[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Infrared Spectrum of Acetylene-d_1[1]

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The vibrational–rotational spectrum of acetylene-d_1 has been observed and measured from 1800 to 9200 cm.$^{-1}$ Rotational structure sufficient to enable an analysis was found for 28 bands. From the average combination-difference values of the 14 best bands the rotational constants were found to be, $B_0 = 0.99169 \pm 0.00015$ cm.$^{-1}$ and $D_0 = 1.08 \pm 0.26 \times 10^{-6}$ cm.$^{-1}$ The vibrational energy system is fully discussed. It is pointed out that the vibrational energy levels cannot be fit by the usual quadratic expansion of the energy in terms of the vibrational quantum numbers. Evidence is presented to show that at least cubic terms must be included in the expansion.

Introduction

Although the infrared spectra of acetylene and acetylene-d_2 have been extensively investigated under high resolution,[2-6] no high resolution work has been reported on the partially deuterated species in the non-photographic infrared. The vibrational energy systems of C_2H_2 and C_2D_2 are still not well understood in spite of the extensive work. Since C_2HD is less symmetric, there are no vibrational transitions which are forbidden by symmetry and hence there is a better chance to observe enough bands to enable an understanding of its energy system and perhaps furnish some clues which will help unravel the other two molecules. The spectrum of C_2HD has been observed from 1800 to 9200 cm.$^{-1}$. In this region 28 bands were observed for which rotational analyses could be made. In addition several Q branches were measured for which the P and R branch absorption was too weak to be observed.

Experimental

In the spectral region from 1 to 5.5 μ, there have been observed 28 bands of C_2HD for which the centers have been determined. These bands varied considerably in intensity and the measurements were made on the gas in two cells of 1 m. and 10 m. in length and at pressures from a few millimeters to 76 cm. (Hg).

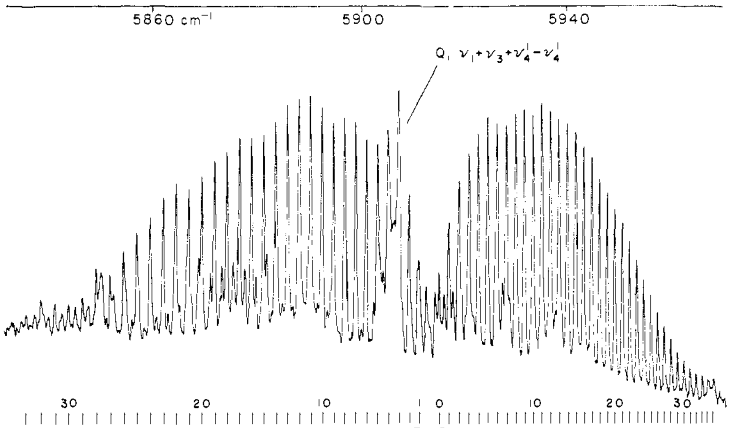

Fig. 1.—The $\nu_1 + \nu_3$ and the $\nu_1 + \nu_3 + \nu_4^1 - \nu_4^1$ bands of C_2HD in the region of 5900 cm.$^{-1}$. The rotational quantum numbers are given below the trace for the $\nu_1 + \nu_2 + \nu_4^1$ band. A ten meter cell with a pressure of 16 cm. (Hg) of C_2HD was used for this region.

Two instruments were used in obtaining the data. One instrument employs a grating of 15,000 lines/in. and a PbS detector. Other details of this spectrometer have been previously published.[7] The second instrument contained a 7500 lines/in. grating and a cooled PbTe cell and it was used for the observations in the region from 3 to 5.5 μ. A detailed description of this instrument has been reported.[8]

The rotational lines were measured by comparison with the fringe system from a Fabry–Perot interferometer. The absorption spectrum and the fringe system were recorded simultaneously on a two-pen recorder. The fringe system was calibrated by superimposing well known spectral lines on the chart at intervals throughout the band. This method of measurement is well suited for high precision measurements. When bands are not seriously overlapped by other bands (hot bands and isotopic bands) the band centers can be determined to a few hundredths of a wave number.

The C_2HD gas was made by Dr. Hellman of this Bureau. The gas was analyzed by a mass spectrometer and showed 16.8% C_2H_2, 47.8% C_2HD and 35.4% C_2D_2. The spectra of the three components caused serious overlapping only in the region of 6600 cm.$^{-1}$.

The results obtained in two regions of the spectrum are shown in Figs. 1 and 2. White recorder paper was used so that photographs could be made of the actual tracing from the instrument. Figure 1 shows the bands $\nu_1 + \nu_3$ and $\nu_1 + \nu_3 + \nu_4^1 - \nu_4^1$ in the region of 5900 cm.$^{-1}$. Figure 2 is the observed trace for the region 2580 and shows the three bands ν_3, $\nu_3 + \nu_4^1 - \nu_4^1$, and $\nu_3 + \nu_5^1 - \nu_5^1$.

Rotational Analysis.—The bands were analyzed by first assigning J values to the observed absorption peaks. An equation for each J value in a given band 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 to obtain values for ν_0, B', B'' and D. The least squares reductions were carried out on SEAC, the NBS electronic computer. The observed absorption frequencies and rotational assignments for several of the stronger bands are given in Table I.

The value of B_0 varied somewhat from band to band. This is believed to be due to the influence of overlapping hot bands. In order to get a best value

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(1) The work reported herein was supported by the U. S. Atomic Energy Commission.

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TABLE I

OBSERVED FREQUENCIES AND ROTATIONAL ASSIGNMENTS FOR SEVERAL C_2HD BANDS

	$\nu_2 = 1853.75$		$\nu_3 = 2583.638$		$\nu_1 = 3335.58$		$\nu_1 + \nu_5^1 = 3995.777$		$\nu_2 + \nu_3 = 4415.882$	
	R	P	R	P	R	P	R	P	R	P
0	1855.775		2585.575		3337.40		3997.72		4417.86	
1	1857.737	1851.807	2587.542	2581.747	3339.37	3333.54	3999.69		4419.75	4413.89
2	1859.674	1849.807	2589.492	2579.688	3341.39	3331.43	4001.68		4421.68	4411.89
3	1861.597		2591.426	2577.678	3343.24	3329.64	4003.61	3989.81	4423.60	4409.85
4	1863.570		2593.344	2575.639	3345.27	3327.64	4005.55	3987.78	4425.51	4407.80
5	1865.500		2595.234	2573.581	3347.32	3325.68	4007.49	3985.75	4427.35	4405.70
6	1867.486	1841.773	2597.128	2571.542+	3349.05	3323.53	4009.35	3983.72	4429.15	4403.64
7		1839.731	2598.996	2569.517+	3351.11	3321.55	4011.26	3981.65	4430.99	4401.52
8	1871.258	1837.687	2600.898	2567.380	3352.99	3319.50	4013.15	3979.63	4432.75	4399.39
9	1873.163	1835.646	2602.735	2565.297	3354.87	3317.48	4015.03	3977.52	4434.51	4397.26
10	1875.051	1833.573	2604.561	2563.214	3356.83	3315.38	4016.91	3975.48	4436.27	4395.05
11	1876.924	1831.491	2606.379	2561.048	3358.55	3313.31	4018.76	3973.39	4437.96	4392.87
12	1878.789		2608.222	2558.976	3360.31	3311.20	4020.59	3971.32	4439.70	4390.65
13	1880.654	1826.351	2610.037	2556.816	3362.30	3309.08	4022.45	3969.22	4441.35	4388.43
14	1882.515		2611.814	2554.682	3364.23	3307.08	4024.28	3967.11	4443.00	4386.12
15	1884.352	1823.143	2613.527	2552.497	3365.99	3304.92	4026.11	3965.18	4444.65	4383.81
16		1821.047	2615.298	2550.286	3367.89	3302.77	4027.96		4446.24	4381.57
17			2617.000	2548.092	3369.65	3300.55	4029.75	3960.67	4447.83	4379.21
18			2618.720		3371.43	3298.46	4031.56	3958.52	4449.38	4376.85
19	1891.607	1814.654	2620.452	2543.633	3373.26	3296.37		3956.40	4450.91	4374.48
20	1893.413	1812.497	2622.141	2541.426+	3374.97	3294.17	4035.06	3954.20	4452.45	4372.11
21			2623.831	2539.242	3376.78	3292.01	4036.80	3952.00	4453.93	4369.74
22	1896.974	1808.22	2625.496	2536.933	3378.52	3289.92	4038.54	3949.86	4455.41	4367.27
23	1898.739	1806.046	2627.157	2534.633	3380.26	3287.71	4040.24		4456.88	4364.82
24	1900.500	1803.869	2628.786	2532.436	3381.94	3285.42	4041.99	3945.40	4458.36	4362.34
25	1902.252	1801.679	2630.420	2530.106	3383.68	3283.08	4043.70		4459.72	4359.82
26	1903.996		2632.035	2527.797	3385.45	3280.75	4045.40		4461.10	4357.32
27	1905.745		2633.652	2525.480	3387.14		4047.06		4462.49	4354.76
28	1907.517		2635.181	2523.186	3388.78		4048.70		4463.79	4352,14
29	1909.182		2636.707	2520.851					4465.16	4349.61
30	1910.872		2638.360	2518.462					4466.46	
31	1912.589		2639.916	2516.048	3393.80				4467.70	4344 .35
32	1914.253		2641.405	2513.679	3395.47				4468.93	
33	1915.248			2511.296					4470.08	
34				2508.828	3398.74				4471.37	
35				2506.430	3400.36					
36				2503.996	3402.00					
37				2501.556						

TABLE I (*Continued*)

J	$\nu_1 + \nu_5^0 = 4643.244$		$\nu_2 + \nu_3 + \nu_4 = 4915.719$		$2\nu_3 = 5123.114$		$\nu_1 + \nu_2 + \nu_5^1 = 5795.014$	
	R	*P*	*R*	*P*	*R*	*P*	*R*	*P*
0					5125.08			
1		4641.22			5126.96	5121.15	5798.93	
2	4649.12	4639.23			5128.92	5119.12	5800.83	
3	4651.13	4637.30	4923.63		5130.74		5802.69+	
4	4653.08	4635.32	4925.41	4907.73		5114.98	5804.51	5786.87
5	4655.02	4633.23	4927.22	4905.75	5134.48	5113.01+	5806.31	5784.73
6	4657.06	4631.24	4929.06	4903.55	5136.22	5110.82	5808.12	5782.73
7	4658.96	4629.26	4930.97	4901.47	5138.00	5108.59	5809.87	5780.58
8	4660.92	4627.27	4932.83		5139.75	5106.56	5811.62	5778.42
9	4662.86	4625.27	4934.49	4897.33	5141.48	5104.32	5813.34	5776.20
10	4664.79	4623.23	4936.32	4895.02	5143.20	5102.13	5815.02	5773.94
11	4666.66+	4621.23	4938.00	4892.89	5144.84	5099.76	5816.63	5771.73
12	4668.68	4619.19	4939.66	4890.62	5146.46	5097.63	5818.28	5769.41
13	4670.60	4617.15	4941.34	4888.31	5148.08	5095.22	5819.88	5767.14
14	4672.52	4615.16	4943.01	4886.18	5149.65	5092.89	5821.47	5764.79
15	4674.46	4613.11	4944.63	4883.89	5151.18	5090.44	5823.00	5762.40
16	4676.34	4611.09	4946.37	4881.62	5152.68	5088.22	5824.50	5759.98
17	4678.26	4609.01	4948.00	4879.40	5154.19	5085.83	5825.94	5757.59
18	4680.14	4606.99		4877.01		5083.27	5827.46	5755.19
19	4682.04	4604.93	4952.56	4874.48	5157.04	5080.96	5828.81	5752.70
20	4683.91	4602.93	4954.14	4871.79	5158.49	5078.40		
21	4685.75	4600.81			5159.98	5075.92		
22	4687.68	4598.74			5161.30	5073.38		
23	4689.56	4596.65			5162.64			
24		4594.53			5163.98	5068.16		
25					5165.18+	5065.64		
26					5166.42	5062.92		
27					5167.64+	5060.16		
28					5168.89+	5057.49		
29					5170.09	5054.91		
30					5171.12	5052.16		
31					5172.28			
32								
33					5174.40			
34					5175.46			

TABLE I (*Concluded*)

J	$\nu_1 + \nu_3 = 5913.312$		$2\nu_1 = 6569.36$		$3\nu_3 = 7620.34$		$2\nu_1 + \nu_2 = 8409.18$		$2\nu_1 + \nu_3 = 9139.02$	
	R	P	R	P	R	P	R	P	R	P
0	5915.26		6571.40+		7622.39		8411.08			
1	5918.20	5911.30	6573.32	6567.46	7624.10		8413.08	8407.27	9142.91	9136.92
2	5919.10	5909.33	6575.18	6565.52	7625.92	7616.32	8414.84	8405.17	9144.72	9135.10
3	5921.08	5907.31	6577.10	6563.38	7627.79	7614.16	8416.83	8403.10	9146.63	9133.06
4	5922.93	5905.30	6578.92	6561.25	7629.66	7612.14	8418.81	8400.99	9148.50	9130.76+
5	5924.72	5903.18	6580.73	6559.19	7631.36	7609.98	8420.56	8398.99	9150.22	9128.78
6	5926.54	5901.06	6582.68+	6557.10	7633.18	7607.88	8422.36	8396.83	9152.06	9126.64
7	5928.36	5898.98		6554.97	7634.85+	7605.59	8424.08	8394.68	9153.74	9124.42
8	5930.18	5896.83	6586.13	6552.79	7636.41	7603.34	8425.79	8392.51	9155.47	9122.29
9	5931.88	5894.64	6587.83	6550.60	7637.94	7601.00	8427.53	8390.27	9157.03	9120.04
10	5933.60	5892.46	6589.54	6548.34	7639.64+	7598.70	8429.19	8388.04	9158.70	9117.70
11	5935.31	5890.24	6591.26	6546.14	7641.06	7596.35	8430.85	8385.87	9160.31	9115.44
12	5936.98	5887.98	6592.93	6543.94	7642.54	7593.90	8432.45	8383.57	9161.83	9113.14
13	5938.66	5885.78		6541.78	7644.01+	7591.49	8434.05	8381.21	9163.37	9110.72
14	5940.29	5883.47	6596.18	6539.41	7645.18	7588.93	8435.62	8378.82+	9164.87	9108.35
15	5941.95	5881.19	6597.70	6536.91	7646.58	7586.39	8437.11	8376.49	9166.34	9105.88
16	5943.50	5878.82	6599.27	6534.48	7647.83	7583.76	8438.65	8374.11	9167.82	9103.39
17	5945.07	5876.50	6600.82	6532.21	7649.13	7581.10	8440.07	8371.70	9169.10+	9100.98
18	5946.60	5874.14	6602.32	6529.83	7650.29	7578.51		8369.19+	9170.51	9098.54
19	5948.14+	5871.70	6603.78	6527.50	7651.54	7575.76	8442.97	8366.73	9171.85	9095.88
20	5949.66	5869.33	6605.20	6525.12		7573.08	8444.47	8364.27	9173.08	9093.28
21	5951.11	5866.83		6522.68+		7570.18+	8445.83	8361.67		9090.73
22	5952.58	5864.40	6608.06	6520.25		7567.42	8447.19	8359.13+		
23	5954.01	5861.97	6609.54				8448.17			9085.17
24	5955.36	5859.47		6515.72			8449.72	8354.00		9082.52
25	5956.77	5856.93	6612.24	6512.58			8450.90	8351.37		9079.87
26	5958.11	5854.44	6613.53	6509.87				8348.16		9077.30
27	5959.44	5851.81	6614.90	6507.36				8345.95		
28	5960.79	5849.24	6616.12	6504.63				8343.16		
29	5962.04	5846.64								
30	5963.32	5843.94								
31	5964.57	5841.36								
32	5965.78	5838.72								
33	5966.94	5835.97								
34	5968.15	5833.22								

+ Overlapped or very weak lines.

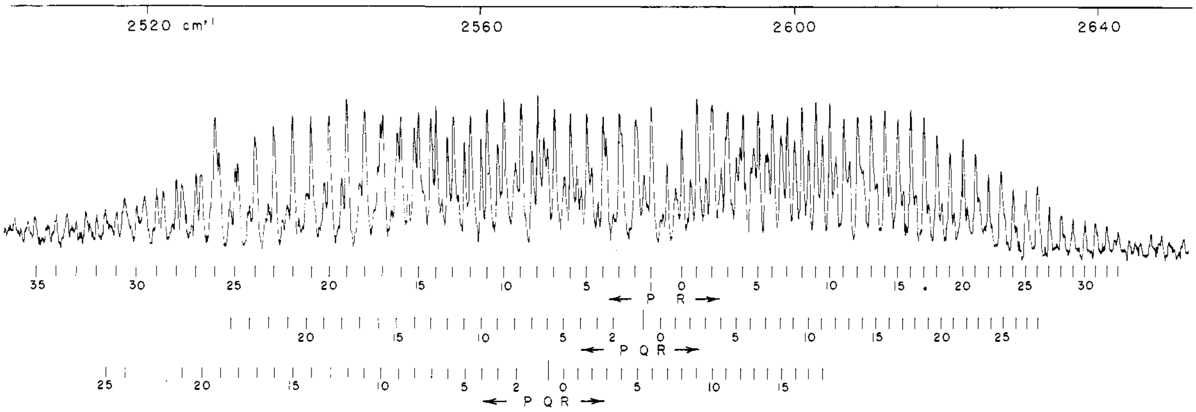

Fig. 2.—The ν_3, $\nu_3 + \nu_4^1 - \nu_4^1$ and $\nu_3 + \nu_5^1 - \nu_5^1$ bands of C_2HD in the region of 2580 cm.⁻¹. The rotational quantum numbers for ν_3 are marked below the spectrum. A one meter cell with a pressure of 1.5 cm. (Hg) was used for observing this band.

TABLE II

INFRARED SPECTRUM OF C_2HD

$\nu_0 + B'l'^2 + B''l''^2$	Upper v_1	Upper v_2	Upper v_3	Upper v_4^1	Upper v_5^1	Lower v_1	Lower v_2	Lower v_3	Lower v_4^1	Lower v_5	$(B' - B'')$ obsd.	$(B' - B'')$ calcd.
1200.63				1^1	1^1						0.0050	
1850.177											.00432	
1852.46		1			1^1					1^1	.0038	0.0042
1853.75		1									.00422	0.00422
2065.24			1						1^1		.00699	
2568.29			1	1^1					1^1		.00645	0.00670
2580.81			1		1^1					1^1	.00677	0.00670
2583.638			1								.00670	0.00670
3086.61			1	1^1							.00614	
3335.58	1										.00480	0.00480
3995.777	1				1^1						.00508	
4362.11	1			2^0							.00128	
4385.76		2			1^1						.0003	
4397.47		1	1	1^1					1^1		.0108	0.0109
4415.882		1	1								.01091	0.01092
4513.57	1			1^1	1^1						.00092	
4643.244	1				2^0						.00198	
4915.719		1	1	1^1							.00941	
5123.114			2								.01338	0.01340
5610.03			2	1^1							.01390	
5795.014	1	1			1^1						.01372	
5894.15	1		1	1^1					1^1		.0113	0.0115
5913.312	1		1								.01143	.01150
6564.24	2				1^1					1^1	.0119	.0960
6569.36	2										.01221	.0960
6932.20		1	2								.01755	.01762
7620.34			3								.02016	.02010
8409.18	2	1									.01386	.01382
9139.02	2		1								.01617	.01630

$B_0 = 0.99169 \pm 0.00015$ cm.⁻¹
$D_0 = 1.08 \pm 0.26 \times 10^{-6}$ cm.⁻¹

for B_0, use was made of the combination difference relation

$$\Delta F_2'' = R(J - 1) - P(J + 1) = 4B''(J + {}^1/_2) + 8D''(J + {}^1/_2)^3 \quad (2)$$

The ΔF_2 values were obtained by averaging the ΔF_2 values of the 14 best bands. These equations were then solved by the method of least squares. The values of the rotational constants obtained in this manner are, $B_0 = 0.99169 \pm 0.00015$ cm.⁻¹ and $D_0 = 1.08 \pm 0.26 \times 10^{-6}$ cm.⁻¹. The values of ν_0 and $B' - B''$ obtained from the solutions of eq. 1 are given in Table II. From the analyses of ν_1, ν_2 and ν_3 one obtains directly values of α_1, α_2 and α_3 in the expansion of the inertial constants in terms of the vibrational constants

$$B_v = B_e + \sum_{i=1}^{5} \alpha_i(V_i + {}^{d_i}/_2) \quad (3)$$

The values of the constants are $\alpha_1 = 0.00480$ cm.⁻¹, $\alpha_2 = 0.00422$ and $\alpha_3 = 0.00670$. These values can be checked by calculating B_v for the states in which only v_1, v_2 and v_3 are greater than zero. This has been done and the results are included in the last column of Table II. It is readily seen that the agreement is excellent in all cases except $2\nu_1$ at 6569.36 cm.$^{-1}$. The reason for this is not immediately apparent. As we shall see later this band is also a misfit in the vibrational analysis. The B_e value cannot be determined until adequate values of α_4 and α_5 are obtained. These values cannot be obtained from the present work since no Q-branches were resolved and no l-type doubling was observed. However B_0 values have been determined in this Laboratory for C_2H_2 and C_2D_2 as well as C_2HD. The values were determined from the average ΔF_2 values of many bands and a least squares reduction of the data. The results are tabulated in Table III along with the bond distances which one can calculate from these inertial constants.

TABLE III

MOLECULAR CONSTANTS OF ACETYLENE[a]

	B_0, cm.$^{-1}$	
C_2H_2	1.17627 ± 0.00016	
C_2HD	0.99169 ± 0.00015	
C_2D_2	0.84788 ± 0.00009	
B_0's used	r_{CH}, Å.	$r_{C\equiv C}$, Å.
C_2H_2 and C_2HD	1.054	1.210
C_2H_2 and C_2D_2	1.056	1.209
C_2HD and C_2D_2	1.055	1.210
Av.	1.055	1.210

[a] The atomic constants used are taken from the recent work of J. A. Bearden and John S. Thomsen "A Survey of Atomic Constants," a report prepared for Bureau of Ordnance, U. S. Navy, 1955.

Vibrational Analysis.—The vibrational energy levels of a molecule are usually expanded in terms of the vibrational quantum numbers in an equation of the form

$$E_v - E_0 = \sum_i \omega_i V_i - \sum_{i,k \geq i} X_{ik} V_i V_k - \sum_{ijk} Y_{ijk} V_i V_j V_k + \ldots \quad (4)$$

In most spectra studied so far, it has been sufficient to neglect terms above those quadratic in the vibrational quantum numbers. For C_2HD this approximation seems to be inadequate. Consider ν_1 and its overtones as is done in Table IV. The first, second and third differences are tabulated. If this series could be represented adequately by a quadratic expression, the second differences would be equal. If this series could be adequately represented by a cubic expression, the third differences would be equal. Clearly neither of these conditions is fulfilled. However if $2\nu_2$ were about 1 cm.$^{-1}$ higher, then the third differences could be equal and a cubic expression would suffice. The C_2HD band at 6569 is badly overlapped by both C_2H_2 and C_2D_2 as well as hot bands of C_2HD. It is conceivable that the analysis here is in error, which would help straighten things out. One can also consider the series $n\nu_1 + \nu_3$ as is done in the second group of Table IV. Again we clearly see that a quadratic term is not adequate. However if one uses the $\Delta_3\nu$ to calculate y_{111}, a set of constants ω_1^0, X_{11} and Y_{111} can be obtained which faithfully calculates the series $n\nu_1$ except for $n = 2$ which it predicts about 1 cm.$^{-1}$ higher than it is observed. Further, if cubic cross terms were not important, then the $\Delta_2\nu$ values for the two series should be equal, a condition which, again, is not fulfilled.

TABLE IV

TABLE SHOWING BAND SERIES REGULARITIES

$v_1v_2v_3v_4^lv_5^l$	ν, cm.$^{-1}$	$\Delta\nu$	$\Delta_2\nu$	$\Delta_3\nu$
00000	0			
		3335.58		
10000	3335.58		101.80	
		3233.78		5.06
20000	6569.36		96.74	
		3137.04		0.10
30000	9706.4		96.64	
		3040.40		
40000	12746.8			
00100	2583.64			
		3329.67		
10100	5913.31		103.96	
		3225.71		2.23
20100	9139.02		101.73	
		3123.98		
30100	12263.0			
00000	0			
		2583.64		
00100	2583.64		44.21	
		2539.43		2.07
00200	5123.07		42.14	
		2497.29		
00300	7620.34			
01000	1853.75			
		2562.13		
01100	4415.88		45.81	
		2516.32		2.08
01200	6932.20		43.72	
		2472.60		
01300	9404.8			

As further evidence the data and differences for the two series $n\nu_3$ and $\nu_2 + n\nu_3$ are also given in Table II. These series cannot be followed to sufficiently high values of v_3 to determine whether or not the third differences are constant. Certainly the third differences are the same for each series, hence an unambiguous value of Y_{333} can be determined. Again the respective values of $\Delta_2\nu$ in the two series are not equal indicating a sizable contribution from such terms as Y_{112} and Y_{122}. This evidence points quite conclusively to the fact that at least terms cubic in the vibrational quantum numbers are necessary to represent the vibrational energy levels. Several constants have been determined and are given in Table V.

TABLE V

VIBRATIONAL CONSTANTS OF C_2HD

$\omega_1^\circ = 3386.92$ cm.$^{-1}$ $X_{11} = 51.77$ $Y_{111} = -0.43$

$\omega_3^\circ = 2606.45$ $X_{33} = 23.16$ $Y_{333} = -0.35$

$X_{23} + Y_{223} = 20.71$ $Y_{233} = 0.80$

$X_{13} + Y_{133} = 4.35$ $Y_{113} = 1.56$

Constants from levels in which all $v_i < 2$

$X_{23} = 21.51$ cm.$^{-1}$ $X_{24} = 3.16$ $X_{34} = 15.26$

$\nu^1_4 = 518.26$ cm.$^{-1}$

One might suggest a resonance phenomenon as the reason for this unexpected situation. It is felt that this is ruled out by the regularities observed in the second and third differences in Table III. Even a small resonance interaction would introduce serious irregularities. It is possible that $2\nu_1$ may be displaced due to some local resonance interaction, but the other resonating level is not obvious. If the transition involving the other level is normally too weak to be seen, one would expect it to borrow intensity enough from $2\nu_1$ to be seen, for $2\nu_1$ is a rather strong band.

Using levels in which no normal mode is excited by more than one quantum of energy, it is possible to evaluate, in several ways, what appear to be constants in a quadratic energy expression. In the light of the information in Table III this is fortuitous. Since no level was excited by $v > 1$, the resulting constants are probably combinations of X_{ij}'s and Y_{ijk}'s. Constants which can be evaluated in this way are given in Table IV where the designation used is that appropriate to a quadratic equation.

A final piece of information which can be deduced is the band center of ν_4^1. This can be determined three different ways: ν_3 and $\nu_3 - \nu_4^0$, $\nu_2 + \nu_3 + \nu_4^1$ and $\nu_2 + \nu_3 + \nu_4^1 - \nu_4^1$, and $\nu_3 + \nu_4^1$ and $\nu_3 + \nu_4^1 - \nu_4$. The values obtained for ν_4^1 are 518.40, 518.25 and 518.32 cm.$^{-1}$. Since there is no reason to prefer any one of these values, the average 518.31 cm.$^{-1}$ should represent the band center satisfactorily. The poor agreement can be explained by the fact that these values were deduced from hot bands which were badly overlapped by a strong C_2HD band. Hence the band centers may be in error as much as 0.1 cm.$^{-1}$.

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Dipole Moments and Structures of Two Heteropolar Cyanine Dye Molecules[1,2]

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The molecular dipole moments of two cyanine dyes have been measured in very dilute solutions in dioxane. Comparison of the observed moment values 9.8 and 13.3 × 10^{-18} with those calculated for the possible resonating structures indicates that a full, or nearly full, electronic charge is carried by the acidic radical of the molecule, while an equal positive charge is equally divided between the nitrogens of the two basic nuclei.

Dipole moment measurements carried out in the Frick Laboratory have been used,[3,4] in conjunction with absorption data in the visible region, to help clarify the resonance conditions in various non-ionized dyes. A long series of papers by Brooker and colleagues dealing with these molecules is listed in reference 4. Two new dyes are of particular interest because of their possibly large polarities. The two compounds are 1,3-bis-(2-methoxyethyl)-5-[bis-1,3-(3-ethyl-2-benzothiazolinylidene)-2-propylidene]-barbituric acid and 1,3-diethyl-5-[bis-1,3-(3-ethyl-2-benzothiazolinylidene)-2-propylidene]-2-thiobarbituric acid, both belonging to the group of dyes known as the holopolar cyanines.[5] They will hereafter be referred to as I and II, respectively.

Experimental

The dipole moments were measured in dioxane solutions at 30°. "Practical" 1,4-dioxane from the Carbide and Carbon Chemicals Corporation was refluxed overnight with sodium and then fractionally distilled as needed. The fraction used boiled at 101.2–101.3° at 758.0 mm. and had a dielectric constant of 2.2005 ± 0.0002 at 30°. Dioxane was chosen as solvent because of the greater solubility of the dyes in this medium than in benzene.

Because of the very slow rate of solution of the dyes, heat was used to dissolve the solids. In the more concentrated solutions, which were evidently supersaturated, the solids recrystallized after two days, so that measurements were carried out as soon as possible after the solutions were prepared.

The dielectric constants of the solutions were measured with a heterodyne-beat apparatus as described elsewhere.[3,6] The dielectric cell was similar to that previously described[7] with one modification. Filaments of lead glass (Corning No. 8871) instead of mica strips were used as spacing material between the concentric condenser plates, the glass being fused to the platinum in a high temperature oven.[8] This construction gave added stability to the cell and thus an invariable cell constant.

Because of the low solubilities of the dyes (range of mole fractions used: I, (0.5–1.5) × 10^{-4}; II, (1.2–4.4) × 10^{-5}), it was considered unprofitable to measure the densities of the more dilute solutions. Consequently, the density of only the most concentrated solution was measured in each case, with an Ostwald–Sprengel pycnometer, and a linear dependence of specific volume v_{12} on the mole fraction c_2 was assumed. The values of the slopes β' in the equation

$$v_{12} = v_1 + \beta' c_2$$

were then calculated from the specific volumes of the pure solvent and the most concentrated solution. The effect of

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[2] This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[8] The cell was constructed by Mr. B. B. Howard of the Frick Laboratory.