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Beryllium Deuteride Spectra

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The spectra of the BeD green bands and of the ultraviolet BeD^+ bands have been photographed at high dispersion. A Be arc in a deuterium atmosphere was the source. Rotational analyses of the BeD bands, and rotational and vibrational analyses of the BeD^+ bands are presented. The electronic isotope shift in the ultraviolet system is 0.8 cm^{-1}. The values $B_e^*=5.6807$ for the lower state of BeD and $B_e^*=5.9546$ for the lower state of BeD^+ are found. Comparison of these values with the corresponding values of the hydrides gives ratios 0.55110 and 0.55073, respectively, whereas $\rho^2=0.55060$. Calculation of the J. L. Dunham corrections to B_e for the anharmonic oscillator are shown to affect the B_e ratio inappreciably. The variation of the ratio of the B_e^*'s from ρ^2 and the small electronic isotope shift are briefly discussed.

INTRODUCTION

An accurate comparison of the spectra of the deuterides with those of the corresponding hydrides is important in the study of the dynamical behavior of diatomic molecules. Such studies as have been made for DCl,[1] AlD,[2] CaD,[3] NaD,[4] LiD,[5] and AgD,[6] CdD[7] show, in many cases, an interesting variation of the ratios of the molecular constants from the predictions of the simple isotope theory. This theory predicts an equality between the ratio of the reduced masses, ρ^2, and the ratio of the rotational constant B_e for the nonrotating vibrationless isotopic molecules, but experiment shows the latter to be appreciably larger than ρ^2 in some cases. In no case has the ratio B_e^i/B_e been found to be smaller than ρ^2. Since different views[2, 8] of the explanation of these departures have developed, it is desirable to compare accurately the spectra of other hydrides and deuterides. The $^1\Sigma\rightarrow{}^1\Sigma$ BeH^+ bands[9, 10, 11] in the region 2200–3100A and the $^2\Pi\rightarrow{}^2\Sigma$ BeH bands[9, 12, 13, 14] near 4990A, which have been carefully analyzed, offer good material for this study. The results of analyses of the corresponding spectra of the deuterides BeD^+ and BeD are here presented.

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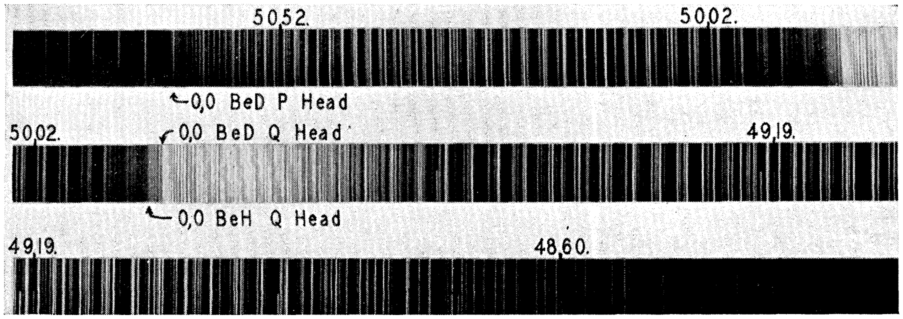

FIG. 1. Spectrogram of the BeD green bands at 4990A.

EXPERIMENTAL PROCEDURE

The light source, used in the production of the BeD^+ and BeD bands, was a d.c. arc between two Be electrodes in an atmosphere of deuterium gas at about 3 cm of Hg pressure. The deuterium was obtained from the reaction of 99 percent deuterium oxide with metallic Ca in a vacuum. The BeD bands near 4990A were photographed in the third order of a 21-ft. concave grating in a stigmatic mounting, with a dispersion of 1.29A/mm. Exposure times of 5 to 10 minutes with currents of 4 to 6 amperes were sufficient to produce intense spectrograms. The BeD^+ bands in the region 2200–3100A were photographed with a Hilger E-1 spectrograph in a Littrow mounting having a dispersion of 2.7A/mm at 2500A. Exposure times for the prism instrument were of the order of 1 to 4 minutes. Although the hydride spectra were present as an impurity on all spectrograms, the hydrogen coming from the hot electrodes and electrode mountings, they were much weaker than those of the corresponding deuteride spectra. The presence of the hydride system did not present any difficulties in the quantum assignments since the spacing of the lines for the hydride is nearly twice that for the deuteride.

BeD GREEN BANDS

It is well known that the green bands of $BeH^{9,12,13,14}$ at 4990A belong to a $^2\Pi\rightarrow{}^2\Sigma$ transition and that the system consists almost entirely of a few bands in the $\Delta v=0$ sequence, the origin of the 1,1 band being very close to that of the 0,0 band. The $^2\Pi$ state can be described as Hund's case *b*, since the ratio $A/B=0.191$ for this state. Only a few of the rotational lines near the origin show a detectable spin doubling due to the $^2\Pi$ level, while the spin doubling for the lower $^2\Sigma$ state is negligible. This means that the bands have the appearance of $^1\Pi\rightarrow{}^1\Sigma$ bands with only three branches, and that the equations for a $^1\Pi\rightarrow{}^1\Sigma$ transition may be used instead of the more complicated ones for $^2\Pi\rightarrow{}^2\Sigma$ bands which have appreciable spin multiplet separations.

Fig. 1 is a spectrogram of the BeD green bands. The strong head is that of the Q branch of the 0,0 band, while the weak head on the long wave-length side is that of the Q branch of the corresponding BeH 0,0 band. Because of the much smaller spacing of the lines in the deuteride spectra, the P and R branches belonging to the hydride can easily be distinguished from

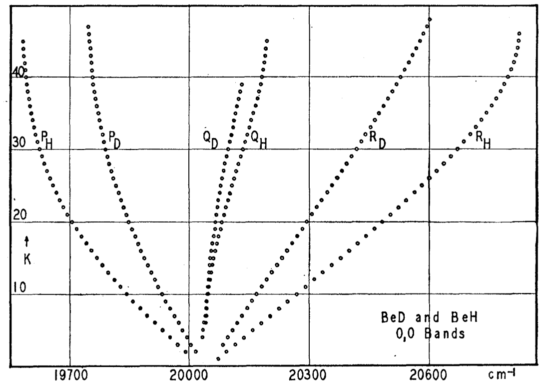

FIG. 2. Fortrat diagram of BeD green bands.

those of the deuteride. Fig. 2 is a Fortrat diagram comparing the 0,0 bands for BeD and BeH. This shows the Q branches rising very rapidly with the P and R branches extending out to either side. The upward curve of the R branches has been attributed to rotational distortion.

ROTATIONAL CONSTANTS

The assignment of frequencies to the P, Q, and R branches of the 0,0 and 1,1 bands is given in Table I. The usual combination differences may be obtained from Table I in the customary manner by means of the relations

$$\begin{aligned} R(K-1)-P(K+1)&=\Delta_2F''(K),\\ R(K)-Q(K+1)&=\Delta_1F''(K+\tfrac{1}{2})+Z_{K+1},\\ Q(K)-P(K+1)&=\Delta_1F''(K+\tfrac{1}{2})-Z_K \end{aligned} \tag{1}$$

for the lower state, and the equations

$$\begin{aligned} R(K)-P(K)&=\Delta_2F_d'(K),\\ R(K)-Q(K)&=\Delta_1F_c'(K+\tfrac{1}{2})+Z_{K+1}\\ &=\Delta_1F_d'(K+\tfrac{1}{2})+Z_K,\\ Q(K+1)-P(K+1)&=\Delta_1F_c'(K+\tfrac{1}{2})-Z_K\\ &=\Delta_1F_d'(K+\tfrac{1}{2})-Z_{K+1} \end{aligned} \tag{2}$$

for the upper state, where Z_K represents the Λ doubling of the $^2\Pi$ state. The expressions for ΔF are easily shown to have the well-known form

$$\Delta_2F(K)=(4K+2)\{B_v+2D_v(K^2+K+1)+F_v(3K^4+6K^3+13K^2+10K+4)\}$$

and

$$\Delta_1F(K+\tfrac{1}{2})=(2K+2)\{B_v+2D_v(K^2+2K+1)+F_v(3K^4+12K^3+19K^2+14K+4)\}.$$

TABLE I. *Rotational assignments for BeD bands.*

	0,0 Band			1,1 Band		
K	P	Q	R	P	Q	R
1						
2	20015.82			20032.02		
3	004.72		20083.65	021.87		
4	19993.92		095.86	011.18		
5	983.31		107.71	000.74		20122.01
6	972.66	20040.51	119.97	19990.44	20056.00	134.16
7	962.46	041.54	132.08	980.25	057.43	146.08
8	952.45	042.60	144.57	970.36	058.29	157.85
9	942.67	043.84	156.89	960.62	059.46	169.85
10	933.05	045.17	169.25	951.16	060.67	181.72
11	923.73	046.64	181.72	941.82	061.94	193.65
12	914.47	048.29	194.32	932.63	063.21	205.76
13	905.50	050.07	206.85	923.73	064.86	217.81
14	896.83	051.92	219.38	915.11	066.45	229.86
15	888.33	053.92	232.06	906.57	068.39	241.92
16	880.07	056.00	244.65	898.31	070.17	253.99
17	872.01	058.29	257.04	890.20	071.95	266.55
18	864.25	060.67	269.99	882.33	074.04	278.08
19	856.72	063.21	282.63	874.67	076.04	289.99
20	849.41	065.76	295.19	867.30	078.81	302.06
21	842.49	068.39	307.78	860.18	080.53	313.95
22	835.69	071.26	320.38	853.17	082.99	325.92
23	829.18	074.04	332.89	846.50	085.57	337.64
24	822.99	077.28	345.26	840.10	087.99	349.26
25	816.86	080.53	357.70	833.85	090.37	360.93
26	811.29	083.65	370.02	827.84		372.44
27	805.71	086.91	382.29	822.11		383.84
28	800.58	090.37	394.39	816.43		395.17
29	795.68	093.67	406.53	810.77		406.53
30	790.92	097.38	418.45	805.71		417.31
31	786.45	101.02	430.38	800.58		428.21
32	782.33	104.63	441.93			438.89
33	778.48	108.67	453.57			449.48
34	774.72	112.31	465.04			459.79
35	771.22	116.12	476.29			470.02
36	768.13	119.97	487.40			480.02
37	765.17	124.04	498.22			489.76
38	762.44	127.98	509.07			499.32
39	759.94	132.08	519.65			508.51
40	757.67		529.95			517.59

The rotational constants B, D, and F for the lower state are evaluated in the usual semi-graphical manner:

(1) The experimental values for $\Delta_2F(K)/(4K+2)$ are plotted against K, using a large scale.

(2) The expression for $\Delta_2F(K)/(4K+2)$ is applied successively to any three points on the curve. The resulting equations are solved simultaneously for the desired constants.

The points are chosen in the region $K=8$ to $K=25$ to eliminate error due to fluctuations of the experimental points for low K values, and the influence of a fourth constant which is effective only for high values of K. An average of ten such determinations for each value gives $B_0''=5.6198\pm0.0004$ and $B_1''=5.4980\pm0.0002$. Using the relation $B_e=B_v+\alpha(v+\frac{1}{2})$ and the above values of B_0 and B_1, one finds $\alpha=0.1218$ and $B_e''=5.6807$. The resulting constants are given in Table II.

TABLE II. *Rotational constants for BeD bands.*

LOWER $^2\Sigma$ STATE	UPPER $^2\pi$ STATE
$B_0^*=5.6198$	$B_{0c}^*=5.6926$
$B_1^*=5.4980$	$B_{0d}^*=5.6937$
	$B_{1d}^*=5.5623$
$D_0=-3.074\times10^{-4}$	$D_0=-3.169\times10^{-4}$
$D_1=-3.204\times10^{-4}$	$D_1=-3.255\times10^{-4}$
$F_0=1.29\times10^{-8}$	$F_0=1.40\times10^{-8}$
$F_1=2.79\times10^{-8}$	$F_1=2.58\times10^{-8}$
$\alpha=0.1218$	$\alpha_d=0.1314$
$B_e^*=5.6198+\frac{1}{2}\alpha=5.6807$	$B_e^*=5.6926+\frac{1}{2}\alpha=5.7583$

The upper state rotational constants may be obtained in a similar manner if the Λ doubling Z_K is evaluated and substituted into Eqs. (2).

TABLE III. *Rotational assignments for BeD$^+$ bands.*

J	R	P	J	R	P	J	R	P	J	R	P
	0,1 BAND			0,2 BAND			0,3 BAND			3,0 BAND	
0	37550.20		0			0			0		
1		37529.09	1			1		34455.73	1		42313.52
2		37513.65	2		35954.15	2		34441.72	2		42296.95
3	37552.93	37494.62	3		35936.50	3		34424.09	3		42276.09
4	37543.61	37471.76	4		35914.50	4		34403.67	4		42252.02
5	37532.29	37446.69	5		35889.95	5	34465.20	34380.62	5		42222.33
6	37519.22	37416.72	6	35963.85	35862.04	6	34455.73	34354.40	6	42287.04	42189.84
7	37501.00	37383.21	7	35947.73	35830.76	7	34441.72	34324.08	7	42265.76	42152.75
8	37479.23	37346.76	8	35928.98	35796.27	8	34424.09	34291.86	8	42237.77	42111.80
9	37454.41	37306.10	9	35907.04	35760.61	9	34403.67	34256.89	9	42206.18	42066.23
10	37426.05	37262.04	10	35880.64	35717.46	10	34380.62	34217.95	10	42172.38	42016.80
11	37393.88	37214.85	11	35851.66	35672.47	11	34354.40	34174.93	11	42134.19	41963.07
12	37358.10	37164.15	12	35818.39	35624.75	12	34324.08	34131.09	12	42089.86	41905.15
13	37319.03	37109.90	13	35783.82	35574.30	13	34291.86	34083.46	13	42043.07	41843.49
14	37276.90	37052.36	14	35744.51	35520.63	14	34256.89	34033.46	14	41990.52	41777.78
15	37230.03	36991.60	15	35702.56	35463.61	15	34217.95	33980.94	15	41936.81	41708.30
16	37180.98	36927.98	16	35656.87	35403.59	16	34174.93	33925.22	16	41876.33	41634.88
17	37127.77	36860.30	17	35608.58	35340.71	17	34132.23	33865.81	17	41812.82	41557.71
18	37072.99	36790.09	18	35556.66	35274.92	18	34088.14	33804.50	18	41745.64	41476.42
19	37012.08	36715.85	19	35501.99	35206.24	19	34039.53	33741.27	19	41673.73	41391.61
20	36949.71	36639.67	20	35442.68	35134.18	20	33985.42	33674.72	20	41598.60	41303.39
21	36882.83	36559.46	21	35383.25	35060.05	21	33929.59	33605.99	21	41519.37	41211.39
22	36813.76	36476.53	22	35319.48	34982.95	22	33872.06	33535.04	22	41436.77	41115.19
23	36741.21	36392.43	23	35253.60	34903.22	23	33811.24	33460.63	23	41350.60	41015.91
24	36665.39	36301.61	24	35183.82	34820.77	24	33748.21	33385.56	24	41260.10	40912.36
25	36587.19	36210.27	25	35112.06	34735.98	25	33681.99	33305.87	25	41166.35	40807.12
26	36505.16	36115.95	26	35036.82	34647.23	26	33614.20	33225.66	26	41069.21	40697.16
27	36421.59	36019.46	27	34959.64	34557.97	27	33545.77	33139.07	27	40969.39	40584.78
28	36334.24	35919.48	28	34880.06	34464.91	28	33471.64		28	40863.73	40468.86
29	36243.79	35818.39	29	34797.55	34370.99	29	33395.00		29	40755.50	40349.17
30	36150.94	35712.38	30	34712.07					30	40645.18	40227.73
31	36056.63	35608.57	31	34623.86					31	40528.61	40100.95
32	35963.85		32	34533.71					32	40411.32	39969.69
33	35862.04		33	34441.48					33	40290.22	
34	35760.61		34	34347.38							
35	35656.87										
	2,0 BAND			3,2 BAND			1,1 BAND				
0			0			0					
1			1			1		38608.58			
2		41254.95	2	39172.22	39134.47	2		38593.67			
3		41234.91	3	39168.29	39115.99	3	38629.83	38575.52			
4	41279.83	41211.39	4		39094.34	4	38620.26	38552.64			
5	41267.07	41183.05	5	39150.02	39067.79	5	38608.58	38524.13			
6	41249.67	41150.30	6	39135.25	39038.15	6	38593.67				
7	41228.26	41115.19	7	39116.48	39004.32	7	38575.52	38458.69			
8	41203.04	41073.94	8	39094.34	38967.62	8	38552.64	38422.02			
9	41173.34	41029.35	9	39067.79	38927.10	9	38527.26	38380.33			
10	41139.61	40981.14	10	39038.15	38882.50	10	38497.34	38335.98			
11	41102.31	40928.34	11	39004.32	38834.40	11		38287.36			
12	41060.79	40872.31	12	38967.62	38783.12	12	38426.41	38235.08			
13	41015.91	40812.15	13	38927.10	38728.59	13	38385.97	38180.25			
14	40965.20	40747.83	14	38882.50	38669.58	14	38342.94	38121.19			
15	40912.36	40679.18	15	38834.40	38608.58	15	38293.66	38058.42			
16	40853.79	40608.30	16	38783.12	38542.86	16	38241.90	37992.60			
17	40792.60	40532.71	17	38728.59	38474.08	17	38187.15	37923.77			
18	40727.38	40453.52	18	38669.58	38402.68	18	38129.33	37851.32			
19	40658.36	40370.77	19	38608.58	38327.84	19	38067.16	37774.80			
20	40584.78	40283.61	20	38542.86	38246.86	20	38000.76				
21	40508.65	40195.35	21	38474.08	38167.60	21	37933.09				
22	40426.47	40100.95	22	38402.68	38083.08	22	37860.62				
23	40344.41	40004.07	23	38327.84	37995.82	23	37786.33				
24	40257.18	39903.86	24	38246.86	37904.50						
25	40165.71	39800.03	25	38167.60	37810.48						

According to Mulliken and Christy,[15] the B_v's in the expression for the rotational energy term for the $^2\Pi$ state represent a more complicated expression than that which the usual B_v signifies and they should be designated as $B_v{}^*$. The B_v's should carry the subscript d or c to indicate the side of the Λ doublet to which they belong. The constants for the $^2\Pi$ state are given in Table II. Of course the B_v constants resulting from this analysis of the lower $^2\Sigma$ state are also B^* values,[15] and we therefore place a superscript (*) on all these constants in Table II.

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[15] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

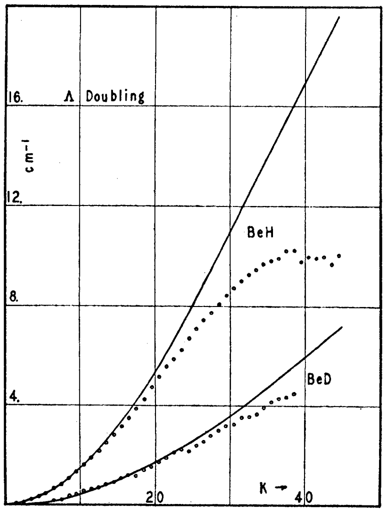

FIG. 3. Λ doubling of $^2\Pi$ state of BeD.

The importance of this in connection with isotope effect theory we shall mention in the last section.

Λ DOUBLING

The doubling of each rotational level, known as Λ doubling, is attributed to a difference of energy resulting from Λ being parallel or anti-parallel to the electric field along the internuclear axis when a magnetic field due to rotation is present. This doubling is zero for Σ states but is appreciable for Π states. For a case $b\Pi$ state Mulliken and Christy[15] express this doubling as

$$\Delta\nu_{dc}(K)=qK(K+1).$$

If allowance is made for rotational stretching, the coefficient q should change with K. Thus

$$q=q_0/[1+u^2K(K+1)]^2.$$

where $u^2=-D_e/B_e$, and q_0 is the value of q for low values of K. Fig. 3 shows the Λ doubling curves for both BeD and BeH. In this figure the points represent experimental values while the solid lines are drawn according to the above expressions. The experimental values for $\Delta\nu_{dc}$ for BeH are the average values from data of Watson[9] and Olsson.[14] Values of $q_0=0.014$ for BeH from Mulliken and Christy and $q_0=0.0043$ for BeD are used. The deviation at high K values of the experimental points from the theoretical curve is well known for BeH and is probably due to failure of the simple relation from which the expression for q was derived. Since the theoretical expression for q_0 contains B_e^2, the transformation ratio for the two isotopic molecules should be equal to ρ^4. The ratio of the above values of q_0 does equal ρ^4 to within the accuracy with which the values can be determined.

ULTRAVIOLET BeD$^+$ BANDS

In contrast to the BeH system, which consists chiefly of a strong $\Delta v=0$ sequence with the band origins of the sequence very closely spaced—indicating a very narrow Condon parabola and a small change in ω_e for the two states—the $^1\Sigma-{}^1\Sigma$ BeH$^+$ system has no long sequences and its strongest bands form a wide Condon parabola. The ω_e values are 1476.1 and 2220.0 cm^{-1}, respectively, for the excited and the ground states. The individual bands, which consist of only two branches, do not form prominent heads since the R branches turn at very low quantum numbers. The appearance of the BeD$^+$ bands is very similar to that of the BeH$^+$ system except for a smaller pattern both for the distribution of the band origins and for the spacing of the lines within a band.

ROTATIONAL ANALYSES

The rotational constants B and D were evaluated in the manner described in the case of the BeD bands. Since no prominent heads are formed, some difficulty was experienced in locating the branches. Table III gives the quantum assignments for seven bands. Table IV gives the results of the rotational analyses. A comparison of the B_e values for the isotopic molecules will be made in a later section.

TABLE IV. *Rotational constants for BeD$^+$ bands.*

	LOWER $^1\Sigma$ STATE		UPPER $^1\Sigma$ STATE	
	B	D	B	D
0	5.8930	−0.0002912	3.9423	−0.0001913
1	5.7714	2986	3.8860	1877
2	5.6464	3036	3.8267	1829
3	5.5038	2783	3.7633	1892
	$\alpha=0.1233$		$\alpha=0.0578$	
	$B_e^*=5.9546$		$B_e^*=3.9712$	

TABLE V. $v'-v''$ *diagram of band origins, * denotes BeD$^+$ others are BeH$^+$.*

$v'v''\rightarrow$ $\downarrow$	0	1	2	3	4
0	39051.4	37540.30* 31911.5	35980.80* 34852.5	34465.89* 32875.3	
1	40496.4	38619.33*		34320.4	32426.9
2	41282.76* 41908.3				
3	42323.95* 43284.5		39161.67*		
4	44621.7				

TABLE VI. *Comparison of vibrational constants.*

	BeH	TRANSFORMATION RATIO	BeD$^+$ CALCULATED	BeD$^+$ EXPERIMENTAL
ν_e	39417.0			39416.2
ω_e'	1476.1	ρ	1095.43	1096.41
$x_e'\omega_e'$	14.8	ρ^2	8.15	8.49
ω_e''	2220.0	ρ	1647.49	1647.64
$x_e''\omega_e''$	39.8	ρ^2	21.92	21.85

VIBRATIONAL ANALYSIS

In order to find the vibrational constants ω_e, $x_e\omega_e$, and $y_e\omega_e$ for both states, it is necessary to determine the origin of each band with all possible accuarcy. Of several methods tried, the most satisfactory one consisted in the application, for example, of the equation of the P branch to an individual line in this branch, using the previously determined values for the B's and D's. This equation was then solved for ν_0. The final value given is the average of ten or more such determinations from the P branch and of a similar set obtained from the R branch. Table V gives a $v'-v''$ table of band origins for BeH$^+$ as given by Bengtsson[10] and for BeD$^+$ as found by the above method, the latter being designated by an asterisk. Bengtsson showed that the constant $y_e\omega_e$ should be included in the vibrational expression for both the lower and upper states of BeH$^+$. If we include these constants for BeD$^+$, it means that we have to evaluate seven constants ν_e, ω_e', $x_e'\omega_e'$, $y_e'\omega_e'$, ω_e'', $x_e''\omega_e''$, and $y_e''\omega_e''$, from seven equations, and that we have no other bands with which to check the result. But Bengtsson's values for the $y_e\omega_e$ constants are not large:

$$y_e'\omega_e'=0.40 \quad \text{and} \quad y_e''\omega_e''=0.15.$$

According to simple isotope theory the transformation ratio of this constant for the two molecules should be ρ^3, which is approximately equal to 0.4087 as calculated from the ratio of the reduced masses. Assuming this transformation ratio to hold exactly, $y_e'\omega_e'=0.16$ and $y_e''\omega_e''=0.06$ for BeD$^+$. On evaluating the remaining constants in the usual way, the vibrational equation is found to be

$$\nu_e=39416.2+1096.4(v'+\tfrac{1}{2})-8.5(v'+\tfrac{1}{2})^2 -0.16(v'+\tfrac{1}{2})^3-[1647.6(v''+\tfrac{1}{2}) -21.9(v''+\tfrac{1}{2})^2-0.06(v''+\tfrac{1}{2})^3].$$

The corresponding equation for BeH$^+$ as given by Bengtsson[10] is

$$\nu_e=39417.0+1476.1(v'+\tfrac{1}{2})-14.8(v'+\tfrac{1}{2})^2 -0.4(v'+\tfrac{1}{2})^3-[2220.0(v''+\tfrac{1}{2}) -39.8(v''+\tfrac{1}{2})^2-0.15(v''+\tfrac{1}{2})^3].$$

Table VI gives a comparison of the vibrational constants for BeH$^+$ with the experimental values for BeD$^+$ and with the calculated values for BeD$^+$ as determined by means of simple isotope theory. The difference in the values of the ν_e for the two isotopic molecules BeH$^+$ and BeD$^+$ indicates a shift of the system origin of about 0.8 cm^{-1}. An explanation of the so-called electronic isotope shifts has been given recently by Dieke[16] as arising from certain terms of the complete Hamiltonian which are usually neglected. On account of the comparatively large B_e values for the BeD$^+$ and BeH$^+$ molecules, that part of these perturbation terms which involves the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis would contribute an electronic isotope shift of about 6 cm^{-1} if a $p\Sigma$ state is involved. Since the electronic configuration for the upper state involved is $(2s\sigma)(2p\sigma)$, the lower state being $(2s\sigma)^2$, the smallness of the observed shift is puzzling. It is possibly to be attributed to a like contribution of the opposite sign from the $\partial^2\phi/\partial r^2$ term.

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[16] G. H. Dieke, Phys. Rev. **47**, 661 (1935).

COMPARISON OF B_e CONSTANTS WITH MASS RATIOS

Simple isotope theory predicts that the ratio of the B_e constants for the isotopic molecules should be exactly equal to ρ^2, the ratio of the reduced masses. With Olsson's[14] value $B_e = 10.308$ for the ground state of BeH and the above value $B_e = 5.6807$ for BeD, the ratio is 0.55110. Although there is some uncertainty in the proper method of calculating ρ^2,[6] the use of atomic weights $H = 1.0081$, $D = 2.0148$, $Be = 9.0155$ gives $\rho^2 = 0.55060$. (The use of the old atomic masses of hydrogen and deuterium increases this value slightly.) Thus the ratio of the B_e constants exceeds ρ^2 by 0.09 percent, the discrepancy being larger than the experimental error.

A possible explanation of this discrepancy which should be considered is the correction to B_e given by J. L. Dunham[17] in his extended treatment of the rotating vibrator. With his notation, the corrected value is $Y_{01} = B_e[1 - 0.00015]$ for BeH. This correction cannot be calculated exactly for BeD without the analysis of at least one additional band, but an approximate solution gives $Y_{01} = B_e[1 - 0.00008]$. The ratio of the corrected B_e values is 0.55110. Apparently the discrepancy can be only partially explained in this way.

It should be recalled that these B values are really B^* values, differing from the true B_v values by uncoupling terms arising from the interaction with certain other states of the molecule. Mulliken and Christy[15] have shown that the two electronic states involved in these BeH bands interact almost solely with each other. Assuming this interaction to be exactly that of "pure precession," the true B_e values may be calculated[3] with the relation $B^* - B_v = -2B_v^2 l \times (l+1)/\nu(\Pi, \Sigma)$. With the known Λ doubling values, however, this correction makes $B_e = 10.3237$ for the normal state of BeH, while for BeD the correction is smaller, so that $B_e = 5.6855$. The ratio of these two B_e's is 0.55072, a value fairly close to that for the ratio of the reduced masses. Since inclusion of these uncoupling terms in order to get true B_e values for the B states of CaH and CaD has been shown by Watson[3] to give similarly near equality of the ratio of the B's and ρ^2, it may be that this effect is responsible for the largest part of the discrepancy between these ratios for all corresponding diatomic hydride and deuteride molecules.

With Bengtsson's[10] value $B_e^* = 10.813$ for the ground state of BeH$^+$ and the above value $B_e^* = 5.9546$ for BeD$^+$, the ratio is 0.55073. This is but very slightly larger, about 0.02 percent, than the value of ρ^2. It is to be noted that the discrepancy is much less for the ionized molecule than for the neutral molecule. An adequate explanation of the discrepancy should account for this fact. Kronig's recent treatment of the diatomic molecule including certain terms in the Hamiltonian of the diatomic molecule which are usually omitted, predicts a variation between the ratio of the B_e's and ρ^2 if the united atom has an L value different from 0, the amount of the variation being dependent upon L. Since the L value of the united atom for BeD$^+$ is 0, while that for BeD is 1, the experimental results are in accordance with his theory. The upper state constants are not compared because of the probable larger influence of nearby levels as discussed by Kronig.

The author wishes to express his appreciation to Professor W. W. Watson, who suggested the problem, for his interest and for many helpful discussions.

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[17] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

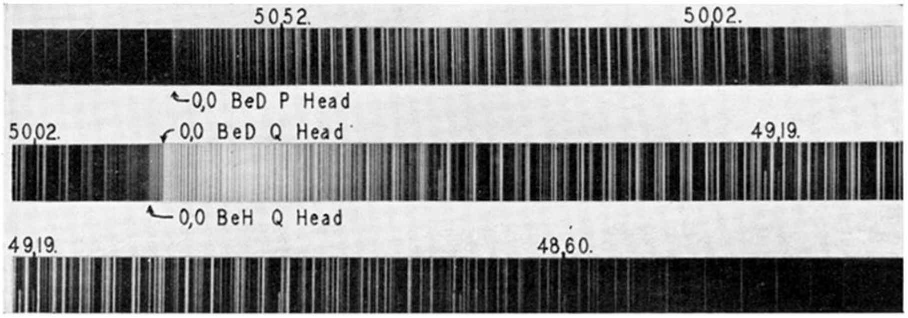

FIG. 1. Spectrogram of the BeD green bands at 4990A.