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Vibrational Spectra of Cubane and Four of Its Deuterated Derivatives

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Abstract: Vibrational spectra are reported for cubane, cubane-d_1, *sym*-cubane-d_2, *sym*-cubane-d_6, and cubane-d_8. Infrared spectra are from 400 to 3600 cm^{-1} for CS_2 and CCl_4 solutions, and for a solid deposited from the vapor at $\sim$100 K. Raman spectra are for the same solutions and for the polycrystalline solid at room temperature. Vibrational assignments have been made for all the fundamentals of all five compounds, 120 modes in all. The fortuitous crystal structure of cubane and cubane-d_8 was an important aid. Of the 18 fundamentals of cubane, only one or two are not certain. The spectra show almost no effect of the severe bond angle strain. Also there are no low molecular modes; the lowest for cubane is 617 cm^{-1}.

Introduction

Cubane, C_8H_8, has the carbon skeleton shown in Figure 1.[2] It is an exceptionally interesting molecule because of having the unusual cubic C_8 cage, very high symmetry, and a great deal of strain. The C-C-C angles are decreased from 109.5 to 90° at each of the eight corners, and this might be expected to produce some unusual vibrational frequencies. Hence a thorough study of its vibrational spectrum seemed desirable.

Cubane was first prepared by Eaton and Cole in 1964.[3] An X-ray diffraction study by Fleischer[4] showed that, within experimental error, the carbon frame is a cube and the hydrogen atoms lie on extensions of the cube diagonals. The C-C distance is 1.55 Å, almost exactly the same as in cyclobutane.

Very little is known about the vibrational spectrum. There are no published Raman data, and the only infrared results are from a survey spectrum obtained at the time of the original synthesis.[3] Only three bands were observed—just the number of fundamentals permitted by cubic symmetry. Recently some unpublished data of King, Cole, and Gayles has been quoted by others.[5] Both the data and the interpretation differ considerably from ours. Thus there is very little usable information on the vibrational spectrum of cubane in the literature.

This work is a cooperative project between our two laboratories. Della and Patney did the chemical preparations, Jones and Miller made the spectroscopic measurements, and McCoy is responsible for the normal coordinate calculation (to be published separately). We have studied five isotopic forms of cubane: cubane-d_0 and -d_8 (O_h symmetry), *sym*-cubane-d_2 and -d_6 (D_{3d}), and cubane-d_1 (C_{3v}). For brevity these will be referred to as d_0, d_1, d_2, d_6, and d_8. The d_2 and d_6 will always mean *sym*-d_2 and *sym*-d_6. Their full names are 1,4-dideuteriocubane and 1,2,3,4,6,7-hexadeuteriocubane.

Experimental Procedures and Results

Origin and Properties of the Samples. The syntheses have been described by Della and Patney.[6] Between 40 and 200 mg of each compound was available for our work.

Cubane is a colorless solid. It melts at 130-131 °C, and decomposes above the melting point. It is soluble in CS_2, CCl_4, $CHCl_3$, and benzene. Surprisingly, it is not sufficiently soluble in cyclohexane to make that a useful solvent for vibrational spectroscopy. It sublimes fairly easily, and is readily transferred on a vacuum line.[7] A small sample left in the open will disappear overnight. One can readily lose cubane while handling it, and we had great difficulty in recovering samples after our experiments. In part this was because the cubane also vaporized when a solvent was evaporated. We suspect, too, that the vapor dissolves readily in stopcock grease.

The purity of the samples will be discussed later.

Infrared Procedures. Initially quite a bit of d_0 was lost in vain attempts to make KBr pressed disks. It just disappeared. We believe now that it may have sublimed when the sample-KBr mixture was evacuated prior to and during the pressing. Solid samples were therefore prepared by depositing the vapor onto a cold window ($\sim$100 K) in a conventional low-temperature cell. Solutions in CS_2 and CCl_4 were also used.

Spectra were obtained from 400 to 3600 cm^{-1} with a Beckman IR-12 spectrophotometer. The lower limit was set by KBr cell windows. In addition a thick deposit of d_0 was measured down to 200 cm^{-1} in a CsI cell. Since no infrared bands were found, the range 200-400 cm^{-1} was not examined for the other compounds. The spectral slit widths were 1-2 cm^{-1} in all cases.

Raman Procedures. Raman spectra were obtained with a Spex Ramalog instrument which has been described elsewhere.[8] Samples were held in thin-walled glass capillary tubes. They were examined as polycrystalline solids at room temperature, and as solutions in CS_2, CCl_4, or benzene as needed to observe each band. Depolarization ratios were measured for the solutions. Excitation was with either the 488.0- or 514.5-nm line of an Ar$^+$ laser. We took the precaution of keeping the laser power at the sample less than 100 mW, and of ro-

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Table I. Cubane-d_0 Infrared and Raman Bands^e

infrared						Raman							
solid (~100 K)		CS_2 soln		CCl_4 soln		solid (~295 K)		CS_2 soln		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int^a	cm^{-1}	int^a	cm^{-1}	int^a	ρ^b	assignments
617	vw			*									8
						665	3	*		667	2		16
						815 827	24 21	821^c	20	*		0.75	15
824 829	w m			*									18
839	m			*									4
848	vw, sh	*		*									12 for ^{13}C compd
853 859	vs vs	851	s	852	s								12
						912	1000	899	235	899	280	0.76	6
						996	sh	~996	sh	~996	sh	p	2 for ^{13}C compd
						1002	970	1001	1000	1001	1000	0.00	2
1030	vw	~1030	vw			~1026	1	~1028	1				imp
1035 1037	m m												17
		~1078	vw										?
						1083	4	1078	3	~1078	1		5
						1130	8						9
		~1133	vvw										?
1144	vw												?
1151 1153	w vw												7
1168	vw												imp.^{d}
						1179 1184	95 60	1182	45	1185	40	0.78	14
1184	vw	~1183	vvw										?
						~1223	2	~1224	2				2 × 617 (I) = 1234? or imp.
1225	m			*									11 for ^{13}C compd or imp.
1227 1230	m vs	1228	s	1231	s								11
1235	m			*									?
1283	w	~1276	vvw										665(R) + 617(I) = 1282
						~1330	1						2 × 665(R) = 1330
~1638	w	*											815(R) + 829(I) = 1644
						~1640	1						2 × 821(R) = 1642
1701	w	1698	w	1700	vw								665(R) + 1036(I) = 1701
		~1717	vvw										899(R) + 829(I) = 1728 (soln)
		~1746	vvw										899(R) + 851(I) = 1750 (soln) 1130(R) + 617(I) = 1747
						~1795	1						665(R) + 1130(R) = 1795
1799	vw	~1794	vvw										1179(R) + 617(I) = 1796
1819	w	1817	w	1820	vw								665(R) + 1151(I) = 1816
		~1850	vvw										821(R) + 1036(I) = 1857 (soln) 1001(R) + 851(I) = 1852 (soln)
1895	vw	~1895	vw										665(R) + 1230(I) = 1895
		~1952	w										1130(R) + 829(I) = 1959
		~1961	vvw										?
1965	vw	~1970	w										821(R) + 1151(I) = 1972
1982	vvw	~1983	vw										1130(R) + 853(I) = 1983
						~2061	1			~2061	1		2× 1036(I) = 2072 839(I) + 1230(I) = 2069
2148	vvw	*											1002(R) + 1151(I) = 2153
						~2154	1						?
						~2205	2			~2205	1		?
2210	w	*											1179(R) + 1036(I) = 2215
						2247 ~2257	4 2			~2252	1		2 × 1130(R) = 2260
						~2309	1						1130(R) + 1182(R) = 2312
										~2328	1	0.0	?
						~2363	2			~2365	1		2 × 1185(R) = 2370 (soln)
						~2454	1						2 × 1230(I) = 2460
2965	s												3 and 10 (a_u)^d
						2970 2978	300 240	2970	180	2973	200	0.75	13

Table I (*Continued*)

infrared						Raman							
solid ($\sim$100 K)		CS_2 soln		CCl_4 soln		solid ($\sim$295 K)		CS_2 soln		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int^a	cm^{-1}	int^a	cm^{-1}	int^a	ρ^b	assignments
2978	vs	2977	vs	2982	vs								10 (e_u)
2992	vs												3 and 10 (a_u)^d
						2995	395	2994	295	2999	280	0.0	1

^{a} Raman intensities are relative peak intensities on a scale of 0-1000, uncorrected for instrument response. ^{b} ρ = depolarization ratio. For depolarized lines, we obtain 0.75 ± 0.03. p, dp = polarized, depolarized. Numerical value of ρ could not be obtained. ^{c} 821 cm^{-1} is a shoulder on the side of the CS_2 band at 796 cm^{-1}. ^{d} See text. ^{e} Notes (also apply to Tables II-V): w, m, s = weak, medium, strong; v = very; b = broad; sh = shoulder; $\sim$ = approximate (±3-5 cm^{-1}), due to breadth, weakness, or being a shoulder; *, solvent interferes; R = Raman value; I = infrared value; imp. = impurity; d_1,d_7 = cubane-d_1, cubane-d_7, etc.; ( ) = estimated from product rule; FR = Fermi resonance.

Table II. Cubane-d_8 Infrared and Raman Bands^e

infrared						Raman					
solid ($\sim$100 K)		CS_2 soln		CCl_4 soln		solid ($\sim$295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int^a	cm^{-1}	int^a	ρ^b	assignment
448	vw	*		*							imp.^{c}
527	vw			*							8
532	vvw			*							8 for d_7
						571	8	570	11	0.0	imp.^{c}
						586	10				16
								606	2	0.0	imp.^{c}
623	vw, b			*							?
638	w	*		*		635	10	636	4	0.75	d_7
						684	585	669	135	0.78	6
								674	sh		6 for d_7?
686	vs	683	vs	684	m						12
$\sim$689	m, sh										
711	m	709	w	*		710	55	710	sh		d_7
$\sim$716	vw, sh										
						715	150	716	35	0.75	15
						739	6	*	$—^d$		?
768	m	764	m	*		766	55	766^b	20^d	0.75	d_7
777	vvw			*							?
791	vw	$\sim$790	vvw	*							d_7?
						$\sim$802	1	*	$—^d$		?
807	vvw			*							4
						$\sim$842	2	*	$—^d$		?
						884	8				9
						923	8				d_7?
924	vw										17 (also in Raman. d_7?)
						950	55	950	sh	0.0	2 for ^{13}C compd
						956	1000	954	1000	0.00	2
						960	140	958	140	0.00	2 for d_7
960	vw										7 (and 2 for d_7)
								972	45	0.0	?
						995	3				?
1005	vw					1004	20	1004	3		d_7
						1027	250	1028	75	0.78	5
						1032	10				5 for d_7
						1072	130	1073	40	0.76	14
1083	m	1081	vw	*							11
1094	vw			*							doublet with 1083?
						$\sim$1144	2				?
1154	w										
1156	m	1154	vw			1154	15	1155	4	0.74	d_7
1169	vvw										imp.^{c}
1185	vvw	1188	vw								d_7
$\sim$1504	vw	*		*							586(R) + 924(I) = 1510
1534	vw	*		*							?
1598	vw										1072(R) + 527(I) = 1599
$\sim$1698	vw	$\sim$1695	vvw								1027(R) + (674)^c = 1701
1801	vvw	$\sim$1795	vvw								715(R) + 1083(I) = 1798 884(R) + 924(I) = 1808
1865	vvw										?
						1908	5				2 × 956(R) = 1912 884(R) + 1027(R) = 1911
						1936	5				?
						1952	5				1072(R) + 884(R) = 1956
1963	w	1962	vw								884(R) + 1083(I) = 1967

Table II (*Continued*)

infrared						Raman					
solid (~100 K)		CS_2 soln		CCl_4 soln		solid (~295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int[a]	cm^{-1}	int[a]	ρ[b]	assignment
2001	w	2000	vw								?
2005	vw, sh										
2029	vvw	2029	vvw								1072(R) + 960(I) = 2032
						2036	10	2040	3	0.77	960(I) + 1083(I) = 2043
2046	w	2044	vw								?
2052	vvw					2052	18	2054	5	0.60	d_7, also 2 × 1027(R) = 2054(R)
2060	w	2060	vw								?
2069	vvw										?
						2093	8	2096	3	0.75	1072(R) + 1027(R) = 2099
2105	w	*									1027(R) + 1083(I) = 2110
2124	vvw	*									?
						2133	10	2137	7	0.0	?
						2141	10	2146	7	0.71	2 × 1072(R) = 2144
2149	w	*									1072(R) + 1083(I) = 2155
						2158	5	2162	3	0.0	2 × 1083(I) = 2166
						2180	5				?
2185	vvw	*									?
2215	vvw	*									?
						2226	300	2230	175	0.75	13
						2232	545				
2229	m										3 and 10 (a_u)[c]
2240	vs	2238	vs	2242	m						10 (e_u)
2248	m										3 and 10 (a_u)[c]
						2259	760	2265	340	0.00	1
2261	w										?
2815	vvw, b	*									586(R) + 2240(I) = 2826
2918	vvw, b	2926	vw								684(R) + 2240(I) = 2924 2232(R) + 686(I) = 2918
2958	vvw										715(R) + 2240(I) = 2955
2975	s	2973	s	2976	vw	2975	40	2978	10	0.20	d_7, also 2259(R) + 715(R) = 2974(R)
~2980	w, sh										
2993	w					2990	10				d_7
3194	vvw										956(R) + 2240(I) = 3196
3216	vw	3216	vw								2259(R) + 960(I) = 3219
3224	vvw										
3303	vw	~3305	vvw								1072(R) + 2240(I) = 3312
3346	vw										2259(R) + 1083(I) = 3342

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] See text. [d] Benzene solution. [e] See footnote *e*, Table I.

Table III. *sym*-Cubane-d_2 Infrared and Raman Bands[f]

infrared						Raman					
solid (~100 K)		CS_2 soln		CCl_4 soln		solid (~295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int[a]	cm^{-1}	int[a]	ρ[b]	assignment
574	w	568	w	568	w						8
						632	30	631	20	0.76	16b
						651	6	651	6	0.33	16a
691	vw										?
711	m	706	m	706	m						18b
724	vw					721	5				d_1
737	vw										g fund. 15b?
						738[c]	130	736	85	0.75	15b
770	vw							*			?
						821	25	820[d]	10[d]	0.74[d]	15a
~827	sh										18a
838	s	838	s	839	s			*			4
844	s							*			12b
851	m	*						*			12a
						875	600	866	220	0.74	6
890	vw					888	80	887	15	~0.73 dp?	d_1
						900	15	~900	2	~0.73 dp?	?
						983	55	983	45	0.0	2 for ^{13}C compd
						991	1000	990	1000	0.0	2
						994	115	994	65	0.0	2 for d_1
995	w	994	w								17b
						1001	55	1002	15	0.0	2 for d_0
						1016	230	1016	95	0.76	5
1020	vw										?
1036	w										17a

Table III (*Continued*)

infrared						Raman					
solid (~100 K)		CS_2 soln		CCl_4 soln		solid (~295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int	cm^{-1}	int[a]	cm^{-1}	int[a]	ρ[b]	assignment
						1100	20	1099	4	0.73	9b
1109	w										7
						1133	6	1134	4	0.10	?
						1168	125	1170	36	~0.57	14a
1169	vw										imp.[e]
						1174	80	1176	24	~0.72	14b
1201	s	1204	s	1205	s						11a
~1208	w, sh										632(R) + 574(I) = 1206
1222	s	1220	s	1221	s						11b
1308	vw										738(R) + 574(I) = 1312
~1342	vw, b										632(R) + 711(I) = 1343
~1625	vw, b	*									632(R) + 995(I) = 1627
~1683	vw, b										651(R) + 1036(I) = 1687
~1744	vw, b										1174(R) + 574(I) = 1748
~1762	vw, b										651(R) + 1109(I) = 1760
~1845	vw, b										738(R) + 1109(I) = 1847
~1853	vw, b										632(R) + 1222(I) = 1854 1016(R) + 838(I) = 1854
~1933	vw, b										1100(R) + 838(I) = 1938
						1975	3	1977	2		2 × 991 (R) = 1982 875(R) + 1100(R) = 1975
1991	w										?
						2024	3	2027	2		2 × 1016(R) = 2032
								2062	2		839(I) + 1221(I) = 2060 (soln)
						2100	3	2101	2		995(I) + 1109(I) = 2104
2122	vw	*									1016(R) + 1109(I) = 2125
2156	vw	*									1168(R) + 995(I) = 2163
2162	vw	*									(1130) + 1036(I) = 2166
2188	w	*									991(R) + 1201(I) = 2192
2194	w	*		2195	vw						1168(R) + 1036(I) = 2204
						2197	2	2199	6	0.10	2 × 1100(R) = 2200
2210	m	*		2214	m						991(R) + 1222(I) = 2213(I)
						2212	2				995(I) + 1222(I) = 2217(R)
2220	vw	*									?
						2237	280	2241	130	0.23	13a
2240	s	~2239	s	2243	s						10a
2248	w					2246	50				?
2278	vw	*									1174(R) + 1109(I) = 2283
2968	s										3
						2970	400	2971	130	dp	13b
						2976	300				738(R) + 2237(R) = 2975; FR with 2970
2977	vs	2977	vs	2980	vs						10b
						2985	180				?
2992	s										d_1?
						2993	440	2991	280	~0.12	1
~3255	vw, b										1016(R) + 2240(I) = 3256
~3410	vw, b										1174(R) + 2240(I) = 3414

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] 738 cm^{-1} is asymmetric on low-cm^{-1} side; unable to resolve. [d] 820 cm^{-1}. In $CHCl_3$ solution. [e] See footnote *d*, Table I. [f] See footnote *e*, Table I.

tating the capillary, to avoid decomposition. It was not possible to obtain the spectrum of molten cubane because it decomposed when slightly above the melting point and under laser illumination. The spectral slit widths were 5 cm^{-1} for survey spectra, and down to 1 cm^{-1} when possible for frequency measurements.

Results. Survey spectra are shown in Figures 2-5 and numerical data are given in Tables I-V. The wavenumber calibration of the instruments was checked just before or after each measurement. The tabulated infrared wavenumbers are thought to be accurate to ±1 cm^{-1}, and the Raman ones to ±2 cm^{-1}, unless a band is marked broad, shoulder, or approximate.

It is noteworthy that the bands seldom change by more than 3 cm^{-1} between solid, CS_2 solution, and CCl_4 solution. This simplifies comparison between these spectra.

Theoretical Considerations

We find that in solution cubane-d_0 follows the selection rules for O_h symmetry, whereas in the polycrystalline solid it follows those for the crystal.

Solutions. Consider first the expectations for the free molecule (gas or solution). If cubane-d_0 and -d_8 are cubic (O_h symmetry), their vibrations are $2a_{1g}(R) + 2e_g(R) + 1f_{1g} + 4f_{2g}(R) + 2a_{2u} + 2e_u + 3f_{1u}(I) + 2f_{2u}$, where R and I mean Raman and infrared active. Note that only three of the nine u modes are active. *sym*-Cubane-d_2 and -d_6 then have symmetry D_{3d}, and their fundamentals are $6a_{1g}(R) + 1a_{2g} + 7e_g(R) + 2a_{1u} + 5a_{2u}(I) + 7e_u(I)$. Finally cubane-$d_1$ is C_{3v}, with $11a_1(R,I) + 3a_2 + 14e(R,I)$.

Table VIA gives the correlation of the vibrations as the symmetry changes from O_h to D_{3d} to C_{3v}.

Product Rule. The Teller-Redlich product rule[9] is a powerful and useful check on the assignments. We prefer to use the reciprocal of the equation given by Herzberg so that the ratios are >1. Data used for calculating the theoretical ratios are given in Table VII. Both theoretical and observed product rule

Table IV. *sym*-Cubane-d_6 Infrared and Raman Bands^g

infrared				Raman					
solid (~100K)		CS_2 soln		solid (~295 K)		CCl_4 soln			
cm^{-1}	int	cm	int	cm^{-1}	int^a	cm^{-1}	int^a	ρ^b	assignment
538	vw								8
				579	6	578	3	0.0	16a
				598	35	597	15	0.78	16b
~623	vvw, b								?
633	vvw								?
~643	w, sh								?
651	m	645	m						18b
662	w	661	vw						?
				671	4	671	1		?
674	vw								18a
690	s	688	m						12a
				704	305	696	110	0.78	6
717	w			716	10	—^{c}			6 for d_5?
				725	35	725^c	10	0.48	15a
736	vw			738	35	736^c	10	0.80	d_5?
~757	vw, b			758	245	753^c	70	0.78	15b
				786	6	—^{c}		?	
{786	s	786	m						12b
{792	s								
				806	1	$*^d$			?
807	m	804	m						4
832	vvw								?
849	vw			847	35	844	8	0.76	d_5?
				884	1				9a
927	vw								17a
				961	55	962	40	0.0	2 for ^{13}C compd
				967	1000	966	1000	0.01	2
				971	250	971	160	0.01	2 for d_5?
975	vvw								17b
				978	15	978	7	0.0	2 for d_4?
				985	90	985	15	0.75	9b
				992	15				9b for d_5?
1014	w								7
				1029	15				?
				1035	155	1036	45	0.80	5
				1067	5	1065	3	0.0	2 × 538(1) = 1076
				1083	25	1083	10	0.65	14a
1100	vw								11a
~1144	vw, b			1145	100	1146	30	0.77	14b
1164	s	1164	m						11b
1169	vw, sh								imp.^{e}
{1184	m	1183	w	1183	1				11b for d_5?
{1187	m								
~1384	vw, b								598(R) + 786(1) = 1384
~1536	vvw, b								758(R) + 786(1) = 1544
~1554	vvw, b								579(R) + 975(1) = 1554
~1615	vvw, b								967(R) + 651(1) = 1618
~1642	vw, b								?
~1680	vw, b								1145(R) + 538(1) = 1683
~1728	vvw, b								1083(R) + 651(1) = 1734
~1769	vw, b								758(R) + 1014(1) = 1772
				1917	1	~1917	1, b		884(R) + 1035(R) = 1919
				1947	1	~1947	1, b		786(1) + 1164(I) = 1950
1955	vw								985(R) + 975(1) = 1960
				1987	3	~1987	1, b		975(1) + 1014(1) = 1989
2006	w								1035(R) + 975(1) = 2010
				2019	1	~2020	1, b		985(R) + 1035(R) = 2020
2032	vvw								?
2043	w								884(R) + 1164(1) = 2048
2053	vvw								1083(R) + 975(1) = 2058
				2061	6	2062	4	0.59	2 × 1035(R) = 2070
2078	w								985(R) + 1100(1) = 2085
2114	vvw								1145(R) + 975(1) = 2120
				2134	3	2135	2	0.0	2 × 1067(R) = 2134? 985(R) + 1145(R) = 2130? 975(1) + 1164(1) = 2139?
2142	vw								985(R) + 1164(1) = 2149
				2162	5	2163	4	0.0	2 × 1083(R) = 2166
2172	vw								?

Table IV (*Continued*)

infrared				Raman					
solid (∼100 K)		CS_2 soln		solid (∼295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int[a]	cm^{-1}	int[a]	ρ[b]	assignment
				2176	5				1014(I) + 1164(I) = 2178 1035(R) + 1145(R) = 2180
2194	w								
2196	w								1035(R) + 1164(I) = 2199
				2196	5	2196	4	0.0	2 × 1100(I) = 2200
2216	vw								?
2220	vw								?
				2229	320	2230	100	0.75	13b
				2234	90				
2231	s								
2236	vs	2234	vs						10b
2239	vs								
2242	vs	2245	s						3
				2254	495	2257	335	0.02	1
				2275	6				?
				2319	1				2 × 1164(I) = 2328
2974	vs	2972	s						10a
				2978	330	2979	110	0.19	13a
2991	s								758(R) + 2236(I) = 2994
				2992	80	*f*			758(R) + 2229(R) = 2987. FR with 2978
3226	vw								2229(R) + 1100(I) = 3229
∼3378	vvw, b								1145(R) + 2236(I) = 3381

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] In benzene solution. [d] 806 cm^{-1}. Both CCl_4 and benzene interfere. [e] See footnote *d*, Table I. [f] 2992 cm^{-1} is not observed in solution, even at 0.5-cm^{-1} resolution. [g] See footnote *e*, Table I.

ratios (τ's) are listed in Table VIII. The observed ratios are expected to be less than the theoretical ones because of anharmonicity. A crude guide is that the difference is about 1% for each C–H(D) stretching mode and about 0.5% for each C–H(D) bending mode.

Effect of Crystal Structure. Fleischer showed that the space group is $R\bar{3}$ (or $C_{3i}{}^2$), with only one molecule per unit cell.[4] The factor group is $C_{3i} \equiv S_6$. This has several useful consequences. (a) Under it, *all* the fundamental modes of d_0 and d_8 become formally allowed. The correlation between modes of the free molecule and of the factor group is shown in Table VIB. (b) There is still a center of symmetry in the factor group so the g–u distinction is preserved and the rule of mutual exclusion still applies. (c) In principle the triply degenerate modes of O_h split into two spectroscopically active components in the crystal. In fact most of them are observed to do just that.

The finding that there is only one molecule per unit cell also has three pertinent consequences. (1) There are no correlation field splittings due to interactions between molecules in the same unit cell. Therefore any observed splittings are due to lowering of the symmetry from the molecular group to the factor group (O_h to S_6). Consequently they will be a dependable guide to locating triply degenerate modes of O_h. (2) There are no translatory lattice modes. (3) There are only two rotatory lattice modes, having symmetry a_g and e_g of S_6. These are Raman allowed, but we found no evidence for them down to 30 cm^{-1}. This is understandable, for they are probably very low in both frequency and intensity. If the molecule were truly cubic in the crystal, rotation or libration would not change the polarizability, and it would be spectroscopically inactive. The molecule is not exactly cubic but the distortion is very small so the librational bands are probably very weak.

The above considerations do not necessarily apply to the intermediate deuterated species. The d_1, d_2, and d_6 molecules have a unique molecular symmetry axis, but it is not necessarily directed along the S_6 axis of the unit cell. The C_3 symmetry axis of these molecules does not present a very different external aspect to neighboring molecules than the other cube diagonals, so some randomness is possible. This will lead to a further relaxation of selection rules in the solid.

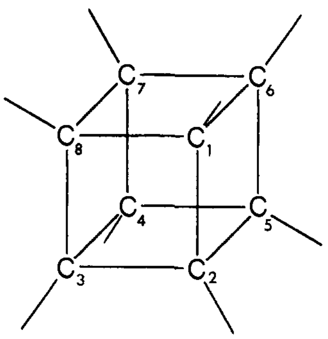

Figure 1. The carbon skeleton of cubane.

Purity of the Samples

A discussion of the purity has been deferred until after presenting the selection rules for solution and solid. We now must consider it before starting on the assignments.

First of all, the infrared spectrum of every solid sample has a very weak band at 1168 or 1169 cm^{-1}. It is not in the empty cell. Although it is hard to imagine how the same impurity can be in every one of the isotopic compounds, we believe that this band must be due to something extraneous to the samples.

d_0. Gas chromatography indicated 1–2% of a chemical impurity whose identity is unknown. A few bands in Table I that we cannot explain may be due to it. The only band that we are certain is an impurity is 1030 cm^{-1} in the infrared, because it appears in solution as well as the solid. Only f_{1u} modes are allowed in solution (i.e., for the free molecule), and all three f_{1u} fundamentals are known with certainty. It cannot be a sum tone because no frequencies are low enough, and it cannot be a difference tone because the solid spectrum was obtained at 100 K. Hence the infrared band is due to an impurity. The Raman band at ∼1026 cm^{-1} may have the same origin.

The remaining samples contained the same 1–2% of *chemical* impurity found in d_0, although it may have been partially deuterated. The isotopic purity seems much more significant, and will now be discussed.

Table V. Cubane-d_1 Infrared and Raman Bands[a]

infrared				Raman					
solid (~100 K)		CS_2 soln		solid (~295 K)		CCl_4 soln			
cm^{-1}	int	cm^{-1}	int	cm^{-1}	int[a]	cm^{-1}	int[a]	ρ[b]	assignment
590	w	585	w	587	11	585	4	0.82	8
654	w	*		652	7	652	4	0.75	16b
				~659	sh	~659	sh		16a
724	m	721	m	722	55	722	20	0.76	18b
				816	25	818[c]	10	0.71	15a
828	w			826	25				15b
834	w								18a
847	vs	844	vs	844	7	843	4	0.56	4, 12b[d]
853	s, sh								12a
~878	w								?
892	m	885	m	898	780	887	200	0.73	6
				~902	sh				?
995	vw			996	1000	995	1000	0.00	2
				1002	100	1002	40	0.26	2 of d_0, plus 17b[d]
1002	w	1001	w						17b
1026	vw			1027	28	1028	5	0.01	?
1036	w								17a
1062	w			1062	18	1062	7	0.76	5
1098	vw			1101	13	1100	3	0.75	9b
				1132	5				9a
1145	w			1145	4				7
1168	vw								imp.[d]
1175	w	1175	w	1174	70	1176	40	0.76	14a
~1179	vw, sh			1179	50	1179	sh		14b
1184	vw								?
1219	vs	1217	s	1217	7	1219	4	0.73	11a
1225	vs	1223	s						11b
1248	vw								590 + 659 = 1249
1308	w	1303	w						590 + 724 = 1314
1381	vw	*							659 + 724 = 1383
~1659	w, b	*							659 + 1002 = 1661
~1690	w, b								590 + 1098 = 1688 654 + 1036 = 1690 847 + 844 = 1691
~1722	w, b								724 + 1002 = 1726
~1762	w, b								590 + 1174 = 1764 724 + 1036 = 1760
~1806	w, b								590 + 1219 = 1809
~1880	vw, b								892 + 996 = 1888 659 + 1225 = 1884
~1945	vw, b								724 + 1225 = 1949
~1962	w, b	~1959	w, b						816 + 1145 = 1961
1984	vw			1982	2	1984	1		2 × 996 = 1992
~2025	vw, b								847 + 1179 = 2026
~2056	vw, b			2054	2	2056	3		996 + 1062 = 2058
~2108	vw, b	*							892 + 1219 = 2111
				2114	1				898 + 1217 = 2115
				2143	1	2145	1		996 + 1145 = 2141
2170	w	*		2168	2				996 + 1174 = 2170
2199	w	*							2 × 1101 = 2202
2204	w	*							1062 + 1145 = 2207
2212	m	*		2212	15	2214	10	0.22	996 + 1217 = 2213
~2230	w, sh					~2233	sh		1101 + 1132 = 2233
2239	m	2241	m	2240	85	2243	36	0.19	10a
2250	w			~2247	sh				1101 + 1145 = 2246
				2269	2	2270	1		1101 + 1174 = 2275
				2349	2	2352	1		2 × 1174 = 2348
2967	s			2969	420	2973	150	dp?	13a,13b
2978	vs	2975	vs	2977	280				3,10b
2992	s			2993	590	2995	260	p	1

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] (818). In $CHCl_3$ solution. [d] See footnote *d*, Table I. [e] See footnote *e*, Table I.

d_8. NMR showed that the deuterium content is 96 ± 1% of the total [D + H]. If the figure is 96%, and if the distribution is statistical, then there is 72% d_8, 24% d_7, and 4% d_6 (not all of which is *sym*-d_6). The spectrum of d_8 does show a considerable amount of isotopic impurity. This not only gives many extraneous bands; it also dilutes the d_8 and makes many of its bands appear to be very weak.

Evidence for isotopic impurity in d_8 consists of the following: (a) Bands which appear in both the infrared and Raman spectra (agreeing within 3 cm^{-1}) (not permitted for O_h or S_6 symmetry except by accident). Examples are 638, 711, 768, 924, 960, 1005, 1156, 2052, 2975, and 2993 cm^{-1}. We do not

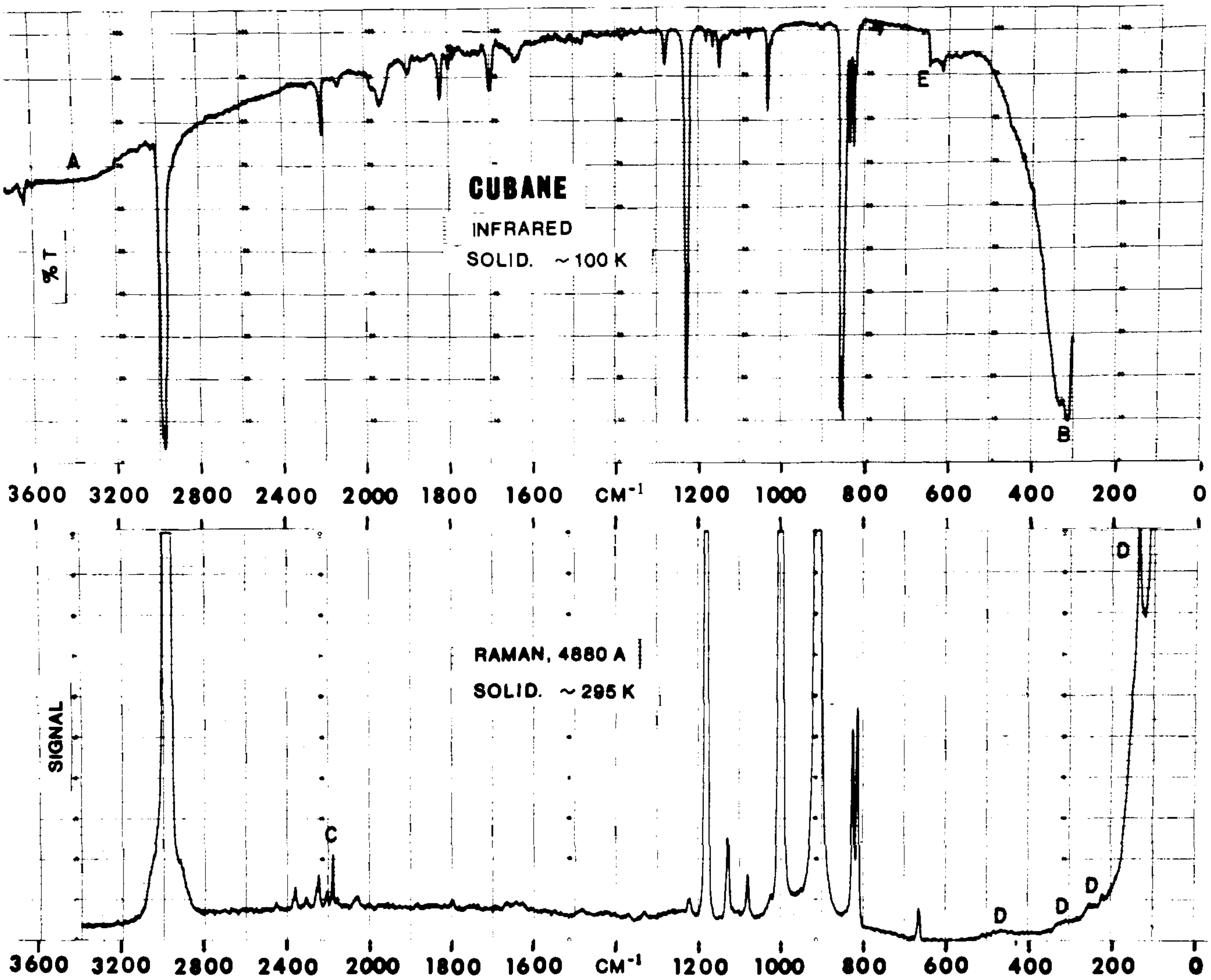

Figure 2. Spectra of cubane. (There is a 2X scale change at 2000 cm^{-1}.) Upper, infrared of solid at ~100 K (1-2 cm^{-1} slits): (A) absorption by water on cell windows; (B) absorption by KBr windows; (E) discontinuity due to grating change. Lower, Raman of solid at room temperature, 4880-Å excitation, 5-cm^{-1} slits; (C) Hg line from room lighting; (D) bands due to glass of sample tube.

attribute 686 (I) and 684 (R) to d_7 because each is very intense. The infrared band is assigned to an allowed f_{1u} fundamental. Also the IR and Raman values in CCl_4 solution differ by 15 cm^{-1}. (b) Weak bands which appear a few cm^{-1} higher than stronger bands of d_8. The former may be due to d_7. Examples are 532, 674, and 1032 cm^{-1}. (c) Some infrared bands which appear in both solid and solution. Assuming that the effective symmetry in solution is O_h, only modes of f_{1u} symmetry are permitted. The three f_{1u} modes are easily identified (see later). Other infrared bands in solution which cannot be explained as F_{1u} combination tones are probably due to d_7. Examples are 711, 768, 791, 1156, and 1185 cm^{-1}.

Two of the above frequencies will actually be assigned to d_8 fundamentals later in spite of the suspicion that they are due to d_7 (924 and 960 cm^{-1}).

The Raman bands of d_8 in solution at 570 and 606 cm^{-1} are attributed to an impurity because they are highly polarized. For d_8 there are only two polarized fundamentals, and they are certainly 956 and 2259 cm^{-1}. There is no way that totally symmetric combination tones can be obtained at 570 and 606 cm^{-1}. These bands must therefore arise from some extraneous substance. Furthermore, a Raman band was observed at 570 cm^{-1} in the CCl_4 solution of every sample of every cubane that we have examined in this work. (This was not true for the solids, however.) For d_8, the intensity of the 570-cm^{-1} band in solution increased with time, further suggesting that it was due to a chemical impurity.

Finally, the 448-cm^{-1} infrared band of d_8 is attributed to an impurity because there is no reasonable corresponding band in any of the other cubanes. Its counterpart in d_0 must not be greater than 448 × 1.35 (the maximum isotopic shift ratio) = 605. The only bands between 448 and 605 cm^{-1} in all the other cubanes can be nicely accounted for in other ways.

d_1. NMR indicated the isotopic labeling to be 99 ± 1% complete.[6] The Raman band at 1002 cm^{-1} could be due to d_0, but if so it seems to also coincide with another mode. This will be discussed later under "Assignments for d_1". There are no other places in the spectrum where one can get a sensitive test for d_0 impurity in d_1.

d_2. NMR indicated the deuterium content at the labeled positions to be 99 ± 1%.[6] The spectrum of d_1 provides a useful check on the purity of d_2. For example, the very strong Raman-active band of each compound near 1000 cm^{-1}, due to the "cube breathing" mode, gives evidence in d_2 for some d_1 (994 cm^{-1}) and a little d_0 (1001 cm^{-1}). Infrared-Raman coincidences should not occur in d_2 except by chance, but several are observed (agreement within 3 cm^{-1}). Two of these are attributed to d_1 impurity: 724 and 890 cm^{-1}. These bands are at least moderately strong in d_1, and for it the coincidence is allowed.

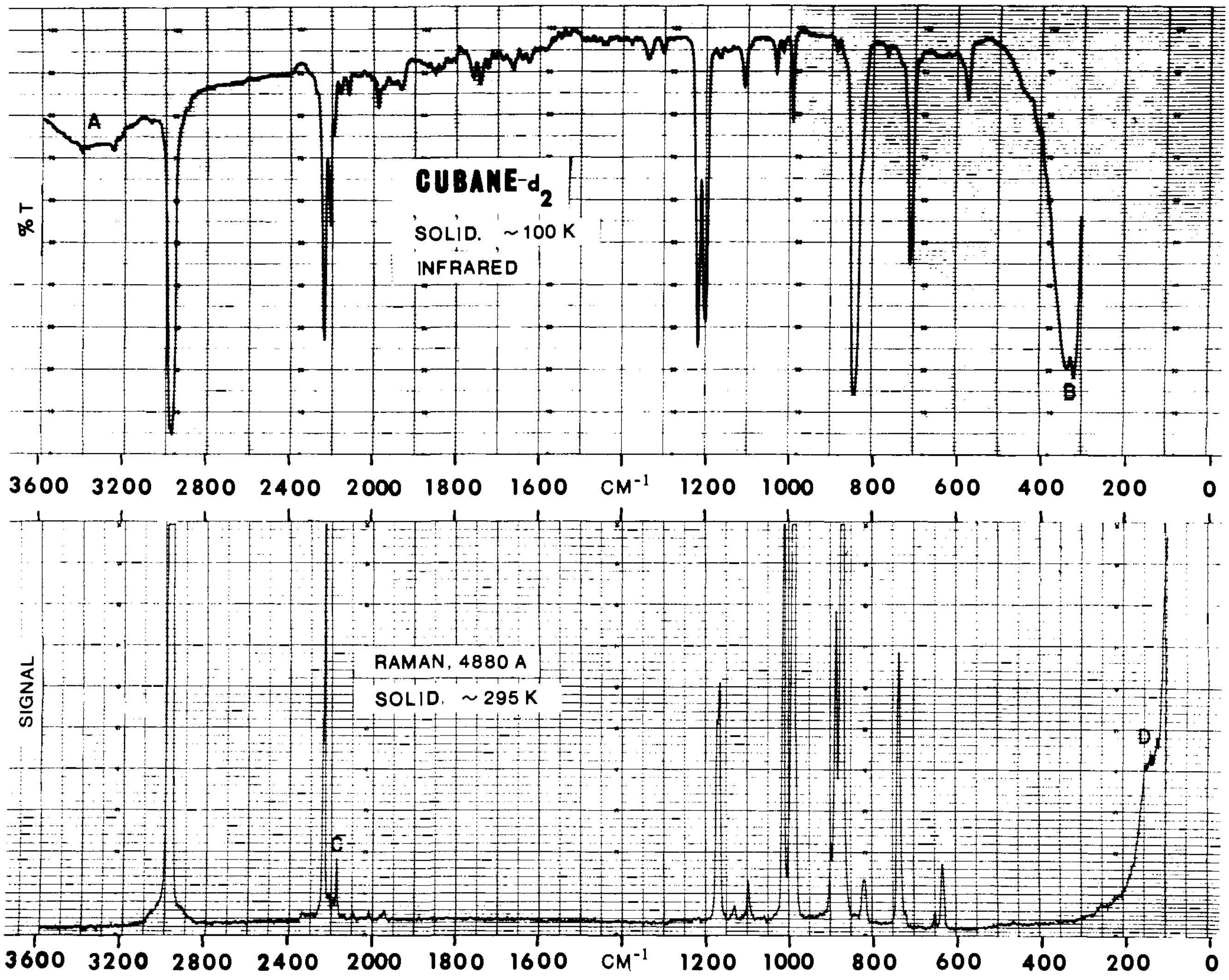

Figure 3. Spectra of *sym*-cubane-d_2. See Figure 2 for full caption.

Table VI. Correlation of the Vibrations[a]

A. On Deuterium Substitution in the Free Molecule

O_h	→	D_{3d}	→	C_{3v}
$a_{1g} + f_{2g}$		a_{1g}		a_1
$a_{2u} + f_{1u}$		a_{2u}		
$a_{1u} + f_{2u}$		a_{1u}		a_2
$a_{2g} + f_{1g}$		a_{2g}		
$e_g + f_{1g} + f_{2g}$		e_g		e
$e_u + f_{1u} + f_{2u}$		e_u		

B. On Crystallization of Cubane-d_0 and -d_8

mol sym O_h	→	factor group S_6 ($\equiv C_{3i}$)
a_{1g}(R,p)		a_g(R)
e_g(R)		e_g(R)
f_{1g}(-)		a_g(R) + e_g(R)
f_{2g}(R)		a_g(R) + e_g(R)
a_{2u}(-)		a_u(I)
e_u(-)		e_u(I)
f_{1u}(I)		a_u(I) + e_u(I)
f_{2u}(-)		a_u(I) + e_u(I)

[a] R = Raman active; I = infrared active; - = forbidden; p = polarized.

Table VII. Data for Calculating Product Rule Ratios[a]

compd	M	I_z	I_{xy}
cubane-d_0	104.15	146.6	146.6
sym-cubane-d_2	106.17	146.6	158.4
sym-cubane-d_6	110.19	177.6	166.1
cubane-d_8	112.21	177.6	177.6

[a] M = molecular weight; I = moment of inertia (in amu A^2). r(C-C) = 1.551 Å; r(C-H) and r(C-D) = 1.06 Å.

***d*₆.** NMR showed the deuterium content at the labeled positions to be 96 ± 2%.[6] The spectra show considerable evidence for isotopic impurity, viz.: (a) Several strong bands assigned as fundamentals for d_6 have weaker satellite bands a few wavenumbers higher which are assigned to d_5. The best example is the very strong Raman cube breathing mode at 967 cm^{-1}, which has highly polarized satellite bands at 971 and 978 cm^{-1} that are attributed to d_5 and d_4, respectively. Other examples are 716 and 992 cm^{-1}. (b) Several bands which are observed in both the infrared and Raman spectra are attributed to d_5 (716, 847, 1184 cm^{-1}).

Assignments for the g Modes of d_0 and d_8

Now having removed at least some of the extraneous features from the data, we are ready to start on the assignments. The g modes for d_0, d_2, d_6, and d_8 will be considered first, followed by their u modes. Since d_1 does not have a center of symmetry, it will be postponed until last.

The assignments are included in Tables I–V, and are summarized in Table IX. In the discussion the frequencies quoted will usually be those for the solid because many frequencies do not appear in solution, especially in the infrared spectra.

Table VIII. Theoretical vs. Observed Product Rule Ratios (τ's) for the Cubanes

		O_h Species							
isotopic pair		a_{1g}	e_g	f_{1g}	f_{2g}	a_{2u}	e_u	f_{1u}	f_{2u}
d_0/d_8	theor	1.414	1.414	1.285	2.000	1.414	1.414	1.927	1.414
	obsd	1.390	1.406	1.278	1.912	1.383	1.404	1.877	1.379

		D_{3d} Species					
		a_{1g}	a_{2g}	e_g	a_{1u}	a_{2u}	e_u
d_0/d_2	theor	1.414	1.000	1.361	1.000	1.401	1.401
	obsd	1.389	1.000	1.345	1.002	1.371	1.378
d_0/d_6	theor	2.000	1.285	2.658	1.414	1.944	2.750
	obsd	1.949	1.278	2.577	1.375	1.912	2.690
d_2/d_6	theor	1.414	1.285	1.953	1.414	1.388	1.963
	obsd	1.404	1.278	1.915	1.371	1.394	1.952
d_2/d_8	theor	2.000	1.285	2.671	1.414	1.945	2.751
	obsd	1.913	1.278	2.555	1.376	1.894	2.637
d_6/d_8	theor	1.414	1.000	1.367	1.000	1.401	1.401
	obsd	1.363	1.000	1.334	1.003	1.359	1.351

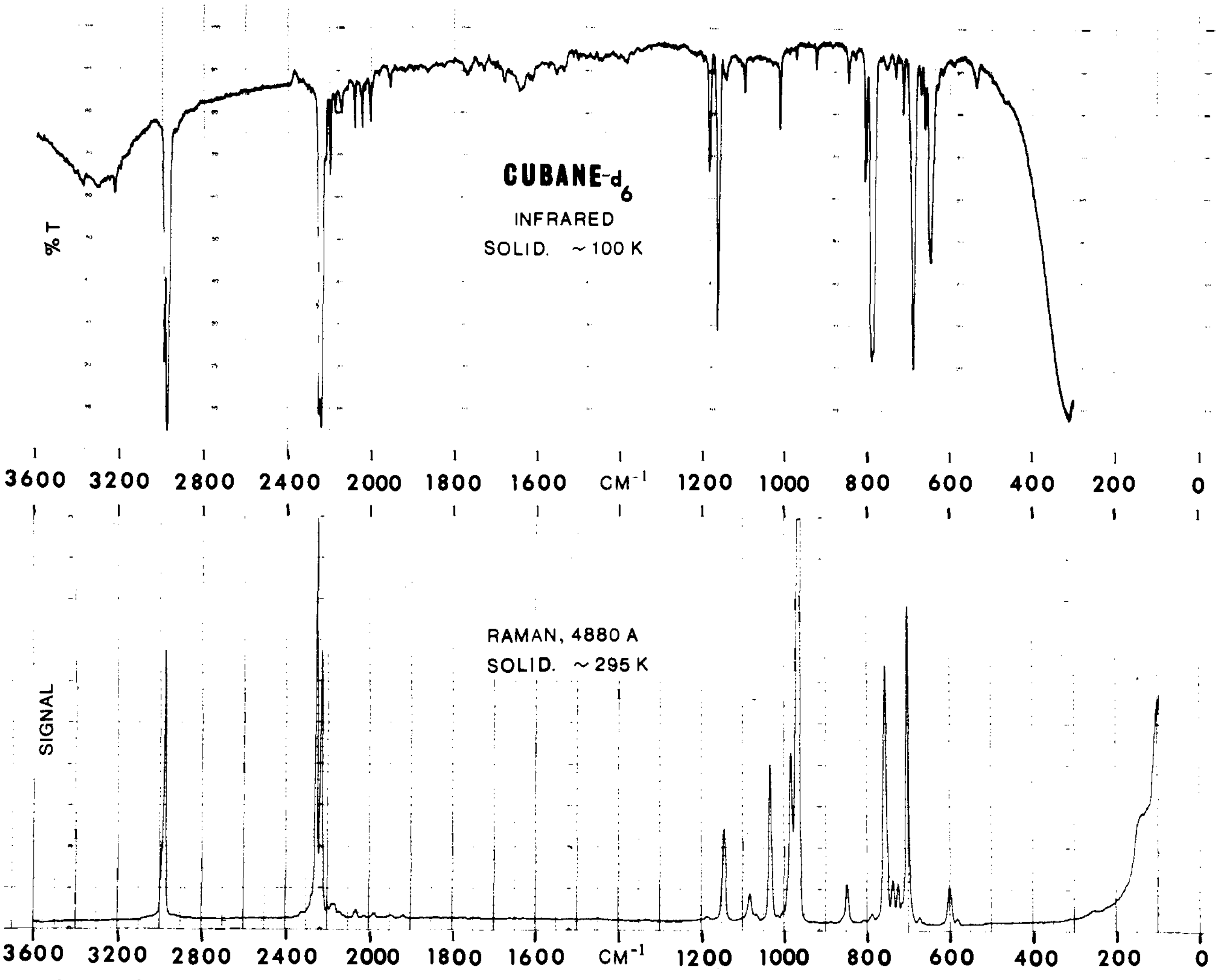

Figure 4. Spectra of *sym*-cubane-d_6. See Figure 2 for full caption.

For O_h symmetry the g fundamentals are $2a_{1g}(R,p) + 2e_g(R) + 1f_{1g} + 4f_{2g}(R)$.

A. g Modes for d_0. It is simplest to start with d_0 because one does not have to worry about incomplete deuteration for it. It does have 1-2% of an unknown chemical impurity which may be responsible for a few weak bands that we cannot explain any other way. We reiterate that the solution follows O_h selection rules, and the solid follows S_6. By examining Table VIB one sees that the g modes for d_0 and d_8 can, in principle, be sorted out in the following way: a_{1g} bands are polarized in solution; f_{1g} bands are forbidden in solution but allowed in the crystal; f_{2g} bands are allowed in both, and give doublets in the crystal; e_g bands are allowed in both, but give singlets in the crystal.

1. a_{1g}. Depolarization ratios and intensities clearly indicate that these two fundamentals are at 2995 and 1002 cm^{-1}. Note that because the molecule is cubic, ρ should be zero, and that it is so within experimental error.

2. f_{1g}. There is only one mode in this species, a C-H bend.

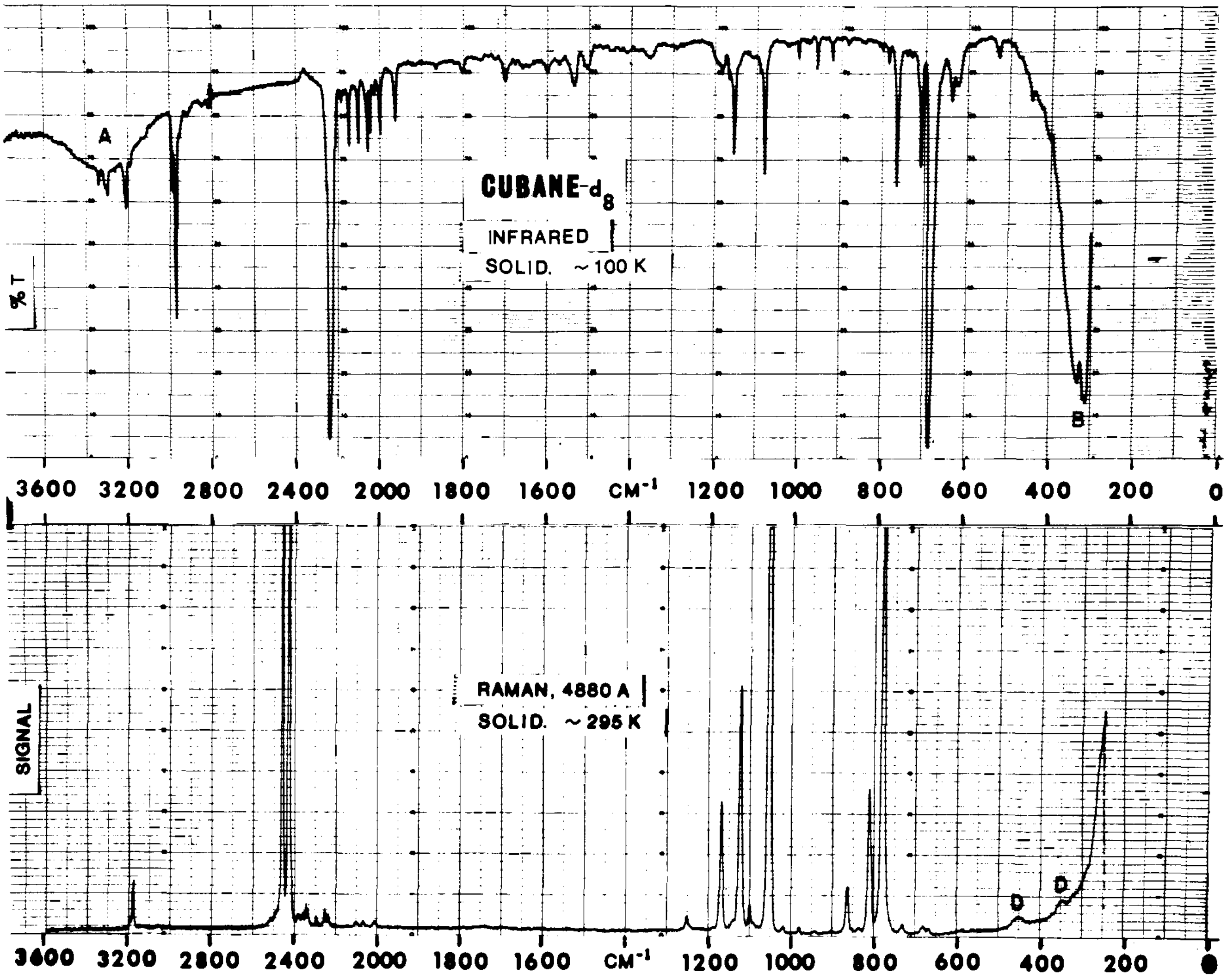

Figure 5. Spectra of cubane-d_8. See Figure 2 for full caption.

It is forbidden in solution but allowed in the crystal. There is only one candidate: the weak band at 1130 cm^{-1}. Although it should be a doublet in the crystal, it is not. The assignment will be verified by d_6 and d_8 results to be given later.

3. f_{2g}. These four fundamentals should occur in both solution and solid, and be doublets in the latter. The doublet property suggests 2970, 1182, and 821 cm^{-1} (all solution values). The fourth one is not obvious and we defer it for a bit.

4. e_g. These two modes are allowed in both solution and solid, but are singlets in the latter. The extremely intense 912-cm^{-1} band is a clear choice, but the second one is not obvious.

There are only five candidates for the two missing g fundamentals: 665, possibly 827 (the separation between 815 and 827 is larger than for any other doublet in d_0 or d_8), ~1026, 1083, and ~1223 cm^{-1}. We will turn to the deuterium derivatives for help in making the selection.

B. g modes for d_8. 1. a_{1g}. Polarization and intensity clearly indicate that these two fundamentals are at 2259 and 956 cm^{-1}. The product rule ratio is satisfactory (Table VIII).

Vibration ν_2, the cube breathing mode, can easily be located in all the intermediate deuterated compounds except d_3, because it decreases linearly by 5.75 cm^{-1} per D atom (Table XA). Adding one atomic mass unit by substituting a ^{13}C for a ^{12}C atom has exactly the same effect as substituting a D for a H atom, viz., ν_2 is lowered by about 6 cm^{-1}. Thus in d_0 ν_2 is lowered from 1002 to 996 cm^{-1} in the ^{13}C compound, and in d_8 from 956 to 950 cm^{-1}. The concentration of molecules containing one ^{13}C atom is 8.2% of the total, so the intensities are reasonable.

2. f_{1g}. This one mode is expected in the solid only. Since the mode is at 1130 cm^{-1} in d_0, the product rule unequivocally selects 884 cm^{-1} in d_0. This choice will be verified later by the data for d_6.

3. f_{2g}. These modes should give doublets in the crystal. Possibilities are 715 (the 710 component is also in the infrared, but the two Raman bands are quite intense for d_7 impurity), 1027, and 2232 cm^{-1}. Again one is missing. It will turn out, too, that we shall later be forced to assign 1027 cm^{-1} to e_g in spite of its being a doublet. Therefore two more f_{2g} fundamentals are needed.

4. e_g. These modes are permitted in both solution and crystal, and are singlets in the crystal. The very strong 684-cm^{-1} band is an obvious choice. It seems to be the counterpart of 912 cm^{-1} in d_0 on the basis of (a) high intensity, (b) the unusually large frequency shift between crystal and solution (13 cm^{-1} for d_0 and 15 cm^{-1} for d_8). This mode can easily be traced through the intermediate compounds (Table XB). We are therefore confident that 912 cm^{-1} in d_0 should be paired with 684 cm^{-1} in d_8. The large decrease shows that they belong to a C–H bend.

This leaves an e_g and one or two f_{2g} fundamentals to be identified in both d_0 and d_8. It is helpful now to look at the data for d_1, d_2, and d_6.

C. Help from the Raman Bands of d_1, d_2, and d_6. The

Table IX. Assignments for the Fundamental Vibrations of Cubane-d_0, -d_2, -d_6, and -d_8[b]

D_{3d} species	O_h species	no.	schematic descripn	d_0	*sym*-d_2	*sym*-d_6	d_8
a_{1g} R(p)	a_{1g} R(p)	1	C-H str	2995	2993	2254	2259
		2	C-C str	1002	991	967	956
	f_{2g} R	13a	C-H str	2970	2237	2978	2232
		14a	C-H bend	1182	1168	1083	1072
		15a	C-C str	821	821	725	715
		16a	C C_3 def	665	651	579	586
a_{2g}	f_{1g}	9a	C-H bend	1130	(1130)	884	884
e_g R	e_g R	5	C-C str	1083	1016	1035[a]	1027
		6	C-H bend	912	875	704[a]	684
	f_{1g}	9b	C-H bend	1130	1100	985[a]	884
	f_{2g} R	13b	C-H str	2970	2970	2229	2232
		14b	C-H bend	1182	1174	1145	1072
		15b	C-C str	821	738	758[a]	715
		16b	C C_3 def	665	632	598	586
a_{1u}	f_{2u}	17a	C-C str	1036	1036	927	924
		18a	C-H bend	829	~827	674	(674)
a_{2u} I	a_{2u}	3	C-H str	[~2978]	2968	2242	[~2239]
		4	C C_3 def	839	838	807	807
	f_{1u} I	10a	C-H str	2978	2240	2974	2240
		11a	C-C str	1230	1201	1100	1083
		12a	C-H bend	853	851	690	686
e_u I	e_u	7	C-H bend	1151	1109	1014	960
		8	C-C_3 def	617	574	538	527
	f_{1u} I	10b	C-H str	2978	2977	2236	2240
		11b	C-C str	1230	1222	1164	1083
		12b	C-H bend	853	844	786	686
	f_{2u}	17b	C-C str	1036	995	975	924
		18b	C-H bend	829	711	651	(674)

[a] To satisfy the noncrossing rule, 1035 and 985 cm^{-1} in d_6 should be interchanged, and so should 704 and 758 cm^{-1}. See text. [b] Values in parentheses were estimated from the product rule; values in brackets were estimated from the resonance pair.

Table X. Some Details for Several Fundamentals

vibration no.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
A. ν_2 (obsd)	1002	996	991		978[a]	971[a]	967	960[b]	956
ν_2 (estd)		996	991	985	979	973	968	962	
B. ν_6	912	898	875			716[a]	704		684
ν_6 (solid) − ν_6 (soln)	13	11	9				8		15
C. ν_{16}	665	~659 sh	651 p				598 dp		586
		652 dp	632 dp				579 p		

[a] From isotopic impurity in the d_6 sample. See Table IV. [b] From isotopic impurity in the d_8 sample. See Table II.

665-cm^{-1} band of d_0 can be traced through the intermediate compounds to 586 cm^{-1} in d_8 as shown in Table XC. In d_1, d_2, and d_6 it gives two bands, and in d_2 and d_6 one of each pair is polarized. This is just what is expected if, and only if, 665 cm^{-1} is an f_{2g} mode, for on going from O_h to D_{3d} symmetry an f_{2g} mode splits into a_{1g}(p) and e_g(dp). An e_g mode does not give two components when the symmetry is lowered to C_{3v} (d_1) or D_{3d} (d_2 and d_6). Therefore we have good evidence that 665 (d_0) and 586 cm^{-1} (d_8) are f_{2g} modes, and since they are the lowest Raman bands they must be ν_{16}. This is nominally a cube deformation, and the numerical value seems reasonable.

D. Completing f_{2g} and e_g. We now know all four f_{2g} fundamentals for d_0 and three of them for d_8. The product rule indicates that the fourth in d_8 is about 1050 cm^{-1}. There is nothing there, but this is roughly midway between the strong depolarized Raman lines at 1072 (singlet) and 1027 cm^{-1} (doublet). One would like to use 1027 cm^{-1} because it is a doublet in the crystal, but it gives a product rule ratio of 1.996, which is too high compared to the theoretical 2.000. We therefore adopt 1072 cm^{-1} (which gives a ratio of 1.912, too low), and assign 1027 cm^{-1} to ν_5 (e_g) of d_8. However, an e_g mode should not give a doublet, so we suggest that the 1032-cm^{-1} component, which is much weaker, is due to d_7.

An alternative possibility is that 1027 and 1072 cm^{-1} in d_8 may be a Fermi resonance pair. Their average is 1050 cm^{-1}. There is a very weak infrared band at 527 cm^{-1} which will later be assigned to an e_u fundamental. It is possible that 2 × 527 = 1054 cm^{-1} (A_{1g} + E_g) could interact with the missing e_g fundamental at about 1050 cm^{-1} to give the two observed bands. However, it is an f_{2g} fundamental which the product rule suggests is about 1050 cm^{-1}, and it would not interact with this overtone. Consequently we reject this possibility.

Turning now to the e_g modes, we have assigned 912 cm^{-1} in d_0 and 1027 and 684 cm^{-1} in d_8. The product rule suggests that the missing one in d_0 is about 1070 cm^{-1}. There is a weak band at 1083 cm^{-1} which we adopt.

If we had interchanged the assignments of 1072 and 1027 cm^{-1} (putting 1072 cm^{-1} in e_g and 1027 cm^{-1} in f_{2g}), we would have had two problems: (a) a high τ for f_{2g} (1.996) and (b) finding a satisfactory frequency for ν_5 of d_0. The product rule indicates that it should be around 1120 $\mathrm{cm^{-1}}$. The closest Raman bands are 1130 $\mathrm{cm^{-1}}$, which is surely ν_9, and 1083 $\mathrm{cm^{-1}}$. The latter gives a τ for e_g of 1.347, which is too low compared to τ(theor) = 1.414. More important is that there are no reasonable Raman frequencies for ν_5 in d_2 and d_6 between 1083 (d_0) and 1072 $\mathrm{cm^{-1}}$ (d_8). Hence we reject this alternative too.

This completes the g fundamentals for d_0 and d_8. We now turn to those for d_2 and d_6.

g Modes for d_2 and d_6

When giving wavenumbers for the four compounds d_0, d_2, d_6, and d_8, we will for brevity list them in that order without specifying the compounds explicitly. For example, ν_2 is 1002, 991, 967, and 956 $\mathrm{cm^{-1}}$. Vibrations ν_2, ν_6, ν_{16a}, and ν_{16b} have already been traced through the series (see Table X).

a_{1g} for D_{3d}. This species contains two C–H stretches. One of them involves the stretching of the H's (or D's) on the C_3 axis. Its frequency will therefore be high for d_0, low for d_2, high for d_6, and low for d_8. We arbitrarily designate this one as ν_{13a}. The other C–H stretch (ν_1) will then be high–high–low–low. The observed depolarizations make it easy to select these. ν_1 is 2995–2993–2254–2259, and ν_{13a} is 2970–2237–2978–2232 $\mathrm{cm^{-1}}$.

It is also easy to trace ν_{14a} and ν_{15a} through the series because they are polarized in d_2 and d_6. Values for ν_{14a} are 1182–1168–1083–1072, and for ν_{15a} are 821–821–725–715 $\mathrm{cm^{-1}}$. The d_2 band at 821 $\mathrm{cm^{-1}}$ is actually depolarized, but this is permissible and the numerical value is appropriate.

a_{2g} for D_{3d}. There is only one mode in this species (ν_{9a}). It is forbidden in solution, but is allowed in the crystal. Since it involves a C–H bend in which H's on the C_3 axis do *not* participate, its frequency should be the same for d_0 and d_2, and also for d_6 and d_8. We have already assigned it to 1130 $\mathrm{cm^{-1}}$ in d_0 and 884 $\mathrm{cm^{-1}}$ in d_8. In d_2 there is a band at 1133 $\mathrm{cm^{-1}}$, but it is present in both solution and solid and it is polarized. It therefore cannot be due solely to ν_{9a}. We do not know its origin. However, d_1 has a band at 1132 $\mathrm{cm^{-1}}$ in the Raman spectrum of the solid which adds support to the assignment. In d_6 there is a very weak band in the solid at 884 $\mathrm{cm^{-1}}$. This also is helpful confirmation of the assignment.

e_g modes for D_{3d}. Vibrations ν_6 and ν_{16b} have already been identified (Table X). The C–H stretch ν_{13b} is straightforward. It will be high–high–low–low, and the values 2970–2970–2229–2232 $\mathrm{cm^{-1}}$ seem reliable. For ν_{14b} the choices 1182–1174–1145–1072 $\mathrm{cm^{-1}}$ are fairly obvious.

There are three nominal C–H bends in this species. One of them (ν_6) has been identified. One of the other two is a bend of the C–H's that lie on the C_3 axis, so in zero approximation it should go high–low–high–low. For ν_{15b} we select the values 821–738–758–715 $\mathrm{cm^{-1}}$ for the following reasons. In d_2 the only candidates are 821 and 738 $\mathrm{cm^{-1}}$. Since 821 $\mathrm{cm^{-1}}$ has already been used for ν_{15a}, we try 738 $\mathrm{cm^{-1}}$ for ν_{15b}. In d_6 there are six bands between 821 and 715 $\mathrm{cm^{-1}}$. The strongest by far is 758 $\mathrm{cm^{-1}}$, so we shall try it. The above sequence goes high–low–high–low, so it may have considerable contribution from the axial C–H bend.

For ν_5 three values are easily selected: 1083–?–1035–1027 $\mathrm{cm^{-1}}$. In d_2 nothing was observed between 1100 and 1016 $\mathrm{cm^{-1}}$. This may be a case of first-order interaction in d_2, with ν_5 being pushed down to 1016 $\mathrm{cm^{-1}}$ and ν_{9b} up to 1100 $\mathrm{cm^{-1}}$. We adopt these two assignments. In d_6 ν_{9b} should be higher than 884 $\mathrm{cm^{-1}}$, the value in d_8. The next higher depolarized band is 985 $\mathrm{cm^{-1}}$, which we use.

This completes the assignments of the g modes for all four molecules. The product rule ratios for all the various isotopic pairs are given in Table VIII, and are generally satisfactory.

In species e_g there are two crossings in going from d_2 to d_6. Vibration ν_{9b} is higher than ν_5 in d_2 and lower than ν_5 in d_6. Similarly ν_6 is higher than ν_{15b} in d_2 and lower than ν_{15b} in d_6. Although in principle this cannot occur because of the noncrossing rule, and we should interchange the designations in d_6 to remove it, in fact it makes no difference. There are advantages to the present arrangement because it is easier to follow a mode through the sequence of molecules. For example, for ν_6 of d_6, 704 $\mathrm{cm^{-1}}$ was chosen rather than 758 $\mathrm{cm^{-1}}$ because of its greater intensity and greater solid-solution frequency shift. However, the two have mixed in d_6 and share these identifying characteristics to some extent. Thus $\Delta\bar{\nu}$ is 8 $\mathrm{cm^{-1}}$ for 704 $\mathrm{cm^{-1}}$ and 5 $\mathrm{cm^{-1}}$ for 758 $\mathrm{cm^{-1}}$, whereas for 684 $\mathrm{cm^{-1}}$ in d_8 it is 15 $\mathrm{cm^{-1}}$. The noncrossing rule does not hold in going from d_6 to d_8 if the two modes that cross are in different species in d_8.

Remaining Raman Bands

Explanations for the remaining Raman bands are included in Tables I–IV. Only binary sum tones were used; ternary combinations were not tried. Difference tones are improbable because even the lowest fundamentals are fairly high. (Even for d_8 all the fundamentals are greater than 525 $\mathrm{cm^{-1}}$). Furthermore, the infrared spectra of the solids were obtained at ~100 K, making difference tones originating from u levels highly unlikely. All the sum tones which are given are symmetry allowed for our assignments. In many cases there are additional explanations which could be given but which we have not bothered to list. A few comments will be made about each molecule.

d_0. There are only three Raman bands of d_0 which cannot be explained: 2154, 2205, and 2328 $\mathrm{cm^{-1}}$. Since they are all very weak, they do not offer an obstacle.

d_8. Many of the remaining bands may be due to d_7. The only one we wish to comment on is 2052 $\mathrm{cm^{-1}}$, for which $\rho = 0.60$. For d_8 ρ should be either 0 or 0.75. We therefore believe that two bands are superimposed here: the overtone of 1027 $\mathrm{cm^{-1}}$ with $\rho = 0$ and a band of d_7 with $\rho = 0.75$.

d_2. The most serious unanswered questions are how to explain 2985 (intensity 180) and 2246 $\mathrm{cm^{-1}}$ (intensity 50). Neither is due to d_1, for we know its spectrum.

d_6. The worst problems here are presented by 738 (intensity 35), 847 (35), and 1029 $\mathrm{cm^{-1}}$ (15). The first two may be due to d_5.

On the whole we are well satisfied with the assignments for the g modes. We turn now to those for the u fundamentals.

Assignments for the u Modes of d_0 and d_8

For O_h symmetry the u fundamentals are $2a_{2u} + 2e_u + 3f_{1u}(I) + 2f_{2u}$. Only the three f_{1u} modes are active. All other u fundamentals are forbidden for O_h, but allowed in the crystal (Table VIB). We assume that the crystal structure of the samples at ~100 K used for the infrared measurements is the same as the crystal structure of the solid at room temperature, so that the S_6 factor group applies also for the infrared data. This is a key assumption. We have no proof that it is correct except that it seems to work.

It is going to be more difficult to assign the u modes than the g ones because most of the u modes are forbidden for O_h symmetry. Even when allowed in the crystal by the S_6 symmetry, they will probably be weak. Also there is no experimental feature to separate a_{2u} and e_u vibrations (Table VIB).

f_{1u}. These three fundamentals are the only u ones allowed for O_h symmetry. They are therefore expected to be relatively intense in solution as well as for the solid. In d_0 they are easily identified as 2978, 1230, and 853 $\mathrm{cm^{-1}}$. In d_8 2240 and 686 $\mathrm{cm^{-1}}$ are surely two of them. Candidates for the third are 1156 and 1083 cm^{-1}, and the product rule shows that 1083 cm^{-1} is the correct choice. These modes should be doublets in the crystal, and all of them are. (See below concerning the C–H stretch.)

C–H Stretches. There are only two u-type C–H stretches for O_h symmetry: ν_3 in a$_{2u}$ and ν_{10} in f$_{1u}$. They present an interesting situation. In d_0 only one C–H stretch is observed in solution as expected (2977 cm^{-1}), but there are three in the solid: 2965 (s), 2978 (vs), and 2992 cm^{-1} (vs). It is impossible to account for the third one as a binary sum tone, so another explanation is needed. We recall that, when the symmetry is changed from O_h to S_6, f$_{1u}$ modes split into a$_u$ and e$_u$ components and a$_{2u}$ modes go to a$_u$ (Table VIB). Thus in the crystal three frequencies are allowed. We believe that the e$_u$ component is 2978 cm^{-1}, close to the solution value of 2977 cm^{-1}. We further believe that the two a$_u$ components have interacted to give 2965 and 2992 cm^{-1}. This would explain why no one of the three is weak; the a$_u$ mode derived from the O_h-forbidden a$_{2u}$ has picked up intensity from the a$_u$ mode derived from the O_h-allowed f$_{1u}$. It also explains why the separations from 2978 cm^{-1} are nearly equal (15 and 14 cm^{-1}), and rather large compared to our other doublets. In Table I we have designated these a$_u$ bands 2965 and 2992 cm^{-1} as "3 and 10(a$_u$)" to imply that each is a mixture. It then appears that the unperturbed a$_u$ fundamental would have been about 2978 cm^{-1}, almost coincident with the e$_u$ component.

In d_8 the situation is analogous. There is one band in solution (2238 cm^{-1}) but three in the solid: 2229 (m), 2240 (vs), and 2248 cm^{-1} (m). Again it seems that the e$_u$ component is 2240 cm^{-1}, nearly coincident with the solution value, whereas the a$_u$ components have interacted and split to give 2229 and 2248 cm^{-1}. We take the unperturbed value to be about 2239 cm^{-1} and use this for ν_3.

ν_8 (e$_u$). In d_0, d_1, d_2, d_6, and d_8 there are bands at 617, 590, 574, 538, and 527 cm^{-1}, respectively, which cannot be ignored. Although they are weak, they are in every compound and are well isolated from other bands. In d_0 617 cm^{-1} is so useful in explaining sum tones that this alone indicates it to be a fundamental. Since these are the lowest observed bands in each of the compounds, they are probably either ν_4 or ν_8. These are nominally cube deformations, and are expected to be the lowest of the fundamentals.

Species a$_{2u}$ of O_h has only two fundamentals: a C–H stretch which we have just assigned for both d_0 and d_8, and a cube deformation. The product rule can therefore be used to see whether 617 and 527 cm^{-1} belong to ν_4 of this species. It is quickly found that they do not. Therefore 617 and 527 cm^{-1} probably belong to the other nominal cube deformation, ν_8 of e$_u$. This gets some further support from the following observations. (1) In d_0 617 cm^{-1} is not a doublet in the solid. This is consistent with not being an f mode (although by no means proof of it). In d_8 527 cm^{-1} is a doublet, but the higher component (532 cm^{-1}) is much weaker and can be due to d_7. (2) The bands of d_2 (574 cm^{-1}) and d_6 (538 cm^{-1}) are singlets in the solid. If they had originated from f$_{2u}$ in d_0, they should be pairs of bands. Therefore they seem to have originated from a$_{2u}$ or e$_u$ in d_0. Since we have just seen that the product rule eliminates a$_{2u}$, the only possibility left is e$_u$. We therefore assign 617 and 527 cm^{-1} to ν_8.

f$_{2u}$ Modes (ν_{17} and ν_{18}). In d_0 doublets in the solid are significant. (Unfortunately this is not necessarily true for d_8 because of the isotopic impurity.) Species f$_{1u}$ and f$_{2u}$ of O_h should give doublets. Since we know the f$_{1u}$ assignments, we can look for candidates for the two f$_{2u}$ modes of d_0 which are (a) doublets in the solid and (b) absent in solution. Possibilities are 829 (m), 1036 (m), and 1151 cm^{-1} (w).

In d_2 and d_6 the f$_{2u}$ modes split into two components because of lowering of the symmetry. We have designated these a and b. Consider the component that is in a$_{1u}$ of D_{3d}. We note that the product rule ratio for d_0/d_2 is 1, and also for d_6/d_8. Consequently one looks in the infrared spectrum of d_2 to see whether any of the above three bands is present there too. Two are: ~827 (sh) and 1036 cm^{-1} (w, solid only). This gives us the assignments for ν_{17a} and ν_{18a} in d_0 and d_2.

Next we look in d_6 and d_8 for bands which (1) have the same wavenumbers in these two compounds (to give $\tau = 1$) and (2) satisfy the product rule for d_0/d_8. There is only one pair with the same wavenumbers in d_6 and d_8: 927 (vw) and 924 cm^{-1} (vw). Unfortunately, the Raman spectrum of d_8 has a band at 923 cm^{-1}, so this could be due to d_7. However, let us try it. We then have 1036 and 829 cm^{-1} in d_0, and 924 and x cm^{-1} in d_8. By using the product rule, x is estimated to be 670 cm^{-1}. A weak band here might be hidden under the very strong one at 686 cm^{-1}. However, in d_6 there is no interference, and there is a band at 674 cm^{-1}, very weak and in the solid only. Therefore we adopt 927 and 674 cm^{-1} for ν_{17a} and ν_{18a} in d_6, and 924 and 674 cm^{-1} (postulated) in d_8. Both assignments for d_8 are uncertain.

a$_{2u}$ Modes (ν_3 and ν_4). We already know ν_3 in both d_0 and d_8. The product rule then gives the ratio $\nu_4(d_0)/\nu_4(d_8) \simeq 1.045$. One can therefore search the spectra for bands giving this ratio. They should be singlets in the solid and missing in solution. The bands may be weak in the solid because they are made allowed only by the crystal symmetry. Furthermore, ν_4 is nominally a CC$_3$ deformation so it is expected to be <1000 cm^{-1}.

An examination of the infrared spectra of d_0 and d_8 gives several possibilities. An additional restriction is that one ought to find the mode in d_2 and d_6 also. A suitable choice seems to be 839 (m)–838 (s)–807 (m)–807 cm^{-1} (vvw). This gives a satisfactory τ for d_0/d_8 (1.383 vs. 1.414). It also follows the expected selection rules. In solution ν_4 is forbidden for d_0 and d_8, but is allowed for d_2 and d_6. The observations for solution are absent, s, w, absent.

e$_u$ Modes (ν_7 and ν_8). We already know ν_8 in both d_0 and d_8. The product rule then gives the ratio $\nu_7(d_0)/\nu_7(d_8) \simeq 1.185$. These modes are forbidden in solution and should be singlets in the solid. The only observed bands which satisfy these requirements are 1144 or 1151 in d_0 and 960 cm^{-1} in d_8. Unfortunately, 1151 cm^{-1} is a doublet, but it is more intense than 1144 cm^{-1} and more useful in explaining sum tones so we use it in spite of its weaker companion at 1153 cm^{-1}. In d_8 960 cm^{-1} is also observed in the Raman spectrum (intensity 140, $\rho = 0.00$). The Raman band is assigned as ν_2 for d_7. This mode of d_7 is also infrared allowed, and this may account for some of the observed infrared intensity. However, by analogy with the infrared and Raman intensities of ν_2 in d_1, where the symmetry is the same as for d_7, the infrared intensity of 960 cm^{-1} seems to have another contribution. We therefore believe that 960 cm^{-1} is also ν_7 of d_8.

u Modes for d_2 and d_6

These have already been selected for ν_8 (quite certain), ν_{17a} and ν_{18a} (from $\tau = 1$), and ν_4. There are three C–H stretches: two in a$_{2u}$ of D_{3d} (ν_3 and ν_{10a}) and one in e$_u$ (ν_{10b}). All are allowed for D_{3d}. One of the a$_{2u}$ modes involves stretching of the C–H or C–D groups lying on the C$_3$ axis. It will therefore be high–low–high–low. We arbitrarily designate this one ν_{10a}. The other two C–H stretches will be high–high–low–low. The following assignments seem reasonable: for ν_3, [~2978]-2968-2242-[~2239]; for ν_{10a}, 2978-2240-2974-2240; for ν_{10b}, 2978-2977-2236-2240 cm^{-1}.

Selection of the remaining u modes for d_2 and d_6 is a matter of looking for bands with reasonable wavenumbers between those of d_0 and d_8, and then checking with the product rule. Given the assignments for d_0 and d_8, there is not a great deal of choice. Our values are given in Table IX, but do not warrant discussion.

Table XI. Assignments for the Fundamental Vibrations of Cubane-d_1 Compared with -d_0 and -d_2[a]

C_{3v} sym			assignment		
species	sel rules	no.	d_0	d_1	d_2
a_1	R(p), I	1	2995	2993	2993
		2	1002	996	991
		13a	2970	2969	2237
		14a	1182	1174	1168
		15a	821	816	821
		16a	665	~659	651
		3	[~2978]	2977	2968
		4	839	844	838
		10a	2978	2240	2240
		11a	1230	1219	1201
		12a	853	853	851
a_2		9a	1130	1132	(1130)
		17a	1036	1036	1036
		18a	829	834	~827
e	R(dp), I	5	1083	1062	1016
		6	912	898	875
		9b	1130	1101	1100
		13b	2970	{2969}	2970
		14b	1182	1179	1174
		15b	821	826	738
		16b	665	652	632
		7	1151	1145	1109
		8	617	590	574
		10b	2978	{2977}	2977
		11b	1230	1225	1222
		12b	853	847	844
		17b	1036	1002	995
		18b	829	722	711

[a] Braces indicate value used twice. See footnote *b*, Table IX.

It may be noted that ν_{18b} is 651 cm^{-1} in d_6 and *rises* to 674 cm^{-1} in d_8. This can be rationalized as follows. The 651-cm^{-1} value is abnormally low in d_6 because ν_{18b} has had first-order interaction with ν_{12b} in the same species, making the latter abnormally high at 786 cm^{-1}. In d_8 this interaction does not occur because ν_{18b} and ν_{12b} are in different species. Consequently ν_{18b} moves up from 651 to 674 cm^{-1}, and ν_{12b} has a 100-cm^{-1} drop from 786 to 686 cm^{-1}.

This completes the assignments of the u modes. The product rule ratios in Table VIII are on the whole quite good. The weakest assignments for d_0 and d_8 are (a) 1151 cm^{-1} for d_0 and (b) 960, 924, and 674 cm^{-1} for d_8.

Remaining Infrared Bands

Explanations for most of these are included in Tables I-IV. The general comments concerning remaining Raman bands apply here too. For d_0 there are six infrared bands for which we cannot supply an explanation. The only serious problem is presented by 1235 cm^{-1} because of its medium intensity. The other five bands are all very weak. For d_8 there are a number of infrared bands for which we cannot account, but all are weak and we know that there is considerable isotopic impurity. Similarly d_2 and d_6 do not present any serious problems.

Assignments for d_1

Because this molecule has a different symmetry from the others, it is discussed separately. Under C_{3v} the fundamentals are $11a_1$(R,I) + $3a_2$ + 14e(R,I). Our assignments are given in Tables V and XI. The assignments for d_0 and d_2 provide a useful guide because they will bracket those for d_1; they are therefore included in Table XI.

One of the C-H stretches of d_0 will drop to about 2250 cm^{-1} in d_1. We arbitrarily call it ν_{10a}, although it could equally well be termed ν_{13a}. The other C-H stretches are fairly obvious: ν_1 2993, ν_3 and ν_{10b} 2977, and ν_{13a} and ν_{13b} 2969 cm^{-1}.

There is no doubt that ν_2 is 996 cm^{-1}. From the large solid-to-solution shift of the 898-cm^{-1} band, this is clearly ν_6 (Table XB). The large infrared intensities confirm 1219 and 1225 cm^{-1} as ν_{11a} and ν_{11b}, and 847 and 853 cm^{-1} as ν_{12b} and ν_{12a}. The reasons for these particular a-b assignments are as follows.

(1) ν_{11}. The polarized Raman sum tone at 2212 cm^{-1} can be explained as 996 + 1217 = 2213 cm^{-1}. Since both 996 and 2213 cm^{-1} are totally symmetrical, 1217 cm^{-1} must be also. Therefore 1217 cm^{-1} (1219 cm^{-1} in the infrared) is assigned to ν_{11a}, leaving 1225 cm^{-1} for ν_{11b}.

(2) ν_{12}. The Raman band at 844 cm^{-1} has ρ = 0.56. Although this value is possible for a C_{3v} molecule, the deviation of d_1 from O_h symmetry is small enough so that all the other observed ρ's are either 0.75 or <0.26. We therefore believe that the value 0.56 indicates an overlap of ν_4(p) with ν_{12b}(dp). This leaves 853 cm^{-1} for ν_{12a}. Incidentally this makes ν_4 5 cm^{-1} higher in d_1 than in d_0 or d_2, possibly owing to interaction with the 816-cm^{-1} band which can occur in d_1 but not in d_0 or d_2. The 816-cm^{-1} band is assigned to ν_{15a} because it may be polarized. It is 5 cm^{-1} lower than expected, supporting the interaction just suggested.

The Raman band at 1002 cm^{-1} has the correct value for d_0 impurity, but for two reasons we believe that it is also overlapping a band of d_1. (1) For d_0, ρ should be zero rather than the observed 0.26. (2) If 1002 cm^{-1} is due to d_0, it should not appear in the infrared spectrum, whereas it is present for both solid and solution. We therefore suggest that the infrared band is due to ν_{17b}, and that the Raman one is a superposition of ν_{17b} of d_1 and ν_2 of d_0.

The three a_2 modes are forbidden for the free molecule. However, they are allowed by the symmetry of the crystal, and we believe that all three occur weakly in the spectrum of the solid only. They are ν_{9a} 1132, ν_{17a} 1036, and ν_{18a} 834 cm^{-1}. The first one is derived from a g mode of d_0 and d_2, and is found in the Raman spectrum only. The other two are derived from u modes, and are seen only in the infrared spectrum. This is pleasing support.

There is no need to discuss the remaining assignments; they are made by analogy with the d_0 and d_2 ones.

Most of the remaining bands can be satisfactorily explained. (The general remarks concerning remaining Raman bands for the other four molecules apply here too.) The only serious problem is presented by the Raman band at 1027 cm^{-1} (intensity 28, ρ = 0.01). Should this replace one of our other a_1 assignments, and by implication lead us to change something in d_0 and d_2? Examination of Table XI leads to the conclusion that there is only one a_1 fundamental which could be changed, viz., ν_4 (844 cm^{-1}). However, replacing it with 1027 cm^{-1} offers more problems in the other four molecules than it solves, so we conclude that 1027 cm^{-1} is not an a_1 fundamental. In d_0 there is a weak band at this position which is ascribed to an impurity. Possibly in d_1 it is also due to the same impurity, although the intensity is disturbingly high for that. We do not have a satisfactory explanation.

Discussion of the Results

It has been possible to make assignments for all the fundamentals of all five molecules—120 modes in all. For d_0 and d_8 we are confident that the assignments of the g modes are correct. Some of their u modes are uncertain—especially ν_7 for d_0 and ν_7, ν_{17}, and ν_{18} for d_8. There are some additional questions about the assignments of d_1, d_2, and d_6. On the whole, though, it is both surprising and gratifying that one can do so well for d_0 and d_8. This is a consequence of the fortunate crystal structure, and to having data for the intermediate isotopic compounds. Both provided essential information. It is perhaps worth noting again, in hindsight, that the spectra of d_0 and d_8 in solution do follow the selection rules for O_h symmetry, whereas in the polycrystalline solid they follow those for S_6.

Cubane may be regarded as six C_4 rings locked together to form a cube. It is a surprising and curious coincidence that the breathing mode of the (nonplanar) cyclobutane ring, 1004.5 cm^{-1},[10] is only 3 cm^{-1} different from the breathing mode of cubane (1002 cm^{-1}).

It was our expectation that the spectra would have some unusual features because of the severely strained bond angles at the cube corners. To our surprise there is no obvious evidence of this. The modes of d_0 come about where one would expect by analogy with unstrained, saturated hydrocarbons, and its spectrum seems to be quite normal. For example, the frequency of a C-H stretch usually rises as the C-C-C bond angle of the saturated carbon becomes smaller. Thus the highest C-H stretch in cyclohexane is 2963 cm^{-1},[11] in cyclopentane is 2966 cm^{-1},[12] in cyclobutane is 2987 cm^{-1},[10] and in cyclopropane the four modes range between 3025 and 3102 cm^{-1}.[13] Many other examples could be cited, but this is enough to show the trend. We had expected to find at least some of the C-H stretches in cubane above 3000 cm^{-1}, but the highest is 2995 cm^{-1}. This is only a little higher than the highest in cyclobutane. A fairer comparison is to use the average of all the C-H stretches weighted for degeneracy. This average is 2916 cm^{-1} for cyclohexane, 2926 cm^{-1} for cyclopentane (averaged over the eight known stretches), 2939 cm^{-1} for cyclobutane, 2977 cm^{-1} for cubane, and 3059 cm^{-1} for cyclopropane. This does reflect the strain in cubane.

It may be that the force field will show the influence of bond strain more clearly. One of us (E.F.M.) expects to publish a normal-coordinate calculation for cubane. We hope that this will give quantitative information on how normal the bonds are. For now the most we can say is that the spectrum of cubane seems remarkably similar to that of the other saturated hydrocarbons.

There is one interesting point of difference, however. Cubane has no low molecular modes; its lowest fundamental is 617 cm^{-1}. The C_8 cube is a "tight" system because it is bonded three dimensionally, and it is therefore not easy to deform even if all the bonds are single ones. By contrast, benzene, although having much stronger C-C bonds, is considerably more floppy and has an out-of-plane bending mode at 404 cm^{-1}.

References and Notes

(1) (a) The Flinders University of South Australia. (b) University of Pittsburgh. (c) A portion of this paper is from a thesis to be submitted by Gerald L. Jones in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh.

(2) The *Chemical Abstracts* name for cubane is pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane. It is *Chemical Abstracts* compound 277-10-1.

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^1H, ^2H, and ^{13}C ENDOR Studies of Phenalenyl Radicals in Nematic and Smectic Mesophases of Liquid Crystals

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Abstract: ESR, ^1H, ^2H, and ^{13}C ENDOR and TRIPLE experiments have been performed on labeled chloro- and methylphenalenyls ("perinaphthenyls") in isotropic, nematic, and smectic phases of liquid crystals. Hyperfine coupling constant shifts were measured and the assignment to molecular positions is discussed. The results suggest that the substituents cause additional alignment effects of the radicals. Smectic A phases have proved to be advantageous as compared to nematic phases in these studies. The first successful detection of ^{13}C ENDOR lines in a nematic mesophase is reported. Quadrupole splittings were observed for all of the ^2H ENDOR lines, and the complete quadrupole coupling tensor of the ring deuterons (e^2qQ/h = (174 ± 10) kHz, η = 0.08 ± 0.04) and the quadrupole coupling of the methyl deuterons ($e^2qQ/h \sim$ 130 kHz) could be determined.

Introduction

Information about the anisotropic hyperfine or **g**-tensor contributions can in principle be obtained from ESR spectra of organic radicals imbedded in amorphous or polycrystalline solid matrices. However, these spectra usually are very complex and poorly resolved. In isotropic fluid solution, on the other hand, the angular-dependent contributions are averaged out by the Brownian motion resulting in well-resolved ESR spectra, but only the isotropic contact hyperfine interactions and the isotropic g factor can be observed and all information about the anisotropic interactions is lost.

Previously it could be shown in a variety of papers that this lack can be overcome by using liquid crystals as solvents.[1] The long axes of the solvent molecules within the nematic liquid crystals tend to be parallel, and they are macroscopically aligned by applying a magnetic field (~0.3 T). Consequently, the molecular motion of dissolved nonspherical molecules is no longer isotropic, and the ordering of the solute will more or less reflect the ordering of the solvent. This alignment of the radical under study constitutes nonvanishing contributions from the anisotropic hyperfine tensors resulting in quite different hyperfine coupling constants as compared to the isotropic splittings. Unambiguous evaluation of the shifts caused by the anisotropic motion of the molecules calls for the proper determination of the respective isotropic hyperfine coupling constants under the same experimental conditions. A more approximate measurement of the isotropic couplings is