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The Raman Spectrum of Tetramethylmethane

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Raman spectra of tetramethylmethane, the mono chloro derivative of tetramethylmethane and *n*-amyl chloride, have been obtained with a spectrograph which gave a dispersion of 14Å/mm at $\lambda 4500$. Filters were employed which permitted the observation of the weaker lines.

The rather simple arrangement of very intense quartz water-cooled vacuum mercury arcs is described. The results for tetramethylmethane confirm the predictions of the theory of the vibration spectrum of the hydrocarbons which was developed by Kohlrausch and Barnes.

INTRODUCTION

KOHLRAUSCH and Barnes¹ have obtained the Raman spectrum of tetramethylmethane, which compound is extremely interesting because of its highly symmetrical character. The above authors have developed a semi-empirical theory of the vibration spectrum of the hydrocarbons from the analysis of the spectrum of this compound and the spectrum of the other lower members of this series of hydrocarbons. The experimental results of Kohlrausch and Barnes leave several points open to question. The purpose of this investigation was to attempt to remove these discrepancies and to verify the predictions of the theory by the use of more adequate experimental procedure.

EXPERIMENTAL

The present experimental arrangement was designed to permit the use of a moderately high dispersion spectrograph and at the same time permit the use of adequate filters.

The mercury arcs consist of simple U tubes of quartz about 30 cm in length and operate in the vertical position. Two of these U arcs were used in the present investigation, arranged in such a manner that each leg of the U is at a corner of the square formed by the four legs. This arrangement is effectually equivalent to four mercury arcs about 12 cm in length.

These arcs are mounted in a suitable container to permit water cooling. The legs of the U's pass through the bottom of the container and are

attached to a vacuum system by means of heavy rubber pressure tubing. The starting of the arcs is accomplished by means of suitable mercury traps, the mercury levels of which could be raised or lowered as necessary. The electrodes are simply the mercury columns of these traps (line connections being made by means of iron rods immersed in the open arms of the traps).

These arcs were operated at a current density of about 30 amperes per cm² of cross section and under such operating conditions have a useful life of from 300 to 400 hours. The black deposit which forms on the walls of the quartz tube after long usage can be removed by means of concentrated hydrofluoric acid followed by heating with an oxy-hydrogen torch which restores the quartz to its original transparency.

The scattering tube was placed in the center of the square formed by the arcs, and surrounded with a cylindrical filter jacket which was designed to permit the use of two separate filter solutions in layers of one cm thickness. The arcs, filter jacket, and scattering tube were surrounded with a cylindrical reflector of silvered glass which has shown itself to be considerably more efficient than the ordinary polished sheet aluminum reflector.

The inside filter jacket contained a 20 percent solution of praseodymium ammonium nitrate² and the outside jacket a saturated solution of sodium nitrite.³ With this combination of filters the excitation is entirely by means of the $\lambda 4358$

¹ K. W. F. Kohlrausch and D. Barnes, *Anales Fisica Y Quimica* **30**, 733 (1932).

² R. W. Wood and Geo. Collins, *Phys. Rev.* **42**, 386 (1932).

³ A. H. Pfund, *Phys. Rev.* **42**, 581 (1932).

group of mercury. For shifts greater than 2000 cm^{-1} a strong solution of crystal violet was substituted for the praseodymium filter, but in the case of the compounds investigated thus far no lines were found by this means which could not also be observed by means of the praseodymium filter. Exposures were also taken using carbon tetrachloride+iodine in conjunction with the praseodymium filter. In this case the excitation is by means of $\lambda 4047$ and $\lambda 4358$ but the $\lambda 4358$ group is considerably reduced in intensity. The object of taking these exposures was to throw the C-H vibrations into the higher dispersion region of the spectrograph so that more accurate measurements could be made of these shifts. However, it was noted that the use of these shorter wave-lengths produced a slight fluorescence with the compounds used in the present investigation.

The spectrograph⁴ employed was a two prism glass instrument (objective F 18) which gave a dispersion of 14Å/mm at $\lambda 4500$. The slit width used was 0.03 mm.

With the experimental arrangement described above, satisfactory unfiltered photographs could be obtained in from one to three hours exposure. When the praseodymium and sodium nitrite filters were used exposures of from 20 to 60 hours were necessary before the continuous background became troublesome. With these filters it required about an hour of exposure in order to photograph the stronger Raman lines.

Measurements of the wave-lengths of the lines were made by means of a large dispersion curve constructed from measurements of the lines of the iron arc spectrum. The frequency shifts tabulated are believed to be accurate $\pm 2 \text{ cm}^{-1}$ except in the cases marked with an asterisk in which cases the errors might be larger because of the faintness and the broad character of these lines. In the case of the sharper lines of good intensity the shifts are probably accurate to a wave number.

The purity of compounds used in work on the Raman effect has in general been relegated to a position of minor importance. However, when intensity ratios as great as 40 to 1 are possible as is the case when the present filter technique is

employed, it is easily seen that even one percent of impurity might cause spurious lines to appear, when one considers the fact that some compounds are considerably better scatterers than others.

The compounds used in the present investigation have been carefully purified chemically as far as possible, and then have been fractionally distilled through very efficient fractionating columns.⁵ The samples investigated were taken from middle cuts from rather large batches of the compounds. The tetramethylmethane and the mono chloro derivative of tetramethylmethane were prepared and purified by Mr. G. H. Fleming of the Chemistry Department working under the direction of Dr. F. C. Whitmore.⁶

The *n*-amyl chloride was purified by Messrs. J. M. Herndon and G. H. Fleming in the following manner. Commercial *n*-amyl chloride (Sharpless Solvents Corp.) was fractionated through a 75×2.2 cm packed column with the use of a high reflux ratio. Material of b. p. $103\text{--}104^\circ\text{C}$ (734 mm) and $N_d^{20} = 1.4120$ was then treated with silver nitrate solution to remove any traces of secondary and tertiary chlorides and then refractionated. The material used had a b. p. $104.0\text{--}104.5^\circ\text{C}$ (732 mm) and $N_d^{20} = 1.4120$, $d_4^{20} 0.8846$. The only probable impurity would be one percent or less of isoamyl chloride.

RESULTS

In Table I, the frequency shifts which were observed for the compounds investigated are tabulated. The results obtained by other authors who have investigated these compounds are also tabulated in this table. Intensities of the lines are indicated by means of the number in parentheses.

TETRAMETHYLMETHANE

The theory of the vibration spectrum of the hydrocarbons developed by Kohlrausch and Barnes¹ demands for each substance that

$$\bar{\omega}^2 = [1/(n-1)] \sum \omega_i^2,$$

where $n-1$ gives the number of C-C links in the molecule and $\sum \omega_i^2$ the sum of the squares of the

⁵ Whitmore and Lux, J. Am. Chem. Soc. **54**, 3451-3 (1932).

⁶ The details of the preparation and purification of these compounds to be published shortly in the J. Am. Chem. Soc.

⁴ D. H. Rank, J. Opt. Soc. Am. **23**, 84 (1933).

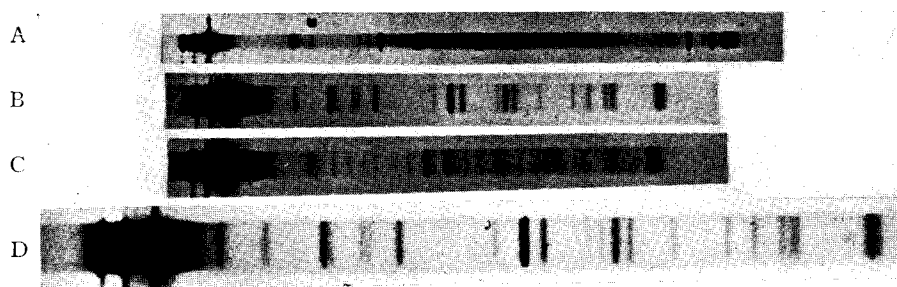


FIG. 1. Raman spectra of (A) tetramethylmethane, (B) tetramethylmethane chloride, (C) *n*-amyl chloride and (D) tetramethylmethane chloride enlarged.

frequencies (vibrations which are doubly or triply degenerate are counted twice or thrice respectively). The above authors have shown $\bar{\omega}^2$ to be nearly constant for homologous molecules. From the constancy of $\bar{\omega}^2$ and consideration of the model employed, Kohlrausch and Barnes have predicted the existence of a triply degenerate vibrational frequency $\Delta\bar{\nu}=400\text{ cm}^{-1}$ for tetramethylmethane which they were unable to observe in their experimental work. In the present investigation this shift was observed and found to be 415 cm^{-1} . (In Fig. 1, A, the spectrum of tetramethylmethane is reproduced and the new

frequency shift predicted by the theory is indicated by means of an ink dot above the line.) By taking the present more accurate values for these shifts for tetramethylmethane and calculating $\bar{\omega}^2$, a value of 96.2×10^4 is obtained which is in good agreement with $\bar{\omega}^2$ calculated for the other members of the series, the mean of which is 98.5×10^4 .

The frequency shift $\Delta\bar{\nu}=794\text{ cm}^{-1}$ observed by Kohlrausch and Barnes did not appear on any of the plates obtained by the author, using tetramethylmethane as the scatterer, although much weaker lines were observed than K. and B. were able to observe. It seems extremely probable that this line is due to isobutane since the strongest line in the isobutane spectrum corresponds to this line within experimental error and isobutane is one of the principal impurities in tetramethylmethane and certainly one of the most difficult to remove.

N-AMYL CHLORIDE AND TETRAMETHYLMETHANE CHLORIDE

Fig. 1, B, is a reproduction of the spectrum of tetramethylmethane chloride, while D is the same spectrum more highly enlarged in order to show several of the close doublets. Fig. 1, C, is a reproduction of the spectrum of *n*-amyl chloride.

The Raman spectrum of *n*-amyl chloride has been obtained by Harkins and Haun⁷ without the use of filters. Their results appear in Table I as well as the results obtained in the present investigation.

The spectrum of tetramethylmethane chloride was obtained for the first time. The spectrum of

⁷ Harkins and Haun, J. Am. Chem. Soc. **54**, 3920 (1932).

TABLE I. Frequency shifts cm^{-1} .

Tetramethyl- methane	Tetramethyl- methane	Tetramethyl- methane chloride	<i>n</i> -amyl chloride	<i>n</i> -amyl chloride
Kohlrausch and Barnes	Rank	Rank	Harkins and Haun	Rank
		123 (5)		268 (6)
		210 (4)		286 (2B)*
		321 (10)		349 (4)
332 (1)	336 (10)	333 (3)		402 (3)
	415 (3)	399 (3)	454 (1)	460 (2)
		412 (3)	658 (10)	657 (20)
		471 (5)		685 (3)
732 (5)	734 (20)	722 (20)	730 (8)	726 (10)
794 (2)		757 (5)		Band 726 to
		883 (2)		782 (3)*
		907 (5)		793 (4)
920 (3a)	925 (15B)	938 (4)		822 (3B)
		1025 (3)		843 (4)
		1144 (4)		881 (3B)
		1199 (4)	893 (1)	898 (5)
1241 (2a)	1253 (20B)	1258 (4)		929 (2)*
		1284 (5B)	970 (1)	981 (3B)*
1448 (4a)	1456 (15)	1451 (10)		1034 (3)
		1467 (5)		1067 (10)
				1097 (4B)
				1114 (4B)
				1177 (1B)*
				1234 (1B)
				1284 (3B)
				1307 (8)
				1452 (20B)
	2713 (5)	2722 (3)	1450 (10)	2871 (20V.B.)
	2746 (3)	2872 (7B)	2877 (8)	2908 (20V.B.)
		2910 (10)	2911 (2)	2939 (20V.B.)
2792 (2a)	2794 (3)	2929 (3)	2941 (4)	2964 (20V.B.)
2866 (5)	2865 (7)	2946 (8)	2967 (4)	3005 (3)
2892 (2)	2893 (5)	Band 2954		
2908 (6)	2913 (10)	to 2996		
	2938 (3)			
2954 (5a)	2957 (7B)			

this compound contrasted with that of tetramethylmethane shows in a striking manner the removal of the degeneracy of an extremely symmetrical molecule by partially destroying its symmetrical character. However, it seems difficult to attempt to assign this splitting to certain definite vibrations of the atoms in the molecule

until more experimental work is available on a series of derivatives of tetramethylmethane, which work is now in progress.

The author wishes to express his appreciation to Dr. F. C. Whitmore of the Chemistry Department for making the compounds available which were used in the present investigation.