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Citation: [The Journal of Chemical Physics](#) **3**, 248 (1935); doi: 10.1063/1.1749648

View online: <http://dx.doi.org/10.1063/1.1749648>

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Raman Spectra of Some Molecules of the Pentatomic Type

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(Received February 18, 1935)

Raman spectra of a number of organic compounds containing a neopentyl group have been obtained. Among these is tetramethyl methane- d_1 . The spectrum of this compound shows the various types of isotope effects to be expected for a polyatomic molecule. It is also apparent from the spectrum that the vibrations of tetramethylmethane- d_1 are less degenerate than the vibrations of tetramethylmethane. The spectrum of tetramethylsilicon has 5 lines in the internal vibration spectrum. The explanation for the existence of this extra line is probably the same as that given by Fermi in the case of CCl_4 .

INTRODUCTION

THE study of organic chemistry has furnished us with an enormous number of different species of molecules whose geometrical structure has been determined quite satisfactorily on the assumption of a static molecule. In dealing with the vibrations of the atoms in a molecule the chemist's static model is invaluable. From this model we are able to predict the number of possible types of vibrations and the degree of degeneracy in the case of symmetrical molecules.

The molecules which have been investigated in the present work have been chosen because of the various degrees of simplicity introduced into their vibration spectrum because of their symmetry properties.

The title of this paper is in one sense a misnomer, since no pentatomic molecules were investigated. Cross and Van Vleck¹ have treated the ethyl halides as though they were triatomic molecules with a fair degree of success. If we consider a methyl group for example as a single atom, then the molecules in the present investigation which will be discussed can be considered to be of the pentatomic type.

The molecules whose Raman spectrum has been investigated were tetramethylmethane- d_1 ; silicon tetramethyl; 2,2,4-trimethylpentene-3; 2,2,4-trimethylpentene-4; 2,2,4-trimethylpentane; 2,2,4,4-tetramethylpentane; 3-hydroxypentane and 2-chloropentane. The structural formulae of these compounds and a schematic diagram

of their Raman spectra are shown in Table I.

The experimental technique employed in the present work has been described by one of us² previously. The spectrograph had a dispersion of 14Å/mm at $\lambda 4500$. However, in the case of silicon tetramethyl and 2,2,4,4-tetramethylpentane the spectrograph was fitted with an $F=9$ lens (dispersion 25Å/mm at $\lambda 4500$). The use of the faster spectrograph in the above two cases was necessary because of the small amounts of these compounds available and the comparative feebleness of the scattered light.

The 2,2,4-trimethylpentene-3 and 2,2,4-trimethylpentene-4 were samples of the compounds separated by Whitmore and Wrenn³ and were considered to be in a high state of purity. The 2,2,4-trimethylpentane, 3-hydroxypentane and 2-chloropentane were furnished us by F. C. Whitmore from a stock of very carefully purified compounds. In the case of the compounds mentioned above samples of approximately 15 cm³ size were used to obtain the Raman spectrum.

Tetramethylmethane- d_1

A 4 cm³ sample of material which consisted of approximately a 50–50 mixture of tetramethylmethane and tetramethylmethane- d_1 was used in this case to obtain the Raman spectrum. The preparation[†] of this material has been described elsewhere.⁴

* D. H. Rank, J. Chem. Phys. **1**, 572 (1933).

² Whitmore and Wrenn, J. Am. Chem. Soc. **53**, 3136 (1931).

[†] A preliminary report on the preparation and the spectrum of tetramethylmethane- d_1 was given by one of us (R) in conjunction with Mr. G. H. Fleming before the Florida meeting of the American Chemical Society.

⁴ Whitmore, Fleming *et al.*, J. Am. Chem. Soc. **56**, 749 (1934).

* From a dissertation submitted by D. H. Rank in partial fulfillment of the requirements for the Ph.D. degree at The Pennsylvania State College.

¹ Paul C. Cross and J. H. Van Vleck, J. Chem. Phys. **1**, 350 (1933).

2,2,4,4-tetramethylpentane

A 4 cm³ sample of this material⁵ which was prepared and purified by Dr. F. C. Whitmore and Dr. H. A. Southgate was used to obtain the Raman spectrum.

Tetramethylsilicon

This material was specially prepared for us by Dr. F. W. Breuer of the Chemistry Department and had the following physical constants:

$$\begin{aligned} \text{Nd} &= 1.37315 \text{ at } -5.5^\circ\text{C}, \\ \text{b.p.} &= 26\text{--}26.5^\circ\text{C at } 720 \text{ mm.} \end{aligned}$$

We have tabulated the frequencies for tetramethylmethane along with that of the mixture of tetramethylmethane and tetramethylmethane-*d*₁ for comparison purposes. The frequency shifts are given in cm⁻¹. The numbers in parentheses are eye estimates of the relative intensity of the lines.

Tetramethylmethane

335 (10)	414 (3)	733 (20)	925 (15B)	1252 (20B)
1455 (15)	2712 (5)	2745 (3)	2794 (3)	2864 (7)
2892 (5)	2911 (10)	2937 (3)	2955 (7B)	

Tetramethylmethane-d₁+tetramethylmethane

283 (3)	338 (6)	418 (4)	723 (20)	736 (20)	819 (6)
930 (15)	1223 (4)	1251 (15)	1302 (3)	1377 (3)	1395 (3)
1453 (15)	2179 (5)	2521 (2)	2714 (6)	2779 (3)	2796 (3)
2870 (10)	2900 (5)	2917 (15 V.B)		2959 (15 V.B)	
2916 (3)	2961 (5 V.B)				

Silicon tetramethyl

202 (20B)	239 (15B)	598 (20)	696 (15B)	863 (10B)
1264 (10B)	1427 (15B)	2905 (10B)	2963 (10B)	

2,2,4-trimethylpentene-3

133 (2B)	202 (2)	300 (2)	327 (8)	506 (2)
568 (8)	760 (20)	820 (4)	924 (10)	940 (2)
1027 (4)	1071 (6)	1159 (4)	1204 (6)	1257 (4)
1357 (4)	1386 (10)	1395 (6)	1450 (15)	1466 (8)
1667 (15)	2903 (10)	2948 (15B)	3000 (15B)	

2,2,4-trimethylpentene-4

124 (4B)	190 (2)	294 (4)	315 (4)	387 (4)
461 (2)	561 (10)	685 (15)	765 (20)	829 (6)
894 (4)	910 (8)	936 (8)	999 (2)	1049 (2)
1101 (2)	1155 (8)	1207 (6)	1240 (10)	1268 (2)
1297 (2)	1328 (2)	1413 (15)	1450 (12B)	1648 (15)
2906 (6)	2947 (10B)	2996 (10)	3021 (6)	

2,2,4-trimethylpentane

302 (2B)	512 (4)	745 (20)	788 (4)	828 (4)
902 (8)	929 (8)	1101 (6)	1167 (4B)	1207 (6)
1250 (6B)	1358 (4)	1458 (10B)	2905 (10B)	2943 (15B)
2998 (15B)				

2,2,4,4-tetramethylpentane

274 (2)	425 (2)	557 (2B)	736 (20)	862 (2)	881 (5)
930 (5B)	1250 (10B)	1450 (10)	1480 (5)	2915 (10B)	2966 (10B)

⁵ Whitmore and Southgate (preparation of this compound to be published).

3-Hydroxypentane

400 (3)	472 (2)	763 (3B)	829 (2)	857 (4)
965 (4B)	1013 (2)	1038 (4)	1128 (2)	1276 (2)
1307 (2)	1363 (2B)	1454 (10B)	2918 (10)	2974 (10B)
3005 (5)				

2-Chloropentane

295 (2B)	342 (3)	380 (3)	399 (3)	426 (3)
442 (3)	511 (2)	536 (3)	612 (10B)	672 (4B)
846 (5)	873 (5)	921 (2B)	1029 (3)	1049 (3)
1087 (3)	1124 (2)	1275 (3)	1309 (3)	1451 (10B)
2914 (5)	2967 (7B)	3013 (4)		

DISCUSSION OF RESULTS

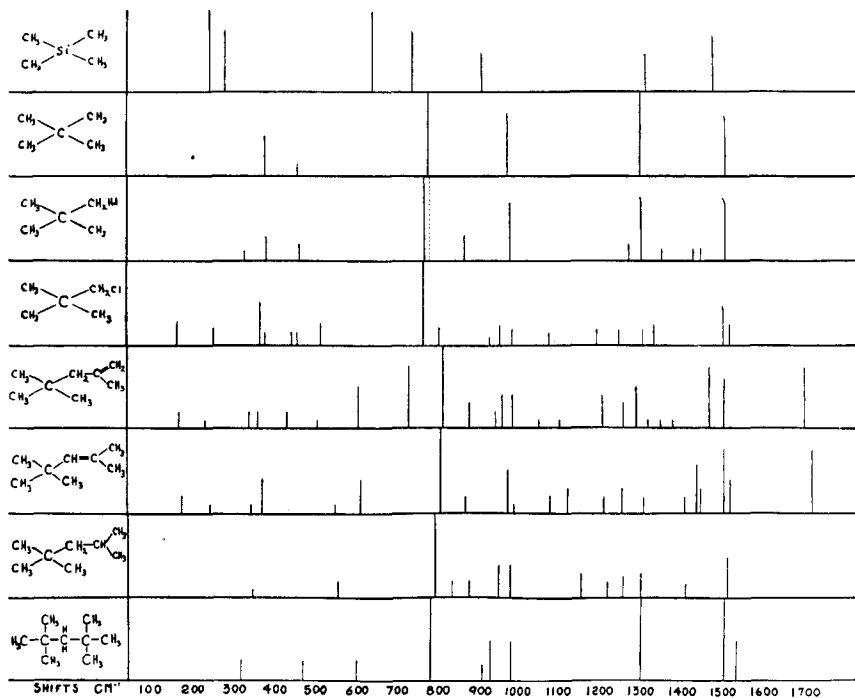
The vibrations of pentatomic tetrahedral molecule are discussed in detail in Born's *Optik*.⁶ As is well known a symmetrical pentatomic molecule has four distinct vibrational frequencies. In the case of CCl₄ for which complete data are available the multiplicities and depolarizations have been completely determined. The lowest frequency has a multiplicity of two and the next lowest a multiplicity of three. The totally symmetric vibration is single while the highest frequency has been shown to be a triple vibration. In the infrared spectrum only the two triply degenerate frequencies make their appearance while in the Raman spectrum all four of these fundamental vibrations are observed. The doublet and triplet lines in the Raman spectrum show a depolarization of $\frac{3}{4}$. However, the totally symmetric single vibration shows a depolarization of zero.

The Raman spectrum of tetramethylmethane shows six lines in the frequency interval 0 to 1500 cm⁻¹. Of these the four lowest can be ascribed to the four fundamental frequencies of a symmetrical pentatomic molecule if we are privileged to consider a CH₃ group as a single atom. The infrared spectrum of tetramethylmethane is not available so there is no direct evidence to allow us to choose the triply degenerate frequencies with certainty. However, there seems to be no good reason why we should not assign the multiplicities of 2, 3, 1, 3 in this molecule for the four vibrations in the order of increasing frequency as has been shown to be true in the case of CCl₄. There can hardly be any doubt as to the fact that this assignment is correct in the case of the higher two of the four frequencies.

The frequencies 1252 and 1455 cm⁻¹ must undoubtedly be ascribed to vibrations of deformation of the methyl groups in which the hydrogens

⁶ Max Born, *Ein Lehrbuch der Electromagnetischen Lichttheorie*, p. 553.

TABLE I.



are directly involved. Regarding the multiplicity of these vibrations we can say practically nothing except that they are probably highly degenerate, since in the case of derivatives of tetramethylmethane we obtain a large number of lines in this region which definitely cannot be ascribed to splitting up of the fundamental "framework" vibrations.

The most striking feature seen on the plates showing the Raman spectrum of these molecules containing the "neopentyl" group is the high intensity and the extreme sharpness of the line which varies from 721 to 765 cm^{-1} depending on the compound. The 598 cm^{-1} line of silicon tetramethyl shows exactly the same characteristics. In the symmetrical compounds no lines of a sharpness comparable to this one are found. In the case of CCl_4 Langseth⁷ has found the 458 cm^{-1} line to be exceedingly sharp as is attested by his beautiful photographs in which he shows the

resolution of the lines which correspond to molecules containing 1 and 2 atoms, respectively, of chlorine 37. It is well known that the usually termed name Raman lines is a misnomer and that actually a Raman line is an unresolved band caused by the overlapping rotational structure. It appears from the plates that the lines corresponding to the totally symmetrical vibration consist only of the closely spaced rotational branches in contradistinction to the other broader lines where apparently the more widely spaced branches were also allowed. The existence of this single extremely sharp line in the spectrum of these compounds shows definitely that rotational structure rather than perturbation of the energy levels by surrounding molecules in the liquid is responsible for the breadth of the other lines.

The spectrum of silicon tetramethyl shows the same degenerate character of the vibration spectrum as tetramethylmethane. The internal vibrations of this molecule lie at somewhat lower frequencies than is the case with tetramethyl-

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

methane. The frequencies 1264 and 1427 cm^{-1} which are undoubtedly associated with the methyl group vibrations, remain substantially the same as in tetramethylmethane. In the case of lead tetramethyl apparently, according to Duncan and Murray,⁸ this is no longer true and these vibrations are degraded to lower frequencies as well as the internal vibrations. In the case of silicontetramethyl we obtain a fairly intense line at 863 cm^{-1} which does not fit into the scheme of vibrations for a pentatomic molecule. It seems quite probable that the same explanation as that used by Fermi⁹ for CCl_4 would hold in this case. If this explanation would be true we must assume that the highest triply degenerate frequency of the internal vibration spectrum is still unknown but very close to the sum of 202+598 cm^{-1} which produces a splitting resulting in the production of the two lines, 696 cm^{-1} and 863 cm^{-1} instead of the single line ordinarily to be expected.

Tetramethylmethane- d_1

The results in the case of this molecule are not entirely unambiguous. About 50 percent of the molecules were ordinary tetramethylmethane and it is not possible to say whether all the lines found in tetramethylmethane are absent in the deuterio derivative or not. The slight differences in the frequencies of lines known to be due to tetramethylmethane as measured on the two sets of plates are in some cases due to experimental error but in other cases may be due to superposition of the two sets of lines from the two different compounds present. For this reason it seems difficult to speculate with any degree of certainty concerning the splitting up of the internal vibrations of the molecule due to partial destruction of the symmetry by the substitution of a deuterium atom for a hydrogen atom. However, the spectrum clearly shows that the vibrational degeneracy of the tetramethylmethane- d_1 molecule is not as complete as that of the tetramethylmethane molecule. The lines 1223, 1302, 1377, 1395 cm^{-1} are almost certainly due to the splitting up of the highly degenerate frequencies which lie at 1252 and 1455 cm^{-1} , respectively, in

the tetramethylmethane molecule. The totally symmetrical vibration exhibits an isotope effect of 13 cm^{-1} . The line appearing at 2179 cm^{-1} is undoubtedly a vibration of the type commonly called C-H "stretching vibrations" in which the deuterium atom forms part of a simple oscillator and is vibrating against part or all of the molecule with little or no interaction with other vibrations. The line at 2521 cm^{-1} is probably of the same type but with the added restriction of interaction with other vibrations of the molecule.

In the case of monochlorotetramethylmethane, 2,2,4-trimethylpentene-3, 2,2,4-trimethylpentene-4, and 2,2,4 trimethylpentane the large number of lines shows that the degeneracy of the tetramethylmethane molecule has been practically completely removed. An inspection of Table I seems to show a grouping of lines of varying separation which might be traced to the fundamental degenerate frequencies of tetramethylmethane.

CONCLUSION

This series of compounds has been studied with the idea in mind to treat them as pentatomic molecules. The spectrum of the symmetrical molecules tetramethylmethane and silicon tetramethyl has been satisfactorily explained by considering the vibrations of a pentatomic molecule. The spectrum of tetramethylmethane- d_1 shows the various types of isotope effects expected for a polyatomic molecule. It also shows that the substitution of a deuterium atom for a hydrogen atom in tetramethylmethane partially destroys the dynamic symmetry and as a consequence partially removes the vibrational degeneracy. The large number of lines appearing in the spectrum of the other tetramethylmethane derivatives shows practically complete removal of vibrational degeneracy.

ACKNOWLEDGMENTS

We wish to express our appreciation to Dean F. C. Whitmore of the School of Chemistry and Physics for making this rare series of compounds available for this investigation. We are also deeply indebted to Dr. F. W. Breuer for the special preparation of the tetramethylsilicon which we have used.

⁸ A. B. F. Duncan and J. W. Murray, J. Chem. Phys. 2, 636 (1934).

⁹ E. Fermi, Zeits. f. Physik 71, 259 (1931).