

## Supersonic jet spectroscopy of floppy molecules

MIHIR CHOWDHURY\*, TAPAS CHAKRABORTY and  
TAPANENDU KUNDU

Department of Physical Chemistry, Indian Association for the Cultivation of Science,  
Jadavpur, Calcutta 700 032, India

**Abstract.** The application of supersonic jet spectroscopy to the study of low-frequency, large-amplitude, anharmonic motions in the excited states of floppy molecules has been discussed. In particular, our work on inversion and torsional vibrations of 9,10-dihydroanthracene and dihydrophenanthrene by laser-induced fluorescence excitation technique has been reviewed. The inversion of dihydroanthracene is nicely fitted with a quadratic Gaussian type potential function and the height of the barrier in the  $S_1$  state is calculated to be  $94\text{ cm}^{-1}$ . The inter-ring torsional frequencies of dihydrophenanthrene appear as a prominent progression and Frank-Condon analysis shows that the  $S_1$  state of the molecule is planar in contrast to a skew configuration in the ground state. A peculiar alternation of band gaps has been noticed.

**Keywords.** Supersonic jet; spectroscopy; floppy molecules.

### 1. Introduction

In flexible large molecules different kinds of large-amplitude intra-molecular motions may occur. The inversion of ammonia, torsional motion of methyl or phenyl groups, and photo-induced isomerisation are some examples of such motions. These are sometimes of chemical significance. The *cis-trans* isomerisation of stilbene or cyanide to isocyanide conversion are consequences of such large-amplitude vibrations and/or rotations. The potential energy curves of such low-frequency vibrations depend on and are very sensitive to the electron density distribution. This might give rise to different conformations in different electronic states. Similarly, the vibrations and librations present in different van der Waals complexes or solvated molecules are caused by a small force field. In still another context, low-frequency vibrations are important, namely in the case of radiationless transitions. According to the Fermi-Golden rule the transition rate depends on the square of the Frank-Condon (FC) factor and on the density of states. Because of the high probability of large differences in the shapes of the potential energy curve in different electronic states, the FC factor is usually large for torsional or librational motions. This property, coupled with a high value for the density of states, makes the low-frequency vibrations the ideal agents for bringing about internal conversions and intersystem crossings.

In view of the significance of the large-amplitude vibrations in chemistry and other radiationless processes, we decided to study these for a few selected interesting molecules. Normal condensed phase or vapour state spectroscopies, however, have

\*For correspondence

serious limitations. In condensed phase, such low force-field vibrations get drastically modified through interactions with other molecules; in addition, spectral bandwidths obliterate their signatures. In the vapour phase, on the other hand, the innumerable hot bands and their large torsional widths do not allow one to draw neat, unambiguous conclusions. Our objective, however, was achieved through supersonic expansion – a technique for preparation in the gas phase of isolated molecules having very low internal temperatures. The principle of cooling by supersonic expansion is discussed below.

## 2. Principle of supersonic expansion and our set-up

When a high-pressure carrier gas is expanded freely through a small orifice into vacuum, the jostling between molecules in the orifice and in the post-orifice region results in a low-temperature translational bath due to conversion of all random velocities to uniform directed translational motion. The final temperature may be calculated from the simple relation,

$$\frac{T}{T_0} = \left( \frac{P}{P_0} \right)^{(\gamma-1)/\gamma}$$

deduced on the assumption that the expansion is iso-entropic. At the same time, the mass flow velocity could exceed the local speed of sound giving a supersonic jet. The cold translational bath produced in this way acts as a refrigerant for other internal degrees of freedom of the seeded molecules of interest which have been carried along by the inert gas. As the expansion proceeds the density of the gas drops and eventually becomes too low to experience any further collision and redistribution of energies. Thus, the non-equilibrated vibrational and rotational temperatures of the isolated seeded molecules are frozen. The rotational and vibrational temperatures attained in the cold supersonic jet of isolated molecules are typically of the order of 10 and 30 K respectively.

Sample molecules in the cold jet may be studied in a number of ways, such as fluorescence, multi-photon ionisation etc. Our set-up records the fluorescence excitation spectrum and is shown in figure 1. The sample vapour is expanded into the vacuum chamber with helium or argon as carrier gas through the orifice (of 0.5 mm diameter) of a pulsed nozzle valve at a frequency of about 10 Hz. A home-made

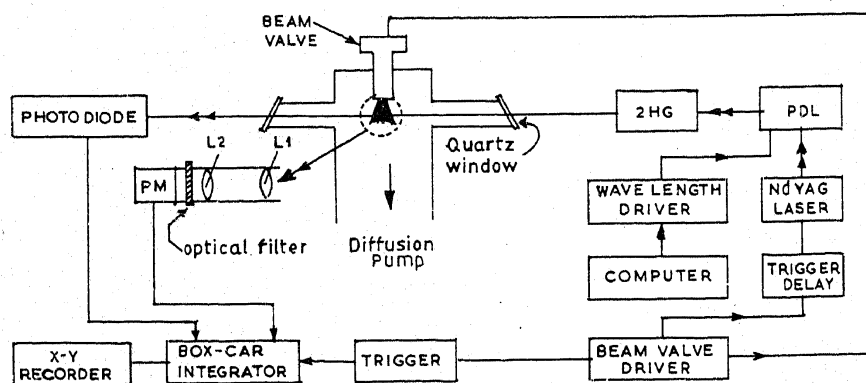


Figure 1. Supersonic jet experimental set-up.

valve gives a reasonably good performance, but the one supplied by the General Valve Corporation is more stable. The sample is taken inside the valve and, to increase the vapour pressure of the sample, it is heated to a temperature of 60–120°C according to requirement. When the valve is on, the background pressure of the vacuum chamber is maintained at less than  $10^{-4}$  torr by a Hind High Vac 6-inch oil diffusion pump backed by a mechanical rotary pump. The output of a dye laser, pumped by an Nd:YAG laser (Quanta Ray DCR 11) is frequency-doubled by a KDP crystal. The phase angle of the KDP crystal is tuned manually and is continuously monitored by an oscilloscope to maintain the intensity of the UV light to a fixed level. The second harmonic output excites the jet-cooled sample molecules at about 1 cm downstream of the nozzle orifice. The fluorescence is collected by a lens assembly and detected by an EMI 9781 R photomultiplier. The electrical output of the photomultiplier is averaged by a boxcar integrator (PAR model 64). The normalized output of the integrator is fed to an X-Y chart recorder.

### 3. Results and discussions

We shall discuss here two molecules with 'soft' modes. The molecule dihydroanthracene is expected to be non-planar with two potential minima with respect to butterfly motion around the central line joining the two methylene C atoms. We studied the potential minima and barrier height between the two minima in the excited electronic state ( $S_1$ ). Figure 2 shows the jet spectrum, which consists of many low-frequency bands over the 0-0 band at  $37217\text{ cm}^{-1}$ . The interesting point is that the spectrum lacks regularity although only one low-frequency mode is expected. The irregular spectrum may be fitted to a double-well potential expressed by

$$V(Q) = \frac{1}{2}\lambda Q^2 + A \exp(-a^2 Q^2),$$

where  $Q$  is the mass-adjusted coordinate, and  $\lambda$ ,  $A$  and  $a$  are empirically fitted parameters. Our spectral analysis gives a barrier height of  $94\text{ cm}^{-1}$  (Chakraborty

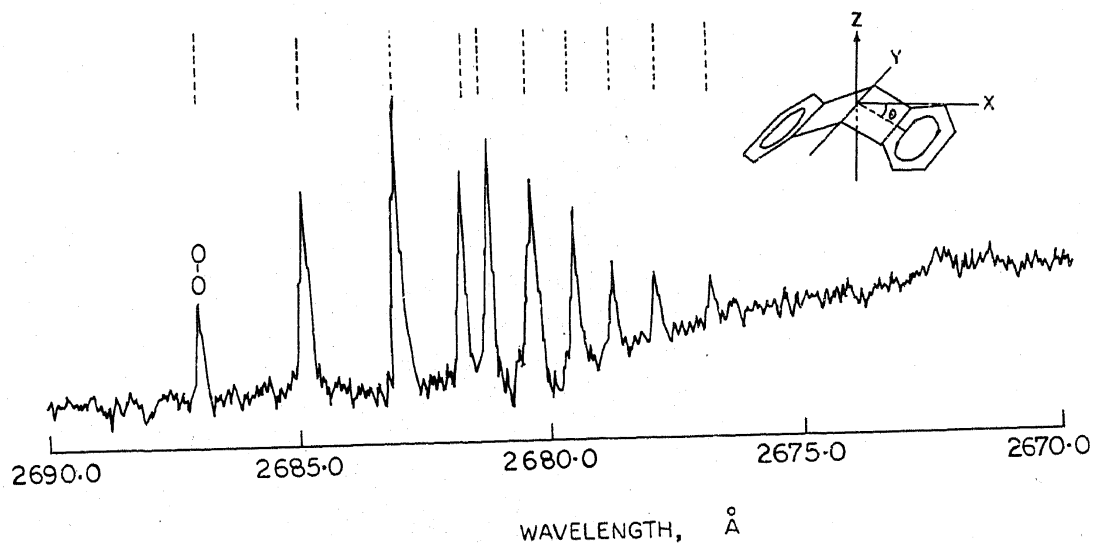


Figure 2. Fluorescence excitation spectrum of 9,10-dihydroanthracene.

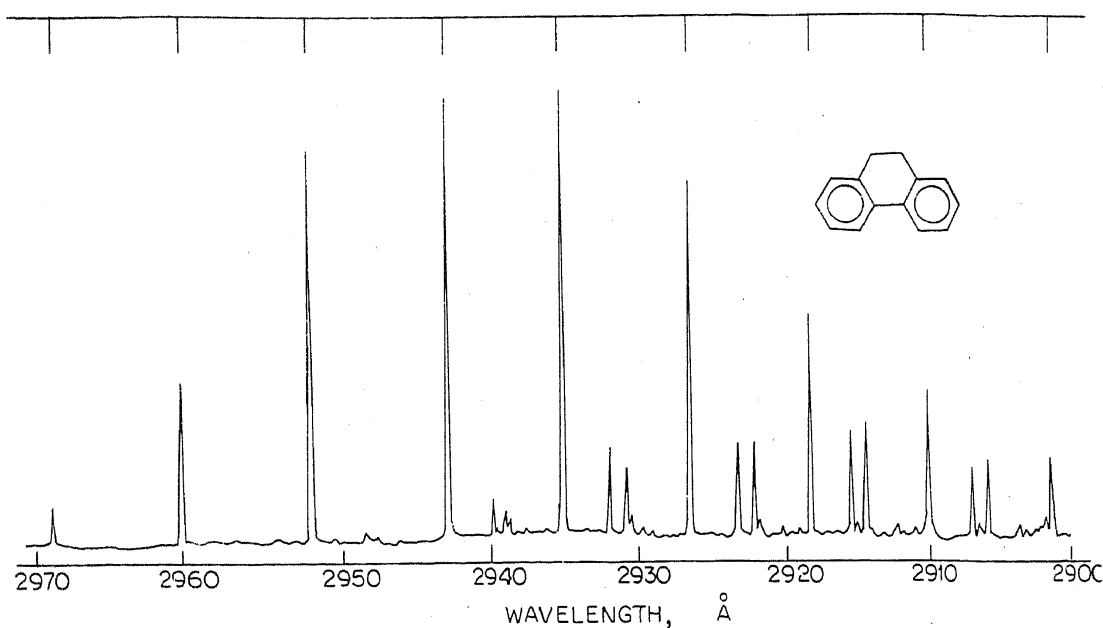


Figure 3. Fluorescence excitation spectrum of 9,10-dihydrophenanthrene.

and Chowdhury 1990). Recently, Lim and coworkers (Shin *et al* 1991) have confirmed the model proposed by us, but their reported barrier height, calculated on the basis of a similar but slightly different expression for potential, is a little lower,  $80 \text{ cm}^{-1}$ . They have additionally analysed the dispersed fluorescence spectrum from which they could determine the ground state barrier height =  $615 \text{ cm}^{-1}$ .

9,10-Dihydrophenanthrene has a completely different type of spectrum as shown in figure 3 (Chakraborty and Chowdhury 1991). The molecule may be considered as a biphenyl system whose amplitude of motion has been restricted by an attached chain. The case of biphenyl has been studied by a number of workers (Im and Bernstein 1988; Takei *et al* 1988). Like the derivative under discussion, the present molecule has a spectrum with very long progression. The 0-0 band of unsubstituted biphenyl is so weak that there is considerable uncertainty in its location. The restriction of free rotation caused by the methylene link introduces the following changes in the spectrum. (1) The 0-0 band becomes distinct, though not very strong. (2) The progression gets limited to ten bands instead of 15 in case of biphenyl (Im and Bernstein 1988). (3) The frequency of torsional motion increases to 97 from  $65 \text{ cm}^{-1}$  in free biphenyl. (4) The methylene-link, expected to destabilise the strained planar conformation and lead to a double-well, shows, however, from the spectrum that the excited state has a harmonic potential with minima corresponding to planar conformation. The mechanism by which the strain of the  $-\text{CH}_2-\text{CH}_2-$  chain is relieved could be shortening of the  $\phi-\phi$  bond length in the excited state. Indeed, a number of calculations conform to this speculation (Imamura and Hoffmann 1968). (5) Although the spectrum corresponds to a simple harmonic well, a peculiar alternation in level spacing has been noticed, which though small is very systematic. We presently favour the idea that this alternation in intervals of the harmonic oscillator is caused by a damped sinusoidal perturbation on the harmonic potential.

Finally, our studies offer an explanation for photo-induced racemisation in some chained biphenyl systems (Mislow and Gordon 1963). The transition from one

potential well to the other in the ground state is facilitated by light because the  $S_1$  state is planar; when the molecule returns to  $S_0$  from  $S_1$  it has an equal probability of getting trapped into either of the two wells, leading to racemisation.

#### 4. Concluding remarks

Although the barrier to potential wells in the ground electronic state has been determined in a number of cases through far IR and laser Raman studies, such barrier height determinations in the excited electronic state are few. The two cases discussed above illustrate the capability of jet spectroscopy in this regard. It may be noted that the effects on excitation are similar for both the molecules, namely the barrier height is reduced on excitation. The opposite is also possible and may be exemplified with octafluoronaphthalene as recently studied by us. The planar molecule undergoes an out-of-plane low-frequency vibration in the excited electronic state where the barrier height between the two equally probable out-of-plane conformations is less than the zero point energy. Similarly, there are cases where the barrier height prevents the interconversion of isomers in both electronic states. One such system, *p*-methoxy-styrene and its derivatives, has recently been studied by us.

The technique of fluorescence excitation discussed above, although powerful, cannot be applied to non-fluorescent molecules. The MPI-jet technique can be adopted for such molecules. Because of greater sensitivity, it is also useful in studying the two-photon spectrum. Additionally, the different species produced can be separately studied by combining mass spectrometry with MPI. We are currently in the process of setting up this apparatus. The proposed MPI experiments are likely to provide further insight into low-frequency vibrations.

#### Acknowledgement

We thank the Department of Science and Technology, Government of India, and the National Institute of Standards and Technology, Gaithersburg, USA, for providing funds which enabled us to carry out the jet experiments.

#### References

- Chakraborty T and Chowdhury M 1990 *Chem. Phys. Lett.* **171** 25
- Chakraborty T and Chowdhury M 1991 *Chem. Phys. Lett.* **177** 223
- Im H -S and Bernstein E R 1988 *J. Chem. Phys.* **88** 7337
- Imamura A and Hoffmann R 1968 *J. Am. Chem. Soc.* **90** 5379
- Mislow K and Gordon A J 1963 *J. Am. Chem. Soc.* **85** 3521
- Shin Y -D, Saigusa H, Zgierski M Z, Zerbetto F and Lim E C 1991 *J. Chem. Phys.* **94** 3511
- Takei Y, Yamaguchi T, Osamura Y, Fuke K and Kaya K 1988 *J. Phys. Chem.* **92** 577