The Electronic States of the Diborane Ion Determined by Photoelectron Spectroscopy

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Summary Five electronic states of the diborane ion are observed in the photoelectron spectrum of diborane using the 584 Å He resonance line and a planar retarding-field, spectrometer.

THE electronic structure of the diborane molecule, B_2H_6, is particularly interesting because of the three-centred bonds.[1] The first ionization potential (I.P.) has been determined only by electron impact[2-4] and there is some question about the molecular orbital corresponding to the first I.P. Values between 12·1 ev [2] and 14·88 ev [4] can be found for the appearance potential of BH_3^+ from B_2H_6 leaving the energy for dissociation of $B_2H_6^+$ into BH_3^+ and BH_3 practically undetermined. The photoelectron spectra of B_2H_6 give direct evidence about the energy of the electronic states of $B_2H_6^+$ and about the bonding properties of the molecular orbitals from which the electrons are ejected.[5]

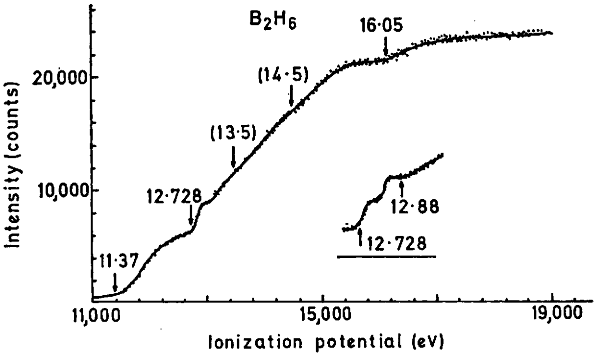

FIGURE. *The retarding-field photoelectron spectrum of* B_2H_6 *plotted against the ionization potential energy, which is the difference between the photon energy* 21·212 ev *and the measured electron energy calibrated with photoelectrons from xenon. The main curve combines the results of* 4 *out of a total of* 12 *runs, the insert shows the fine structure of the second electronic state.*

In our apparatus resonance radiation of He (584 Å) emerging from a He-discharge crosses a molecular beam from a multichannel jet. Electrons ejected perpendicular to the plane of the crossed beams are energy-analysed by an electron spectrometer consisting of an einzeln lens and a planar retarding field.[6] The electrons are counted and registered with a 400-channel analyser. The energy resolution is 12 mev as measured by the step width (10%—90%) of photoelectrons from argon (*i.e.* 10 mev f.w.h.m.).

Five electronic states of diborane are found (Table and Figure). Strictly speaking the reported adiabatic I.P.'s, *i.e.* energy of transitions to the lowest vibrational states of the ion, are upper limits of the true values for all but the second state where vibrational structure was observed. The vertical I.P.'s are the energies at the point of steepest slope in the retarding field curve. Included in the Table are the orbital energies and classification calculated by Buenker *et al.*[7] The rather poor agreement between the calculated energies and vertical I.P.'s is reasonable despite Koopmans' theorem[8] that the ionization potential should be equal to the negative of the orbital energy. The calculated numbers are the energies necessary to extract one electron from that orbital without changing the motion of either the nuclei or other electrons, while for the measured vertical I.P.'s only the motion of the nuclei can be assumed to remain unchanged (Franck–Condon principle).[5]

The lowest energy state has the broad shape typical of removal of a σ-bonding electron. The absence of resolvable vibrational structure at its onset indicates a large change

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in the nuclear framework of the ion compared with the molecule. In agreement with the theoretical results[7] and the low value for the appearance potential of $B_2H_5^+$ [2,3] the ground state of the $B_2H_6^+$ ion is identified as the $(1b_{3g})^{-1}$ state.‡ As expected,[5] our value for the first I.P. ($\leqslant$11·37 ev) is smaller than the electron impact data[2,3] but well within the range of 11—12 ev derived by Price from vacuum u.v. absorption measurements.[9]

TABLE

Ionization potentials of B_2H_6

This work			Calculated[7]	
Adiabatic I.P. (ev)	Vertical I.P. (ev)	Suggested orbital vacated	Orbital energy (ev)	Orbital vacated
11·37	11·9 ± 0·1	$1b_{3g}$	−12·91	$1b_{3g}$
12·728 ± 0·001[a]	—	$1b_{3u}$	−14·16	$3a_g$
(13·5)[b]	13·9 ± 0·2	$1b_{2u}$	−14·38	$1b_{2u}$
(14·5)[b]	14·9 ± 0·2	$3a_g$	−14·95	$1b_{3u}$
16·05	16·4 ± 0·1	$2b_{1u}$	−17·49	$2b_{1u}$
—	—	$2a_g$	−23·77	$2a_g$

[a] In contrast to the other states which are broad and without vibrational structure, this state shows two, equal intensity, sharp steps with a spacing of 0·075 ± 0·005 ev. The sudden breakoff of the vibrational structure precludes evaluation of a vertical I.P.

[b] Values are rough estimates because the onset for these states is covered by the previous state.

The sharp onset and the two vibrational steps of equal height observed for the second state (Table and insert of the Figure) indicate a stable state has been formed. Since it occurs at an energy about 1 ev and 0·5 ev above the appearance potentials of $B_2H_5^+$ and $B_2H_4^+$, respectively,[2,3] the state can be stable only if the electron removed does not contribute significantly to the bonding of the terminal hydrogens. Tentatively, we assign this state to $(1b_{3u})^{-1}$ since the symmetry of this orbital excludes any contribution to the terminal B–H bonds.§ The observed intensity distribution of the vibrational progression, two steps of equal height but no third step detectable, and the spacing of 0·075 ev cannot be explained by a set of Franck–Condon factors connecting discrete vibrational states. The more consistent interpretation of these observations and the onset of a continuous spectrum is, that a dissociation process starts at 12·88 ev. The bridge bonding character of this orbital would favour dissociation of the bridge bonds. These results support the value[3] of 13·1 ± 0·2 ev, for the appearance potential of BH_3^+ from B_2H_6 and leads to $D(BH_3^+–BH_3) \leqslant 1·5$ ev.

It is hard to see how these arguments can be reconciled with the result of Wilson and McGee[4] of 14·88 ev for the appearance potential of BH_3^+ from B_2H_6 unless the cross section of BH_3^+ production increases markedly at 14·88 ev. A comparatively small contribution to the cross section at lower energies may not be detected by the scale-shift method used by these authors. This is expected if our fourth state of $B_2H_6^+$ at 14·9 ev is assigned to $(3a_g)^{-1}$, the other state where an electron is removed from an orbital with partial contribution to the bridge bonding. This leaves the $1b_{2u}$ and $2b_{1u}$ orbitals for the third and fifth states, respectively, in agreement with the ordering from theoretical calculations.[7]

All of the electronic states found in the photoelectron spectrum are thus identified in a manner consistent with the existing evidence. Some question remains whether the second state is the $(1b_{3u})^{-1}$ or $(3a_g)^{-1}$. The redetermination of all the appearance potentials using photoionization techniques being carried out in our laboratory will help resolve this question.

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‡ The designation of the ion states determined by photoelectron spectroscopy by the orbital vacated follows a suggestion by R. S. Mulliken at the symposium on photoelectron spectroscopy at The Royal Society, London, February 1969.

§ Assignment of the second state to the calculated less tightly bound $(3a_g)^{-1}$ state cannot be ruled out but leads to a less consistent overall explanation considering the observed broad structureless shape of the other states.

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