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Some spectroscopic studies on cold isolated molecules

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Abstract. Cold isolated molecules produced in seeded supersonic jets are ideal systems for obtaining information on the nature of potential energy surfaces of excited states. The power of the technique is illustrated with examples of molecules having one or two out-of-plane low-frequency vibrations.

Keywords. Cold isolated molecules; seeded supersonic jets; potential energy surfaces; molecular conformation.

Introduction

The purpose of this overview is to draw attention to the need for spectroscopy of isolated molecules. Although the condensed phase at room temperature is our most favourite medium for carrying out chemical transformation, it is not necessarily the best system for obtaining molecular information. Random interactions between similar (solute–solute) or dissimilar (solute–solvent) molecules and simultaneous population of a number of levels at room temperature interfere seriously with our efforts for obtaining neat molecular information and drawing unambiguous conclusions. An isolated molecule in a definite level is what a molecular scientist aspires for. Fortunately, one can produce such isolated molecules in the lowest vibronic state in a fairly easy manner. If a gas is passed through a small orifice from a high pressure to a low pressure ($\sim 10^{-5}$ torr), the translational temperature of the gas drops down to about 1 K due to rapid isentropic expansion. A microscopic picture might help one to understand this cooling process. Temperature is essentially the average random kinetic energy. It is necessary to emphasize the word 'random', for uniformly directed kinetic energy, as present in, for example, the molecules of a gas bag within a speeding rocket, does not contribute to temperature. In other words, temperature is proportional to the width of the velocity distribution of an assembly of molecules. Before expansion through the orifice, the molecular velocities vary in direction and magnitude as per the Maxwell distribution law. However, after the expansion, the velocities are directed, specially so if one chooses a subgroup of molecules crossing a small opening (skimmer) downstream. The jostling between the molecules as they come out through a small hole causes exchange of velocities making their velocity-amplitudes also equal. Thus the translational temperature drops down to about 1 K or less. If now the chemically inert carrier gas (He, Ar etc.) contains other seeded

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molecules, the various types of energies of these guest molecules try to equilibrate with that of the host carrier gas. Partial exchange of translational and rotational/vibrational energies produces non-equilibrium rotational and vibrational temperatures. Typically, rotational temperatures of the order of 10 K and vibrational temperatures of the order of 30 K may be attained. However, the actual non-equilibrium temperature depends upon the seeded molecule as well as on the condition of the jet. The cooling effect takes place not only during the passage through the hole, but also in regions immediately following the hole. However, at an approximate distance about 10 times the diameter of the hole, the molecules become isolated and no collision or further cooling occurs. Such an assembly of frozen isolated molecules about 1 cm downstream from the orifice is frequently employed for carrying out spectroscopy of various types, such as fluorescence excitation, single vibronic level luminescence, multiphoton ionisation, mass spectrometry, microwave and IR absorption. Here we would like to illustrate the power of jet-fluorescence spectroscopy in providing information on low-frequency, large-amplitude potential energy surfaces of fairly large molecules; the examples will be chosen from our own previous and recent studies (Chakraborty and Chowdhury 1993).

Some results and brief discussion

Although in aromatic organic molecules of moderate size a large number of vibrations are possible, most of the vibrations are of high frequency. Occasionally, however, there occurs one (or two) out-of-plane low-frequency, large-amplitude vibrations. These vibrations hardly interact with the high frequency vibrations of the aromatic part because of the large difference in their energies, and can indeed be treated separately. The molecule dihydroanthracene may be used to illustrate the point. This molecule is not planar, but bent around the bond joining the two CH_2 groups. By the symmetry of the problem there are two equivalent minimum-energy bent structures while the planar form is of higher energy. The butterfly motion converting one bent conformation into its mirror image may be treated separately from all other vibrations.

The model one-dimensional potential for such a case is simply a double-minima curve with a barrier in between the minima. Such a potential can be mathematically represented in many ways, one common form being AZ^4-BZ^2 where B/A represents the barrier height. Whatever be the mathematical approach, the solutions are of the following nature. If the barrier height is high and the energy of the level considered is much below the barrier height, the two levels arising from the two equivalent potential wells are degenerate. As long as the level energies are below the barrier, the separations between degenerate pair of levels are nearly though not exactly harmonic. The anharmonicity is due to the asymmetric shape of each well. The effect of this anharmonicity is to decrease the level spacings slightly, as shown in figure 1a. The molecule that illustrates such behaviour is dihydronaphthalene (Chakraborty and Chowdhury 1992a). The case of the small barrier is interesting. Near the top of the barrier the levels start splitting, the magnitude increasing progressively (figure 1b). In the region slightly below and above the barrier the level spacings vary considerably. In fact, this irregularity is a clear signature of a double minima well with a low barrier. The separations of vibronic levels representing the butterfly motion in dihydroanthracene are irregular. The low-frequency (less than 150 cm^{-1}) fluorescence

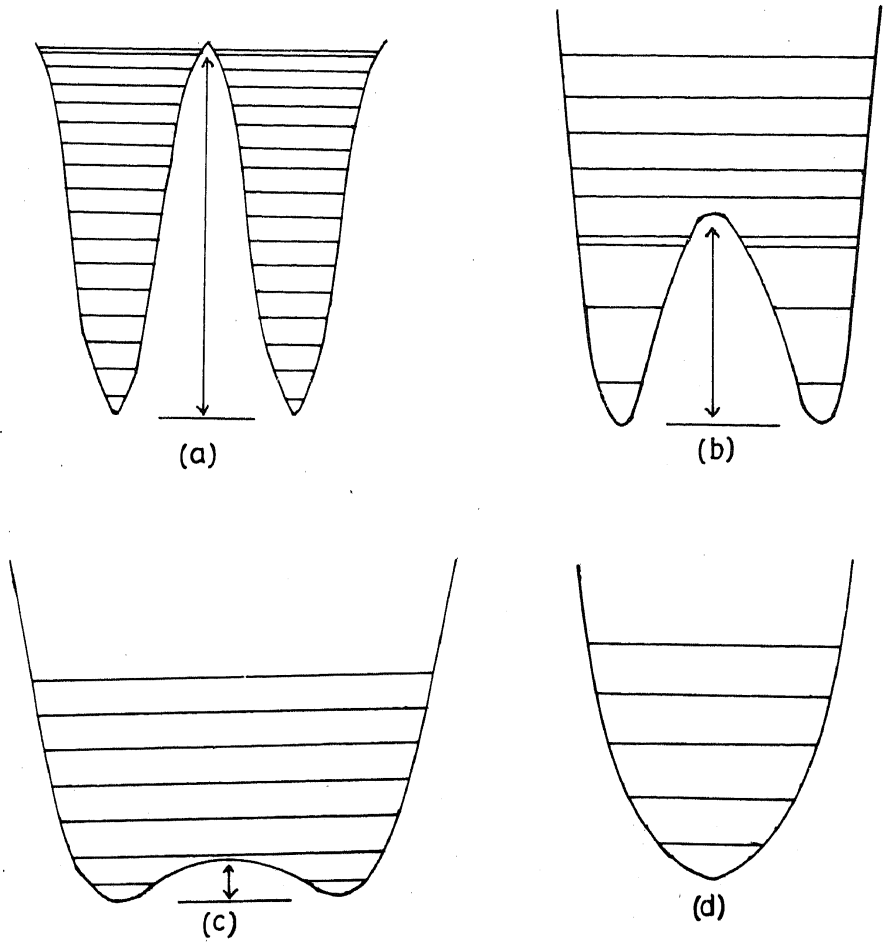

Figure 1. Energy levels of double-well potentials with barriers of various heights: barrier $\gg h\nu$ (**a**), $\approx 3h\nu$ (**b**), $\approx h\nu$ (**c**), $= 0$ (**d**).

excitation spectrum (S_0–S_1) of this molecule fits with a double-minima potential model having a barrier of 94 cm^{-1} in the S_1 state (Chakraborty and Chowdhury 1990). The model has been confirmed by Shin *et al* (1991) who found a slightly lower barrier of 84 cm^{-1} for the S_1 state. Similarly, the barrier for the S_0 state was 615 cm^{-1} from analysis of the dispersed fluorescence spectra originating from each of the single vibronic levels (Shin *et al* 1991). An interesting situation occurs when the barrier exists but is close or below the zero-point energy. In such cases, a negative anharmonicity usually results (figure 1c). The molecule octafluoronaphthalene exhibits such negatively anharmonic series of levels (Chakraborty *et al* 1992). If the barrier totally disappears, then of course, the levels become harmonic as expected (figure 1d). Examples are dihydrophenanthrene and xanthene (Chakraborty and Chowdhury 1991; Guchhait *et al* 1992). We may point out here the interesting consequences of replacing one CH_2-group of DHA by one O-atom. The O-atom allows π-conjugation through it and thus the planar structure gets stabilised. The DHA has a barrier of 94 cm^{-1} separating the double minima but for xanthene the barrier is zero and the vibronic level separations are uniform.

The situation gets a bit more complicated when two or more low-frequency vibrations occur (Chakraborty and Chowdhury 1992b). These vibrations may interact amongst themselves. A commonly used mathematical expression for a two-dimen-

sional potential energy surface is $AZ_1^4 + BZ_1^2 + CZ_2^4 + DZ_2^2 + EZ_1^2Z_2^2$. Depending on the relative values of the parameters, different types of potential energy surfaces and, hence, different types of energy level patterns result. One particular case is when Z_1 and Z_2 are equivalent. The contour diagram consists of a central hill with a valley going all round it. If the valley is a flat one i.e. without any barrier, pseudorotation results (figure 2a). If one takes a cut of the potential energy surface in any direction a double minima well results, and this may be treated as a one-dimensional 'radial' PEC whose level separations have already been discussed. The angular motion in Z_1–Z_2 space around the valley will result in levels of very small spacings; the spacings increase with increasing quantum number. Such pseudorotational levels for the S_0 state of cyclopentane and other five-membered ring derivatives have been discussed in detail (Laane *et al* 1972). However, if the two motions are not equivalent, the hindrance to pseudorotation increases (figure 2b) and separation to two independent variables, r and ϕ, is no longer possible. In such cases, appropriate two-dimensional treatment is needed. Some potential energy surfaces are shown in figure 2.

Recently we have investigated the vibronic structure of the S_0–S_1 transition of tetrahydronaphthalene (THN) (Guchhait *et al* 1994a). The benzene-ring vibrations are all of the high-frequency type; the low-frequency vibrations result from the out-of-plane puckering motion of the C_2 and C_3 carbon atoms. By coupling the two motions, twisting and bending vibrations are possible (Rivera-Gaines *et al* 1991). As

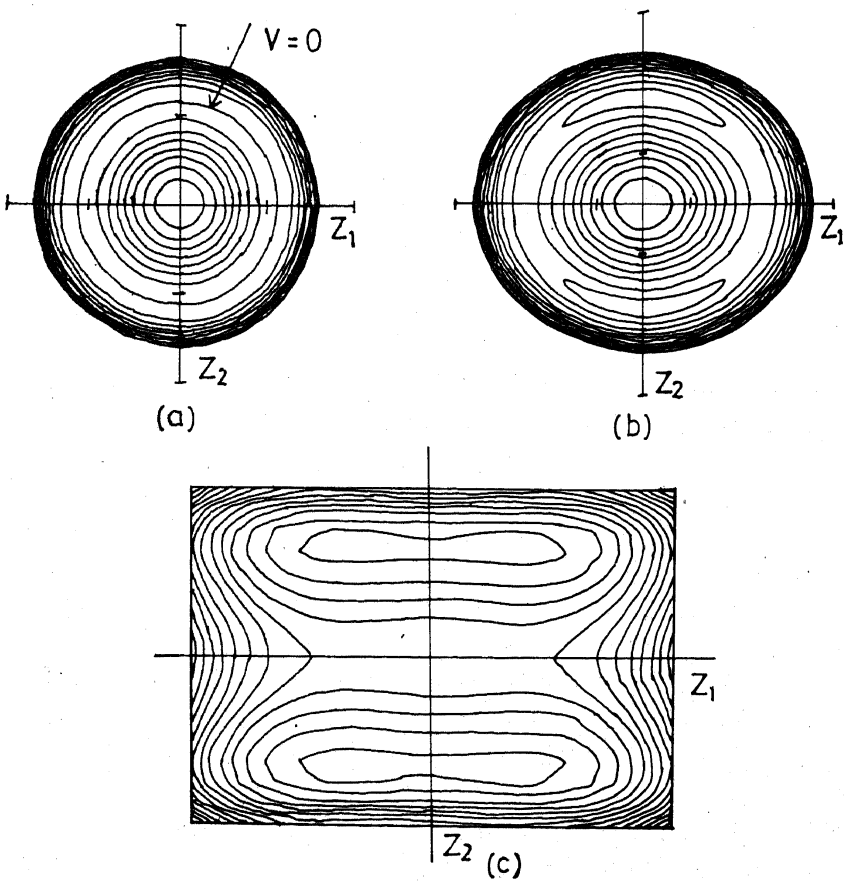

Figure 2. Contour diagrams for potential energy surfaces corresponding to two interacting large amplitude co-ordinates: (**a**) pseudorotation, (**b**) hindered pseudorotation, (**c**) small barrier along Z_1 but large barrier along Z_2.

far as the low frequency vibrations are concerned, the molecule THN may be considered as a pseudo-six-membered ring system, just like cyclohexene. By analysing the anharmonicity in twisting frequencies, it is possible to estimate the barrier height as the molecule distorts itself from one twisted form to the other through the planar conformation. On the other hand, by analysing the twisted frequencies over different bent levels, it is possible to find out the barrier via the bent configuration. Another case where coupling between two low-frequency motions occur is that of indoline (Guchhait *et al* 1994b). The low-frequency motions originate from the out-of-plane motions of the saturated five-membered ring system. Because of the presence of a double bond, the ring system behaves as a pseudo-five membered ring with one low-frequency CH_2 puckering motion. In addition, however, there could be N-inversion. Thus, two vibrational frequencies result from coupling of the CH_2-puckering and the N-inversion. Out of these two coupled motions, one is found to be nearly harmonic in nature, i.e. the sequence of frequencies occur at regular intervals, while the other consists of a negatively anharmonic sequence. The latter series of vibronic bands can be analysed in terms of a double-well potential with a low barrier of $33\,cm^{-1}$. The general type of potential surface that is consistent with our observed spectrum is shown in figure 2c.

Concluding remarks

The examples given demonstrate that it is possible to obtain experimentally S_1 potential energy surfaces in some simple cases of symmetry-equivalent double wells. Potential energy surfaces which permit large amplitude motion become chemically significant only when the wells are not equivalent. We are currently investigating some such cases. The connection between such an experimentally determined S_1 potential energy surface and photo-induced isomerisation is still a long way off. In the meantime, accurately determined S_1 potential energy surfaces may be offered as a challenge to the theoreticians who might test the accuracy of their excited state PES calculations by comparison with the surface obtained spectroscopically.

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