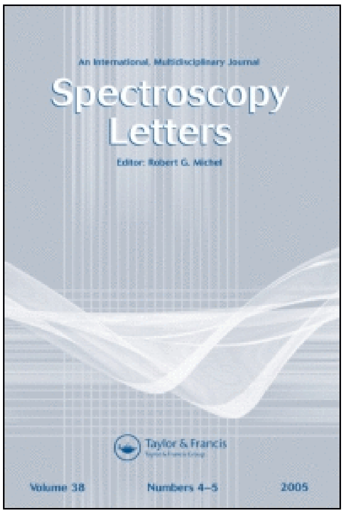

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Far Infrared Study of Solid Cyclohexanol-OD

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

To cite this Article Ściesińska, E. and Ściesiński, J.(1980) 'Far Infrared Study of Solid Cyclohexanol-OD', Spectroscopy Letters, 13: 12, 895 — 904

To link to this Article: DOI: 10.1080/00387018008064076

URL: http://dx.doi.org/10.1080/00387018008064076

SPECTROSCOPY LETTERS, 13(12), 895-904 (1980)

FAR INFRARED STUDY OF SOLID CYCLOHEXANOL-OD

Key words: Far infrared spectra, Hydrogen bond, Isotope effect

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

ABSTRACT

The far infrared absorption spectra of cyclohexanol-OD have been measured in the 20 - 500 cm^{-1} frequency range for crystal III, II, I and liquid phases. Comparison with cyclohexanol-OH and the isotope effect is discussed.

INTRODUCTION

Far infrared studies of solid alcohols are meager. Some data are available for methanol[1], tert-butanol[2] and ethanol[3]. Therefore it was considered to be useful to extend far infrared investigations of cyclohexanol-OH /CHOL/[4] to its deuterated derivative cyclohexanol-OD /CHOL-OD/.

The polymorphism of cyclohexanol was fully discussed in Reference 4. This discussion was based on the far infrared spectra as well as on other presently available experimental data. Here only the main results need to be reported. Cyclohexanol exists in two ordered crystalline modifications: crystal III and crystal II. Crystal III transforms to crystal II at ca. 245 K, but both phases are stable below their transition points at least on a time scale of several days. In addition CHOL shows two disordered crystalline phases: crystal I plastic and a metastable crystal MS /Fig. 6 of Reference 4/. Crystal I can be obtained through the crystal II - crystal I transition at 265 K or from the liquid phase at the freezing point 299 K. It can also be supercooled down to liquid nitrogen temperature. All phases reveal both axial and equatorial conformers of the molecules. The following description of the phases is proposed on the basis of the far infrared spectra. Crystal III consists of chain polymers of hydrogen-bonded equatorial conformers and chain polymers of hydrogen-bonded axial conformers. The line group of the chain is the C_2 group. Crystal II is built up of cyclic dimers of hydrogen-bonded equatorial conformers and cyclic dimers of axial conformers. The point group symmetry of the dimers is the C_i group.

RESULTS AND DISCUSSION

Absorption measurements on polycrystalline samples of CHOL-OD were carried out with a DIGILAB FTS-14 spectrometer in the 20 - 500 cm^{-1} frequency range and 96 - 305 K temperature range. TPX and polyethylene was used as window materials below 120 and over 50 cm^{-1}, respectively. Resolution was kept at 2 cm^{-1}. An experimental method is described in Reference 4. Figure 1 and Tables 1 and 2 summarise the results. Figure 1 shows the representative spectra of crystals III and II at low and high experimental temperatures. The spectra of liquid and plastic phase I are also given for comparison. The last two spectra are practically identical, as is usually observed for plastic crystals. In the range of internal modes they show only three bands: a weak one at 310, a strong and broad one at 343 and a medium one at 405 cm^{-1}. The range above ca. 420 cm^{-1} was hardly measured for CHOL-OD on account of the high background of the OD out of plane bending mode. Therefore the two highest modes could not be located for disordered phases. But for ordered crystals the OD mode shifts upward and becomes narrowed, which allows for quite good quality of the spectra. The range of external modes for the liquid and crystal I spectra is covered by a broad absorption showing one distinct maximum at 177 cm^{-1} and wings peaking at 95, 135 and 235

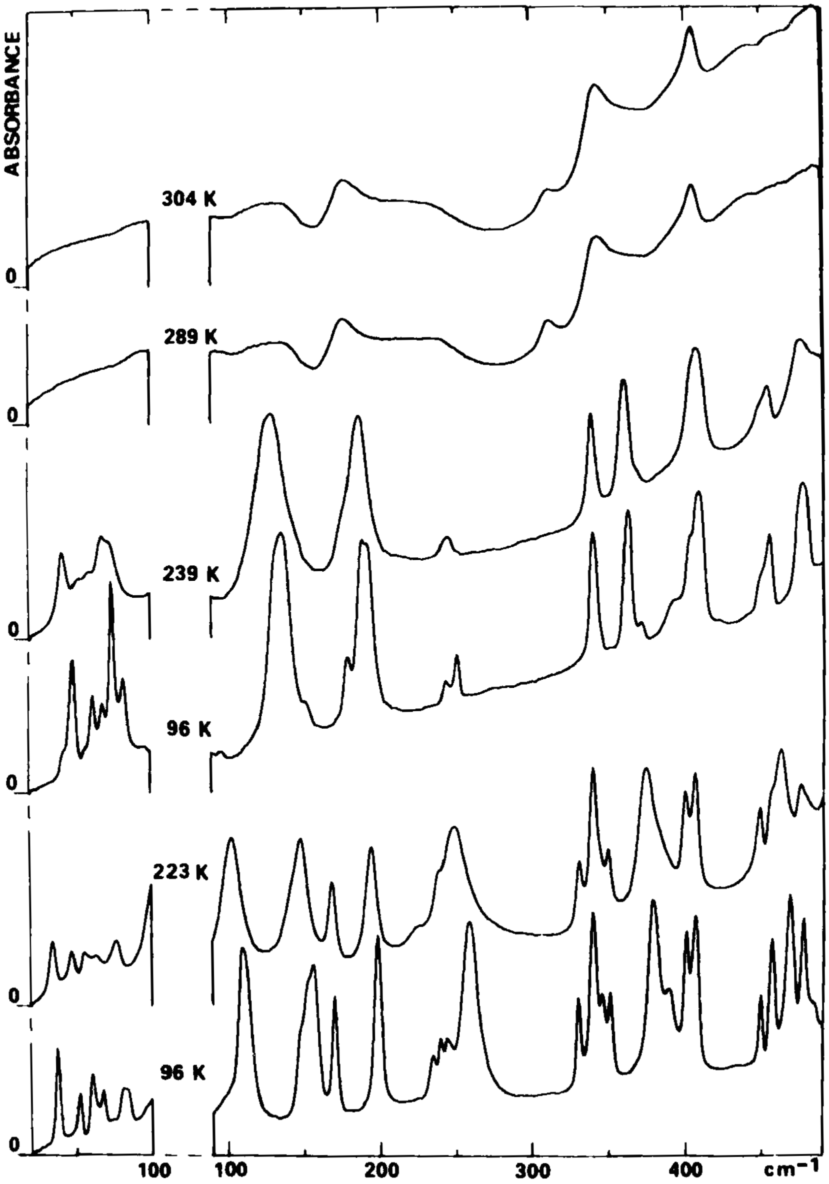

Fig. 1 Far infrared spectra of cyclohexanol-OD. From the top: liquid, crystal I, crystal II /239 and 96 K/, and crystal III /223 and 96 K/.

TABLE 1

Internal Mode Frequencies /cm^{-1}/ and Assignment

Assignment		Crystal III			Crystal II		
		CHOL	CHOL - OD		CHOL	CHOL -OD	
	C_s	93 K	97 K	225 K	94 K	95 K	241 K
ν_{32} E_u	A′	240	240 w		243	243 w	
	A″	245	244 w	238 sh			
		247	247 sh		251	251 m	245
ν_6 A_{1g} and ν_{24} E_g	A′	332	331 m	331	341		
	A′	345	340 s	340	343	340 s	339
		347	346 w				
	A″	357	352 m	350	346		
a CO ipb	A′	383	379 vs	373	372	363 s	360
		396	389 m			372+ w	
						392 bw	
e CO opb	A″	404	401 s	400		403+sh	
		409	407 s	406	411	408 vs	407
a CO opb	A″	451	450 m	448		450+sh	
		461	457 s	455 sh	459	455 m	453
e CO ipb	A′	480	468 vs	462	478	477 vs	475
		485	478 s	476			
			485+sh				

Notation: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder; a, axial and e, equatorial conformer; ipb, in plane and opb, out of plane bending modes; +, spurious band.

TABLE 2

Lattice Mode Frequencies /cm^{-1}/ and Assignment of Cyclohexanol-OD

Crystal III					Crystal II				
Assignment	96 K	223 K	S	%	Assignment	96 K	238 K	S	%
	38 m	35	1.03	2		43 sh			
Inter-					Inter-	49 s	42	1.00	3
	52 w	47	1.02	1					
chain					dimer	57 sh			
	60 w	55	1.01	1		62 m	53	1.00	2
modes					transla-				
	67 w	63	1.00	2		68 w	60		
and					tions	75 s	68	1.005	2
	81 w								
ν_γ/R/	84 w	76				82 m	73	1.006	2
ν_γ/T/	110vs	103	1.00	2		96 w			
	148sh								
ν_β/R/	153sh				Intra-	136bvs	129	1.00	3
and	156 s	147			dimer	152 sh			
ν_β/T/	171 s	168	1.012	0.5	libra-	180 m	176		
						189bvs	185	1.005	2
ν_σ/T_x/	198vs	193	1.011	0.5	tions	192 sh			
38+198	235 w	224							
ν_σ/T_x/	259vs	248	1.01	1					

Notation as in Table 1. Additional notation: ν_σ, ν_β and ν_γ hydrogen bond stretching, in plane and out of plane bending modes. T and R, translational and librational modes. x, the chain axis. S and %, isotopic shift factor and its % error.

cm^{-1}. These features are connected with the hydrogen bond stretching ν_σ and bending ν_β modes.

The investigated spectral region include the low energy internal modes of the molecule above ca. 220 cm^{-1} and lattice modes below this value. Table 1 gives a tentative assignment of internal modes. For all skeletal modes symmetry species under the C_s point group are given. In fact this group holds only for the metastable phase MS. For the ordered phases III and II the molecule shows only the C_1 point group symmetry probably due to a gauche position of the OH group. Hence the actual symmetry species of all the modes is A. Ring deformation modes are also described in terms of corresponding cyclohexane ring modes under the D_{3d} point group[5]. These modes are common to both equatorial and axial conformers. The majority of the modes show intrapolymer correlation splitting at low temperature. Some of them, mainly the CO bending modes are sensitive to isotopic substitution. The frequencies of CHOL[4] are quoted in Table 1 for comparison. Some skeletal modes change markedly on phase transition. These are three higher ring deformation modes which come close together at the crystal III - II transition, giving only one band under worse resolution. This indicates that some constraints are operating in the crystal. The change of the axial CO ipb mode seems to be connected mainly with the changeable character of the hydrogen bond for both crystals. There are some weak spurious bands /marked by + in Table 1/ in the range of internal modes. These can be assigned to CHOL contamination. But some of them might be due to a phase III admixture. It was a hard experimental task to grow the pure phase.

Lattice mode frequencies and qualitative assignments are given in Table 2. These modes divide into intrapolymer hydrogen bond stretching and bending modes derived from translations and rotations of the molecules, and interpolymer translations and rotations of the entire polymers. But because of the C_1 site point group for ordered phases, there can be mixing of the translational and librational motions. In spite of this a description of the lattice modes in terms of translations and rotations is given in Table 2. This is expected to hold at least qualitatively under weak mixing. The amount of mixing could be, in principle, estimated from experimental isotopic shift factors. But it would demand that the accuracy be much better. The predicted shift factors are 1.005 for translations, for rotations 1.013, 1.020 and 1.032 for an axial conformer, and 1.012, 1.016 and 1.005 for an equatorial conformer. The moments of inertia of CHOL are 245.0, 185.6, 143.1 and 313.7, 227.3, 116.0 amuÅ^2, respectively. The experimental error of shift factors varies between 0.5 and 4.0 per cent depending on the energy and the shape of the band.

The second question is the isotope effect itself. According to Novak[6] some positive isotope effect can be expected for alcohols causing the shift factors to increase. The reported results exclude any significant effect. Somewhat lower values of the shift factors for crystal II in comparison to crystal III seem to support the cyclic polymer character of crystal II.

The extension of measurements down to 20 cm^{-1} for both CHOL-OD and CHOL, and the overall behaviour of the spectra in this range make the existence of further modes below, unlikely. This means that five interpolymer and sixteen intrapolymer modes predicted for crystal III /Reference 4/ should be found among the fourteen experimental lattice modes. This indicates that some accidential degeneracies are very probable for intrapolymer modes in this case.

REFERENCES

1.P.T.T. Wongang and E. Whalley, J. Chem. Phys. 55, 1830 /1971/.

2.J.R. Durig, S.M. Craven, J.H. Mulligan, C.W. Hawley and J. Bragin, J. Chem. Phys. 58, 1281 /1973/.
E. Ściesińska and J. Ściesiński, Acta Phys. Pol., in press.

3.Y. Mikawa, J.W. Brasch and R.J. Jakobsen, Spectrochim. Acta 27A, 529 /1971/.

4. E. Ściesińska and J. Ściesiński, Mol. Cryst. Liq. Cryst. 51, 9 /1979/.
5. R.J. Obremski, C.W. Brown and E.R. Lippincott, J. Chem. Phys. 49, 185 /1968/.
6. A. Novak, Structure and Bonding, 18, 177 /1974/.

Received: October 15, 1980
Accepted: November 6, 1980