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The far i.r. absorption of a single crystal of pentachloronitrobenzene

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Abstract—A far i.r. spectrum for a single crystal of the disordered solid pentachloronitrobenzene (PCNB) is presented and used to characterise the absorptions observed in a pressed disc of the same substance. The spectrum, recorded with the hexad axes of the PCNB molecules aligned parallel to the transmitted beam, enables the four separate absorptions observed in this terahertz frequency range to be assigned to inter or intra-molecular modes of motion. The absorption at lowest frequency is attributed to molecular librations about the hexad axes whereas the high frequency absorptions are considered to be intramolecular arising from torsions of the NO_2 group.

INTRODUCTION

Recently we reported [1] a far i.r. study of the disordered solids pentachloronitrobenzene (PCNB) and pentachloroaniline (PCA). We tried to impress in the article that the k.z. absorption observed by AIHARA [2] for a pressed disc of a sample of PCNB necessarily has an associated librational mode at terahertz frequencies (far i.r.). We used a model of itinerant oscillations [3], corrected for molecular moment of inertia, to represent the whole molecule hexad torsion whereby the two absorptions were linked by causality and thus analytically. Theory predicted a near delta function arising at terahertz frequencies that coincided with an experimentally observed absorption. It seemed reasonable to assign this absorption to the individual stages of the slow diffusive process, to molecular librations. In addition we proposed that higher frequency absorptions observed were intramolecular in nature probably arising from torsions of the NO_2 group.

In the present note we report a spectrum for a single crystal of pentachloronitrobenzene measured with the plane face of the crystal mounted perpendicular to the transmitted beam. In this orientation the close packed molecules have their hexad axes aligned parallel to the measuring beam. X-ray studies [4] have shown that crystals of pentachloronitrobenzene are rhombohedral of space group R3 with three molecules per hexagonal cell. They have a disordered structure with an apparent molecular symmetry of 6 and may perform rotational reorientations between three equivalent equilibrium positions. The nitro group is tilted significantly out of the plane of the benzene ring and has two orientations about the C–N axis.

EXPERIMENTAL

The far i.r. spectrum was recorded with a Mark III, Grubb–Parsons/N.P.L. fourier transform spectrometer employing phase modulation of the detected signal. A solid state, low noise i.r. detector type IR50 was used to detect the modulated signal which was synchronously amplified and fourier transformed using digital methods. A power absorption coefficient $\alpha(w)$ (nep cm^{-1}) was calculated from the ratio of intensities penetrating the single crystal of the sample to that through free vacuum. Using a Space Optics reflective off-axis beam reducer/collimator, designed for precision work from visible to far i.r. wavelengths, it was possible to reduce our transmitted beam to one of only 10 mm in diameter. The detected intensity is considerably increased enabling electronic noise to be minimised. We estimate an uncertainty of ± 2 over 90% of the frequency range for a series of recorded spectra. The maximum resolution was 4 cm^{-1}.

Attempts were made to purify the sample by repeated recrystallisation from benzene, vacuum sublimation and zone refining in an inert atmosphere. Here, single crystals are grown from material in the central portion of the zone refining tube by a vapour growth technique [5]. This method allows, in principle, the preparation of thick crystals the dimensions of which are large enough to be amenable to our measuring technique. Also the crystals are generally cleaner than corresponding melt grown crystals which are prone to relatively large number of dislocations.

RESULTS

The observed room temperature spectrum for PCNB is shown in Fig. 1. An earlier result for the pressed disc at ambient temperature and 113K is displayed for comparison. The distinguishing features are the medium intensity bands in the 35–45 wavenumber region of the spectra and three further bands at higher frequencies. These absorptions, previously designated to intramolecular modes of motion, are significantly decreased in intensity in the single crystal relative to the pressed disc sample. We account for this observation as follows. Firstly, using a single crystal we eliminate uncertainties in the absolute absorption intensity arising from interstitial effect on the dispersion in the powdered crystal sample. More importantly the single crystal is mounted with the hexad axes of the molecules parallel to the transmitted beam so that any anisotropy of the intramolecular modes is reflected in the spectrum by a decrease in the intensities of the bands associated with the modes. This is what we observe experimentally. It lends support to our assignment of these modes to intramolecular motion, probably torsions of the NO_2

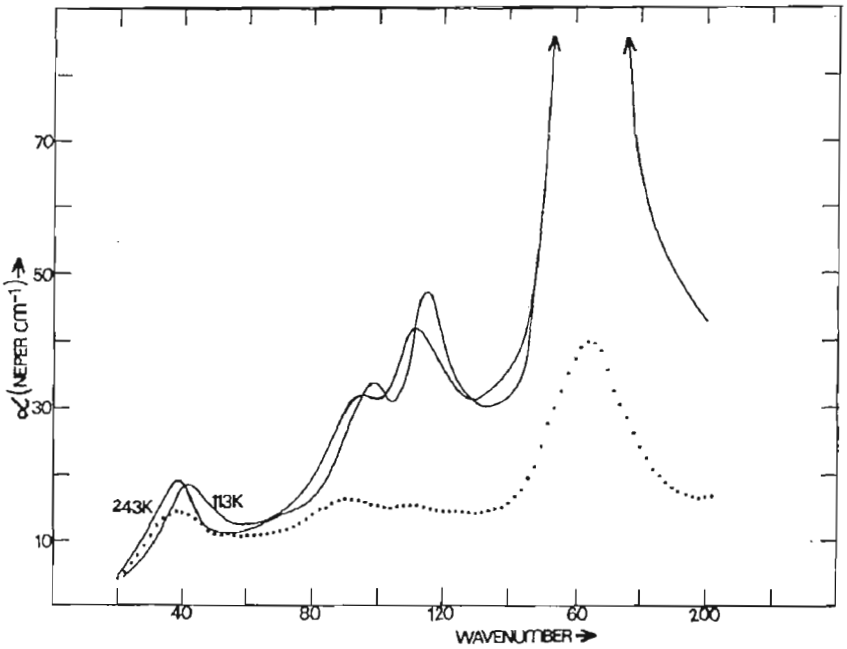

Fig. 1. The far i.r. spectra of a single crystal of PCNB at ambient temperature and a pressed disc of the same substance at room temperature and 113 K. ···· single crystal data; —pressed discs.

group. We recall that these groups are deflected some 62° out of the plane of the benzene ring which satisfactorily accounts for the observed incomplete inactivity of the modes in the particular crystal orientation studied here.

Since the slow Debye-type diffusive process, located at kilohertz frequencies, necessarily has an associated terahertz absorption the single absorption at 38 cm^{-1} must be attributable to torsional oscillations or librations of the whole molecule about their hexad axes. We observe that the absorption intensity of the band is decreased only slightly in the single crystal compared to the powdered sample, this small deviation probably arising from interstitial effects.

In concluding, this single crystal experiment lends support to an earlier assignment of the four absorption bands observed at terahertz frequencies in the disordered crystal PCNB. The absorption at 38 cm^{-1} certainly appears to be intermolecular in nature. In a following article [6] we use an amended version of a planar itinerant oscillator model to link this absorption to its associated Debye-type, kilohertz absorption. The model contains only one adjustable parameter which enables the near delta functions at tetrahertz frequencies, corresponding to the limiting case of $\beta_2=0$ and discussed elsewhere [1] to be broadened so that theory more closely approximates experiment.

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