

The Near Ultraviolet Bands of Acetylene

ShoChow Woo, TaKong Liu, T. C. Chu, and Wu Chih

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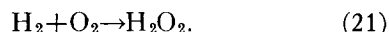
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hydrogen from this reaction combines with oxygen to form hydrogen peroxide according to:



(4) This reaction (21) accounts for the increased production of hydrogen peroxide and increased consumption of oxygen.

The decrease in carbon dioxide shows us to what extent the effect of the rays on formic acid is suppressed by the presence of the oxygen and it is given in the following tabulation:

6 cm O ₂	1.0 mM HCOOH	$\Delta\text{CO}_2 = 3.2 - 2.1 = 1.1 \mu\text{M CO}_2$
	0.03 mM HCOOH	$\Delta\text{CO}_2 = 2.7 - 1.6 = 1.1 \mu\text{M CO}_2$
70 cm O ₂	1.0 mM HCOOH	$\Delta\text{CO}_2 = 3.2 - 2.0 = 1.2 \mu\text{M CO}_2$

The decrease in carbon dioxide is independent of

the formic acid concentration and of the oxygen pressure and equals $\Delta\text{CO}_2 = 1.1 \mu\text{M}$. This value equals the rate at which oxygen is consumed when it is irradiated alone.

Apparently the formic acid decomposition can be only partially suppressed by adding oxygen. This result takes on a special significance when we note that water activated with ultraviolet light causes the decomposition of formic acid, but it has no effect on oxygen. Possibly, therefore, the reason for the inability of oxygen to completely suppress the formic acid reaction may be that the x-ray activated water molecules, which act on formic acid, do not all react with oxygen.

We are indebted to D. M. Gallagher for his assistance during the greater part of this work.

The Near Ultraviolet Bands of Acetylene

SHO-CHOW WOO, TA-KONG LIU, T. C. CHU AND WU CHIH
National Research Institute of Chemistry, Academia Sinica, Shanghai, China

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The present investigation is a part of the program of a series of studies aiming at a satisfactory analysis of the near ultraviolet spectrum of acetylene. The spectrum of C_2H_2 at room temperature and 300°C was taken with a Bausch and Lomb large quartz spectrograph. The spectrum extends from $\lambda 2430\text{\AA}$ down to the ultraviolet limit of the instrument. More than 1000 bands and lines have been measured. Most of the bands revealed intensification at elevated temperature. Some of them have been partially resolved into rotational lines with alternating intensities. Seven main progressions all with frequency difference $\sim 1050 \text{ cm}^{-1}$ have been found. Only the bands of three of

the progressions showed no intensification at higher temperature. From the differences between these bands, a frequency 580 cm^{-1} has been observed. Weaker bands on the red side of stronger ones have been proved through temperature variation to be due to transitions from the excited $2\nu_b''(E_g)$ level in the ground state. Through a tentative assignment, $2\nu_b' = 1050 \text{ cm}^{-1}$ and $\nu_4'(E_u) = 580 \text{ cm}^{-1}$ and the empirical selection rules, all of the bands in the seven progressions can be satisfactorily explained. Other possible assignments and the nature of the electronic transition have also been briefly discussed.

THE complexity of the ultraviolet spectra of polyatomic molecules usually prevents a complete analysis in the present state of knowledge. Attempts toward simplification have been made by working with those molecules which possess a structure of high symmetry. For this reason, we have recently been working mainly on molecules which are considered to be of the symmetrical and collinear type. Acetylene is particularly suitable in this category since its structure and fundamental frequencies in the ground state have been thoroughly investigated through the infra-red and Raman spectrum

measurements. Unfortunately, no satisfactory analysis which makes use of these results in the ground state has been attained, in spite of the numerous investigations¹ made in recent years.

¹ (a) J. Stark and P. Lipp, *Zeits. f. physik. Chemie* **86**, 36 (1913); (b) H. Hese, A. Rose and R. Gräffin Zu Dohna, *Zeits. f. Physik* **81**, 745 (1933); (c) G. Kistiakowsky, *Phys. Rev.* **37**, 276 (1931); (d) M. A. Jonesco, *Comptes rendus* **199**, 710 (1934); (e) M. A. Jonesco, *Comptes rendus* **200**, 817 (1935); (f) H. Göpfert, *Zeits. f. wiss. Phot.* **34**, 156 (1935); (g) It is uncertain if the bands beginning at $\lambda 2070\text{\AA}$ found by Herzberg (*Trans. Faraday Soc.* **27**, 378 (1931)) are a continuation of the system here discussed, since the distances between the main bands were found to be 1365 and 865 cm^{-1} , which are quite different from what we have found here.

A program has thus been planned in this laboratory to investigate this problem in the following three steps. (1) The spectrum of C_2H_2 is to be taken at different temperatures in order to ascertain which of the bands are due to transitions from the vibrationless level, and which are from the higher vibrational levels in the ground state. The frequency differences between these two groups of bands are then compared with the results of infra-red and Raman spectrum measurements. (2) The vibrational isotopic shifts of the bands are to be determined by a study of the spectrum of pure C_2D_2 . This will help us not only to identify the (0,0) band, but also to prove the correctness of the assignment of the vibrational levels in both the ground as well as the excited states, since by a simple computation the frequencies of C_2D_2 may be obtained from those of C_2H_2 . (3) The rotational structure of some of the bands is to be analyzed with a grating spectrograph of high dispersion, so that the nature of the electronic transition and hence the vibrational selection rules may be clearly understood.

With the above outlined program, we could certainly hope to attain a satisfactory solution of the problem. Unfortunately our work has been interrupted by the Sino-Japanese war just before the beginning of step (2). We are much obliged to Drs. Vaughan and McQuigg of the Union Carbide and Carbon Company for their kindness in offering us the purest calcium carbide available in their company.

Thus only step (1) of the program has been finished. With this part of the data, a complete analysis may not be attained. However, a plausible vibrational analysis may still be made and this part of experimental results may assist in the future investigation of the problem.

EXPERIMENTAL

The acetylene gas used in this investigation was obtained from a commercial tank. It was thoroughly purified by passing through a train of Milligan wash-bottles containing, respectively, water, cupric nitrate in nitric acid, mercuric chloride in hydrochloric acid and chromic acid in sulphuric acid. After being dried with soda-lime and P_2O_5 and collected in a liquid-air trap, the gas was then fractionated under reduced

pressure, only the middle portion being taken for use. A large excess quantity of the gas was thus prepared and reserved for use in round-bottomed flasks provided with glass stopcocks and connections with the traps. After the gas had been condensed in the liquid-air traps, the complete system was thoroughly evacuated in order to remove any gaseous impurities which might be present.

The experimental arrangement was as usual. A hydrogen discharge tube, the same as one described before² was used as the continuous light source. The spectrum was taken with a Bausch and Lomb large Littrow type spectrograph with a dispersion of 2.1Å/mm at 2430Å and 1.2Å/mm at 2040Å. Glass tubes 50 cm and 350 cm long, fitted with quartz windows and connections to traps, manometer and vacuum pump, were used as our absorption cells. The amount of the absorbing gas varied from a few millimeters pressure in the short tube, to 1040 mm in the long tube. Plates were taken at adjusted pressure intervals in order to reveal the bands as completely as possible. Ilford Empress and Eastman 40 plates sensitized with mineral oil were used. Exposure for one hour was usual and in some cases two or three hours were found necessary. Iron arc and copper spark lines were taken as comparison spectra.

For the study of the intensity variation of the bands with temperature, quartz absorption cells with fused-on windows of 10 cm and 100 cm length were used. They were heated with tube-form electric heaters connected to rheostats for temperature regulation. For every amount of the absorbing gas in the cell, two spectra were taken side by side on the same plate with one at room temperature and the other at a higher temperature ($\sim 300^\circ C$). By varying the amount of the absorbing gas from a few mm pressure in the 10 cm tube to half an atmosphere in the 100 cm tube, the temperature effect, if any, on most of the bands could be observed. Photo-polymerization was found to become more prominent at the higher temperature. In the case of higher pressures, the product of polymerization was found to deposit on the light-entering window whose transparency was thereby diminished. Conse-

² Sho-Chow Woo and Ta-Kong Liu, *J. Chem. Phys.* **5**, 161 (1937).

TABLE I. The acetylene bands in the region $\lambda\lambda 2430-2050$.

$\nu(\text{cm}^{-1})$ (IN VACUUM)	DESIG- NATION	I	$\nu(\text{cm}^{-1})$ (IN VACUUM)	DESIG- NATION	I	$\nu(\text{cm}^{-1})$ (IN VACUUM)	DESIG- NATION	I	$\nu(\text{cm}^{-1})$ (IN VACUUM)	DESIG- NATION	I
41227.1*	a_3	00	$\nu 43490.4^*$	b_6	3	$\nu 44660.5$	A_7	7	$\nu 45993.4$	c_{10}	4
41393.9*		00	$\nu 43502.9^*$		4	$\nu 44672.6$		8	$\nu 45998.7$		5
41406.1*		00	$\nu 43505.1^*$		1	$\nu 44675.0$		7	$\nu 46028.6^*$		5
41456.6*	b_2	00	43524.6		1	$\nu 44685.0$		4	46041.7		5
41644.8	B_0	00	43530.3*		1	$\nu 44686.8$		4	46046.0		5
41819.2*		0	43610.5		2	44694.4*		4	$\nu 46060.0^*$		7
41929.8*		0	43617.1*		1	44707.0		4	$\nu 46061.9^*$		8
$\nu 42024.3$	c_2	1	$\nu 43660.0$	A_5	3	$\nu 44733.8$	B_6	6	$\nu 46073.3$	c_9	6
$\nu 42029.2$			$\nu 43663.8$		5	$\nu 44736.0$		8	$\nu 46074.6$		7
$\nu 42041.4^*$		1	$\nu 43674.1$		3	$\nu 44747.0$		2	$\nu 46121.6^*$		4
42044.0*	c_1	00	$\nu 43676.9$	B_4	3	$\nu 44749.4$	c_8	5	$\nu 46123.7^*$	C_8	4
$\nu 42045.3^*$		1	43682.9*		3	44815.2*		4	$\nu 46133.7^*$		6
42128.9*		00	43686.7*		3	$\nu 44830.5^*$		5	$\nu 46135.6^*$		7
42142.6*	C_0	1	$\nu 43719.4$		4	$\nu 44879.2^*$		00	46173.6		4
42226.6		00	$\nu 43730.8$		6	44888.9*		4	46182.7		4
42335.5*		00	$\nu 43733.3$		1	44892.5		5	$\nu 46288.4$		6
42376.3*	a_5	00	43797.5*		1	$\nu 45057.2$		5	$\nu 46290.1$	b_{12}	4
42395.8*		00	$\nu 43800.8^*$		1	$\nu 45058.4$		5	$\nu 46305.1$		6
42421.2*		0	$\nu 43803.8^*$		3	$\nu 45059.8^*$		4	$\nu 46307.4$		4
42430.2*	b_4	0	$\nu 43816.5^*$		0	45067.9*		6	$\nu 46449.0^*$		4
42432.2*		0	$\nu 43819.2^*$		0	$\nu 45073.2^*$		4	$\nu 46462.2^*$		4
42472.9		00	43859.9		0	$\nu 45075.2^*$		4	46480.7		4
$\nu 42476.2^*$	A_3	00	$\nu 43861.9$		0	$\nu 45103.1$		6	46546.5		5
$\nu 42487.5^*$		1	$\nu 43873.0^*$		2	$\nu 45106.2$		3	46558.4		7
$\nu 42489.4^*$		2	$\nu 43874.8^*$		00	$\nu 45116.9$		6	46582.5		5
42631.0	B_2	2	43947.7*		3	$\nu 45118.6$		3	$\nu 46594.7$	A_{11}	4
$\nu 42632.8$		2	44007.2		5	$\nu 45191.4^*$		6	$\nu 46596.8$		7
$\nu 42646.3$		2	$\nu 44068.3^*$		2	$\nu 45193.6^*$		8	46625.3		4
42656.3*	c_4	2	$\nu 44072.8^*$		5	$\nu 45203.4^*$		8	46636.6		5
$\nu 42683.6$		2	$\nu 44081.0^*$		2	$\nu 45206.7^*$		6	46655.3		7
$\nu 42696.4$		3	$\nu 44082.7^*$		5	45251.7		8	46666.7		4
$\nu 42697.9$	c_3	00	$\nu 44085.0^*$		5	45260.5		8	46691.5		5
42762.1*		00	$\nu 44087.4^*$		1	45289.6		6	$\nu 46703.3$	B_{10}	10
42829.5*		00	44132.5		1	$\nu 45300.3$		8	$\nu 46705.2$		4
42832.1*	c_2	00	44157.3		3	$\nu 45302.4$		10	47009.0		4
42838.4*		0	44193.4		5	$\nu 45317.6$		7	47026.6		4
42949.9*		00	$\nu 44205.5^*$		2	$\nu 45319.6$		5	$\nu 47045.2$		5
42961.7*	c_1	00	$\nu 44208.4^*$		2	$\nu 45397.0^*$		7	$\nu 47048.3$		7
$\nu 43057.0^*$		3	44213.3*		3	$\nu 45455.4$		5	$\nu 47057.4$		5
$\nu 43059.0^*$		4	44216.1*		5	$\nu 45457.5$		6	$\nu 47061.0$		9
$\nu 43074.6^*$	c_3	2	$\nu 44286.7$		5	$\nu 45472.4^*$		6	$\nu 47111.5$		5
$\nu 43169.1^*$		4	$\nu 44289.5$		5	$\nu 45474.2^*$		5	$\nu 47114.8$		9
43176.9*		0	$\nu 44304.8$		2	45596.4*		9	$\nu 47124.8$		4
$\nu 43184.4^*$	c_2	4	$\nu 44307.2$		5	$\nu 45659.3$		10	$\nu 47126.4$		5
$\nu 43190.5^*$		00	44344.3*		2	$\nu 45660.9$		9	47156.4		4
$\nu 43192.2^*$		00	44415.6*		5	$\nu 45670.7$		10	47172.2		5
43203.6*	C_2	1	$\nu 44427.9^*$		5	$\nu 45672.4$		9	47204.7		6
$\nu 43256.9$		2	44443.3*		3	45691.4		5	$\nu 47223.2$		5
$\nu 43257.6$		3	$\nu 44447.2^*$		3	45703.1		7	$\nu 47225.0$		5
$\nu 43273.0$	a_7	00	$\nu 44458.7^*$		1	$\nu 45725.9$		3	47247.8		4
$\nu 43274.8$		00	$\nu 44460.9^*$		0	$\nu 45728.0$		3	$\nu 47258.9$		7
43309.0*		0	44480.3*		5	$\nu 45739.5$		10	$\nu 47260.4$		5
43365.7*	b_8	00	$\nu 44485.0$		1	$\nu 45741.1$		3	$\nu 47275.5$	C_{10}	7
43378.1*		0	$\nu 44493.5^*$		5	45814.9*		2	$\nu 47277.3$		4
$\nu 43411.6$		3	$\nu 44497.3^*$		1	$\nu 45827.1$		0	47418.3		4
$\nu 43412.8$	a_7	4	44553.4		4	$\nu 45831.7$		3	47434.3		5
$\nu 43430.1^*$		4	44567.3*		3	45869.4		4	47569.9		5
$\nu 43442.0^*$		1	44597.5		3	$\nu 45881.4$		3	47582.4		7
43458.1		0	44611.2		3	$\nu 45885.4$		4	47676.1		8
43467.7						$\nu 45974.2$			$\nu 47692.4$		
						$\nu 45979.5$			$\nu 47694.7$		

* Bands which showed intensification at higher temperature.

† Bands whose intensification at elevated temperature was anticipated, but not observed. Probably the crowding of bands and lines as well as the diminished transparency at 300°C make the observation difficult.

quently after a few exposures, the window had to be cleaned.

Measurement of bands and lines was made with an S.I.P. comparator. The error of measurement for most of the bands was less than $\pm 1 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The spectrum of acetylene extends from $\lambda 2430\text{\AA}$ down to the ultraviolet limit of the instrument. More than 1000 bands and lines have been measured. A number of the bands have been partially resolved into rotational lines with alternating intensities. However, on account of the limited dispersion of the instrument, great accuracy for the rotational lines cannot be claimed. In Table I, are given the wave-lengths and wave numbers of the band heads with their visually estimated intensities. Because of the fact that the bands and lines are so numerous and closely spaced in some cases of weak absorption it was difficult to tell their real nature. Consequently, it may be that some of the weak band heads have been left unlisted in Table I while some of the lines may have been mistaken for band heads. It will be seen that our results agree very well with those of Göpfert.¹⁷ Most of the bands showed intensification at elevated temperature. Seven progressions with reasonable intensity distribution and all with frequency difference $\sim 1050 \text{ cm}^{-1}$ have been found. These are listed in Table II, where the bands without intensification at higher temperature are designated by the capital letters.

All of the bands are double headed and with a degradation toward the red, showing an increase in moment of inertia by the electronic excitation. The separations of the doublets remain almost constant for each progression but vary from one progression to another, the greatest one being that in the bands of progression C. This indicates that in the upper levels of the C bands, the molecule possesses a moment of inertia nearest to that in the ground state. Hence if we take $C_0 - B_0$ as a vibrational frequency, it must be a deformational one, since it has been shown in the infra-red spectrum that the moment of inertia of acetylene in the ground state is decreased slightly by deformational oscillations³

and this is probably true also for the excited state.

The second differences in each of the progressions show considerable variations which exceed our experimental error. It is, however, interesting to note that these variations, though irregular, show a general tendency of increasing at first, followed by a decrease. This fact may help us to a better understanding of the nature of these bands, although no definite conclusion could be drawn here from this fact alone.

The complexity of the spectrum results from the fact that the bands are so numerous and crowded that it can hardly be understood how all of their frequency differences can be ascribed to the fundamental frequencies in the lower and upper states. The study of the intensity variation with temperature has simplified the analysis enormously. Thus it can be seen that only three progressions of bands showed no intensification at higher temperature and hence they must be the only ones which arise from transitions from the vibrationless level in the ground state to different vibrational levels in the excited state. Consequently there remain at most only three frequency differences, namely, $\sim 1050 \text{ cm}^{-1}$, $\sim 1000 \text{ cm}^{-1}$ ($A_3 - B_0$), and $\sim 580 \text{ cm}^{-1}$ ($C_0 - B_0$) which may be ascribed to the fundamentals or their multiples in the excited state. All of the other bands arise from transitions from higher vibrational levels in the ground state. These bands must be on the red side of the A, B and C bands by distances which are multiples of the fundamental frequencies in the ground state.

Before the meaning of $\sim 1050 \text{ cm}^{-1}$, $\sim 1000 \text{ cm}^{-1}$ and $\sim 580 \text{ cm}^{-1}$, and the nature of the transitions of these bands can be understood, a reference to the fundamental frequencies in the ground state appears to be necessary. From the infra-red and Raman spectrum measurements, it has been proved that the acetylene molecule is symmetrical and collinear and possesses the following frequencies: $\nu_1''(\text{Ag}) = 1974$, $\nu_2''(\text{Ag}) = 3370$, $\nu_3''(\text{Au}) = 3288$, $\nu_4''(\text{Eu}) = 729$, $\nu_5''(\text{Eg}) = 612$.⁴ Now if the electronic transition is not a forbidden one and the excitation is at the C-C bond, by which the symmetry of the molecule is not altered, the most natural assignment is

³ K. Hedfeld and R. Mecke, *Zeits. f. Physik* **64**, 151 (1930); G. Herzberg and J. W. T. Spinks, *Zeits. f. Physik* **91**, 386 (1934).

⁴ Gösta W. Funke and Einar Lindholm, *Zeits. f. Physik* **106**, 518 (1937).

and C 's by a frequency difference of $\sim 1240\text{ cm}^{-1}$ or $2\nu_5''$. It can hardly be understood why only one quantum of ν_5' is excited in the case of the C and c bands. Moreover, no satisfactory explanation can be given for the small separation of each pair of A 's and B 's which cannot be regarded as electronic doublets, since the ground state of acetylene is $^1\Sigma$ and hence its excited state should be either singlet or triplet. Again, the assignment is not able to account for the bands, c_1 , c_3 , c_5 , etc.

The last two difficulties may be removed by assigning $\nu_1' = 1050 \text{ cm}^{-1}$, $\nu_4' = 580 \text{ cm}^{-1}$ and $2\nu_5' = 1000 \text{ cm}^{-1}$. However, the other difficulties are still left unsolved. Although the bands, c_1 , c_3 , $c_5 \dots$ are situated just in the middle of B_0-A_3 , B_2-A_5 , $B_4-A_7 \dots$ with comparatively low intensity as should be expected, it cannot be explained why they should show remarkable intensification at higher temperature. Moreover, the appearance of bands with $\Delta\nu_4' = 1$ with con-

⁵ W. C. Price, Phys. Rev. **47**, 444 (1935).

⁶ G. Herzberg and E. Teller, *Zeits. f. physik. Chemie* **B21**, 410 (1933).

TABLE II. Main progressions in the near ultraviolet spectrum of C_2H_2 .

A		B		C		
A_1	B_0	41645	C_0	42227	$C_0 - B_0 = 582$
A_3	$\left. \begin{array}{l} 42633 \\ 42646 \end{array} \right\} 13$	B_2	$\left. \begin{array}{l} 42684 \\ 42698 \end{array} \right\} 14$	C_2	$\left. \begin{array}{l} 43258 \\ 43275 \end{array} \right\} 17$	$C_2 - B_2 = 577$
A_5	$\left. \begin{array}{l} 43664 \\ 43677 \end{array} \right\} 13$	B_4	$\left. \begin{array}{l} 43719 \\ 43733 \end{array} \right\} 14$	C_4	$\left. \begin{array}{l} 44290 \\ 44307 \end{array} \right\} 17$	$C_4 - B_4 = 574$
A_7	$\left. \begin{array}{l} 44661 \\ 44675 \\ 44687 \end{array} \right\} 14$	B_6	$\left. \begin{array}{l} 44736 \\ 44749 \end{array} \right\} 13$	C_6	$\left. \begin{array}{l} 45302 \\ 45320 \end{array} \right\} 18$	$C_6 - B_6 = 571$
A_9	$\left. \begin{array}{l} 45661 \\ 45672 \end{array} \right\} 11$	B_8	$\left. \begin{array}{l} 45728 \\ 45741 \end{array} \right\} 13$	C_8	$\left. \begin{array}{l} 46290 \\ 46307 \end{array} \right\} 17$	$C_8 - B_8 = 566$
A_{11}	$\left. \begin{array}{l} 46625 \\ 46637 \end{array} \right\} 12$	B_{10}	$\left. \begin{array}{l} 46692 \\ 46705 \end{array} \right\} 13$	C_{10}	$\left. \begin{array}{l} 47260 \\ 47277 \end{array} \right\} 17$	$C_{10} - B_{10} = 572$
A_{13}	$\left. \begin{array}{l} 47570 \\ 47582 \end{array} \right\} 12$					

siderable intensity is also in disagreement with the selection rules of Herzberg and Teller.

In order to remove most of the above difficulties, an alternative assignment has to be considered. This assignment, though quite peculiar, may be suitable for a forbidden transition with which we are probably dealing, judging from its low intensity as compared with those in the far ultraviolet. Let us assume $\nu_4' = 580 \text{ cm}^{-1}$ and $2\nu_5' = 1050 \text{ cm}^{-1}$. Thus the bands in the progressions, *A*, *B*, and *C* are considered as arising from transitions from the vibrationless level in the ground state to levels in the excited state with $\nu_4' = 0, \nu_5' = 1, 3, 5 \dots$; $\nu_4' = 1, \nu_5' = 0, 2, 4 \dots$; and $\nu_4' = 2, \nu_5' = 0, 2, 4 \dots$ respectively. The bands *a*'s, *b*'s and c_{even} 's are on the red side of the corresponding *A*, *B*, and *C* bands by a distance of ~ 1240 which is approximately $2\nu_5''$ (see Table III). The c_{even} bands may as well as considered as being separated from the *A* bands by $1\nu_5''$

(thus $A_3 - c_2 = 601$; $A_5 - c_4 = 602.3$; $A_7 - c_6 = 599.4$; $A_9 - c_8 = 597.2$). However, the former interpretation is preferred on account of its unique validity for all of the *a*, *b*, c_{even} bands.

It will be seen from the above discussion that most of the prominent progressions may be fitted into the last scheme of analysis. The only difficulty which confronts this assignment is, however, its peculiar selection rules which do not quite agree with those of Herzberg and Teller and are not quite consistent among themselves. Despite this fact, if these selection rules be empirically followed, bands due to transitions from $\nu_5'' = 1$ to $\nu_5' = 0, 2, 4 \dots$ (for *A* group of bands) or to $\nu_5' = 1, 3, 5 \dots$ (for *B* and *C* groups) should also be expected to appear in the spectrum. This is just the case with the bands, $c_1, c_3, c_5 \dots$. This may be shown as follows:

The frequencies of the bands, $C_0, C_2, C_4 \dots$ may be approximately represented by the follow-

TABLE II.—Continued.

<i>a</i>	<i>b</i>	c_{even}	c_{odd}
<i>a</i> ₁	<i>b</i> ₀	<i>c</i> ₀	<i>c</i> ₁ 42129 } 42143 } 14
<i>a</i> ₃ 41394 } 41406 } 12	<i>b</i> ₂ 41457 } 42476 } 1032 42489 } 13	<i>c</i> ₂ 42029 } 42045 } 16	<i>c</i> ₃ 43169 } 43184 } 15
<i>a</i> ₅ 42421 } 42432 } 11	<i>b</i> ₄ 42476 } 42489 } 13	<i>c</i> ₄ 43059 } 43075 } 16	<i>c</i> ₅ 44193 } 44208 } 15
<i>a</i> ₇ 43430 } 43442 } 12	<i>b</i> ₆ 43490 } 43505 } 15	<i>c</i> ₆ 44073 } 44087 } 14	<i>c</i> ₇ 45194 } 45207 } 13
<i>a</i> ₉ 44416 } 44428 } 12	<i>b</i> ₈ 44480 } 44497 } 17	<i>c</i> ₈ 45060 } 45075 } 15	<i>c</i> ₉ 46183(?)
	<i>b</i> ₁₀ 45458 } 45474 } 16	<i>c</i> ₁₀ 46046(?)	
	<i>b</i> ₁₂ 46449 } 46462 } 13		

TABLE III.

$A_1 - a_1 = \text{---}$	$B_0 - b_0 = \text{---}$	$C_0 - c_0 = \text{---}$	$C_1 - c_1 = 612$
$A_3 - a_3 = 1240$	$B_2 - b_2 = 1241$	$C_2 - c_2 = 1230$	$C_3 - c_3 = 610$
$A_5 - a_5 = 1245$	$B_4 - b_4 = 1244$	$C_4 - c_4 = 1232$	$C_5 - c_5 = 606$
$A_7 - a_7 = 1245$	$B_6 - b_6 = 1244$	$C_6 - c_6 = 1233$	$C_7 - c_7 = 607$
$A_9 - a_9 = 1244$	$B_8 - b_8 = 1244$	$C_8 - c_8 = 1232$	$C_9 - c_9 = 612$
	$B_{10} - b_{10} = 1231$	$C_{10} - c_{10} = 1231$	

ing formula if the interaction coefficient between v_4' and v_5' is neglected:

$$\nu = 42227.51 + 529.56v_5' - 2.450v_5'^2, v_5' = 0, 2, 4 \dots$$

The term values of the levels, $C_1, C_3, C_5 \dots$ can be obtained by letting $v_5' = 1, 3, 5 \dots$. In Table IV are given the calculated term values and the observed frequencies while in the last column of Table III, the calculated differences $C_1 - c_1, C_3 - c_3, C_5 - c_5 \dots$ which, as will be seen, agree well with the ν_5'' found from infra-red and Raman spectrum measurements.

The ground state of acetylene has been identified as $^1\Sigma$. In the far ultraviolet systems studied by Price, the electronic transitions have been determined to be of $^1\Sigma \leftarrow ^1\Sigma$ and $^1\Pi \leftarrow ^1\Sigma$. From a study of the rotational structure of the bands C_2 (designated by Jonesco as a_1), Jonesco^{1d} has suggested a $^1\Sigma \leftarrow ^1\Sigma$ transition for the near ultraviolet system. On account of the interruption of

our research plan, we are not able to judge the correctness of Jonesco's interpretation. However, the numerous mistakes and typographical errors in this author's article make his experimental results doubtful. For example, from the data given in his equation $\nu = 44292.20 \pm 2.236J - 0.08J^2$, we cannot obtain his values of moments of inertia, $I'' = 23.89 \times 10^{-40}$ and $I' = 24.21 \times 10^{-40}$, but $I'' = 23.92 \times 10^{-40}$ and $I' = 25.66 \times 10^{-40}$ instead. We cannot understand why the author's measurements of the band heads should be so different from ours which are in satisfactory agreement with those of Göpfert and Kistiakowsky. This discrepancy may be the reason why our results cannot be represented by his simple formula $\nu = \nu_0 + 1034.6v' - v'^2$, where, again, the coefficient of v'^2 has been dropped, probably through a misprint. Thus whether the transition involved in this system is $^1\Sigma \leftarrow ^1\Sigma$ is still uncertain. From the low intensity of the system and the small vibrational frequencies we are inclined to consider that it is probably a forbidden transition.

It is to be noted that the analysis suggested here is not claimed to be the uniquely correct one. However, we feel that our interpretation may not be far from the truth and that the program we suggested would certainly point to the way for the complete solution of the problem.

In conclusion, the authors of this paper want to express their sincere thanks to Professor Richard M. Badger for his kindness in reading the manuscript before publication.

TABLE IV.

		ν calc.	ν obs.
C_0	C_1	42227.5	42226.6
		42754.6	
C_2	C_3	43276.8	43274.8
		43794.1	
C_4	C_5	44306.6	44307.2
		44814.1	
C_6	C_7	45316.7	45319.6
		45814.4	
C_8	C_9	46307.2	46307.4
		46795.1	
C_{10}		47278.1	47277.3