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Raman frequencies, relative intensities, and depolarization factors are reported for hexachloroethane and hexabromoethane. The relative intensities and depolarization factors were obtained by use of a Gaertner microdensitometer. The fundamental frequencies of hexachloroethane were used to calculate force constants from the equations used by Stitt for ethane. The Raman data indicate that the equilibrium configuration for hexachloroethane is that corresponding to the point group D_{3d}. The force constants so obtained were then used to calculate the values of the frequencies that are allowed by the selection rules in the infra-red spectrum. Selection rules for the fundamentals, binary combinations, overtones of non-degenerate frequencies, and overtones of degenerate frequencies up to the fourth overtone for any molecule whose symmetry is D_{3h}, D'_{3h}, or D_{3d} were worked out and are discussed.

INTRODUCTION

ETHANE-LIKE molecules are especially interesting in view of the many investigations[3-6] of the ethane molecule during the last few years. These studies have been concerned particularly with the orientation of the methyl groups and the potential barrier restricting internal rotation about the carbon-carbon single bond. Karweil and Schäfer[6] concluded that the stable equilibrium configuration for ethane was that corresponding to the point group D_{3h}, but Stitt[4] in his paper on C_2D_6 regarded the evidence for this conclusion as insufficient and decided after analyzing the data for both the symmetries D_{3h} and D_{3d} that the equilibrium configuration could not be reliably determined from the data then available for C_2H_6 and C_2D_6.

It appeared that it might be interesting to extend the above studies to include molecules of the ethane type, with larger atoms substituted for the hydrogen atoms. For such molecules the potential barrier restricting the internal rotation would be expected to be greater than in ethane and it could be expected that a more definite decision in regard to the equilibrium configuration might be obtained.

The molecules chosen for this investigation were hexachloroethane and hexabromoethane. Raman frequencies, relative intensities, and depolarization factors were obtained (in solution) for these molecules. The more complete spectrum of hexachloroethane seems to indicate clearly that the equilibrium configuration for this molecule is D_{3d}, in agreement with the conclusion of Mizushima and Morino.[7] Force constants were calculated for hexachloroethane, using the Raman fundamental frequencies, and the fundamental frequencies allowed in the infra-red spectrum by the selection rules were then obtained by use of these force constants. Considerable previous data[7-12] were available for hexachloroethane, but there was some uncertainty in regard to three of the frequencies, the depolarization data were incomplete, and the relative intensities were only visual estimates. Hexabromoethane had been investigated only once[13] and the Raman frequencies and relative intensities obtained in that

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investigation are not in satisfactory agreement with those obtained in the present study. No previous polarization data seem to exist for this molecule.

EXPERIMENTAL

The spectrograms were obtained with apparatus previously described.[14-16] The relative intensities and depolarization factors were obtained with the aid of a Gaertner microdensitometer, calibrated by methods described in recent papers.[17] Excitation was by Hg 4358A.

Exposures of from ten to thirty-five hours were made for the following solutions: C_2Cl_6 dissolved in carbon tetrachloride, chloroform, and carbon disulfide; C_2Br_6 dissolved in dioxane, ethylene bromide, and ethyl bromide. The hexachloroethane and hexabromoethane were Eastman grade chemicals obtained from the Eastman Kodak Company. A portion of the solvent used in preparing each solution was used to obtain an exposure equal to that of the longest exposure made on the solution in order to be sure that no solvent lines were attributed to the hexachloroethane or hexabromoethane.

RESULTS

The results obtained for hexachloroethane are compared with the previous data in Table I.

TABLE I. Comparison of the present Raman data for hexachloroethane with that of previous investigators.*

N	Previous data Δν	I_e	ρ	Present results Δν	I	ρ
3	144	1	r	162	vw	P
9	220	4	v	±223	450	0.80
12	340	4	v	±340	370	0.86
12	432	7	r	±431	1000	0.15
1	673	0				
9	858	3	v	859	220	0.81
3	978	1		975	33	0.35

* N is the number of times the line has been observed previously in different investigations, Δν is the Raman frequency in cm⁻¹, I_e is the estimated relative intensity, I is the relative intensity obtained with the aid of the microdensitometer, r or v indicates right or left circularly polarized, respectively, ρ is the depolarization factor, P indicates a polarized line that was too weak to permit a quantitative determination of ρ, vw (very weak) designates a line that was too weak to measure with the microdensitometer, and the ± sign means that the line was observed both as a Stokes and as an anti-Stokes line.

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Several independent measurements made on three different spectrograms consistently locate a very weak line at about 162 cm⁻¹, which is somewhat higher than the average of the values previously reported. Since this line was very

TABLE II. Comparison of the present Raman data for hexabromoethane with previous data.

Gockel Solid C_2Br_6 Δν	I_e	Present results C_2Br_6 in solution Δν	I	ρ
154	3	139	530	0.47
177	1			
211	½	±204	780	0.83
264	1	±255	1000	0.13
		768	460	0.70

weak and in some cases difficult to measure due to overlapping by the Rayleigh wing, its exact location is not readily established. The line at 975 cm⁻¹ appeared as a polarized line and was strong enough to be easily observed and measured. The line previously reported by one investigator at 673 cm⁻¹ was not found in the present investigation.

The results obtained for hexabromoethane are compared with the previous results of Gockel[13] in Table II. The present Δν values are somewhat lower than the corresponding values obtained by Gockel and the intensities show very poor agreement. Furthermore, no line corresponding to the 177 cm⁻¹ frequency could be observed on the several spectrograms of hexabromoethane obtained in this laboratory, although these spectrograms did show a line at 768 cm⁻¹, strong enough to be readily observed, that was not reported in the previous investigation.

In comparing the Raman data for hexachloroethane and hexabromoethane, one notices that the frequencies of the hexabromoethane lie somewhat lower than the corresponding frequencies of hexachloroethane; this is what one would expect in view of the larger masses of the bromine atoms and of the inferior strength of the C—Br bonds. Had a better solvent been known for hexabromoethane, lines corresponding to the weak lines at 162 and 975 cm⁻¹ in the hexachloroethane spectrum might have appeared. Since these two lines could not be observed for hexabromoethane, it was not possible to calculate force constants for this molecule. It is to be hoped that later in-

vestigations may succeed in obtaining the complete Raman spectrum.

CALCULATIONS

The six Raman frequencies observed for hexachloroethane were used to calculate force constants for this molecule from the equations used by Stitt[4] for C_2H_6 and C_2D_6. The particular equations used were those obtained by Stitt from a six-constant potential function of the modified valence force type.* Two cubic equations were involved, one for the three A_{1g} frequencies, another for the three E_g frequencies. Substitution of the observed values of the A_{1g} and E_g frequencies thus would give six equations with six unknown force constants. However, it did not seem practicable to solve these equations directly for the force constants since such complicated expressions were involved. Consequently the procedure followed was to establish relations[18] between the roots (observed $\Delta\nu$ values) and the coefficients for each cubic equation. These relations were simplified by omitting certain terms, but in spite of this omission one could obtain good approximations of the force constants by use of the simplified relations.

Since the analysis of the two cubic equations yielded two sets of approximate values for the force constants, subsequent adjustment of the values was necessary in order to establish a single set which would best satisfy both cubic equations, i.e., would yield the best "test values" for the frequencies (see Table IV).

TABLE III. Force constants in 10^5 dynes/cm for ethane and hexachloroethane.

Force constant	C_2Cl_6	C_2H_6
K_C	4.00	4.60
K_{Cl}	2.00	
K_H		4.79
K_α	0.75	0.46
K_β	0.35	0.46
$K_{\alpha\beta}$	−0.65	−0.015
$K_{C\gamma}$	−1.36	−0.47

* See Eq. (2) of reference 4, page 303.
[18] Relations between the roots and coefficients of an equation: If $a_1, a_2, a_3, \cdots, a_n$ are the n roots of the equation $x^n + p_1 x^{n-1} + p_2 x^{n-2} + \cdots + p_{n-1}x + p_n = 0$, then

$$p_1 = -(a_1 + a_2 + a_3 + \cdots + a_n),$$
$$p_2 = (a_1 a_2 + a_1 a_3 + \cdots),$$
$$p_3 = -(a_1 a_2 a_3 + a_1 a_2 a_4 + \cdots),$$
$$\cdots \qquad \cdots$$
$$p_n = (-1)^n a_1 a_2 a_3 \cdots a_n.$$

The best set of force constants resulting from these calculations is given in Table III, along with the corresponding constants calculated by Stitt for ethane. K_C is the carbon-carbon force constant, K_{Cl} and K_H are, respectively, the

TABLE IV. Calculated and observed frequencies for hexachloroethane.

Type	Raman observed	Test values	Type	Infra-red Calculated
A_{1g}	162	282	A_{2u}	310
	431	313		1001
	975	972		
E_g	223	209	E_u	100
	340	341		325
	859	869		869

carbon-chlorine and carbon-hydrogen force constants, K_α and K_β are, respectively, the bond angle force constants for the $Cl-C-Cl$ and $Cl-C-C$ angles, and $K_{\alpha\beta}$ and $K_{C\gamma}$ are associated with interactions within a CCl_3 or CH_3 group, respectively. The bond distances used in the calculations were obtained from electron diffraction data for similar molecules; they were $C-Cl = 1.76A$ and $C-C = 1.54A$.

As a test of the accuracy and reliability of the above set of force constants and as a safeguard against errors of calculation, the calculations were repeated in reverse order, the frequencies being obtained from the force constants. The extent to which the force constants reproduce the six observed Raman frequencies may be seen in Table IV in which the so-called "test values" are the values calculated from the A_{1g} and E_g equations by use of the force constants listed in Table III.

Having now more or less reliably established the force constants, the A_{2u} and E_u frequencies, allowed only in the infra-red spectrum, were calculated. The calculated A_{2u} and E_u frequencies, as yet unmeasured, are of interest in that they give the neighborhood in which the infra-red bands may be expected to appear.

DISCUSSION

There are three possibilities in regard to the orientation of the two CCl_3 groups: (1) *free rotation*, in which there is no potential restricting rotation about the $C-C$ bond, symmetry D_{3h}';

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(2) *eclipsed*, the orientation in which the Cl atoms are as close together as possible, symmetry D_{3h}; and (3) *staggered*, the orientation in which the Cl atoms are as far apart as possible, symmetry D_{3d}. The selection rules for fundamentals, binary combinations, non-degenerate overtones, and doubly degenerate overtones up to the fourth overtone have been worked out for each of the three cases by methods described elsewhere,[19] but will not be listed here since they have been published in a condensed form already.[20]

The selection rules show that three polarized Raman lines are allowed for each of the three configurations, but that the number of depolarized Raman lines allowed is smaller for the D_{3d} than for the D_{3h} or the D_{3h}' configurations. For D_{3d} only *three* depolarized lines are allowed, while for D_{3h}

TABLE V. Comparison of the Raman data and assignments for hexachloroethane and hexabromoethane.

	Hexachloroethane					Hexabromoethane			
$\Delta\nu$	I	ρ	Type	D^*	$\Delta\nu$	I	ρ	Type	D
162	vw	P	A_{1g}	1	—	—	—	—	—
431	1000	0.15	A_{1g}	1	255	1000	0.13	A_{1g}	1
975	33	0.35	A_{1g}	1	—	—	—	—	—
223	450	0.80	E_g	2	139	530	0.47	E_g	2
340	370	0.86	E_g	2	204	780	0.83	E_g	2
859	220	0.81	E_g	2	768	460	0.70	E_g	2

* D is the degeneracy.

or D_{3h}' *six* depolarized lines are permitted. Since only three depolarized lines were observed, the Raman spectra data thus establish the equilibrium configuration as D_{3d}, unless one makes the improbable assumption that three of the depolarized lines were so weak as to escape observation. This conclusion could be tested further if the infra-red data were available since the selection rules for combinations and overtones for D_{3d} are quite different from those for the other two configurations.

The D_{3d} configuration seems probable on other grounds as well, for the potential barrier restricting internal rotation in ethane is about 3000

calories per mole and since the chlorine atoms are larger and the interactions therefore presumably larger, it seems quite reasonable to suppose that the orientation of the CCl_3 groups should be that in which the Cl atoms in different CCl_3 groups are as far apart as possible. Mizushima and Morino[7] have discussed this point.

Using the calculated infra-red frequencies given in Table IV in conjunction with the selection rules for D_{3d}, one can predict the regions in which infra-red absorption should occur. The numerical values of these expected infra-red frequencies are not written down here since it is not known just how reliable the calculated infra-red frequencies may be. The three lowest infra-red frequencies fall in a region where their observation would be difficult, but it is possible that they may be established by observation of overtone or combination frequencies. Only the second, fourth, sixth, etc., overtones of the A_{2u} and E_u frequencies are permitted in the infra-red spectrum, but six combinations, $A_{1g}\times A_{2u}$, $A_{1g}\times E_u$, $A_{1u}\times E_g$, $A_{2g}\times E_u$, $A_{2u}\times E_g$, and $E_g\times E_u$, are allowed. Especially interesting are those combinations of the torsional A_{1u} frequency, which is forbidden in both the Raman and infra-red spectra, with the three frequencies of the E_g type. From these three combination frequencies, if they could be observed and identified in the infra-red spectrum, one might be able to get a value for the torsional A_{1u} frequency. If this frequency and the A_{2u} and E_u fundamentals could be established by an infra-red investigation, it would then be possible to calculate thermodynamical quantities for hexachloroethane.

With the results for hexachloroethane as a guide, one can make tentative assignments of the observed frequencies for hexabromoethane, assuming that its equilibrium configuration is likewise D_{3d}. The spectra of the two compounds and the assignments are compared in Table V.

ACKNOWLEDGMENT

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