SPECTROSCOPIC MANIFESTATIONS OF PHASE TRANSITIONS IN CRYSTALLINE CYCLOPENTANE

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Fig. 1

Figure 1: Fig. 1

Abstract

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SPECTROSCOPIC MANIFESTATIONS OF PHASE TRANSITIONS IN CRYSTALLINE CYCLOPENTANE

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It is known that during phase transitions in molecular crystals a number of changes occur in the infrared absorption spectra (1−3), including splitting and shifts of bands, decreases in their widths, and changes in intensities. A decrease in the widths of infrared absorption bands after phase transitions has been noted repeatedly (2), but quantitative measurements were not made; this was hindered, in particular, by the splitting of bands into several components (3).

In studying the infrared absorption spectrum of cyclopentane at low temperatures, we chose the absorption band at 546 cm^{-1}, for which it proved possible to trace changes in width in the temperature interval 300–80°K.

In this temperature interval crystallization of the sample occurs (179.6°K), and two other phase transitions are observed: 138.1°K (crystal I → crystal II) and 122.4°K (crystal II → crystal III) (4). All of them are clearly visible on the graph we obtained experimentally of the dependence of width on temperature (Fig. 1). At the crystallization point the slope of the graph changes noticeably, and at the points of the phase transitions I→II and II→III a discontinuous change in the band width is observed.

Fig. 1. Dependence of the width of the 546 cm^{-1} band of cyclopentane on temperature.
1—layer thickness 35 μ; $2, 3$—layer thickness 100 μ. The solid lines were drawn by the method of least squares in the sections II and I through points 1 and 2, and in the liquid section through points 3.

The spectra of the liquid, crystal I, and crystal II (Fig. 2) differ little from one another, and only with careful measurement of the width (with an accuracy of 0.5 cm^{-1}) is it possible to notice the transition between these phases (during the liquid—crystal I transition, in addition, the absorption background increases somewhat). Neither the I nor the II crystalline modification exhibits infrared dichroism, although it should have been observed in the I modification, which belongs to the hexagonal system (according to X-ray structural analysis data (^{5})).

In contrast to crystals I and II, crystal III has a clearly observed infrared dichroism (Fig. 3), which indicates the anisotropy of crystal III. It arises after the low-temperature phase transition and testifies, together with other facts (see below), to the cessation of rotational reorientations. Analysis of the infrared spectrum of the III crystalline modification and of the dichroism observed by us makes it possible to assert that the cyclopentane molecules in this crystal occupy positions with C_s symmetry and themselves possess this symmetry, and not D_{5h} (^{6}).

and C_2, C_1 (^{7}). For this conclusion we used the data (^{8}) from the vibrational calculation of two low-symmetry conformations of cyclopentane. Although their frequencies proved to be very close to one another, the polarization of many transitions with identical frequencies must be opposite (Table 1).

Table 1

Comparison of dichroism data with the calculated interpretation of the spectrum of low-symmetry conformations of cyclopentane (^{8})

Experiment	Experiment	Experiment	Calculation	Calculation	Calculation
frequency, cm^{-1}	intensity	polarization	C_2	C_s	frequency, cm^{-1}
546	medium	$a > b$	B	A'	557
775	med.-str.	$a < b$	B	A'	797
860	medium	$a > b$	B	A'	880
880	strong	$a > b$	A	A'	891
895	strong	b			
897	strong	a	B	A''	930
902	strong	$a = b$			
953	strong	$a < b$	A	A'	933
958	strong	$a > b$			
984	strong	$a < b$	B	A''	1034
1290		$a > b$	A	A'	1280
1295		$a > b$	B	A''	1273
1316	strong	$a > b$	B	A''	1305

Upon transition to the III crystalline modification, the greatest jump in the width (~ 7 cm^{-1}) of the cyclopentane band at 546 cm^{-1} is observed (Fig. 1). At this same transition, a jump in the width was also observed in the NMR spectra (^{9}). The NMR data were insufficient for judging the degree of hindered rotation of the molecules in crystals II and I, i.e., for determining the reorientation barriers. In (10) the reorientation barrier was determined from the Raman spectrum only for liquid cyclopentane (1.4 ± 0.5 kcal/mol). Having data on the temperature behavior of the width, we determined the reorientation barriers in each of the phases, except crystal III.

In crystal III, over the temperature interval studied (from 122.4 to 70°K), the band width practically did not change. However, from (11) it is known that at 10°K its width was ~ 1.6 cm^{-1}. The slow change of the width with temperature, together with the presence of IR dichroism in modification III, allowed us to suggest that rotational reorientations of the molecules are absent in it, and that they appear upon transition from crystal III to crystal II. In the latter, rotational reorientations are indicated by the considerable band width, the noticeable temperature behavior of the width, and the absence of dichroism. It should be assumed that hindered rotation occurs about almost all symmetry axes that a planar cyclopentane molecule may have, since only in this case, apparently, can the considerable entropy jump at the transition III → II be explained (1) (4). Rearrangement of the crystal at the transition II → I leads to certain changes in the character of the rotational reorientations, which is manifested in a much smaller jump in the width S_i and in a change in the slope of the graph $S_i = f(T)$.

Similarly to how this was done in (10), we assumed that the width depends on temperature in the following manner:

$$S_i(T) = S_{i0} + A_i e(-U_i/RT). \tag{1}$$

Here S_{i0} is the residual width, assumed not to depend on temperature within phase i; U_i is the barrier of rotational reorientations in the given phase; A_i is the frequency factor. The second term in (1) corresponds to the contribution to the width from Brownian reorientations.

Having determined, from three values of the width at three temperatures, the quantities S_{i0}, we found the values of U_i from the slope of the plots $\ln(S_i - S_{i0}) - 1/T$. This method of finding the residual width, and then U_i, appears to us more correct than in (10), where the residual width of Raman lines was determined by extrapolation to infinite viscosity.

The values of S_{i0}, U_i, and A_i obtained by us are given in Table 2. From these

from the data it is first of all evident that the mechanism of rotational reorientations, while explaining the observed temperature dependence of the width, accounts only partially for the jumps in width at the phase transitions. The latter are due mainly to jumps in the residual width. This applies especially to the jump in width at the II → III transition.

Fig. 2. IR absorption spectra of cyclopentane at different temperatures: 1 – 300° K, 2 –205° K (liquid), 3 –146° K (crystal I), 4 –132° K (crystal II), 5 –

Figure 2. IR absorption spectra of cyclopentane at different temperatures: 1 –300° K, 2 –205° K (liquid), 3 –146° K (crystal I), 4 –132° K (crystal II), 5 –88° K (crystal III).

Figure 2: Figure 2. IR absorption spectra of cyclopentane at different temperatures: 1 –300° K, 2 –205° K (liquid), 3 –146° K (crystal I), 4 –132° K (crystal II), 5 –88° K (crystal III).

Fig. 3. Portion of the spectrum of cyclopentane crystal III in polarized light. Curves a and b correspond to two mutually perpendicular directions of polarization of the incident light

Figure 3: Fig. 3. Portion of the spectrum of cyclopentane crystal III in polarized light. Curves a and b correspond to two mutually perpendicular directions of polarization of the incident light

88° K (crystal III).

The value of the barrier in the liquid is somewhat smaller than that obtained in Ref. (10). However, in contrast to Ref. (10), the barriers in crystals II and I are significantly smaller than the barrier in the liquid. In Ref. (10), by contrast, agreement was noted between the barrier values in the liquid and in the plastic crystal (1), using other molecules of this class as examples. We note that the difference between the barriers in crystals I and II correlates with the course of their heat capacities (12).

All phase transitions in cyclopentane belong to first-order transitions (1), and supercooling of the high-temperature phases is characteristic of them. In Fig. 1 the vertical lines mark the phase boundaries observed in careful thermophysical measurements (4). It is easy to see that, upon lowering the temperature, the higher-temperature phases persisted down to lower temperatures than the indicated boundaries (by 5-6°). The transi-

cooling of the liquid phase was also observed in one of the experiments (points 3 in Fig. 1).

The spectra were measured on a Hitachi-225 IR spectrophotometer; the spectral slit width in the region of 546 cm^{-1} was 0.7 cm^{-1}, which made it possible to record the band contour over the entire temperature interval investigated practically without slit distortions.

Fig. 3. Portion of the spectrum of cyclopentane crystal III in polarized light. Curves *a* and *b* correspond to two mutually perpendicular directions of polarization of the incident light.

IR dichroism in crystal III could be observed only on some specimens. They were selected by visual observation of the state of the crystal (the specimen was placed between crossed Polaroids). For polarization of the IR radiation, a polarizer based on transparent GOI diffraction gratings (13) and an IPSh-12 polarizer were used (in some additional measurements carried out on a Leitz IR spectrophotometer, FRG). When working on the Hitachi-225 diffraction spectrophotometer, the polarization directions made angles of 45° with the slit, which eliminated the polarizing action of the instrument.

Table 2

	Liquid	Crystalline modifications	Crystalline modifications	Crystalline modifications
	300—179.6°K	I, 179.6—138.1°K	II, 138.1—122.4°K	III, 122.4°K—80°K
S_{i0}, cm^{-1}	10.5	9.8	8.2	2.8
U_i, kcal/mol	1.2 ± 0.1	0.8 ± 0.1	0.4 ± 0.1	–
A_i, cm^{-1}	88.5 ± 0.5	29 ± 0.5	10 ± 0.3	–

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