

ROTATIONAL COOLING IN A SEEDED OCS BEAM

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Supersonic nozzle beams of pure OCS and argon seeded OCS (10% OCS–90% Ar and 5% OCS–95% Ar) were studied. Typical nozzle source conditions were: total backing pressure 0.73 bar, nozzle diameter 60 μm , and nozzle source at room temperature. The translational temperatures of the beams were determined from measured velocity distributions. Intensity measurements of electric resonance transitions of OCS originating in rotational states up to $J = 5$ have been used to obtain the rotational temperatures: 14(4) K for a pure OCS beam and 3.5(7) K for the argon seeded OCS beams. The rotational beam temperatures deduced from the observed rotational energy distributions agree (within experimental uncertainties) with the translational temperatures.

1. Introduction

Molecular beams formed by nozzle expansion of gases into vacuum have found a large number of important applications in spectroscopy [1,2]. The reasons are well known: nozzle beams can be made nearly univelocity and rotational degrees of freedom can be cooled to very low temperatures. For molecular beam electric or magnetic resonance spectroscopy and for beam maser spectroscopy the rotational cooling provides a considerable enhancement of the intensity of transitions originating in the lower rotational states [3–6]. This is of special importance for the study of large molecules with low rotational constants and with internal rotation [7,8].

Rotational cooling has been studied by spectroscopic methods in nozzle beams of HCN [3], OCS [4] and H_2 [6], while the rotational state distribution of CsF molecules in a Xe seeded CsF nozzle beam has been determined from its deflection spectrum in an electrostatic quadrupole field [5]. A nonthermal behaviour was observed for H_2 and OCS. In the case of H_2 this is not so unexpected in view of the very large energy spacings between the rotational levels ($\hbar B/k = 85$ K). However, "rotational temperatures" of 15 K, 40 K and 170 K for the $J = 0$, $J = 1$ and $J = 2$

states, respectively, obtained for an OCS nozzle beam [4] are surprising since in this molecule $\hbar B/k$ is only 0.3 K.

In the present experiments we used a molecular beam electric resonance (MBER) spectrometer to study the rotational state distribution in pure and argon seeded OCS nozzle beams. Rotational temperatures of OCS were deduced from the observed line intensities. The $J = 1$ and $J = 2$ states of the ground vibrational state and the $J = 1$ through $J = 5$ states in the first excited bending vibrational state were investigated. It was found that the rotational population distribution could be described by a Boltzmann distribution. Rotational temperatures for OCS of 14(4) K and 3.5(7) K were obtained for a pure OCS beam and for an argon seeded OCS beam, respectively.

Measurements of velocity distribution have been performed using a high resolution velocity selector. The parallel translational temperatures obtained from these measurements agree, within the experimental errors, with the observed rotational temperatures.

2. Experiment

The nozzles for the beam source were made by electrical sparking between a sharpened 0.3 mm \emptyset tungsten wire and a stainless steel tube or a brass plate. At the place where the orifice is formed the thickness

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of the wall was made 0.5 mm. Nozzle diameters as small as 20 μm were obtained with this method. Recently, we employ electron microscope lenses which are commercially available with holes larger than 5 μm in diameter.

The electric resonance spectrometer is basically the one described by van Wachem [9]. The source chamber, modified to handle a large gas load, was pumped by a 6000 ℓ/s oil diffusion pump. A skimmer with a diameter of 1.5 mm with an apex angle of 90° separates the source from a buffer chamber pumped by a 1500 ℓ/s oil diffusion pump. An electron bombardment ionizer (Extranuclear, Type II) in combination with a quadrupole mass analyzer (Model 324-9) was used to detect the beam.

The gas mixtures were prepared in a 4 ℓ steel vessel in which a small fan was mounted to provide good mixing. All experiments were performed at room temperatures, with a nozzle having a diameter $d = 60 \mu\text{m}$ and backing pressures (p_0) up to about 1 bar.

The velocity distribution measurements have been performed in another beam machine equipped with a high resolution slotted disc velocity selector under the same conditions as used in the electric resonance spectrometer. The resolution of this selector $\delta v/v$ (full width at half maximum) was 6%.

3. Beam velocity distribution

When a Maxwell-Boltzmann velocity distribution is assumed the beam intensity $I(v)$ as a function of the velocity v for a density detector is given by [10]

$$I(v) \propto v^3 \exp[-(v/\alpha_s - S)^2]. \quad (1)$$

where

$$\alpha_s = (2kT_t/m)^{1/2}.$$

Herein S is the speed ratio defined as the ratio between the stream velocity and α_s , m is the molecular mass, T_t is the effective translational temperature in the beam, and k is the Boltzmann constant. The most probable velocity v_p , defined as the velocity for which the derivative of eq. (1) equals zero, is

$$v_p = \frac{1}{2}\alpha_s[S + (S^2 + 6)^{1/2}]. \quad (2)$$

A small computer program written by Dr. S. Stolte was used to calculate the value of $\Delta v/v_p$ as a function of S for the distribution of eq. (1), with Δv defined as the half width at half height of the velocity distribution. To derive the experimental value of $\Delta v/v_p$ as a function of S , corrections have to be made for the finite resolution of the velocity selector. These corrections were obtained numerically.

Velocity distribution measurements have been carried out for pure Ar and OCS beams and for 10% OCS - 90% Ar and 5% OCS - 95% Ar seeded beams at a backing pressure of 0.73 bar. For seeded beams the distributions have been measured for both compounds.

The values of $\Delta v/v_p$ (corrected for finite resolution), S and v_p for the various nozzle beams observed are given in table 1. From eq. (2) and the definition of α_s the translational temperatures were calculated.

From table 1, it is clear that the translational temperatures of OCS in the two seeded beams are equal within the experimental error and are considerably lower than in a pure OCS beam. Further, it is interesting that even a small admixture of OCS molecules in an argon beam drastically increases the translational temperatures of the argon atoms.

Table 1
Velocity distribution of pure argon and OCS beams and argon seeded OCS beams

	Pure argon	Pure OCS	10% OCS - 90% Ar		5% OCS - 95% Ar	
			OCS	Ar	OCS	Ar
$v_p(\text{m/s})^{\text{a)}}$	545	547	550	553	546	548
$\Delta v/v_p$	0.075	0.17	0.090	0.12	0.095	0.10
S	22 (2)	8.6 (9)	18 (2)	14 (1)	17 (2)	16 (2)
T_t (K)	1.5 (3)	14 (3)	3.4 (7)	3.7 (5)	3.7 (7)	2.8 (7)

^{a)} The experimental error in v_p is about 1.5%.

4. Determination of the rotational temperature

4.1. Theory

The rotational temperature of the OCS molecules has been determined from intensity measurements of electric resonance transitions in specific rotational states. We studied the $J = 1$ and $J = 2$ rotational states in the ground vibrational state and the $J = 1$ through $J = 5$ in the first excited bending vibrational state (01^10). In the ground vibrational state normal radio-frequency transitions of the type $\Delta J = 0$, $\Delta M_J = \pm 1$ were observed in an external electric field [11], in the bending state the zero field, $\Delta J = 0$, l -doubling transitions [12]. These were the only transitions for which an efficient state selection was possible at the maximum voltage available for the quadrupole state selectors.

Since all the transitions are of the type $\Delta J = 0$ the observed intensities are a measure of the population of the state. However, in order to derive the rotational temperature from the relative population measurements, efficiency of the state selection for the states in question has to be taken into account. This problem is discussed below.

By comparing the intensities of the two transitions in the ground vibrational states with the corresponding ones in the (01^10) state, we concluded that the effect of vibrational cooling was too small to be detected under the present experimental conditions (moderate p_{0d}). This conclusion applies both for a pure OCS beam and for the Ar seeded beams. Consequently, the measurements were concentrated on the (01^10) state since this allowed us to study five rotational states (instead of two).

The observed line intensity $I_l(J)$ in a rotational state J is given by

$$I_l(J) = I_{\text{tot}} f_F(J, T_1) f_J(T_1) f_v(T_v). \quad (3)$$

Herein I_{tot} represents the total beam intensity and $f_J(T_1)$ and $f_v(T_v)$ the population factors for the rotational and vibrational states, respectively, with corresponding rotational (T_1) and vibrational (T_v) temperatures. The quantity $f_F(J, T_1)$ stands for the efficiency of the quadrupole system in selecting a particular rotational state. This efficiency depends not only on the rotational quantum number, i.e., on the Stark effect, but also on the velocity distribution in the beam determined by T_1 .

Since the discussion is restricted to the rotational state distribution a normalized line intensity $\bar{I}_l(J) = I_l(J)/I_l(1)$ will be used. This intensity can be written as

$$\bar{I}_l(J) = \bar{f}_F(J, T_1) \bar{f}_J(T_1), \quad (4)$$

where $\bar{f}_F(J, T_1) = f_F(J, T_1)/f_F(1, T_1)$ and $\bar{f}_J(T_1) = f_J(T_1)/f_J(1, T_1)$. At thermal equilibrium the rotational population function $\bar{f}_J(T_1)$ is given by

$$\bar{f}_J(T_1) = \frac{1}{3}(2J + 1) \exp\left[-(hB/kT_1)[J(J + 1) - 2]\right], \quad (5)$$

with h as the Planck constant and B as the rotational constant.

Since the state selector efficiency depends also on the geometry of the apparatus one would prefer to determine $f_F(J, T_1)$ experimentally. Unfortunately, it is impossible to separate the product of $f_J(T_1)$ and $f_F(J, T_1)$ from the observed intensities $I_l(J)$. Also measurements with different mixture parameters and nozzle pressures will not solve this problem, because usually both $f_J(T_1)$ and $f_F(J, T_1)$ are affected by changes of the source conditions. However, the state selector efficiency $f_F(J, T_1)$ can be obtained numerically rather accurately from the equation

$$f_F(J, T_1) = \int \Omega_J(v) I(v) dv. \quad (6)$$

Herein $I(v)$ is the velocity distribution from eq. (1), which has been measured experimentally, and $\Omega_J(v)$ is defined as the transmission function of molecules with a velocity v in a specific quantum state J . The trajectory of a molecule entering the state selection system at a given angle, with a velocity v and in a state J was found by solving the equation of motion numerically [13]. A summation over the entrance angles of all possible trajectories through the molecular beam apparatus yields $\Omega_J(v)$. The function $\Omega_J(v)$ contains all the geometrical quantities of the spectrometer in a proper way. Furthermore by solving the equation of motion numerically the exact form of the Stark effect can be taken into account resulting in reliable results for $\Omega_J(v)$. Integration of eq. (6) over v yields $f_F(J, T_1)$.

The results of the calculations for the pure OCS beam and the two Ar seeded beams showed that the value of $\bar{f}_F(J, T_1)$ was about the same for each of the three beams. This can easily be understood from the

Table 2

Observed normalized line intensities $\bar{I}_l(J)$ and calculated normalized state selector efficiencies $\bar{f}_F(J, T_1)$ for the l -doubling transitions in rotational states $J = 2, 3, 4$ and 5

J	Normalized intensities $\bar{I}_l(J)^{a)}$			$\bar{f}_F(J, T_1)$
	pure OCS	10% OCS - 90% Ar	5% OCS - 95% Ar	
2	2.80	2.15	2.15	1.65
3	3.48	1.78	1.36	1.77
4	3.84	1.24	0.92	1.80
5	3.29	0.70	0.45	1.73

a) Total backing pressure 0.73 bar, nozzle diameter 60 μm .

fact that the most probable velocity of the OCS molecules was found to be practically the same in the various beams while the changes in the width of the velocity distributions were too small to have any influence upon $\bar{f}_F(J, T_1)$. The resulting values for $\bar{f}_F(J, T_1)$ are given in table 2. The errors in these quantities are $\pm 7\%$ due to estimated uncertainties in the trajectory calculations because of the fringe field effects.

4.2. Experiment

The intensities of the total OCS beam and of the line intensities of the $\Delta J = 0$ transitions in the $(01^1 0)$ vibrational state have been measured as a function of the total backing pressure. The measurements were performed with a pure OCS beam and with a seeded beam of 5% OCS-95% Ar. The results are depicted in fig. 1. It is seen from this figure that for a pure OCS beam both the slopes of the line intensity curves $I_l(J)$ and the pressures at which the maximum intensities were reached (p_{max}^J) are the same for the various rotational states. This indicates that the rotational temperature is well above 10 K.

It should be emphasized at this point that the bend over of the line intensity curves (fig. 1) is mainly a consequence of the rotational cooling in the beam and only partly (at pressures above 0.8 bar) of scattering of the molecules out of the beam. This conclusion is based on the total beam intensity curves which show a much less pronounced bend over behaviour.

Drastic rotational cooling is observed for the argon seeded OCS beams, demonstrated by the variation of $I_l(J)$ with J and the shift of p_{max}^J to lower pressures for increasing J . Moreover, the slopes of the line intensity curves are clearly larger than those of the total

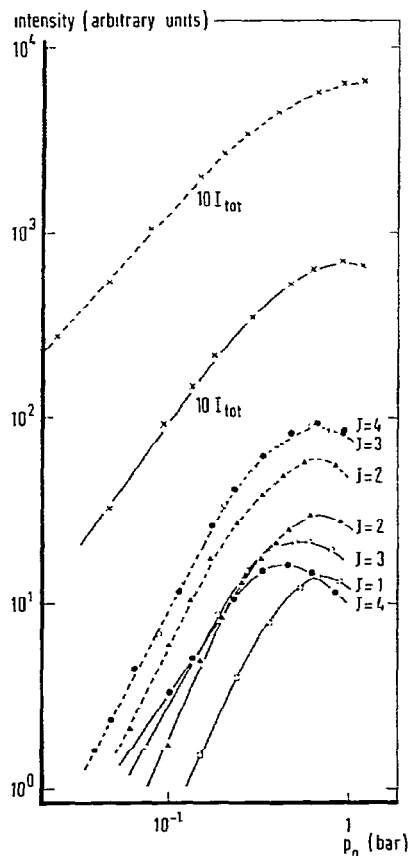


Fig. 1. Intensity versus total backing pressure for a pure OCS beam (dashed curves) and an argon seeded 5% OCS beam (solid lines). For clarity the total beam intensities (I_{tot}) are multiplied by 10. The observed line intensities are indicated by \square for $J = 1$, \triangle for $J = 2$, \circ for $J = 3$ and \bullet for $J = 4$.

beam intensities. This again is a consequence of the substantial rotational cooling in the seeded beams.

Quantitative measurements have been performed at $p_0 = 0.73$ bar. Because of the limited pumping capacity in the source chamber this is the maximum backing pressure at which scattering of molecules out of the beam is still negligible (see I_{tot} , fig. 1). The source chamber background pressure at $p_0 = 0.73$ bar was 2×10^{-4} mbar. The corresponding distance of the mach disk from the source was 75 mm [14]. Since the nozzle skimmer distance in the present experiment was only 15 mm the effect of background scattering and skimmer interference do not cause rotational state changes.

The observed normalized intensities, $\bar{I}_l(J)$, are given in table 2 for a pure OCS beam and two seeded beams of 10% OCS and 5% OCS with argon. Using eq. (4) the observed normalized intensities of table 2 and the computed values for $\bar{f}_F(J, T_r)$ we calculated the functions $\bar{f}_J(T_r)$. The results are plotted in fig. 2 together with the theoretical numbers derived from eq. (5) for several values of T_r . The errors indicated on the experimental values in fig. 2 are determined by uncertainties in both $\bar{f}_F(J, T_r)$ and $\bar{I}_l(J)$. The uncertainties in the latter quantity are based on the reproducibility of the measurements and on the signal to noise ratios of the spectral lines.

Fig. 2 demonstrates clearly that the rotational energy distribution of the OCS molecules both in a pure beam and in the argon seeded beams can be described by a Boltzmann distribution with an appropriate rotational temperature. Although the data plotted in fig. 2 suggest a somewhat lower rotational temperature for the mixture of 5% OCS with argon than for 10% OCS with argon the measurements do overlap within the experimental uncertainties. The final result for T_r is 14(4) K and 3.5(7) K for the pure and argon seeded OCS beams, respectively.

At a lower backing pressure $p_0 = 0.3$ bar the same method was used for a 5% OCS–95% Ar mixture. The rotational distribution in this case could again be described by a Boltzmann distribution with a slightly higher rotational temperature of 6.5 (1.5) K.

5. Discussion

The values for the rotational temperatures as determined from spectroscopic observations compare very

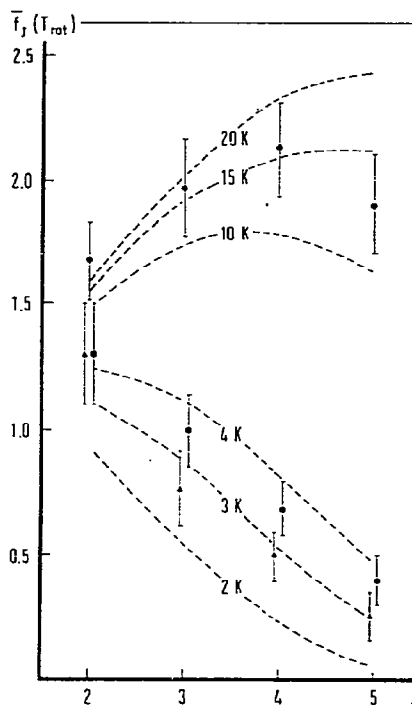


Fig. 2. Reduced rotational population function $\bar{f}_J(T_r)$ of OCS as observed in pure and seeded nozzle beams ($p_0 = 0.73$ bar, $d = 60 \mu\text{m}$) and calculated from eq. (4) for various values of T_r . Experimental points: \bullet pure OCS; \blacksquare 10% OCS – 90% Ar; \blacktriangle 5% OCS – 95% Ar. The dashed lines are drawn to form a visual guide to the calculated points.

well with the translational temperatures obtained from measured velocity distributions. This is found both for a pure OCS and for an argon seeded OCS nozzle beam. A similar agreement was found by Borkenhagen et al. [5] for a Xe seeded CsF beam.

The present results indicate a Boltzmann distribution of rotational levels at appropriate rotational temperatures for all OCS beams. This is in disagreement with the results of Kukolich et al. [4]. This is surprising since the source conditions in both experiments are comparable $p_0 d = 4.4 \times 10^{-2}$ bar mm and 2.0×10^{-2} bar mm in this work and that of Kukolich et al., respectively. On the basis of the dynamic similarity principle one would expect an identical behaviour. Furthermore effects of background scattering can be ruled out in our experiments as has been discussed in the previous section. Our results are obtained from intensity measurements of $\Delta J = 0$ transitions in five rotational states. This type of transition is a direct

measure for the population of a specific rotational state. Moreover, changes in transmission properties (i.e. state selection efficiencies) were carefully taken into account via computer calculations of molecular trajectories. Kukolich et al. were well aware of these changes and made a correction (for the "focusing effects"), apparently only for the $J = 2$ state. It is not clear how exactly the correction was obtained and to what extent the influence of the change in transmission properties due to the change in velocity distribution as a function of the backing pressure were taken into account. These uncertainties in combination with the fact that line intensities in the beam-maser experiment of Kukolich et al. depend on population differences between the rotational states, and not on the populations themselves as in the present experiment, might be the explanation of the discrepancy.

Borkenhagen et al. [5] also concluded that the rotational population distribution of CsF was thermal in a Xe seeded CsF beam.

The strong cooling of internal degrees of freedom that is obtained in a seeded beam will permit the spectroscopic study of large molecules and/or high temperature species. Since only a small fraction of the gas mixture used in a seeded beam consists of the molecule one wants to investigate spectroscopically, the MBER study of expensive and/or enriched isotopic species may become more accessible. The observed signal to noise (S/N) ratio in an MBER spectrometer is determined by the population of the specific rotational state and by the noise, which is in many applications proportional to the square root of the total beam intensity. From fig. 1 one expects then the same S/N ratio for corresponding transitions observed with a pure OCS and with an argon OCS beam. This was confirmed experimentally.

A gain in S/N ratio of the transitions originating in the lower rotational states will generally be achieved by using a seeded beam of a heavy molecule with an inert carrier gas rather than a pure nozzle beam. We performed some test measurements on the electric resonance spectrum in the $J = 1$ rotational state of CF_3H . An improvement of the S/N ratio for these transitions by a factor of four was obtained by using

a 5% CF_3H -95% Ar seeded beam instead of a pure CF_3H beam. The recent electric resonance studies performed in our laboratory on the heavy symmetric top molecules OPF_3 [7] and ClH_3CF_3 [8] have become possible only by the use of the seeded beam technique.

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