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In a molecule such as CH_3OH it is difficult to know how many electrons to assign to the carbon and how many to the oxygen and so one cannot say with certainty just what the area under a peak should be. There are eighteen electrons to be assigned to the molecule; this gives a definite (undoubtedly too large) upper limit to the area under the peak corresponding to $\text{C}-\text{O}$ of $2 \times 9^2 = 162$. The observed area is about 130. If we assign approximately 9 scattering electrons to the oxygen atom then from the measured area under the peak at 2.7\AA we may calculate the number of oxygen neighbors at this distance: $\text{Area} = n \times 9^2$. It is hard to know just how much to include in the area under this peak but in any case it is of the order of 200 units. Thus $n \approx 2$ in agreement with Zachariasen's picture. The positions of the other peaks are

practically the same as Zachariasen obtained from Stewart and Morrow's data and accordingly agree completely with his interpretation. It is felt that the peak in the distribution curve at 2.7\AA together with its disappearance at high temperatures gives very strong evidence for the truth of Zachariasen's picture of the molecular arrangement in liquid methyl alcohol.

It was planned to carry out a similar analysis on a whole series of the normal alcohols and some work has been completed on ethyl alcohol. Due to unavoidable delay and also to the fact that diffraction patterns from the higher alcohols are not nearly so straightforward of interpretation it is thought worthwhile to record the present results. The author is indebted to Professor B. E. Warren for his encouragement and interest throughout the work.

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The Isotope Effect in the Vibration Spectrum of CCl_4

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The fine structure in certain of the Raman lines of CCl_4 observed by Langseth and interpreted by him as being due to a lack of symmetry in the four carbon valencies has been shown to be accountable for as a purely isotopic effect. Rosenthal's general theory of the isotope effect in molecules of this type has been applied to the case of CCl_4 in an attempt to differentiate between two types of potential function which have been proposed for this molecule. The fine structure patterns predicted on the different theories have been worked out. Unfortunately the existing experimental data are not sufficiently good to allow a decision to be made as to which is the better function.

IN 1931 A. Langseth¹ reported that the Raman lines of carbon tetrachloride possessed a fine structure which he concluded was due to the different varieties of the compound arising from the presence of the two chlorine isotopes. Thus the five isotopic compounds CCl^{35}_4 , $\text{CCl}^{35}_3\text{Cl}^{37}$, $\text{CCl}^{35}_2\text{Cl}^{37}_2$, $\text{CCl}^{35}\text{Cl}^{37}_3$, CCl^{37}_4 should be present in the following relative percentages 31.6, 42.2, 21.1, 4.7 and 0.4. The proportion of $\text{CCl}^{35}\text{Cl}^{37}_3$ and CCl^{37}_4 being so small it may be taken that the Raman lines from those varieties of tetrachloride will be too weak to be observed; the remaining three varieties should each have their

own Raman spectrum differing slightly from one another and so giving rise to an apparent fine structure. The theory of the effect was worked out on very elementary lines by Langseth who found that although he could explain the fine structure in one of the Raman frequencies he could not account for the observed structure in the case of the two other frequencies in which it was observed. It occurred to us that the theory of this effect can be treated much more accurately now since the general equations have been developed by Rosenthal.² However in order to make numerical predictions it is necessary to

¹ Langseth, *Zeits. f. Physik* **72**, 350 (1931).

² Rosenthal, *Phys. Rev.* **45**, 538 and **46**, 730 (1934).

TABLE I.

CX ₄	CX ₃ X'	CX ₂ X ₂ '	LANGSETH	
			PREDICTED	OBSERVED
$\nu_1(1)$	$\nu_1'(1)$	$\nu_1''(1)$	$\nu_1 - \nu_1' = \nu_1' - \nu_1'' = 3.15 \text{ cm}^{-1}$	$\nu_1 - \nu_1' = 3.10 \text{ cm}^{-1}$ $\nu_1' - \nu_1'' = 3.20 \text{ cm}^{-1}$
$\nu_2(2)$	$\nu_2'(2)$	$\nu_{2a}''(1)$ $\nu_{2b}''(1)$	$\nu_2 - \nu_2' = 1.49 \text{ cm}^{-1}$	Doublet with spacing = $2.2 \pm .2 \text{ cm}^{-1}$
$\nu_3(3)$	$\nu_{3ab}'(2)$ $\nu_{3c}'(1)$	$\nu_{3a}''(1)$ $\nu_{3b}''(1)$ $\nu_{3c}''(1)$	—	Unresolved
$\nu_4(3)$	$\nu_{4ab}'(2)$ $\nu_{4c}'(1)$	$\nu_{4a}''(1)$ $\nu_{4b}''(1)$ $\nu_{4c}''(1)$	$\nu_4 - \nu_4' = 2.16 \text{ cm}^{-1}$	Doublet with spacing = $2.93 \pm .2 \text{ cm}^{-1}$

know the potential constants of CCl₄. Several different sets of those have been proposed by various authors. What we have done then is to compute the isotopic fine structure of the Raman spectrum of CCl₄ using two of the most generally accepted models of this molecule to see whether the predicted isotope effect agrees better with the observations in the one case than in the other. This method of using the isotope effect to discriminate between different force fields is likely to be of great importance in the near future more especially now that methods of concentrating heavy nitrogen have been developed.

The CX₄ molecule in which the X atoms are situated at the corners of a regular tetrahedron possesses nine fundamental modes of vibration. These are not all distinct, falling into groups of 3, 3, 2 and 1 and are conventionally denoted by ν_4 , ν_3 , ν_2 , and ν_1 . Suppose now we have the isotopic molecule CX₃X' the nine fundamentals then group themselves into three single frequencies ν_1' , ν_{3c}' and ν_{4c}' and three double frequencies ν_2' , ν_{3ab}' and ν_{4ab}' . In the case of the isotopic molecule CX₂X₂' all the nine frequencies are distinct. The correspondence between the three cases is illustrated in Table I where the notation of Rosenthal has been used for convenience in reference. From this table it is clear that the effect of the Cl isotopes on the various frequencies will be qualitatively very different. In the case of ν_1 we should expect simply three lines one due to each isotopic variety; in the case of ν_2 there should be four lines while in the case of ν_3 and ν_4 we should

expect a sextet. The actual fine structure observed by Langseth is indicated in Table I together with his predicted effect on a very simplified model. For ν_1 Langseth observed the triplet and the separations between the constituents were in good agreement with his calculated value. For ν_2 he observed not a quartet but a doublet having a separation of $2.2 \pm 0.2 \text{ cm}^{-1}$; this he interpreted as due to the frequencies ν_2 and ν_2' , leaving the nonappearance of ν_{2a}'' and ν_{2b}'' unexplained. The value he calculated for this doublet separation was 1.49 cm^{-1} . In the case of ν_3 he was unable to resolve the fine structure so it was not considered further while for ν_4 he again obtained a doublet having a separation of $2.9 \pm 0.2 \text{ cm}^{-1}$. This he interpreted as due to ν_4 and the group ν_{4ab}' , ν_{4c}' , the separation between which he calculated should be 2.16 cm^{-1} . The fact that the observed separations did not agree with the calculated ones together with the apparent nonappearance of the frequencies due to CCl³⁵₂Cl³⁷₂ led Langseth to conclude that this structure was not due to the isotope effect at all but was due to a lack of tetrahedral symmetry in the molecule of carbon tetrachloride. This result has been quoted and accepted in much of the subsequent literature.³ Our purpose here is to show that the separations obtained by Langseth are consistent with those due to an isotope effect although exact agreement with calculated values cannot be expected since the dispersion used by Langseth was not suf-

³ Roussët, Comptes rendus **202**, 654 (1936). Schaefer and Kern, Zeits. f. Physik **78**, 605 (1932).

ficient to reveal all of the fine structure caused by the isotope effect.

The general equations for the isotope effect in a tetrahedral molecule of the type YX_4 have been given by Rosenthal² and need not be re-discussed here. In order to apply them to a specific example it is necessary to know the five potential constants of the molecule. Since CCl_4 has only four distinct frequencies it is not possible to determine the five constants without making some additional assumption regarding the nature of the field in the molecule. Several attempts have been made to do this but we shall only concern ourselves with two of them now for reasons which will appear later. The first is that of Voge and Rosenthal⁴ who extended the method of independent groups suggested by Sutherland and Dennison⁵ and by using the known five constants for methane were able to deduce first the constants of $ClCH_3$ and then those of CCl_4 . The assumptions involved are essentially that the CH_3 group is unaltered in going from CH_4 to $ClCH_3$ and secondly that the $C-Cl$ force constant is the same in $ClCH_3$ and in CCl_4 . The former assumption is almost certainly correct,⁶ the latter is more open to criticism. The second field is that of Urey and Bradley;⁷ this assumes

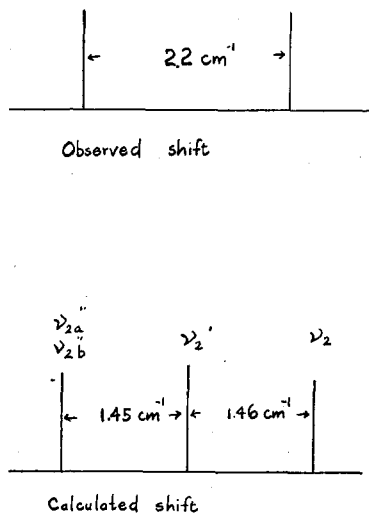


FIG. 1. ν_2 frequency of CCl_4 at 217 cm^{-1} .

⁴ Voge and Rosenthal, J. Chem. Phys. **4**, 137 (1936).

⁵ Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935).

⁶ Sutherland, Trans. Faraday Soc., February (1938).

⁷ Urey and Bradley, Phys. Rev. **38**, 1969 (1931). For convenience we have here used the slightly modified form of this field employed by Rosenthal. See reference 2.

TABLE II.

	OBSERVED	ROSENTHAL AND VOGE	UREY AND BRADLEY	
			1	2
$\nu_1 - \nu_1'$	3.10	3.2	3.1	3.1
$\nu_1' - \nu_1''$	3.28	3.2	3.1	3.1

that the potential energy is due to central forces plus forces perpendicular to the bond lines and has been found very satisfactory in correlating the four frequencies of molecules of this type although no independent check of its correctness has yet been discovered. The connection of Urey and Bradley's assumptions with the more general treatment has been very fully discussed by Rosenthal.² We shall deal with the frequencies individually to avoid unnecessary repetition.

THE FREQUENCY ν_1 AT 458 cm^{-1}

The comparison between the observed triplet separations and the predicted ones is made in Table II. It is clear that either force field gives very good agreement with observation. Actually the slight difference is due solely to the fact that Rosenthal and Voge used "corrected frequencies" which are higher than those observed in an effort to approximate to the values of the frequencies in the gaseous state. It should be explained that the two different fields of Urey and Bradley are due to the two different values of ν_3 which exist. There are actually two different fields on the Voge and Rosenthal theory too but for a different reason since there the two values of ν_3 have simply been averaged. The cause of these two fields is an inherent ambiguity in the determination of the potential constants. It happens however that for ν_1 those two fields give identical isotopic shifts. The figures in Table II are given in the usual frequency units *viz.* cm^{-1} ; the exact frequencies of the lines have not been given since these are not important.

THE FREQUENCY ν_2 AT 217 cm^{-1}

The results of the calculations on this frequency are illustrated in Fig. 1 where they are also compared with the observed doublet. First it will be noticed that in each case ν_{2a}'' and ν_{2b}'' are not separated giving a triplet instead of a

quartet. Theoretically there is a separation but it is too small to be shown on the diagram and we shall therefore regard them as coincident. Next it will be observed that the separation of the extreme lines of the triplet is identically 2.9 cm^{-1} , in each case as compared with the ob-

have done or choose each value in turn as has been done for Urey and Bradley's method. Strictly, this will not give the exact pattern but it is sufficient for our purpose to show that the separations are such that it is understandable that they were not resolved by Langseth. The calculated separations are shown in Fig. 2.

In Figs. 2 and 3 the lines due to the different isotopic species have been shown with heights proportional to the relative abundance of that species. This does not imply that the intensity is proportional to the height shown. When one considers that the intensities of all of those lines may vary relative to one another within wide limits it is understandable except on Vogé and Rosenthal (2) that Langseth obtained only broad diffuse lines with the resolving power he employed.

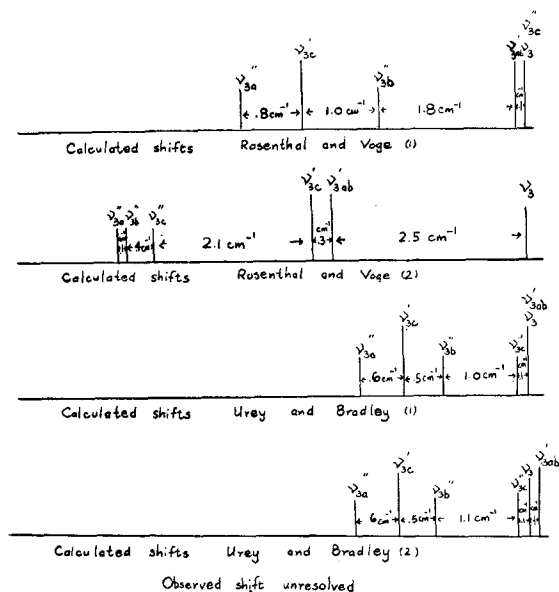


FIG. 2. ν_3 frequency of CCl_4 at 775 cm^{-1} .

served doublet separation of $2.2 \pm 0.2 \text{ cm}^{-1}$. At first this might seem further evidence in favor of Langseth's contention that the doubling is not due to an isotope effect but one must remember that we know nothing of the intensities of ν_{2a}'' and ν_2' relative to ν_2 . It may well be that under the resolution of Langseth's instrument two weaker lines due to ν_2'' and ν_2' combine to give the appearance of one line at about 2.2 cm^{-1} from ν_2 . A repetition of the observations with higher resolving power is required to make this certain.

THE FREQUENCY ν_3 AT 775 cm^{-1}

In this case the issue is complicated by the fact that the frequency is double, one line being at 762 cm^{-1} , the other at 790 cm^{-1} . This is now known to be due to a resonance between the frequency ν_3 and the combination frequency $\nu_1 + \nu_4$. A full treatment of this effect would be very tedious and is not necessary for calculations of the isotope effect for which one may either average the two values as Vogé and Rosenthal

THE FREQUENCY ν_4 AT 311 cm^{-1}

The patterns calculated on the different theories are shown in Fig. 3 on which the observed doublet is plotted on the same scale. It is again difficult to say what this pattern would aggregate into under dispersion too low to resolve it completely but it is fairly likely that the most intense lines would be those due to ν_4 and ν_{4c}' .

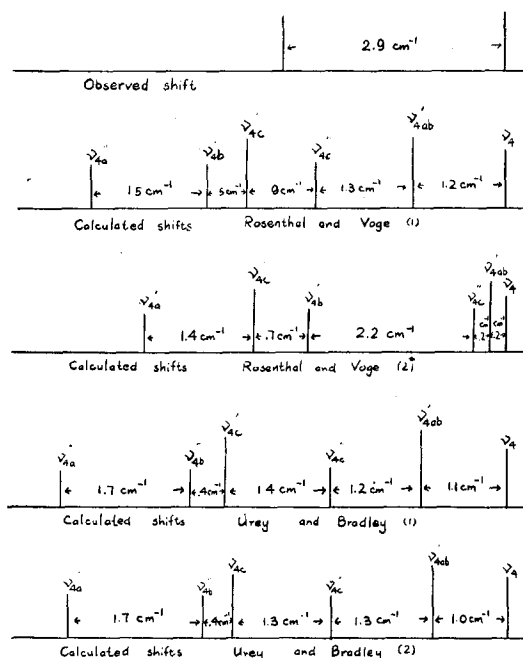


FIG. 3. ν_4 frequency of CCl_4 at 311 cm^{-1} .

The calculated separations between that pair are 3.4 cm^{-1} , 3.3 cm^{-1} (Rosenthal and Voge 1 and 2), 3.7 cm^{-1} and 3.6 cm^{-1} (Urey and Bradley 1 and 2) as compared with the observed doublet separation of $2.9 \pm 0.2\text{ cm}^{-1}$. One must remember that the presence of the other frequencies must modify to some extent the apparent position of ν_4 and ν_{4c}' and so the observation of a doublet is at least compatible with an isotope effect and we may even go so far as to say that the magnitude of the observed separation would here seem to indicate that the potential function of Voge and Rosenthal seems slightly better than that of Urey and Bradley in predicting the order of this effect. The latter conclusion should be accepted with considerable reserve however, as the following discussion will show.

DISCUSSION

Considering the results as a whole, the first conclusion we may draw is that the fine structure observed by Langseth in the Raman lines of CCl_4 can certainly be attributed a purely isotopic origin and there is no need to make any assumption of a lack of symmetry in the molecule from the conventional regular tetrahedral model. Although it has been possible to account for the exact structure observed in only one of the four frequencies the failure in the other cases is almost certainly due to the fact that the fine structure has not been completely resolved. In the case of the frequency (ν_3) where no fine structure at all was observed the theory indicates that the spread of the separate components is probably less in this frequency than in the others. It has not been possible (as had been hoped originally) to use the isotope effect to discriminate between different potential functions which have been proposed for the molecule as the existing data are not yet accurate enough. We would emphasize here that the isotopic shifts in ν_1 and ν_2 are practically independent of the potential function used and it is only from ν_3 and ν_4 that large differences can be expected on the different theories. From the fact that no fine structure was observed for ν_3 it would seem that the field

designated as "Rosenthal and Voge (2)" may be ruled out since it predicts three rather widely separated groups of lines. This is interesting in as much as it seems physically less admissible than "Rosenthal and Voge (1)." The considerably closer grouping of all of the components in the Urey and Bradley fields would indicate a slight superiority of this function over the "Rosenthal and Voge (1)" in this frequency. On the other hand for ν_4 , as we have remarked, the opposite would appear to be the case. It is clear that a resolving power at least capable of separating frequencies 0.4 cm^{-1} apart will be needed to enable one to decide between the different functions.

One must remember that the intensities of the different isotopic frequencies will not be simply in the ratio of their abundance. When a degenerate frequency is split up by the isotope effect the separate components may possess very different intensities. The work of McWood and Urey⁸ on the Raman spectra of the deuteromethanes illustrates this point very well. In the case of chlorine isotopes it is not to be expected that there will be such large differences as in the case of the hydrogen isotopes but there certainly will be differences about which we can as yet say very little. It does seem reasonable to suppose however that the semi-empirical rules which have been found to hold good for molecules of a similar type will again hold good here. For instance in molecules of the ZYX_3 type (e.g. methyl halides) it is generally found that in the Raman spectrum the three single frequencies are more intense than the three doubly degenerate ones. This is why we think it likely that ν_{4c}' may be more intense than ν_{4ab}' in the structure of this frequency. On the other hand this rule does not seem to be completely obeyed in the molecules CH_3D and CD_3H ,⁸ and so we must not apply it until more data are available by which to judge. It is to be hoped that the isotopic fine structure of the CCl_4 Raman lines will be reinvestigated more minutely in the light of the above calculations in the not too distant future.

⁸ McWood and Urey, J. Chem. Phys. **4**, 402 (1936).