a simple immobilization of the negative ions by the usual negative charge of both glass and paraffin. This is true even though this charge is subject to specific ion effects.

A single tube prepared with sealing wax instead of paraffin gave the same type of data. The only difference which was observed was a much slower increase of conductivity and generally more stable properties.

Because of its partial specificity and its response to low concentrations of calcium, even this type of system may have usefulness as an electrode. This and the nature of the effect are being studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS AND THE AGRICULTURAL EXPERIMENT STATION, UNIVERSITY OF FLORIDA]

The Infrared Absorption Spectrum of Vitamin C[1]

BY DUDLEY WILLIAMS AND LEWIS H. ROGERS

The isolation, identification, and synthesis of Vitamin C and its ultraviolet absorption spectrum are well known.[2,3] The spectral region previously studied, however, lies between 200 and 400 mμ. In order to obtain additional information on the molecular structure of this compound, it was decided to make a study of its infrared absorption spectrum in the region from 2 to 8 μ. Although the infrared absorption spectrum of any polyatomic molecule is necessarily complex, the interpretation in terms of atomic groups is more direct than in the case of the visible and ultraviolet regions where electronic energy changes are involved. Complete theoretical analyses of vibrational–rotational spectra have been made only for diatomic and triatomic molecules and for benzene, but semi-empirical explanations of the spectra of organic molecules have proved valuable in many cases. From the study of large numbers of organic compounds it has been found that every organic radical gives rise to a characteristic series of bands, its characteristic frequencies being practically unaffected by other groups present in the same molecule or in neighboring molecules. Thus, for example, one finds a band arising from a C–H vibration which varies in frequency from about 3100 cm.$^{-1}$ in a simple molecule like methane to about 2800 cm.$^{-1}$ in a complex molecule like stearic acid.[4] Those frequencies of particular interest in the present discussion are

$$\nu(\mathrm{C{-}H}) \cong 3000 \text{ cm.}^{-1}$$
$$\nu(\mathrm{O{-}H}) \cong 3300$$
$$\nu(\mathrm{C{=}C}) \cong 1500 \text{ to } 1800$$
$$\nu(\mathrm{C{-}O}) \cong 1500 \text{ to } 1800$$
$$\nu(\mathrm{C{-}C}) \cong 900$$
$$\delta(\mathrm{CH_2}) \cong 1440$$

where ν symbolizes a linear vibration and δ a deformation vibration. With the aid of these experimentally obtained results it is possible to gain some general ideas concerning molecular structure from a study of infrared absorption spectra. Lists of other characteristic oscillation frequencies have been given by other workers.[5]

The spectrometer used in the present work was an instrument of the minimum deviation type equipped with a rock salt prism. The effective slit widths ranged from 0.04 μ in the 2.5 μ region to 0.09 μ in the 8 μ region. Fifteen to twenty readings were made per micron of spectral range. The absorption cells were made with fluorite plates separated by mica washers of approximately 0.02 mm. thickness. In obtaining the absorption data the transmission of a vitamin solution was compared with the radiation transmitted by a cell of equal thickness containing water. Other experimental details are given in another paper soon to appear. Baird and his co-workers[6] have pointed out the unstable nature of Vitamin C due to oxidation. Hence, in this work, the material was kept in sealed ampoules until immediately before preparing the solutions used in making the measurements. The samples used were obtained from Merck. Saturated

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(1) Presented before the Organic Division, American Chemical Society, Chapel Hill, N. C., April 12, 1937.

(2) Szent-Gyorgi, *Biochem. J.*, **22**, 1387 (1928); Haworth, Hirst, *et al.*, *Chemistry and Industry*, **221**, 482, 645 (1933); *Nature*, **130**, 888 (1932); *J. Chem. Soc.*, 1270, 1419 (1933); *ibid.*, 62 (1934); Reichstein, Grussner, and Oppenauer, *Nature*, **132**, 280 (1933); *Helv. Chim. Acta*, **16**, 561 (1933).

(3) Hirst and Hubert, *Nature*, **129**, 205 (1932); *J. Chem. Soc.*, 1270, 1564 (1933).

(4) Coblentz, Carnegie Inst. of Wash. Pub. No. 35 (1905).

(5) Barnes, *Rev. Sci. Instruments*, **7**, 265 (1936).

(6) Baird, *et al.*, *J. Chem. Soc.*, 63 (1934).

solutions were used in all cases in order to ensure intense absorption.

In Fig. 1 are shown transmission curves for cells containing water and Vitamin C solution. The curves are the result of a typical determination, although each absorption band shown has been repeated several times. The water curve shows the well-known absorption maxima at 3, 4.7, and 6.2 μ. As may readily be seen from the figure, the Vitamin C solution is more strongly absorbing in all regions studied with intense bands near 3, 6, and 7.5 μ.

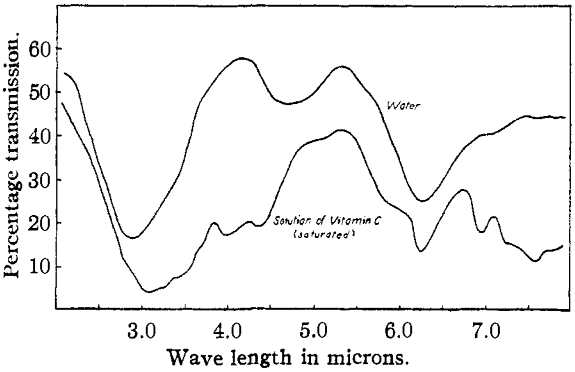

Fig. 1.—The percentage transmission of water and of an aqueous solution of vitamin C in the region between 2 and 8 μ.

Figure 2 shows the transmission of Vitamin C alone and is the average result of numerous determinations. The transmission curve shows several minima in the 3–3.5 μ region where bands arising from OH and CH groups would be expected to occur. Characteristic hydrocarbon bands are known to occur at 6.9 and 7.3 μ; both of these are found in the spectrum of Vitamin C. Although the 7.3 μ band appears as an inflection point in the curve showing the average of the results obtained, this band was actually well resolved in a number of runs. The comparative weakness of these bands may be attributed to the presence of only one CH_2 group in the Vitamin C molecule. The intense bands at 5.9 and 6.2 μ appear in the region in which one would expect to find absorption due to the C=C and C=O groups. Two well-defined bands are found which are not characteristic of any other recognized inner vibrations of the groups appearing in ascorbic acid. The first band appears at 4 μ, the second at 7.8 μ. These may possibly be vibrations involving the lactone linkage. In order to check this point, the spectrum of a sugar known to contain this type of linkage was mapped and bands were found at these wave lengths. Further studies of compounds containing this linkage are in progress.

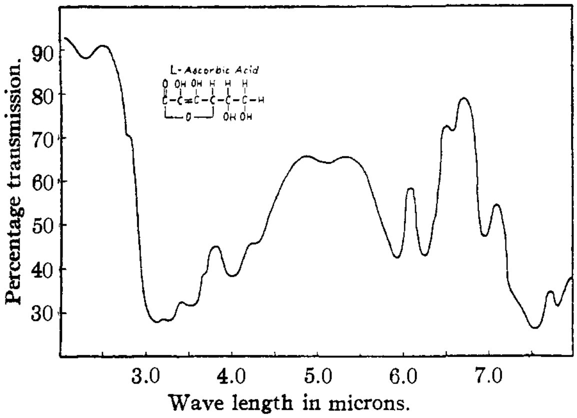

Fig. 2.—The infrared absorption spectrum of Vitamin C in the 2–8 μ region.

Summary

Although no strictly theoretical interpretation is possible for the infrared absorption spectrum of a molecule as complex as Vitamin C, it seems that the results obtained thus far are in agreement with the molecular structure suggested by Haworth and Hirst. From considerations of this structure, it appears that there should be six absorption bands in the infrared region between 2 and 8 μ. These bands have been observed and, in addition, two other bands which may arise from the lactone linkage.

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