

# Photoionization studies of $(\text{BH}_3)_n$ ( $n=1,2$ )

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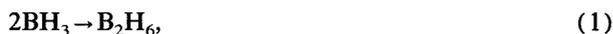
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The results of photoionization mass spectrometric studies on  $\text{B}_2\text{H}_6$ , and  $\text{BH}_3$  (produced by pyrolysis of  $\text{B}_2\text{H}_6$ ) are presented. The photoion yield curves of  $\text{B}_2\text{H}_n^+$  ( $n=2-6$ ) and  $\text{BH}_n^+$  ( $n=2-3$ ) from  $\text{B}_2\text{H}_6$ , as well as  $\text{BH}_n^+$  ( $n=1-3$ ) from  $\text{BH}_3$  have been obtained. It is shown that the combination of appearance potential measurements for  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ) and  $\text{BH}_3^+$  ( $\text{BH}_3$ ) yields a poor upper limit for  $-\Delta H_{\text{dimerization}, 0\text{K}}(\text{BH}_3)$  of 52.7 kcal/mol, while the combination of  $\text{BH}_2^+$  ( $\text{B}_2\text{H}_6$ ) and  $\text{BH}_2^+$  ( $\text{BH}_3$ ) provides a better upper limit ( $46.6 \pm 0.6$  kcal/mol) for this quantity. However, the threshold for  $\text{BH}^+$  ( $\text{BH}_3$ ), combined with auxiliary data, provides the best current experimental value,  $(34.3 - 39.1) \pm 2$  kcal/mol. This experimental value is in good agreement with a recent *ab initio* calculation, and is arrived at by using the best current estimate of  $\Delta H_f(\text{B}_2\text{H}_6)$ , rather than a radically different value proposed in that paper. The ionization potential of  $\text{BH}_3$ ,  $\Delta H_f(\text{BH}_2^+)$ , and the atomization energy of  $\text{BH}_3$  obtained experimentally are in excellent agreement with other *ab initio* calculations. The upper limits on heats of formation for the ionic species  $\text{B}_2\text{H}_n^+$  ( $n=2-6$ ) are obtained, and plausible structures are discussed for these species, based on the current energetics and various *ab initio* calculations. Finally, the fragmentation behavior of photoions from diborane is shown to have a more facile explanation by quasiequilibrium theory than by a molecular orbital picture, with the probable exception of  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ).

## I. INTRODUCTION

Some recent articles<sup>1-3</sup> have focused attention on the dimerization energy of borane,



and its pivotal role in determining  $\Delta H_f(\text{BH}_3)$  and other boron-hydrogen bond energies. Fehlner and Housecroft<sup>2</sup> summarize four approaches: thermodynamic, kinetic, mass spectrometric, and by way of *ab initio* calculations. The thermodynamic approach, rather indirect and with assumptions, was used to estimate  $\Delta H_{298} = -43$  kcal/mol for reaction (1). Two kinetic studies yield  $-35.0$  and  $-36$  kcal/mol. Two types of mass spectrometric measurements have been reported—a determination of the equilibrium constant<sup>4</sup> for reaction (1) at elevated temperatures (773–925 K) from which  $\Delta F$ , and then  $\Delta H$  were obtained, and electron impact measurements of the appearance potential (AP) of  $\text{BH}_3^+$  from  $\text{B}_2\text{H}_6$ , together with the ionization potential (IP) of  $\text{BH}_3$  performed in a separate, pyrolysis experiment. The equilibrium approach<sup>4</sup> yielded  $\Delta H_0 = -55 \pm 8$  kcal/mol for reaction (1). Early electron impact measurements<sup>5</sup> yielded  $-39$  and  $-37.1 \pm 4$  kcal/mol, but these were subsequently criticized (with good justification, as we shall show) by McGee and co-workers in two articles,<sup>6,7</sup> in both of which they obtained  $-59$  kcal/mol for reaction (1).

*Ab initio* results are usually referred to the bottom of the respective electronic potential wells, which we call  $\Delta H_e$ . The results summarized in the ensuing paragraph refer to  $\Delta H_e$ . Early *ab initio* calculations which did not take electron correlation into account<sup>3</sup> appeared to converge on a Hartree-

Fock limit of  $\sim -19.0$  kcal/mol. More recent calculations using various correlation methods yield  $-36.6$  kcal/mol<sup>8</sup> (coupled electron pair approximation, or CEPA),  $-37.4$  kcal/mol<sup>9</sup> (many-body perturbation theory),  $-40.3$  kcal/mol<sup>10</sup> (third-order perturbation theory), and  $-43.14$  kcal/mol<sup>3</sup> (fourth-order Møller-Plesset perturbation theory). The latter authors calculate a difference between  $\Delta H_e$  and  $\Delta H_{298}$  of 3.5 kcal/mol, i.e.,  $\Delta H_e = -43.1$  kcal/mol becomes  $\Delta H_{298} = -39.6$  kcal/mol.

Page *et al.*<sup>3</sup> summarize the experimental work as falling into two categories, either "high" (55–59 kcal/mol) or "low" (28–39 kcal/mol), the mass spectrometric being high and the kinetic, low. They regard their own calculations, being the most recent and the most extensive, as being the most accurate, but they estimate a residual error of 2–3 kcal/mol. Fehlner and Housecroft,<sup>2</sup> after summarizing the experimental and calculational results, appear to be convinced that "... the value of  $D(\text{B}_2\text{H}_6)$  lies between 35 and 40 kcal/mol." [Their  $D(\text{B}_2\text{H}_6)$  is equivalent to  $-\Delta H_{298}$  for reaction (1).] To reach this conclusion, they have had to place considerable weight on the calculational results.

The dimerization energy of borane is the link between  $\Delta H_f(\text{B}_2\text{H}_6)$  and  $\Delta H_f(\text{BH}_3)$ . If two of these enthalpies are well known, the third can be inferred. Although many experiments have been performed to determine  $\Delta H_{f,298}(\text{B}_2\text{H}_6)$ , there is still some uncertainty. The latest JANAF table<sup>11</sup> lists experimental values between 6.5 and 17.3 kcal/mol, and selects  $9.8 \pm 4.0$  kcal/mol. The recent Russian compilation<sup>12</sup> chooses  $8.7_5 \pm 0.5$  kcal/mol. Page *et al.*<sup>3</sup> utilize their calculated dimerization energy and  $\Delta H_{f,298}(\text{BH}_3)$  to deduce  $\Delta H_{f,298}(\text{B}_2\text{H}_6) = 2.7$  kcal/mol, which is lower than any of the experimental values considered by JANAF<sup>11</sup> or the Russian compilation.<sup>12</sup> However, in order to obtain  $\Delta H_{f,298}(\text{BH}_3)$  they have had to combine their calculated atomization energy of  $\text{BH}_3$  with the heat of formation (or heat of

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sublimation) of boron. This quantity has also been the subject of numerous experiments, and uncertainties of the order of 3–4 kcal/mol persist. We shall return to this question, and attempt to interrelate  $\Delta H_f(\text{B}_2\text{H}_6)$ ,  $\Delta H_f(\text{B})$ , and the dimerization energy of borane following presentation of our own data.

The technique we shall employ is photoionization mass spectrometry. It is similar in principle to electron impact mass spectrometry, but considerably more precise and detailed. We shall demonstrate the existence, and upper limits to the heats of formation, of  $\text{B}_2\text{H}_5^+$ ,  $\text{B}_2\text{H}_4^+$ ,  $\text{B}_2\text{H}_3^+$ ,  $\text{B}_2\text{H}_2^+$ , and  $\text{BH}_2^+$ , as well as determine the ionization potentials of  $\text{B}_2\text{H}_6$  and  $\text{BH}_3$ . These species have been identified earlier by electron impact mass spectrometry. In view of the interesting structures manifested by the electron deficient neutral boranes, it is rather surprising that of the diboron hydride ions, only  $\text{B}_2\text{H}_5^+$  has been studied by *ab initio* methods and reported in the open literature, and only by two groups.<sup>13,14</sup> We hope that the present results will spur further calculations of these species.

## II. EXPERIMENTAL ARRANGEMENT

The photoionization mass spectrometer, consisting of a 3 m vacuum ultraviolet monochromator (McPherson) and a quadrupole mass spectrometer (Extranuclear) has been described previously.<sup>15,16</sup> The diborane sample, which contained 50%  $\text{B}_2\text{H}_6$  and 50% He, was "electronic grade" and was obtained from Airco. The quartz pyrolysis reactor was identical to that described earlier.<sup>15</sup> The measurements were performed with a wavelength resolution of 0.28 Å, using the Hopfield continuum of helium for shorter wavelengths and the many-line pseudocontinuum of hydrogen at longer wavelengths.

## III. EXPERIMENTAL RESULTS

### A. $\text{B}_2\text{H}_6$ sample

The photoion yield curves of all of the ions produced by photoionization of diborane with intensities  $\geq 0.1\%$  of the major mass ( $m/e = 27$ ) were recorded. These include  $m/e = 28$ , which is  $^{11}\text{B}^{11}\text{BH}_6^+$ ;  $m/e = 27$ ,  $^{11}\text{B}^{11}\text{BH}_5^+$  and  $^{10}\text{B}^{10}\text{BH}_6^+$ ;  $m/e = 26$ ,  $^{11}\text{B}^{11}\text{BH}_4^+$ ,  $^{10}\text{B}^{11}\text{BH}_5^+$ , and  $^{10}\text{B}^{10}\text{BH}_6^+$ ;  $m/e = 25$ ,  $^{11}\text{B}^{11}\text{BH}_3^+$ ,  $^{10}\text{B}^{11}\text{BH}_4^+$ , and  $^{10}\text{B}^{10}\text{BH}_5^+$ ;  $m/e = 24$ ,  $^{11}\text{B}^{11}\text{BH}_2^+$ ,  $^{10}\text{B}^{11}\text{BH}_3^+$ , and  $^{10}\text{B}^{10}\text{BH}_4^+$ ; and  $m/e = 23$ ,  $^{10}\text{B}^{11}\text{BH}_2^+$  and  $^{10}\text{B}^{10}\text{BH}_3^+$ . The extremely weak signal at  $m/e = 22$  attests to the absence of  $\text{B}_2\text{H}^+$  in our energy domain.

In addition, we have examined  $m/e = 14$ ,  $^{11}\text{BH}_3^+$ ;  $m/e = 13$ ,  $^{11}\text{BH}_2^+$  and  $^{10}\text{BH}_3^+$ ; and  $m/e = 12$ ,  $^{10}\text{BH}_2^+$ . These experimental data sets have each been fitted with a spline smoothing function. In Fig. 1, the data points, together with the smoothed functions, are shown for  $m/e = 27, 26, 25, 24$ , and 23. The corresponding data sets and smoothed functions for  $m/e = 28, 14, 13$ , and 12, considerably weaker than the first group, are collected and displayed in Fig. 2.

It is immediately apparent that the parent ion,  $^{11}\text{B}_2\text{H}_6^+$ ,  $m/e = 28$  is extremely weak ( $\sim 0.1\%$  of  $m/e = 27$ ). Hence,  $m/e = 27$  is essentially attributable in its entirety to

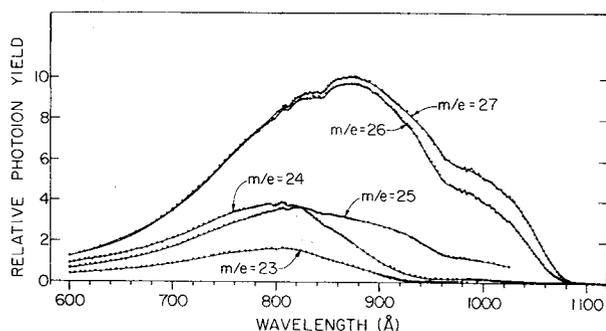


FIG. 1. The photoion yield curves of  $m/e = 27, 26, 25, 24$ , and 23 from  $\text{B}_2\text{H}_6$  obtained with 0.28 Å resolution (FWHM). The smooth curve through each data set represents a fitting with a polynomial spline function, except for  $m/e = 23$ . There, the smooth curve is a simulation obtained by summing up the contributions from isotopically pure species (see Fig. 3) and serves as a check.

$^{11}\text{B}_2\text{H}_5^+$ . Using the isotopic abundances of boron<sup>17</sup> ( $^{11}\text{B} = 0.801$ ,  $^{10}\text{B} = 0.199$ ) and a small factor due to the mass discrimination of the quadrupole mass spectrometer, we have subtracted the  $\text{B}_2\text{H}_5^+$  contribution from  $m/e = 26$ . The residue is  $^{11}\text{B}_2\text{H}_4^+$ . The digital subtraction was performed with the smoothed functions for  $m/e = 27$  and 26. The  $\text{B}_2\text{H}_4^+$  function thus derived, together with the  $\text{B}_2\text{H}_5^+$  function, could now be subtracted in turn from  $m/e = 25$ , leaving as residue  $^{11}\text{B}_2\text{H}_3^+$ . The  $\text{B}_2\text{H}_4^+$  and  $\text{B}_2\text{H}_3^+$  functions were then subtracted from  $m/e = 24$ , leaving as residue  $\text{B}_2\text{H}_2^+$ . This could be compared with  $m/e = 23$ , which is mostly  $^{10}\text{B}^{11}\text{BH}_2^+$ , with only a small contribution from  $^{10}\text{B}^{10}\text{BH}_3^+$ . The agreement between these two  $\text{B}_2\text{H}_2^+$  functions was quite good, providing a check on our subtraction procedure. A similar strategy was employed for  $m/e = 14, 13$ , and 12, yielding the  $\text{BH}_3^+$  and  $\text{BH}_2^+$  ion yield functions. The photoion yield curves thus derived for  $\text{B}_2\text{H}_5^+$ ,  $\text{B}_2\text{H}_4^+$ ,  $\text{B}_2\text{H}_3^+$ , and  $\text{B}_2\text{H}_2^+$  are shown in Fig. 3. The relative intensities shown in this figure are true representations of the relative abundances of these species. The weaker species  $\text{B}_2\text{H}_6^+$ ,  $\text{BH}_3^+$ , and  $\text{BH}_2^+$  are shown in Fig. 4, with an appropriate scale factor.

The ionization potential of  $\text{B}_2\text{H}_6$ , and the appearance potentials of  $\text{B}_2\text{H}_5^+$ ,  $\text{B}_2\text{H}_4^+$ ,  $\text{B}_2\text{H}_3^+$ ,  $\text{B}_2\text{H}_2^+$ ,  $\text{BH}_3^+$ , and  $\text{BH}_2^+$

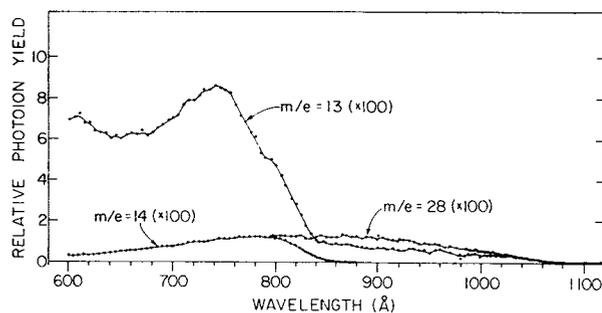


FIG. 2. The photoion yield curves of  $m/e = 28, 14$ , and 13 from  $\text{B}_2\text{H}_6$ , obtained with 0.28 Å resolution (FWHM). The  $m/e = 28$  curve was not followed below 800 Å, because of interference from autoionizing lines of a small  $\text{N}_2$  impurity.

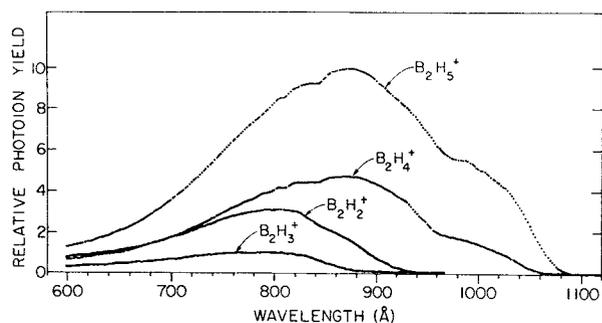
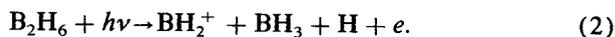


FIG. 3. The photoion yield curves of  $\text{B}_2\text{H}_5^+$ ,  $\text{B}_2\text{H}_4^+$ ,  $\text{B}_2\text{H}_3^+$ , and  $\text{B}_2\text{H}_2^+$  from  $\text{B}_2\text{H}_6$ . These curves have been obtained by a subtraction procedure described in the text, which sorts out the  $^{10}\text{B}$  and  $^{11}\text{B}$  contributions. The relative intensities shown are true representations of the relative abundances of these species.

are summarized in Table I. The appearance potentials have been corrected<sup>18</sup> to 0 K, by adding to the observed onset energy the internal thermal energy<sup>11,12</sup> (0.0618 eV) of  $\text{B}_2\text{H}_6$  at 298 K. The actual thresholds were determined either by linear extrapolation, or in the cases of marked curvature (as in  $\text{B}_2\text{H}_6^+$  and  $\text{B}_2\text{H}_5^+$ ), a subjective judgment of the departure from the background level. In all cases, the appearance potentials must be regarded as upper limits.

The species  $\text{BH}_2^+$  requires further discussion. This species has a rather sharp increase at  $\sim 839 \text{ \AA}$ , but a signal persists to much longer wavelengths, and it appears both at  $m/e = 13$  and 12, with an intensity ratio corresponding to that of boron isotopes. Hence, it is almost certainly  $\text{BH}_2^+$ . As we shall see later, the threshold at  $839 \text{ \AA}$  is a plausible one for the process



Since  $\text{BH}_4$  is not stable, a possible process at lower energy could be the simultaneous formation of the ion pairs  $\text{BH}_2^+ + \text{BH}_4^-$ , the latter having been calculated<sup>19</sup> to be quite stable. We thereupon made a search for the  $\text{BH}_4^-$  ion, having first established from a study of ion-pair formation in  $\text{Cl}_2$  (giving  $\text{Cl}^+ + \text{Cl}^-$ ) that our sensitivity for negative ions was at least as good as for positive ions. No evidence for  $\text{BH}_4^-$  was found. Subsequently, we tested the intensity of  $\text{BH}_2^+$  at selected wavelengths in the tail region (above 839

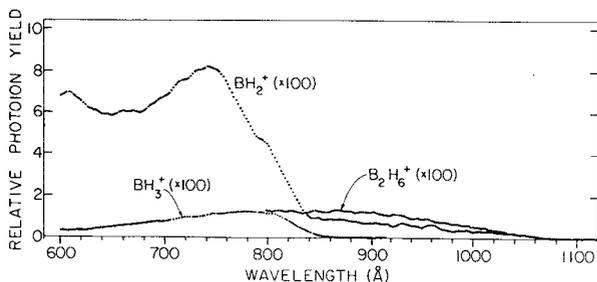


FIG. 4. The photoion yield curves of  $\text{B}_2\text{H}_6^+$ ,  $\text{BH}_3^+$ , and  $\text{BH}_2^+$  from  $\text{B}_2\text{H}_6$ . Note the scale, which distinguishes those weaker species from those in Fig. 3.

TABLE I. Ionization potential and appearance potentials<sup>a</sup> of ionic species from photoionization of  $\text{B}_2\text{H}_6$ .

Process	Threshold potential, eV
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{B}_2\text{H}_6^+ + e$	$< 11.37 \pm 0.05$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{B}_2\text{H}_5^+ + \text{H} + e$	$< 11.40 \pm 0.05$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{B}_2\text{H}_4^+ + \text{H}_2 + e$	$< 11.75$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{B}_2\text{H}_3^+ + \text{H} + \text{H}_2 + e$	$< 14.15$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{B}_2\text{H}_2^+ + 2\text{H}_2 + e$	$< 13.25$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{BH}_3^+ + \text{BH}_3 + e$	$< 14.31\text{--}14.39$
$\text{B}_2\text{H}_6 + h\nu \rightarrow \text{BH}_2^+ + \text{BH}_3 + \text{H} + e$	$< 14.84_0 \pm 0.01_7$

<sup>a</sup> Observed appearance potentials have been reduced to equivalent 0 K thresholds by adding the internal thermal energy of  $\text{B}_2\text{H}_6$  at 298 K, 0.0618 eV.

$\text{ \AA}$ ) as a function of  $\text{B}_2\text{H}_6$  pressure. The dependence on pressure was greater than linear, but less than quadratic (going as  $\sim P^{1.5}$ ). Our tentative conclusion is that this tail is partially due to collisional processes of second order (such as  $\text{B}_2\text{H}_5^+ + \text{B}_2\text{H}_6$ ) and partially to some small impurity. Weak intensities were also observed at  $m/e = 15$  and 16. Proceeding on the hypothesis that  $m/e = 15$  could be  $^{11}\text{BH}_4^+$ , and thus provide us with a measure of the proton affinity of  $\text{BH}_3$ , we followed both  $m/e = 15$  and 16 to their thresholds. The  $m/e = 16$  peak had the lower energy threshold, and it was in the vicinity of the ionization potential of  $\text{CH}_4$ . The  $m/e = 15$  peak had a threshold close to that of  $\text{CH}_3^+$  from  $\text{CH}_4^+$ .<sup>20</sup> Hence, the tentative conclusion is that both  $m/e = 15$  and  $m/e = 16$  are attributable to a small methane impurity in our sample, although the relative abundance of  $m/e = 15$  to  $m/e = 16$  was about 20% larger than that previously reported.<sup>20</sup>

## B. $\text{BH}_3$ from pyrolysis of $\text{B}_2\text{H}_6$

Diborane was introduced into the pyrolysis reactor, and the temperature was gradually increased while monitoring the  $m/e = 14$  ion intensity below the threshold for  $^{11}\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ). The intensity of  $\text{BH}_3^+$  increased from the background level, and optimized at  $\sim 530^\circ\text{C}$ . Above that temperature, the  $\text{BH}_3^+$  signal decreased, although the thermal decomposition of  $\text{B}_2\text{H}_6$  was not complete. Others<sup>6</sup> have also observed such behavior. With the temperature stabilized at  $\sim 530^\circ\text{C}$ , the photoion yield curves of  $m/e = 14$ ,  $^{11}\text{BH}_3^+$ ;  $m/e = 13$ ,  $^{11}\text{BH}_2^+$  and  $^{10}\text{BH}_3^+$ ;  $m/e = 12$ ,  $^{11}\text{BH}^+$  and  $^{10}\text{BH}_2^+$ ; and  $m/e = 11$ ,  $^{10}\text{BH}^+$  were measured from below their respective thresholds to  $\sim 790 \text{ \AA}$ . The peaks in the spectrum of the hydrogen lamp were utilized in the long wavelength region, down to  $927 \text{ \AA}$ . There was some overlap with the helium continuum data, which extended to  $\sim 790 \text{ \AA}$ . The photoion yield curves for these masses are shown in Fig. 5. The mass 14 signal, which is entirely attributable to  $\text{BH}_3^+$  ( $\text{BH}_3$ ), increases slowly from threshold, peaks at about  $974 \text{ \AA}$ , and declines to shorter wavelength. The gradual increase from threshold suggests that the geometrical structure of  $\text{BH}_3^+$  in its ground state is significantly different from that of  $\text{BH}_3$  neutral, and has implications for the presumed Jahn-Teller distortion in  $\text{BH}_3^+$ . The peaking at

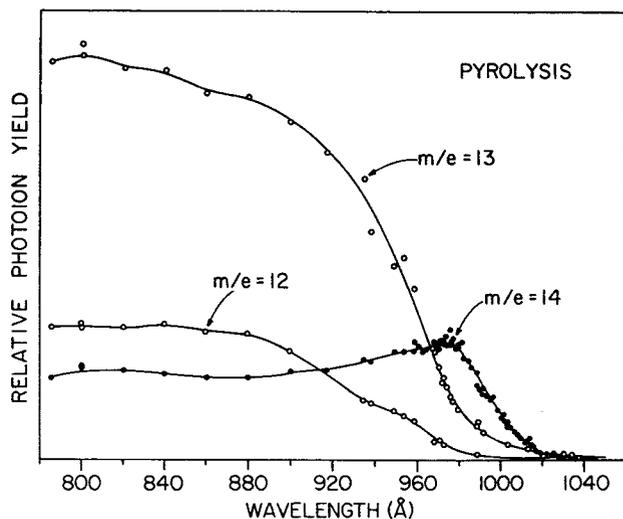


FIG. 5. The photoion yield curves of  $m/e = 14, 13,$  and  $12$  from  $\text{BH}_3$ . The monoborane target is obtained by pyrolysis of diborane at  $\sim 530^\circ\text{C}$ .

$\sim 974 \text{ \AA}$  occurs close to the onset of  $\text{BH}_2^+$  ( $\text{BH}_3$ ). This characteristic feature is rather similar to the photoionization<sup>21</sup> of  $\text{CH}_4$ , which exhibits a peak for  $\text{CH}_4^+$  formation just before the onset of  $\text{CH}_3^+$ . The curve for  $m/e = 13$  begins an abrupt rise at  $\sim 980 \text{ \AA}$ , and exceeds the intensity of  $m/e = 14$  below  $\sim 967 \text{ \AA}$ . Hence, at wavelengths lower than  $967 \text{ \AA}$ , the  $m/e = 13$  curve is predominantly attributable to  $\text{BH}_2^+$ . At wavelengths much longer than  $980 \text{ \AA}$ , a tail persists on the  $m/e = 13$  curve (but not on the  $m/e = 14$  curve), which presumably is attributable to the same processes responsible for such a tail in the photoionization of  $\text{B}_2\text{H}_6$  (see Sec. III A, above).

The inherent structure of the photoion yield curve for  $\text{BH}_2^+$  was obtained by subtracting the  $^{10}\text{BH}_3^+$  contribution from  $m/e = 13$ , using the relative abundance ratio of  $^{10}\text{B}$ : $^{11}\text{B}$  and the ion yield curve of  $m/e = 14$ , and incorporating a quadrupole transmission correction. In addition, since the threshold for  $\text{BH}_2^+$  ( $\text{BH}_3$ ) is one of the important results we hope to extract from the present study, we plotted the ratio of intensities at  $m/e = 13$  to  $m/e = 14$  as a function of wavelength. Below the energy threshold for  $\text{BH}_2^+$  ( $\text{BH}_3$ ), this ratio should just represent the abundance ratio of  $^{10}\text{B}$  to  $^{11}\text{B}$ ; above this threshold, the new process should cause an increase in the  $m/e = 13$  to  $m/e = 14$  intensity ratio. Both methods of treating this set of data are shown in Fig. 6, and (within experimental error) yield the same result.

The photoion yield curve for  $m/e = 12$  has a substantial contribution from  $^{10}\text{BH}_2^+$  which obscures the inherent behavior of  $^{11}\text{BH}^+$ . Nevertheless, a subtraction of the  $^{10}\text{BH}_2^+$  component has been performed, and a residue obtained. The results of this, as well as the earlier subtraction, are summarized in Fig. 7, which displays the inherent photoion yield curves of  $\text{BH}_3^+$ ,  $\text{BH}_2^+$ , and  $\text{BH}^+$  from  $\text{BH}_3$ . The relative intensities in this figure represent true relative abundances of these ions. We note that  $\text{BH}^+$  has a relatively small abundance. The  $^{10}\text{B}$  isotope of this species is still weaker, by a factor 4. However, the  $\text{BH}^+$  ( $\text{BH}_3$ ) threshold has consider-

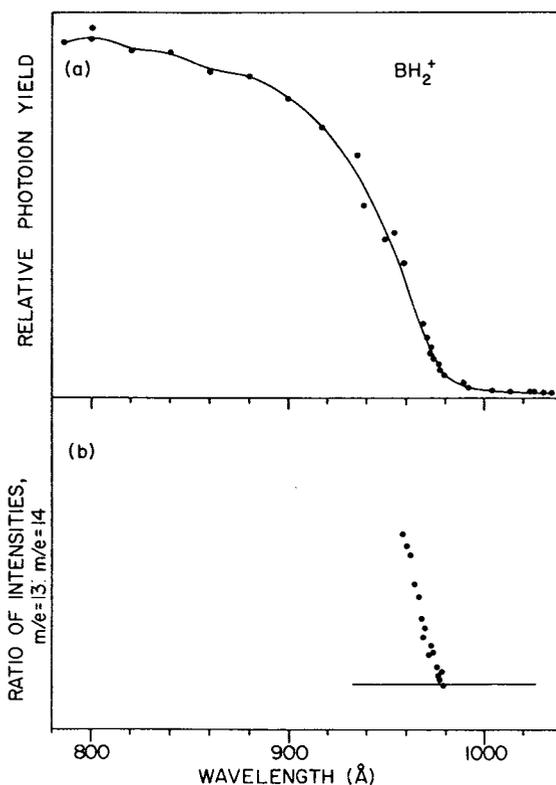


FIG. 6. (a) The photoion yield curve of  $\text{BH}_2^+$  ( $\text{BH}_3$ ), obtained by subtracting the  $^{10}\text{BH}_3^+$  contribution to  $m/e = 13$ . (b) The ratio of intensities of  $m/e = 13$  to  $m/e = 14$  as a function of wavelength. At long wavelengths, this ratio should become a constant, which represents the relative abundance of  $^{10}\text{BH}_3^+$  to  $^{11}\text{BH}_3^+$ . The ratio increases at shorter wavelengths, when  $^{11}\text{BH}_2^+$  adds to the intensity of  $m/e = 13$ .

able significance in the ensuing discussion, and  $m/e = 11$  is essentially entirely attributable to  $\text{BH}^+$ . Hence we explored the threshold region for  $m/e = 11$  with longer counting times. The resulting curve is recorded in Fig. 8.

The final results for the ionization potential of  $\text{BH}_3$ , and

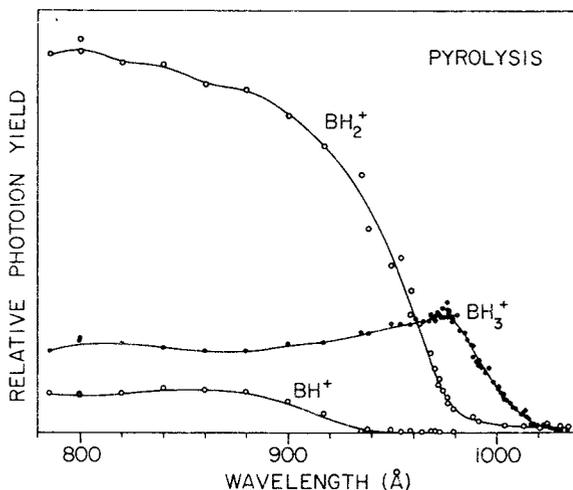


FIG. 7. The photoion yield curves of  $\text{BH}_3^+$ ,  $\text{BH}_2^+$ , and  $\text{BH}^+$  from  $\text{BH}_3$ , after taking into account the isotopic contributions. The relative intensities in this figure represent the true relative abundances of these ions.

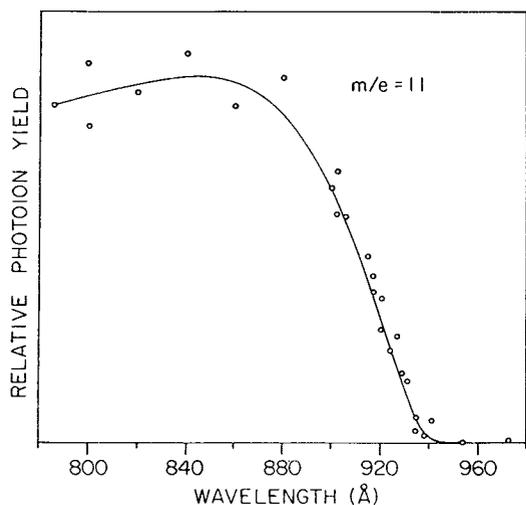


FIG. 8. The photoion yield of  $m/e = 11$ , which is  $^{10}\text{BH}^+$ , from  $\text{BH}_3$ , taken with longer counting times.

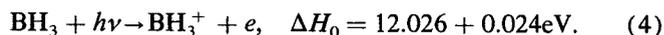
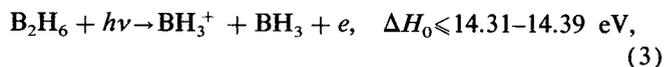
the appearance potentials of  $\text{BH}_2^+$  and  $\text{BH}^+$  from  $\text{BH}_3$ , are summarized in Table II. The appearance potentials of  $\text{BH}_2^+$  and  $\text{BH}^+$  have been corrected to 0 K by taking into account the internal thermal energy of  $\text{BH}_3$  at 800 K. This internal thermal energy (0.1609 eV) was obtained by subtracting  $5/2 RT$  from the heat content ( $H_{800} - H_0$ ).<sup>11</sup>

#### IV. INTERPRETATION OF RESULTS

##### A. The dimerization energy of borane

###### 1. Combining the thresholds for $\text{BH}_3^+$ ( $\text{B}_2\text{H}_6$ ) and $\text{BH}_3^+$ ( $\text{BH}_3$ )

From the results summarized in Tables I and II, we can extract



By subtracting reaction (4) from reaction (3), we obtain an upper limit to the dimerization energy of diborane at 0 K,  $\leq 2.28\text{--}2.37 \text{ eV} \equiv 52.7\text{--}54.7 \text{ kcal/mol}$ .

This approach is independent of prior knowledge about  $\Delta H_f(\text{B}_2\text{H}_6)$  and  $\Delta H_f(\text{BH}_3)$ . It is analogous to the earlier electron impact studies. Fehlner and Koski<sup>5</sup> obtained  $13.1 \pm 0.2 \text{ eV}$  for reaction (3), and  $11.4 \pm 0.2 \text{ eV}$  for reaction (4), both significantly lower than the present photoionization data. In the vast majority of such comparative studies to date, the photoionization data yield lower thresholds. Another dubious observation reported by Fehlner and Koski<sup>5</sup> was the presence of free  $\text{BH}_2$  in the pyrolysis of  $\text{B}_2\text{H}_6$  at a concentration two to three times as large as the  $\text{BH}_3$  concentration. From the results of the present investigation, it can readily be shown that the formation of  $\text{BH}_2$  from the pyrolysis of  $\text{B}_2\text{H}_6$  is much more endothermic than the formation of  $\text{BH}_3$ , and hence that the presence of free  $\text{BH}_2$  is unlikely, and unobserved in the present experiment.

Wilson and McGee<sup>6</sup> obtained  $14.88 \pm 0.05 \text{ eV}$  for reac-

tion (3), and  $12.32 \pm 0.1 \text{ eV}$  for reaction (4). Both of these values are higher than the corresponding photoionization results, which conform to the expected behavior. Furthermore, Wilson and McGee made a special effort to detect  $\text{BH}_2$  in their pyrolysis experiment, trying to reproduce Fehlner and Koski's<sup>5</sup> experimental conditions as closely as possible. They state that "... at no time was this ( $\text{BH}_2$ ) free radical detected." Hence, the electron impact measurements of Wilson and McGee,<sup>6</sup> which yield an upper limit to the dimerization energy of diborane of  $2.56 \text{ eV} \equiv 59 \text{ kcal/mol}$ , appear to be on much firmer ground than the corresponding data of Fehlner and Koski,<sup>5</sup> which give  $1.7 \text{ eV} \equiv 39 \text{ kcal/mol}$  for this quantity.

A detailed examination made possible by the present study reveals why this approach, whether performed by photon or electron impact ionization, is likely to produce too high a value for the dimerization energy. Reaction (4) is a primary ionization of a parent ion and, apart from the problem of low Franck-Condon factors near threshold, can in principle yield a rather good threshold. Reaction (3) represents a very weak process at best, for which the threshold will be very hard to find. We have seen that  $\text{B}_2\text{H}_6^+$  is an extremely weak parent ion, 1000 times less abundant than  $\text{B}_2\text{H}_5^+$ . Almost at threshold,  $\text{B}_2\text{H}_5^+$  appears and at 0.35 eV higher energy,  $\text{B}_2\text{H}_4^+$ . At still higher internal energies, these species fragment further to give  $\text{B}_2\text{H}_3^+$  and  $\text{B}_2\text{H}_2^+$ , respectively. If the quasiequilibrium theory of mass spectra were rigorously valid, no  $\text{B}_2\text{H}_6^+$  would survive at the internal energies necessary to produce  $\text{BH}_3^+ + \text{BH}_3$ . The photoionization data indicate an initial increase in the photoion yield curve of  $\text{B}_2\text{H}_6^+$  above threshold, and thereupon a rather flat region, suggesting that most of the higher electronic states formed in the photoionization of  $\text{B}_2\text{H}_6$  fragment, rather than producing excited  $\text{B}_2\text{H}_6^+$ . (However, see Sec. IV C.) Hence, we are drawn to the conclusion that the probability of reaction (3) occurring is very small, and that it must compete with much more probable processes. The asymptotic approach to the apparent threshold which we observe for  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ) is in agreement with this view.

The present situation is analogous to trying to determine the dimerization energy of methyl radicals by measuring the thresholds for  $\text{CH}_3^+$  ( $\text{C}_2\text{H}_6$ ) and  $\text{CH}_3^+$  ( $\text{CH}_3$ ). In this case, the dimerization energy is well known, as is the ionization potential of  $\text{CH}_3$ . Hence, one can predict that the thermochemical threshold for  $\text{CH}_3^+$  ( $\text{C}_2\text{H}_6$ ) should be 13.586 eV. However, photoionization of  $\text{C}_2\text{H}_6$  yields substantial  $\text{C}_2\text{H}_6^+$  at low energy, followed by  $\text{C}_2\text{H}_4^+$  and  $\text{C}_2\text{H}_5^+$ , the latter two ions ultimately dissociating into  $\text{C}_2\text{H}_2^+ + \text{H}_2$  and  $\text{C}_2\text{H}_3^+ + \text{H}_2$ .<sup>22</sup> In the midst of these strong, competing processes, the  $\text{CH}_3^+$  ion grows slowly from an apparent threshold at  $\sim 13.96 \text{ eV}$ .<sup>22</sup> Hence, an attempt to deduce the dimerization energy of methyl radicals by using this appearance potential would yield too high a value, by  $\sim 0.374 \text{ eV} = 8.6 \text{ kcal/mol}$ .

It may be argued that  $\text{B}_2\text{H}_5^+$  can itself decompose at higher energies to produce  $\text{BH}_3^+ + \text{BH}_2$ . This, of course, would be a different process from reaction (3) as written. However, it too, is an unfavored process. Curtiss and Pople<sup>26</sup>

TABLE II. Ionization potential and appearance potentials<sup>a</sup> of ionic species from photoionization of BH<sub>3</sub>.

Process	Threshold potential, eV
BH <sub>3</sub> + <i>hν</i> → BH <sub>3</sub> <sup>+</sup> + <i>e</i>	12.026 ± 0.024
BH <sub>3</sub> + <i>hν</i> → BH <sub>2</sub> <sup>+</sup> + H + <i>e</i>	<12.819 ± 0.020
BH <sub>3</sub> + <i>hν</i> → BH <sup>+</sup> + H <sub>2</sub> + <i>e</i>	< 13.372 ± 0.015

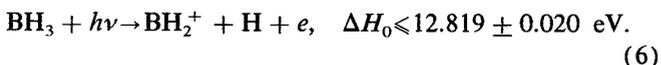
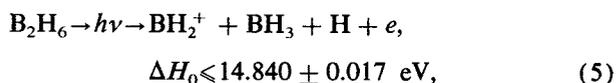
<sup>a</sup> Observed appearance potentials have been reduced to equivalent 0 K thresholds by adding the internal thermal energy of BH<sub>3</sub> at 800 K, 0.1609 eV.

have calculated, and our experiments to a large extent verify, that the ionization potential of BH<sub>2</sub> is 3.75 eV lower than that of BH<sub>3</sub>. Therefore, the dissociation of B<sub>2</sub>H<sub>5</sub><sup>+</sup> to form BH<sub>2</sub><sup>+</sup> + BH<sub>3</sub> should occur at much lower energy than that to form BH<sub>3</sub><sup>+</sup> + BH<sub>2</sub>, tending to retard the latter process both in onset energy and in intensity.

In summary, although this combination of processes [BH<sub>3</sub><sup>+</sup> (BH<sub>3</sub>) and BH<sub>3</sub><sup>+</sup> (B<sub>2</sub>H<sub>6</sub>)] provides an upper limit to the dimerization energy of borane, it is not a very useful or practical upper limit. Our results and analysis help to explain why the "mass spectrometric measurements tend to give the high values."<sup>3</sup>

## 2. Combining the thresholds for BH<sub>2</sub><sup>+</sup> (B<sub>2</sub>H<sub>6</sub>) and BH<sub>2</sub><sup>+</sup> (BH<sub>3</sub>)

Once again referring to the results summarized in Tables I and II, we recall



By subtracting reaction (6) from reaction (5), we obtain an alternative upper limit to the dimerization energy of borane at 0 K, <2.021 ± 0.026 eV ≡ 46.6 ± 0.6 kcal/mol. This value, about 6.1 kcal/mol lower than that deduced from BH<sub>3</sub><sup>+</sup> thresholds, is clearly a more useful upper limit. Of the two threshold measurements entering into this determination that corresponding to reaction (6) is much more likely to be not just an upper limit, but the true threshold (within experimental error). It corresponds to the first fragment of a simple molecule, it is a simple bond cleavage, and the experimental photoion yield curve rises rapidly from threshold. It is analogous to CH<sub>3</sub><sup>+</sup> (CH<sub>4</sub>), which also is well behaved and yields the correct thermochemical onset. On the other hand, BH<sub>2</sub><sup>+</sup> (B<sub>2</sub>H<sub>6</sub>) most likely occurs as a result of successive fragmentations, i.e., B<sub>2</sub>H<sub>5</sub><sup>+</sup> (itself a fragment, although in this case almost a parent ion) acquires enough internal energy to finally dissociate into BH<sub>2</sub><sup>+</sup> + BH<sub>3</sub>. (To be discussed more fully in Sec. IV E) The experimental photoion yield curve for this process displays a rather sharp onset (above the previously discussed weak, asymptotic tail), suggesting that the excess energy at the threshold of reaction (5) is probably less than that of CH<sub>3</sub><sup>+</sup> from C<sub>2</sub>H<sub>6</sub>, i.e., < 8.6 kcal/mol.

Wilson and McGee<sup>6</sup> report threshold values for reaction (5), 15.5 ± 0.05 eV, and reaction (6), 12.95 ± 0.05 eV,

which are in fair agreement with the present data, recognizing that electron impact methods usually result in higher values. However, the dimerization energy obtained from these numbers is once again 59 kcal/mol.

## 3. Combining D<sub>0</sub> (BH), ΔH<sub>f</sub><sup>0</sup> (B), and ΔH<sub>f</sub><sup>0</sup> (B<sub>2</sub>H<sub>6</sub>)

This is an important, though rather cumbersome analysis. It requires experimental values for D<sub>0</sub> (BH), IP(BH), our measured threshold for BH<sup>+</sup> (BH<sub>3</sub>), the heat of sublimation of boron and ΔH<sub>f</sub><sup>0</sup> (B<sub>2</sub>H<sub>6</sub>).

D<sub>0</sub> (BH) is given by Huber and Herzberg<sup>23</sup> as 3.42 eV, by Meyer and Rosmus<sup>24</sup> as 3.42 ± 0.04 eV, and by the Russian compilation<sup>12</sup> as 3.45 ± 0.05 eV. It is based on an observed predissociation. There is apparently a hump in the potential curve of A<sup>1</sup>Π. The estimated height of this hump has been subtracted from the extrapolated energy of the potential maximum. Meyer and Rosmus<sup>24</sup> have calculated D<sub>0</sub> (BH) = 3.34 eV by CEPA, while Pople *et al.*<sup>1</sup> obtain 3.51 eV by fourth-order Møller–Plesset perturbation theory. A value of 79.0 ± 1.1 kcal/mol ≡ 3.42<sub>6</sub> ± 0.05 eV appears to be reasonable, with a conservative error limit.

The ionization potential of BH obtained by Bauer, Herzberg, and Johns<sup>25</sup> from the observation of Rydberg states in the absorption spectrum is 9.77 ± 0.05 eV. Curtiss and Pople<sup>26</sup> have recently calculated 9.87 eV. We retain here the value of Bauer *et al.*<sup>25</sup> Our measured threshold for BH<sup>+</sup> (BH<sub>3</sub>) is <13.372 ± 0.015 eV, as given in Table II. By combining these quantities with the well-known D<sub>0</sub> (H<sub>2</sub>) = 4.4781 ± 0.0001 eV, we obtain the atomization energy of BH<sub>3</sub>, <11.50<sub>6</sub> ± 0.07<sub>2</sub> eV ≡ 265.3 ± 1.7 kcal/mol, entirely from experimental measurements. Pople *et al.*<sup>1</sup> have obtained 266.9 kcal/mol, (with a presumed error of ± 2 kcal/mol) by fourth-order Møller–Plesset perturbation theory. Comparison of these quantities provides support for the view that the upper limit for the BH<sup>+</sup> (BH<sub>3</sub>) threshold obtained in the present experiment is in fact very close to the true value.

However, to relate the atomization energy of borane to ΔH<sub>f</sub>(BH<sub>3</sub>) one requires an accurate value for the heat of sublimation of boron. The alternative values discussed in the following paragraph refer to ΔH<sub>f</sub><sup>0</sup><sub>298</sub> (B), since this is the quantity most often cited by the researchers and compilers. The JANAF<sup>11</sup> (1983) tables give 133.8 ± 2.9 kcal/mol, which is also the CODATA (1978) value. This analysis does not include the later results of Mar and Bedford<sup>27</sup> (1976), Storms and Mueller<sup>28</sup> (1977), Andrievskii *et al.*<sup>29</sup> (1982), and Nordine and Schiffman (1985).<sup>30</sup>

The Russian compilation<sup>12</sup> (1982) considers Mar and Bedford,<sup>27</sup> and Storms and Mueller,<sup>28</sup> but not the latter two investigations. They choose 135.0 ± 1.2 kcal/mol. In Table III, we tabulate these various selections, after converting each to ΔH<sub>f</sub><sup>0</sup> (B, g). By combining ΔH<sub>f</sub><sup>0</sup> (B, g) with the enthalpy of atomization of BH<sub>3</sub> deduced previously, 265.3 ± 1.7 kcal/mol, and D<sub>0</sub> (H<sub>2</sub>) we can compute ΔH<sub>f</sub><sup>0</sup> (BH<sub>3</sub>). Hence, we also list in Table III the value of ΔH<sub>f</sub><sup>0</sup> (BH<sub>3</sub>) corresponding to a particular choice of ΔH<sub>f</sub><sup>0</sup> (B, g). The values of ΔH<sub>f</sub><sup>0</sup> (BH<sub>3</sub>) range from 22.2 ± 3.4 to 25.8 ± 1.7 kcal/mol.

TABLE III. Alternative choices for  $\Delta H_f^0$  (B, g) and the correlated values of  $\Delta H_f^0$  ( $\text{BH}_3$ ) (in kcal/mol).

$\Delta H_f^0$ (B,g)	Ref.	$\Delta H_f^0$ ( $\text{BH}_3$ )
$132.6 \pm 2.9$	JANAF (CODATA) <sup>11</sup>	$22.2 \pm 3.4$
$133.8 \pm 1.2$	Russian compilation <sup>12</sup>	$23.4 \pm 2.1$
$133.5 \pm 6.1$	Mar and Bedford <sup>27</sup>	$23.1 \pm 6.3$
$132.9 \pm 0.6$		$22.5 \pm 1.8$
$134.1 \pm 2.6$		$23.9 \pm 3.1$
$136.2 \pm 0.2$		$25.8 \pm 1.7$
$133.8 \pm 1.7$	Storms and Mueller <sup>28</sup>	$23.4 \pm 2.4$
	Nordine and Schiffman <sup>30</sup>	

In the Introduction, we reviewed briefly the current knowledge regarding the heat of formation of diborane. The JANAF compendium<sup>11</sup> selects  $\Delta H_f^0$  ( $\text{B}_2\text{H}_6$ ) =  $13.5 \pm 4.0$  kcal/mol, while the Russian compilation<sup>12</sup> gives  $12.5 \pm 0.5$  kcal/mol. The extremum values for the dimerization energy of borane (0 K) resulting from this range for  $\Delta H_f^0$  ( $\text{BH}_3$ ) and  $\Delta H_f^0$  ( $\text{B}_2\text{H}_6$ ) are 30.9–39.1 kcal/mol. If we eliminate the JANAF value from our consideration, we reduce this spread to  $(34.3\text{--}39.1) \pm 2$  kcal/mol. (The data of Andrievskii *et al.*<sup>29</sup> are not considered to be of sufficient accuracy for inclusion here.) The corresponding values for  $\Delta H_{\text{dim},298}$  are  $(36.2 - 41.0) \pm 2$  kcal/mol, which can be compared with the recent *ab initio* calculation of Page, *et al.*,<sup>3</sup>  $39.6 \pm 2\text{--}3$  kcal/mol. These results, currently the best available for the dimerization energy of borane, are clearly in reasonable accord with one another, and indicate that there is no need to suggest a new heat of formation of diborane which is outside the bounds of all measurements, as Page *et al.*<sup>3</sup> have done.

The upper limit for  $\Delta H_{\text{dim},0\text{K}}$  we deduced in Sec. IV A 2 from  $\text{BH}_2^+$  thresholds is  $46.6 \pm 0.6$  kcal/mol, or  $48.5 \pm 0.6$  kcal/mol at 298 K. In that section, we noted that the relatively sharp increase of the photoion yield curve of  $\text{BH}_2^+$  ( $\text{B}_2\text{H}_6$ ) suggested that the excess energy at this threshold was probably  $< 8.6$  kcal/mol. This surmise favors the upper part of the experimental range for  $\Delta H_{\text{dim},298}$  given above, i.e., around 40–41 kcal/mol. If  $\Delta H_f^0$  ( $\text{B}_2\text{H}_6$ ) is as firm as the Russian compilation implies ( $12.5 \pm 0.5$  kcal/mol), then the various considerations in this section favor the highest value for  $\Delta H_{\text{sub}}(\text{B})$ , i.e., the result of Storms and Mueller.<sup>28</sup>

## B. The bond energies and ionization potentials of $\text{BH}$ , $\text{BH}_2$ , and $\text{BH}_3$

We have shown in Sec. IV A 3 that the experimental atomization energy of  $\text{BH}_3$  at 0 K is  $265.3 \pm 1.7$  kcal/mol, and that Pople *et al.*<sup>1</sup> have obtained 266.9 kcal/mol by *ab initio* calculation at the level of fourth-order Møller–Plesset perturbation theory. Page *et al.*<sup>3</sup> report an *electronic* atomization energy (i.e., from the minimum of the  $\text{BH}_3$  potential surface) of 280.3 kcal/mol. We can relate this number to an experimental atomization energy by incorporating the zero point energy of  $\text{BH}_3$ . This quantity is 18.10 kcal/mol using the JANAF<sup>11</sup> frequencies, and 17.98 kcal/mol using the frequencies in the Russian compilation, but is calculated by Page *et al.*<sup>3</sup> to be 15.3 kcal/mol. If we combine their calculated electronic atomization energy with their calculated zero point energy, we obtain 265.0 kcal/mol, in excellent agree-

ment with the experimental atomization energy. With experimental frequencies, this becomes 262.3 kcal/mol, in which case the two values based on *ab initio* calculations bracket the experimental value.

From our experimental threshold for  $\text{BH}^+$  ( $\text{BH}_3$ ), the ionization potential of  $\text{BH}$  and  $D_0$  ( $\text{H}_2$ ), we can readily compute



$$\Delta H_0 \leq 8.080 \pm 0.052 \text{ eV} \leq 186.3 \pm 1.2 \text{ kcal/mol.}$$

Pople *et al.*<sup>1</sup> obtain 186.0 kcal/mol for the energy to remove two hydrogen atoms from  $\text{BH}_3$ . The agreement is fortuitously good, but supports the contention of Pople *et al.* that their calculations should be accurate to  $\pm 2$  kcal/mol.

The threshold for the process (given in Table II)



$$\Delta H_0 \leq 12.819 \pm 0.020 \text{ eV} \leq 295.6 \pm 0.5 \text{ kcal/mol}$$

represents the sum of  $D_0$  ( $\text{H}_2\text{B-H}$ ) and the ionization potential of  $\text{BH}_2$ . Pople *et al.*<sup>1</sup> obtain 105.8 kcal/mol for  $D_0$  ( $\text{H}_2\text{B-H}$ ), while Curtiss and Pople<sup>26</sup> have calculated  $\text{IP}(\text{BH}_2) = 8.18 \text{ eV} \equiv 188.6 \text{ kcal/mol}$ , or a sum equal to 294.4 kcal/mol. Once more, the agreement between experiment and *ab initio* calculation is excellent. In this instance, the experimental number is based solely on the present photoionization threshold measurement.

Although we are unable to measure the individual  $D_0$  ( $\text{H}_2\text{B-H}$ ) and  $D_0$  ( $\text{HB-H}$ ) bonds and  $\text{IP}(\text{BH}_2)$ , since we have not generated free  $\text{BH}_2$ , the excellent agreement shown above between experiment and the *ab initio* calculations of Pople and co-workers<sup>1,26</sup> for the sum of two bond energies, and the sum of a bond energy and  $\text{IP}(\text{BH}_2)$ , provides strong circumstantial support for the calculated individual bond energies and the calculated  $\text{IP}(\text{BH}_2)$ . Since we (and Wilson and McGee<sup>6</sup>) have shown that the  $\text{BH}_2$  observed by Fehlner and Koski<sup>5</sup> is spurious, it is not surprising that the latter's reported  $\text{IP}(\text{BH}_2) = 9.8 \pm 0.2 \text{ eV}$  is far from the calculated value.

Curtiss and Pople<sup>26</sup> point out that the highest occupied molecular orbitals in  $\text{BH}_3$  form a doubly degenerate  $e'$  set. Removal of an electron from this orbital leads to a degenerate  ${}^2E'$  state, which must then distort to lower symmetry according to the Jahn–Teller theorem. They state that this is the smallest molecule to exhibit such a distortion. To the best of our knowledge, the present data are the first to provide any experimental probe of this Jahn–Teller distortion. The experimental photoion yield curve of  $\text{BH}_3^+$  ( $\text{BH}_3$ ) rises gradually from a threshold at  $12.026 \pm 0.024 \text{ eV}$  to peak at  $\sim 12.73 \text{ eV}$ , declining noticeably thereafter. This behavior is rather similar to that of  $\text{CH}_4^+$  ( $\text{CH}_4$ ), where Jahn–Teller distortion also occurs in the ion. The implication of the gradual rise in the photoion yield curve is that a geometry change accompanies the photoionization transition (Franck–Condon effect), although it could also be conceivably attributed to a marked change in electronic transition moment (for a direct ionization process), or an increase in the relative rate of autoionization to predissociation (for an indirect ionization process). Pople *et al.*<sup>1</sup> calculate that  $\text{BH}_3$  has  $D_{3h}$  symmetry, with a B–H bond length of 1.188 Å. Cur-

tiss and Pople<sup>26</sup> conclude that the <sup>2</sup>E' state of BH<sub>3</sub><sup>+</sup> distorts into a lower <sup>2</sup>B<sub>2</sub> [IP = 11.93 eV, C<sub>2v</sub> structure, bond angles = 75.0°, 142.5° (2), bond lengths 1.164 Å, 1.266 Å (2)] and an upper <sup>2</sup>A<sub>1</sub> [IP = 12.09 eV, C<sub>2v</sub> structure, bond angles = 162.6°, 98.7° (2), bond lengths 1.574 Å, 1.171 Å (2)]. The large changes in bond angle between BH<sub>3</sub> and BH<sub>3</sub><sup>+</sup>, as well as some changes in bond length, imply a broad Franck-Condon range, and hence a slowly increasing photoion yield curve.

Our selected threshold is about 0.1 eV higher than the lowest IP calculated by Curtiss and Pople.<sup>26</sup> Since this photoion yield curve rises so slowly, it is quite possible that we were unable to detect the lowest ionization, above the background level. Even in the case of methane, which is a permanent gas and far more easily measured, it is difficult<sup>31</sup> to establish the adiabatic threshold.

Wilson and McGee<sup>6</sup> obtained 12.32 ± 0.1 eV for IP(BH<sub>3</sub>) by electron impact. As noted earlier, this is a plausible result, characteristically higher than the photoionization value. Fehner and Koski<sup>5</sup> reported IP(BH<sub>3</sub>) = 11.4 ± 0.2 eV, which indicates some error in their energy scale.

### C. The heats of formation of B<sub>2</sub>H<sub>n</sub><sup>+</sup> (n=2-6) and implications for the geometrical structure of these species.

#### 1. B<sub>2</sub>H<sub>6</sub><sup>+</sup> and B<sub>2</sub>H<sub>5</sub><sup>+</sup>

As noted earlier, the parent ion B<sub>2</sub>H<sub>6</sub><sup>+</sup> is extremely weak. Its photoion yield curve declines gradually toward the background level, over a span of at least 100 Å. The difficulty of selecting an onset is exacerbated by the possibility of a Boltzmann tail extending below the 0 K adiabatic threshold. In the absence of structural features, it is difficult to distinguish between diminishing Franck-Condon factors and a Boltzmann tail. The dynamical intensity range of the data does not warrant a semilogarithmic plot.<sup>18</sup> With these qualifications, we have selected the first significant departure from the background level, 1090 ± 5 Å ≡ 11.37 ± 0.05 eV as the adiabatic IP of B<sub>2</sub>H<sub>6</sub>. Three prior studies, using photoelectron spectroscopy, have obtained < 11.37,<sup>32</sup> 11.38 ± 0.01,<sup>33</sup> and 11.41 ± 0.02 eV.<sup>34</sup> The older electron impact value obtained by Koski *et al.*<sup>35</sup> was 11.9 ± 0.1 eV.

The photoion yield of B<sub>2</sub>H<sub>5</sub><sup>+</sup> is about three orders of magnitude larger than that of B<sub>2</sub>H<sub>6</sub><sup>+</sup>, but the difficulties of choosing a threshold are similar, and the corresponding photoion yield curves have very similar shapes near the threshold region. In fact, within experimental error, the threshold for B<sub>2</sub>H<sub>5</sub><sup>+</sup> is the same as for B<sub>2</sub>H<sub>6</sub><sup>+</sup>. The observation of B<sub>2</sub>H<sub>6</sub><sup>+</sup> in our experiment proves that it can survive as an entity for at least several microseconds. We cannot distinguish in this experiment between a B<sub>2</sub>H<sub>6</sub><sup>+</sup> entity which is indefinitely stable in its lowest vibrational states, or a metastable B<sub>2</sub>H<sub>6</sub><sup>+</sup> which will eventually decay, even in its lowest vibrational state. What implication does this observation have for the structure of B<sub>2</sub>H<sub>6</sub><sup>+</sup>, and of B<sub>2</sub>H<sub>5</sub><sup>+</sup>?

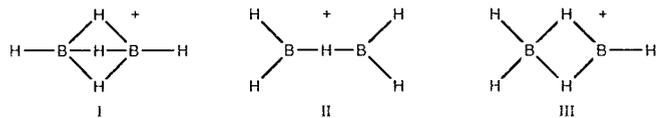
Early on, Koski *et al.*<sup>35</sup> had noted that B<sub>2</sub>H<sub>5</sub><sup>+</sup> had the same appearance potential (11.9 ± 0.1 eV) as the ionization potential of B<sub>2</sub>H<sub>6</sub>, by electron impact. They argued from

available thermochemical evidence that it required less energy to break a *terminal* B-H bond than to withdraw a *bridged* H atom (in the neutral molecule) and therefore it was the terminal hydrogen which was liberated in the formation of B<sub>2</sub>H<sub>5</sub><sup>+</sup>.

Support for this conclusion can be obtained from an entirely different line of reasoning. There have been several *ab initio* calculations of B<sub>2</sub>H<sub>6</sub> which reported orbital eigenvalues.<sup>36-39</sup> Most agree quite well with the energies of the ionic states obtained in photoelectron spectroscopy. One of these calculations<sup>39</sup> uses the Green's function method, and hence goes beyond the Koopmans' Theorem approximation. A conclusion of the latter calculation is that<sup>39</sup> "...the one-particle picture is well adapted to describe the (B<sub>2</sub>H<sub>6</sub>) ionization process." In every one of the calculations cited, and consequently in the assignments of the photoelectron spectra, the uppermost occupied orbital in B<sub>2</sub>H<sub>6</sub> is identified as b<sub>3g</sub> (or b<sub>2g</sub>, depending upon convention). Both Rose *et al.*<sup>32</sup> and Lloyd and Lynaugh<sup>34</sup> conclude that the vibrational progression they observe in the first photoelectron band is a bending motion in the *terminal* B-H bonds, and hence the molecular orbital from which electron ejection occurs is mainly localized in the region of boron atoms and *terminal* hydrogen atoms. Furthermore, "...the B-H (terminal) overlap population is 0.23 with all other contributions to the total population very small."<sup>34</sup>

Hence, the molecular orbital picture can be simply summarized: an electron is ejected from the vicinity of the B-H (terminal) bond, it weakens that bond and a terminal hydrogen drops off. Actually, the molecular orbital in question seems to affect the bending rather than the B-H stretch which one might expect to be diagnostic of a bond rupture, but the argument certainly favors the removal of a terminal H atom, rather than a bridged H atom. A calculation of B<sub>2</sub>H<sub>6</sub><sup>+</sup> might be more revealing, but we are unaware of any such attempt.

However, there have been two calculations of B<sub>2</sub>H<sub>5</sub><sup>+</sup> reported in the literature. The one by Duke and Stephens<sup>13</sup> used a modest basis set and the POLYATOM SCF program. These authors considered three structures, a triple bridge (I), a single B-H-B bonding arrangement (II), and a double bridge (III).



They found that structure II was the most stable, structure I at least 12.68 kcal/mol higher, and structure III (the one in which a terminal H atom is removed from B<sub>2</sub>H<sub>6</sub><sup>+</sup>) higher in energy by 19.36 kcal/mol. Rastogi and Ray<sup>14</sup> used a floating spherical Gaussian orbital (FSGO) model, and considered three similar structures—an "acetylenic structure," analogous to I (above); a "planar structure," analogous to II (above); and a "nonsymmetric structure," analogous to III (above), where a terminal H atom is missing from a B<sub>2</sub>H<sub>6</sub> structure. Their conclusions were quite different from those of Duke and Stephens. They found the acetylenic structure

(I) to be the most stable, the nonsymmetric structure (III) to be 1.25 kcal/mol less stable, and the planar structure (II) to be the least stable, by 27 kcal/mol.

In summary, Duke and Stephens found that the single hydrogen bridged structure was the most stable, while Rastogi and Ray concluded that this was the least stable, the triple bridged structure being the most stable. On the basis of total energy, the Duke and Stephens calculation would be preferred, since they obtain  $-51.4577$  a.u., whereas the most favored structure of Rastogi and Ray is reported to have a total energy of  $-43.881$  a.u. This enormous difference in total energy could be due to the method of treatment of core orbitals used by Rastogi and Ray.

A criticism of the Duke and Stephens calculation already put forward by Rastogi and Ray is that fixed bond distances and bond angles were used, rather than optimization of these parameters.

Clearly, a more modern calculation on  $\text{B}_2\text{H}_5^+$  (as well as the aforementioned  $\text{B}_2\text{H}_6^+$ ) is desired to resolve this marked discrepancy. Curtiss and Pople<sup>40</sup> have recently performed such a calculation for  $\text{B}_2\text{H}_5^+$ , with optimization of geometry. At the HF/3-21G level, roughly comparable to the basis set used by Duke and Stephens, they find the three structures to have nearly the same stability, the triple bridged structure being about 3 kcal/mol more stable than the other two. With an improved basis set (HF/6-31G\*), the triple bridged structure is 11.9 kcal/mol more stable than the double bridged structure, and 21.7 kcal/mol more stable than the single bridged structure. Finally, with the inclusion of correlation effects (MP4/6-311G\*\*) they find the triple bridged structure 20.2 kcal/mol more stable than the double bridged structure, and 41.0 kcal/mol more stable than the single bridged structure. Even at the HF/3-21 G level, their total energy is lower than that given by Duke and Stephens.

Thus, the calculation of Curtiss and Pople<sup>40</sup> provides convincing evidence that the most stable structure of  $\text{B}_2\text{H}_5^+$  has three hydrogen bridges. In hindsight, this result is not too surprising. DeFrees *et al.*<sup>41</sup> have recently reported that the most stable structures of  $\text{LiBH}_4$  and  $\text{BeBH}_5$  are tribridged, and cite earlier calculations by others which had arrived at the same conclusion for these species. In these latter cases, the tribridged structure is about 6 kcal/mol more stable than the dibridged structure.

The prevailing evidence is that  $\text{B}_2\text{H}_6$  has a dibridged structure, and  $\text{B}_2\text{H}_5^+$  a tribridged structure. Somehow, the process of ionization provides a pathway from one structure to the other. A calculation of the  $\text{B}_2\text{H}_6^+$  potential energy surface would be helpful in following this path. For the present, it appears as if the ionization process drastically weakens a B-H (terminal) bond, leading to dissociation, while a terminal H on the opposite boron atom moves into a bridged position.

The simple molecular orbital would predict the loss of a terminal H atom, leaving essentially a dibridged structure. The large difference in the stability of tribridged and dibridged structures (20.2 kcal/mol) obtained by Curtiss and Pople<sup>40</sup> strongly favors the formation of  $\text{B}_2\text{H}_5^+$  in the tribridged form, and hence reorganization following ioniza-

tion. We shall show below that the further decomposition of  $\text{B}_2\text{H}_6$  following ionization is much better characterized by a quasiequilibrium theory, where it is the total energy of the molecular ion which governs the decomposition, rather than a localized molecular orbital picture (which has been used in previous discussions by other authors<sup>32,33</sup>) where the nature of the orbital from which an electron is ejected governs the mode of decomposition.

## 2. $\text{B}_2\text{H}_4^+$

Although neutral  $\text{B}_2\text{H}_4$  has not been observed experimentally, this molecule has been the subject of numerous *ab initio* calculations. The two most recent<sup>42,43</sup> ones include references to earlier work. There seems to be general agreement on the structure of the ground state—staggered,  $D_{2d}$ , two H-B-H planes perpendicular to one another. Mohr and Lipscomb<sup>42</sup> give  $r(\text{B-B}) = 1.6534$  Å,  $r(\text{B-H}) = 1.1902$  Å and  $116.15^\circ$  for the H-B-H angle at the MP2/6-31G\*\* level, while Vincent and Schaeffer<sup>43</sup> obtain  $r(\text{B-B}) = 1.669$  Å,  $r(\text{B-H}) = 1.195$  Å and  $116.6^\circ$  for the H-B-H angle at the double beta plus polarization plus configuration interaction level. The barrier for rotation about the B-B bond is given as 12.6<sup>42</sup> or 11.9 kcal/mol.<sup>43</sup> However, Mohr and Lipscomb<sup>42</sup> have found that a staggered double-bridged structure with  $C_{2v}$  symmetry gains significantly in relative stability as one includes polarization functions and correlation corrections, being 32.6 kcal/mol less stable than the  $D_{2d}$  structure at the HF/6-31 G level, but only 1.5 kcal/mol less stable at the MP2/6-31 G\*\* level.

The photoion yield curve of  $\text{B}_2\text{H}_4^+$  ( $\text{B}_2\text{H}_6$ ) has a threshold only  $\sim 0.35$  eV higher than that of  $\text{B}_2\text{H}_5^+$  and  $\text{B}_2\text{H}_6^+$ . It occurs well within the first photoelectron band; the curve increases rapidly from threshold, rather than approaching the threshold asymptotically. In the terminology of unimolecular rate theory (or quasiequilibrium theory) this suggests a transition state that is not extremely tight.

A description of the mode of decomposition, and hence the transition state, depends critically on the structure assumed by the  $\text{B}_2\text{H}_4^+$  fragment ion. High quality calculations have been performed for  $\text{B}_2\text{H}_4$ ,<sup>42,43</sup> and for  $\text{Be}_2\text{H}_4$ <sup>41</sup> (the latter isoelectronic with  $\text{B}_2\text{H}_5^+$ ). The  $\text{B}_2\text{H}_4$  structure is  $D_{2d}$  (i.e., perpendicular  $\text{BH}_2$  planes), with a barrier to rotation about the B-B bond of only  $\sim 12$  kcal/mol.<sup>42,43</sup> The  $\text{Be}_2\text{H}_4$  structure, on the other hand, has a double hydrogen bridge.<sup>41</sup> Such a double bridged structure for  $\text{B}_2\text{H}_4^+$  has also been reported recently by Sana and Leroy,<sup>44</sup> whose calculations were performed at the 6-31G/MP2 level.

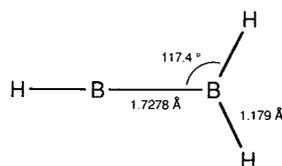
Our experimental data lead to the conclusion<sup>45</sup> that  $\text{B}_2\text{H}_4^+$  is formed from  $\text{B}_2\text{H}_6^+$  by release of  $\text{H}_2$ , rather than from  $\text{B}_2\text{H}_5^+$  by loss of an H atom. The most likely scenario, given the present level of information, is that terminal hydrogen atoms from opposite boron atoms gradually come together to form  $\text{H}_2$ , while maintaining the bridging hydrogen atoms. The remaining terminal hydrogen atoms simultaneously adjust to an H (terminal) -B-B-H (terminal) linear structure.

From the appearance potential of  $\text{B}_2\text{H}_4^+$  given in Table I and  $\Delta H_f^0(\text{B}_2\text{H}_6) = 12.5$  kcal/mol, we can compute

$\Delta H_f^0(\text{B}_2\text{H}_4^+) \leq 283.5$  kcal/mol. Dill, Schleyer, and Pople<sup>46</sup> have estimated  $\Delta H_f(\text{B}_2\text{H}_4)$  from *ab initio* calculations at the 6-31G\* level, and give 58 kcal/mol for this quantity. This number is based on *ab initio* calculations of the hydrogenation reaction  $\text{H}_2 + \text{B}_2\text{H}_4 \rightarrow 2\text{BH}_3$  which they believe to have an accuracy of  $\pm 4$  kcal/mol, based on prior experience. [Their choice of  $\Delta H_f(\text{BH}_3)$  at that time differs by 1–2 kcal/mol from our present preferred value, but we shall ignore such differences for the relatively crude purpose at hand. We also ignore differences between  $\Delta H_{f_{298}}^0$  and  $\Delta H_f^0$ .] Combining our  $\Delta H_f^0(\text{B}_2\text{H}_4^+)$  with the calculated value of  $\Delta H_f(\text{B}_2\text{H}_4)$ , we obtain  $\text{IP}(\text{B}_2\text{H}_4) \leq 9.78$  eV. This seems a plausible, though rough value; the ionization energy of the uppermost occupied ( $\pi$ ) orbital in  $\text{C}_2\text{H}_4$  is 10.51 eV,<sup>47</sup> and a comparison of ionization potentials of the various saturated and unsaturated boron hydrides and hydrocarbons indicates that the boron species typically has the lower IP. We shall return to this topic in Sec. V.

### 3. $\text{B}_2\text{H}_3^+$

From the appearance potential of  $\text{B}_2\text{H}_3^+$  given in Table I, we can readily compute  $\Delta H_f^0(\text{B}_2\text{H}_3^+) \leq 287.2$  kcal/mol. The Pople group<sup>48</sup> has computed the geometry of bridged and nonbridged  $\text{C}_{2v}$  structures and found the more stable structure of  $\text{B}_2\text{H}_3^+$  at the 6-31G\* level to be a nonbridged geometry, i.e.,



They calculate the total energy at the HF/6-31G\*\* level to be  $-50.733\,963$  a.u., but conversion of this quantity to a heat of formation (which could be compared to our experimental value) has not yet been attempted.

### 4. $\text{B}_2\text{H}_2^+$

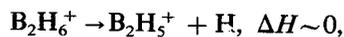
*Ab initio* calculations<sup>46</sup> predict that the neutral HBBH has a linear triplet ground state ( $^3\Sigma_g^-$ ) and an excited  $^1\Delta$  state, as in  $\text{O}_2$ . This pattern persists at the MP4/6-31G\* level.<sup>48</sup> The optimum 6-31G\* structures are:  $^3\Sigma_g^-$ ,  $r(\text{B}-\text{B}) = 1.499$  Å,  $r(\text{B}-\text{H}) = 1.172$  Å;  $^1\Delta$ ,  $r(\text{B}-\text{B}) = 1.510$  Å,  $r(\text{B}-\text{H}) = 1.170$  Å. The heat of formation of the  $^1\Delta$  state has been estimated<sup>46</sup> to be 148 kcal/mol. From the appearance potential of  $\text{B}_2\text{H}_2^+$  given in Table I, we compute  $\Delta H_f^0(\text{B}_2\text{H}_2^+) \leq 318.1$  kcal/mol. Thus, the estimated ionization potential from the  $^1\Delta$  state is  $\leq 7.37$  eV. At the MP4/6-31 G\* level, the  $^3\Sigma_g^-$  state lies 0.87 eV below that of  $^1\Delta$ , and the IP of  $\text{B}_2\text{H}_2$  from its ground state is estimated to be  $\leq 8.25$  eV. The uppermost occupied orbital in  $\text{B}_2\text{H}_2$  is calculated<sup>46</sup> to be  $\pi_u$ . The heats of formation of  $\text{B}_2\text{H}_n^+$  discussed in this section are summarized in Table IV.

### D. Bond energies of $\text{B}_2\text{H}_n^+$ ; comparison with $\text{C}_2\text{H}_n^+$

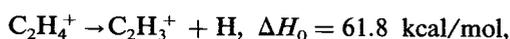
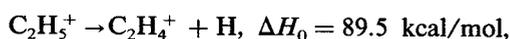
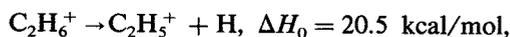
It is instructive to examine the successive bond energies of the various diborane ions, as deduced from the appearance potentials in our experiment. Thus

TABLE IV. Heats of formation (0 K) of diboron hydride ions.

Ionic species	$\Delta H_f^0$ (kcal/mol)
$\text{B}_2\text{H}_2^+$	$\leq 318.1$
$\text{B}_2\text{H}_3^+$	$\leq 287.2$
$\text{B}_2\text{H}_4^+$	$\leq 283.5$
$\text{B}_2\text{H}_5^+$	$\leq 223.7 \pm 1.3$
$\text{B}_2\text{H}_6^+$	$\leq 274.7 \pm 1.3$

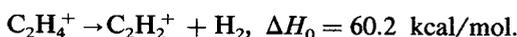
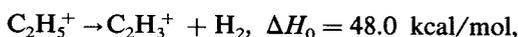
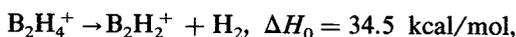
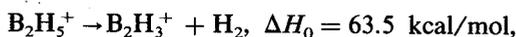


These results indicate that the structures with odd numbers of hydrogen atoms are distinctly more stable than the even numbered ones. A similar pattern exists in the photodissociative ionization of  $\text{C}_2\text{H}_6$ , given below.<sup>22</sup>



These observations can be readily rationalized by noting that the ions containing odd numbers of hydrogen atoms are actually closed shell structures, while those with even numbers of hydrogen atoms retain only one electron in some bonding orbital.

It is also instructive to compare the following  $\text{H}_2$  loss processes:



There is a reversal in the relative reaction energies in the borohydride and hydrocarbon species. One possible explanation focuses on the exceptional stability of  $\text{B}_2\text{H}_5^+$  and its isoelectronic analog,  $\text{C}_2\text{H}_3^+$ . Recently, it has been reported<sup>49</sup> that the most stable structure of  $\text{C}_2\text{H}_3^+$  is bridged, i.e., that this structure is more stable than the "classical" structure. The tentative conclusion we have reached earlier is that  $\text{B}_2\text{H}_5^+$  is exceptionally stable because of its tribridged structure. Hence,  $\text{B}_2\text{H}_5^+$  is more difficult to decompose, and  $\text{C}_2\text{H}_3^+$  forms more readily.

Another interesting, though not quite isoelectronic analogy concerns  $\text{B}_2\text{H}_4$  and  $\text{C}_2\text{H}_4$ . The *ab initio* calculations conclude that  $\text{B}_2\text{H}_4$  has a  $D_{2d}$  structure, i.e., the two  $\text{BH}_2$  planes are perpendicular. Ethylene is, of course, a planar structure. However, both calculations<sup>50</sup> and Franck-Condon analysis<sup>51</sup> of the photoelectron spectrum show that  $\text{C}_2\text{H}_4^+$  is no longer planar, but that the two  $\text{CH}_2$  planes are twisted. The isoelectronic analog to  $\text{B}_2\text{H}_4$  would be  $\text{C}_2\text{H}_4^{+}$ , which is not stable (though metastable). It appears that  $\text{C}_2\text{H}_4^+$  prefers a structure which has partially moved to the  $D_{2d}$  geometry.

## E. Partial and total ionization derivatives and the photoelectron spectrum

In Sec. IV C 1, we noted that there were contrasting ways of explaining the mass spectrum of a molecule. One approach, which we shall designate the MO viewpoint, is closely connected with the photoelectron spectrum and its interpretation. In a single-electron model, which is evidently<sup>39</sup> quite a good model for explaining the photoelectron spectrum of  $\text{B}_2\text{H}_6$ , there is a good correlation between the energy ordering of the orbitals in the neutral species and the negative of the successive ionization potentials (Koopmans' theorem). An electron removed from the uppermost occupied orbital gives rise to the lowest state of the ion, etc. Furthermore, if the electron is removed from a  $\text{B-H}_{\text{terminal}}$  bonding orbital, it should cause weakening or rupture of the  $\text{B-H}_{\text{terminal}}$  bond in the ion; if it is removed from an orbital which has  $\text{B-H}_{\text{bridge}}$  or  $\text{B-B}$  bonding character, it could result in rupture of the  $\text{B-B}$  bond.

Thus, Brundle *et al.*<sup>33</sup> related the first band in the photoelectron spectrum to electron ejection from a bonding orbital involving  $2p$  orbitals in boron and the terminal hydrogen atoms. They found it "striking" that the appearance potential of  $\text{B}_2\text{H}_5^+$  given by Koski *et al.*<sup>35</sup> nearly coincided with the breaking off of vibrational structure in the first photoelectron band, "indicating a possible dissociative process in this region."<sup>33</sup> We now know that the appearance potential of  $\text{B}_2\text{H}_5^+$  given by Koski *et al.*<sup>35</sup> is about 0.5 eV too high, vitiating this apparent correlation.

Rose, Frey, and Brehm<sup>32</sup> observed vibrational fine structure in the second band, which was shown early on to be due to an HCl impurity. Nevertheless, the argument they employed is illustrative of the application of the MO picture to fragmentation processes. They knew from the electron impact appearance potentials that the vibrational structure in the second band occurred well above the threshold for  $\text{B}_2\text{H}_5^+$  and  $\text{B}_2\text{H}_4^+$ , both of which originate at energies corresponding to the first band. They therefore concluded that the second band, in the region of vibrational structure, must relate to electron emission from an orbital which does *not* involve bonding between boron and terminal hydrogen, since otherwise dissociation would occur and vibrational structure would be absent. Whereas others<sup>33,34</sup> have assigned this second band to  $(3a_g)^{-1}$ , they preferred  $(1b_{3u})^{-1}$ , "since the symmetry of this orbital excludes any contribution to the terminal  $\text{B-H}$  bonds."<sup>32</sup> They also noted the onset of a continuous spectrum in this band at 12.88 eV, which signaled to them the beginning of a dissociation process. The bridge bonding character of the  $1b_{3u}$  orbital, together with the appearance potential of  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ) =  $13.1 \pm 0.2$  eV given by Koski *et al.*<sup>35</sup> appeared to make a self-consistent picture. On this basis, they could not reconcile the appearance potential of  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ) = 14.88 eV given by Wilson and McGee.<sup>6</sup> The present photoionization data show that the appearance potential of  $\text{BH}_3^+$  ( $\text{B}_2\text{H}_6$ ) given by Wilson and McGee<sup>6</sup> is much more acceptable than that of Koski *et al.*<sup>35</sup> and of course, the vibrational structure which becomes continuous structure is false, and hence the MO picture is once again inappropriate for this example.

A very different view of fragmentation processes is provided by quasiequilibrium theory. Here, the basic assumption is that the total internal energy is the dominant parameter determining the modes of fragmentation of a molecular ion, regardless of the mechanisms by which this excitation energy was achieved. The best test of such a model is a coincidence experiment, in which analysis and detection of the photoelectron provides a measure of the internal energy of the parent molecular ion, and the ion(s) in coincidence with this electron yield information about the fragmentation probability into alternative channels. A so-called breakdown diagram can then be constructed, and compared with the prediction of quasiequilibrium theory. Both experiment and theory have been performed for  $\text{C}_2\text{H}_6$  and the agreement between the two is quite satisfactory.<sup>22,52</sup> We have not performed coincidence experiments in the present study. However, we have treated the current data in a fashion which permits a crude test of quasiequilibrium theory. The approach we use here was pursued with some success in earlier work from this laboratory on the photodissociative ionization of  $\text{CH}_3\text{OH}$ .<sup>53</sup> We shall confine ourselves here to some salient features.

Direct photoionization (distinguished from autoionization) is presumed to exhibit step-function behavior. On this hypothesis, the derivative of total ionization with respect to energy should look like the photoelectron spectrum. Since differentiation and summation are both linear operators, the sum of the differentiated curves of the individual species should be the same as the derivative of the sum of the individual photoion yield curves (suitably normalized).

We have summed the smoothed photoion yield curves of the individual species (Figs. 3 and 4), and then differentiated the sum. The resulting curve is shown in Fig. 9(a), and a He I photoelectron spectrum<sup>34</sup> in Fig. 9(b). The differentiated photoion yield curve resembles the experimental photoelectron spectrum, in the sense that the peaks occur at the same energies. However, the intensities of the peaks seem to decline with increasing energy, when compared to the photoelectron spectrum. This remains the case even if one takes into account the transmission function of the Perkin-Elmer apparatus with which the photoelectron spectrum was obtained. We attribute this discrepancy to a departure from step-function behavior in the individual photoion yield curves. This is not at all surprising, since step-function behavior is only appropriate, if at all, to a small energy region beyond threshold, and typically the cross section for formation of a particular state declines with increasing photon energy.<sup>22</sup> The derivatives of the individual photoion yield curves are displayed in Fig. 10.

It is now possible to draw conclusions regarding the fragmentation ensuing upon formation of various states of  $\text{B}_2\text{H}_6^+$ , within the assumption of step-function (or near step-function) behavior. By comparing the derivatives of the individual photoion yield curves (Fig. 10) with the photoelectron spectrum (Fig. 9), we can conclude that  $\text{B}_2\text{H}_5^+$  results as soon as the lowest ionic state is created (which is no surprise), and continues to be formed through the second and third photoelectron band. In the region between the third and fourth photoelectron band,  $\text{B}_2\text{H}_5^+$  declines and  $\text{B}_2\text{H}_3^+$

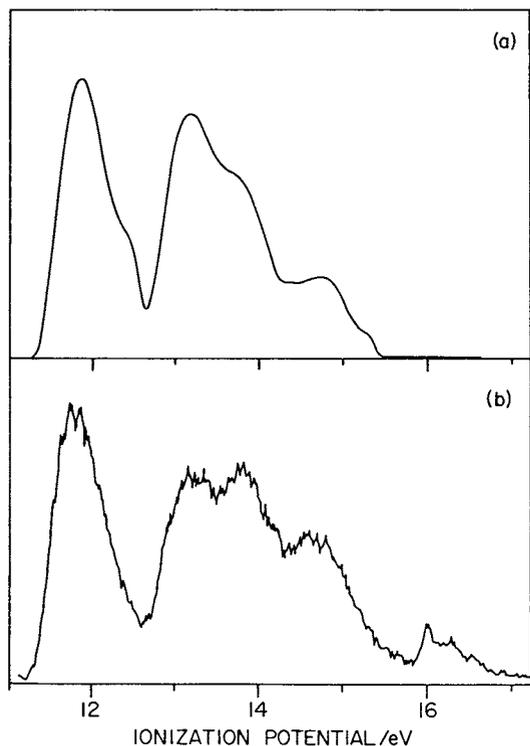


FIG. 9. (a) The derivative with respect to energy of the total ion yield from  $\text{B}_2\text{H}_6$ . The individual photoion yields were smoothed before summing. (b) The He I photoelectron spectrum of  $\text{B}_2\text{H}_6$  (from Ref. 34, with permission of the authors).

appears to take over. This pattern will become clearer when we examine the breakdown diagram. The  $\text{B}_2\text{H}_4^+$  species is also initially formed in the energy range of the first photoelectron band. Its relative importance increases (i.e., the derivative increases from threshold) throughout the first and

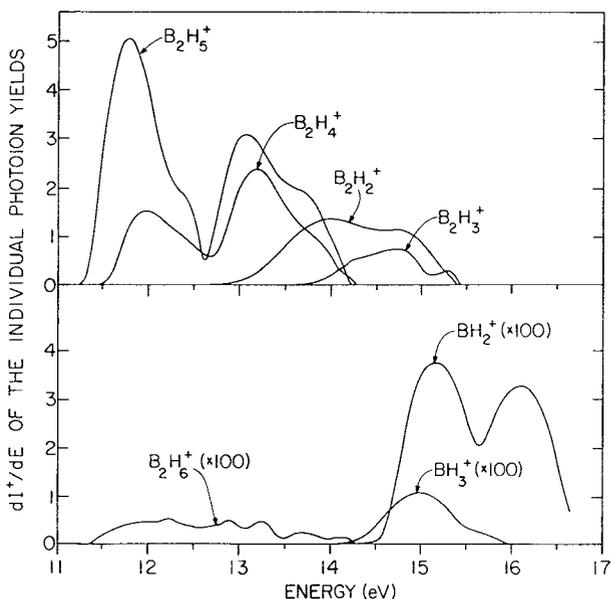


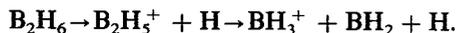
FIG. 10. The derivatives with respect to energy of the individual photoion yield curves of  $\text{B}_2\text{H}_6^+$ ,  $\text{B}_2\text{H}_5^+$ ,  $\text{B}_2\text{H}_4^+$ ,  $\text{B}_2\text{H}_3^+$ ,  $\text{B}_2\text{H}_2^+$ ,  $\text{BH}_3^+$ , and  $\text{BH}_2^+$  from  $\text{B}_2\text{H}_6$ .

second bands. Between the second and third bands, the  $\text{B}_2\text{H}_4^+$  derivative decreases, and the  $\text{B}_2\text{H}_2^+$  species appears to take over.

The weaker species containing a single boron atom ( $\text{BH}_3^+$ ,  $\text{BH}_2^+$ ) require further consideration. The onset of the  $\text{BH}_3^+$  derivative curve corresponds to an energy between the third and fourth photoelectron bands. On thermochemical (i.e., energetic) grounds, this onset must correspond to the process

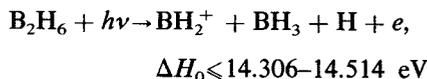


It cannot correspond to the process

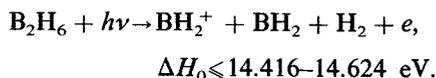


In the simplest, so-called strong form of quasiequilibrium theory, this should not occur. The onset energy of  $\text{BH}_3^+$  is almost 3 eV above the adiabatic ionization potential of  $\text{B}_2\text{H}_6$ , and hence the internal energy of  $\text{B}_2\text{H}_6^+$  is almost 3 eV. The  $\text{B}_2\text{H}_6^+$  should have dissociated completely, to either  $\text{B}_2\text{H}_5^+ + \text{H}$  or  $\text{B}_2\text{H}_4^+ + \text{H}_2$ , at much lower energy, somewhere in the energy domain of the first photoelectron band. Hence, the implication is that a  $\text{B}_2\text{H}_6^+$  species is formed again by photoionization at higher energy, and decays to form  $\text{BH}_3^+ + \text{BH}_3$ . In the language of quasiequilibrium theory, it acts like an isolated state, or region of phase space, not equilibrating with the other modes at this energy. A similar departure from quasiequilibrium theory was noted in the study of  $\text{CH}_3\text{OH}$ ,<sup>53</sup> where the formation of  $\text{CH}_3^+$  (+ OH) appeared to result directly from an isolated state. In both cases, an MO description provides a plausible interpretation. In the present case, the onset of  $\text{BH}_3^+$  corresponds very nearly to the adiabatic threshold for electron ejection from the  $1b_{2u}$  orbital, which is  $\sigma$ -bonding between boron and hydrogen bridges, and hence could facilitate the decomposition into  $\text{BH}_3^+ + \text{BH}_3$ . There is some indication in the derivative curve of  $\text{B}_2\text{H}_6^+$  (Fig. 10) that this species is formed again at energies between  $\sim 11.5$ – $14.1$  eV. If this observation is verified by future, more definitive coincidence studies it would indicate that step-function behavior has some validity for this process, but that quasiequilibrium theory in its strong form is violated.

The  $\text{BH}_2^+$  onset occurs at slightly higher energy, just beyond the adiabatic threshold of the fourth photoelectron band. On thermochemical grounds, the  $\text{BH}_2^+$  onset could correspond to either of two processes:



or



In the first case, it would point to the decomposition of  $\text{B}_2\text{H}_5^+$  into  $\text{BH}_2^+ + \text{BH}_3$ ; in the second, to the decomposition of  $\text{B}_2\text{H}_4^+$  into  $\text{BH}_2^+ + \text{BH}_2$ . Both  $\text{B}_2\text{H}_5^+$  and  $\text{B}_2\text{H}_4^+$  derivatives approach zero at nearly the same energy, which is just about the onset energy of  $\text{BH}_2^+$ . Perhaps both processes provide mechanisms of comparable intensity for generating  $\text{BH}_2^+$ .

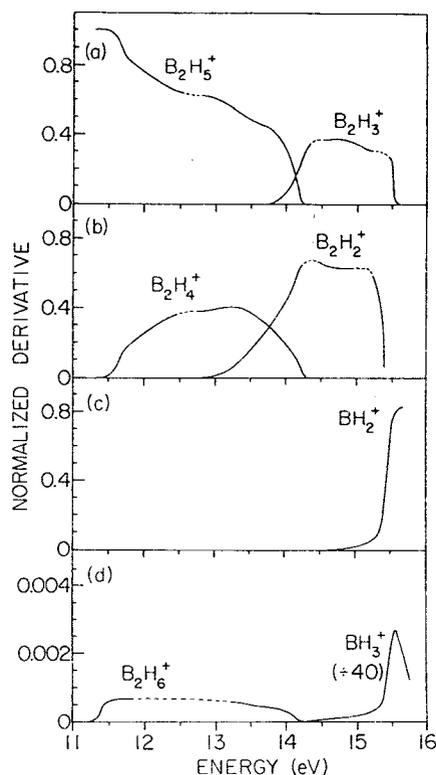


FIG. 11. The normalized derivative curve, or breakdown diagram, from the photoionization of  $\text{B}_2\text{H}_6$ . (a)  $\text{B}_2\text{H}_5^+$  and  $\text{B}_2\text{H}_3^+$ , (b)  $\text{B}_2\text{H}_4^+$  and  $\text{B}_2\text{H}_2^+$ , (c)  $\text{BH}_2^+$ , (d)  $\text{B}_2\text{H}_6^+$  and  $\text{BH}_3^+$ .

Within the aforementioned limitations of the step-function approximation, we have constructed a crude breakdown diagram. This is obtained by evaluating the magnitude of the derivative of each ion species at a particular energy, normalizing to unity, and thus ascertaining the fraction of the total derivative to be assigned to each species. This procedure is performed throughout the relevant energy domain. In this approximation, the normalized derivative curve is the breakdown diagram, although the latter can be more reliably obtained from a coincidence experiment. In Fig. 11, we present the results in four panels, as was previously done for<sup>50,22</sup>  $\text{C}_2\text{H}_6$ . In the uppermost panel, we can follow the decline of  $\text{B}_2\text{H}_5^+$ , and its replacement by its daughter,  $\text{B}_2\text{H}_3^+$ . In the second panel,  $\text{B}_2\text{H}_4^+$  initially rises, then declines as its daughter,  $\text{B}_2\text{H}_2^+$  takes over. In the lowermost panel, we can observe the weak reappearance of  $\text{B}_2\text{H}_6^+$  and its decline as  $\text{BH}_3^+$  appears, and in the third panel, the appearance of  $\text{BH}_2^+$ , from either/or  $\text{B}_2\text{H}_5^+$  and  $\text{B}_2\text{H}_4^+$ . Thus, most of the fragmentation behavior of  $\text{B}_2\text{H}_6$  appears to be plausibly explained by quasiequilibrium theory. A more rigorous test requires coincidence experiments and a calculated breakdown diagram based on quasiequilibrium theory.

## V. DISCUSSION

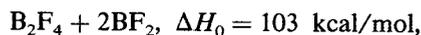
Since considerable discussion has accompanied our interpretation of results, we confine ourselves here to a comparison of  $\text{B}_2\text{H}_4$ ,  $\text{B}_2\text{Cl}_4$ , and  $\text{B}_2\text{F}_4$ . Both  $\text{B}_2\text{Cl}_4$  and  $\text{B}_2\text{F}_4$  are

relatively stable species which can readily be prepared and investigated. The geometrical structure of  $\text{B}_2\text{Cl}_4$  is reported<sup>54-56</sup> to have  $D_{2d}$  symmetry (twisted planes) while that of  $\text{B}_2\text{F}_4$  is said to have a planar,  $D_{2h}$  symmetry.<sup>57</sup>

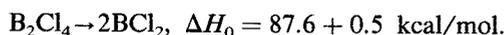
We have already referred to several calculations which appear to agree that  $\text{B}_2\text{H}_4$  has  $D_{2d}$  symmetry in its ground state, but experimental evidence is lacking because  $\text{B}_2\text{H}_4$  has not yet been isolated. The adiabatic ionization potentials of  $\text{B}_2\text{F}_4$ <sup>58</sup> and  $\text{B}_2\text{Cl}_4$ <sup>59</sup> have been measured to be 12.07 eV and 10.32 eV, respectively.

We have inferred an ionization potential of  $\text{B}_2\text{H}_4$  by combining a calculated  $\Delta H_f$  ( $\text{B}_2\text{H}_4$ ) with our measured  $\Delta H_f$  ( $\text{B}_2\text{H}_4^+$ ), and obtain  $\lesssim 9.78$  eV. Our attempt to rationalize these observations rest partially on electron withdrawing power from the vicinity of the B-B bond. It has been pointed out<sup>46</sup> that B-B, unlike C-C, eschews the double bond and prefers to twist to avoid the  $\pi$  bonding. Pauling's electronegativity scale<sup>60</sup> assigns 2.0 to B, 2.1 to H, 3.0 to Cl and 4.0 to F. Thus, in  $\text{B}_2\text{F}_4$  we can anticipate the maximum withdrawal of charge from the B-B bond. This may be a reason why this structure is planar (unlike  $\text{B}_2\text{Cl}_4$ , and presumably  $\text{B}_2\text{H}_4$ ). If the lowest ionization potential in all three molecules is correlated with electron emission from an orbital involving the B-B bond, which seems reasonable, then the order of ionization potentials follows from the difference in electronegativities—in  $\text{B}_2\text{H}_4$  there is almost no tendency toward withdrawal of charge from the B-B bond (lowest IP), in  $\text{B}_2\text{Cl}_4$  the difference in electronegativity is 1.0 (intermediate IP), and in  $\text{B}_2\text{F}_4$  this difference is 2.0 (highest IP).

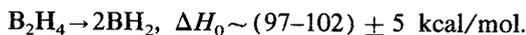
Available evidence also permits us to compare the strength of the B-B bond in these three structures. Photoionization measurements by Dibeler and Liston<sup>58</sup> have produced



and other such studies by Dibeler and Walker<sup>59</sup> have resulted in



If we combine the estimated heat of formation of  $\text{B}_2\text{H}_4$  based on an *ab initio* calculation<sup>46</sup> with  $\Delta H_f^0$  ( $\text{BH}_2$ ) inferred from the current measurements [77.6–80.0 kcal/mol, depending on  $\Delta H_{\text{sub}}(\text{B})$ ], we can compute



Hence, to zeroth order, the B-B bond strength in  $\text{B}_2\text{X}_4$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}$ ) is about 90–100 kcal/mol. If we wish to engage in speculation about the differences in these values, we may offer the following explanation. In  $\text{B}_2\text{Cl}_4$ , the bond is weaker than in  $\text{B}_2\text{H}_4$ , because some charge has been withdrawn from the B-B bond region. In  $\text{B}_2\text{F}_4$ , more charge has been withdrawn, but this results in a more stable, planar structure, thereby increasing the bond strength.

## ACKNOWLEDGMENTS

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