

A MODEL CALCULATION OF INFRARED SPECTRA IN CYCLOHEXANOL

M. NOWINA KONOPKA AND T. WASIUTYŃSKI

H. Niewodniczański Institute of Nuclear Physics
Radzikowskiego 152, 31-342 Kraków, Poland

(Received February 18, 1999, revised version May 18, 1999)

A model calculation based on semiempirical methods for the cyclohexanol molecules is presented. Energetically preferred molecular conformations and possibility of different hydrogen bond networks in the crystal are discussed. The calculated and the experimental infrared spectra are compared. The results corroborate earlier suggestions that the rich polymorphism of cyclohexanol is due to the existence of both axial and equatorial isomers in solid phases and different architecture of hydrogen bonds network.

PACS numbers: 61.50.Ah, 63.20.Dj, 78.20.Bh, 78.30.Jw, 78.30.Ly

1. Introduction

The polymorphism of solid cyclohexanol $C_6H_{11}OH$ was the subject of many papers since the pioneering work of Adachi et al. [1]. It is in that paper that the term of "glassy crystal" was used for the first time. Then a number of papers was devoted to the phase diagram and dynamical properties of solid cyclohexanol. In the careful calorimetric study by Mayer et al. [2] the following sequence of phases was established: plastic phase I, when cooled down it rapidly transforms to its glassy form below 150 K. On the other hand, when cooled down to about 180 K the supercooled phase I transforms into a metastable phase (MS) which then relaxes slowly into a phase III in the region of 190–220 K. The phase III transforms into the phase II in the temperature range of 220–240 K. The phase II when heated up transforms back to the phase I at 265 K. The detailed enthalpy calculations based on calorimetry data [2] as well as infrared absorption spectra [3] show that both the phase II and the phase III are ordered crystalline phases. They form a monotropic system, i.e. the transition III–II is irreversible. The dielectric absorption [4] and neutron scattering experiments [5] reveal that there are fast stochastic motions in the phase I but not in the phase II or III. The second moment of magnetic resonance is well below the value for rigid lattice even at 100 K [6]. The crystal structure of the phase I and glassy phase are determined to be face centered cubic — space group $Fm\bar{3}m$ [7]. The detailed structures of

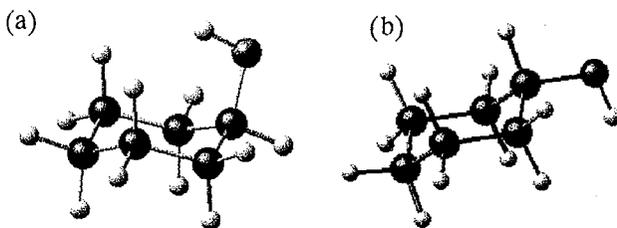


Fig. 1. Cyclohexanol molecule in axial (a) and equatorial (b) conformation.

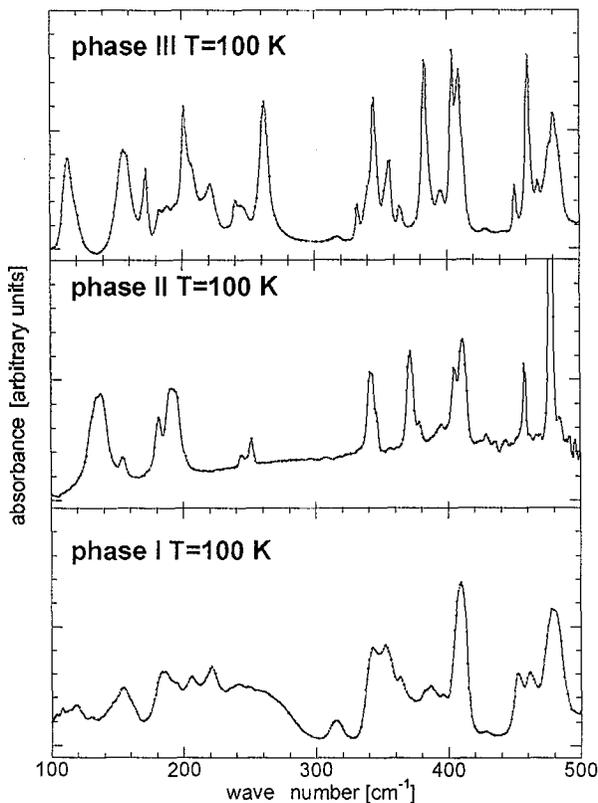


Fig. 2. Far infrared spectra of solid cyclohexanol in glassy (I) and ordered (II and III) phases at $T = 100$ K.

the phase II and phase III are not known till now because of the difficulties in growing single crystals. However, Ściesińska et al. [5] using ir spectra and neutron diffraction data suggested that the phases II and III differ by the architecture of hydrogen bonding network in the lattice. The nature of molecular disorder in the phase I is not clear either. The quasi globular shape of the cyclohexanol molecule (see Fig. 1) might suggest the type of reorientations similar to cyclohexane. On the other hand, the intermolecular hydrogen bonds are clearly seen in the plastic phase in infrared spectra [3].

The rich polymorphism of cyclohexanol is due to the variety of its molecular conformations and ability of forming hydrogen bond networks. It is generally accepted that all molecules are in chair conformation of C_6 skeleton (see Fig. 1) while the boat and twisted boat conformations are more than 20 kJ/mole higher in energy. The OH group can be attached in either axial (Fig. 1a) or equatorial position (Fig. 1b). There is a controversy concerning the abundance of the two forms. James et al. [8] concluded from the temperature dependence of their Raman spectra that in the ordered phases only the equatorial conformation is present. The other authors agree that both isomers are present in solid phases. André et al. [6] found that there is the equal distribution of axial and equatorial forms in the glassy phase. In addition there is freedom in the OH group rotation around C-O bond.

Slow kinetics of the phase transitions allowed Ściesińska and Ściesiński [3] to measure infrared spectra of various phases at the same temperature 100 K. Their results are presented in Fig. 2. One can see that the spectra differ in the region of 300–500 cm^{-1} , i.e. in the internal modes region. It is the open question, how different crystal environment influences the internal vibrations of cyclohexanol.

The lack of the full structural information and the controversies in the matter of abundance of particular conformations have actuated us to perform the present model calculations. We expect to reveal the energetically preferred conformations and hydrogen bonded aggregates of the cyclohexanol molecules appearing in condensed phases. The details of the model used are described in Sec. 2. The results allowing one to compare the energies of the particular conformations and their vibrational spectra are presented in Sec. 3.

2. Model

To enumerate the possible local conformations of the cyclohexanol in the condensed phases we have started our calculations from a single molecule. With all possible conformations of single molecule in hand we have subsequently studied aggregates of 2, 3, and 4 molecules allowing them to form hydrogen bonds among them. To model the intermolecular potential we made use of a semi-empirical method. From various sets of parameters (MNDO, MINDO/3, AM1, PM3) tried in our study, the AM1 [9] set turned out to give the best agreement in the case of the structure and vibrational spectra of cyclohexane molecule, used by us as a test system. The hydrogen bond interaction between an oxygen atom from one molecule and a hydrogen atom belonging to a hydroxyl group of another molecule is described by the AM1 set provided that

1. distance r between them is less than 3.2 Å,
2. bond angle O-H...O is greater than 150°.

With the aim of the above we established the structure of the single molecule, dimer, and trimer of cyclohexanol in their various conformations by finding global minima of total energy. The vibrational frequencies and the corresponding infrared intensities have been evaluated so as to enable a comparison with the spectroscopic data.

3. Results

The test calculations performed on the cyclohexane allowed us to reveal the influence of the hydroxyl group onto the bond length, bond angles, and the vibrations of the cyclohexane ring. Some of the results for cyclohexane are summarized in Table.

TABLE
Structural parameters of cyclohexane.

Parameter	Calculated	Experiment [10]
R_{C-C}	1.515	1.536
R_{C-H}	1.121	1.106
α_{H-C-H}	107°	107°
α_{C-C-C}	111°	111°
α_{C-C-H}	110°	110°

3.1. Static properties of cyclohexanol

The results of the calculations are presented in Fig. 3, where the energy, as a function of torsional angle H-C-O-H for two isomers: axial and equatorial, is given. The calculated potential can be approximated by the following formula:

$$V(\phi) = a_0 + a_1 \cos(\phi) + a_2 \cos(2\phi) + a_3 \cos(3\phi), \quad (1)$$

where

$$a_1^{\text{axial}} = 5.8 \text{ kJ/mol}, \quad a_1^{\text{equatorial}} = 7.4 \text{ kJ/mol}, \quad (2)$$

$$a_2^{\text{axial}} \approx a_2^{\text{equatorial}} = 0.8 \text{ kJ/mol}, \quad (3)$$

$$a_3^{\text{axial}} \approx a_3^{\text{equatorial}} = 3.1 \text{ kJ/mol}. \quad (4)$$

Since the main difference in energy barrier between the two isomers comes from the term $a_1 \cos(\phi)$, it is the charge distribution responsible for it. As it is seen the most stable isomer is equatorial with OH group in *trans* position. The axial *trans* isomer has the energy about 2 kJ/mol higher. Figure 3 shows also the results for 30° twisted boat conformation of C₆ skeleton. In this case there is no difference between the axial and equatorial position of OH. It is then an estimate of the energy barrier for equatorial to axial conversion for the chair conformation. We attribute to it the value of 17 kJ/mol. Our results are in contradiction to the *ab initio* quantum chemistry calculations by Jansen et al. [11]. They found isomer *gauche* (i.e. 60° twisted) more stable than *trans*, axial, and equatorial isomers being about the same energy. The authors [11] conclude however that there is a need for *ab initio* computation of cyclohexanol molecule with even larger basis sets. It is doubtful however that *ab initio* computation with a large enough basis set will be done soon for aggregates of a few molecules. Anyway it is obvious that with such a small energy difference and very small moment of inertia of OH group there is

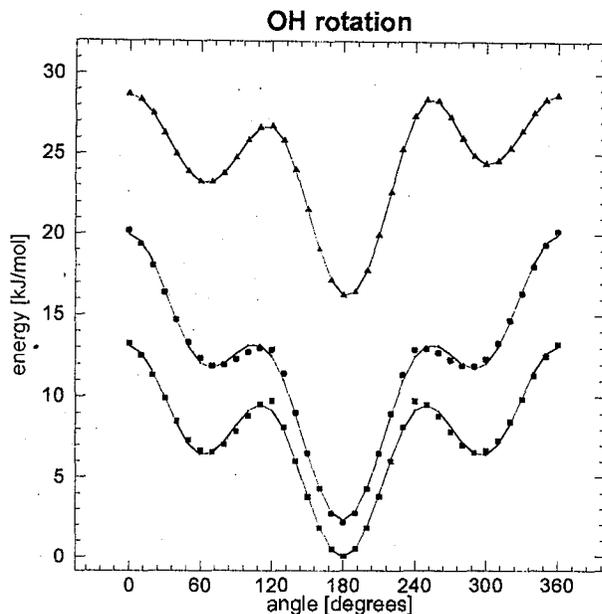


Fig. 3. Calculated energy barriers for OH rotation around C-O axis. Solid lines correspond to the fit, squares denote equatorial conformation and circles — axial conformation. Triangles correspond to twisted conformation of C₆ skeleton, where axial and equatorial isomers are of the same energy.

free rotation of OH at any temperature. Axial and equatorial isomers are about the same energy separated by a large barrier of 17 kJ/mol. It is very likely that both are present in cyclohexanol crystal.

In all further calculations we assume *trans* configuration for both isomers. The molecule is invariant under symmetry plane and all normal modes are either symmetric or antisymmetric with respect to that plane.

3.2. Dynamic properties

3.2.1. Cyclohexanol monomer

The vibrational spectrum of cyclohexanol molecule differs from the cyclohexane in a few aspects. All the skeleton modes are shifted towards lower frequencies, there are new bands connected with C-O bond and O-H bond. The difference between the axial and equatorial isomers are not significant. The most striking feature is a shift of the H-C-O-H in plane deformation from 700 cm⁻¹ in axial to 608 cm⁻¹ in equatorial isomer. The other difference concerns C-O stretching frequency that shifts from 1086 cm⁻¹ to 1058 cm⁻¹. The strongest bands at 352 cm⁻¹ (axial) and 323 cm⁻¹ (equatorial) correspond to the out of plane C-O-H deformation. Average agreement of the calculated and experimental [3] values is about 10%.

3.2.2. Cyclohexanol dimers and trimers

In this case we have additional bands coming from hydrogen bonds. Figure 4 presents the results of the calculations for eight different trimers in the spectral range up to 1500 cm^{-1} . Both positions and intensities of the modes depend strongly on the mutual geometry of the molecules in the trimer. The intense bands in the range of $300\text{--}500\text{ cm}^{-1}$ correspond to the deformation of the hydrogen bond. We do not show here bands in the region of 3500 cm^{-1} corresponding to O-H stretching which do not strongly depend on the molecule geometry. We believe that the modes in the range of $300\text{--}500\text{ cm}^{-1}$ are essential in understanding the differences in experimental spectra of various crystal phases.

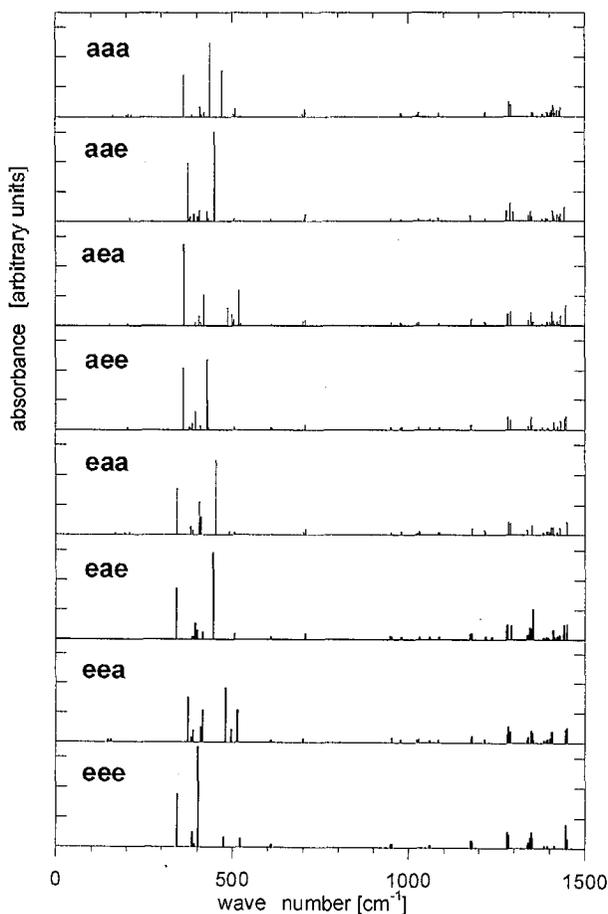


Fig. 4. Calculated infrared spectra for eight trimers of cyclohexanol.

4. Discussion

As it was pointed out by Ściesińska and Ściesiński [3] the phases II and III have spectra typical of ordered crystalline phases. The difference between them comes from the different architecture of hydrogen bonds. Although our calculations do not concern an infinite crystal but only aggregates of molecules some correspondence is easily visible. Figure 5 shows how the calculated spectra depend on the length of the chain. It is exemplified for equatorial isomer. One can see that the differences between them are not too large. We thus assume that plausible statements can be made on the basis of our approximate calculations. Figure 6 shows the spectra derived from those presented in Fig. 4. The upper part presents the simulations of the spectra in the case of separated chains of axial and equatorial isomers. The lower part of Fig. 6 shows simulation of the spectra for the chains of the form ...equatorial-axial-equatorial... We assume an equal concentration of both isomers and the simplest possible way of constructing an ordered lattice

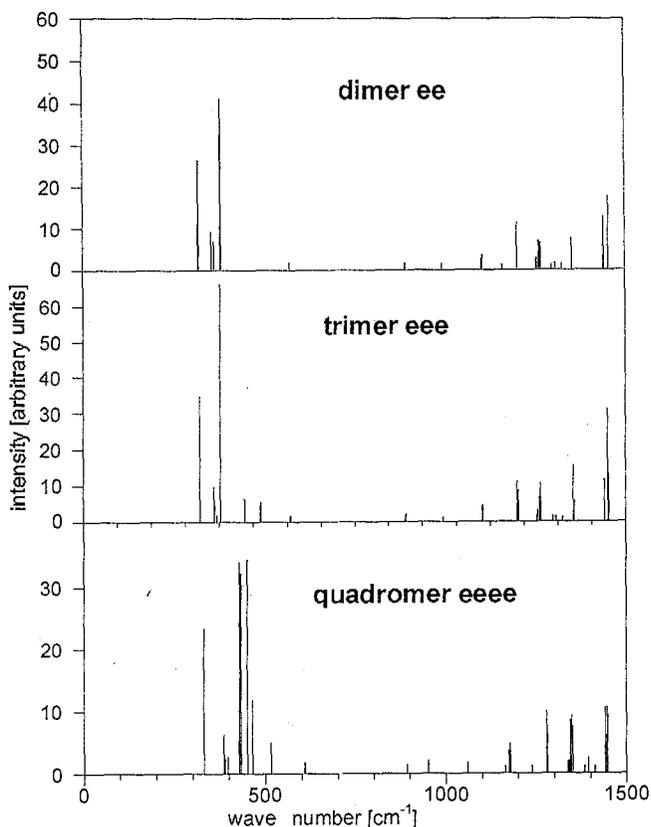


Fig. 5. Calculated infrared spectra for dimer, trimer, and quadromer of equatorial cyclohexanol.

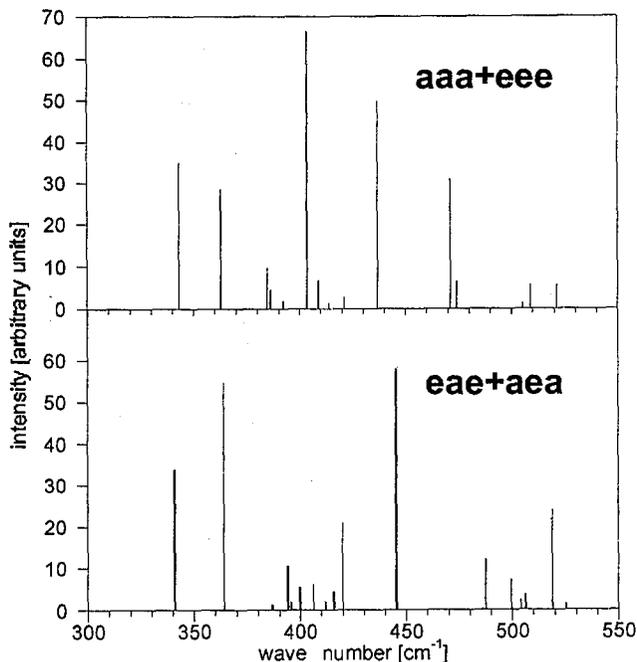


Fig. 6. Calculated spectra for ordered phase of cyclohexanol consisting of equatorial and axial segregated chains (upper part) and axial-equatorial mixed chains (lower part).

of hydrogen bond networks. By comparing Figs. 4, 5 and 6 we draw the following conclusions:

1. there is a disorder in the phase I concerning hydrogen bonds between different axial and equatorial isomers,
2. the phase III is an ordered phase, probably it consists of the segregated chains of bonds axial-axial and equatorial-equatorial. It is seen in a strong line around 400 cm^{-1} (exper. 382 cm^{-1}) that disappears in the phase II. The same concerns to the line at 450 cm^{-1} ,
3. the phase II is a stable phase, the hydrogen bond chains are of the mixed architecture . . . equatorial-axial-equatorial. . . Such configuration has a lower energy than the previous one so the transformation is irreversible.

Consequently, the phase II has a higher symmetry than the phase III and the experimental ir spectra have less features in the phase II than in the phase III.

5. Conclusions

Our calculations showed that the axial and equatorial isomers have energy that differs only by 2 kJ/mol so both are present in equal concentration at the high temperatures. Since the barrier for the conversion between them is relatively high, about 17 kJ/mol, we assume that their concentration is constant. On the basis of the calculated infrared spectra we concluded that the stable crystal phase is the one that consist of extended hydrogen bond chains between the isomers:

...equatorial-axial-equatorial... It is obvious that further calculations on real lattice are needed to confirm the present results. There is a need for extensive studies of crystal structure by neutron diffraction.

Acknowledgments

The authors gratefully acknowledge valuable discussions with E. Ścieszńska, J. Ścieszński and P. Zieliński. This work was partly financed by the Committee for Scientific Research (Poland) grant No. 2P03B 027 13.

References

- [1] K. Adachi, H. Suga, S. Seki, *Bull. Chem. Soc. Jpn.* **41**, 1073 (1968).
- [2] J. Mayer, M. Rachwalska, E. Ścieszńska, J. Ścieszński, *J. Phys. (France)* **51**, 857 (1990).
- [3] E. Ścieszńska, J. Ścieszński, *Mol. Cryst. Liq. Crystals* **51**, 9 (1979).
- [4] K. Adachi, H. Suga, S. Seki, S. Kubota, S. Yamaguchi, O. Yano, Y. Wada, *Mol. Cryst. Liq. Crystals* **18**, 345 (1972).
- [5] E. Ścieszńska, J. Mayer, I. Natkaniec, J. Ścieszński, *Acta Phys. Pol. A* **76**, 617 (1989).
- [6] D. André, D. Ceccaldi, H. Szwarc, *J. Phys. (France)* **45**, 731 (1984).
- [7] D. Ceccaldi, *Phys. Rev. B* **31**, 8221 (1985).
- [8] D.W. James, H.F. Shurvell, R.M. Parry, *J. Raman Spectrosc.* **5**, 201 (1976).
- [9] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
- [10] K.B. Wiberg, V.A. Walters, W.P. Dailey, *J. Am. Chem. Soc.* **107**, 4860 (1985).
- [11] C. Jansen, D. an Mey, G. Raabe, J. Fleischhauser, *J. Mol. Struct.* **398**, 395 (1997).
- [12] A. Dworkin, A.H. Fuchs, M. Ghelfenstein, H. Szwarc, *J. Phys. Lett.* **43**, L21 (1982).
- [13] A.H. Fuchs, J. Virlet, D. André, H. Szwarc, *J. Chim. Phys.* **82**, 293 (1985).