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## The Absorption Spectrum of Diacetylene in the Near Ultraviolet

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The absorption spectrum of diacetylene gas was investigated down to  $\lambda 1900\text{\AA}$ . In the region  $\lambda\lambda 2860\text{--}1900\text{\AA}$  more than eighty bands were found. Some regularities in the spectrum and the similarity with the cyanogen ultraviolet absorption spectrum are described. Resemblance between the diacetylene and cyanogen molecules is briefly discussed.

A GREAT deal of interesting and useful results regarding the structure of diatomic molecules in the normal as well as in the excited states have been obtained from their spectroscopic investigations. For polyatomic gases, however, on account of their increasing complexity, only in few of the simplest cases have their spectra and structure been completely understood. Very interesting results regarding the structure of simple polyatomic molecules in the excited states could, however, be obtained through an investigation of their ultraviolet absorption spectra in cases where the structure in the normal states has been definitely established. Some three years ago, the ultraviolet absorption spectrum of cyanogen was studied by Badger and one of the present authors.<sup>1</sup> It was found that the spectrum is extremely complex, and no complete analysis could be made. A comparison of the diacetylene molecule with that of cyanogen would immediately suggest that these molecules are isosteric and probably have similar electronic states. This has actually been proved to be the case in the normal state.<sup>2</sup> It seems to be probable that a study on the ultraviolet absorption spectrum of diacetylene may throw some light on the structure of both of these molecules in the excited states.

### EXPERIMENTAL PROCEDURE

The diacetylene gas used in the investigation was prepared by the method of Straus and Kollek.<sup>3</sup> The gas generated was condensed in a solid  $\text{CO}_2$  trap when thoroughly washed and dried. It was purified by repeated fractionation

under vacuum, until the first, middle and last portions showed no difference in the spectrum.

A glass tube of about 130 cm long, fitted with fused quartz windows and connections to trap, manometer and vacuum pump, was used as the absorption cell. The spectrum was taken with a Hilger E 31 quartz spectrograph. A hydrogen discharge tube of the type described by Scheibe<sup>4</sup> was used as the continuous light source. The authors want to express their sincere thanks to Dr. Herzberg through whose kindness the discharge tube was obtained. The tube was excited with a power of about 1 kva through a 9000 v transformer. Eastman 40 plates sensitized with light oil were used. As comparison spectrum copper spark lines were employed. Exposure of one hour was found sufficient.

After the introduction of freshly distilled diacetylene in the liquid air trap, the system was thoroughly evacuated with an oil pump to get rid of any volatile impurities which might be present during the preparation. The pressure of the absorbing gas varied from 1 mm to 252 mm. It was found that the development of the bands was very critical to pressure. Plates were thus taken at adjusted pressure intervals in order to develop the system as completely as possible, and for each pressure two or three plates were taken.

During the exposure, slight polymerization of the gas was observed, but it had no influence on the nature of the spectrum.

Measurement of the bands were made with a S. I. P. Comparator\* for 16 plates, each being measured three to six times. On account of the

<sup>1</sup> Sho-Chow Woo and Richard M. Badger, *Phys. Rev.* **39**, 932 (1932).

<sup>2</sup> B. Timm and R. Mecke, *Zeits. f. Physik* **94**, 1 (1935).

<sup>3</sup> F. Strauss and L. Kollek, *Ber. d. Deutsch. chem. Ges.* **59**, 1664 (1926).

<sup>4</sup> G. Scheibe, F. Povenz and C. F. Linström, *Zeits. f. physik. Chemie* **B20**, 283 (1933).

\* Our thanks are due to Professor S. L. Ting and Dr. Z. W. Ku for the privilege of using the instrument of the Physics Institute.

great pressure broadening on part of the bands, great accuracy may not be expected. Great difficulty was also experienced in deciding exactly what part of a band to measure, for the appearance of the bands varies considerably from band to band. But in the case of sharp bands the error may not be greater than  $10\text{ cm}^{-1}$ .

### RESULTS AND DISCUSSION

At 1 mm pressure (130 cm absorption length), diacetylene was found to be completely transparent to  $\lambda 2490\text{A}$ , where a group of strong bands set in and extended to the short wavelength limit of the spectrograph. Some of the strong bands are degraded to the red, while most of them do not show any sharp edge. With increasing pressure, the bands became broadened and appeared finally as an apparent continuum, which shifted gradually toward the red side, till at a pressure of about 10 mm, all of the low pressure bands were completely obliterated and another group of bands began to appear. This last group of bands extended toward the red side with increasing pressure, until at 252 mm it extended as far as  $\lambda 2860\text{A}$ .

Because of the varying appearance of the bands, it is rather difficult to determine how best to describe their general nature, until our more detailed investigation with higher dispersion is finished. It may, however, be said that the low pressure group of bands shows somewhat different gross structure from that of the higher pressure group. Table I gives the wavelengths and wave numbers of the bands measured, their relative intensities being estimated visually.

The fundamental frequencies of diacetylene in the normal state have been discussed by Mecke.<sup>2</sup> The valence vibrational frequencies may not be expected to appear as differences in the ultraviolet absorption spectrum at room temperature. On the other hand, weaker bands should appear on the red side of the strong bands at distances equal to the deformation vibrational frequencies from the latter. It is rather curious why these bands should be absent in the spectrum.

Six progressions of reasonable intensity distribution are given in Table II. It will be noticed that all of them have a frequency difference of

TABLE I. The diacetylene bands in the near ultraviolet.

<i>M</i>	$\lambda(\text{A})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>M</i>	$\lambda(\text{A})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>D</i>
	2861.4	34938	00		2498.9	40006	0	
	2851.5	35059	00		2485.3	40224	3	
	2808.4	35597	00		2476.5	40367	1	
	2805.2	35638	0	VE	2467.3	40518	4	
	2802.1	35677	00		2460.3	40633	0	
	2798.3	35725	00		2450.2	40801	0	
	2793.2	35791	00		2446.3	40866	0	
	2787.6	35863	00	VE	2429.5	41148	10	A
	2782.3	35931	00		2422.0	41276	5	B
	2777.6	35992	00		2407.7	41521	5	C
D	2755.0(?)	36287	3		2403.5	41593	5	D
D	2751.3(?)	36336	2	VE	2393.0	41776	6	E
D	2746.3(?)	36402	3		2388.7	41851	0	
D	2738.4	36507	0		2384.6	41923	0	
D	2732.0	36592	0		2380.3	41999	0	
D	2724.2	36697	0		2375.7	42080	3	F
D	2716.8	36797	0		2364.4	42281	1	
VE, (D)	2698.8	37043	4		2359.3	42372	2	
	2694.0	37109	3		2351.9	42506	1	
	2688.5	37184	0		2346.7	42600	3	
	2683.6	37252	0	VE	2310.8	43262	9	A'
D	2677.9	37332	1		2303.0	43408	4	B'
D	2670.2	37439	3		2292.6	43605	4	C'
	2664.5	37519	2		2287.9	43695	4	D'
	2657.5	37618	0	VE, (D)	2281.8	43811	5	E'
	2652.6	37688	2		2276.3	43917	2	
D	2648.8	37742	4		2263.2	44172	3	F'
	2641.9	37840	1		2254.9	44334	1	
	2637.7	37901	2		2246.8	44494	1	
D	2630.5	38004	1		2236.9	44691	3	
	2623.5	38106	0	VE	2204.2	45354	5	A''
D	2617.3	38196	3		2196.5	45513	2	B''
	2606.9	38348	2		2189.3	45662	2	C''
	2599.1	38463	1		2179.3	45872	2	E''
	2592.9	38555	0		2161.4	46252	2	F''
	2586.8	38646	0		2117.9	47202	1	
VE, (D)	2553.4(?)	39152	2	VE	2108.2	47419	3	A'''
	2513.6	39772	0		2100.8	47586	1	B'''
	2506.3	39887	0		2085.3	47939	1	E'''

In columns *M*, VE indicates the violet edge of the bands measured, for other bands not specified centers of them being measured. *D* means diffused.

Columns *I* and *D* give respectively the estimated relative intensities and designations.

TABLE II. Some progressions in the diacetylene spectrum.

$\nu(\text{cm}^{-1}) \Delta \nu$	$\nu(\text{cm}^{-1}) \Delta \nu$	$\nu(\text{cm}^{-1}) \Delta \nu$
<i>A</i>	<i>B</i>	<i>C</i>
<i>A</i> 41148	<i>B</i> 41276	<i>C</i> 41521
<i>A'</i> 43262	<i>B'</i> 43408	<i>C'</i> 43605
<i>A''</i> 45354	<i>B''</i> 45513	<i>C''</i> 45662
<i>A'''</i> 47419	<i>B'''</i> 47586	
<i>D</i>	<i>E</i>	<i>F</i>
<i>D</i> 41593	<i>E</i> 41776	<i>F</i> 42080
<i>D'</i> 43695	<i>E'</i> 43811	<i>F'</i> 44172
	<i>E''</i> 45872	<i>F''</i> 46252
	<i>E'''</i> 47939	

about  $2100\text{ cm}^{-1}$ . Other similar progressions could have been assigned by including the higher pressure bands. But the peculiar intensity distribution make them uncertain. Without considering the coupling effect between different vibrations which causes its variation from one progression to another, the frequency difference

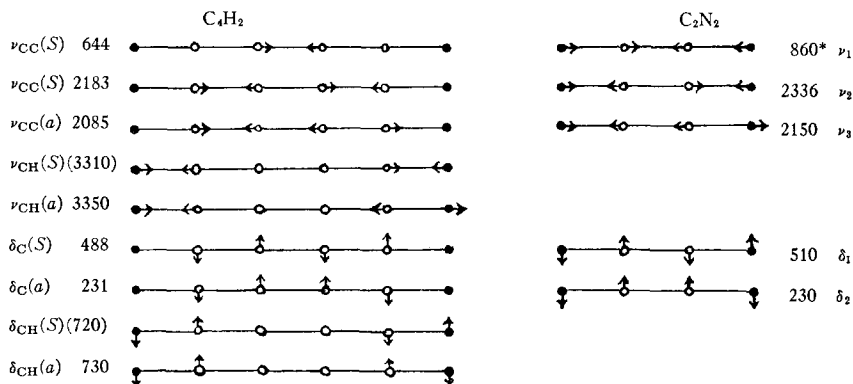


FIG. 1.

$\sim 2100 \text{ cm}^{-1}$  is considered to be approximately the frequency of a longitudinal vibration in the excited state.

The similarity between the structure of diacetylene and cyanogen in the normal state has been pointed out by Mecke through an investigation of their infrared and Raman spectra. The normal vibration frequencies are given in Fig. 1. Because these compounds contain the same number of electrons, it may be inferred that they should possess similar electronic states. An examination of their ultraviolet absorption spectra shows fairly definitely that these systems are due to transitions between corresponding electronic states, the lower states being the normal. First of all, these spectra appear almost in the same region. The spectrum of diacetylene as in the case of cyanogen will certainly extend farther into the vacuum region than what we have reported here. Secondly, the gross structure of these spectra shows marked similarities. Thus in both of them the strongest and longest progressions have a frequency difference of  $\sim 2100 \text{ cm}^{-1}$ , which represents a normal vibrational frequency in the excited states probably having similar symmetrical character in both cases. Before the complete analysis of the spectra is obtained, one may not be able to ascertain the exact structure of these molecules in the excited state and the selection rules governing the transitions in the ultraviolet spectra. But it

may be pointed out that the probability of transitions is influenced by two factors. Firstly the symmetry of the molecule determines the selection rule. Secondly transitions which may be allowed by the symmetry characters may still be excluded for reasons which are analogous to those leading to the Franck-Condon principle for diatomic molecules. If the vibration  $\sim 2100 \text{ cm}^{-1}$  in the excited states is taken to be of similar symmetry character for the two molecules, a reference with the vibration diagram given above will show that the excited electronic states of diacetylene and cyanogen molecules are similar in symmetry character, and that the internuclear distances in the excited states with those in the normal states have the same kind of relation in both cases.

The above argument does not necessarily mean that the structures of the diacetylene and cyanogen molecules should not differ from each other in details. For example, one of the molecules may be slightly bent, while the other is collinear. This may not affect some of the vibrational frequencies very much, but will certainly modify the selection rules considerably. This effect has already been observed in the infrared and Raman spectra of diacetylene.

\* According to our recent calculation (to appear in the J. Chinese Chem. Soc.) there may still be some doubt about the value  $860 \text{ cm}^{-1}$  assigned to the longitudinal vibration  $\nu_1$ , which seems to be  $756 \text{ cm}^{-1}$  as observed in Raman spectrum (A. Petrikahn und J. Hochberg, Zeits. f. physik. Chemie B8, 440 (1930)).