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Raman Spectrum of Trimethyl Silicon Chloride

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August 18, 1948

THE analysis of the Raman spectra of substances like trimethyl-silicon chloride, which belongs to the symmetry C_{3v} ,¹ seems highly desirable in connection with the study of the structural properties of silanes and with recent theoretical considerations put forward for the similar carbon compounds.²

Our results for the Raman spectrum of this substance in the liquid state are given in the following table, in which we indicate the Raman frequencies (cm^{-1}), the rough relative intensities, and the exciting mercury lines which are referred to by letters as follows: $e=4358\text{\AA}$, $k=4047\text{\AA}$. The spectrograph was a "Huet" glass prism instrument giving a dispersion of about 20 $\text{\AA}/\text{mm}$ in the region involved. Diffuse and sharp lines are designated d and s , respectively. The mean error of our measurements is about 3 cm^{-1} for most lines.

± 187 (3, dd) (e,k)	846 (o,dd) (e,k)
± 242 (3, dd) (e,k)	1260 (o,sd) (e,k)
330 (oo,d) (e)	1315 (oo,dd) (e)
± 467 (5, d) (e,k)	1375 (oo,d) (e)
± 637 (6, s) (e,k)	1415 (1, d) (e,k)
700 (1, dd) (e,k)	1446 (oo,d) (e)
760 (2, sd) (e,k)	2902 (5, d) (e,k)
	2970 (4, dd) (e,k)

The intense lines observed at 2902 and 2970 cm^{-1} correspond, respectively, to symmetric and antisymmetric valency C—H vibrations. These values are in agreement with the frequencies found with hydrocarbons. The C—H deformation frequencies appear at 1375 (1315) and 1415 (1446) cm^{-1} and are abnormally weak. If we can correlate the former with the symmetric vibration and the latter with the antisymmetric one, these too are in good agreement with the frequencies found with the corresponding vibrations in hydrocarbon compounds. Finally, the line observed at 1260 cm^{-1} may involve hydrogen motions as well, and in that case would be assigned to a methyl rocking frequency in agreement with the interpretation given to an infra-red band situated at 1257 cm^{-1} in methylpolysiloxanes.³ It should be remarked, however, that in our experiments this line could be considered alternatively as the first overtone of the 637- cm^{-1} frequency.

Assuming now that the methyl groups behave like single atoms R of atomic weight 15, six vibrations are to be expected to characterize the ClSiR_3 radical.

In order to correlate the observed frequencies with the normal modes, we have used a simple valency force field and have adopted for the force constants the values

$$\begin{aligned} f_1(\text{Si}-\text{R}) &= 3.3 \times 10^5 \text{ dynes/cm}; \\ f_\theta(\text{R}-\text{Si}-\text{R}) &= 0.13 \times 10^5 \text{ dynes/cm}; \\ f_\beta(\text{Cl}-\text{Si}-\text{R}) &= 0.2 \times 10^5 \text{ dynes/cm}; \\ f(\text{Si}-\text{Cl}) &= 5 \times 10^5 \text{ dynes/cm}. \end{aligned}$$

The excellent agreement obtained between calculated (in brackets) and observed frequencies justifies the follow-

ing assignment, where ν_1, ν_3, ν_5 are the parallel and ν_2, ν_4, ν_6 the perpendicular frequencies according to the usual notation:

$$\begin{aligned} \nu_1 &= 760 \text{ cm}^{-1} (810), & \nu_2 &= 846 \text{ cm}^{-1} (850), \\ \nu_3 &= 187 \text{ cm}^{-1} (191), & \nu_4 &= 242 \text{ cm}^{-1} (224), \\ \nu_5 &= 637 \text{ cm}^{-1} (595), & \nu_6 &= 330 \text{ cm}^{-1} (330). \end{aligned}$$

The constants f_1 and f_θ are nearly the same as those found by Wall and Eddy⁴ for tetramethylsilicon, whereas f_β has been chosen by analogy with the ratio f_θ/f_β present in $\text{CH}_3\text{Cl} \cdot f_{\text{Si}-\text{Cl}}$ has been adjusted to calculate a satisfactory value for ν_5 (symmetric Si—Cl vibration) which we had already assigned to 637 cm^{-1} because of its sharpness and intensity. It should be noticed that the infra-red spectrum of compounds such as the linear methylpolysiloxanes, which contain the group $\text{Si}(\text{CH}_3)_3$, show bands at 753 and 841 cm^{-1} which have been assigned to Si—C vibrations.³ This provides further evidence of the correctness of our assignments.

The 467- and 700- cm^{-1} frequencies must remain unassigned until a more detailed analysis of the vibrational modes has been made.

It will be observed that the value of $f_{\text{Si}-\text{Cl}}$ is greater than the corresponding value for the C—Cl bond in CH_3Cl (3.30). This result is in qualitative accordance with recent measurements¹ showing that the Si—Cl bond distance in $\text{ClSi}(\text{CH}_3)_3$ is markedly contracted (2.09 \AA) with respect to the sum of the covalent radii (2.16 \AA), whereas this is not the case with the C—Cl bond length. On the other hand, there is an increase in the Si—Cl bond as well as in the C—Cl bond in going from SiCl_4 to $\text{Si}(\text{CH}_3)_3\text{Cl}$ (or SiH_3Cl), or from CCl_4 to CH_3Cl .

These facts can be explained in terms of two distinct effects: (1) resonance effect, and (2) changes of hybridization at the central atom.

The resonance effect must be due to the part played by structure like $(\text{CH}_3)_2(\text{CH})_3\text{Si}=\text{Cl}^+$ which strengthen the Si—Cl bond. The changes of hybridization at the silicon atom with respect to an sp^3 state are illustrated by the opening of the C—Si—C angle to about 113°, which means more s -character in the hybridized Si orbital from which the Si—C bonds are formed, and more p -character in the corresponding orbital for the Si—Cl bond. This results in the Si—Cl bond increasing and in the Si—C bond decreasing. This agrees qualitatively with the facts, as the SiCl bond is only 2.02 \AA in SiCl_4 and as Si—C is a little smaller (1.88 \AA) than the sum of the covalent radii (1.94 \AA). Hence this second factor which seems to exert only a small influence in carbon compounds such as CH_3Cl (2) is much enhanced in the silicon compounds.

Thus we believe that we have here an important indication in favor of the existence of the small effects predicted for the carbon compounds which are probably so small that it would be difficult to measure them directly. It should also be noticed that the frequencies of the methyl group are not noticeably affected when it is bound to a silicon atom.

A full account of this work will be published later. We are very indebted to Dr. W. F. Gilliam and to Dr. E. L.

Warrick who have kindly supplied us with samples of the trimethyl silicon chloride.

Our best thanks are due Professor C. A. Coulson and to Dr. D. M. Simpson who have read the manuscript and kindly revised the English.

¹ R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.* **68**, 719 (1946).

² C. A. Coulson, *V. Henri Memorial Volume* (Deseer, Liège, 1947); C. A. Coulson, J. Duchesne, and C. Manneback, *ibid.*; A. D. Walsh, *Trans. Faraday Soc.*, meeting on free radicals (in the press); J. Duchesne, *Nature* **159**, 62 (1947).

³ N. Wright and M. J. Hunter, *J. Am. Chem. Soc.* **69**, 803 (1947).

⁴ F. T. Wall and C. R. Eddy, *J. Chem. Phys.* **6**, 107 (1938).

Errata: A Relation between Bond Order and Covalent Bond Distance

[*J. Chem. Phys.* **15**, 284 (1947)]

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IN the table for CN, CO, and NO bonds, the bond orders are 0, 1, and 2 for single, double, and triple bonds instead of 1, 2, and 3 as in the table; the C≡O distance is 1.11 instead of 1.15.

Errata: "Volume Effect" and Random Flights

[*J. Chem. Phys.* **16**, 839 (1948)]

R. C. BRIANT

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IN a previous Letter to the Editor the proposed solution is wrong, in part, because the definition of "loop" is ambiguous. Also, multiple loop configurations are over-weighted. The writer regrets the error.

A Note on the Structure of Insulin*

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August 16, 1948

A COMPREHENSIVE x-ray study of a "wet" insulin crystal has been carried out by Dr. Crowfoot and her collaborators. Much of the work is at present unpublished because of the war. A preliminary publication gave the

space group $R3$, cell dimensions $a=83.0\text{\AA}$, $c=34.0\text{\AA}$, and the Patterson projection on the basal plane.¹ A report to the Rockefeller Foundation in 1942 by Dr. Crowfoot included her calculation of the basal section of the Patterson-Harker map and calculations by Dr. K. Schiff of lines parallel to the trigonal axis, including those extending over a 5\AA region about it and an estimate of molecular weight 36,000. A general account based on this report appeared in Russian in 1946.² Dr. Crowfoot has generously given me a list of the intensities recorded. We are very greatly indebted to Dr. W. J. Eckert and the International Business Machine Corporation for making available the facilities of the Watson Scientific Computing Laboratory, to Dr. L. H. Thomas for planning, and to Miss E. A. Stewart for carrying out the calculation of the complete three-dimensional Patterson-Harker map derived from these intensities, for z in thirtieths, and for x and y in sixtieths.

Figure 1 shows sections from this map parallel to the basal plane, in the neighborhood of the trigonal axis. The following features may be remarked: a *positive* region A enclosing the origin with circumscribing sphere of radius 8.2\AA ; a *negative* region B completely inclosing A ; and a *positive* region C extending slightly further than from $z=\frac{1}{2}\pm\frac{1}{6}$. Since the full extent of the insulin structure or of any molecule in it cannot be represented by so small a region as A , the region B suggests the presence of a lower electron density distribution within each molecule, i.e., a cage structure for each molecule comprising a closely integrated space-enclosing atomic fabric. Structures of this morphological type³ were suggested for protein molecules in 1936. These include the C_1 cage which, it is now seen,⁴ can comprise 72 to 48 residues per skeleton, the C_2, \dots, C_n, \dots cages with maximum skeletal residue numbers $288, \dots, 72n, \dots$.

A possible picture of the insulin structure is thus as follows: each particle comprises m trigonal molecules ($m=0, 1, \dots$) and n triads of molecules not necessarily trigonal ($n=0, 1, \dots$), each being a cage structure. Oncley's recent finding⁵ that the insulin structure ($MW\sim 36,000$) may be dissociated into 3 subunits suggests that $m=0$, leaving n , the number of molecules per subunit, to be determined.

These new data, so far as suggestions of the "cage" type are concerned, thus appear to favor the suggestion of an insulin structure made up of C_1 cages⁶—say 6—or of 3

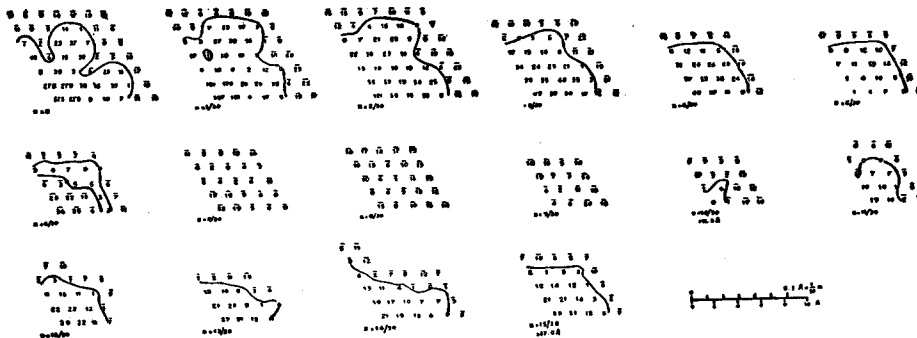


FIG. 1. Sections of the Patterson-Harker map of the "wet" insulin crystal in the neighborhood of the trigonal axis, parallel to the basal plane, calculated from Crowfoot's intensities.