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The Smekal-Raman Spectra of $SiHCl_3$, $CHFCl_2$ and CF_2Cl_2

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The Smekal-Raman spectra of the compounds $SiHCl_3$, $CHFCl_2$ and CF_2Cl_2 have been investigated using a quartz mercury arc as the primary source. There are six frequency displacements in the case of silicochloroform all somewhat less than the corresponding displacements of chloroform. The so-called transverse hydrogen bond frequency is not observed. Eight frequencies of $CHFCl_2$ and nine of CF_2Cl_2 have been observed. The transverse hydrogen bond vibration is not observed in the former. An assignment of the observed frequencies to particular modes of vibrations is made.

Introduction

The Smekal-Raman effect proves to be of great value in the study of molecular structure from a correlation between the observed frequencies and the mechanical modes of vibration of particular molecular models. Considerable success has been obtained in the explanation of the spectra of molecules of the type YX_4.[1] Thus it was thought that by observing the Smekal-Raman spectra of molecules in which some of the X atoms had been replaced by others more information could be gained concerning their structure and modes of vibration.

Experimental Procedure

The apparatus used in these experiments was designed to serve for liquids boiling at −40° to −50°C.[2] The observation tube was a Pyrex glass tube 2.5 cm in diameter with a plane window on one end, a straight portion of 12.5 cm length, and the lower portion tapering off to a point. The tapering portion was surrounded by a jacket filled with black enamel.[3] This took the place of the usual black curved light horn. A sidearm close to the window served for filling. The observation tube was mounted vertically in an unsilvered Dewar flask filled with anhydrous liquid ammonia. The outside of the Dewar, except for a narrow vertical strip, was covered with a piece of highly polished aluminum. Two Hanovia quartz mercury arcs operating on 220 volts were mounted vertically in front of the open strip in the aluminum. A piece of asbestos board was placed over the whole set-up, and the light scattered by the liquid in the observation tube was taken out through a small hole in the board, and reflected by a prism through a lens into the slit of a Hilger D78 glass spectrograph. The copper spectrum was used for comparison.

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[1] B. Trumpy, Zeits. f. Physik **66**, 790 (1930); H. C. Urey and C. A. Bradley, Jr., Phys. Rev. **38**, 1969 (1931).

[2] H. C. Urey and C. A. Bradley, Jr., Phys. Rev. **37**, 843 (1931).

[3] Black Duco of E. I. du Pont de Nemours and Company, Inc.

When one mercury arc was used and run hot, it gave out considerable continuous background. Two arcs were therefore mounted parallel and as close together as possible, and cooled with a current of air. This eliminated most of the continuous, and reduced the consumption of the ammonia. Ammonia was added as needed by pumping some in from a supply in another Dewar flask.

Some of the exposures were made on panchromatic plates, but the best spectra were obtained on Cramer Isopresto plates. The lengths of the exposures were ten and twenty hours.

The first compound studied was silicochloroform. It was prepared by passing dry hydrogen chloride over amorphous silicon at a temperature of 250° to 350°C. The product was condensed in a flask surrounded by solid CO_2. The product was fractionated into another flask, and sealed off. This fraction was distilled under vacuum into the observation tube.

The other compounds studied were dichloromonofluoromethane and dichlorodifluoromethane. These compounds were supplied to us by the Frigidaire Corporation through the kindness of Dr. R. M. Buffington and were reported by their laboratories as "better than 99 percent pure." They were redistilled twice in vacuo and finally distilled into the observation tube, and sealed off. The average measurements of several plates for each of these compounds are given in Tables I, II and III. The mercury arc lines from which Smekal-Raman lines were observed were λλ4047, 4078, 4348, 4358, 5462, 5771, 5792, 3985, 3907, 3651A. They are referred to in the tables as *a*, *b*, *e*, *f*, *g*, *i*, *m*, *n*, *o*, and *r* respectively.

TABLE I. *Silicochloroform*

$\tilde{\nu}$(cm^{-1})	Exciting line	$\Delta\tilde{\nu}$ (cm^{-1})	Note	$\tilde{\nu}$ (cm^{-1})	Exciting line	$\Delta\tilde{\nu}$ (cm^{-1})	Note
24885	*a*	+182	v.w.	22447	*a* *f*	−2256 −491	s.b.
24454	*a*	−248	s.sh.	22350	*f*	−588	w.b.
24265	*b*	−248	w.	22256	*b*	−2257	w.
24215	*a*	−488	v.s.	22135	*f*	−803	w.b.
24116	*a*	−586	b.w.	20677	*f*	−2260	s.b.
24026	*b*	−488	s.sh.	18130	*g*	−178	m.
23906	*a*	−797	s.b.	18057	*g*	−250	w.
23717	*b*	−797	v.w.	17816	*g*	−491	m.s.
23428	*f*	+490	w.	17512	*h*	+185	v.w.
23171	*e*	+176	v.w.	17448	*i*	+185	v.w.
23114	*f*	+176	v.w.	17149	*h*	−178	w.sh.
22759	*f*	−179	w.	17087	*i*	−176	w.sh.
22685	*f*	−253	w.	16838	*h*	−489	w.sh.
22506	*e*	−490	v.w.	16775	*i*	−488	w.sh.

Notes: w. = weak; s. = strong; sh. = sharp; b. = broad; m. = medium; v. = very.

$CHCl_3$*		$SiHCl_3$		$CHCl_3$*		$SiHCl_3$	
$\Delta\tilde{\nu}$	*I*	$\Delta\tilde{\nu}$	*I*	$\Delta\tilde{\nu}$	*I*	$\Delta\tilde{\nu}$	*I*
261	4	179	5	762	3 *d*	587	4 *d*
367	5	250	6	1218	2 *d*	799	6 *d*
669	4	489	10	3019	3 *d*	2258	7 *d*

* Proc. Roy. Soc. **A127,** 360 (1930).

TABLE II. *Dichloromonofluoromethane*

$\tilde{\nu}$ (cm^{-1})	Exciting line	$\Delta\tilde{\nu}$ (cm^{-1})	Note
24429	*a*	−273	m.d.
24368	*r*	−3020	b.
24274	*o*	−3016	w.
24250	*a*	−453	s.sh.
24063	*b* *c*	−451 −270	w.
23982	*a*	−721	v.b.s.
23914	*a*	−789	v.w.
23792	*b*	−722	v.w.
23397	*a* *f*	−1306 +459	m.
23215	*f*	+277	w.
22662	*f*	−276	s.
22572	*n* *f*	−3019 −366	m.w.
22483	*f*	−455	s.sh.
22213	*e* *f*	−783 −726	s.v.b. (band like)
22152	*f*	−786	w.b.
21687	*a* *e*	−3016 −1309	m.
21631	*f*	−1307	w.
21493	*b*	−3021	v.w.
19918	*f*	−3021	w.

$CHFCl_2$

$\Delta\tilde{\nu}$	*I*
274	7
366	4
454	7
723	9
786	4
(1065)*	1
1307	3
3019	5

* $\Delta\tilde{\nu} = 1065$ estimated from the microphotometer curve.

TABLE III. *Dichlorodifluoromethane*

˜	Exciting line	$\Delta\tilde{\nu}$	Note
24443	*m* *a*	−650 −260	v.w.
24383	*a*	−320	v.w.
24272	*a*	−431	w.
24249	*a*	−454	m.
24060	*b*	−454	v.w.
24040	*a*	−662	s.
23850	*b*	−663	v.w.
23626	*a*	−1076	v.w.
23564	*a*	−1139	v.v.w.
23393	*f*	+455	v.w.
23199	*f*	+261	v.w.
22677	*e* *f*	−319 −261	m.
22617	*f*	−321	w.
22502	*f*	−436	w.
22481	*f*	−457	m.
22272	*f*	−666	s.
22061	*f*	−877	v.w.
22019	*f*	−919	v.w.
21850	*f*	−1088	w.b.
21782	*f*	−1156	v.w.

CF_2Cl_2

$\Delta\tilde{\nu}$	*I*
260	5
320	3
433	5
455	7
664	10
877	1
919	2
1082	3
1147	1

THE MODES OF VIBRATION AND THE ASSIGNMENT OF FREQUENCIES

Brester[4] has determined the number of characteristic frequencies of these types of molecules and Dennison[5] has described the character of the vibrations of the chloroform and carbon tetrachloride types of molecules. Brester's

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[4] C. J. Brester, Kristallsymmetrie und Reststrahlen, Dissertation, Utrecht, 1923.

[5] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

work shows that the number of vibrational frequencies of CCl_4, $SiHCl_3$, CF_2Cl_2 and $CFHCl_2$ are 4, 6, 9, and 9 respectively.

In order to assign the frequencies one should have a physical idea as to the character of the motion. The simplest of the above types is carbon tetrachloride. Its four frequencies Brester calls A, B, C_1, and C_2. We may describe them in the following manner. Let the carbon atom be at the origin of the coordinate system. The axes are chosen so that they pass through the midpoints of the lines joining the corner chlorine atoms. Frequency A will consist of a perfectly symmetric motion of the chlorine atoms moving along the lines joining them to the carbon atom, which will remain stationary. This will be an inactive single vibration. Frequency B also is inactive and consists of a twisting motion of pairs of the chlorine atoms; i.e., the chlorine atoms move on the surface of a sphere. The pairs may be selected in three ways, but only two are independent. Thus B is a double frequency.

Frequencies C_1 and C_2 are of a similar character, but very different magnitude. The larger, which we will choose as C_1, will consist of a motion in which the chlorine atoms move nearly along the valence bonds, while for C_2 their motion will be more perpendicular to the bonds. In C_1 the chlorine atoms move in the positive while the carbon atom moves in the negative X direction; the two chlorine atoms with positive X coordinates move away from the X axis, while those with negative X coordinates move toward the X axis. There are three independent ways of choosing the axes in this manner, thus C_1, is a triple vibration. In C_2 the chlorine atoms with positive X coordinates move toward while those with negative X coordinates move away from the X axis, and this frequency is triple.

The most intense Smekal-Raman lines should be those corresponding to inactive frequencies. A will, of course, be larger than B, and more intense. B will be the smallest, C_1 the largest, and C_2 should lie between A and B.

In the Smekal-Raman spectrum of CCl_4 five frequency displacements have been observed. The appearance of the doublet $\Delta\tilde{\nu} = 760$ and $790\ cm^{-1}$ probably is due to accidental degeneracy,[6] although it has been attributed to an asymmetry of the carbon atom.[7] Thus, the assignment for CCl_4 is $A = 460\ cm^{-1}$, $B = 214\ cm^{-1}$, $C_1 = 760\text{–}790\ cm^{-1}$, and $C_2 = 311\ cm^{-1}$.

In the case of CF_2Cl_2, all degeneracy has been removed, and nine frequency displacements are expected in the Smekal-Raman effect. We may describe the nine modes of vibration in the following manner. Let us take for the Z axis the symmetry axis, and let the origin be at the center of the mass. The two fluorine atoms may be considered as lying in the $X-Z$ plane, and the two chlorine atoms in the $Y-Z$ plane. There will be one frequency, A_1^1, which will be somewhat similar to the A vibration for CCl_4. However, it will be active in this case, and the electric moment will vibrate parallel to the Z axis. There will be two vibrations characterized by a twisting motion. We shall call these A_2 and A_1^2. A_2 will be an inactive frequency consisting of a twisting of the pairs of F atoms and Cl atoms about the symmetry axis. A_1^2

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[6] E. Fermi, Zeits. f. Physik **71**, 250 (1931).

[7] A. Langseth, Zeits. f. Physik **72**, 350 (1931).

will consist of a sort of twisting of Cl–F pairs of atoms around some axis perpendicular to the Z axis. It will be an active vibration, and the electric moment will vibrate parallel to the Z axis.

The other six frequencies, we shall group as follows A_1^3, B_1^1, B_2^1 and A_1^4, B_1^2, B_2^2. The first group will be of a character similar to C_1 for CCl_4, and the second group similar to C_2. In A_1^3 the electric moment will vibrate $\|$ to the Z axis; in B_1^1 $\|$ to the X axis; in B_2^1 $\|$ to the Y axis. The motion of the corner atoms will be such that they move nearly along the bonds to the central atom. In A_1^4 the electric moment will be $\|$ to the Z axis, B_1^2 $\|$ to X, and B_2^2 $\|$ to Y and the motion is more perpendicular to the bonds.

It is impossible to assign every frequency displacement observed to the actual modes of vibration. However, it is possible to group them with considerable certainty. Since the F atoms are lighter than the Cl atoms, we would expect A_1^1, to be larger than the A for CCl_4, and to be rather intense. Thus $\Delta\tilde{\nu} = 664$ cm^{-1} becomes A_1^1; A_2 and A_1^2 should be the smallest frequency displacements, and become 260 cm^{-1} and 320 cm^{-1}. In assigning the groups A_1^3, B_1^1, B_1^2 and A_1^4, B_2^1, B_2^2 we expect the first to possess the largest frequencies, and all be rather closely grouped, while the second group should lie between 360 cm^{-1} and 664 cm^{-1}, and also all be rather close to one another. However, I find four frequency displacements in the region of the first group and two in the region of the second. In the first group I assign immediately $\Delta\tilde{\nu} = 1147$ cm^{-1} and 1082 cm^{-1}. The appearance of the two lines $\Delta\tilde{\nu} = 919$ cm^{-1} and 877 cm^{-1} may be due to combinations and accidental degeneracy, for we see that $260 + 664 = 924$ cm^{-1}, $455 + 433 = 888$ cm^{-1}, $1147 - 260 = 887$ cm^{-1}. Therefore, as in the case of C_1 for CCl_4, I must group the frequency displacements, 1147, 1082, 919, and 877 cm^{-1} in the group of vibrations A_1^3, B_1^1, B_1^2. For A_1^4, B_2^1, B_2^2, there are the frequencies $\Delta\tilde{\nu} = 455$ and 433 cm^{-1}. I should expect the third frequency to be close to these two. However, neither the original plate nor the microphotometer curve show any line in this region.

The case of $CHCl_3$ is somewhat simpler. Here one expects six frequency displacements, and they are all observed in the Smekal-Raman effect. Let us take the origin of the coordinate system at the center of mass of the molecule; the Z axis as the symmetry axis and the three chlorine atoms on a plane perpendicular to the symmetry axis. There will be three modes of vibration with the electric moment oscillating $\|$ to the Z axis, and three perpendicular to it. The first three will all be single, and the latter all double vibrations. We will call the $\|$ vibrations A, C_1^1, and C_2^1, and the perpendicular ones B, C_1^2, and C_2^2, corresponding to their similarity with CCl_4. The character of A will in this case be determined by the Cl atoms and consequently, while larger than A for CCl_4, will be of the same order of magnitude, and intense. Thus I ascribe $\Delta\tilde{\nu} = 669$ cm^{-1} to A. In the case of C_1^1 and C_2^1, the character seems to be determined mostly by the vibration of the hydrogen with respect to the rest of the molecule and is very large as a result. One thus expects C_1^1 to be 3019 cm^{-1} and $C_2^1 = 1218$ cm^{-1}. In order to justify this assignment I set up the equations of motion for the parallel vibrations assuming pure valency forces, and used the force constants calculated from CCl_4, (reference 1, p. 1972). The only change made being that one of the corner atoms now had 1/35 of the previous mass. With these very simplifying assumptions, the numerical solution gave for the three parallel vibrations $\Delta\tilde{\nu} = 3015$, 1497, and 466 cm^{-1}; the agreement is quite as good as found in the case of CCl_4 assuming pure valency forces. Frequency B will again be a twisting motion, and the smallest observed frequency displacement; thus B is 261 cm^{-1}. C_1^2 and C_2^2 will be $\perp$ vibrations, as Dennision describes, as tilting of the plane containing the chlorine atoms relative to the line joining the carbon and hydrogen atoms. From analogy, I expect C_1^2 to be larger than C_2^2. Thus C_1^2 is 762 cm^{-1} and C_2^2 is 367 cm^{-1}.

In the case of $SiHCl_3$, again six frequency displacements are observed and they are all somewhat smaller than those for $CHCl_3$, as one would expect from the increased mass of the central atom. The intensities of the observed lines for $SiHCl_3$ are in the same order as those of $CHCl_3$. One may, therefore, immediately assign the frequencies as follows: A is 489 cm^{-1}, B is 179 cm^{-1}, C_1^1 is 2258 cm^{-1}, C_1^2 is 587 cm^{-1}, C_2^1 is 799 cm^{-1}, and C_2^2 is 250 cm^{-1}.

In the compound $CHFCl_2$, all degeneracy is removed and one expects nine frequency displacements in the Smekal-Raman effect. From the intensities of the observed lines, and comparison with the assignment of frequencies for $CHCl_3$, I make the following correlation: A, 723 cm^{-1}; B_1, and B_2, 274 cm^{-1}, and 366 cm^{-1}; C_1^1, 3019; C_1^2, 786 cm^{-1}; C_2^1, 1307 and C_2^2, 454 cm^{-1}. We still must find C_1^3 and C_2^3. C_1^2 shows on the microphotometer curve as being a very close doublet, and as one would expect C_1^3 to lie near C_1^2, 786 cm^{-1} may be both C_1^2 and C_1^3. However, a very faint line is observed also at $\Delta\tilde{\nu} = 1065$ cm^{-1}. This may be C_1^3; it may also be due to the combination $786+274=1060$ or $723+366=1089$. I expect C_2^3 to be close to C_2^2, but no line is observed in that region.

In Table IV I have collected and tabulated the observed frequencies and my assignment to the various types of vibration.

TABLE IV.

$CHFCl_2$	$SiHCl_3$	$CHCl_3$	CCl_4	CF_2Cl_2
$A-723$	$A-489$	A (single $-\parallel$ to Z) -669	$A-460$	$A_1^1-(\parallel$ to $Z)-664$
B_1- 274 B_2- 366	$B-179$	B (double $-\perp$ to Z) -261	$B-214$	A_2-(Inactive)$-$ 260 $A_1^2-(\parallel$ to $Z)$ 320
C_1^1-3019 C_1^2- 786 C_1^3 1065	C_1^1-2258 C_1^2-587	C_1^1 (single $-\parallel$ to Z) -3019 C_1^2 (double $-\perp$ to Z) -762	C_1-760 790	$A_1^3-(\parallel$ to $Z)$ $B_1^1-(\parallel$ to $X)$ $B_1^2-(\parallel$ to $Y)$ 1147 1082 919 877
C_2^1-1307 C_2^2-454 C_2^3- ?	C_2^1-799 C_2^2-250	C_2^1 (single $-\parallel$ to Z) -1218 C_2^2 (double $-\perp$ to Z) -367	C_2-311	$A_1^4-(\parallel$ to $Z)$ $B_2^1-(\parallel$ to $X)$ $B_2^2-(\parallel$ to $Y)$ 455 433

I should like to express my appreciation to Professor Harold C. Urey for his very helpful assistance and advice during the course of this work. I should also like to thank Dr. R. M. Buffington of the Frigidaire Corporation for the samples of $CHFCl_2$ and CF_2Cl_2. And I wish to express my appreciation to the E. I. du Pont de Nemours and Company, Incorporated for the awarding of a fellowship.