

¹Vibrational Constants of Acetylene-d₂

Harry C. Allen, Jr., L. R. Blaine, and Earle K. Plyler

The infrared spectrum of acetylene-d₂ has been investigated in the region from 1 to 5 microns. The new data have enabled a consistent interpretation of the 16 bands in which only the stretching modes are excited. It is shown that there is a resonance interaction present between the vibrational levels (v_1, v_2, v_3) and ($v_1 - 2, v_2, v_3 + 2$) analogous to that present in C₂H₂. The new vibrational constants enable the calculation of band centers that are in excellent agreement with the observed band centers. By combining the photographic infrared results with those obtained in this work it is found that $B_0 = 0.84770 \pm 0.00007 \text{ cm}^{-1}$ and $D = (7.04 \pm 0.63) \times 10^{-7} \text{ cm}^{-1}$.

1. Introduction

The infrared spectrum of C₂D₂ has been studied by several workers. Recently, Saksena [1]² has observed and measured 12 bands in the photographic infrared region. He obtained an excellent value of B_0 , but his efforts to evaluate vibrational constants were hampered by an insufficient knowledge of the spectrum at longer wavelengths. Subsequently, Talley and Nielsen [2] have published, in detail, their measurements on the spectrum from 500 to 7,800 cm⁻¹. These workers observed 39 bands, which were more than enough to evaluate the constants in the quadratic expression for the vibrational energy. Unfortunately, the constants they deduced do not satisfactorily account for the frequencies in the photographic region. It is believed that the difficulty arises from a second-order resonance due to the near equality of ν_1 and ν_3 , because such an effect has been found in the spectrum [3] of C₂H₂. Furthermore, a new analysis of the band, $\nu_1 - \nu_5^1$, near 2,167 cm⁻¹ places this band center one line spacing higher than the previous work [4]. As the determination of the frequency of ν_1 , which is not active in the infrared, depends directly on the frequency of this band, a new band center for this band leads to a new frequency for ν_1 . This work was undertaken in order to obtain a more complete understanding of the C₂D₂ spectrum in view of the new value obtained for ν^1 and the suspected resonance interaction.

2. Experimental Procedure

The spectra were recorded on the two grating instruments of the Radiometry Section [5, 6]. The gas was prepared by M. Hellman of the Polymer Structure Section of the Bureau. The gas contained a small amount of C₂HD (<1 percent), which was not sufficient in quantity to interfere with the observations of the C₂D₂ bands. The region 1 to 2.8 μ was scanned with a 6-m cell and a pressure of 62 cm (Hg), and the region 3 to 5 μ was scanned with a 1-m cell and 28-cm pressure (Hg). Seventeen regions of absorption were observed, and some sections contained several overlapping bands. The pressure of the gas

was varied for the different regions so that both the weak and the strong lines could be measured; the pressures in the slow-speed measurements ranged from 1 to 11 cm (Hg).

The frequencies of the rotational lines of the bands were measured by using the white-light fringes of a Fabry-Perot interferometer. The fringes served as a scale with a spacing of about 0.40 cm⁻¹. The maxima of the fringe system were determined in wavenumbers by using the wavenumbers of well-known emission lines of the noble gases. The emission lines, fringe system, and the absorption spectrum were recorded on a two-pen recorder. The absorption spectrum and the emission spectrum were detected by PbS and cooled PbTe cells, and the fringes were recorded with a 1P28 photomultiplier.

As an example of the spectrum of C₂D₂, a recorder trace on white paper was made of two regions. In figure 1 is shown the absorption band of one of the stretching vibrations, ν_3 . The band center is at 2,439.24 cm⁻¹. It is overlapped by the weaker hot band at 2,433.76 cm⁻¹. Figure 2 is the trace obtained for the combination band $\nu_2 + \nu_3$. It is overlapped by two weak bands.

3. Rotational Analysis

The bands were analyzed by first assigning J -values to the observed absorption peaks. An equation for each J -value was then obtained of the form

$$\nu = \nu_0 + (B' + B'')m + (B' - B'')m^2 + 4Dm^3, \quad (1)$$

where $m = J + 1$ for the R -branch and $m = -J$ for the P -branch. The set of equations for each band was solved by the method of least squares for the best estimates of ν_0 , B' , B'' , and D . The calculations were carried out on SEAC, the NBS electronic computer. The observed line frequencies and rotational assignments are given for several of the stronger bands in table 1. Blank spaces correspond to lines too weak to measure precisely or to lines badly overlapped by lines of hot bands or atmospheric water-vapor absorption. The results of the analyses are given in table 2. The six strong bands in the photographic infrared region are also included. These bands were reanalyzed in order to have a consistent set of anal-

¹ This work was supported by the United States Atomic Energy Commission.

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

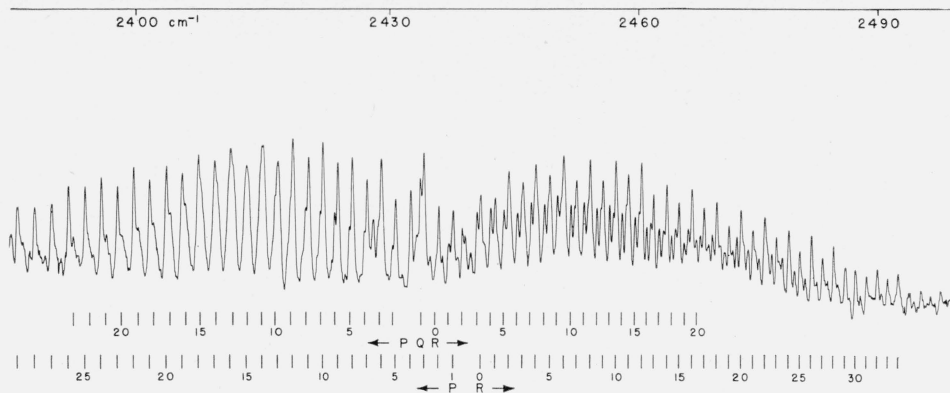


FIGURE 1. Fundamental band ν_3 of C_2D_2 .
The pressure was 4 cm (Hg), and the cell length was 1 m.

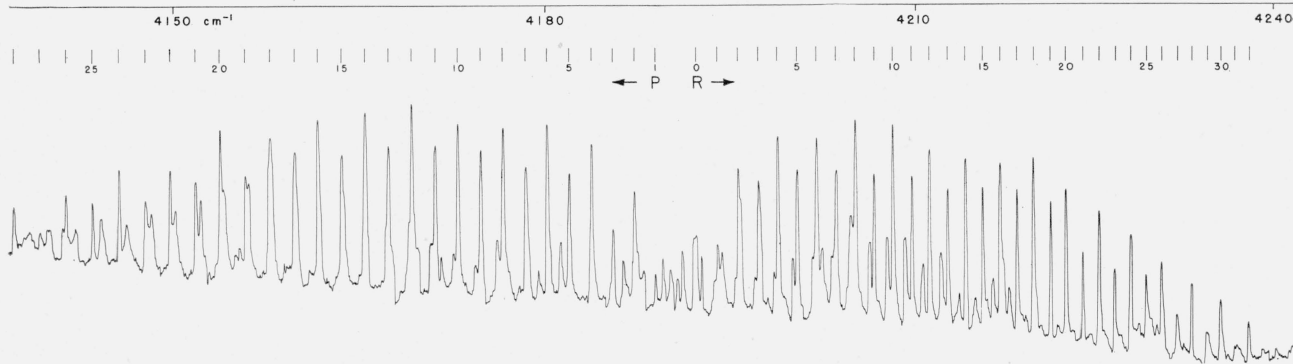


FIGURE 2. Combination band $\nu_2 + \nu_3$ of C_2D_2 .

The pressure was 11 cm (Hg), and the cell length was 6 m. Nonlabeled peaks belong to $\nu_2 + \nu_3 + \nu_4 - \nu_4'$ at 4181.22 cm^{-1} and $\nu_2 + \nu_3 + \nu_3' - \nu_3'$ at about 4187.0 cm^{-1} .

yses for a determination of B_0 and D . The B_0 and D values varied somewhat from band to band as can be seen from table 2. This variation is believed to arise from blended lines that could not be completely eliminated. The B_0 estimates were combined to get a best estimate for the constant. An average estimate was obtained by weighing each value according to the reciprocal of its estimated variance [7]. Such an averaging process gives $B_0 = 0.84770 \pm 0.00007 \text{ cm}^{-1}$ as a best estimate where the quoted uncertainty represents one standard deviation. It should be emphasized that the uncertainties quoted here and in table 2 are essentially an indication of the internal consistency of the measurements. They do not mean that the absolute frequencies of the band centers are known to the precision indicated, although the fit for the over-all spectrum would seem to indicate that the absolute frequencies are known to better than 0.1 cm^{-1} .

There is a wide spread in the individual values obtained for D . The quantity D is extremely small and such a spread is to be expected, especially since the analyses could not be extended to high J -values. An average value of D was obtained in a manner analogous to that used for B_0 , giving $D = (7.04 \pm 0.63) \times 10^{-7} \text{ cm}^{-1}$.

From the bands at $2,439 \text{ cm}^{-1}$, $4,190 \text{ cm}^{-1}$, and $6,868 \text{ cm}^{-1}$, values for α_1 , α_2 , and α_3 were determined as $0.00588 \pm 0.00003 \text{ cm}^{-1}$, $0.00316 \pm 0.00003 \text{ cm}^{-1}$, and $0.00442 \pm 0.00002 \text{ cm}^{-1}$, respectively. Unfortunately these constants do not predict the excited state inertial constants as well as those suggested by Saksena, even after the resonance correction has been applied. This is a bit puzzling because these values are apparently more reliable than his, for he did not allow for the effect of any resonance in his work, and the present values were determined from levels involving fewer quanta of excitation.

TABLE 1. Wave numbers of lines in C₂D₂ bands (cm⁻¹)

J	ν ₃ -ν ₄ ν ₀ =1928.596		ν ₁ -ν ₅ ν ₀ =2167.481		ν ₃ ν ₀ =2439.236		ν ₂ +ν ₃ ν ₀ =4190.577		ν ₁ +ν ₃ ν ₀ =5097.17		ν ₁ +ν ₂ +ν ₃ ν ₀ =6828.816	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
0	-----	-----	-----	-----	2440.87	-----	4192.12	-----	-----	-----	6829.85	-----
1	-----	-----	-----	-----	-----	-----	4193.92	-----	5100.52	5094.98	6831.54	6826.59
2	1933.59	-----	-----	-----	2444.22	-----	4195.58	4187.15	5102.15	5093.46	6833.14	6824.78
3	1935.27	-----	-----	-----	2445.92	-----	4197.23	4185.48	5103.78	5092.02	6834.65	-----
4	1936.94	1921.78	2175.78	-----	2447.58	-----	4198.83	4183.72	5105.42	5090.38	6836.29	6821.24
5	1938.56	1919.99	2177.37	-----	2449.25	-----	4200.43	-----	5106.96	5088.52	6837.80	6819.40
6	1940.18	-----	2179.04	2157.20	2450.86	-----	4201.98	4180.17	5108.49	5086.73	6839.23	6817.57
7	-----	1916.50	2180.58	2155.34	2452.46	-----	4203.58	4178.40	5110.02	5084.88	6840.80	6815.72
8	1943.38	1914.78	2182.20	2153.56	2454.10	2425.42	4205.13	4176.60	5111.54	5083.04	6842.21	6813.84
9	1945.04	1912.97	2183.76	2151.74	2455.65	2423.66	4206.67	4174.78	5112.99	5081.20	6843.66	6811.94
10	-----	1911.18	2185.30	2149.94	2457.28	2421.88	4208.22	4172.99	5114.45	5079.31	6845.02	6810.00
11	1948.16	1909.42	2186.81	2148.12	2458.90	2420.16	4209.72	-----	5115.93	5077.36	6846.41	6808.01
12	1949.73	1907.62	2188.33	2146.26	2460.44	2418.36	4211.24	4169.26	5117.37	5075.46	6847.74	6806.02
13	1951.28	1905.78	2189.94	2144.46	2462.00	2416.61	4212.72	4167.38	5118.71	5073.55	6849.00	6804.02
14	1952.84	1903.96	2191.42	2142.54	2463.58	2414.80	4214.18	4165.47	5120.09	5071.51	6850.27	6801.99
15	1954.36	1902.14	2192.86	2140.70	2465.12	2412.90	4215.61	4163.56	5121.47	5069.58	6851.61	6799.95
16	1955.91	1900.28	2194.34	2138.82	2466.69	2411.12	4217.05	4161.68	5122.84	5067.55	6852.87	6797.79
17	1957.44	-----	2195.76	2136.92	2468.23	2409.25	4218.48	4159.75	5124.13	5065.61	6854.04	6795.74
18	1958.92	-----	2197.24	2134.97	2469.74	2407.38	4219.88	4157.77	5125.44	5063.54	6855.19	6793.52
19	1960.43	1894.73	2198.74	2133.08	2471.28	2405.47	4221.26	4155.80	5126.72	5061.40	6856.36	6791.36
20	1961.91	1892.82	2200.15	2131.10	2472.80	2403.67	4222.62	4153.81	5127.97	5059.32	6857.51	6789.15
21	1963.40	1890.94	2201.56	2129.20	2474.26	2401.74	4223.99	4151.85	5129.21	5057.16	6858.58	6786.96
22	1964.84	-----	2202.96	2127.20	2475.75	2399.87	4225.32	4149.79	5130.39	5055.03	6859.67	6784.70
23	-----	1887.13	2204.36	2125.24	2477.26	2397.98	4226.68	4147.76	5131.60	5052.91	6860.70	6782.46
24	-----	-----	2205.76	2123.26	2478.70	2396.09	4227.98	4145.72	5132.74	5050.86	6861.75	6780.09
25	1969.16	1883.28	-----	2121.30	2480.17	2394.20	4229.28	4143.68	5133.87	5048.56	6862.71	6777.76
26	1970.63	1881.29	-----	2119.29	2481.64	2392.38	4230.56	4141.60	5135.03	5046.40	6863.68	6775.38
27	1972.06	1879.33	-----	2117.24	2483.07	-----	4231.83	4139.52	5136.15	5044.26	6864.62	-----
28	1973.44	-----	-----	-----	2484.49	2388.48	4233.06	4137.48	5137.23	5041.82	6865.54	6770.55
29	1974.80	-----	-----	-----	2485.95	2386.58	4234.34	4135.39	5138.25	5039.50	6866.36	6768.16
30	1976.21	-----	-----	-----	2487.28	2384.72	-----	4133.20	5139.28	5037.30	6867.27	6765.74
31	-----	-----	-----	-----	2488.70	2382.55	-----	4131.04	-----	5035.04	6868.12	6763.27
32	-----	-----	-----	-----	2490.14	2380.71	-----	-----	-----	-----	6868.85	-----
33	-----	-----	-----	-----	2491.50	-----	-----	-----	-----	-----	-----	-----

TABLE 2. Observed bands and rotational constants of C₂D₂

Observed	Upper					Lower					B ₀	B' - B''	D × 10 ⁷	B''	
	v ₁	v ₂	v ₃	l ₄	l ₅	v ₁	v ₂	v ₃	l ₄	l ₅					
cm ⁻¹															
1928.596 ± .005			1					1 ¹							0.84764 ± .00020
2167.481 ± .008	1							1 ¹							.84825 ± .00035
2433.76 ± .02			1	1 ¹											.84710 ± .00100
2439.236 ± .009			1								0.84741 ± .00034	0.00442 ± .00002	5.08 ± 2.32		
2944.49 ± .03			1	1 ¹											
3234.82 ± .02	1				1 ¹										
4190.577 ± .004		1	1					1 ¹			.84714 ± .00019	.00758 ± .00001	3.99 ± 1.50		
5083.72 ± .04	1		1	1 ¹											
5097.17 ± .02	1		1								.84830 ± .00077	.01041 ± .00004	10.40 ± 5.9		
5197.66 ± .02		1	1	1 ¹	1 ¹						.84508 ± .00099	.00131 ± .00009			
5907.64 ± .01	2										.84693 ± .00053	.01125 ± .00003			
6828.816 ± .007	1	1	1		1 ¹						.84759 ± .00029	.01346 ± .00002	9.73 ± 2.14		
7733.85 ± .02	2		1								.84405 ± .00116	.01637 ± .00008			
8550.11 ± .03 ^a	1	2	1								.84706 ± .00133	.01637 ± .00009	24.72 ± 13.52		
8952.880 ± .006 ^a		1	3								.84812 ± .00026	.01644 ± .00001	9.95 ± 2.11		
9444.517 ± .004 ^a	2	1	1								.84773 ± .00017	.01914 ± .00001	4.38 ± 1.70		
9794.069 ± .003 ^a	1	3									.84774 ± .00017	.01966 ± .00001	8.30 ± 2.76		
10347.931 ± .004 ^a	3	1									.84761 ± .00017	.02186 ± .00001	6.47 ± 1.88		
11492.666 ± .002 ^a	1	1	3								.84794 ± .00013	.022457 ± .000008	8.94 ± 1.24		

^a Data from reference [1].

4. Vibrational Analysis

The new band center of $\nu^1-\nu_5^1$, together with the previously measured value [2] of $\nu_5^1=537.81\text{ cm}^{-1}$, is sufficient to determine the infrared fundamental ν_1 as $2,705.29\text{ cm}^{-1}$. In order to obtain enough band centers to evaluate the nine constants involving only the stretching modes in the vibrational energy expression,

$$\nu_0 = \sum_{i=1}^3 \omega_i^0 \nu_i - \sum_{i=1}^3 \sum_{j \geq i}^3 X_{ij} \nu_i \nu_j + \dots, \quad (2)$$

it is necessary to use some of the bands observed in the photographic infrared. However, with one exception, these are just the bands whose excited states were suspected of having resonance interactions. The criterion for resonance is that the two energy levels have quantum numbers (ν_1, ν_2, ν_3) and $(\nu_1-2, \nu_2, \nu_3+2)$. In order to eliminate the resonance effects so the X_{ij} 's could be determined, only the average of the levels suspected of resonating were used. In this way 9 equations can be formed to evaluate the 9 constants in (2). These equations are given in table 3. A straightforward evaluation of these constants leads to the values given in table 4.

If one calculates the observed energy levels by using these constants, it is found that the levels suspected of resonating are not predicted correctly, thus confirming the presence of the resonance interaction. The results of such a calculation are given for unperturbed levels in table 5, column 3.

TABLE 3. Equations used to evaluate the vibrational constants of C_2D_2

$2705.29 = \omega_1^0 - X_{11}$.
$2439.24 = \omega_3^0 - X_{33}$.
$4190.58 = \omega_2^0 + \omega_3^0 - X_{22} - X_{33} - X_{23}$.
$5097.17 = \omega_1^0 + \omega_3^0 - X_{11} - X_{33} - X_{13}$.
$6828.82 = \omega_1^0 + \omega_2^0 + \omega_3^0 - X_{11} - X_{22} - X_{33} - X_{12} - X_{13} - X_{23}$.
$8550.11 = \omega_1^0 + 2\omega_2^0 + \omega_3^0 - X_{11} - 4X_{22} - X_{33} - 2X_{12} - X_{13} - 2X_{23}$.
$9198.70 = \omega_1^0 + \omega_2^0 + 2\omega_3^0 - 2X_{11} - X_{22} - 5X_{33} - X_{12} - X_{13} - 2X_{23}$.
$10071.00 = 2\omega_1^0 + 2\omega_3^0 - 5X_{11} - 5X_{33} - 3X_{13}$.
$11764.77 = 2\omega_1^0 + \omega_2^0 + 2\omega_3^0 - 5X_{11} - X_{22} - 5X_{33} - 2X_{12} - 3X_{13} - 2X_{23}$.

TABLE 4. Vibrational constants of C_2D_2 (cm^{-1})

$\omega_1^0 = 2717.74$	$X_{11} = 12.45$	$X_{12} = 19.64$
$\omega_2^0 = 1774.86$	$X_{22} = 5.24$	$X_{13} = 47.34$
$\omega_3^0 = 2452.14$	$X_{33} = 12.90$	$X_{23} = 18.28$
$\gamma = 23.86$ (1-0.20 ν_2)		$X_{14} = 7.97$
		$X_{15} = 8.28$
$\omega_4^0 - X_{44} - g_{44} = 510.64^a$		$X_{34} = 5.48$

^a Following G. Herzberg, Infrared and Raman spectra of polyatomic molecules (D. Van Nostrand Co., Inc., New York, N. Y., 1945). The additive constant from the rotational constant is absorbed into the g_{44} term.

The theory of this second-order resonance has been worked out adequately and is in the literature [3, 8]. It is found that the matrix element connecting the resonating levels, to a second order of approximation, is,

$$(\nu_1, \nu_2, \nu_3 | E | \nu_1-2, \nu_2, \nu_3+2) = \frac{1}{2} \gamma [\nu_1(\nu_1-1)(\nu_3+1)(\nu_3+2)]^{\frac{1}{2}}, \quad (3)$$

where to this degree of approximation, γ is a constant, which depends on the coefficients of the cubic and quartic terms in the potential-energy expansion. In the case of C_2D_2 , it is found, as was found for water vapor [9] and hydrogen cyanide [10], that γ is also a function of the vibrational quantum numbers. The presence of $\nu_2 > 0$ in a pair of resonating levels seems to have a very marked effect on γ , although pairs of levels in which $\nu_2 = 0$ seem to be accounted for by a constant γ . When more bands are available a dependence of γ on ν_1 and ν_2 will undoubtedly be found. The expression for γ given in table 4 gives the fit shown in table 5. Column 4 gives the band centers after the resonance correction has been applied to the upper-state levels. The bands with upper states that resonate are indicated by a bracket. In cases where only one-half the resonating pair has been observed, the other half has been calculated and included in the table. The fit obtained in this work is superior to either of the two previous determinations with the exception of the bands, (0,0,5) and (2,0,3). The possibility of wrong assignments is extremely unlikely. The difficulty is believed to arise from the omission of terms cubic in the vibrational quantum numbers from eq (2). For instance, a coefficient of ν_3^3 as small as 0.1 cm^{-1} would make a difference of 12.5 cm^{-1} in the calculated value of the (0,0,5) band and drastically affect the perturbed levels. With present data, it is not possible to evaluate the cubic terms in eq (2). It is felt that the excellence of the fit for other bands is sufficient justification for the inclusion of the resonance interaction.

TABLE 5. Vibrational spectrum of C_2D_2 bands involving only ν_1, ν_2 , and ν_3

Observed	Upper state $\nu_1 \nu_2 \nu_3$	Calculated	
		Unperturbed	Perturbed
cm^{-1}			
2439.24	1	1769.62	
	1 1	2439.24	
4190.58	1 1 1	2705.29	
5097.19	1 1 1	4190.58	
6828.89	1 1 1	5097.19	
	1 1 1	6828.89	
	3	[7240.32]	7236.84
7730.60	2 1 1	[7730.24]	7733.70
8550.12	1 2 1	8550.11	
8952.89	1 1 3	[8955.10]	8952.87
9444.51	2 1 1	[9442.30]	9444.53
9794.06	1 1 3	[9803.59]	9794.19
10347.92	3 1 1	[10338.39]	10347.79
	2 3	[10659.40]	10658.14
11146.0	2 2 1	[11143.88]	11145.15
11492.66	1 1 3	[11498.73]	11492.64
12036.87	3 1 1	[12030.81]	12036.90
11905.34	1 1 5	11938.20	11924.21
12344.50	2 3	12341.96	12338.61
	4 1	12921.96	
13181.9	1 2 3	13183.39	13179.93
	3 2 1	13712.75	13716.21

As a result of the analysis of several hot bands in the course of this work it is possible to evaluate some of the interaction terms in eq (2) between the stretching modes and the bending modes. For example, from ν_3 and $\nu_3 + \nu_4^1 - \nu_4^1$, X_{34} can be obtained, and from $\nu_2 + \nu_3 + \nu_4^1 - \nu_4^1$ the sum of X_{24} and X_{25} can be obtained. Likewise from ν_3 and $\nu_3 - \nu_4^1$ a value for ν_4^1 can be obtained. The interaction terms that could be determined unambiguously are given in table 4. In addition, *P*- and *R*-branch transitions were resolved for several bands involving ν_4^1 and ν_5^1 , for which only *Q*-branches were previously reported. The band centers of these bands are also listed in table 2. Only bands for which improved values could be obtained are included. It is felt that there are not enough bands, in which ν_4 and ν_5 are excited, to make it worthwhile to evaluate all the anharmonic and interaction terms at this time. It seems highly likely, as ν_4^1 and ν_5^1 are separated by only 27 cm^{-1} , that there should also be a second-order resonance between levels with quantum numbers $(\nu_1\nu_2\nu_3\nu_4\nu_5^1)$ and $(\nu_1\nu_2\nu_3\nu_4^1 + 2, \nu_5^1 - 2)$. Such an interaction, if present, cannot be found in the presently available data. Although this work accounts for a large part of the spectrum, there is still much work to be done before the spectrum is completely understood. This will have to await the precise measurement of a sufficient number of appropriate bands.

In conclusion, the authors express their appreciation to M. Hellman for preparing the compound, and to Joseph Cameron and Carroll Dannemiller for carrying out the computations on SEAC.

5. References

- [1] B. D. Saksena, *J. Chem. Phys.* **20**, 95 (1952).
- [2] R. M. Talley and A. H. Nielsen, *J. Chem. Phys.* **22**, 2030 (1954).
- [3] N. H. Nordin and R. N. H. Haslam, *Can. J. Research [A]* **26**, 279 (1948).
- [4] H. C. Allen, Jr., and E. K. Plyler, *J. Chem. Phys.* (in press).
- [5] N. Gailar and E. K. Plyler, *J. Research NBS* **48**, 392 (1952) RP2327.
- [6] E. K. Plyler, L. R. Blaine, and W. S. Connor, *J. Opt. Soc. Am.* **45**, 102 (1955).
- [7] W. G. Cochran and S. P. Carroll, *Biometrics* **9**, 447 (1953).
- [8] B. T. Darling and D. M. Dennison, *Phy. Rev.* **57**, 128 (1940).
- [9] W. S. Benedict and E. K. Plyler (private communication).
- [10] H. C. Allen, Jr., E. D. Tidwell, and E. K. Plyler, *J. Chem. Phys.* (in press).

WASHINGTON, December 12, 1955.