Spectroscopy of molecules seeded in cold jet : study of conformers

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Conformers of two molecules, *sym*-hexahydropyrene (*s*-HHP) and tetrahydroisoquinoline (THIQ) have been investigated in seeded cold molecular beams by laser spectroscopic techniques. Observed fluorescence excitation, dispersed emission and two-colour hole-burning spectra are consistent with the geometries obtained through semi-empirical calculations.

Conformers originate when a set of atoms reorganize themselves. The primary requirement is, of course, the existence of multiple minima in the potential energy surface into which the set of atoms may be trapped. Chemical and spectroscopic methods are widely applied to investigate structure and dynamics of conformers. Difficulties, however, arise when (i) conformers are energetically and structurally very close and (ii) when barriers between the minima are very low, permitting rapid interconversion between conformers. For investigating rapidly interconverting and/or energetically close conformers, it is necessary to have enough time-resolution and/ or frequency-resolution of the spectroscopic tool used. Nuclear magnetic resonance[1], for example, has proved to be a very effective tool for conformational studies. It has an excellent frequency resolution, through which the structure of conformers can be determined, but at the best, a reasonable time resolution of the order of 10^{-7} s. Problems arise when the conformers interconvert within a time-period shorter than 10^{-7} s. The options are to slow down the interconversion by cooling the liquid medium and to increase the frequency of the NMR spectrometer. The first approach is limited by the freezing of the liquid medium and the second by the power of the electromagnet employed. A simple rule of the thumb[2] is that conformers separated by a barrier less than 8 kcal mol^{-1} at room temperature can not be distinguished by NMR.

Technique employed in the present study :

Cooling by supersonic jet : In the last two decades a simple method of cooling the vapors, known as supersonic jet cooling[3], has become highly popular, and coupled with microwave and/or laser spectroscopy[4,5], it has become a very effective tool for investigating rapidly interconverting, near-isoenergetic conformers. It consists of mixing the vapor of the desired substance with an inert gas, and the mixture kept at high pressure (1–7 atm.) is allowed to rush through a tiny hole (size ~0.1–0.5 mm) into high vacuum (~10^{-5} torr)[5]. As the rare gas molecules with random velocities (in direction and in magnitude) come out through the tiny hole jostling against each other, their velocities get equalized in both direction and magnitude till they travel upto ~0.5 cm down from the tiny hole, at which point the collision ceases, and in consequence, further velocity reorganisation stops. In as much as translational temperature is an index of randomness of velocities, the translational temperature of the streaming gas becomes very low (<1 K). The non-equilibrium vibrational or rotational temperature of the seeded molecule also gets very low. By this process a rotational temperature of 10 K and a vibrational temperature of ~30 K is often attained by the collisionless, uniformly moving stream of molecules. The different conformations that exist in the high temperature gas get frozen in the collisionless stream. Low temperature prevents interconversion between conformers if the barrier is reasonably high. In the collisionless cold jet, not only are the conformers of the bare molecule stabilized, new adducts are also formed by loose attachment of two or more molecules and stabilized in their various conformations.

Spectroscopy of the conformers cooled in the jet : The original molecule or its adduct with rare gas or other molecules, or itself, can be studied *in situ* by interrogating the molecular stream with a laser beam of tunable frequency, preferably at right angles, for thereby the Doppler broadening can be largely avoided. The width of the absorption band in the laser excitation spectrum becomes less than 1 cm^{-1} – sufficient for distinguishing conformers' electronic origin transitions or vibronic bands. The laser excitation spectrum consists of absorption bands of all conformers or species. It is necessary to separate the absorption spectrum of each conformer. This is commonly done by two-colour experiments[7,8]. If two of the observed bands have the same ground

state, and the pump beam 1 fixed on one of the bands depopulates the common ground state, the fluorescence caused by probe beam 2 fixed on the other band decreases in intensity when the pump beam is on. Thus it is possible to identify bands of the same conformer by pump-probe hole-burning experiment. Once we know which absorption band corresponds to which conformer, it is further possible to obtain the emission spectrum of each conformer, or even of each level of the conformer, by fixing the exciting light on a particular band and scanning the emission by means of a monochromator. The resolution of single vibronic level luminescence spectra obtained in this way is limited by the resolution of the monochromator. Various multi-colour experiments[9] have been proposed to improve the resolution of single vibronic level (SVL) luminescence.

Results

In order to illustrate the power of jet spectroscopy, we shall discuss here two typical examples from our own work.

Hexahydropyrene (HHP) :

Basically HHP is a derivative of naphthalene. The fluorescence excitation spectrum of naphthalene and HHP are compared in Fig. 1. It may be noticed that in HHP there are
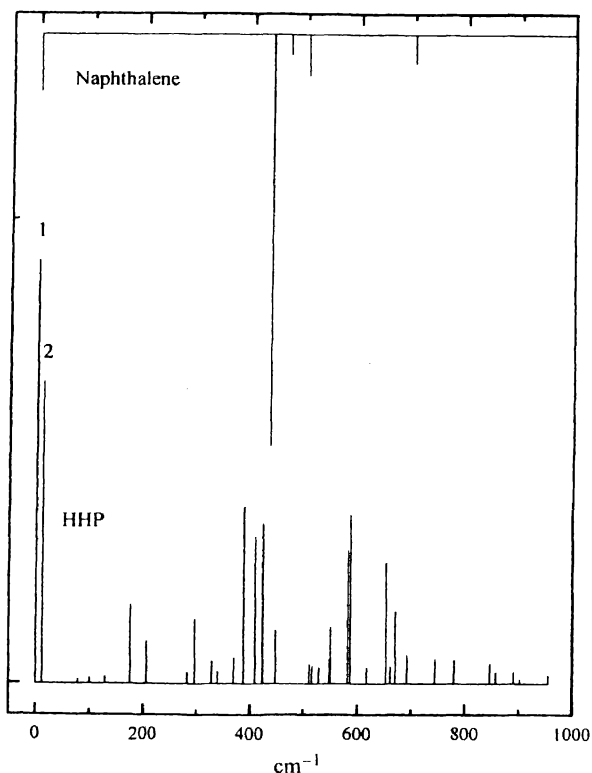
additional low-frequency bands, which are absent in naphthalene[10]. These may, therefore, reasonably be ascribed to vibrations of the methylenic chain. The second point to note is that at the origin of the series of vibronic bands in the HHP[11] spectrum there lies a doublet 12 cm^{-1} apart (unlike the naphthalene case), the nature of which needs to be ascertained. Apparently it has to be associated with the connecting methylene chain – either with its vibrations, or with its equilibrium configurations such as boat and chair forms. Had one of the two been a 0-0 band and the other a vibronic band of the same conformer, their ground state populations would have been same and the difference in intensity of the two bands could only be ascribed to a difference in transition probability to the two levels of the excited state. In such a case, when the stronger band gets saturated on increasing the laser power, the weaker one does not. On increasing the laser power further, the weaker one only should continue to grow[12]. However, this is not what is observed; the two bands reach saturation together, and the ratio of two intensities remains the same when the laser power is varied. We conclude that the second of the doublet bands can not arise from a vibration. This is corroborated by S_0 frequency calculation through MOPAC-AM1 where the lowest vibration frequency was found to be 78 cm^{-1}. A second possibility could be that both are vibronic bands, but one is hot and the other cold. This is also negated by the observations already stated, and additionally by changing the temperature of the cold beam – an action which does not affect the intensity ratio of the two bands. We, therefore, associate the two observed 0-0 bands to two different equilibrium conformations of the methylenic chain, chair and boat. The question, however, remains – which band is due to which conformer? We have carried out theoretical calculations in order to decide this point. Optimization of ground state geometry for boat and chair forms was done by semi-empirical AM1 Hamiltonian through MOPAC (version 5.0). The energies calculated using semi-empirical methods (AM1, MM2) and *ab initio* (6–31 G basis) starting from different initial geometries indicate that the boat form is stabler than the chair form by a number which varies from 2 to 6 cm^{-1}, depending on the method applied. The barrier between the two forms is found to be about 1600 cm^{-1} (~4.7 kcal mol^{-1}) in the ground S_0 state but about 1200 cm^{-1} in the S_1 state. These values are qualitatively consistent with our jet spectrum. The analysis of the SVL spectrum is another important tool to assign the conformers. Vibronic bands at an interval of 200 cm^{-1} are present in SVL's and in the fluorescence excitation spectrum. These out-of-plane modes are getting allowed because of the nonplanarity in the saturated chain (at C_2 and C_7) of the two conformers. AM1 calculation shows

that in both conformers there are two out-of-plane modes of vibration of frequencies at about 180 and 200 cm^{-1}, respectively. Although the two forms do not differ in vibrational frequencies, they differ in one important respect – in the symmetry groups and in the symmetry representations to which the modes belong. The details of selection rules have been worked out elsewhere[11]. The former mode (180 cm^{-1}) is allowed in the boat form and the latter (200 cm^{-1}) in the chair form. This distinguishing feature can be utilized to identify the conformers. It might be noticed in Fig. 2 that
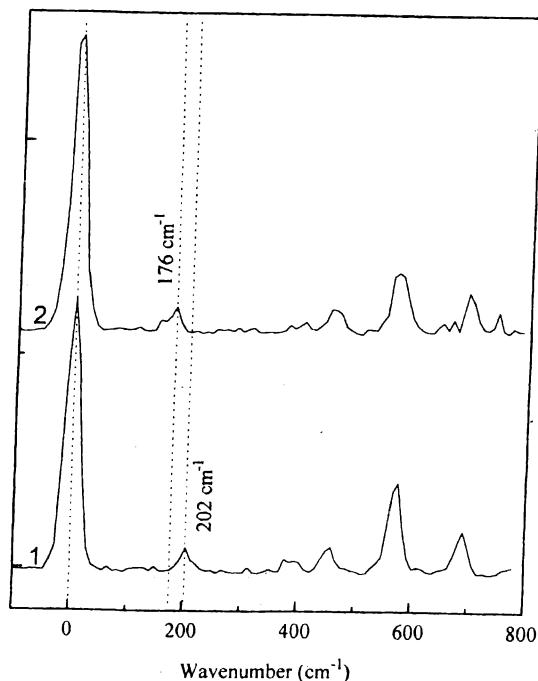

Fig. 2. A comparison of dispersed fluorescence spectra of HHP when excited at origin band 1 and at origin band 2.

SVL of band 1 bear the signature of the chair form, namely, that the frequency interval between the origin band and the weak band is greater than 200 cm^{-1}. On the other hand, the SVL of band 2 bear the signature of the boat form, with the said interval being only 180 cm^{-1}. We conclude, therefore, that band 1 belongs to the chair form and band 2 to the boat form. This conclusion is tentative and needs to be verified by hole burning experiment.

Tetrahydroisoquinoline (THIQ) :

The second molecule we would like to discuss is THIQ[13] which can exist in a number of symmetry-inequivalent conformations. Four conformers of this molecule – two bent and two twisted – are formed by out-of-plane puckering of adjacent carbon and nitrogen atoms of the saturated chain. All four conformers of THIQ are inequivalent and hence,

all of them, in principle, can leave signatures in the spectrum under favourable conditions. Fig. 3, the FE excitation spectrum of THIQ, shows that while the origin band 1 appears as a singlet at 36781 cm^{-1}, three close-lying bands 2, 3 and 4 appear clustered at 92, 98 and 103 cm^{-1} on the blue side of the band origin. All the three bands could not be assigned as vibronic bands of the molecule in the excited S_1 state. Theoretical calculations for the ground state have been performed with MOPAC-AM1 Hamiltonian. The results show that only two such low-frequency modes exist close to 100 cm^{-1}. We suspected, therefore, at least one of the three clustered bands ought to be an origin transition of a different conformer. We measured their response to the variation of laser intensity following Levy *et al.*'s' prescription for conformer identification[12] – a technique that has also been successfully used by Topp *et al.*[14] for the same purpose. The principle of the method has already been explained in the previous section. Had the band 4 been a vibronic feature over the origin band 1, the rate of increase of intensity with laser power for bands 1 and 4 would have been different; but this is not what is observed. So, we conclude that the two bands 1 and 4 in the FE spectra arise from different conformers.
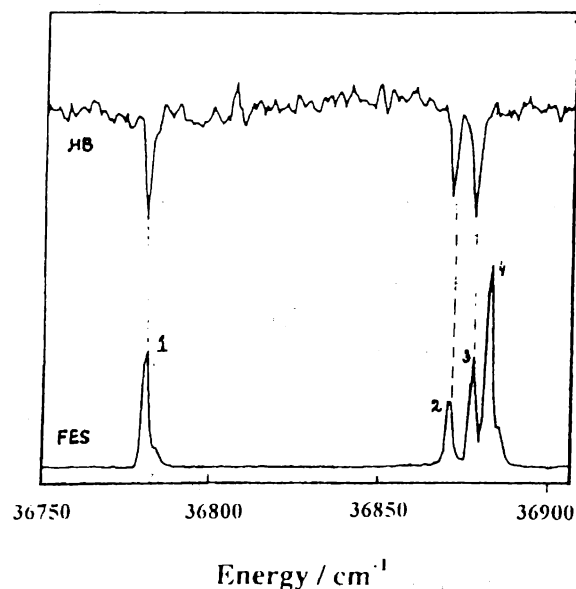

Fig. 3. Fluorescence excitation spectrum (FES) of jet-cooled THIQ, combined with the hole burning (HB) spectrum, when probe laser is fixed at band 1.

Further experimental confirmation came from dispersed emission spectra corresponding to excitations at these two bands. Small *et al.*[15] and Pratt *et al.*[16] argued that 0-0 SVL's should have a strong origin in the emission spectra relative

to the vibronic manifold. This test confirms our suspicion, that bands 1 and 4 are origin bands corresponding to two different conformers.

Finally, we have carried out UV-UV hole-burning experiment. One laser, say of the same frequency as band 1, excites the molecules and the resulting fluorescence is sensed. A second laser (called pump laser) scans the frequency region of bands 2, 3, 4. When the pump laser frequency corresponds to bands 2 or 3, a dip occurs in the luminescence resulting from excitation of molecules by probe laser. This shows that bands 2 and 3 are indeed vibronic bands of the origin band 1. However, no dip was found when the pump laser is at the frequency corresponding to the band 4. The relationship is reciprocal. This is, when the probe laser is fixed at the frequency of the band 4 and the pump laser at the frequency of band 1, no dip is observed. Thus, it follows that bands 4 and 1 belong to different conformers.

The question remains – what are the structures of the two conformers? From MOPAC-AM1 calculations we have found that two lowest energy conformers corresponding to twisted axial hydrogen (TA) and twisted equatorial hydrogen (TE) forms, TA being stabler than TE by a number varying between 0.33 and 3.3 kcal mol^{-1}, depending on the method employed for calculation. From the observed area under the peaks of 0-0 bands we estimate the difference in energy to be 0.86 kcal mol^{-1}. Calculations further show that the 0-0 band of the equatorial form should appear 145 cm^{-1} to the red of that of the TA form. The experimental number is 103 cm^{-1}. On the basis of these calculations we assign the 0-0 band at 36781 cm^{-1} to the TE form and that at 36884 cm^{-1} to the stabler TA form.

Concluding remarks :

The two examples of jet spectroscopic studies of conformers show that the structure-spectra correlation can indeed be fine-tuned and extended to conformers. The difference in frequency of absorption between two conformers is small – but nevertheless, measurable. Spectral signature of each conformer can be obtained through different types of jet spectroscopies. The water cluster formation capabilities of different conformers are different and need to be investigated in depth. It may also be mentioned that recently interesting studies on the difference in geometries of LE (locally excited) and the CT (charge-transfer) states of naphthalene clusters have been carried out by Das et al.[17].

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