

The Vibrational Spectra of Chloro-, Bromo- and Iodocyclohexane

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The IR spectra of chloro-, bromo- and iodocyclohexane as liquids at various temperatures, as solids and as solutes in different solvents were recorded in the region $4000-50\text{ cm}^{-1}$. High pressure IR spectra of the pure samples ($0-40\text{ kbar}$) in a diamond anvil cell were obtained, and dichroism of oriented crystalline films was measured. Raman spectra of the amorphous and crystalline solids at low temperature were recorded, and semiquantitative polarization ratios were measured for liquid chloro- and bromocyclohexane. In addition, FIR spectra ($600-50\text{ cm}^{-1}$) of the cyclohexanes as guest molecules in thiourea clathrates were obtained.

A normal coordinate analysis was performed for both conformers of all the three molecules, using a constrained valence force field analogous to that of the *trans*-1,4-dihalocyclohexanes. Tentative assignments of the fundamentals belonging to the *e*- and *a*-conformers are presented in agreement with the results from the normal coordinate calculations.

Chloro-, bromo- and iodocyclohexane have been studied in great detail by a variety of physical methods. In the vapour phase, in solution, in the liquid state and as amorphous solids at 90 K , they exist as equilibrium mixtures of equatorial and axial conformers, although the *e*-conformers are invariably in higher abundance.¹⁻¹⁰ The compounds all crystallize in the *e*-conformer at low temperature¹¹⁻¹⁴ and under high pressure.¹¹

IR and Raman spectra of the three title compounds¹¹⁻¹⁶ have earlier been obtained of the vapours, liquids and solid phases (at low temperature and under high pressure). Spectra have also been recorded of the halocyclohexane-thiourea clathrates in the Raman effect,¹⁷ in the IR^{18,19} and FIR²⁰ regions. Moreover, the intensities of a few bands in the IR spectra of the liquids have been measured as a function of

temperature.²¹ Special studies of some IR bands obtained from solutions with different concentrations and solvents^{8,9,22} indicate that the vibrational frequencies and the ratio of the amounts of *e*- and *a*-conformers are almost the same for different solutions.

Previous attempts to make normal coordinate analyses for chloro-, bromo- or iodocyclohexane are incomplete.^{14,20,23,24} In order to improve the assignments of the fundamental vibrations of both conformers, we have collected new spectral data from solutions in the IR region and from the liquids, crystalline and amorphous solids in the Raman effect as well. Careful inspection of the spectra reveals a number of shoulders and splittings of bands which have not been reported before.^{11,12} By comparing the different spectra we have been able to assign the bands to the respective conformer with great reliability. Polarization measurements of oriented crystal of the *e*-conformers under high pressure in the IR region have made the division of fundamentals between the *a'* and *a''* species of the *e*-conformer more certain than in the earlier studies^{20,23,24} in which only Raman polarization data for the liquids were available.

In the FIR region we have recorded spectra of the samples at low temperatures, at high pressures, as liquids and as solutes in different solvents and concentrations. FIR spectra were also obtained from the three compounds in thiourea clathrates between 100 and 600 cm^{-1} . These data, as well as the Raman results, give strong criteria with which to interpret the spectra in this region.

Recently we have made a complete normal coordinate analysis of fluorocyclohexane²⁵ by using a force field slightly modified from that developed for several dihalogenated *trans*-1,4-cyclohexanes.²⁶ This force field²⁶ has also been used in the analyses of the chloro-, bromo- and iodocyclohexanes.

Table 1. Infrared and Raman spectral data^a for chlorocyclohexane.

| IR | | Raman | | Assignments | |
|------------------------------|--------------------------|-----------------------------|-----------------------------|--------------------------|----------------------|
| Solution CCl ₄ | Crystalline ^b | Liquid | Cryst. ^b 90 K | ^e | ^a |
| | 90 K | | | | |
| | | | | | ~ 15 kbar |
| 3021 vw ^{c,d} | 3015 vw | | 3017 vw | $\nu_3 + \nu_{27}$ | comb. |
| 2955 s sh | 2957 s } 2950 s } | | 2957 s } 2952 w sh } | ν_1 A' | |
| | | 2946 s P | 2943 s | ν_2 A' | ν_1 A' |
| ~ 2940 s sh | 2937 vs | 2935 s sh | 2937 s | ν_{28} A'' | ν_{28} A'' |
| 2925 s sh | 2930 s sh } 2923 s } | | 2930 m | ν_{29} A'' | |
| | | 2921 m sh P | | | ν_2 A' |
| 2907 m | 2905 m | 2908 s P | 2907 m | ν_3 A' | ν_3 A' |
| 2898 m sh | 2898 m | 2903 m sh | 2900 m | ν_4 A' | ν_{29} A'' |
| 2889 w sh | 2870 w sh } | 2891 w sh | 2859 s sh | ν_5, ν_{30} | ν_4 A' |
| 2866 s sh | 2863 m sh } | | | | ν_{30} A'' |
| 2860 s | 2855 s | ~ 2860 s I | 2861 s P | ν_6, ν_7, ν_{31} | ν_5, ν_6 A' |
| 2844 w sh | * | | 2845 w sh | | ν_7, ν_{31} |
| 2819 vw | 2813 w | ~ 2820 w sh I | | $2 \times \nu_{10}$ | |
| 2797 w | 2793 w | 2796 w I | | $\nu_8 + \nu_{11}$ | |
| 2703 vw | 2702 vw | | 2704 m P | $\nu_8 + \nu_{13}$ | |
| 2677 w | 2672 w | | 2678 m P | $2 \times \nu_{35}$ | |
| 2670 w sh | 2662 w | | | $2 \times \nu_{36}$ | |
| 2656 w | 2655 w | | 2659 m P | $2 \times \nu_{12}$ | |
| | | | 2623 w P | $\nu_{10} + \nu_{15}$ | |
| 2609 vw | 1466 w } | | 2602 w P | $\nu_{11} + \nu_{13}$ | |
| 1465 m | 1462 m } | 1464 s sh I | 1466 w sh P | ν_8 A' | comb. |
| 1461 m | | | | | ν_8 A' |
| | 1456 m | 1459 s sh I | | $2 \times \nu_{22}$ | |
| | 1452 s } | | | | |
| 1452 s } | 1448 m } | 1445 vs bd I | 1448 s | ν_9, ν_{32} | ν_{32} A'' |
| 1449 s } | 1446 s } | | | | |
| | 1443 s } | | | | |
| | 1440 m } | | | ν_{33} A'' | ν_9 A' |
| 1441 m sh | 1437 w } | | | | |
| 1437 vw sh | | | | | ν_{33} A'' |
| 1430 m | 1429 w | 1435 m sh | 1432 m sh | ν_{10} A' | ν_{10} A' |
| 1405 vw | 1402 vw | 1414 vw sh I | 1404 vw P | $\nu_{39} + \nu_{48}$ | |
| 1388 vw | | | | | comb. |
| 1369 w sh | 1363 w | 1388 vw I _⊥ | | ν_{34} A'' | |
| | 1361 w | 1375 vw sh I | | $\nu_{15} + \nu_{27}$ | |
| 1359 w sh | * | * | | | ν_{34} A'' |
| | 1351 m } | 1354 s I } | 1355 m sh } | | |
| 1354 m | ~ 1350 w sh } | 1352 m sh I _⊥ } | 1350 m } | ν_{11}, ν_{35} | ν_{35} A'' |
| | 1347 w } | | | | |
| | 1341 m } | | | | |
| 1340 m | 1338 m } | 1344 s I _⊥ | 1343 s P | ν_{36} A'' | ν_{11}, ν_{36} |
| | 1333 m } | | | | |
| 1334 w sh | 1330 w sh } | 1334 s I | 1333 w sh | ν_{12} A' | |
| | 1326 m } | | | | |
| 1326 w } | 1323 m sh } | 1330 s sh I | 1322 vw | $\nu_{18} + \nu_{25}$ | ν_{12}, ν_{37} |
| 1321 w } | 1331 vw | 1315 vw | | $\nu_{19} + \nu_{24}$ | |
| | 1301 m } | | | | |
| 1303 w | 1299 w sh } | 1304 s I _⊥ | 1302 m | ν_{37} A'' | |

Table 1. Continued.

| | | | | | | |
|-------------------------|----------------------------|--|------------|-----------|---|--|
| 1272 m sh | 1273 w sh } 1271 w sh } | 1285 vw sh | | | $\nu_{42} + \nu_{48}$ | $\nu_{38} A''$ |
| 1268 s | 1270 m } 1268 s } | 1271 s I_{\parallel} | 1269 s P | 1273 m | $\nu_{13} A'$ | $\nu_{14} A'$ |
| 1260 s | 1262 w sh } 1259 m } | 1263 s sh I_{\perp} } 1260 s I_{\parallel} } | 1261 s P | 1261 s | $\nu_{20} + \nu_{24}$ ν_{14}, ν_{38} | $\nu_{13} A' \cdot$ $\nu_{43} + \nu_{47}$ |
| 1245 vw | * | | | | | |
| 1228 vw | 1236 w } 1232 w } | 1240 vw | | | $\nu_{22} + \nu_{23}$ | |
| 1215 s | 1218 m } 1216 s } | 1220 s I_{\parallel} } 1218 s I_{\perp} } | 1216 s P | 1218 m | $\nu_{15} A'$ | $\nu_{15} A'$ |
| 1185 w | 1186 m } 1184 m } | 1189 m I_{\perp} | 1186 m | 1186 m | $\nu_{39} A''$ | |
| 1180 vw sh ^c | 1177 w | 1182 w sh | | | $\nu_{20} + \nu_{25}$ | |
| 1146 w | * | * | 1146 w | * | | $\nu_{39} A''$ $\nu_{26} + \nu_{44}$ |
| 1138 vw sh ^c | | | | | | |
| 1133 w | 1134 m } 1132 m } | 1135 m I_{\parallel} | 1132 s P | 1133 m | $\nu_{16} A'$ | |
| 1119 vw | 1130 w } 1121 vw } | | | | comb. $\nu_{44} + \nu_{47}$ | $\nu_{40} A''$ |
| 1099 m | 1103 vw sh } 1100 w } | 1102 vw sh | 1099 w | * | $\nu_{44} + \nu_{48}$ | $\nu_{16} A'$ |
| 1089 w | 1090 w sh } 1088 m } | 1093 m I_{\perp} | | 1089 vw ? | $\nu_{40} A''$ | |
| 1074 vw | 1075 w } 1073 w } | 1079 w } 1077 w sh I_{\perp} } | 1075 m | 1076 m | $\nu_{41} A''$ | $\nu_{41} A''$ |
| | 1067 w } 1062 vw } | 1073 vw | | | $\nu_{21} + \nu_{47}$ | |
| 1052 w | 1052 w sh } 1050 m } | 1053 m I_{\perp} | 1052 m | 1053 m | $\nu_{42} A''$ | |
| 1031 m } 1023 vw } | 1040 vw } 1033 m } | 1040 w sh I_{\parallel} } 1035 w sh } 1030 w I_{\parallel} } | 1030 s P | 1028 s | $\nu_{45} + \nu_{48}$ $\nu_{17} A'$ | ν_{17}, ν_{42} |
| 1015 m | * | * | | | | ν_{18} |
| 1010 vw sh | * | * | | | | $\nu_{22} + \nu_{47}$ |
| 994 s | 996 s } 995 s } | 999 s I_{\parallel} | 995 s P | 996 s | $\nu_{18} A'$ | |
| | 993 s } 990 m } | 997 s sh | | | $\nu_{20} + \nu_{27}$ | |
| 949 vw ^c | 948 w } 940 vw sh } | 965 vw | | | $\nu_{22} + \nu_{48}$ $\nu_{23} + \nu_{46}$ $\nu_{23} + \nu_{24}$ | $2 \times \nu_{24}$ $\nu_{43} A''$ |
| 929 w sh | 928 vw } | | | | | |
| 921 w | 922 m } | 925 w I_{\perp} | 922 vw | 922 w | $\nu_{43} A''$ | |
| 917 w sh ^c | 919 m } | | | | | |
| 889 s | 892 s } 888 s } | 892 s I_{\parallel} | 890 w | 890 w | $\nu_{19} A'$ | |
| | 881 vw sh } 876 w sh } | 879 w sh | | | $\nu_{44} A''$ | |
| 869 m | 869 vw | * | 869 w sh P | * | $2 \times \nu_{46}$ | $\nu_{19} A'$ |
| 863 w sh | * | * | | | | $\nu_{44} A''$ |
| 859 m | * | * | | | | $\nu_{20} A'$ |

Table 1. Continued.

| | | | | | | |
|------------------------|----------------------------|---|-------------|----------------------|---|-----------------------|
| 852 m | 850 s | 853 m I_{\parallel} | 853 s P | 851 s | ν_{20} A' | |
| 843 vw | 846 vw sh } 843 vw sh } | 847 vw ? | | | | $2 \times \nu_{24}$ |
| 819 s | 818 vs } 812 m } | 823 s I_{\parallel} | 819 s P | 819 s | ν_{21} A' | |
| 807 m ^c | 809 w sh | | 809 s P | * | | ν_{21} A' |
| 789 w ^c | 792 m } 789 w sh } | 795 w I_{\perp} | ~ 790 w sh | 791 w | ν_{45} A'' | |
| 775 vw ^c | * 773 vw | * | ~ 775 vw sh | | ν_{45} A'' $\nu_{24} + \nu_{25}$ | |
| 733 s | 728 vs | 730 s } 725 s sh } I_{\parallel} } | 732 s P | 726 s | ν_{22} A' | |
| 718 vw sh | 721 w sh } 718 vw sh } | | | | $\nu_{23} + \nu_{48}$ | |
| | 713 w } 710 w } | | | 710 vw sh | | |
| | 707 w sh | | | | $\nu_{46} + \nu_{47}$ | |
| 686 s | 687 vw sh } 680 w } | ~ 685 w | 687 s P | * | $\nu_{24} + \nu_{47}$ | ν_{22} A' |
| | 669 w | | | | $2 \times \nu_{25}$ | |
| 648 vw | 659 vw sh } 654 w } | | | | comb. | $\nu_{46} + \nu_{48}$ |
| 613 vw | 640 vw } 637 vw } | | | | $2 \times \nu_{26}$ | comb. |
| 560 s | * | * | 560 s P | * | | ν_{23} A' |
| 513 s | 513 s } 510 s } | 517 s I_{\parallel} | 513 s P | 513 m | ν_{23} | |
| | 498 w sh | | | | $\nu_{47} + \nu_{48}$ | |
| | 485 w | 490 vw | | | $\nu_{25} + \nu_{27}$ | |
| 472 m | 477 vw } 474 w } | * | 473 m P | | $\nu_{26} + \nu_{27}$ | ν_{24} A' |
| 455 w | 452 vw | 467 vw | 453 vw | | $2 \times \nu_{48}$ | ν_{46} A'' |
| | 441 m | 443 w sh I_{\perp} | 440 m | 440 m sh | ν_{46} A'' | |
| 435 m ^e | 434 m | 438 s I_{\parallel} | 437 s P | 436 s | ν_{24} A' | |
| 394 vw sh ^e | | | | | | $2 \times \nu_{48}$ |
| 383 w ^d | 384 vw | 390 vw | 383 w P | * | $\nu_{27} + \nu_{48}$ | ν_{25} A' |
| 340 s | 340 s | 348 s | 341 s P | 342 s | ν_{25} A' | |
| 336 m sh | | | 337 m sh | | | ν_{47} A'' |
| 328 w ^e | 330 w | 337 s sh | 330 w sh | 332 w | ν_{26} A' | |
| 307 vw ^e | 303 vw | | | | $2 \times \nu_{27}$ | |
| 286 w ^e | * | * | 287 m P | * | | ν_{26} A' |
| 258 m | 260 m | 270 s | 260 m | 260 m | ν_{47} A'' | |
| 222 vw ^e | 245 w } 236 w } | 257 w | | | ν_{48} A'' | |
| 199 w ^e | * | * | 200 w | * | | ν_{48} A'' |
| 148 m ^e | 166 m } 155 m } | 180 w } 167 w } | 145 w P | 167 vw } 150 vw } | ν_{27} A' | ν_{27} A' |

^aWeak bands in the regions 4000–3050 and 2600–1500 cm^{-1} are omitted. ^bAnisotropic phase. ^cLiquid. ^ds, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; asterisks (*), bands which are absent; P, polarized; I_{\perp} and I_{\parallel} , dichroic measurements; comb., combination band. ^eCyclohexane solution.

EXPERIMENTAL

The samples of chloro-, bromo- and iodocyclohexane were all commercial products from Baker. When checked by gas chromatography iodocyclohexane was 97–98% pure, while chloro- and bromocyclohexane were found to have an even higher purity. All the compounds were treated by preparative gas chromatography, after which several bands disappeared from the spectra of the impure iodocyclohexane. For chloro- and bromocyclohexane no differences were observed in the spectra before and after the preparative gas chromatography.

The Raman spectrometer, the high pressure diamond anvil cell and the low temperature cryostats have been described.²⁵ Two infrared instruments were used, a Perkin-Elmer model 225 spectrometer ($4000-200\text{ cm}^{-1}$) and a fast scan Fourier transform spectrometer from Bruker (IFS 114c) ($3000-50\text{ cm}^{-1}$).

RESULTS

The Raman spectrum of chlorocyclohexane as an anisotropic solid at 90 K is shown in Fig. 1, and the FIR spectra of bromocyclohexane dissolved in

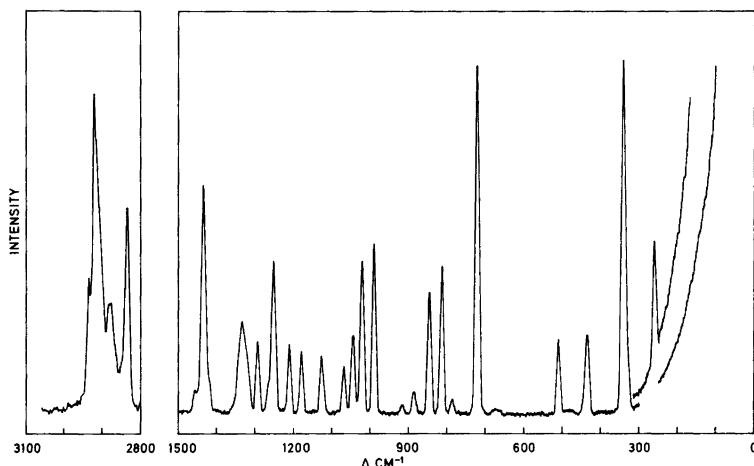


Fig. 1. The Raman spectrum of chlorocyclohexane (anisotropic phase) at 90 K.

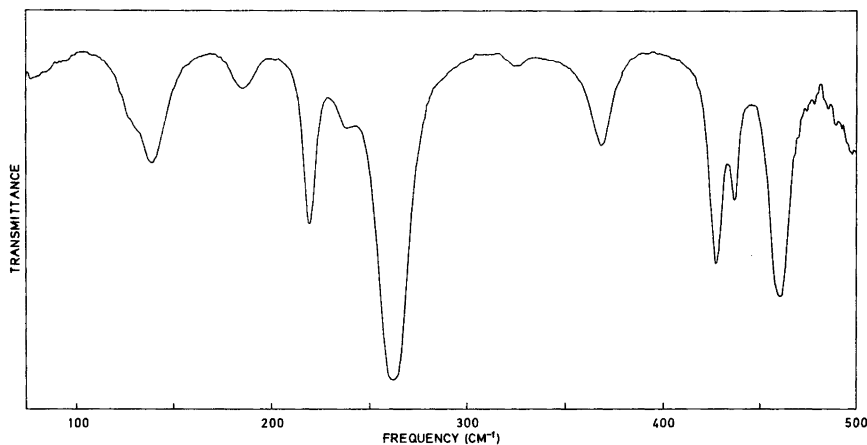


Fig. 2. Far infrared spectrum ($75-500\text{ cm}^{-1}$) of bromocyclohexane dissolved in cyclohexane ($\sim 40\%$ solution), 1 mm cell thickness, $6\text{ }\mu\text{m}$ beamsplitter, 1 cm^{-1} resolution.

Table 2. Infrared and Raman spectral data^a for bromocyclohexane.

| IR | | Raman | | Assignments | | |
|------------------------------|--------------------------|---|--------------------------|-----------------------------|--|----------------------|
| Solution CCl ₄ | Crystalline ^b | | Liquid | Cryst. ^b 90 K | ^e | ^a |
| | 90 K | ~ 15 kbar | | | | |
| 2956 s sh ^c | 2962 s | 2971 s I_{\perp} | | 2964 vs | ν_1 A' | |
| | 2951 s | 2955 s I_{\parallel} | 2943 vs P | 2952 s | ν_2 A' | ν_1 A' |
| 2941 s | 2936 s } 2930 s } | ~ 2945 s | | 2937 vs } 2926 s } | ν_{28} A'' | ν_{28} A'' |
| 2924 s sh | 2920 s | 2930 s I_{\perp} | 2922 s P | 2918 m sh | ν_{29} A'' | ν_2 A' |
| 2905 m | ~ 2905 s sh | ~ 2915 s I_{\parallel} | 2905 s | 2900 s bd | ν_3 A' | ν_3, ν_{29} |
| 2895 w | 2891 m | 2900 m I_{\parallel} | 2896 s P | | ν_4 A' | |
| 2886 m | * | * | 2885 s P | * | | ν_4 A' |
| 2867 s sh | 2862 m sh | ~ 2865 m I_{\perp} | | 2863 w sh | ν_5, ν_{30} | ν_{30} A'' |
| 2860 s | 2860 s } 2853 s } | 2860 s I_{\parallel} | 2861 s sh } 2857 vs } | 2855 vs | ν_6, ν_7, ν_{31} | ν_5, ν_6 A' |
| 2849 s sh ^d | * | * | 2840 s P | * | | ν_7 A' |
| 2839 m | * | * | | | | ν_{31} A'' |
| 2817 w | 2817 w | | | | $2 \times \nu_{10}$ | |
| 2796 w | 2794 w | 2795 w I_{\parallel} | 2803 w P | | $\nu_8 + \nu_{11}$ | |
| 2770 vw sh ^e | 2772 w | | | | comb. | |
| 2747 vw | 2744 vw } 2738 vw } | | | | comb. | |
| | 2709 vw | | 2710 w sh P | | $\nu_{33} + \nu_{37}$ | |
| 2701 w | 2702 w | | 2700 m P | | $\nu_8 + \nu_{13}$ | $2 \times \nu_{34}$ |
| 2676 w | 2675 w sh | | 2678 m P | | $2 \times \nu_{11}$ | $2 \times \nu_{35}$ |
| 2669 w sh | 2667 w | | 2670 w sh | | $2 \times \nu_{35}$ | |
| 2654 w | 2653 w | | 2654 m P | | $2 \times \nu_{12}$ | $2 \times \nu_{11}$ |
| 2645 vw sh | 2648 vw sh | | 2645 w sh P | | comb. | $2 \times \nu_{36}$ |
| 2629 vw ^e | 2627 vw | | | | comb. | |
| 2616 vw ^d | * | | 2613 w | | | $2 \times \nu_{12}$ |
| 2597 vw | 2595 w | | 2596 w P | | $\nu_{11} + \nu_{13}$ | |
| 1473 w | 1477 w | 1484 w I_{\perp} | | | comb. A'' | |
| 1464 m | 1466 m } 1465 w sh } | 1469 m I_{\parallel} | 1465 w P | 1468 m | ν_8 A' | |
| 1459 w sh ^e | 1461 m } 1453 s sh } | 1461 m I_{\parallel} | | | $\nu_{12} + \nu_{27}$ | ν_8 A' |
| 1451 s } | 1450 s } | 1453 s sh I_{\parallel} } 1445 s I_{\perp} } | 1446 s | 1453 m sh } 1441 s } | $\nu_{38} + \nu_{47}$ } ν_9, ν_{32} } | ν_{32} A'' |
| 1447 s } | 1445 s } | | | | | |
| 1438 m | 1437 m | 1439 w sh | 1440 m sh P | | ν_{33} A'' | ν_9, ν_{33} |
| 1433 w sh ^d | * | * | | | | |
| 1429 w sh ^e | * | * | 1427 w | * | | ν_{10} A' |
| 1425 w sh | 1426 w | 1425 w sh I_{\parallel} | | | ν_{10} A' | |
| 1416 w sh ^e | 1419 w } 1370 w } | | | | $\nu_{27} + \nu_{37}$ | |
| | * | * | 1357 w sh | * | ν_{34} A'' | ν_{34} A'' |
| 1358 m | | | | | | |
| 1351 m sh ^e | 1354 m } 1349 w sh } | 1357 w sh | 1350 m | 1353 m | ν_{11} A' | |
| 1348 m ^e | 1346 m } 1342 m } | 1348 m } 1345 m sh I_{\perp} } | | 1345 w sh | ν_{35} A'' | ν_{35} A'' |
| 1337 m | 1339 m } 1334 s } | 1340 m sh I_{\parallel} | 1337 s P | 1335 s | ν_{12} A' | ν_{11}, ν_{36} |
| 1332 vw sh | 1332 m sh } 1329 s } | 1335 s I_{\perp} | | | ν_{36} A'' | |

Table 2. Continued.

| | | | | | | |
|------------------------|--|---|-------------|--------|--|-----------------------|
| ~1325 w | 1323 w | 1326 w sh | 1325 vw sh | * | $\nu_{15} + \nu_{27}$ | $\nu_{12} A'$ |
| 1310 w | * | * | | | | $\nu_{37} A''$ |
| 1300 m | 1301 w sh } 1297 m } 1293 w } 1285 vw } | 1309 vw } 1299 m } I_{\perp} | 1299 m | 1300 m | $\nu_{37} A''$ | $\nu_{20} + \nu_{24}$ |
| 1279 vw ^e | 1278 vw | | | | comb. | |
| 1273 m | 1273 w | * | 1273 m | * | $\nu_{24} + \nu_{44}$ $\nu_{41} + \nu_{48}$ | $\nu_{38} A''$ |
| 1264 w sh | 1265 s } 1263 s sh } | 1268 s } 1265 m sh } I_{\parallel} | 1265 w sh | 1266 s | $\nu_{13} A'$ | |
| 1257 s | 1257 s | 1259 s I_{\parallel} | 1257 s P | 1257 s | $\nu_{20} + \nu_{24}$ ν_{14}, ν_{38} | $\nu_{13} A'$ |
| 1254 s | 1250 w sh | 1254 w sh | 1252 m sh P | | | $\nu_{14} A'$ |
| 1225 vw | 1226 w | | | | $\nu_{21} + \nu_{24}$ $\nu_{45} + \nu_{46}$ | |
| 1215 vw ^d | 1217 w | | | | | |
| 1193 s | 1196 s } 1191 w sh } | 1199 s I_{\parallel} | 1193 s P | 1187 s | $\nu_{15} A'$ | $\nu_{15} A'$ |
| 1184 w sh ^e | 1184 w } 1182 m } 1177 m } | 1185 w sh } 1181 m } I_{\perp} | 1185 m sh | 1183 m | $\nu_{22} + \nu_{23}$ } $\nu_{39} A''$ } | |
| 1144 w | 1142 vw | | 1144 w | * | $\nu_{43} + \nu_{47}$ $\nu_{19} + \nu_{26}$ | $\nu_{39} A''$ |
| 1135 vw | 1134 w | | | | | |
| 1119 m | 1124 m } 1120 m } | 1127 m } 1123 m } I_{\parallel} | 1119 m P | 1123 m | $\nu_{16} A'$ | $\nu_{40} A''$ |
| | 1117 w sh } 1114 w } | | | | comb. | |
| 1097 vw | 1100 vw | | | | $\nu_{22} + \nu_{24}$ | |
| 1089 m | 1086 m } 1081 vw } | 1091 m I_{\perp} } 1086 vw sh } | 1087 w | 1087 w | $\nu_{40} A''$ | $\nu_{16} A'$ |
| 1080 vw sh | 1071 w | | 1076 m | 1075 s | $\nu_{41} A''$ | $\nu_{41} A''$ |
| 1075 w ^e | 1066 vw | 1074 w I_{\perp} | | | $\nu_{21} + \nu_{26}$ | |
| 1050 w | 1052 w } 1049 w } | 1057 w I_{\perp} } 1053 w } | 1052 m | 1051 s | $\nu_{42} A''$ | |
| | 1044 w } 1035 w } | 1041 w sh | | | $\nu_{21} + \nu_{47}$ | |
| 1030 m | | | 1030 s | | | $\nu_{42} A'$ |
| | | | 1026 s sh | | | $\nu_{17} A'$ |
| 1023 w | 1027 m } 1023 m } | 1031 m } 1026 w sh } I_{\parallel} | 1023 m sh | 1027 s | $\nu_{17} A'$ | |
| 1011 m | | | 1014 w sh P | * | | $\nu_{18} A'$ |
| 1008 w sh ^e | 1007 m | 1012 w sh I_{\parallel} | | | $\nu_{45} + \nu_{47}$ | |
| 990 s | 994 s } 989 s } | 1000 m sh } 992 s } I_{\parallel} | 991 s P | 991 s | $\nu_{18} A'$ | |
| 992 s sh ^d | 986 m } 980 w sh } | | | | $2 \times \nu_{23}$ | |
| 963 vw | 950 vw | 963 vw | | | $\nu_{21} + \nu_{27}$ $\nu_{22} + \nu_{26}$ | $\nu_{23} + \nu_{24}$ |
| 931 vw | 931 vw | 940 vw | | | | |
| 921 m | | | 920 vw | | | $\nu_{43} A''$ |
| 918 w sh | 920 m } 917 w sh } | 924 m I_{\perp} | | 920 vw | $\nu_{43} A''$ | |
| 887 s | 887 s } 883 w } | 890 s I_{\parallel} | 887 m P | 888 m | $\nu_{19} A'$ | |
| 873 w | 876 w sh | 873 vw sh ? | | | $\nu_{44} A''$ | |
| 866 m | * | * | 865 w P | * | | $\nu_{19} A'$ |
| 864 m | 861 vw | 865 vw | | | $2 \times \nu_{46}$ | $\nu_{44} A''$ |
| 853 m | * | * | 854 w sh ? | * | | $\nu_{20} A'$ |

Table 2. Continued.

| | | | | | | |
|------------------------|-----------------------|------------------------------------|-------------|------------------------|-----------------------|-----------------------|
| 849 w sh | 852 w } 845 m } | 855 w } 848 m } I_{\parallel} | 848 s P | 852 s } ~845 m sh } | $\nu_{20} A'$ | |
| | 842 w | 843 vw sh I_{\parallel} | | | $2 \times \nu_{24}$ | |
| 811 s | 817 w } 813 m } | 816 s I_{\parallel} | 811 s P | 816 s | $\nu_{21} A'$ | |
| 804 m ^e | 810 m } 808 m } | 812 s sh I_{\parallel} | 805 s P | * | $\nu_{22} + \nu_{27}$ | $\nu_{21} A'$ |
| 800 vw sh ^e | 798 vw | 800 vw I_{\parallel} | | | $\nu_{23} + \nu_{25}$ | |
| 789 w ^e | 790 m | 793 m I_{\perp} | | 791 m | $\nu_{45} A''$ | |
| 776 w ^e | * | * | ~780 vw sh | * | | $\nu_{45} A''$ |
| 761 vw ^e | 758 vw | 770 vw ? | 761 vw P | | $\nu_{23} + \nu_{26}$ | |
| 729 vw ^e | 728 w } 727 w sh } | | | | $\nu_{24} + \nu_{25}$ | |
| | 723 vw } | | | | $\nu_{23} + \nu_{47}$ | |
| | 720 vw } | | | | | |
| 705 vw ^e | 714 vw } 701 vw } | | | | $\nu_{23} + \nu_{48}$ | |
| 689 vs | ~686 vs | 689 s I_{\parallel} | 687 vs P | 686 s | $\nu_{22} A'$ | |
| 674 vw | 671 m | 674 m | | 673 w | $\nu_{24} + \nu_{26}$ | |
| 660 s | 655 vw | * | 658 s P | * | | $\nu_{22} A'$ |
| 648 vw | * | * | | | | $2 \times \nu_{47}$ |
| | 638 vw | | | | $\nu_{24} + \nu_{48}$ | |
| 549 vw ^e | 551 vw | 552 vw | | | $\nu_{25} + \nu_{47}$ | $\nu_{27} + \nu_{46}$ |
| 541 vw ^e | | | | | | $\nu_{25} + \nu_{48}$ |
| 508 m | 523 vw } 511 vw } | * | ~510 m sh P | * | $2 \times \nu_{26}$ | $\nu_{23} A'$ |
| | 499 m } | | | | | |
| 501 s | 492 s } | 499 s | 502 s P | 500 s } 490 vw sh } | $\nu_{23} A'$ | $2 \times \nu_{26}$ |
| 460 s | * | * | 460 s P | * | | |
| 449 vw sh | * | * | | | | $\nu_{24} A'$ |
| | | | | | | $\nu_{46} A''$ |
| 437 m | 436 m } 434 m } | 439 m | 436 w sh | ~440 w sh | $\nu_{46} A''$ | |
| 427 m | 429 m | 431 m | 427 s P | 429 s | $\nu_{24} A'$ | |
| 368 m | * | * | 368 m P | * | | $\nu_{25} A'$ |
| 327 vw | | | | | | $\nu_{47} A''$ |
| 324 vw | 331 w | 335 w | 324 m P | ~325 m | $\nu_{25} A'$ | |
| 262 s | 260 s | 264 s | 262 s P | 262 vs | $\nu_{26} A'$ | |
| 251 m sh | | | | | | $\nu_{26} A'$ |
| 237 w | 252 s } 232 w } | 239 vw | 240 w sh | 245 w | $\nu_{47} A''$ | |
| 219 m | 216 m | 219 m | 219 m | 216 m | $\nu_{48} A''$ | |
| 185 w | * | * | 185 m | * | | $\nu_{48} A''$ |
| 138 m | 146 m } 137 m } | 153 m } 138 m } | 140 m sh P | ~140 w bd | $\nu_{27} A'$ | |
| 129 w | * | * | 129 s P | * | | $\nu_{27} A'$ |

^a Weak bands in the regions 4000–3000 and 2590–1500 cm^{-1} are omitted. ^b Anisotropic phase. ^c For abbreviations, see Table 1. ^d Amorphous solid at 90 K. ^e Liquid.

cyclohexane and as an anisotropic crystal at 90 K are presented in Figs. 2 and 3, respectively. The IR dichroism spectrum of a single crystal of iodocyclohexane under high pressure is given in Fig. 4. Additional spectra of chloro-,^{11–13} bromo-^{11,12} and iodocyclohexane¹² in the vapour (IR), in the

solid (IR) and liquid states (IR, Raman) have previously been reported. The wave numbers of the observed IR and Raman bands are listed in Tables 1–3 for chloro-, bromo- and iodocyclohexane, respectively. Data from the vapour phase for chloro- and bromocyclohexane as well as Raman data for

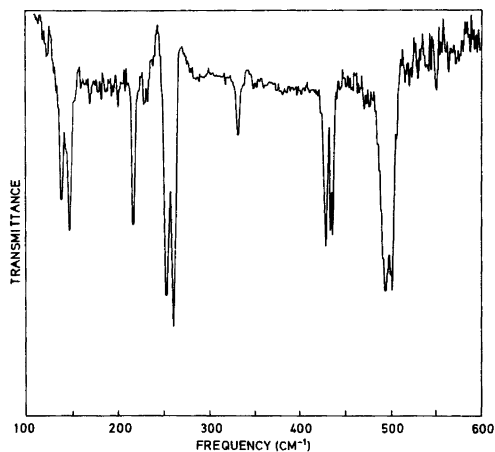


Fig. 3. Far infrared spectrum (100–600 cm^{-1}) of bromocyclohexane (anisotropic phase) at 90 K, 3.5 μm beamsplitter, 1 cm^{-1} resolution.

liquid iodocyclohexane can be found in Ref. 11. The present IR and Raman frequencies agree fairly well with the earlier values,^{11–13} but a careful inspection of the new IR and Raman spectra has revealed a number of “doublets” and shoulders which were formerly not observed. The data for the FIR region are also much more complete than those reported earlier.¹²

Both conformers of chloro-, bromo- and iodocyclohexane will obviously have C_s symmetry, and the 48 fundamentals of each will accordingly divide themselves into the symmetry species as follows: $27 a' + 21 a''$. All the fundamentals are active

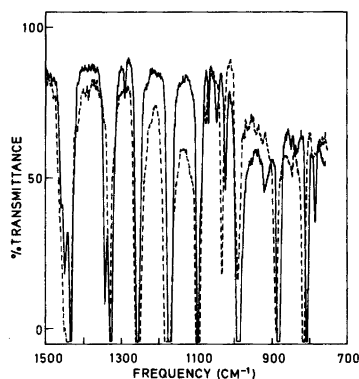


Fig. 4. The infrared dichroism spectrum of a single crystal of iodocyclohexane in the diamond anvil cell at ca. 15 kbar pressure and at ambient temperature.

in both IR and Raman; those belonging to species a' will give rise to polarized Raman lines.

Assignments of the fundamental vibrations of the e-conformers. Vibrational spectra of the pure e -conformers can easily be obtained since all the compounds crystallize in this conformer both at low temperature and at high pressure. The crystal structures of the three compounds are to our knowledge unknown. However, the Davydov splitting of the bands into two components indicates crystal structures with at least two molecules in the unit cells. The agreement between observed IR and Raman frequencies is usually good, and the unit cells are probably not centrosymmetrical.

Three criteria are used in the assignments of the observed bands to the a' or a'' species:

- (1) Raman polarization data, obtained from the liquids.
- (2) IR dichroism measurements of the anisotropic crystals under high pressures.
- (3) Normal coordinate calculations.

From the Raman polarization data several of the a' fundamentals can easily be identified. Since the liquids consist of an equilibrium mixture of the e - and a -conformers, the observed Raman bands often belong to fundamentals of both conformers. Moreover, some of the a' fundamentals tend to be very weakly polarized, and the distinction from a depolarized band may be difficult to make. In Tables 1–3 only bands which are clearly polarized are marked with a P.

From the molecular structure it is obvious that, for an oriented crystalline film of a monohalogenated cyclohexane, all vibrations belonging to species a'' must have the same dichroistic ratio in the IR spectra. When chlorocyclohexane is compressed in the diamond anvil cell a plastic solid containing both conformers is formed at rather low pressures.¹¹ When higher pressures are applied, a phase transition between the plastic and the anisotropic phases will occur, and a single crystal of the e -conformer can be obtained. For chlorocyclohexane we were not able to grow one single crystal. When the anisotropic crystal was formed as the pressure increased, we obtained at least two or three single crystals. However, the IR spectra gave good dichroistic measurements with the a'' bands almost vanishing in one polarization direction. No plastic crystals have been observed for bromo- and iodocyclohexane,^{11,23} and when the pressure was increased an anisotropic single crystal was grown over the entire diamond surface. The spectra

Table 3. Infrared and Raman spectral data^a for iodocyclohexane.

| IR Solution CCl ₄ | Crystalline ^b | | Raman | | Assignments | |
|------------------------------------|--|--------------------------|----------------------------|-----------------------------|---|---|
| | 200 K | ~ 15 kbar | Amorphous 90 K | Cryst. ^b 90 K | e | a |
| | | | | | | |
| 2944 m sh | 2956 s ^c | | | 2958 vs | v ₁ A' | |
| 2936 s | 2945 m | | | 2946 s | v ₂ A' | v ₁ A' |
| | | | 2936 s | 2936 s | v ₂₈ A'' | v ₂₈ A'' |
| 2920 m sh | 2929 s bd | | 2927 w sh } 2918 w sh } | 2927 vs | v ₂₉ A'' | v ₂ A' |
| | 2913 s | | | 2918 w sh | 2 × v ₈ | |
| 2903 w | 2898 m | | 2897 m bd | 2900 m bd | v ₃ , v ₄ | v ₃ , v ₂₉ |
| 2881 m | 2883 w | | 2884 w | 2873 w | 2 × v ₃₂ | v ₄ A' |
| | 2860 s sh } 2855 s } 2851 s sh } | | 2854 s } 2850 s sh } | 2855 vs | v ₅ , v ₆ , v ₇ v ₃₀ , v ₃₁ | v ₃₀ A'' v ₅ , v ₆ A' |
| 2833 m | * | | 2832 m | * | | v ₇ , v ₃₁ |
| 2813 vw | 2809 vw | 2815 w | | | 2 × v ₁₀ | 2 × v ₁₀ |
| 2796 vw | 2794 w } | | | | v ₈ + v ₁₁ | |
| 2782 vw | 2787 w } | 2796 w | | | comb. | comb. |
| 2769 vw ^d | 2766 w | | | | comb. | |
| 2707 w sh ^d | * | | | | | comb. |
| 2698 vw | 2698 w | 2701 w | | | v ₈ + v ₁₃ | 2 × v ₃₄ |
| | 2691 w sh | | | | comb. | |
| | 2673 m } | | | | 2 × v ₁₁ | |
| 2668 w | 2665 w } | 2669 m | | | 2 × v ₃₅ | 2 × v ₃₅ |
| 2652 vw | 2652 w | 2652 w | | | comb. | |
| | 2645 w | | | | 2 × v ₁₂ | |
| | 2629 vw } | | | | 2 × v ₃₆ | |
| 2621 w ^d | 2626 vw } | | | | | 2 × v ₁₂ |
| 2597 w ^d | 2597 w | | | | v ₁₁ + v ₁₃ | |
| 2583 w ^d | 2583 w | | | | comb. | |
| 1495 vw ^d | 1496 vw | | | | comb. | |
| 1461 m | 1464 m | 1464 m I | 1461 vw | 1467 w | v ₈ A' | |
| 1457 vw ? | 1459 w sh } | | | | v ₁₄ + v ₂₆ | v ₈ A' |
| | 1457 w } | | | | v ₁₂ + v ₂₇ | |
| | 1451 m | 1457 s I | | | | |
| | 1448 s | 1452 s I _⊥ | | | | |
| 1450 s } | 1444 s } | 1445 s I | 1440 s | 1447 s } | v ₉ , v ₃₂ | v ₃₂ A'' |
| 1446 m sh } | 1441 m } | 1441 s I | | 1443 s } | | |
| 1437 m | 1437 w sh | 1433 w sh I _⊥ | | | v ₃₃ A'' | v ₉ A' |
| 1435 w sh | * | | | | | v ₃₃ A'' |
| 1429 m | | | 1425 w sh | | | v ₁₀ A' |
| 1417 w sh ^d | 1424 w | 1429 vw sh } | | | v ₁₀ A' | |
| | | 1424 vw sh } | | | | |
| | | 1413 vw I | | | v ₁₆ + v ₂₅ | |
| | | 1392 vw I | | | v ₁₈ + v ₂₄ | |
| 1368 vw ^d | 1367 vw | 1362 vw sh | | 1362 vw ? | v ₃₄ A'' | |
| 1355 m | * | * | | | | v ₃₄ A'' |
| 1352 w sh | 1352 m | 1352 m I | | 1351 w | v ₁₁ A' | |
| 1349 m | 1347 m } | 1348 m I _⊥ | 1347 w } | | v ₃₅ A'' | v ₃₅ A'' |
| 1337 w sh | 1342 m } | 1344 m sh } | 1337 w sh } | 1339 m | v ₂₇ + v ₃₈ | v ₁₁ A' |
| | | 1342 m | | | | |
| | | 1337 w sh } | | | | |
| 1333 m | 1332 s | 1334 s I | 1330 s | 1333 s | v ₁₂ A' | v ₃₆ A'' |

Table 3. Continued.

| | | | | | | |
|------------------------|-------------------------|---|------------|-------------|-----------------------|-----------------------|
| 1326 w sh ^d | 1324 m | 1330 s I_{\perp} | | | $\nu_{36} A''$ | |
| 1318 w sh ^d | 1318 vw | 1324 w sh | | | $\nu_{24} + \nu_{43}$ | $\nu_{12} A'$ |
| 1303 w | 1306 w | 1314 w | | | $\nu_{19} + \nu_{46}$ | $\nu_{37} A''$ |
| 1298 m | 1296 m | 1297 w I_{\perp} | 1296 m | 1299 w | $\nu_{37} A''$ | |
| ~1290 vw ? | 1292 vw } 1288 w } | 1292 w sh | | | $\nu_{15} + \nu_{27}$ | |
| 1278 vw | * | * | | | | $\nu_{20} + \nu_{24}$ |
| 1270 w | * | * | | | | $\nu_{38} A''$ |
| 1263 w sh | 1265 w sh } 1259 m } | 1262 s I_{\parallel} | ~1265 m sh | 1262 s | $\nu_{13} A'$ | |
| 1254 s | 1254 s | 1257 s I_{\perp} } 1250 s sh I_{\parallel} } | 1252 s | 1251 s | ν_{14}, ν_{38} | $\nu_{13} A'$ |
| 1246 s | 1244 w | 1245 w sh I_{\parallel} | 1241 w sh | * | $\nu_{20} + \nu_{24}$ | $\nu_{14} A'$ |
| 1224 vw | 1229 w } 1226 w } | 1232 w I_{\perp} | | | $\nu_{25} + \nu_{43}$ | |
| 1208 vw | 1209 vw | 1215 vw I_{\parallel} | | | $\nu_{45} + \nu_{46}$ | |
| 1191 w | 1193 w | 1199 vw | | | comb. | |
| 1181 m sh | | 1182 s } 1178 s } | | 1183 w sh ? | $\nu_{39} A''$ | |
| 1174 s | 1178 s | 1176 m I_{\parallel} } 1173 s I_{\perp} } | 1176 s | 1178 s | $\nu_{15} A'$ | $\nu_{18} + \nu_{48}$ |
| 1167 s | 1171 m sh | 1170 w sh | ~1165 m sh | * | $\nu_{27} + \nu_{42}$ | $\nu_{15} A'$ |
| | 1158 vw | | | | $\nu_{20} + \nu_{25}$ | |
| 1144 vw ? | 1148 vw | | | | $\nu_{17} + \nu_{27}$ | |
| 1139 vw | 1138 vw | 1136 vw | ~1140 vw | * | $\nu_{22} + \nu_{23}$ | $\nu_{39} A''$ |
| 1128 vw | 1129 vw | 1128 vw | | | $\nu_{26} + \nu_{43}$ | |
| 1118 w | 1119 vw | 1118 vw I_{\parallel} | | | $\nu_{21} + \nu_{24}$ | $\nu_{40} A''$ |
| 1106 w | 1106 m | 1110 w sh I_{\parallel} | | | $\nu_{43} + \nu_{48}$ | |
| 1096 s | 1095 s | 1101 s sh I_{\perp} } 1098 s I_{\parallel} } | 1097 m | 1100 m | $\nu_{16} A'$ | $\nu_{16} A'$ |
| | | 1094 s sh | | | comb. | |
| 1082 vw | 1082 w | 1088 w sh I_{\perp} | | 1082 vw sh | $\nu_{40} A''$ | |
| 1075 m | 1071 m | 1073 w | 1075 m | 1077 w | $\nu_{41} A''$ | $\nu_{41} A''$ |
| | 1049 w } 1046 vw } | 1051 w sh } 1049 w I_{\perp} } | 1050 w | 1050 w | $\nu_{42} A''$ | |
| 1029 m | 1038 w } 1031 w } | 1037 w } 1033 vw sh } | 1032 m sh | 1032 vw sh | comb. | ν_{17}, ν_{42} |
| 1021 w | 1023 m | 1026 m I_{\parallel} } 1024 w sh I_{\perp} } | 1023 s | 1024 s | $\nu_{17} A'$ | |
| 1006 m | * | 1003 vw sh } 998 w sh } | 1006 vw ? | * | comb. | $\nu_{18} A'$ |
| | 992 m } 987 s } | 993 s sh I_{\perp} } 987 s I_{\parallel} } | 988 s | 990 s | $\nu_{18} A'$ | |
| 983 m sh | 980 m sh | 983 m sh I_{\perp} | | | $\nu_{21} + \nu_{48}$ | |
| 953 vw | 952 vw | 954 w I_{\parallel} | | | $\nu_{45} + \nu_{48}$ | $2 \times \nu_{23}$ |
| 917 m | 916 w | 920 w I_{\perp} | | | $\nu_{43} A''$ | $\nu_{43} A''$ |
| 884 s | 883 s | 888 s I_{\parallel} } 885 s I_{\perp} } | 886 m | 886 m | $\nu_{19} A'$ | $2 \times \nu_{24}$ |
| | 871 w | 874 vw sh } 870 vw sh } | | | $\nu_{44} A''$ | |
| 864 m | * | * | 868 w | * | | $\nu_{19} A'$ |
| 863 m | * | * | | * | | $\nu_{44} A''$ |
| 849 m | 843 w | 850 vw I_{\perp} } 845 w I_{\parallel} } | 846 s | 848 s | $\nu_{20} A'$ | $\nu_{20} A'$ |
| | | 835 vw I_{\parallel} | | | $2 \times \nu_{24}$ | |

Table 3. Continued.

| | | | | | | |
|--------------------|--|-------------------------|----------|------------------------------|-----------------------------------|-----------------------------------|
| 806 s ^d | 807 s 805 m sh } 802 m 788 w ^d 779 w ^d 719 w ^d 687 w ^d | 811 s I | 806 m | 814 m 808 m sh } 790 w | v ₂₁ A' | |
| | | 807 m sh I _⊥ | | | v ₂₃ + v ₂₅ | v ₂₁ A' |
| | | 790 w I _⊥ | | | v ₄₅ A'' | v ₄₅ A'' |
| | | * | | | v ₂₃ + v ₄₇ | v ₂₄ + v ₂₆ |
| | | * | | | v ₂₂ A' | v ₂₂ A' |
| 656 s | ~ 655 s | 655 s I | 656 s | 656 s | v ₂₄ + v ₂₆ | v ₂₂ A' |
| 640 s | 639 m | 642 m sh | 641 m | 641 w sh | v ₄₆ + v ₄₈ | v ₂₃ + v ₂₇ |
| 621 w | * | 622 vw | | | | v ₂₅ + v ₂₆ |
| 600 vw | * | * | | | | |
| 584 vw | * | * | | | | |
| 494 m | 493 m } 485 m } | 501 m sh } 490 m } | 492 s | 495 s | v ₂₃ A' | |
| 480 w sh | * | * | | | | v ₂₃ A' |
| 459 vw | * | * | | | | 2 × v ₂₆ |
| 446 m | * | 448 w | 448 s | ~ 445 vw | 2 × v ₂₆ | v ₂₄ , v ₄₆ |
| 436 w | 435 m | 439 m | | | v ₄₆ A'' | |
| 421 w | 423 w } 419 w } | 421 w | 422 m | 421 m | v ₂₄ A' | |
| 402 vw | * | * | | | | v ₂₆ + v ₄₈ |
| 359 w | * | * | 360 s | * | | v ₂₅ A' |
| 355 w sh | * | * | | | | 2 × v ₄₈ |
| 328 vw | 334 vw | 336 vw | ~ 325 vw | 325 w | v ₂₅ A' | v ₄₇ A'' |
| 314 vw | * | * | | | | |
| 260 vw | 257 w } 250 w } | 257 w | | | 2 × v ₂₇ | |
| 237 w | * | * | 240 m | * | | v ₂₆ A' |
| 235 vw sh | 232 vw | | | | v ₄₇ A'' | |
| 223 m | 221 m } 220 m } | 222 m | 226 s | 223 s | v ₂₆ A' | |
| 196 vw | 192 vw | ~ 185 vw | 188 w | 193 m | v ₄₈ A'' | |
| 175 vw | * | * | | | | v ₄₈ A' |
| 133 w | 141 vw sh } 134 w } | 138 w | 141 vw | 140 vw | v ₂₇ A' | |
| 121 vw | | | | | | v ₂₇ A' |

^aWeak bands in the regions 4000–3000 and 2580–1500 cm⁻¹ are omitted. ^bAnisotropic crystal. ^cFor abbreviations, see Table 1. ^dLiquid.

showed the same trend as for chlorocyclohexane, with the bands belonging to the *a''* species almost vanishing in one of the polarization directions (Fig. 4). Hence all bands having a strong component with this direction must therefore belong to species *a'* and are marked I_{||} in Tables 1–3, while the components which are vanishing are designated I_⊥.

In a few cases, one band of the liquid corresponds to more than two bands of the crystal. This has been taken as a criterion for more than one fundamental at this frequency or for a fundamental overlapping a combination mode. An example is found in chlorocyclohexane where the band at 1354 cm⁻¹ of

the liquid corresponds to three components of the anisotropic crystal. Hence the three components observed for the crystal are interpreted as two overlapping *e*-fundamentals. For bromo- and iodocyclohexane a similar feature occurs at 1184 and *ca.* 1345 cm⁻¹, respectively, where the three bands in the spectra of the crystals are assigned to a fundamental overlapping a combination band.

Our final assignments of the fundamentals for the *e*-conformers are quite different from those presented earlier^{20,23,24} especially in the frequency region above 800 cm⁻¹. By far the most complete normal coordinate analyses for chloro-, bromo- and

Table 4. Observed^a and calculated fundamental frequencies for chloro- and iodocyclohexane.

| | Chlorocyclohexane | | | | Iodocyclohexane | | | |
|------------------------|-------------------|-------|----------|-------|-----------------|-------|----------|-------|
| | <i>e</i> | | <i>a</i> | | <i>e</i> | | <i>a</i> | |
| | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| <i>a'</i> | | | | | | | | |
| <i>v</i> ₁ | 2955 | 2956 | 2946 | 2956 | 2955 | 2955 | 2944 | 2955 |
| <i>v</i> ₂ | 2946 | 2922 | 2921 | 2922 | 2944 | 2922 | 2920 | 2922 |
| <i>v</i> ₃ | 2908 | 2916 | 2908 | 2916 | 2900 | 2916 | 2900 | 2916 |
| <i>v</i> ₄ | 2903 | 2914 | 2889 | 2914 | 2900 | 2914 | 2879 | 2914 |
| <i>v</i> ₅ | 2865 | 2857 | 2860 | 2857 | 2855 | 2857 | 2850 | 2857 |
| <i>v</i> ₆ | 2860 | 2853 | 2860 | 2853 | 2855 | 2853 | 2850 | 2853 |
| <i>v</i> ₇ | 2860 | 2851 | 2845 | 2851 | 2855 | 2851 | 2832 | 2851 |
| <i>v</i> ₈ | 1466 | 1456 | 1461 | 1456 | 1461 | 1456 | 1457 | 1455 |
| <i>v</i> ₉ | 1449 | 1440 | 1439 | 1437 | 1440 | 1439 | 1437 | 1437 |
| <i>v</i> ₁₀ | 1429 | 1425 | 1429 | 1422 | 1417 | 1425 | 1428 | 1422 |
| <i>v</i> ₁₁ | 1353 | 1351 | 1343 | 1345 | 1352 | 1346 | 1337 | 1344 |
| <i>v</i> ₁₂ | 1333 | 1340 | 1326 | 1343 | 1332 | 1337 | 1318 | 1342 |
| <i>v</i> ₁₃ | 1268 | 1265 | 1268 | 1283 | 1263 | 1250 | 1254 | 1257 |
| <i>v</i> ₁₄ | 1259 | 1251 | 1260 | 1251 | 1254 | 1241 | 1244 | 1234 |
| <i>v</i> ₁₅ | 1216 | 1221 | 1216 | 1226 | 1173 | 1178 | 1166 | 1173 |
| <i>v</i> ₁₆ | 1133 | 1121 | 1099 | 1105 | 1094 | 1090 | 1094 | 1088 |
| <i>v</i> ₁₇ | 1026 | 1020 | 1030 | 1026 | 1021 | 1019 | 1029 | 1024 |
| <i>v</i> ₁₈ | 994 | 992 | 1015 | 985 | 987 | 984 | 1006 | 988 |
| <i>v</i> ₁₉ | 889 | 892 | 869 | 870 | 883 | 886 | 864 | 859 |
| <i>v</i> ₂₀ | 852 | 839 | 859 | 853 | 848 | 833 | 848 | 846 |
| <i>v</i> ₂₁ | 819 | 819 | 807 | 806 | 806 | 800 | 801 | 801 |
| <i>v</i> ₂₂ | 732 | 733 | 685 | 680 | 655 | 666 | 639 | 627 |
| <i>v</i> ₂₃ | 512 | 508 | 559 | 552 | 494 | 493 | 482 | 483 |
| <i>v</i> ₂₄ | 436 | 428 | 473 | 482 | 421 | 418 | 446 | 449 |
| <i>v</i> ₂₅ | 341 | 342 | 384 | 380 | 328 | 321 | 359 | 349 |
| <i>v</i> ₂₆ | 328 | 324 | 286 | 290 | 222 | 224 | 236 | 249 |
| <i>v</i> ₂₇ | 148 | 154 | 148 | 136 | 133 | 129 | 121 | 93 |
| <i>a''</i> | | | | | | | | |
| <i>v</i> ₂₈ | 2943 | 2918 | 2943 | 2917 | 2936 | 2917 | 2936 | 2917 |
| <i>v</i> ₂₉ | 2930 | 2913 | 2903 | 2913 | 2920 | 2913 | 2900 | 2913 |
| <i>v</i> ₃₀ | 2865 | 2855 | 2865 | 2855 | 2855 | 2855 | 2855 | 2855 |
| <i>v</i> ₃₁ | 2860 | 2852 | 2845 | 2851 | 2855 | 2852 | 2832 | 2851 |
| <i>v</i> ₃₂ | 1449 | 1448 | 1452 | 1440 | 1446 | 1445 | 1450 | 1440 |
| <i>v</i> ₃₃ | 1439 | 1434 | 1436 | 1434 | 1436 | 1434 | 1435 | 1434 |
| <i>v</i> ₃₄ | 1366 | 1383 | 1358 | 1368 | 1368 | 1380 | 1355 | 1367 |
| <i>v</i> ₃₅ | 1353 | 1351 | 1353 | 1350 | 1348 | 1349 | 1348 | 1349 |
| <i>v</i> ₃₆ | 1340 | 1345 | 1340 | 1342 | 1326 | 1345 | 1332 | 1341 |
| <i>v</i> ₃₇ | 1302 | 1299 | 1321 | 1320 | 1296 | 1298 | 1303 | 1309 |
| <i>v</i> ₃₈ | 1260 | 1245 | 1273 | 1261 | 1254 | 1245 | 1269 | 1259 |
| <i>v</i> ₃₉ | 1185 | 1182 | 1146 | 1145 | 1181 | 1179 | 1138 | 1142 |
| <i>v</i> ₄₀ | 1089 | 1100 | 1119 | 1144 | 1082 | 1090 | 1117 | 1137 |
| <i>v</i> ₄₁ | 1075 | 1068 | 1075 | 1083 | 1073 | 1066 | 1073 | 1080 |
| <i>v</i> ₄₂ | 1052 | 1051 | 1030 | 1034 | 1048 | 1051 | 1029 | 1033 |
| <i>v</i> ₄₃ | 917 | 916 | 921 | 928 | 916 | 913 | 916 | 924 |
| <i>v</i> ₄₄ | 877 | 886 | 862 | 856 | 873 | 883 | 863 | 854 |
| <i>v</i> ₄₅ | 789 | 787 | 775 | 792 | 788 | 785 | 779 | 787 |
| <i>v</i> ₄₆ | 440 | 457 | 454 | 461 | 437 | 456 | 446 | 454 |
| <i>v</i> ₄₇ | 259 | 263 | 337 | 330 | 235 | 228 | 314 | 286 |
| <i>v</i> ₄₈ | 240 | 221 | 200 | 182 | 196 | 191 | 175 | 155 |

^aWhen possible, frequency values for the liquids are given.

iodocyclohexane until now are found in Ref. 23. However, some of the assignments reported²³ are in conflict with our experimental data. As an example, the IR bands at *ca.* 1030 and 890 cm^{-1} observed for all three compounds cannot be assigned to fundamentals of species *a''* as the dichroistic measurements reveal strong components in the I_{\parallel} direction for both bands.

Assignments of the fundamental vibrations of the a-conformers. The earlier attempts at assigning the vibrational spectra of the *a*-conformers of chloro-, bromo- and iodocyclohexane are rather incomplete,^{20,23,24} especially in the region above 1000 cm^{-1} where many bands of the *e*- and *a*-conformers are overlapping. New spectral data and the normal coordinate calculations have given a more complete and reliable interpretation of the spectra of the *a*-conformers although some uncertainties still persist.

All attempts to crystallize the *a*-conformers have failed, and no spectra are available of these conformers in the pure state. Since the three halocyclohexanes crystallize in the *e*-conformer, bands vanishing upon crystallization (marked with an asterisk (*)) in Tables 1–3) must belong to the *a*-conformer. Hence the pure "axial" bands can be attributed with certainty, but the distinction between "equatorial" bands and bands common to both conformers is in some cases uncertain.

In the liquid phase the *e*-conformer is the more stable, and the ΔG° values are of the order of -2 kJ/mol^{1-6} for all three compounds. Upon cooling the liquids, the *e*-conformers should be even more preferred. With a computer-controlled interferometer it has been possible to record IR spectra of the liquids as a function of temperature and to subtract the spectra. When a spectrum obtained at a lower temperature is partially subtracted from a high temperature spectrum, the result should be a spectrum with bands mostly belonging to the *a*-conformer. Although this technique is somewhat hampered by the variations of band widths with temperature, it has been of great value for the interpretation of the IR spectra of the liquids, especially in the regions where several bands overlap.

In thiourea clathrates the *a*-conformer of chloro- and bromocyclohexane are strongly preferred in the channels,¹⁷⁻²⁰ while iodocyclohexane^{17,18} has a certain amount of *e*-conformer in addition. Since the thiourea bands are strongly dominating in the vibrational spectra of the adducts, the information about the *a*-conformers is limited, though in the area

below 1000 cm^{-1} some very valuable IR and Raman data have been obtained.¹⁷⁻²⁰ When these data are compared with the results from the annealing and cooling techniques, it is possible to identify most of the bands belonging to the *a*-conformers even when bands are common to both conformers.

Only the Raman polarization measurements give experimental criteria for assigning the *a*-conformer vibrations to species *a'* and *a''*, and the assignments are based on these data as well as on the normal coordinate calculations. Since our model force field²⁶ has given excellent agreement between observed and calculated frequencies for a variety of axially substituted cyclohexanes^{27,28} including fluorocyclohexane,²⁵ we believe that this should also be the case for *a*-chloro-, *a*-bromo- and *a*-iodocyclohexane. Moreover, it seems to be a very good approximation to use a similar force field for the *a*- and *e*-conformer of a cyclohexane derivative, and the agreement between observed and calculated frequencies for the *e*-conformer of chloro-, bromo- and iodocyclohexane is quite satisfactory.

Normal coordinate calculations and spectral correlations. Only one torsional force constant had to be adjusted when the force field previously derived for six *trans*-1,4-dihalocyclohexanes,²⁶ was transferred to the three monohalocyclohexanes. For fluorocyclohexane the force constant, τ_s , for the torsion around the C_1-C_2 bond ($X-C_1-C-C_2-C_2-C-C_1$) was found to be 0.046 mdyn \AA/rad^2 .²⁵ Using the new data from both conformers of chloro-, bromo- and iodocyclohexane we have determined τ_s to be 0.0437 mdyn \AA/rad^2 when the molecular parameters are the same as in Ref. 26.

The observed and calculated frequencies for chloro- and iodocyclohexane are given in Table 4. Corresponding values for bromocyclohexane are listed in Table 5, and for this compound the potential energy distribution (PED) is given in terms of the internal coordinates. The PED of Table 5 is representative also for chloro- and iodocyclohexane although the fundamentals with the same number do not always correspond according to the PED. For example, for the *e*-conformers, ν_{26} of chlorocyclohexane has the same PED as ν_{25} of bromo- and iodocyclohexane, and ν_{25} of chloro- corresponds to ν_{26} of bromo- and iodocyclohexane.

For *e*-bromocyclohexane ν_{47} and ν_{48} at 240 and 219 cm^{-1} , respectively, are strongly coupled and both are observed in the Raman effect, ν_{48} giving rise to the more intense line. ν_{47} of chlorocyclohexane is assigned to a medium intense Raman line as is ν_{48} of

Table 5. Observed^a and calculated fundamental frequencies for bromocyclohexane.

| | <i>e</i> | | <i>a</i> | | | |
|------------------------|------------------------|------|----------|------------------------------|------|-------|
| | PED ^b | Obs. | Calc. | PED | Obs. | Calc. |
| <i>a'</i> | | | | | | |
| <i>v</i> ₁ | 97d(X) ^c | 2956 | 2956 | 99d(X) | 2943 | 2956 |
| <i>v</i> ₂ | 96d | 2943 | 2922 | 96d | 2922 | 2922 |
| <i>v</i> ₃ | 95d | 2905 | 2916 | 95d | 2905 | 2916 |
| <i>v</i> ₄ | 98d | 2896 | 2914 | 97d | 2885 | 2914 |
| <i>v</i> ₅ | 96d | 2867 | 2857 | 94d | 2860 | 2857 |
| <i>v</i> ₆ | 95d | 2860 | 2853 | 95d | 2860 | 2853 |
| <i>v</i> ₇ | 96d | 2860 | 2851 | 96d | 2840 | 2851 |
| <i>v</i> ₈ | 71δ + 18γ | 1464 | 1456 | 69δ + 17γ | 1459 | 1456 |
| <i>v</i> ₉ | 68δ + 19γ | 1447 | 1439 | 66δ + 22γ | 1438 | 1437 |
| <i>v</i> ₁₀ | 68δ + 20γ | 1426 | 1425 | 71δ + 18γ | 1429 | 1422 |
| <i>v</i> ₁₁ | 81γ | 1350 | 1347 | 82γ | 1336 | 1345 |
| <i>v</i> ₁₂ | 83γ + 21R | 1336 | 1338 | 81γ + 23R | 1323 | 1343 |
| <i>v</i> ₁₃ | 76γ | 1264 | 1251 | 64γ | 1257 | 1262 |
| <i>v</i> ₁₄ | 63γ | 1257 | 1246 | 71γ | 1252 | 1239 |
| <i>v</i> ₁₅ | 36γ + 31θ + 18γ(X) | 1193 | 1199 | 37θ + 32γ + 17γ(X) | 1193 | 1207 |
| <i>v</i> ₁₆ | 51γ + 17θ | 1119 | 1109 | 58γ | 1088 | 1097 |
| <i>v</i> ₁₇ | 50R + 29γ | 1023 | 1020 | 51R + 29γ | 1026 | 1025 |
| <i>v</i> ₁₈ | 41γ + 31ω | 989 | 988 | 46γ + 29ω | 1011 | 993 |
| <i>v</i> ₁₉ | 53R + 39γ | 886 | 890 | 65R + 25γ | 866 | 864 |
| <i>v</i> ₂₀ | 47R + 43γ | 847 | 836 | 60γ + 21R | 852 | 851 |
| <i>v</i> ₂₁ | 64R + 15γ | 811 | 807 | 75R | 804 | 804 |
| <i>v</i> ₂₂ | 49X + 30γ + 18ω + 16Ξ | 687 | 696 | 31γ + 29X + 20ω + 16Ξ | 658 | 648 |
| <i>v</i> ₂₃ | 41ω + 41γ | 501 | 499 | 58X + 27ω + 26γ | 510 | 504 |
| <i>v</i> ₂₄ | 50ω | 427 | 423 | 51ω + 22X | 459 | 471 |
| <i>v</i> ₂₅ | 39ω + 35τ _s | 324 | 325 | 41ω + 32τ | 368 | 362 |
| <i>v</i> ₂₆ | 49X | 261 | 263 | 27ω + 24Ξ + 22τ _s | 251 | 269 |
| <i>v</i> ₂₇ | 38τ(X) + 22Ξ + 22ω | 139 | 141 | 35τ(X) + 19Ξ | 129 | 110 |
| <i>a''</i> | | | | | | |
| <i>v</i> ₂₈ | 98d | 2941 | 2917 | 98d | 2941 | 2917 |
| <i>v</i> ₂₉ | 98d | 2924 | 2913 | 98d | 2901 | 2913 |
| <i>v</i> ₃₀ | 97d | 2867 | 2855 | 96d | 2867 | 2855 |
| <i>v</i> ₃₁ | 97d | 2860 | 2852 | 96d | 2839 | 2851 |
| <i>v</i> ₃₂ | 66δ + 16γ | 1447 | 1447 | 73δ + 16γ | 1451 | 1440 |
| <i>v</i> ₃₃ | 66δ + 21γ | 1438 | 1434 | 61δ + 21γ | 1438 | 1434 |
| <i>v</i> ₃₄ | 46γ + 24R + 23γ(X) | 1370 | 1382 | 70γ + 20R | 1357 | 1368 |
| <i>v</i> ₃₅ | 67γ + 19R | 1348 | 1350 | 83γ | 1348 | 1350 |
| <i>v</i> ₃₆ | 88γ | 1331 | 1345 | 63γ + 15γ(X) | 1336 | 1342 |
| <i>v</i> ₃₇ | 76γ | 1299 | 1299 | 42R + 39γ + 22γ(X) | 1309 | 1317 |
| <i>v</i> ₃₈ | 72γ | 1257 | 1245 | 77γ | 1272 | 1261 |
| <i>v</i> ₃₉ | 77γ + 18R | 1184 | 1181 | 95γ | 1144 | 1144 |
| <i>v</i> ₄₀ | 57γ + 42R | 1088 | 1096 | 61γ + 27R | 1119 | 1142 |
| <i>v</i> ₄₁ | 61γ + 23R + 21γ(X) | 1075 | 1068 | 57γ + 27R | 1079 | 1082 |
| <i>v</i> ₄₂ | 59R + 24γ | 1050 | 1051 | 53R + 21γ | 1030 | 1034 |
| <i>v</i> ₄₃ | 52γ + 34R | 918 | 915 | 83γ | 921 | 927 |
| <i>v</i> ₄₄ | 49γ + 32R | 873 | 885 | 68R + 15γ | 864 | 855 |
| <i>v</i> ₄₅ | 78γ + 15R | 789 | 788 | 79γ | 776 | 791 |
| <i>v</i> ₄₆ | 60ω | 436 | 457 | 64ω | 449 | 458 |
| <i>v</i> ₄₇ | 40Ξ + 31ω + 20τ | 240 | 237 | 58Ξ + 24τ + 17ω | 327 | 308 |
| <i>v</i> ₄₈ | 46Ξ + 22τ + 15ω | 219 | 211 | 31Ξ + 24ω + 21τ | 185 | 167 |

^a When possible, frequency values taken from the liquid spectra are given. ^b The potential energy distribution is defined as $X_{ik} = 100F_{ik}L_{ik}^2/\lambda_k$. ^c d(X) and γ(X), C-H stretching and C-C-H bending in the Br-C-H group; d and γ, C-H stretchings and C-C-H bendings in the C-CH₂ groups; R, C-C stretchings; X, C-Br stretching; δ, H-C-H bendings; θ, H-C-Br bending; ω, C-C-C bendings; Ξ, C-C-Br bending; τ_s and τ(X), torsions around the C₃-C₄ and the C₁-C₂ bonds (BrHC¹-C²H₂-C³H₂-C⁴H₂-C⁵H₂-C⁶H₂); τ, the sum of τ_s, τ(X) and the torsion around the C₂-C₃ bond.

iodocyclohexane, while ν_{48} of chloro- and ν_{47} of iodocyclohexane are not observed in the Raman effect at all. Therefore ν_{47} of *e*-chlorocyclohexane corresponds to ν_{48} of iodocyclohexane, and according to the PED can be interpreted as an almost pure C–C–X (X=Cl,I) bending vibration.

For both the *e*- and *a*-conformers ν_{13} and ν_{15} are somewhat coupled, especially for chlorocyclohexane where ν_{13} can be interpreted as the H–C–Cl bending vibration, while for bromo- and iodocyclohexane the H–C–X (X=Br,I) bending seems to be dominating for the ν_{15} mode.

The C–X (X=Cl,Br,I) stretchings of the *a*-conformers are not well-localized vibrations.^{14,24} For chlorocyclohexane the bands at 685 and 559 cm^{-1} (ν_{22} and ν_{23}) could both be assigned to this mode according to the PED, while for bromocyclohexane the corresponding vibrations are found at 510 and 658 cm^{-1} , respectively. For iodocyclohexane ν_{24} at 446 cm^{-1} as well as ν_{22} and ν_{23} at 639 and 482 cm^{-1} all have major contributions from stretching of the C–I bond.

Except for the vibrations with strong contribution from C-halogen stretching or bending, the fundamental frequencies are rather similar for the different molecules of the same conformer, while the frequency variations for the different conformers of the same compound are often considerably larger. Especially for species *a'* the differences between the fundamental vibrations of chloro-, bromo- and iodocyclohexane are very small.

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