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Mass Spectra of Diborane-d_6 and Ethane-d_6

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The complete mass spectra of B_2D_6 and C_2D_6 and the partial spectrum of B_2D_5H have been obtained for ionizing voltages of 50 volts and 70 volts. An analytical procedure is given for deriving the contribution of all ions containing a hydrogen atom from the polyisotopic spectrum of a mixture of B_2D_6 and B_2D_5H. A comparison of spectra of B_2D_6 and B_2H_6 and of C_2D_6 and C_2H_6 indicates that substitution of deuterium for hydrogen has only a slight effect on the dissociation probabilities in diborane and ethane. An exception is the occurrence of a metastable transition in B_2D_6 that does not occur in B_2H_6 viz $B_2D_5^+ \rightarrow B_2D_3^+ + 2D$.

Simple statistical considerations, based upon the assumption of equal probabilities for the removal of a deuterium or a protium, give a dissociation pattern that differs by more than experimental error from that observed.

I. Introduction

A number of theories have been proposed [1][1] on the structure of electron-deficient molecules, particularly the hydroborons. Of these, the hydrogen bridge model and "protonated double bond" model have received support from recent measurements of the infrared absorption spectrum of diborane [2] and the mass spectra of diborane [3] and pentaborane [4]. In the case of diborane, a possible structural correspondence with ethane is ruled out and the presence of an ethylenic linkage is indicated. It is also apparent from the mass spectra of diborane and pentaborane that not all hydrogens are bound in the molecule by equivalent bonds.

In the present investigation, we have obtained the mass spectrum of diborane-d_6 for comparison with normal diborane to obtain information on the stability of the molecule ion as well as the effect of deuterium substitution on dissociation processes in diborane.

It is convenient at this time also to report the mass spectrum of ethane-d_6. This spectrum is compared with normal ethane to demonstrate the effect of complete deuterium substitution in hydrocarbons. Similar data for methane and methane-d_4 have been published by Turkevich, Friedman, Solomon, and Wrightson [5].

II. Experimental Details

Mass spectra were obtained with a type 21–102 Consolidated mass spectrometer. The temperature of the ionization chamber was controlled at 245° C. Ionizing electron energies were nominally 50 and 70 v.

The B_2D_6 was synthesized according to Finholt, Bond, and Schlesinger [6]. Approximately 0.3 g of 98-percent lithium aluminum deuteride [2] [7] were dissolved in 25 ml of anhydrous dibutyl ether contained in a flask provided with a reflux condenser and connections to a vacuum system. Solution was accomplished after several hours of stirring under an atmosphere of nitrogen at a temperature just below the boiling point of the ether. The solution was frozen with liquid nitrogen, the flask evacuated, and approximately 1.5 g of boron trichloride distilled onto the frozen solution. The flask and contents were allowed to warm slowly to room temperature, stirring when possible. The reaction was moderate, and after completion, the volatile material was drawn off

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The deuteride, deuterium gas, and deuterium oxide used in the preparations of B_2D_6 and C_2D_6 were obtained through the Isotopes Branch of the USAEC.

by a Toepler pump through a trap at −120° C. A mass spectrometric analysis showed no hydroborons heavier than diborane, although approximately 7 percent of B_2D_5H was present. The BCl_3 originally obtained from Kahlbaum in 1906 was quite yellow and probably contained some HCl. This may account for the more than expected amount of protium in the product. The rate of decomposition of B_2D_6 to give deuterium gas and heavier hydroborons is apparently slow even at room temperature, as a sample showed no appreciable increase in noncondensibles or heavier hydroborons over a period of several weeks. Before admitting a sample to the mass spectrometer, however, the precaution was always taken to pump off possible noncondensibles at liquid nitrogen temperature.

The ethane-d_6 was kindly supplied by L. A. Wall of this Bureau. It was made by the catalyzed reduction of acetylene-d_2. Mass spectrometric analysis indicated impurities of approximately 1 percent of deuteromethane, 2 percent of deuteropropane, and 1 percent of deuterobutane, in addition to approximately 1 percent of C_2D_5H. The isotopic purity of nearly 99 percent is exceptionally good for a compound containing six deuterium atoms.

III. Results

The computation of the monoisotopic spectrum of B_2D_6 is complicated by the presence of B_2D_5H. The method used, however, is similar to that already described for B_2H_6 [3]. By trial approximation, the abundance ratio, $B^{10}/B^{11}=0.250$, was found to give the best fit. This is in agreement with the ratio obtained for normal diborane (0.251) and pentaborane (0.250). Using the ratio 0.250, one derives the abundance ratios

$$B^{10}B^{11}/B_2^{11}=0.500 \text{ and } B_2^{10}/B_2^{11}=0.0625.$$

With these values it is possible to calculate the spectrum of ions containing only deuterium and of ions containing 1 protium atom. As relatively few molecules contain protium atoms, the first spectrum is to a first approximation the B_2D_6 spectrum, and the second spectrum is the partial spectrum of B_2D_5H accounting for all ions that contain protium. There is no basis for distinguishing between ions from B_2D_6 and from B_2D_5H with protium removed.

Table 1 shows the B_2 portion of the B_2D_6 and B_2D_5H mixture spectra at 70 v ionizing voltage and summarizes the calculations of the complete monoisotopic spectrum of B_2D_6 and the partial spectrum of B_2D_5H. Column 1 lists the mass numbers of the recorded ions; column 2 gives the mixture spectrum with the ion intensities relative to the maximum peak at $m/e=32$ taken as 100. The monoisotopic spectra are separated by starting at the heavy mass end and applying the abundance values calculated above to determine the contribution of each B_2 ion to each value of m/e. The peak at $m/e=34$ comes entirely from

TABLE 1. *Summary of the monoisotopic spectrum calculations for the* B_2 *group of* B_2D_6 *and* B_2D^5H *for 70-v electrons*

m/e	Mixture spectrum	B_2D_6 [a]				B_2D_5H [a]			
		$B_2^{11}D_x$	$B^{10}B^{11}D_x$	$B_2^{10}D_x$	ΣB_2D_x	$B_2^{11}D_xH$	$B^{10}B^{11}D_xH$	$B_2^{10}D_xH$	ΣB_2D_xH
20	0.10	-----	-------	0.10	2.55	------	--------	------	-------
21	.82	-----	0.82	----	------	------	--------	------	-------
22	1.92	1.63	-------	.29	7.22	------	--------	------	-------
23	2.43	-----	2.31	----	------	0	--------	0.12	3.09
24	9.79	4.62	-------	4.18	104.47	------	0.99	------	-------
25	35.49	-----	33.43	----	------	1.98	--------	.08	1.97
26	68.97	66.86	-------	1.48	36.89	------	.63	------	-------
27	13.25	-----	11.80	----	------	1.26	--------	.19	4.64
28	28.00	23.61	-------	2.91	72.66	------	1.48	------	-------
29	26.64	-----	23.25	----	------	2.97	--------	.42	10.62
30	56.15	46.50	-------	6.25	156.24	------	3.40	------	-------
31	56.80	-----	50.00	----	------	6.80	--------	------	-------
32	100	99.99	-------	0.01	0.26	------	--------	------	-------
33	0.07	-----	0.08	----	------	------	--------	------	-------
34	.17	0.17	-------	----	------	------	--------	------	-------

[a] x assumes integral values from 0 to 6.

the $B_2^{11}D_6^+$ ion; therefore, the $B^{10}B^{11}D_6^+$ ion (m/e=33)=0.17×0.50=0.08 and the $B_2^{10}D_6^+$ ion (m/e=32)=0.17×0.0625=0.01. The difference between the calculated and observed values at m/e=33 is in the region of experimental uncertainty, since this peak is very small. The $B_2^{11}D_5^+$ ion is 100−0.01=99.99. The principal contribution is from B_2D_6 but with a small contribution from B_2D_5H. The $B^{10}B^{11}D_5^+$ ion (m/e=31) is 99.99×0.50=50.00, and the $B_2^{10}D_5^+$ ion (m/e=30) is 99.99×0.0625=6.25. We now have a measure of the $B_2^{11}D_4H^+$ ion, which is the difference 56.80−50.00=6.80. From this value we compute the contributions of the $B^{10}B^{11}D_4H^+$ and $B_2^{10}D_4H^+$ ions as before. The $B_2D_4^+$ ion is now obtained by subtracting the contributions of $B_2^{10}D_5^+$ and $B^{10}B^{11}D_4H^+$ from the 30 peak; i. e., 56.15−(6.25+3.40)=46.50. The $B^{10}B^{11}D_4^+$ and $B_2^{10}D_4^+$ ions are computed and the cycle continued until all contributions to all peaks are obtained. There are two checks on the calculations. The abundance of the 21 and 20 peaks is calculated to be 0.82 and 0.10, respectively, in exact agreement with the observed abundance.

Table 2 is a summary of the monoisotopic spectra calculations of the B_1 group for ionizing electron energies of 70 v. Starting with the heaviest mass in that group, m/e=17 is assumed to be entirely the $B^{11}D_3^+$ ion. Therefore, the $B^{10}D_3^+$ ion (m/e=16) is 0.84×0.250=0.22. By subtraction, the $B^{11}D_2H^+$ ion is 0.29−0.22=0.07 and the $B^{10}D_2H^+$ ion (m/e=15) is 0.02. After all contributions are obtained, the single check point is m/e=10. The observed discrepancy is considerably larger than the experimental uncertainty, requiring a B^{10}/B^{11} ratio of approximately 0.26 to obtain a zero residual. A similar effect was noted and discussed in a previous paper [4]. The B_2D_6 and B_2D_5H dissociation patterns are obtained by summing the contributions of all ions with the same number of deuterium atoms regardless of boron isotopic species. The most abundant ion of B_2D_6 ($B_2D_5^+$) and of B_2D_5H ($B_2D_4H^+$) are taken as 100. Other values of ion abundance are relative to the maximum peak. The complete spectrum of B_2D_6 and the partial spectrum of B_2D_5H for 50- and 70-v electrons are given in table 3. The spectrum of B_2H_6 is included for comparison. Sensitivities (ion current in arbitrary units per unit of sample pressure) are given for the maximum peaks of B_2D_6 and B_2H_6.

TABLE 2. *Summary of the monoisotopic spectrum calculations for the* B_1 *group of* B_2D_6 *and* B_2D_5H *for 70-v electrons*

m/e	Mixture spectrum	B_2D_2 [a]			B_2D_5H [a]		
		$B^{11}D_x$	$B^{10}D_x$	ΣBD_x	$B^{11}D_xH$	$B^{10}D_xH$	ΣBD_xH
10	5.54	-------	5.37	26.85	--------	--------	--------
11	21.53	21.48	-------	-------	--------	0.05	0.25
12	3.94	-------	3.74	18.71	0.20	--------	--------
13	15.19	14.97	-------	-------	--------	.22	1.09
14	7.63	-------	6.76	33.81	.87	--------	--------
15	27.07	27.05	-------	-------	--------	.02	.09
16	.29	-------	.21	1.05	.07	--------	--------
17	.84	.84	-------	-------	--------	--------	--------

[a] x assumes integral values from 0 to 3.

TABLE 3. *Monoisotopic dissociation patterns of* B_2D_6, B_2H_6, *and the partial pattern of* B_2D_5H *for 50 and 70-v electrons*

B_2D_6			B_2H_6			B_2D_5H		
Ion	50 v	70 v	Ion	50 v	70 v	Ion	50 v	70 v
B^+	17.7	17.3	B^+	21.7	21.5	B^+	-----	-----
BD^+	12.0	12.1	BH^+	10.2	10.6	BH^+	2.5	1.4
BD_2^+	22.8	21.8	BH_2^+	19.9	19.5	BDH^+	10	10
BD_3^+	.68	.67	BH_3^+	.58	.65	BD_2H^+	.8	.8
B_2^+	1.56	1.63	B_2^+	2.84	3.22	B_2^+	-----	-----
B_2D^+	5.27	4.62	B_2H^+	8.46	7.72	B_2H^+	0	0
$B_2D_2^+$	69.2	66.9	$B_2H_2^+$	76.2	74.6	B_2DH^+	30	29
$B_2D_3^+$	24.3	23.6	$B_2H_3^+$	29.6	28.8	$B_2D_2H^+$	19	18
$B_2D_4^+$	46.9	46.5	$B_2H_4^+$	53.2	52.9	$B_2D_3H^+$	42	44
$B_2D_5^+$	100	100	$B_2H_5^+$	100	100	$B_2D_4H^+$	100	100
$B_2D_6^+$	.18	.17	$B_2H_6^+$	.34	.31	$B_2D_5H^+$	-----	-----
Sensitivity	23.6	24.3	Sensitivity	23.0	23.7	Sensitivity	-----	-----

Omitted from the B_2D_6 spectrum in table 2 is a small peak at $m/e=12.5$ amounting to 0.36 percent of the maximum at 50 v and 0.40 percent at 70 v. This peak is due to the double charged ion, $B^{10}B^{11}D_2^{++}$. The two isotope peaks expected coincide with large peaks at $m/e=12$ and 13. A similar doubly charged peak appears in B_2H_6 at $m/e=11.5$, amounting to 0.39 percent of the maximum at 50 v and 0.43 percent at 70 v. This doubly charged ion of mass 23 was ascribed [3] to either $B_2^{11}H^{++}$ or $B^{10}B^{11}H_2^{++}$. It is very likely $B^{10}B^{11}H_2^{++}$ corresponding to the $B^{10}B^{11}D_2^{++}$ peak in the B_2D_6 spectrum.

Also omitted from the B_2D_6 spectrum are the four small peaks listed in columns 2 and 3 of table 4. These are the result of dissociation of ions after they have traversed the electric field [8]. The peaks at 21.6 and 22.6 are isotopic as indicated by their relative abundance and are due to the transitions $B^{10}B^{11}D_4^+ \rightarrow B^{10}B^{11}D_2^+ + 2D$ and $B_2^{11}D_4^+ \rightarrow B_2^{11}D_2^+ + 2D$. The peaks at $m/e=23.6$ and 24.6 are also isotopic and are a result of the transitions $B^{10}B^{11}D_5^+ \rightarrow B^{10}B^{11}D_3^+ + 2D$ and $B_2^{11}D_5^+ \rightarrow B_2^{11}D_3^+ + 2D$. The transition $B_2^{10}D_5^+ \rightarrow B_2^{10}D_3^+ + 2D$ may also contribute to $m/e=22.6$, but the contribution is very small and below the threshold of observation. The two metastable transitions observed in diborane are also given in table 4. These are also isotopic and result from the transitions $B^{10}B^{11}H_4^+ \rightarrow B^{10}B^{11}H_2^+ + 2H$ and $B_2^{11}H_4^+ \rightarrow B_2^{11}H_2^+ + 2H$. The apparent mass of each metastable ion is calculated from the usual relation $m_a = (m_f)^2/m_i$, where m_i and m_f are respectively the ion masses before and after metastable dissociation. The calculated and observed values agree within 0.1 mass unit.

TABLE 4. *Percentage abundance of metastable ions relative to the maximum peak in* B_2D_6 *and* B_2H_6

m/e	B_2D_6		B_2H_6	
	50 v	70 v	50 v	70 v
21.1	--------	--------	0.05	0.06
21.6	0.07	0.09	--------	--------
22.1	--------	--------	.13	.15
22.6	.16	.17	--------	--------
23.6	.07	.08	--------	--------
24.6	.13	.14	--------	--------

Table 5 gives the dissociation patterns of ethane and ethane-d_6 at 50 and 70 v. The sensitivities of the maximum peak in each compound are also given. The peaks at the odd mass numbers in the C_2D_6 spectrum have been corrected for carbon isotope and represent contributions from an estimated 1.5 percent of C_2D_5H in the sample. The two peaks indicated by the footnote very probably include contributions due to the doubly charged ions $C_2D_3^{++}$ and $C_2D_5^{++}$. Analogous doubly charged ions appear in C_2H_6 at $m/e=13.5$ and 14.5. The relative abundance of these ions is given in the C_2H_6 spectrum. Three metastable ions not included in table 5 are observed in the C_2D_6 spectrum. One appearing near mass 24.5 amounting to 0.19 percent of the maximum peak at 50 v and 0.18 percent at 70 v is a result of the transition $C_2D_4^+ \rightarrow C_2D_2^+ + 2D$. Another, near $m/e=26.5$, of 0.19 percent at 50 v and 0.17 percent at 70 v, comes from the transition $C_2D_5^+ \rightarrow C_2D_3^+ + 2D$. The third, near $m/e=28.4$, of 0.08 percent at 50 v and 0.09 percent at 70 v, comes from the transition $C_2D_6^+ \rightarrow C_2D_4^+ + 2D$. Analogous transitions are observed for ethane at $m/e=24.1$, 25.1, and 26.1. They are 0.10, 0.17, and 0.30 percent, respectively, of the maximum peak at 50 v and 0.12, 0.17, and 0.30 percent at 70 v.

TABLE 5. *Monoisotopic dissociation patterns of* C_2D_6 *and* C_2H_6 *for 50 and 70 v electrons*

C_2D_6				C_2H_6			
m/e	Ion	50 v	70 v	*m/e*	Ion	50 v	70 v
12	C^+	0.54	0.67	12	C^+	0.52	0.66
13	CH^+	--------	--------				
14	CD^+	1.27	1.47	13	CH^+	1.11	1.34
15	CDH^+	[a].04	[a].08	13.5	$C_2H_3^{++}$	.05	.07
16	CD_2^+	3.44	3.71	14	CH_2^+	4.27	4.68
17	CD_2H^+	[a].33	[a].54	14.5	$C_2H_5^{++}$	.56	.70
18	CD_3^+	4.29	4.45	15	CH_3^+	4.67	4.90
19	CD_3H^+	.03	.02				
20	CD_4^+	.04	.04	16	CH_4^+	.08	.10
24	C_2^+	.32	.44	24	C_2^+	.56	.82
25	C_2H^+	--------	--------				
26	C_2D^+	2.28	2.61	25	C_2H^+	3.73	4.39
27	C_2DH^+	.04	.04				
28	$C_2D_2^+$	17.9	18.4	26	$C_2H_2^+$	22.9	23.5
29	$C_2D_2H^+$	.12	.11				
30	$C_2D_3^+$	24.4	24.4	27	$C_2H_3^+$	32.3	32.7
31	$C_2D_3H^+$	.82	.83				
32	$C_2D_4^+$	100	100	28	$C_2H_4^+$	100	100
33	$C_2D_4H^+$	.23	.21				
34	$C_2D_5^+$	15.3	16.4	29	$C_2H_5^+$	18.7	18.8
35	$C_2D_5H^+$	.28	.23				
36	$C_2D_6^+$	19.1	19.9	30	$C_2H_6^+$	23.7	23.5
Sensitivity.	----------	45.8	46.4	Sensitivity.	----------	44.1	45.1

[a] Includes contributions from the doubly charged ions $C_2D_3^{++}$ and $C_2D_5^{++}$.

IV. Discussion

As evidenced by table 3, the mass spectra of diborane and diborane-d_6 are quite similar. The 34 peak in B_2D_6 is considered a good measure of the $B_2D_6^+$ ion as an impurity on this peak is unlikely in diborane. The lower value of the relative abundance of the $B_2D_6^+$ ion (0.18) compared to the $B_2H_6^+$ ion (0.34) is perhaps not significant. The latter value suggests that a trace of nitrogen impurity may contribute to the 28 peak of normal diborane. Although the molecule ion is very unstable, it is evidently not completely absent from the mass spectrum as first supposed [9]. The sensitivities of the maximum peaks of both compounds agree within 3 percent, which is the estimated uncertainty, demonstrating the nearly equal probability of dissociating a deuterium from B_2D_6 and a protium from B_2H_6. In the B_2 group the relative probabilities of dissociating successive deuterium atoms from B_2D_6 and successive protium atoms from B_2H_6 are similar but always somewhat less for the deuterated compound. In the B_1 group the probabilities are roughly equal. This compares reasonably well with the similarities previously reported [5] and those observed for ethane and ethane-d_6 discussed below.

Metastable transitions with the loss of mass 2 are by far the most frequent type found in hydrocarbons [10]. It is not surprising, therefore, to find this transition readily occurring in deutero- and normal diborane. An interesting difference between B_2D_6 and B_2H_6, however, is the occurrence of a metastable dissociation of the $B_2D_5^+$ ion in diborane-d_6, whereas the analogous transition is absent in normal diborane. As observation of a metastable ion indicates a delay of roughly 10^{-6} second in the dissociation process, it is evident that substitution of deuterium for protium in diborane has materially changed the mean life of the transition involved. The other metastable dissociations are similar and have nearly equal probability in diborane and diborane-d_6.

The formula $B^{10}B^{11}D_2^{++}$ is unambiguously assigned to the ion appearing at $m/e=12.5$ in the diborane-d_6 spectrum. The similarity of relative abundance of this peak and the doubly charged ion appearing in diborane at $m/e=11.5$ suggests an unique interpretation of the latter that is not possible from the B_2H_6 spectrum alone. From the foregoing, it is probable but not certain that the doubly charged peak in B_2H_6 has the formula $B^{10}B^{11}H_2^{++}$ analogous to the doubly charged ion in B_2D_6.

The part of the B_2D_5H spectrum that contains protium atoms has been included in table 3. The method of computation and the small magnitude of the residuals from which the pattern is derived give a relatively large uncertainty for this pattern. As expected, the pattern is not like the patterns of either B_2D_6 or B_2H_6. One would predict that the abundance of the ions $B_2D_5^+$ plus $B_2D_4H^+$ from B_2D_5H should be compared with the abundance of the $B_2D_5^+$ ion from B_2D_6; the abundance of $B_2D_4^+$ plus $B_2D_3H^+$ should be compared with the abundance of $B_2D_4^+$ from B_2D_6, and so forth. If the probability of removing a dueterium or protium atom is merely a statistical matter, then the abundance ratio $B_2D_4H^+/B_2D_5^+$ from B_2D_5H would be 5 to 1. From table 1 the $B_2D_4H^+$ peak is 6.8 percent of the $B_2D_5^+$ peak, and on the above basis, B_2D_5H contributes 1.36 percent to the $B_2D_5^+$ peak. As the $B_2D_5H^+$ ion is immeasurably small, there is no check on this. The probability of removing a deuterium rather than a protium from $B_2D_4H^+$ is 4 to 1, and it might be expected that the pattern coefficient of $B_2D_3H^+$ from $B_2D_4H^+$ is 4/5 of the pattern coefficient of $B_2D_4^+$ from $B_2D_5^+$. The value thus calculated (37) is not in agreement with the observed value of 44. The probability of removing two deuteriums rather than a deuterium and a protium from $B_2D_4H^+$ is $3/4\times4/5=3/5$, and one would predict a pattern coefficient of 14 compared with 18 observed. Similarly, for B_2DH^+ one would predict $0.4\times66.9=27$ instead of 29, and for BDH^+, 8.8 instead of 10. For B_2H^+ one would expect 0.9 instead of zero, and for BH^+, 2.4 as observed. Analysis of the mass spectra of simple hydrocarbons containing one deuterium atom [5, 11] indicates that removal of the deuterium and protium atoms is not equally probable but in a ratio of about 0.5 to 1 for these molecules. It is not surprising, therefore, that purely statistical considerations fail to account for the B_2D_5H spectrum. The case of diborane, however, is more complicated as, according to recent theory [1], the six hydrogen atoms are not equivalent, but two of the atoms are bound loosely to an ethylene-type structure.

Insofar as the statistical method roughly accounts for the spectrum, the following conclusions can be drawn. The amount of B_2D_5H in the mixture is about 8.5 percent. The contribution of this to most peaks in the B_2D_6 pattern amounts to a few tenths of a percent of the $B_2D_5^+$ peak. (The B_2D_6 pattern is normalized with $B_2D_5^+$ taken as 100, therefore only differential effects enter as errors in the pattern.) The peaks resulting from the ions $B_2D_5H^+$ and B_2H^+ are very small and near the threshold of observation, and it is not unexpected to observe a pattern coefficient of zero for these peaks.

From table 5, the mass spectra of C_2D_6 and C_2H_6 are also quite similar. The sensitivities of the most abundant ion in both compounds agree to about 3 percent, which is the approximate uncertainty of the measurements. The similarity of the spectra extends to the doubly charged ions and the metastable transitions. The amount of C_2D_5H present is too small to permit conclusions concerning the dissociation of this molecule compared to ethane-d_6. The abundance of the molecule ion in ethane permits an estimate of the amount of C_2D_5H assuming only equality in sensitivity of the two ethanes. The 35 peak indicates approximately 1.5 percent C_2D_5H in the mixture. The dissimilarities of C_2H_6 and B_2H_6 spectra are already noted [3]. The same observations are applicable to C_2D_6 and B_2D_6, namely, the low abundance of the molecule ion and the BD_3^+ ion in the latter molecule compared to the analogous ions in ethane-d_6. In addition, a metastable transition of the $B_2D_5^+$ ion observed in diborane-d_6 has no analog in ethane-d_6.

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