

Infrared Spectrum of Acetylene¹

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The spectrum of acetylene has been observed and measured under high resolution from 1,900 to 8,500 cm^{-1} . Many of the bands observed have been analyzed and precise values obtained for ν_0 and $B' - B''$. A good value of B_0 (1.17684 ± 0.00016) has been obtained by combining the results of the present work with previous data in the photographic infrared. The vibrational-energy problem is discussed.

1. Introduction

The photographic region of the infrared spectrum of acetylene was studied many years ago [1].² More recently, high-resolution work has been reported [2] for the region below 4,000 cm^{-1} , and in a short note [3] the band centers for many of the bands from 4,000 to 8,000 cm^{-1} have been reported. Many of the latter band centers were reported only to the nearest wave number, and no attempt was made to evaluate the constants in the vibrational-energy expression. Present spectrometers and measuring techniques make it possible to get better data and hence more precise band centers. The present investigation was undertaken in order to obtain these more precise band centers and to attempt to evaluate the constants in the expression for the vibrational energy as a function of the vibrational quantum numbers.

2. Experimental Procedure

The bands in the spectral region from 1,900 to 8,500 cm^{-1} were observed by the use of two spectrometers [4], one having a grating with 15,000 lines/in. and a lead sulfide cell as the detector, and the other instrument having a grating with 7,500 lines/in. and a cooled lead-telluride cell as the detector. In the region from 4,000 to 8,500 cm^{-1} a resolution of about 0.1 cm^{-1} was obtained, and from 1,900 to 3,500 cm^{-1} the resolution was about 0.2 cm^{-1} when a cell of 1 m was used. With a 10-m multiple-reflection cell the resolution was reduced by a factor of two. This resolution was ample to bring out all the main lines of the band and in some cases to resolve the lines of overlapping hot bands.

Examples of the spectra obtained are shown in figures 1 and 2. The figures are photographs of the recorder paper, which were obtained when the instrument was scanned over the band. The wavelengths of the lines were determined by making measurements from the superimposed fringe system and standard atomic lines. These are not shown in the figures, but details of the method of measurement have been given in a previous paper [5].

Figure 1 represents the absorption spectra in the region from 4,600 to 4,770 cm^{-1} of acetylene at a pressure of 1 atm and with a 10-m cell. Two bands

have been analyzed from the rotational structure, and the assignments of the lines are shown below the spectra. The centers of the two bands occur at 4673.38 and 4722.72 cm^{-1} . Figure 2 represents the absorption spectra in the region from 5,750 to 6,000 cm^{-1} . Although the cell length was 10 m and the pressure was 1 atm, the bands are weak. There are several bands in this region, but the rotational structure was only of sufficient intensity to allow an assignment of the rotational lines for two bands. The centers of these two bands occur at 5,850.75 and 5,944.40 cm^{-1} .

3. Analysis

The bands were analyzed by the method of combinations and differences. Values of ν_0 and $B' - B''$ for each band were obtained from the expression,

$$R(J+1) + P(J) = 2\nu_0 + 2(B' - B'')J^2.$$

As many combinations as possible were set up for each band, and the resulting equations were solved by the method of least squares. The results of these calculations for the various bands are given in table 1.

Values for B_0 and D_0 were obtained in the same manner from the expression,

$$\Delta F_2 = R(J-1) - P(J+1) = 4B(J + \frac{1}{2}) - 8D(J + \frac{1}{2})^3.$$

The value of B_0 obtained in this manner varied somewhat from band to band because of the strong overlapping of bands in all spectral regions. In order to minimize this effect, the ΔF_2 values for the six best bands were averaged, omitting all differences that depended on absorption peaks that were obviously the blend of two or more transitions. The value of B_0 determined in this manner agrees very well with the value obtained from photographic infrared bands [6]. Because the earlier workers reduced their data graphically, their results were reworked in the manner described above. The uncertainty in the B_0 value was further reduced by averaging the ΔF_2 values of Herzberg and Spinks with the values obtained in this work. These three values are compared in table 2. The uncertainties given are one standard deviation. Because of the large uncertainties and the fact that the values of $J > 25$ were not used in the ground-state calculations, very little significance can be attached to the values of D_0 given in table 2.

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² Figures in brackets indicate the literature references at the end of this paper.

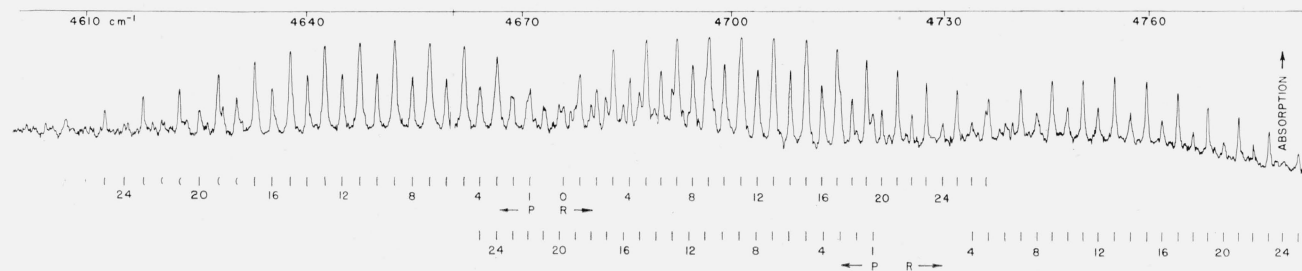


FIGURE 1. *Acetylene absorption bands at 4673.38 and 4722.72 cm⁻¹.*

The cell length was 10 m and the gas pressure was 1 atm.

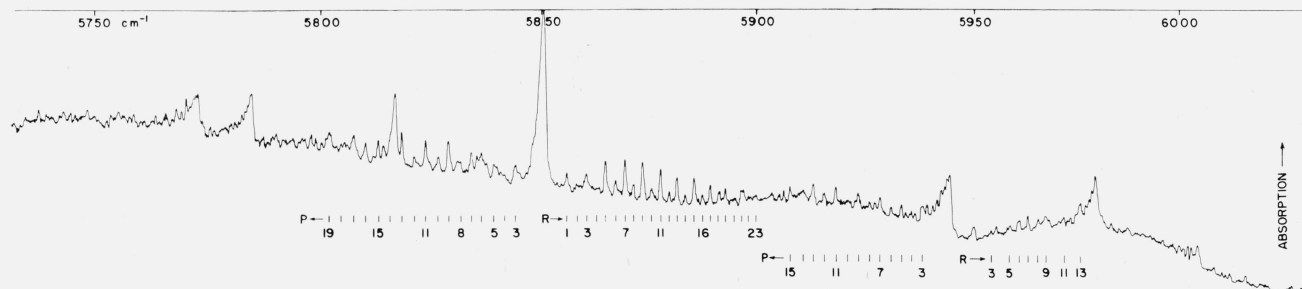


FIGURE 2. *Absorption spectrum of acetylene in the region from 5,750 to 6,000 cm⁻¹.*

The two bands with the most intense rotational structures occur at 5850.75 and 5944.40 cm⁻¹. The cell length was 10 m and the gas pressure was 1 atm.

TABLE 1. *Assignments of the observed bands of acetylene*

Observed	Calculated	D, D, Resonance	Excited					Lower					<i>B'</i> - <i>B''</i>
			<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	<i>v</i> ₄ ^{<i>l</i>}	<i>v</i> ₅ ^{<i>l</i>}	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	<i>v</i> ₄ ^{<i>l</i>}	<i>v</i> ₅ ^{<i>l</i>}	
<i>cm</i> ⁻¹	<i>cm</i> ⁻¹												
	611.58					1 ¹							
	729.25						1 ¹						
1328.18 ^a	1328.18					1 ¹	1 ¹						-0.00090
1940.11	1940.07					2 ⁰	1 ¹						-, .00171
1973.8 ^b	1973.8												-, .00892
2169.24	2169.15			1			3 ¹						-, .01134
2560.51	2560.52					3 ¹	1 ¹						-, .00303
													-, .00003
2644.58	2644.45		1								1 ¹		-, .00329
2670.35	2670.27			1						1 ¹			-, .00658
2683.38	2683.42			1		1 ¹	1 ¹						-, .00529
2690.78	2690.97			1			2 ⁰						-, .00534
2702.20	2702.20			1			1 ¹						-, .00243
													-, .00194
3281.85	3281.93				1								-, .0015
3294.96	3294.98			1		1 ¹	1 ¹						-, .00704
3373.7 ^b	3373.7		1										-, .00372
4062.00	4062.11		1			1 ¹	1 ¹			1 ¹			-, .00154
4068.57	4069.93		1				2 ⁰				1 ¹		
4080.3	4079.89		1				2 ²						
4091.20	4091.20		1				1 ¹						
4138.82	4138.81			1			3 ¹						
4673.68	4673.67		1			1 ¹	1 ¹						-, .00372
4722.72	4719.45				1		2 ⁰						-, .00154
5772.99	5783.23	5771.61		2							1 ¹		Q only.
5850.75	5850.64			1	1	1 ¹							-, .01286
5944.40	5945.06		1		1					1 ¹			Q only.
5979.37	5969.99	5981.61	2								1 ¹		Q only.
6530.00	6531.10		1	1	1 ¹					1 ¹			-, .01590
6556.62	6556.62		1		1								-, .01286
6623.33	6623.53		1	1		1 ¹	1 ¹						-, .00924
7141.22	7142.66		1		1	1 ¹							-, .01072
7217.6	7230.27	7217.95			2		1 ¹						Q only.
7416.51	7404.99	7417.31	2				1 ¹						-, .01396
8512.09	8512.10		1	1	1								-, .01872

^a From reference [2].

^b Raman lines from reference [1].

TABLE 2. Values of B_0 and D_0 for acetylene

	B_0	D_0
	cm^{-1}	
This work.....	1.17665 ± 0.00024	$2.12 \pm 1.1 \times 10^{-6}$
Herzberg and Spinks.....	1.17684 ± 0.00021	1.75 ± 1.1
Combination of both.....	1.17684 ± 0.00016	2.19 ± 0.85

In addition to the bands for which P and R structure was observed, several Q branches were observed without P and R structure. These bands are appropriately marked in table 1. For all perpendicular-type bands, the $B'-B''$ values refer only to the effective inertial constant from the P and R branches. No Q branches were sufficiently resolved to enable the other effective inertial constant to be determined for the state involved.

4. Vibrational Energy

It is customary to express the vibrational energy in terms of the vibrational quantum numbers as

$$E_{v'} - E_0 = \sum_i \omega_i^0 + \sum_{ik} X_{ik} V_i V_k + \sum_i \sum_k g_{ik} l_i l_k.$$

For the acetylene molecule, if there are no vibrational interactions, there are 22 constants to be evaluated. Herzberg [1] has suggested that, as in the water-vapor spectrum, states described by the quantum numbers $(v_1, v_2, v_3, v_4^l, v_5^l)$ ($v_1+2, v_2, v_3-2, v_4^l, v_5^l$) enter into a second-order Fermi resonance. This has been investigated [7] and shown to exist. Such a resonance introduces another constant, γ , to be evaluated.

Attempts were made to evaluate these 23 constants from the observed band centers. No set of 23 constants was found that would predict all the observed bands precisely. This is not surprising because in the case of water vapor [8] it was found that one constant, γ , would not predict the correct splitting for all the resonating states. Likewise it seems likely that states characterized by the quantum numbers, $[v_1, v_2, v_3, v_4^l, v_5^l]$ and $[v_1, v_2, v_3, (v_4+2)^l, (v_5+2)^l]$, also interact resonance-wise. All these complications make it quite difficult to get a unique set of constants for the energy expression. The set given in table 3 predicts the bands below $8,500 \text{ cm}^{-1}$ as shown in table 1. No claim is made that these are unique, for several other sets are nearly as good. These constants do not predict the photographic bands nearly as well. The values of ω_4^0 , X_{44} , g_{44}

do not agree well with those found in the ultraviolet [9].

From the several difference bands observed, values of ν_4^l and ν_5^l have been obtained. The frequency for $\nu_4^l + \nu_5^l$ used to evaluate these constants was obtained from reference [2] and the Raman frequencies from reference [1].

Because of the serious problem of overlapping bands, one cannot place too much faith in the $B'-B''$ values obtained from the analyses. As a result, no α values are given.

TABLE 3. Vibrational constants of acetylene (cm^{-1})

$\omega_1^0 = 3397.78$	$X_{11} = -24.08$	$X_{12} = -16.94$	$X_{13} = -99.01$	$X_{14} = -16.46$
$\omega_2^0 = 1981.72$	$X_{22} = -7.92$	$X_{23} = -1.38$	$X_{24} = -6.15$	$X_{25} = -0.85$
$\omega_3^0 = 3307.62$	$X_{33} = -25.69$	$X_{34} = -9.06$	$X_{35} = -5.73$	$X_{15} = -11.75$
$\omega_4^0 = 607.28$	$X_{44} = 5.38$	$X_{45} = -12.65$	$g_{44} = 1.10$	$g_{55} = 2.49$
$\omega_5^0 = 729.03$	$X_{55} = -2.27$	$\gamma = 49$		

Several regions could not be investigated because of atmospheric absorption. Several important bands could thus not be observed. It is felt that when these bands are available some improvement can be made in the vibrational constants.

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5. References

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