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FTIR study of the conformational dynamics in the solid phases of fluorocyclohexane and bromocyclohexane

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The infrared spectra of the solid phases of fluorocyclohexane (FCH) and bromocyclohexane (BCH) have been investigated at temperatures between 77 and 286 K and between 77 and 216 K, respectively. The solid films were formed by cooling liquid films and by condensing vapors of FCH or BCH onto a cold window. During annealing of the deposited film of the FCH a metastable phase, which was interpreted to be the undercooled plastic phase, was observed in the temperature interval between 100 and 143 K; in this phase both axial (a) and equatorial (e) conformers are present with similar concentrations. Near 143 K, an irreversible transition from the undercooled plastic phase to an anisotropic phase was observed. In this phase a non-negligible and reproducible amount of the a-conformer remains. Using dissolution experiments in liquid krypton, the concentration ratio of the conformer $(c_e/c_a)_{solid}$ in the anisotropic phase was determined to be 17(1). At 188 K the reversible phase transition from the anisotropic to the plastic phase was observed. The infrared spectra of the plastic phase of FCH in the temperature interval between 188 and 283 K indicate the existence of a conformational equilibrium e ⇆ a. The similarity of the spectra suggests this phase is identical to the phase observed between 77 and 143 K. The standard enthalpy difference ΔH° between the conformers in this phase is found to be 1.16(5) kJ mol^{-1}, with the e-conformer being more stable. During the annealing of the deposited BCH film a new metastable, anisotropic phase, crystal I, was observed in the temperature interval between 77 and 160 K. At ca. 160 K an irreversible phase transition from crystal I to another anisotropic crystalline phase, crystal II, takes place. In both crystalline phases only the e-conformer is present. From the experiments it was concluded that the conformational mobility dominates the formation of the anisotropic phase of FCH and of the lower temperature anisotropic phase I of BCH.

Introduction

The vibrational spectra of solid fluorocyclohexane (FCH) have been the subject of different studies.[1–4] The solids were formed either by cooling a liquid film[1–3] or by condensing vapors onto a cold window.[4] In the latter case, an amorphous solid is formed upon deposition which by annealing is transformed into an anisotropic crystalline phase. During the phase transition, the bands of the axial conformer were observed to disappear nearly completely. Upon warming this phase, a reversible phase transition to a plastic (cubic, isotropic) crystalline phase is observed at 180 K. This phase contains both the axial (a) and equatorial (e) conformers.[4]

In this study we have set out to obtain more detailed information on the anisotropic and plastic phases. In particular, we have determined the conformational composition of the anisotropic phase, and we have shown that an equilibrium conformational distribution is present in the temperature interval in which the plastic phase is stable. It will be shown that this equilibrium is characterized by a standard enthalpy difference ΔH° very similar to the solution phase value.

In order to find supporting evidence for an interpretation of the thermal behaviour of FCH, to be discussed below, we have also performed low temperature experiments on bromocyclohexane (BCH). The solid state of this compound has been studied by vibrational spectroscopy between 300 and 77 K[1–3,5,6] and by scanning calorimetry between 300 and 7 K.[7,8] In the latter studies only one phase transition, from liquid to solid, was found by the slow cooling of BCH.[7] This is consistent with the vibrational studies, all of which report a single anisotropic crystalline phase. Close scrutiny of the vibrational frequency tables reported by Klaboe[2] and by Woldbaek,[6] however, reveals several discrepancies. These can be interpreted as an indication that different crystalline phases were detected, which would be in contradiction to the conclusion from the calorimetry experiments. Therefore, collateral to the above aim, we have carefully re-investigated the behavior upon annealing of a solid film of BCH. It will be shown below that two different anisotropic crystalline phases have been detected, the spectral characteristics of one of them being in agreement with the data of Klaboe,[2] while those of the other agree with the data described by Woldbaek.[6]

Experimental

The samples of fluorocyclohexane (Lancaster Synthesis, purity 98+%, $T_{mp} = 13\,^\circ C$, ref. 9) and bromocyclohexane (Acros Organics, purity 99%, $T_{mp} = -56.5\,^\circ C$, ref. 9) were used without further purification. The krypton was obtained from L'Air Liquide and had a stated purity of 99.998%.

The infrared spectra were recorded using a Bruker IFS 66v spectrometer equipped with a globar source, a Ge/KBr beamsplitter and LN$_2$ cooled broad band MCT detector. The interferograms were recorded with a resolution of 0.5 cm^{-1} and Fourier transformed using a Blackman–Harris apodization function. A zero-filling factor of 4 was used for all experiments.

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It is well known[10] that the structure of the solid phase of an organic compound often depends on the way the sample was prepared. Therefore, we have prepared the solids in two different ways, either by condensation of vapor onto a cold KBr or Ge window, and by slowly cooling a liquid film placed between KBr windows. The cell used for solutions in liquid Kr (LKr) is made of brass, it has a path length of 40 mm and is equipped with silicon windows.[11] The cryostats were cooled with liquid nitrogen. The temperature was measured by a Pt-100 thermo-resistor and was kept constant manually to ensure a standard deviation smaller than 0.5 K. With the type of cryostat for the solids films used here, the temperature accuracy is supposed to be about ±5 K.

Band areas of spectral bands were obtained from least-squares fittings using Gauss/Lorentz sum functions. These calculations were performed using Peakfit 4.01.[12] Linear regression analysis of the data derived from the vibrational spectra were carried out using Origin 6.0.[13] The uncertainties reported are the standard deviations obtained from the regression analysis.

Results and discussion

In the following paragraphs, just as in the introduction, we will refer to phase transitions as being reversible or irreversible in the kinetic meaning, *i.e.* depending on the transition being reversed or not when the temperature evolution is reversed.

Phase transitions in fluorocyclohexane

The vibrational frequencies of FCH, and their assignments, have been discussed before,[4] and will not be described in detail here. In this study we have mainly used data from the 900–800 cm^{-1} region. In this region four bands of medium intensity are observed. Two of them, at 830 and 866 cm^{-1}, are assigned to the a-conformer, while the other two, with maxima at 845 and 894 cm^{-1}, belong to the e-conformer.

The spectra recorded from a film of FCH pressed between two KBr plates indicate the formation of solid phases in agreement with previous observations.[4] Thus, when the liquid film is slowly cooled at a rate close to 1.5 K min^{-1}, crystallization to an anisotropic phase is observed. The anisotropy was confirmed by visual inspection of the film between crossed polarizers. The spectrum of this phase agrees with that reported by Christian *et al.*,[4] *i.e.* it is dominated by bands assigned to the e-conformer, but weak bands due to the a-conformer persist. By slowly warming the anisotropic phase, a transition is observed at 188 K, resulting in the plastic phase. In this phase a- and e-conformers are present in similar populations, and the phase transition is found to be reversible, as described before.[4]

A different behavior was observed when starting from a film of FCH deposited on a 77 K KBr window. This is illustrated by the spectra shown in Fig. 1. The freshly deposited film is amorphous. Its spectrum is given in Fig. 1a. Annealing of the amorphous film at approximately 100 K induces a number of changes in the spectrum: bandwidths decrease, relative intensities change and many bands undergo small frequency shifts, as indicated in Table 1. These changes signal a transition to a new phase, which we shall describe as phase A, and which we shall identify below. This transition is irreversible, *i.e.* upon recooling of phase A it does not transform back in the amorphous phase. The spectrum of phase A is shown in Fig. 1b. It is clear from, for instance, the 845/830 and 894/866 cm^{-1} conformational doublets, that in this phase both conformers are present. When heated to approximately 143 K, phase A undergoes a transition to a new phase, the spectrum of which is given in Fig. 1c. This spectrum is in excellent agreement with that of the anisotropic phase, and we identify this phase accordingly. Attention is drawn to the fact that also in this case the bands
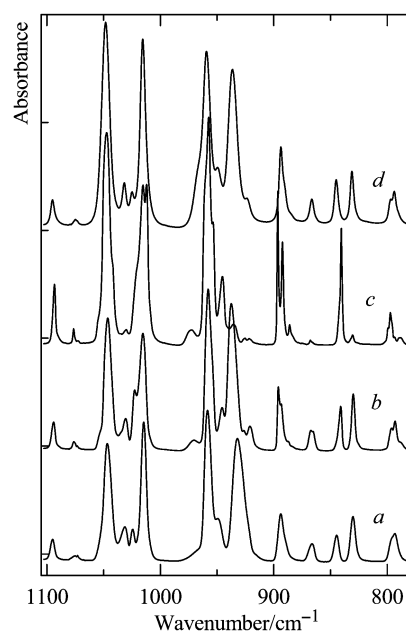

Fig. 1 Infrared spectra of solid fluorocyclohexane: (a) spectrum recorded immediately after condensing vapor of FCH onto a KBr window at 77 K, (b) spectrum of the undercooled plastic phase, recorded after annealing to 98 K and re-cooling to 77 K, (c) spectrum of the anisotropic phase recorded after annealing to 165 K and re-cooling to 123 K and (d) spectrum of the plastic phase at 188 K. The ordinate tick marks are separated by 0.2 absorbance units. The spectra have been shifted vertically for clarity.

due to the axial conformer are strongly reduced in relative intensity but have not completely disappeared. The transition from A to the anisotropic phase was found to be irreversible. Together with the fact that the formation of A is also irreversible, this leads to the conclusion that phase A is metastable. When heated to 188 K the anisotropic phase reversibly transforms to the plastic phase; the spectrum of this phase is given in Fig. 1d. It is clear, as was said above, that in this phase the a–conformer has re-appeared.

Detailed comparison shows there is a strong similarity of the spectrum of phase A with that of the plastic phase, not only in terms of relative intensities, but also in terms of the postitions of the bands. Comparison in Fig. 1 suggests a slightly better resolution in the spectrum of phase A than in that of the plastic phase, but this is readily accounted for by considering the lower temperature at which phase A was investigated. Although there are several possibilities for the nature of phase A, including that it is an oriental glass, in view of the above similarity we prefer the interpretation that phase A is the undercooled form of the plastic phase observed above 188 K. The amorphous phase being the undercooled liquid phase, below the melting point of the plastic phase the chemical potential of the latter is lower than that of the amorphous phase, so that thermodynamically the plastic phase is accessible from the amorphous phase at 100 K. Below the temperature at which the anisotropic and plastic phases are in equilibrium, 188 K, the chemical potential of the anisotropic phase is below that of the plastic phase, so that at 100 K the latter is metastable with respect to the former.

At first sight, the similarity of the relative intensities in the conformational doublets in the spectra of the plastic phase with those of the undercooled plastic phase, obvious from Fig. 1, is somewhat surprising, as in the former the intensity ratio is determined thermodynamically, while in the latter it is related to the population ratio in the amorphous phase (*vide infra*). It is well-known that upon deposition onto a cold window of an amorphous film from the vapor phase a conformer

Table 1 Vibrational frequencies (in cm^{-1}) of solid fluorocyclohexane[a]

Amorphous, 77 K	Undercooled plastic phase, 77 K	Amorphous, 77 K	Undercooled plastic phase, 77 K
474.1	472.4	1119.0 sh	1119.0 sh
479.5	477.8	1125.4	1124.7
487.6	487.6		1140.5
546.7	546.7	1153.3 sh	1151.5
660.6	660.6	1158.5	1158.0
	788.0 sh	1190.6	1187.9
793.2	793.0		1191.1 sh
796.3 sh	796.3	1234.9	1234.5
830.3	830.0	1243.2	1242.1
844.6	841.0	1246.8 sh	1246.8
866.0	865.3	1257.6	1258.3
	867.3	1271.4	1270.4
890.0 sh	886.8 sh	1307.6	1307.6 sh
893.8	893.5		1312.1
	896.0	1315.3	1315.3
	920.9	1327.4	1326.7
932.1 br	926.3		1332.5 sh
	937.4	1340.2	1339.3
949.1 sh	945.6	1345.9	1344.6
958.5	957.9		1348.7
969.0 sh	971.0	1367.6	1366.6
1014.6	1015.4	1377.2 sh	1375.3 sh
1024.4	1022.7	1431.4	1434.7 br
1031.1	1030.5	1438.7	1444.1
1046.8	1046.4	1449.7	1449.7 sh
1054.0 sh	1054.0 sh	1456.8 sh	1455.6
1072.9	1073.2	1463.0 sh	1461.2
1075.4	1076.2	1470.0	1468.3
1095.0	1094.0		

[a] sh: shoulder, br: broad band.

population ratio is obtained that does not reflect the low temperature equilibrium value, but is usually closer to the vapor phase equilibrium value. Therefore, the above similarity must be accidental, the conformer ratio in the amorphous phase being fortuitously close to the 188 K equilibrium value in the plastic phase.

To summarize the data obtained during the annealing processes, the temperature intervals in which the different solid phases of FCH occur are summarized in Fig. 2.

Solid phase formation and conformational interconversions

The changes observed while annealing the solid phases can be explained if the conformational mobility of FCH is taken into account. The kinetics of the conformational transitions in the FCH dissolved in LKr have been investigated,[14] and the activation Gibbs energy for the transition from axial to equatorial conformer was derived to be $\Delta G^{\ddagger} = 42(2)$ kJ mol^{-1} at $T = 140$ K.
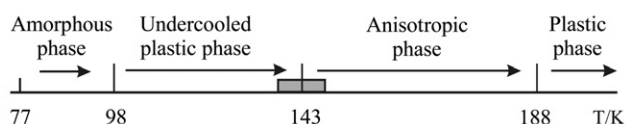

Fig. 2 Temperature intervals in which the anisotropic and the plastic phases of fluorocyclohexane occur. The phase transition at 188 K is reversible, the phase transitions at *ca.* 98 and 143 K are irreversible. The rectangle shows the temperature interval, 137–148 K, in which the kinetics of the conformational transition was investigated in liquid Kr.[14]

The relaxation time τ for the axial to equatorial transitions essentially depends on the temperature. The spectra obtained during isothermal studies have shown[14] that at 148 K τ is close to 190 s, while at 137 K it equals 3300 s. On the high temperature side of this narrow interval the conformational equilibration is near-instantaneous, while on the low temperature side the rate of conformational interconversion becomes negligible. Techniques have been described to determine the "temperature of conformational freezing", T_0,[15] at which, on the time scale of the present experiments, the former regime switches into the latter. The T_0 for FCH dissolved in LKr was estimated to be 148 K.[14]

The phase transition between the amorphous phase and undercooled plastic phase takes place at $T = 98$ K, well below T_0. At this temperature, the conformational interconversion is frozen, so the relative populations in the undercooled plastic phase must equal those in the amorphous phase. This conclusion is confirmed by the comparison of the band areas of the a- and e-conformers in the different phases. In the amorphous phase the ratios are $I_a(865)/I_e(892) = 0.33(1)$ and $I_a(831)/I_e(845) = 1.90(2)$, whereas in the undercooled plastic phase the ratios are $I_a(865)/I_e(892) = 0.34(1)$ and $I_a(831)/I_e(845) = 1.41(2)$. Although it cannot be excluded that the change in the 831/845 cm^{-1} doublet reflects an orientational effect, it is not very likely that in different experiments an identical degree of orientation of a polycrystalline sample is obtained. The reproducibility of the above ratio, observed in this study, not only in experiments using the same KBr substrate to deposit the film, but also in experiments using a Ge window, suggests that the intensity ratio change is connected with changes in the extinction coefficients of the bands during the phase transition.

It was noted above that both the amorphous phase and phase A contain bands due to the a- and the e-conformers, while in the anisotropic crystal the bands of the a-conformer are dramatically reduced in relative intensity. The phase transition between phase A and the anisotropic phase takes place at temperatures in the vicinity of 145 K, *i.e.* close to the temperature T_0 (Fig. 2). This suggests that the main factor which determines the temperature of this phase transition is the conformational mobility. If the Gibbs energy for transition from undercooled plastic to anisotropic phase, ΔG_t°, would be large, the energy released in the process could be used in the interconversion of the conformers, so that the transition could take place well below T_0. The fact that this not observed supports the suggestion that ΔG_t° is much smaller than the conformational activation Gibbs energy $\Delta G^{\ddagger}$, which was determined[14] to be 42 kJ mol^{-1} in LKr.

Enthalpy difference measurements in the plastic phase of FCH

It was noted above that in the plastic phase of FCH both the e- and the a-conformer are present. The plastic phase is stable at temperatures well above the temperature of conformational freezing, and it may consequently be assumed that in this phase, a conformational equilibrium is present. To characterize this equilibrium, we have studied the spectra of the plastic phase between 188 and 283 K. The intensities were measured both during heating and cooling of the sample, and the changes were found to be reversible. Typical spectra in the 855–820 cm^{-1} region obtained during this study are shown in Fig. 3.

The conformational equilibrium can be described by a combination of Van't Hoff's isochore and Beer's law,[16] resulting in the following relation between $\ln(I_a/I_e)$ and the inverse temperature:

$$\ln \frac{I_a}{I_e} = \ln \frac{\varepsilon_a}{\varepsilon_e} + \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}, \qquad (1)$$
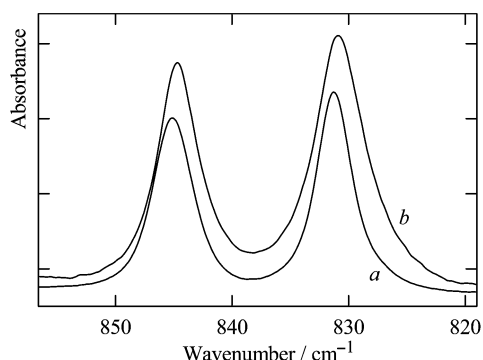
Fig. 3 Infrared spectra of the plastic phase in the 855–820 cm^{-1} region. The spectra were recorded at 283 K (a) and 188 K (b). The ordinate tick marks are separated by 0.05 absorbance units. The spectra have been shifted vertically for clarity.

in which I_a and I_e are infrared intensities in a conformational doublet, ΔS° and ΔH° are the standard entropy and standard enthalpy differences between the conformers, and ε_a and ε_e are the extinction coefficients for the conformational doublet, respectively. The slope B of the relation between $\ln(I_a/I_e)$ and the inverse temperature can be written as:

$$B = \frac{d}{dT^{-1}}\left(\ln\frac{I_a}{I_e}\right)$$
$$= \frac{d}{dT^{-1}}\left(\ln\frac{\varepsilon_a}{\varepsilon_e}\right) - \frac{\Delta H^\circ}{R} + \frac{T}{R}\frac{d(\Delta H^\circ)}{dT} - \frac{T^2}{R}\frac{d(\Delta S^\circ)}{dT} \quad (2)$$

It has been shown,[15] that the two last terms on the right hand side of this expression cancel each other. In most experimental studies the first term on the right hand side of eqn. (2) is neglected, but this assumption is rarely justified. In Fig. 4a, the plot of $\ln(I_a/I_e)$ versus $1/T$ for the 833/845 cm^{-1} doublet for the plastic phase is shown. It can be seen that a linear relation exists, with a slope B equal to $-140(6)$ K.

The data from the equilibrium plastic phase alone do not allow the measurement of the contribution of $d[\ln(\varepsilon_a/\varepsilon_e)]/dT^{-1}$ to this slope. This quantity, however, can be measured for phase A, for which it has been argued above that the relative populations of the conformers do not change with temperature. The $\ln(I_a/I_e)$ for the 833/845 cm^{-1} doublet measured between 93 and 133 K for this phase are shown against inverse temperature in Fig. 4b. The slope of the linear regression through the points equals 11.4(7) K. Assuming that phase A is indeed the undercooled plastic phase, it appears not unreasonable to assume that the temperature variations of ε_a and

ε_e are very similar in both temperature intervals. It then follows that the slope of the regression line in Fig. 4a is largely dominated by the shift of the conformational equilibrium. The standard enthalpy difference ΔH° between the conformers derived from Fig. 4a, accounting for the temperature dependence of ε_a and ε_e, equals 1.16(5) kJ mol^{-1}, with the e-conformer being more stable. This value is acceptably similar to the value measured in LKr,[14] 1.3(4) kJ mol^{-1}, and to the value obtained for FCH dissolved in liquid CS$_2$,[17] 0.9(3) kJ mol^{-1}.

In their study, Christian *et al.*[4] noted that no conversion from the plastic to the anisotropic phase was observed when the plastic phase was quenched to liquid nitrogen temperature. A possible explanation for this is that the quenching lowers the temperature of the plastic phase too quickly, so that the transformation to the anisotropic phase, which has to set in at 188 K, cannot take place to a measurable extent before the temperature reaches $T_0 = 148$ K. Beyond this temperature, the conformational interconversion is no longer possible,[14] so that the path from plastic to anisotropic phase becomes effectively blocked.

Determination of the conformer ratio $(c_e/c_a)_{cryst}$ in the anisotropic crystal of FCH

The literature data[4] and the present study show that in the anisotropic solid a small but significant and reproducible amount of the a-conformer remains. (Fig. 1c). Especially the latter fact suggests that the anisotropic solid is single-phased. Because no information was available on the extinction coefficient ratio of conformational doublets, $\varepsilon_a/\varepsilon_e$, previous studies were unable to determine the relative concentrations of the conformers in this phase. We have measured this quantity in the following way.

It was noted above that the anisotropic phase is stable up to 188 K. Upon dissolution of this phase in a solvent at temperatures well below $T_0 = 148$ K, the conformers will pass unchanged from the solid into the solution, and the changes in the conformer concentrations in the solution will reflect the conformer populations in the dissolving solid phase.

This can be expressed by equating the ratio of the changes, dc_e/dc_a, of the solution concentrations during the dissolution to the population ratio in the solid phase, $v = (c_e/c_a)_{solid}$:

$$dc_e/dc_a = \nu = (c_e/c_a)_{solid} \quad (3)$$

Combination of this equation with Beer's law yields:

$$\frac{dI_e}{\varepsilon_e l} = \nu\frac{dI_a}{\varepsilon_a l}. \quad (4)$$

Integrating between $t = t_0$ and $t = t$ results in:

$$I_e = \frac{\varepsilon_e}{\varepsilon_a}\nu I_a + \mu \quad (5)$$

where μ is a constant whose value is determined by the initial conditions.

We have studied the kinetics of the dissolution of the anisotropic phase in LKr at 123 K, using samples prepared with the following procedure. Initially, the cell was cooled to 285 K and vapors of FCH were allowed to condense in the cell. Subsequently, the cell was slowly cooled to 153 K, during which crystallization of the condensed liquid takes place. To ensure complete conversion to the anisotropic phase, the sample was annealed by slowly heating the cell to 168 K, at a heating rate of 0.01 K s^{-1}. After this, the cell was cooled to 123 K and Kr gas was slowly added to the cell in small batches. At this temperature the Kr liquefies and the FCH starts to dissolve.

The manifold used to fill the cell does not allow pre-cooling of the solvent gas, which, therefore, has to be manipulated at room temperature. This makes the condensation of the solvent gas the critical step in the process. The experience is that when
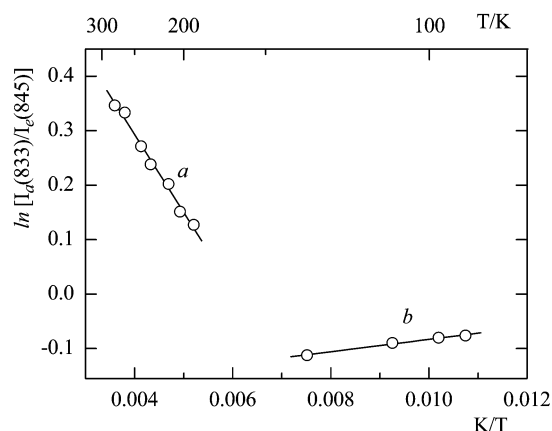

Fig. 4 Dependence of $\ln[I_a(833)/I_e(845)]$ on $1/T$ for the plastic phase of fluorocyclohexane in the stable (a) and in the undercooled (b) region.

the solvent gas is admitted with long intervals in sufficiently small batches most of it condenses in the filling tube. As the gas is admitted at a pressure of 6–8 bar, the temperature of the condensing liquid initially is approximately 150 K, after which it rapidly cools to 123 K, the temperature of the cell body. The initial liquid temperature of 150 K is well below the temperature of 188 K at which the anisotropic solid transforms into the plastic phase. Hence, during the formation of the liquid, the composition of the undissolved solid is not affected. Because every newly added batch of solvent may locally, and temporarily, heat the solution already present to temperatures near $T_0 = 148$ K, the conformational composition of FCH in solution may differ from that in the anisotropic solid with which it is in contact. When the cell is completely filled with liquid, it is allowed to equilibrate its temperature, and then the evolution in time of the solution is followed spectroscopically for 2 h, the beginning of this study being identified with the time $t = t_0$. During the 2 h interval the band areas of the absorption bands of both conformers increase, signalling further dissolution of anisotropic solid. The evolution of the band areas was analyzed using eqn. 5. It may be remarked that the difference in conformational composition between the solution at t_0 and the anisotropic solid is of no consequence for this analysis.

In this study, 6 independent dissolution experiments were carried out at 123 K. Typical infrared spectra in the 855–825 cm^{-1} region, obtained during such a study, are shown in Fig. 5. The spectra were recorded at t_0, and 10 and 16 min later. It can be seen that the ratios of the band area increases of the e- and a-bands differ from the band area ratio of the same bands at t_0, which, as explained above, is a consequence of the difference in conformational composition of the liquid at t_0 compared to that of the solid which is being dissolved. For each experiment, the band area $I_e(844)$ of the 844 cm^{-1} e-conformer band was plotted against the band area $I_a(833)$ of the 833 cm^{-1} a-conformer band. A typical plot is shown in Fig. 6. It can be seen that band areas are linearly related. The slopes of the linear regression lines obtained equal, in descending order, 6.78(5), 6.38(7), 6.13(13), 5.25(11), 5.06(6), and 2.69(2). Obviously, there is a large scatter on these slopes. The experiments resulting in the smaller slopes had changes of a-conformer band area that are relatively higher than in the experiments that result in the higher slopes. This means that in the former experiments the changes of the concentration of the a–conformer in the solution were too high. It is believed that the reasons for this are either that the anisotropic phase was incompletely formed, or that during formation of the liquid some uncondensed, and thus warm, krypton had penetrated the cell and locally transformed part of the anisotropic solid into the plastic phase, or a combination of both.
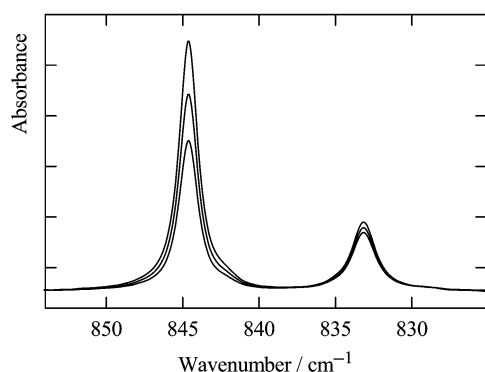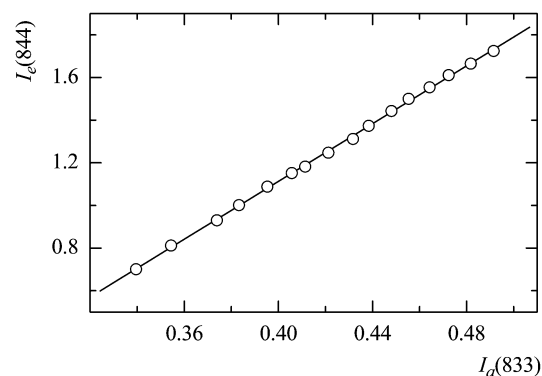

Fig. 6 Dependence of the 844 cm^{-1} band area on that of the 833 cm^{-1} band, obtained from the study of the dissolution as a function of time, of fluorocyclohexane in LKr at 123 K.

Eqn. (3) shows that the calculation of the population ratio ν requires knowledge of the ratio $\varepsilon_e/\varepsilon_a$ of the extinction coefficients in LKr at a temperature sufficiently similar to that used in the present experiments. This ratio was determined recently[14] in LKr at 136 K and equals $\varepsilon_e/\varepsilon_a = 0.38(4)$. Using this value, the concentration ratios $(c_e/c_a)_{solid}$ were determined to be 17.8(19), 16.8(18), 16.1(17), 13.8(15), 13.3(13) and 7.1(7).

The comparison of the infrared spectra of fluorocyclohexane in different solid phases shows (Fig. 1a–d), that in the anisotropic crystal the ratio $(c_e/c_a)_{solid}$ is significantly larger than that observed for the other solid phases. Within their uncertainties, the three higher values of $(c_e/c_a)_{solid}$ are equal. Their grouping suggests that this set represents experiments in which the solution population was not altered by the dissolution and, hence, correctly reflects the stoichiometry of the anisotropic phase. Therefore, we propose the average of the three values, 17(1) as the population ratio c_e/c_a in this phase.

There is a variety of reasons why a small amount of a second conformer can be present in the sample. For instance, it may be that microcrystals of each pure conformer coexist in the solid film with kinetics preventing evolution to the more stable variety, of that the second conformer occupies special deffective sites such as present in the grain boundaries. The non-equilibrium nature of these posibilities appears to contradict the grouping of the c_e/c_a ratios and, therefore, are judged to be less likely in the present case. Other possibilities are that the obtained crystals are homogeneous, with an equilibrium but otherwise random distribtution of the second conformers in the unit cell, or that the c_e/c_a ratio reflects the true stoichiometry of the unit cell. Although these are more likely possibilities, the present experiments, with their lack of direct control of the structure of the crystals, do not allow to distinguish between them.

Phase transitions in bromocyclohexane

The solid state behavior of bromocyclohexane was mainly studied by recording infrared spectra of samples prepared by depositing vapors of the compound on either a KBr or a Ge substrate kept at 77 K. After deposition, the thin film was allowed to slowly warm up: the temporal evolution of the temperature in a typical run is given in the lower part of Fig. 7, while in the upper part the evolution of the band area of the spectral feature(s) near 1120 cm^{-1} (open circles) (ν_{16} e- and ν_{40} a-conformer[6]) and of the maxima of the band(s) near 1195 cm^{-1} (closed circles) (ν_{15} e- and a-conformer[6]) are given.

It can be seen that four temperature intervals can be distinguished. Below $T_a = 121$ K the spectrum is typical for an amorphous film. At a temperature T_a some changes in the spectra start to appear. For example, the areas of the 1120 and 1193 cm^{-1} bands suddenly decrease, and the bandwidth

Fig. 5 The infrared spectra of fluorocyclohexane dissolved in LKr at 123 K. From top to bottom, the spectra were recorded immediately after filling the cell, and 10 and 16 min later. The ordinate tick marks are separated by 0.1 absorbance units.
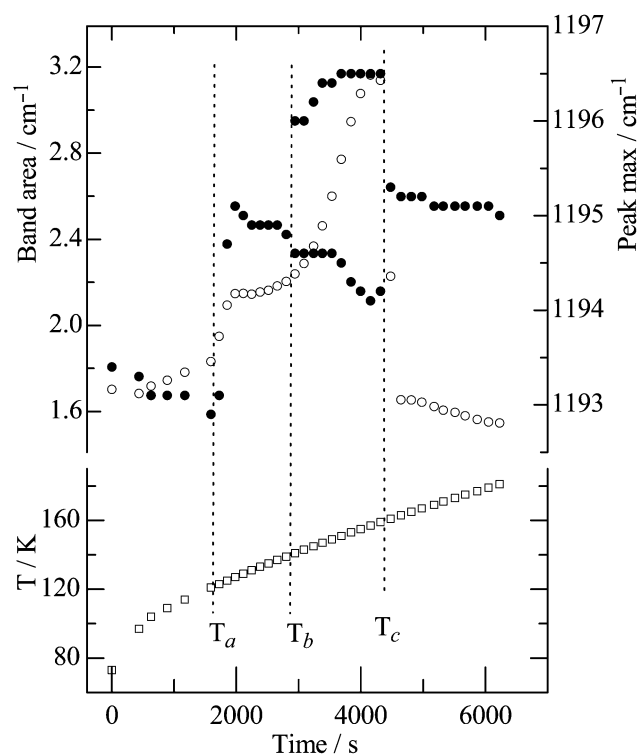
Fig. 7 Dependencies of the 1120 cm^{-1} band area (light circles), peak maximum of the 1193 cm^{-1} band (dark circles) and temperature (squares) on the time during the annealing of a bromocyclohexane film deposited on a KBr substrate.

Fig. 9 The temperature intervals in which the spectra of the different solid phases of bromocyclohexane were observed. T_a, T_b and T_c are the temperatures of the phase transitions. The indications 'crystal I' and 'crystal II' above the arrows a, b and c indicate which crystal form is obtained when the warming of the sample is stopped at the temperature corresponding to the starting point of the arrow, followed by cooling to liquid nitrogen temperature. The shady rectangle shows the temperature interval, 145–153 K, in which the kinetics of the conformational transitions was observed in liquid ethane and liquid Kr.

of several of the bands decreases (the 1193 and 1120 cm^{-1} bands are narrowed about by 15 and 20%, respectively). These changes are similar to those observed in the spectra of FCH during the transition from the amorphous to the undercooled plastic phase. We therefore suggest that also for BCH an undercooled plastic phase is formed. Near $T_b = 139$ K the bands of the a-conformer disappear, while the bands of the e-conformer are shifted and in a number of cases are split into multiplets. This is illustrated in Fig. 8a. Visual inspection of the film between crossed polarizers shows that these changes are due to a transition to an anisotropic phase, crystal I. Temperature cycling suggests that this phase is stable in the temperature interval from 77 to $T_c = 160$ K (Fig. 9, line a). Annealing of the sample at temperatures above 160 K (T_c) results in new changes in the spectra, as is evident from Figs. 7 and 8b, which again signal a phase transition. Analysis using crossed polarizers shows that also this new phase, crystal II,
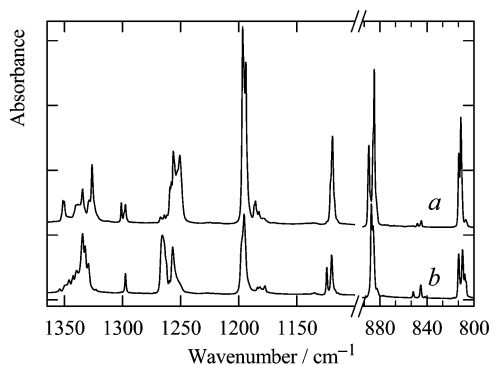
is anisotropic. Crystal II remains stable up to the melting point of BCH ($T_{mp} = 216.7$ K[9]). The phase transition from crystal I to crystal II is irreversible, testifying that crystal I is a meta-stable solid phase (Fig. 9, line a, b).

It should be noted that the temperature T_b at which the phase transition from the amorphous to the crystal I phase takes place is close to the temperature interval from 145 to 153 K in which the conformational relaxation of BCH was observed in liquid ethane[15,18] and in liquid Kr[19] (Fig. 9, hatched rectangle). This is in agreement with our observation for FCH, and it confirms our conclusion that the main factor which determines the temperature of this phase transition is the conformational mobility. This result also shows that for BCH the the Gibbs energy of the phase transition, ΔG_t°, at that temperature is significantly smaller than the activation Gibbs energy controlling the conformational transitions $\Delta G_t^\circ \ll 44$ kJ mol^{-1}.[15]

Experiments in which a liquid film was cooled have also been perfomed, and these reveal that the solid phase obtained depends on the cooling rate. At slow rates, about 2 K min^{-1}, crystal II is formed and this phase remains stable, as mentioned above, in the temperature range from 77 K to the melting point (Fig. 9c). This result agrees with the calorimetric investigation[7] in which the heat capacity of BCH was measured between the temperatures 7 and 300 K and only one phase transition, melting, was observed. In contrast, rapid cooling of the liquid film, with a rate close to 15 K min^{-1}, yields crystal I.

Finally, it is interesting to compare the spectrum of crystal phases I and II with those reported in the literature.[2,6] Taking into account the lower temperatures used in our experiments and the better resolution, the spectrum of crystal phase I matches closely that reported by Klaboe,[2] while the spectrum of crystal phase II is in better agreement with that described by Woldbaek.[6]

Acknowledgements

Fig. 8 Infrared spectra of solid bromocyclohexane: crystal I (a) and crystal II (b) at 77 K. The ordinate tick marks are separated by 0.2 absorbance units. Spectrum a has been shifted for clarity.
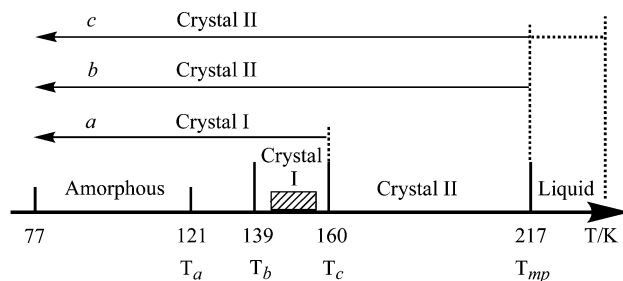
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