Study of butterfly motion of xanthene through jet spectroscopy

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Abstract : The supersonic jet cooled excitation spectrum of xanthene has been obtained. It has been found that the excited state is planar in contrast to other similar type of molecules, eg. dihydroanthracene. The spectrum fits reasonably well by assuming a single well model for the excited state.

1. Introduction

Butterfly type of motion involving out-of-plane bending of atoms in an aromatic system can be conveniently studied by fluorescence jet spectroscopy. The potential energy curves with respect to out-of-plane displacement co-ordinate may exhibit symmetrical double-minima in ground and/or excited states, as has been observed for 1, 2, 4, 5-tetrafluoro benzene (Okuyama *et al* 1986), octafluoronapthalene (Chakraborty *et al* 1992) and dihydroanthracene (Chakraborty and Chowdhury 1990). In the case of dihydroanthracene (Shin *et al* 1991), the molecule has been found to be bent in both excited and ground states, but the barrier between the two equivalent conformations was found to be around 90 cm^{-1} in the S_1 state (Chakraborty and Chowdhury 1990 ; Shin *et al* 1991) and around 650 cm^{-1} in the ground state (Shin *et al* 1991). Apparently, the CH_2–bridge is more effective in bringing about a conjugation between the two benzene rings in the S_1 state than the S_0 state. It will be interesting to see what happens when one or more of the CH_2–bridges are replaced by other atoms such as oxygen or nitrogen. With this in mind, we have chosen xanthene for our study. The molecule has been found to be bent in the S_0 state by electron diffraction (Iijjima *et al* 1990) and other studies (Aroney *et al* 1969), the interplanar angle being about 160/165^0. NMR studies indicated rapid interconversion between equivalent non-planar forms at room temperature (Schaefer and Sebastian 1990). Ab initio theoretical

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calculations have been carried out for the ground state (Schaefer and Sebastian 1990) and it has been found that although minima occurs at a interplanar dihedral angle of 180^0, the potential energy curve is flat and the "expectation" value of the dihedral angle at room temperature is about 165^0. It is doubtful whether the quantum mechanical calculation of potential energy surface can provide accuracy of the order of a few tens of wavenumbers. Our spectrum of xanthene study is interpreted assuming a bent structure for the ground state and a planar one for the excited state.
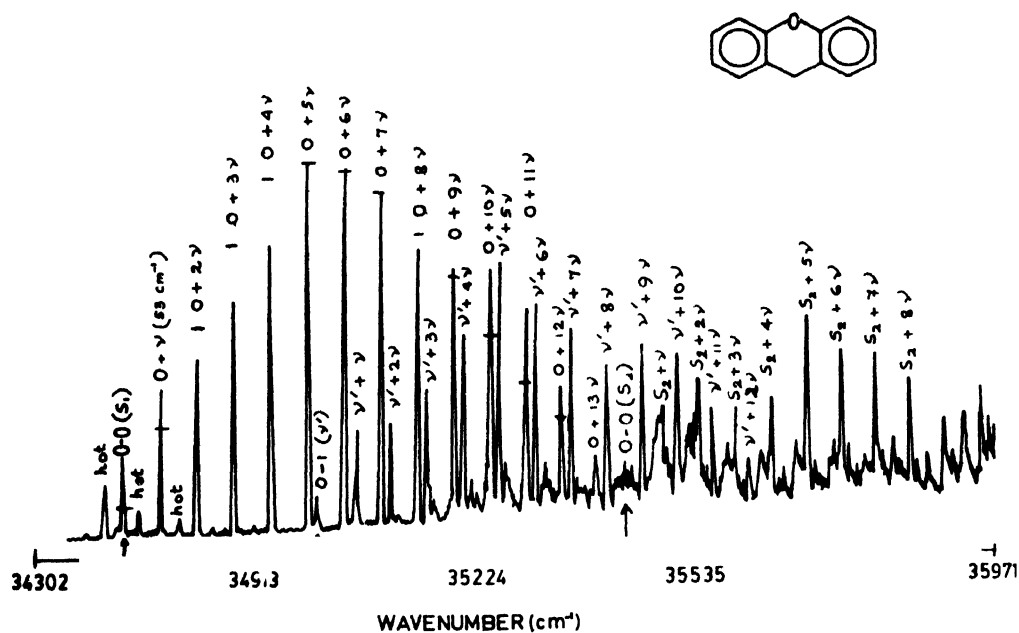
Figure 1. The excitation spectrum of jet cooled xanthene. The horizontal bars represent the theoretically estimated values. The O-O (S_1),O-O (S_2) and false vibronic origin are marked by arrows.

2. Results and discussion

The excitation spectrum is shown in Figure 1. The 0-0 band is located at 34726 cm^{-1}. It is about 2500 cm^{-1} to the red of that obtained for dihydroanthracene. Obviously, the lone pair of oxygen atom extends the conjugation between the two benzene rings. A long progression of 53 cm^{-1} rides over not only the 0-0 origin but also on false origins of 0-1 vibration of other types. The low frequency progression is presumably due to the soft out-of-plane butterfly type vibration, indicating considerable change in this coordinate on excitation. The extent of the change in the dihedral angle θ may be obtained from the intensity distribution amongst the various members of the progression. Since the emission is weak, we have been unable to study dispersed fluorescence spectrum and obtain any information on the

ground state potential energy surface from SVL studies. The hot bands that appear in the spectrum indicate that the ground state frequency is only half of the S_1 frequency. We assume a ground state with minima at $\theta = 165^0$ as shown by electron diffraction and other studies (Iijima *et al* 1990; Aroney *et al* 1969; Schaefer and Sebastian 1990). Since the transitions are originating from $v = 0$ level, little error will be involved if we assume a harmonic well. Actually, two such harmonic wells should be located at $\theta = 180 \pm 15^0$, but if the barrier is greater than 3 or 4 v_0 ($v_0 = 26$ cm^{-1}) the tunnelling splitting will be negligible. We therefore assume that the bands are originating from the degenerate $0^{\pm}$ level and no symmetry selection rule operates (Chakraborty and Chowdhury 1991). In such a case, one can ignore the double well feature (about the nature of which we have no information) and work with a single harmonic well at $\theta = 165^0$. The results obtained for a double-well calculation will essentially be same as that obtained for a single-well model if the tunneling splitting is 0 (Chakraborty and Chowdhury 1991).

Since there is a long pregression without any sign of tunnelling splitting or anharmonicity, we assume a single harmonic well for the excited S_1 state corresponding to planar conformation. With the above assumptions, the intensities may be calculated by using the formula

$$\frac{I_{0 \to n}}{I_{0 \to 0}} = \frac{1}{2}(\alpha^2)^n \times \frac{1}{n!} \quad (1)$$

which we have used before for dihydrophenanthrene (Chakraborty and Chowdhury 1991). In this formula α is a dimensionless constant ($\alpha = \frac{\phi}{\phi_0}$) where ϕ is the rotational displacement on excitation and $\phi_0 = (h / \pi J v_0)^{1/2}$ where J is the reduced moment of inertia for the rotational motion around the O-CH$_2$ axis. J was calculated to be 1.8628×10^{-38} gm.cm^2 and using $v_0 = 53$ cm^{-1}, we calculate ϕ_0 to be 6.2^0. With an assumed value of $\phi = 15^0$, a displacement which will make the excited state planar, the relative intensities of different members of the butterfly progression were calculated. The agreement between the calculated and experimental intensities is reasonable. The above formula is based on equal frequencies for S_0 and S_1 state, but our hot bands indicate that the ground state frequency is half of the excited state frequency. We have therefore obtained the relative intensities by direct calculation of the Franck-Condon factor by a using a ground state frequency of 25 cm^{-1} and an excited state frequency of 53 cm^{-1} and assuming a 15^0 change of ϕ following calculational method described in ref (dutta and bhattacharyya 1992). The calculated intensities are shown in figure 1. The general agreement leads to the cnclusion that the excited state is planar. Apparently the o-atoms is sp^2-hybridised in the excited, but incompletely so in the ground state.

The second feature that we would like to point out is that there are other false origins over which the same progression rides. The progression that starts from O-O +280 cm^{-1} has practically the same intensity distribution as the progression starting from the O-O

band—both peaking at the 0-6 level. It is reasonale to assume that O-O +280 cm^{-1} false origin is a vibration over S_1 state. However, the progression that starts around O-O +730 cm^{-1} has distinctly different intensity distribution and features such as width of the bands. This could be the origin of S_2 state. In molecules containing two insulated benzene rings, exciton and/or through-bond interaction will spilt the benzene states. The extent of this splitting was shown to be about 140 cm^{-1} in dihydroanthracene from a comparison of one-photon and two-photon spectrum (Chakraborty and Chowdhury 1991; Samanta *et al* 1987). It is expected that the through-bond interaction will be larger in xanthene than in dihydroanthracene. The observed tentative assignment of S_2 state therefore seems reasonable.

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