ON THE ULTRAVIOLET ABSORPTION SPECTRUM OF ACETYLENE*

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Abstract

It is shown that the ultraviolet absorption bands reported previously do not belong to acetylene but to some impurity. In pure acetylene, bands are observed only below 2400A. These bands are arranged into three progressions and their interpretation is proposed using information from the work on the infrared absorption spectrum of acetylene.

THE more recent investigations of the infrared absorption spectrum of acetylene have revealed a very simple structure of these bands[1] leading to the conclusion that the acetylene molecule has all four atoms in a straight line and is therefore characterised by rotational quantum levels typical of a diatomic molecule. It seemed promising to undertake a study of the ultraviolet absorption spectrum of acetylene in the hope that here also a more complete analysis could be achieved than is possible with the majority of polyatomic molecules. Not much work has been done on acetylene spectrum. Stark and Lipp[2] investigated the absorption spectrum in gaseous acetylene and reported bands between 2200–1900A without giving their wave-lengths. On the other hand, Henri and Landau[3] studying gaseous acetylene and using a 40 cm absorption tube found numerous bands at longer wave-lengths which they divide into three groups: bands with fine structure from 3157 to 2872A; partly sharp, partly diffuse bands in the region 2960 to 2495A and bands with fine structure between 2327 and 2236A.

In the present work absorption tubes up to 2 meters length were used. As a light source a hydrogen discharge tube was employed and the photographs taken first with a medium size and later with a large Hilger E1 spectrograph. Acetylene was taken from a small "Prestolyte" tank and was purified[4] by passing it slowly through a series of five Milligan wash bottles containing water, chromic acid in sulfuric acid, mercuric chloride in hydrochloric acid, copper nitrate in nitric acid and sodium hydroxide solutions, respectively. It was finally dried over phosphorus pentoxide.

Acetylene thus purified was found to be completely transparent down to 2400A and even using plates of the most contrast no traces of the some 70 bands reported by Henri and Landau could be detected. Exposures were also made with acetylene prepared from commercial calcium carbide and only crudely purified. Here a continuous absorption was found extending from

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[1] Levin and Meyer, Journ. Opt. Soc. Am. 16, 137 (1928); Hedfeld and Mecke, Zeits. f. Physik 64, 151 (1930); Mecke, Ibid. 64, 173 (1930).

[2] Stark and Lipp, Zeits. f. phys. Chem. 86, 36 (1913).

[3] Landau, C. R. 156, 697 (1913).

[4] Beilstein. Handbuch d. Organischen Chemie, Vol. 1.

shorter wave-lengths up to about 3200A. It became evident that the spectrum described by Henri and Landau is due to some impurity and a further search for it was abandoned.

In the short ultraviolet a number of bands was observed. The wave numbers of the band heads will be found in Table I. Most of these bands are extremely faint and, in addition, a continuous absorption sets in at about

TABLE I. *Absorption bands of acetylene.*

1st progression		2nd progression		3d progression	
Wave number	Estimated intensity	Wave number	Intensity	Wave number	Intensity
42056	1	42961	1	44084⎫ 44100⎭	5
42156	1	43074⎫ 43088⎭	5	44205⎫ 44220⎭	3
42433	1	43184⎫ 43199⎭	3	44304⎫ 44318⎭	3
42504	1	43290	1	44475	3
42648⎫ 42660⎭	2	43441⎫ 43455⎭	2		
42698⎫ 42712⎭	3	43502⎫ 43518⎭	2		
		43674⎫ 43687⎭	10		
		43730⎫ 43744⎭	10		

Unassigned 44441 (3) and 44514 (3)

2300–2350A and becomes so strong below 2250A that not more than 5 percent of the light of this wave-length is transmitted by a 2 meter layer of acetylene at 760 mm pressure. In view of this, no great precision can be claimed for the wave-length determinations, the error for the fainter bands being probably of the order of 5 cm^{-1}. The bands are shaded to the red and have double heads with a spacing of about 14 cm^{-1}. The resolution obtained was not sufficient to show rotational structure near the heads, but in the stronger bands (43674–43687 and 43730–43744 cm^{-1}) evidence of structure was observed some distance away. Even in this spectral region the bands reported by Henri and Landau must be attributed to impurities for, with the exception of 42961 cm^{-1}, none of them coincides with the now observed ones within less than 20 cm^{-1}. It is of course not excluded that the bands here reported are also to be ascribed to impurities. On the other hand every precaution exercised in purifying acetylene seemed not to effect them in the least.

The bands recorded in Table I can be arranged into three progressions at a distance of 1032 and 1012 cm^{-1} apart. These progressions can be described by the same equation, as will be best seen from Fig. 1 in which the wave-numbers of the shorter wave-length band heads (after subtracting from the second and third progressions 1032 and 2044 cm^{-1}, respectively) have been plotted against an arbitrary number v. A quadratic expression in v is, however, certainly insufficient to describe the progressions since they show a pronounced convergence for the lowest values of v, but for $v = 5$ to 10 the bands become nearly equidistant. It is also unusual that both the first and the second progression break off abruptly after the strongest band ($v = 10$). A tenta-

tive interpretation of the observed regularities is possible using information obtained from the vibration-rotation bands of acetylene. Mecke[1] has pointed out that a normal acetylene molecule possesses three modes of vibration parallel to the molecular axis, of which one is optically active in the infrared ($\nu_2 = 3312.83$ cm^{-1}), and two transversal vibrations of lower frequencies ($\theta_1 = 729.27$ and $\theta_2 = 1328.5$). It is quite likely that the three progressions here reported are due to transitions into successive quantum states of either of the longitudinal vibrations of the excited molecule—probably ν_2—while the bands within each progression are caused by transitions to successive quantum states of one of the transversal modes of vibration. Against this interpretation speaks mainly the abnormal intensity distribution within each progression, but perhaps this, as also the rather unusual law of binding force necessary to account for the observed spacing of the bands can be attributed to the transversal character of the vibrations involved.
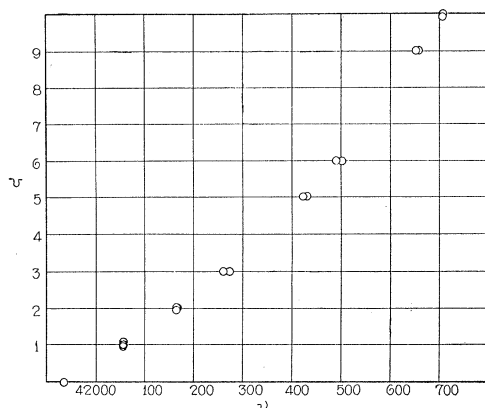

Fig. 1. A plot of three progressions of the acetylene bands.

Although a calculation of the fundamental frequencies of the excited molecule is impossible at present, it can be pointed out at least that they are probably lower than those of the normal molecule, the bands being shaded to the red, thus indicating a larger moment of inertia and presumably weaker binding force in the excited molecule. Assuming that the rotational structure of the acetylene bands is similar to that of diatomic molecules and that the double band heads are due to R and Q branches, one can estimate from their separation and the known moment of inertia of the normal molecule,[5] the moment of inertia of the excited one. One obtains thus $25.6 \pm 0.3 \times 10^{-40}$ gm cm^2 as compared with 23.509×10^{-40} gm cm^2 of the normal molecule.

The origin of the continuous absorption, mentioned in the beginning of this note, remains uncertain. It is likely, though, that this absorption is due to residual traces of impurities, because Stark and Lipp[2] were able to observe absorption bands down to 1900A.

It is a pleasant duty to thank Mr. Alfred L. Loomis for his kind permission to work in the Loomis Laboratory and for the facilities put there at my disposal.

[5] Assuming that the head of the Q branch coincides with the zero line of the band, that the equation of the R branch is $\Delta\nu = (B' + B'')K + (B' - B'')K^2$ and that for its head $K = -B' + B''/2(B' - B'')$.