

## The Infra-Red Spectrum of Heavy Water Vapor

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The vibration-rotation bands  $\nu_2$  and  $\nu_3$  in the heavy water vapor ( $D_2O$ ) spectrum have been remeasured. An analysis of the rotational structure has been carried out. From the interpretation of the data the values of the normal frequencies have been determined as well as the values of the reciprocals of inertia effective in these two vibration states. The frequency  $\nu_2$  is found to be  $1178.30\text{ cm}^{-1}$ , and the frequency  $\nu_3$ ,  $2787.23\text{ cm}^{-1}$ . For the state  $\nu_2$  the effective reciprocals of inertia are  $A(V)=16.60\text{ cm}^{-1}$ ,  $B(V)=7.35\text{ cm}^{-1}$ ,  $C(V)=4.84\text{ cm}^{-1}$ . For the state  $\nu_3$ ,  $A(V)=14.88\text{ cm}^{-1}$ ,  $B(V)=7.24\text{ cm}^{-1}$ ,  $C(V)=4.84\text{ cm}^{-1}$ .

### I. INTRODUCTION

THE vibration-rotation spectrum of water vapor has probably been studied more extensively than that of any other molecule. The fine structure is quite extensive since the moments of inertia are small and the rotational energies large. The rotational structure is, moreover, quite irregular since no two moments of inertia of the molecule are equal and thus the molecule is an asymmetric rotator. The spectrum of heavy water vapor is equally as extensive as that of ordinary water vapor. The band centers of the vibration-rotation bands occur at somewhat lower frequencies than the corresponding water vapor bands, however, because the reduced masses of the molecule are increased by the substitution of deuterium for hydrogen.

The far infra-red spectrum of heavy water vapor ( $D_2O$ ), corresponding to transitions between the rotational energy levels only, has been measured by Fuson, Randall and Dennison<sup>1</sup> and term values have been assigned. Two of the fundamental vibration-rotation bands,  $\nu_2$  and  $\nu_3$ , have been measured by Barker and Sleator.<sup>2</sup> Their resolution of the lines was not good enough to enable them to make any analysis of the rotational structure beyond the identification of a few lines in the band  $\nu_2$ . The third fundamental vibration band,  $\nu_1$ , has been observed by Bender<sup>3</sup> as a Raman line.

The incompletely resolved band  $\nu_2$  as given by Barker and Sleator has recently been interpreted

<sup>1</sup> N. Fuson, H. M. Randall, and D. M. Dennison, *Phys. Rev.* **56**, 982 (1939).

<sup>2</sup> E. F. Barker and W. W. Sleator, *J. Chem. Phys.* **3**, 660 (1935).

<sup>3</sup> D. Bender, *Phys. Rev.* **47**, 252 (1935).

by King,<sup>4</sup> who has used a punch card system to obtain the band contour which most resembles that obtained experimentally. From the most satisfactory fit he has obtained values for the moments of inertia.

The potential constants of  $H_2O$  have been evaluated by Bonner<sup>5</sup> from the observed frequencies and from the dimensions for the molecule given by Mecke.<sup>6</sup> Using this information, Bonner has predicted the fundamental vibration frequencies of  $D_2O$ . More recently Darling and Dennison,<sup>7</sup> using more complete data, have evaluated the normal frequencies of  $H_2O$  and  $D_2O$  together with values for the moments of inertia of the molecule in many of the vibrational states. The recent measurements by Nielsen<sup>8,9</sup> corroborate essentially the values given by them.

### II. EXPERIMENTAL

The absorption spectrum of heavy water vapor was examined with a prism grating spectrometer. The absorption cell which contained the  $D_2O$  vapor was 2.54 cm in diameter and 8 cm long. Built onto one side of the cell, and connecting to it, was a small reservoir which contained a sample of liquid  $D_2O$ . The windows of the cell were silver chloride. By using this material for the windows there were no etching effects on them due to the heavy water vapor. The windows were sealed onto the cell with red glytal.

<sup>4</sup> G. W. King, *J. Chem. Phys.* **15**, 85 (1947).

<sup>5</sup> L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).

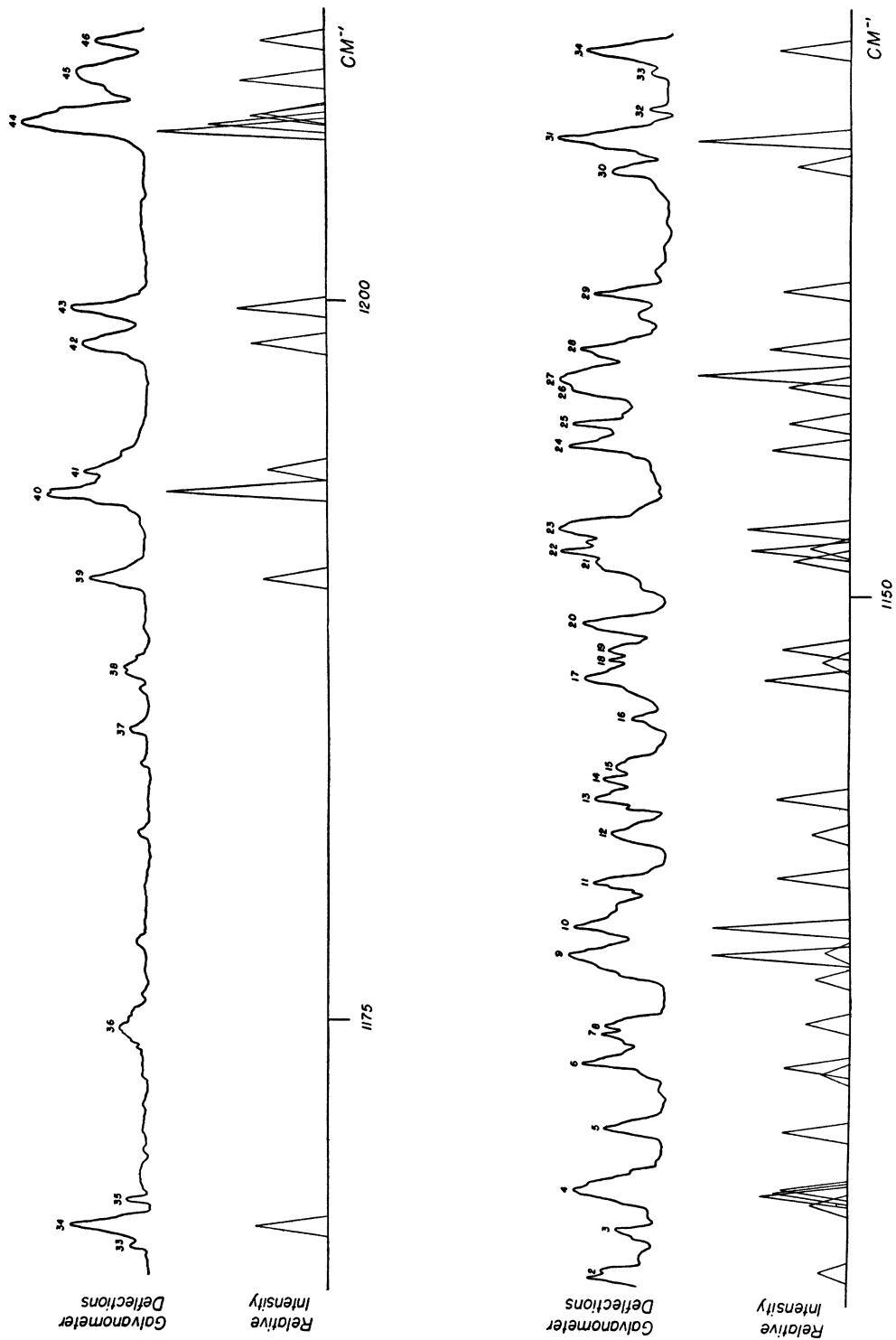
<sup>6</sup> R. Mecke, *Zeits. f. Physik* **81**, 313 (1933).

<sup>7</sup> B. T. Darling and D. M. Dennison, *Phys. Rev.* **55**, 128 (1940).

<sup>8</sup> H. H. Nielsen, *Phys. Rev.* **59**, 565 (1941).

<sup>9</sup> H. H. Nielsen, *Phys. Rev.* **62**, 422 (1942).

FIG. 1. Absorption band  $\nu_2$  for  $D_2O$ .



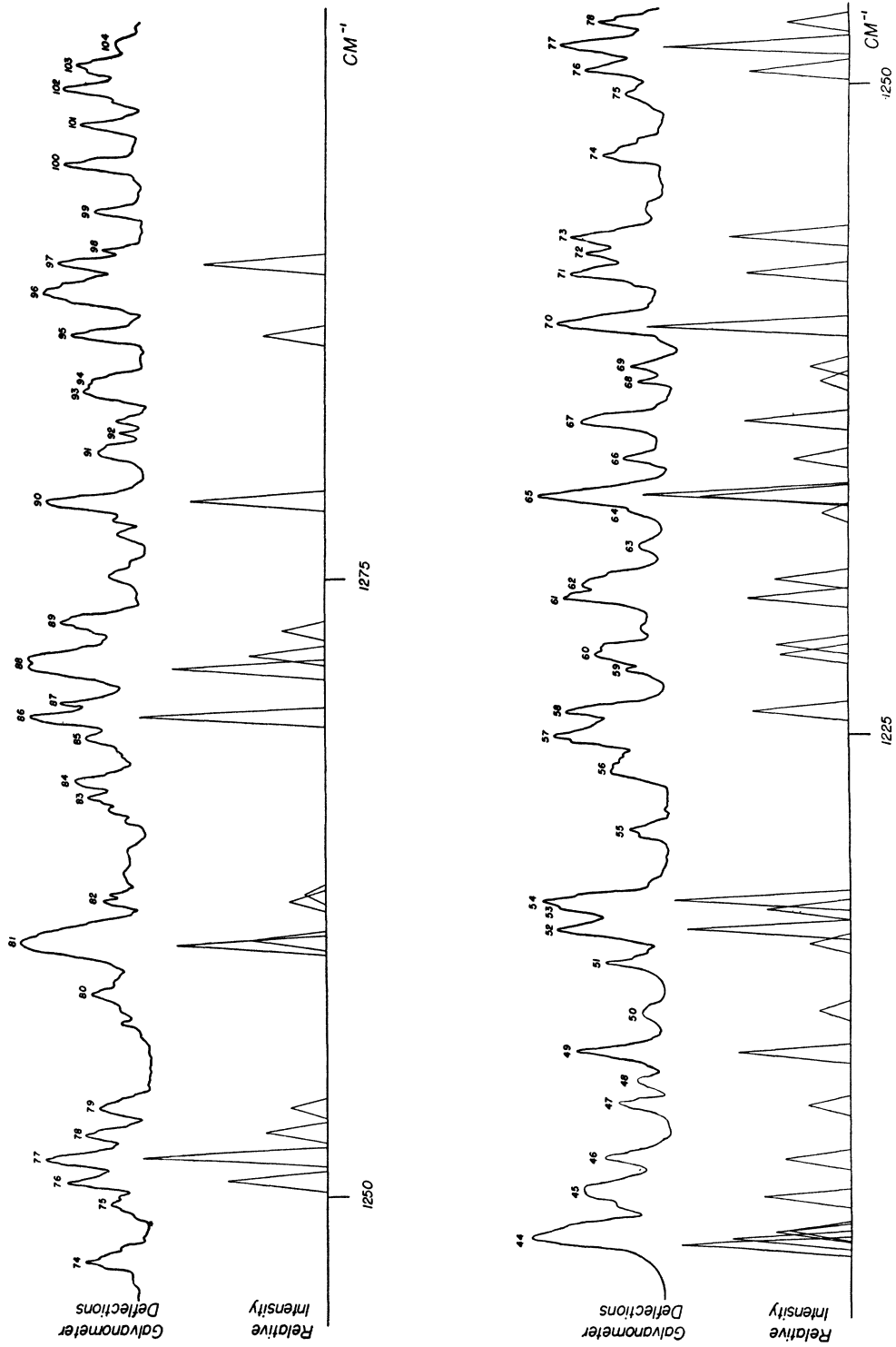


FIG. 2. Absorption band  $\nu_2$  for  $D_2O$ .

The sample of heavy water used was obtained from the Stuart Oxygen Company and contained a minimum of 99.9 percent D<sub>2</sub>O. The sample was introduced into the reservoir of the cell through a stopcock and then frozen by immersing the reservoir in liquid air. The cell was then evacuated and the stopcock closed. When the reservoir was removed from the liquid air, the heavy water melted, and heavy water vapor filled the cell. To prevent the vapor from condensing on the windows, and a resulting loss in the amount of transmitted energy, the windows of the cell were kept slightly warmer than the rest of the cell.

The gratings used for these measurements were replicas made by R. W. Wood. The one used in measuring the band  $\nu_2$  was a grating ruled with 3600 lines per inch. The one used in measuring the band  $\nu_3$  was ruled with 7200 lines per inch. The grating constants were determined by observing lines of the mercury spectrum in high orders. The position of the lines in wave numbers were reduced to their values in vacuum, and thus the corrected wave numbers are strictly proportional to the oscillation frequencies, the more fundamental figure, since these are not changed when the medium is changed.

The fundamental vibration-rotation band  $\nu_2$  was observed in the region between 1125 cm<sup>-1</sup> and 1300 cm<sup>-1</sup> with the effective slit width of the spectrometer set to 0.35 cm<sup>-1</sup>. Readings of the transmitted energy were made and recorded for every five seconds of arc of the grating circle. The results of the measurements may be seen by referring to the upper curves of Figs. 1 and 2. The numbers appearing over the various lines are arbitrary numbers assigned to them. These numbers are useful in quickly picking out any one line. Frequencies in wave numbers, corrected to vacuum, for the lines are given in Table I.

The fundamental vibration-rotation band  $\nu_3$  was observed in the region between 2650 cm<sup>-1</sup> and 2900 cm<sup>-1</sup>. The effective slit width was 0.35 cm<sup>-1</sup>, and readings of the transmitted energy were made and recorded for every five seconds of arc of the grating circle. The results of these measurements may be seen by referring to the upper curves of Fig. 3. Frequencies in wave numbers, corrected to vacuum, for these lines are given in Table II.

After these measurements were taken and an analysis of the bands carried out, the automatic recording vacuum spectrometer described by

TABLE I. Frequency positions and identifications of heavy water vapor lines in  $\nu_2$ .

Line No.	Obs. $\nu_{(vac)}$ (cm <sup>-1</sup> )	Transition	Line No.	Obs. $\nu_{(vac)}$ (cm <sup>-1</sup> )	Transition
1	1128.66		53	1218.58	3 <sub>0</sub> -3 <sub>-2</sub>
2	1128.89	4 <sub>2</sub> -4 <sub>4</sub>	54	1218.91	4 <sub>-4</sub> -3 <sub>-2</sub>
3	1130.14		55	1221.46	
4	1131.43	3 <sub>-3</sub> -4 <sub>-3</sub>	56	1223.85	
		5 <sub>-4</sub> -5 <sub>-2</sub>	57	1225.08	
		6 <sub>-6</sub> -6 <sub>-4</sub>	58	1225.95	4 <sub>-3</sub> -3 <sub>-3</sub>
5	1133.78	5 <sub>-2</sub> -5 <sub>0</sub>	59	1227.54	
6	1135.41	4 <sub>-1</sub> -4 <sub>-3</sub>	60	1228.50	5 <sub>-2</sub> -5 <sub>-4</sub>
		4 <sub>-1</sub> -5 <sub>-3</sub>			6 <sub>-4</sub> -6 <sub>-6</sub>
7	1136.27		61	1230.23	5 <sub>-5</sub> -4 <sub>-3</sub>
8	1136.54	3 <sub>0</sub> -3 <sub>2</sub>	62	1231.16	5 <sub>-2</sub> -5 <sub>-4</sub>
9	1138.78	3 <sub>2</sub> -4 <sub>-4</sub>	63	1232.30	
		3 <sub>1</sub> -3 <sub>3</sub>	64	1233.44	3 <sub>3</sub> -3 <sub>1</sub>
		4 <sub>-3</sub> -4 <sub>-1</sub>	65	1234.12	2 <sub>1</sub> -1 <sub>1</sub>
		2 <sub>-2</sub> -3 <sub>-2</sub>			4 <sub>2</sub> -4 <sub>0</sub>
10	1139.72				5 <sub>-4</sub> -4 <sub>-4</sub>
11	1141.10	4 <sub>0</sub> -4 <sub>2</sub>			3 <sub>2</sub> -3 <sub>0</sub>
12	1142.63	5 <sub>-5</sub> -5 <sub>-3</sub>	66	1235.52	2 <sub>2</sub> -1 <sub>0</sub>
13	1143.71	3 <sub>-2</sub> -3 <sub>0</sub>	67	1236.97	6 <sub>-3</sub> -6 <sub>-5</sub>
14	1144.31		68	1238.45	4 <sub>1</sub> -4 <sub>-1</sub>
15	1144.69		69	1239.02	6 <sub>-6</sub> -5 <sub>-4</sub>
16	1146.27		70	1240.65	6 <sub>-5</sub> -5 <sub>-6</sub>
17	1147.54	6 <sub>-2</sub> -6 <sub>0</sub>	71	1242.68	
18	1148.07	2 <sub>-1</sub> -2 <sub>1</sub>	72	1243.46	
19	1148.42	1 <sub>-1</sub> -2 <sub>-1</sub>	73	1243.98	3 <sub>0</sub> -2 <sub>0</sub>
20	1149.09		74	1247.24	
21	1151.26	2 <sub>-1</sub> -3 <sub>-3</sub>	75	1249.64	
22	1151.74	3 <sub>0</sub> -4 <sub>-2</sub>	76	1250.46	7 <sub>-7</sub> -6 <sub>-5</sub>
		6 <sub>-4</sub> -6 <sub>-2</sub>	77	1251.47	7 <sub>-7</sub> -6 <sub>-6</sub>
		4 <sub>-4</sub> -4 <sub>-2</sub>	78	1252.39	4 <sub>-1</sub> -3 <sub>-1</sub>
23	1152.22		79	1253.45	3 <sub>1</sub> -2 <sub>-1</sub>
24	1154.94	2 <sub>0</sub> -2 <sub>2</sub>	80	1258.06	
25	1155.65	5 <sub>-3</sub> -5 <sub>-1</sub>	81	1259.98	8 <sub>-8</sub> -7 <sub>-6</sub>
26	1156.80	3 <sub>-1</sub> -3 <sub>1</sub>			8 <sub>-7</sub> -7 <sub>-7</sub>
27	1157.16	4 <sub>-2</sub> -4 <sub>0</sub>	82	1261.90	4 <sub>4</sub> -4 <sub>2</sub>
28	1158.10	0 <sub>0</sub> -1 <sub>0</sub>			4 <sub>4</sub> -4 <sub>1</sub>
29	1159.91	3 <sub>-3</sub> -3 <sub>-1</sub>			
30	1163.95	1 <sub>0</sub> -2 <sub>-2</sub>	83	1266.09	
31	1164.94	2 <sub>-2</sub> -2 <sub>0</sub>	84	1266.73	
32	1165.89		85	1268.40	
33	1167.10		86	1269.27	9 <sub>-9</sub> -8 <sub>-7</sub>
34	1167.80	1 <sub>-1</sub> -1 <sub>1</sub>			9 <sub>-8</sub> -8 <sub>-8</sub>
35	1168.80		87	1270.00	
36	1174.56		88	1271.64	3 <sub>2</sub> -2 <sub>2</sub>
37	1184.74				3 <sub>3</sub> -2 <sub>1</sub>
38	1187.04		89	1273.29	4 <sub>0</sub> -3 <sub>-2</sub>
39	1190.29	1 <sub>1</sub> -1 <sub>-1</sub>	90	1278.13	10 <sub>-10</sub> -9 <sub>-8</sub>
40	1193.28	2 <sub>0</sub> -2 <sub>-2</sub>			10 <sub>-9</sub> -9 <sub>-9</sub>
41	1194.06	2 <sub>-2</sub> -1 <sub>0</sub>	91	1280.31	
42	1198.53	3 <sub>-1</sub> -3 <sub>-3</sub>	92	1281.00	
43	1199.80	1 <sub>0</sub> -0 <sub>0</sub>	93	1282.63	
44	1206.41	3 <sub>-3</sub> -2 <sub>-1</sub>	94	1283.20	
		3 <sub>1</sub> -3 <sub>-1</sub>	95	1285.21	4 <sub>1</sub> -3 <sub>-3</sub>
		4 <sub>-2</sub> -4 <sub>-4</sub>	96	1287.14	
		4 <sub>0</sub> -4 <sub>-2</sub>	97	1288.27	4 <sub>2</sub> -3 <sub>0</sub>
45	1207.93	2 <sub>2</sub> -2 <sub>0</sub>	98	1288.92	
46	1209.38	2 <sub>-1</sub> -1 <sub>-1</sub>	99	1290.57	
47	1211.36	4 <sub>-2</sub> -3 <sub>0</sub>	100	1292.52	
48	1212.21		101	1294.19	
49	1213.26	6 <sub>-2</sub> -6 <sub>-4</sub>	102	1295.81	
50	1214.73	2 <sub>1</sub> -2 <sub>-1</sub>	103	1296.58	
51	1216.57		104	1297.78	
52	1217.84	3 <sub>-2</sub> -2 <sub>-2</sub>			
		5 <sub>-3</sub> -5 <sub>-5</sub>			

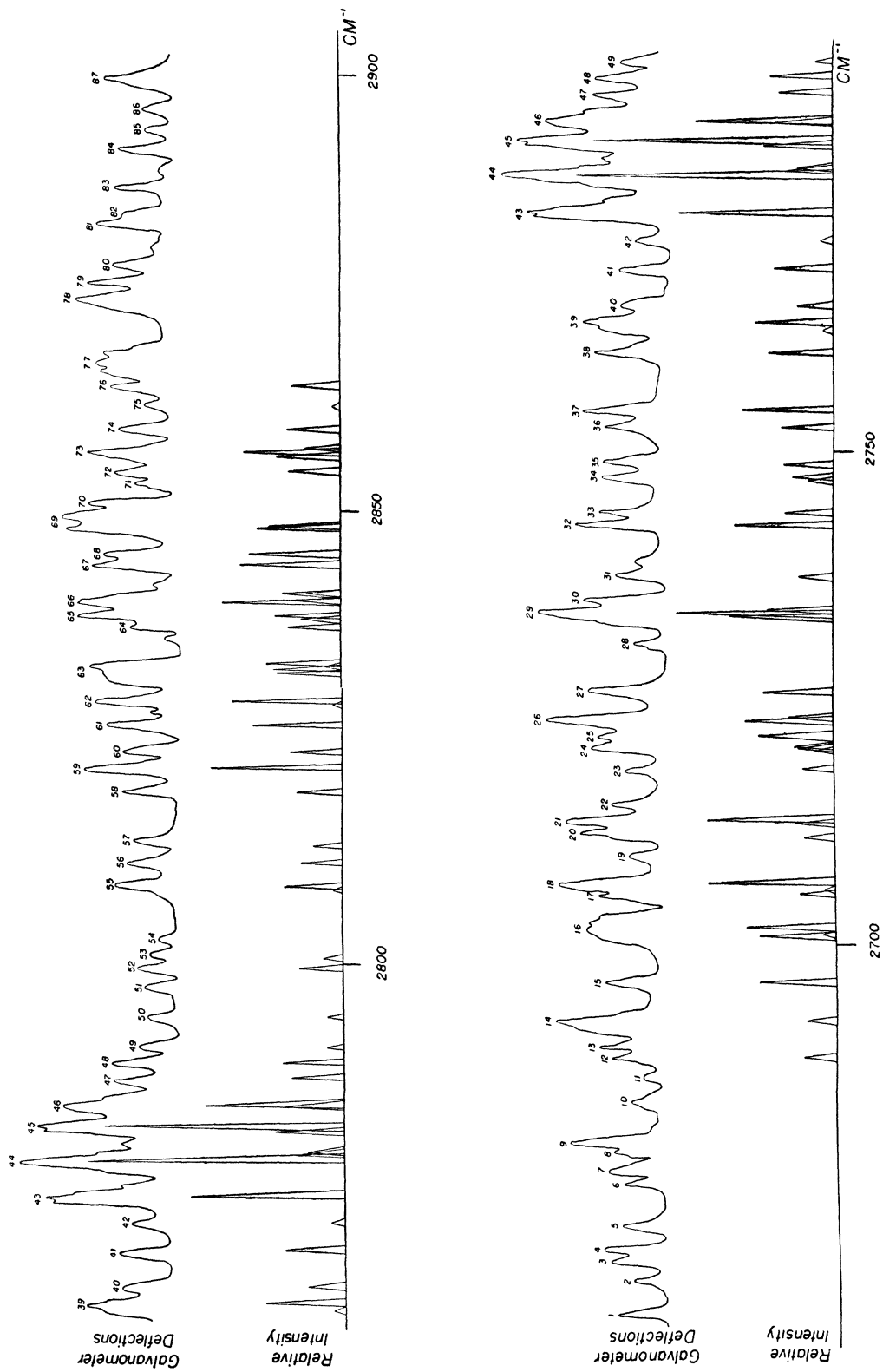


FIG. 3. Absorption band  $\nu_3$  for  $D_2O$ .

TABLE II. Frequency positions and identifications of heavy water vapor lines in  $\nu_3$ .

Line No.	Obs. $\nu(\text{vac})$ (cm <sup>-1</sup> )	Transition	Line No.	Obs. $\nu(\text{vac})$ (cm <sup>-1</sup> )	Transition
1	2663.78		29	2733.40	3 <sub>-1</sub> -4 <sub>-2</sub>
2	2666.96				3 <sub>1</sub> -4 <sub>0</sub>
3	2668.80				3 <sub>2</sub> -4 <sub>1</sub>
4	2669.85				3 <sub>3</sub> -4 <sub>2</sub>
5	2672.10				4 <sub>-4</sub> -5 <sub>-5</sub>
6	2676.33				4 <sub>-3</sub> -5 <sub>-4</sub>
7	2677.78		30	2734.48	
8	2679.44			2734.71	
9	2680.47		31	2737.32	3 <sub>0</sub> -4 <sub>-1</sub>
10	2684.32		32	2742.35	3 <sub>-3</sub> -4 <sub>-4</sub>
11	2686.50		33	2743.67	3 <sub>-2</sub> -4 <sub>-3</sub>
12	2688.60		34	2747.30	2 <sub>0</sub> -3 <sub>-1</sub>
13	2689.75	6 <sub>0</sub> -7 <sub>-1</sub>			2 <sub>-2</sub> -2 <sub>-1</sub>
14	2692.26	6 <sub>-2</sub> -7 <sub>-3</sub>			3 <sub>-3</sub> -3 <sub>0</sub>
15	2696.15	5 <sub>0</sub> -6 <sub>-1</sub>	35	2748.90	2 <sub>1</sub> -3 <sub>0</sub>
		6 <sub>-1</sub> -7 <sub>-2</sub>	36	2752.82	2 <sub>-2</sub> -3 <sub>-3</sub>
16	2700.69	5 <sub>-1</sub> -6 <sub>-2</sub>	37	2754.26	2 <sub>-1</sub> -3 <sub>-2</sub>
		5 <sub>4</sub> -6 <sub>3</sub>	38	2760.36	1 <sub>1</sub> -2 <sub>0</sub>
		5 <sub>5</sub> -6 <sub>4</sub>	39	2762.81	4 <sub>-3</sub> -4 <sub>-2</sub>
	2701.33	5 <sub>1</sub> -6 <sub>0</sub>		2763.79	1 <sub>-1</sub> -2 <sub>-2</sub>
		6 <sub>-4</sub> -7 <sub>-5</sub>	40	2765.38	1 <sub>0</sub> -2 <sub>-1</sub>
	2701.96		41	2768.74	6 <sub>5</sub> -6 <sub>6</sub>
	2702.49			2769.30	6 <sub>6</sub> -6 <sub>5</sub>
17	2704.82	5 <sub>2</sub> -6 <sub>1</sub>	42	2772.11	3 <sub>-2</sub> -3 <sub>-1</sub>
		5 <sub>3</sub> -6 <sub>2</sub>	43	2774.70	
18	2705.88	5 <sub>-3</sub> -6 <sub>-4</sub>		2775.15	0 <sub>0</sub> -1 <sub>-1</sub>
		6 <sub>-3</sub> -7 <sub>-4</sub>			5 <sub>4</sub> -5 <sub>5</sub>
19	2708.65				5 <sub>5</sub> -5 <sub>4</sub>
20	2710.89	5 <sub>-2</sub> -6 <sub>-3</sub>			6 <sub>3</sub> -6 <sub>4</sub>
21	2712.28	6 <sub>-6</sub> -7 <sub>-7</sub>			6 <sub>4</sub> -6 <sub>3</sub>
		6 <sub>-5</sub> -5 <sub>-4</sub>		2776.27	
22	2713.99		44	2779.21	2 <sub>-1</sub> -2 <sub>0</sub>
23	2717.41	4 <sub>3</sub> -5 <sub>2</sub>			4 <sub>-1</sub> -4 <sub>0</sub>
		4 <sub>4</sub> -5 <sub>3</sub>			4 <sub>3</sub> -4 <sub>4</sub>
24	2719.77	4 <sub>-2</sub> -5 <sub>-3</sub>			4 <sub>4</sub> -4 <sub>3</sub>
		4 <sub>0</sub> -5 <sub>-1</sub>			5 <sub>2</sub> -5 <sub>3</sub>
		4 <sub>2</sub> -5 <sub>1</sub>			5 <sub>3</sub> -5 <sub>2</sub>
25	2720.95	4 <sub>-2</sub> -5 <sub>-3</sub>			6 <sub>1</sub> -6 <sub>2</sub>
		4 <sub>1</sub> -5 <sub>1</sub>			6 <sub>2</sub> -6 <sub>1</sub>
26	2722.56	5 <sub>-3</sub> -6 <sub>-6</sub>	45	2782.50	
		5 <sub>-4</sub> -6 <sub>-5</sub>		2782.95	3 <sub>0</sub> -3 <sub>1</sub>
27	2725.48	1 <sub>-1</sub> -2 <sub>2</sub>			3 <sub>2</sub> -3 <sub>3</sub>
		4 <sub>-1</sub> -5 <sub>-2</sub>			3 <sub>3</sub> -3 <sub>2</sub>
28	2730.25				4 <sub>1</sub> -4 <sub>2</sub>
					4 <sub>2</sub> -4 <sub>1</sub>

Bell, Noble, and Nielsen<sup>10</sup> became available at the laboratory, and as a matter of interest, the bands were remeasured on this instrument. The results of these measurements of the band  $\nu_2$  are shown in Fig. 4. It should be noted that the gain was increased on the high frequency side of the band. The measurements of the band  $\nu_3$  are shown in Fig. 5. Here the gain was reduced over the region occupied by the strong central lines of the Q branch, that is lines 42 to 50, and was somewhat different over the region occupied by lines 51 to 79. A section of the automatic

<sup>10</sup> E. E. Bell, R. H. Noble, and H. H. Nielsen, Rev. Sci. Inst. 18, 48 (1947).

TABLE II.—Continued.

Line No.	Obs. $\nu(\text{vac})$ (cm <sup>-1</sup> )	Transition	Line No.	Obs. $\nu(\text{vac})$ (cm <sup>-1</sup> )	Transition
46	2784.77	1 <sub>0</sub> -1 <sub>1</sub>	66	2839.90	5 <sub>-5</sub> -4 <sub>-4</sub>
		2 <sub>1</sub> -2 <sub>2</sub>		2840.80	5 <sub>-2</sub> -4 <sub>-1</sub>
		2 <sub>2</sub> -2 <sub>1</sub>			5 <sub>1</sub> -4 <sub>2</sub>
47	2787.62	3 <sub>1</sub> -3 <sub>0</sub>			5 <sub>2</sub> -4 <sub>3</sub>
48	2789.44	1 <sub>1</sub> -1 <sub>0</sub>			5 <sub>3</sub> -4 <sub>4</sub>
49	2791.27	4 <sub>0</sub> -4 <sub>-1</sub>	67	2844.00	5 <sub>-3</sub> -4 <sub>-2</sub>
50	2794.30	2 <sub>0</sub> -2 <sub>-1</sub>	68	2845.15	5 <sub>-1</sub> -4 <sub>0</sub>
51	2797.57		69	2847.90	6 <sub>-5</sub> -7 <sub>-6</sub>
52	2799.63	1 <sub>-1</sub> -0 <sub>0</sub>			6 <sub>-6</sub> -5 <sub>-5</sub>
53	2800.90	3 <sub>-1</sub> -3 <sub>-2</sub>		2849.34	
54	2802.52		70	2850.66	
55	2808.53	2 <sub>-1</sub> -1 <sub>0</sub>	71	2853.07	
		4 <sub>-2</sub> -4 <sub>-3</sub>	72	2854.26	6 <sub>1</sub> -5 <sub>2</sub>
56	2811.09	2 <sub>-2</sub> -1 <sub>-1</sub>			6 <sub>2</sub> -5 <sub>3</sub>
57	2813.41	2 <sub>0</sub> -1 <sub>1</sub>	73	2856.44	6 <sub>-3</sub> -5 <sub>-2</sub>
58	2819.13	3 <sub>-2</sub> -2 <sub>-1</sub>			6 <sub>-1</sub> -4 <sub>0</sub>
59	2821.36	3 <sub>-3</sub> -2 <sub>-2</sub>			6 <sub>0</sub> -5 <sub>1</sub>
		3 <sub>0</sub> -2 <sub>1</sub>	74	2859.34	6 <sub>-4</sub> -5 <sub>-3</sub>
60	2823.24	2 <sub>1</sub> -2 <sub>-2</sub>	75	2861.40	3 <sub>1</sub> -2 <sub>-2</sub>
		3 <sub>1</sub> -2 <sub>2</sub>	76	2864.06	6 <sub>-2</sub> -5 <sub>-1</sub>
61	2826.16	3 <sub>-1</sub> -2 <sub>0</sub>	77	2865.29	
62	2828.89	4 <sub>-3</sub> -3 <sub>-2</sub>		2865.88	
		4 <sub>-1</sub> -4 <sub>-4</sub>		2866.74	
63	2830.89			2867.96	
	2831.13	4 <sub>-4</sub> -3 <sub>-3</sub>	78	2872.95	
	2831.91	4 <sub>1</sub> -3 <sub>2</sub>		2874.18	
		5 <sub>0</sub> -4 <sub>1</sub>	79	2876.02	
	2832.19	4 <sub>2</sub> -4 <sub>3</sub>	80	2877.79	
	2832.77		81	2882.90	
	2832.90	4 <sub>-1</sub> -3 <sub>0</sub>	82	2884.01	
64	2836.93	4 <sub>-2</sub> -3 <sub>-1</sub>	83	2886.85	
65	2838.36	4 <sub>0</sub> -3 <sub>1</sub>	84	2891.43	
		5 <sub>-4</sub> -4 <sub>-3</sub>	85	2893.54	
			86	2896.25	
			87	2899.77	

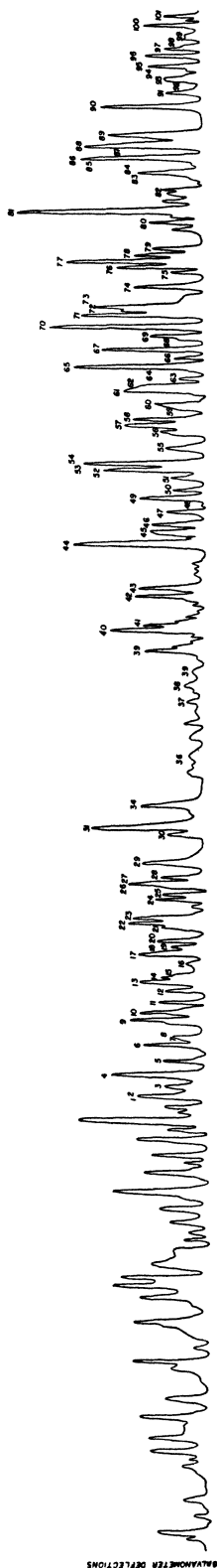
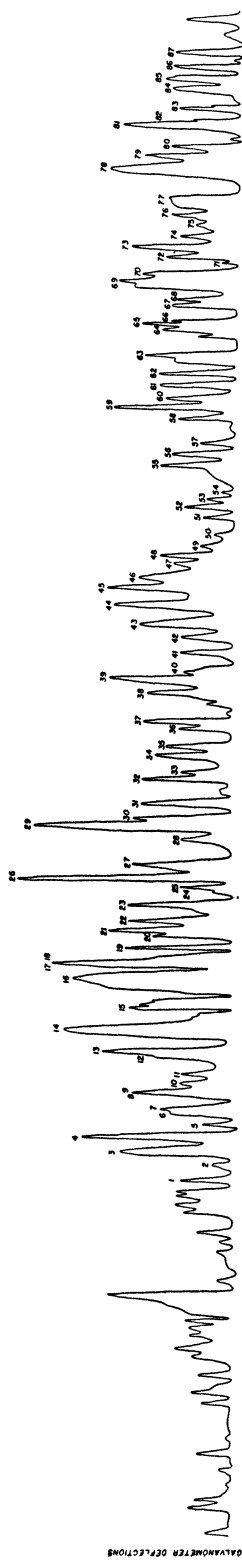
recorded spectrum tracing may be seen in Fig. 6. This includes the region from the center of the band  $\nu_2$  to line 67.

III. IDENTIFICATION OF THE OBSERVED LINES

The identification of the lines measured in the two bands was made by following the method used by Nielsen<sup>8,9</sup> in identifying the lines in the spectrum of water vapor. Each line in one of the bands  $\nu_i$  is due to the molecules making a transition from a rotation level in the normal vibration state to a rotation level in the vibration state  $\nu_i$ , and the frequency of such a line will be the difference between a term value in  $\nu_i$  and one in the normal state. The selection rules governing what transitions may take place have been given by Dennison.<sup>11</sup>

Term values for the normal state have been determined experimentally by Fuson, Randall

<sup>11</sup> D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

FIG. 4.  $\nu_2$  for  $D_2O$  measured with automatic recording spectrometer.FIG. 5.  $\nu_3$  for  $D_2O$  measured with automatic recording spectrometer.

and Dennison.<sup>1</sup> Term values for the state  $\nu_i$  will be the sum of the vibrational energy plus the rotational energy. Shaffer and Nielsen<sup>12</sup> have given the following expression for the rotational energies of the non-linear triatomic molecule:

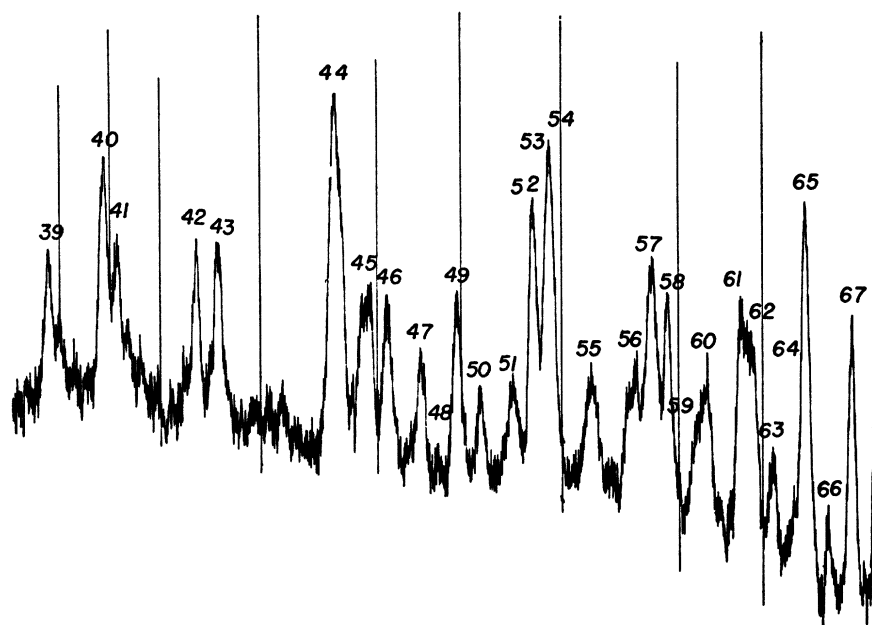
$$E(V, J, \tau) = J(J+1)\frac{1}{2}(A(V) + B(V)) + \rho_1 - J^2(J+1)^2\rho_2 + \epsilon_\tau, \quad (1)$$

where  $\rho_1$  and  $\rho_2$  are constants;  $A(V)$ ,  $B(V)$ , and  $C(V)$  are the reciprocals of inertia;  $V_1$ ,  $V_2$  and  $V_3$  are the vibrational quantum numbers,  $J$  is the quantum number of total angular momentum, and  $\epsilon_\tau$  is one of the  $2J+1$  roots of the secular determinant which is used to diagonalize the rotational part of the Hamiltonian. Nielsen<sup>8</sup> has expanded this determinant for all values of  $J$  up through  $J=6$ , and given the algebraic relations for  $\epsilon_\tau$ . Constants which occur in (1) may be evaluated by first identifying, by trial and error, enough lines in the spectrum of  $\nu_i$  to enable the determination of the term values for  $J=0$ ,  $J=1$ , and  $J=2$ . When these term values are known, enough relationships of (1) will be available to permit an evaluation of the constants for the state  $\nu_i$ . For example, if a line is identified as being due to the transition  $1_1-1_{-1}$ , then the term value for  $1_1$  in the state  $\nu_i$  will be equal to the frequency of the line plus the term value for  $1_{-1}$  in the normal state. The correctness of these term values may be checked by using them, together with the term values in the normal state and the selection rules, to see if lines which would occur from such values are actually found in the measured spectrum.

Once the constants of (1) are known, rotational energies and then term values for  $J=3$  may be calculated. These term values will give rise to additional spectral lines. A check is then made of the measured spectrum to see if such lines occur. Once these lines are located in the measured spectrum new term values for  $J=3$  may be determined from the experimental data. The new term values may be used to improve the values of the constants of (1). The process is then repeated for still higher values of  $J$ .

In an attempt to evaluate the centrifugal stretching coefficients from the data of Fuson, Randall, and Dennison<sup>1</sup> by fitting the energy

<sup>12</sup> W. H. Shaffer and H. H. Nielsen, Phys. Rev. 56, 188 (1939).


 FIG. 6. Section of record of absorption band  $\nu_2$  for  $D_2O$ .

relations up to  $J=6$  to their term values, no constant values could be obtained. This was interpreted to mean that the effect of the centrifugal stretching on these levels was so small that it was less than the experimental accuracy. Since our evaluation of the moments of inertia of the molecule is made from transitions where  $J$  is not greater than 6, the effect of centrifugal stretching has been neglected. It may, in fact, be seen by reference to the relations (39) and (42) of the work of Shaffer and Nielsen<sup>12</sup> that the centrifugal stretching might here be expected to be approximately  $\frac{1}{16}$  the magnitude of those for  $H_2O$ .

As a further aid in identifying the lines of the spectrum, the relative intensities of the lines have been calculated by using the line strengths given by Cross, Hanier, and King.<sup>13</sup> That is:

$$\sum_{X'Y'Z'} \sum_{M''} \sum_{M'} |(\phi_{F_0^A})_{J''\tau''M''; J'\tau'M'}|^2, \quad (2)$$

where  $\phi_{F_0}$  represents the direction cosine element of the asymmetric rotator and  $X'Y'Z'$  are the space fixed Cartesian coordinates. Their values are for various parameters of asymmetry. That

<sup>13</sup> P. C. Cross, R. M. Hanier, and G. W. King, J. Chem. Phys. 12, 210 (1944).

is:

$$K = \frac{2B(V) - A(V) - C(V)}{A(V) - C(V)}. \quad (3)$$

The values used were those tabulated for  $K = -0.5$ , since the parameter of asymmetry of  $D_2O$  in the normal state is  $-0.54$ , in the state  $\nu_2 - 0.57$ , and in the state  $\nu_3 - 0.53$ .

Term values determined in this manner for the frequencies  $\nu_2$  are tabulated in Table III.

 TABLE III. Vibration-rotation term values for the frequencies  $\nu_2$ .

$J_\tau$	$\nu_2$	$J_\tau$	$\nu_2$
0 <sub>0</sub>	1178.30 cm <sup>-1</sup>	4 <sub>0</sub>	1347.51 cm <sup>-1</sup>
1 <sub>1</sub>	1202.37	4 <sub>-1</sub>	1341.16
1 <sub>0</sub>	1199.75	4 <sub>-2</sub>	1321.16
1 <sub>-1</sub>	1190.39	4 <sub>-3</sub>	1296.20
2 <sub>2</sub>	1257.15	4 <sub>-4</sub>	1293.56
2 <sub>1</sub>	1256.70	5 <sub>-2</sub>	1401.19
2 <sub>0</sub>	1229.00	5 <sub>-3</sub>	1386.12
2 <sub>-1</sub>	1221.50	5 <sub>-4</sub>	1348.83
2 <sub>-2</sub>	1214.20	5 <sub>-5</sub>	1348.60
3 <sub>3</sub>	1345.44	6 <sub>-2</sub>	1492.79
3 <sub>2</sub>	1345.33	6 <sub>-3</sub>	1471.05
3 <sub>1</sub>	1295.39	6 <sub>4</sub>	1460.43
3 <sub>0</sub>	1293.18	6 <sub>-5</sub>	1411.56
3 <sub>-1</sub>	1268.79	6 <sub>-6</sub>	1410.61
3 <sub>-2</sub>	1253.55	7 <sub>-6</sub>	1483.39
3 <sub>-3</sub>	1248.67	7 <sub>-7</sub>	1483.06
4 <sub>4</sub>	1468.00	8 <sub>-7</sub>	1565.30
4 <sub>3</sub>	1468.00	8 <sub>-8</sub>	1565.22
4 <sub>2</sub>	1398.06	9 <sub>-8</sub>	1657.07
4 <sub>1</sub>	1397.29	9 <sub>-9</sub>	1657.02



TABLE IV. Vibration-rotation term values for the frequencies  $\nu_3$ .

$J_r$	$\nu_3$	$J_r$	$\nu_3$
0 <sub>0</sub>	2787.23 cm <sup>-1</sup>	5 <sub>5</sub>	3186.33 cm <sup>-1</sup>
1 <sub>1</sub>	2809.58	5 <sub>4</sub>	3186.33
1 <sub>0</sub>	2807.36	5 <sub>3</sub>	3110.05
1 <sub>-1</sub>	2799.57	5 <sub>2</sub>	3110.05
2 <sub>2</sub>	2859.10	5 <sub>1</sub>	3046.64
2 <sub>1</sub>	2858.71	5 <sub>0</sub>	3037.68
2 <sub>0</sub>	2836.05	5 <sub>-1</sub>	3009.18
2 <sub>-1</sub>	2828.78	5 <sub>-2</sub>	2998.50
2 <sub>-2</sub>	2823.14	5 <sub>-3</sub>	2985.40
3 <sub>3</sub>	2939.40	5 <sub>-4</sub>	2955.63
3 <sub>2</sub>	2939.39	5 <sub>-5</sub>	2954.61
3 <sub>1</sub>	2897.42	6 <sub>6</sub>	3351.00
3 <sub>0</sub>	2895.00	6 <sub>5</sub>	3351.00
3 <sub>-1</sub>	2875.36	6 <sub>4</sub>	3260.56
3 <sub>-2</sub>	2861.04	6 <sub>3</sub>	3260.56
3 <sub>-3</sub>	2857.11	6 <sub>2</sub>	3185.20
4 <sub>4</sub>	3048.27	6 <sub>1</sub>	3184.95
4 <sub>3</sub>	3048.27	6 <sub>0</sub>	3126.60
4 <sub>2</sub>	2988.71	6 <sub>-1</sub>	3122.79
4 <sub>1</sub>	2988.36	6 <sub>-2</sub>	3094.53
4 <sub>0</sub>	2949.97	6 <sub>-3</sub>	3073.91
4 <sub>-1</sub>	2943.00	6 <sub>-4</sub>	3065.33
4 <sub>-2</sub>	2925.72	6 <sub>-5</sub>	3017.80
4 <sub>-3</sub>	2903.47	6 <sub>-6</sub>	3017.10
4 <sub>-4</sub>	2901.37	—	—

Term values for the frequencies  $\nu_3$  are tabulated in Table IV. The identification of lines is given in the third columns of Tables I and II. Immediately below the measured spectrum shown in Figs. 1, 2, and 3 is shown a spectrum which one would expect using the term values given in Tables III and IV. The lines are drawn as triangles, where the base is twice the equivalent slit width and the height is proportional to the relative intensity, which was determined in the manner described. The term values given for the state  $\nu_2$  with values of  $J$  higher than 6 were not determined in the manner discussed but rather from the characteristics of the spectrum and the calculated relative intensities.

The term values up to  $J=6$  have been employed to calculate the values of the reciprocals

of inertia  $A(V)$ ,  $B(V)$ , and  $C(V)$ . The values which seem most consistent with the term values given in Tables I and II are stated in Table V. In the same table are stated the values of the corresponding effective moments of inertia  $I_A$ ,  $I_B$ , and  $I_C$  for the normal state and the states  $\nu_2$  and  $\nu_3$ .

Darling and Dennison<sup>7</sup> have shown that the quantity  $\Delta = I_C - I_A - I_B$  is one which, for planar molecules, is independent of the coefficients of the anharmonic part of the potential energy. Its value may therefore be computed from a knowledge of the normal frequencies and the shape of the molecule. The values of  $\Delta$  for the states  $\nu_2$  and  $\nu_3$  computed with the aid of the relation of Darling and Dennison, are also given in Table V, together with the experimentally determined values. It is somewhat disappointing that the computed value of  $\Delta$  for the state  $\nu_3$  seems to differ appreciably from the measured value.

The data of Barker and Sleator<sup>2</sup> has been analyzed by King,<sup>4</sup> using a punch card method developed by them. His values for the moments of inertia, which were originally chosen to obey the  $\Delta$  condition, vary slightly from the values given by us. The values of the moments of inertia chosen by King are such as to give the best over-all agreement with the contour of the incompletely resolved absorption pattern reported by Barker and Sleator. The values are therefore those which fit the term values of high  $J$  values best. No compensation has been made by him for centrifugal stretching. While the centrifugal stretching is much smaller here than in the case of ordinary water vapor, it can probably not be neglected for the higher values of  $J$ .

We have, of course, never employed the

TABLE V. Values of  $A(V)$ ,  $B(V)$ ,  $C(V)$ ,  $I_A$ ,  $I_B$ ,  $I_C$ , and  $\Delta$ .

	Normal state*	$\nu_2$	$\nu_3$
$A(V)$	15.38 cm <sup>-1</sup>	16.60 cm <sup>-1</sup>	14.88 cm <sup>-1</sup>
$B(V)$	7.25	7.35	7.24
$C(V)$	4.83	4.84	4.84
$I_A$	$1.820 \times 10^{-40}$ g cm <sup>2</sup>	$1.686 \times 10^{-40}$ g cm <sup>2</sup>	$1.881 \times 10^{-40}$ g cm <sup>2</sup>
$I_B$	$3.860 \times 10^{-40}$	$3.808 \times 10^{-40}$	$3.866 \times 10^{-40}$
$I_C$	$5.794 \times 10^{-40}$	$5.782 \times 10^{-40}$	$5.782 \times 10^{-40}$
$\Delta_{\text{obs.}}$	$0.114 \times 10^{-40}$	$0.288 \times 10^{-40}$	$0.035 \times 10^{-40}$
$\Delta_{\text{calc.}}$	$0.105 \times 10^{-40}$	$0.327 \times 10^{-40}$	$0.084 \times 10^{-40}$

\* See reference 1.

method of King and are, therefore, not really qualified to criticize it. We do know, however, that his values of the moments of inertia do not yield lines at positions which fit our data as well as the values of the moments of inertia which we have given in Table V. We believe this to be because his values are chosen so as to give the best agreement at considerable distances from the center of the band where the centrifugal distortion is of considerable significance. They must, therefore, deviate from the values which would give the best fit near the center of the band. In our determination, compensation for

centrifugal stretching has also been neglected. The values of the moments of inertia were, however, determined from term values of small  $J$  value where the centrifugal stretching is small and may be neglected. Since the lines which have been used to determine these term values are known accurately to about  $0.05 \text{ cm}^{-1}$ , we believe the values obtained by us for the moments of inertia are somewhat more reliable.

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### The Conservation of Momentum in the Beta-Decay of $Y^{90}$ \*

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Monolayer sources of yttrium (90) are formed by evaporation in a vacuum of  $10^{-7}$  mm of Hg. The momentum of individual recoil ions is measured by timing their flight in a field free space. The positively charged Zr (90) recoils appear to lose about 6-electron volts energy as they escape from the surface. If a 6-electron volt correction is made to the observed recoil spectra, there is good agreement regarding shape and absolute amplitude with those recoil spectra calculated on the assumption of a neutrino-electron angular correlation function of  $(1 - \beta \cos\theta)^2$ . For this function the most probable angle between the neutrino and the electron is  $\sim 135^\circ$ . These results are in agreement, within experimental error, with earlier data obtained with  $P^{32}$ . The exact limits of error due to chemical effects at the surface cannot yet be assigned, so it is not possible to make a definite selection of the form of the neutrino-electron angular correlation function.

#### 1. INTRODUCTION

**I**N earlier experiments<sup>1</sup> the momentum spectra of the recoil ions from monolayer sources of  $P^{32}$  ( $E_{\text{max}} = 1.72$  Mev, half-life, 14.3d) were measured. It was concluded that momentum is not conserved between the electron and the recoil nucleus. If one assumes the existence of a neutrino, which is most probably emitted in the opposite hemisphere from the electron, one accounts for the experimentally observed recoil momentum spectra. The experiments reported here measure the recoil momentum spectra of yttrium (90) ( $E_{\text{max}} = 2.16$  Mev, half-life, 62 hr.).

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<sup>1</sup> C. W. Sherwin, *Phys. Rev.* **73**, 216 (1948).

These experiments permit a rather critical test of the previous results, since the  $Zr^{90}$  recoil ion from  $Y^{90}$  is very different from the  $S^{32}$  recoil ion from  $P^{32}$ . The recoil ions in these two cases differ appreciably regarding (1) maximum velocity, (2) maximum energy, (3) maximum momentum, (4) mass, (5) ionization potential ( $S = 10.3$  volts,  $Zr = 6.92$  volts), and (6) the fraction of the recoils that escape in the charged state. If one assumes a  $(1 - \beta \cos\theta)^2$  neutrino-electron angular correlation function for both cases, about 8 percent of the sulfur, and about 87 percent of the zirconium recoils escape charged.

In addition, the nature of the freshly evaporated foundation surface on which the monolayer is deposited is different.  $P^{32}$  was deposited on