

Structure and bonding in the B_2H_5 radical and cation

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The B_2H_5 radical has been generated by the $F + B_2H_6$ reaction, and studied by photoionization mass spectrometry. The photoion yield curve for $B_2H_5^+$ (B_2H_5) is extremely weak at the adiabatic threshold (~ 6.945 eV), at least three orders of magnitude weaker than at its maximum (~ 9.67 eV). This observation provides support for recent *ab initio* calculations, which predict a singly bridged B_2H_5 and a triply bridged $B_2H_5^+$ as ground states. Evidence is presented for the coexistence of a doubly bridged B_2H_5 isomer, ~ 3 kcal/mol higher in energy. From the appearance potential of $B_2H_3^+$ (B_2H_5), a B_2H_5-H bond energy of ≤ 102.7 kcal/mol is obtained. From the photoion yield curve of $B_2H_3^+$ (B_2H_5), at least one, and perhaps two, excited states of $B_2H_5^+$ can be inferred. The lower one also branches into parent B_2H_5 , an apparent violation of QET.

I. INTRODUCTION

Scarcely four decades have elapsed since the dibridged, D_{2h} geometry became accepted as the structure of B_2H_6 . In Herzberg's 1945 volume,¹ an ethane-like structure was still considered more likely. Two key experiments, one by Price² in 1947 on the analysis of the rotational structures of bands in the infrared, the other by Shooley³ in 1955 on the nuclear magnetic resonance spectrum of $^{11}B_2H_6$, clearly established the dibridged structure. Various theoretical descriptions have been proposed, and found wanting,⁴⁻⁶ until the advent of modern molecular orbital calculations.⁷

Until quite recently, almost nothing was known about the species B_2H_5 and B_2H_4 . The latter had been predicted to be stable,^{8,9} but had never been successfully isolated. Last year, Curtiss and Pople,¹⁰ motivated by our photoionization study of B_2H_6 ,¹¹ calculated (MP4/6-311G** theory) that the most stable structure of $B_2H_5^+$ was tribridged, with dibridged and singly bridged structures lying 20.2 and 41.0 kcal/mol, respectively, above the tribridged structure. Each of these structures, D_{3h} , C_{2v} , and D_{2d} , represent different portions of the ground state potential surface, but the single-bridged (D_{2d}) does not correspond to a minimum on the potential energy surface.

Still more recently, Trachtman *et al.*¹² have calculated (MP4/6-31G* theory) that the most stable form of B_2H_5 was singly bridged, about 5 kcal/mol more stable than a doubly bridged structure, with a barrier between them of about 5 kcal/mol (~ 2.5 kcal/mol with inclusion of zero point energies). In addition, they calculated the B_2H_5-H bond energy to be 98.80 kcal/mol at the MP4 (SDTQ) level, but presumably without zero point energy corrections. These authors note that "at all computational levels a hydrogen atom is more easily removed from the bridging positions in diborane than the nonbridging positions..." To our knowledge, there are no experimental data on the structures of B_2H_5 and $B_2H_5^+$. Manocha *et al.*¹³ have estimated the B_2H_5-H bond energy by reacting B_2H_6 with F atoms, and measuring the vibrational distribution of the HF product. In their words, "the shape of the HF (ν) distribution...implies

direct abstraction from the terminal position with D^0 ($H-B_2H_5$) ≈ 100 kcal/mol." Thus, the calculated and experimental bond energies are in rough agreement, but the authors differ about the bond which is broken (if, in fact, one can describe the dissociation in such terms).

The goal of the present research was to make an experimental test of the calculated structures of B_2H_5 and $B_2H_5^+$, and to provide an independent measurement of the B_2H_5-H bond energy. The method employed was the photoionization mass spectrometric study of the B_2H_5 radical, in combination with earlier studies on B_2H_6 .¹¹

II. EXPERIMENTAL ARRANGEMENT

The radical B_2H_5 was readily prepared *in situ* by the reaction of F atoms with B_2H_6 . The fluorine atoms were generated in a microwave discharge through pure F_2 . The description of the flow tube and reaction cup has been given previously,¹⁴ as has the photoionization mass spectrometric method. The fast-flowing fluorine is trapped in a helium cryopump. Initial experiments utilizing a 50% He, 50% B_2H_6 mixture (Aircro, Inc.) were unsuccessful, because the back diffusion of this mixture through a 0.5 mm orifice was sufficient to overwhelm the cryopump. Use of a 50% Ar, 50% B_2H_6 mixture (Matheson Gas Products) avoided this problem. Initial data were obtained with a wavelength resolution of 0.5 Å (FWHM). Later data, particularly at weak signal levels, were obtained with a resolution of 1.4 Å (FWHM). Most of the measurements utilized the hydrogen many-lined spectrum. Since the adiabatic ionization potential of B_2H_5 is quite low, and in a region of weak hydrogen lamp intensity, some strong emission lines of atomic iodine were generated between 1640–1830 Å to extend the effective range of measurement. Light intensities were monitored with a sodium salicylate coated window, coupled to a photomultiplier tube which measured the fluorescence generated by the vacuum ultraviolet radiation.

The B_2H_4 species could also be generated in this experiment, by adjusting the flow rates of F_2 and B_2H_6 . The study of this species will be the subject of a future report.

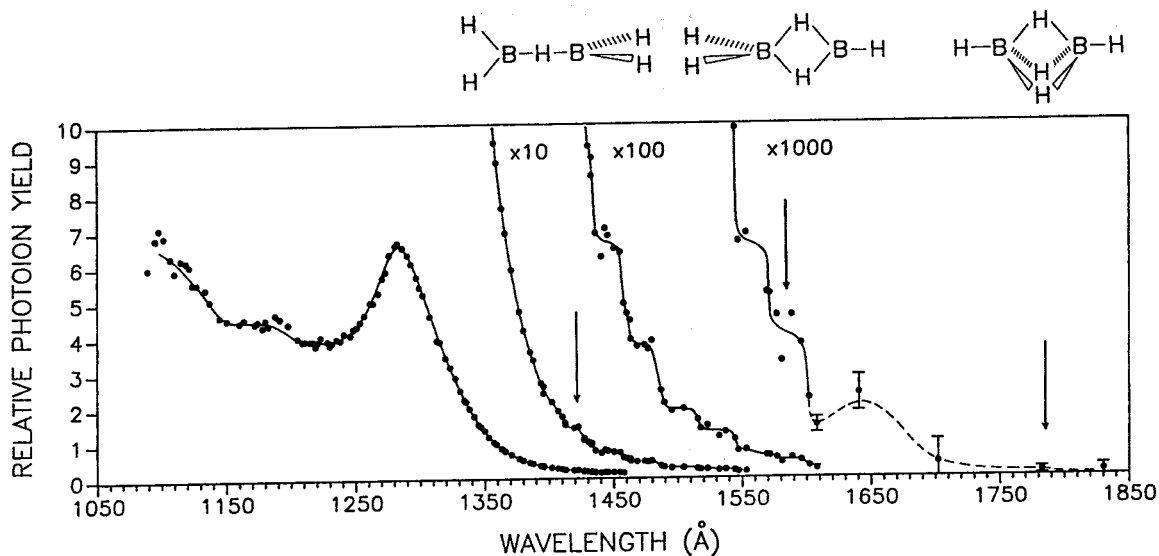


FIG. 1. Photoion yield curve of $B_2H_5^+$ (B_2H_5) where B_2H_5 is produced by the $F + B_2H_6$ reaction. The increasing yield below 1160 Å has been corrected for the presence of $B_2H_5^+$ from unreacted B_2H_6 . Arrows indicate the adiabatic thresholds obtained by *ab initio* calculations (Refs. 10 and 15) for the ionic structures shown.

III. EXPERIMENTAL RESULTS

The photoion yield curve of $B_2H_5^+$ (B_2H_5) is displayed in Fig. 1. The maximum of this curve occurs at 1282 Å. The curve declines more-or-less monotonically to longer wavelengths. We have monitored this decline to ~1800 Å. The ordinate scale has been expanded in three sections, each stage of magnification corresponding to a factor of 10. Thus, the last measured point distinctly above background, at ~1640 Å, is more than 3 orders of magnitude lower than the

maximum at 1282 Å. The point at ~1702 Å is also believed to be above background. The anticipated onset (see below) should occur at ~1787 Å (6.94 eV), and is significantly weaker still.

At wavelengths shorter than 1282 Å, the $B_2H_5^+$ ion yield curve initially declines, and then levels off. Almost exactly at the maximum, the fragment ion $B_2H_3^+$ has its onset (see Fig. 2).

The fragment ion yield increases very rapidly from its threshold (~1287 Å) to about 1190 Å. Between 1190 Å–

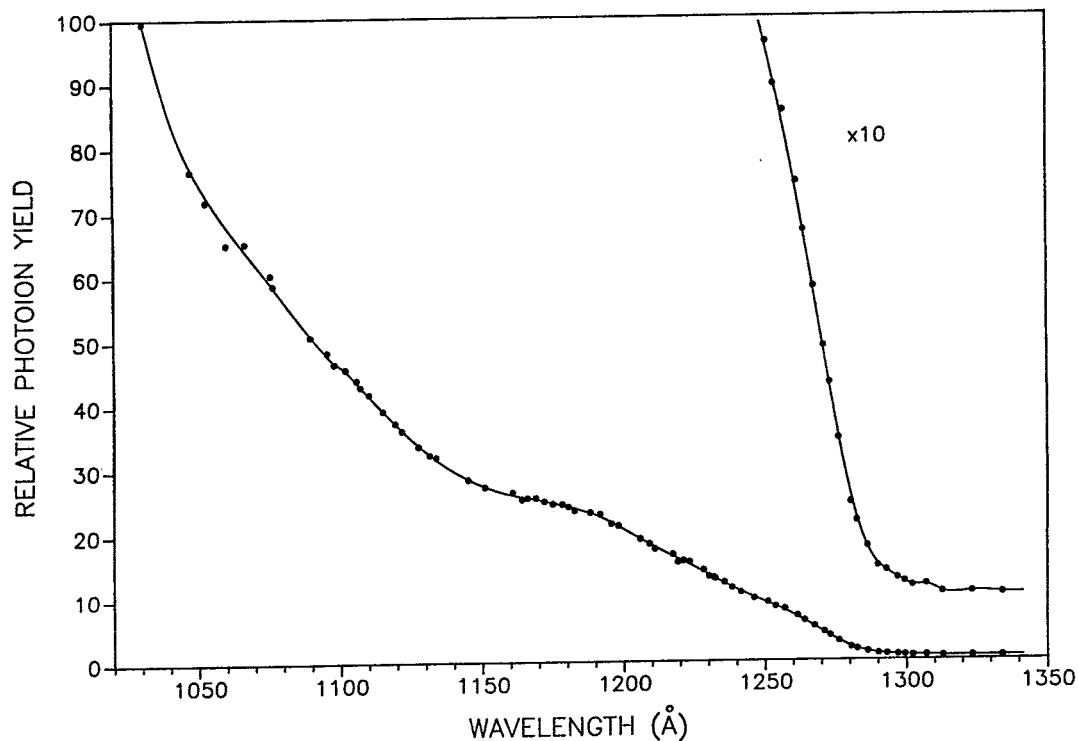


FIG. 2. Photoion yield curve of $B_2H_3^+$ (B_2H_5). The ordinate scales of this figure and Fig. 1 are matched, that is, $B_2H_3^+$ and $B_2H_5^+$ from B_2H_5 are equal in intensity at ~1265 Å.

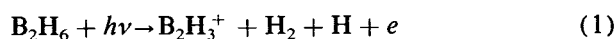
1160 Å it is relatively flat, then increases again to ~1100 Å. Here, there appears to be a change in slope, beyond which there is a further increase to 1030 Å (the limit of measurement). The parent B₂H₅⁺ ion also experiences a growth between ~1160 and 1107 Å (see Fig. 1), paralleling that of B₂H₃⁺. This increase must be attributed to direct ionization of the B₂H₅ radical. A very small contribution due to the tail of the process B₂H₆ → B₂H₅⁺ + H + e, beginning at 1110 Å, has been subtracted in the construction of Fig. 1. The huge contribution of this latter process below 1107 Å thwarted attempts to follow the B₂H₅⁺ parent ion to shorter wavelengths.

The above evidence is indicative of two excited states of B₂H₅⁺, one with an adiabatic onset at ~1160 Å ≡ ~10.7 eV, and the other with an adiabatic onset at ~1080–1070 Å ≡ ~11.5–11.6 eV. Surprisingly, the first excited state branches partially to the parent ion, although this energy is well beyond the onset of fragmentation. This decomposition appears to be at least partially state specific, rather than statistical, but detailed calculations have not been performed. The second state, with its onset at ~11.5–11.6 eV might correspond to a triplet state of B₂H₅⁺ calculated by Curtiss and Pople¹⁵ to have an adiabatic value of 11.5 eV.

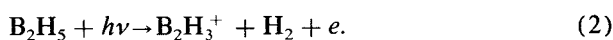
The sum of the B₂H₅⁺ and B₂H₃⁺ ion yield curves, i.e. the total ion yield, is shown in Fig. 3(a). If this curve is attributable to direct ionization, rather than autoionization (which seems plausible), and if step function behavior is assumed, then the energy derivative of total ionization should simulate a photoelectron spectrum. This derivative function is displayed in Fig. 3(b). The peak of the first band, at ~10.3 eV, corresponds to the vertical ionization potential (IP), calculated by Curtiss and Pople¹⁵ to occur at 10.21 eV. [Our value, ~10.3 eV, tends to decrease toward ~10.2 eV, if more smoothing is applied to the data while constructing the total ion yield curve in Fig. 3(a).] The peak at ~11.1–11.2 eV corresponds to the vertical IP of the first excited state of B₂H₅⁺ (with an adiabatic onset at ~10.7 eV), while the second excited state (presumably triplet) appears to have a vertical IP ≈ 11.7 eV.

IV. INTERPRETATION OF RESULTS

In our earlier work,¹¹ the photodissociative ionization threshold corresponding to the process



was found to be ≤14.15 eV. This value also corresponded to the crossover point between B₂H₅⁺ and B₂H₃⁺ in a breakdown diagram (see Fig. 11 of Ref. 11). However, Curtiss and Pople¹⁶ have calculated 13.93 eV for this threshold, 0.22 eV below our upper limit, and their anticipated margin of error is ±0.1 eV. In the present experiment, the onset for B₂H₃⁺ (B₂H₅) occurs at ~1287 Å ≡ 9.633 eV. By applying an approximate internal energy correction for B₂H₅ (assumed to be at 300 K) equal to that of B₂H₆ (0.062 eV), we obtain 9.695 eV as the 0 K threshold for the process

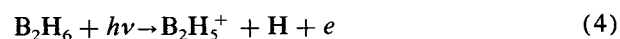


Subtraction of Eq. (2) from Eq. (1) yields



i.e., a bond energy of ~4.455 eV, or ~102.7 kcal/mol. This is best interpreted as an upper limit. The experimental threshold for reaction (1), which can be viewed as a successive decomposition (B₂H₆⁺ → B₂H₅⁺ → B₂H₃⁺) is more likely to exceed the true thermochemical threshold than is reaction (2). The deduced value is thus in fairly good agreement with the earlier experimental value¹³ (~100 kcal/mol). The *ab initio* value of $D_e = 98.80$ kcal/mol¹² has recently been improved¹⁵ using a larger basis set and an isogyric correction, so that $D_e = 107.9$ kcal/mol and $D_o = 100.0 (\pm 2)$ kcal/mol.

Also, by comparing the previously obtained¹¹ threshold (≤11.40 ± 0.05 eV) for the process



with the enthalpy of ≤102.7 kcal/mol deduced for the bond-breaking reaction (3), we obtain ≈6.945 eV for the adiabatic ionization potential of B₂H₅. This experimentally deduced number is in excellent agreement with a recently calculated value of 6.94 eV by Curtiss and Pople.¹⁵

The gap between the inferred vertical ionization potential (~10.3 eV) and the adiabatic value is unusually large (~3.36 eV). For example, the gap between vertical and adiabatic IPs in SiH₄^{14(b)} is 1.82 eV, and in GeH₄¹⁷ is 1.95 eV. In both those cases, the transition occurs from a tetrahedral neutral species to a highly Jahn–Teller distorted ionic species. The extremely slow ascent of the photoion yield curve of B₂H₅ is also quite remarkable. However, the structures and energies of B₂H₅ and B₂H₅⁺ forthcoming from the recent *ab initio* calculations provide a plausible basis for this behavior, or inversely, the current experimental results provide support for the calculational results. Clearly, if the ground state structure of B₂H₅ is singly bridged, while the most stable structure of B₂H₅⁺ in its ground state is tribridged, the Franck–Condon factors involved in this ionizing transition should be vanishingly small. The Franck–Condon factors might improve slightly, but remain small when sufficient energy is available to access the dibridged isomer of B₂H₅⁺. When the incident photon energy is high enough to access that portion of the B₂H₅⁺ ground state potential surface in the neighborhood of a singly bridged configuration, the Franck–Condon factors should maximize.

The *ab initio* calculations of Trachtman *et al.*¹² indicate that a dibridged structure of neutral B₂H₅ lies only slightly higher (~6 kcal/mol, with inclusion of zero point energies) than the singly bridged B₂H₅. If the B₂H₅ species we generate produces a significant abundance of the dibridged isomer, one might anticipate relatively large Franck–Condon factors in the transition from dibridged neutral to dibridged cation, which would appear at lower energy.

There is, in fact, some evidence for contribution of this transition in the photoion yield curve of B₂H₅⁺ (Fig. 1). Distinct step structure can be seen, beginning at ~1600 Å and extending to ~1430 Å. A derivative with respect to energy of this region is displayed in Fig. 4. If step-function behavior characteristic of direct ionization is assumed, this

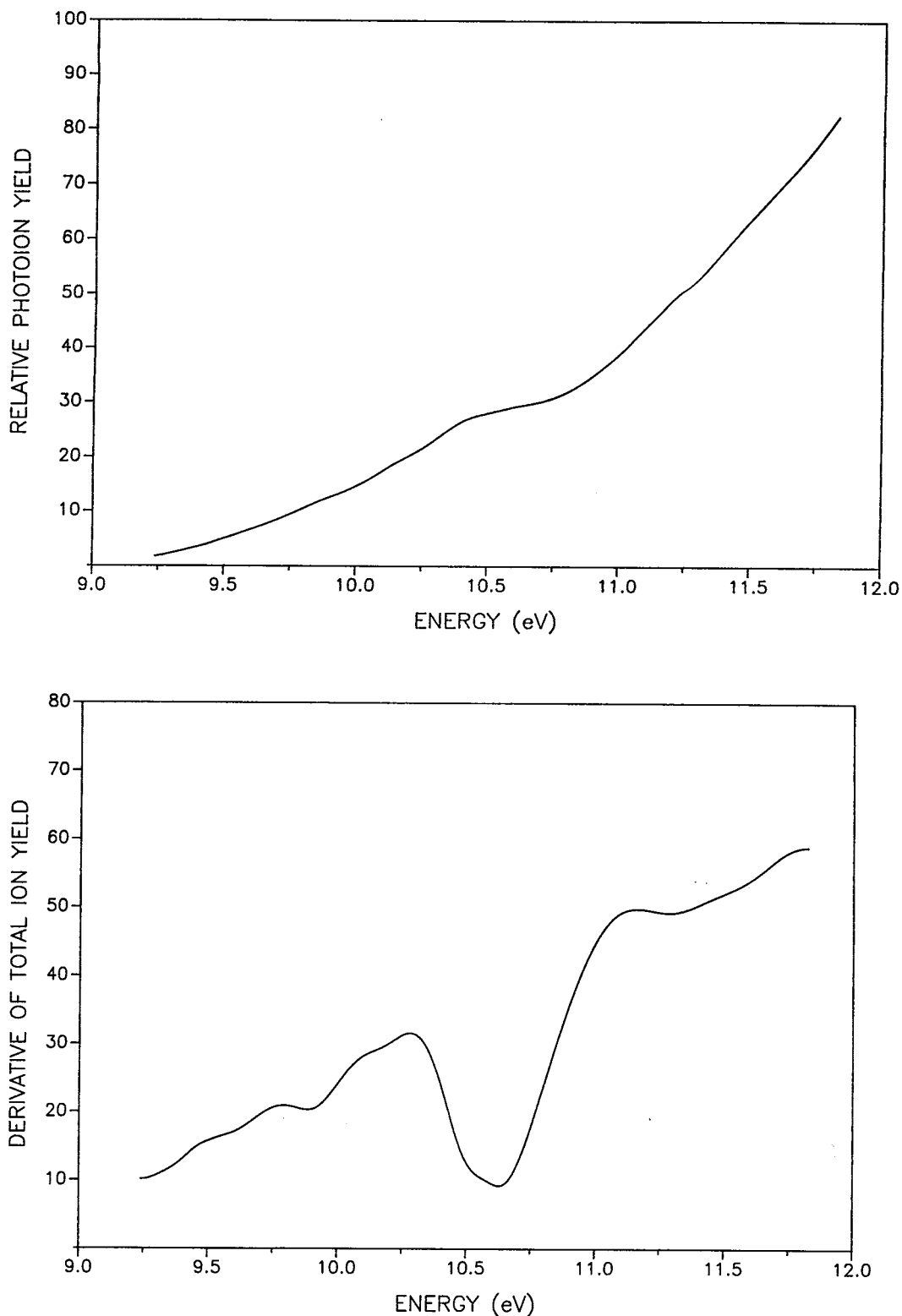


FIG. 3. (a) The sum of the $B_2H_5^+$ and $B_2H_3^+$ ion yield curves, plotted as a function of photon energy. The $B_2H_5^+$ contribution for $h\nu > 11.2$ eV is assumed equal to that at 11.2 eV, since higher energy measurements were not possible for this species. Since $B_2H_3^+ \gg B_2H_5^+$ at 11.2 eV, this assumption should not influence the curve significantly. (b) The derivative with respect to energy of the smoothed total ion yield (a). This curve should simulate a photoelectron spectrum.

derivative should simulate a photoelectron spectrum. One can readily discern a vibrational progression with a spacing of $0.16 \text{ eV} \equiv 1290 \text{ cm}^{-1}$, with a few additional oscillations which may be the result of scatter in the data or possibly evidence for another vibrational excitation. In the ion yield curve (Fig. 1), the maximum intensity of this spectral region

at $\sim 1430 \text{ \AA}$ (comparable to a sum over Franck-Condon factors) is about 180 times weaker than the strength of the first band attributable to the singly-bridged to singly bridged transition (measured as the sum of $B_2H_3^+$ and $B_2H_5^+$ at $\sim 1188 \text{ \AA}$). The weakness of this staircase region can be attributed either to poor Franck-Condon factors (singly

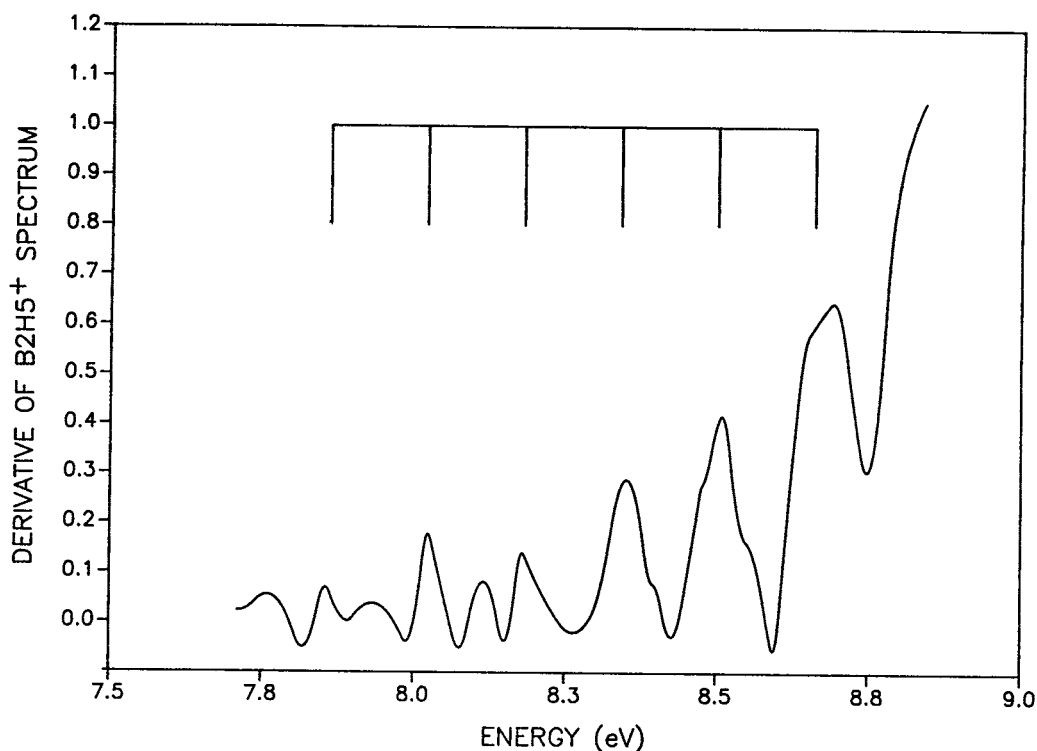


FIG. 4. Derivative with respect to energy of the step structure region (~ 1430 – 1600 Å) of Fig. 1. One distinct vibrational progression, with a spacing of 1290 cm^{-1} , can be discerned. Other undulations present could conceivably indicate other active vibrations, but they may also be a consequence of experimental uncertainty.

bridged to doubly bridged transition) or to a Boltzmann factor representing the population of the doubly bridged above the singly bridged neutral species. If we assume that these structures are in equilibrium at ~ 300 K, and that the respective photoionization transition probabilities are approximately equal, then we can calculate an excitation energy of ~ 3.1 kcal/mol for the doubly bridged neutral species, which is somewhat smaller than the value obtained by *ab initio* calculations. Curtiss and Pople¹⁵ obtain 4.0 kcal/mol for this difference and 5.0 kcal/mol with inclusion of zero point energies. (Our calculation assumes equal partition functions for the two neutral species.) The simple vibrational progression, increasing rather rapidly from the apparent adiabatic onset of ~ 7.8 eV, is suggestive of a small geometry change (doubly bridged to doubly bridged) rather than singly bridged to doubly bridged. The *ab initio* value for a vertical ionization potential (doubly bridged to doubly bridged)¹⁵ is 8.55 eV $\equiv 1450$ Å.

Curtiss and Pople¹⁰ have calculated the structure of doubly bridged $B_2H_5^+$. Trachtman *et al.*,¹² and later, Curtiss and Pople,¹⁵ have calculated the structure of doubly bridged B_2H_5 . These structures are described in Table I. The major differences in these structures are: (a) the unique terminal hydrogen is in plane with the bridge in the cation, but is bent from the approximate plane in the neutral, and (b) the B–H–B–H ring is more distorted (difference in B–H bond lengths) in the cation than in the neutral. Curtiss and Pople¹⁵ have calculated the normal mode frequencies of the doubly bridged cation. Of the 15 frequencies, the two whose eigenvectors approximate the geometrical changes are b_2 (1029 cm^{-1}), a bending of the unique terminal hydrogen, and a_1 (1592 cm^{-1}), a distortion of the bridge, involving hydrogen motion. These *ab initio* frequencies are normally

scaled by a factor 0.89 to more closely approximate experimental frequencies. Also, the totally symmetric species conform to selection rules and are the ones usually observed. Hence, the scaled a_1 frequency (1417 cm^{-1}) can be identified with the observed progression, having a spacing of 1290 cm^{-1} .

V. CONCLUSIONS

The free radical B_2H_5 has been prepared and studied by photoionization mass spectrometry for the first time. The parent $B_2H_5^+$ and fragment $B_2H_3^+$ are the only ions observed. From the appearance potential for $B_2H_3^+$, and earlier measurements, we deduce $D_o(B_2H_5-H) \leq 102.7$ kcal/

TABLE I. Geometries^a of doubly bridged B_2H_5 and $B_2H_5^+$ from *ab initio* calculations.^b

	B_1B_2	B_1H_1	B_1B_b	B_2H_2	B_2H_b	$H_1B_1H_1$	$B_1B_2H_2$
Neutral	1.758	1.185	1.330	1.181	1.298	122	128
Cation	1.726	1.176	1.438	1.166	1.236	131.4	180

^a Bond lengths in angstroms, bond angles in degrees.

^b From Refs. 10 and 15. The geometry of neutral B_2H_5 given here is very close to that given in Ref. 12, at the UHF/6-31 G* level.

mol, and the adiabatic ionization potential of B₂H₅ is ≈ 6.945 eV. This value for the adiabatic ionization potential cannot be determined directly, because the transition probability is extremely low ($\ll 10^{-3}$ of the maximum) at the adiabatic onset. The very weak and gradual onset and the large gap between vertical and adiabatic ionization potentials, together with good agreement between *ab initio* calculations and experiment on the adiabatic IP and the B₂H₅-H bond energy, provide strong, though indirect support for a singly bridged B₂H₅ and a tribridged B₂H₅⁺ as the most stable structures. Step structure observed between ~ 1600 – 1430 Å can be interpreted as evidence for a doubly bridged isomer of B₂H₅, lying ~ 3 kcal/mol higher in energy.

If indeed both isomers of B₂H₅ coexist under the present experimental conditions, they could conceivably be produced concurrently by H atom abstraction from either the bridged or terminal positions, or alternatively, equilibrium could be established by the few collisions occurring on the wall or in the gas phase.

Bridged structures are no longer as exotic as they may have been 40 years ago. Bridged halogen species such as Al₂Cl₆¹⁸ and Be₂Cl₄^{5(b),18} are known, as well as lithium alkyls.^{7,19} Current evidence favors bridged structures for the ground states of vinyl^{20,21} and ethyl²² cations. Even tribridged structures have been calculated for LiBH₄ and BeBH₅.²³ However, some of these bridged structures may be attributable to ionic bonding, whereas others are not. The bridged aluminum and beryllium halides are reminiscent of the cyclic alkali halide dimers. In these cases, the difference in electronegativity between the metal and halogen is substantial, and the ionic nature of the bonding may be the principal explanation for a bridged structure. Thus, one may view the tribridged LiBH₄ as a Li cation residing on the threefold axis of a BH₄⁻ tetrahedral anion. However, the difference in electronegativity between B and H is very small, and hence the tribridged B₂H₅⁺ must be viewed in molecular orbital terminology as three, three centered bonds.

ACKNOWLEDGMENT

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