

Raman Effect in Solutions of some Amino Acids

THE purpose of this letter is to report some measurements of Raman frequencies in solutions of glycine, alanine, tyrosine and cystine, which have been observed as a preliminary to the development of a spectroscopic method of analysis for molecules of this class.

An air-cooled quartz-capillary mercury arc furnished the exciting light, filter solutions of sodium nitrite and praseodymium ammonium nitrate permitting excitation by the 4358 Å. line. The spectrograph was a two-prism glass instrument having a dispersion of 23 Å./mm. at 4500 Å.

Solutions (in water) of samples of glycine and alanine which had been recrystallised several times to remove impurities exhibited some fluorescence; this, however, decreased upon still further recrystallising. Introduction of a small amount of potassium iodide to these solutions quenched the fluorescence very effectively.

The observed Raman frequencies (in cm^{-1}) together with visual estimates of the relative intensities are as follow:

Glycine (15 per cent solution in water, 10 per cent KI):—506 (3), 899 (8), 1036 (4), 1112 (2), 1332 (8), 1411 (10), 1445 (4);

Alanine (15 per cent in water, 8 per cent KI):—528 (2), 851 (6), 1305 (4), 1358 (5), 1383 (1), 1417 (10), 1466 (6), 1715 (4);

Tyrosine (5 per cent in 0.9 *N* HCl):—646 (3), 844 (9), 1216 (6), 1359 (4), 1448 (1), 1620 (10);

Cystine (8.33 per cent in 1.1 *N* HCl):—503 (10), 670 (10), 1633 (3), 1736 (3).

These lists are not to be regarded as complete for the spectral region covered, as weaker lines have been no doubt obscured by scattered continuous radiation from the mercury arc. The range of error of the measurements is roughly $\pm 3 \text{ cm}^{-1}$.

To test the effect of varying the concentration, three solutions of glycine having concentrations of 7.5, 15 and 22.5 per cent were examined. The Raman lines showed no shift in position greater than 2 cm^{-1} . Varying the amount of potassium iodide in these solutions from zero to 40 per cent also produced no shift greater than the error of measurement.

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July 10.

Initiation of the High-Frequency Discharge

WHEN the gas hydrogen in a wide tube is excited by means of a high-frequency alternating potential $V \sin 2\pi nt$, applied between two parallel plate electrodes, the relation between the sparking potential $V_s \sin 2\pi nt$, the gas pressure p , and the inter-electrode distance d for values of pd in excess of the critical value is of the simple form $V_s = A + Bpd$, where B is a gas constant and A depends upon the frequency n and the electrode surfaces¹.

This form of Paschen's law is consistent with the hypothesis that the peak potential V_s just before the initiation of the discharge is made up of two parts, (1) an electrode fall V_E and (2) a uniform field in the gas Bp . At pressures considerably in excess of the critical value, it may be assumed that V_E occurs in a very small fraction of the distance d . Then V_E will be approximately equal to A .

In the accompanying diagram (Fig. 1) an experimental curve is shown which exhibits the variation of V_s with p in a tube the electrodes of which were

of copper, 8 cm. in diameter and 2.58 cm. apart. The frequency of the applied potential was 2.03×10^7 c.p.s. This curve is typical of those which have been determined for frequencies between 8×10^6 c.p.s. and 9×10^7 c.p.s. It can be explained in terms of (1) ionisation by positive ions at the cathode and (2) ionisation by electronic impact in the gas. The former is connected with the electrode fall (72 volts) and the latter with the gradient $B = 21.6$ volts/cm./mm. of mercury.

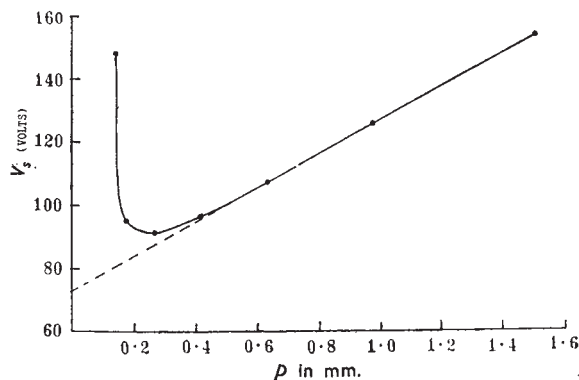


FIG. 1.

If it is assumed that a typical free electron moves under the action of the electric field so that $m\ddot{x} = E \cos(2\pi nt - \phi)$ and that a discharge occurs when the electron gains its ionising velocity at a given distance $L = K/p$ from its starting point, it can be shown that the mode of variation of E with p for a discharge is,

$$E = \frac{\pi n \sqrt{\frac{2V_0}{e/m}}}{\sin \frac{2\pi n K}{p \sqrt{(2V_0 e/m)}}} \dots \dots \dots (1)$$

For large values of p , $E = V_0 p / K$, giving the constant gradient $B = V_0 / K$.

When various experimental curves are examined by these hypotheses, the following facts emerge:

(a) The ionisation potential V_0 of the gas is correctly predicted.

(b) The value of K is much larger than that deduced from the kinetic theory on the assumption that L is the electronic mean free path.

(c) In discharges at all high frequencies, the critical pressure p_c is such that $d = K/p_c$ where K is calculated from the gradient V_0/K .

This last fact indicates that the minimum E predicted by equation (1) is not in general observed. Owing to the relatively large electrode fall, the equation only holds at the minimum for certain frequencies or for tubes in which d is very large. Fig. 1 is drawn for a value of n for which the theory of equation (1) holds very exactly down to the critical pressure.

A detailed account of the experiments which have led to these conclusions, and of others relating to the initiation of discharges by means of constant potentials, will be published elsewhere in due course.

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July 1.

¹ J. Thomson, *Phil. Mag.*, 18, 696; 1934. The value given for B in this paper is in error, due to a mistake in the estimate of a capacity. The correct value for the experiments there described is 26 volts/cm./mm.