

The Absorption Spectrum of Diacetylene in the Near Ultraviolet. II

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would be to consider the effect of ionic concentration. Unfortunately the data in Table IV do not give a unique answer; but, considering the difficulties in making absolute measurements in this region of the spectrum and the possibility of accumulative errors in calculating, the data in general justify the assumption that the properties of the ions and water molecules are additive.

7. The validity of Stokes' law of friction

Calculating the motion of ions in the electrolytes due to the intensity of radiation of the infrared frequencies we used shows that the displacement of the ions is small compared with 10^{-8} cm. Therefore it is not altogether justified to apply Stokes' law of friction, which was derived for macroscopic processes, to the microscopic phenomenon we investigated.

We introduced Stokes' law as a means of determining the ion radii and possibly it is not surprising that our values are somewhat too small. However, it is to be observed that Stokes' law at least gives the right order of magnitude for the ion radii; or stated otherwise, the calculated frictional forces acting on the ions are in fair agreement with Stokes' law.

The electrical conductivity of ions we obtained without taking account of their radii was greater than is observed for static fields. This might indicate that Stokes' law can be applied to both static and very high frequency fields for calculating ion radii but the effective radii depend on frequency. In view of the difficulties already mentioned in assigning a value to the absorption due only to the ions, it seems possible that we have overestimated their absorption and hence obtained in general too high values for the electrical conductivities. However, if such were the case it would mean that Stokes' law of friction can be used very well for even microscopic movements of ions in electrolytes.

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The Absorption Spectrum of Diacetylene in the Near Ultraviolet. II

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The absorption spectrum of diacetylene has been reinvestigated with an instrument of higher dispersion. The bands in the region $\lambda\lambda 2970-2650\text{\AA}$ are sharp and narrow, and very closely spaced. Two progressions with a frequency difference $\sim 690\text{ cm}^{-1}$ have been found. Those below $\lambda 2650\text{\AA}$ are very diffuse, but with a comparatively simpler gross structure. Ten progressions all with a frequency difference $\sim 2100\text{ cm}^{-1}$ have been found. Through a brief and qualitative discussion of the normal vibrations and symmetry properties of the molecule, the frequency differences $\sim 2100\text{ cm}^{-1}$ and $\sim 1900\text{ cm}^{-1}$ are respectively ascribed as the totally symmetrical $\nu'_{c\equiv c}(s)$ and unsymmetrical $\nu'_{c\equiv c}(a)$ longitudinal frequencies in the excited state. The frequency $\sim 635\text{ cm}^{-1}$ is assigned as one of the fundamental frequencies in the normal state, since bands with this frequency difference were relatively intensified at higher temperatures.

IN a recent communication¹ (which will hereafter be designated as I), the results of our

¹ Sho-Chow Woo and T. C. Chu, *J. Chem. Phys.* **3**, 541 (1935).

previous investigation of the absorption spectrum of diacetylene were reported. The spectrum was then taken with a small Hilger quartz spectrograph. The gross structure of the spectrum

seemed to point to the necessity of a more detailed study with a more powerful instrument. Experiments have thus been carried out with our since then available instrument of higher dispersion.

The experimental arrangement was essentially the same as that used by Woo and Liu.² The Bausch and Lomb large quartz spectrograph has a dispersion in the region of interest about ten times greater than the Hilger E31 used in our previous experiments. Absorption tubes of 3 cm, 50 cm and 350 cm long with varying pressures up to 745 mm were used in order to develop the bands as far as possible. Besides the repeated fractionation under reduced pressure, the purity of the gas was further evidenced by being passed through an ammoniacal solution of cuprous chloride and regenerated from the precipitated copper diacetylide with dilute hydrochloric acid. The contamination of the gas with acetylene, which may not be removed by the above treatment, was excluded by the absence of the well-known spectrum of acetylene. On account of the easy polymerization of the diacetylene gas, absorption at higher temperature ($\sim 250^{\circ}\text{C}$) has been carried out only at very low pressures ($< 1\text{--}2.5$ mm) of the absorbing gas. Microphotometer tracings for a number of plates were made through the kindness of Dr. Ny Tsi-Zé and Mr. Chyan San-Chyang, to whom the authors wish to express their sincere gratitude.

The results of the present investigation agree well with those of I. However, since we used greater dispersion and wider variation of the experimental conditions in the present investigation, the spectrum was much better developed than before. Many of the previously overlapping bands have been resolved to some extent and numerous new ones have come into appearance. Table I gives the wave-lengths and wave numbers of the bands measured with their relative intensities visually estimated. Because of the strong pressure broadening of the low pressure bands and a comparatively finer adjustment of the pressure in the present investigation, the measured wave-lengths of these bands differ somewhat from those of the corresponding ones given before. The spectrum extends from $\lambda 2970\text{\AA}$

down to the ultraviolet limit of the spectrograph with increasing intensity. The complete spectrum consists of two parts of apparently very different gross structure. They constitute probably two different electronic systems which will be treated separately.

HIGH PRESSURE BANDS

The bands on the longer wave-length side began to appear only at comparatively high pressures. These bands are so sharp and narrow that they appear as individual lines, the average separation between almost any two of them being about $4\text{--}5\text{ cm}^{-1}$. The "lines" are so numerous and closely spaced that the spectrum appears apparently very open and without any prominent head. Very little regularity could be found from the gross structure. Many weak bands on the red side of some stronger ones have been found with frequency differences ~ 230 , ~ 460 , ~ 488 and $\sim 644\text{ cm}^{-1}$. These could be ascribed as due to transitions from excited vibrational levels in the ground state. However, since the "lines" are so closely spaced that any scheme of analysis could fit in with some satisfaction, it is not advisable at present to draw any conclusion about these possibilities, unless an unambiguously consistent analysis could be provided. Two progressions of stronger bands with reasonable intensity distribution can, however, be assigned with certainty. These are listed in Table II. Each pair of the bands may be considered as doublets with a separation of about 50 cm^{-1} . The complexity of the gross structure of this system of bands is possibly due to the transformation of the diacetylene molecule into the bent form in the excited state by the electronic excitation. This changes the symmetry properties of the molecule and modifies the selection rules applicable to symmetrical collinear molecules. Besides, the molecule in the excited state will then possess three moments of inertia, one of which is probably much smaller. This will also cause the spectrum to assume an open structure.

LOW PRESSURE BANDS

The bands below $\lambda 2650\text{\AA}$ become increasingly diffuse. Those below 2500\AA are specially so, so that no resolution could be effected by varying

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

TABLE I. *The diacetylene bands in the near ultraviolet.*

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I
2970.0	33660.2	00	2826.5	35369.1	00	2782.6	35927.0	0	2736.8	36528.2	0	2688.1	37190.0	1
2958.4	33792.2	00	2826.3	35371.6	00	2782.34	35930.4	2	2736.4	36533.6	0	2687.4	37199.7	1
2917.70	34263.6	1	2826.0	35375.3	00	2781.33	35943.4	0	2735.5	36545.6	0	2686.4	37213.5	1
2917.02	34271.6	1	2825.8	35377.8	00	2781.0	35947.7	00	2735.16	36550.1	1	2685.8	37221.8	0
2916.96	34272.3	0	2825.5	35381.6	00	2780.7	35951.6	00	2734.36	36560.8	2	2685.2	37230.1	1
2913.30	34315.3	0	2825.3	35384.1	00	2780.27	35957.1	3	2733.84	36567.8	1	2684.5	37239.8	0
2912.40	34325.9	0	2825.1	35386.6	00	2779.45	35967.7	0	2733.2	36576.3	1	2684.2	37244.0	0
2911.75	34332.6	1	2824.9	35389.1	00	2779.1	35972.3	00	2732.18	36590.0	1	2683.3	37256.5	0
2911.45	34337.1	1	2822.0	35425.5	00	2778.69	35977.6	00	2731.86	36594.3	1	2682.3	37270.4	0
2909.7	34357.8	0	2821.7	35429.2	00	2778.47	35980.5	00	2731.3	36601.8	0	2680.4	37296.8	3
2908.95	34366.6	0	2820.82	35440.3	1	2777.7	35990.4	00	2730.8	36608.5	0	2680.1	37301.0	1
2908.65	34370.2	0	2820.35	35446.2	1	2776.14	36010.6	0	2730.4	36613.9	1	2679.85	37304.5	3
2908.3	34374.3	0	2820.0	35450.6	0	2775.28	36021.8	2	2730.0	36619.2	1	2679.4	37310.7	1
2907.65	34382.0	1	2819.50	35456.9	3	2774.72	36029.1	0	2729.2	36629.9	2	2679.09	37315.0	3
2907.3	34386.1	0	2819.2	35460.6	00	2774.26	36035.0	0	2728.7	36636.7	1	2678.6	37321.9	2
2906.3	34398.0	0	2818.7	35466.9	0	2773.66	36042.8	0	2727.5	36652.8	1	2678.3	37326.0	2
2904.95	34413.9	0	2818.4	35470.7	0	2773.3	36047.5	00	2726.8	36662.2	1	2677.9	37331.6	2
2900.32	34468.9	1	2818.1	35474.5	0	2773.08	36050.4	3	2726.5	36666.2	2	2677.5	37365.1	2
2899.64	34477.0	0	2817.7	35479.5	0	2771.8	36067.0	00	2726.2	36670.3	1	2677.0	37372.1	2
2898.8	34487.0	0	2817.45	35482.6	1	2771.42	36071.9	2	2725.72	36676.7	3	2674.7	37376.3	2
2897.7	34500.0	0	2816.4	35495.9	0	2771.04	36076.9	0	2725.17	36684.1	3	2674.4	37380.5	2
2897.4	34503.6	0	2815.8	35503.5	00	2770.47	36084.3	1	2724.84	36688.5	0	2673.9	37387.5	3
2896.53	34514.0	1	2815.4	35508.5	0	2769.88	36092.0	1	2724.6	36690.8	0	2673.2	37397.3	2
2895.5	34526.3	0	2815.00	35513.5	2	2769.36	36098.8	2	2724.3	36695.8	1	2672.3	37409.8	2
2880.9	34701.2	0	2814.52	35519.6	1	2768.86	36103.3	0	2723.99	36700.0	0	2672.0	37414.0	2
2878.3	34732.6	0	2814.23	35523.3	2	2768.3	36112.6	00	2723.4	36708.0	0	2671.6	37419.6	4
2875.5	34766.4	0	2813.8	35528.7	00	2768.02	36116.3	1	2722.7	36717.4	1	2671.3	37423.8	4
2874.1	34783.3	0	2813.5	35532.5	00	2767.6	36121.7	00	2722.08	36725.8	3	2670.9	37429.5	4
2871.2	34818.4	0	2813.33	35534.6	3	2766.0	36142.6	00	2721.5	36733.6	1	2670.3	37437.9	2
2870.7	34824.5	0	2813.0	35538.8	0	2765.36	36151.0	1	2721.09	36739.1	3	2669.6	37447.7	3
2866.6	34874.3	0	2812.71	35542.5	2	2764.63	36160.6	0	2720.8	36743.0	1	2668.9	37457.5	1
2865.26	34890.6	2	2812.5	35545.1	0	2763.60	36174.0	0	2720.51	36746.9	2	2668.3	37465.9	1
2865.0	34893.8	0	2812.03	35551.0	1	2762.46	36188.9	0	2720.09	36752.6	2	2667.3	37480.0	3
2864.73	34897.1	0	2811.4	35559.0	0	2761.99	36195.1	1	2719.85	36755.8	1	2666.7	37488.4	3
2864.37	34901.5	0	2810.63	35568.8	4	2761.61	36200.1	0	2719.45	36761.3	2	2666.0	37498.2	3
2864.03	34905.6	2	2810.25	35573.6	0	2760.95	36208.7	0	2718.63	36772.4	1	2665.5	37505.3	2
2863.74	34909.2	0	2810.03	35576.4	1	2760.34	36217.3	0	2718.5	36774.1	0	2664.6	37519.7	1
2863.45	34912.7	3	2809.80	35579.3	5	2759.94	36222.0	0	2717.93	36781.8	4	2664.2	37523.6	1
2862.5	34924.3	0	2809.51	35582.9	1	2759.60	36226.5	0	2717.04	36793.9	3	2663.7	37530.6	1
2861.85	34932.2	4	2809.29	35585.7	3	2758.91	36235.5	2	2716.33	36803.5	2	2663.1	37539.1	1
2860.84	34944.7	1	2808.99	35589.5	2	2758.36	36242.7	3	2712.1	36809.0	0	2661.3	37564.5	1
2859.89	34956.1	1	2808.6	35594.5	00	2757.78	36250.3	2	2711.9	36863.6	0	2660.5	37575.8	2
2859.2	34964.6	0	2808.02	35602.3	0	2757.51	36252.9	3	2709.7	36893.5	1	2660.1	37581.4	2
2858.64	34971.4	1	2807.41	35609.6	4	2757.12	36259.0	1	2709.3	36899.0	1	2659.4	37591.3	3
2858.1	34978.0	0	2806.71	35618.4	0	2756.87	36262.3	1	2707.4	36924.9	2	2659.0	37597.0	3
2857.04	34991.0	2	2806.50	35621.1	3	2756.58	36266.1	4	2707.1	36929.0	1	2658.7	37601.2	3
2856.7	34995.2	00	2806.25	35624.3	5	2756.28	36270.1	1	2706.89	36931.8	3	2658.9	37626.7	1
2856.38	34999.2	0	2805.9	35628.7	00	2756.06	36273.0	1	2706.53	36936.6	1	2658.1	37638.0	2
2856.1	35002.5	00	2805.7	35631.3	00	2755.74	36277.2	5	2706.1	36942.6	3	2657.5	37646.5	2
2855.90	35005.0	2	2805.51	35633.7	3	2755.50	36280.4	0	2705.4	36952.2	1	2656.9	37655.0	2
2855.67	35007.8	2	2805.29	35635.9	2	2755.27	36283.4	1	2704.97	36958.0	2	2656.4	37660.9	4
2855.2	35013.6	00	2805.02	35639.3	3	2755.03	36286.5	0	2704.51	36964.3	3	2656.2	37664.9	4
2854.9	35017.2	0	2804.78	35642.7	2	2754.77	36291.3	0	2704.2	36968.6	2	2655.4	37677.8	4
2854.7	35019.7	0	2804.56	35647.5	1	2754.52	36296.8	0	2703.85	36973.4	7	2655.3	37684.9	3
2854.25	35025.2	2	2804.30	35653.4	0	2754.27	36303.0	0	2703.3	36980.8	1	2655.2	37693.4	3
2853.63	35032.8	1	2804.03	35659.1	1	2754.02	36311.3	1	2703.0	36985.0	0	2654.4	37695.3	3
2853.34	35036.4	4	2803.77	35664.8	1	2753.77	36314.4	1	2702.7	36989.1	2	2654.1	37697.6	4
2852.84	35042.5	2	2799.41	35711.3	3	2753.52	36317.7	3	2702.45	36992.5	2	2653.7	37700.4	4
2852.20	35050.4	0	2799.2	35714.0	0	2753.27	36322.5	4	2702.18	36996.2	4	2653.4	37704.7	4
2851.54	35058.5	3	2798.92	35717.6	3	2753.02	36327.8	1	2701.8	37001.4	0	2653.1	37709.0	4
2851.1	35063.9	0	2798.67	35720.7	1	2752.77	36333.1	0	2701.6	37004.1	0	2652.8	37713.2	5
2850.8	35067.6	0	2798.3	35725.1	1	2752.52	36338.4	0	2701.3	37008.3	2	2652.5	37717.5	2
2850.5	35071.3	00	2798.0	35728.0	1	2752.27	36343.7	0	2701.0	37012.4	2	2652.2	37721.1	7
2850.25	35074.3	3	2797.7	35730.6	0	2752.02	36349.0	0	2700.5	37019.2	2	2651.9	37727.5	4
2849.7	35081.1	0	2797.4	35733.3	0	2751.77	36354.3	1	2700.2	37023.3	2	2651.6	37731.7	2
2849.1	35088.5	0	2797.1	35736.0	1	2751.52	36359.6	1	2699.93	37027.0	3	2651.3	37736.0	2
2848.3	35098.4	0	2796.8	35738.7	0	2751.27	36364.9	1	2699.5	37032.9	2	2651.0	37751.7	1
2847.7	35105.8	0	2796.5	35741.4	1	2751.02	36370.2	1	2699.2	37039.9	1	2650.7	37757.6	2
2847.0	35114.4	0	2796.2	35744.1	2	2750.77	36375.5	0	2698.9	37046.9	2	2650.4	37761.7	1
2846.4	35121.8	0	2795.9	35746.8	3	2750.52	36380.8	0	2698.6	37053.9	2	2650.1	37767.4	2
2845.4	35134.1	0	2795.6	35749.5	4	2750.27	36386.1	0	2698.3	37060.9	2	2649.8	37773.4	2
2844.8	35141.5	0	2795.3	35752.2	5	2750.02	36391.4	0	2698.0	37068.0	2	2649.5	37779.5	2
2844.3	35147.7	0	2795.0	35754.9	6	2749.77	36396.7	1	2697.7	37075.0	2	2649.2	37785.9	2
2844.08	35150.5	1	2794.7	35757.6	7	2749.52	36402.0	2	2697.4	37082.1	2	2648.9	37792.1	1
2843.0	35163.8	00	2794.4	35760.3	8	2749.27	36407.3	3	2697.1	37089.2	3	2648.6	37798.2	1
2842.7	35167.5	0	2794.1	35763.0	9	2749.02	36412.6	4	2696.8	37096.3	4	2648.3	37804.3	1
2842.3	35172.5	0	2793.8	35765.7	10	2748.77	36417.9	5	2696.5	37103.4	5	2648.0	37810.2	2
2841.76	35179.1	2	2793.5	35768.4	11	2748.52	36423.2	6	2696.2	37110.5	6	2647.7	37816.0	2
2841.23	35185.7	0	2793.2	35771.1	12	2748.27	36428.5	7	2695.9	37				

TABLE I.—Continued.

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>
2632.6	37974.0	2	2620.6	38147.8	2	2616.3	38210.5	2	2607.9	38333.6	4	2601.7	38424.9	2
2632.0	37982.6	3	2620.3	38152.2	2	2615.8	38217.8	2	2607.6	38338.0	4	2601.3	38430.8	3
2631.8	37985.5	3	2620.0	38156.6	2	2611.5	38280.8	1	2606.9	38348.3	3	2600.9	38436.8	5
2631.5	37989.8	3	2619.5	38163.8	4	2610.9	38289.5	2	2606.3	38357.1	3	2600.1	38448.6	5
2631.2	37994.2	2	2619.2	38168.2	2	2610.6	38293.9	2	2606.1	38360.1	3	2599.7	38454.5	2
2630.7	38001.4	1	2618.9	38172.6	6	2609.9	38304.2	2	2605.7	38366.0	1	2597.5	38487.1	2
2626.5	38062.1	1	2618.5	38178.4	3	2609.2	38314.5	3	2604.5	38383.6	1	2596.8	38497.4	2
2623.6	38104.2	1	2618.0	38185.7	6	2608.9	38318.9	3	2603.3	38401.3	1	2595.7	38513.7	2
2622.2	38124.6	1	2617.5	38193.0	2	2608.5	38324.8	5	2603.1	38404.3	1	2594.7	38528.6	2
2621.5	38134.7	2	2617.2	38197.4	3	2608.2	38329.2	5	2602.7	38410.2	3	2593.3	38549.4	1

<i>M</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>D</i>	<i>M</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>D</i>	<i>M</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>D</i>	<i>M</i>	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	<i>I</i>	<i>D</i>
C	2588.3	38624	3			2460.6	40628				2377.8	42043				2257.8	44277	1	
C	2585.2	38670	1			2459.7	40643	2		MI	2376.9	42059	5	F		2256.5	44303		
C	2582.4	38712	1			2455.6	40711	1			2374.5	42101				2254.2	44348	2	G'
C	2579.2	38760	1			2451.8	40774				2365.8	42256	3	G		2252.2	44387		
C	2575.8	38811	2			2450.5	40796	1			2364.2	42285				2247.4	44482	2	H'
	2565.7	38964	1			2448.2	40834				2361.6	42331	4	H		2246.4	44502		
	2565.2	38972	2			2446.0	40871	1			2358.6	42385			C	2243.8	44553	1	
	2563.8	38993	3			2440.4	40965				2353.6	42475	3			2240.1	44627		
	2563.3	39001	3			2439.6	40978		J		2351.1	42520				2239.2	44645	1	
	2562.8	39008	3			2439.0	40988	2			2349.0	42558				2237.7	44675		
	2560.6	39042	4			2433.8	41076			MI	2346.5	42605	5	I'	C	2236.8	44693	4	I''
	2560.2	39048	5	A°	C	2433.3	41089	10			2345.8	42617				2235.8	44713		
	2559.8	39054	5			2432.3	41100				2340.6	42711	1		C	2232.6	44777	1	
	2559.4	39060	4		L	2431.3	41118	4	A		2337.0	42777			C	2214.9	45135	1	J''
	2557.8	39084	3		L	2430.8	41125	4			2332.0	42869	1		MI	2209.6	45243		
	2556.8	39100	3			2430.3	41130				2330.8	42891				2205.5	45327	6	A''
	2555.8	39115	3			2429.9	41135	5			2328.0	42942	2			2204.6	45346		
C	2555.4	39121	3			2429.9	41141				2325.6	42986				2197.9	45484	3	B''
C	2554.6	39133	2			2422.9	41260	7	B	C	2322.7	43040				2196.1	45521		
C	2554.0	39143	2			2421.8	41269				2321.3	43066	2	J'		2189.9	45650	3	C''
	2541.8	39330				2419.5	41279				2319.7	43096				2188.7	45675		
	2541.5	39335	2			2418.5	41318	1			2314.7	43189			C	2185.3	45746	3	D''
	2541.3	39338				2418.5	41335			C	2313.8	43207	9		C	2181.4	45828	2	
	2534.0	39451				2413.5	41421	1			2313.1	43219			C	2178.9	45880	3	E''
	2532.8	39470	2			2412.1	41445			L	2312.6	43229	4	A'	C	2175.1	45960	2	
	2529.1	39528	3			2408.6	41505	7	C		2312.1	43239				2162.6	46226	3	F''
	2525.0	39592	3			2408.2	41512			C	2311.9	43242	5			2160.4	46273		
	2515.7	39738	3			2407.8	41519				2311.7	43245			C	2155.3	46383	1	
	2512.5	39789	3			2404.8	41571				2304.9	43373	5	B'	C	2151.2	46471	1	G''
	2509.7	39833	3			2404.2	41581	7	D		2302.8	43411			C	2144.3	46621	1	H''
	2505.7	39897	3			2403.6	41592				2294.7	43565	5	C'	C	2138.2	46759	1	I''
	2502.9	39942	3			2395.7	41730				2292.6	43605			C	2118.1	47197	1	J''
	2498.5	40012	3			2395.0	41740	8	E		2289.3	43668	5	D'	MI	2111.1	47354		
C	2486.8	40200				2394.5	41750				2288.3	43687				2109.2	47396	3	A'''
	2485.9	40215	4			2394.1	41756				2285.1	43748				2108.8	47405		
	2485.3	40224				2393.8	41761	5		MI	2282.9	43790	6	E'		2101.3	47574	1	B'''
	2477.8	40346				2393.5	41766				2281.6	43815				2100.0	47604		
	2476.5	40367	3			2390.5	41820	2		C	2277.2	43900				2097.0	47672	1	C'''
	2471.5	40449				2389.2	41842				2276.3	43917	3			2095.1	47715		
L	2469.3	40486	5			2386.8	41884				2275.7	43929			C	2090.8	47813	1	D'''
L	2468.8	40494	6	I		2385.1	41914	1			2272.7	43987	1			2084.8	47951	1	E'''
L	2468.3	40502				2382.3	41963			C	2269.6	44047	1			2070.4	48284	1	F'''
	2467.5	40515				2380.8	41990	1			2264.7	44142	4	F'		2068.5	48329		
	2463.9	40574									2262.1	44194							
	2462.2	40602	1																

In columns *M*, broader bands are given under brackets. *C* or *MI* specifies the center or the part of maximum intensity of the band measured. *L* = "Line" or very narrow band. In columns *I* and *D* are given their estimated relative intensities and designations.

the experimental conditions such as pressure, plates and slit width. Since it will be seen later that the electronic excitation has taken place at the C≡C bond, it is probable that predissociation must have occurred at the C—C bond. This being the case, the estimated energy of dissociation amounts approximately to 107 kcal./mole.

The gross structure of the low pressure system is comparatively simple and some regularities of the vibrational structure may be observed. The strongest band *A* at 2430 Å has been resolved to some extent at pressures less than 1 mm with an absorbing path of 50 cm. But further improve-

ment could not be made with further adjustment of the experimental conditions. In Table III are given the progressions found in the low pressure system of bands including those previously reported. All of these progressions have a frequency difference of about 2100 cm⁻¹. The frequency differences between bands of different progressions should usually be assigned as fundamentals or combinations in the excited state. But they are too many here to be all so assigned. Moreover, these differences are far from being approximate constants and vary rather irregularly. Complications might have come in from two possibilities: (1) the resonance between

TABLE II. Progressions in C_4H_2 "high pressure systems."

$\nu(\text{cm}^{-1})$	I	$\delta\nu$	$\Delta\nu$
24932	4	45	692
35579	5		
35624	5		
36277	5	46	698
36323	4		699
36973	7	54	696
37027	3		704
37668	4	53	695
37721	7		694
38360	3	50	692
38410	3		689
39054	5	46	694
39100	3		690

nearly coincident levels of fundamentals and harmonics of the different vibrations in the excited state and (2) the interaction between the excited electronic state and the deformation oscillations, if the former be degenerate. Nevertheless, certain plausible assignments may still be made from what we have known about the fundamental frequencies of the molecule in the ground state and the selection rules governing the transitions in an electronic system of a symmetrical collinear molecule.

The fundamental frequencies of the diacetylene molecule in the ground state have been discussed by Timm and Mecke.³ The assignment of these authors has recently been examined by Wu and Shen⁴ with a detailed calculation of the force constants and a critical discussion of the selection rules for infrared and Raman spectra. It is true

³ B. Timm and R. Mecke, *Zeits. f. Physik* **94**, 1 (1935).

⁴ Ta-You Wu and S. T. Shen, *Chinese J. Phys.* **2**, 128 (1936).

TABLE III. Progressions in C_4H_2 "low pressure system."

$\nu(\text{cm}^{-1})$	$\Delta\nu$	$\nu(\text{cm}^{-1})$	$\Delta\nu$	$\nu(\text{cm}^{-1})$	$\Delta\nu$
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p><i>A</i></p> <p>A° 39048 } A 41135 } A' 43242 } A'' 45327 } A''' 47396 }</p> </div> <div style="width: 30%;"> <p><i>B</i></p> <p>B 41279 } B' 43411 } B'' 45521 } B''' 47604 }</p> </div> <div style="width: 30%;"> <p><i>C</i></p> <p>C 41519 } C' 43605 } C'' 45675 } C''' 47715 }</p> </div> </div>					
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p><i>D</i></p> <p>D 41592 } D' 43687 } D'' 45746 } D''' 47813 }</p> </div> <div style="width: 30%;"> <p><i>E</i></p> <p>E 41761 } E' 43815 } E'' 45880 } E''' 47951 }</p> </div> <div style="width: 30%;"> <p><i>F</i></p> <p>F 42101 } F' 44194 } F'' 46273 } F''' 48329 }</p> </div> </div>					
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p><i>G</i></p> <p>G 42285 } G' 44387 } G'' 46471 }</p> </div> <div style="width: 30%;"> <p><i>H</i></p> <p>H 42385 } H' 44502 } H'' 46621 }</p> </div> <div style="width: 30%;"> <p><i>I</i></p> <p>I 40502 } I' 42605 } I'' 44693 } I''' 46759 }</p> </div> </div>					
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p><i>J</i></p> <p>J 40978 } J' 43066 } J'' 45135 } J''' 47197 }</p> </div> <div style="width: 30%;"> <p>2087 2107 2085 2069 2095 2059 2067 2102 2084</p> </div> <div style="width: 30%;"> <p>2132 2110 2083 2054 2065 2071 2117 2119</p> </div> <div style="width: 30%;"> <p>2086 2070 2040 2093 2079 2056 2103 2088 2066</p> </div> </div>					
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p>2088 2069 2062</p> </div> <div style="width: 30%;"> <p>$A - I = 633$ $A' - I' = 637$ $A'' - I'' = 634$ $A''' - I''' = 637$</p> </div> </div>					

TABLE IV. Deformation force constants.

MOLECULE	$\nu(\text{CM}^{-1})$	$k_1 \left(\frac{\text{DYNE CM}}{\text{RADIAN}} \right)$	$k_2 \left(\frac{\text{DYNE CM}}{\text{RADIAN}} \right)$	REFERENCE
H-C \equiv N	δ 709	2.41×10^{-12}	—	6
H-C \equiv C-H	$\delta(a)$ 730	2.44×10^{-12}	0.92×10^{-12}	5
	$\delta(s)$ 605			
N \equiv C-C \equiv N	$\delta(a)$ 230	2.93×10^{-12}	-0.24×10^{-12}	6
	$\delta(s)$ 510			
H-C \equiv C-C \equiv C-H	$\delta_C(a)$ 231	2.6×10^{-12} (H-C and C \equiv C)	0.14×10^{-12}	4
	$\delta_C(s)$ 488			
	$\delta_{CH}(a)$ 730	3.6×10^{-12} (C-C and C \equiv C)	0.15×10^{-12}	
	$\delta_{CH}(s)$ 720			

k_1 = force constant of bending between the neighboring single and triple bonds, *vis.*, $o-o \equiv o$.

k_2 = force constant of interaction between the bendings of two single bonds with a common triple bond, *vis.*, $o-o \equiv o-o$, or of two triple bonds with a common single bond, *vis.*, $o \equiv o-o \equiv o$.

that the assignment of the deformation frequencies of Timm and Mecke is confronted with serious difficulties from the selection rules. It may, however, be interesting to note that the force constants calculated from the values of these authors seem to be comparable with those of other similar molecules (Table IV).⁷ We agree with the suggestion of Wu and Shen that a re-examination of the Raman spectrum of diacetylene is necessary to settle this problem. But in the present analysis we are essentially concerned with the longitudinal vibrations for which there seems to be not much difficulty.⁸ Regarding the symmetry properties of the diacetylene molecule and the selection rules governing the transitions between the different

vibrations, what has been discussed in the spectrum of cyanogen² may be essentially applicable here. Thus the frequency difference $\sim 2100 \text{ cm}^{-1}$ must be the frequency $\nu'_{c \equiv o}(s)$ of the totally symmetrical vibration in the excited state and the electronic excitation has probably taken place mainly at C \equiv C bond. The difference $\sim 1900 \text{ cm}^{-1}$ ($J-A=1931, 1893, 1870 \text{ cm}^{-1}$) which only weakly appeared in the spectrum, is probably the frequency of the vibration $\nu'_{c \equiv o}(a)$. The differences between the *A* and *B*, and the *C* and *D* bands are too small to be ascribed to fundamental frequencies. Whether they may be described as doublets given rise through resonance between nearly coincident levels of fundamentals and harmonics of the different vibrations is uncertain. The only bands which showed appreciably relative intensification at higher temperatures are the *I* bands. Thus they are considered as due to transitions from the excited vibrational levels with $\nu \sim 640 \text{ cm}^{-1}$ ($633, 637, 634, 637 \text{ cm}^{-1}$) in the ground state.

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

⁵ W. F. Colby, Phys. Rev. **47**, 388 (1935).

⁶ Unpublished results.

⁷ It may be admitted that the force constant K_2 plays also a considerable part in affecting the deformation frequencies and the values here obtained vary considerably for different molecules. However, the values of K_1 , which is of primary importance here, are of the same order of magnitude for these molecules.

⁸ The value 644 cm^{-1} seems to be too small for the frequency $\nu'_{c \equiv o}(s)$ (see reference 4). For the corresponding force constant $k_1(c-c)$ of cyanogen, see reference 2, Table V.