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Substituted Propanes. XIII. The Vibrational Spectra of 2,2-Dichloropropane-d_6

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The infrared spectra of 2,2-dichloropropane-d_6 as a vapour, liquid and crystalline solid at −180 °C were recorded in the region 4000 – 200 cm^{-1}. Raman spectra of the liquid were obtained and polarization data presented.

The fundamental frequencies have been assigned in terms of C_{2v} symmetry. A normal coordinate analysis reproduced the fundamentals of 2,2-dichloropropane and the d_6-derivative satisfactorily. The assignments for the parent molecule were slightly changed on the basis of this work.

We have been interested in halogenated propanes for some time and have reported the vibrational spectra of certain 2-halopropanes[1-3] and 2,2-dihalopropanes[4] as well as force fields derived for these molecules.[5,6] Since the spectra of isopropylhalides are not complicated by the conformational equilibria present in the propyl halides, they can therefore be interpreted with some confidence. The spectra of 2,2-difluoropropane were published by Crowder and Jackson[7] who also derived a force field for this compound.

The spectra of 2,2-dichloropropane were reinvestigated by Green and Harrison[8] (hereafter referred to as GH) who changed some of the earlier[4] assignments.

Since the fully deuterated molecule 2,2-dichloropropane-d_6 is now commercially available, we decided to study its spectrum. We hoped that these data would be useful for developing a more reliable force field which might settle some of the controversial assignments for the parent molecule.

EXPERIMENTAL

The sample of 2,2-dichloropropane-d_6 was a commercial product from Merck, Sharp & Dohme of Canada Limited, investigated without purification. No impurity peaks were detected by gas chromatographic analysis. The isotopic purity was high since no IR or Raman bands were observed which could be attributed to C – H stretch. Moreover, the most intense IR vapour bands at 1119 and 669 cm^{-1} of the parent compound[4,8] were not detected in the spectra of the fully deuterated species.

The infrared spectra were recorded in the region 4000 – 200 cm^{-1} with a Perkin-Elmer model 225 spectrometer. Vapour cells with windows of KRS-5 and CsI had path lengths of 1 m and 10 cm, respectively. Sealed cells having KBr and CsI windows were used for the liquid, while a conventional cryostat with CsI windows was employed for the crystalline solid at −180 °C.

Raman spectra of the liquid were obtained with a modified[9] Cary 81 spectrometer using the 5145 and 4880 Å lines from an argon ion laser (CRL 52 G) for excitation.

SPECTRAL INTERPRETATION

2,2-Dichloropropane-d_6. The present compound, obviously has C_{2v} symmetry like the parent molecule. Assuming tetrahedral angles and the bond distances: C – C = 1.54, C – D = 1.09 and C – Cl = 1.795 Å we calculated the following principal moments of inertia: $I_A = 170.57$, $I_B = 228.06$ and $I_C = 260.06$ a.m.n. Å.[2] Since the orientation of the I_A, I_B and I_C axes were parallel with those of the parent molecule[4] the various IR active fundamentals should have the same rotational contours for both molecules. The *PR* sparations were esti-

Table 1. Infrared and Raman spectral data for 2,2-dichloropropane-d_6.

Infrared			Raman	Assignments
Vapour	liquid	Solid (−180 °C)	liquid	
2960 vw	2960 vw	2960 vw	2962 vw	
2430 vw		2405	2395 vw	
2258 m, 2252 s	2265	2265	2264 m,P	ν_1 a_1 fund
	2246 s	2252	2247 s,D	ν_{22} b_2 fund
2248 m, 2242 s, 2235 w C	2238 s	2249, 2239	2242, m,D	ν_{15} b_1 fund
			2215 w,D	ν_{10} a_2 fund
2160 m	2151	2155		
2153 m	2142	2140	2142 m,P	A_1 comb
2131 m	2122		2122 vs,P	ν_2 a_1 fund
2118 m	2110		2111 s,P	A_1 comb FR
2109, 2101 m, 2092 C?	2093		2095 w,D	ν_{16} b_1 fund
2077 w	2070	2065	2069 w,P	A_1 comb
2025 w	2015		2022 w,P	A_1 comb
1288 w	1275	1280		
1212 m, 1207 s, 1205 vs, 1203 s, 1202 s, 1200 s, 1194 m C	1200	1205, 1198	1204 w,D	ν_{17} b_1 fund hot bands
1143 s, 1138 s, 1135 s, 1129 s B	1127	1132	1134 m,P	ν_3 a_1 fund
1113 w, 1105 w, 1097 w	1105	1108, 1090	1108 vw	ν_{23} b_2 fund
			1068 vw	ν_{11} a_2 fund
	1056 w	1055		
1062 s, 1052 s, 1048 s A	1048	1058, 1045	1049 m,D	ν_{24} b_2 fund
1042 s C	1037	1035	1037 w	ν_{18} b_1 fund
1023 s, 1016 s, 1013 s, 1006 s B	1005	1011, 1005	1011 vs,P	ν_4 a_1 fund
980 vs, 973 vs, 962 s C?	963	952	963 m,P	ν_5 a_1 fund
932 s, 920 vs, 914 s C	922	919	924 vw	ν_{19} b_1 fund
852 m	839			
830 m,C	826	827		

Table 1. Continued.

822 m 813 w 788 s		806			
782 s 779 s 772 s	B	778	785 780	782 s,P?	ν_6 a_1 fund
				744 w	ν_{12} a_2 fund
750 w 739 m 732 w	C	736	740		ν_{20} b_1 fund
654 s 649 s 646 s 638 s	B?	648	668 652		*A* comb?
618 vs 610 vs 602 vs	A	598	604 582	598 vs,D	ν_{25} b_2 fund
538 s 530 s 527 m 520 s	B	526	530 523 520	525 vs,P	ν_7 a_1 fund
485 vw		482	470	487 vw	
450 w			455	430 vw?	
359 m 350 m 341 m	C	350	353	352 w	ν_{21} b_1 fund
329 w 322 w 319 w 313 w	B	325	324	327 s,P	ν_8 a_1 fund
302 w		291		290 vw	ν_{26} b_2 fund
				252 s,D	ν_{13} a_2 fund
240 m		245	250	244 m,P?	ν_9 a_1 fund
		204 vw	205 m	204 vw	ν_{27} b_2 fund

[a] The weak infrared and Raman bands in the regions 5000 – 2400 cm^{-1} and 2000 – 1300 cm^{-1} are omitted. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; P, polarized; D, depolarized; A, B and C denote vapour contours.

mated[10] to be 14, 16 and 18 cm^{-1} for *A* (b_1), *B* (a_1) and *C* (b_2) contours, respectively.

Many of the observed vapour contours were well resolved, while others were more diffuse and not as valuable for the assignments as in the parent molecule. The Raman polarization data are very useful for determining the polarized a_1 modes, but cannot differentiate between the b_1 and b_2 modes. Moreover, the IR inactive a_2 fundamentals are often very weak in the Raman spectra and their identification therefore uncertain.

The actual IR and Raman spectral curves are not reproduced for the sake of brevity, but the wave numbers for the observed bands are listed in Table 1. In Table 2 the assigned fundamentals are collected together with the results of the normal coordinate calculations.

The nine fundamentals of species a_1 can be assigned with considerable confidence to strongly polarized Raman bands of generally high intensities at 2264, 2122, 1134, 1011, 525 and 327 cm^{-1} while those at 963, 782 and 244 cm^{-1} were only slightly polarized. Generally, these Raman bands corresponded to infrared bands with prominent *B*-contours in the vapour, such as 1136, 1014, 780, 528 and 320 cm^{-1} which had the expected *PR* as well as the *QQ* splitting. Exceptions were the vapour bands around 973 cm^{-1} which had a sharp *Q*-branch

Table 2. Observed and calculated fundamental frequencies (in cm^{-1}) for 2,2-dichloropropane-d_6.

Species	No.	Obs.[a]	Calc.	Potential energy distribution[b]	Approximate motions
a_1	ν_1	2252	2250	$97(s-t)$	CD_3 as.str.
	ν_2	2131	2131	$97(s+t)$	CD_3 sym.str
	ν_3	1136	1169	$52r+33\gamma^+$	C−C str.
	ν_4	1014	1023	$85\gamma^-$	CD_3 as.bend
	ν_5	973	981	$43\gamma^+ + 23(\varepsilon-\delta)+23\alpha$	CD_3 sym.bend
	ν_6	781	764	$47(\varepsilon-\delta)+21r$	CD_3 rock
	ν_7	528	523	$44d+26r$	C−Cl str.
	ν_8	320	315	$112\beta+90\alpha$	mixed
	ν_9	240	247	$31\beta+22\alpha$	
a_2	ν_{10}	2215[c]	2223	$98(s-t)$	CD_3 as.str.
	ν_{11}	1068[c]	1061	$90\gamma^-$	CD_3 as.bend
	ν_{12}	744[c]	766	$91(\varepsilon-\delta)$	CD_3 rock
	ν_{13}	252[c]	248	92β	ClCC bend
	ν_{14}	–	203	83τ	torsion
b_1	ν_{15}	2242	2237	$98(s-t)$	CD_3 as.str.
	ν_{16}	2101	2116	$97(s+t)$	CD_3 sym.str.
	ν_{17}	1205	1233	$65r+19\gamma^+$	C−C str.
	ν_{18}	1042	1038	$90\gamma^-$	CD_3 as.bend
	ν_{19}	920	917	$66\gamma^+$	CD_3 sym.bend
	ν_{20}	739	738	$72(\varepsilon-\delta)$	CD_3 rock
	ν_{21}	350	351	$72\beta+17r$	ClCC bend
b_2	ν_{22}	2246[d]	2238	$98(s-t)$	CD_3 as.str.
	ν_{23}	1105[d]	1101	$41(\varepsilon-\delta)+21\beta+21d$	CD_3 rock
	ν_{24}	1052	1044	$81\gamma^-$	CD_3 as.bend
	ν_{25}	610	586	$54(\varepsilon-\delta)+48d$	C−Cl str.
	ν_{26}	302	304	$49\beta+28d+22\tau$	ClCC bend
	ν_{27}	204	200	66τ	torsion

[a] Infrared vapour values except when noted. [b] Terms below 15 are omitted. [c] Raman liquid values. [d] Infrared liquid values.

suggesting *C*-contour.

Our remaining four a_1 fundamentals had vapour contours which were ill-defined and of no aid to the assignments. Some additional Raman bands appeared polarized (*e.g.* at 2142, 2111, 2069 and 2022 cm^{-1}) which could all be explained as combination bands or overtones of species A_1.

The a_2 fundamentals ($\nu_{10}-\nu_{12}$) were assigned to the weak or very weak Raman bands at 2215, 1068, 744 with unknown polarization ratios. Since the 2215 and 744 cm^{-1} bands were 23 and 8 cm^{-1} removed from IR liquid bands they are not as definite choices for a_2 as would be preferred. A strong, depolarized Raman band at 252 cm^{-1} appears as a good choice for ν_{13}. No likely Raman band was observed for the CD_3 torsional mode ν_{14}.

Vapour bands, having *C*-type contours with sharp central *Q*-branches were observed at 2242, 2101, 920, 739 and 350 cm^{-1} and should therefore be assigned as b_1-modes. The polarization ratios for some of the Raman counterparts were not known because of low intensities. The sharp peaks commencing at 1207 cm^{-1} with 2 cm^{-1} spacing and diminishing intensities apparently form a hot band progression of the *Q*-branches. A very sharp band at 1042 cm^{-1} is apparently the central branch of a *C*-type band but the contours are obscured by the neighbouring *A*-type band. As mentioned previously, the a_1 modes at 973 and 530 cm^{-1} have contours more like *C* than *B*, but the polarized Raman counterparts rule out the possibility for b_1-modes.

Vapour bands with definite *A*-contours were

Table 3. Observed and calculated fundamental frequencies (in cm^{-1}) for 2,2-dichloropropane.

Species	No.	Obs.	Calc.	Potential energy distribution[a]	Approximate motions
a_1	ν_1	3010	3012	$99(s-t)$	CH_3 as.str.
	ν_2	2943	2943	$99(s+t)$	CH_3 sym.str.
	ν_3	1440	1427	$85\gamma^- + 16(\varepsilon-\delta)$	CH_3 as.bend
	ν_4	1391	1360	$86\gamma^+ + 16r$	CH_3 sym.bend
	ν_5	1163	1163	$57(\varepsilon-\delta)+20\alpha$	CH_3 rock
	ν_6	915	937	$48r+17d$	C–C str.
	ν_7	562	575	$44d+26r+19\alpha$	C–Cl str.
	ν_8	359	358	$112\beta+89a+18d$	mixed
	ν_9	258	249	$34\beta+20\alpha$	mixed
a_2	ν_{10}	*2990*[b]	2978	$99(s-t)$	CH_3 as.str.
	ν_{11}	1447	1470	$88\gamma^-$	CH_3 as.bend
	ν_{12}	*1020*[c]	1000	$90(\varepsilon-\delta)$	CH_3 rock
	ν_{13}	*287*	294	$67\tau+20\beta$	torsion
	ν_{14}	–	269	$78\beta+19\tau$	ClCC bend
b_1	ν_{15}	2993	3000	$99(s-t)$	CH_3 as.str.
	ν_{16}	2943	2922	$99(s+t)$	CH_3 sym.str.
	ν_{17}	1453	1457	$83\gamma^-$	CH_3 as.bend
	ν_{18}	1377	1352	$64\gamma^+ + 30r$	CH_3 sym.bend
	ν_{19}	1119[c]	1121	$27\gamma^+ + 27r + 27(\varepsilon-\delta) + 16\beta$	mixed
	ν_{20}	954	954	$58(\varepsilon-\delta)+25r$	CH_3 rock
	ν_{21}	388	387	$77\beta+17r$	ClCC bend
b_2	ν_{22}	*2993*[c]	2998	$99(s-t)$	CH_3 as.str.
	ν_{23}	1463	1480	$83\gamma^-$	CH_3 as.bend
	ν_{24}	*1192*[b]	1198	$51(\varepsilon-\delta)+19\beta$	CH_3 rock
	ν_{25}	669	704	$52r+35(\varepsilon-\delta)+28\beta$	C–Cl str.
	ν_{26}	*359*[c]	339	$41\tau+32d+29\beta$	mixed
	ν_{27}	–	271	$44\tau+28\beta$	torsion + ClCC bend

[a] Terms below 15 are omitted. [b] In variance with Ref. 4 and GH Ref. 8. [c] According to GH, Ref. 8, in variance with Ref. 4.

observed at 1052 and 610 cm^{-1}, most certainly the b_2-fundamentals ν_{24} and ν_{25}. The remaining modes of this symmetry species are more uncertain; thus ν_{22} was assigned to the strong bands at 2246 cm^{-1} (IR liquid) and 2247 cm^{-1} (Raman), overlapping ν_1 and ν_{15} in the vapour phase. A weak IR vapour band at 1105 cm^{-1} with possible *A*-contour appeared as a shoulder on the intense ν_3, but having a very weak Raman couterpart was assigned as ν_{23}. The two low frequency b_2 fundamentals ν_{26} and ν_{27} are tentatively attributed to the weak IR bands at 302 cm^{-1} (vapour) and 204 cm^{-1} (liquid), respectively, both having very weak Raman counterparts.

2,2-Dichloropropane. From the force field developed for these molecules (see below) and from spectral analogies with the fully deuterated compound, we have revised the assignments for the parent molecule. The fundamentals which are revised compared to our earlier assignments are written in italics in Table 3, in many cases they agree with those of GH.[8] No revisions were made for the a_1 modes ($\nu_1-\nu_9$). The CH stretch of species a_2 was reassigned to the depolarized Raman band at 2990 cm^{-1} which overlaps ν_{15} as a consequence of the force constant calculations. The Raman band at 2908 cm^{-1} previously[4] assigned as ν_{15} can be explained as $\nu_{17}+\nu_{23}$. Moreover, we agree with GH's[8] attributions of the Raman bands at 1020 and 287 cm^{-1} as ν_{12} and ν_{13}, respectively, while the torsional mode ν_{14} remains unobserved.

Among the b_1 fundamentals all our previous assignments[4] were supported by the force field calculations. Since the CH_3 rocking mode of species b_2 according to the calculations is expected at higher

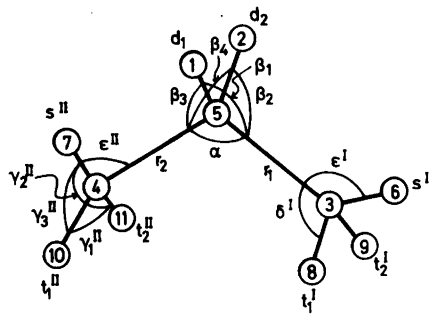

Fig. 1. Definition of the valence coordinates for the propane molecular model. r, d, s and t are stretchings. The γ type bendings are shown only for the methyl group II while the δ's are exemplified by δ_1^I only. The torsions τ_1 and τ_2 (not shown on the figure) involve the atoms 6-3-5-4 and 7-4-5-3, respectively.

wavenumbers than the corresponding b_1 fundamental, we have not followed GH in substituting 1119 cm^{-1} with 1192 cm^{-1} for ν_{19}, although the contour looks more like *A* than *C*. The asymmetric CH_3 stretch ν_{22} of species b_2 has been considered accidentally degenerate with ν_{15} (b_1). For ν_{24} we have assigned the band at 1192 cm^{-1}, previously attributed[4] to ν_{12}, but shown by GH[8] to have an IR counterpart. We have verified that our previous[4] weak band at 332 cm^{-1} was due to an impurity. Thus, there is no other apparent choice for ν_{26} than assuming overlap with ν_8 at 359 cm^{-1} as suggested by GH.[8] No good choice was found for ν_{27}, which as a torsional fundamental should be very weak and might be hidden by ν_9.

NORMAL COORDINATE ANALYSIS

As a help in the assignment discussed above a normal coordinate analysis based on symmetry coordinates was performed. It seems of little interest to go into any details of these calculations here. Finally calculated frequencies for 2,2-dichloropropane-d_6 and 2,2-dichloropropane including the potential energy distributions (PED) are given in Tables 2 and 3, respectively. The potential energy distributions are expressed in terms of the valence coordinates defined in Fig. 1.

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