

## The InfraRed Spectrum of Acetylene

E. E. Bell and H. H. Nielsen

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$$\alpha = \alpha_0 - \frac{(M_2 - M_1)}{\bar{M}} \left[ \left( \frac{2a}{\bar{V}^2} - \frac{RT\bar{V}}{(\bar{V} - b)^2} \right) \times \left[ \frac{1}{p - \frac{a}{\bar{V}^2} + \frac{2ab}{\bar{V}^3}} \right] + 1 + \frac{2a}{RT\bar{V}} \right] \quad (16)$$

Now the experimental data in the critical region are for the system ethane-xenon. The van der Waals' constants for these gases do not differ greatly. To the first approximation we can consider these as a mixture of isotopes of molecular weights 133 and 30, using  $\alpha_0$  evaluated from kinetic theory.

Figure 1 is a plot of  $T_r$  versus  $\rho_r$  with lines of constant  $\alpha$ . Figure 2 shows the results of experiment. It can be seen that the calculated curves reproduce all the essential features of the experiment. While the agreement is entirely qualitative nevertheless it seems very

remarkable that the double sign change in  $\alpha$  with increasing density could be predicted using no empirical constants.

It is of particular interest to note that this calculation has been made for a mixture of isotopes. In the original papers<sup>7,8</sup> the phenomenon was attributed to a selective clustering of the ethane molecules. No such selective clustering would be conceivable among isotopes, so that this seems rather to be a phenomenon of molecular interaction explainable directly from kinetic theory. It is hoped that the consideration of ternary collisions now being undertaken by Kirkwood and Hirschfelder will permit the prediction of the pressure coefficient of thermal diffusion.

It is planned to treat thermal diffusion in nonisotopic mixtures, diffusion and thermal conductivity in dense gases, and transport properties of van der Waals' liquids in later papers.

## The Infra-Red Spectrum of Acetylene\*

E. E. BELL AND H. H. NIELSEN  
Ohio State University, Columbus, Ohio  
(Received June 29, 1950)

New measurements of the infra-red absorption spectrum of acetylene between 16 and  $2.5\mu$  have established many new bands. A cooling experiment has demonstrated that the central line of the parallel band  $\nu_4^1 + \nu_5^1$  ( $1328.18 \text{ cm}^{-1}$ ) belongs to a difference band,  $2\nu_4^0 + \nu_5^1 - \nu_4^1$  ( $1328.46 \text{ cm}^{-1}$ ). Resolution sufficient to distinguish the center of the fundamental  $\nu_3$  ( $3282.5 \text{ cm}^{-1}$ ) from the combination band  $\nu_2 + \nu_4^1 + \nu_5^1$  ( $3295.56 \text{ cm}^{-1}$ ) has been obtained. An interesting  $\Pi_u - \Pi_g$ -band, identified as  $\nu_1 + \nu_3^1 - \nu_4^1$ , is shown. Frequencies of the infra-red inactive fundamentals are derived and many anharmonic coefficients are evaluated. Diagrams of the absorption regions and tables of the line frequencies are included.

ACETYLENE is known to be a linear, symmetrical molecule. Because of its simplicity and small moment of inertia, a large amount of experimental and theoretical work has been done with respect to its infra-red absorption spectrum. Expressions for the vibration-rotational energy levels have been obtained through second-order contributions by Shaffer and Nielsen.<sup>1</sup> Assignments of bands and numerical evaluations of the anharmonicity constants have been made by many workers.<sup>2</sup> Experimentally, the photographic infra-red bands have been well measured, and the Raman spectrum of the liquid has been obtained. The bolometric infra-red bands of acetylene have been measured with high dispersion by Levin and Meyer.<sup>3</sup>

\* A part of the material of this paper was presented at the Symposium on Molecular Structure and Spectroscopy at Ohio State University, in Columbus, Ohio (June, 1947).

<sup>1</sup> W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. **9**, 847 (1941).

<sup>2</sup> Note the many references given by G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

<sup>3</sup> Levin and Meyer, J. Opt. Soc. Am. **16**, 137 (1928).

This early work of Levin and Meyer left several questions unanswered. A parallel-type band,  $\nu_4^1 + \nu_5^1$ , seemed to have an absorption line at the center, suggestive of a Q branch.<sup>4</sup> This line was also observed later by Nielsen and Williams.<sup>5</sup> The work of Levin and Meyer did not allow an accurate determination of the center of the  $\nu_3$ -fundamental band because of the interference of an overlapping band.

A more extensive measurement of this region of the

<sup>4</sup> In agreement with G. Herzberg (see reference 2) the vibrational frequencies will be designated as follows:

$\nu_1$ , species  $\Sigma_g^+$ , about  $3373 \text{ cm}^{-1}$ , parallel vibration in which the C atoms are approaching while the H atoms are separating.

$\nu_2$ , species  $\Sigma_g^+$ , about  $1974 \text{ cm}^{-1}$ , parallel vibration in which the CH groups vibrate against each other.

$\nu_3$ , species  $\Sigma_u^+$ , about  $3282 \text{ cm}^{-1}$ , parallel vibration in which the C atoms are moving together against the H atoms.

$\nu_4$ , species  $\Pi_g$ , about  $613 \text{ cm}^{-1}$ , perpendicular vibration in which the C atoms move opposing each other and H atoms move against each other.

$\nu_5$ , species  $\Pi_u$ , about  $731 \text{ cm}^{-1}$ , perpendicular vibration in which the C atoms move together against the H atoms.

<sup>5</sup> A. H. Nielsen and D. Williams, Phys. Rev. **59**, 911A (1941).

infra-red spectrum of acetylene has now been made and the results will be given in this paper.

The notation used to designate the anharmonic coefficients is that used by Shaffer and Nielsen. The vibrational energy of acetylene is given by

$$G_V = G_0 + \sum_{n=1}^5 \omega_n (V_n + g_n/2) + \sum_{n=1}^5 x_{nn} (V_n + g_n/2)^2 \\ + \sum_{n=1}^5 \sum_{n' > n=1}^5 x_{nn'} (V_n + g_n/2) (V_{n'} + g_{n'}/2) \\ + \sum_{k=4}^5 X_{kk} (l_k^2 - 1),$$

where  $V_n$  is the vibrational quantum number associated with the normal frequency  $\omega_n$ , and  $g_n$  is the degree of degeneracy of the mode  $\omega_n$ .  $g_1 = g_2 = g_3 = 1$  and  $g_4 = g_5 = 2$ .  $l_k$  is the quantum number associated with the internal angular momentum arising from the twofold degenerate vibrations and may assume the values  $\pm V_k$ ,  $\pm(V_k - 2)$ ,  $\dots \pm 1$  or 0. The values of  $G_0$ ,  $x_{nn}$ ,  $x_{nn'}$ , and  $X_{kk}$  are given in terms of the generalized force constants in the paper by Shaffer and Nielsen.

The rotational energy of acetylene is

$$F_R = B_V [J(J+1) - l^2], \quad l = l_4 + l_5$$

where  $J$  is the quantum number associated with the total angular momentum and may have integral values such that  $J \geq |l_4 + l_5|$  and the centrifugal stretching term is omitted because it was not of significance in this molecule. It is to be noted that the band frequencies are  $G_V' - G_V''$  and these do not correspond to the positions

of the  $Q$  branches (or band centers, where  $\Delta J = 0$ ) unless  $\Delta l = 0$ .

### EXPERIMENTAL

The absorption bands were measured with an automatic recording vacuum grating instrument.<sup>6</sup> The gratings were calibrated by measuring several orders of two strong mercury arc emission lines near  $1\mu$ . The measured wave-lengths of the absorption lines in this paper are the wave-lengths in vacuum obtained directly without correction, by making all band measurements with the spectrograph evacuated. The records of the bands were obtained on a Speedomax recorder and were marked at every 10 min. of arc of the grating position (sometimes every 5 min.). The frequency, in  $\text{cm}^{-1}$ , at these calibration points was computed. The frequencies of the lines were obtained by interpolation between the calibration points. Repeated measurements extending over several months time indicated that the measurements were consistent within one-tenth  $\text{cm}^{-1}$  for the lines tested. Measurements to one-hundredth of a wave number were used with the combination principles to obtain band centers, etc., and some frequencies will be given to this accuracy, even though all frequencies are of questionable absolute accuracy even in the fifth significant figure.

The acetylene used in these measurements was made by the action of water on calcium carbide. No special precautions were made to assure the purity of the acetylene used. The gas was passed through drying towers filled with calcium chloride before it was admitted to the absorption cell. The absorption cells each contained a small boat of anhydrous phosphorus pentoxide to remove the last traces of water vapor. By preevacuation

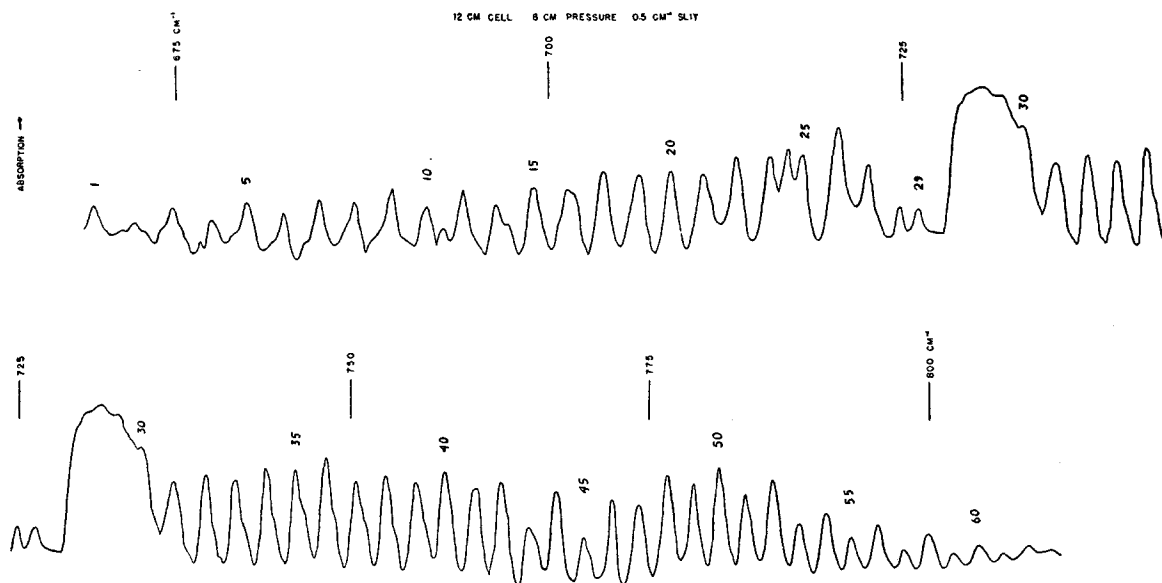


FIG. 1. The  $\nu_5^1$ -band of acetylene as measured with the 1800 lines per inch grating. For the values of the line frequencies see Table I.

<sup>6</sup> Bell, Noble, and Nielsen, Rev. Sci. Inst. 18, 48 (1947).

TABLE I. The  $\nu_5^1$ -band frequencies, see Fig. 1.

Line No.	$\nu_5^1$	cm <sup>-1</sup>	Line No.	$\nu_5^1$	cm <sup>-1</sup>
1	<i>P</i> (25)	670.67	31	<i>R</i> (2)	736.98
2	<i>P</i> (24)	673.02	32	<i>R</i> (3)	738.97
3	<i>P</i> (23)	675.34	33	<i>R</i> (4)	741.27
4	<i>P</i> (22)	677.83	34	<i>R</i> (5)	743.58
5	<i>P</i> (21)	680.02	35	<i>R</i> (6)	746.01
6	<i>P</i> (20)	682.39	36	<i>R</i> (7)	748.36
7	<i>P</i> (19)	684.75	37	<i>R</i> (8)	750.81
8	<i>P</i> (18)	687.07	38	<i>R</i> (9)	753.33
9	<i>P</i> (17)	689.54	39	<i>R</i> (10)	755.53
10	<i>P</i> (16)	691.66	40	<i>R</i> (11)	757.96
11		692.81	41	<i>R</i> (12)	760.40
12	<i>P</i> (15)	694.19	42	<i>R</i> (13)	762.70
13	<i>P</i> (14)	696.46	43	<i>R</i> (14)	764.93
14		697.20	44	<i>R</i> (15)	767.23
15	<i>P</i> (13)	698.88	45	<i>R</i> (16)	769.45
16	<i>P</i> (12)	701.26	46	<i>R</i> (17)	771.84
17		701.58	47	<i>R</i> (18)	774.14
18	<i>P</i> (11)	703.68	48	<i>R</i> (19)	776.53
19	<i>P</i> (10)	706.00	49	<i>R</i> (20)	778.88
20	<i>P</i> (9)	708.34	50	<i>R</i> (21)	781.20
21	<i>P</i> (8)	710.47	51	<i>R</i> (22)	783.50
22	<i>P</i> (7)	713.01	52	<i>R</i> (23)	785.87
23	<i>P</i> (6)	715.44	53	<i>R</i> (24)	788.23
24		716.67	54	<i>R</i> (25)	790.63
25	<i>P</i> (5)	717.75	55	<i>R</i> (26)	792.94
26	<i>P</i> (4)	720.27	56	<i>R</i> (27)	795.31
27	<i>P</i> (3)	722.46	57	<i>R</i> (28)	797.57
28	<i>P</i> (2)	724.72	58	<i>R</i> (29)	799.87
29		726.13	59	<i>R</i> (30)	802.04
30	<i>R</i> (1)	734.24	60	<i>R</i> (31)	804.53

of the gas generating system and the cell, atmospheric carbon dioxide was eliminated from the absorption cell.

The absorption bands shown in this paper were traced from the original records in such a manner as to eliminate most of the drift of the thermocouple (a "dc" amplification system was used as described in reference 6). Some of the peculiar intensities on the middle of the *R* branch of Fig. 1 were introduced by shifting the foreprism while this portion of the spectrum was being recorded. For the other bands a single setting of this prism was used for the whole range.

The values for the band centers, for  $B''$ , and for  $B' - B''$  were obtained by use of the combination principles<sup>7</sup> in the bands for which the rotational lines were well-enough resolved.

### EXPERIMENTAL RESULTS

In describing the results it will be convenient to indicate the absolute value of the quantum number  $l$  by the usual superscript appended to the frequency. For example, the notation  $\nu_5^1 + 2\nu_4^0 - \nu_4^1$  will mean the vibrational frequency for a transition from a lower state with  $V_4=1$ ,  $|l_4|=1$  to a state with  $V_5=1$ ,  $|l_5|=1$ ,  $V_4=2$ ,  $|l_4|=0$ , all other vibrational quantum numbers being zero. The active fundamental band regions will be discussed first and the derived values of the infra-red inactive, but Raman active, fundamentals will be given. The combination bands will be discussed in the order of increasing frequencies. Finally the de-

rived results and anharmonic coefficients will be discussed.

### THE FUNDAMENTAL BANDS AND FREQUENCIES

#### $\nu_5^1$ -Band

Of the five fundamental frequencies of acetylene only  $\nu_3$  and  $\nu_5^1$  are observed in the infra-red spectrum. The appearance of the  $\nu_5^1$ -band, which has a frequency of 730.74 cm<sup>-1</sup>, is shown in Fig. 1, and the line frequencies are given in Table I. The lines in Table I are numbered to correspond with the line numbers in Fig. 1. A combination principle applied to the *P* and *R* branch lines gives a *Q* branch position of 729.56 cm<sup>-1</sup>. If this band were the  $\nu_5^1$ , ( $\Pi_u - \Sigma_g$ ), band only, it would consist of a strong central *Q* branch and *P* and *R* branches with alternating intensities and a missing *P* (1) line. That this absorption region consists of more than the  $\nu_5^1$ -band is easily seen. Line No. 24 at 716.67 cm<sup>-1</sup> is identified as the *Q* branch of the difference band  $\nu_4^1 + \nu_5^1 - \nu_4^1$ , ( $\Sigma_u^-$ ,  $\Sigma_u^+ - \Pi_g$ ), with  $l=0$  in the upper state. The vibrational frequency for this difference band is therefore 715.49 cm<sup>-1</sup>. The band  $\nu_4^1 + \nu_5^1 - \nu_4^1$ , ( $\Delta_u - \Pi_g$ ), with  $l=2$  in the upper state would be expected to produce a *Q* branch (weaker relative to its *P* and *R* branch lines than the  $\Sigma_u^-$ ,  $\Sigma_u^+ - \Pi_g$ -band *Q* branch) with a frequency  $4B''$  smaller than line No. 24. A *Q* branch at this expected position, 712.06 cm<sup>-1</sup>, is not seen in the spectrum except in disturbing the resolution of lines No. 21 and No. 22. The bands  $2\nu_5^0 - \nu_5^1$ , ( $\Delta_g$ ,  $\Sigma_g^+ - \Pi_u$ ), would also lie in this region of the spectrum. The *Q* branch of the  $2\nu_5^0 - \nu_5^1$ -band adds to the intensity of line No. 26 and the *Q* branch of  $2\nu_5^0 - \nu_5^1$  is at 730 cm<sup>-1</sup> and hence is masked by the *Q* branch of  $\nu_5^1$ . The assignment of these bands is consistent with anharmonic coefficients  $x_{55}$  and  $X_{55}$  which are obtained from bands in the region of  $3\nu_5^1$ . The frequency  $2\nu_5^0 - \nu_5^1$  is therefore 719.09 cm<sup>-1</sup> with a *Q* branch at 720.27 cm. The presence of bands other than  $\nu_5^1$  in this spectrum is also indicated by the presence of line No. 29 which is not at the right position to be a *P* (1) line of the  $\nu_5^1$  [the *P* (1) line should have zero intensity], by the lack of proper three to one intensity alternation in the lines of the *P* and *R* branches, and by the presence of satellites on the *R* branch lines near the center of the band.

A combination principle applied to the lines in the *P* and *R* branches gives a value  $B' - B'' = -0.0008$  cm<sup>-1</sup>. The convergence of the *Q* branch, however, is consistent with a positive value of  $B' - B''$ . This may be understood in the following manner.\* The levels in the upper state are split by an  $l$ -type doubling. These component states have, effectively, two different  $B'$  values which we shall designate by  $B_{\pm}'$ . The lines in the *P* and *R* branches are due to transitions from the normal vibration state to the lower components in the upper state. The components of the *Q* branch, however, are due to transitions from the normal state to the upper component states.

\* Note added in proof: this anomaly has been discussed by G. Herzberg in Rev. Mod. Phys. 14, 219 (1942).

<sup>7</sup> See reference 2, p. 340 ff.

The quantities  $B_{\pm}'$  are equal to  $B_{\pm}' = B' \pm \Delta$  where  $B'$  are the  $B$ , given by Shaffer and Nielsen and where  $\Delta$  for a state  $V_5 = |l_5| = 1$  is equal<sup>8</sup> to  $B(B/\omega_5)[1 + \Sigma_s \zeta_{5s}^2 4\omega_5^2/(\omega_s^2 - \omega_5^2)]$ . It is readily verified that  $\zeta_{53}^2 = 1$  and  $\zeta_{51}^2 = \zeta_{52}^2 = 0$  so that  $\Delta$  reduces to  $B(B/\omega_5)[1 + 4\omega_5^2/(\omega_3^2 - \omega_5^2)]$ . Insertion of the constants  $B_1$ ,  $\omega_5$ , and  $\omega_3$  into  $\Delta$  leads to a value  $\Delta = 0.0023 \text{ cm}^{-1}$ . The value  $B' - B'' = -0.0008$  referred to earlier is in reality  $B_- - B''$ . From the definition of  $B_+$  we have that  $B_+ - B'' = B_- - B'' + 2\Delta$ . We obtain, therefore,  $B_+ - B'' = +0.0038 \text{ cm}^{-1}$  which is positive as indicated by the convergence of the  $Q$  branch.

### $\nu_3$ -Band

The fundamental  $\nu_3$ ,  $(\Sigma_u^+ - \Sigma_g^+)$ , which has a frequency of  $3282.5 \text{ cm}^{-1}$ , is shown in Fig. 2. This band is overlapped by the combination band  $\nu_2 + \nu_4^1 + \nu_5^1$ ,  $(\Sigma_u^+ - \Sigma_g^+)$ . The resolution is sufficient to separate these two bands as is indicated by the schematic diagram of the two bands shown in Fig. 2. The relative intensities of the two bands in the schematic spectrum were chosen to approximate the observed spectrum by giving the combination band twice the intensity of the fundamental. The  $B' - B''$  values for these bands, given

in Table XI, cannot be accurate because of the inability to measure the frequencies of the lines of either band without interference from the lines of the other band. The line frequencies for these two bands are given in Table II. It is strange that the intensity of the fundamental should appear weaker than the combination band and it is possible that these assignments may have to be interchanged. A test of the validity of the assignment may be obtained from the anharmonic constants after the band  $\nu_2 + \nu_4^1 - \nu_5^1$  or the band  $\nu_2 + \nu_5^1 - \nu_4^1$  is observed. The  $\nu_2 + \nu_4^1 - \nu_5^1$ -band was not observed with our instrument with a 30-in. cell containing acetylene at atmospheric pressure. In view of the anharmonic constants, as presently evaluated (see later), it seems that it would be possible to invert this assignment of  $\nu_3$  and  $\nu_2 + \nu_4^1 + \nu_5^1$ .

The band  $\nu_3 + \nu_4^1 - \nu_4^1$ ,  $(\Pi_u - \Pi_g)$ , is expected at  $3270.7 \text{ cm}^{-1}$  and may therefore be adding to the intensity of line No. 27 at  $3270.9 \text{ cm}^{-1}$ . Line No. 27 is not significantly larger than one would expect without the addition of the  $Q$  branch of  $\nu_3 + \nu_4^1 - \nu_4^1$ . One of the components of  $\nu_2 + 2\nu_4^{0,2} + \nu_5^1 - \nu_4^1$ ,  $(2\Pi_u, \Phi_u - \Pi_g)$ , is expected at  $3286.6 \text{ cm}^{-1}$  and the  $Q$  branch probably adds to distort the intensities of lines No. 38 and No. 39.

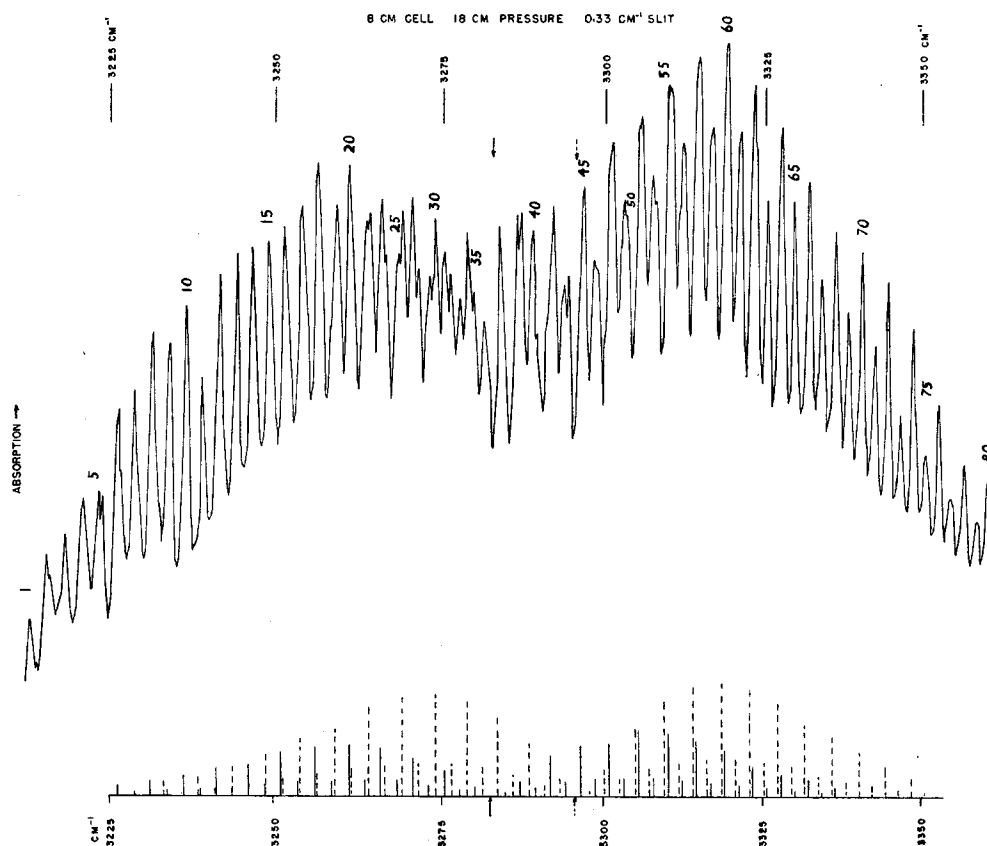


FIG. 2. The  $\nu_3$ - and  $\nu_2 + \nu_4^1 + \nu_5^1$ -bands of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table II.

<sup>8</sup> H. H. Nielsen, Phys. Rev. 77, 130 (1950).

TABLE II. The  $\nu_3$ - and  $\nu_2+\nu_4^1+\nu_5^1$ -band frequencies, see Fig. 2.

Line No.	$\nu_3$	$\nu_2+\nu_4^1+\nu_5^1$	cm <sup>-1</sup>	Line No.	$\nu_3$	$\nu_2+\nu_4^1+\nu_5^1$	cm <sup>-1</sup>
1	<i>P</i> (28)		3213.5	41	<i>R</i> (2)		3289.4
2	<i>P</i> (27)		3215.8	42	<i>R</i> (3)		3291.7
3	<i>P</i> (26)		3218.7	43		<i>P</i> (1)	3293.2
4	<i>P</i> (25)		3221.2	44	<i>R</i> (4)		3294.1
5	<i>P</i> (24)		3223.7	45	<i>R</i> (5)		3296.4
6	<i>P</i> (23)		3226.3	46		<i>R</i> (0)	3297.9
7	<i>P</i> (22)		3228.8	47	<i>R</i> (6)		3298.6
8	<i>P</i> (21)		3231.6	48	<i>R</i> (7)		3300.8
9	<i>P</i> (20)		3234.0	49		<i>R</i> (2)	3302.5
10	<i>P</i> (19)		3236.6	50	<i>R</i> (8)		3303.1
11	<i>P</i> (18)		3239.2	51		<i>R</i> (3)	3304.2
12	<i>P</i> (17)		3241.7	52	<i>R</i> (9)		3304.7
13	<i>P</i> (16)	<i>P</i> (21)	3244.2	53		<i>R</i> (4)	3307.2
14	<i>P</i> (15)	<i>P</i> (20)	3246.5	54	<i>R</i> (10)		3307.8
15	<i>P</i> (14)	<i>P</i> (19)	3249.0	55		<i>R</i> (5)	3309.7
16	<i>P</i> (13)	<i>P</i> (18)	3251.5	56	<i>R</i> (11)		3310.0
17	<i>P</i> (12)	<i>P</i> (17)	3254.0	57	<i>R</i> (12)	<i>R</i> (6)	3311.9
18	<i>P</i> (11)	<i>P</i> (16)	3256.3	58	<i>R</i> (13)	<i>R</i> (7)	3314.3
19	<i>P</i> (10)	<i>P</i> (15)	3259.1	59	<i>R</i> (14)	<i>R</i> (8)	3316.6
20	<i>P</i> (9)	<i>P</i> (14)	3261.2	60	<i>R</i> (15)	<i>R</i> (9)	3318.8
21	<i>P</i> (8)		3263.6	61	<i>R</i> (16)	<i>R</i> (10)	3321.0
22		<i>P</i> (13)	3264.2	62	<i>R</i> (17)	<i>R</i> (11)	3323.3
23	<i>P</i> (7)		3265.8	63	<i>R</i> (18)	<i>R</i> (12)	3325.3
24		<i>P</i> (12)	3266.5	64	<i>R</i> (19)	<i>R</i> (13)	3327.6
25	<i>P</i> (6)		3268.4	65	<i>R</i> (20)	<i>R</i> (14)	3329.8
26		<i>P</i> (11)	3269.1	66	<i>R</i> (21)	<i>R</i> (15)	3332.0
27	<i>P</i> (5)		3270.9	67	<i>R</i> (22)	<i>R</i> (16)	3334.0
28		<i>P</i> (10)	3271.4	68	<i>R</i> (23)	<i>R</i> (17)	3336.2
29	<i>P</i> (4)		3273.0	69	<i>R</i> (24)	<i>R</i> (18)	3338.3
30		<i>P</i> (9)	3273.9	70	<i>R</i> (25)	<i>R</i> (19)	3340.4
31	<i>P</i> (3)		3275.3	71		<i>R</i> (20)	3342.7
32		<i>P</i> (8)	3276.2	72		<i>R</i> (21)	3344.7
33	<i>P</i> (2)		3277.5	73		<i>R</i> (22)	3346.7
34		<i>P</i> (7)	3278.7	74		<i>R</i> (23)	3348.8
35	<i>P</i> (1)		3279.8	75		<i>R</i> (24)	3350.7
36		<i>P</i> (6)	3281.3	76		<i>R</i> (24)	3352.8
37		<i>P</i> (5)	3283.6	77		<i>R</i> (25)	3354.9
38		<i>P</i> (4)	3286.2	78		<i>R</i> (26)	3356.9
39	<i>R</i> (1)		3287.0	79		<i>R</i> (27)	3359.1
40		<i>P</i> (3)	3288.5	80		<i>R</i> (28)	3360.9

 $\nu_1$ -,  $\nu_2$ -,  $\nu_4^1$ -Frequencies

No other fundamental bands of acetylene are infrared active. The fundamental Raman frequencies of acetylene gas may be obtained from some difference bands which will be discussed later. These fundamental frequencies are the following:  $\nu_1=3373.2$  cm<sup>-1</sup>,  $\nu_2=1974.0$  cm<sup>-1</sup>, and  $\nu_4^1=613.3$  cm<sup>-1</sup>.

## COMBINATION BANDS

 $\nu_2-\nu_5^1$ -Band

A weak perpendicular band with a frequency of 1243.3 cm<sup>-1</sup> has a *Q* branch which may be seen among the *P* branch lines of the  $\nu_4^1+\nu_5^1$ -band as shown in Fig. 3. This band must be  $\nu_2-\nu_5^1$ , ( $\Sigma_g^+-\Pi_u$ ). The majority of the lines seen on the two sides of the *Q* branch must be associated with the  $\nu_4^1+\nu_5^1$ -band. The *Q* branch peak which was taken for the band center, as marked in the Fig. 3, is at 1244.5 cm<sup>-1</sup>.

 $\nu_4^1+\nu_5^1$ -Band

A very intense summation band is found at 1328.18 cm<sup>-1</sup>, which is identified as  $\nu_4^1+\nu_5^1$ , ( $\Sigma_u^+-\Sigma_g^+$ ). This

should be a parallel-type band with no *Q* branch and alternating intensities. The experimentally obtained band, Fig. 4C appears to have a line at the center and does not have the expected three to one intensity alternation in the rotation lines. The record shown in Fig. 4B was obtained by placing dry ice around the absorption cell, except at the windows, and thereby reducing the temperature to about -75°C. The record of Fig. 4C was obtained with the same instrumental conditions (slit widths, etc.) after the dry ice had sublimed away and the cell has warmed up to room temperature. It is easily seen that the central line, which is marked by an arrow in Fig. 4, is temperature sensitive. The alternating intensity is more marked in the cooled sample. We conclude that there must be a difference band in this region which arises from an excited  $V_4=1$  or  $V_5=1$  state, because the intensity of a difference band would be reduced by cooling, i.e., by reducing the number of molecules in the initial thermally excited level.

This difference band, with a *Q* branch in the center of the  $\nu_4^1+\nu_5^1$ -band, is found to be one of the two bands  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$ , ( $2\Pi_u-\Pi_g$ ), with a central *Q* branch at 1328.46 cm<sup>-1</sup>. The center of the  $\nu_4^1+\nu_5^1$ -band is at 1328.18 cm<sup>-1</sup> as found by a combination principle applied to the rotational lines of the cooled gas record, Fig. 4B. The fact that the 1328.46-cm<sup>-1</sup> *Q* branch is not quite at the center of the  $\nu_4^1+\nu_5^1$ -band was apparent on the original records. The bands  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$  and  $2\nu_4^2+\nu_5^1-\nu_4^1$  would be of the same type, ( $\Pi_u-\Pi_g$ ), but not at the same position because of the  $X_{44}l_4^2$  term in the vibrational energy of the two upper states would be different. A difficulty of assignment of this band will be reviewed later in the discussion of anharmonicity coefficients. The addition of a band of the  $\Pi_u-\Pi_g$ -type together with  $\nu_4^1+\nu_5^1$  seems to explain the apparent intensities of the main lines in this region of the spectrum. The appearance of a  $\Pi_u-\Pi_g$ -type band is shown in Fig. 9.

The record shown in Fig. 4A was made with a cell whose windows had not been fogged by the cooling procedure. The additional lines seen between the main lines are difficult to explain. The most abundant expected isotope,  $H^1-C^{12}\equiv C^{13}-H^1$ , would be asymmetrical and would not show the apparent intensity alternations which these minor lines seem to show. The difference bands  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$ , discussed above, and the difference bands  $\nu_4^1+2\nu_5^{0,2}-\nu_5^1$ , ( $\Pi_g-\Pi_u$ ), also would not show this intensity alternation. The very weak bands  $\nu_3-\nu_2(\Sigma_u^+-\Sigma_g^+)$ , and  $\nu_2+\nu_4^1+\nu_5^1-\nu_2$ , ( $\Sigma_u^+-\Sigma_g^+$ ), while of the proper type, would be expected to have a center in the *P* branch near 1310 and 1320 cm<sup>-1</sup>. There are some additional lines in the *P* branch, but good records of them were not obtained. An isotope band might account for these additional *P* branch lines.

The line frequencies for the  $\nu_4^1+\nu_5^1$ -band are given in Table III. The combination relations applied to the

lines of the cooled gas records give  $B''=1.1769\text{ cm}^{-1}$  and  $B'-B''=+0.003\text{ cm}^{-1}$ .

The upper state level  $V_5=1$ ,  $V_4=2$  which is involved in producing the central line in the  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$ -band has been measured in transitions from the ground state, see Fig. 5 and the next paragraph. The value of the lower state level  $V_4=1$  has been derived from several difference bands. From the knowledge of the upper and lower levels it is possible to predict the position of the  $Q$  branch of the  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$ -band. The predicted<sup>9</sup> value is  $1328.4\text{ cm}^{-1}$  compared with the experimental value of  $1328.46\text{ cm}^{-1}$ .

### $2\nu_4^{2,0}+\nu_5^1$ -Band

There are two  $Q$  branches with frequencies  $1940.52$  and  $1960.66\text{ cm}^{-1}$  shown in Fig. 5. It is natural to identify these as  $2\nu_4^0+\nu_5^1$ ,  $(\Pi_u-\Sigma_g^+)$ , and  $2\nu_4^2+\nu_5^1$ ,  $(\Pi_u-\Sigma_g^+)$ , which would immediately give the value of the separation  $4X_{44}$  as  $\pm 20.14\text{ cm}^{-1}$  with a sign depending upon which of the two ways the assignment is made. There is difficulty with both ways, however, as will be seen later when an evaluation of the constant  $X_{44}$  is made. The difference bands  $3\nu_4^{3,1}+\nu_5^1-\nu_4^1$ ,  $(\Sigma_u^+, \Sigma_u^-, 2\Delta_u-\Pi_g)$ , and  $2\nu_4^{2,0}+2\nu_5^{2,0}-\nu_5^1$ ,  $(2\Sigma_g^+, \Sigma_g^-, 2\Delta_g-\Pi_u)$  will also lie in this region. A cooling experiment to determine whether either one of the two  $Q$  branches in this region belonged to a difference band was inconclusive but seemed to indicate that it did not. An investigation of the possible vibrational resonance interactions and coriolis interactions has not disclosed any reasonable explanation for a shift in the positions of these bands.

TABLE III. The  $\nu_4^1+\nu_5^1$ -band frequencies, see Fig. 4.

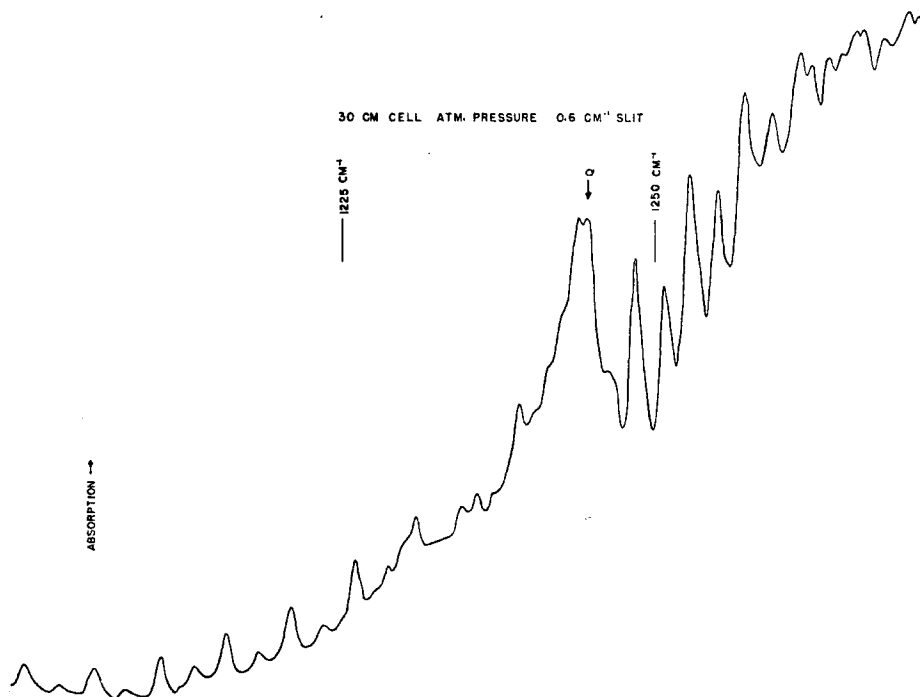
Line No.	$\nu_4^1+\nu_5^1$	$\text{cm}^{-1}$	Line No.	$\nu_4^1+\nu_5^1$	$\text{cm}^{-1}$
1	$P(20)$	1282.3	21		1328.46
2	$P(19)$	1284.6	22	$R(0)$	1330.6
3	$P(18)$	1286.8	23	$R(1)$	1333.0
4	$P(17)$	1289.0	24	$R(2)$	1335.3
5	$P(16)$	1291.2	25	$R(3)$	1337.7
6	$P(15)$	1293.5	26	$R(4)$	1340.1
7	$P(14)$	1295.8	27	$R(5)$	1342.4
8	$P(13)$	1298.0	28	$R(6)$	1344.9
9	$P(12)$	1300.3	29	$R(7)$	1347.1
10	$P(11)$	1302.7	30	$R(8)$	1349.7
11	$P(10)$	1304.9	31	$R(9)$	1352.1
12	$P(9)$	1307.2	32	$R(10)$	1354.4
13	$P(8)$	1309.5	33	$R(11)$	1356.9
14	$P(7)$	1311.8	34	$R(12)$	1359.3
15	$P(6)$	1314.2	35	$R(13)$	1361.8
16	$P(5)$	1316.4	36	$R(14)$	1364.2
17	$P(4)$	1318.7	37	$R(15)$	1366.6
18	$P(3)$	1321.1	38	$R(16)$	1369.1
19	$P(2)$	1323.5	39	$R(17)$	1371.5
20	$P(1)$	1325.8	40	$R(18)$	1373.9

No resonance would be expected to induce infra-red activity in a band here either. The line frequencies are given in Table IV, and  $B'-B''=0.0032\text{ cm}^{-1}$  for the lines associated with the  $1940.52\text{-cm}^{-1}$   $Q$  branch. A tentative assignment of  $2\nu_4^0+\nu_5^1$  to the stronger  $Q$  branch gives this band a vibrational frequency of  $1941.70\text{ cm}^{-1}$ .

### $3\nu_5^1$ -Band

A perpendicular band attributed to  $3\nu_5^1$ ,  $(\Pi_u-\Sigma_g^+)$ , is found with a frequency of  $2170.84\text{ cm}^{-1}$  and is shown

FIG. 3. The  $\nu_1-\nu_5^1$ -band  $Q$  branch as measured with the 3600 lines per inch grating.



<sup>9</sup> The  $2\nu_4^{2,0}+\nu_5^1-\nu_4^1$ -band was used together with the  $\nu_4^1+\nu_5^1$ -band to obtain one experimental value of the  $V_4=1$  level, but the  $V_4=1$  level could be obtained from other pairs of bands and thus predict the position of the  $Q$  branch  $2\nu_4^{0,2}+\nu_5^1-\nu_4^1$ .

in Fig. 6. The intensity alternation shows very well in this band. The value of  $B' - B''$  equal to  $0.0020 \text{ cm}^{-1}$  and the band center of  $2169.67 \text{ cm}^{-1}$  were obtained from the combination relations. The line frequencies are given in Table V. There are several extra lines in the spectrum whose intensities relative to the other lines seemed to be decreased by cooling. Among these lines are Nos. 17 and 22, which are undoubtedly  $Q$  branches of difference bands. The difference bands which may be expected in this region are  $\nu_4^1 + 3\nu_5^{3,1} - \nu_4^1$ ,  $(\Sigma_u^-, \Sigma_u^+, 2\Delta_u - \Pi_g)$ , and  $4\nu_5^{2,0} - \nu_5^1$ ,  $(\Sigma_g^+, \Delta_g - \Pi_u)$ . Anharmonic constants derived from other bands indicate that the  $Q$  branch of  $3\nu_5^1 + \nu_4^1 - \nu_4^1$  would be near  $2122 \text{ cm}^{-1}$ . Near this position there is no obvious  $Q$  branch. The expected position of  $4\nu_5^0 - \nu_5^1$  is near  $2151 \text{ cm}^{-1}$  so we believe that line No. 17, which occurs at  $2152.0 \text{ cm}^{-1}$ , is of the  $Q$  branch of this band. Thus the frequency of  $4\nu_5^0 - \nu_5^1$  is  $2150.8 \text{ cm}^{-1}$ . The line No. 22 is chosen as the  $Q$  branch of  $4\nu_5^2 - \nu_5^1$  because the bands  $\nu_5^1$ ,  $3\nu_5^1$ ,  $4\nu_5^0 - \nu_5^1$ , and  $4\nu_5^2 - \nu_5^1$  give values for the anharmonic constants  $x_{55}$  and  $X_{55}$  which are consistent with the assignment of  $2\nu_5^0 - \nu_5^1$ . The frequency  $4\nu_5^2 - \nu_5^1$  is taken to be  $2165.0 \text{ cm}^{-1}$ . It is not possible to interchange the assignments of  $4\nu_5^2 - \nu_5^1$  and  $4\nu_5^0 - \nu_5^1$  without leading to an inconsistency in the anharmonic constants.

### $3\nu_4^1 + \nu_5^1$ -Band

A weak parallel band attributed to  $3\nu_4^1 + \nu_5^1$ ,  $(\Sigma_u^+ - \Sigma_g^+)$ , is found at the edge of the  $3.7\mu$  absorption

group. Figure 7 shows this band and the overlapping of the lines of the  $3.7\mu$  bands on the high frequency side. Only a few of the weak lines show in the record because of the poor resolution, and therefore it is difficult to find the center. The center has been chosen as  $2556.5 \text{ cm}^{-1}$  as indicated in Fig. 7. The center might very well be  $4B$  larger than this value. The frequencies of the lines are given in Table VI.

$$\nu_1 - \nu_6^1, \nu_3 - \nu_4^1, \nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1, \text{ and } \nu_2 + \nu_5^1\text{-Bands}$$

Four distinct  $Q$  branches are found in the  $2700\text{-cm}^{-1}$  region as shown in Fig. 8. The frequencies of these lines are given in Table VII. These bands are:  $\nu_1 - \nu_6^1$ ,  $(\Sigma_g^+ - \Pi_u)$ , with a  $Q$  branch at  $2643.69 \text{ cm}^{-1}$  and a frequency of  $2642.51 \text{ cm}^{-1}$ ;  $\nu_3 - \nu_4^1$ ,  $(\Sigma_u^+ - \Pi_g)$ , with a  $Q$  branch at  $2670.33 \text{ cm}^{-1}$  and a frequency of  $2669.15 \text{ cm}^{-1}$ ;  $\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$ ,  $(\Sigma_u^-, \Sigma_u^+ - \Pi_g)$  with a  $Q$  branch at  $2683.09 \text{ cm}^{-1}$  and a frequency of  $2681.81 \text{ cm}^{-1}$ ; and  $\nu_2 + \nu_5^1$ ,  $(\Pi_u - \Sigma_g^+)$ , with a  $Q$  branch at  $2702.46 \text{ cm}^{-1}$  and a frequency of  $2703.63 \text{ cm}^{-1}$ . The  $Q$  branch of the band  $\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$ ,  $(\Delta_u - \Pi_g)$ , with  $l=2$  in the upper state, is expected at a frequency  $4B$  less than  $2683.09 \text{ cm}^{-1}$ . A strong absorption at this position is not seen in the records. The  $Q$  branch of the band  $\nu_2 + 2\nu_5^0 - \nu_5^1$ ,  $(\Sigma_g^+ - \Pi_u)$ , is thought to be at  $2691.7 \text{ cm}^{-1}$ , line No. 48, and thus the frequency would be  $2690.5 \text{ cm}^{-1}$ . This is conjecture, however, since the  $Q$  branch does not tower over the other lines of the spectrum. Such a position for

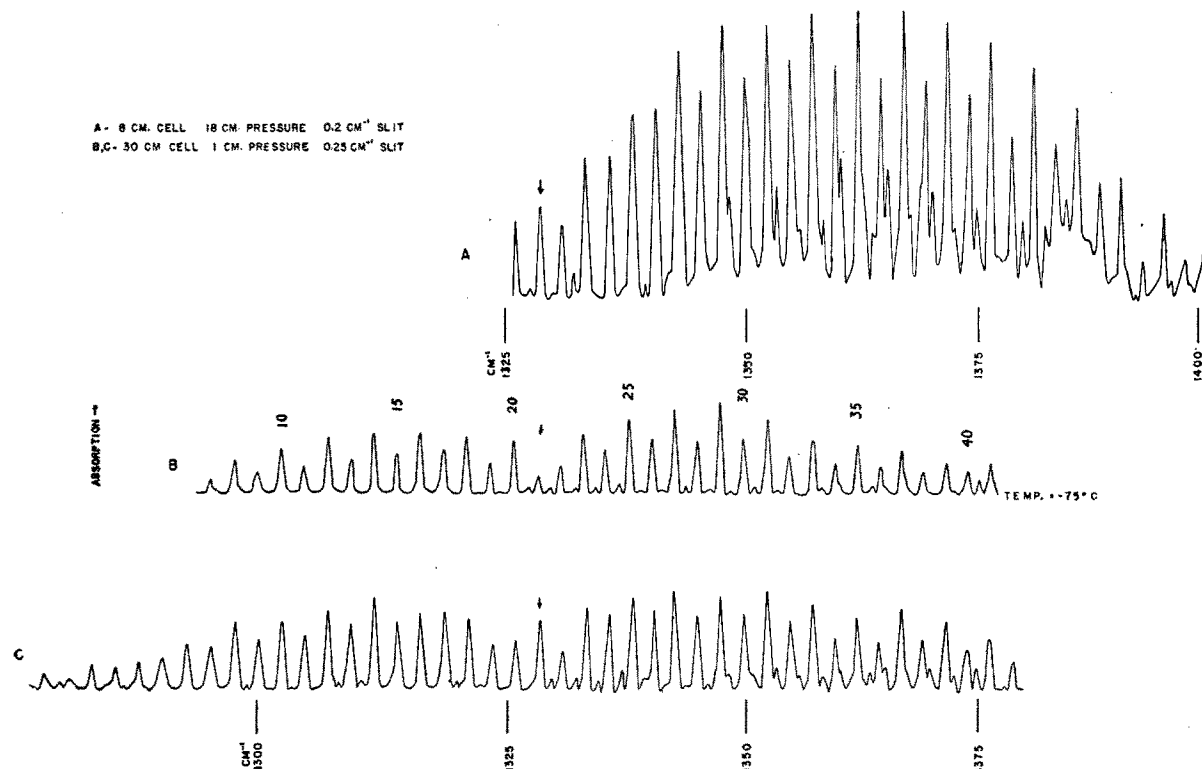


FIG. 4. The  $\nu_4^1 + \nu_5^1$ -band of acetylene as measured with the 3600 lines per inch grating. The values of the line frequencies are given in Table III.



TABLE IV. The  $2\nu_4^0 + \nu_5^1$ -band frequencies, see Fig. 5.

Line No.	$2\nu_4^0 + \nu_5^1$	cm <sup>-1</sup>	Line No.	$2\nu_4^0 + \nu_5^1$	cm <sup>-1</sup>	
1	<i>P</i> (19)	1896.4	31	<i>R</i> (7)	1959.6	
2	<i>P</i> (17)	1901.1	32		1960.66	
3		1902.7	33	<i>R</i> (9)	1964.2	
4	<i>P</i> (16)	1903.4	34		<i>R</i> (1)	1964.9
5	<i>P</i> (15)	1906.2	35	<i>R</i> (10)	1966.7	
6		1907.4	36		<i>R</i> (2)	1967.2
7	<i>P</i> (14)	1908.2	37	<i>R</i> (11)	1969.0	
8	<i>P</i> (13)	1910.1	38		<i>R</i> (3)	1969.7
9	<i>P</i> (12)	1912.5	39	<i>R</i> (12)	1971.5	
10	<i>P</i> (11)	1914.8	40	<i>R</i> (13)	1973.8	
11		1916.1	41		<i>R</i> (5)	1974.6
12	<i>P</i> (10)	1917.4	42	<i>R</i> (14)	1976.2	
13		1918.8	43		<i>R</i> (6)	1977.0
14	<i>P</i> (9)	1919.6	44	<i>R</i> (15)	1978.7	
15		1920.7	45		<i>R</i> (7)	1979.5
16	<i>P</i> (8)	1921.8	46	<i>R</i> (16)	1980.8	
17	<i>P</i> (7)	1924.1	47		<i>R</i> (8)	1981.7
18	<i>P</i> (6)	1926.3	48	<i>R</i> (17)	1983.2	
19	<i>P</i> (5)	1928.9	49		<i>R</i> (9)	1984.5
20		<i>P</i> (13)	50		<i>R</i> (10)	1986.6
21	<i>P</i> (4)	1931.3	51	<i>R</i> (19)	1988.0	
22	<i>P</i> (3)	1933.4	52		<i>R</i> (11)	1989.4
23		<i>P</i> (11)	53	<i>R</i> (21)	1993.6	
24	<i>Q</i>	1941.17	54		<i>R</i> (13)	1994.3
25	<i>R</i> (1)	1945.8	55		<i>R</i> (14)	1996.0
26	<i>R</i> (3)	1950.1	56	<i>R</i> (23)	1997.4	
27		1952.2	57		<i>R</i> (15)	1999.5
28	<i>R</i> (5)	1954.9				
29	<i>R</i> (6)	1957.2				
30		1957.4				

TABLE V. The  $3\nu_5^1$ -band frequencies, see Fig. 6.

Line No.	$3\nu_5^1$	cm <sup>-1</sup>	Line No.	$3\nu_5^1$	cm <sup>-1</sup>
1	P (23)	2115.8	26		2174.8
2	P (21)	2121.1	27		2175.7
3	P (20)	2123.4	28	R (2)	2176.5
4	P (19)	2125.6	29	R (3)	2179.0
5	P (18)	2128.1	30		2180.1
6	P (17)	2130.3	31	R (4)	2181.4
7	P (16)	2132.5	32	R (5)	2183.9
8	P (15)	2134.8	33	R (6)	2186.4
9	P (14)	2137.1	34	R (7)	2188.8
10	P (13)	2139.4	35	R (8)	2191.2
11	P (12)	2141.7	36	R (9)	2193.6
12	P (11)	2144.0	37	R (10)	2195.9
13	P (10)	2146.3	38	R (11)	2198.3
14		2147.0	39	R (12)	2200.8
15	P (9)	2148.5	40	R (13)	2203.0
16	P (8)	2150.9	41	R (14)	2205.4
17		2152.0	42	R (15)	2207.9
18	P (7)	2153.2	43	R (16)	2210.2
19	P (6)	2155.6	44	R (17)	2212.6
20	P (5)	2158.0	45	R (18)	2214.8
21	P (4)	2160.3	46	R (19)	2217.4
22		2161.5	47	R (20)	2219.8
23	P (3)	2162.6	48	R (21)	2222.1
24	Q	2170.19	49	R (22)	2224.7
25	R (1)	2173.9	50	R (23)	2226.8

couple the base line of the cooled records has been somewhat distorted.

#### $\nu_1 + \nu_5^1 - \nu_4^1$ -Band

A beautiful example of a  $\Pi_u - \Pi_g$ -band is found at 3480.51 cm<sup>-1</sup>. This band lies in a region where it may be seen without interference by other bands. The appearance of this band is shown in Fig. 9, and the line frequencies are given in Table VIII. The outstanding features of this band are the weak Q branch, the missing P (1) and R (1) lines, and the lack of intensity alterna-

$\nu_2 + 2\nu_5^0 - \nu_5^1$  would be in good agreement with the anharmonic constants, however. Confidence in the choice of the  $V_4=1$  and  $V_5=1$  as the lower levels for the bands in this region is gained by noting that  $\nu_1 - \nu_5^1$  is apparently reduced in intensity relatively more by cooling than either  $\nu_3 - \nu_4^1$  or  $\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$ . This is expected since  $V_5=1$  is a higher energy level than  $V_4=1$ . In compensating for the drift of the thermo-

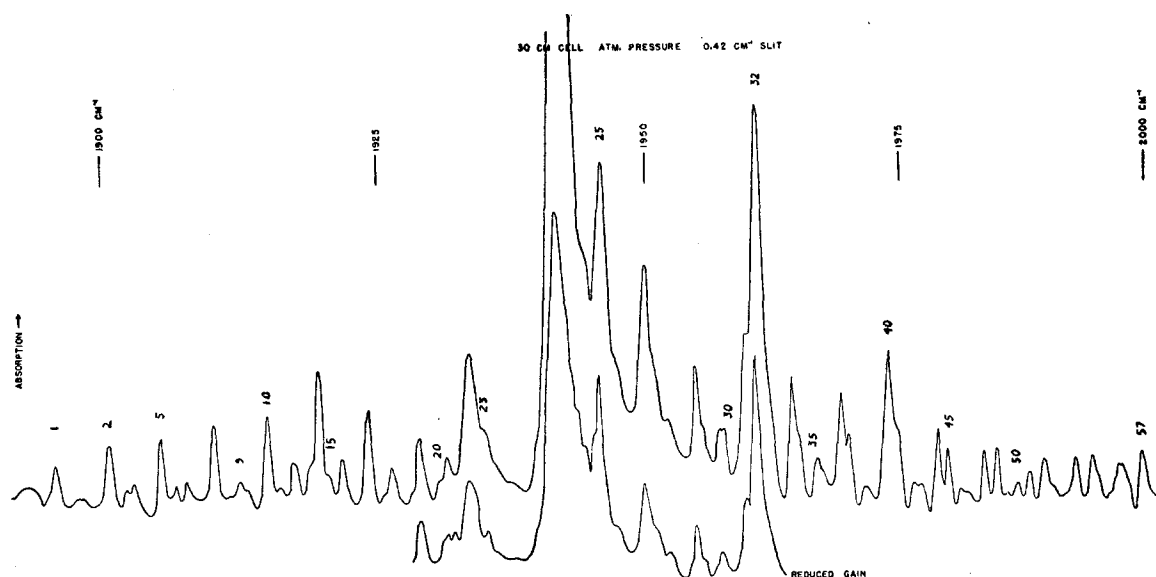


FIG. 5. The  $2\nu_4^2 + \nu_5^1$ -band region of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table IV.

TABLE VI. The  $3\nu_4^1 + \nu_5^1$ -band frequencies, see Fig. 7.

Line No.	$3\nu_4^1 + \nu_5^1$	cm <sup>-1</sup>	Line No.	$3\nu_4^1 + \nu_5^1$	cm <sup>-1</sup>
1	<i>P</i> (17)	2520.1	12		2563.5
2	<i>P</i> (15)	2524.0	13	<i>R</i> (3)	2565.9
3	<i>P</i> (13)	2528.1	14		2568.2
4	<i>P</i> (11)	2532.0	15	<i>R</i> (5)	2571.0
5	<i>P</i> (9)	2536.2	16		2573.6
6	<i>P</i> (7)	2540.5	17	<i>R</i> (7)	2576.0
7	<i>P</i> (5)	2544.8	18		2578.9
8	<i>P</i> (3)	2549.4	19	<i>R</i> (9)	2580.9
9	<i>P</i> (1)	2554.0	20		2584.5
10	<i>R</i> (0)	2558.9	21	<i>R</i> (11)	2586.0
11	<i>R</i> (1)	2562.0	22		2590.0

tion. The lack of the *P* (1) and *R* (1) lines follows from the fact that there is no  $J=0$  level in either the upper or lower state. The lack of the three-to-one intensity alternation is a result of the fact that each *P* branch line and each *R* branch line is the superposition of a weak line and a strong line (split by  $l$ -type doubling which is too small to be resolved). This band must be assigned to  $\nu_1 + \nu_5^1 - \nu_4^1$ .

#### $\nu_3 + \nu_4^1$ , $\nu_2 + 2\nu_4^{2,0} + \nu_5^1$ -Bands

Two absorption regions are shown in Fig. 10. The separation of the lines of the bands  $\nu_2 + 2\nu_4^{2,0} + \nu_5^1$ , ( $2\Pi_u - \Sigma_g^+$ ), and  $\nu_3 + \nu_4^1$ , ( $\Pi_u - \Sigma_g^+$ ), is indicated by the predicted bands shown in Fig. 10 and in Table IX. The predicted bands were drawn with the intensity of the  $\nu_3 + \nu_4^1$ -band equal to three-fourths the intensity of the  $\nu_2 + 2\nu_4^{2,0} + \nu_5^1$ -band. The fact that  $\nu_3 + \nu_4^1$  is weaker

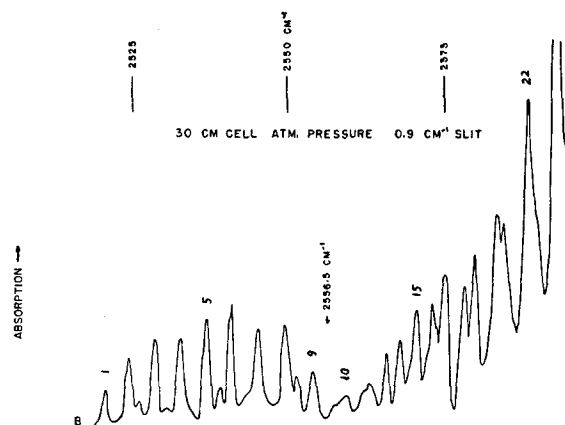


FIG. 7. The  $3\nu_4^1 + \nu_5^1$ -band of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table VI.

than  $\nu_2 + 2\nu_4^{2,0} + \nu_5^1$  is as disturbing as the fact that the  $\nu_3$ -band is weaker than the  $\nu_2 + \nu_4^1 + \nu_5^1$ -band. The center of the  $\nu_3 + \nu_4^1$ -band is at  $3882.81 \text{ cm}^{-1}$  and the center of the  $\nu_2 + 2\nu_4^{2,0} + \nu_5^1$ -band is at  $3898.81 \text{ cm}^{-1}$  so that the frequencies are  $3883.97$  and  $3899.97 \text{ cm}^{-1}$ , respectively. Another possible assignment would, of course, be that these two bands could be the two components  $\nu_2 + 2\nu_4^0 + \nu_5^1$  and  $\nu_2 + 2\nu_4^2 + \nu_5^1$ . The value of  $X_{44}$  resulting from this reassignment would be in good agreement with some other data. We prefer, however, to leave the assignment unchanged and have a band to attribute to  $\nu_3 + \nu_4^1$ . The value of  $B' - B''$  is  $-0.0067$

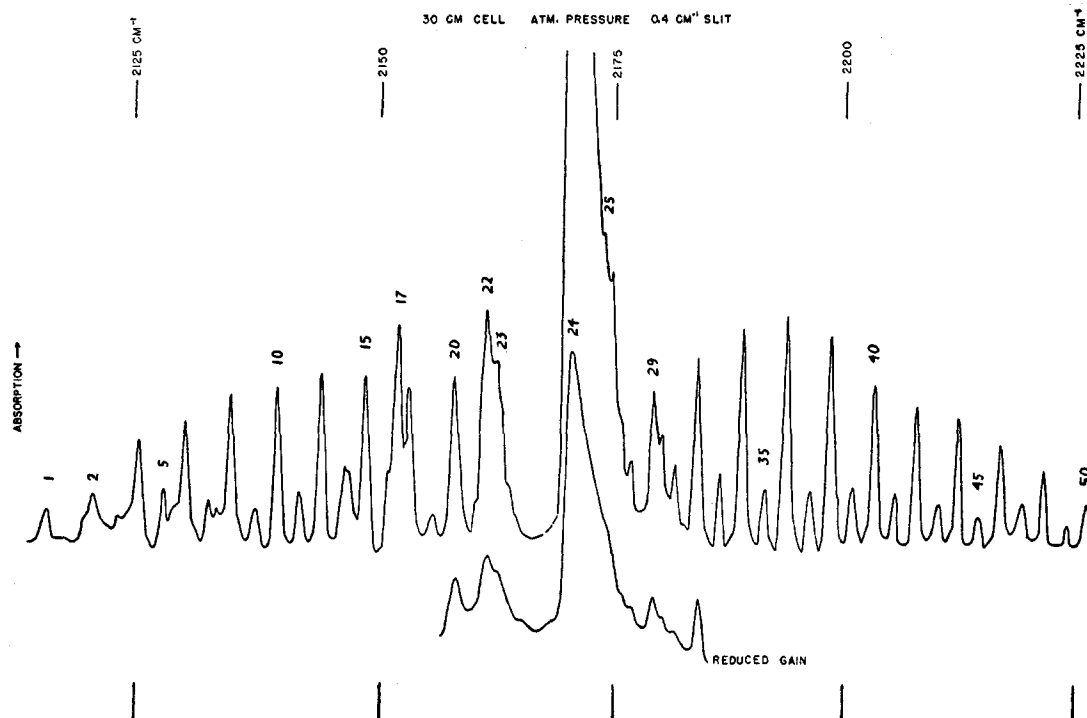


FIG. 6. The  $3\nu_5^1$ -band of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table V.

$\text{cm}^{-1}$  for the  $\nu_3+\nu_4^1$ -band and  $-0.0074 \text{ cm}^{-1}$  for the  $\nu_2+2\nu_4^{2,0}+\nu_5^1$ -band.

#### $\nu_1+\nu_4^1+\nu_5^1-\nu_4^1$ , $\nu_1+\nu_5^1$ -Bands

The high frequency absorption region shown in Fig. 10 is identified as the combination of the bands  $\nu_1+\nu_4^1+\nu_5^1-\nu_4^1$ , ( $\Sigma_u^-$ ,  $\Sigma_u^+$ ,  $\Delta_u-\Pi_g$ ), with  $Q$  branch near  $4080 \text{ cm}^{-1}$  and  $\nu_1+\nu_5^1$ , ( $\Pi_u-\Sigma_g^+$ ), with a  $Q$  branch at  $4092.75 \text{ cm}^{-1}$ . The rotation lines associated with the  $\nu_1+\nu_5^1$ -band are easily identified after reducing the intensity of the  $\nu_1+\nu_4^1+\nu_5^1-\nu_4^1$ -band by cooling the gas. This is shown in Fig. 10 also. The frequencies are given in Table X. The vibrational frequency of  $\nu_1+\nu_5$

is  $4093.92 \text{ cm}^{-1}$  and the value of  $B'-B''$  is  $-0.0078 \text{ cm}^{-1}$ .

The  $\Sigma_u^\pm-\Pi_g$ -component of  $\nu_1+\nu_4^1+\nu_5^1-\nu_4^1$  (with  $l=0$  in the upper state) was thought to give rise to a  $Q$  branch at  $4080.86 \text{ cm}^{-1}$  and have a frequency  $4079.7 \text{ cm}^{-1}$ , line No. 126. The  $\Delta_u-\Pi_g$ -components (with  $l=2$  in the upper state) would have a  $Q$  branch at  $4076.3 \text{ cm}^{-1}$ , line No. 124, and thus the same vibrational frequency of  $4079.7 \text{ cm}^{-1}$ . At the Symposium on Molecular Structure and Spectroscopy at Ohio State University, Columbus, Ohio (June 13, 1950), R. M. Talley and A. H. Nielsen reported on recently measured  $\text{C}_2\text{H}_2$  absorption bands in the  $4000$ - to  $7000\text{-cm}^{-1}$  region.

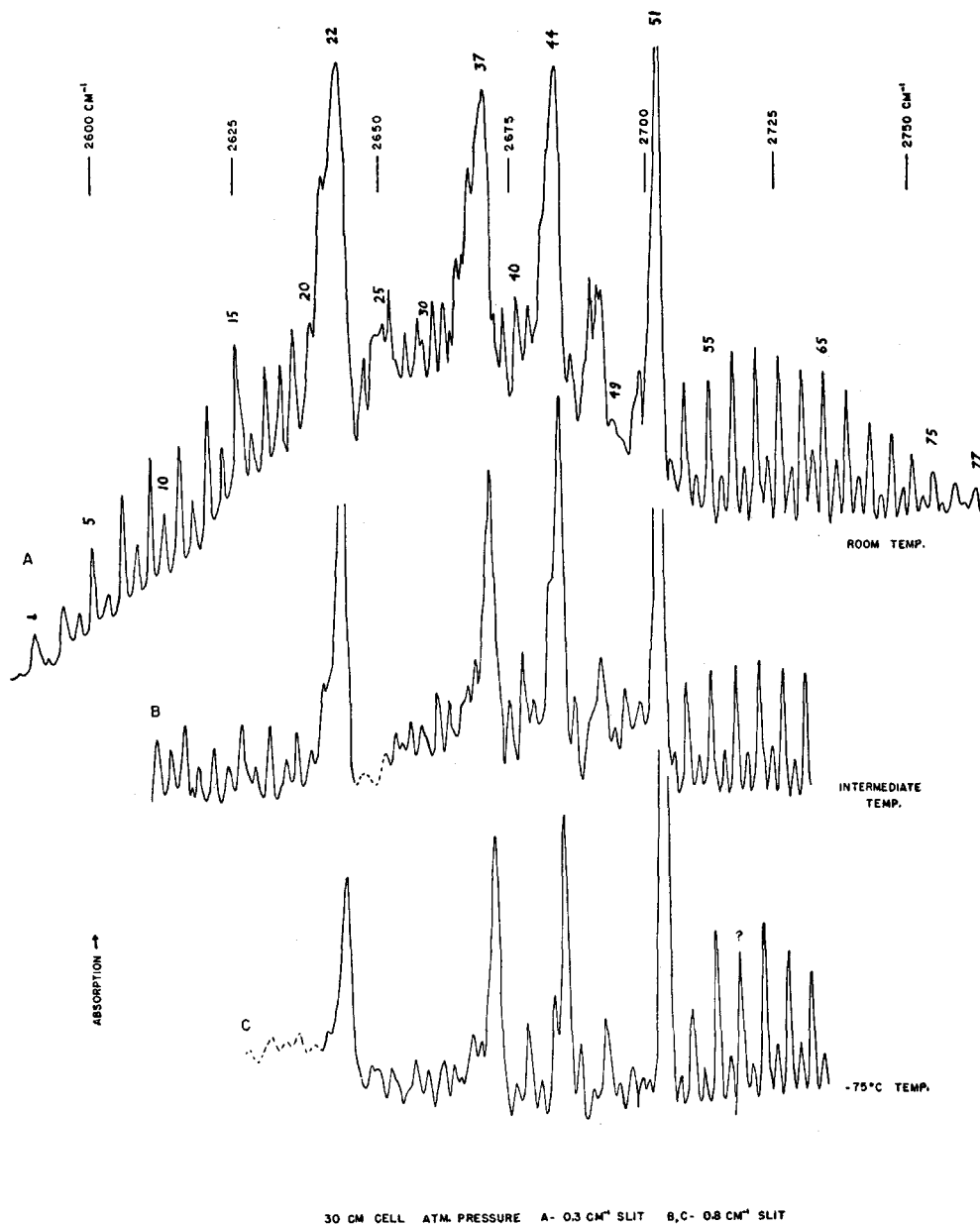


FIG. 8. The  $\nu_1-\nu_5^1$ ,  $\nu_3-\nu_4^1$ ,  $\nu_2+\nu_4^1+\nu_5^1-\nu_4^1$ , and  $\nu_2+\nu_5^1$ -bands of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table VII.

TABLE VII. The  $\nu_2 + \nu_5^1$ -band frequencies, see Fig. 8.

Line No.	$\nu_2 + \nu_5^1$	cm <sup>-1</sup>	Line No.	$\nu_2 + \nu_5^1$	cm <sup>-1</sup>
1		2589.8	39		2673.8
2		2591.9	40	P (11)	2676.2
3		2594.7	41		2678.3
4		2597.5	42		2680.6
5		2600.0	43	P (9)	2681.4
6		2602.7	44		2683.09
7		2605.3	45	P (7)	2686.6
8		2607.6	46		2689.6
9		2610.2	47	P (5)	2690.9
10		2612.7	48		2691.7
11		2615.3	49		2693.8
12		2617.8	50		2699.0
13		2620.4	51	Q	2702.46
14		2622.9	52	R (0)	2704.9
15		2625.5	53	R (1)	2707.3
16		2628.1	54	R (2)	2709.6
17		2630.4	55	R (3)	2711.8
18		2632.9	56	R (4)	2714.2
19		2635.2	57	R (5)	2716.4
20		2638.3	58	R (6)	2718.5
21		2640.2	59	R (7)	2720.7
22	Q	2643.69	60	R (8)	2723.0
23		2648.0	61	R (9)	2725.3
24		2649.9	62	R (10)	2727.5
25		2651.3	63	R (11)	2729.7
26		2652.8	64	R (12)	2731.9
27		2654.0	65	R (13)	2734.1
28	P (19)	2655.7	66	R (14)	2736.3
29		2657.6	67	R (15)	2738.5
30		2658.5	68	R (16)	2740.6
31	P (17)	2660.3	69	R (17)	2742.8
32		2662.5	70	R (18)	2744.9
33		2663.6	71	R (19)	2746.9
34		2665.0	72	R (20)	2748.9
35	P (15)	2665.9	73	R (21)	2751.2
36		2667.2	74	R (22)	2753.1
37	Q	2670.33	75	R (23)	2755.2
38		2672.1	76	R (25)	2759.0
			77	R (27)	2762.9

In this work was a parallel band at 4673.2 cm<sup>-1</sup> attributed to  $\nu_1 + \nu_4^1 + \nu_5^1$ . The Q branches at 4076.3 and 4080.86 cm<sup>-1</sup> cannot, therefore, be  $\nu_1 + \nu_4^1 + \nu_5^1 - \nu_4^1$ . The Q branch at 4061.0 cm<sup>-1</sup>, line No. 119 in Fig. 10, must be one of the difference band Q branches. The other Q branch would be expected at 4056.4 cm<sup>-1</sup>, between lines No. 117 and No. 118, and is not seen in the records. In order to accommodate these new data the

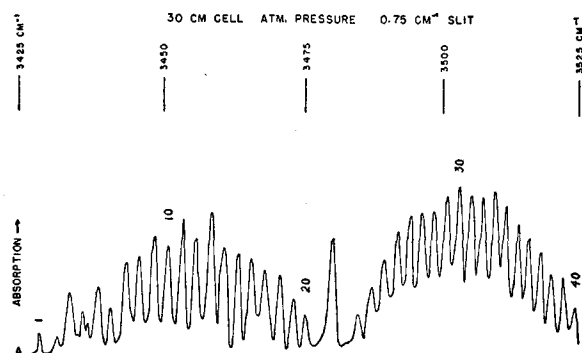


FIG. 9. The  $\nu_1 + \nu_5^1 - \nu_4^1$ -band ( $\Pi_u - \Pi_g$ ) of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Table VIII.

TABLE VIII. The  $\nu_1 + \nu_5^1 - \nu_4^1$ -band frequencies, see Fig. 9.

Line No.	$\nu_1 + \nu_5^1 - \nu_4^1$	cm <sup>-1</sup>	Line No.	$\nu_1 + \nu_5^1 - \nu_4^1$	cm <sup>-1</sup>
1	P (21)	3428.4	21	Q	3480.58
2	P (20)	3430.9	22	R (1)	3485.2
3	P (19)	3433.8	23	R (2)	3487.3
4	P (18)	3436.2	24	R (3)	3489.7
5	P (17)	3438.7	25	R (4)	3492.1
6	P (16)	3441.1	26	R (5)	3494.4
7	P (15)	3443.9	27	R (6)	3496.5
8	P (14)	3446.1	28	R (7)	3498.8
9	P (13)	3448.8	29	R (8)	3501.1
10	P (12)	3451.3	30	R (9)	3503.3
11	P (11)	3453.9	31	R (10)	3505.5
12	P (10)	3456.3	32	R (11)	3507.6
13	P (9)	3458.9	33	R (12)	3509.8
14	P (8)	3461.3	34	R (13)	3512.0
15	P (7)	3463.7	35	R (14)	3514.2
16	P (6)	3466.2	36	R (15)	3516.3
17	P (5)	3468.7	37	R (16)	3518.5
18	P (4)	3471.2	38	R (17)	3520.6
19	P (3)	3473.6	39	R (18)	3522.7
20	P (2)	3475.7	40	R (19)	3524.9

original assignments have been denoted with question marks in Tables XI and XII and the new assignment is marked by parentheses.

The extra intensity of line No. 148 at 4140.35 cm<sup>-1</sup> is attributed to Q branch of  $\nu_2 + 3\nu_5^1$ . The frequency of  $\nu_2 + 3\nu_5^1$  is, then, 4141.5 cm<sup>-1</sup>.

A summary of the bands observed is presented in Table XI. The value of  $l_4$  for states in which  $V_4 = 2$  has been labeled as zero for lack of evidence contrariwise. The centers of bands for which  $B' - B''$  are given where obtained from a combination principle. Very weak bands of questionable intensity and assignment are labeled with a "w."

## DERIVED RESULTS

The inactive infra-red fundamentals are fairly well determined by several difference bands.  $\nu_4^1$  may be found as follows: (the parentheses about a frequency combination is used to denote an observed frequency or a derived fundamental):

$$(\nu_4^1) = (\nu_3) - (\nu_3 - \nu_4^1) = 613.35 \text{ cm}^{-1}$$

$$(\nu_4^1) = (\nu_1 + \nu_5^1) - (\nu_1 + \nu_5^1 - \nu_4^1) = 613.41 \text{ cm}^{-1}$$

$$(\nu_4^1) = (\nu_2 + \nu_4^1 + \nu_5^1) - (\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1) = 613.75 \text{ cm}^{-1}$$

$$(\nu_4^1) = (\nu_5^1 + 2\nu_4^0) - (\nu_5^1 + 2\nu_4^0 - \nu_4^1) = 613.24 \text{ cm}^{-1}$$

$$(\nu_4^1) = (\nu_4^1 + \nu_5^1) - (\nu_4^1 + \nu_5^1 - \nu_4^1) = 612.69 \text{ cm}^{-1}$$

The value 613.3 cm<sup>-1</sup> has been chosen as the value of  $\nu_4^1$ , but the evidence is that  $\nu_4^1$  is slightly higher than this. The two other infra-red inactive frequencies are determined as follows:

$$(\nu_2) = (\nu_2 - \nu_5^1) + (\nu_5^1) = 1974.0 \text{ cm}^{-1}$$

and

$$(\nu_1) = (\nu_1 - \nu_5^1) + (\nu_5^1) = 3373.2 \text{ cm}^{-1}$$

The fundamental Raman frequencies are in good agreement with the frequencies given by other observers.<sup>2</sup>

TABLE IX. The  $\nu_3+\nu_4^1$ - and  $\nu_2+2\nu_4^0+\nu_5^1$ -band frequencies, see Fig. 10.

Line No.	$\nu_3+\nu_4^1$	$\nu_2+2\nu_4^0+\nu_5^1$	cm <sup>-1</sup>	Line No.	$\nu_3+\nu_4^1$	$\nu_2+2\nu_4^0+\nu_5^1$	cm <sup>-1</sup>
1		P (35)	3792.2	29		Q	3882.55
2		P (33)	3797.9	30	P (5)	R (1)	3886.8
3		P (31)	3803.6	31		R (2)	3889.8
4		P (29)	3809.1	32	P (3)	R (3)	3891.9
5		P (27)	3814.8	33	P (2)	R (4)	3894.1
6		P (26)	3817.7	34			3898.85
7		P (25)	3820.1	35	R (0)	R (7)	3901.1
8		P (24)	3822.6	36	R (1)	R (8)	3903.4
9		P (23)	3825.6	37	R (2)	R (9)	3905.7
10		P (22)	3827.3	38	R (3)	R (10)	3908.1
11		P (21)	3830.9	39	R (4)	R (11)	3910.2
12		P (20)	3833.2	40	R (5)	R (12)	3912.8
13		P (19)	3836.1	41	R (6)	R (13)	3914.7
14		P (18)	3638.7	42	R (7)		3917.0
15		P (17)	3841.3	43		R (15)	3918.7
16		P (16)	3843.4	44	R (9)		3921.7
17		P (15)	3846.3	45		R (17)	3922.8
18	P (20)	P (14)	3848.2	46	R (11)		3925.9
19	P (19)	P (13)	3851.2	47		R (19)	3927.0
20	P (18)	P (12)	3853.4	48	R (13)		3930.5
21	P (17)	P (11)	3856.2	49	R (15)		3934.1
22	P (16)	P (10)	3858.5	50	R (16)		3936.6
23	P (15)	P (9)	3861.2	51	R (17)		3938.8
24	P (13)	P (7)	3866.7	52	R (19)		3942.9
25			3868.4	53	R (20)		3944.9
26	P (11)	P (5)	3871.6	54	R (21)		3946.8
27		P (3)	3875.5	55	R (23)		3950.9
28	P (9)	P (2)	3877.8	56	R (25)		3954.8

Numerous anharmonic coefficients may be determined from these data. Table XII gives the relations used to obtain the values of some of the coefficients. Because of the inaccuracies of the measurements these anharmonic coefficients may have a large percentage

TABLE X. The  $\nu_1+\nu_5^1$ -band frequencies, see Fig. 10.

Line No.	$\nu_1+\nu_5^1$	cm <sup>-1</sup>	Line No.	$\nu_1+\nu_5^1$	cm <sup>-1</sup>
100	P (33)	4007.9	127	P (3)	4085.8
101	P (31)	4013.4	128	Q	4092.56
102	P (30)	4015.9	129	R (1)	4097.4
103	P (29)	4018.5	130	R (2)	4099.9
104	P (28)	4021.2	131	R (3)	4102.0
105	P (27)	4023.9	132	R (4)	4104.1
106	P (26)	4027.0	133	R (5)	4106.6
107	P (25)	4029.7	134	R (6)	4108.8
108	P (24)	4032.2	135	R (7)	4110.9
109	P (23)	4034.7	136	R (8)	4113.1
110	P (22)	4037.6	137	R (9)	4115.3
111	P (21)	4040.3	138	R (10)	4117.5
112	P (20)	4042.7	139	R (11)	4119.8
113	P (19)	4045.5	140	R (12)	4121.9
114	P (18)	4048.1	141	R (13)	4124.1
115	P (17)	4050.8	142	R (14)	4126.0
116	P (16)	4053.4	143	R (15)	4128.0
117	P (15)	4055.9	144	R (16)	4130.2
118	P (14)	4058.5	145	R (17)	4132.4
119	P (13)	4061.0	146	R (18)	4134.4
120	P (12)	4063.3	147	R (19)	4136.5
121	P (11)	4066.2	148	R (21)	4140.35
122	P (10)	4068.7	149	R (23)	4144.5
123	P (9)	4071.0	150	R (25)	4148.1
124	P (7)	4076.3	151	R (27)	4152.1
125	P (6)	4078.2	152	R (29)	4156.2
126	P (5)	4080.9	153	R (31)	4159.9

error. The most serious difficulty which arises from a consideration of the anharmonic constants revolves about the assignment of the  $2\nu_4^2+\nu_5^1$ -band. The upper vibration level consists of two  $\Pi_u$ -components and a  $\Phi_u$ -component. Both of the  $\Pi_u$ -components will be infra-red active in transitions from the ground state

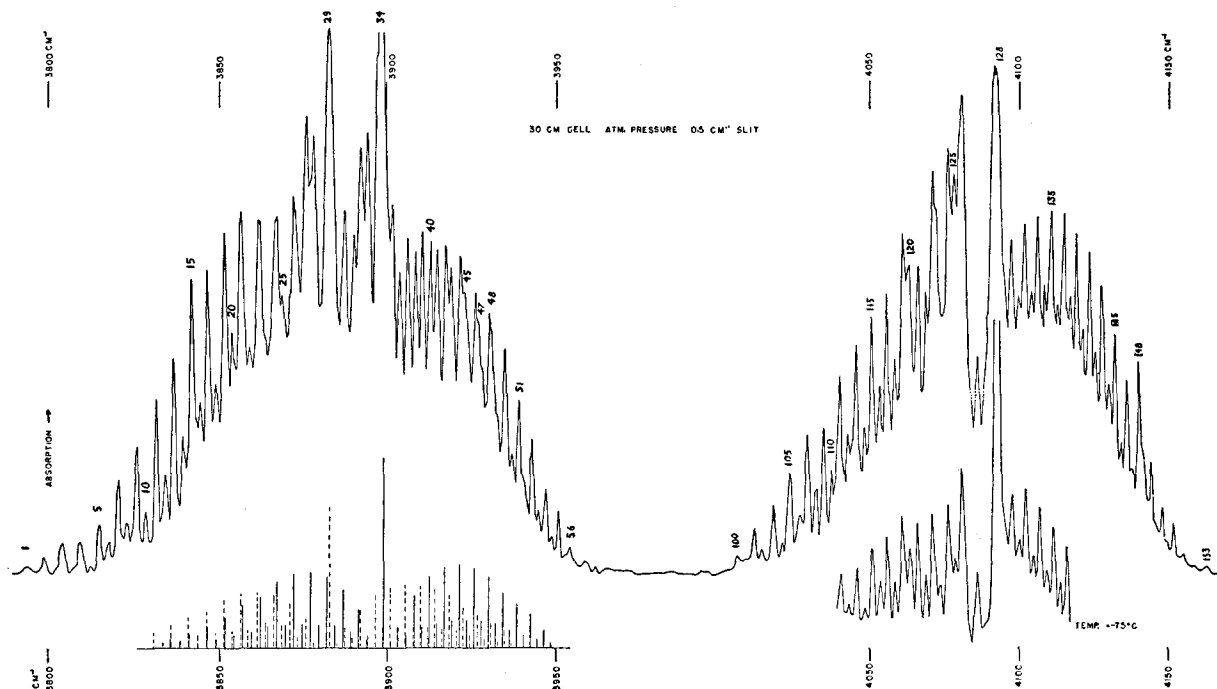


FIG. 10. The  $\nu_3+\nu_4^1$ -,  $\nu_1+2\nu_4^2+\nu_5^1$ -,  $\nu_1+\nu_4^1+\nu_5^1$ -, and  $\nu_1+\nu_5^1$ -bands of acetylene as measured with the 7500 lines per inch grating. The values of the line frequencies are given in Tables IX and X.

TABLE XI. Band assignments and frequencies.

Band	Band center cm <sup>-1</sup>	Band frequency cm <sup>-1</sup>	B' - B'' cm <sup>-1</sup> or remarks	Figure
Fundamental bands				
$\nu_4^1$	—	613.3	Derived	1
$\nu_6^1$	729.56	730.74		
$\nu_2$	—	1974.0	Derived	2
$\nu_3$	3285.5	3282.5	-0.0043	
$\nu_1$	—	3373.2	Derived	
Combination bands				
$\nu_4^1 + \nu_5^1 - \nu_4^1$	712.06(?)	715.49	$\Delta_u - \Pi_g; w$	1
$\nu_4^1 + \nu_5^1 - \nu_4^1$	716.67	715.49	$\Sigma_u^-, \Sigma_u^+ - \Pi_g$	1
$2\nu_6^0 - \nu_5^1$	720.27	719.09	w	1
$\nu_2 - \nu_5^1$	1244.5	1243.3		3
$\nu_4^1 + \nu_5^1$	1328.18	1327.18	+0.003	4
$2\nu_4^0 + \nu_5^1 - \nu_4^1$	1328.46	1328.46		4
$2\nu_4^0 + \nu_5^1$	1940.52	1941.70	+0.0032	5
$2\nu_4^2 + \nu_5^1(?)$	1960.66	1961.84		5
$3\nu_5^1$	2169.67	2170.84	+0.0020	6
$4\nu_5^0 - \nu_5^1$	2152.0	2150.8		6
$4\nu_5^2 - \nu_5^1$	2161.5	2165.0		6
$3\nu_4^1 + \nu_5^1$	2556.5	2556.5		7
$\nu_1 - \nu_5^1$	2643.69	2642.51		8
$\nu_3 - \nu_4^1$	2670.33	2669.15		8
$\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$	2683.09	2681.81		8
$\nu_2 + 2\nu_5^0 - \nu_5^1$	2691.7	2690.5	w	8
$\nu_2 + \nu_5^1$	2702.46	2703.63	-0.0079(?)	8
$\nu_2 + \nu_4^1 - \nu_4^1$	3270.9	3270.9	w	2
$\nu_2 + 2\nu_4^0 + \nu_5^1 - \nu_4^1$	3286.6	3286.6	w	2
$\nu_2 + \nu_4^1 + \nu_5^1$	3295.56	3295.56	-0.0050	2
$\nu_1 + \nu_5^1 - \nu_4^1$	3480.51	3480.51	-0.0068	9
$\nu_3 + \nu_4^1$	3882.81	3883.97	-0.0067	10
$\nu_2 + 2\nu_4^0 + \nu_5^1$	3898.81	3899.97	-0.0074	10
$\nu_1 + \nu_4^1 + \nu_5^1 - \nu_4^1(?)$	4076.3	4079.7	$\Delta_u - \Pi_g; w$	10
$\nu_1 + \nu_4^1 + \nu_5^1 - \nu_4^1(?)$	4080.86	4079.7	$\Sigma_u^-, \Sigma_u^+ - \Pi_g; w$	10
$\nu_1 + \nu_5^1$	4092.75	4093.92	-0.0078	10
$\nu_2 + 3\nu_5^1$	4140.35	4141.53	w	10
$(\nu_1 + \nu_4^1 + \nu_5^1 - \nu_4^1)$	(4061.0)	(4059.9)	$(\Sigma_u^-, \Sigma_u^+ - \Pi_g; w)$	10

and the  $\Pi_u$ -components will differ by  $2X_{44}$  cm<sup>-1</sup> in vibrational energy. One would expect, therefore, that the two strong Q branches seen in Fig. 5 might be the  $2\nu_4^0 + \nu_5^1$ , ( $\Pi_u - \Sigma_g^+$ ), at 1940.52 cm<sup>-1</sup>, and  $2\nu_4^2 + \nu_5^1$ , ( $\Pi_u - \Sigma_g^+$ ), at 1960.66-cm<sup>-1</sup>, bands with a separation  $4X_{44} = +20.14$  cm<sup>-1</sup>. The evaluation of  $4X_{44}$  from other bands gives a value of -15 cm<sup>-1</sup>. An interchange of the assignments of these two bands would give  $4X_{44} = -20.14$  cm<sup>-1</sup>. This interchange would also demand that the 1328.46-cm<sup>-1</sup> Q branch should belong to  $2\nu_4^2 + \nu_5^1 - \nu_4^1$  because the 1941.70-cm<sup>-1</sup> frequency must arise from a transition from the ground state to the upper level of the 1328.46-cm<sup>-1</sup> band. ( $\nu_4^1$  is well established by other difference bands as 613.3 cm<sup>-1</sup>, and the 1328.46-cm<sup>-1</sup> band is quite evidently a difference band with  $V_4 = 1$  in the initial state.) The result of this interchange would be an evaluation of  $4X_{44}$  from bands other than  $2\nu_4^2 + \nu_5^1$  of +7.5 cm<sup>-1</sup>. Even a  $4B$  change in the assigned value of the center of  $3\nu_4^1 + \nu_5^1$ , see Fig. 7, which

TABLE XII. Evaluation of anharmonic coefficients.

	cm <sup>-1</sup>
1: $(\nu_4^1 + \nu_5^1) - (\nu_4^1) - (\nu_5^1) = x_{45}$	-15.86
2: $(2\nu_4^0 + \nu_5^1 - \nu_4^1) - (\nu_4^1 + \nu_5^1) = x_{45} + 2x_{46} - 2X_{44}$	+0.28
3: $(3\nu_4^1 + \nu_5^1) - 3(\nu_4^1) - (\nu_5^1) = 3x_{45} + 6x_{46} - 2X_{44}$	-14.13
4: $(2\nu_4^0 + \nu_5^1) - 2(\nu_4^1) - (\nu_5^1) = 2x_{45} + 2x_{46} - 2X_{44}$	-15.63
5: $(\nu_1 + \nu_4^1 + \nu_5^1 - \nu_4^1) - (\nu_1 + \nu_5^1) = x_{14} + x_{45}$	-14.22? (-34.02)
6: $(\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1) - (\nu_2 + \nu_5^1) = x_{24} + x_{45}$	-21.82
7: $(\nu_2 + \nu_5^1) - (\nu_2) - (\nu_5^1) = x_{25}$	-1.11
8: $(\nu_1 + \nu_5^1) - (\nu_1) - (\nu_5^1) = x_{15}$	-10.02
9: $(\nu_2 + \nu_4^1) - (\nu_2) - (\nu_4^1) = x_{24}$	-11.83
10: $(\nu_2 + 3\nu_5^1) - (\nu_2 + \nu_5^1) - 2(\nu_5^1) = 2x_{25} + 6x_{55} - 2X_{55}$	-23.98
11: $(4\nu_5^0 - \nu_5^1) - (3\nu_5^1) = 6x_{55} - 2X_{55}$	-20.04
12: $(4\nu_5^2 - \nu_5^1) - (4\nu_5^0 - \nu_5^1) = 4X_{55}$	+14.2
13: $(\nu_2 + 3\nu_5^1) - (\nu_2) - (3\nu_5^1) = 3X_{25}$	-3.31
14: $(3\nu_5^1) - 3(\nu_5^1) = 6x_{55} - 2X_{55}$	-21.38
15: $(\nu_2 + \nu_4^1 + \nu_5^1) - (\nu_2) - (\nu_4^1 + \nu_5^1) = x_{24} + x_{25}$	-6.62
$x_{14} = +1.64? (-18.16)$	$x_{15} = -10.02$
$x_{24} = -5.96, -5.52$	$x_{25} = -1.1$
$x_{34} = -11.83$	$x_{45} = -15.86$
$x_{44} = +4.38$	$x_{55} = -2.17$
$X_{44} = -3.74$	$X_{55} = +3.55$

is used in this computation, would not improve the situation. The fact that only one band of the type  $2\nu_4^2 + \nu_5^1 - \nu_4^1$  appears in the 7.5 $\mu$  region, see Fig. 4, is also strange.

The interchange of the assignments of  $\nu_2$  and  $\nu_2 + \nu_4^1 + \nu_5^1$  would necessitate the interchange in the assignments of  $\nu_3 - \nu_4^1$  and  $\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$  because of the known value of  $\nu_4^1$ . The band  $\nu_2 + \nu_5^1$  seems well established, however, as the only temperature-insensitive band in the 2700-cm<sup>-1</sup> region. The resulting value of the anharmonic constant  $x_{24}$ , through relation No. 6 in Table XII, would be -18.62 cm<sup>-1</sup>. This reasonably small value for the anharmonic constant  $x_{24}$ , a likewise small value from  $x_{34}$  from relation No. 9 in Table XII, and a reasonably consistent value of  $x_{25}$  from relations Nos. 13 and 15 would not prevent an interchange of the assignments of  $\nu_3$  and  $\nu_2 + \nu_4^1 + \nu_5^1$ . The fact that  $\nu_3$  is less intense than  $\nu_2 + \nu_4^1 + \nu_5^1$ , that  $\nu_3 + \nu_4^1$  is less intense than  $\nu_2 + 2\nu_4^0 + \nu_5^1$ , and that  $\nu_3 - \nu_4^1$  is less intense than  $\nu_2 + \nu_4^1 + \nu_5^1 - \nu_4^1$  is not taken as sufficient evidence in itself to warrant an interchange of the assignments as previously given.

The value of  $B''$  as determined by the combination principles from the data in any of these bands will be poor because of the fact that all bands are more or less spoiled by the overlapping of other bands. The data from the cooled gas run, Fig. 4, curve C, were used to obtain a value  $B'' = 1.1769$  cm<sup>-1</sup>. This is in good agreement with previously obtained values. The values of  $B' - B''$  which were obtained are given in Table XI. Needless to say, we cannot place much faith in these values.

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