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FAR INFRARED STUDY OF SOLID tert-BUTANOL

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The temperature dependence of the FIR absorption spectra of tert-butanol has been measured in the 40–500 cm^{-1} frequency range and 97–303 K temperature range. Three solid phases were identified: phase I, phase II, and phase III. Crystal II is built on hydrogen bonded chain polymers of C_{2v} line group symmetry. The most likely crystal space groups are given. Phase I and III are probably disordered crystals built on chain polymers. The kind of disorder which may be encountered here is proposed.

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1. *Introduction*

tert-Butanol C_4H_9OH is a hydrogen bonded crystal, similarly as other alcohols [1–3]. An adiabatic calorimetric study of the phase polymorphism was carried out by Oetting [4] in the 15–330 K temperature range. Two solid phases, the low-temperature phase II and the high-temperature phase I, were found to exist. The II–I phase transition takes place at 286.14 K, but the direct melting of phase II is also possible at 298 K. There is some indication of a phase III in the 281.5–294.5 K range, but experimental evidence of this is very poor. On the basis of X-ray powder measurements Oetting has concluded that both phases II and I show crystal symmetry lower than cubic.

Spectroscopic studies of tert-butanol have been made by several authors. Complete vibration assignments for the intramolecular modes and references to earlier works are given by Beynon and McKetta [5]. There are also two papers dealing with the far infrared region. Lake and Thompson [6] have examined this region for the liquid and solid in order to find the hydrogen bond stretching mode ν_σ. Durig et al. [7] have measured the spectra of C_4H_9OH and C_4D_9OH for phase II in order to determine the methyl torsional frequencies and the corresponding barrier height for methyl group rotation.

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The nature of phase I was controversial for a long time. It is mainly due to the low entropy of melting [4] that this phase was considered to be a rotatory phase. Hence, tert-butanol was classified as a plastic crystal [8], similary as many other compounds of the type $(CH_3)_3CX$ (X = Cl, Br, NO_2, SH) [9], as well as some alcohols [1, 3]. However, dielectric constant measurements have revealed a small effect. The most recent study was by Neu [10]. This author has ascribed the whole effect solely to some kind of crystal defects and concluded that tert-butanol is not a plastic crystal.

The aim of this work is to clarify the phase situation and to provide more information about the properties of the various phases.

2. *Experimental and results*

Absorption measurements were carried out with a DIGILAB FTS-14 spectrometer. The investigated spectral region was 40–500 cm^{-1}, resolution was 2 cm^{-1}. The sample cell with polyethylene windows was filled with the liquid and then the temperature dependence of the absorption spectra was measured several times under various cooling and heating conditions. The sample temperature was stabilized and measured to an accuracy of ± 1 K.

Representative results are shown in the figures. Figure 1 compares spectra of different phases at similar temperatures. Figure 2 shows the temperature dependence of phase II spectra. Tables I and II contain the observed frequencies as well as proposed mode assignments for all phases.

3. *Discussion*

3.1. Internal modes

The tert-butanol molecule C_4H_9OH contains fifteen atoms. From the total of thirty nine internal modes only the skeletal modes of low energy and torsional modes of methyl groups should fall into the experimental range. The correlation method [11] gives for nine internal modes of the skeleton C_3CO of the point group symmetry C_{3v} the irreducible representation $\Gamma_1 = 3A_1+3E$. After the subtraction of four high energy stretching modes there remains for the five low-energy skeletal modes the representation $\Gamma_2 = 1A_1+2E$. Methyl group hydrogens do not change the symmetry of the molecule but add three torsional degrees of freedom of the A_2 and E symmetry species. The OH group hydrogen should lower the symmetry to the C_s point group and add three further degrees of freedom. But according to earlier papers [5, 7] all OH group modes appear at higher frequencies for condensed phases and the tert-butanol molecule can be approximated by the C_{3v} point group at least for the gas and liquid, as no systematic splitting in the assigned E bands was observed. Finally, the irreducible representation Γ_m of low energy intramolecular modes of the molecule is $\Gamma_m = 1A_1+1A_2+3E$ and contains two methyl torsional modes and three skeletal bending modes. These are the modes which should be expected in the investigated spectral region.

3.2. General characteristic of results

Measurements performed for the liquid and solid state give evidence of three different solid phases: phase I, phase II and phase III (Fig. 1). The experimental frequency range includes the range of lattice modes below 210 cm^{-1} and that of the internal modes over this value. A characteristic feature of the first part is the qualitative similarity of the liquid, phase I and phase III spectra. As was discussed earlier [3], the liquid and plastic phase spectra are seen to be almost identical for all known plastic crystals, even for alcohols. Here, the differences are much more pronounced, in agreement with Neu's conclusion. The two broad bands in this range are connected with hydrogen bonding. The higher mode was observed by Lake [6] and assigned to the ν_σ mode. It is reasonable to assign the lower one to the hydrogen bond in-plane bending mode ν_β (this is discussed below). Hence, the close resemblence of the spectra seems to indicate that the hydrogen bond character is similar for the liquid, I and III phases. As usual, the bond is stronger for solids, which causes a shift of the modes towards higher frequencies. There are also some differences in the bond geometry, which is revealed by the relative intensity of the ν_σ and ν_β modes.

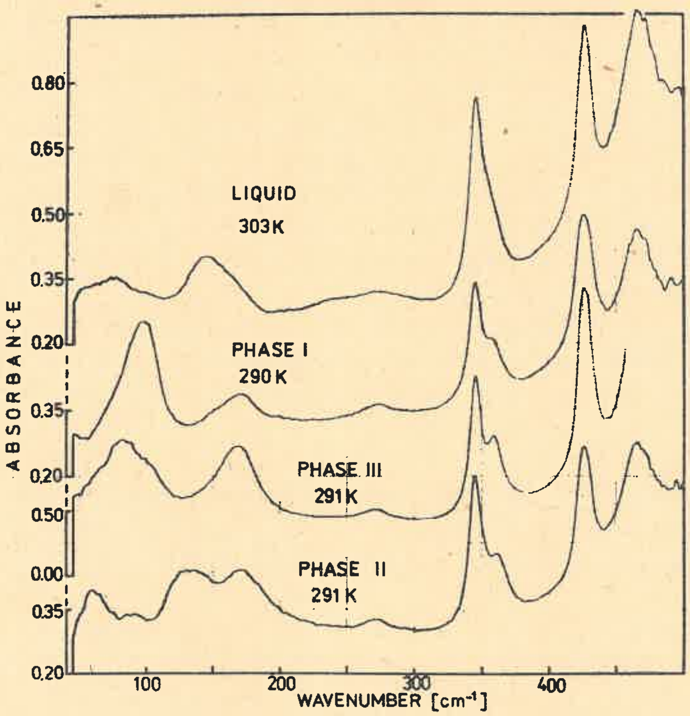

Fig. 1. Far infrared spectra of tert-butanol. From the top: liquid (303 K), phase I (290 K), phase III (291 K) and phase II (291 K)

As was mentioned, the evidence for phase III was controversial in earlier studies. These results support its existence. Phase III and phase I spectra are very similar, indeed, but there is a significant difference in the ν_β mode frequencies and relative intensities of the ν_σ and ν_β modes.

The lattice range of phase II spectra still shows some qualitative similarity to the other phases, clearly seen at higher temperatures (Fig. 1). However, two additional bands appear at 90 and 60 cm^{-1}. The 60 cm^{-1} band is likely to be the out-of-plane hydrogen bond bending mode ν_γ. The appearance of this mode and the further strong shift of the ν_β mode indicates that the hydrogen bonded polymers take definite conformations at phase II. This kind of behaviour should be expected for the normal-crystalline phase II. It is shown below that crystal II is built from plane hydrogen bonded chain polymers. Therefore, we come to the following conclusions: the liquid and solid phases contain chain polymers; phases I and III are probably disordered phases; disorder is probably associated with a curl-like flexible character and variable length of the chains. There can also be an admixture of cyclic multimers especially in the liquid phase. The significant contribution of cyclic multimers for tert-butanol solutions was ascertained by Małecki [12] through linear and nonlinear dielectric effect measurement.

The internal mode range of all phases is almost identical at similar temperatures (Fig. 1). The only difference is the 360 cm^{-1} shoulder. It is seen clearly for the solid phases. For the liquid it is only evident as a distinct asymmetry of the 344 cm^{-1} band.

3.3. Phase II

Careful analysis of the low-temperature spectrum of phase II can provide valuable information concerning crystal II properties. It is seen from Fig. 2. that under these conditions all subtle details which smear out completely at higher temperatures appear clearly in the spectrum.

It is appropriate to begin our discussion from the internal mode range. As was shown earlier, this region should contain two methyl torsional modes (A_2 and E) and three skeletal bending modes (one A_1 and two E). This range was measured by Durig [7] and he gave the final assignments. Comparison of our results and that of Durig (see Table II and Table I of Ref. [7]) shows a small discrepancy for one methyl mode (220 cm^{-1} instead of Durig's 235 cm^{-1}). The 235 cm^{-1} mode is not observed in our spectrum. Two modes are seen instead, a weak one at 220 cm^{-1} and another, almost indiscernible one at 230 cm^{-1}. It proved that the 230 cm^{-1} mode is a trace of the strong 229.2 cm^{-1} ice mode [13] caused by hoar-frosting at the cell windows if pumping is not sufficient. Hence, the 220 cm^{-1} mode must be assumed to be the A_2 torsional mode. This correction gives values of 4.01 and 0.58 kcal/mol for the torsional barrier and the coupling term, instead of 4.13 and 0.44 kcal/mol obtained by Durig (Table VIII from Ref. [7]). The method of calculation and the remaining data were adopted from Durig's paper.

Fig. 2 shows that there are three bands at 344, 424 and 465 cm^{-1}, besides the methyl bands. Hence, these are the skeletal modes, to be expected in this region. But at the lowest temperature these broad bands give rise to eight distinct sharpened bands. The lowering of the symmetry to the C_s point group alone cannot explain this result, as it could give five modes at most (A_1 changes to A' and E splits into A' and A''). The only possible explanation is that Davydov splitting is seen in the spectrum. This correlation splitting is caused by the strongest intermolecular interaction, i.e. the hydrogen bonding. The sequence of the modes is also significant. They form a doublet (350 cm^{-1}), singlet (367 cm^{-1}), doublet (425 cm^{-1}) and triplet (475 cm^{-1}) by turns. The first doublet and singlet together form the triplet. This structure can be unambiguously understood if it is assumed that the molecular symmetry is lowered to the C_s point group and the correlation splitting is subject to the C_{2v} factor group. A more detailed discussion of this can be found in Ref. [3]. We should only add that cyclic polymers which exhibit C_s molecular symmetry and weak hydrogen bonding[1] should have C_{nh} point group symmetry. Hence, both A' and A'' internal modes should remain as singlets in infrared absorption under intrapolymer interaction, in contrast to the Raman effect. Therefore, the experimental evidence of the occurrence of both singlets and doublets in our spectra leaves only one possible polymer structure, namely, the C_{2v} chain polymer (the same as phase MS of cyclohexanol, Ref. [3]). The skeletal mode assignments (Table II) agree with earlier interpretation [5, 7] and give it strong experimental corroboration.

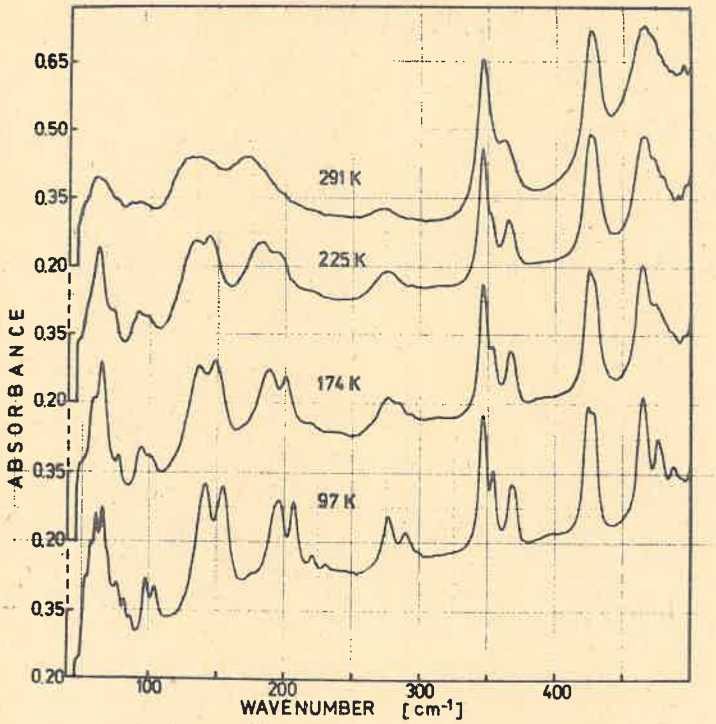

Fig. 2. Temperature dependence of phase II spectra. Temperatures: 291, 225, 174 and 97 K

In order to get further information about the crystal structure the range of lattice modes should be examined. There are thirteen unquestionable modes there (Table I). Two modes at 81 and 85 cm^{-1} may be spurious bands caused by the polyethylene mode,

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[1] All alcohols show a rather weak hydrogen bond [14].

TABLE I

Lattice mode frequencies (cm^{-1}) and tentative assignment

Liquid 303 K	Phase I 290 K	Phase III 291 K	Phase II				Assignment	
							Chain line group C_{2v}	
			291 K	225 K	174 K	97 K	Hydrogen bond modes	Lattice modes
						46 sh		interchain
					47	52 sh		translations
						56 sh		and
					57	60 s		$B_2(R_x, R_y)$
			60	60	63	65 s	$\nu_\gamma^{1,2}$	and
						68 sh		
				72	75	75 w	$\nu_\beta^{1,2}$	$A_1(R_z)$
						*81 w		
						*85 vw		
			90	90	93	97 m	$\nu_\beta^{1,2}$	$B_1(R_z)$
				97	99	104 m		
75 m,b	97 vs,b	83 vs,b	135	132	135	141 vs	$\nu_\beta^{1,2}$	$A_1(T_y)$
				142	147	154 vs		
143 s,b	170 m,b	167 vs,b	170	180	186	195 s	$\nu_\sigma^{1,2}$	$B_1(T_x)$
				192	199	206 s		

Notation: s = strong, m = medium, w = weak, b = broad, sh = shoulder, vw = very weak and vs = very strong. Asterisks mark spurious bands.

TABLE II

Internal mode frequencies (cm^{-1}) and assignment

Liquid 303 K	Phase I 290 K	Phase III 291 K	Phase II				Molecular symmetry species		Approximate description
			291 K	225 K	174 K	97 K	C_s	C_{3v}	
					219	220 w	A''	A_2	CH_3 torsion
						*230 vw			
270 w,vb	272 w	270 w	270	275	274	275 s	A', A''	E	CH_3 torsion
					283	288 m			
344 vs	343 vs	345 vs	344	344	344	345 vs	A'	$> E$	CC_3 deformation
				350 sh	351	353 s			
	357 sh	358 s	360	363	365	367 s	A''		
425 vs	425 vs	425 vs	424	425	425	423 vs	A'	A_1	CC_3 deformation
						427 vs			
465 vs	465 vs	465 vs	465	465	463	464 vs	A', A''	E	CC_3 rocking
					473	475 s			
						486 w			

Notation as in Table I.

as these modes were not seen by Durig [7] and he did not use polyethylene windows. Therefore, the most likely crystal space group is the D_{2h}^9 group with $Z = 8$ (Fig. 8 and Table III from Ref. [3]). This means that the crystal unit cell is built up by four chain units of four different chains. The second discussed group C_{2v}^2 with $Z = 4$ is equally likely in this case, as the crystal is built up from identical molecules and the crystal correlation splitting is not seen in the spectrum. Hence, both arguments against the C_{2v}^2 group [3] lose their validity.

Table I also contains tentative assignments for the lattice modes. The guidelines for this are the following. The intrachain stretching and bending modes are connected with external translational and rotational degrees of freedom of the molecule. The chain unit contains two molecules. The representation Γ_c of eight intrachain modes under the C_{2v} line factor group is $\Gamma_c = 2A_1\ (T_y, R_z)+2\,A_2(T_z, R_y)+2\,B_1(T_x, R_z)+2\,B_2(R_x, R_y)$ (Fig. 8 of Ref. [3]). The chain axis is $2_1(x)$ and the chain plane is $\sigma(x, y)$. Thus, the ν_σ mode corresponds approximately to the $B_1(T_x)$ mode, the ν_β modes to $A_1(T_y)$, $A_1(R_z)$ and $B_1(R_z)$ and the ν_γ modes correspond to $A_2(T_z)$, $A_2(R_y)$, $B_2(R_x)$ and $B_2(R_y)$. All modes except those of symmetry species A_2 are infrared active. The crystal unit cell contains two or four very similar or identical chains, so each mode should appear twice. This explains the characteristic doublet structure of the higher lattice modes. Hence, the highest doublet denoted $\nu_\sigma^{1,2}$ (Table I) is the ν_σ mode of both chains. The next one should be the $\nu_\beta^{1,2}A_1(T_y)$ mode, because its intensity is similar to the first one. Translational modes can be expected to be much stronger than rotational ones in infrared absorption [15]. Hence, the 100 cm^{-1} doublet should be rotational in origin. The $B_1(R_z)$ mode should be chosen from two possibilities, as it is likely to appear at a higher energy [16]. The rest of the intrachain modes and interchain modes form the group of lattice modes at 60 cm^{-1}. At first sight there are discrepancies between this assignment of the intrachain modes and Durig's isotopic shift factors (Table I of Ref. [7]). Nevertheless, there are good reasons why this interpretation is acceptable. Firstly, all the modes are not pure translational or librational modes but can couple together, as the site point group does not contain an inversion center. Moreover, this coupling may depend on isotopic substitution. Secondly, under the assumptions of the localized hydrogen bond model the modes should not shift at all [6]. Hence, the proposed assignments (Table I) require experimental corroboration.

4. *Conclusions*

Three solid phases were identified: crystal I, crystal II and crystal III. Crystal II is built on hydrogen bonded chain polymers of C_{2v} line group symmetry. The most likely crystal space group is the C_{2v}^2 or D_{2h}^9 group. Conclusions regarding phases I and III are not founded so soundly, but there are indications that both phases are disordered crystals built on chain polymers. The kind of disorder which may be encountered here is proposed.

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