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Vibrational Spectra and Structure of Four-Membered Ring Molecules. II. Chlorocyclobutane, Chlorocyclobutane-d_1, and Chlorocyclobutane-d_4*

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The infrared spectra of chlorocyclobutane, α-chlorocyclobutane-d_1, and $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ in both the gaseous and liquid states have been recorded from 4000 to 250 cm^{-1}. The far-infrared spectrum of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ in the vapor state has been recorded down to 33 cm^{-1}. The Raman spectra of the three isotopic species of chlorocyclobutane have also been recorded of the liquid phases and depolarization values measured. The spectra have been interpreted by considering the molecule to have a plane of symmetry and belonging to point group C_s. Assignment of the frequencies of the fundamental vibrations is based on position, isotopic shift, band type, and depolarization values. The ring-puckering vibration in chlorocyclobutane was observed in the Raman spectrum at 165 cm^{-1}, and found at 159 cm^{-1} in the far-infrared spectrum of the vapor. The data shows that the first upper-state transition of the ring-puckering vibration is centered at 142 cm^{-1}. For the tetradeuterated molecule the ring-puckering vibration was found at 144 cm^{-1} in the far-infrared spectrum of the vapor. The nature of the potential energy function governing the ring-puckering vibration is discussed.

INTRODUCTION

RECENTLY we published the Raman and far-infrared spectra of several four-membered ring molecules.[1] Assignment of the normal vibrations, with the exception of the ring-puckering vibration and the halogen bending and stretching vibrations, was not given because isotopic data were not available. We felt such an assignment would be highly tentative.[1] We now have the infrared and Raman spectra of three isotopic species of chlorocyclobutane and with the measured depolarization values, band contours, and isotopic shifts it is possible to give rather conclusive assignments for most of the normal vibrations of chlorocyclobutane.

A microwave investigation of chlorocyclobutane by Kim and Gwinn[2] has shown the molecule to be puckered in the equilibrium position with a dihedral angle of 20°±1°. The chlorine atom was found in the equatorial position and no spectrum attributable to the axial conformation was observed. From the microwave intensity measurements they predicted a ring-puckering vibration at 155 cm^{-1} and a first overtone at 300 cm^{-1}. In our earlier far infrared investigation[1] we confirmed these predictions when we located the $1\leftarrow 0$ and $2\leftarrow 0$ transitions of the ring-puckering vibration at 159 and 303 cm^{-1}, respectively. From the decrease in the spacing of the higher-energy levels it was concluded that the potential function governing the ring-puckering vibration of this molecule had the usual anharmonic deviation. Such a potential function was in marked contrast to that needed to predict the far-infrared spectra of trimethylene oxide,[3–5] trimethylene sulfide,[6] and cyclobutanone.[6,7] In order to better understand the vibrational spectra of chlorocyclobutane we investigated the infrared and Raman spectra of chlorocyclobutane, α-chlorocyclobutane-d_1, and $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$.

EXPERIMENTAL

The initial step in the synthesis of chlorocyclobutane was the reduction of cyclobutanone to cyclobutanol with $LiAlH_4$. The alcohol was treated with $SOCl_2$ under conditions similar to those described by Caserio *et al.*,[8] and the chlorination products were separated with an Aerograph Model 30-P3 gas chromatograph. An 8-ft column of di-isodecyl phthalate was used under the following conditions: column temperature, 55°C; helium flow rate, 150 ml/min; collector, 200°C; injector, 220°C; detector, 240°C; and bridge power, 150 mA. The chlorocyclobutane collected was shown to be better than 99% pure by vapor-phase chromatography (VPC). The synthesis of α-chlorocyclobutane-d_1 was initiated by reducing cyclobutanone with $LiAlD_4$ to α-cyclobutanol-d_1. The monodeuterated alcohol was then treated with $SOCl_2$ and the chlorination products were separated by the same procedure as described above. Vapor-phase chromatography showed the compound to be better than 99% pure. In order to prepare the chlorocyclobutane-d_4, we first prepared $\beta,\beta,\beta',\beta'$-

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* For Part I of this series, see J. Chem. Phys. **45**, 1269 (1966).

† Taken in part from the thesis submitted by A. C. Morrissey to the Department of Chemistry in partial fulfillment for the degree of Ph.D.

[1] J. R. Durig, W. H. Green, and N. C. Hammond, J. Phys. Chem. **70**, 1989 (1966).

[2] H. Kim and W. D. Gwinn, J. Chem. Phys. **44**, 865 (1966).

[3] W. J. Lafferty, Ph.D. thesis, MIT, June 1961.

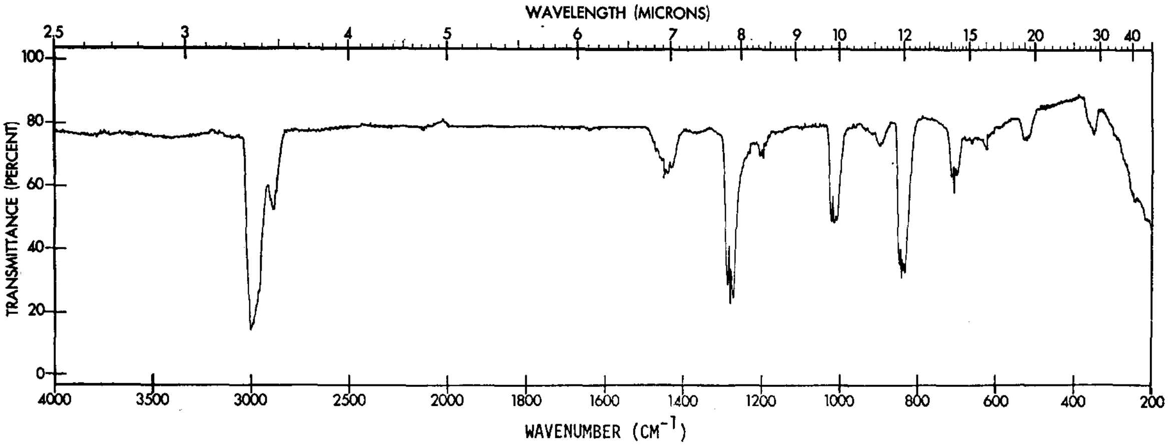
[4] A. Danti, W. J. Lafferty, and R. C. Lord, J. Chem. Phys. **33**, 294 (1960).

[5] S. I. Chan, T. R. Borgers, J. W. Russel, H. L. Strauss, and W. D. Gwinn, J. Chem. Phys. **44**, 1103 (1966).

[6] J. R. Durig and R. C. Lord, J. Chem. Phys. **45**, 61 (1966).

[7] T. R. Borgers and H. L. Strauss, J. Chem. Phys. **45**, 947 (1966).

[8] M. C. Caserio, W. H. Graham, and J. R. Roberts, Tetrahedron **11**, 171 (1960).



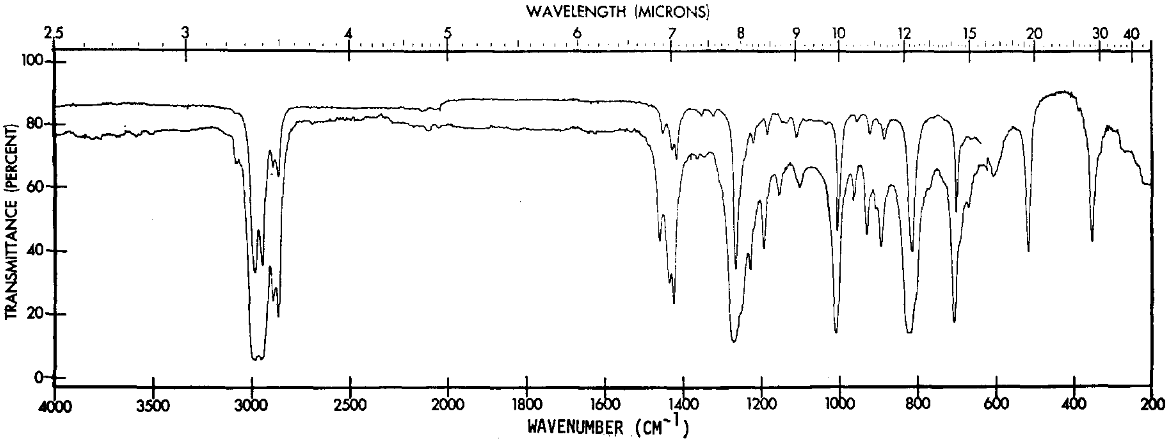


FIG. 1. Infrared spectra of chlorocyclobutane. Top: gas phase recorded with pressure of 30 torr and a path length of 10 cm. Bottom: liquid phase recorded neat and with cell thickness of 0.05 mm (see Experimental section).

cyclobutanone-d_4 by the method of Frei and Günthard.[9] After five exchanges of the cyclobutanone in an acidified solution which contained a 20:1 mole excess of D_2O, the NMR spectrum showed the four β positions to be better than 99% deuterated. The $\beta,\beta,\beta',\beta'$-cyclobutanone-$d_4$ was reduced to the alcohol with $LiAlH_4$ and the alcohol was chlorinated as before. The products were separated as described previously and the purity of the $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ was greater than 98%. Because of the chlorination procedure followed the isomeric purity was expected to be greater than 86%.[10]

The infrared spectra of liquid and gaseous chlorocyclobutane and the deuterium analogues have been measured from 250 to 4000 cm^{-1} with a Perkin–Elmer Model 521 spectrophotometer. The spectrophotometer housing was purged with dry nitrogen to remove atmospheric water vapor and carbon dioxide. The instrument was calibrated in the usual manner.[11,12] The infrared spectra of gaseous chlorocyclobutane and the deuterium analogs were recorded over this frequency range at pressures of 15, 30, 40, and 60 torr in a 10-cm cell equipped with CsBr windows. Original tracings of the infrared spectra of liquid and gaseous chlorocyclobutane, α-chlorocyclobutane-d_1, and $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ are shown in Figs. 1, 2, and 3, respectively, and the frequencies of the observed bands are listed in Tables I, II, and III. The infrared spectra of the liquid samples were recorded over the same frequency range by utilizing a Perkin–Elmer liquid cell with a 0.06-mm Teflon spacer and equipped with CsBr windows. To establish the frequency of the strong bands, a 0.012-mm Teflon spacer was used to record the spectra of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ and α-chlorocyclobutane-d_1, and the spectrum of chloro-

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[9] K. Frei and Hs. H. Günthard, J. Mol. Spectry. **5**, 218 (1960).

[10] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, J. Am. Chem. Soc. **81**, 4390 (1959).

[11] *IUPAC Tables of Wavenumbers for the Calibration of Infrared Spectrometers* (Butterworths Inc., Washington, D.C., 1961).

[12] H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, Phys. Rev. **52**, 160 (1937).

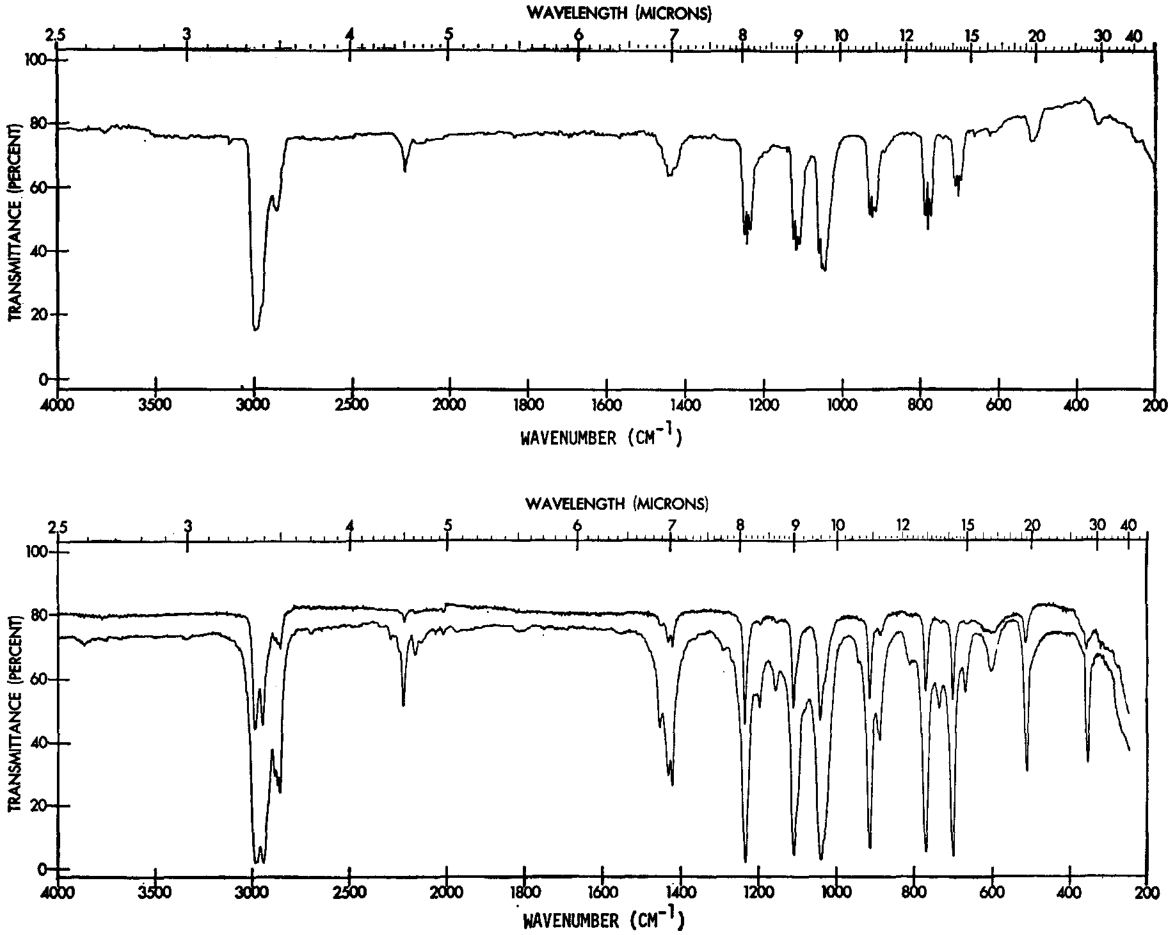

FIG. 2. Infrared spectra of α-chlorocyclobutane-d_1. Top: gas phase recorded with pressure of 15 torr and a path length of 10 cm. Bottom: liquid phase recorded with cell thickness of 0.012 and 0.05 mm (see Experimental section).

cyclobutane was examined neat between two CsBr discs.

The far infrared spectrum of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ was measured on a Beckman IR-11 far-infrared spectrophotometer[13] from 33 to 300 cm^{-1}. The instrument was calibrated with atmospheric water vapor and the assignments of Randall *et al.*[12] The far infrared spectrum of the vapor was recorded at a pressure of 9 torr in an 8.2-m gas cell equipped with polyethylene windows. A reproduction of the original spectrum is shown in Fig. 4 and the frequencies are listed in Table III.

The infrared spectrum of chlorocyclobutane was also recorded 4000 to 250 cm^{-1} in an isolated argon matrix at 20°K. The low temperature was achieved by an Air Products and Chemicals, Inc. AC-2-100 cryotip refrigerator, described by White and Mann.[14] Forty μM of chlorocyclobutane were vaporized into the evacuated system and Ar was introduced to give a mole ratio of 1000:1. The sample mixture was then deposited at a rate of 1 mm/min on a CsBr plate. The infrared spectrum of the matrix isolated material is shown in Fig. 5 and the frequencies are listed in Table IV.

The Raman spectra of the liquid samples were recorded on a Cary Model 81 spectrophotometer described in a previous publication.[1] Original tracings of the Raman spectra of chlorocyclobutane, α-chlorocyclobutane-d_1 and $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ are shown in Figs. 6, 7, and 8, respectively, and the wavenumbers, intensities, and depolarization values are listed in Tables I, II, and III. All frequencies reported are believed to be accurate to ±2 cm^{-1} or better.

DISCUSSION AND ASSIGNMENT OF FUNDAMENTALS

The recent microwave studies[2] have established the chlorocyclobutane molecule as being puckered and belonging to point group C_s. The thirty normal vibrations, which are both infrared and Raman active, are separated into the following symmetry species: $18A'+12A''$. The eighteen vibrations of symmetry species A' should show polarized Raman lines and the remaining twelve

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[13] The far-infrared spectrophotometer was purchased with funds from a National Science Foundation Grant, GP-5827.

[14] D. White and D. E. Mann, Rev. Sci. Instr. **34**, 1370 (1963).

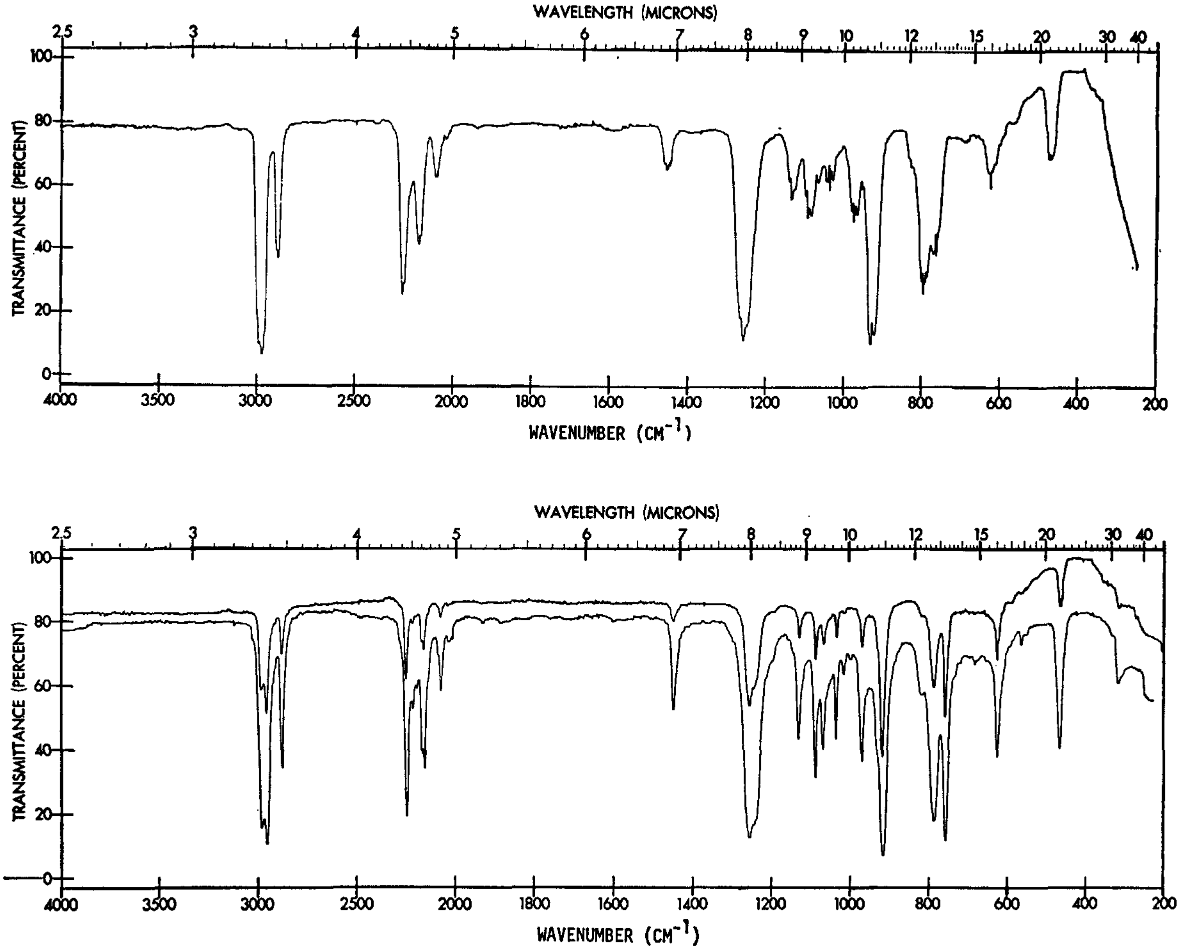


FIG. 3. Infrared spectra of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$. Top: gas phase recorded with pressure of 40 torr and path length of 10 cm. Bottom: liquid phase recorded with cell thickness of 0.012 and 0.05 mm (see Experimental section).

vibrations are antisymmetric with respect to the plane of symmetry and should give rise to depolarized Raman lines. The three moments of inertia of chlorocyclobutane[2] are such that the intermediate and greatest moments are nearly the same, whereas the least moment of inertia is considerably smaller than the other two moments. Vibrations with a dipole moment change along the least axis should give rise to Type *A* bands and belong to symmetry species A'. The greatest moment of inertia also lies in the plane of symmetry of the molecule and vibrations with a dipole moment oscillation along this axis should give rise to Type *C* band envelopes. However, since both of these moments lie in the plane of the molecule and the molecule has only a plane of symmetry, the vibrations of symmetry species A' will give infrared band contours that are mixtures of both Type *A* and Type *C* bands. The relative intensity of the *Q* branches of these bands will be determined by the amount of "*C*" character of the band. The intermediate moment of inertia is perpendicular to the plane of symmetry and vibrations with a dipole moment change along this axis should show Type *B* bands and belong to symmetry species A''. However, the contours of the Type *B* bands are not expected to be very distinct and vibrations of symmetry species A'' will show in most instances very ill-defined band contours. In order to alleviate confusion in the

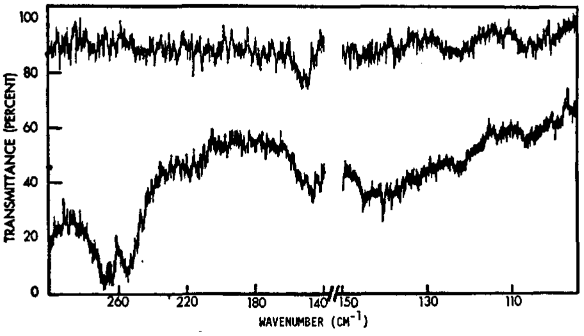


FIG. 4. Far infrared spectrum of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ recorded in a Beckman model IR-11 spectrophotometer. Gain: 5.55×10; period: 8; speed: 20; slits: standard. Top curve, background of 8.2-m empty cell with polyethylene windows versus two pieces of polyethylene; bottom curve, sample cell containing chlorocyclobutane-d_4 at 9 torr.

TABLE I. Infrared and Raman spectra of chlorocyclobutane.[a]

Infrared gas (cm^{-1})	Band type	Relative intensity	Infrared liquid (cm^{-1})	Relative intensity	Raman (Δcm^{-1})	Relative intensity	Depolarization factor	Assignment
			3083	vw				Impurity
3005 *Q*		vs			2979	68	0.50	ν_1, ν_2
2989 *Q*		vs(sh)	2989	vs(brd)	2979	68	0.50	ν_{19}, ν_{20}
2967 *Q*		vs(sh)	2949	vs(brd)	2953	100	0.30	ν_3
2954 *Q*		s(sh)			2923	45	0.25	ν_4
2903 *Q*		m(sh)	2890	s	2880	11	0.33	$2\times\nu_6=2930$
2885 center		m						$2\times\nu_{21}=2884$
2872 center		m(sh)	2862	s	2854	12	0.64	ν_5
2375 center		vvw						$\nu_8+\nu_{10}=2380$
2350 center		vvw						$\nu_{23}+\nu_{25}=2358$
			2185	vvw				$\nu_{11}+\nu_{24}=2184$
			2115	vvw				$\nu_8+\nu_{12}=2120$
			2058	vvw				$\nu_{12}+\nu_{25}=2062$
1740 center		vvw						$\nu_9+\nu_{16}=1737$
1480 *Q*	*A* or *C*	w(sh)	1468	m	1465	5	6/7	ν_6
1455 *Q*	*A* or *C*	m	1442	m	1442	12	6/7	ν_7
1442 center		w(sh)	1430	m				ν_{21}
1292 *R*		vs						
1288 *Q*	*A*	vs	1279	s	1277	6	0.77	ν_8
1280 *P*		vs						
			1261	m(sh)	1255	3		ν_{22}
1241 *Q*	*A* or *C*	vvw	1235	w	1232	3		ν_{23}
1214 *R* ?								
1207 *Q*	*A*	w	1200	m	1198	4	6/7	ν_9
1200 *P* ?								
			1161	w	1164	2		ν_{24}
			1123	m				ν_{25}
			1100	vvw	1103	7	0.24	ν_{10}
					1080	1		$\nu_{15}+\nu_{17}=1081$
1031 *R*								
1024 *Q*	*A*	s	1018	s	1018	25	0.26	ν_{11}
1017 *P*								
			971	w				ν_{26}
947 *R*								
940 center	*B* ?	vw	938	m	934	4	6/7	ν_{27}
932 *P*								
910 center	*B* ?	w	902	m	901	21	6/7	ν_{28}
856 *R*								
851 *Q*	*A*	vs	830	vs(brd)	829	20	0.30	ν_{12}
848 *Q*	*A* ?	vs	830	vs (brd)	829	20	0.30	ν_{13}
843 *P*			815	m(sh)				ν_{29}
			795	vvw(sh)				?
			780		781	2		ν_{14}
724 *R*								
717 *Q*	*A*	s	715	s	715	12	0.35	ν_{15}
711 *P*								
			702	w(sh)				$2\nu_{30}+\nu_{18}=719$
675 center		vvw	679	vvw				$\nu_{16}+\nu_{18}=690$
630 center		vw	615	vvw	618	5	0.48	ν_{16}
538 *R*								
530 *Q*	*A*	m	525	m	528	17	0.42	ν_{16}
524 *P*								
376 *R*								
370 *Q*	*A*	m	363	m	366	24	0.38	ν_{17}
365 *P*								
355 *Q*								
303 center		w						$2\nu_{18}=301$
291 *R*								
286 center	*B*	s			287	9	6/7	ν_{30}
280 *P*								
215 *R*								
207 center		vw						Impurity
199 *P*								
171 ?								ν_{18} hot band
159 *Q*		w			165	8	*p*	ν_{18} 1←0
142 *Q*		w						ν_{18} 2←1

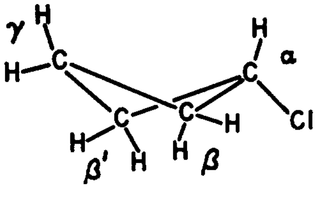
[a] s, m, w, v, p denote strong, medium, weak, very, and polarized, respectively; *P*, *Q*, *R* refer to rotational branches of a single band; sh and brd denote shoulder and broad.

TABLE II. Infrared and Raman spectra of chlorocyclobutane-d_1.[a]

Infrared gas (cm^{-1})	Band type	Relative intensity	Infrared liquid (cm^{-1})	Relative intensity	Raman (Δcm^{-1})	Relative intensity	Depolarization factor	Assignment
2999 *Q*		vs						ν_2
			2989	vs	2977	87	0.48	ν_{19}, ν_{20}
2985 *Q*		s						
2967 *Q* ?		ms	2950	vs	2949	100	0.32	ν_3
2957 *Q*		ms	2920	w(sh)	2921	49	0.47	ν_4
			2890	m				$\nu_6+\nu_7=1501$
2885 center		m	2875	m	2877	25	0.48	$2\times\nu_6=2922$
			2860	m	2853	24	0.52	ν_5
			2290	vw				$\nu_9+\nu_{11}=2294$
			2250	vw(sh)				$2\times\nu_{10}=2240$
2233 center		w	2223	m	2226	33	0.40	ν_1
			2165	w	2167	<1		$\nu_{10}+\nu_{11}=2170$
			1461	m	1461(sh)	4		ν_6
1452 *Q*	*A*	w	1442	s	1441	19	0.40	ν_7
1445 ?		vw(sh)	1431	s				ν_{21}
			1295	w				$\nu_{14}+\nu_{16}=1299$
1258 *R*								
1251 *Q*	*A* and *B*	m	1244	vs	1244	4		ν_9, ν_{22}
1244 *P*								
1212 ?		vvw	1206	w	1207	7	0.71	ν_{23}
			1165	w	1167	4		ν_{24}
1133 *R*								
1127 *Q*	*A*	m	1119	s	1120	7		ν_{10}, ν_{25}
1119 *P*								
			1092	vvw	1089	<1		$\nu_8+\nu_{18}=1088$
1065 *R*								
1054 *Q*	*A*	s	1050	s	1050	20	0.28	ν_{11}
1051 center	?	m	1042	w	1040(sh)	8		$2\times\nu_{16}$
1047 *R*								
938 *R*		m						
932 *Q*	*A*	m	924	s	924	49	0.30	ν_8, ν_{27}
924 *P*		m						
905 ?		vvw	900	m	903	28	6/7	ν_{28}
			820	vvw(sh)	824	2		ν_{12}, ν_{29}
797 *R*		m						
790 *Q*	*A*	m	780	s	779	15	0.42	ν_{13}, ν_{14}
783 *P*		m						
			745	w	745	4		ν_{26}
720 *R*		mw						
713 *Q*	*A*	mw	710	s	712	25	0.32	ν_{15}
705 *P*		mw						
677 center		vvw	675	w				$\nu_{16}+\nu_{18}=675$
620 center		vvw(brd)	610	w	613	3		ν_{16}'
525 center		w(brd)	520	s	522	25	0.30	ν_{16}
360 center		w(brd)	361	s	365	37	0.34	ν_{17}
					285	14	6/7	ν_{30}
					163	4		ν_{18}

[a] s, m, w, v, p, denote strong, medium, weak, very, and polarized, respectively; *P*, *Q*, *R* refer to rotational branches of a single band; sh and brd denote shoulder and broad.

discussion of the various vibrational motions, the carbons and associated hydrogens in chlorocyclobutane are denoted using the Greek letters α, β, β', and γ:



The fundamental frequency assignments of chlorocyclobutane have been made using isotopic substitution at the α and β, β' positions, the band envelopes in the infrared spectra of the vapor phases of both the normal and deuterium compounds, along with the other following pertinent data: the intensity of both the Raman and infrared absorptions, the depolarization values of the Raman lines, and information about expected location of analogous vibrations from spectra of similar molecules. It is believed that these assignments are reasonably accurate since the product rule is obeyed in all cases, and there is no crossing within a given symmetry species.[15] The discussion of the normal modes appears in the following order: (1) C–H stretching

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[15] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1945), p. 269.

TABLE III. Infrared and Raman spectra of chlorocyclobutane-d_4.[a]

Infrared gas (cm^{-1})	Band type	Relative intensity	Infrared liquid (cm^{-1})	Relative intensity	Raman (Δcm^{-1})	Relative intensity	Depolarization factor	Assignment
2997 *R* ?		m(sh)						
2990 *Q*		vs	2975	vs	2974	72	0.57	ν_1, ν_2
2972 *Q*		vs	2955	vs	2953	100	0.31	ν_3
2963 *R* ?		s(sh)						
2892 center		m	2879	s	2877	30	0.19	$2\times\nu_6=2920$
2257 *Q*		s	2247	vs	2245	53	6/7	ν_{19}, ν_{20}
2248 *R* ?		m(sh)						
			2215	w				$\nu_{11}+\nu_{22}=2216$
			2195	w	2198	52	0.26	ν_4
			2168	m(sh)				
2171 *Q*		m	2156	s	2156	44	0.35	ν_5
2162 ?		m(sh)						
					2124	30	0.34	$2\nu_{21}=2144$
2083 center		w(brd)	2074	m				$\nu_6+\nu_{15}=2082$
			2035	vw				$\nu_{12}+\nu_{22}=2033$
1465 *R*								
1460 *Q*	*A* ?	w	1453	m	1452	13	0.60	ν_6
1454 *P*								
1273 *Q*		s(sh)	1262	vs	1263	5		ν_8
1264 *Q*		vs	1254	s(sh)				$\nu_{17}+\nu_{25}=1253$
1254 ?		s(sh)	1242	s(sh)	1242	7	6/7	ν_{22}
			1205	vvw(sh)	1204	3		$\nu_{10}+\nu_{30}=1200$
					1149	2		$\nu_{17}+\nu_{28}=1153$
1143 center	*A* or *C*	w	1136	m	1133	25	0.22	ν_7
1107 *R* ?								
1100 *Q* ?			1092	m	1092	7	6/7	ν_{24}
1193 *P*								
1074 center		vvw	1074	m				ν_{21}
1052 *R*								
1045 *Q*	*A*		1040	m	1038	12	0.53	ν_9
1037 *P*								
			1024	w				$\nu_{16}+\nu_{16}'=1034$
			1004	vvw	1005	5		$\nu_{13}+\nu_{30}=1025$
987 *R*								
982 *Q*	*A*	m	975	m	974	24	0.27	ν_{11}, ν_{23}
973 *P*								
939 *R*			936 (sh)	m	934	14	6/7	ν_{10}
931 center	*B*	vs	924	vs	924	12	6/7	ν_{25}
927 *P*			824	vw(sh)	824	24	6/7	ν_{28}
809 *R* ?								
805 *Q*	*A* ?	s	794	s	794	26	0.30	ν_{12}, ν_{27}
801 *Q*								
798 *P* ?								
779 *P*								
772 *Q*	*A*	m(sh)	765	s	761	56	0.36	ν_{13}
765 *R*								
			725	vvw	727	4		$\nu_{16}+\nu_{30}=737$
691		vvw	684	vvw				$\nu_7+\nu_{30}=688$
639 *R*								
634 *Q*	*A* ?		634	m	630	7	0.72	ν_{15}, ν_{29}
622 *P*								
573 center		vvw	570	vw	561	2		ν_{16}'
484 *R*								
477 center	*A*	m(brd)	474	s	473	41	0.40	ν_{16}
474 *P*								
326 center		vvw	324	vvw	329	32	0.42	ν_{17}
268 *R*								
262 center	*B*	w			264	19	6/7	ν_{30}
255 *P*								
219 center								Impurity ?
144 *Q*								ν_{18} 1←0
139 *Q*								ν_{18} hot band
131 *Q* ?								ν_{18} 2←1

[a] s, m, w, v, p denote strong, medium, weak, very, and polarized, respectively; *P*, *Q*, *R* refer to rotational branches of a single band; sh and brd denote shoulder and broad.

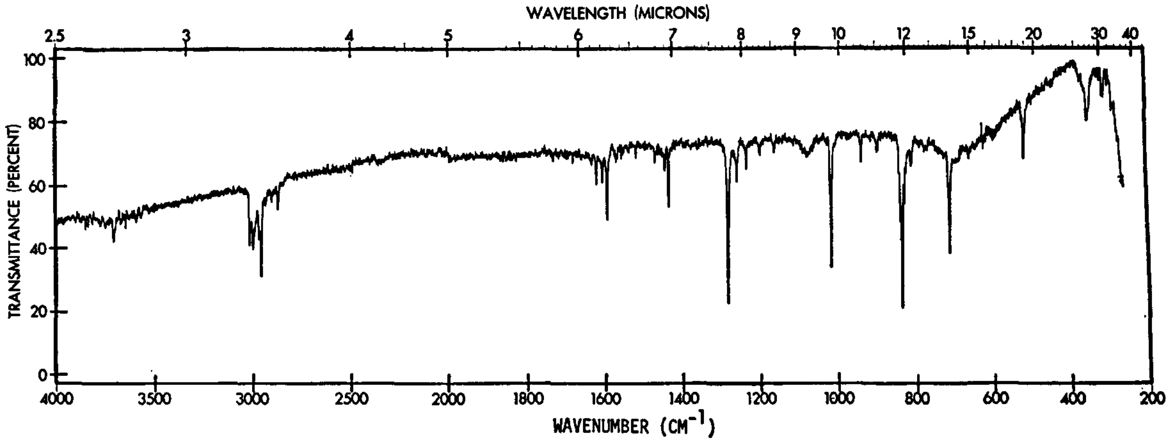

FIG. 5. Infrared spectrum of chlorocyclobutane isolated in a 1000:1 Ar matrix.

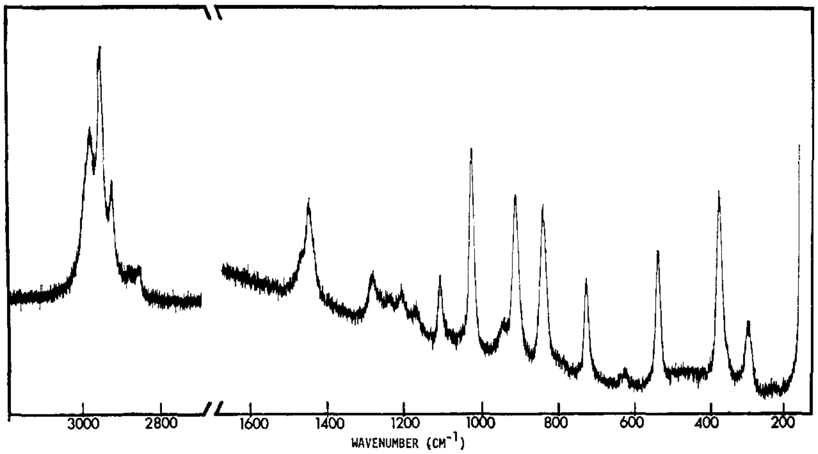

FIG. 6. Raman spectrum of chlorocyclobutane. Cell, 0.2 ml, 2-mm diam; slit double 10 cm×10 cm^{-1}; sensitivity, 2.6×200; period, 2.0 sec; scan, 0.5 cm^{-1}/sec; zero suppression, 1.90.

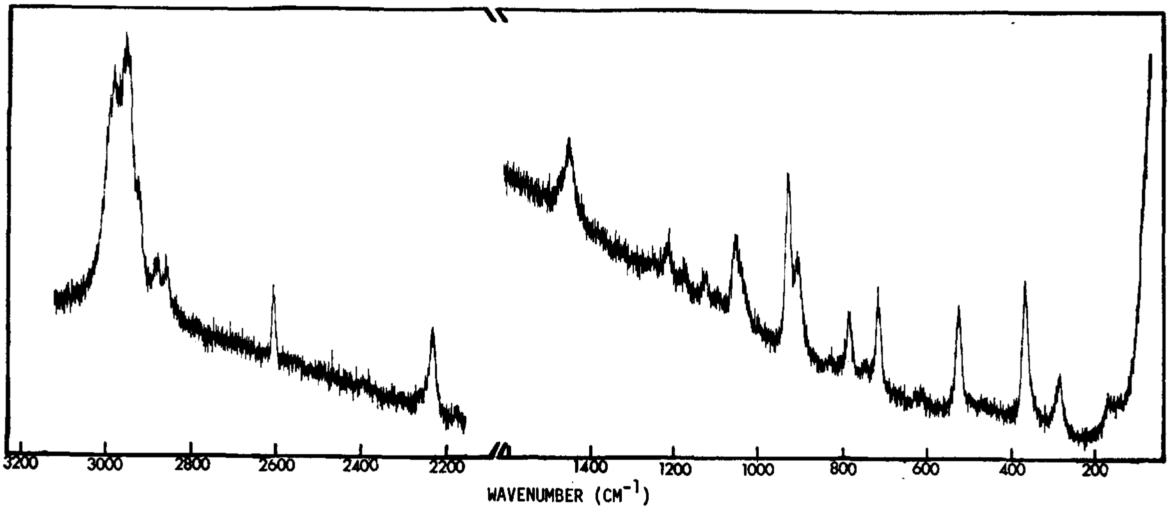

FIG. 7. Raman spectrum of α-chlorocyclobutane-d_1. Cell, 0.2 ml, 2-mm diam; slit single, 10 cm×10 cm^{-1}; sensitivity, 2.0×500; period 2.5 sec; scan, 0.5 cm^{-1}/sec; zero suppression 4.85.

TABLE IV. Infrared spectrum of chlorocyclobutane in an argon matrix[a]

Frequency (cm^{-1})	Intensity	Assignment	Frequency (cm^{-1})	Intensity	Assignment
3015	m	ν_1	1242	m	ν_9
3000	m	ν_2	1207	vw	ν_{23}
2984 sh	w	ν_{19}	1172	vw	ν_{24}
2977 sh	m	ν_{20}	1100	vvw	ν_{10}
2957	s	ν_3	1075	w	Impurity[b]
2902	vvw	2×6	1018	vs	ν_{11}
2887	vvw	$\nu_7+\nu_{21}$	940	w	ν_{27}
2870	w	ν_5	900	w	ν_{28}
1620	w	νH_2O	842 sh	m	ν_{12}
1603	w	νH_2O	837	vs	ν_{13}
1592	m	νH_2O	831 sh	m	$\nu_{16}+\nu_{30}$
1460	vw	ν_6	815	w	ν_{29}
1447	w	ν_7	722 sh	w	$2\nu_{17}$
1435	m	ν_{21}	715	s	ν_{15}
1289	vs	ν_8	525	ms	ν_{16}
1266	m	ν_{22}	361	ms	ν_{17}

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder.

[b] This band varied in intensity depending on purity of compound.

vibrations, (2) CH_2 bending modes, (3) ring deformations, (4) halogen and α-hydrogen bending vibrations, and (5) combinations, overtones, and matrix spectrum. Each of these categories is discussed with respect to the two symmetry species.

CH STRETCHING VIBRATIONS

Species A'

There are five vibrations symmetric to the plane of symmetry which can adequately be described as CH stretching motions and which belong to symmetry species A'. In both the Raman and infrared spectra these vibrations are very near coincident in frequency (see Figs. 1, 5, and 6). The Raman depolarization values and the shifts observed upon deuteration have made the assignment of these vibrational modes relatively certain. In order to cut out some of the overlapping of the bands in the 3000-cm^{-1} region, the infrared spectrum of chlorocyclobutane in an argon matrix was investigated (mole ratio 1:1000). A weak band at 3015 cm^{-1} is assigned as the α-CH stretching vibration. The corresponding band in the spectrum of bromocyclobutane has been shown to disappear upon α deuteration.[16] The Raman line centered at 2979 cm^{-1} is very broad (see Fig. 6) and would obscure a weak absorption near 3000 cm^{-1}. In the Raman spectrum of the monodeuterated molecule, the α-CD vibration is found at 2226 cm^{-1} and the band is polarized. The shift of 1.34 is approximately what one might expect for a carbon–hydrogen stretching vibration. For the tetradeuterated molecule, this vibration is again part

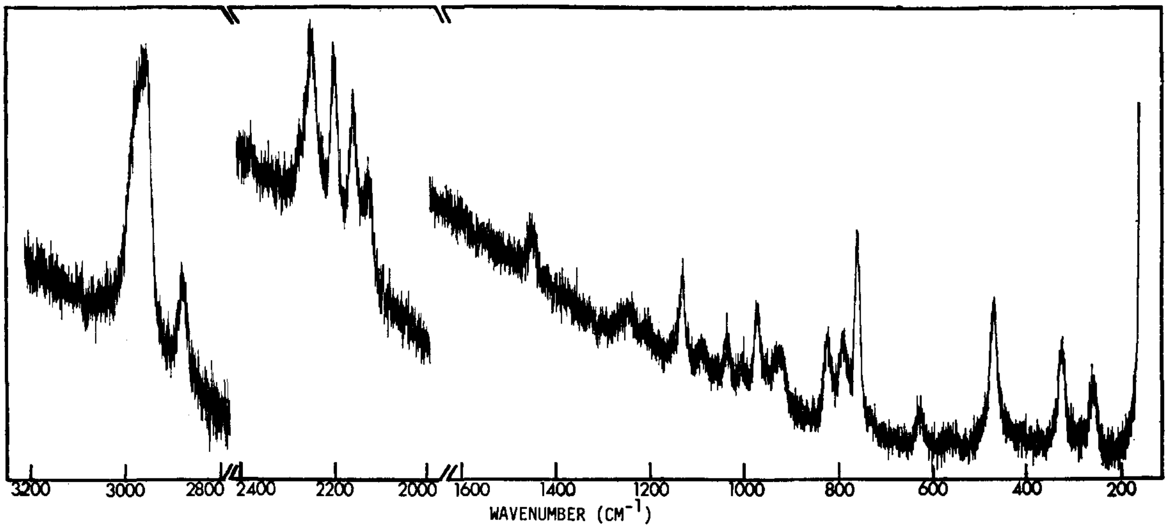

FIG. 8. Raman spectrum of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$. Cell, 0.2 ml, 2-mm chain; slit double 10 cm^{-1}×10 cm; sensitivity, 1.7×100; period, 2.5 sec; scan, 0.5 cm^{-1}/sec; zero suppression 4.67, 6.44, and 9.50.

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[16] J. R. Durig and W. H. Green, "Vibrational Spectra and Structure of Four-Membered Ring Molecules. III. Bromocyclobutane, Bromocyclobutane-d_1, Bromocyclobutane-d_4, and Bromocyclobutane-d_5." J. Chem. Phys. (to be published).

of a very broad Raman line centered at 2974 cm^{-1} (see Fig. 8). The γ-CH_2 symmetric and antisymmetric[17] stretching vibrations should remain at relatively the same frequency in the spectra of the light and heavy molecules. The γ-CH_2 antisymmetric stretching vibration is normally found at the higher frequency and it is, therefore, assigned to the Raman lines at 2979 cm^{-1} for normal chlorocyclobutane, at 2977 cm^{-1} for the monodeuterated molecule, and at 2974 cm^{-1} for the tetradeuterated compound. The γ-CH_2 symmetric stretching vibration is assigned to the strongly polarized Raman lines at 2953 cm^{-1}, 2949 cm^{-1}, and 2953 cm^{-1} for the normal, monodeuterated, and tetradeuterated compounds, respectively.

The polarized Raman line at 2877 cm^{-1} in the spectrum of chlorocyclobutane-d_4 was first thought to be the α-CH stretching mode. However, the Raman spectra of both $\alpha,\beta,\beta,\beta',\beta'$-bromocyclobutane-$d_5$ [16] and $\alpha,\beta,\beta,\beta',\beta'$-cyclobutanol-$d_5$ [16] showed a corresponding polarized line of approximately the same intensity and frequency. Therefore, the 2877-cm^{-1} Raman line is assigned as the first overtone of the γ-CH_2 deformation found at 1452 cm^{-1} and its intensity results from Fermi resonance with the γ-CH_2 stretching vibrations.

The two β-CH_2 in-phase stretching vibrations belong to symmetry species A'. The antisymmetric stretching mode is assigned to the polarized Raman line at 2923 cm^{-1} for the normal compound and to the 2921 cm^{-1} Raman line for the monodeuterated molecule. The line shifts to 2198 cm^{-1} upon tetradeuteration. The β-CH_2 symmetric stretching vibration is assigned to the relatively weak, polarized Raman line at 2854 and 2853 cm^{-1} in the spectra of the light and monodeuterated compounds, respectively. Upon deuterium substitution at the β positions, the Raman line shifts to 2156 cm^{-1}.

Species A''

The two out-of-phase stretching motions of the β-hydrogens should give rise to depolarized Raman lines. The antisymmetric and symmetric stretching vibrations are assigned as near coincident lines. In the infrared and Raman spectrum of liquid chlorocyclobutane (see Figs. 1 and 6), the absorption centered at 2979 cm^{-1} is very broad. The infrared spectrum of the matrix shows a splitting of this intense absorption into several overlapping bands (see Fig. 5). Thus, the shoulder at 2989 cm^{-1} in the infrared spectrum of the light compound is assigned as the β-CH_2 antisymmetric stretching vibration and the absorption centered at 2979 cm^{-1} is assigned to the corresponding symmetric vibration. The Raman line at 2979 cm^{-1} can be considered depolarized even though the factor is less than 6/7. Some of the intensity is certainly coming from coincident polarized lines previously discussed. The spectrum of chlorocyclobutane-d_1 shows the same pattern with the frequencies being unchanged. Deuteration at the β-positions results in a shift of the Raman line to 2245 cm^{-1}. There appears to be a shoulder on the 2245 cm^{-1} Raman line (see Fig. 8) which we have assigned as the β-CD_2 antisymmetric stretching vibration and the main line is assigned as the symmetric mode. The infrared spectrum of the vapor showed ill defined band envelopes in both the C–H and C–D stretching regions and, consequently were of little assistance in making the fundamental assignments.

CH_2 BENDING MODES

Species A'

In the methylene scissoring region, three absorption bands were observed in the infrared spectrum of liquid chlorocyclobutane whereas only two Raman lines were found. As noted for other four-membered ring molecules,[9] the γ-CH_2 scissoring motion is assigned to the highest frequency observed in the 1400-cm^{-1} region. Therefore, the Raman line at 1465 cm^{-1} is attributed to the γ-CH_2 deformation; the line appears to be depolarized, but the depolarization value of 6/7 has been observed for the similar vibration in other compounds.[18] The infrared spectrum of the liquid shows the corresponding band to be centered at 1468 cm^{-1}. For chlorocyclobutane-d_1, the γ-CH_2 deformation is observed at 1461 cm^{-1} in both the Raman and infrared spectra of the liquid and upon tetradeuteration the band shifts to 1452 cm^{-1} and the Raman line appears to be slightly polarized. The Raman line at 1442 cm^{-1} which is the strongest in this region is assigned to the β-CH_2 in-phase deformation. The infrared spectrum of the liquid shows a band centered at the same frequency. The exchange of the α hydrogen with deuterium causes no shift in the frequency of this normal mode. Deuterium substitution in the β positions causes the band to shift to 1133 cm^{-1}. The infrared spectrum of the vapor shows a band envelope which appears to be a mixture of Type *A* and Type *C* band contours which is the expected envelope for a band of this symmetry species.

The 1207-cm^{-1} band which has a central *Q* branch and must belong to symmetry species A' has been assigned to the β-CH_2 wagging (in-phase) vibration. The band is believed to be in coincidence with the γ-CH_2 wagging vibration at 1251 cm^{-1} for the monodeuterated compound. With tetradeuteration the band shifts to the Type *A* band at 1045 cm^{-1} and the corresponding Raman line is observed at 1038 cm^{-1} and it is polarized. The β-CH_2 twisting vibration (in phase) is assigned to the polarized Raman line at 1103 cm^{-1}. However, the band appears to shift to a slightly higher frequency with monodeuteration and the band center

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[17] The term antisymmetric here does not imply that the vibration is antisymmetric with respect to the plane of symmetry but rather that the two hydrogens on the γ-carbon atom are moving out of phase with one another, i.e., one CH bond is compressed, while the other CH bond is being stretched.

[18] R. C. Lord and D. G. Rea, J. Am. Chem. Soc. **79**, 2401 (1957).

is obscured by the near coincidence of the 1127-cm^{-1} band. The infrared spectra of both the liquid and vapor phases of chlorocyclobutane-d_1 show very intense absorption near 1120 cm^{-1} and we believe the coupling of some of the vibrations in the 1100-cm^{-1} region for the light compound is entirely different from that observed for the monodeuterated molecule. Therefore, the 1127-cm^{-1} band is assigned to the β-CH$_2$ twisting vibration of symmetry species A'' and the Q branch is contributed by the β-CH$_2$ twisting vibration for chlorocyclobutane-d_1. On deuterium substitution at the β positions, the β-CH$_2$ twisting mode is believed to have shifted to the 934-cm^{-1} Raman line.

Two CH$_2$ bending modes remain to be assigned in symmetry species A' and both are rocking motions. The assignment of rocking vibrations is very difficult since they are usually very weak in intensity and their frequency shifts drastically with the change of environment of the CH$_2$ group. Therefore, the assignment of these rocking motions is somewhat arbitrary. The γ-CH$_2$ rocking mode is assigned to a shoulder on the high-frequency side of the 830-cm^{-1} band which was observed in the infrared spectrum of liquid chlorocyclobutane. The infrared matrix spectrum shows the frequency of this shoulder to be about 842 cm^{-1}. The band shifts to 824 cm^{-1} upon monodeuteration and to 794 cm^{-1} with tetradeuteration. The latter two frequencies are Raman values. This rocking vibration should give rise to a Type C band in the infrared spectrum of the vapor, and the observed envelope (see Fig. 3) appears to have predominantly "C" character with the main Q branch at 805 cm^{-1}. The β-CH$_2$ rocking vibration is assigned to the weak Raman line at 781 cm^{-1} for the light compound and it remains unchanged in frequency and in coincidence with a ring deformation at 779 cm^{-1} for the monodeuterated compound. This vibration was not observed in the spectra of the tetradeuterated species, but bromocyclobutane and its deuterated analogs have nearly comparable vibrational assignments[16] with only slightly lower frequencies and the β-CH$_2$ rocking mode for bromocyclobutane-d_4 has been assigned to a polarized Raman line at 576 cm^{-1}. Thus, it is estimated with good certainty, that the frequency of β-CH$_2$ rocking vibration of chlorocyclobutane-d_4 is near 600 cm^{-1}.

Species A''

Six CH$_2$ bending vibrations fall in the symmetry species A''. These vibrations can be approximately described as a β-CH$_2$ scissoring (out of phase), γ-CH$_2$ twisting, β-CH$_2$ twisting (out of phase), γ-CH$_2$ wagging, β-CH$_2$ wagging (out of phase), and a β-CH$_2$ rocking (out of phase) vibrations. The β-CH$_2$ scissoring vibration is attributed to the infrared band at 1430 cm^{-1} observed in the spectrum of liquid chlorocyclobutane. This deformation is unchanged in frequency in the spectrum of chlorocyclobutane-d_1, but it shifts to 1074 cm^{-1} for the tetradeuterated compound. There appears to be no corresponding Raman lines for these infrared bands. The two shoulders at 1261 and 1235 cm^{-1} on the 1279-cm^{-1} band in the infrared spectrum of liquid chlorocyclobutane are assigned to the γ-CH$_2$ and β-CH$_2$ wagging vibrations, respectively. For the monodeuterated molecule, the γ-CH$_2$ wagging is in coincidence with the wagging of symmetry species A' and shifts to 1254 cm^{-1} with tetradeuteration. The β-CH$_2$ wagging vibration shifts to 1207 cm^{-1} on α-deuteration and to 974 cm^{-1} with deuteration at the β-positions. The latter two frequencies are taken from the Raman spectra. The 1164-cm^{-1} Raman line which appears to be depolarized is assigned as the γ-CH$_2$ twisting vibration for chlorocyclobutane and it shifts to 1092 cm^{-1} with tetradeuteration. The β-CH$_2$ twisting mode has been assigned to the 1123-cm^{-1} infrared liquid band and discussed previously. With deuterium substitution at the β positions the vibration shifts to the 931-cm^{-1} band which has a well-defined Type B contour. The methylene bending vibration which remains to be assigned is a β-CH$_2$ rocking motion. The matrix infrared spectrum shows a splitting of the intense band at 830 cm^{-1} with a well-defined band at 815 cm^{-1} which is assigned as this final rocking mode. No shift is observed on monodeuteration, but on tetradeuteration it is believed that the band shifts in coincidence with a symmetric ring deformation at 634 cm^{-1}.

RING DEFORMATIONS

Species A'

In addition to the ring-puckering vibration, there are three symmetric ring vibrations which belong to symmetry species A'. They are assigned to the polarized lines at 1018, 829, and 715 cm^{-1} in the Raman spectrum of the light compound. The 1018-cm^{-1} line can be described as a ring-breathing mode. The description is based on the intensity and depolarization value of the Raman line. The line shifts to 1050 cm^{-1} upon monodeuteration and back to 974 cm^{-1} for chlorocyclobutane-d_4. The rather large shift with deuterium substitution in the α position shows the vibration is strongly coupled with the other hydrogenic atom motions. Also, it should be pointed out that what may be an appropriate description of a vibration for the normal molecule may not be at all descriptive of the vibration after deuterium substitution. Therefore, it is believed that these normal modes cannot be characterized as strictly ring deformations, but that they are ring modes with a considerable amount of mixing with other motions. The second symmetric ring deformations shifts from 829 to 779 cm^{-1} with monodeuteration. The envelope of the 848-cm^{-1} band for the light molecule is poorly defined, mainly because additional vibrational fundamentals are observed in the same general frequency range. The infrared spectrum (see Fig. 5) of the matrix shows the general complexity of the absorption near 837 cm^{-1}. The second ring deformation continues to shift to lower frequency with the substitution of deuterium at the β positions and the very strong Raman line at 761 cm^{-1} is assigned to this normal mode for chlorocyclobutane-d_4. The third symmetric ring mode which is assigned to the 715-cm^{-1} Raman line shifts to 712 cm^{-1} on single deuterium substitution and to 630 cm^{-1} on tetradeuteration. In the infrared spectrum of both chlorocyclobutane and chlorocyclobutane-d_1 Type *A* bands are found at 717 and 713 cm^{-1}, respectively, but the band contour of the 634 cm^{-1} infrared band for the tetradeuterated molecule is probably distorted by a CD_2 rocking vibration in near coincidence.

The ring-puckering vibration is the most interesting vibration of the chlorocyclobutane molecule. The vibration is expected to be the band of lowest frequency and it is readily assigned to the weak absorption in the 120–160-cm^{-1} region of the far infrared spectrum. In our earlier investigation[1] of the far infrared spectrum of chlorocyclobutane we assigned the *Q* branch at 159 cm^{-1} as the ring-puckering fundamental and the 142-cm^{-1} band as the first "hot band." The Raman spectrum of liquid chlorocyclobutane has a band at 165 cm^{-1}. The frequency of the vibration in the liquid phase is expected to be higher than that found in the gas phase[19] which provides part of the basis for assigning the 159-cm^{-1} band as the fundamental transition. Additional evidence for assigning the fundamental transition to the 159-cm^{-1} band is provided by the gas-phase contour itself. If the potential well is broader than an harmonic well the hot bands will fall on the low-frequency side of the fundamental transition and the band is expected to have a broad "tail" on the low-wavenumber side. However, if the potential function is quartic or near quartic, then the hot bands are expected to fall at higher wavenumbers than the fundamental transition. The band contour of the ring-puckering vibration of chlorocyclobutane clearly shows the "hot bands" fall on the low-frequency side of the zero to one transition. Since the publication of our earlier far-infrared studies of chlorocyclobutane Rothschild[20] has proposed an asymmetric potential function in which the molecule becomes more and more planar with increasing quanta of the ring-puckering vibration. With this potential function Rothschild[20] has calculated the expected "hot bands" for bromocyclobutane. From this calculation one would predict the first hot band transition for the ring-puckering vibration of chlorocyclobutane to fall near 140 cm^{-1} which compares well with the 142 cm^{-1} observed. Although the agreement may seem fortuitous, the over-all band shape certainly supports the potential function proposed by Rothschild.

The far-infrared spectrum of $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$ was recorded from 300 to 33 cm^{-1} (see Fig. 4). The fundamental transition has shifted to 144 cm^{-1} and there are possibly two additional *Q* branches on the low-frequency side of the main peak. The shift by a factor of 1.1 with tetradeuteration is considerably smaller than the 1.2 factor found for the cyclobutanone molecule with similar deuteration.[6] However, the gross differences in the nature of the potential governing the ring-puckering vibration for the two molecules along with the differences in the masses does not make the result too surprising. The shift with deuteration is expected to be relatively constant for successive hot-band transitions. Thus, the 139-cm^{-1} band cannot represent the one to two transition, but the 131-cm^{-1} band has the expected frequency for the first hot band. There was also an apparent peak near 122 cm^{-1}, but a dip is found in the background at the same frequency and the band is thought to be the result of background absorption (see Fig. 4). There was a very small amount of absorption in the 45 to 95 cm^{-1} range, but below 45 cm^{-1} the absorption became quite pronounced. This latter absorption is the result of pure rotation and not associated with the ring-puckering vibration. There was also a very weak band centered at 219 cm^{-1}. The band appeared to have a Type *B* contour and it is considered to arise from a small amount of cyclopropylcarbinyl chloride impurity rather than from a hot band of the ring-puckering vibration. Although the *Q* branches for the ring-puckering vibration of tetradeuterated chlorocyclobutane are not pronounced, the over-all band contour is very similar to that found for the corresponding vibration for the "light" molecule. Again, the band contour supports the potential function proposed by Rothschild. The transitions are not definite enough for quantitative calculations on the potential function, but there is little question that the potential function is broad, which is in marked contrast to the quartic function used to predict the ring-puckering transitions of trimethylene oxide[3–5] and cyclobutanone.[6,7]

Species A''

There are two antisymmetric ring deformations which should give rise to depolarized Raman lines. Two depolarized Raman lines are found at 934 and 901 cm^{-1} which appear to have the expected shift upon deuteration for ring modes. The corresponding bands in the infrared spectrum appear quite weak, but this is not unusual for ring modes. The substitution of deuterium for the α-hydrogen makes the 938-cm^{-1} band shift in coincidence with the α-CD in-plane bending vibration at 924 cm^{-1}. In the Raman spectrum of chlorocyclobutane-d_4 these ring deformations are found at 794 and 824 cm^{-1}, respectively. The Raman line at 824 cm^{-1} is depolarized and the corresponding infrared band is very weak whereas the 794-cm^{-1} ring mode is in coin-

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[19] W. G. Fateley, I. Mastubara, and R. E. Witkowski, Spectrochim. Acta **20**, 1461 (1964).

[20] W. G. Rothschild, J. Chem. Phys. **45**, 1214 (1966).

cidence with ν_{12}. The relative intensity of the 934-cm^{-1} Raman line was only 4 in the normal compound and the intensity could be considerably less than that for the tetradeuterated molecule and thus it might contribute very little to the intensity of the 794-cm^{-1} Raman line.

VIBRATIONS ASSOCIATED WITH THE α-CARBON ATOM

Species A'

There are six normal vibrations which can be associated with the α-carbon atom. Three are carbon–hydrogen motions and three are associated with the carbon–chloride bond. All the vibrations of the α-carbon group are quite readily assigned, although the carbon–halogen motions are found at a considerably lower frequency than generally reported for other monochloro-substituted hydrocarbons. The intensity and depolarization values of the Raman lines which result from the C–Cl motions, makes the assignment of these fundamental modes quite certain. The assignment of the two α-CH bending modes is also confidently given since deuterium substitution was carried out at the α position.

The α-CH stretching vibration has been assigned earlier and the in-plane bending vibration is assigned to the Raman line at 1277 cm^{-1} with the corresponding band in the infrared spectrum found as an intense absorption at 1279 cm^{-1}. The infrared spectrum of the vapor shows the band to have a typical Type *A* contour (see Fig. 1). The frequency of this CH bending vibration is considerably higher than might be expected for such a motion. The main basis for our assignment is the disappearance of the Raman line at 1277 cm^{-1} on monodeuteration and its reappearance on tetradeuteration. The infrared absorption at 1288 cm^{-1} appears too intense for the α-CH in-plane bending (Fig. 1) but there is more than one vibration contributing to the intensity of the 1288-cm^{-1} band. Upon monodeuteration a medium intense Type *A* band appears at 932 cm^{-1} and is assigned to the α-CD in-plane bending vibration. Upon tetradeuteration, the line reappears at 1263 cm^{-1} in the Raman spectrum and at 1262 cm^{-1} in the infrared spectrum of the liquid. It was not possible to decipher the infrared spectrum of the vapor for band contours in 1200–1300-cm^{-1} region (see Fig. 3).

The carbon–chloride stretching vibration is found at 530 cm^{-1} in the vapor spectrum. The strong, polarized Raman line at 528 cm^{-1} confirms the assignment. The frequency is considerably lower than that found for most other carbon-chloride stretching vibrations which normally appear between 700–750 cm^{-1}. The band shifts to 522 and 473 cm^{-1} upon mono- and tetradeuteration, respectively. Such a shift shows some coupling of the carbon–chloride motions with other vibrations of the molecule. The chloride in-plane bending vibration is assigned to the strong, polarized Raman line at 366 cm^{-1}, in the light compound. This vibration shifts in the Raman effect to 365 and 329 cm^{-1} on mono- and tetradeuteration, respectively. The band contours of the infrared spectra of the vapors are very ill defined.

Species A''

There are two motions of the α carbon which belong to symmetry species A'' and these are out-of-plane bending vibrations of the chloride and hydrogen atoms. The α-CH bending is expected to be weak in both the Raman and infrared spectrum. In the Raman spectrum of monodeutero-chlorocyclobutane a weak depolarized Raman line appears at 745 cm^{-1} which was not observed in the Raman spectrum of the normal compound and it is thus assigned as the α-CD bending mode. Assuming a reasonable shift upon deuteration one would expect the corresponding vibration to be near 1000 cm^{-1} for the light molecule. In the infrared spectrum of the liquid a weak band is observed at 971 cm^{-1} which is assigned as the α-CH bending vibration. On deuteration at the β carbons the band is masked by the intense absorption of the ring-breathing vibration at 982 cm^{-1}, but it is estimated to be near 970 cm^{-1}. The C–Cl bending mode is assigned to the Type *B* band centered at 286 cm^{-1} in the infrared spectrum of gaseous chlorocyclobutane. This vibration is observed at 285 cm^{-1} in the Raman spectrum on monodeuteration. The shift observed upon tetradeuteration is to the well-defined Type *B* band at 262 cm^{-1} in the far-infrared spectrum (see Fig. 4) of the vapor. The above vibrational assignments of chlorocyclobutane and the deuterium derivatives are summarized in Table V.

OVERTONES, COMBINATIONS, AND MATRIX SPECTRUM

The low symmetry of the molecule, C_s, allows all combinations and overtones to be both Raman and infrared active. Many of the weak absorption bands can not be uniquely assigned, but reasonable assignments are given in Tables I, II, and III. Because of the large number of combinations and overtones, only the most interesting and questionable are discussed. The polarized Raman lines at 2880, 2877, and 2877 cm^{-1} for chlorocyclobutane, chlorocyclobutane-d_1, and chlorocyclobutane-d_4, respectively, are assigned as overtones of the γ-CH$_2$ deformation in Fermi resonance with the C–H stretching vibrations. In the region of the C–D stretching vibration for the tetradeuterated molecule, there are more absorptions bands than one would predict from the fundamental modes alone. However, this is not unexpected since the combination and overtone bands which normally fall in this region gain

TABLE V. Summary of fundamental frequencies of chlorocyclobutane, chlorocyclobutane-d_1, and $\beta,\beta,\beta',\beta'$-chlorocyclobutane-$d_4$.

Fundamental	Approximate description	Chlorocyclobutane frequency (cm^{-1})[a]	Chlorocyclobutane-d_1 frequency (cm^{-1})[a,b]	Chlorocyclobutane-d_4 frequency (cm^{-1})[a]
1	α-CH stretching	3015	2233	2974
2	γ-CH_2 antisymmetric stretching	3005	2985	2990
3	γ-CH_2 symmetric stretching	2967	2967	2972
4	β-CH_2 antisymmetric stretching	2923*	2921*	2198*
5	β-CH_2 symmetric stretching	2854*	2853*	2156*
6	γ-CH_2 scissoring	1480	1461*	1460
7	β-CH_2 scissoring	1455	1452	1133*
8	α-CH bending (in plane)	1288	932	1273
9	β-CH_2 wagging	1207	1251	1045
10	β-CH_2 twisting	1103*	1127	934*
11	Ring breathing	1024	1054	982
12	γ-CH_2 rocking	851	824*	794*
13	Ring deformation	848	790	772
14	β-CH_2 rocking	781*	790	(600)
15	Ring deformation	717	713	634
16	C–Cl stretching	530	525	477
17	C–Cl bending (in plane)	365	360	324
18	Ring puckering	159	163*	144
		Species A''		
19	β-CH_2 antisymmetric stretching	2989†	2989†	2247†
20	β-CH_2 symmetric stretching	2979*	2979*	2245*
21	β-CH_2 scissoring	1430†	1431†	1074†
22	γ-CH_2 wagging	1266	1251	1254
23	β-CH_2 wagging	1242	1207*	974*
24	γ-CH_2 twisting	1172	1167*	1092*
25	β-CH_2 twisting	1123†	1127	931
26	α-CH bending (out of plane)	971†	745*	(970)
27	Ring deformation	940	932	794*
28	Ring deformation	910	903*	824*
29	β-CH_2 rocking	815	820†	634
30	C–Cl bending (out of plane)	286	285*	262

[a] An asterisk denotes Raman frequencies and a dagger denotes infrared frequencies. Other frequencies are either infrared frequencies from the gas or matrix spectra.

[b] The apparent violations of Rayleigh's rule could arise from errors in determining band centers, use of values for different states, or obscure anharmonicity effects.

additional intensity from the relatively strong C–D stretching modes. There is one Raman line at 2124 cm^{-1} which is not assigned as a fundamental vibration and merits comment. The line is polarized and it can arise from any combination except those involving fundamentals of Species $A'+A''$. There are several combinations which fall near 2124 cm^{-1}, but all belong to symmetry species A''. It is believed that this line must be in Fermi resonance with a fundamental of higher frequency and shifted to a lower wavenumber. Thus, this polarized Raman line is tentatively assigned to $2\times\nu_{21}$ in Fermi resonance with the polarized Raman line at 2156 cm^{-1}.

The infrared spectrum of chlorocyclobutane isolated in an argon matrix was invaluable in making assignments of fundamentals which were in near coincidence. For example, in the carbon–hydrogen stretching region the Raman and infrared spectra of the liquid showed only broad absorption bands, but in the matrix spectrum these bands were well separated into the various fundamentals. This separation makes the assignment of the bands in the C–H stretching region, as previously discussed, rather certain. The very broad, intense band centered at 830 cm^{-1} in the infrared spectrum of the liquid was thought to be a multiple band. The matrix spectrum showed the band to be split into at least four resolved bands. The γ-CH_2 rocking, β-CH_2 rocking (in phase) and a symmetric ring deformation were assigned to three of the observed peaks. The fourth band was thought to be a combination of $\nu_{16}+\nu_{30}$.

Of particular interest is the 615-cm^{-1} infrared band (618-cm^{-1} Raman line) which apparently disappears in the matrix spectrum. Such behavior would be expected for a difference band but corresponding bands are found in the spectra of both chlorocyclobutane-d_1 and chlorocyclobutane-d_4. The shift of this band with deuteration at the α- and β-positions is the same as that found for the C–Cl stretching vibrations for the respective compounds which would suggest a difference band of the carbon–chloride stretching vibration. Difference bands give exact frequencies of the fundamentals which requires absorption bands at 1146 and 1135 cm^{-1} for the "light" and monodeuterated molecules, respectively, in order that the 618- and 613-cm^{-1} (α-deuterated compound) bands be difference bands involving the C–Cl stretching mode. Neither molecule has a fundamental within 15 wavenumbers of these values and the difference band assignment is disregarded. Thus, the data tend to support the existence of conformers as reported by Rothschild.[20] In the tetradeuterated chlorocyclobutane the additional C–Cl stretching vibration is observed at 561 cm^{-1} in the Raman spectrum. Thus, again the shift with deuteration is about the same as that observed for the main C–Cl stretching mode for β,β,β′,β′-chlorocyclobutane-d_4.

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Antiferromagnetic Structure of Anhydrous Cupric Sulfate $CuSO_4$

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The antiferromagnetic structure of anhydrous cupric sulfate is considered theoretically. The collinear magnetic structure determined from neutron-diffraction data is explained by the isotropic exchange and the dipole interactions, and the effect of the antisymmetric-exchange interaction is discussed.

INTRODUCTION

Recently, Almodovar *et al.*[1] have determined the antiferromagnetic structure of anhydrous cupric sulfate $CuSO_4$ by a neutron-diffraction study. Anhydrous cupric sulfate is antiferromagnetic below about 34.5°K.[2–6] Magnetic measurements reported by several authors revealed interesting behavior. Susceptibility measurement on a single crystal by Kreines[5] showed a large anisotropy in the antiferromagnetic state, particularly, an anomalous growth of $\chi_\perp$ with decreasing temperature near the antiferromagnetic transition point.

According to an analysis of the crystal structure,[7,8] $CuSO_4$ crystallizes in the orthorhombic space-group *Pbnm* (D_{2h}^{16}). The unit cell contains four Cu^{++} ions at sites 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Let the spins on each ion be represented by the vectors $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$, and $\mathbf{S}_4$, respectively. If the magnetic cell is identical with the chemical cell, it may be reasonable to assume a four-sublattice model. The sublattices are denoted as 1, 2, 3, and 4 corresponding to $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$, and $\mathbf{S}_4$ (Fig. 1). The spin configuration for the antiferromagnetic state determined by Almodovar *et al.* is the collinear ordering $+-+-$ on the sublattices 1, 2, 3, and 4 with the spin axes parallel to the *a* axis.

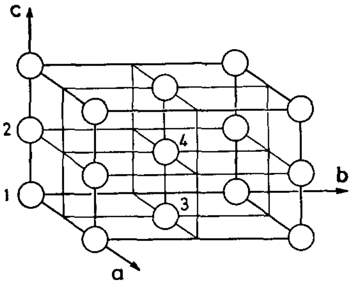

Fig. 1. The orthorhombic crystal structure of $CuSO_4$. The circles show the Cu^{++} site, and the numbers 1, 2, 3, and 4 indicate the four magnetic ions which constitute the sublattices, respectively. Lattice constants are $a=4.791$ Å, $b=8.391$ Å, and $c=6.811$ Å.

The purpose of the present paper is to discuss the ordered spin arrangement. The free Cu^{++} ion is in a $^2D_{5/2}$ state and a crystalline electric field of cubic

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