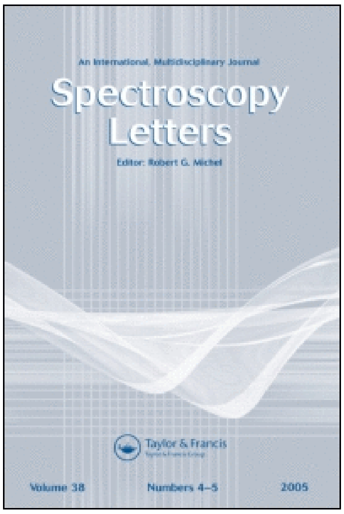

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Very Low Frequency Far-Infrared Spectra of Mixtures of Dioxan with the Halogens and Related Molecules

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VERY LOW FREQUENCY FAR-INFRARED SPECTRA OF MIXTURES OF DIOXAN WITH THE HALOGENS AND RELATED MOLECULES

Key Words: far-infrared, dioxan, halogens.

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INTRODUCTION

There has been considerable interest recently in the study of the submillimetre (or very far-infrared) absorption shown by both polar[1-4] and non-polar molecules.[2,5-8] Such absorption, in the ~5-100 cm^{-1} region, for non-polar molecules is thought[2,6] to be caused by fluctuating dipoles associated with classical quadrupole-induced dipole interactions (in general multipole-induced dipole interactions). These effects are said to be "collision-induced" and can be thought of as being due to "collision" complexes in the liquid phase. For polar molecules the absorption is now thought[1-4] to be due to libration of the dipole in a "cage" of surrounding molecules (either molecules of the same species or of solvent). This so-called Poley-Hill model[9,10] is not inconsistent with the idea[1,2] of a residual rotation of the molecular dipole in the liquid phase. This similarity is underlined by the fact that some simple polar molecules[11,12] have a liquid phase Poley-Hill absorption the general shape and position of which follow quite closely that of the pressure broadened,gas phase spectrum. Our interest in the far-infrared region stems from our studies on halogen complexes with various n and bπ donors.[13,14] The pyridine-I_2 system (in cyclohexane) for example shows two bands in the far-infrared not present in either component. The band at ~183 cm^{-1} is thought to be the stretching mode of the iodine, perturbed in the complex. The band at ~96 cm^{-1}, which is very broad and which has a completely different shape to the ν(I-I) band, has so far been interpreted[14,15] as an "intermolecular" stretching mode between donor and acceptor, ν(D-A). This interpretation was completely accepted by us until recently when we have observed such low frequency absorptions in the systems p-dioxan-XY/cyclohexane (X = Y = I, Br,Cl; X = I, Y = Cl, Br, CN). Unlike the pyridine-XY complexes which are thermodynamically quite stable,[15] the corresponding p-dioxan complexes are very weak[16] and it is doubtful whether such bands (Fig.1) can be reasonably interpreted as due to the internal mode of a "rigid" complex. We have recently observed such bands in other systems (e.g. CS_2, C_6H_6, $(C_2H_5)_2O$, $(C_2H_5)_2S$ with I_2 and ICN) and some of these have also been observed elsewhere[17] so the phenomenon is now established for solutions of a weak donor containing a halogen.

RESULTS

The observed bands (obtained using a Beckman-RIIC FS720 interferometer) are shown in Fig.1 along with the spectrum of dioxan itself. For solutions containing a halogen molecule the spectra have been obtained in the double beam mode by ratioing the solution spectrum against a "blank" containing the same concentration of dioxan. For this reason we are reasonably sure that the bands observed are not simply due to a perturbation of the dioxan band at ~70 cm^{-1}. Our transmission values are, we believe, accurate to about 3-5% above 20 cm^{-1}. In Table 1 we show the spectral parameters for the observed bands along with some additional data necessary for a discussion of their origin.

TABLE 1

Low Frequency Infrared Bands Observed for p-dioxan-XY in Cyclohexane at 20°C

Halogen	Conc. (mole l^{-1})	$\bar{\nu}_{max}$ (cm^{-1})	$\Delta\nu_{\frac{1}{2}}^{a}$ (cm^{-1})	Intensity^{b} (l $mole^{-1}$ cm^{-2})	A^{c} (l $mole^{-1}$ cm^{-2})	Complex dipole moment^{e}	α_{11}^{d} (x 10^{25} cm^{3})	$\bar{\nu}_{max}\Big/\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}$
I_2	0·054	80 ± 4	55 ± 5	1250	3·9	1·0D	175	610
Br_2	0·145	85	50	800	10	1·3D	99·5	640
Cl_2	-^{h}	140^{g}		-		-	66	870
ICl	0·132	102	51	1020	106	4·0D	136	
IBr	0·082	97	49	700	63	3·6D		
ICN	0·084	78	54	940	129	4·4D		

(b) Intensities, based on total halogen concentration, are $\frac{1}{cl}\int \ln(T_o/T)_\nu d\nu$. (c) intensity calculated from Gordon Formula (1). (d) polarisabilities α_{11} for the halogens from M.W. Hanna, J. Am. Chem. Soc., 90, 285 (1968). (e) from ref.17. (g) this band, obtained in chloroform solution, is possibly due to Cl_3^- but no other evidence for ionic species has so far been obtained. (h) concentration not known accurately.

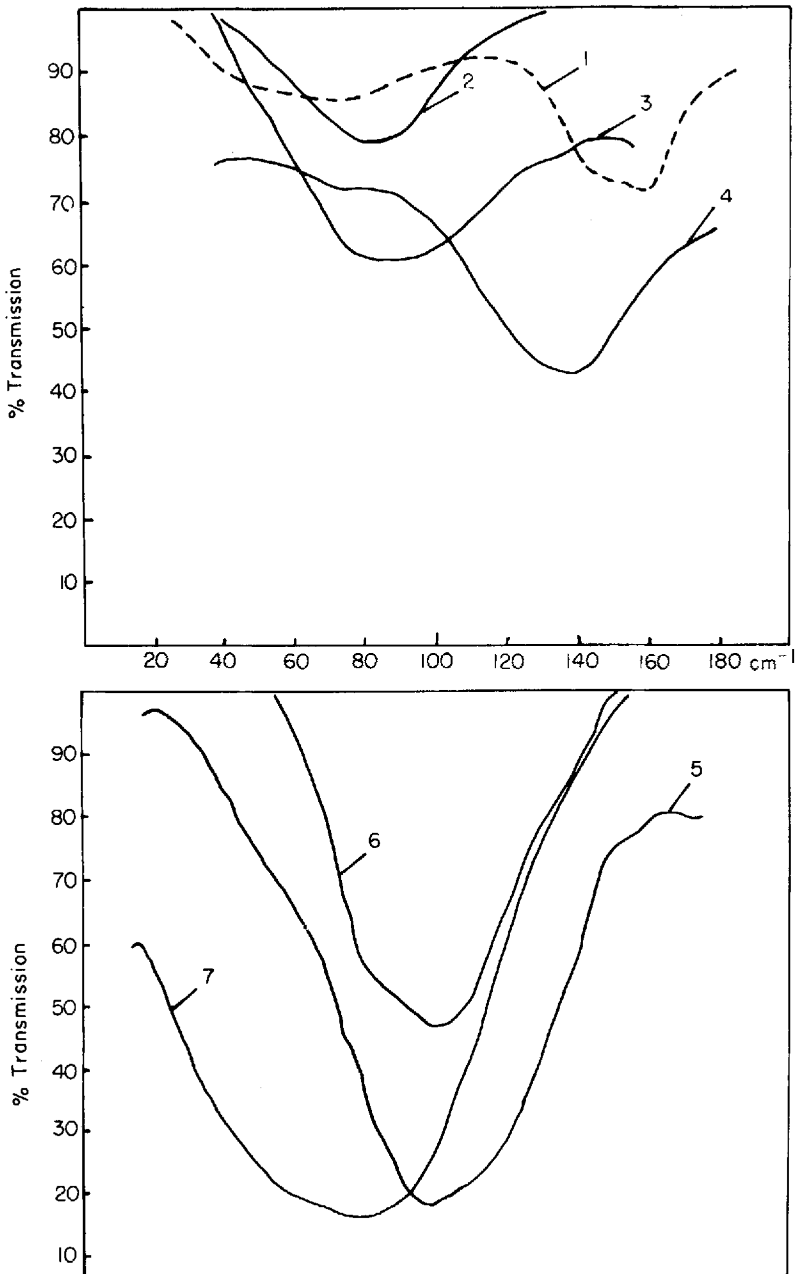

Fig. 1. Far-infrared spectra of 1.3M dioxan in cyclohexane with added halogen. Concentrations of halogen are (1) zero (2) I_2, 0.054M (3) Br_2, 0.145M (4) Cl_2, conc. not known (5) ICl, 0.132M (6) IBr, 0.082M (7) ICN, 0.084M. (NB In cases 2-7 the spectrum of 1.3M dioxan has been substracted off).

DISCUSSION

Although neither p-dioxan nor iodine are polar (p-dioxan having a very small dipole moment of about 0.1D[18] due to a small concentration of the "boat" form) the "complex" has a moment of about 1D[19]. It is possible to calculate from the work of Gordon[20] the intensity which might be expected for a condensed phase "rotational" band of the rigid complex since this depends only on the dipole moment, $\vec{\mu}_z$, and moments of inertia, I_x and I_y.

$$A = \frac{N\pi}{3c^2} \vec{\mu}_z^{\,2} \left(\frac{1}{I_x} + \frac{1}{I_y} \right) \qquad (1)$$

This expression, valid strictly for a symmetric top molecule, gives estimated A values shown in table 1 for "rigid complex" molecules between the donors and acceptors studied. Although (1) gives the intensity for "pure" complex molecules, it is clear that the Poley-Hill model is unlikely to account for the intensities observed, at least for dioxan-X_2 systems. It therefore seems likely that the bands we have observed arise mainly by a collision induced mechanism - the dioxan having, of course, quite large local dipoles despite having only a very small overall permanent moment. According to the equations for the calculation of classical "collisional" frequencies[2] the value of $\bar{\nu}_{max}$ ought to be proportional, at a given temperature, to $(2/M)^{\frac{1}{2}}$ where M is the molecular mass. For unlike molecules, A and B, $\bar{\nu}_{max}$ is proportional to $\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}}$. The values of $\bar{\nu}_{max} / \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}}$ are shown in table 1 for dioxan-X_2 systems and reasonably good agreement is observed (the value of $\bar{\nu}_{max}$ for dioxan-Cl_2 could be elevated by a solvent effect in chloroform). We also have evidence accumulating that both the frequencies and intensities (areas) depend quite drastically on the concentrations of both components. Further, the intensities seem highest for iodine which also has the highest polarisability. We feel therefore that we have good evidence for the collision-induced nature of the observed bands. This could be the reason why we previously observed anomalous results for the ν(I-I) band at $\sim$ 200 cm^{-1}.[21] These data were obtained using a very small range of concentrations and were interpreted using the idea of a "well-defined" complex. There is evidence[19] that the "complexes" formed have lifetimes of the order of 10^{-12}sec. The "frequency" of complex dissociation is therefore of the same order as that of the vibrations concerned and so it is doubtful if such an interpretation is possible.

The situation is somewhat more complicated for systems containing IX molecules since dipole-induced dipole forces probably lead to a much stronger interaction and, possibly, to a contribution due to Poley-Hill absorption of the rigid complex. However, the frequencies and intensities of the observed bands tend to decrease as the dipole moment of the "complex" increases. This again indicates that the contribution from induced dipole fluctuations is considerable since equation 1 predicts a drastic increase in intensity as the "complex" dipole moment increases.

The problem now arises as to how we should interpret the low frequency band for the pyridine-I_2 system. The value of A obtained from (1) is 145 l $mole^{-1}cm^{-2}$ compared with an observed intensity of $\sim$ 2000 l $mole^{-1}$ cm^{-2} so Poley-Hill absorption could make a contribution. We have shown recently[14] that a simple electrostatic model for dipole-induced dipole interaction between pyridine and iodine gives a transition dipole ($\partial\mu/\partial r$) which amounts to 25% of the observed value. It therefore seems likely that there are at least two contributions to this band besides that due to "electron delocalisation"[14] which, for this relatively strong complex, may still have a considerable effect.

We are now continuing our studies on these and other weak "complex" systems using systematic concentration, solvent and temperature variations. Much more data is clearly needed before existing or "new" theories of intermolecular interaction can be tested.

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