

## Gas dynamic flow and laser spectroscopy of molecules

P K Chakraborti

Bhabha Atomic Research Centre, M.D.R.S., Bombay-85

**Abstract :** A novel technique for overcoming the difficulties involved in high resolution gas phase spectroscopic studies of complex molecules is described. A desirable spectroscopic sample would be an ensemble of molecules, all in a particular well defined quantum state (usually the lowest energy state) travelling in free space with a narrow velocity distribution, and at a sufficiently low density so that intermolecular interactions are unimportant. A supersonic expansion of molecules in a monatomic carrier gas seems, to a large degree, satisfy the requirement of an ideal spectroscopic sample. Some applications of this technique to the study of both stable and unstable molecules and its usefulness in relation to laser isotope separation will be discussed.

### 1. Introduction

An extremely high level of occupancy of the low lying levels of complex heavy molecules makes them unattractive species for high resolution spectroscopic studies. The difficulties are very much aggravated with increasing number of atoms in the molecule and with increasing molecular weight. Theoretically the solution to this problem is to supercool the vapour to very low temperature without condensation and without losing vapour phase characteristics. Isolation of the molecules in an inert gas crystal lattice (Lewis and Kasha 1944, Robinson *et al* 1957, McClure 1954, Paine *et al* 1976) solve the problem only partially. This technique can not determine all the energy states of the free molecule, since the intermolecular interaction results in a loss of information on the rotation of the molecule, and the geometry of the molecule can become strongly distorted. Thus, it is necessary to have a more effective method of reducing the vibrational and rotational structure of the spectra.

Use of hydrodynamic flow source for high intensity molecular beams was first suggested in 1951 (Kantrowitz and Grey 1951). Since then great advances have been made in the design and operation of nozzle beam sources and they are adequately described in the literature (Anderson *et al* 1966, Pauly and Toennis 1968, Fluendy and Lawley 1973). In conventional molecular beam studies such sources are now routinely used (Parson *et al* 1972, Ng *et al* 1974, Vehmeyer *et al* 1976). Hydrodynamic source has also been used for studying unstable species e.g. van der Waals' complexes (Milne *et al* 1970, Golomb *et al* 1972, Gordon *et al* 1971, Van Deursen *et al* 1975, Vehmeyer *et al* 1976). The formation

of van der Waals complex in a nozzle beam is due to the extensive cooling produced in the jet. This well-known phenomenon of supercooling of gases and vapours in a supersonic stream and their use in spectroscopy was first suggested by Milne and Green (1969). The translational temperature as low as 0.03°K can be achieved in some cases through nozzle expansion. Polyatomic molecules seeded into this expanding jet communicate with this refrigeration media through binary collision causing considerable cooling of the different degrees of freedom. Free, collisionless flow is achieved very quickly, permitting the highly unstable cold species to survive for a period determined by the size of the apparatus. Three body collision leading to condensation is minimized due to the sudden nature of the cooling.

Over the last few years this technique of supersonic expansion has been used by a number of works for visible fluorescence studies (Smalley *et al* 1974, 1975, 1976, 1978), electronic absorption studies (Kataev 1976) and infra red absorption studies (Jensen *et al* 1976, Travis *et al* 1976, Miller 1977). In this account we will discuss some of the characteristics of a supersonic jet flow and also trace very briefly the progress of research in the application of supersonic beams and jets towards the solution of a number of problems in molecular optical spectroscopy and to illustrate the promise such experiments hold.

## 2. Cooling in supersonic beams and jets

A molecular beam source consists of a high-pressure gas reservoir, an orifice in the reservoir to allow the escape of gas, collimating apertures to shape the downstream flow pattern, and sufficient pumping speed to maintain low downstream pressure. If collimating apertures are absent and there is no attempt to control the downstream flow pattern, a supersonic source is called a free jet. For supersonic operation the source pressure must satisfy the condition  $D \gg \lambda_0$ , where  $D$  is the orifice diameter and  $\lambda_0$  stagnation mean free path.

The most important features of a hydrodynamic beam derive from the fact that the nozzle converts the random kinetic energy of the source gas into directed mass flow with velocity  $U$  and with a lower local gas temperature  $T$  (defined in terms of the width of the velocity distribution). Under adiabatic reversible flow condition (no shock waves, no shear forces, no heat source or sink and no heat conductivity) the expansion is isentropic. Conservation of energy along a flow stream-line require that at any point in the flow,

$$H_0 = H + \frac{1}{2}U^2 \quad (1)$$

where  $H = C_p T + \text{Const.}$  is the enthalpy per unit mass and the subscript 0 refer to stagnation condition in the source.

From this we derive

$$T/T_0 = \left[ 1 + \frac{\gamma-1}{2} M^2 \right]^{-1} \quad (2)$$

It therefore follows that cooling can be quite extensive, for example for a jet with  $M = 10$  and  $\gamma = 5/3$ ,  $T/T_0 = 3 \times 10^{-2}$ .

For continuous flow the Mach number dependence on distance from the nozzle (Ashkenas and Sharman 1966) is given by

$$M = A(X/D)^{\gamma-1} \quad (3)$$

where  $X$  is the distance from the nozzle and  $D$  is the nozzle diameter. The quantity  $A$  is a constant which depends on  $\gamma$  and is 3.26 for a monatomic gas.

There are practical limitations to the usefulness of equation (3) and to the extent of cooling that can be achieved. These are:

a) *Rarefaction.*

Binary collision rate decreases rapidly with progress of expansion and very soon the collision rate becomes too low to change the velocity distribution appreciably. Anderson and Fonn (1965) predict for the asymptotic terminal Mach number

$$\begin{aligned} M_T &= \text{Const.} (\lambda_0/D)^{\frac{1-\gamma}{\gamma}} \\ &= 133(P_0 D)^{0.4} \text{ (for argon)} \end{aligned} \quad (4)$$

where  $P_0$  is the stagnation pressure in atmosphere and  $D$  is the nozzle diameter in centimetres. Substitution of equation (4) in equation (2) gives for the terminal temperature for argon.

$$\frac{T_T}{T_0} = [1 + 5896(P_0 D)^{0.8}]^{-1} \quad (5)$$

Participation of the internal degrees of freedom of a polyatomic molecule slows down the cooling rate, thus expansion of pure polyatomic gas produces much higher terminal temperature. Polyatomic molecules must therefore be used in low concentration in a monatomic carrier gas to achieve lowest possible internal temperatures. In general we expect  $T_0 > T_{vib} > T_{rot} > T_{tr}$ .

b) *Pumping speed:*

Inadequate pumping speed or obstacles in the flow pattern can create standing shock waves which must be avoided if experiments are to be performed

on solid molecules. Campargue (Campargue *et al* 1976) discussed the limitations and important practical means of mitigating the effects of finite pumping speeds.

c) *Condensation* :

The condensation rate is very low in a fast expanding supersonic flow. Nevertheless, at some point in the flow the formation of dimers, polymers and eventually crystals and droplets will begin and this will limit the ultimate translational temperature attainable. In Figure 1 we present the measured intensity

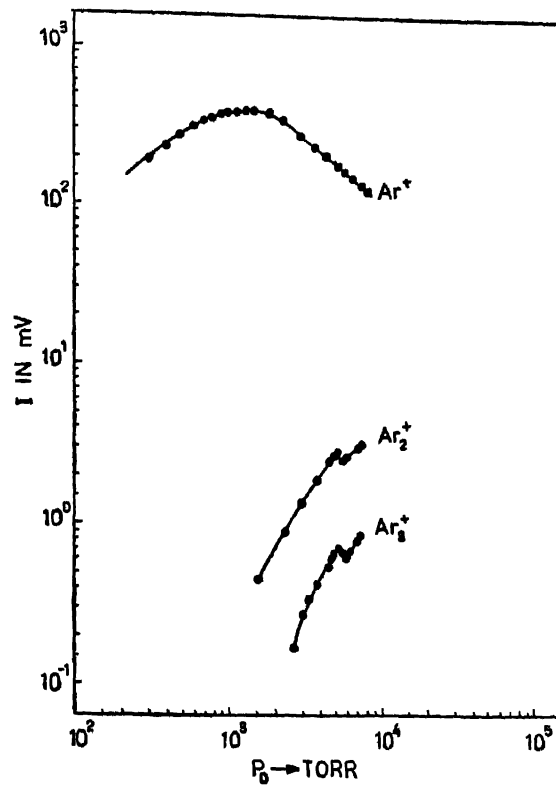


Figure 1. Intensity VS stagnation pressure at stagnation temperature,  $T_0 = 308^\circ\text{K}$ .

data for argon as obtained by the present author. It is observed that the monomer intensity passes through a peak. This is in conformity with the observations

made by other worker in the field (Leckenby *et al* 1964, Golomb *et al* 1970, 1972, Van Dourson *et al* 1974). Intensity decrease for the monatomic species could primarily be attributed to loss of particles due to condensation. However, additional loss of monomer particles from the collimated beam can be attributed to additional momentum gain from heat of condensation. Proper assignment of the detected signal is complicated by dissociative ionization of higher clusters in the ionizer of the detection system. Several workers (Van Deussen *et al* 1975, Vehmeyer *et al* 1976) have utilized the measured dimer collision cross section as a function of stagnation pressure and stagnation temperature to locate the initiation point for the formation of higher clusters. Figure 2 shows the data

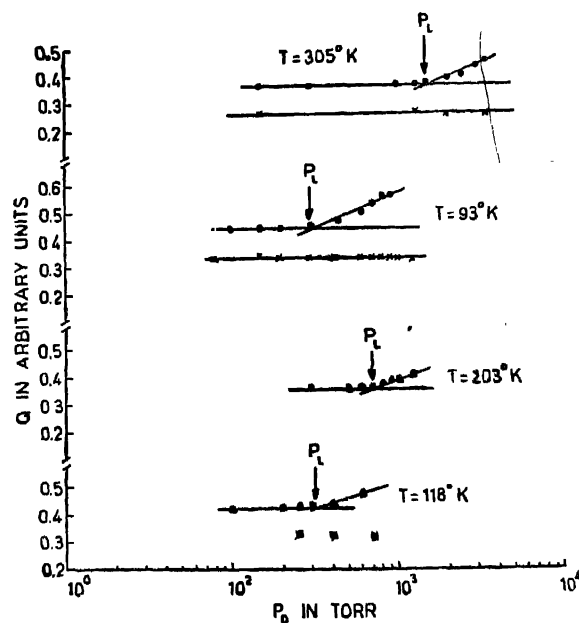
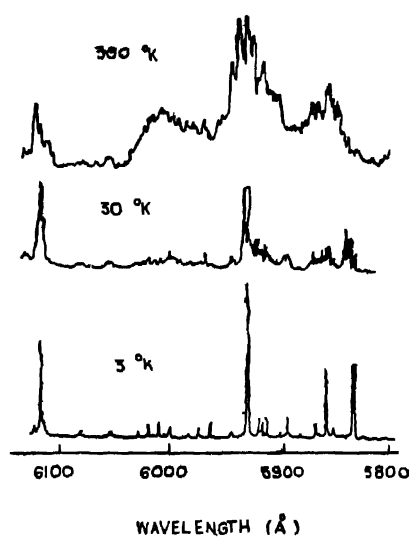


Figure 2. Total collision cross-section data (without velocity selection) for Ar<sub>2</sub>-Ne (●) and for Ar-Ne (×) as a function of stagnation pressure for different source temperatures. The limiting pressure  $P_L$  for each temperature is indicated by an arrow. (From Vehmeyer H *et al* 1976).

for argon dimers scattered by neon (Vehmeyer *et al* 1976). The points marked by  $P_L$  mark the beginning of the formation of clusters higher than dimers. The frequency of three body collisions necessary to initiate condensation depend upon the mass and interatomic potential of atoms in question. Condensation

is minimized by using lighter species e.g. He or H<sub>2</sub> in particular helium which has very weak intermolecular force. There is no bound He<sub>2</sub> molecule (Van Deursen and Reuss 1975), the formation of pure helium cluster requires at least four body collision for initiation, and thus the growth of such clusters is a very slow process. In fact, the growth of clusters of helium with molecules of spectroscopic interest is much faster than the growth of helium clusters. Such cluster formation is minimized by limiting the concentration of molecules to a low value.



**Figure 3.** A portion of the fluorescence excitation spectrum of NO<sub>2</sub> for (top) a conventional room temperature sample of pure NO<sub>2</sub> at 0.04 torr pressure, (middle) a supersonic beam of pure NO<sub>2</sub>, and (bottom) a supersonic beam of 5% NO<sub>2</sub> in Ar. All spectra were taken using a CW dye laser. Laser bandwidth was 0.5 Å for the lower two spectra. (From Smalley R E *et al* 1974).

Probability of binary collision is proportional to  $D/\lambda_0$  and that of trimayr collision is proportional to  $D/\lambda_0^2$ . The ratio of three body to two body collision is proportional to the number density of atoms  $n_0$ . Since the terminal temperature is a function of  $n_0 D$ , a fixed terminal temperature with minimum complex formation is achieved by decreasing  $n_0$  and increasing  $D$ , keeping  $n_0 D$  constant. Mass throughput is proportional to  $n_0 D^2$ , thus increasing nozzle diameter increases pump size.

### 3. Optical spectroscopy with supersonic beams and jets

The availability of tunable lasers along with the prospect of isolating supercooled molecules, complexes and free radicals in a jet or a beam has given a new momentum to molecular spectroscopists. It is now within our means to separate the individual vibronic bands and make proper rotational assignment of the bands even for the most complex molecules.

Isotopic features in the i.r. absorption spectra of complex molecules has clearly been resolved using flow cooled method. All these have fundamental importance as well as practical implications. Here we will project some selected optical studies carried out with supercooled beams and jets to demonstrate the capability of this technique.

#### a) Fluorescence studies :

Since 1974 Levy and Wharton group at Chicago has measured the visible fluorescence spectra of a number of molecules and complexes using supersonic jets and beams and a tunable CW dye laser. The system most thoroughly studied by them include molecules e.g., NO<sub>2</sub>, I<sub>2</sub>, S-tetrazine and their complexes with helium. As a typical example we have taken the case of NO<sub>2</sub> in the wavelength region 6700 to 5700 Å. The magnitude of simplification in the observed flow cooled spectra for NO<sub>2</sub> (Smalley *et al* 1974) is demonstrated in Figure 3. The peak detected fluorescence intensity is  $\sim 10^5$  photon/sec. In the seeded beam data vibronic bands are now clearly separated and the rotational structure appear to be dominated by a triplet. The ratio of intensity of the central member of a triplet to that of the other two components provide a measure of rotational temperature, and this gives a rotational temperature of  $3 \pm 1^\circ\text{K}$  for the seeded beam. Subsequently using a dilute mixture of NO<sub>2</sub> in helium at 100 atm. they were able to achieve a rotational temperature of  $0.7^\circ\text{K}$ . In the case of S-tetrazene a rotational temperature of  $0.5^\circ\text{K}$  was achieved and this permitted a complete analysis of the rotational structure.

#### b) Infrared Absorption :

Apart from basic interest in high resolution spectroscopy, absorption studies with supercooled molecules has practical implication in laser isotope separation. For any feasible model for laser isotope separation, the most fundamental requirement is the existence and identification of isolated isotopic spectral feature. Room temperature spectra of polyatomic molecules e.g. SF<sub>6</sub>, UF<sub>6</sub> etc. are very complex due to 'hot band' transitions. Supercooling the molecules in a supersonic flow can produce the desired spectroscopic result. Using a tunable diode laser and flow cooling, high resolution spectra of SF<sub>6</sub> and UF<sub>6</sub> molecules have

been reported (Jensen *et al* 1976, Travis *et al* 1976). In Figure 4 we have shown the room temperature spectra of the  $\nu_3$  band of  $\text{SF}_6$  which can be compared with

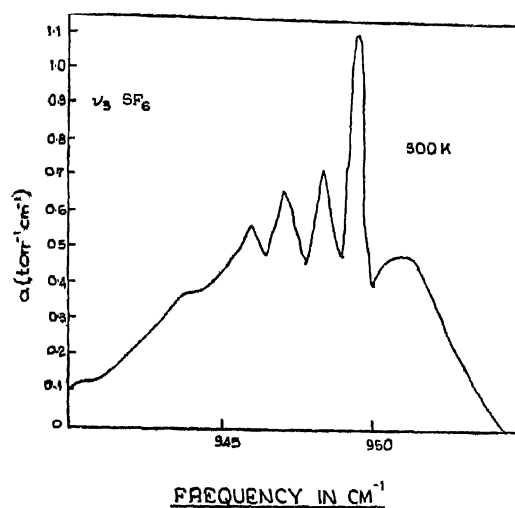


Figure 4. Infrared absorption spectrum of  $\text{SF}_6$  at room temperature. (From Jensen R. J. *et al* 1976).

the spectra of  $\text{SF}_6$  (Jensen *et al* 1976) in Figure 5 flow-cooled to  $\sim 55^\circ\text{K}$ . The cooling makes the Q-branch much sharper than the room temperature spectra, indicating the extent of reduction in the "hot-band" absorption from that at room temperature.

A composite high resolution  $\nu_3$ -band spectra of flow cooled  $\text{UF}_6$  (Jensen *et al* 1976) is shown in Figure 6. The isotope effects are very clearly resolved. This spectra may be compared with the corresponding room-temperature spectra Figure 7.

Supersonic flow and its relevance to high resolution laser spectroscopy has been clearly documented in the cited results.



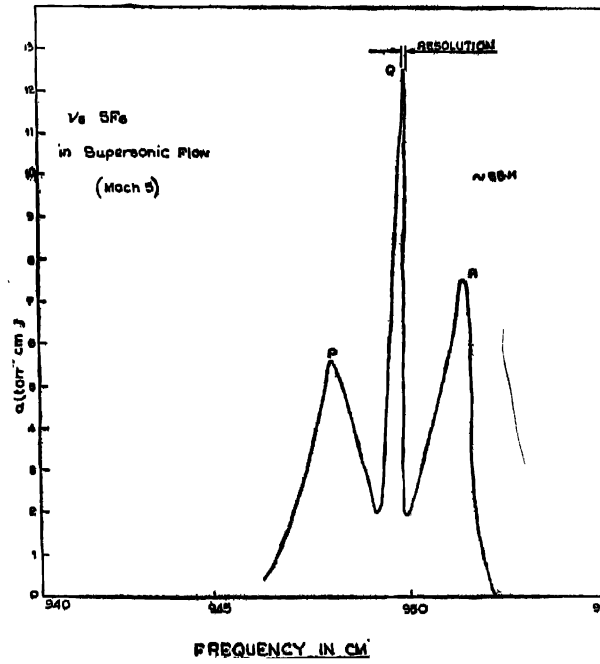


Figure 5. Spectrum of flow cooled  $\text{SF}_6$  (From Jensen R. J. *et al* 1976).

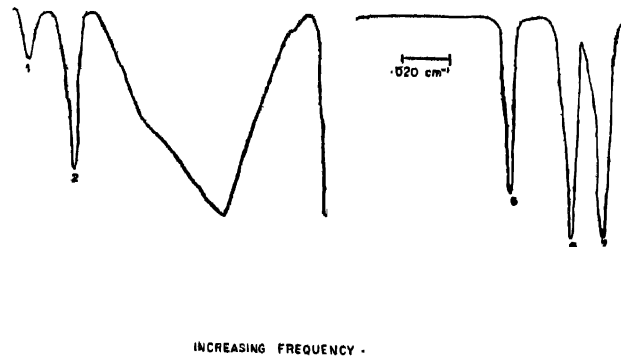


Figure 6. Composite spectrum of flow-cooled  $\text{UF}_6$  taken with tunable diode lasers. Peaks 2, 4 and 5 are *R*-branch lines of  $^{238}\text{UF}_6$ , peak 3 is the *Q* branch of  $^{238}\text{UF}_6$  and peaks 1, 6 and 7 are from reference gases. (From Jensen *et al* 1976).

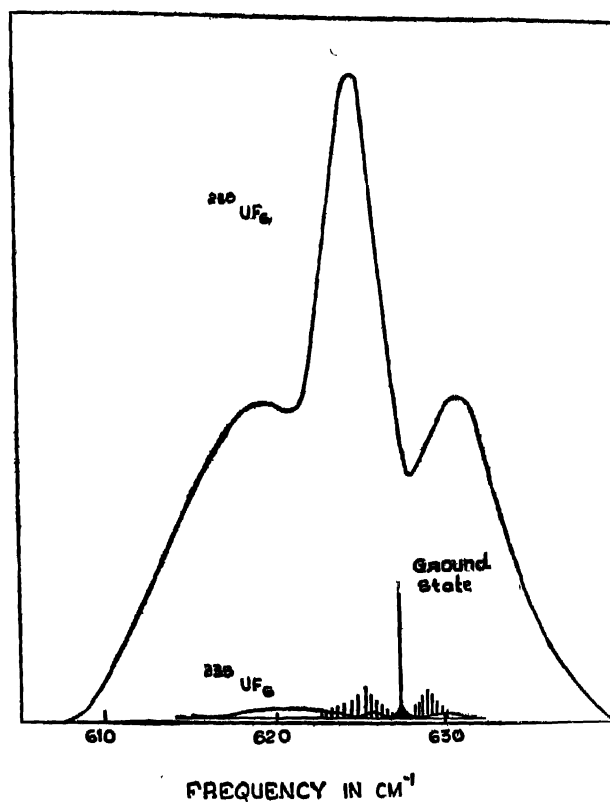


Figure 7. Spectrum of  $^{235}\text{UF}_6$  at room temperature with ground state PQR structure for  $\nu_3$  band, spectrum  $^{238}\text{UF}_6$  is shown at bottom for comparison.

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