

Hindered Rotation I. The Configuration of the Cyclohexane Molecule

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it is necessary to introduce a steric factor of 10^{-4} if $E=8$ kcal., and state that this small steric factor would be unnecessary if the trimolecular process were assumed. Such a steric factor is, however, a logical consequence of the small probability of the activated state in reactions between complex radicals and molecules on the basis of the activated complex theory of Eyring. The problem is, therefore, not how to explain an anomalous steric factor but whether the steric factor for the trimolecular process may reasonably be expected to be any smaller than 10^{-4} . The present comparison of the effects of added

hydrogen on zinc and mercury diethyls affords further evidence of the existence of a chain reaction initiated by hydrogen atoms formed by the bimolecular mechanism.

The activation energies for the reaction of methyl radicals with hydrocarbons as determined by Smith and Taylor² will probably be approximately valid for the corresponding ethyl radical reaction and although the entropy of activation may be somewhat less for the ethyl radical reaction, in general the reactivity of ethyl may be expected to be not appreciably inferior to that of methyl.

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Hindered Rotation

I. The Configuration of the Cyclohexane Molecule

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A restriction of the free rotation about the carbon-carbon single bond will play an important role in the potential function of the cyclohexane molecule. Any force whose nature is such that it will produce a hindrance to the free rotation about the C—C bond must also give rise to different potential energies for the "chair" and "tub" forms of cyclohexane even if these forms are "strainless" in the Baeyer theory sense. According to the nature of the rotational restriction (stabilizing "staggered" or "opposed" configurations) either the "chair," the "tub," or even the hexagonally symmetrical form with a plane

carbon ring could be the most stable form. From considerations of the obtained Raman spectra of cyclohexane, cyclohexane- d_1 , and cyclohexane- d_{12} it is shown that the only form present in measurable quantities is the form with a D_{6h} symmetry, i.e., the form with the plane of the carbon ring as a reflection plane for the hydrogen atoms. The rotational restriction about the C—C single bond, therefore, is of such a nature that it stabilizes this D_{6h} configuration, in which the H atoms are in "opposed" positions.

INTRODUCTION

AS first pointed out by H. Sachse¹ it is possible to construct two different nonplanar models for the cyclohexane molecule without deforming the tetrahedral angles of the carbon atoms (Fig. 1). Of these two forms I (the "chair") has a high symmetry, D_{3d} , and is rigid in the sense that it cannot be deformed without altering the C—C—C angles in the ring. The symmetry of II (the "tub") is not defined because of a certain flexibility of the model. Without any alteration of the tetrahedral angles it is possible by simple

rotation about the C—C bonds to bring any one of the six carbon atoms up in the ends of the "tub." During this operation the symmetry changes between C_{2v} (for the "tub"), C_2 , and D_2 . On the basis of the simple valence force picture the two forms, I and II, should have the same potential energy because they are both strainless. In ordinary cyclohexane they should therefore both be present in the ratio of their statistical weights 1 : 3. If this proportion is found experimentally to be shifted towards one side or the other it is necessary to introduce a new restriction upon the potential function in order to explain the difference in potential energy of the

¹H. Sachse, Ber. Deutsch. Chem. Ges. 23, 1363 (1890); Zeits. f. physik. Chemie 10, 203 (1892).

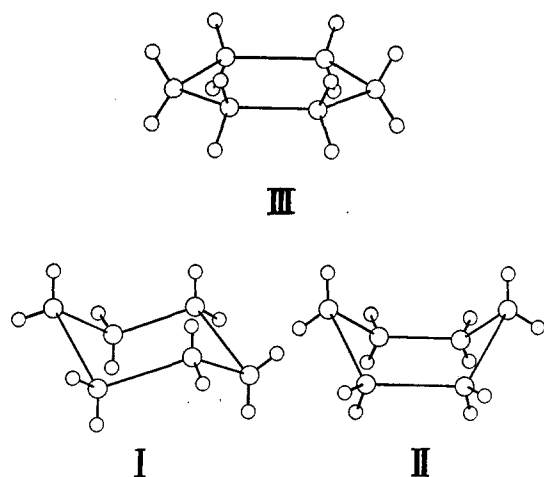


FIG. 1.

two forms. It is easily seen (from a model) that any restriction having the required properties will be equivalent to a restriction of the internal rotation about the carbon-carbon single bond.

As for the qualitative nature of the rotational restriction there are two possibilities to be considered. In the first case each methylene group in cyclohexane will have a tendency to place its H atoms in a staggered position with respect to the H atoms of the neighboring CH_2 groups (as in the centro-symmetrical D_{3d} form of ethane). This will stabilize the puckered D_{3d} form of cyclohexane. If, in the second case, the rotational restriction for the C—C single bond is of such a nature that it will tend to place the H atoms of the different CH_2 groups in opposed positions with respect to each other (as in the D_{3h} form of ethane), this will make the less symmetrical "tub" forms— C_{2v} , C_2 , and D_2 —more stable than the "chair" form— D_{3d} —and tend to produce the most stable plane D_{6h} form (III, Fig. 1). It is important to note that in the last case the rotational restriction will be opposed to the restriction due to the angular restoring force, i.e., the C—C—C angles will be deformed in tending to make the ring plane. It depends on the nature as well as on the order of magnitude of the competing restrictions whether the cyclohexane molecule reaches the plane D_{6h} configuration in which the potential energy due to internal rotation has its minimum. Thus the determination of the configuration of cyclohexane will give valuable

information concerning the nature of the rotational restriction about the carbon-carbon single bond.

EXPERIMENTAL

The cyclohexane used was a commercial product carefully purified by rectification through a 1.0-meter high column: $bp_{760} = 80.6^\circ\text{C}$. Even a strongly exposed Raman spectrum showed no trace of lines due to the presence of benzene, the impurity most likely to be present.

The cyclohexane- d_1 , $\text{C}_6\text{H}_{11}\text{D}$, was prepared from pure bromocyclohexane, $\text{C}_6\text{H}_{11}\text{Br}$, by a Grignard reaction carried out in such a way (which will be described in detail elsewhere) that neither cyclohexane nor cyclohexene could be present as impurities. In order to check the method, a sample of C_6H_{12} was prepared in exactly the same way, using ordinary water instead of D_2O for decomposition of the Grignard compound. Its Raman spectrum was absolutely identical with that of the commercial product purified in the way mentioned above.

Cyclohexane- d_{12} was prepared by deuterating benzene- d_6 at 180°C in the presence of a Ni-catalyst:



The equilibrium mixture thus obtained was purified by treatment with bromine and a small quantity of iron powder in the dark. Under these conditions the benzene- d_6 is rapidly brominated, whereas the cyclohexane- d_{12} is scarcely attacked. After washing and drying it was rectified: $bp_{760} 77.8^\circ\text{--}78.0^\circ\text{C}$.

The Raman spectra were obtained with a newly-built spectrograph. The dispersion at 4500A is 7A per mm and the resolving power

TABLE I. Raman spectrum of cyclohexane.

RAMAN FREQUENCY IN CM^{-1}	INTENSITY	STATE OF POLARIZATION	RAMAN FREQUENCY CM^{-1}	INTENSITY
384.1	1	D	2630.0	1
427.0	2	D	2665.4	2
762	0	—	2701.9	1
801.7	10	P	2853.8	10
1028.6	5	D	2888.3	2
1158.3	3	P	2896.7	2
1267.0	5	D	2908.1	1
1347.6	2	D	2924.0	8
1426.5	$\frac{1}{2}$	—	2934.7	8
1445.1	5	D		
1465.6	$\frac{1}{2}$	—		

sufficiently high to separate lines 1 cm^{-1} apart. The Raman apparatus is of a new construction using six mercury lamps and having a high light gathering power. Raman spectra were taken both without and with filter (sat. NaNO_2 -solution) cutting off the violet lines.

The complete Raman spectra of cyclohexane, cyclohexane- d_1 and cyclohexane- d_{12} are given in the Tables I, II and III. The frequencies of the lines were measured from photographic enlargements by interpolation between standard lines of the iron arc. The positions of the polarized lines may be considered accurate to $\pm 0.2 \text{ cm}^{-1}$. The frequencies of the depolarized lines may usually be trusted to $\pm 0.5 \text{ cm}^{-1}$.

In Tables I and III the state of polarization for the low frequency lines are given. These estimations are based upon the observed shape of the lines.² It is well known that the state of polarization of a Raman line is intimately connected with the rotational structure of the "line," which is really an unresolved vibration-rotation band. If therefore the Raman spectrum is taken with a high dispersion instrument the strongly polarized lines appear as sharp lines (intense Q branch) and the depolarized as bands with no well-defined intensity maximum. Partially polarized lines have shapes in between these two limits with more or less sharp maxima according to their total polarization factor.

TABLE II. Raman spectrum of cyclohexane- d_1

RAMAN FREQUENCY CM^{-1}	INTENSITY	RAMAN FREQUENCY CM^{-1}	INTENSITY	RAMAN FREQUENCY CM^{-1}	INTENSITY
321	0	1034.1	4	2114.9	1
370.7	1	1052.8	2	2144.1	2
375.9	1	1076.5	1	2164.7	2
423.2	2	1106.5	0	2171.8	2
427.4	2	1133.6	2	2180.7	0
566	0	1147.8	1	2192	0
589	0	1151.8	1		
(699?)	0)	1162.4	1	2631.6	0
725.8	3	1168.5	0	2656.0	0
745	0	1199.8	1	2669.3	0
778.3	$\frac{1}{2}$	1255.1	1	2688.3	0
798.7	2	1264.7	4	2697.6	0
801.2	10	1301.0	2		
811	0				
821.3	$\frac{1}{2}$	1348	2	2853.8	10
852	0	1441.3	5	2882.4	2
940.5	1	1447.1	4	2922.1	7
963.1	$\frac{1}{2}$	1464.1	1	2936.6	8
1027.1	5				

² Cf. Langseth and Walles, Zeits. f. physik. Chemie B27, 214 (1934).

TABLE III. Raman spectrum of cyclohexane- d_{12}

RAMAN FREQUENCY CM^{-1}	INTENSITY	STATE OF POLARIZATION	RAMAN FREQUENCY CM^{-1}	INTENSITY
298.2	1	<i>D</i>	2064.3	1
373.2	2	<i>D</i>	2082.8	10
385	0	—	2097.6	4
593	0	—	2106.6	5
637	0	—	2127.0	1
696	0	—	2154.6	6
715.9	0	—	2173.8	1
723.8	10	<i>P</i>	2199.7	6
746.2	1	<i>P</i>	2239.3	1
795.6	5	<i>D</i>	2298.1	$\frac{1}{2}$
931	3	<i>D</i>	2320.9	1
937.2	5	<i>P</i>	2390.9	$\frac{1}{2}$
1014.8	1	<i>P</i>		
1070.6	3	<i>D</i>		
1119.8	2	<i>P</i>		
1214.1	2	<i>D</i>		
1305	0	—		

Our measurements of the Raman frequencies of cyclohexane agree—except for a couple of faint lines—with previous investigations.³ Discrepancies between our estimation of the state of polarization of certain lines in the spectrum of cyclohexane and previous measurements will be discussed later on.

DISCUSSION

1. Cyclohexane

As already mentioned it is necessary to consider D_{6h} , D_{3d} , D_2 , C_{2v} , and C_2 as possible symmetries for the cyclohexane molecule. According to the selection rules for the symmetries D_2 , C_{2v} , and C_2 all 48 vibrational frequencies are Raman active. Hence the presence of molecules of these symmetries in the cyclohexane should give rise to a very complicated spectrum. As Table I shows this is far from being the case. In fact the spectrum is surprisingly simple for a vibrational system of 18 atoms and immediately indicates a high symmetry of the molecule. Although the Raman spectrum of C_6D_{12} may appear more complicated than that of C_6H_{12} , it is still indicative of a higher symmetry than D_2 , C_{2v} , or C_2 for the molecule.⁴ Also, it is immediately evident, on comparison of the complexity of the spectra of C_6H_{12} (or C_6D_{12}) and $\text{C}_6\text{H}_{11}\text{D}$ (Table II) that a change from a high to a low symmetry has been

³ For literature see Kohlrausch, *Smekal-Raman-Effekt*, Ergänzbd., p. 229.

⁴ The spectrum of C_6D_{12} will be discussed in detail in the latter part of the article.

affected. We feel therefore justified in excluding the possibility of symmetries as low as D_2 , C_{2v} , and C_2 for the cyclohexane molecule as well as the possibility of cyclohexane being a mixture of different stereo-isomers. The remaining question is to decide between the only possible symmetries: D_{6h} and D_{3d} .

In Table IV the selection rules for the D_{6h} and D_{3d} symmetries are summarized. It is a well-known fact that Raman spectra of molecules containing several hydrogen atoms show a very complicated structure in the 3000-cm^{-1} region because of the high probability for accidental degeneracy between overtones (and combination tones) of hydrogen deformation frequencies and hydrogen stretching frequencies.⁵ For this reason in Table IV the fundamentals corresponding to hydrogen stretching frequencies $2800\text{--}3000\text{ cm}^{-1}$ are separated out, and in the following only the region below *ca.* 1500 cm^{-1} will be considered.

From Table IV, the principal difference between the two symmetries is that the D_{6h} symmetry allows only 2 totally symmetric fundamentals, whereas the D_{3d} symmetry allows 4 totally symmetric frequencies, all of which should appear in the Raman spectrum as polarized lines. According to our observations the spectrum of cyclohexane contains 2 strongly polarized, and 6 depolarized lines corresponding to fundamentals with frequencies below 1500 cm^{-1} .⁶ The 3 additional lines observed in this region are weak and can plausibly be explained as overtones and combination tones. The low frequency part of the Raman spectrum is therefore in perfect accordance with the selection rules for a D_{6h} structure of the cyclohexane molecule.

Furthermore, the D_{6h} symmetry is strongly supported by the following argument. From

⁶ The same applies to the corresponding deuterium frequencies. This is illustrated most strikingly by the spectrum of $C_6H_{11}D$. For this molecule only one deuterium stretching frequency around 2200 cm^{-1} is to be expected. Five out of the six lines observed in this region must therefore be due to overtones and combination tones taking up intensity by interaction with the active fundamental.

⁶ In a discussion of the structure of the cyclohexane molecule Kohlrausch and Stockmair (Zeits. f. physik. Chemie **B31**, 382 (1936)) decided in favor of the D_{3d} symmetry on the basis of previous polarization measurements, which seemed to indicate that 4 of the low frequency lines were polarized. According to Hanle and Heidenreich (Zeits. f. Physik **97**, 277 (1935)) the two rather faint lines, 384.1 cm^{-1} and 1347.6 cm^{-1} , seem to be polarized, whereas the shape of these lines on our plates definitely indicates a depolarization factor very close to $6/7$. The following discussion of the spectrum confirms our estimation of $\rho = 6/7$ for these two lines.

TABLE IV.

SYMMETRY OF THE MOLECULE	VIBRATIONAL SYMMETRY CLASS	NUMBER OF RAMAN ACTIVE FUNDAMENTALS WITH FREQUENCIES	
		<1500 cm^{-1}	>1500 cm^{-1}
D_{6h}	A_{1g}	2 non-deg. (P)	1 non-deg. (P)
	E_g^+	4 deg. (D)	1 deg. (D)
	E_g^-	2 deg. (D)	1 deg. (D)
D_{3d}	A_{1g}	4 non-deg. (P)	2 non-deg. (P)
	E_g	6 deg. (D)	2 deg. (D)

Table I it is seen that the two fundamentals with the lowest frequencies must have a combination tone whose frequency happens to fall close to the strongest Raman active fundamental, which must be assigned to a totally symmetrical (A_{1g}) vibration:

$$384.1 + 427.0 = 811.1\text{ cm}^{-1} \sim 801.7\text{ cm}^{-1}.$$

Because of the closeness of this accidental degeneracy an interaction may be expected to occur *if the combination tone has totally symmetrical properties*. Even if this interaction for some special reason was weak, we still might expect the combination frequency (which in itself must be allowed in Raman effect) to take up enough intensity from the very strong totally symmetrical fundamental to make it appear on a strongly exposed Raman plate. We have, however, *not* been able to detect any line which could be assigned to this combination tone, although the corresponding interaction in the spectrum of cyclohexane- d_1 , where it must be allowed, is observed very distinctly.⁷ From this we conclude that the said combination frequency in cyclohexane is *not allowed* to interact with the totally symmetrical vibration, and therefore has too low an intensity to be observed, as is usually the case for combination frequencies.

If cyclohexane had D_{3d} symmetry, fundamentals belonging to two different symmetry classes only would be Raman active, namely A_{1g} and E_g (cf. Table IV). A combination tone between any two frequencies from these symmetry classes will have totally symmetrical properties (A_{1g} or $A_{1g} + E_g$) and therefore will always be allowed to interact with the A_{1g} frequency.

⁷ The fact that the interaction in the cyclohexane- d_1 spectrum is observed to cause an *intensification* of the combination tone indicates that we should expect the same effect in the spectrum of C_6H_{12} even if a *weakening* theoretically might be the result of an interaction.

However, since no interaction has been observed cyclohexane cannot have D_{3d} symmetry. If on the other hand we assume D_{6h} symmetry for the molecule the Raman active frequencies belong to three different symmetry classes: A_{1g} , E_g^+ , and E_g^- . A combination tone between an E_g^+ and an E_g^- frequency will have the symmetry ($B_{1g} + E_g^-$) and is therefore not allowed to interact with a totally symmetrical frequency. This supports the assignment in Table V of the Raman lines 381.1 and 427.0 cm^{-1} to $E_g^-(\nu_{10})$ and $E_g^+(\nu_6)$, respectively, on the basis of a D_{6h} symmetry.

The first overtones of both of the degenerate frequencies ($2\nu_{10} = 768.2 \text{ cm}^{-1}$ and $2\nu_6 = 854.0 \text{ cm}^{-1}$) are allowed in Raman effect and might be expected to appear as weak lines in the spectrum. The theoretically possible interaction with the totally symmetrical vibration ($\nu_1 = 801.7 \text{ cm}^{-1}$) is not likely to play any important role because of the large separation. We have in fact only been able to find the first as an extremely weak line at 762 cm^{-1} .

Without intending to give a detailed discussion of the observed spectra at the present stage of the investigation we have in Table V given an assignment of the observed low frequency lines in cyclohexane. This assignment is fairly certain as it is based on the knowledge we have of the corresponding modes of vibration in the benzene molecule.⁸ For the sake of comparison the assignment of the cyclohexane- d_{12} spectrum is also given in Table V. This assignment will be discussed in some detail in the latter part of this article. We have numbered the modes of vibration in such a way that their relation to the corresponding normal frequencies in the benzene molecule is obvious.⁹ A schematical diagram of the modes of vibration discussed in this article is given in Fig. 2.

2. Cyclohexane- d_1

The cyclohexane- d_1 molecule cannot have any symmetry higher than C_s (i.e., one plane of symmetry only). All the degenerate vibrations will therefore split up into two components and all frequencies forbidden in the Raman spectrum of cyclohexane (because of its high symmetry) are now allowed. As already mentioned, this is

⁸ Cf. A. Langseth and R. C. Lord, Jr., Kgl. Danske Vidensk. Selsk. math.-fys. Medd. XVI, p. 6 (1938).

⁹ Langseth and Lord, reference 8, p. 10. This notation is—except for a few minor alterations—identical with that given by Wilson, Phys. Rev. 45, 706 (1934).

confirmed by the experiment insofar as there is a very considerable increase in the number of lines observed in the Raman spectrum of $\text{C}_6\text{H}_{11}\text{D}$ as compared with that of C_6H_{12} . Also the predicted release of degeneracy is observed for the two frequencies ν_{10} and ν_6 . The two components of each of these close doublets correspond in the cyclohexane- d_1 molecule to nondegenerate vibrations, one of which is symmetrical (A') and the other antisymmetrical (A'') to the plane of symmetry which is now the only symmetry-element of the molecule.

It is of interest to consider the overtones and combination tones of the frequencies $10a$, $10b$, $6a$, and $6b$ also in cyclohexane- d_1 . They are all allowed in Raman effect and are also observed as will be seen from Table VI. But the important point is that the interaction to be expected between the totally symmetrical fundamental ν_1 and the combination frequencies ($\nu_{10a} + \nu_{6a}$) and ($\nu_{10b} + \nu_{6b}$), respectively—both of which are totally symmetrical—is observed as a spreading of the two lines to both sides of ν_1 . For the same reason the two lines are more intense than unperturbed combination tones usually are. As already emphasized, the observation of this interaction in cyclohexane- d_1 strengthens our conclusion, that the reason why we did not find the corresponding interaction in the spectrum of cyclohexane is the fact that it is forbidden because of the D_{6h} symmetry of the molecule. The antisymmetrical combination frequencies ($\nu_{10a} + \nu_{6b}$) and ($\nu_{10b} + \nu_{6a}$)—which are not allowed to interact with ν_1 —are found almost exactly at the calculated frequency

TABLE V. Assignment of frequencies below 1500 cm^{-1} .

C_6H_{12} FREQ. cm^{-1}	SYMMETRY CLASS	MODE OF VIBRATION	C_6D_{12} FREQ. cm^{-1}
384.1	E_g^-	ν_{10}	298.2
427.0	E_g^+	ν_6	373.2
—	—	?	385
762	$(A_{1g} + E_g^+)$	$2\nu_{10}$	593
—	A_{1g}	$(\nu_1 + \nu_{10}) - \nu_{10}$	637
—	A_{1g}	$(\nu_1 + \nu_6) - \nu_6$	696
—	A_{1g}	$(\nu_1 + \nu_{10}) - \nu_{10}$	715.9
801.7	A_{1g}	ν_1	723.8
—	A_{1g}	$(\nu_1 + \nu_6) - \nu_6$	746.2
1028.6	E_g^+	ν_9	795.6
1158.3	A_{1g}	ν_{2x}	937.2
1347.6	E_g^-	ν_{10y}	931
—	$(A_{1g} + E_g^-)$	$\nu_1 + \nu_{10}$	1014.8
1267.0	E_g^+	ν_{7x}	1070.6
—	$(A_{1g} + E_g^+)$	$\nu_1 + \nu_6$	1119.8
1445.1	E_g^+	ν_8	1214.1
—	$(A_{1g} + E_g^+)$	$\nu_{2x} + \nu_6$	1305
1465.6	$(A_{1g} + E_g^+)$	$\nu_6 + \nu_9$	—

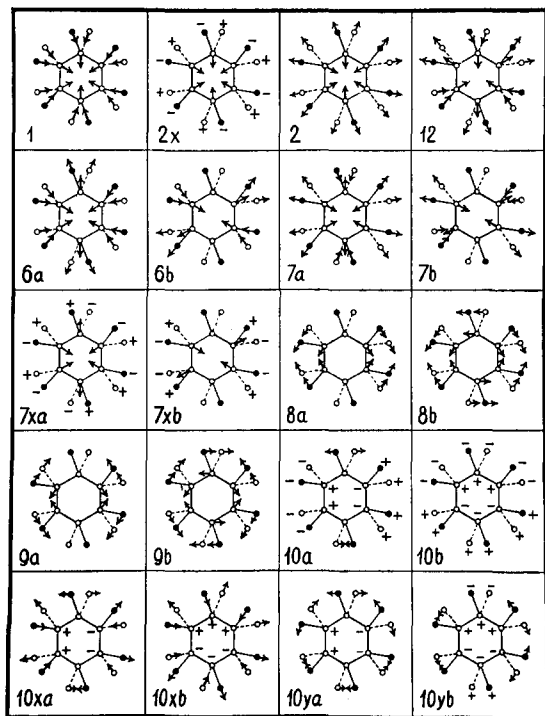


FIG. 2.

close to the strong ν_1 where they are overlapping a sharp line due to $C_5^{12}C^{13}H_{11}D$ molecules. This accounts for the intensity of this line being a little higher than one would expect for a pure carbon isotopic line.

3. Cyclohexane- d_{12}

As already mentioned the Raman spectrum of the heavy cyclohexane is more complicated than that of the light compound. This arises from two cases of accidental degeneracy between fundamentals and combination tones. The resulting interaction causes an increase in the number of Raman lines in the low frequency region of the C_6D_{12} -spectrum and thus complicates the simple structure of the spectrum which is found for C_6H_{12} . The assignment of the fundamentals given in Table V explains the strongest of the observed lines in the spectrum of C_6D_{12} and is supported by the "product rule." Although the use of the product rule is to some extent limited in this case because of the uncertainty in the assignment of hydrogen and deuterium stretching frequencies¹⁰ it shows nevertheless that the given

¹⁰ The complexity of the spectra in these regions is caused by the chaotic mixture of interacting fundamentals, overtones and combination tones.

assignment, on the basis of a D_{6h} symmetry, is the only one plausible. In Table VII the theoretical¹¹ and the observed products (τ 's) are given for the three Raman active symmetry classes. The agreement is satisfactory when the anharmonicity of the observed frequencies is taken into account.

The strongest of the interactions mentioned above is that between the combination frequency $\nu_1 + \nu_6 (A_{1g} + E_g^+)$ observed at 1119.8 cm^{-1} (calc.: $723.8 + 373.2 = 1097.0 \text{ cm}^{-1}$) and the fundamental, $\nu_{7x} (E_g^+)$ observed at 1070.6 cm^{-1} . Because of this interaction the combination tone appears as a rather strong line shifted towards higher frequencies. As the wave functions for ν_{7x} and $(\nu_1 + \nu_6)$ are mixed because of the interaction, we should expect two other lines in the spectrum corresponding to transitions from the first excited level of ν_6 (which is densely populated at ordinary temperatures) up to the two resonance levels. These transitions correspond to an excitation of the strongly Raman active ν_1 . The two difference tones should therefore be present in the spectrum if the given interpretation is correct. In fact, they are both observed at their calculated positions. As the frequencies of the starting level as well as of both end levels are observed in the spectrum, the frequencies of the expected lines are given accurately by the differences: $1070.6 - 373.2 = 697.4 \text{ cm}^{-1}$, obs. 696 cm^{-1} , and $1119.8 - 373.2 = 746.6 \text{ cm}^{-1}$, obs. 746.2 cm^{-1} .

The fortuitous degeneracy between $(\nu_1 + \nu_6)$

TABLE VI. Combination frequencies in cyclohexane- d_{12} .

SYMMETRY CLASS	ASSIGNMENT	FREQUENCY IN cm^{-1}	
		CALC.	OBS.
A'	$2\nu_{10a}$	742	745
A''	$\nu_{10a} + \nu_{10b}$	747	
A'	$2\nu_{10b}$	752	
A'	$2\nu_{6a}$	846	852
A''	$\nu_{6a} + \nu_{6b}$	850	
A'	$2\nu_{6b}$	854	
A''	$\nu_{10a} + \nu_{6b}$	798	799
A''	$\nu_{10b} + \nu_{6a}$	799	
A'	$\nu_{10a} + \nu_{6a}$	794	Inter-action { 778
A'	ν_1	801.2	
A'	$\nu_{10b} + \nu_{6b}$	803	

¹¹ The moments of inertia contained in the theoretical τ for the E_g^- class are calculated on assumption of the C-C distance as 1.51 Å and the C-H distance as 1.08 Å.

and ν_{7x} cannot be complete because the two Raman lines have different intensities and states of polarization. As the 1119.8-line is weaker and more polarized than the 1070.6-line, the wave function for the 1119.8 cm^{-1} resonance level must contain the greater part of the $(\nu_1 + \nu_6)$ wave function. Therefore, according to expectation the 746.2 cm^{-1} line is the stronger of the two difference tones.¹²

Another case of interaction is observed in the cyclohexane- d_{12} spectrum between the combination frequency $\nu_1 + \nu_{10}(A_{1g} + E_g^-)$ and the two almost coinciding fundamentals $\nu_{2x}(A_{1g}) = 937.2 \text{ cm}^{-1}$ and $\nu_{10y}(E_g^-) = 931 \text{ cm}^{-1}$. Here the resonance is weaker (because of the larger separation of the interacting levels) and is responsible only for an intensification of the combination tone, which is observed at 1014.8 cm^{-1} almost at the calculated position: $\nu_1 + \nu_{10} = 1022.0 \text{ cm}^{-1}$. This assignment is verified by the observation of the expected difference tone: 715.9 cm^{-1} , calculated $1014.8 - 298.2 = 716.6 \text{ cm}^{-1}$. A slight mixing of the $(\nu_1 + \nu_{10})$ with the ν_{2x} and ν_{10y} wave functions is also indicated by the very faint and broad line observed at 637 cm^{-1} which can be explained as the unresolved difference tones: $937.2 - 298.2 = 639.0 \text{ cm}^{-1}$ and $931 - 298.2 = 633 \text{ cm}^{-1}$.

THE ABSENCE OF C^{13} -ISOTOPIC LINE IN CYCLOHEXANE

Finally we want to call attention to a very puzzling feature in the Raman spectrum of cyclohexane, even if this has no close relation to the problem we are discussing. It is the fact (which has been bothering one of us ever since he took his first Raman spectrum of cyclohexane in 1931) that no C^{13} -isotopic satellite is to be found close to the strong 801.7 cm^{-1} line in cyclohexane. The spectrum of $\text{C}_6\text{H}_{11}\text{D}$ reveals the mystery. The explanation is the same as the one which accounts for the surprisingly small shift in the frequency of ν_1 from 801.7 cm^{-1} in C_6H_{12} to 801.2 cm^{-1} in $\text{C}_6\text{H}_{11}\text{D}$. In cyclohexane as well as in benzene the trigonally symmetrical frequency

¹² Unfortunately the weak overtone of ν_6 (calc. 746.4 cm^{-1}) falls very close to the difference tone which it is partly overlapping. It served therefore no useful purpose to make quantitative measurements of the relative intensities of the two difference tones. Cf., the discussion of an exactly corresponding interaction, observed in the Raman spectrum of benzene; Langseth and Lord, J. Chem. Phys. 6, 203 (1938); Kgl. Danske Vidsk. Selsk. Medd. XVI, p. 51 (1938).

ν_{12} (see Fig. 2) has a value in the neighborhood of the totally symmetrical ν_1 .¹³ In benzene ν_{12} has a somewhat higher frequency but in cyclohexane its frequency is a little lower than ν_1 . In cyclohexane itself ν_{12} is inactive and not allowed to interact with ν_1 . As soon, however, as the symmetry of the molecule is destroyed—e.g. by introduction of one deuterium atom or of one C^{13} atom— ν_{12} becomes a totally symmetrical vibra-

TABLE VII.

τ	A_{1g}	E_g^+	E_g^-
Theoretical	2.00	2.83	2.50
Calculated	1.9	2.7	2.4

tion and a strong interaction with ν_1 springs into being. The result of this interaction is firstly, a transfer of intensity from ν_1 to ν_{12} , which causes ν_{12} to show up in the spectrum of cyclohexane- d_1 as a fairly strong and polarized line at 725.8 cm^{-1} , and secondly, that the two frequencies are pressed apart: ν_{12} towards lower and ν_1 towards higher frequencies. Now it happens that the increase in frequency for ν_1 due to the interaction cancels almost exactly the decrease in frequency due to the greater mass of the D or the C^{13} atom. For this reason ν_1 has almost exactly the same frequency in $\text{C}_6\text{H}_{11}\text{D}$ or in $\text{C}_5^{12}\text{C}^{13}\text{H}_{12}$ as in C_6H_{12} . However, if the mass of the molecule is increased further, as it is in $\text{C}_5^{12}\text{C}^{13}\text{H}_{11}\text{D}$, then a slight decrease in the frequency of ν_1 is observed as a C^{13} -isotopic satellite at 798.7 cm^{-1} in the spectrum of cyclohexane- d_1 .

Apparently, the same conditions as in C_6H_{12} are prevailing also in C_6D_{12} as we have been unable to find a C^{13} -isotopic line in its spectrum.

SUMMARY

The Raman spectra of cyclohexane, cyclohexane- d_1 and cyclohexane- d_{12} have been obtained.

From considerations of: (1) number and state of polarization of fundamentals observed, (2) selection rules, in particular for cases of interaction between fundamentals and overtones or combination tones, and (3) Teller's product rule, the configuration of the cyclohexane molecule has been assigned a D_{6h} symmetry.

¹³ Cf. A. Klit and A. Langseth, J. Chem. Phys. 5, 925 (1937); Langseth and Lord, reference 12, p. 25.