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ABSTRACT

The frequency spectra of cyclohexanol in three crystalline phases and in the liquid state were determined by incoherent inelastic neutron scattering. The measurements were performed using a Beryllium Filter Time-of-Flight Spectrometer. Neutron inelastic scattering spectra and frequency spectra fitted to a sum of Gaussian functions show evidences for events around 36-44, 62-79, 120-148, 216-260 and 384-509 cm^{-1} assigned as hindered rotation of molecules, lattice vibrations, hydrogen bond stretching, out-of-plane and in-plane ring bending modes respectively.

I – INTRODUCTION

There is a large interest in the study of globular compounds(21) because of their peculiar physical properties, attributed to the almost spherical symmetry of their molecules. The globular compounds show high triple point, small entropy of melting and a phase transition, in solid state, with large entropy change. This phase transition occurs from a low symmetry crystalline phase, stable at low temperatures, to a crystalline phase with high symmetry, stable at temperatures between the transition point and the melting point. The high symmetry phase is called plastic crystal or rotational phase due to display a certain degree of plasticity and an unhindered rotation of molecules around their lattice positions.

In particular, cyclohexanol has been classified as a globular compound(21) due to its small entropy of fusion (1.37 cal/K.mol)(12) and to show a plastic crystal phase near below the melting point. It freezes at 298.5 K into a f.c.c. structure with a lattice spacing 8.83 Å(12). Investigations by dieletric(11) and ultrasonic(12) methods indicate the existence of three phases in solid state, one plastic and two non-plastic, occuring phase transitions at 264.7 and 244.2 K. The solid phases of cyclohexanol were named here according to Green and Scheie(12) convention: crystal I (plastic phase); crystal II (non-plastic) with transition II-I at 244.2 K and crystal III (non-plastic) with transition III-I at 264.7 K. These phase transitions possesse high entropy of transformation, around 7.5 cal/K.mol(12). The presence of OH in the molecule causes a molecular asymmetry and associations of molecules through hydrogen bonds, responsable for the high viscosity of liquid cyclohexanol.

The study of cyclohexanol becomes more interesting because of the duality of dynamical behavior of this globular compound: freedon for rotations, at least in the plastic crystal phase, and restrictions of mouvements due to the hydrogen bonds.

The molecular dynamics of cyclohexanol has been studied by Raman(15) and infrared(4) spectroscopy, in the frequency region from 300 to 3000 cm^{-1}, being the lower assigned frequencies

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attributed to ring vibrations. It is well know that inelastic neutron scattering is a powerful technique to investigate the low-frequency atomic motions of hydrogenated molecules in condensed states. In these cases, the neutron scattering is essentially incoherent and due to hydrogen atoms, since the incoherent scattering cross section of H atom is about 20 times that for C and O.

In order to investigate the dynamical behavior of cyclohexanol in different phases, determining the characteristic atomic motions in the low-frequency region, below 600 cm^{-1}, neutron inelastic scattering spectra were measured in the temperature interval 100-300 K.

II – RELATIONS BETWEEN CORRELATION FUNCTION, DIFFERENTIAL SCATTERING CROSS SECTION AND GENERALIZED FREQUENCY SPECTRUM

A system of particles and its evolution in time can be described by the Van Hove space-time correlation function[22], $G(\vec{r},t)$. This function describes the correlation between the presence of a particle in position $\vec{r}' + \vec{r}$ at time $t' + t$ and the presence of a particle in position $\vec{r}'$ at time t', averaged over $\vec{r}'$. The function $G(\vec{r},t)$ is defined by the equation

$$G(\vec{r},t) = \frac{1}{N} < \sum_{l,i=1} \int d\vec{r}'\, \delta(\vec{r} + \vec{r}_l(0) - \vec{r}')\, \delta(\vec{r}' - \vec{r}_i(t)) >$$

Informations about changes in the system of particles are contained in the self-correlation function $G_s(\vec{r},t)$ and in the distinct (particles) correlation function $G_d(\vec{r},t)$, corresponding to terms $l = i$ and $l \neq i$ in the sum respectively. In the study of characteristic mouvements of molecules only the self-correlation function is used.

In the study of molecular dynamics by slow neutron scattering technique, energy and momentum transfers in the collision process are determined experimentally. The energy and momentum transfers in the scatering process are

$$E_1 - E_0 = \hbar w \qquad h(\vec{k}_1 - \vec{k}_0) = \hbar\vec{Q}$$

Here E_1 and E_0 are the scattered and incident energy of neutron and $\vec{k}_1$ and $\vec{k}_0$ the respective wave vectors.

Thus, it is convenient to change from space $(\vec{r},t)$ to $(\vec{Q},w)$. The incoherent scattering law $S_{inc}(\vec{Q},w)$ is obtained by Fourier transform over $\vec{r}$ and t of $G_s(\vec{r},t)$[13]

$$S_{inc}(\vec{Q},w) = \frac{N}{2\pi} \int d\vec{r}\, dt\, e^{i(\vec{Q}\cdot\vec{r} - wt)}\, G_s(\vec{r},t)$$

The differential incoherent scattering cross section is related to the scattering law through equation[22]

$$\frac{d^2\sigma^{inel}_{inc}}{d\Omega\, dw} = \frac{k_1}{k_0}\, b^2_{inc}\, S_{inc}(\vec{Q},w)$$

were b_{inc} is the incoherent scattering length of nuclei of the scattering system.

The generalized frequency spectrum f(w) for liquids can be obtained as an extension of the frequency spectrum for solids[1,2,7,8,9,18,19]. The frequency spectrum is calculated from the scattering law through the exact relation[9,20].

$$f(w) = \frac{4M}{\hbar w} \, \text{senh} \left(\frac{\hbar w}{2KT}\right) w^2 \lim_{\vec{Q} \to 0} \frac{\tilde{S}(\vec{Q},w)}{Q^2}$$

where M is the mass of scattering atom, K is the Boltzmann's constant, T is the absolute temperature and $\tilde{S}_{inc}(\vec{Q},w)$ is the sysmmetrical scattering law given by

$$\tilde{S}_{inc}(\vec{Q},w) \;\; \exp\left(\frac{-\hbar w}{2KT}\right) S_{inc}(\vec{Q},w)$$

In the case of isotropic systems, it is more convenient to work with an admensional frequency spectrum[6,9,10], obtained defining new variables α and β and redefining the scattering law:

$$\alpha = \frac{hQ^2}{2MKT} \qquad \beta = \frac{\hbar w}{KT} \qquad S(\alpha,\beta) = \frac{KT}{\hbar} \tilde{S}_{inc}(\vec{Q},w)$$

The resultant frequency spectrum is given by

$$f(\beta) = 2\,\beta \, \text{sen} \frac{\beta}{2} \lim_{\alpha \to 0} \frac{S(\alpha,\beta)}{\alpha}$$

The limit for $\vec{Q} \to 0$ or $\alpha \to 0$ can be substituted by a generalized Debye-Waller factor[2,7,8].

Thus, using above relations, generalized frequency spectrum can be obtained from differential scattering cross section, determined experimentally by slow neutron scattering measurements.

III – EXPERIMENTAL

The measurements of scattered neutron distributions were carried out using a conventional cold neutron time-of-flight spectrometer[11] at IEA-R1 research reactor.

A polycrystalline beryllium filter, cooled in liquid nitrogen, transmits a cold neutron spectrum with an average energy of 3.5 meV and a full width at half-height of 2.0 meV. Neutrons scattered by the sample at a certain solid angle are pulsed by a curved slit slow-neutron chopper operated usually at 13000 rpm and are detected by a bank of eight ^{3}He detectors after a flight path of 3.15 m. The time-of-flight analysis of scattered neutrons and the data record are performed by a multichannel analyser.

Cyclohexanol of "pro analysi" quality, purchased from J. T. Baker Co. with purity higher than 99% were used. The sample, sealed in an aluminium holder while in liquid state, has a tickness of 0,02 cm ensuring a 90% transmission to avoid multiple scattering. The sample holder was mounted in a cryostat with a cold finger and a heat system permiting measurements at temperatures in the range 100-300 K, controlled within 2 K. All measurements have been performed in transmission geometry with the sample plane forming an angle of 45° with the incoming beam.

IV – RESULTS AND DISCUSSION

The energy distributions of scattered neutrons in cyclohexanol were measured at the scattering angle 50° for the sample at the following temperatures: 300 K (liquid state), 287 K (crystal I), 253 K (crystal III), 183 K, 143 K and 100 K (crystal II).

After subtraction of background and sample holder scattering, spectra were corrected for chopper transmission, detector efficiency and air absorption and scattering.

Corrected time-of-flight spectra for six measured temperatures are shown in Figures 1, 2 and 3. In all spectra five peaks are observed, plus the peak reffering to the quasi-elastic scattering.

The corrected spectrum corresponds to $d^2\sigma/d\Omega dt$, which is transformed in $d^2\sigma/d\Omega dw$ by the relation

$$\frac{d^2\,\sigma_{inc}^{inel}}{d\Omega\,dw} \sim E^{-3/2}\ \frac{d^2\,\sigma_{inc}^{inel}}{d\Omega\,dt}.$$

The generalized frequency spectra for cyclohexanol were calculated from $d^2\sigma/d\Omega dw$ using the formalism described in part II. Figures 4 and 5 show a spectrum for each cyclohexanol phase.

In order to allow a most precise determination of characterist frequencies, frequency spectra have been fitted to a sum of Gaussian functions[1,2], using the least-squares fit method. A Gaussian function was associated an each peak, thus each spectrum is described as a sum of five Gaussian functions

$$f(\beta) = \sum_{j=1}^{5} A_j \exp\left[-\frac{1}{2}\left(\frac{\beta-\beta_{oj}}{\Delta\beta_j}\right)^2\right]$$

Where A_j, β_{oj} and $\Delta\beta_j$ are Gaussian function parameters: height, peak position and half width respectively. Fitted curves together with experimental results are shown in Figures 4 and 5. Determined frequencies are listed in Table I.

For each peak, shifts in frequency are observed for different phases. These shifts are principally due to changes in intermolecular and intramolecular forces at the phase transitions, and partially attributed to the effect of temperature variation.

The peak at 40 cm^{-1}, observed in all phases, is attributed to hindered rotations or molecular reorentation. This peak is better defined in the crystal plastic phase (crystal I).

The peak observed in the region 70 cm^{-1} corresponds to vibration modes of crystalline lattice. Similar results have been obtained for cyclohexane[5] using slow neutron scattering technique. As temperature decreases, this peak becomes better defined in the neutron scattered spectra, specially for the non-plastic crystalline phases; on the other hand the decrease in intensity of this peaks is caused by the reduction of thermal energy of the crystal. The presence of this peak in the spectrum obtained from liquid state indicates the existence of region with crystalline structure in liquid. The origen of those regions can be attributed to the association of molecules through hydrogen bonds. Dielectric measurements[13] have shown that molecules in cyclohexanol are associated in dimers, at least in the plastic crystal phase.

As it has been suggested for other globular compounds, the peaks at 40 and 70 cm^{-1} could permit another assignment: vibrational and librational modes of molecules associated in dimers.

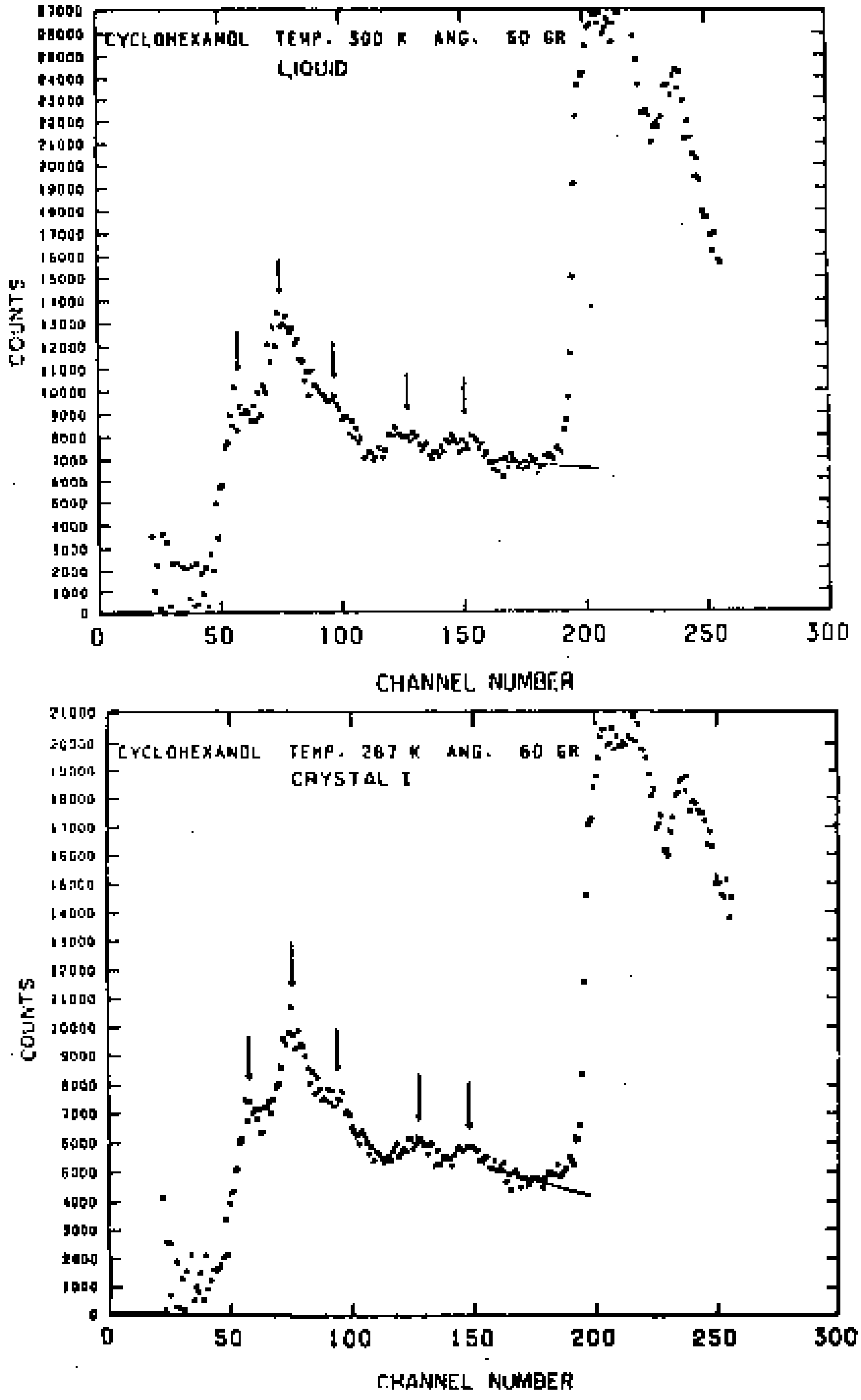

Figure 1 -- Corrected Time-of-Flight Spectra of Neutrons Scattered at an Angle of 60° by Cyclohexanol in its Liquid and Solid (Crystal I) Phases.

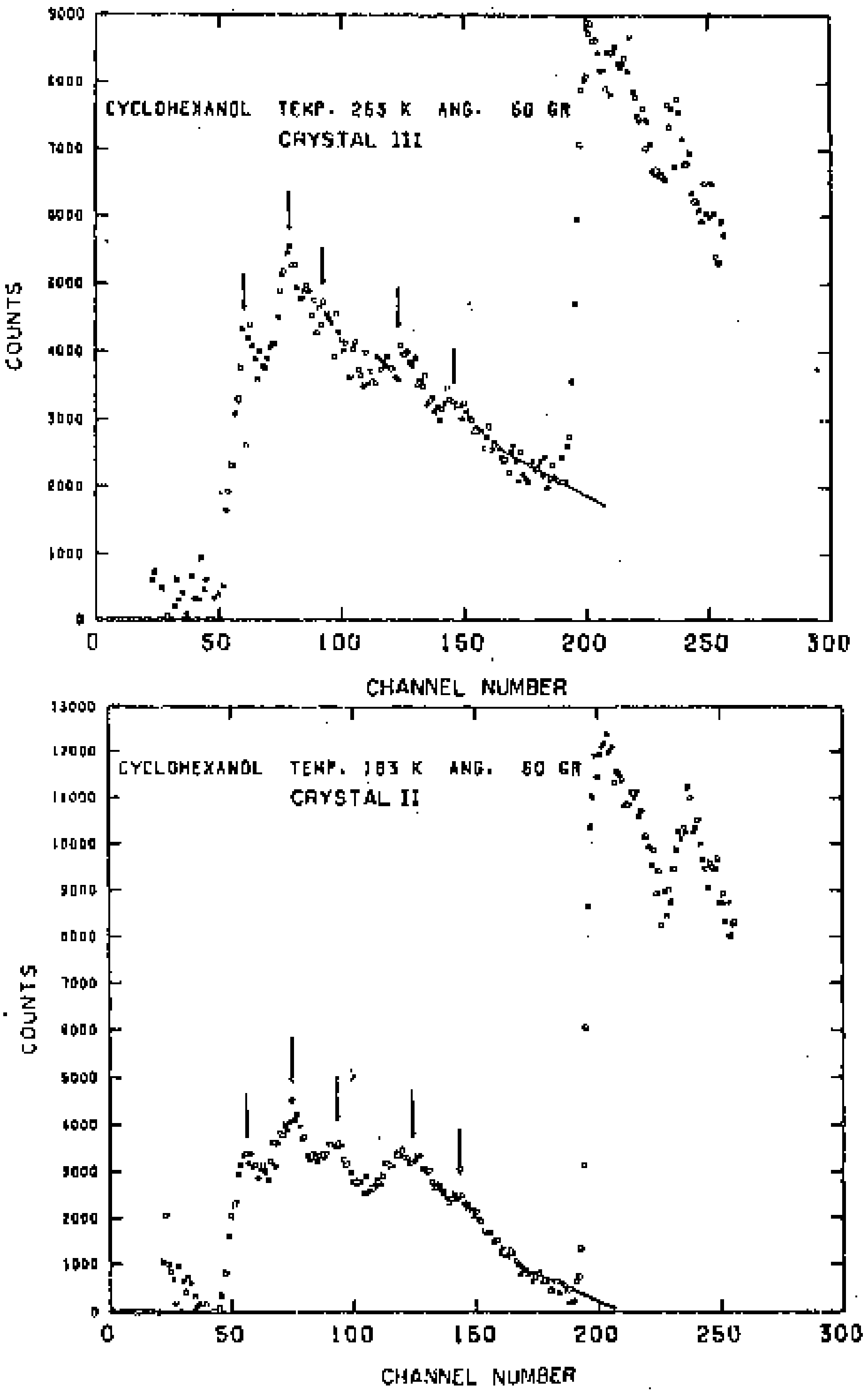

Figure 2 – Corrected Time-of-Flight Spectra of Neutrons Scattered at an Angle of 60° by Cyclohexanol in its Crystall III and Crystal II Phases.

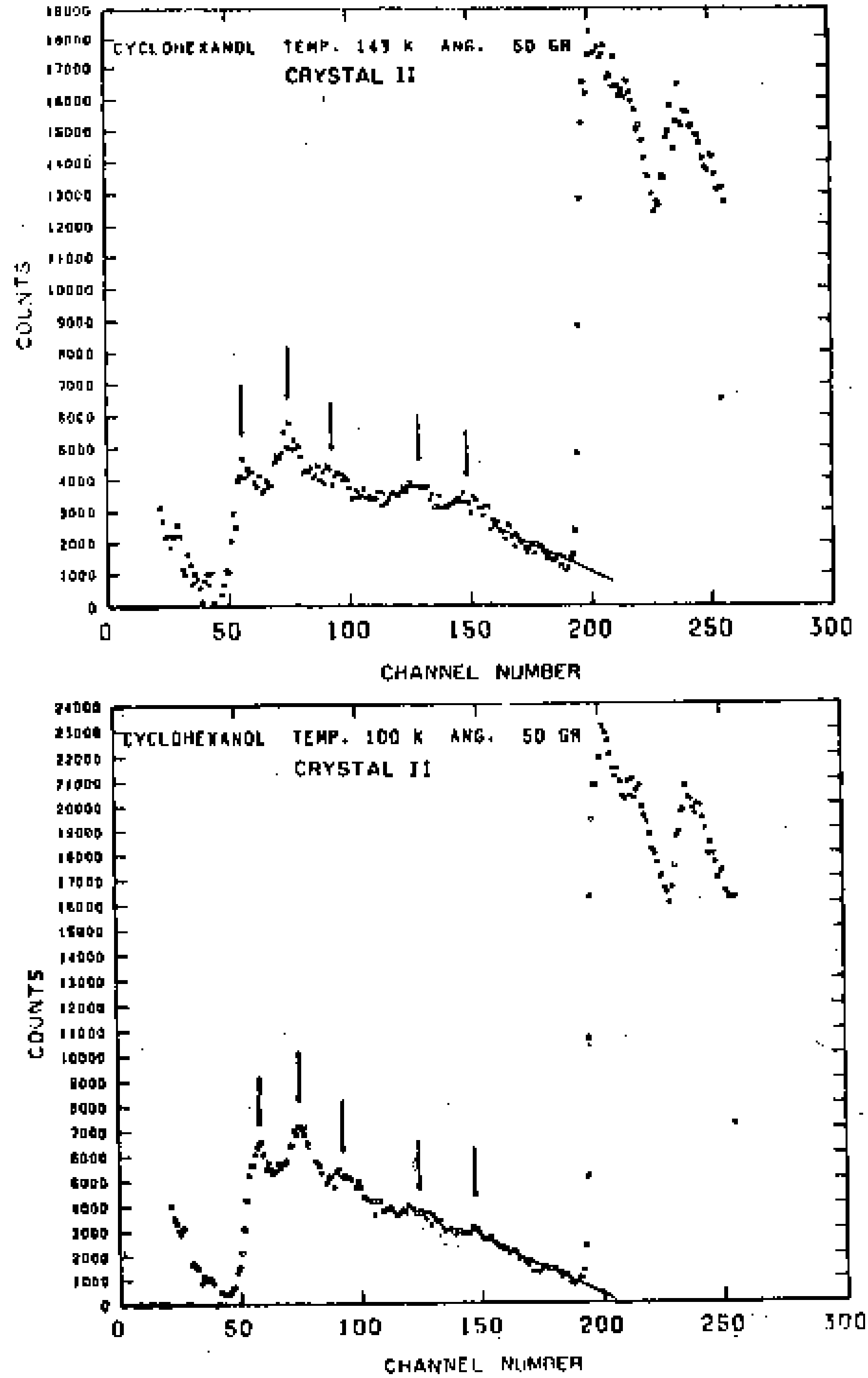

Figure 3 – Corrected Time-of-Flight Spectra of Neutrons Scattered at an Angle of 50° by Cyclohexanol in its Crystal II Phase.

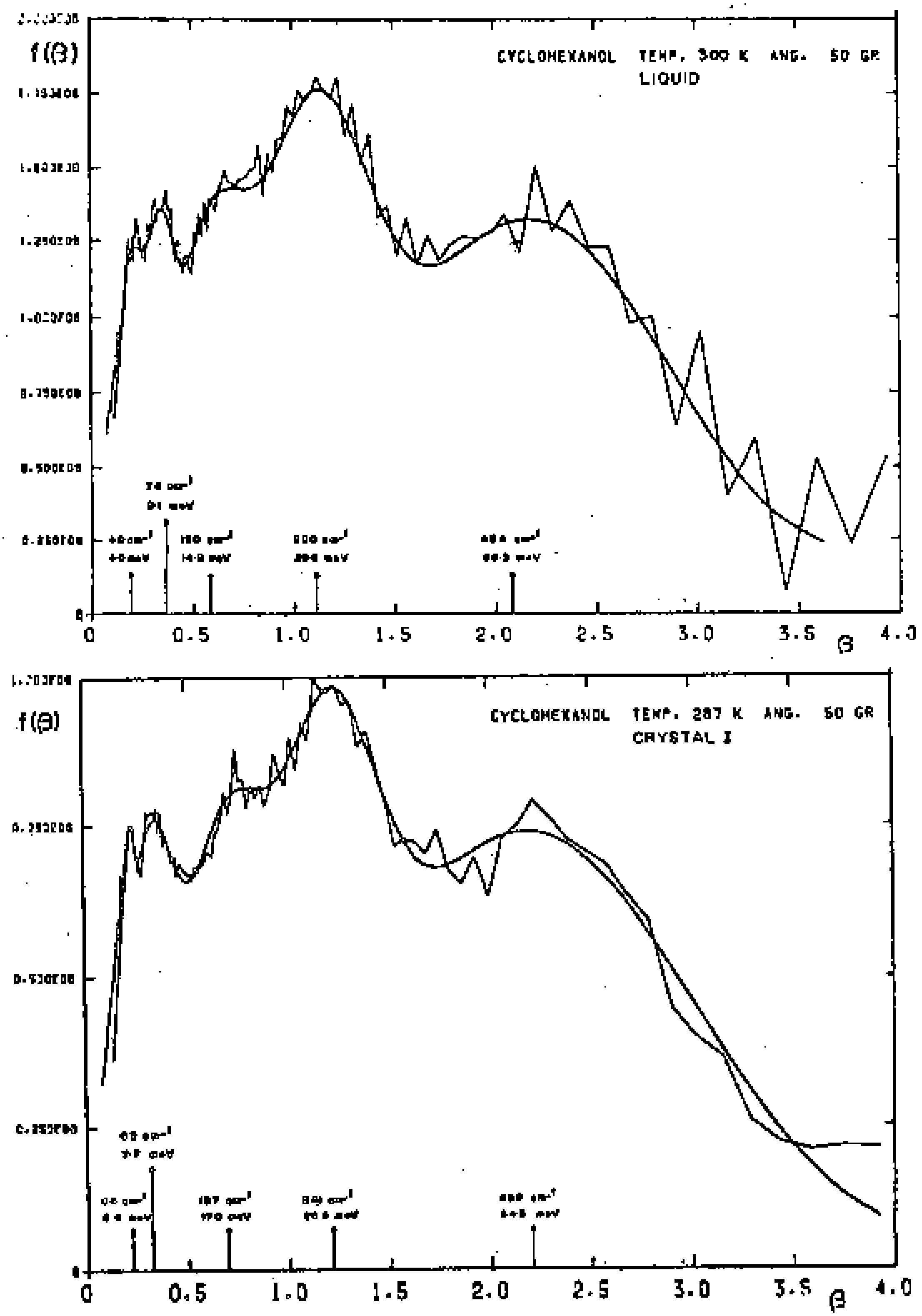

Figure 4 — Generalized Frequency Spectra as a Function of $\beta = \hbar w/KT$. Smooth curve denotes the Best Fitted Spectrum, Calculated as Sum of Five Gaussian Functions. The arrows Mark the Positions of Peaks.

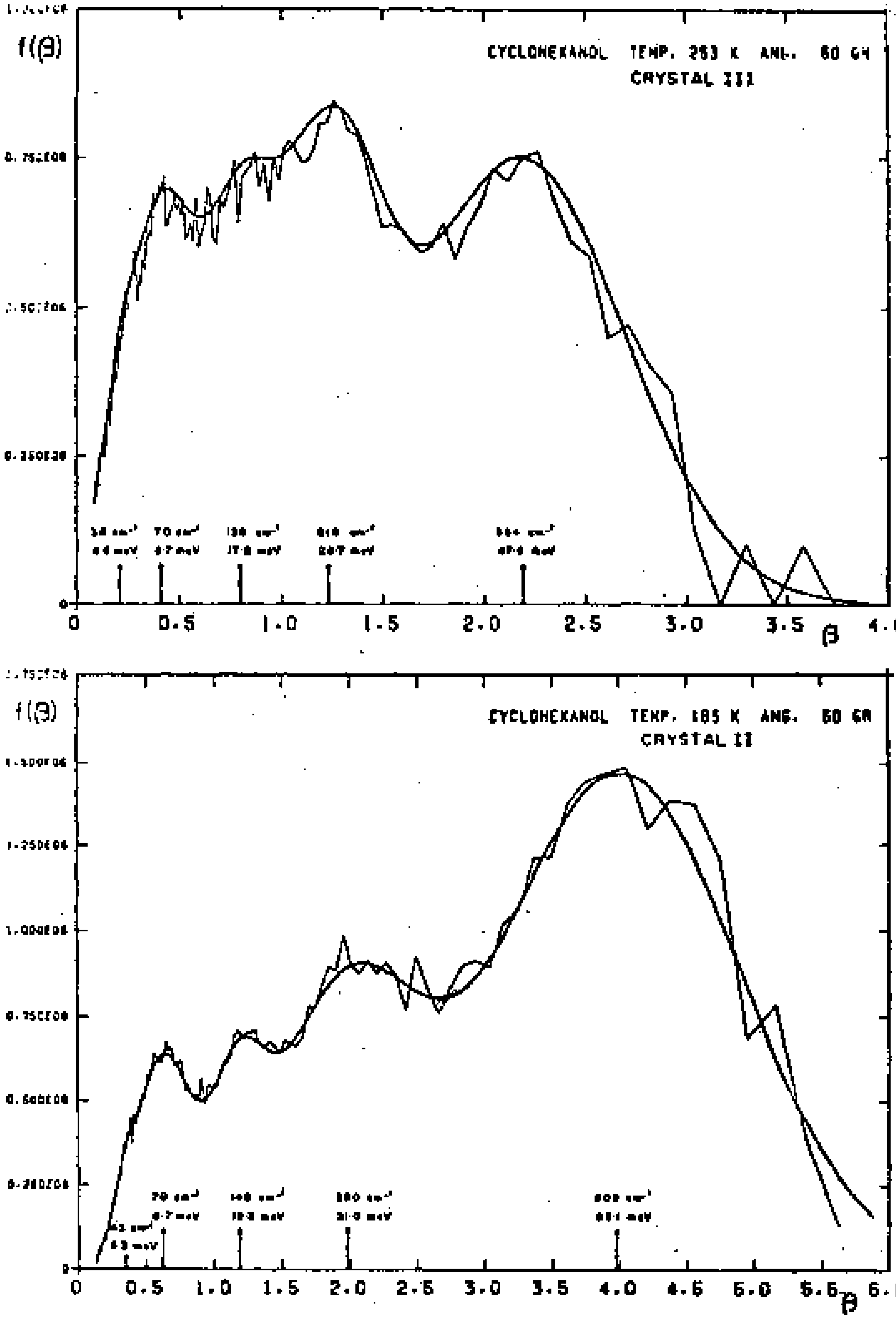

Figure 5 – Generalized Frequency Spectra as a Function of $\beta = \hbar w/KT$. Smooth curve denotes the Best Fitted Spectrum, Calculated as Sum of Five Gaussian Function. The arrows Mark the Positions of Peaks.

Table I

Observed Frequencies and Assignment for Cyclohexenol

Liquid (300K)		SOLID						Assignment
		crystal I (287K)		crystal III (253K)		crystal II (183K)		
(cm^{-1})	(mev)	(cm^{-1})	(mev)	(cm^{-1})	(mev)	(cm^{-1})	(mev)	
40	4.9	44	5.4	36	4.5	43	5.3	hindered rotation or molecular reorientation
74	9.1	62	7.7	70	8.7	79	9.7	crystalline lattice vibration mode
120	14.8	137	17.0	138	17.1	148	18.3	stretching of hydrogen bonds
230	28.5	241	29.9	216	26.7	250	30.9	out-of-plane ring bending modes
454	56.2	438	54.3	384	47.6	509	63.1	out-of-plane and in-plane ring bending modes

The peak observed in the region 120-150 cm^{-1} is originated from the straching of hydrogen bonds, H. . .O, between two molecules[17]. The frequency increases with the decrease of temperature, indicating that the height of barrier for hydrogen bond stretching varies inversely with temperature.

The peak observed at frequencies in the range 216-250 cm^{-1} must be attributed to ring bending modes with 1-0 transition dipole moment[3,14,16], characteristic of out-of-plane atomic motions. These ring vibrations are represented schematically in Figure 6[16].

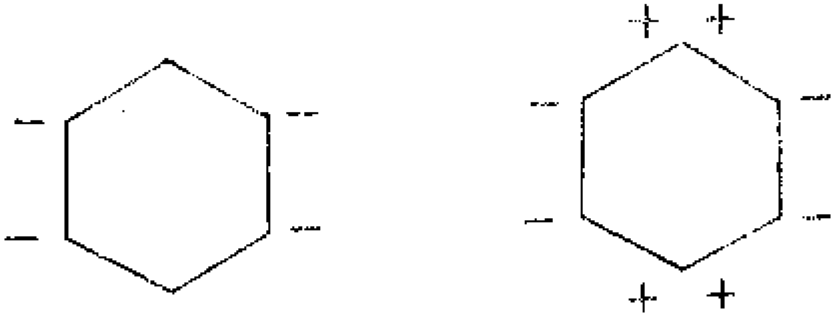

Figure 6 – Schematic View of the Ring Bending Modes Where the Signs + and – Indicate the Direction of Atoms Mouvements Perpendiculary to the Mean Plane of Molecule.

A peak in this frequency region could be assigned as stretching of hydrogen bond; however due to the high intensity observed for this peak in scattered neutron spectra and in frequency spectra, it must correspond to mouvement envolving large number of hydrogen atoms, as a ring vibration, and not to mouvement of one hydrogen in the bond.

In the frequency range 380-500 cm^{-1}, in all spectra a broaded peak was observed. It must be attributed to ring bending modes[16], including in plane and out-of-plane modes. These vibrations are schematically represented in Figure 7[16].

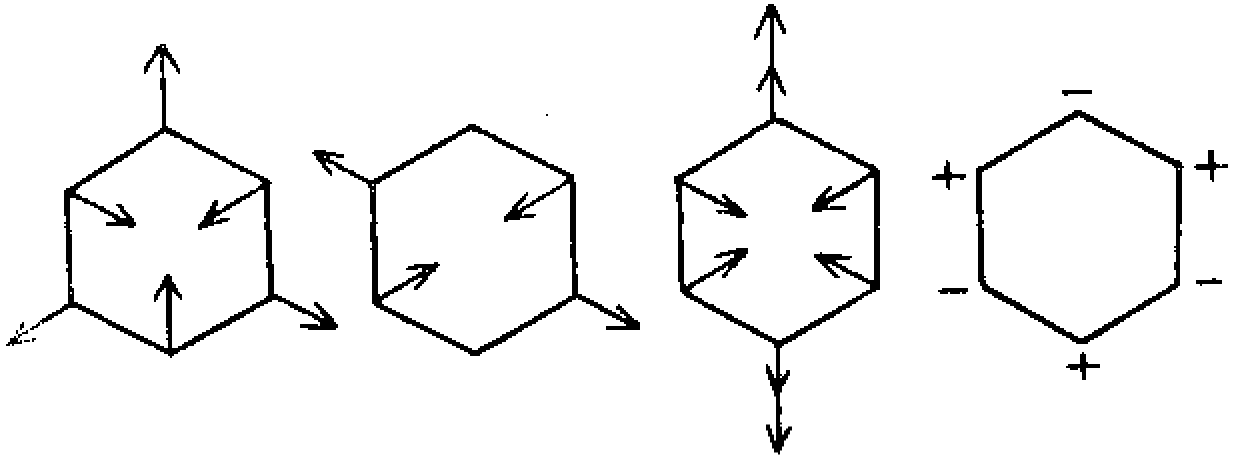

Figure 7 – Schematic View of the Ring Bending Modes

In infrared measurements reported by Cummins and Page[4], four peaks were observed in this frequency region. In the spectra obtained from neutron scattering technique, only a broaded peak was observed. This band probably represents the unresolved four peaks, corresponding to different ring vibration modes. The resolution of the neutron spectrometer, which varies with $E^{3/2}$, is poor in this region of energy and insufficient to resolve the four peaks.

The predominance of one ring band mode in each phase could explain the large displacement in frequency and the differences in the peak profile occured in phase transitions.

RESUMO

Determinou-se por meio do espalhamento incoerente inelástico de nêutrons os espectros de frequência do ciclohexanol em três fases cristalinas e no estado líquido. As medidas foram realizadas utilizando-se o dispositivo experimental Filtro de Berílio Espectrômetro de Tempo de Vôo. Os espectrômetros de nêutrons espalhados e os espectros de frequência ajustados por uma soma de funções gaussianas apresentam cinco acidentes nos intervalos de frequência 36-44, 62-79, 120-148, 216-250 e 384-509 cm^{-1}. Esses picos foram atribuídos respectivamente a rotações restritas da molécula, vibrações da rede cristalina, estiramento de pontes de hidrogênio, modos vibracionais do anel carbônico no plano ou fora do plano médio das moléculas.

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