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E. ściesinska [a] & J. Ściesiński [b]

[a] Institute of Physics of the Jagiellonian University, Cracow

[b] Institute of Nuclear Physics, Cracow

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Infrared Study of Solid Cyclohexanol

E. ŚCIESIŃSKA† and J. ŚCIESIŃSKI‡

†*Institute of Physics of the Jagiellonian University, Cracow*
‡*Institute of Nuclear Physics, Cracow*

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Mid infrared absorption for cyclohexanol-OH and -OD in the 400–3700 cm^{-1} frequency range and 93–304 K temperature range has been examined. The presence of both equatorial and axial conformers of the molecule for ordered crystals III and II is confirmed. Conclusions on crystal III and II structures on the basis of the OH modes behavior are drawn.

INTRODUCTION

Earlier far infrared studies of polymorphism in cyclohexanol[1,2] have revealed that both equatorial and axial conformers of the molecules are present in the ordered crystalline phases III and II. Such a behavior contradicts that usually observed for molecular crystals: only the most stable conformer persists in an ordered phase. A mixture of conformers appears only for the disordered plastic phase I. Such normal properties were also ascertained for a variety of halogenocyclohexanes by Klaeboe[3] and Rey-Lafon.[4] The exceptional position of cyclohexanol clearly needs further examination. The aim of this work has been to test the conclusions reached from far infrared investigations for the mid infrared region. Also, further information on the structure of the hydrogen bonded polymers was sought.

EXPERIMENTAL AND RESULTS

Absorption measurements were carried out with a DIGILAB FTS-14 spectrometer in the 400–3700 cm^{-1} frequency range and 93–304 K temperature range. Resolution was kept at 2 cm^{-1}. KRS-5 cell windows were used. The experimental method used here is described in Ref. 1. Measurements were per-

formed for pure cyclohexanol-OH (CHOL-OH) and for CHOL-OH_m and CHOL-OD_m doped with cyclohexanol-OD and -OH, respectively. Some measurements for CCl_4 solution of CHOL-OH and CHOL-OD were included.

The main results are shown in Figure 1. These are phase III and II spectra of CHOL-OH and CHOL-OD_m at liquid nitrogen temperature. The phase III–II transition is especially clearly seen on the OH_a stretching admixture band. This is shown in Figure 2. Figure 3 presents the plastic phase I spectra of CHOL-OH and CHOL-OD_m. The spectra of the liquid phase are practically identical, as is always observed for plastic crystals. Slight differences were noted only for the OH and OD band parameters (see Tables II–IV).

The infrared frequencies observed for CHOL-OH and CHOL-OD_m in the fundamental region are listed in Table I. A great many bands appear above 1900 and 2500 cm^{-1} for CHOL-OD_m and CHOL-OH, respectively. They can all be explained as overtones or combination bands, but interpretation is not always unique. Furthermore, additional information about the fundamental region contained there is meager in the case of such low symmetry. Hence these frequencies have been omitted to avoid an excessively long table. The sample thickness had to be fitted to the low absorption region, hence some information about the CH and OH stretching band structure has been lost. The OH and OD band parameters are given separately in Tables II–IV. [A comment on the comparison with Raman studies by James[5] should be added. From the far infrared region the conclusion was drawn[1] that James' phase III corresponds with crystal II. Although the most characteristic OH modes were not observed by James, the specific behavior of the 1139 and 1173 cm^{-1} bands supports this conclusion.]

DISCUSSION

Evidence of conformers

Complete vibrational assignment for cyclohexanol is lacking so far.[5] However, the CO stretching band is known to appear at 970 cm^{-1} for an axial and at 1070 cm^{-1} for an equatorial conformer, respectively. Figure 1 shows that both bands are present for phases III and II. Neither does their relative intensity change significantly under phase transitions. This is a direct proof that both ordered phases are built up of both equatorial and axial conformers. Also, a systematic disappearance of bands is not observed under phase transitions. Only three weak bands common to the CHOL-OH and -OD plastic and liquid phases (*d* bands in Table I) are not seen for ordered crystals. All these can be assigned as combinations involving the 312 cm^{-1} band characteristic only for disordered phases.[1]

The multiplicity of the CO bands is supposed to result from the intrapolymer correlation splitting. The C_i cyclic dimer structure would demand internal

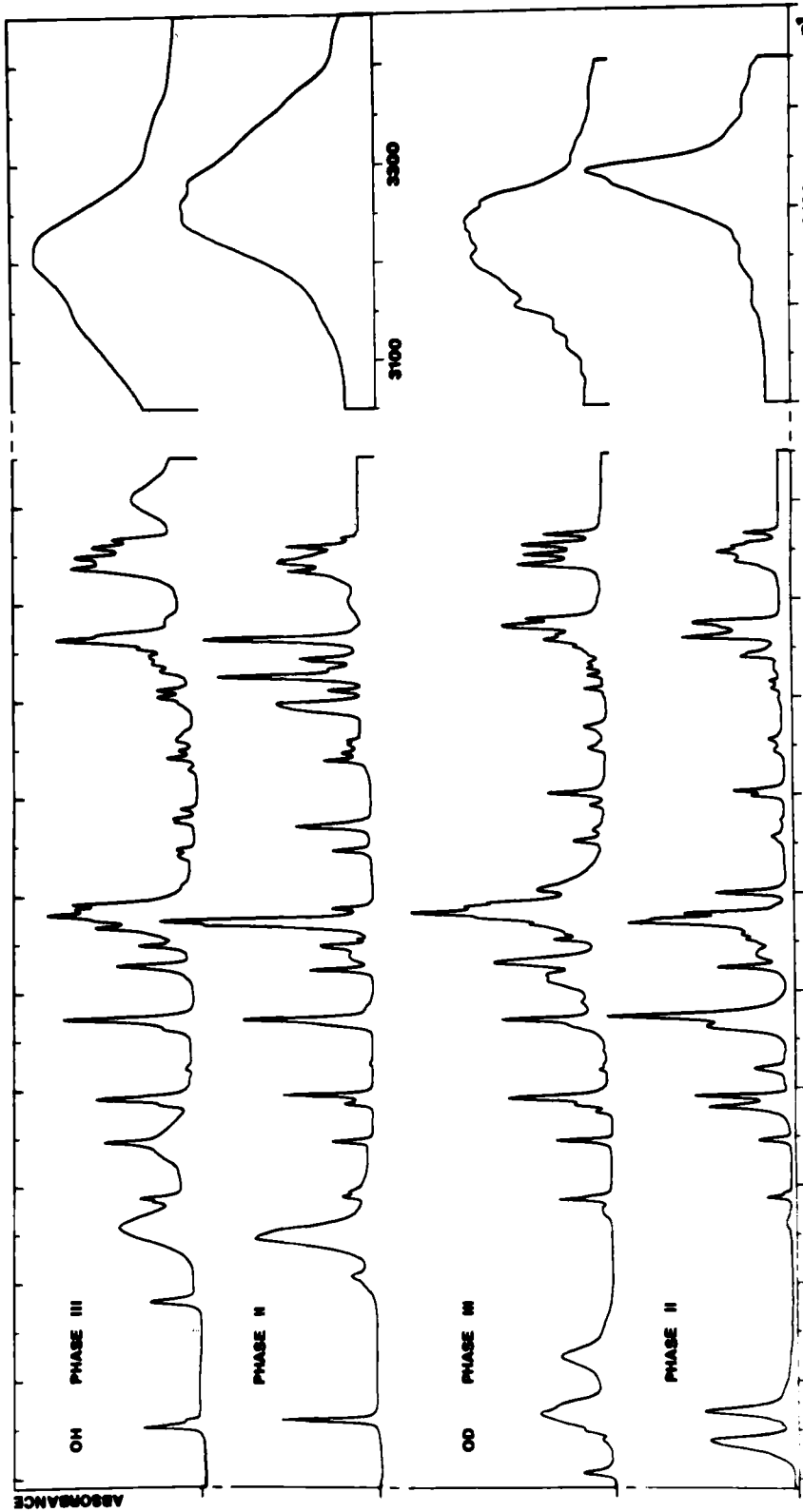

FIGURE 1 Mid infrared spectra of cyclohexanol-OH and -OD at 95 K. From the top: CHOL-OH crystal III, crystal II; CHOL-OD crystal III and crystal II.

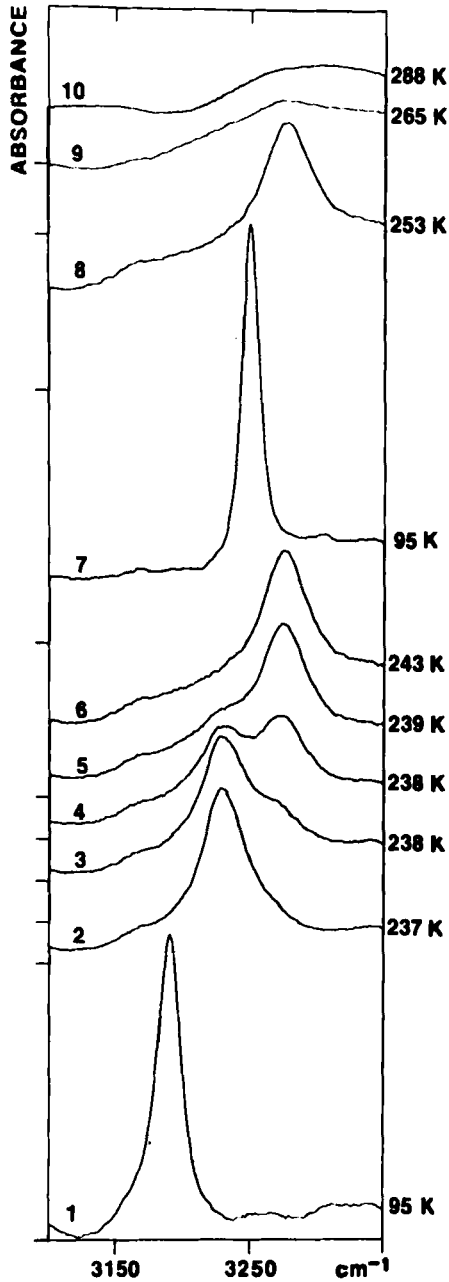

FIGURE 2 Temperature behavior of the OH_a admixture stretching band in cyclohexanol-OD. Crystal III (1,2), crystal II (6,7,8), crystal I (9,10) spectra and crystal III-II phase transition at 238 K (3–5). The spectra are numbered in time sequence.

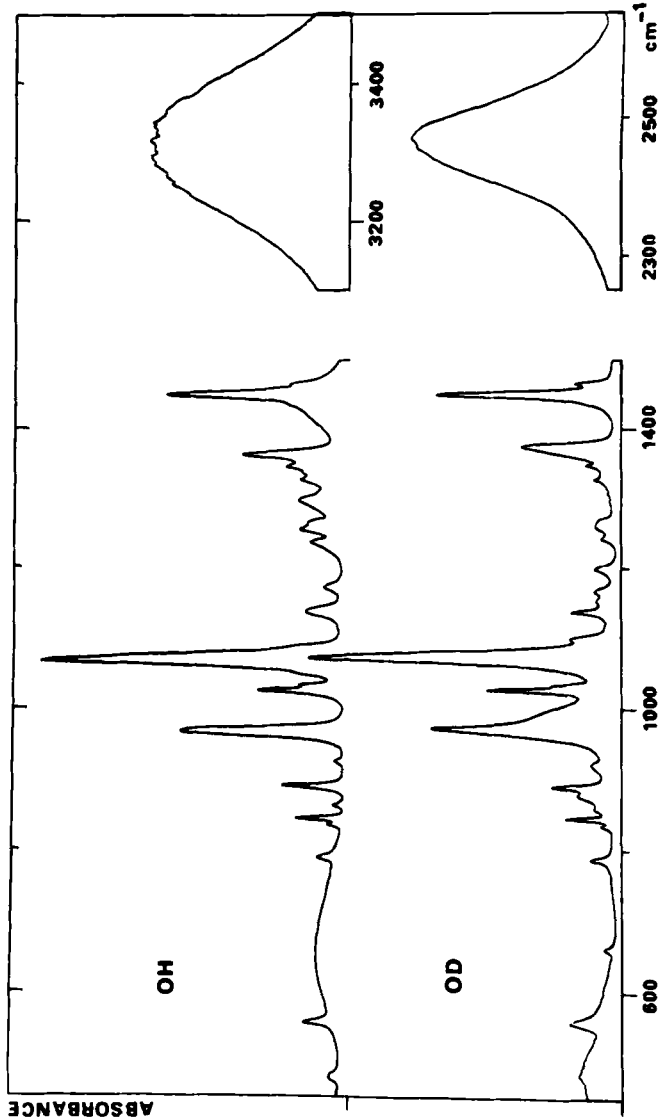

FIGURE 3 Mid infrared spectra of cyclohexanol-OH and -OD. Crystal I spectra at 288 K.

TABLE I

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

Crystal I		Crystal II		Crystal III		
CHOL-OH	CHOL-OD_m	CHOL-OD_m	CHOL-OH	CHOL-OH	CHOL-OD_m	Assignment
				551 m	542 W	
556 m	557 m	567 vs	558 s	558 sh	550 W	$\nu_{16}(A_{2u})$ D
	662 w					350 + 312 d
789 m	786 m	787 w	788 w	784 sh	785 m	$\nu_5(A_{1g})$ a, e
		791 sh	793 sh	788 m	788 sh	
835 w	832 w					1139 − 312 d
844 m	843 m	845 m	845 m	846 m	845 m	CH_2 rock
863 w	860 m					ν_{16} + 312 d
890 s	876 sh	879 s	883 m	883 sh	881 sh	$\nu_{31}(E_u)$
	889 s	890 s	893 s	889 s	888 s	
926 w	922 m	918 m	925 vw	920 w	918 w	CH op bend
970 s	970 s	973 vs	971 s	962 sh	963 sh	CO stretch a, D
				972 s	970 s	
1025 m	1026 m	1022 m	1022 m	1027 m	1029 s	$\nu_{22}(E_g)$
1033 sh	1032 sh	1035 m	1036 m			
1050 sh		1050 w	1048 m	1048 m	1052 w	CH_2 rock
		1056 w	1054 vw	1051 sh	1058 sh	
		1068 s	1069 sh	1066 m	1067 sh	CH_2 twist
				1074 sh	1072 sh	
1068 vs	1071 vs	1072 sh	1073 vs	1079 vs	1081 vs	CO stretch e
				1091 s	1091 sh	
1090 sh		1077 m	1086 m	1086 sh	1087 sh	$\nu_9(A_{1u})$
	1099 sh	1098 s			1103 s	$2\nu_{16}$
1139 m	1138 m	1155 w	1144 m	1141 w	1153 m	CH_2 twist D
	1153 vw			1146 w	1164 w	

1173 m	1200 m	1203 m	1169 s	1175 w	1202 m	CH_2 rock
				1178 w		
		1197 m		1188 w	1189 w	
1237 m	1240 w	1242 w	1237 m	1229 vw	1248 w	CH_2 wag
				1241 w		
		1245 w	1245 w	1248 w	1253 sh	
1256 m	1262 m	1255 w	1253 w	1259 w	1270 w	CH_2 twist
1267 sh			1257 w	1267 sh		
1310 sh		1307 w	1310 m	1311 m	1309 w	CH_2 twist
1329 w	1327 w	1315 w	1332 sh	1331 w	1322 w	CH_2 twist
1338 vw		1340 m	1342 m	1338 w	1330 w	CH_2 wag
1346 m	1347 w			1346 w	1335 w	
				1354 vw	1352 vw	
1363 s	1373 s	1360 vs	1362 vs	1363 vs	1360 m	CH_2 wag
					1365 sh	
		1375 vs	1324 vs	1368 sh	1375 s	CH ip bend D
					1382 m	
			1400 wb	1384 wb		$2\nu_{OH}$ op bend
1452 vs	1449 vs	1438 w	1433 s	1437 s	1437 s	CH_2 scissor
		1447 s	1442 s	1448 s	1447 s	
			1447 sh			
		1452 sh	1457 s	1458 s	1457 s	CH_2 scissor
		1466 m	1466 w	1466 m	1467 m	
2850 vs	2850 vs	2855 vs	2855 vs	2855 vs	2855 vs ?	CH_2 stretch
2930 vs	2930 vs	2930 vs	2930 vs	2920 vs	2920 vs ?	

Crystal I data at 288 K, crystal II and III at 95 K.

Notation: v, w, m, s, b and sh denotes very, weak, medium, strong, broad and shoulder, respectively; ip bend and op bend, in plane and out of plane bending mode; a, axial and e, equatorial conformer; d, bands characteristic only for disordered phases; D, correlation doublet; ?, estimated band center; subscript m, doped crystal; W, Evans transmission window [*Spectrochim. Acta*, **18**, 507 (1962)].

mode singlets and the C_2 chain polymer structure internal mode doublets. These polymer structures were predicted for phases II and III respectively on the basis of the CO bending and lattice modes behavior. A full discussion is given in Ref. 1. The 970 cm^{-1} band of the axial conformer fits these expectations by appearing as a singlet for phase II and as a doublet for phase III (Figure 1 and Table I). The 1070 cm^{-1} band of the equatorial conformer behaves less clearly. Five components for phase III and three components for phase II are seen for this band at low temperature. This is undoubtedly due to accidential degeneracy with some other skeletal or methylene group modes. A tentative assignment is given in Table I.

The reported experimental results do not suffice for vibrational assignment. However considerable changes in the spectrum are observed under sample deuteration and phase transitions. These give evidence of complicated intermode couplings. Qualitative analysis of these effects and comparison with the literature infrared and Raman data for cyclohexanol[5] and related compounds[3,4,6,7] has enabled the assignment shown in Table I to be proposed. The assignment below 1000 cm^{-1} is rather fixed. Skeletal modes were described in terms of the corresponding cyclohexane ring modes,[6] as is frequently done. Actually, the CHOL molecule can show, at best, the C_s symmetry. In contrast to halogenocyclohexanes, there seems to be no clear difference between conformers for ring deformation and stretching modes of cyclohexanol. Only the ν_5 mode undoubtedly shows splitting of 4 cm^{-1} into the *e* and *a* components.

OH and OD modes

The most valuable information on the properties of a cyclohexanol crystal is certainly concealed in the behavior of these modes. Some relevant data are listed in Tables II–IV. These results are discussed below for OH(OD) stretching, in plane and out of plane bending modes. Features revealing peculiar polymer structure of crystal III and II are stressed.

1 OH(OD) stretching modes As was mentioned, the OH stretching band was not reliably measured for a pure sample, but it seems to show no structure beside the shoulders listed in Table II. The OD stretching band, on the other hand, reveals rich structure especially for phase III, due certainly to overtones and combination bands. Approximate positions of the band centers and band widths are given in Table II. The OH_a and OD_a admixture bands are hardly seen for the liquid and plastic phase on account of its broadness (Figure 2). But for crystal II and III the bands are quite narrow and these give further evidence of the ordered structures.[8,9] The significant feature is the considerable narrowing of the OH and OD bands and their shift upwards ca. 55 cm^{-1} at the phase III–II transition. Both features[10,11] strongly support the chain polymer-cyclic polymer transition model.

TABLE II

OH and OD stretching band parameters

PHASE	OH	OH_a	θ_a^H	OD_m	OD_a	θ_a^D	S_a	S_m
III	3185/180/vs 3350 sh	3190/21/m	0.85	2365/120/vs	2364/27/m	0.97	1.3494	1.347
II	3150 sh 3275/150/vs 3370 sh 3435 sh	3250/14/m	0.54	2427/55/vs	2416/15/m	051	1.3452	1.349
I	3315/240/vs			2465/140/vs				1.345
L	3330/290/vs			2480/140/vs				1.343
S	3621/22/m,F 3490 sh,B 3345/250/s,B	3621/21/ w,F 3490 sh,B 3350/260/w,B		2673/17/m,F 2590 sh,B 2480/160/s,B				1.3547 1.35 1.349

Band positions and full band widths at half maximum in parenthesis (cm^{-1}); crystal III and II data at 95 K, crystal I at 288 K, liquid L at 303 and solution S at 298 K. Additional notation in comparison to Table I: F and B, monomer and associated molecule bands; subscript a and m, admixture and matrix bands; superscript H and D, a parameter of the OH and OD bands, θ, linear temperature shift coefficient (in 10^{-4} K^{-1}) defined as $d\nu/\nu_0 dT$, where ν_0 corresponds to 95 K, $d\nu$ and dT denote frequency and temperature change, respectively; S_a and S_m, isotopic shift factors for admixture and matrix bands. Estimated errors: 5–10% for θ and 0.04–4% for S_a and S_m, depending on band shapes and positions.

2 OH(OD) ip bending modes The assignment of these modes was not obvious even though a comparison of the CHOL-OH and -OD spectra was made. The OH ip bending mode is known to be highly sensitive to intermode mixing[9,12] and as a consequence less specific. This mode was suspected[13] at ca. 1400 cm^{-1} from CCl_4 solution studies. However, practically identical results were obtained here for CHOL-OH and CHOL-OD solutions above 1320 cm^{-1}. Clear differences were instead seen at ca. 1230 and 1290 cm^{-1}. Hence these bands were assigned to the OH ip bending mode of the free and associated molecule, respectively. A somewhat higher isotopic shift factor (Table III) for the free molecule is reasonable for this mode. The CHOL-OH crystal III shows one component of the OH ip bending mode at 1507 cm^{-1} as a very strong and broad band, similarly as with methanol.[14] For the deuterated sample this band appears at ca. 1010 cm^{-1} and its structure is connected with the OD op bending overtone. There also appears a clear band at 874 cm^{-1} for $CHOL\text{-}OD_m$ which most probably is the second component. The corresponding band for CHOL-OH is found at 1304 cm^{-1}. The value of the shift factor gives evidence of significant intermode coupling, but is still much lower than 1.67 as observed for methanol.[15] Some doubts are caused by the OD_a band located at 1003 cm^{-1} (Table III), which seems to be too far removed from the correlation doublet center. The character of the OH ip bending band for crystal II is different; the band is rather narrow. For CHOL-OD an influence on the ν_{31} and CH op bending modes is revealed, but the shift factor remains at a normal level (Figure 1).

TABLE III

OH and OD ip bending band parameters

PHASE	OH	θ^H	OH_a	OD_m	OD_a	S_a	S_m
III	1304(5) m			874 sh	998 sh 1003 w		1.492
				987 w			
	1507(32) vs	−0.79		1010(18) s			1.488
				1015 sh			
II	1295(12) s	−0.14	1297w	962 sh	980 sh	1.323	1.346
I	1298 m			990 sh			1.31
	1430 ?						
L	1297 m			990 sh			1.31
	1430 ?						
S	1230 m,F			854(10) m,F			1.440
	1292 w,B			935 w,B			1.382

For notation, see footnotes to Table II.

3 OH(OD) op bending modes The OH op bending mode has not received much attention in earlier hydrogen bonding studies. More recently its diagnostic value has been appreciated.[9,16] Zerbi and coworkers have done an experimental[14] and theoretical[17] analysis of this mode for methanol. Figure 4 shows the temperature dependence of this mode for CHOL-OH. For crystal III the mode behaves qualitatively very similarly to that of methanol,[14] but two broad components are clearly separated at low temperature. The methanol band is like that of cyclohexanol but at a much higher temperature. Even the frequencies are nearly coincident. The same is observed for the OH ip bending and OH stretching modes. This similarity can hardly be understood if the polymer structures of methanol and cyclohexanol were different. Hence this strongly supports the chain polymer model for phase III. The existence of the OH op bending triplet instead of the expected doublet need not mean that the postulated two-molecule chain unit is wrong. The band is not well understood in detail so far. Recently, Pellegrini[17] has explained the breadth of the band for methanol through a distribution of hydrogen bond geometries along the chain. But there is still no reasonable explanation why the lowest component is so narrow. The highest frequency component for methanol was seen as a broad shoulder and interpreted through two-phonon processes. It seems quite possible that a theory of vibrational excitons involving strong coupling with relevant hydrogen bond modes, similar to that of Fischer and Rice,[18] would give a similar triplet for the two-molecule unit cell. This problem certainly demands further study.

The behavior of the OH op bending mode for phase II is quite different. The band consists of two medium broad components, one weak and the other very strong. For CHOL-OD this band is significantly distorted by coupling with the ν_{16} mode, so the first component is only marked as a shoulder. This coupling reveals itself in the somewhat anomalous value of the isotopic shift factor (Table IV). Both the intensity and position of the ν_{16} mode are noticeably perturbed (Figure 1 and Table I). The appearance of a doublet instead of a singlet for the C_i cyclic dimer structure is comprehensible under the strong coupling conditions with appropriate hydrogen bond modes. Due to arguments similar to those of Witkowski,[19] these can cause the gerade mode to be infrared active. The peculiar behavior of this band for a CHOL-OH_m doped crystal is also very interesting. Here a third weak component at 717 cm^{-1} is seen between two others. It has to be the OH_u uncoupled mode in the middle of the correlation doublet. The appearance of this mode cannot be understood for the C_2 chain polymer structure with a low concentration of the admixture. For crystal III the OH op bending band is identical for pure CHOL-OH and doped CHOL-OH_m. But for the cyclic polymer structure the smallest admixture unavoidedly breaks the intrapolymer coupling for some polymers. Hence

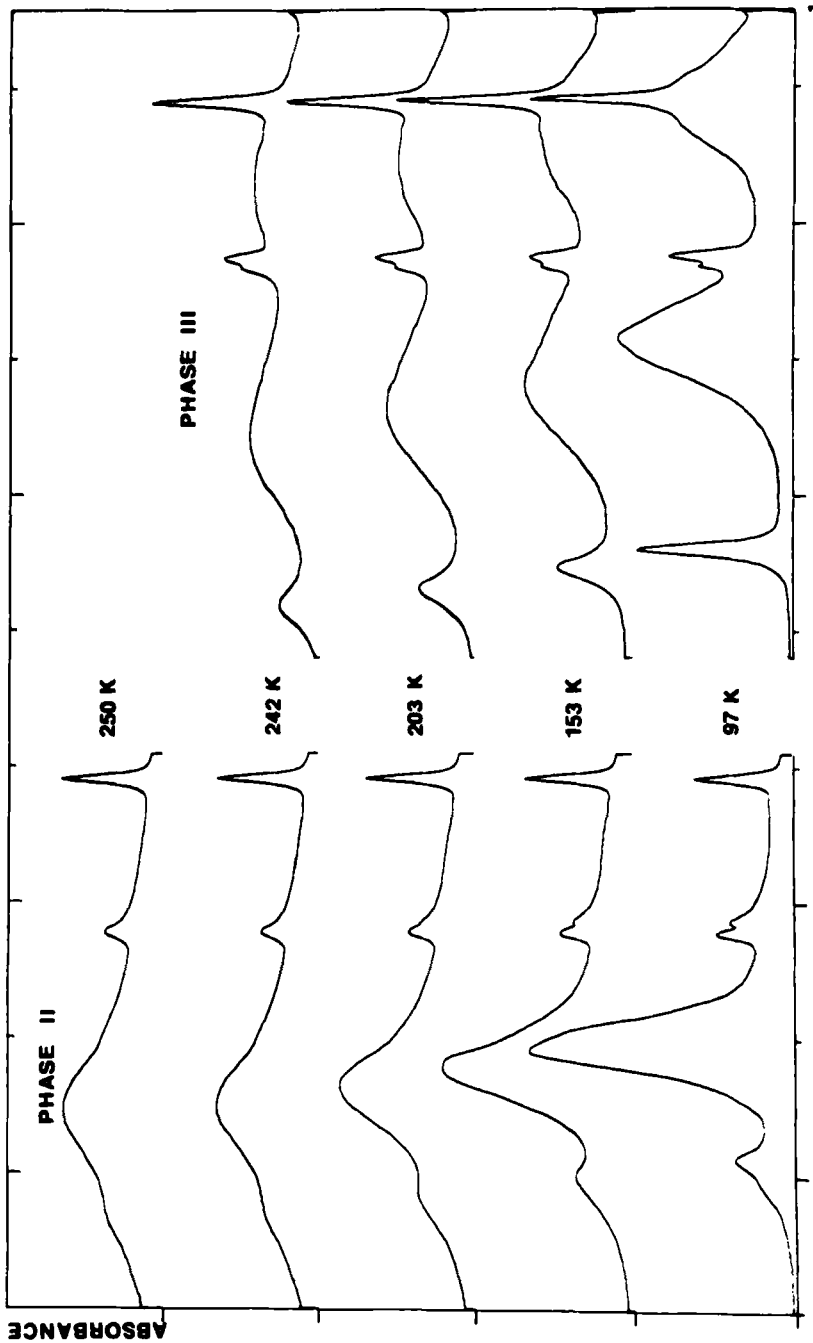

FIGURE 4 Temperature dependence of the infrared spectrum of cyclohexanol-OH in the OH op bending mode region. Crystal II (left) and crystal III (right) at 97, 153, 203, 242 and 250 K. (The modes ν_5 at 789 and CH_2 rock at 844 cm^{-1} are also seen.)

TABLE IV

OH and OD op bending band parameters

PHASE	OH	θ^H	OH_a	θ_a^H	OD_m	θ^D	OD_a	S_a	S_m
III	680(6) s	−2.07	770 w	−2.34	505(6) s	−1.22	562 w	1.375	1.347
	758(34) vs	−3.11	775 w		565(27) vs				1.342
	844(39) s	−2.31			624(24) s	−3.00			1.353
II	706 m		761 w		523 sh		543 w	1.401	
	745(22) vs	−1.79			539(14) vs	−2.69			1.382
I	650(200) s				500 m				1.30
L	650(200) s				490 m				1.33

For notation, see footnotes to Table II.

both the OH_u and OD_a uncoupled modes should appear, as is observed. These experimental data seem to be a strong argument in favor of the C_i cyclic dimer structure of phase II. The shift of 44 cm^{-1} between the OH_a and OH_u modes is worth noting. According to Prased,[20] this shift can be due to the difference of the static site shift for a CHOL-OH and -OD environment, or it can be due to the translational shift resulting from the interactions between translationally equivalent molecules. Hence these interactions seem to be strong for crystal II of cyclohexanol.

4 Appearance of conformers So far, the problem of two conformers has been omitted from the OH mode discussion. It would have been expected that two correlation multiplets should be observed for each of the three OH modes, independently for the axial and equatorial conformer. But it is known that the behavior of OH modes is decided by hydrogen bond properties for bonded molecules. Experimentally, it looks like the bands were common to both conformers. The OH_a and OD_a stretching admixture narrow bands are single. The structure of the ip and op bending multiplets is also due to correlation splitting. The OH_a op bending mode for phase III, however, seems to show a slight doublet structure, close to the limit of experimental error (Table IV and Figure 1). The most likely solution seems to be an accidential degeneracy of the OH modes for both conformers. The geometrical structure of the conformers and the closest packing conditions can provide similar, or even equal parameters of the hydrogen bond for both conformers.[1] Alternatively, one might postulate that only different conformers bond together for cyclohexanol II and III crystals. But then the intrapolymer splittings observed in the far[1] and mid infrared region for some modes would seem to be unexpectedly high for the second neighbor interaction. The intrapolymer splitting of methanol, observed only for the OH op bending and OH and CO stretching modes, is similar to that of cyclohexanol.

5 Temperature behavior of OH(OD) modes The temperature dependence of the OH modes is worth discussing. It is shown in Figures 2 and 4. Relevant data are given in Tables II–IV. The linear frequency vs temperature dependence was fitted for all the bands. The error of the temperature shift coefficient θ is estimated to be 5–10%. The OH and OD stretching bands show equal θ coefficients, as one would expect. For op bending modes agreement is lacking probably due to intermode mixing for the CHOL-OD crystal. Temperature broadening and neighboring band behavior make the data for bending modes less accurate and informative. Nevertheless, these coefficients were also included in Tables III and IV merely to complete the experimental results. In accordance with expectation, the coefficients show a stronger temperature effect for the op bending mode. An interesting feature is also the definite difference between the θ coefficients for the op bending mode components of crystal III. The most reliable and valuable data relate to the OH_a and OD_a stretching admixture bands. It is seen that the θ coefficient of crystal II is almost two times lower than that of crystal III (Table II). The temperature effect for the OH stretching mode has been studied both theoretically and experimentally.[21,22] Generally, the positive effect is expected and observed. But potassium bicarbonate which forms a cyclic dimer structure, shows no effect. Such a behavior was predicted for isolated cyclic dimers by Marechal.[23] The factor two between θ coefficients of crystals III and II of cyclohexanol would be hard to understand for similar polymer structures. This is a further valuable and convincing argument for the chain and cyclic polymer structures of crystal III and II, respectively.

6 Isotopic effect According to Novak,[9] valuable information about the isotopic effect in a crystal can be obtained by comparing the isotopic shift factors for the OH stretching and op bending modes. Unfortunately, the OH op mode factors for cyclohexanol are significantly distorted due to intermode coupling. The OH stretching mode alone suggests a minor positive isotopic effect, as is expected for alcohols. Some further data on the isotopic effect for cyclohexanol can be found in Ref. 2.

CONCLUSIONS

The presence of both equatorial and axial conformers of the molecule for ordered crystals III and II of cyclohexanol was confirmed. Many peculiar features of the OH modes, supporting the chain polymer and cyclic dimer structure of crystal III and II, respectively, were found. So far, there seem to be no convincing experimental arguments against the C_i cyclic dimer and C_2 chain polymer structures, proposed in Ref. 1.

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