line represents the case of the Boltzmann distribution for the rotational temperature of 4.9 K.

This observed anomalous line shape is of instrumental nature and is caused by three different effects. Two of the three effects on the line profile can be accounted for in a somewhat simplified model, which we would like to suggest. The observed line profile is explained as a superposition of the line shapes of two different molecular distributions: (i) the cold jet gas embedded in the (ii) warmer surrounding ambient gas. The third effect, the asymmetry in the line profile stems from a Doppler shift of the jet's absorption profile, caused by the non-perpendicular crossing of the laser – and molecular jet beam.

The molecules in the jet form an interaction length of  $L_j$ , in the ambient gas of  $2L_a$  (i.e.  $L_a$  on side either of the jet, see Fig. 1), where  $L_a \gg L_j$ . In our experiment underlying Fig. 6,  $L_j$  was about 4 mm (half width of the column density distribution) and  $2L_a$  was 650 mm.

The transmitted laser intensity at the detector is

$$I^{(1)} = I_0 \exp[-S_{mn}(2f_a q_a^{(1)} L_a + f_j q_j L_j)] \quad (3)$$

for the period of the open valve and

$$I^{(2)} = I_0 \exp[-S_{mn} f_a q_a^{(2)} (2L_a + L_j)] \quad (4)$$

for the period of the closed valve, where the parameters are defined as follows:

$I_0$ : incident laser intensity,  $S_{mn}$ : line strength of the transition from state  $n$  to  $m$ ,  $f_a, f_j$ : line shape func-

tions in the surroundings and in the jet; for simplicity we assume that they are constant in either of the two areas,  $q_a, q_j$ : density of the molecules in the lower state of the transition for the ambient gas and the gas in the jet; for simplicity we also assume that the densities are constant in each area.

The density  $q_a$  is not the same for the open and the closed valve. It is modulated with a slight phase delay by the pulsed operation of the nozzle. This delay can be explained by three overlappings effects which are of instrumental and physical nature: (i) Because of the finite exhausting speed of the pump, the molecules injected from the nozzle can not be pumped out instantaneously. (ii) Because of the finite expansion speed of the injected molecules, the molecular density in the background does not rise instantaneously when the molecules are injected. (iii) The nozzle released cold molecules require a certain delay time to repopulate the rotational level from which the transition is to be observed. Due to relaxation processes the delay time of the last effect is larger for higher  $J$  states. Thus we have

$$q_a^{(2)} - q_a^{(1)} = q_d \neq 0. \quad (5)$$

Since a lock-in amplifier is used to detect the signal synchronously to the valve repetition rate, the recorded signal represents the difference of  $I^{(1)}$  and  $I^{(2)}$ ;

$$|I_{\text{psd}}| = |I^{(1)} - I^{(2)}|. \quad (6)$$

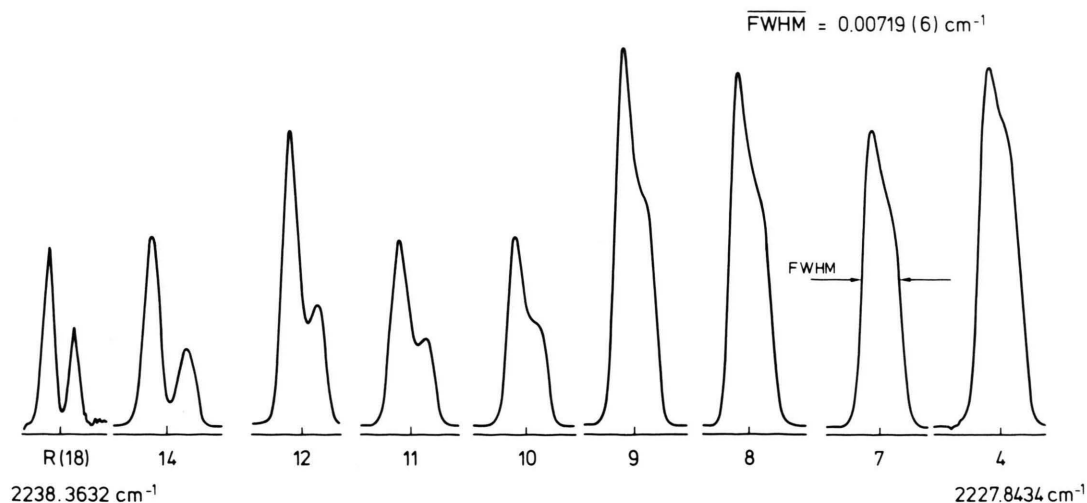


Fig. 6. Observed line shapes are illustrated for transitions of NNO in the  $\nu_1$  band. Since the intensities are not normalized to the incident laser power the peak heights of the lines can not be compared in this picture. A constant line width of 216 MHz ( $0.00719 \text{ cm}^{-1}$ ) was observed for low  $J$  transitions ( $J \leq 9$ ). For higher  $J$  transitions the lines are split and the line width has no well defined physical meaning.



By expanding the exponential to second order an approximate relation is obtained:

$$|I_{\text{psd}}| \cong I_0 (S_{mn} f_j Q_j L_j - 2 S_{mn} f_a Q_d L_a - \frac{1}{2} S_{mn}^2 f_j^2 Q_j^2 L_j^2 - 2 S_{mn}^2 f_a Q_d^{(1)} f_j Q_j L_a L_j) . \quad (7)$$

This equation shows that the detected signal represents an absorption of the molecules in the jet (first and third term) reduced by the absorption of the ambient gas (second and fourth term). Crude estimates indicate that for the present experimental condition the second term should be much larger than the fourth.

Since the line shape  $f_j$  of the molecules in the jet is broader than that of the ambient molecules  $f_a$ , the second and fourth term in (7) give rise to a dip centered on the line position of the jet molecule.

In the present observation the line center of the ambient gas is not coincident with the line center caused by the jet molecules, because the jet beam is not exactly perpendicular to the laser beam. The absorption due to molecules in the jet show a very slight Doppler shift, which causes the asymmetry in the lines.

Since the temperature of the molecules in the ambient gas is higher than of those in the jet, one can assume that the absorption intensity of the former becomes larger for increasing  $J$ . On the other hand the absorption intensity in the jet decreases with increasing  $J$ . Therefore the dip is larger for high  $J$  lines as shown in Figure 6.

The model has been supported by the following experiments:

(i) Smaller center dips on the absorption lines were observed after shortening the path length through the vacuum chamber.

(ii) A cold trap filled with liquid  $N_2$  causes the same effect by decreasing the density of the ambient molecules.

(iii) The asymmetry of the line shape was observed to be dependent on the particular nozzle in use. The geometry of the nozzle determines the angle between the jet and the laser beam. Different nozzles cause slightly varying angles resulting in different Doppler shifts in the jet spectrum.

(iv) The dip was dependent on the lock-in amplifier phase, which indicates the effect of  $Q_d$ , which shows a finite phase delay.

## Conclusion

The main result is the determination of the rotational temperature. It has been found to decrease with increasing distance from the nozzle and ranges between 29 and 3 K. The accuracy of the temperature measurements was limited experimentally by the purity of the laser mode, which caused an error for  $I_0$  in (1), and by the fluctuation of the number of molecules contained in each pulse. It was also limited theoretically by the weak-absorption approximation used for (1). In the present study the accuracy of the temperature determination was estimated to be less than  $\pm 1$  K. With this accuracy the behavior of the rotational temperature along the jet axis was found to fall monotonically within the range of our distance measurements. No increase of temperature for large nozzle distances was observed.

Since the distribution was found to be non-Boltzmann the global rotational temperature could not be determined. Therefore the excitation temperatures between several pairs of transitions were determined. A Boltzmann distribution was found only for short nozzle distances, where frequent collisions of molecules take place. At larger distances the rotational distribution is frozen out indicating a limited collisional energy transfer.

The observations of the absorption line shape of NNO transitions showed that the distorted shape is caused by the absorption due to background gas not participating in the jet action. However, it should be noted that the simple model proposed here is not adequate to account for the large variety of dips of jet spectra described in the literature. For example Baldacchini *et al.* observed the total absorption, jet and background together [4, 9], and they found a doubly peaked structure for  $NH_3$  and  $CH_2Cl_2$  near  $900\text{ cm}^{-1}$ . This double peak structure cannot be explained by our model.

The dipped line shapes appeared, in our experiments, only for molecules with very strong absorption lines. For example, we have observed single peak line shapes for  $^{13}CO_2$  molecules in natural abundance and OCS molecules seeded in Ar. The pure OCS jet is expected to show the double peak structure. However, we could not observe the jet spectrum of pure OCS, because the molecule seemed to decompose at the pin hole; the nozzle was plugged immediately by solid material, which may be sulphur.

The dipped line shapes in the present study were artificially produced by observing the molecules in the cold and warm states simultaneously with a lock-in amplifier. With respect to this, we would like to draw the attention of the reader to the similarity in certain line shape profiles observed in interstellar space. In molecular clouds the radiation against which molecular absorption can be seen, may be provided by emission of the line itself [10]. Thus the absorption dip in the interstellar emission

line occurs, when the geometry of the interstellar cloud configuration places a cold cloud in front of a warm cloud, which is a rather common interstellar phenomenon: the warmer cloud is surrounded by a cold "envelope".

#### *Acknowledgement*

We are very grateful to Dr. M. Takami for detailed information about his apparatus.

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