High accuracy submillimetre-wave solution measurements

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Abstract. Submillimetre-wave measurements of the power absorption coefficient α and refractive index n of room temperature solutions of p-difluorobenzene in nonpolar solvents are reported. A room temperature detector was used and careful precautions, which included phase modulation, have given very small estimated uncertainties: as low as $\pm 0.1\%$ in α and $\pm 0.02\%$ in n. Some variations with molar concentration are given.

1. Introduction

Since the submillimetre-wave Poley absorption was explicitly discovered in polar liquids (Chantry and Gebbie 1965) and, shortly afterwards, a weaker absorption of similar profile was found in nonpolar liquids (Chantry *et al* 1967), much work has been done with a view to explaining the origins of the process. As the absorption phenomenon is especially characteristic of the liquid state it must be associated with the fluctuating force field in which a given molecule finds itself. Variation of both the molecular parameters and the environment of a given molecule provide clues about the force field. Thus, dipole moment, moment of inertia, molecular shape, molecular rigidity, temperature and pressure have been used as variables (Davies *et al* 1968, 1970, Leroy *et al* 1967, Garg *et al* 1968, Bulkin 1969, Kroon and van der Elsken 1967 and Bradley *et al* 1966) and solutions have also been studied (Pardoe 1970).

In all such spectral studies, high accuracy is important, not least in measurements on solutions. If the dependences on concentration of such things as absorption coefficient, integrated strength, permittivity, etc, are to be tested, reliable measurements are essential. Some workers have resorted to the use of liquid helium cooled detectors for this reason. We report here some results for p-difluorobenzene which are typical of those obtained in a wide ranging study in which Golay cells were the detectors. Full details and analysis will be published later.

2. Experimental

Measurements of refractive index (n) and power absorption coefficient (α) were made over the broad spectral range 1500 to $20\,000\ \mathrm{m}^{-1}$ (15 to $200\ \mathrm{cm}^{-1}$) using Fourier transform spectrometry (FTS) (Vanasse and Sakai 1967). Some spot-frequency measurements of n were made at $2971\ \mathrm{m}^{-1}$ ($29.71\ \mathrm{cm}^{-1}$) using an HCN laser as source (Chamberlain *et al* 1971). Attempts were then made to correlate the found variations with concentration.

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For the broad-band experiments an NPL–Grubb Parsons cube interferometer with Golay cell detector was used (Chantry *et al* 1969). The lamp housing was water cooled and the radiation was phase modulated (PM) (Connes *et al* 1967, Chamberlain 1971, Chamberlain and Gebbie 1971a, 1971b). An AIM system 5 synchronous amplifier[†] was used to produce a DC signal. A Moore-Reed electromechanical encoder[‡] converted this signal to digital form with a resolution of 1 in 256. This was, in fact, inadequate, for the PM interferograms showed signal-to-noise ratios (as defined by Chamberlain 1971) of up to about 1000. Both nondispersive and dispersive interferograms (Chamberlain *et al* 1969) were obtained to give α and n respectively. When n and α are known, the real and imaginary parts of the complex relative permittivity can be evaluated.

Precautions taken included the careful drying of the liquids over 4A zeolite[§], the virtual elimination from the calculations of reflection effects at the liquid boundaries by comparing the transmissivities of thick and thin specimens (for α) and by a careful choice of low resolution and sufficient thickness (for n). For the α measurements the liquid was placed in a plane parallel space between wedged crystalline quartz windows in a slightly convergent beam (f/2). No correction for convergence was made (Fleming 1970). The temperature was held near $20 \pm 2\,°C$.

The refractive index was measured at $2971\ m^{-1}$ using a PM Mach–Zehnder interferometer irradiated by an HCN laser. The technique of Chamberlain *et al* (1971) was used. The values of n so-obtained were used to fix the levels of the refraction spectra.

3. Results

Figure 1 gives one of the best examples of the high signal-to-noise ratio and reproducibility achieved for the power absorption coefficient of a solution of *p*-difluorobenzene (6·16 M
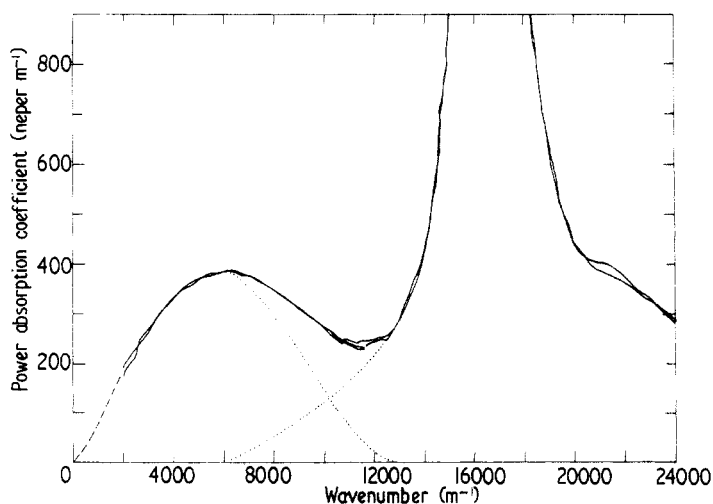

Figure 1. Three independent determinations of power absorption coefficient of a solution of *p*-difluorobenzene (6·16 M in carbon tetrachloride) showing reproducibility obtainable. The dotted line shows a hypothetical decomposition of the spectrum.

† AIM Electronics Limited, Cambridge.
‡ Moore-Reed (Industrial) Limited, Andover, Hampshire.
§ Union Carbide Limited.

in carbon tetrachloride). The three independent spectra shown have a total scatter of as little as ± 3 neper m^{-1} (0·03 neper cm^{-1}) equivalent to $\pm 0·1\%$ at peak α. The effective thickness was 5 mm and uncertainty in this probably provides the overall limiting error. Three independent refraction spectra are shown in figure 2 (2·05 M in
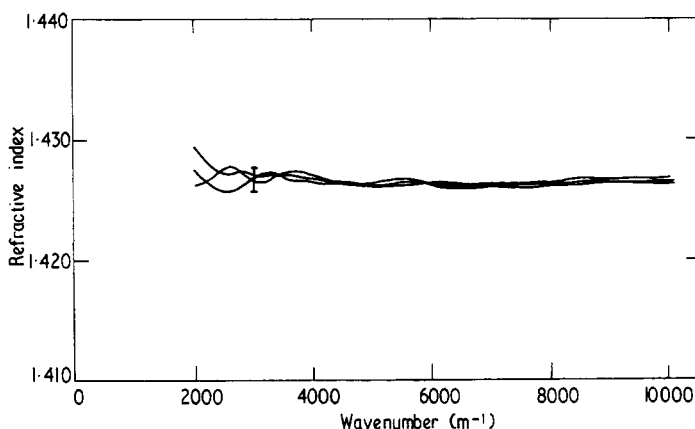

Figure 2. Three independent determinations of refractive index spectra for a solution of *p*-difluorobenzene (2·05 M in cyclohexane) showing reproducibility obtainable. The level of the curves was fixed by the laser measurement.

cyclohexane) together with a laser measurement. The total scatter in n is $\pm 0·0003$ which is equivalent to $\pm 0·02\%$. The levels were fixed by the laser value which has a precision of better than 0·1%. With such accuracy obtainable, families of curves like those shown in figures 3 and 4 (for various concentrations in cyclohexane at 20 °C) have a quantitative significance.
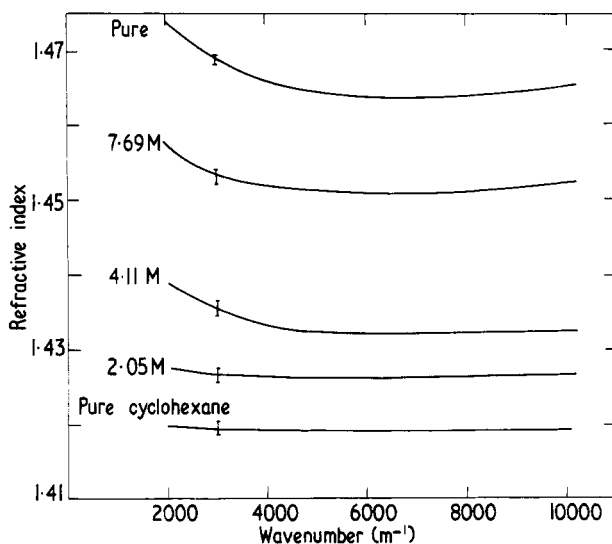

Figure 3. Refractive index for solutions of *p*-difluorobenzene in cyclohexane. Each curve is the average of about 3 spectra.
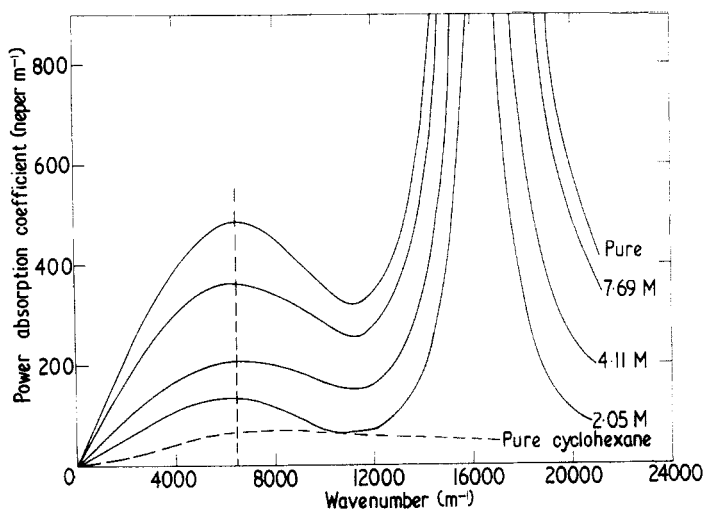
Figure 4. Power absorption coefficient for solutions of p-difluorobenzene in cyclohexane. Each curve is the average of about 3 spectra.

The peak in α at $16\,400\ \text{m}^{-1}$ ($164\ \text{cm}^{-1}$) is the out-of-plane CF deformation mode (Steele *et al* 1963) of p-difluorobenzene, the broader weaker absorption near $6500\ \text{m}^{-1}$ ($65\ \text{cm}^{-1}$) is the submillimetre-wave absorption. The peak value of this does not increase linearly with concentration nor does the integrated area (figure 5), except at
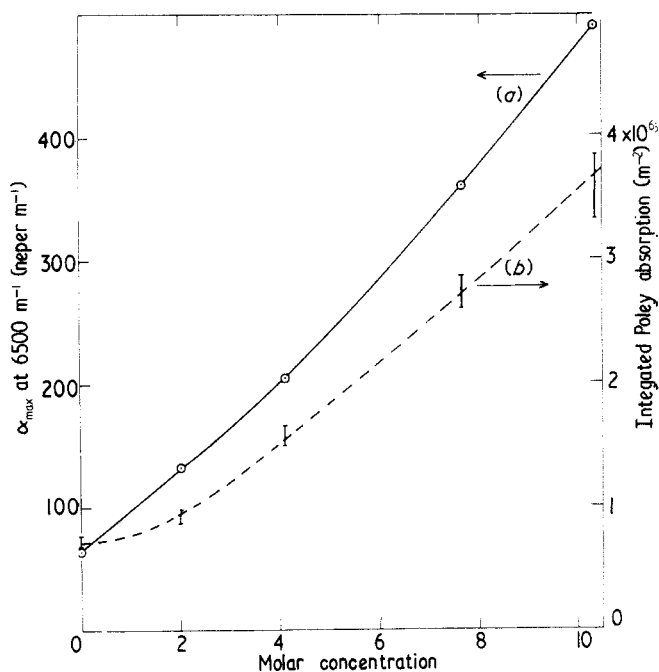

Figure 5. Plots of (*a*) power absorption coefficient at $6500\ \text{m}^{-1}$ ($\sim \alpha_{max}$) and (*b*) integrated area of Poley absorption for solutions of p-difluorobenzene in cyclohexane.

higher concentrations. There is no significant shift of the band. Variations at other representative wavenumbers can also be studied; in particular, 2971 m^{-1}. The variation of n for p-difluorobenzene in a number of solvents is given in figure 6. The fitted curves are of diverse shapes. Plots of relative permittivity are no more easily recognized as simple functions although *trans*-dichloroethylene in cyclohexane is an exception for it shows a quadratic dependence of the relative permittivity on concentration.
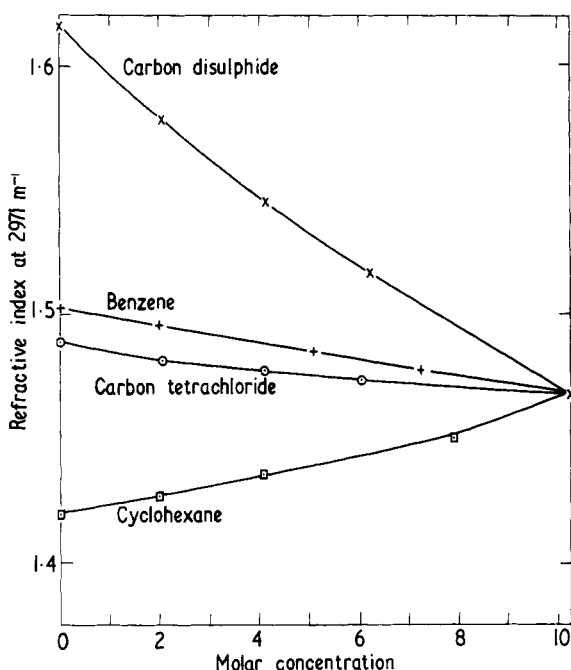

Figure 6. Variation of refractive index at 2971 m^{-1} of solutions of p-difluorobenzene in various solvents. The variations are not linear.

This preliminary account shows the type of data that are obtainable using a room temperature detector and FTS with a cube interferometer. Even better signal-to-noise ratios would be achieved if a liquid helium cooled detector were used but this is not necessary for most applications.

Acknowledgments

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