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Mass Ratio of the Boron Isotopes from the Spectrum of BO

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Wave number data. New measurements are made of the rotational structure of the α bands of BO, and the wave numbers of the lines in the $^2\Pi_{1/2}$, $^2\Sigma$ component up to about $J=20$ are tabulated for the (0, 0), (0, 1), (0, 2), (1, 0), (1, 1), (1, 2), (2, 0), (3, 0), and (4, 0) bands of both the $B^{11}O$ and $B^{10}O$ systems. The $^2\Pi_{1/2}$, $^2\Sigma$ component of (5, 0) is also measured for $B^{11}O$ and the $^2\Pi_{3/2}$, $^2\Sigma$ component of (1, 0) for $B^{11}O$ and $B^{10}O$.

Vibrational isotope effect. Values of ΔG_v are computed by least-squares methods, and from the ratio $\Delta G_e^i/\Delta G_e$, the isotopic mass coefficient $\rho=(\mu/\mu^i)^{1/2}$ is found to be 1.02908 ± 0.00003, from the data on the $^2\Sigma$ state, and 1.02913 ± 0.00004, from that on $^2\Pi_{1/2}$. The latter figure is less trustworthy than the former, because of the presence of perturbations in the upper state. The mass-spectrograph measurements of Aston give $\rho=1.02908\pm0.00003$. The relation $\rho=x_e^i/x_e$ is verified to within the probable error, one part in 500. Improved values are obtained for the vibrational constants of the $^2\Sigma$ state, while for the $^2\Pi_{1/2}$ state, the equations $\Delta G_v=1260.415-21.870(v'+\frac{1}{2})$ and $\Delta G_v^i=1297.130-23.228(v'+\frac{1}{2})$ are considered to give the constants least influenced by perturbation effects.

Rotational isotope effect. From the rotational term-differences, the constants B_v and α are computed, also by least squares. The equations $B_v''=1.7803-0.01648(v''+\frac{1}{2})$, $B_v''^i=1.8850-0.01772(v_,''+\frac{1}{2})$, $B_v'^i{}_{-1/2}=1.4277-0.0196(v'+\frac{1}{2})$, and $B_{v,-1/2}'^i=1.5115-0.0211\ (v'+\frac{1}{2})$ give values of $\rho^2=B_e^i/B_e$ and $\rho^3=\alpha_e^i/\alpha_e$ which yield values of ρ equal to those obtained from the vibrational constants to within the probable error, one part in 4000 for the B_e's and one in 100 for the α_e's. A perturbation is found in the rotational levels of $^2\Pi_{1/2}{}^{(4)}$, which reaches its maximum at $J'=13\frac{1}{2}$. It is caused by the crossing of these levels by those of $^2\Sigma^{(17)}$, and affects only one component of the Λ-doublets, as expected. The Λ-doubling is investigated, and its constants computed.

Electronic isotope effect The spin coupling constant, A, is evaluated by the 1, 0 band, and found to be the same for $B^{11}O$ and $B^{10}O$, having the value 122.36 ± 0.03 cm^{-1}. The origins of the two isotopic band systems, $^2\Pi_{1/2}$, $^2\Sigma$, are found to be $\nu_{2e}=23{,}958.85\pm0.05$, $\nu_{2e}^i=23{,}959.18\pm0.06$, giving an electronic shift of 0.33 ± 0.08 cm^{-1}, the $B^{10}O$ origin being displaced toward the violet.

INTRODUCTION

MANY verifications of the theory of the isotope effect in band spectra[1] have established the fundamental correctness of the theory. They have also led to the discovery of new isotopes of low abundance. The frequencies of the band lines of a suspected isotopic molecule can be predicted with great certainty. The possibility of reversing the usual procedure, and of computing accurately the relative masses of isotopic atoms from the observed frequen-

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[1] F. W. Loomis, Bull. Nat. Res. Council **57,** 250 (1926). R. Mecke, Geiger and Scheel's Handbuch der Physik **21,** 565–573 (1929).

cies was first explicitly mentioned by Giauque,[2] although of course it was implied in Mulliken's original work.[3] Thus far the only case in which data of sufficient accuracy and completeness were available has been the atmospheric bands of oxygen, from which the mass ratio $O^{18}:O^{16}$ has now been found by Babcock and Birge[4] with an apparent accuracy of one part in 100,000. Since the oxygen isotopes have not yet been observed with the mass-spectrograph,[4a] the band-spectrum method is the only one at present available for determining the atomic weights of O^{18} and O^{17}.

It therefore appears highly desirable to apply this method to an element for which the isotopic masses have already been found by Aston's precision mass-spectrograph. This would allow us to decide whether the theory of the isotope effect is sufficiently correct in its finer details to be reliable in such an exacting application. For this purpose the most accurate results are obtained in the case of a light element where the proportional difference in mass of the isotopes is large. Boron and lithium are especially suitable, and in the present work it will be shown that the spectrum of BO gives satisfactory agreement with Aston's values for the mass-ratio $B^{11}:B^{10}$. Work on the $Li^7:Li^6$ ratio from the Li_2 bands is now in progress.

The BO spectrum excited in active nitrogen was used by Mulliken in his first and most accurate test of the isotope effect.[5] Of the three band systems in this spectrum, the α system is the most favorable for precise work, because it occurs at longer wave-lengths where an advantageous ratio of wave-length interval to frequency interval exists. The rotational structure of these bands was first shown by one of us[6] to be that of a $^2\Pi$, $^2\Sigma$ transition, in which the $^2\Pi$ level is inverted and constitutes a good example of the case *a* type of spin coupling. The complete experimental material was not given in this article, because further measurements, particularly of the bands of the less abundant isotopic molecule $B^{10}O$, were anticipated. In the meantime Scheib[7] has published extensive measurements of four bands of the α system as developed in the arc. Because of the higher temperature, many more rotational lines of each band are observed than in active nitrogen. All of Scheib's measurements concern the bands of the more abundant isotope, $B^{11}O$, since none of the $B^{10}O$ bands were identified in his work. Furthermore, the data given by Scheib for the (0,1), (0,2), (0,3) and (0,4) bands, while they suffice for the determination of the molecular constants of the lower, $^2\Sigma$ state, do not

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[2] W. F. Giauque, Nature **124**, 127 (1929).

[3] R. S. Mulliken, Phys. Rev. **25**, 119 (1925).

[4] H. D. Babcock and R. T. Birge, Phys. Rev. **37**, 233A (1931). See also the preliminary account and discussion given by Birge in Trans. Farad. Soc. **25**, 718 (1929). In the work of Mecke and Wurm, Zeits. f. Physik **61**, 37 (1930), the data were insufficient, and the methods not sufficiently rigorous, to yield a result of much significance.

[4a] F. W. Aston, Nature **130**, 21, July 2 (1932). Here is recorded the observation of the oxygen isotopes O^{17} and O^{18} by the mass-spectrograph and their abundance is estimated but no accurate mass determinations are made.

[5] R. S. Mulliken, Phys. Rev. **25**, 259 (1925).

[6] F. A. Jenkins, Proc. Nat. Acad. Sci. **13**, 496 (1927).

[7] W. Scheib, Zeits. f. Physik **60**, 74 (1930).

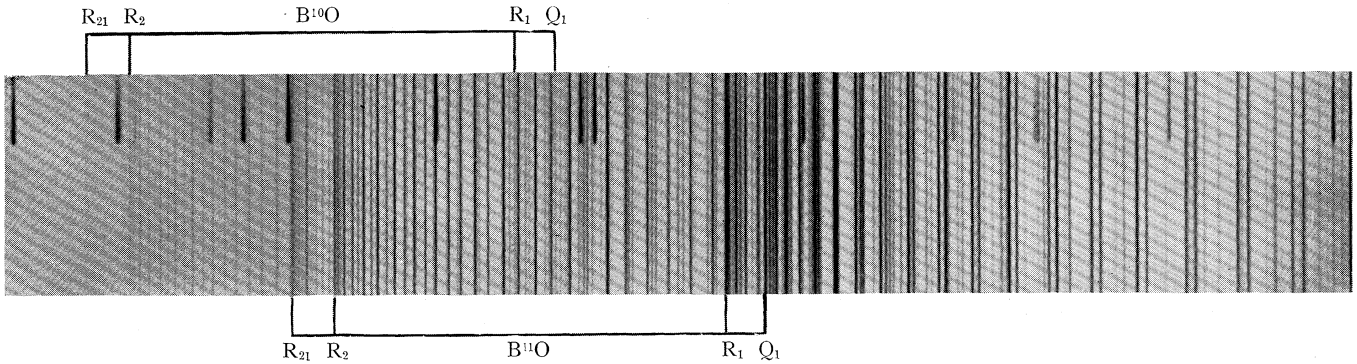

Fig. 1. The 2, 0 band of the α system of BO. First order of the 21-foot grating. The origin of the fainter, $B^{10}O$, band lies 8.876A further to the violet (i.e., to the left) in this case, and its rotational structure is seen to be almost an exact replica of that in the $B^{11}O$ band, but on a slightly larger scale.

yield all the constants of the $^2\Pi$ state, because these bands involve only $v'=0$. Hence the present article, besides giving the first measurements on the $B^{10}O$ system, also supplements Scheib's data for the upper state of the $B^{11}O$ system.

EXPERIMENTAL DATA

The spectrograms used in our analyses have already been briefly described in connection with the preliminary work mentioned above.[6] For a source, BCl_3 vapor was mixed with a stream of flowing active nitrogen containing traces of oxygen. The spectrum was photographed in the first and second orders of the Harvard 21-foot grating of 120,000 lines, which is mounted on the Paschen system. Double exposures of the iron arc spectrum were used to insure correct placing of the standards.

These plates have been completely remeasured with a Société Génevoise comparator. Independent measurements of the same band gave results differing on the average by less than 0.01 cm^{-1}. For the purpose in hand, it was not necessary or desirable to measure all the lines of each band, since an analysis of the $^2\Pi_{1/2}$, $^2\Sigma$ component only will give the required data. Also this sub-band is much freer from blends than the other, particularly for the fainter

TABLE I. *1, 0 band.*

K''	R_{21} λ4014.962	R_2 λ4017.087	R_2^i λ4012.781	Q_2	Q_2^i	P_2	P_2^i
0					24,911.64		
1	24,894.06	14,886.66	24,913.36	24,882.42			
2	896.66	886.66	913.36	879.51	905.90		
3	898.36	885.72	912.46	875.88	901.98		
4	899.48	884.14	910.75	871.47	897.30	24,861.83	
5	899.84	881.83	908.27	866.33	891.88	853.80	
6	899.84	878.71	905.04	860.44	885.72	845.16	24,869.41
7	898.36	874.92	900.94	853.80	878.71	835.81	859.47
8	896.66	870.35	896.15	846.38	870.77	825.60	848.77
9	894.06	865.02	890.50	838.24	862.14	814.71	837.00
10	890.75	858.94	884.14	829.34	852.67	803.07	824.87
11	886.66	852.10	876.79	819.70	842.50	790.66	811.64
12	881.83	844.50	868.78	809.31	831.51	777.47	797.93
13	876.26	836.15	859.92	798.16	819.70	763.54	783.06
14	870.25	827.05	850.27	786.30	807.10	748.84	767.42
15		817.19	839.83	773.61	793.75	733.52	750.99
16		806.57	828.61	760.15	779.34	717.32	733.52
17		795.24	816.55	745.98	764.48	700.31	715.99
18		783.06	803.54	731.15	748.84	682.77	
19		770.16	790.09	715.45	732.18	664.33	
20		756.58	775.56	698.99	714.75	645.16	
21		742.08		681.85	696.36	625.26	
22		726.99		663.91		604.59	
23		710.75		645.16		583.07	
24		694.28		625.71		560.91	
25		676.82		605.54		537.97	
26		658.43		584.54		514.25	
27		639.47		562.82		489.74	
28		619.77		540.24		464.59	
29		599.14		517.01			
30				492.68			
31				467.79			
32				442.10			

TABLE I. (*Continued*). *1, 0 band*

K''	R_1 λ4035.467	R_1^i λ4031.039	Q_1 λ4037.415	Q_1^i λ4033.112	P_1	P_1^i	P_{12}
0	24,764.96						
1	768.27		24,761.36	24,787.78			
2	770.94		761.19	787.78	24,754.45	24,780.54	
3	772.50	24,799.63	760.15	786.62	750.53	776.54	
4	773.31	800.52	758.23	784.55	745.98	771.52	
5	773.31	800.52	755.55	781.74	740.50	765.77	24,728.19
6	772.50	799.63	752.07	778.02	734.22	759.14	719.38
7	770.94	798.16	747.75	773.31	727.27	751.49	709.54
8	768.63	795.24	742.65	767.97	719.38	743.31	698.96
9	765.43	792.05	736.72	761.63	710.75	734.22	687.60
10	761.36	787.78	730.01	754.45	701.31	724.15	675.38
11	756.58	782.63	722.45	746.48	691.03	713.10	662.34
12	750.99	776.54	714.10	737.58	679.95	701.31	648.55
13	744.54	769.82	704.96	727.87	668.04	688.93	633.97
14	737.30	762.00	695.02	717.32	655.39	675.38	618.57
15	729.27	753.55	684.23	705.88	641.90	661.02	602.44
16	720.40	744.03	672.67	693.55	627.61	645.85	585.34
17	710.75	733.52	660.29	680.41	612.53	629.88	567.50
18	700.31	722.45	647.14	666.36	596.59	612.92	548.89
19	688.93	710.75	633.12	651.53	579.87	595.21	529.45
20	676.82	697.61	618.34	635.76	562.37	576.48	509.24
21	663.91	684.23	602.74	619.18	544.03	557.10	488.23
22	650.18	669.28	586.32	601.74	524.86	536.83	466.44
23	635.76		569.06	583.48	504.97	515.70	443.79
24	620.32		551.07		484.24		
25	604.32		532.23		462.68		
26	587.13		512.62		440.37		
27	569.49		492.18		417.24		
28	551.07		470.90		393.25		
29			448.90				
30			426.06				
31			402.37				
32			377.92				

TABLE I. (*Continued*). *1,1 band.*

K''	R_{21} λ4339.369	R_2 λ4341.931	R_2^i λ4346.957	Q_2	Q_2^i	P_2
0				23,024.05	22,997.43	
1	23,031.71	23,024.78	22,998.16	020.45	993.48	
2	034.49	024.78	998.16	017.55	990.50	
3	036.50	024.05	997.43	014.12	986.73	23,007.27
4	037.86	022.57	995.80	009.91	982.18	000.20
5	038.37	020.45	993.48	004.92	977.23	22,992.34
6	038.37	017.55	990.50	22,999.23	971.08	983.96
7	037.46	013.96	986.73	992.83	964.29	974.80
8	035.93	009.61	982.18	985.65	956.78	964.89
9	033.66	004.56	976.81	977.82	948.48	954.27
10	030.67	22,998.82	970.70	969.25	939.31	942.95
11	026.96	992.34	963.83	959.97	929.60	930.89
12	022.57	985.13	956.24	949.99	919.04	918.17
13	017.55	977.23	947.92	939.31		
14	011.50	968.62	938.77	927.84		
15	004.92	959.25	928.88	915.70		
16	22,997.43	949.16	918.17			
17	989.42	938.33				
18	980.64	926.81				
19	971.08	914.55				
20	960.89					
21	949.99					
22	938.33					

TABLE I. (*Continued*). *1, 2 band.*

K''	R_{21} λ4715.525	R_2 λ4718.660	R_2^i λ4736.250	Q_2	Q_2^i	P_2
0				21,185.85	21,107.19	
1	21,193.24	21,186.55	21,107.87	182.20	103.85	
2	196.20	186.55	107.87	179.47		21,175.35
3	198.39	185.85	107.19	175.96	096.63	168.95
4	199.40	184.56	105.75	171.87	092.28	162.29
5	200.64	182.51	103.85	167.02	087.28	154.61
6	200.64	179.86	100.84	161.52	081.28	146.37
7	199.99	176.51	097.30	155.33	074.94	137.33
8	198.82	172.46	092.97	148.49	067.59	127.71
9	196.84	167.73	088.05	140.95		117.40
10	194.11	162.29	082.38	132.70		106.38
11	190.81	156.18	075.88	123.80		094.70
12	186.55	149.38		114.21		082.38
13	182.20	141.91		103.85		068.97
14	176.51	133.72		092.97		
15	170.42	124.87		081.28		
16	163.61	115.26				
17	156.18	105.04				
18		094.07				
19		082.38				

TABLE I. (*Continued*). *0,0 band.*

K''	R_{21}	R_2 λ4227.480	R_2^i	Q_2	Q_2^i	P_2
0				23,646.02	23,637.42	
1		23,648.13		643.86	634.99	
2		648.13		641.02	632.03	
3		647.40	23,638.71	637.42	628.20	
4		646.02	637.42	633.19	623.77	
5	*not observed*	643.86	634.99	628.20	618.43	23,615.57
6		641.02	632.03	622.50	612.45	606.98
7		637.42	628.20	616.09	605.66	
8		633.19	623.77	609.00	598.13	587.84
9		628.20	618.43	601.12	589.93	577.27
10		622.50	612.45	592.60	580.81	565.87
11		616.09	605.66	583.31	571.02	553.85
12		609.00	598.13	573.35	560.47	540.93
13		601.12	589.93	562.67		527.62
14		592.60	580.81	551.23	537.20	
15		583.31	571.02	539.14	524.27	
16		573.35	560.47	526.33		
17		562.67				
18		551.23	537.20			
19		539.14	524.27			
20		526.33				

TABLE I. (*Continued*). *0,1 band.*

K''	R_{21} λ4585.702	R_2 λ4588.759	R_2^i λ4601.883	Q_2	Q_2^i	P_2
0	21,789.96			21,783.90		
1	793.32	21,786.30	21,724.17	781.94	21,719.77	
2	796.15	786.30	724.33	779.22	716.84	21,775.06
3	798.41	785.73	723.64	775.75		768.70
4	799.89	784.45	722.40	771.59	708.64	761.73
5	800.83	782.50	720.35	766.76	703.80	754.11
6	800.83	779.84	717.50	761.27	697.84	745.83
7	800.42	776.54	714.06	755.08	691.33	736.86
8	799.17	772.52	709.86	748.26	684.09	727.23
9	797.31	767.83	704.90	740.74	676.22	716.84
10	794.76	762.51	699.28	732.52		705.83
11	791.48	756.44	692.89	723.64		694.20
12	787.56	749.71	685.78	714.06		681.78
13		742.31	678.04	703.80		
14		734.21		692.89		
15		725.45		681.29		
16		715.94				
17		705.83				
18		694.99				
19		683.45				

TABLE I. (*Continued*). *0,2 band.*

K''	R_{21} λ5007.846	R_2 λ5011.650	R_2^i λ5040.468	Q_2	Q_2^i	P_2
0						
1		19,947.96	19,833.91	19,943.72	19,829.65	
2	19,958.11	947.96	833.91	940.82		19,936.67
3	960.39	947.55	833.35	937.49		
4	961.93	946.48	832.34	933.46		923.60
5	962.84	944.61	830.45	928.90		916.22
6	963.12	942.16	827.85	923.60		908.17
7	962.84	938.94	824.61	917.66	802.01	899.35
8	961.93	935.34		911.05	794.98	889.94
9	960.39	930.97		903.81	787.37	879.99
10	958.11	925.93	810.87	895.96	779.07	869.29
11	955.26	920.24	804.89	887.44		857.97
12	951.69	913.91	798.19	878.25		845.90
13		906.92	790.86	868.43	749.96	833.35
14		899.35	782.81	857.97		
15		891.05	774.06	846.84		
16		882.09	764.69	835.09		
17		872.48	754.55			
18		862.18				
19		851.33				

TABLE I. (*Continued*). *2,0 band.*

K''	R_{21} λ3828.047	R_2 λ3829.857	R_2^i λ3820.962	Q_2	Q_2^i	P_2
0				26,101.49		
1		26,103.26	26,164.03	099.18	26,159.69	
2	26,112.75	103.26	164.03	096.22	156.58	
3	114.48	102.18	162.84	092.45	152.56	26,085.55
4	115.61	100.38	161.06	087.91	147.78	078.34
5	115.61	097.91	158.36	082.61	142.09	070.30
6	115.13	094.56	154.79	076.51	135.68	061.47
7	113.73	090.45	150.43	069.60	128.39	051.82
8	111.40	085.55	145.23	061.96	120.26	041.42
9	108.57	079.88	139.25	053.45	111.40	030.19
10	104.81	073.38	132.38	044.23	101.49	018.25
11	100.38	066.13	124.64	034.16	090.86	005.47
12		058.10	116.14	023.43	079.41	25,991.96
13		049.22	106.77	011.75	067.10	977.63
14		039.58	096.51	25,999.35	053.95	
15		029.14	085.55	986.19	039.94	
16		017.91	073.38		025.08	
17		005.91	060.65		009.26	
18		25,993.03	047.15		25,992.42	
19		979.45	032.79			
20			017.53			
21			001.43			

TABLE I. (*Continued*). *3,0 band.*

K''	R_{21} λ3660.631	R_2 λ3662.205	R_2^i λ3649.691	Q_2	Q_2^i	P_2
0						
1	27,304.88	27,298.22	27,391.80	27,294.37	27,387.41	
2	307.45	298.22	391.80	291.30	384.25	
3	309.14	297.12	390.50	287.44	380.23	27,280.77
4	309.95	295.14	388.37	282.77	375.31	273.25
5	309.95	292.38	385.56	277.29	369.60	265.18
6	309.14	288.85	381.78	271.00	362.97	255.95
7	307.45	284.46	377.79	263.88	355.33	246.46
8	304.52	279.21	371.59	255.95	346.98	235.70
9	301.52	273.25	365.16	247.14	337.64	224.22
10	297.12	266.28	357.87	237.54	327.44	211.91
11	292.38	258.70	349.67	227.13	316.36	198.88
12		250.13	340.61	215.89	304.52	184.89
13		240.76	330.65	203.79	291.44	
14		230.63	319.96	190.90	277.84	
15		219.57	308.20	177.03	263.42	
16		207.74			247.76	
17		195.06			231.57	
18		181.60	267.95		214.43	
19			252.58		196.40	
20			236.45			
21			219.57			
22			201.64			
23			183.44			

TABLE I. (*Continued*).

	4,0 band				5,0 band	
K''	R_2 λ3511.222	R_2^i λ3495.848	Q_2	Q_2^i	R_2	Q_2
0						
1	28,472.01	28,597.22				29,621.18
2	472.01	97.22	28,465.22	28,590.06	29,624.75	617.95
3	470.71	95.65	461.25	85.58	623.49	613.87
4	468.66	93.40	456.45	80.41	621.18	608.93
5	465.71	90.41	450.80	74.50	617.95	603.11
6	461.90	86.15	444.31	67.61	613.87	596.43
7	457.20	81.38	436.91	59.80	608.93	588.87
8	451.70	75.39	428.70	51.01	603.11	580.29
9	445.31	68.60	419.62	41.45	596.43	570.89
10	438.05	60.86	409.61	30.76	588.87	560.61
11	430.00	52.21	398.80	19.33	580.29	549.41
12	421.08	42.77	387.16	06.98	570.89	537.36
13	411.75	32.20	374.61	28,493.69	560.61	524.31
14	400.10	20.83	361.18		549.41	
15	388.60	08.58			537.36	
16	376.20				524.31	
17	362.98					

isotopic system. This will be evident from the enlargement, Fig. 1. All the four branches of the $^2\Pi_{1/2}$, $^2\Sigma$ sub-band, which are designated in order R_{21}, R_2, Q_2, and P_2, could be accurately measured in most cases for the stronger system, $B^{11}O$, but the R_{21} branch (and sometimes the P_2) of $B^{10}O$ was too faint to measure. To get the constants of the lower state, the two progressions $v'=0$ and $v'=1$ were measured from $v''=0$ to 2, while for the upper state four additional bands of the strong $v''=0$ progression, (2,0), (3,0), (4,0) and (5,0), were investigated. Of these ten bands, only 0,1 and 0,2 had been measured by Scheib. Our results are systematically lower by 0.21 cm^{-1} in the former band, and by 0.16 cm^{-1} in the latter. The possibility of a constant error of this magnitude in our measurements was eliminated by checking against the lines of the 0,9 β-band of NO and the boron doublet, λλ2496.778, 2497.733 (in the second order), which were present in the band source.

In Table I will be found the wave numbers in vacuum of all of the measured lines assigned to the various branches in these bands, with the wavelength in I.A. of the observed heads at the top of the appropriate columns. The column headings for the less intense system, that of $B^{10}O$, carry the superscript *i*. For 1,0 the low-frequency sub-band $^2\Pi_{1\,1/2}$, $^2\Sigma$ was also measured and analyzed in order to find the constants of the $^2\Pi_{1\,1/2}$ state and the electronic coupling coefficient, A. The 0, 0 band was unsatisfactory for this purpose because it is fainter, and confused with the 3,2 band.

VIBRATIONAL ISOTOPE EFFECT

The vibrational terms of the two isotopic molecules may be represented[8] by the following equation:

$$\begin{aligned} B^{11}O\ G &= \omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 + y_e\omega_e(v+\tfrac{1}{2})^3 + \cdots \\ B^{10}O\ G^i &= \omega_e^i(v+\tfrac{1}{2}) - x_e^i\omega_e^i(v+\tfrac{1}{2})^2 + y_e^i\omega_e^i(v+\tfrac{1}{2})^3 + \cdots \qquad (1) \\ &= \rho\omega_e(v+\tfrac{1}{2}) - \rho^2 x_e\omega_e(v+\tfrac{1}{2})^2 + \rho^3 y_e\omega_e(v+\tfrac{1}{2})^3 + \cdots, \end{aligned}$$

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[8] R. S. Mulliken, Phys. Rev. **25**, 125 (1925).

in which ρ^2 is the ratio of the reduced masses μ/μ^i. We shall use the superscript i to distinguish quantities pertaining to the less abundant molecule $B^{10}O$. The problem of finding the relative masses thus becomes one of evaluating as accurately as possible the constant ρ from the relation

$$\omega_e{}^i/\omega_e = \rho. \tag{2}$$

Other values of this constant, though much less accurate, can be found from the higher power term; since

$$x_e{}^i/x_e = \rho, \quad y_e{}^i/y_e = \rho^2. \tag{3}$$

From the spectrum we can evaluate the term-differences

$$\Delta G_v = \omega_e - 2x_e\omega_e(v + \tfrac{1}{2}) + 3y_e\omega_e[(v + \tfrac{1}{2})^2 + 1/12] + \cdots \tag{4}$$

by finding the separation of the origins of two adjacent bands in a progression. This separation is best determined by a study of the combination differences of the type

$$\begin{aligned} R_2{}^{(0,0)}(K) - R_2{}^{(0,1)}(K) &= Q_2{}^{(0,0)}(K) - Q_2{}^{(0,1)}(K) = P_2{}^{(0,0)}(K) - P_2{}^{(0,1)}(K) \\ &= \Delta G_{1/2}'' - (B_0'' - B_1'')(K + \tfrac{1}{2})^2 + \cdots \\ &= \Delta G_{1/2}'' - \alpha''(K + \tfrac{1}{2})^2 + \cdots \end{aligned} \tag{5a}$$

$$\begin{aligned} R_2{}^{(1,0)}(K) - R_2{}^{(0,0)}(K) &= Q_2{}^{(1,0)}(K + 1) - Q_2{}^{(0,0)}(K + 1) \\ &= P_2{}^{(1,0)}(K + 2) - P_2{}^{(0,0)}(K + 2) \\ &= \Delta G'_{1/2} - (B'_{0,-1/2} - B'_{1,-1/2})(K + \tfrac{1}{2})^2 + \cdots \\ &= \Delta G'_{1/2} - \alpha'(K + \tfrac{1}{2})^2 + \cdots \end{aligned} \tag{5b}$$

in which the higher power terms can be shown to be negligible for all practical purposes. $B_{v,-1/2}$ represents the effective B_v for the component ${}^2\Pi_{1/2}$ of the upper state. These term-differences, which we shall refer to as ΔT, are fitted by least squares to a parabola having its vertex at $K = -\frac{1}{2}$. The constant term in this solution yields the best value of the vibrational term-difference ΔG, which is required. Fig. 2c shows by diagrams the relation of pairs of lines, connected by arrows, whose wave-number difference gives a single value of ΔT (and of ΔT^i) for the lower state. This will be clear from the term diagram in Fig. 2b.

The first step in the computation is obviously to prove from the experimental data that the vertex of the $\Delta T{:}K$ parabola actually does occur at $K = -\frac{1}{2}$ to within the error of the measurements. Fig. 2d shows the data from the R_2 branches of the 1,0 and 1,1 bands and their least squares solution in the form of Eq. (5a). By carrying through the solution, admitting a linear term in $(K+\frac{1}{2})$, a value of the constant term was obtained which differed from the first value by less than its probable error. This justifies the assumption that the vertex occurs at $K = -\frac{1}{2}$, an assumption made in obtaining all of the results discussed below. To show the extent to which Eq. (5a) is capable of representing the data, we give in Table II the results of the solution for $Q_2{}^{(0,0)}(K) - Q_2{}^{(0,1)}(K)$. This is a typical example from the

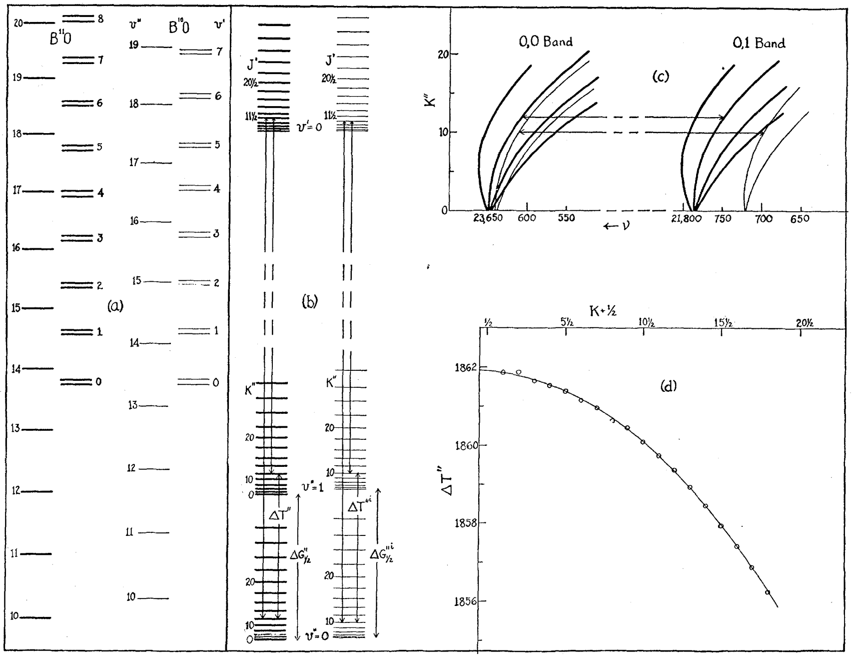

Fig. 2. (a) Some vibrational levels of the two isotopic molecules drawn to scale. The single levels on the left belong to the lower, $^2\Sigma$ state, and the double levels are $^2\Pi$. For $B^{11}O$, the $v''=17$ level of $^2\Sigma$ lies very close to $v'=4$ of $^2\Pi_{1/2}$, the upper component. This explains the observed perturbation in the $v'=4$ rotational levels (cf. Fig. 3 and text, p. 478). (b) Alternate rotational levels associated with $v''=0$ and 1 of $^2\Sigma$ and with $v'=0$ of $^2\Pi_{1/2}$. The difference in frequency of the two lines whose transitions are indicated by the long vertical arrows, $R_2^{(0,0)}$ (12) and $R_2^{(0,1)}$ (12), gives the term-difference $\Delta T''$ (12) in the lower state. As explained in the text, the various values of $\Delta T''$ and $\Delta T''^i$ are extrapolated to $\Delta T''(-\frac{1}{2})$, giving accurate values of the vibrational term-differences $\Delta G''$ and $\Delta G''^i$. (c) Fortrat diagrams of the $^2\Pi_{1/2}$, $^2\Sigma$ components of the 0, 0 and 0, 1 bands. Heavy curves represent branches of the $B^{11}O$ bands, and light curves those measured for $B^{10}O$. The arrows indicate the differences $\Delta T''$ (12) and $\Delta T''^i$ (10). (d) A typical $\Delta T : K+\frac{1}{2}$ parabola, derived from the R_2 branches of the 1, 0 and 1, 1 bands. Circles are observed values, while the curve is the least squares solution, which intersects the axis, $K+\frac{1}{2}=0$, at the value of $\Delta G_{1/2}''$.

TABLE II. $\Delta T''=\Delta G_{1/2}''-(B_0''-B_1'')\,(K+1/2)^2=1861.937-0.01698\,(K+1/2)^2$.

K''	$\Delta T''$ (*Obs.*)	$\Delta T''$ (*Calc.*)	$O-C$
1	1861.92	1861.899	+0.021
2	1861.80	1861.831	−0.031
3	1861.67	1861.729	−0.059
4	1861.60	1861.593	+0.007
5	1861.44	1861.423	+0.017
6	1861.23	1861.220	+0.010
7	1861.01	1860.982	+0.028
8	1860.74	1860.710	+0.030
9	1860.38	1860.404	−0.024
10	1860.08	1860.065	+0.015
11	1859.67	1859.691	−0.021
12	1859.29	1859.284	+0.006
13	1858.87	1858.842	+0.028
14	1858.34	1858.367	−0.027
15	1857.85	1857.857	−0.007

42 least squares solutions carried out in evaluating the various values of $\Delta G_v''$ and $\Delta G_v'$.

TABLE III. *Vibrational constants of the* $^2\Sigma$ *state.*

B¹¹O	*Branch*	*Bands*	$\Delta G_v''$	α''	*Wt.*
	R_2	0,0–0,1	1861.86 ±0.01	0.0164	19
	Q_2	0,0–0,1	1861.94 ±0.01	0.0170	15
	P_2	0,0–0,1	1861.92 ±0.04	0.0171	6
			Av. 1861.896±0.018		
	R_2	0,1–0,2	1838.37 ±0.01	0.0164	18
	Q_2	0,1–0,2	1838.37 ±0.01	0.0164	14
	P_2	0,1–0,2	1838.38 ±0.03	0.0162	8
			Av. 1838.375±0.002	*Av.* 0.01656±0.00013	
B¹⁰O	R_2^i	0,0–0,1	1915.28 ±0.02	0.0189	11
	Q_2^i	0,0–0,1	1915.29 ±0.01	0.0173	6
			1915.286±0.003		
	R_2^i	0,1–0,2	1890.41 ±0.02	0.0179	11
	Q_2^i	0,1–0,2	1890.10 ±0.02	0.0138	3
			1890.343±0.078	0.01774±0.00082	
			$\omega_e=1885.417\pm0.037$	$\omega_e^i=1940.229\pm0.078$	$\rho=\mathbf{1.02907}$ $\pm\mathbf{0.00004}$
			$x_e=0.006238$	$x_e^i=0.006428$	$\rho=1.030$
B¹¹O	*Branch*	*Bands*	$\Delta G_v''$	α''	*Wt.*
	R_2	1,0–1,1	1861.90 ±0.01	0.0164	18
	Q_2	1,0–1,1	1861.94 ±0.01	0.0169	14
	P_2	1,0–1,1	1861.86 ±0.02	0.0160	9
			1861.903±0.015		
	R_2	1,1–1,2	1838.34 ±0.01	0.0164	19
	Q_2	1,1–1,2	1838.36 ±0.01	0.0164	14
	P_2	1,1–1,2	1838.33 ±0.03	0.0167	10
			1838.348±0.005	0.01641±0.00007	
B¹⁰O	R_2^i	1,0–1,1	1915.27 ±0.02	0.0177	15
	Q_2^i	1,0–1,1	1915.40 ±0.06	0.0189	9
			1915.318±0.044		
	R_2^i	1,1–1,2	1890.36 ±0.03	0.0179	11
	Q_2^i	1,1–1,2	1890.29 ±0.04	0.0154	6
			1890.336±0.025	0.01770±0.00040	
			$\omega_e=1885.458\pm0.031$	$\omega_e^i=1940.300\pm0.092$	$\rho=\mathbf{1.02909}$ $\pm\mathbf{0.00005}$
			$x_e=0.006246\pm0.000006$	$x_e^i=0.006438\pm0.000013$	$\rho=1.031$ ±0.002

Lower state

The $^2\Sigma$ state is the easiest and most satisfactory to deal with because it does not involve complicated interactions of electronic and rotational motions. That the spin doubling is negligible, even for large rotation, is shown by an examination of Scheib's results.[9] Further advantages of the $^2\Sigma$ state over the $^2\Pi$ for the precise determination of ρ lie in the greater magnitude of ω_e, as well as in the fact that this is the normal state, and therefore should be free from perturbations.

Table III contains the results of the various solutions for $\Delta G_v''$, with the probable error of each computed from the residuals by the accepted least squares formulas.[10] It will be noticed that the faint R_{21} branch has not been used at all, nor the P_2 branch in the case of $B^{10}O$. The mean values have been taken separately for the progressions $v'=0$ and $v'=1$, so that two independent evaluations of the vibrational constants are obtained. Computation of the probable errors of the mean $\Delta G_v''$ values based on their internal consistency[10] (on the probable errors of the individual determinations of ΔG_v) showed that these are considerably smaller than the probable errors found from external consistency (determined from the deviation of the individual determinations from their mean). Therefore, following the recommendation of Birge,[10] we have adopted the probable errors from external consistency even though these are based on such a small number of items. The items are then logically weighted according to the number of observations, or values of ΔT, used in the evaluation of each, rather than inversely as the squares of their probable errors. In this way the most consistent set of values of a given vibrational term-difference is obtained, as well as a conservative estimate of the probable error of the mean.

Following each set of results in Table III are given the ω_e and x_e calculated by Eq. (4) The data, involving as they do only $v''=0$, 1, and 2, are not sufficient to determine the term $y_e\omega_e(v+\frac{1}{2})^3$ or higher powers. But these terms are usually negligibly small for the ground states of stable molecules, and in fact Mulliken's data on band heads shows no departure from a linear dependence of ΔG_v on v up to $v''=8$. Hence we obtain the constants on the assumption that these terms are zero. Our best values of ρ, from the ratio ω_e^i/ω_e, are listed in Table III. The values from x_e^i/x_e are much less accurate but agree to well within the probable error.

Upper state

In the determination of the vibrational constants for the $^2\Pi$ state, there are several complications not present in the $^2\Sigma$ state. In the first place, since the spin lies coupled to the figure axis by the field of the orbit, the electronic level is two-fold with a separation of about 122 cm^{-1}. Assuming no interaction of the spin with the molecular rotation, we could work exclusively with the one component, $^2\Pi_{1/2}$, $^2\Sigma$, as a separate band system. This procedure is largely justified, as will be shown below in the discussion of the rotational energy function. However, there are unknown additive constants,[11] such as

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[9] Cf. R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931). We have also reexamined the data and find no evidence of an appreciable spin doubling.

[10] R. T. Birge, Phys. Rev. **40**, 207 (1932).

[11] R. S. Mulliken, Rev. Mod. Phys. **2**, 114 (1930).

$\overline{G^2}$ and C_Σ, in the energy function which, though small, cannot be corrected for in obtaining the true ΔG values. Finally, the most serious difficulty is the possibility of perturbations, which may affect the vibrational, as well as the rotational terms. These are known in the analogous band system of CN,[12] and are also found here, though to a lesser degree. Because of these draw-

TABLE IV. *Vibrational constants of the ${}^2\Pi$ state.*

$B^{11}O$	*Branch*	*Bands*	$\Delta G_v'$	α'	*Wt.*
	R_2	1,0–0,0	1238.58	0.0196	18
	Q_2	1,0–0,0	1238.53	0.0193	14
	P_2	1,0–0,0	1238.49	0.0181	7
			Av. 1238.545 ±0.016		
	R_2	2,0–1,0	1216.65	0.0196	18
	Q_2	2,0–1,0	1216.70	0.0200	15
	P_2	2,0–1,0	1216.67	0.0204	9
			1216.675 ±0.010		
	R_2	3,0–2,0	1195.08	0.0193	18
	Q_2	3,0–2,0	1195.10	0.0196	13
	P_2	3,0–2,0	1195.11	0.0195	8
			1195.095		
	R_2	4,0–3,0	1173.87	0.0194	11
	Q_2	4,0–3,0	1173.92	0.0200	13
			1173.896		
	R_2	5,0–4,0	1152.88	0.0195	10
	Q_2	5,0–4,0	1152.73	0.0193	11
			1152.799	0.01959	
$B^{10}O$	R_2^i	1,0–0,0	1273.93	0.0213	15
	Q_2^i	1,0–0,0	1273.87	0.0214	13
			1273.902 ±0.021		
	R_2^i	2,0–1,0	1250.66	0.0209	18
	Q_2^i	2,0–1,0	1250.69	0.0211	14
			1250.674 ±0.008		
	R_2^i	3,0–2,0	1227.83	0.0210	17
	Q_2^i	3,0–2,0	1227.81	0.0206	14
			1227.823		
	R_2^i	4,0–3,0	1205.426	0.0214	14
	Q_2^i	4,0–3,0	1205.329	0.0210	11
			1205.383	0.02111	
	With only $\Delta G'_{1/2}$ *and* $\Delta G'_{1\,1/2}$: $\omega_e = 1260.415 \pm 0.033$ $x_e = 0.008676$		$\omega_e^i = 1297.130 \pm 0.048$ $x_e^i = 0.008954$		$\rho = \mathbf{1.02913}$ $\mathbf{\pm 0.00004}$ $\rho = 1.032$

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[12] F. A. Jenkins, Y. K. Roots and R. S. Mulliken, Phys. Rev. **39**, 16 (1932).

backs the resulting values of ρ are of little importance in bettering those already obtained. However, the analysis has been done since it gives fairly reliable values of the vibrational constants, and affords a check on the ρ already found from the lower state.

Our measurements include bands of the $v''=0$ progression up to $v'=5$ for $B^{11}O$, and $v'=4$ for $B^{10}O$. All of the values were computed from the ΔT parabolas of the type of Eq. (5b), using least squares in exactly the same way as for the lower state. The results are shown in Table IV. The probable errors of the individual ΔG_v's have not been calculated because internal consistency is of little value in getting the probable error of the mean, as explained above. But the residuals were always examined, and where a trend was noted, the worst value or values were discarded, and a new solution made. In the solutions for $\Delta G'_{3\,1/2}$ and $\Delta G'_{4\,1/2}$ from the R_2 branch, the residuals grew suddenly large above $K=11$, showing the presence of a large perturbation in the R_2 branch of the 4,0 band. The Q_2 branch is perfectly regular. The perturbation reaches its maximum (0.66 cm^{-1}) at $J'=13\frac{1}{2}$ of the $^2\Pi_{1/2}$ state. Fig. 3 is a plot of the residuals from the final, adopted solution for $\Delta G'_{3\,1/2}$ (R_2 branch), and shows the usual form characteristic of a large perturbation.

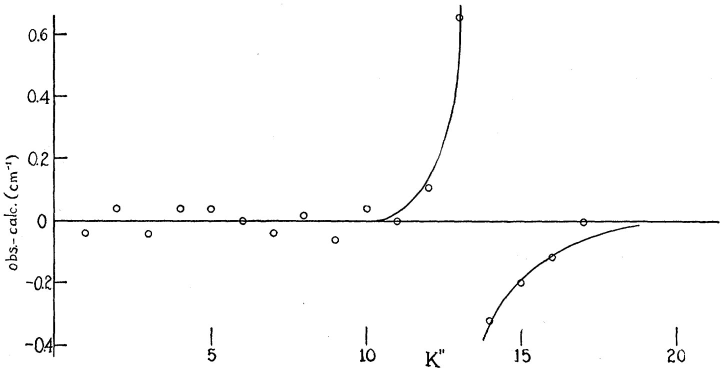

Fig. 3. Residuals of the ΔT parabola $R_2^{(4,0)}-R_2^{(3,0)}$ from the solution adopted. The large discontinuity in the curve at $K=13$ represents a perturbation in the rotational terms of the upper state.

This perturbation is obviously analogous to one of those occurring in the $v'=6$ levels of the $^2\Pi$ state in CN.[12] It results from the near equality of energy levels with the same J in the $^2\Pi$ and the lower $^2\Sigma$ states. When we computed the terms in these two states from the data already established, it was found that by far the closest approach of any two terms is $^2\Sigma^{(17)}$ to $^2\Pi_{1/2}{}^{(4)}$. The levels are drawn to scale in Fig. 2a, and one sees that the lowest $^2\Pi_{1/2}$ terms are far removed from the $^2\Sigma$ terms, and hence not likely to be seriously perturbed. But for the vibrational states near $v'=4$, we expect irregularities in the ΔG values, such as were found in CN. Actually, anomalies are present, the ΔG curve departing greatly from a straight line, and showing a large "positive" curvature (positive y_e).[13] It does not seem of value to attempt an analytical representation of all the observed vibrational terms of the upper state.

For the determination of ρ, the states $v'=0$, 1, and 2 only have been used, to avoid as far as possible the effect of the perturbations. The resulting values, shown in Table IV, agree surprisingly well with those from the normal state, considering the difficulties and approximations in their evaluation.

ROTATIONAL ISOTOPE EFFECT

Although the rotational effect is capable of yielding values of ρ which are only about one-tenth as accurate as those from the vibrational effect, we have studied it to obtain the best possible values of the rotational constants for both "main" ($B^{11}O$) and "isotopic" ($B^{10}O$) systems. This is essential if conclusions are to be drawn about the electronic effect, as will be done below. The principal constant, B_v, which occurs in the expressions for the rotational energy, differs for the two isotopic molecules according to the following equations.[8]

$$\mathbf{B^{11}O}: B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \cdots \tag{6a}$$

$$\begin{aligned}\mathbf{B^{10}O}: B_v{}^i &= B_e{}^i - \alpha_e{}^i(v+\tfrac{1}{2}) + \gamma_e{}^i(v+\tfrac{1}{2})^2 + \cdots \\ &= \rho^2 B_e - \rho^3\alpha_e(v+\tfrac{1}{2}) + \rho^4\gamma_e(v+\tfrac{1}{2})^2 + \cdots .\end{aligned} \tag{6b}$$

Here the only value of ρ which is at all accurate is found from

$$B_e{}^i/B_e = \rho^2,$$

the constants α_e and γ_e being too small to permit much precision.

Lower state

For the main system, values of B_v'' could be calculated directly by least squares from the combination differences

$$\Delta_2F_2''(K) = R_2(K-1) - P_2(K+1) = 4B_v''(K+\tfrac{1}{2}) + 8D_v''(K+\tfrac{1}{2})^3 + \cdots \tag{7}$$

after eliminating the cubic term as usual[14] by preliminary calculation of D_v from the theoretical relation with B_e and ω_e. We have used $D_e''=-6.29\times10^{-6}$ $\beta''=0$ $D_e''{}^i=\rho^4D_e''=7.05\times10^{-6}$. For the isotopic system, however, where the P_2 branch was not available, we must use the quantities

$$\begin{aligned}\Delta_1F''(K) &= R_2(K-\tfrac{1}{2}) - Q_2(K+\tfrac{1}{2}) - \Delta\nu_{dc} \cdots \\ &= 2B_v''(K+\tfrac{1}{2}) + 4D_v''(K+\tfrac{1}{2})^3 - \Delta\nu_{dc} \cdots\end{aligned} \tag{8}$$

The term $\Delta\nu_{dc}$ represents the Λ-doubling in the upper state from which the two lines come. It can easily be corrected for, as we shall show later, and we have proved by tests on the main system that the resulting B_v's agree exactly

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[13] Although it is commonly said that a negative curvature is the normal one (Birge and Sponer), it appears that in the few cases where extensive and accurate measures of band origins are available (NOβ, SiN) a positive curvature for the upper state is most common. However, perhaps perturbing effects are also at work in these cases.

[14] Reference 1, p. 174.

with those from Eq. (7). The chief results of these calculations are collected in Table V. No values are quoted for $v''=2$, since the data from the isotopic system for this state are too fragmentary to be of value here.

The data of Table V were derived from the analysis of the rotational term-differences alone, and thus furnish a valuable independent check on the results from the vibrational analyses contained in Tables III and IV. It is possible to improve somewhat the accuracy of the value of ρ from rotational constants, by assuming the more accurate values of α_e obtained in connection with the vibrational analysis. Thus, if we fix $\alpha_e''=0.01648\pm0.00008$, $\alpha_e''=0.01772\pm0.00042$ and us the B_v'' values of Table V, we find:

TABLE V. *Rotational constants of the* $^2\Sigma$ *state.*

$B^{11}O$ *Bands*	B_v''		B_v''	$B^{10}O$ *Bands*	$B_v''^i$		$B_v''^i$
0,0	1.7715	0,1	1.7569	0,0	1.8738	0,1	1.8600
1,0	1.7720	1,1	1.7545	1,0	1.8763	1,1	1.8581
2,0	1.7725		1.7557 ±0.0008	2,0	1.8768		1.8587 ±0.0009
3,0	1.7719			3,0	1.8753		
Av.	1.7720 ±0.0001				1.8758 ±0.0006		
$B_e''=1.78015\pm0.0004$ $\alpha_e''=0.0163\pm0.0008$				$B_e''^i=1.88465\pm0.0008$ $\alpha_e''^i=0.0171\pm0.0011$			
$\rho^2=B_e''^i/B_e''=1.0587\pm0.0005$ $\rho^3=\alpha_e''^i/\alpha_e''=1.05$					$\rho=1.0289\pm0.00025$ $\rho=1.02$		

$$B_e = 1.7803 \pm 0.0004$$

$$B_e^i = 1.8850 \pm 0.0005$$

$$\rho^2 = 1.0588 \pm 0.0004 \qquad \rho = 1.0290 \pm 0.0002$$

$$\rho^3 = \alpha_e''^i/\alpha_e'' = 1.075 \pm 0.024 \qquad \rho = 1.024 \pm 0.008$$

Upper state

As stated above, the initial state of these bands is an inverted $^2\Pi$. Because of the large multiplet separation, it is obviously very near to case *a* type of spin coupling, at least for small rotation. The form of the rotational energy function is in general complicated in such a state, because of the spin uncoupling which occurs as the rotation increases. In the present instance, however, the departure toward case *b* should be inappreciable at small rotational quantum numbers. This was found to be true, by investigating graphically the combination differences

$$\begin{aligned} \Delta_2F_2'(K) &= R_2(K) - P_2(K) = 4B'_{v,-1/2}(K+\tfrac{1}{2}) + 8D'_{v,-1/2}(K+\tfrac{1}{2})^3 + \cdots \\ \Delta_2F_1'(K) &= R_1(K) - P_1(K) = 4B'_{v,+1/2}(K+\tfrac{1}{2}) + 8D'_{v,+1/2}(K+\tfrac{1}{2})^3 + \cdots \end{aligned} \qquad (7)$$

using the very complete data for the 1,0 band. The quantities $B_v'{}_{,-1/2}$ and $B_v'{}_{,+1/2}$, although not equal, were found to be practically constant below $J\sim30$. Hence, if lines of low J are used, the spin uncoupling need not be considered. Probably this $^2\Pi$ state departs more toward case *c*, where the two components can be considered as separate electronic levels (each with its own constants) than toward case *b*. Fortunately, this makes it possible to apply the usual least squares methods for the evaluation of B_v, and in doing so we have confined ourselves to lines having rotational quantum numbers below 15.

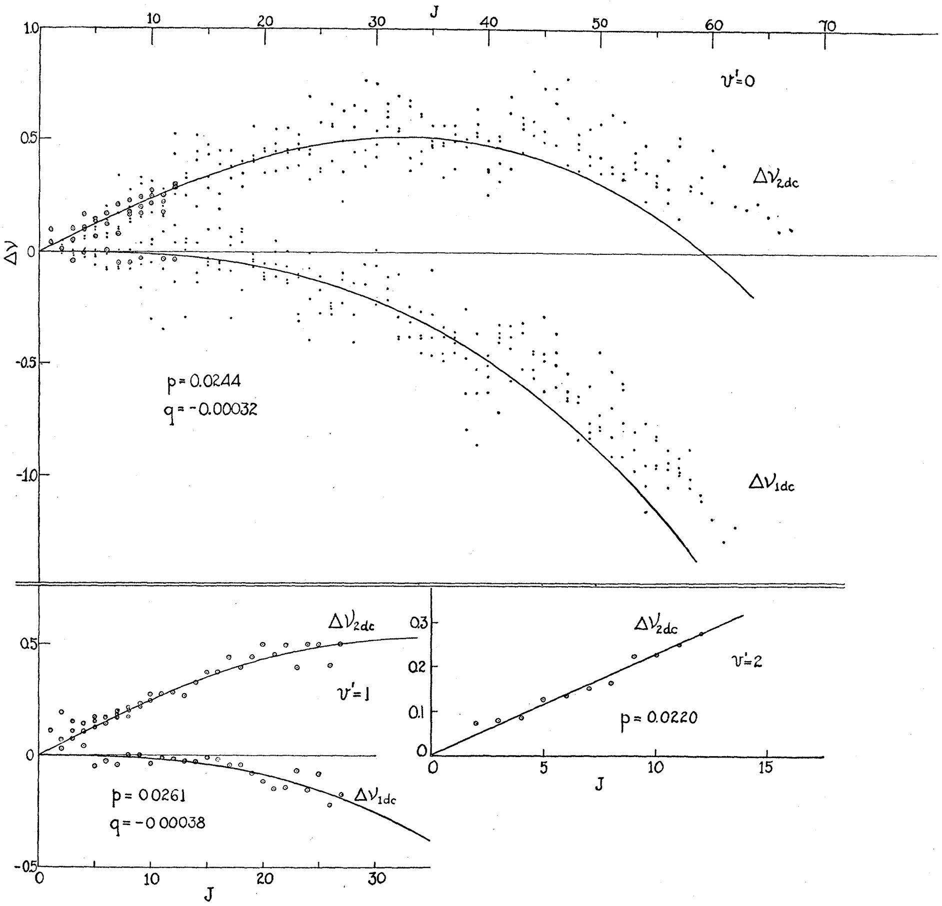

Fig. 4. Λ-doubling in the upper states $v'=0$, 1 and 2. Values indicated by circles are from our data, and the small dots are from the measurements of Scheib.[7] The curves are the theoretical ones, drawn according to the constants indicated.

Another factor which must be considered is the Λ-doubling, which splits all the $^2\Pi$ rotational states into two. Particularly, this must be corrected for in the $B^{10}O$ combination differences, where only R_2 and Q_2 branches are available. For the main system, the Λ-doubling could be evaluated directly as the combination defect:

$$2\Delta\nu_{dc}(J+\tfrac{1}{2}) = [R(J) - Q(J)] - [Q(J+1) - P(J+1)]. \qquad (8)$$

Fig. 4 shows graphically the course of $\Delta\nu_{2dc}$ (in $^2\Pi_{1/2}$) and $\Delta\nu_{1dc}$ (in $^2\Pi_{1\ 1/2}$)

for the lowest three vibrational levels. Below about $J=15$, they may be well represented by the equation[15] of Van Vleck for inverted case a states:

$$\begin{aligned}\Delta\nu_{2dc} &= p(J+\tfrac{1}{2})\\ \Delta\nu_{1dc} &= -(p/Y^2+2q/Y)(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+1\tfrac{1}{2}).\end{aligned}\tag{9}$$

Y stands for A/B_v, A being the spin coupling constant, while p and q are small constants. Their values, as found graphically, are given in Table VI.

TABLE VI. *Constants of the Λ-doubling.*

$B^{11}O$	v'	p	q	$B^{10}O$	p (calc.)
	0	0.0244	−0.00032		0.0257
	1	0.0261	−0.00038		0.0277
	2	0.0220			0.0233
	3	0.0244			0.0258
	4	0.0188			0.0199

For $v'=0$ and 1, we have used the more general expression given by Mulliken and Christy,[9] for states intermediate between cases a and b. The curves in Fig. 4 for these states are the theoretical ones, based on these equations. For $B^{10}O$, not enough branches are observed to permit the direct determination of $\Delta\nu_{dc}$. However, an examination of the theoretical expression,[9] for these constants shows that the magnitude of p depends on B_v and of q on B_v^2. In connection with Eqs. (9), this requires that $\Delta\nu_{2dc}$ be greater for $B^{10}O$ than for $B^{11}O$ by the factor ρ^2, and $\Delta\nu_{1dc}$ greater by ρ^6. Thus we obtain the values in the last column of Table VI. The determination of $B_{v,\Sigma}$ was then made by correcting the combination difference, so that

$$\begin{aligned}R_2(K)-Q_2(K)-\Delta\nu_{2dc}(K+\tfrac{1}{2}) &= \Delta_1F_2'(K+\tfrac{1}{2})\\ &= 2B_{v,-1/2}(J+\tfrac{1}{2})+4D_v(J+\tfrac{1}{2})^3\\ R_1(K)-Q_1(K)-\Delta\nu_{1dc}(K+\tfrac{1}{2}) &= \Delta_1F_1'(K+\tfrac{1}{2})\\ &= 2B_{v,+1/2}(J+\tfrac{1}{2})+4D_v(J+\tfrac{1}{2})^3.\end{aligned}$$

The cubic term was first eliminated, with

$$\begin{aligned}D_v &= -7.09\times10^{-6}+5.08\times10^{-8}(v'+\tfrac{1}{2})\\ D_v^i &= -7.92\times10^{-6}+5.86\times10^{-8}(v'+\tfrac{1}{2}).\end{aligned}$$

The resulting values of $B_{v,\Sigma}$ are collected in Table VII. As before, a considerably better ρ is obtained if we use the more accurate α_e's from the ΔT parabolas. Adopting these, and solving by least squares the values of $B_{v,-1/2}$ from $v'=0$ to 3, we find

$$\begin{aligned}B_{e,-1/2} &= 1.4277\pm0.0005 & B^i_{e,-1/2} &= 1.5115\pm0.0006\\ \rho^2 &= 1.0587\pm0.0006 & \rho &= 1.0289\pm0.0003\\ \alpha_e &= 0.0196 & \alpha_e^i &= 0.0211\\ \rho^3 &= 1.078\pm0.008 & \rho &= 1.025\pm0.003.\end{aligned}$$

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[15] R. S. Mulliken, Rev. Mod. Phys. **2**, 109 (1930).

TABLE VII. *Rotational constants of the* $^2\Pi$ *state.*

$B^{11}O$	B_v	*From bands*			$B^{10}O$	B_v^i
$B_{0,-1/2}$	1.4172	0,0	0,1	0,2	$B^i_{0,-1/2}$	1.4991
$B_{1,-1/2}$	1.3969	1,0	1,1	1,2	$B^i_{1,-1/2}$	1.4793
$B_{1,+1/2}$	1.3679		1,0		$B^i_{1,+1/2}$	1.4488
$B_{2,-1/2}$	1.3789		2,0		$B^i_{2,-1/2}$	1.4605
$B_{3,-1/2}$	1.3609		3,0		$B^i_{3,-1/2}$	1.4382
$B_{4,-1/2}$	1.3450		4,0		$B^i_{4,-1/2}$	1.4243
$B_{5,-1/2}$	1.3346		5,0			

With only data for $v'=0, 1, 2,$ *and* 3

$B_{e,-1/2}=1.4266$ $B^i_{e,-1/2}=1.5092$

$\rho=1.0286$

$\alpha_e=0.0188$ $\alpha_e^i=0.0203$

$\rho=1.03$

In computing ρ, the values of $B_{e,-1/2}$ have been used rather than the "true" B_e, which the theory of case *a* states shows to be the mean of $B_{v,-1/2}$ and $B_{v,+1/2}$. This was done because it appeared that the difference between $B_{1,-1/2}$ and $B_{1,+1/2}$ was less than the theoretical value, $2B_1^2/A$ by from 5 to 10 percent and it was therefore uncertain how well the state approximates the theoretical case *a*.

ELECTRONIC ISOTOPE EFFECT

It is important to note that the above results, because they are derived from analyses of the vibrational and rotational term-*differences*, involve no assumption as to the presence or absence of differences in the electronic terms of the two molecules. It is only when one is concerned with the frequency differences between corresponding bands of the two molecules, the "isotope shift," that the electronic effect enters. Since we have now fixed the relative position of all the terms of each type of molecule, within a given electronic state, it remains to find the separations of the terms of the $^2\Pi$ state from those of $^2\Sigma$. This requires the determination of the origin of one band, and we have chosen to do it for 1,0. The lines of the R_2 and Q_2 branches are given by the differences:

$$\begin{aligned} R_2(J) &= [T_{2e}' + G_1' + F_2'(J+1)] - [T_e'' + G_0'' + F''(J)] \\ Q_2(J) &= [T_{2e}' + G_1' + F_2'(J)] - [T_e'' + G_0'' + F''(J)]. \end{aligned} \tag{11}$$

Hence, the band origin may be expressed:

$$\begin{aligned} \nu_2^{(1,0)} = (T_{2e}' - T_e'' + G_1' - G_0'') &= R_2(J) - F_2'(J+1) + F''(J) \\ &= Q_2(J) - F_2'(J) + F''(J). \end{aligned} \tag{12}$$

In the lower state, we have

$$F''(J) = B_0''(K+\tfrac{1}{2})^2 = B_0''(J+1)^2. \tag{13}$$

In the upper state, we can use the expansion of the Hill and Van Vleck equation for large negative values of $Y=A/B_v$. Neglecting the small, unknown constants, this reduces to

$$F'(J) = B_{v,-1/2}(J+\tfrac{1}{2})^2 + B_v/Y \pm \tfrac{1}{2}p(J+\tfrac{1}{2}) + \cdots. \tag{14}$$

The positive sign applies to R_2, and the negative to Q_2. Y has the value -88.51, as shown ahead. From the first eight lines of these two branches, sixteen values of the origins were computed for both main and isotope bands. The results are

$$\nu_2^{(1,0)} = 24{,}885.09 \pm 0.01 \text{ cm}^{-1} \quad \nu_2^{(1,0)i} = 24{,}911.73 \pm 0.01 \text{ cm}^{-1}.$$

The two system-origins are then readily obtained from the relation

$$\nu_{2e} = \nu_2^{(1,0)} - [\omega_e'(1\tfrac{1}{2}) - 2x_e'\omega_e'(1\tfrac{1}{2})^2] + [\omega_e''(\tfrac{1}{2}) - 2x_e''\omega_e''(\tfrac{1}{2})^2]. \tag{15}$$

We find

$$\mathbf{B^{11}O}{:}\,\nu_{2e} = 23{,}958.85 \pm 0.05 \qquad \mathbf{B^{10}O}{:}\,\nu_{2e}^{i} = 23{,}959.18 \pm 0.06.$$

Thus there remains a discrepancy of 0.33 ± 0.08 cm^{-1} which in all probability represents an electronic isotope effect. It agrees in sign and order of magnitude with the value 0.47 cm^{-1} obtained by one of us[6] in 1927 from measurements on the main and isotope Q_2 head of the 0,0 bands, a less accurate method. Although it is commonly supposed that electronic isotope effects are smaller than the above, recent work both experimental and theoretical on the atomic spectrum of lithium[16] have yielded shifts even greater than this. Our result appears to be the first evidence of any sort of an electronic isotope effect in molecular spectra.

In the above, we have treated the $^2\Pi_{1/2}$ component as a separate band system. This is justified if the value of the coupling coefficient, A, is the same for $B^{11}O$ and $B^{10}O$ in different vibrational levels of the $^2\Pi$ state. The data are insufficient for testing this point except in the case of the 1,0 band. Here the values of A have been calculated separately for main and isotope systems. The term-formula for $^2\Pi_{1\ 1/2}$, corresponding to Eq. (14) is

$$F_1'(J) = B_{v,+1/2}(J+\tfrac{1}{2})^2 - B(2 - 1/Y), \tag{16}$$

omitting the Λ-doubling, which is negligible for small J. The separation of pairs of terms of the same J in the two components may thus be expressed as follows:

$$\begin{aligned} T_2(J) - T_1(J) &= (T_{2e} - T_{1e}) + (B_{1,-1/2} - B_{1,+1/2})(J+\tfrac{1}{2})^2 \\ &\quad + 2B_1(1 + 1/Y) \pm \tfrac{1}{2}p(J+\tfrac{1}{2})^2 \\ &= -A - [2B_1/\alpha](J+\tfrac{1}{2})^2 + 2B_1(1+1/Y) \pm \tfrac{1}{2}p(J+\tfrac{1}{2})^2. \end{aligned} \tag{17}$$

This separation was evaluated from the combination differences

$$R_2(J-1) - Q_1(J) \text{ and } Q_2(J) - P_1(J+1),$$

the positive sign in the final term of Eq. (17) being applicable in the former, and the negative in the latter case. The A computed in this way was constant below about $J = 10$, and the mean values adopted are

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[16] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930); D. S. Hughes, Phys. Rev. **38**, 857 (1931).

$$A = -122.36 \pm 0.03 \text{ cm}^{-1} \qquad A^i = -122.36 \pm 0.05 \text{ cm}^{-1}.$$

Hence $Y = A/B_v = -88.51$, from the mean value of B_1. It is not surprising to find the spin coupling coefficients equal for the two isotopic molecules, since they should be practically uninfluenced by the nuclear masses.

DISCUSSION OF RESULTS

The different determinations of the coefficient ρ are summarized in Table VIII. It will be seen that the accuracy in this quantity obtainable from the four important constants decreases in the order of their size; thus in the order ω_e, B_e, x_e and α_e. For these the probable error is roughly one part in 20,000, 4000, 500 and 100, respectively. The agreement between the several values is always of the order of magnitude of their probable errors, and more often closer than the computed errors would indicate. This shows that the latter represent conservative estimates. We note a slight tendency of the x_e to give too high a value of ρ, while α_e gives values too low. Considering the probable errors, however, it seems that little significance can be attached to these trends.

TABLE VIII. *Results from analysis of vibrational structure.*

Constants used	*Bands used*			ρ	*Probable error*
ω_e''	0,0	0,1	0,2	1.02907	±0.00004
ω_e''	1,0	1,1	1,2	1.02909	±0.00005
x_e''	0,0	0,1	0,2	1.030	—
x_e''	1,0	1,1	1,2	1.031	±0.002
α_e''	0,0	0,1	0,2	1.023	±0.018
α_e''	1,0	1,1	1,2	1.026	±0.009
ω_e'	0,0	1,0	2,0	1.02913	±0.00004
x_e'	0,0	1,0	2,0	1.032	—
α_e'	0,0	1,0	2,0		
	3,0	4,0		1.025	±0.003
Results from analysis of rotational structure.					
B_e''	0,0	1,0	2,0	1.0289	±0.00025
	3,0	1,1	0,1	1.0290*	±0.0002
α_e''	0,0	1,0	2,0	1.02	—
	3,0	1,1	0,1		
B_e'	0,0	1,0	2,0	1.0286	—
	3,0	1,1	0,1	1.0289*	±0.0003
α_e'	0,0	to	5,0	1.03	—
	0,1	1,1			

* These values obtained if the more accurate α_e from the vibrational analysis is used.

Aston[17] has measured the masses of the boron isotopes with the precision mass-spectrograph, and found the following results:

B^{10}: 10.0135 Limit of error 0.0015
B^{11}: 11,0110 " " " 0.0016.

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[17] F. W. Aston, Proc. Roy. Soc. **115A**, 509 (1927).

The masses are based on $O^{16}=16$. From these we find

$$(\mu/\mu^i)^{1/2} = \rho = 1.02908. \quad \textit{Limit of error } 0.00009$$
$$= 1.02908 \pm 0.00003$$

assuming the probable error to be one-third of the assigned limit of error. This agrees strikingly well with the best results in Table VIII. Thus the mean of the two determinations from ω_e'' is exactly the above value, with the same probable error. The value from ω_e' is untrustworthy for reasons given above, while those from the B_e's should be given negligible weight, because of the magnitude of their probable errors. Hence the agreement with Aston's result is complete, and constitutes the first independent check on the accuracy of his relative masses.

Since it is ρ, the square root of the ratio of the reduced masses, which is obtained from the band spectrum, one must assume one of the absolute masses to evaluate their ratio. This is because the ratio of the vibration frequencies is dependent not only on the ratio of the masses of the molecules, but also on their absolute values. If we let m_{11} and m_{10} be the respective atomic weights, we have

$$m_{11}/m_{10} = 16\rho^2/[m_{10}(1-\rho^2)+16] = [m_{11}(\rho^2-1)+16\rho^2]/16$$

Assuming Aston's value, $m_{10}=10.0135$, our mean value of ρ gives for the mass ratio

$$m_{11}/m_{10} = 1.09961 \pm 0.00006$$

and from Aston's two masses, directly

$$m_{11}/m_{10} \doteq 1.09962. \quad \text{Limit of error } 0.00032$$
$$= 1.09962 \pm 0.00011.$$

We have therefore verified the value of the slope of the packing fraction curve of Aston, assuming the absolute value of the packing fraction, at atomic weight 10.

In closing, we wish to acknowledge the kind assistance of Professor R. T. Birge on the methods of treating the data. Most of the above methods have already been applied by him in his very accurate computation of the masses of the oxygen isotopes.

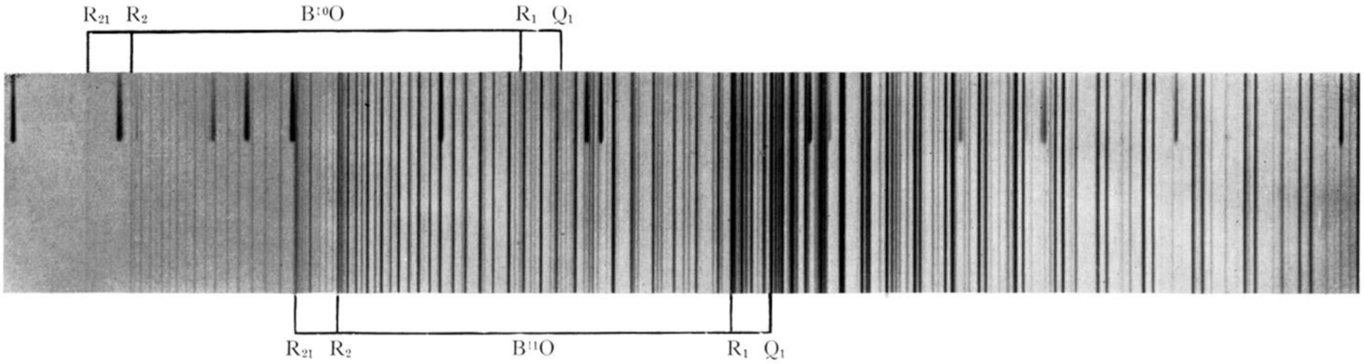

Fig. 1. The 2, 0 band of the α system of BO. First order of the 21-foot grating. The origin of the fainter, B^{10}O, band lies 8.876A further to the violet (i.e., to the left) in this case, and its rotational structure is seen to be almost an exact replica of that in the B^{11}O band, but on a slightly larger scale.