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A STUDY OF THE INTRINSIC, ORIENTATIONAL DYNAMICS OF THE MOLECULES OF TWO MOLECULAR CRYSTALS

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ABSTRACT

A far infra-red study of pentachloronitro benzene and pentachloro aniline is presented. These molecular crystals exhibit, as an intrinsic property, a considerable molecular orientational freedom. The spectra of the first is treated with two models of the molecular dynamics. The first, due to Frenkel, assumes that the dynamics of the disorder conform to a description of the motion in terms of random jumps occurring between discrete orientational sites. The second, of more recent origin, is the itinerant oscillator model corrected for inertia which is formally identical to a Mori three variable formalism. These molecular cystals, in which the Debye and librational absorptions are separated by some eleven decades of frequency, provide a severe test for this model.

INTRODUCTION

Pentachloronitrobenzene and pentachloroaniline are molecular crystals in which the molecules exhibit considerable degrees of orientational freedom about their hexad axes. Aihara et al. [1] investigated pentachloronitrobenzene dielectrically, in the temperature range 293 K → 372 K, and found absorptions at frequencies between 30 Hz and 1 MHz. These absorptions they attributed to the rotational transitions occurring between several equilibrium sites, equivalent in energy but separated from each other by barriers of different energy which equalize only at higher temperature (> 283 K) when a single relaxation time is approached.

In the present study we present the far infra-red spectra (20–200 cm^{-1}) for both these molecular crystals. We use two models to treat the molecular dynamics of pentachloronitrobenzene. Darmon and Brot [2] have shown that Frenkel's model [3] is a quantitatively good approximation of the motion in crystals presenting a molecular orientational freedom, even in the limit of frequent reorientations. This model restricts molecules to discrete orientations.

The planar itinerant oscillator model of molecular motion is our second model. It has been reformulated [4] to take account of inertial effects and used recently to match experimental data from depolarized Rayleigh scattering, from molecular dynamics computations [5] and from a far infra-red study of a highly dipolar species in dilute solution [6]. This model gives an angular velocity auto-correlation function formally identical to the "three variable" Mori theory used extensively [7] to approximate the orientational auto-correlation functions of dipolar gases and liquids [8].

It is a mathematical consequence of three variable Mori theory that a low frequency Debye absorption has an associated high frequency librational absorption. The planar itinerant oscillator model affords a clearer physical insight. The central feature of the model is that a molecule is supposed to execute torsional oscillations arising from a mechanical potential generated by the rigid cage of its neighbours which itself undergoes rotational Brownian motion. The torsional oscillations of the central molecule are deemed to account for the far infra-red absorption while the Debye absorption has its origin in the rotational motion of the cage. A stringent test for this model is provided by pentachloronitrobenzene where the Debye absorptions arise at less than 1 MHz.

EXPERIMENTAL

The far infra-red spectra were recorded with a Mark III, Grubb-Parsons/N.P.L. fourier transform spectrometer employing phase modulation [9] of the detected signal. A solid state, low noise infra-red detector type IR50 detected the modulated signal which was synchronously amplified and digitally fourier transforme A power absorption coefficient $\alpha(\omega)$ (neper cm^{-1}) was calculated from the ratio of intensities penetrating a pressed disc of the sample to free vacuum space. A series of spectra were recorded until a reproducibility in the absolute intensity of ± 5% over 90% of the frequency range was established. The maximum resolution was 2 cm^{-1}.

The samples were prepared in the manner of Aihara _et_ _al_.[1]. Commercial product was recrystallized from ethanol and purified by zone-refining. Several discs, of varying thicknesses were prepared by pressing at 3 ton/cm^2.

RESULTS and DISCUSSION

Pentachloronitrobenzene (P.C.N.B.)

Until recently it was thought that hexasubstituted benzenes with the nitro-group as a substituent underwent no rotation in the molecular crystal. However, Aihara et al. [1] in 1970 detected a dielectric absorption between 30 Hz and 1 MHz in the temperature range 293-372 K with an energy barrier for rotation (assumed to be the measured Arrhenius activation enthalpy) of $V \approx 16.1$ k cal mole^{-1}. The data indicate that the rotational transition in the solid state is about an axis perpendicular to the molecular plane (the so-called hexad axis). An Eyring entropy difference ΔS between the stationary and transitional positions was calculated on the basis of plane reorientation between two opposite Frenkel wells with the angular frequency of oscillation ($2\pi f$) of the dipole about its equilibrium position set at half the pre-exponential factor in the Arrhenius equation. An entropy value ΔS is produced which suggests a fairly regular arrangement of molecules in the crystalline solid in the above range of temperature.

However, the assumption $f_o = 10^{12}\pi s^{-1}$ is arbitrary, made in the absence of relevant far infra-red measurements of the peak librational wavenumber $\bar{\nu}_o = f_o/c$. This may be estimated in the harmonic approximation for reorientation of six fold symmetry in the manner of Darmon and Brot [2] by assuming that the angular movement of the molecule occurs in a fixed crystalline potential. The frequency $\bar{\nu}_o$ is then defined for simple symmetries such as that of benzene by:

$$\bar{\nu}_o = \frac{3}{\pi c}\left(\frac{V}{2I}\right)^{\frac{1}{2}} \tag{1}$$

where I is the moment of inertia about the hexad axis (3.86×10^{-37} gm cm^2). Naturally, eqn. (1) is an approximation for PCNB, especially since the large NO_2 group will set up potential barriers to rotation of different magnitude resulting in an observed distribution of dielectric relaxation times which become nearly idential only at ca 372 K. No account is taken by eqn. (1) of intermolecular coupling. This results in a distribution of librational frequencies and sets up vibrational waves throughout the lattice. Nevertheless, eqn. (1) yields $\bar{\nu}_o$ = 38 cm^{-1} ($f_o = 1.1 \times 10^{12}$ s^{-1}), about three times lower a frequency than that guessed at by Aihara et al. This means their ΔS will be increased to 14.9 cal (mole K)$^{-1}$ from 12.8 cal (mole K)$^{-1}$.

Eqn. (1) has been used very successfully by Brot et al.[2] to predict the observed Raman or far infra-red peak libration frequencies in crystalline benzene, furan, and some other hexa-substituted benzenes which all lie in the range 30-60 cm^{-1}. This supports our claim that the PCNB band at 38 cm^{-1} is librational and roughly harmonic in origin. The a priori relevance in PCNB of the Frenkel model, where each molecule can take only certain orientations, is revealed by calculating the proportion of molecules in levels higher than the mean barrier height from

$\exp(-V/KT) = 4 \times 10^{-10}$ even at 372 K, where the kHz absorption/dispersion approaches an almost pure Debye process. Converting the calculated $\bar{\nu}_o$ to 108 cals/mole gives a rough estimate of the mean librational energy at 293 K. The Pitzer theory [10] of the hindered rotator and its associated thermodynamics may be used to check the validity of the harmonic oscillator approximation and to estimate the contribution of molecules "in a state of jump" to the overall process. Brot and Darmon have pointed out that this theory can be applied to molecular asymmetric tops rotating in a rigid frame made up of the crystal lattice. We obtain at 293 K a mean hindered rotator energy as in Table 1, where are listed for comparison Brot and Darmon's equivalent results for benzene and furan.

TABLE 1

Hindered rotator entropies and enthalpies

Molecule	Temp (K)	Entropy (cal(mole K)$^{-1}$)	Enthalpy (cal mol^{-1})	$\bar{\nu}_o$ (cal mol^{-1})
PCNB	293	9.0	498	108 (38 cm^{-1})
	392	9.6	706	108 (38 cm^{-1})
PCA	293	9.7	571	74 (26 cm^{-1})
Benzene	100	2.2	122	189 (66 cm^{-1})
Furan	171	7.1	296	150 (52.5 cm^{-1})

The $\bar{\nu}_o$ value and the hindered rotor mean energy are best matched for benzene, and worst for PCNB at 392 K. The frequency $\bar{\nu}_o$ is temperature independent, and is the mean librator energy (as is the Arrhenius enthalpy V) taken over all temperatures. Darmon and Brot derive also a mean librator energy from the Crawford formalism, which agrees closely with the hindered rotor mean energy of benzene and furan. It seems that the Crawford model [2] is not applicable to PCNB and PCA without modification, but the discrepancy between the last two columns of Table 1 in these molecules suggests that torsions of the NO_2 and NH_2 groups will be responsible for further far infra-red absorption at higher frequencies than $\bar{\nu}_o$, which is taken to represent hexad libration in the whole molecule. Intense absorptions in the 50-200 cm^{-1} region are apparent in Fig. (1). Aihara et al. suggest that the twisting of the nitro group in PCNB (due to steric repulsion from positions ortho to the NO_2) may result in two equilibrium isomers, adding to the total entropy in the system as a whole. However, their derived value of ΔS is approximate since plane reorientation among two opposite wells is clearly an extremely rare event with a barrier between each sixfold well of about twenty times the thermal energy available even at 392 K ($V/RT = 20.7$).

Pentachloroaniline (PCA)

Garrington et al. [11] have measured recently the dielectric loss of PCA as a function of temperature and deduce an Arrhenius activation enthalpy of 13.1 kcal mole^{-1}. The moment of inertia of PCA about the hexad axis is 3.08 x 10^{-37} gm cm^2 so that eqn. (1) produces $\bar{\nu}_o$ = 38 cm^{-1} (f_o = 1.1 x 10^{12} s^{-1}). The far infra-red results on PCA at 293 K and at N_2 (l) temperature, Fig. (2), reveal a shoulder at ca 30 cm^{-1} which shifts very slightly to higher frequencies at the lower temperature. Of course, eqn. (1) predicts no shift of $\bar{\nu}_o$ at all with temperature and a delta function peak in the far infra-red, but this is to neglect factors such as vibrational coupling to the lattice, well depth distributions and anharmonicity.

The Pitzer model yields a hindered rotational mean energy of 571 cal mole^{-1} at 293 K which is large compared with $\bar{\nu}_o$ = 74 cal mole^{-1} (26 cm^{-1}). This

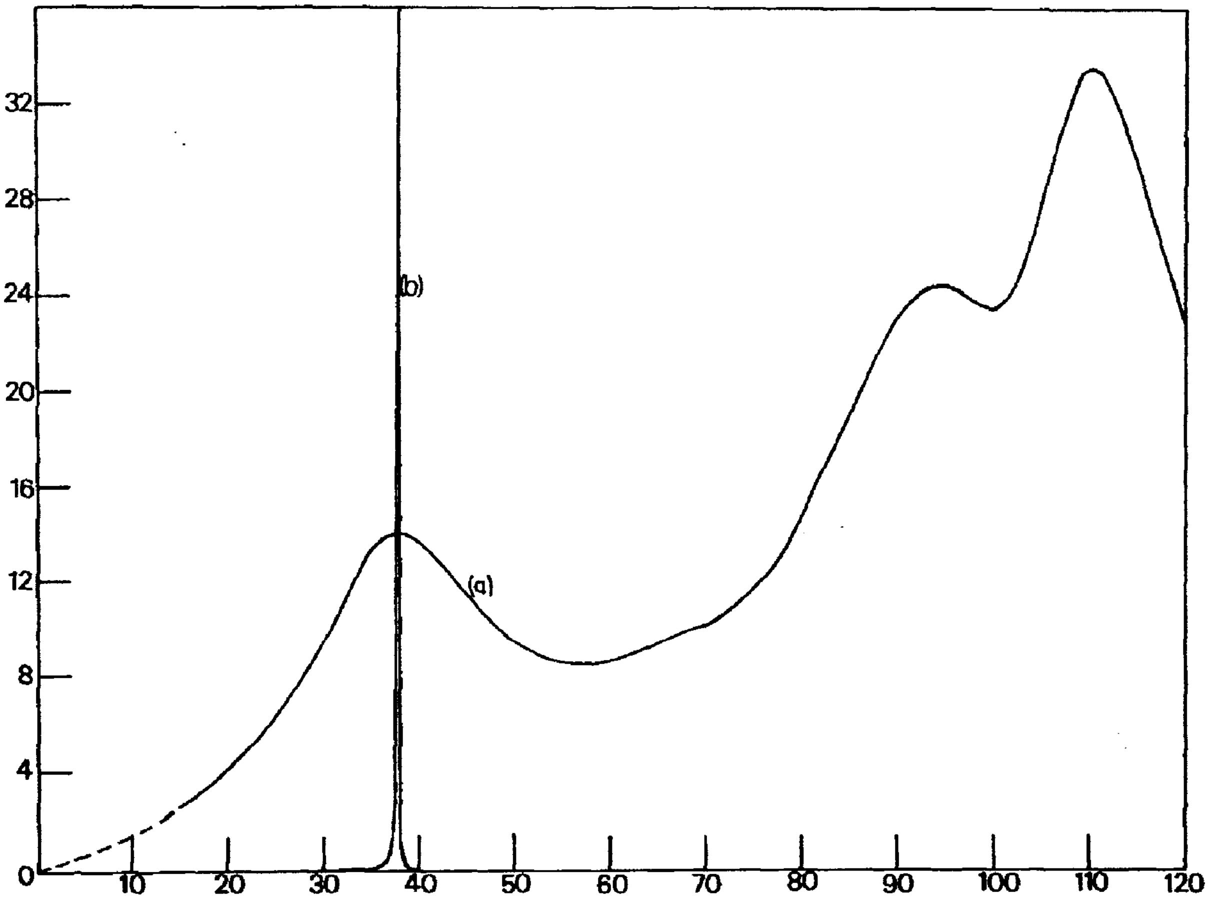

Fig. 1. (a) Far infra-red spectrum of PCNB at 296 K, 1 bar. (b) Theoretical absorption predicted with the itinerant oscillator model.
Ordinate: $\alpha(\omega)/(\text{neper cm}^{-1})$; abscissa: $\bar{\nu}/\text{cm}^{-1}$.

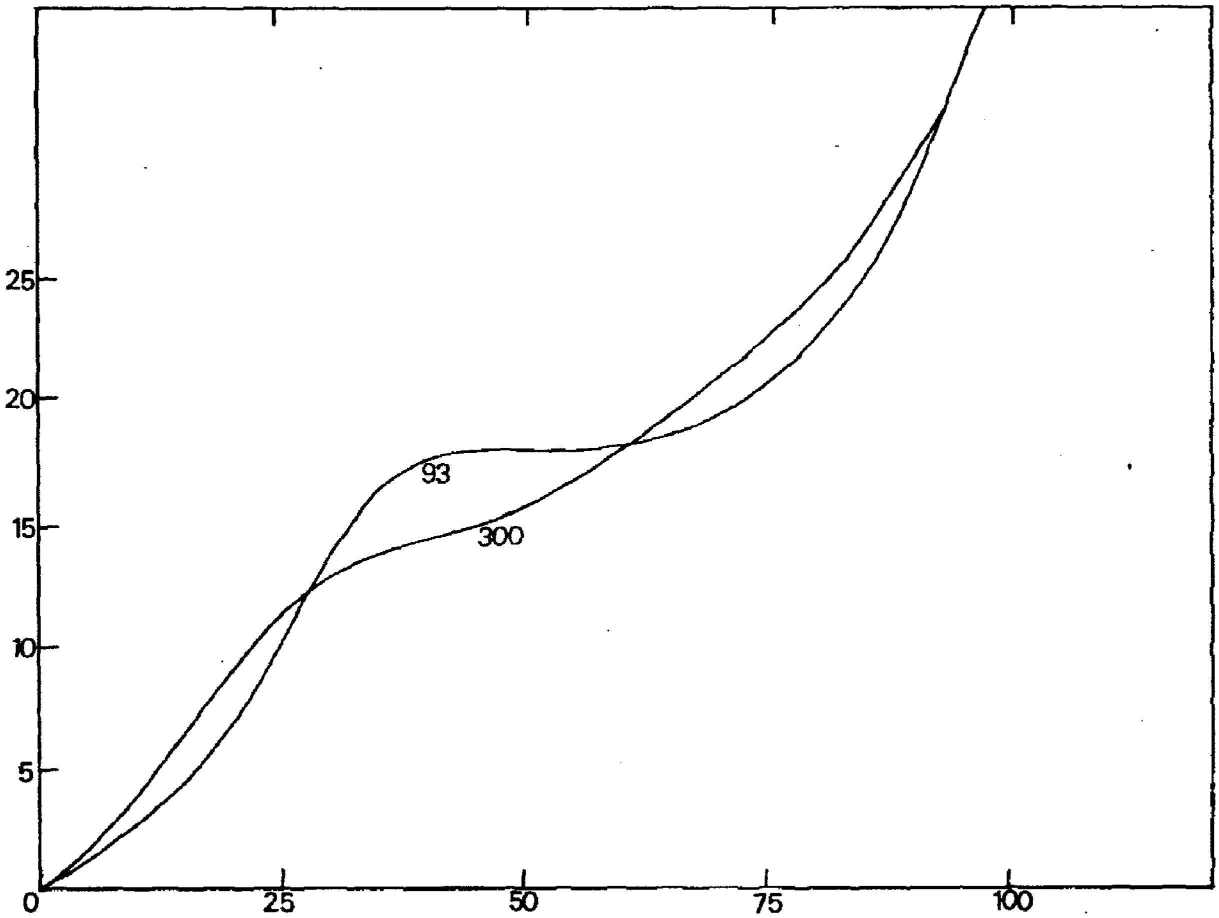

Fig. 2. (a) Far infra-red spectrum of PCA at 298 K, 1 bar. (b) Far infra-red spectrum of PCA at 93 K, 1 bar. Ordinate: $\alpha(\omega)/(\text{neper cm}^{-1})$; abscissa: $\bar{\nu}/\text{cm}^{-1}$.

suggests again that higher frequency absorptions ought to be present in the far infra-red due to rotations of the NH_2 group (with or without quantum tunnelling) or due to residual anharmonicity at the bottom of each potential well.

Model Dynamical Interpretation - The Itinerant Oscillator

It is necessary to produce a mechanism for the whole molecule hexad torsion whereby the far infra-red and kHz absorptions (compounded of the same origin) are linked to each other by causality, and thus analytically. In its simplest form this would produce a near-delta function corresponding to the librational frequency and a Debye type absorption at the lower frequencies. It is not possible on general statistical grounds to consider a Debye model in isolation [4-8] since there cannot be a return to transparency at high frequencies in the power absorption coefficient $\alpha(\omega) = \omega\varepsilon''/n(\omega)$ where ε'' is the loss factor and $n(\omega)$ the refractive index. The Debye orientational a.c.f. (autocorrelation function) is an exponential ($\exp(-t/\tau_D)$) (whereas a true a.c.f. is time reversible with zero slope as $t \to o$) and is a consequence of solving the Langevin equation for a spherical top with neglect of the inertia term [12].

Recently, Coffey et al. [4] have developed the Hill/Wyllie [13] itinerant oscillator to include inertial effects in two dimensions. A central molecule, represented by a disc of moment of inertia I_2 performs harmonic oscillations inside a rigid annulus of moment of inertia I_1 (representing the cage of nearest neighbours) which is itself undergoing rotational Brownian motion. The disc carries a dipole $\underset{\sim}{\mu}$ along one of its diameters, whose direction is specified by an angle $\theta(t)$ relative to a fixed axis which is taken for convenience to coincide with the direction of a steady electric field E. The position of a point on the rim of the annulus is specified by an angle $\psi(t)$ relative to the same fixed axis. Further, the dipole is attracted towards the direction specified by $\psi(t)$ by a restoring torque proportional to the displacement $(\theta(t) - \psi(t))$. We suppose that the steady field E is suddenly removed at $t = o$, so for any time $t > o$ the motion of the system is governed by the equations:

$$I_1 \ddot{\psi}(t) + \zeta\dot{\psi}(t) - \gamma(\theta(t) - \psi(t)) = \lambda(t), \tag{2}$$

$$I_2 \ddot{\theta}(t) + \gamma(\theta(t) - \psi(t)) = 0 \tag{3}$$

In eqns. (2) and (3), γ is the restoring torque constant, $\zeta\dot{\psi}$ is the frictional couple acting on the annulus, arising from the surroundings, and $\lambda(t)$, which is represented by a Wiener process, is the couple caused by random collisions of the Brownian motion type. Defining the following:

$\beta = \zeta/I_1$,

$\omega_o^2 = \gamma/I_2$,

$\Omega_o^2 = (I_2/I_1)\omega_o^2$,

we have for $(kT/I_2\omega_o^2) \lesssim 0.1$ the real and imaginary parts of the complex polarisability defined by:

$$\frac{\alpha'_\mu(X)}{\alpha_\mu(o)} = \frac{[1-(a_1-a_2)X^2](1-X^2a_3)+X^2(a_2-1+a_1X^2)(a_5-X^2a_4)}{(1+X^2)[(1-X^2a_3)^2+X^2(a_5-X^2a_4)^2]}$$

$$\frac{\alpha''_\mu(X)}{\alpha'_\mu(o)} = \frac{[1-(a_1-a_2)X^2](a_5-X^2a_4)-(1-X^2a_3)(a_2-1+a_1X^2) \quad X}{(1+X^2)[1-X^2a_3)^2+X^2(a_5-X^2a_4)^2}$$

$$\text{where } a_1 = \left(\frac{kT}{I_2\omega_o^2}\right)^2 \left(\frac{I_2}{I_1}\right) \left(\frac{\omega_o}{\beta}\right)^2 ,$$

$$a_2 = \left(\frac{kT}{I_2\omega_o^2}\right) ,$$

$$a_3 = \left(\frac{kT}{I_2\,{}_o^2}\right)^2 \left(\frac{I_2}{I_1}\right)^2 \left(\frac{\omega_o}{\beta}\right)^2 ,$$

$$a_4 = \left(\frac{kT}{I_2\omega_o^2}\right)^3 \left(\frac{I_2}{I_1}\right)^3 \left(\frac{\omega_o}{\beta}\right)^4 ,$$

$$a_5 = \left(\frac{kT}{I_2\omega_o^2}\right) \left(\frac{I_2}{I_1}\right) \left(1 + \frac{I_2}{I_1}\right) \left(\frac{\omega_o}{\beta}\right)^2 ,$$

$$X = \omega\tau_D,$$

with the Debye relaxation time τ_D as:

$\tau_D = I_1\beta/kT.$

The frequency ω_o, which is that of the disc libration with the annulus stationary can be taken as $2\pi\bar{\nu}_o c$. The factor β is defined experimentally through the Debye time τ_D, which for simplicity we take as the inverse of the kHz peak absorption frequency, since the itinerant oscillator as presented here uses but one relaxation time. The disc moment of inertia can be taken as that of the PCNB or PCA molecule, though only PCNB is considered here, and the annulus moment of inertia I_1 can be either calculated roughly using X-ray data or adjusted for best fit with the kHz-THz peak frequencies.

Making no attempt at any correction for the internal field, or dipole-dipole coupling (which introduces a $-\underset{\sim}{\mu}X\underset{\sim}{F}$ term and makes insoluble eqn. (2)), the dielectric loss and dispersion; and the power absorption coefficient $\alpha(\bar{\nu})$, may be expressed as:

$$\varepsilon'' = \frac{3A}{D}\,\frac{\alpha_\mu''(X)}{\alpha'_\mu(o)} ;$$

$$\varepsilon' = \frac{3}{D}\left(1 - \frac{A\alpha'_\mu(X)}{\alpha'_\mu(o)}\right) - 2;$$

$$\alpha(\bar{\nu}) = \frac{2\sqrt{2}\pi\bar{\nu}\varepsilon''}{((\varepsilon''^2 + \varepsilon'^2)^{\frac{1}{2}} + \varepsilon')^{\frac{1}{2}}} ;$$

where $$D = \frac{A^2 \alpha''_\mu(X)^2}{\alpha'_\mu(o)^2} + \left(\frac{A\,\alpha'_\mu(X)}{\alpha'_\mu(o)} - 1 \right)^2 ;$$

$$A = (\varepsilon_o - 1)/(\varepsilon_o + 2) \;;$$

with ε_o as the static permittivity.

We use these expressions to evaluate the far infra-red/Debye type absorption spectra, which are treated as an entity even though separated by some eleven decades of frequency in this a limiting case of slow molecular reorientation. No "force fitting" of the molecular parameters of the itinerant oscillator model is attempted. Rather the moment of inertia of the annulus I_1 is estimated using the X-ray data of Tanaka et al. [14]. Values of the molecular parameters used are listed in Table 2. Debye-type dielectric absorptions, Fig. (3), are predicted in the frequency range experimentally observed. The theoretical curves are significantly sharper, the experimental arising from a distribution of relaxation times, but follow the shift of $\bar{\nu}_{max}$ to higher frequencies and the decrease in intensity of the maximum absorption with increasing temperature. The analytical expressions allow one to both extrapolate to higher frequencies, Fig. (1), and to evaluate the respective dispersion curves (Figs. (3) and (4)).

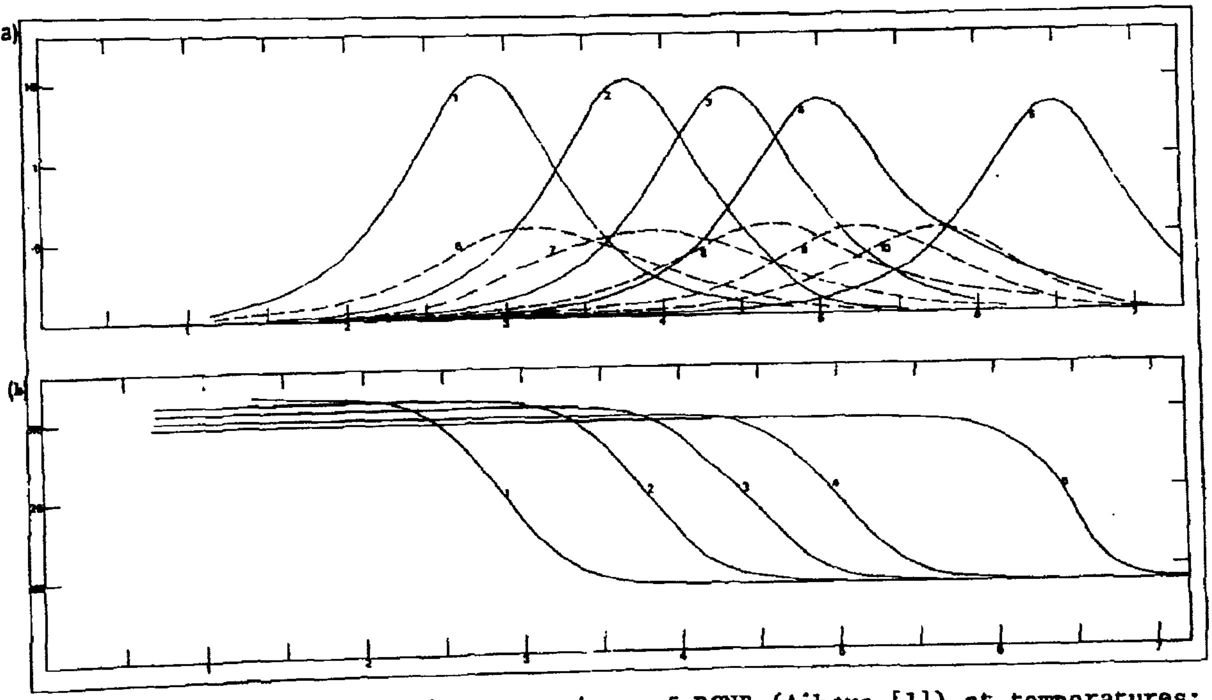

Fig. 3. (a) --- The dielectric absorptions of PCNB (Aihara [1]) at temperatures: (1) 293 K, (2) 313.4 K, (3) 33 K, (4) 353.7 K, (5) 372.1 K. —— The Theoretical absorptions: (6) 293 K, (7) 313.4 K, (8) 333 K, (9) 353.7 K, (10) 372.1 K. Ordinate: ε"; abscissa: log f/Hz. Ordinate: ε'; abscissa: log f/Hz.
N.B. The theoretical curves 5 are drawn one decade too high in frequency.

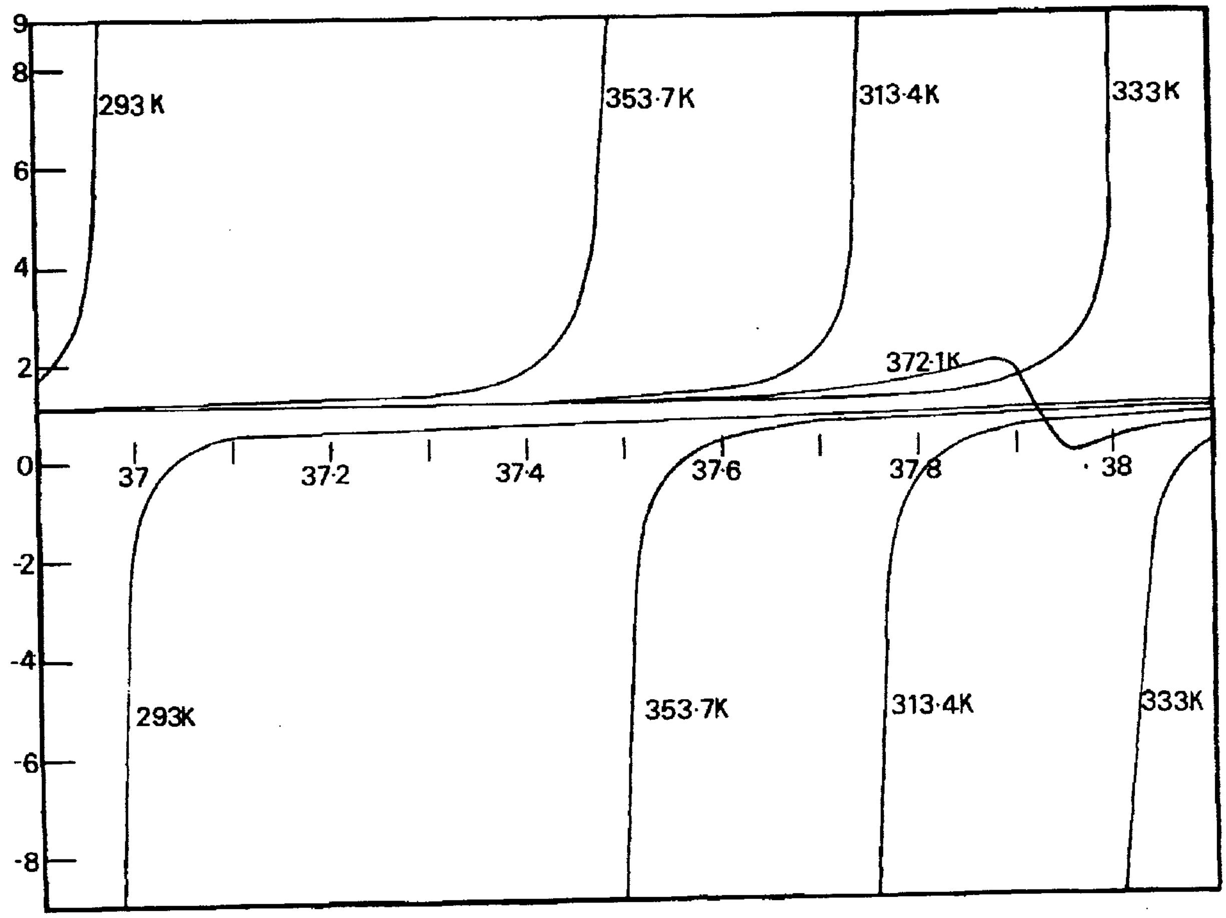

Fig. 4. Theoretical dispersions at far infra-red frequencies. Ordinate: ε'; abscissa: $\bar{\nu}$/cm^{-1}.

TABLE 2

Parameters for PCNB used in the itinerant oscillator model

Temp/K	τ_D/sec	$kT/I_2\omega_o^2$	I_2/I_1	ω_o/β
293	1.072×10^{-4}	0.0021	0.1	6.372×10^{-6}
313.4	1.306×10^{-5}	0.0022	0.1	4.890×10^{-5}
333	3.073×10^{-6}	0.0023	0.1	1.974×10^{-4}
353.7	8.243×10^{-7}	0.0025	0.1	6.865×10^{-4}
372.1	2.694×10^{-8}	0.0026	0.1	1.997×10^{-3}

At far infrared frequencies the theoretical absorptions are near delta-functions arising at the experimentally observed frequency of maximum absorption (38 cm^{-1}). The absorption arises from the torsional oscillation or libration of the molecules, at a unique frequency, in the field of their neighbours which are temporarily fixed in one of their allowed orientations. In practice, a distribution of librational frequencies exists, a consequence of the small but definitive differences existing between the depths of the two potential wells accessible to a molecule. These differences arise from the different potential barriers to rotation set up by the large NO_2 groups and, however small, produce a relevant displacement of the librational level of the various molecules in the crystal which results in a statistical broadening of the observed libration band. Also, intermolecular coupling, which causes librations in the crystal to take the form of vibrational waves [15] with some frequency distribution, has been disregarded in our calculations. The dispersions at high frequencies are predictably sharp, though broadening slightly at the highest temperature as the statistical distribution of librational frequencies increases.

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