

The vibrational spectra of 1-chloro-2,2-dimethylpropane

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(Received for publication 10 June 1985)

Abstract—Infrared and Raman spectra in the region $5000\text{--}20\text{ cm}^{-1}$ were recorded at low temperature and high pressure of gaseous, liquid and crystalline solid 1-chloro-2,2-dimethylpropane. Quantitative Raman polarization data were obtained. The fundamental frequencies of vibration were assigned according to C_s symmetry and compared with the results of a normal coordinate analysis.

Under high pressure a plastic crystalline phase and two anisotropic crystalline phases were observed.

INTRODUCTION

Our work on 1-chloro-2,2-dimethylpropane (CDMP) represents part of a series of studies on halogenated neopentanes, including 1,3-dichloro-2,2-dimethylpropane [1], 2(chloromethyl)-1,3-dichloro-2-methylpropane [2] and 1,3-dichloro-2,2-di(chloromethyl)propane [3] and 1,3-dibromo-2,2-di(bromomethyl)propane [3]. These compounds can all be considered as halogenated neopentanes, being the monochloro-, dichloro-, trichloro-, tetrachloro- and tetrabromoneopentane, respectively.

We have now established that the monochloro-, dichloro- and trichloroneopentanes all possess a plastic phase in common with the parent compound, neopentane (2,2-dimethylpropane) [4]. For the tetrachloro and tetrabromo compounds, however, no such phase has been observed either on heating or cooling [5] or under high pressure [3].

The vibrational spectra of CDMP as a liquid have been briefly reported by CROWDER and LIN [6]. We have now extended their results into the far i.r. region, observed i.r. and Raman spectra of the crystalline phases at low temperatures and recorded i.r. spectra of various crystalline phases under high pressure.

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EXPERIMENTAL

The sample of CDMP was a commercial product from Ventron GmbH. Prior to use, the sample was distilled *in vacuo* and the purity was checked by gas chromatography.

Infrared spectra of CDMP as a vapour, as a liquid and as a crystalline solid at 80 K were recorded on a Perkin-Elmer model 225 spectrometer ($5000\text{--}200\text{ cm}^{-1}$) and with a Bruker FTIR model 114C ($4000\text{--}20\text{ cm}^{-1}$). The Raman spectra of the liquid, including quantitative polarization measurements, and of the crystalline solid at 80 K were recorded on a Cary 81 spectrometer, modified for perpendicular illumination and on a Dilor RTI-30 (triple monochromator) interfaced to the Aspect 2000 datasystem of the Bruker FTIR.

A diamond anvil cell with type IIa diamonds equipped with gaskets of brass and inconel with holes of 0.4 mm was employed for the high pressure studies. The compressed samples were observed in a polarization microscope between spectral recordings. A $4\times$ beam condenser from Perkin-Elmer was employed in the Perkin-Elmer 225 and the Bruker FTIR spectrometers.

RESULTS AND DISCUSSION

The i.r. and Raman spectra of CDMP in the liquid state are shown in Figs 1 and 2. Three i.r. curves recorded under varying pressures in the diamond anvil cell, covering the region $1500\text{--}1240\text{ cm}^{-1}$, are given in Fig. 3. The spectral curves represent three solid high pressure phases of CDMP, obtained under different pressure conditions. The various i.r. and Raman spectra obtained at low temperatures have not been

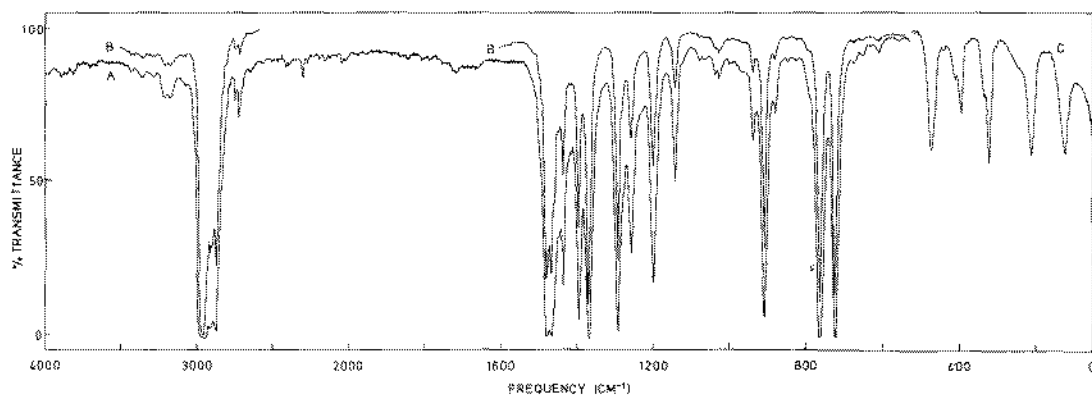


Fig. 1. The i.r. spectrum of 1-chloro-2,2-dimethylpropane (CDMP) as a liquid.

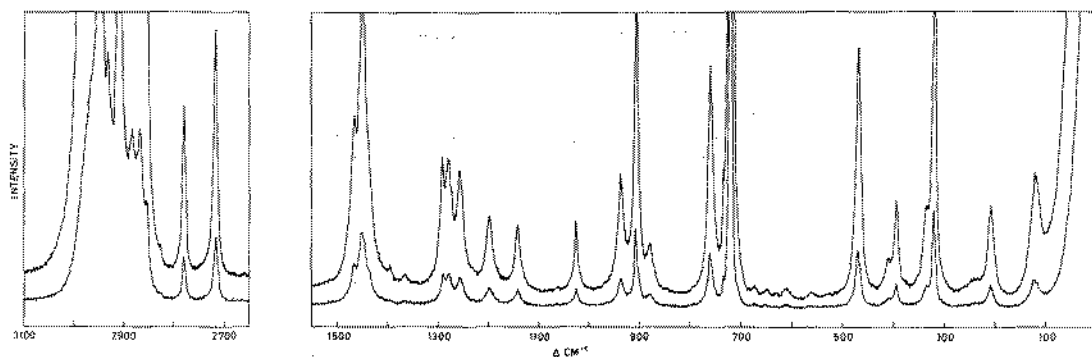


Fig. 2. The Raman spectrum of 1-chloro-2,2-dimethylpropane (CDMP) in the liquid state.

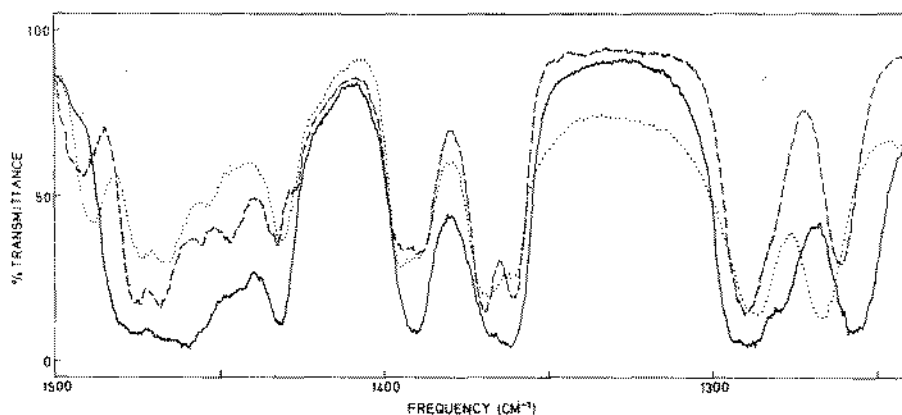


Fig. 3. The i.r. spectra of 1-chloro-2,2-dimethylpropane (CDMP) under pressure in a diamond anvil high pressure cell; solid curve (3–5 kbar) plastic crystal; dotted curve (20 kbar) anisotropic crystal, initially formed; dashed curve (20 kbar) anisotropic crystal formed after 20 h.

reproduced for the sake of brevity. The maxima of the observed i.r. and Raman bands are listed in Table 1.

Spectral assignments

Unlike the di-, tri- and tetrahalogenated neopentanes studied simultaneously, CDMP can only exist in one staggered conformation of C_s symmetry. The spectral assignments are therefore fairly simple compared with those of the trichloro compound [2(chloromethyl)-1,3-dichloro-2-methylpropane] in which three conformers are abundant [7] and tetrachloroneopentane [1,3-dichloro-2,2-di(chloromethyl)propane] which has two abundant conformers [8].

The vibrational fundamentals of CDMP divide into 25 modes of species a' and 20 of species a'' . The A and C axes lie in the symmetry plane; thus the a' modes should have A/C hybrid vapour contours, while the a'' modes should have B -type contours. The i.r. vapour band contours were calculated [9] for a HWHH of 1 cm^{-1} (Fig. 4); the A -type bands having a PR separation of ca 13 cm^{-1} and a prominent central O -branch, the B - and C -type bands appearing almost identical and contourless as can be expected for a near prolate rotor with large moments of inertia.

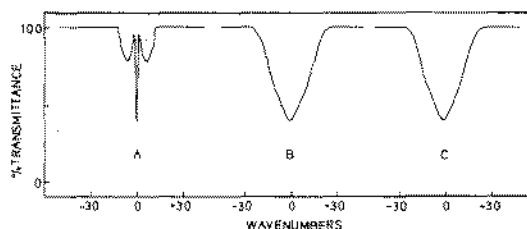


Fig. 4. Predicted vapour contours for the A -, B - and C -type bands of 1-chloro-2,2-dimethylpropane (CDMP).

The other way of distinguishing between the a' and a'' modes is offered by Raman polarization measurements. Very careful Raman polarization measurements were carried out with the setup, giving a depolarization ratio of 6/7 for the a'' modes. The depolarization ratios are also listed in Table 1.

Based upon the experimental band intensities in the i.r. and in Raman, the i.r. vapour contours, the Raman polarization measurements and the results of the force constant calculations (see below) the vibrational spectrum of CDMP was interpreted. Unfortunately, we

Table 1. Vibrational spectral data* for 1-chloro-2,2-dimethylpropane (CDMP)

Vapour	Infrared		Raman			Interpretation
	Liquid	Cryst. 15 kbar	Liquid	Depol. ratio	Cryst. 80 K	
2989 } 2984 } s, sh 2976 }	~ 2990 m, sh†		2990 m		2990 m	$\nu_{26} a''$
2970 s 2965 s	~ 2975 m, sh 2962 s		2965 s		2969 s	$\nu_{11}, \nu_{27} a', a''$ $\nu_{28}, \nu_{29} a''$
2955 m, sh	2950 m, sh		2948 s	<0.1	2950 m	$\nu_{2}, \nu_{3}, \nu_4 a'$
	~ 2940 m ~ 2930 m		2933 m	<0.1	2931 vw	$2 \times \nu_7 A'$
2915 w	2915 m 2902 m		2911 m	0.25	2915 m	Comb. A' Comb. A', A''
2880 m	2870 m ~ 2855 m 2832 w 2812 w		2868 m 2857 w		2869 m 2853 w	$\nu_{5}, \nu_{6}, \nu_{30}, a', a''$ Comb. A', A'' Comb. A', A'' Comb. A', A''
	2780 w		2782 w	<0.1	2786 vw 2776 w	Comb. A', A'' Comb. A', A''
~ 2750 vw	2751 w					Comb. A', A''
~ 2730 vw	2722 w		2717 w	<0.1	2712 w	Comb. A', A''
1488 } 1483 } m, A 1476 }	1478 m	1476 m			1477 w	$\nu_7 a'$
1472 m	1466 m ~ 1445 w	1467 m 1447 w	1466 m 1450 s	0.6 0.80	1468 s 1454 m	ν_8, ν_{31}, a', a'' $\nu_9, \nu_{32}, \nu_{33} a', a''$
1447 } 1440 } m, A 1334 }	1435 m	1431 m	1435 m, sh		1447 m	$\nu_{10} a'$
1418 vw 1404 }	~ 1420 vw		~ 1420 vw, sh			Comb. A', A''
1397 } 1391 }	1394 m	{ 1396 m 1389 m	1395 vw		1397 vw?	$\nu_{11} a'$
1373 s, bd	1367 s	{ 1368 s 1361 s	1367 vw		1368 w, bd	$\nu_{12}, \nu_{34} a', a''$
1300 } 1295 } m, A 1288 }	1290 s		1291 m	0.69	1298 m	$\nu_{13} a'$
	1279 w	1287 m	1280 m	0.84	1283 m	$\nu_{35} a''$
1266 } 1260 } m, A 1254 }	1256 m	1269 m	1258 m	0.83	1262 s	$\nu_{14} a'$
	~ 1235 vw	1239 w	~ 1235 vw		1223 vw	Comb. A''
1209 } 1203 } w, A/C 1197 }	1198 m	1205 m	1199 m	0.81	1202 m	$\nu_{15} a'$
1144 w, B?	1155 vw 1141 m 1122 vw, sh	1153 m	1142 m ~ 1125 vw ~ 1110 vw	0.87	1148 m	Comb. A', A'' $\nu_{36} a''$ $\nu_{20} + \nu_{41} A''$ Comb. A', A''
1091 } 1085 } w, B 1077 }	1078 vw		~ 1080 vw			$\nu_{19} + \nu_{23} A'$
	1063 vw 1035 w	1041 w	1063 vw ~ 1035 w, sh		1042 vw	$\nu_{39} + \nu_{45} A'$ $\nu_{37} a''$
1033 } 1026 } w, A/C 1020 }	1025 w	1031 w	1025 m	0.50	1033 w	$\nu_{16} a'$
970 vw, B?	994 vw 978 vw 968 vw 952 vw					Comb. A', A'' $\nu_{38} a''$ $\nu_{19} + \nu_{23} A'$ $\nu_{39} a''$
941 } 935 } w, A/C 929 }	936 w	949 m	936 m	0.80	942 m, bd	$\nu_{17} a'$

Table 1. (Contd.)

Vapour	Infrared		Raman		Cryst. 80 K	Interpretation
	Liquid	Cryst. 15 kbar	Liquid	Depol. ratio		
915 } 909 } 902 } m, A	906 s	914 s	906 s	0.53	911 s	$\nu_{18} a'$
880 w 840 vw	879 w 846 vw ~ 825 vw ~ 790 vw	886 m	878 m 848 vw 790 vw	0.87	883 m	$\nu_{40} a''$ $\nu_{21} + \nu_{22} A'$ $\nu_{20} + \nu_{45} A''$ Comb. A''
773 } 768 } 762 } s, A	760 s	764 s	760 m	0.68	760 s	$\nu_{19} a'$
730 } 724 } 718 } s, A	719 s	722 s	720 s	0.05	718 vs	$\nu_{20} a'$
	~ 705 vw 672 vw 654 vw 648 vw 628 vw 609 vw ~ 560 vw 525 vw 515 vw	707 w	~ 705 vw 674 vw 655 vw 649 vw 631 vw 610 vw 560 vw 527 vw 515 vw			Comb. A', A'' $\nu_{21} + \nu_{25} A'$ $\nu_{23} + \nu_{42} A''$ Comb. A', A'' Comb. A', A'' $\nu_{25} + \nu_{41} A''$ Comb. A', A'' Comb. A', A'' $\nu_{22} + \nu_{45} A''$
474 } 469 } 464 } m, A/C	470 m	478 w	469 m	0.27	469 m	$\nu_{21} a'$
	438 vw 410 w 395 m 335 w	410 w 396 w	~ 440 vw 410 w 395 m 335 m, sh	0.85 0.46 0.9	414 w 400 m 341 m	$\nu_{23} + \nu_{45} A''$ $\nu_{41} a''$ $\nu_{22} a'$ $\nu_{42} a''$
325 } 318 } 312 } w, A	322 s	337 s	321 s	0.41	329 s	$\nu_{23} a'$
	~ 250 w, bd		240 w, bd		229 w	$\nu_{24}, \nu_{43}, \nu_{44} a', a''$
205 w 116 w	210 m 124 m		210 m 122 m	0.40 0.91	206 m 131 m	$\nu_{25} a'$ $\nu_{45} a''$

* Bands above 3100 cm^{-1} and in the region $2700\text{--}1500 \text{ cm}^{-1}$ have been omitted.

† Abbreviations: s, strong; m, medium; w, weak; v, very; bd, broad; sh, shoulder; A, B and C denote bandcontours; comb. A' or comb. A'' when various explanations are possible.

have not observed any $^{35}\text{Cl}/^{37}\text{Cl}$ splitting in the spectra, which would have lent support to our assignments. The assigned fundamentals are listed together with the calculated values and an approximate description in Table 2; for the most part they agree with those of CROWDER and LIN [6].

As suspected previously [6] the polarized band at 210 cm^{-1} does not originate from the three methyl torsions but must rather be interpreted as the CCCl bending mode. The methyl torsions are instead assigned to the weak, broad band at $\text{ca } 240 \text{ cm}^{-1}$ observed in both the far i.r. and Raman spectra of the liquid.

Force constant calculations

Force fields for the series of halogenated neopentanes were transferred from the work of SNYDER and SCHACHTSCHNEIDER [10]. The force constants were refined by an overlay procedure described earlier [11] and will be listed in a forthcoming paper [2].

Solid phases

As is apparent from Fig. 3 three different high pressure solid phases were recorded. At rather low pressure (ca 3–5 kbar) a solid was formed which showed no colours in polarized light. However, the sample was clearly different from the liquid since small wavy lines were detected in the polarization microscope. The i.r. spectrum (solid line in Fig. 3) was quite similar to that of the liquid. We believe strongly that this is a plastic phase as has been observed in various neopentanes. Calorimetric data for the phase transitions between the plastic and anisotropic crystals of various chlorinated neopentanes at atmospheric pressure will be given separately [12].

When the pressure was increased to approximately 20 kbar, a phase transition took place. An anisotropic polycrystalline phase was formed as was apparent from strongly coloured crystallites in the polarization microscope. The dotted curve in Fig. 3 and the listed wavenumbers of the high pressure crystal in Table 1 represent i.r. data for this phase.

Table 2. Fundamental frequencies of 1-chloro-2,2-dimethylpropane (CDMP)

	Obs.	Calc.*	Approximate description
a' ν_1	2975	2967	CH ₂ sym. str.
ν_2	2950	2963	CH ₃ asym. str.
ν_3	2950	2963	CH ₃ asym. str.
ν_4	2950	2961	CH ₃ asym. str.
ν_5	2870	2883	CH ₃ sym. str.
ν_6	2870	2883	CH ₃ sym. str.
ν_7	1478	1467	CH ₃ asym. def.
ν_8	1466	1465	CH ₃ asym. def.
ν_9	1450	1453	CH ₃ asym. def.
ν_{10}	1435	1431	CH ₂ def.
ν_{11}	1394	1383	CH ₃ sym. def.
ν_{12}	1367	1375	CH ₃ sym. def.
ν_{13}	1290	1285	CH ₂ wag.
ν_{14}	1256	1270	CC str./CH ₃ rock.
ν_{15}	1198	1204	CC str./CH ₃ rock.
ν_{16}	1025	1023	CH ₃ rock.
ν_{17}	936	926	CC str./CH ₃ rock.
ν_{18}	906	906	CC str.
ν_{19}	760	761	CC str.
ν_{20}	719	726	CCl str.
ν_{21}	470	467	CCC bend.
ν_{22}	395	393	CCC bend.
ν_{23}	322	316	CCC bend.
ν_{24}	240	246	CH ₃ tors.
ν_{25}	210	207	CCC bend./CCCl bend.
a'' ν_{26}	2990	3008	CH ₂ asym. str.
ν_{27}	2975	2963	CH ₃ asym. str.
ν_{28}	2962	2960	CH ₃ asym. str.
ν_{29}	2962	2959	CH ₃ asym. str.
ν_{30}	2870	2883	CH ₃ sym. str.
ν_{31}	1466	1460	CH ₃ asym. def.
ν_{32}	1450	1453	CH ₃ asym. def.
ν_{33}	1450	1452	CH ₃ asym. def.
ν_{34}	1367	1374	CH ₃ sym. def.
ν_{35}	1279	1289	CC str./CH ₂ twist.
ν_{36}	1141	1140	CC str./CH ₂ twist.
ν_{37}	1035	1029	CH ₃ rock.
ν_{38}	978	990	CH ₃ rock.
ν_{39}	952	938	CH ₂ twist./CH ₃ rock.
ν_{40}	879	864	CC str.
ν_{41}	410	408	CCC bend.
ν_{42}	335	341	CCC bend.
ν_{43}	240	240	CH ₃ tors.
ν_{44}	240	236	CH ₃ tors.
ν_{45}	124	125	CH ₂ Cl tors.

*The force field will be given in Ref. [2].

After the sample had been standing overnight in the diamond anvil cell without adjusting the pressure, the crystallites had changed in appearance, the small crystallites had grown into a rod-like pattern. The i.r.

spectrum of this solid is given as the dashed curve of Fig. 3. As can be easily seen, the bands were shifted and the intensities changed relative to the dotted curve. From the visual microscopic observations and from the spectral changes it seems clear that another high pressure phase was formed with time. When the dashed curve was "formed" we could not get the dotted curve "back" by manipulating the pressure. We therefore believe that the dotted curve represents a metastable high pressure phase which is gradually transformed into the "dashed" phase.

Complete sets of low temperature i.r. and Raman spectra were obtained by condensing the vapour on the CsI or polyethylene window (i.r.) or copper block (Raman) kept at ca 80 K. The amorphous deposit gave a spectrum fairly similar to that of the liquid, but after annealing to ca 150 K and recooling to 80 K the sample looked crystalline. The Raman frequencies listed in Table 1 were observed from the annealed sample.

Acknowledgements—D. L. P. is grateful to the Norwegian Research Council for Science and the Humanities and the Norwegian Marshall Fund for financial support.

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