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# Low Frequency Vibrational Spectra of Molecular Crystals

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# Low Frequency Vibrational Spectra of Molecular Crystals

## XXI†. Cyclopentane, Cyclopentane-$d_1$ and Chlorocyclopentane

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The infrared and Raman spectra of the three crystal modifications of cyclopentane-$d_1$ were recorded at temperatures in the respective ranges of each of the three phases. The spectra of the two plastic modifications are so similar that no evidence could be observed for a phase transition. Many of the very broad bands observed in crystal forms I and II become multiplets of sharp bands in crystal III. Upon comparing the infrared to the Raman spectrum of crystal III, one readily observed an alternation of intensity of the bands in the two spectra; bands which are intense in the Raman are weak in the infrared spectrum and vice versa. Six bands were observed in the C–D stretching region and it is concluded that Fermi resonance and conformational multiplicity are responsible for this complex spectral pattern. Each of the three components of the C–D stretch of the low temperature phase coalesce into one band in crystal phase III apparently due to the pseudorotational and reorientational motion of the molecules in the plastic modification. Lattice modes were observed for both cyclopentane-$d_0$ and cyclopentane-$d_1$ in crystal phase III at 116, 108, 89, 71, 58, and 48 $cm^{-1}$.

In the far infrared spectrum of chlorocyclopentane in crystal phase I, a very broad band centered at 50 $cm^{-1}$ was observed which is very similar to the spectrum of the liquid in this spectral region. With the transition to crystal phase II, this band sharpens and pronounced bands are observed at 51, 69 and 75 $cm^{-1}$. This behavior is consistent with a transition from a

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‡ Soviet-American Scientific Exchange Scholar.

disordered to an ordered crystalline state. Changes in the 622 and 584 $cm^{-1}$ doublet in the infrared spectrum of chlorocyclopentane on the transition from solid phase I to solid phase II clearly showed the transition involves the change from a mixture of axial and equatorial conformations to an axial conformation only.

## INTRODUCTION

Previous vibrational studies of solid cyclopentane and monohalocyclopentanes have yielded considerable information about both the molecular and crystal symmetries[1–10] of these globular molecules. The changes in the observed vibrational spectra of solid cyclopentane[2,3,5,7,9] at the phase transition of crystal II to crystal III (122.9°K) have been explained by: (1) the lowering of the molecular symmetry in crystal III, (2) the change in the crystal symmetry below the phase transition, and (3) the supposition that molecular reorientational motion or conformational change is largely absent in the low temperature phase. These proposals were based on the appearance of the infrared dichroisms[3,5] in the spectrum of cyclopentane in crystal phase III and the very pronounced sharpening of several of the infrared bands[7] in the lowest temperature crystal modification.

In order to separate the effects on the spectra of the molecular symmetry changes from those of order-disorder phenomena, an investigation of the substituted cyclopentanes seemed in order. The simplest of the substituted cyclopentanes are monohalocyclopentanes; however, only chlorocyclopentane is known[11] to possess a first-order phase transition in the solid state. Two of the other monosubstituted cyclopentanes (Br, I) crystallized only as rigid crystals.[12] No information concerning possible solid state phase transitions in fluorocyclopentane is presently available. However, since monodeutero-cyclopentane on which no vibrational data has been reported should have the same physical properties as cyclopentane-$d_0$ and have the same molecular symmetry as the monohalocyclopentanes, the investigation of the vibrational spectra of the three solid state crystal modifications was undertaken. Thus, we report the study of the vibrational spectra in the various crystalline modifications of cyclopentane-$d_1$ and chlorocyclopentane with reference to complimentary data from the Raman[13] spectrum of cyclopentane-$d_0$. Near the completion of our studies, Schettino and Marzocchi[9] reported the laser Raman spectra of crystal III of cyclopentane and cyclopentane-$d_{10}$. Their data in the higher frequency region for the "light" compound are in complete agreement with our results, but our data differ significantly in the low frequency region of the spectrum of cyclopentane-$d_0$. The temperature dependence of the shape and width of several of the infrared bands will also be discussed.

## EXPERIMENTAL

The sample of chlorocyclopentane used in the present work was obtained from Chemicals Procurement Laboratories, Inc. and was purified by vapor phase chromatography (16 ft. diisodecyl phthalate column) as previously described.[4] The sample of cyclopentane-$d_1$ was prepared by the method previously described[14] and checked by mass-spectrometry. It contained 80% cyclopentane-$d_1$ and ~20% cyclopentane-$d_0$. Spectroquality reagent-grade cyclopentane was obtained from Matheson, Coleman and Bell, but the sample required purification by vapor phase chromatography as described earlier.[15]

The Raman spectra of the solid and gaseous samples were obtained with a Cary Model 82 Raman spectrophotometer[16] employing a Coherent Model 53A argon ion laser as a source. All data were taken with the 5145Å line for excitation with a power of approximately 2 watts at the sample. The spectra of the solid samples were obtained by using the spray-on technique with a cell similar in design to that described earlier,[17] except it was adapted for the Raman instrument. The spectrum of the gas was obtained with the sample contained in the standard Cary multipass gas cell. Depolarization measurements were made by using the analyzer method.

The mid-infrared spectra were recorded with a Digilab Fourier transform spectrometer FTS-14 and a Perkin–Elemer Model 621 spectrophotometer. The far infrared spectra were recorded with a RIIC FS-720 Fourier spectrometer. Frequencies for all well defined infrared and Raman bands are expected to be accurate to $\pm 1$ cm$^{-1}$.

## RESULTS AND DISCUSSION

*Cyclopentane*-$d_1$ The infrared and Raman spectra of the three crystal modifications of cyclopentane-$d_1$ were recorded at temperatures in the respective ranges of each of the phases for cyclopentane-$d_0$ (138.1°–179.6°K, crystal I; 122.4°–138.1°K, crystal II; and below 122.4°K, crystal III). The vibrational data are summarized in Figures 1–3 and Table I. As in cyclopentane-$d_0$ the spectra of the two plastic modifications are so similar that no evidence for a phase transition could be observed.

The spectrum recorded at 110°K (see Figure 1B) differs significantly from those for the plastic modifications. Many of the very broad bands observed in crystal forms I and II (see Figure 1A) become multiplets of sharp bands in crystal III. Further cooling of the sample to 25°K did not change the appearance of the spectrum significantly.

While the spectrum of crystal III of monodeuterocyclopentane contains most of the bands observed in cyclopentane-$d_0$, eight additional bands

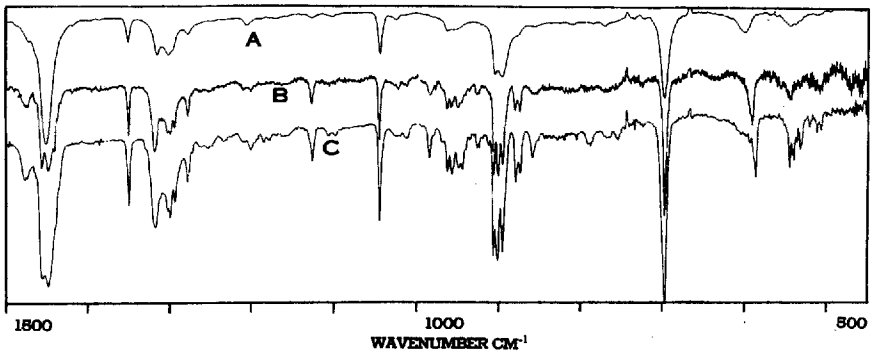


FIGURE 1 Mid-infrared spectra (450–1500 $cm^{-1}$) at different temperatures of solid cyclopentane-$d_1$: A, phase I at 155 K; B, phase III at 110 K; C, phase III at 25 K.

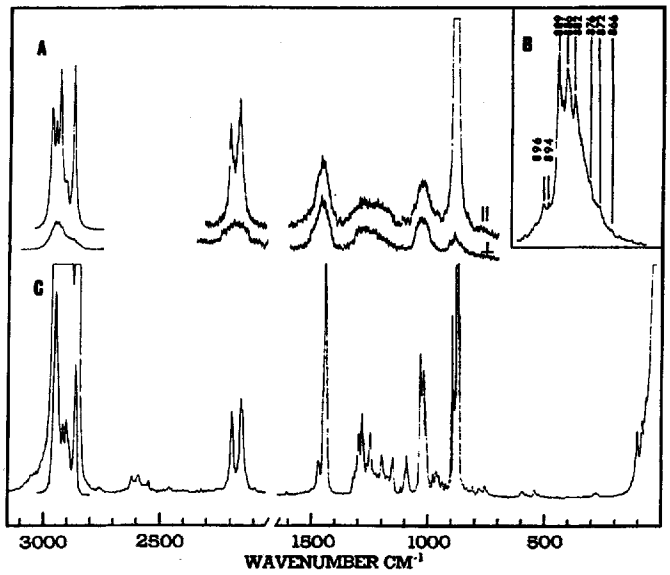


FIGURE 2 Raman spectra of cyclopentane-$d_1$: A—mutually orthogonal polarizations, gas, 240 mm Hg, multipass cell, slitwidth 1.5 $cm^{-1}$; B—the 889 $cm^{-1}$ band with slitwidth 0.8 $cm^{-1}$; C—crystal III, spectral slit 3 $cm^{-1}$.

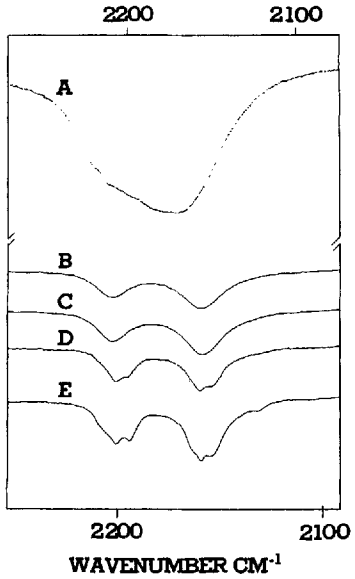


FIGURE 3 The C–D stretch vibration region in infrared spectrum of cyclopentane-$d_1$: A—gas, p = 60 mm Hg, path length 250 mm (P.-E. 621); solid sample at the temperatures: B—155°K, C—128°K, D—110°K, E—25°K, spectral slitwidth 2 $cm^{-1}$.

attributed to the vibrations of the deuterium are observed at 2200, 2160, 1350, 1127, 1045, 906, 698, and 590 $cm^{-1}$. Bands observed at 985, 813, 775, and 546 $cm^{-1}$ suffered a loss of intensity upon deuteration.

Upon comparing the infrared to the Raman spectrum of crystal III, one readily observed an alternation of intensity of the bands in the two spectra. Bands which are intense in the Raman are weak in the infrared spectrum and vice versa. This phenomenon was also observed in the low temperature modification of cyclopentane-$d_0$. This observation can be attributed to the unit cell of crystal III having a center of symmetry as reported by Schettino and Marzocchi[9] who concluded the factor-group to be either $C_{2h}$ or Ci for cyclopentane. It is easy to rationalize the appearance of forbidden transitions (ungerade vibrations in the Raman effect and gerade vibrations in the infrared spectrum) in the spectra of cyclopentane-$d_1$ since the center of inversion is destroyed for this crystal with the random distribution of the deuterium atom relative to the rigid $C_s$ conformation of the cyclopentane ring (see below) and possibly by crystal defects which should be common to crystalline forms III for both cyclopentane and cylopentane-$d_1$. However, an explanation for these forbidden transitions in the spectra of cyclopentane-$d_0$ is not so readily apparent and this problem will be discussed later.

TABLE I

Observed vibrational frequencies of cyclopentane-$d_1$.[a]

| Raman | | Infrared | |
|---|---|---|---|
| Gas $\Delta\nu(cm^{-1})$ | Crystal III 110°K $\Delta\nu(cm^{-1})$ | Crystal I 155°K $\nu(cm^{-1})$ | Crystal III 110°K $\nu(cm^{-1})$ |
| | | 3060 w | 3060 m |
| 2975 vs,p | | | 2960 vs |
| 2957 vs,p | 2950 vs | 2950 vs | 2950 vs |
| 2952 p | | | |
| 2941 vs,p | 2942 sh | | |
| | 2930 sh | | 2935 sh |
| | 2920 s,b | | 2925 sh |
| 2915 v,b,p | 2907 | 2915 sh | 2915 sh |
| | 2903 | | |
| | 2898 | | |
| | 2894 | | 2895 sh |
| 2880 vs,p | | | |
| | 2870 sh | | 2875 vs |
| | 2865 vs | | |
| | 2860 vs | 2865 s | 2865 vs |
| | | 2850 sh | |
| | | | 2845 sh |
| 2212 vs,p | 2212 sh | | |
| 2203 sh | 2202 vs | 2203 s | 2201 s |
| | 2195 s | | 2196 s |
| | 2189 sh | | |
| | 2177 sh | | |
| 2170 vs,p | | | |
| | 2164 vs | 2162 s | 2163 s |
| | 2156 vs | | 2159 s |
| | 2142 sh | | |
| | 2138 sh | | |
| 1494 sh | | | |
| 1484 sh | | | |
| 1478 sh | | 1473 sh | 1475 m,b |
| 1472 sh | | | |
| | | 1465 sh | 1464 sh |
| 1460 s | 1458 s | | 1456 vs |
| 1452 s | | 1452 vs | |
| 1449 sh | 1448 vs | | 1448 vs |
| | | | 1440 s |
| | 1438 s | | 1436 sh |
| 1434 sh | | | 1432 sh |
| 1424 sh | | 1420 w | 1478 w |
| | | 1350 m | 1350 m |
| 1328 vw | 1328 w | | 1329 sh |
| | 1318 w,b | | 1318 m |
| | | 1315 m | |
| | 1304 m | 1303 m | 1303 m |
| | 1300 sh | 1297 m | 1299 m |
| | 1290 m | | 1294 m |
| | 1286 sh | | |

TABLE I (*Continued*)

| Raman | | Infrared | |
|---|---|---|---|
| Gas | Crystal III 110°K | Crystal I 155°K | Crystal III 110°K |
| $\Delta\nu(cm^{-1})$ | $\Delta\nu(cm^{-1})$ | $\nu(cm^{-1})$ | $\nu(cm^{-1})$ |
| 1280 m,p | 1280 w | 1278 w,b | 1278 m |
| | 1270 w | | 1270 sh |
| | 1255 m | | 1250 w,b |
| | 1243 w | | |
| | 1239 w | | |
| | 1230 w | | 1235 vw,b |
| | 1208 sh | | 1210 w,b |
| | 1205 m | 1205 w,b | |
| | 1199 sh | | 1200 w,b |
| | 1194 w | | |
| | 1183 w | | |
| 1180 p | | | |
| | 1177 w | | |
| | 1160 sh | | |
| | 1156 m | | 1160 vw,b |
| | 1120 w | | 1127 m |
| 1110 w,p | 1105 w,b | | 1106 w,vb |
| | 1099 m | | |
| | 1096 sh | | |
| 1090 w,p | 1090 w | | |
| | | 1044 m | 1045 m |
| | 1040 s | | |
| | 1030 m | | |
| 1020 m,b | 1024 s | | 1022 w |
| | 1016 m | | |
| | 1010 m | | 1010 w,b |
| | 928 w | | 984 m |
| | | | 978 sh |
| | 970 w | | 970 sh |
| | | 964 w | 964 m |
| 960 w | 957 w | | 958 m |
| | | 953 w | 950 m |
| | | | 946 sh |
| | 942 w | | 941 sh |
| | | | 936 sh |
| | 904 m | | 906 s |
| | 900 sh | 903 s | 900 s |
| | | 897 s,b | |
| 889[b]vb,p | 894 vw | | 895 s |
| | 881 vs | | 880 m |
| | 876 m | 878 sh,b | 877 sh |
| | 874 m | | 875 m |
| | 873 m | | |
| | 872 sh | | |
| | 853 vw | | 856 w,b |
| | 804 w | | 808 w,b |
| | 790 w,b | | 790 w,b |
| | 764 w | | 770 w,b |
| | | | 725 w,b |

(*Continued*)

TABLE I (*Continued*)

| Raman | | Infrared | |
|---|---|---|---|
| Gas | Crystal III 110°K | Crystal I 155°K | Crystal III 110°K |
| $\Delta\nu(cm^{-1})$ | $\Delta\nu(cm^{-1})$ | $\nu(cm^{-1})$ | $\nu(cm^{-1})$ |
| | | 698 s | 698 s |
| | | 687 sh | |
| | 675 w,b | | |
| | 635 w,b | | 640 w,vb |
| | | | 590 m |
| | 570 w,b | | 569 w |
| | | | 558 sh |
| | | 545 w,vb | 545 m,b |
| | 540 vw,b | | |
| | | | 510 w,b |
| | | | 470 w,b |
| | | | 460 w,b |
| | 290 w,vb | | |
| | 115 sh | | |
| | 107 | | |
| | 87 | | |
| | 69 | | |
| | 58 | | |
| | 46 | | |

[a] Abbreviations used: m, medium; s, strong; w, weak; v, very; b, broad; sh, shoulder; p, polarized; dp, depolarized.
[b] For the details of this band, see insert on Figure 2.

The two bands at 2200 and 2160 $cm^{-1}$ are really two doublets (2201, 2196, 2163, 2159) in crystal form III which show additional splitting when the sample is cooled to 25°K (see Figures 3D and 3E). These multiplets of bands which are observed in the crystal phase III become averaged by the molecular motion resulting in a smoothed doublet for both plastic phases I and II (see Figures 3B and 3C). In the gas state, the infrared doublet is still discernible but not nearly as pronounced. However, in the Raman spectrum of the gas (see Figure 4A) these two bands are well resolved into a broad doublet with each band having the same polarization ratio. In crystal III this doublet again splits into four well defined bands with two shoulders so there may be as many as six components for the C–D stretching vibrations. Since the same pattern of splitting is observed in a solid solution of 10% cyclopentane-$d_1$ cyclopentane in both the infrared and Raman (see Figure 4D) spectra, this splitting cannot be attributed to Davidov splitting.

The multiplicity of the observed bands in this region may be explained in three different ways. Since the molecule is of low symmetry ($C_s$ or $C_1$) Fermi

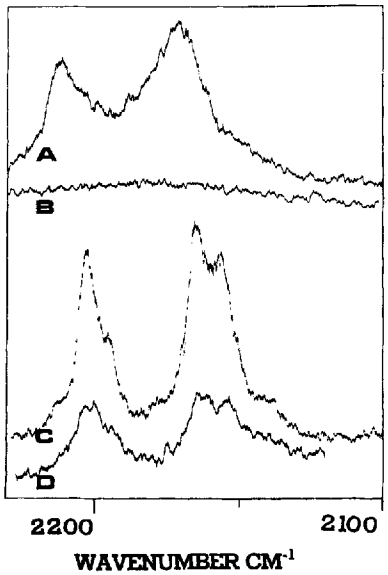


FIGURE 4 The C-D stretching and vibrational region in Raman spectrum of cyclopentane-$d_1$: A and B—gas spectra at two mutually orthogonal polarizations; C—pure crystal III at 110°K, D—10% solid solution of cyclopentane-$d_1$ in cyclopentane, spectral slitwidth 2 $cm^{-1}$.

resonance may account for the doublet.[18] There are several overtones or combination bands which fall in this frequency region and anyone of these bands could be in resonance with the C–D stretching mode. A second possibility is that several overtones or combination bands fall at near the same frequency and add up to give a band near the intensity of the fundamental of the C–D stretching mode; this second possibility seems quite remote. The third possibility is that these six components are just the ones expected for the unequivalent positions of the deuterium atom on a molecule with $C_s$ symmetry such as that found for the cyclopentane ring[3,5,7,11]. For this case the relative statistical weights of the six possible conformations are 1 (axial: 1 (equatorial): 2:2: 2:2: where the last four numbers correspond to the deuterium atom being attached to the other four carbon atoms which make up the "envelope" of the five-membered ring and the first two to the deuterium attached to the "flap" carbon. This ratio does not really correspond to the observed relative intensities of the components. In essence it is difficult to give a completely satisfactory explanation for the multiplicity of bands in this spectral region.

It is quite possible that both Fermi resonance and conformational multiplicity are responsible for the complex spectral pattern. For support of the conformational explanation, we can reference the study of the infrared

spectrum of 1-chloro-1-deuterocyclopentane which was reported by Ekejiuba and Hallam[6]. These authors observed a doublet at 2190 and 2168 $cm^{-1}$ for the C–D stretching mode and according to the temperature dependence measurements the two bands correspond to the deuterium atom being on either the equatorial and axial positions, respectively. The existence of the doublet for the chlorocyclopentane case is possible because of the shape of the potential function where the axial and equatorial positions for the chlorine atom are significantly more stable than the conformations where the chlorine atom is attached to one of the carbon atoms of the envelope. In the absence of the chlorine atom (our case for monodeuterocyclopentane) all positions for the deuterium atom are close to being identical in energy but with possibly slightly different frequencies which could give rise to six different components.

In the infrared spectrum at 25°K the components of the C–D stretch were found to have the following wavenumbers: 2158, 2163, 2166 and 2195, 2201, 2209 $cm^{-1}$. The total bandwidth of the high frequency doublet component is considerably larger than the bandwidth of the same component in the plastic crystal II phase (see Figure 3C). Thus, it appears that the three components of the low temperature phase coalesce into one band due to the fast pseudorotational and reorientational motion of the molecules in the plastic modification. The free or nearly free pseudorotational motion[15] of gaseous cyclopentane-$d_0$ or cyclopentane-$d_1$ is transformed in the condensed state to a slightly restricted pseudorotation due to the change in the potential function caused by intermolecular forces. The restriction is quite temperature dependent with a low enough activation energy in the plastic crystal for pseudorotation to take place on the vibrational time scale but too large in the solid phase III for a conformational change to take place on the same time scale.

In Figure 5A are shown the points corresponding to the changes with temperature of the band width for the infrared band at 698 $cm^{-1}$. At the phase transition from crystal I to crystal II the bandwidth becomes narrower by about 6 $cm^{-1}$.

In Figure 6 are shown the low frequency lattice modes in crystal phase I (Figure 6A) and crystal phase III (Figure 6B–D) for cyclopentane-$d_0$ and for crystal phase III of cyclopentane-$d_1$. The observed frequencies for both compounds in phase III are practically identical: 116 (sh), 108, 89, 71, 58 (w), 48 $cm^{-1}$ for cyclopentane-$d_0$ (see Table I for comparison). The broad band in the spectrum of cyclopentane-$d_0$ in crystal phase I is characteristic of disordered crystal systems. Lassier *et al.*[19] have observed a similarly broad band in the far infrared spectrum of methylchloroform in its plastic crystalline phase. This band is probably due in part to the interaction of the lattice modes with the activated pseudorotational motion in the crystal phase I. This latter effect considerably shifts the position of the band maximum to a higher frequency.

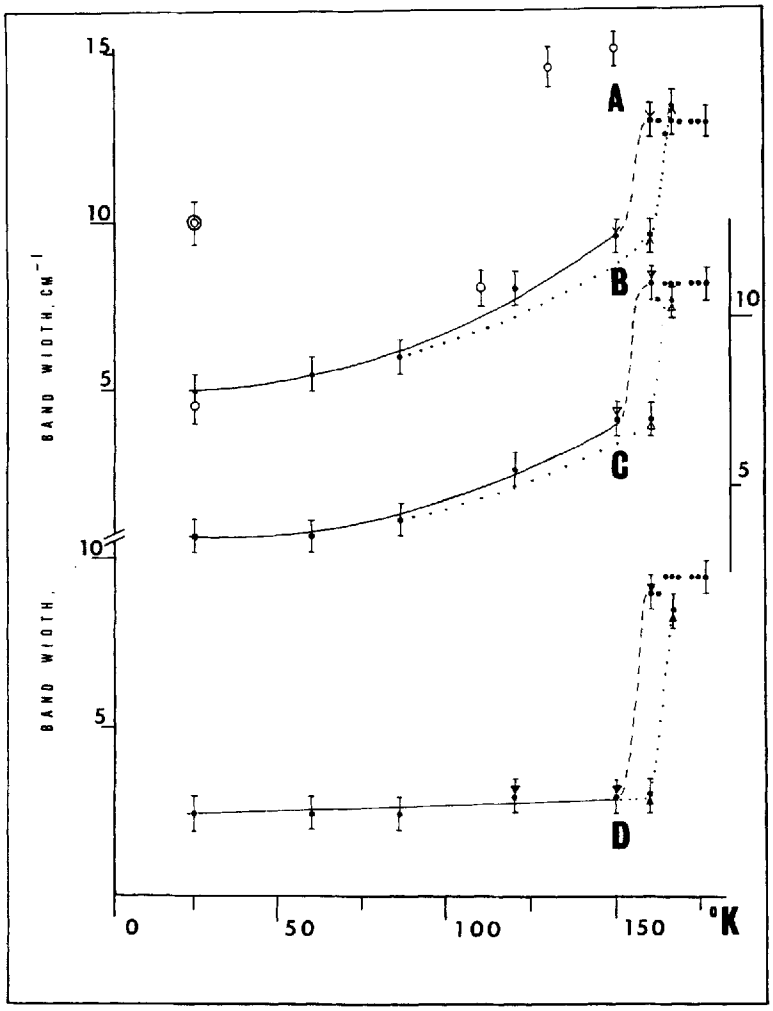


FIGURE 5 Temperature dependence of bandwidth in solids: A—cyclopentane-$d_1$, band 700 $cm^{-1}$; Chlorocyclopentane: B—942 $cm^{-1}$, C—1142 $cm^{-1}$, D—1068 $cm^{-1}$, spectral slitwidth 2 $cm^{-1}$.

*Chlorocyclopentane.* This compound exists in a plastic crystalline phase from its melting point at 178.8°K to 168°K and this phase is called crystal form I. At 168°K the crystal undergoes a first-order phase transition to form a rigid crystal (form II) for which no crystallographic data have been reported. No other phase transitions have been reported. Although there have been four previous vibrational studies[4,6,8,10] of chlorocyclopentane, there

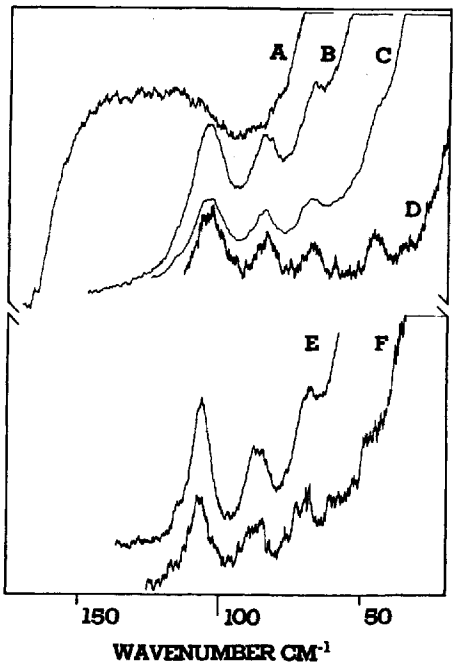


FIGURE 6 The low frequency Raman spectra of solid cyclopentane: A—crystal I, close to the melting point, 110°K at different spectral slitwidths, B—4 $cm^{-1}$, C—3 $cm^{-1}$, D—1 $cm^{-1}$; solid cyclopentane-$d_1$: E—4 $cm^{-1}$, F—1.5 $cm^{-1}$.

are no data available for the plastic crystal. Since this phase is of major importance in understanding the nature of the changes involved in going from the liquid to the rigid crystal phase, our primary focus was on the data of phase I.

In a previous study[4] of chlorocyclopentane in the fluid states, we presented evidence for at least two distinct conformations for chlorocyclopentane and these were thought to correspond to structures with the Cl in the axial and equatorial orientations. Later work on the infrared[6] and Raman[8] spectra of the solid in phase II confirmed the presence of two conformations in the fluid state and Ekejiuba and Hallam[6] concluded that the axial was more stable than the equatorial by 0.7 ± 0.3 kcal/mole in a $CS_2$ solution. Vovelle *et al.*[10] in the most recent vibrational study came to similar conclusions from normal coordinate calculations and comparisons of the data for the liquid and crystal II but unfortunately these results were not discussed in light of previous studies.[4,6,8]

In Figure 7 are shown the infrared spectra for both crystal phases I(A) and II. The observed frequencies are listed in Table II along with the relative

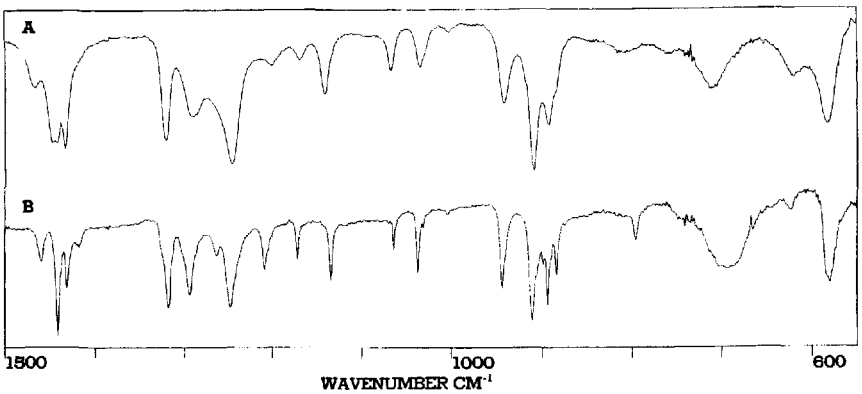


FIGURE 7 Mid-infrared spectrum of solid chlorocyclopentane: A—crystal I (170°K), B—crystal II (25°K). Spectral slitwidth 2 $cm^{-1}$ (FTS–14).

intensities. The most striking difference between the spectra of the two phases is the coalescence of many of the bands in going from phase II to phase I as well as distinct changes in the bandwidths. Although there are some differences in the frequencies for the fundamentals in the two phases, there were no definite trends.

One unusual reproducible feature of the spectra upon going from phase I to phase II and vice versa is the apparent extreme broadening of the band centered around 700 $cm^{-1}$. Closer examination of these data indicated that the band envelope is composed of at least two broad bands. The width change can be accounted for by an increase in the intensity of the lower frequency component relative to the higher. This relative intensity change may be due to a change in the mixing of these vibrations in the two phases.

Plastic crystals have been characterized by considerable rotational mobility of the molecules that allows disordering of the lattice structure. For cyclopentane and cyclohexane this rotational mobility has been reported with the barrier to reorientation approximately the same in the plastic modification as in the liquid.[7] In chlorocyclopentane, disorder could also arise from the positioning of the chlorine atom in the axial and equatorial conformations.

It has been reported[6,15] for liquid chlorocyclopentane that the carbon-chlorine stretching frequencies for the axial and equatorial positions are 593 and 624 $cm^{-1}$, respectively. In the recent work of Vovelle, *et al.*[10] they also attributed bands at 584 and 627 $cm^{-1}$ to the presence of axial and equatorial isomers but assigned the higher frequency band to a bending motion and assigned the equatorial C—Cl stretch to a frequency of 761 $cm^{-1}$. On the basis of the Raman intensities we have to agree with the earlier assignments.[6,15] Upon solidification to crystal phase II the 624 $cm^{-1}$ band

TABLE II

Observed vibrational frequencies of chlorocyclopentane.[a]

| Infrared | | Raman |
|---|---|---|
| Crystal I 170°K | Crystal II 25°K | Crystal II 110°K |
| | 2972 vs | |
| 2970 vs,b | | |
| | 2960 s | |
| | 2948 sh | |
| 2928 sh,b | | |
| | 2922 s | |
| | 2915 s | |
| 2904 sh,b | | |
| | 2899 s | |
| 2874 s | 2872 sh | |
| | 2868 s | |
| 2851 s | 2852 s | |
| 2788 w | 2780 w | |
| 1468 m | | 1470 vw |
| | 1460 m | |
| 1449 s | | 1450 m |
| 1443 s | | |
| | 1437 s | 1438 s |
| 1434 s | 1431 m | |
| | 1418 w | |
| | 1325 sh | |
| 1320 s | 1319 s | 1320 vw |
| | 1317 s | |
| | 1300 sh | |
| 1290 m,b | 1293 s | 1295 w |
| | 1288 sh | |
| | 1263 w | 1267 w |
| 1247 s | 1248 s | 1245 m |
| | 1242 sh | |
| | 1237 sh | |
| | 1209 m | 1220 w |
| | 1205 sh | 1205 w |
| 1200 w | 1201 sh | |
| 1170 w | 1172 m | 1170 w |
| 1141 m | 1139 w,sh | 1140 m |
| 1136 w,sh | 1135 m | |
| | 1130 w,sh | |
| | 1070 w,sh | |
| 1067 m | 1064 m | 1065 m |
| | 1061 w,sh | |
| 1035 m | 1036 m | 1040 s |
| 1028 sh | 1031 w | |
| 1003 vw | 1005 vw | 1000 w |
| 943 m | 944 s | 945 w |
| 910 vs | 911 s | 910 s |
| | 906 sh | |

TABLE II (*Continued*)

| Infrared | | Raman |
|---|---|---|
| Crystal I 170°K | Crystal II 25°K | Crystal II 110°K |
| | 899 m | |
| 893 s | 894 s | |
| 885 sh | 884 m | |
| 810 w,b | | |
| | 795 m | 800 vw |
| 760 w,b | | |
| 710 m,b | | 700 w |
| | 683 m,vb | 690 sh,b |
| 620 m,b | 622 vw | |
| 583 s,b | 585 sh | |
| | 580 s | 580 s |
| | 575 sh | |
| | 570 | |
| | 565 sh | |
| | 560 | |
| | | 363 sh |
| | 352[c] | 355 m |
| | 320[c] | 320 w |
| | 174[c] | 170 w,b |
| | 115[c] | |
| | 75[b] sh | |
| | | 72 m |
| | 69[b] s | |
| 50 w,vb | 51[b] m | 50 m |
| | | 39 m |
| | | 26 w,b |

[a] Abbreviations used: see Table I.

[b] These frequencies were obtained from a sample which was prepared by slow freezing of a liquid layer in a quartz cell. Data were obtained on a Fourier-spectrometer FS-720 (see Figure 8).

[c] Taken from reference 8.

has been reported to disappear indicating the presence of only the axial form. Our data on phase II are in agreement with this conclusion. From the data on phase I, however, it is clear that both the axial and equatorial conformations are present. A comparison of the relative intensities of the two bands indicates the presence of a much greater amount of the axial form; this same observation was also reported[6,15] for the liquid phase.

The shapes of the infrared bands studied are Gaussian in both crystal modifications. This may be interpreted to mean that the broadening of the bands in phase I is predominantly inhomogeneous and the barrier to reorientation of the molecules in the plastic phase is much higher than in

cyclopentane.[7] The barrier to pseudorotation in chlorocyclopentane was calculated[4] to be about 1.1 kcal/mole for the gas phase. In a more recent report[8] experimental data were used to estimate a maximum for the barrier of 4 kcal/mole.

Three well separated bands (942, 1068 and 1142 $cm^{-1}$) were selected for the investigation of the dependence of bandwidths on temperature and phase. The bands chosen did not show any distinct splitting with phase change or the lowering of the temperature. The half-widths of the bands are plotted against temperature in Figure 5. From this graph, it can be seen that just below the phase transition temperature, the bandwidths decrease by 4–6 $cm^{-1}$. In the range of the plastic modification the bandwidths are constant within the limits of error. The temperature dependence of the bandwidths of the 942 and 1142 $cm^{-1}$ band is very similar with the widths asymptotically going to the limiting value at 0°K after the phase transitions I → II. The difference in the temperature dependence of the bandwidth of the 1068 $cm^{-1}$ band is explained by the extreme sharpness of this band at low temperatures (at 25°K the bandwidth is about 1.2 $cm^{-1}$) so that the observed bandwidth at temperatures between 24 and 150°K corresponds mainly to the instrumental function of the Fourier spectrometer (FTS-14).

If the change in bandwidth is connected with order-disorder changes in the crystal, the value of the entropy of the phase transition can be estimated[20] from the equation

$$\Delta S = R \ln\left(\frac{N_2}{N_1}\right)$$

where the quantities $N_2$ and $N_1$ are the number of states of disorder. Taking the values of the bandwidths as proportional to $N$ and considering the limiting values of the widths, the relation becomes

$$\Delta S = R \ln \frac{S_I^2 - S_0^2}{S_{II}^2 - S_0^2}$$

where $S_I$, $S_{II}$, $S_0$ are the bandwidths at half height of the bands in phase I, phase II and at 25°K, respectively. For the three bands measured, the value of $\Delta S$ varies between 2.2 and 0.8 e.u. For these calculations bandwidths measured for warming from phase II to phase I were used in order to avoid the complications of supercooling. The thermodynamic data for this compound are unknown but this range of values is reasonable when compared with the entropy of transition of other substituted cyclopentane molecules.[20]

The low frequency spectra of chlorocyclopentane are shown in Figure 8. The far infrared spectrum of crystal phase I shows a broad band centered at 50 $cm^{-1}$ which is very similar to that of the liquid. After the transition to

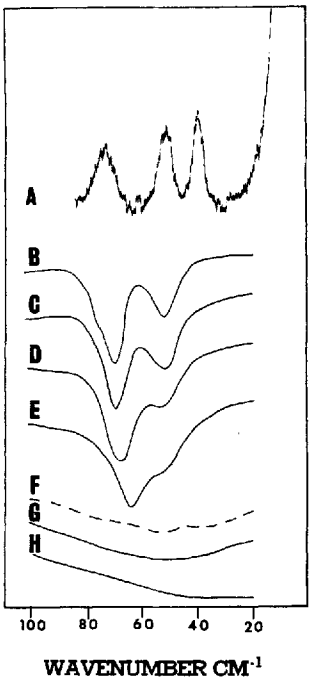


FIGURE 8. Low frequency vibrations of chlorocyclopentane: A—Raman spectrum of crystal II; Far infrared spectrum: Crystal II: B—25°K, C—110°K, D—128°K, E—155°K, F—Crystal I, G—cooled liquid (190°K), H—liquid at room temperature, spectral slitwidth = 2.5 $cm^{-1}$, FS-720.

crystal phase II, this band becomes relatively sharper. This is consistent with a transition from a disordered to a more ordered state.

## CONCLUSION

The changes in the 622 and 584 $cm^{-1}$ doublet in the infrared spectrum of chlorocyclopentane on the transition from solid phase I to solid phase II clearly show that the transition involves the change from a mixture of axial and equatorial conformations to axial conformation only. The axial-equatorial interconversion can theoretically occur by ring inversion through the planar conformation or via the pseudorotational pathway. Altona *et al.*[21] calculated the barrier to the axial-equatorial conversion to be 5.21 kcal/mole via the planar conformation, but only 1.1 kcal/mole via pseudorotation. Furthermore, CNDO calculations[22] indicate that the only stable forms of chlorocyclopentane are the envelope ($C_s$) conformations in which the halogen

atom occupies the flap. In addition these calculations found that the axial conformation is preferred. Our data seem to substantiate these calculations. While we cannot rule out the possibility that non-flap conformations may contribute to the disorder, there is no need to invoke these to interpret the data. The splittings that occur on phase change may be factor group splitting. The band narrowing on going to phase II may be explained by the increased ordering in the crystal in the absence of the equatorial conformation.

The infrared and Raman spectra of the two plastic phases of cyclopentane-$d_1$, are so similar that no evidence could be observed for a phase transition. Many of the very broad bands observed in the crystal phases I and II become multiplets of sharp bands in crystal phase III. Six bands were observed in the C–D stretching region and it is concluded that Fermi resonance and conformational multiplicity are responsible for the complexity in this spectral region. These six bands coalesce into two bands in crystal phase II which is apparently due to the pseudorotational and reorientational motions of the molecules in the plastic modification.

In the low frequency spectral region, broad bands were observed for the plastic crystal modifications which is consistent with a disordered crystal. With the transition to the low temperature crystal phase, the broad band sharpened and discrete lattice modes were observed for this phase.

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