SOME NEW FEATURES IN THE RAMAN SPECTRA OF CARBON AND SILICON TETRACHLORIDES.

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Received October 4, 1935.
(Communicated by Sir C. V. Raman, R.S., F.R.S., N.L.)

1. Introduction.

The Raman spectrum of CCl₄ has been the subject of numerous papers.¹ The great intensity of the lines observed with this substance, the appearance of several anti-stokes components and the striking differences in the state of polarisation of the radiations, are some of the features which make the case one of special experimental interest. From the theoretical standpoint, the chemically indicated tetrahedral symmetry of the molecule makes the comparison of the results to be expected from dynamical theory with those actually observed a matter of considerable importance. Classical mechanics indicates that a molecule with five atoms should, in general, possess nine characteristic frequencies. In the case of CCl₄ and other molecules with tetrahedral symmetry, however, only four out of the nine frequencies are distinct—one being single (the total symmetric vibration) (ν₁), one doubly degenerate (ν₂) and two triply degenerate (ν₅ and ν₆). All the four modes of vibration are Raman-active so that one would expect four lines in the Raman spectrum of CCl₄. Actually, however, the triply degenerate vibration ν₄ in CCl₄ is observed to be split up into a pair of lines of equal intensity. Moreover, a fifth line (faint and diffuse) has been observed in the Raman spectrum of CCl₄ which is found to correspond roughly to the octave of ν₄.

The splitting of the fourth frequency has been attributed by Fermi² to a "quasi-degeneracy" arising from the fact that the frequency which is split up happens to be almost exactly equal to the sum of two other fundamental frequencies, ν₄ ≈ (ν₁ + ν₅). This gives rise to a coupling of the terms which, according to wave mechanics, leads to splitting. Another interesting feature of the Raman spectrum of CCl₄ is the fine structure of the Raman lines ν₁, ν₂ and ν₃. This has been studied in some detail by Langseth.³ Since chlorine consists of two different isotopes of masses 35 and 37 with a relative abundance ratio 3:1, the substance CCl₄ is a mixture of five different kinds of molecules, CCl₄³⁵, CCl₄³⁷, Cl³⁵CCl₃⁷, Cl³⁵Cl³⁷, Cl³⁷CCl₃⁷ and CCl₃⁷ which occur in the proportion 31.6:42.2:21.1:4.7:0.4. The total-symmetric
vibration should therefore consist of five close components with a relative separation of 3.15 cm.$^{-1}$ and with intensities in the above ratio. The presence of the first three components with the expected order of intensity and separation has been recorded by Langseth.

Investigations on SiCl$_4$ are not so numerous. The Raman spectrum of this substance has been found to show three strong lines corresponding to $v_1$, $v_2$ and $v_3$ and a broad and diffuse line corresponding to $v_4$.

The author has undertaken a careful study of the Raman spectra of these two substances, and has succeeded in getting some new results which are recorded in the present paper.

2. Experimental.

Two different instruments have been employed in the present investigation for the study of the Raman spectra:

(i) A Hilger two-prism spectrograph of great light-gathering power giving a dispersion of about 25 Å/mm. in the $\lambda$ 4358 region.

(ii) A spectrograph of Littrow model, with two glass prisms of large size, one 60° and the other 30°, also supplied by the firm of Adam Hilger Ltd. The dispersion in the region $\lambda$ 4358 is about 10 Å/mm. In spite of its lesser light-gathering power, well-exposed Raman spectra taken with this instrument are found to show many finer details which are not so strikingly brought out in the pictures with smaller dispersion.

Ilford hypersensitive panchromatic plates were employed to photograph the Raman spectra with the first instrument, and an exposure of about 10 to 12 hours was sufficient to get well-exposed pictures with a slit width of 40 μ. With the instrument of higher dispersion, the time of exposure required varied from 40 to 50 hours. Ilford "golden isozenith" plates with special backing were used in this case.

The liquids employed were very pure chemicals, and special care was taken to free them from dust by repeated slow distillation in vacuum. Wood's arrangement was used for photographing the Raman spectra. The Raman tubes were of pyrex glass with fused on end window, and contained the dust-free liquids sealed off in vacuum. The illumination was from a quartz mercury lamp placed in direct contact with a water jacket surrounding the Raman tube. Concave reflectors of polished aluminium one below the tube and the other above the arc served to enhance the illumination. For making accurate measurements of the modified lines, an iron arc comparison