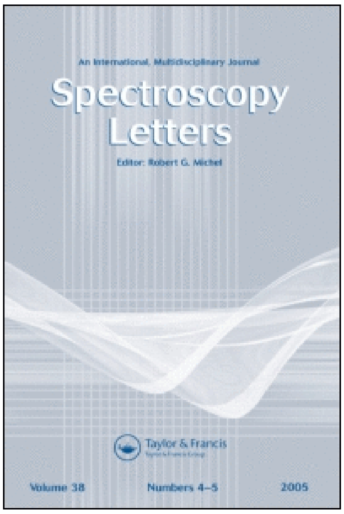

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INFRARED STUDY OF SOLID CYCLOHEPTANOL

Key words: polymorphism, hydrogen bond, infrared spectra

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ABSTRACT

Infrared absorption spectra of cycloheptanol-OH have been measured in the 50 - 3700 cm^{-1} frequency range for crystal II', II, I and liquid phases. Order-disorder behaviour concerning orientational, conformational and hydrogen-bond properties is discussed.

INTRODUCTION

This investigation of polymorphism of cycloheptanol by means of infrared spectroscopy is an extension of previous works on the cyclic alcohols[1-3]. The phase behaviour of cycloheptanol is intricate. Eight kinds of stable and metastable crystalline phases including the glassy crystal were revealed by means of an adiabatic calorimetry method[4]. Among these stable crystals I, II and III are considered to be plastic, i.e. orientationally disordered according to the Timmermans criterion[5]. This is supported by the motional narrowing phenomenon of the NMR spectra[4] and by dielectric measurements for phases I and II[6]. On the contrary, the entropy of II-II' transition amounting to 17.2 J $mol^{-1}K^{-1}$ would rather indicate crystal II' to be a normal ordered crystal[4]. Crystal II' is the low-temperature stable phase. The II-II' transition takes place from the supercooled phase II denoted sII. The aim of this work is to study this order-disorder behaviour of different phases in more detail[7]. In general, three kinds of order i.e. conformational, hydrogen bonding and orientational order should be considered.

EXPERIMENTAL AND RESULTS

IR absorption spectra in the frequency of 50 - 3700 cm^{-1} and temperature of 96 - 300 K range under various heating and cooling conditions for the sample holder with polyethylene or KRS-5 windows filled with liquid $C_7H_{13}OH$ were measured with a Fourier transform FTS-14 Digilab spectrometer with 2 cm^{-1} resolution. Phase sequence of liquid, phases I, II, sII and II' was studied in this way. Representative results are shown in Fig.1 for the 30 - 500 and in Fig.2 for 450 - 1550 cm^{-1} range. An erroneous structure is observed for stronger bands i.e. for 472 and 1035 cm^{-1}, because the sample thickness was to be fitted to weaker features of the spectra. Observed frequencies below 600 cm^{-1} are listed in Table 1.

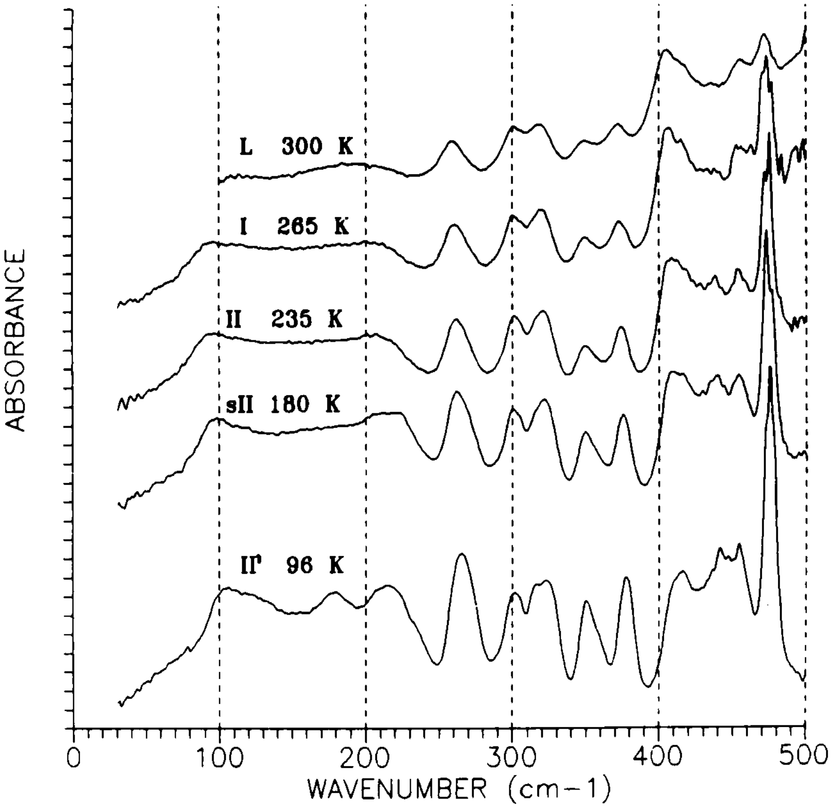

FIG. 1. Infrared absorption spectra of cycloheptanol-OH in the lattice and skeletal mode range: from the top liquid at 300 K, phase I at 265 K, phase II at 235 K, supercooled phase II i.e. sII at 180 K and phase II' at 96 K.

DISCUSSION

The cycloheptanol molecule can occur in several conformations. This depends on the cycloheptane ring conformation and the OH group position. Rotational isomerism of the OH group could be neglected here. The most stable conformation for cycloheptane is the twist-chair one of the C_2 symmetry but an energy

TABLE 1

Low-Energy Skeletal Modes (frequencies cm^{-1} at 96 K) and Tentative Assignment

Eight ring deformations		Two CO bending modes		
out of plane	in plane	C_s^1	C_s^2	C_2
180 a 215 b 265 300 315 a 322 b	375 472 510 548	413	440 453	348

a and b randomly mark the C_s and C_2 ring conformations identical to skeletal conformations; superscripts 1 and 2 randomly mark axial and equatorial conformations.

barrier to the chair conformation of the C_s symmetry is low[8]. The boat of C_s symmetry and the twist-boat of C_2 symmetry conformations are not excluded either. The OH substituant could leave the skeletal symmetry unchanged and introduces axial - equatorial differentiation in the case of C_s symmetry. Among the possible sixty internal modes of the molecule, ten low energy modes below ca 600 cm^{-1} should appear at most. These are the following skeletal modes: four out-of-plane and four in-plane ring deformation modes and two CO angle bending modes. Some of them could show conformation and/or phase sensitivity.

The only spectroscopic data for cycloheptane derivatives we could find are those by Adachi[4]. These are the Raman and mid IR spectra (above 450 cm^{-1}) for liquid state and mid IR for crystals II and II' of cycloheptanol-OH. Two lowest internal modes at 179 and 255 cm^{-1} are seen there.

A general view of the spectra in Figs 1 and 2 is very similar. No appearance or disappearance of new bands in the range of internal modes is observed at phase transitions. Phase sensitive modes are clearly the 435 and 1220 cm^{-1} bands showing characteristic intensity changes. No additional structure, i.e. splittings, peculiar to an ordered crystal is visible either. An important feature of the spectra, however, is an observation of thirteen low energy internal modes. It means that some skeletal modes are conformation sensitive and that at least two different conformations of the molecule appear for all the phases of cycloheptanol. A tentative assignment of skeletal modes in Table 1 is based on the following: Adachi data[4]; compatibility for all the phases; comparison with cyclopentanol[1]. The reason for the last point is that the ring strain energies for cyclopentane and cycloheptane are similar[9]. It is seen from Table 1 that conformation sensitive modes are mostly the CO modes; the CO stretching modes are assigned at 1035 and 1130 cm^{-1} for the two ring i.e. skeletal conformations. The OH torsion at ca 700 and stretching at ca 3300 cm^{-1} broad and structureless bands behave similarly to linear polymer phases of other alcohols (the bands at 725, 755, 792, 816, 830 and 850 cm^{-1} do not belong to the OH torsion band, these are CH_2 rocking and CC stretching modes). The OH stretching range is not shown here to make the paper shorter. The position $\nu(cm^{-1})$ of OH stretching band of roughly 210 cm^{-1} halfwidth in the temperature T range of 96 - 300 K is given by a linear equation $\nu(T)=3186+0.487\ T$ within ± 6 cm^{-1} limit.

The most important conclusions concerning order - disorder behaviour of the phases come from the lattice mode range of the spectra below ca 250 cm^{-1}. One broad structureless band similar for all the phases is seen

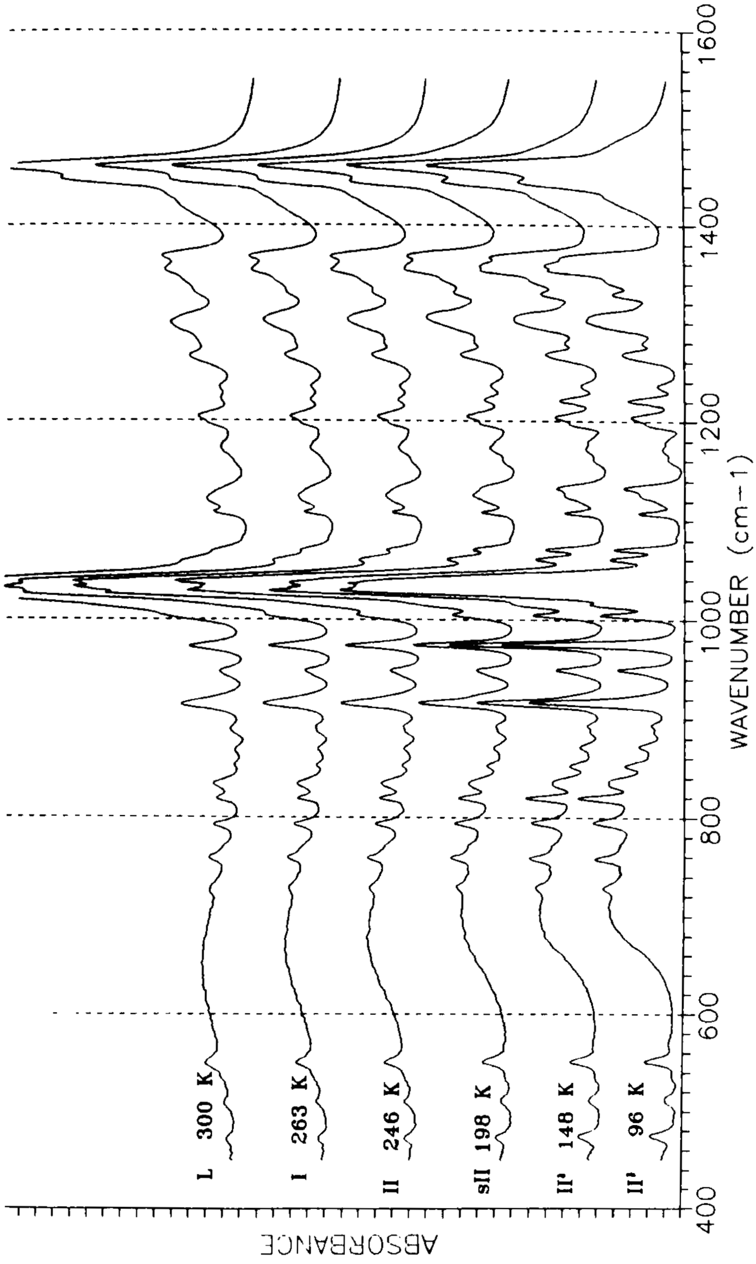

FIG. 2. Infrared absorption spectra of cycloheptanol-OH in the internal mode range: from the top liquid at 300 K, crystals I (263 K), II (246 K), sII (198 K) and II' (at 148 and 96 K).

there. Below ca 130 cm^{-1} those bands are indistinguishable for all the phases. The lowest ring deformation at 180 and a band at 215 cm^{-1} are more pronounced at 96 K. It is supposed that the two bands correspond to each other in the two different conformations of the ring. The 215 cm^{-1} band might escape detection by Adachi due to a low abundance of that conformation. Both the 180 and 215 cm^{-1} bands are superposed on a broad band of hydrogen bond stretching and bending vibrations. Hence it is seen that the low temperature phase II' of cycloheptanol shows no distinct lattice bands above 30 cm^{-1} (the quality of measurements below 50 cm^{-1} is worse). Such a behaviour of the lattice range is characteristic for a disordered crystal and was earlier observed for the plastic phases of cyclopentanol[1] and cyclohexanol[2]. In contrast, ordered phases of the alcohols (phase IV of cyclopentanol and phases II and III of cyclohexanol) show rich and highly structured spectra in the lattice range[1,2]. Therefore, it is concluded that the low-temperature phase II' of cycloheptanol is a disordered crystal. Hence cycloheptanol does not show any ordered phase.

CONCLUSIONS

Plastic character of phases I and II of cycloheptanol is supported. Conformational disorder is ascertained for the liquid and phases I, II and II'. In spite of the summarized transition entropy of 26.31 $Jmol^{-1}K^{-1}$ being somewhat too high, the low-temperature phase II' is an orientationally disordered phase. Contrary to a dynamical disorder of plastic phases, the orientational, conformational and hydrogen bond disorders of phase II' are of static type.

Although there are no full data for cyclobutanol[10] and cyclooctanol[10,11,12], more general statements on the polymorphism of cyclic alcohols are put for consideration here. Concerning the low-temperature ordered phases it is believed that: a hydrogen bonding is forcing different conformations of the molecule to appear, a hydrogen bonding is forcing a conformational order to set up due to some steric effects, the steric effects are ring-size dependent, therefore for the hydrocarbon rings bigger than that of cyclohexanol no ordered phases appear.

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