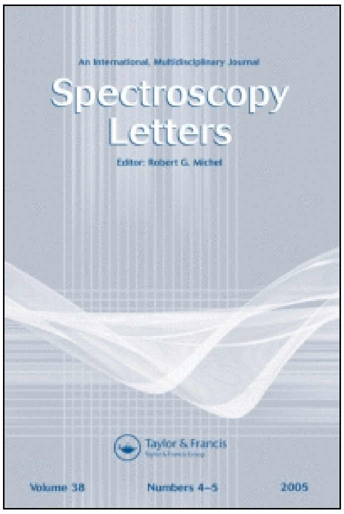

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E. Ściesińska[a]; J. Ściesiński[ab]; M. Godlewska[a]
[a] Institute of Physics of the Jagiellonian University, Kraków [b] Institute of Nuclear Physics, Kraków, Poland

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INFRARED STUDY OF SOLID CYCLOPENTANOL

Key words: polymorphism, hydrogen bond,
infrared spectra

E. Ściesińska, J. Ściesiński⁺,
and M. Godlewska
Institute of Physics of the Jagiellonian
University, Reymonta 4, 30-059 Kraków,
+Institute of Nuclear Physics, Kraków,
Poland

ABSTRACT

Infrared absorption spectra of cyclopentanol-OH and -OD have been measured in the 16 - 3700 cm^{-1} frequency range for crystal IV, III, II, I and liquid phases. The role of both the hydrogen bond and the conformation of a molecule in polymorphism is discussed.

INTRODUCTION

The polymorphism of cyclopentanol has been previously investigated by several methods. In calorimetric measurements[1,2] the temperatures of phase transitions and their thermodynamic parameters were determined. Dielectric studies[3] showed that phases I and II were rotator phases and allowed the length of hydrogen bonded chain polymers to be estimated. Fundamental data on the crystal structure of rotator phases are also known[4]. However, information on the mechanism of phase transitions is not complete and the factors influencing polymorphism are not known yet. The aim of this work was to study the role of both the hydrogen bond and the conformation of a molecule in polymorphism of cyclopentanol. In view of the results obtained recently for cyclohexanol[5] it seemed that the use of the infrared spectroscopy method may give interesting information.

RESULTS AND DISCUSSION

The temperature dependence of the absorption spectrum of C_5H_9OH and OD was measured in the temperature range of 90 - 300 K and in the frequency range of 16 - 3700 cm^{-1} with a DIGILAB FTS 14 spectrometer. The temperature range studied covers all known crystalline phases and the liquid phase. The frequency range covers both the lattice mode region (below ca 270 cm^{-1}) and the internal vibration region (above 270 cm^{-1}). Representative results are shown in Fig. 1 - 3. Figure 1 shows the absorption spectra of phases I and IV of cyclopentanol-OH (CPOL-OH) and -OD above 450 cm^{-1}. The spectrum of phase II as well as that of liquid is practically identical with the spectrum of phase I. This fact, found for all plastic crystals investigated, confirms the rotational character of phases I and II. In spite of the above mentioned close similarity of the spectra the phase II - phase I transition and the melting transition are noticeable due to slight changes of

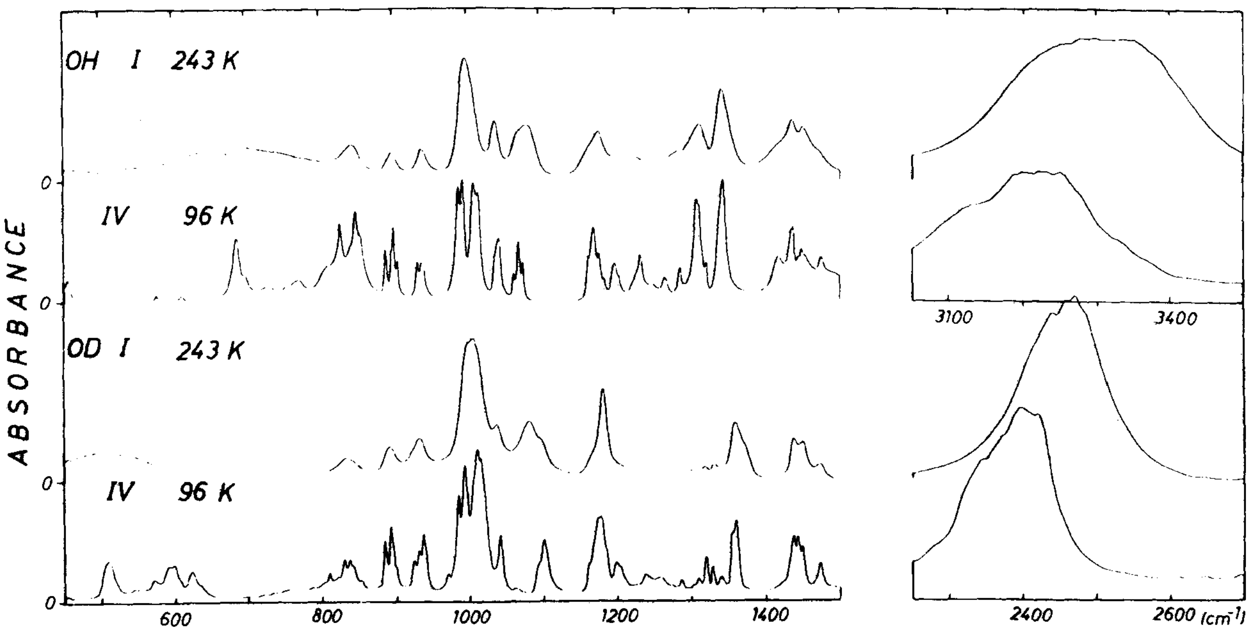

FIG. 1 Infrared absorption spectra of cyclopentanol-OH and -OD in the internal mode range: phase IV at 96 K and phase I at 243 K.

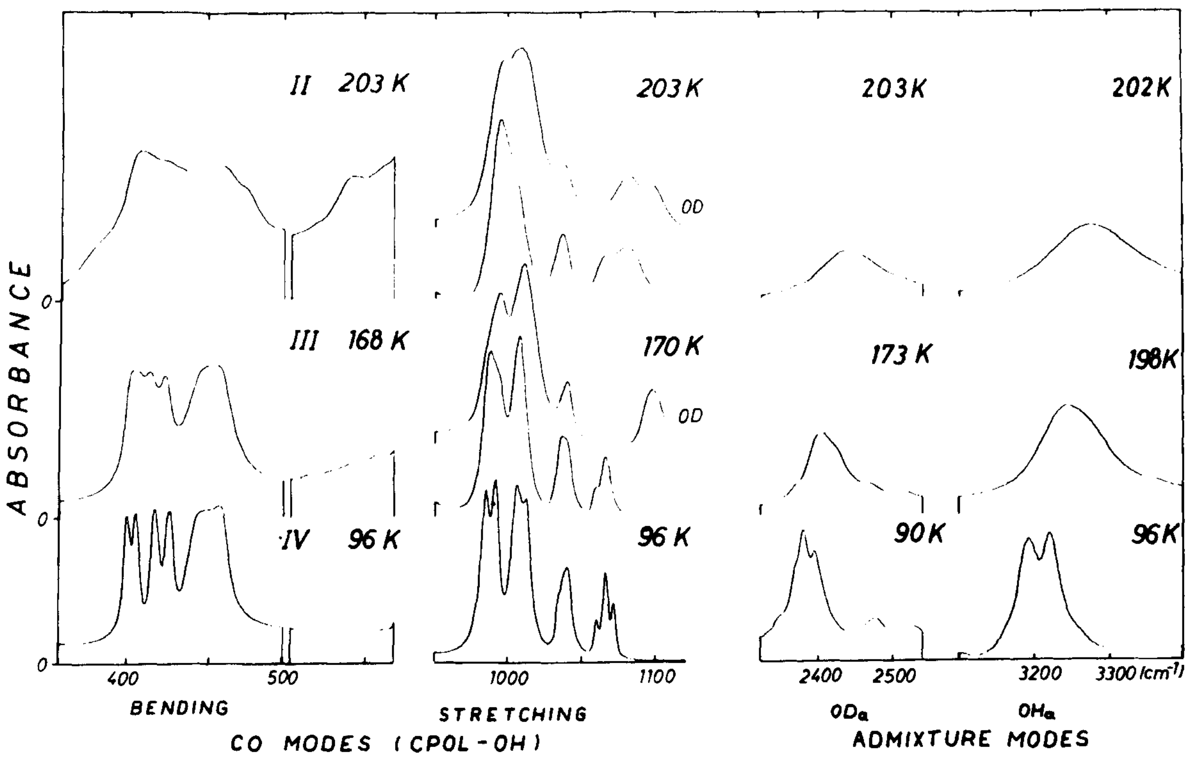

FIG. 2 The range of CO bands /op and ip bending and stretching modes/ and OH_a /OD_a/ admixture stretching band for phases IV, III and II.

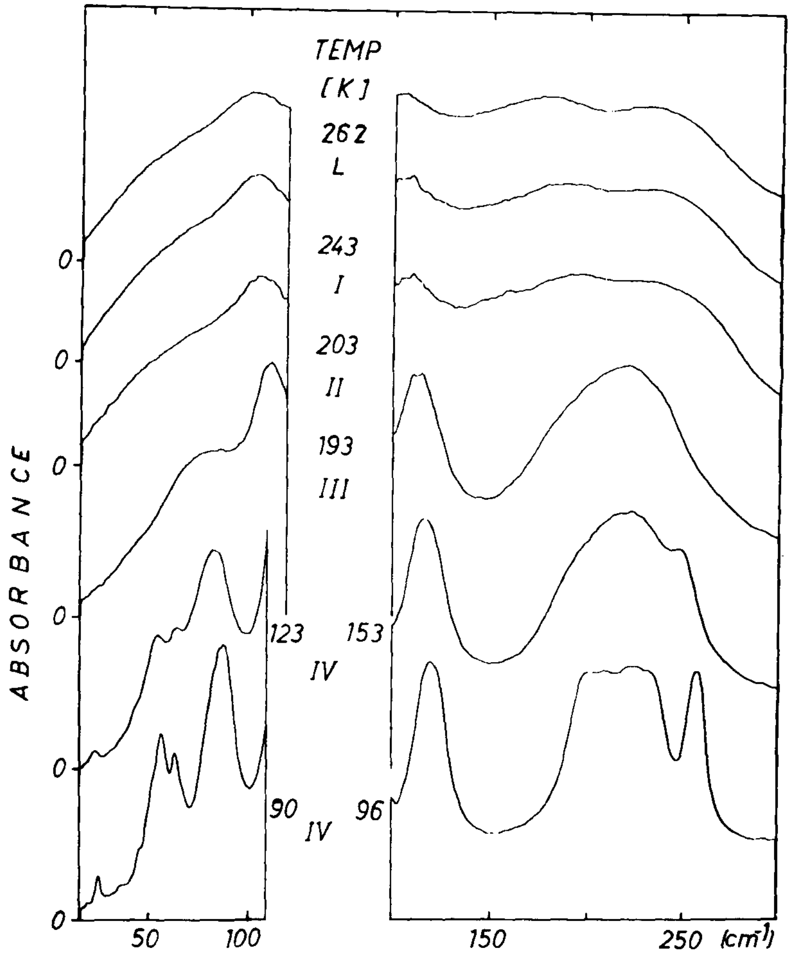

FIG. 3 Infrared absorption spectra of cyclopentanol-OH in the lattice mode range. From the top: liquid (262 K), phase I (243 K), phase II (203 K), phase III (193 K) and phase IV at two temperatures.

peak intensities of certain bands (1000, 1080, 1130 cm^{-1}). The comparison of the spectra for CPOL-OH and -OD makes it possible to assign the modes of OH and OD groups. Some uncertainty still remains about the OD in plane bending band (OD ip bend) which overlaps the strong band at 1000 cm^{-1}. A few of OH and OD bands parameters are given in Tables 1 and 2. It can be added that a rich structure of the OH and OD out of plane bending bands smears out gradually under heating and disappears completely just at the phase III - phase II transition.

Figure 2 presents the characteristic changes visible at the phase IV - phase III and phase III - phase II transitions in the internal modes range. The most important fact for further analysis is the disappearance of a rather strong band at 1080 cm^{-1} in the phase II - phase III transition. This has been observed for both OH and OD compounds. There are also certain changes of the strong band at 1000 cm^{-1}. So it seems reasonable to assume that the 1080 and 1000 cm^{-1} bands must be assigned to the CO stretching mode of two different conformations of the CPOL molecule, one of the conformations vanishing in phase III. This assumption disagrees with that made by Durig[7] and leads to further differences. For example, weak bands at 377 and 540 cm^{-1} disappearing together with the 1080 cm^{-1} band,

TABLE 1

OH and OD Stretching Band Parameters

PHASE	OH	OH_a	OD_m	OD_a
IV 96K	3210(260)	3195(30) 3222(30)	2400(150)	2380(23) 2394(23)
		$\theta=1.4$		$\theta=1.3$
III 196K	3245(220)	3250(105)	2420(115)	2415(70)
II 203K	3270(235)	3275(127)	2445(127)	2437(105)
		$\theta=2.0$		$\theta=1.8$
I 240K	3290(245)	3300(155)	2455(124)	2455(110)
L 256K	3325(220)	3307(170)	2465(130)	2463(110)
0.3 M CCl_4	3624(18) F 3505 sh P 3345(230)P		2676(14) F 2600 sh P 2485(155)P	

Band positions and full band widths at half maximum in parenthesis (cm^{-1}) for phase IV, III, II, I, liquid L and 0.3 M CCl_4 solution of cyclopentanol.
Notation: F and P, monomer and associated molecule bands; subscript a and m, admixture and matrix bands; θ, estimated linear temperature shift coefficient (in 10^{-4} K^{-1}) defined as $d\nu/\nu_0\, dT$, where ν_0 corresponds to 96K, $d\nu$ and dT denote frequency and temperature change, respectively; sh stands for shoulder.

TABLE 2

OH and OD Bending Band Parameters

PHASE		OH	OH_a	OD_m	OD_a
		ip Bending			
IV	96K	1417 m		1010 o	
0.03M	CCl_4	1245 w, F 1385 w, F		875 m, F	
		op Bending			
IV	96K	686 s 697 sh 730 w,b 770 w,b 820 m,b		510 s 595 m,b 625 m,b	560 vw, M_c 535 vw, D_c 567 vw, D_c
II	203K	690(200?)		520(120?)	
L	300K	660 vb		490 vb	
0.03M	CCl_4	245(110)	250 b	185(100)	

Additional notation in comparison to Table 1: s, m, w, v, b, denote strong, medium, weak, very and broad, respectively; o, overlaped band; M_c and D_c, monomer and dimer cluster states[6].

we assign rather to the CO bending vibrations ν_{40} and ν_{22} of the same conformation. Internal mode frequencies of CPOL-OH and -OD below 1500 cm^{-1} observed for phase IV at 96 K are listed in Table 3. (OH and OD modes are given separately in Tables 1 and 2.) Assignment is based on Durig's paper[7] and his numbering of the fundamentals is followed.

The changes of CO bands at the transformation to phase IV are very characteristic. Stretching and out of plane bending bands give quartets consisting of two close doublets. The splitting of the 450 cm^{-1} in plane bending band is smaller and only its doublet structure is visible. At the same time the OH_a and OD_a admixture doublet bands (Fig. 2 and Table 1) indicate that in phase IV there must be two different sublattices of hydrogen bonds. These facts suggest that phase IV is an ordered structure of two types of chain polymers differing only in the conformation of their molecules. As the "twisted" C_2 conformation of a molecule would give one possibility only, it is assumed that in one type of the polymers the molecules are in their "envelope" axial form C_s^{ax} while in the other type the equatorial conformation C_s^{eq} is found. This C_s symmetry plane relates only to the skeleton of the molecule. A final symmetry can be lower depending on the OH group position. The splitting of the CO bands into doublets

TABLE 3

Internal Mode Frequencies (cm^{-1}) and Assignment

CPOL-OH	CPOL-OD	Assignment
217 w,b	215 w,b	23,42
395 w 400 w	390 w 397 w	40
413 w 423 w	407 w 414 w	40
446 w 455 w	430 w 440 w	22
575 vw	573 w	39
610 vw	610 sh	21
	810 w	$2\nu_{40}$
826 s	830 m	19,38
846 vs 852 sh	837 m 842 sh	37
	852 vw	$2\nu_{22}$
886 s	883 m	20
894 sh 897 s	892 m 895 sh	18
902 m	900 sh	36
	923 m	34
927 m	930 m	17
935 m	936 m	34
	969 vw	$\nu_{40}+\nu_{39}$
985 vs 991 vs	983 s 992 vs	13

CPOL-OH	CPOL-OD	Assignment
1006 vs 1012 vs	1010 vs 1016 sh	13
1040 s	1041 m	35
1060 w 1066 s 1072 m	1093 sh 1101 m	14,33
1161 sh 1168 s 1175 m 1182 sh	1161 sh 1173 s 1176 s	15,16
1196 m 1202 sh	1197 m 1203 sh	32
1231 m	1237 w	12
1245 vw		?
1264 w	1257 w	?
1285 m	1286 w	31
1306 vs	1354 sh 1359 s	9
1319 m	1319 m	10
1342 vs	1327 w	30
1435 sh 1437 s	1437 m	8
1444 sh 1449 m 1454 sh	1442 m 1449 m	28,29
1475 m	1473 m	7

Notation as in Tables 1 and 2. Numbering of the fundamentals according to Durig[7].

is connected with the intrapolymer Davydov splitting for Z=2 while the separation of the doublets corresponds with the energy difference between the C_s^{ax} and C_s^{eq} conformations. Other sources[7] estimate such a difference as 50 cal/mole. This interpretation determines at the same time the conformation vanishing at the phase II - phase III transition as a "twisted" C_2 conformation (the CO stretching, ip and op bending modes at 1080, 540 and 377 cm^{-1} and the ring puckering ν_{23} and ν_{42} modes probably at 245 cm^{-1} for the liquid phase).

The analysis of the spectra in the lattice region shown in Fig. 3 yields further information on the structure of polymers. The clear disappearance of certain bands (24, 56 and 63 cm^{-1}) at the phase IV - phase III transition is of vital importance; it indicates that the symmetry of a polymer becomes higher. Proposed assignments are given in Table 4. So, phase IV is built up of polymers of the C_2 (or C_s) line group symmetry. A growing amplitude of librations during heating leads to the phase IV - phase III transition at which the symmetry of polymer rises up to the C_{2v} symmetry. Simultaneously the strength of hydrogen bonds slightly weakens and on the average becomes equal for both the sublattices (see Tables 1 and 4 - note the increase of OH_a and OD_a band frequency, the decrease of $\dot{\nu}_{\sigma}$ frequen-

TABLE 4

Lattice Mode Frequencies (cm^{-1}) and Tentative Assignment

L	I	II	III	IV		Mode Assignment	
261K	243K	208K	173K	96K OD	90K OH	Hydrogen Bond	Polymer C_{2v}
					24 w		$A_2(R_x)$
					36 vw		
					45 sh		
					52 sh		
					56 m	ν_γ	$A_2(R_y)$ and
					63 m		$A_2(T_z)$
					67 sh		
					83 sh		
					86 sh	ν_γ	$B_2(R_y)$ and
			80		88 s		$B_2(R_x)$
102 vb	105 vb	106 vb	115	120 s	118 s	ν_β	$A_1(R_z)$ and
					120 sh	ν_β	$A_1(T_y)$
180 vb	188 vb	190 vb					
				198sh	200 sh	ν_β	$B_1(R_z)$
235 vb	235 vb	225 vb	220	215sb	217 sb	$\nu_\sigma;\nu_{23};\nu_{42}$	$B_1(T_x)$ and $\nu_{23};\nu_{42}$
				254 s	258 s	ν_σ	$B_1(T_x)$

Notation as in Tables 1,2,3. Additional notation: ν_σ, ν_β, ν_γ, hydrogen bond stretching, in plane and out of plane bending modes; T and R, translational and librational modes; $2_1(x)$ and $\sigma(x,y)$, the chain polymer axis and plane.

Remarks: CPOL-OD was not measured below 100 cm^{-1}; the representation of eight intrapolymer modes for two molecule chain unit under the C_{2v} line factor group is $A_1(T_y) + A_1(R_z) + A_2(T_z) + A_2(R_y) + B_1(T_x) + B_1(R_z) + B_2(R_x) + B_2(R_y)$. For the crystal unit cell containing two C_s^{ax} and two C_s^{eq} molecules all modes could be doubled.

cy and a large increase of the OH_a and OD_a band widths). Some modes of A symmetry in the C_2 group change into modes of A_2 symmetry in the C_{2v} group and thus become infrared inactive. Simultaneously the temperature broadening of the bands smears the Davydov structure (see Fig. 2) but the difference between the C_s^{eq} and C_s^{ax} conformations is still visible.

At the phase III - phase II transition the C_2 "twisted" conformation appears. This probably makes possible fast transitions between C_s^{ax} and C_s^{eq} conformations and the conformational structure of CO bands is smeared out (see Fig. 2). It also introduces the conformational disorder into the crystal. The character of the spectrum in the lattice mode range (i.e. the decrease of the ν_β and especially of ν_γ frequency) also suggests the transition from the rigid C_{2v} polymer conformation to a flexible disordered structure of C_∞ symmetry on the average. The transition to phase I is accompanied by further disordering of the structure. The decrease in the rigidity of hydrogen bond also in the plane of bonding (note blurring of ν_β) leads to some deviations of the polymer linearity. X-Ray diffraction studies[4] suggest that the isotropic reorientation of molecules is already possible in this phase. The absorption spectra of phase I and of the liquid phase are qualitatively indistinquishable in either the internal vibration region or in the lattice mode region (see Fig. 3).

The proposed interpretation finds some support in the results of the calorimetric study.[1,2] It remains in agreement with the small entropy change at the phase IV - phase III transition and with the big change at the phase III - phase II transition (high contribution of the conformation mixing entropy). On the other hand this interpretation enables one to explain the interesting pressure effects[2] observed for the phase III - phase II transition by the influence of pressure on the conformational equilibrium of molecules.

SUMMARY

It was found that firstly, in phases I, II and liquid molecules of C_s^{ax}, C_s^{eq} and C_2 conformations are present, the difference between C_s^{ax} and C_s^{eq} conformations becoming visible but in the lower phases. Secondly, in the phase II - phase III transition the C_2 conformation disappears. Thirdly, phase IV is an ordered structure of C_s^{ax} and C_s^{eq} conformations built up of two sublattices of hydrogen bonds. On the basis of these results a model of phase transformations in cyclopentanol was proposed.

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