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# Photoelectron spectroscopy of BH<sub>3</sub><sup>-</sup>

C. Tom Wickham-Jones, Sean Moran,<sup>a)</sup> and G. Barney Ellison Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

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We have studied the photoelectron spectra of  $BH_3^-$  and  $BD_3^-$  and have measured the electron affinities of borane; we find EA(BH<sub>3</sub>) =  $0.038 \pm 0.015$  eV and EA(BD<sub>3</sub>) =  $0.027 \pm 0.014$  eV. The peak splittings and intensities demonstrate that the  $BH_{3}^{-}$  ion and the  $BH_{3}$  neutral have very similar geometries; our spectra are consistent with a planar structure for both species. Variational calculations of a coupled oscillator basis over an *ab initio* potential give an excellent fit to the experimental frequencies and photodetachment Franck-Condon factors. This ab initio model leads to equilibrium geometries with both BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> as planar molecules with  $r_e(BH_3^-) = 1.207$  Å and  $r_e(BH_3) = 1.188$  Å. We find  $\Delta H_{f0}^{\circ}(BH_3^-)$  $= 23.1 \pm 3.8 \text{ kcal mol}^{-1}$ .

# **I. INTRODUCTION**

Borane has long been known to be a highly unstable species.<sup>1</sup> This is due to the empty p orbital on the boron atom which makes it a strong Lewis acid. In the gas phase BH<sub>3</sub> readily dimerizes to form diborane, B<sub>2</sub>H<sub>6</sub>. The transient existence of BH<sub>3</sub> has been postulated to be an intermediate in such processes as the isotopic self-exchange between  $B_2H_6$ and  $B_2D_6$  and the pyrolysis of diborane to yield higher boranes.<sup>2</sup> Mass spectroscopic studies of pyrolysis of diborane<sup>3</sup>  $(B_2H_6)$  and borane carbonyl<sup>4</sup> (BH<sub>3</sub>CO) have demonstrated the existence of  $BH_3$  in the gas phase.

Optical studies of BH<sub>3</sub> have failed to record any electronic spectrum. This has been attributed to the fact that the excited electronic states are dissociative. Infrared spectra of the ground electronic state of BH<sub>3</sub> trapped in a cryogenic Ar matrix have been measured.<sup>5</sup> Three infrared active modes were observed:  $v_2$  (out-of-plane bend) = 1125 cm<sup>-1</sup>,  $v_3$ (doubly degenerate asymmetric B-H stretch) = 2808 cm<sup>-1</sup>, and  $v_4$  (doubly degenerate in-plane bend) = 1604 cm<sup>-1</sup>. Recently the  $v_2$  out-of-plane bend has been observed at 1140.9 cm<sup>-1</sup> via diode laser infrared spectroscopy of BH<sub>3</sub> in the gas phase.<sup>6</sup>

Borane hydride anions have been observed with ESR spectroscopy in solid matrices<sup>7,8</sup> following  $\gamma$  irradiation of borohydrides and by hydrogen abstraction from borohydride (BH<sub>4</sub><sup>-</sup>) with tert-butoxyl radicals in ether-alcohol solutions.<sup>9</sup> The ESR coupling constants suggest that  $BH_3^-$  has a planar structure; an observed temperature dependence of the coupling constants in the solution work was due to excitation of the out-of-plane bending  $v_2$  mode.

We have succeeded in making beams of  $BH_3^-$  from BH<sub>3</sub>CO in an electron discharge ion source. The mass-selected ions are detached with a fixed frequency ( $\hbar\omega_0$ ) Ar II laser. A measurement of the kinetic energy of the ejected electron forms the technique of negative ion photoelectron spectroscopy. This experiment measures the electron affinity of the neutral and, in many cases, it determines the energies of accessible excited vibrational and electronic states of the neutral. Vibrationally or electronically excited ions, if present, will also be observable in the spectrum. The general

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method has been reviewed recently.<sup>10</sup>

BH<sub>3</sub> can be expected to have an  ${}^{1}A'_{1}$  electronic state and a planar  $D_{3h}$  geometry. The boron atom forms bonds to the hydrogen atoms by  $sp^2$  hybridization and the molecule will be planar as this arrangement minimizes the hydrogen-hydrogen interactions. This is a similar situation to BF<sub>3</sub> which is experimentally established to be a planar  $D_{3h}$  species.<sup>11</sup> No other electronic state of BH<sub>3</sub> can be formed without exciting electrons from B-H bonds or from the boron inner core. These are clearly unfavorable processes and will lead to electronic states which are higher in energy and almost certainly dissociative.

The electron, which is added to  $BH_3$  to form  $BH_3^-$ , can be expected to take up residence in the empty p orbital and leads to an  ${}^{2}A_{1}^{"}$  electronic state. The hydrogen atoms have no electrons other than those forming bonds to the boron and thus the electron in the p orbital does not interact with other electrons in the molecule. We thus expect the  $BH_3^-$  ion to be roughly planar. A representation of the detachment process is shown in Eq. (1)



since<sup>12</sup> We expect the  $EA(BH_3)$  to be low  $EA(B) = 0.277 \pm 0.010 \text{ eV}$ . Such a small electron binding energy ( $\simeq 2200 \text{ cm}^{-1}$ ) suggests that very few vibrationally excited ions,  $(BH_3^-)^{\dagger}$ , will be formed, as they will autodetach rather rapidly. It is instructive to recall that  $BH_3^-$  is isoelectronic with  $CH_3$  and  $BH_3$  with  $CH_3^+$ . We can expect the structure of isoelectronic pairs to be similar and our spectra to show similarities with the photoelectron spectra<sup>13,14</sup> of  $CH_3$ ;  $IP(CH_3) = 9.843 \pm 0.001 \text{ eV}.^{15}$ 

This paper is organized as follows. Section II gives a description of the experimental method and results and Sec. III analyzes the thermochemistry. Section IV reports on ab initio electronic structure calculations which have been carried out on BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup>. This portion also discusses the

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a) Present address: Department of Chemistry, University of Rochester, River Station, Rochester, NY 14627.

vibrational modes of these species and details calculations of Franck-Condon factors which can be compared with the experimental spectra. Section V compares the calculated spectra with the experimental results and states our final conclusions. The synthesis of BH<sub>3</sub>CO and BD<sub>3</sub>CO is outlined in Appendix A while Appendix B details the coordinates and G matrix elements which have been used in these calculations. Finally, the vibrational potentials are detailed in Appendix C.

#### **II. EXPERIMENTAL**

## A. General

BH<sub>3</sub><sup>-</sup> ions can be generated in a high pressure (roughly 0.1 Torr) magnetically confined plasma. A 1:2 mixture of BH<sub>3</sub>CO or BD<sub>3</sub>CO and Ar is introduced into the plasma which is driven by a 0.015 in. tungsten filament heated to produce an 8 mA emission current. The ions are mass selected with a Wien filter and beams of up to 100 pA of BH<sub>3</sub><sup>-</sup> and 30 pA of BD<sub>3</sub><sup>-</sup> achieved. Typically 80 pA of BH<sub>3</sub><sup>-</sup> and 25 pA of BD<sub>3</sub><sup>-</sup> can be maintained for 2–3 h. An Ar II laser operating cw on a single line ( $\lambda_0 = 488.0$  nm) is crossed with the ion beam. So as to increase the number of photons interacting with the ion beam, the latter is incorporated inside the cavity of the laser. In this fashion the ions interact with about 75 W of laser power.

Detached electrons are collected and analyzed with a pair of hemispherical analyzers. The maximum resolution of this system is about 20 meV as measured with an O<sup>-</sup> ion beam. The photoelectron spectrum is calibrated with a reference ion and transformed to the center of mass (CM) frame. It is the energy in the CM frame which is reported in this paper. In these experiments  $NH_2^-$  (EA = 0.772 ± 0.005 eV) was used as the calibration ion.<sup>16</sup>

The apparatus outlined here has been detailed in previous publications<sup>17</sup> except for two modifications. We have removed the hemispherical analyzer's ceratron electron detector and installed a multichannel plate array detector. Second, a new 6 in. Wien filter has been incorporated in the place of the earlier 3 in. model. The new 6 in. device is liquid cooled so that greater electrical currents, up to 15 A, can be passed through the magnet coils and higher magnetic fields achieved. The new Wien filter now gives us an approximate mass resolution of  $M/\Delta M \approx 100$ . A detailed description of the installation and operation of these new features has been published elsewhere.<sup>18</sup>

#### **B. Mass spectra**

A mass scan obtained from a discharge in argon and BH<sub>3</sub>CO is shown in Fig. 1. The mass scale is fixed by the presence of a small amount of O<sup>-</sup> (m/z = 16 amu) which is identified by its photoelectron spectrum. The peak at 14 amu is due to <sup>11</sup>BH<sub>3</sub><sup>-</sup> and that at 13 amu to <sup>10</sup>BH<sub>3</sub><sup>-</sup>. The 1:4 intensity ratio of these peaks reflect the relative abundance of the two naturally occurring isotopes of boron ( $^{10}B \approx 20\%$ ,  $^{11}B \approx 80\%$ ). BH<sub>4</sub><sup>-</sup>, which is isoelectronic with methane, will not detach electrons with 488 nm photons and the mass peak at 15 amu is due to <sup>11</sup>BH<sub>4</sub><sup>-</sup>. The peak at 14 amu will contain a



FIG. 1. BH<sub>3</sub><sup>-</sup> mass scan.

small proportion of  ${}^{10}BH_4^-$  but since this ion does not detach electrons with 488 nm photons, its presence can be ignored. The second cluster of mass peaks around 25 amu is comprised of various isotopic combinations of  $B_2H_4^-$ ,  $B_2H_5^-$ , and  $B_2H_7^-$ . We have seen photodetachment<sup>18</sup> from  $B_2H_4^-$ , but the other ions do not detach. The third group of peaks at 35-40 amu is made up of anions containing three boron atoms.

When BD<sub>3</sub>CO is used as an ion precursor, the mass scan in Fig. 2 results. O<sup>-</sup> stays at 16 amu while BD<sub>3</sub><sup>-</sup> shifts to 17 and BD<sub>4</sub><sup>-</sup> to 19. The peak at 27 amu cannot contain just boron and hydrogen since an odd mass can only be obtained by having <sup>10</sup>B and <sup>11</sup>B in the same ion; this would lead to a mass peak with two <sup>11</sup>B atoms having an intensity four times greater. A possible ion with this mass is BO<sup>-</sup> which has an EA<sup>19</sup> of  $3.12 \pm 0.09$  eV; mass 30 is B<sub>2</sub>D<sub>4</sub><sup>-</sup>, and mass 32 is B<sub>2</sub>D<sub>5</sub><sup>-</sup>. Chloride is a contaminant of argon and shows up as the major anion (*m/z* 35 and 37) when a discharge is run with only argon.



FIG. 2. BD<sub>3</sub><sup>-</sup> mass scan.

## **C. Photoelectron spectra**

A photoelectron spectrum of  $BH_3^-$  over the full energy range for possible detachment from the 2.540 eV photons is shown in Fig. 3. Two facts are immediately evident from this spectrum. (a) The anion is barely bound since photoelectrons with almost the full laser energy ( $\hbar\omega_0 = 2.540 \,\text{eV}$ ) are observed. Thus  $EA(BH_3)$  is nearly zero. (b) The geometry change in going from the radical anion to the neutral is small because the photoelectron spectrum shows a nearly vertical transition. Most of the photodetachment intensity is in the origin. A more detailed spectrum of the region showing detachment is shown in Fig. 4, while Fig. 5 is a spectrum of  $BD_3^-$  taken under the same conditions. The peak which is labeled A in both spectra can be identified as the (0,0) transition since it shifts the least upon deuteration:  $BH_{1}^{-}$  to  $BD_{1}^{-}$ . The splitting between peaks A and B is  $2480 \pm 180$  cm<sup>-1</sup> for  $BH_3^-$  and  $1800 \pm 180$  cm<sup>-1</sup> for  $BD_3^-$ . The energies of the peaks in Figs. 4 and 5 are listed in Table I. The identity of the second feature, peak B is discussed in subsequent sections of this paper. In our spectra we see no other features which can be identified as peaks.

### **III. THERMOCHEMISTRY**

## A. Electron affinities

Feature A in the BH<sub>3</sub><sup>-</sup> and BD<sub>3</sub><sup>-</sup> spectra are the (0,0) transitions; these are collected together in Table I. Use of these values and the laser photon energy at 2.540 eV then affords the uncorrected or raw electron affinities: raw  $EA(BH_3) = 0.040 \pm 0.014$  eV and raw  $EA(BD_3) = 0.029 \pm 0.013$  eV. In order to calculate the proper electron affinities of BH<sub>3</sub> and BD<sub>3</sub>, it is necessary to correct these energies for differences in the rotational constants in the ion and neutral. BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> are both planar (or near planar)  $D_{3h}$  molecules and they are thus perfect (or near) oblate symmetric tops. The rotational correction for this type of rotor has been previously derived<sup>20</sup> where B and C are the constants (in cm<sup>-1</sup>) while T is the rotational temperature (K) and  $k_B$  is Boltzmann's constant. The final expression is given by



FIG. 4. BH<sub>3</sub><sup>-</sup> photoelectron spectrum detailed range.

$$\Delta_{\rm rot} = k_B T \left[ \frac{B'}{B''} + \frac{C'}{2C''} - \frac{3}{2} \right] + \frac{B'' - B'}{3}.$$
 (2)

Using the bond lengths from the *ab initio* calculations (described in the next section) the rotational constants listed in Table II are obtained. There are no hot bands due to the very low energy with which BH<sub>3</sub> binds an electron; thus the rotational temperature of the  $BH_3^-$  ions must be estimated. Assuming  $T_{\rm rot} = 500 \pm 200$  K and using the rotational constants in Table II, an uncertainty of  $\pm 5\%$  leads to  $\Delta_{rot} (BH_3) = 0.002 \pm 0.004$ eV and  $\Delta_{\rm rot}$  (BD<sub>3</sub>) = 0.002 + 0.004 eV. The lack of hot bands due to the low EA obviates the need for a sequence band correction, so the final EA's are  $0.038 \pm 0.015$  eV for BH<sub>3</sub> and  $0.027 \pm 0.014$ eV for BD<sub>3</sub>. These final results are listed in Table I. Notice that 38 meV = 306 cm<sup>-1</sup>; consequently it is little surprise that no hot bands are evident. All vibrationally excited ions will autodetach:

$$(\mathbf{B}\mathbf{H}_3^-)^{\dagger} \to \mathbf{B}\mathbf{H}_3 + e^- . \tag{3}$$



FIG. 3. BH<sub>3</sub><sup>-</sup> photoelectron spectrum full range.

FIG. 5. BD<sub>3</sub><sup>-</sup> photoelectron spectrum detailed range.

TABLE I. Experimental results. Laser ene	$\lambda_0 = 488 \text{ nm} (2.540 \text{ eV}).$
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CM transition energies (eV)	BH <sub>3</sub>	BD <sub>3</sub>
Peak A	$2.500 \pm 0.014 \text{ eV}$	$2.511 \pm 0.013 \text{ eV}$
Peak B	$2.192 \pm 0.018 \text{ eV}$	$2.288 \pm 0.018 \text{ eV}$
	$\begin{aligned} \mathbf{EA(BH_3)} &= 0.038 \pm 0.015 \text{ eV} \\ \Delta H_{f0}^{\circ}(\mathbf{BH_3}) &= 22.2 \pm 3.4 \text{ kcal/mol} \\ \Delta H_{f0}^{\circ}(\mathbf{BH_3^{-}}) &= 23.1 \pm 3.8 \text{ kcal/mol} \end{aligned}$	$EA(BD_3) = 0.027 \pm 0.014 \text{ eV}$

# B. Heat of formation of BH<sub>3</sub><sup>-</sup>

The heat of formation of  $BH_3^-$  can be extracted from our measurement of the electron affinity of  $BH_3$ . Recently a photoionization mass spectrometric study of  $B_2H_6$  has been reported which established the dimerization energy:  $2BH_3 \rightarrow B_2H_6$ . This photoionization paper thoroughly discussed the heat of formation of  $BH_3$ .<sup>21</sup> Using JANAF values<sup>22</sup> for associated thermochemical data the PIMS study reports  $\Delta H_{f0}^{\circ}(BH_3) = 22.2 \pm 3.4$  kcal/mol. Combined with EA(BH\_3) = 0.88  $\pm$  0.35 kcal/mol and the assertion that the heat of formation of a free electron is 0 kcal/mol, a  $\Delta H_{f0}^{\circ}(BH_3^-) = 23.1 \pm 3.8$  kcal/mol is obtained. This result is shown in Table I.

#### IV. AB INITIO GEOMETRIES AND FREQUENCIES

In both the borane and  $d_3$ -borane spectra, peak A has been identified as the (0,0) band. This assignment is based on the small isotopic shift between  $BH_3^-$  and  $BD_3^-$ . In each scan there is another, lesser feature which is labeled peak B. We shall now try to identify this peak and draw any pertinent conclusions about  $BH_3^-$  and  $BH_3$ .

In the  $BH_3^-$  spectrum peak **B** is displaced 2480 cm<sup>-1</sup> from peak **A**. This value is of the correct magnitude for a stretching frequency. Bending frequencies are typically less than 1000 cm<sup>-1</sup>, but an overtone of such a motion could fall at 2480 cm<sup>-1</sup>. In this case two simple possibilities for the nature of peak **B** arise. (A) Peak **B** is due to excitation in the fundamental of a stretching mode. (B) It is due to excitation in the overtone of a bending mode. (C) The value of the bending frequency is twice that of the stretch and anharmonic coupling gives rise to a two-to-one Fermi resonance.<sup>23</sup> It is these mixed levels which are excited.

In order to properly model our photoelectron spectra we must have some estimates of the vibrational frequencies and equilibrium geometries of BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup>. We resort to electronic structure calculations as a starting point. The electronic energy and geometry of BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> have been computed with the GAUSSIAN 86 set of computer programs.<sup>24</sup> The results of a number of calculations are shown in Table III. In the calculations of BH<sub>3</sub>, the molecule was fixed at a  $D_{3h}$  geometry while the BH<sub>3</sub><sup>-</sup> was only constrained to have  $C_{3v}$  symmetry. The planarity of the BH<sub>3</sub> molecule was confirmed with a HF/6-31G(2*d*,*p*) calculation constrained to  $C_{3v}$  symmetry. This resulted in a minimum geometry of  $\theta = 0.0006^{\circ}$  and R = 1.1879 Å.

For electronic structure calculations it is very important to use a basis set which is appropriate for the system of interest. For a molecule with a weakly bound electron a basis set which includes diffuse orbitals is necessary.<sup>25</sup> The basis set 6-31G\*\* has no diffuse functions,  $6-31 + G^{**}$  has diffuse functions on the boron and  $6-31 + G^{**}$  has them on both the boron and hydrogen. We find that the calculations using a basis set without diffuse functions result in an ion which is nonplanar but those which include diffuse functions produces a planar ion. It can be seen that the inclusion of diffuse functions on the hydrogens does not have a strong influence on the optimized geometry; this conclusion has been reported for other systems.<sup>25</sup>

The contribution of electron correlation to the potential energy surface has been investigated by calculating a fourth order Møller–Plesset correction (MP4). Table III shows that this alters the total energy in a significant fashion but the final equilibrium geometry is rather insensitive to the degree of electron correlation in the calculation. Notice that the  $BH_3^-$  ion is not bound with respect to  $BH_3$  and a free electron; the ion sits up in the continuum by 28.7 mhartrees or + 0.78 eV. Recall that the measured value for EA(BH<sub>3</sub>) is  $0.038 \pm 0.015$  eV so this is not an easy *ab initio* calculation to do.

BH<sub>3</sub><sup>-</sup> is isoelectronic with methyl radical, CH<sub>3</sub>, and it is interesting to compare the two. CH<sub>3</sub> is known to be planar and to have a C-H bond length<sup>26</sup> of 1.079 Å. A UHF/6-31 + G\*\* calculation of the optimized geometry has been carried out, wherein the methyl radical was constrained to have  $C_{3v}$  symmetry. The optimized structure is a planar spe-

TABLE II. Rotational constants<sup>a</sup> (cm<sup>-1</sup>).

	В	С
BH <sub>3</sub>	7.896	3.948
BH <sub>3</sub> <sup>-</sup>	7.653	3.826
BD,	3.947	1.974
BD <sub>3</sub>	3.829	1.915

<sup>a</sup> Calculated with constrained bond lengths as BH<sub>3</sub> ( $R_{B-H}$ ) = 1.188 Å and BH<sub>3</sub><sup>-</sup> ( $r_{B-H}$ ) = 1.207 Å.

	BH <sub>3</sub> optimized	at D <sub>3h</sub> symmetry	$BH_3^-$ optimized at $C_{3\nu}$ symmetry			
Calculation	Energy	B-H length (Å)	Energy	B-H length (Å)	θ°	
HF/6-31G**	- 26.392 869	1.1882	- 26.333 996	1.2293	12.4	
MP4/6-31G**	- 26.507 547	1.1865	- 26.459 715	1.2185	10.7	
HF/6-31 + G**	- 26.393 535	1.1884	- 26.364 598	1.2185	0.1	
MP4/6-31 + G**	- 26.508 684	1.1869	- 26.494 303	1.2071	0.1	
HF/6-31 + + G**	- 26.393 542	1.1884	- 26.364 771	1.2071	0.1	
	H N	e R	Н			
		Β Γ <sub>1</sub> θ <sub>1</sub>	$= R_1 - r_e$ $= \Theta_1 - \pi/2$			

TABLE III. Ab initio energies (in hartrees) and geometries.

cies with C–H bond length of 1.073 Å which is within 1% of the known value. This provides some confidence in our ability to calculate a geometry for  $BH_3^-$ . Our most extensive calculations, as shown in Table III, suggest that both  $BH_3$ and  $BH_3^-$  are planar species with a B–H bond length equal to 1.188 Å for  $BH_3$  while the  $BH_3^-$  ion has a bond length equal to 1.207 Å. Our UHF/6-31 + G\*\* calculations on BH<sub>3</sub><sup>-</sup> lead to a wave function with  $\langle S^2 \rangle = 0.754$ .

These results suggest to us that we have computed proper structures for the equilibrium geometries of  $BH_3$  and  $BH_3^-$ . We must now extract vibrational energy levels from these *ab initio* borane potentials.

### A. Modes

An AB<sub>3</sub> molecule of  $D_{3h}$  symmetry possesses six vibrational degrees of freedom: two singly degenerate modes of

TABLE IV. Hartree–Fock harmonic frequencies<sup>a</sup> (cm<sup>-1</sup>).

Mode	BH <sub>3</sub>	BD <sub>3</sub>
$\omega_1$	2668	1887
$\omega_2$	1223	954
	(1140.9) <sup>b</sup>	
	(1125)°	
$\omega_3$	2783	2082
-	(2808)°	
$\omega_4$	1297	956
	(1604) <sup>c</sup>	
Mode	BH <sub>3</sub> <sup>-</sup>	$\mathbf{BD}_{3}^{-}$
ω	2525	1779
$\omega_2$	563	439
$\omega_3$	2606	1947
$\omega_4$	1244	918

\*HF/6-31 + G\*\* potential.

<sup>b</sup>Diode laser, Ref. 6.

<sup>e</sup> Matrix IR, Ref. 5.

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FIG. 6. BH<sub>3</sub> normal modes.

symmetry  $A'_1$  (symmetric stretch) and  $A''_2$  (out-of-plane bend) and two doubly degenerate modes of symmetry E'(scissors and asymmetric stretch). A representation of these vibrations<sup>27</sup> is shown in Fig. 6. As mentioned in the introduction, matrix infrared spectroscopy<sup>5</sup> has assigned some of the BH<sub>3</sub> modes. These are  $v_2 = 1125$  cm<sup>-1</sup>,  $v_3 = 2808$ cm<sup>-1</sup>, and  $v_4 = 1604$  cm<sup>-1</sup>; the symmetric stretch  $v_1$  is IR inactive and has not been observed experimentally. A gas phase study of  $v_2$  has been carried out with a laser diode experiment<sup>6</sup> and the value of the fundamental measured to be 1141 cm<sup>-1</sup>.

Harmonic approximations to the vibrational frequencies of a molecule can be estimated from an ab initio calculation. Harmonic frequencies are determined by the second derivatives of the potential with respect to the molecular nuclear coordinates. It is possible to calculate these derivatives in analytic form from a Hartree–Fock wave function. In this manner harmonic frequencies for  $BH_3$  and  $BH_3^-$  have been obtained for the  $6-31 + G^{**}$  basis set and these are shown in Table IV. The frequencies are calculated for planar  $D_{3h}$  molecules with B-H bond lengths which correspond to the minimum energy geometry. This is necessary as the force constants only give the harmonic frequencies at a minimum in the potential energy surface. The harmonic frequencies of BH<sub>3</sub> have been calculated previously by a Hartree-Fock calculation using the 6-31G\*\* basis set,<sup>28</sup> i.e., without the use of diffuse functions. These are within  $30 \text{ cm}^{-1}$  of our frequencies in Table IV. Also included in Table IV are the measured infrared energies and it is evident that some of the calculated frequencies disagree with the experimental values by as much as 25%. This is a common level of accuracy for Hartree-Fock, harmonic frequencies.<sup>28,29</sup>

#### **B. Franck–Condon factors**

In our experiment we can observe transitions from electronic and vibrational quantum states in the  $BH_3^-$  ion to electronic and vibrational states in the final  $BH_3$  neutral. Due to our energy resolution of 20 meV and the large number of rotational states which are populated, we cannot resolve rotational transitions. For a given electronic transition, the measured relative intensities of the vibrational levels of the neutral are governed by the Franck–Condon principle<sup>30</sup> and the distribution of vibrational states in the ion. The latter is fixed by the temperature of the ion source and the constraint that vibrationally excited ions may be absent if the electron affinity is sufficiently small. This is the case in these experiments.

The Franck–Condon factor is the square of the integral over the vibrational wave functions of ion and neutral:

$$I(v' \leftarrow v'') \propto |\langle \Psi_{v'} | \Psi_{v''} \rangle|^2.$$
(4)

In this expression, v' labels the vibrational quantum state in the neutral and v'' the vibrational state in the ion. In order for Eq. (4) to be nonzero, the integral must be totally symmetric with respect to the symmetry operations of the molecular point group. Thus the direct product of the representation of v' with that of v'' must contain the totally symmetric representation. The wave function of the ground vibrational state is always totally symmetric. Consequently, only the totally symmetric vibrational modes in the neutral (or even quanta of the nontotally symmetric modes) can be reached by detachment. Both of these cases are illustrated in Figs. 7(a) and 7(b). Excitation in a symmetric mode (such as the  $a'_1$  B-H stretching mode,  $v_1$ ) is depicted in Fig. 7(a) while an active asymmetric oscillator (such as the  $a''_2$  umbrella mode,  $v_2$ ) is represented by Fig. 7(b).

Can we anticipate which  $BH_3$  vibrational modes will be active in the detachment of the ion? This is the heart of the three different assignments offered for peak **B** at the beginning of Sec. IV. We must decide if the detachment process excites the B-H stretch (A), an overtone of the umbrellalike mode (B), or some complicated coupling mode (C).

The symmetric stretch of BH<sub>3</sub> is the only  $a'_1$  mode in the molecule (see Fig. 6) and levels in this manifold can be accessed by detachment. This is assignment (A). One might be skeptical that  $v_1$  would be excited upon detachment since the scattered electron originates from an  $a''_2$  p-like orbital residing upon the boron atom [see Eq. (1)]. The electrons comprising the three B-H bonds are orthogonal to the active electron. Nevertheless, our *ab initio* geometries (Table IV) indicate that the bonds in the borane ion are greater than neutral borane by 0.018 Å:  $r_e$  (BH<sub>3</sub><sup>-</sup>) >  $r_e$  (BH<sub>3</sub>). Conse-



FIG. 7. Symmetry selection rules for Franck-Condon factors.

quently, we must carefully consider that feature **B** in our spectrum is simply excitation of v' = 1 of an harmonic mode,  $v_1$ .

The assumption that peak **B** is due to excitation in the symmetric stretch can now be modeled. We must calculate a value of the Franck-Condon integral, (4), for v' = 0, 1 with the  $Q_1$  the active mode. We use harmonic modes for both the ion and the neutral; consequently, the vibrational functions  $\Psi_v(Q_1)$  are eigenfunctions of a linear oscillator:

$$H_{\rm vib}(Q_1) \equiv \frac{1}{2} g_{11}^0 P_1^2 + \frac{1}{2} k_{11} Q_1^2 .$$
 (5)

In expression (5),  $Q_1$  is coordinate for the symmetric B-H stretch (Fig. 6), and  $k_{11}$  is the stretching force constant. The first term is the kinetic energy and depends upon the momentum operator  $P_1$  and the effective inverse mass expressed as an element of the G matrix,  $g_{11}^0$ . The form of the G matrix is discussed in Appendix B.

Under interpretation (A), our experimental spectra indicate that 2480 cm<sup>-1</sup> is  $\omega_1(Q_1)$  and we empirically choose  $k_{11}$  in Eq. (5) to reproduce this. This is not outrageously different from our *ab initio* results since it is within 7% of the calculated value, 2668 cm<sup>-1</sup> (Table IV). As we have no



FIG. 8. (a) BH<sub>3</sub><sup>-</sup> Franck–Condon simulation with harmonic  $\nu_1 = 1$ . (b) BD<sub>3</sub><sup>-</sup> Franck–Condon simulation with harmonic  $\nu_1 = 1$ .

experimental value for the frequency in the ion, it is approximated by the frequency in the neutral, 2480 cm<sup>-1</sup>. The *ab initio* calculations of these frequencies shown in Table IV show  $\omega_1$  to be similar for BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup>.

The Franck–Condon factors can be calculated in a variationally correct manner by diagonalizing Eq. (5) in a basis set of harmonic oscillator wave functions. Using experimental values for  $\omega_1$ , we find  $\Psi_0(Q_1)$  and  $\Psi_1(Q_1)$  and then numerically integrate Eq. (4). The Franck–Condon factors are then folded with an experimental line shape. This model uses Gaussians with a 35 meV FWHM for BH<sub>3</sub><sup>-</sup> and 30 meV for BD<sub>3</sub><sup>-</sup>. We are simply varying the difference in the B–H bond lengths ( $\delta r_{eq}$ ) in order to fit the experimental spectra. Our results are compared with the experimental spectra in Figs. 8(a) and 8(b). The best fit for  $\delta r_{eq}$  is 0.035 Å which allows spectra for both BH<sub>3</sub><sup>-</sup> and BD<sub>3</sub><sup>-</sup> to be reproduced. A change in the B–H bond length of 0.035 Å seems too long to be compatible with our *ab initio* findings in Table III ( $\delta r_{eq} = 0.019$  Å).

A much more plausible active mode would be the umbrella mode,  $v_2$  (see Fig. 6); this is the second interpretation, (B), for the **B** peak. Detachment of the electron [Eq. (1)] might give the boron atom a "kick" and lead to excitation of out-of-plane motion or an umbrella-like oscillation in the final BH<sub>3</sub>. Notice, however, that the  $v_2$  mode is not totally symmetric; consequently, the circumstances of Fig. 7(b) apply. However states of this mode with even number of quanta are totally symmetric and it is possible for the first overtone,  $2v_2$ , of the out-of-plane bending mode to be reached by detachment from the ground vibrational state of the BH<sub>3</sub><sup>-</sup> ion.

Hypothesis (B), that transition B is due to excitation in the out-of-plane bend, strongly suggests that either the BH<sub>3</sub> or  $BH_3^-$  is pyramidal. In light of earlier matrix infrared studies of BH<sub>3</sub> and *ab initio* results, we treat the  $BH_3^-$  ion as having a nonplanar geometry with a double minimum potential. The overtone of the out-of-plane bend is therefore excited. As in model (A), we assume that the neutral is harmonic and use the frequency from the experimental data. In this case, since we can only observe overtone excitation, we assume that the frequency of the fundamental is half that of the experimental splitting; consequently,  $2\omega_2 \equiv 2480 \text{ cm}^{-1}$ . Due to the minimal structure in our spectra the ion cannot be extremely far from planarity and hence the barrier to inversion cannot be large. A convenient form for an inversion potential is a quadratic oscillator perturbed by a quartic term:

$$H_{\rm vib}(Q_2) \equiv \frac{1}{2}g_{22}^0 P_2^2 + a_2 Q_2^2 + b_2 Q_2^4 . \tag{6}$$

If the two constants  $a_2$  and  $b_2$  are positive (as for BH<sub>3</sub>) the potential is planar with a single minimum at  $Q_2 = 0$ , but if  $a_2$  is negative, Eq. (6) has a double minimum. The constants are chosen to give a particular barrier height and position of minimum. The Franck–Condon factors which result are extraordinarily sensitive to the location of the minimum  $(\theta_{eq})$  while the shape of the potential has a lesser influence. Values for  $\theta_{eq}$  (which is defined in Table III) can then be varied and the corresponding Franck–Condon factors calculated until the area under peak **B** agrees with that of the experiment. This has been done for BH<sub>3</sub><sup>-</sup> and it was found

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that it was necessary to have an ion which was 7° bent out-ofplane with a barrier of  $100 \text{ cm}^{-1}$ . Using these constants for  $BH_3^-$  the corresponding spectra have been calculated for  $BD_3^-$ . The experimental fits are shown in Figs. 9(a) and 9(b).

Although the calculated spectra seem to be reasonable for both BH<sub>3</sub><sup>-</sup> and BD<sub>3</sub><sup>-</sup> (as shown by Fig. 9), one is somewhat anxious with interpretation (B). This naive view that feature **B** is just  $2\omega_2$  and  $\omega_2 = 1240$  cm<sup>-1</sup> does not permit the ion to be planar. This model requires that the BH<sub>3</sub><sup>-</sup> ion be slightly pyramidal with  $\theta_{eq} \cong 7^\circ$ . Our *ab initio* results contradict this and suggest that  $\theta_{eq} = 0^\circ$ ; likewise the isoelectronic neutral CH<sub>3</sub> is well known to be a  $D_{3h}$  species. The value for  $\omega_2$  which model (B) employs (1240 cm<sup>-1</sup>) is quite a bit different from the most recent experimental values (Table IV), 1125 and 1140.9 cm<sup>-1</sup>.

There is another model, which we refer to as interpretation (C), that is beguiling. Examination of the *ab initio*, harmonic frequencies in Table IV shows that there is nearly a resonance between  $\omega_1$  and  $2\omega_2$ ; for BH<sub>3</sub> the situation is  $2 \times 1223 \cong 2668 \text{ cm}^{-1}$ , while  $2 \times 954 \cong 1887 \text{ cm}^{-1}$  in the case of BD<sub>3</sub>. One suspects that there may be a strong mixing



FIG. 9. (a) BH<sub>3</sub><sup>-</sup> Franck-Condon simulation with harmonic  $v_2 = 2$ . (b) BD<sub>3</sub><sup>-</sup> Franck-Condon simulation with harmonic  $v_2 = 2$ .

between  $\omega_1$  and  $2\omega_2$ , i.e., a 2:1 Fermi resonance. The experimental feature **B** is then assigned as a mode resulting from this coupling.

This general picture closely parallels the analysis presented<sup>31</sup> to elucidate the fine structure found in the photoionization spectrum<sup>14</sup> of CH<sub>3</sub>. These spectra show considerably more structure than our photodetachment spectra due to vibrationally excited CH<sub>3</sub> and other obscuring species, such as CH<sub>3</sub>CH<sub>2</sub>, being present. However the features in the spectrum which can be identified as being due to detachment from the ground vibrational state of CH<sub>3</sub> have strong similarities with our spectra. They show an intense peak due to detachment from the ground vibrational state of  $CH_3$  to the ground vibrational state of  $CH_3^+$  with a smaller peak due to photoionization to an excited state of the ion. This was originally identified as being due to excitation in the overtone of the bending mode. However a subsequent theoretical study<sup>31</sup> of the process showed that detachment was taking place to a mixed state of the fundamental of the symmetric stretch and the overtone of the bending mode.

We would like to present an *ab initio* analysis based on a similar resonance to explain the features we find in the photodetachment spectra of  $BH_3^-$  and  $BD_3^-$ . To examine the influence of anharmonicity on the symmetric stretch  $(v_1)$  and the overtone of the bend  $(2v_2)$  and possible coupling between these two modes, a considerably more complex calculation was carried out. This has been done by computing an *ab initio* potential and then carrying out a variational calculation of the vibrational levels over this surface. The symmetry coordinates which describe the motion of the two vibrational degrees of freedom are defined as follows (see definitions for  $r_i$  and  $\theta_i$  in Table III):

$$S_1 = 3^{-1/2} (r_1 + r_2 + r_3) , \qquad (7a)$$

$$S_2 = 3^{-1/2} (\theta_1 + \theta_2 + \theta_3)$$
 (7b)

We have to solve a two-dimensional vibrational problem. Thus we seek solutions of the following Schrödinger equation:

$$[T_{\rm vib}(S_1,S_2) + V(S_1,S_2)]\Psi_v(S_1,S_2) = E_v\Psi_v(S_1,S_2).$$
(8)

In order to deal with Eq. (8), we must formulate the kinetic energy  $T_{vib}(S_1,S_2)$  in a useful manner and use our electronic structure programs to generate a realistic potential,  $V(S_1,S_2)$ .

The variables  $\{S\}$  are curvilinear coordinates and these simplify the calculation of the potential surface but complicate the kinetic energy. The correct form of the kinetic energy is more elaborate since the *G* matrix elements will not necessarily commute with the momentum operators.<sup>32</sup> Sibert *et al.*<sup>33</sup> have discussed this problem and they describe first order corrections to the kinetic energy as in Eq. (9):

$$T_{\text{vib}} \cong T^0 + T^1,$$
  

$$T^0 = \frac{1}{2} \sum_{ij=1}^{2} g_{ij}^0 p_i p_j,$$
  

$$T^1 = \frac{1}{2} \sum_{ijk=1}^{2} \left(\frac{\partial g_{ij}}{\partial S_k}\right)^0 p_i p_j S_k.$$
(9)

This expression resembles the zero order kinetic energy of the linear oscillator in Eq. (5) with a first order correction

featuring derivatives of the *i j*th G matrix element with respect to the k th coordinate,  $(\partial g_{ij}/\partial S_k)^0$ . The precise form of G matrix elements and their derivatives with respect to  $S_1$  and  $S_2$  is sketched in Appendix B.

In order to find  $V(S_1,S_2)$ , we must use GAUSSIAN 86 to generate the "stretch/umbrella" surface. The potential energy surface has been obtained as a grid of points in  $(S_1,S_2)$ space by an MP4 calculation with a 6-31G $(2d_xp)$  basis set. The grid consisted of 107 points from  $S_1 = 1.6$  to 2.8 bohr in steps of 0.1 bohr and from  $S_2 = 0$  to 35° in steps of 5° with a substantial number of cross variations. The upper and lower limits of this grid were chosen to include the limits of the Gaussian quadrature which was used. A further set of 118 terms which included steps in  $S_1$  of 0.05 bohr and in  $S_2$  of 2.5° were calculated to check the convergence of the calculation with respect to the grid. Including this further set changed the value of  $v_2 = 1$  by less than 1 cm<sup>-1</sup> and the calculation was considered to be converged with respect to the potential grid.

The basis set which was used to calculate the potential surface contains no diffuse functions but has two d orbitals on the boron atom and one p orbital on the hydrogen atoms. The minimum energy geometry of this calculation was a planar molecule with an  $r_{eq}$  of 1.188 Å. The points on this surface were used to calculate coefficients for an analytic representation of the following form:

$$V(S_1,S_2) = V^0 + V^1,$$
  

$$V^0 = a_2 S_1^2 + b_1 S_2^2,$$
  

$$V^1 = \sum_{i=3}^8 a_i S_1^i + \sum_{j=2}^4 b_j S_2^{2j} + \sum_{i=1}^6 \sum_{j=1}^3 c_{ij} S_1^i S_2^{2j}.$$
(10)

Only even powers of the coordinate  $S_2$  are present since it describes motion perpendicular to a plane of symmetry. A total of 29 coefficients were used and the maximum deviation of the *ab initio* potential from the fit,  $(V - V_{\rm fit})/V$ , was  $2 \times 10^{-4}$ . The coefficients which result from this process are collected together in Appendix C in Table VII.

The vibrational Hamiltonian has now been defined [Eq. (8)] and a variational calculation over a suitable basis will determine the energies  $E_v$  and wave functions of BH<sub>3</sub>,

 $\Psi_{n}(S_{1},S_{2})$ . We believe that a harmonic oscillator basis has a number of advantages. First, many of the matrix elements over momentum and position operators are available in analytic form. Second, in cases where numerical matrix elements are required highly efficient Gaussian-Hermite quadrature is available. In this work 16 point Gaussian-Hermite quadrature was used. Finally, if the basis is related to that of the harmonic vibrations then the wave functions will have a real physical meaning. It is this last advantage which makes a harmonic oscillator basis useful as a particular state can be labeled either as a bend or a stretch or a mixture thereof. The disadvantage is that as the system becomes more anharmonic, more computational effort is required. Simpler basis sets such as cubic splines do not suffer from this problem as they are not founded on the harmonic description. However in these calculations the determination of the potential (10) consumes by far the most computer time and the use of a harmonic oscillator basis is no computational liability.

The results of these calculations are shown in Table V. This shows the lowest three vibrational levels for three separate calculations. (a) The first entry shows the results using only the harmonic potential and kinetic terms  $(H_{\rm vib} = V^0 + T^0)$ , (b) the second set use potential coupling but no kinetic coupling  $(H_{vib} = V^0 + V^1 + T^0)$ , and (c) the third shows both kinetic and potential coupling  $(H_{\rm vib} = V^0 + V^1 + T^0 + T^1)$ . The last entry shows the measured diode laser absorption frequency. The first entry in Table V shows better agreement with experiment than is shown by the analytical Hartree-Fock values in Table IV. This is because the potential surface is superior to the Hartree-Fock surface which was used for Table IV. The potential coupling does not change this substantially but the kinetic coupling has a larger influence. The latter calculation produces a result, 1159  $cm^{-1}$ , which agrees with the laser diode value of 1141 cm<sup>-1</sup> within 2%.

To calculate Franck-Condon factors it is necessary to have knowledge of the potential of both the upper state (the neutral) and the lower state (the ion). The vibrational wave function for ground state BH<sub>3</sub><sup>-</sup>,  $v_1$  and  $v_2 = 0$ , has been obtained with a similar but less detailed calculation. The BH<sub>3</sub><sup>-</sup>

TABLE V. Ab initio variational frequencies  $(cm^{-1})$ . Vibrational energies calculated with two coupled modes,  $S_1$  and  $S_2$ . Different Hamiltonians are used to examine the importance of kinetic and potential coupling. The particular forms for the kinetic  $(T^0 \text{ and } T^1)$  and potential  $(V^0 \text{ and } V^1)$  operators are defined in Eqs. (9) and (10). All potentials calculated with a MP4 6-31G(2d,p) surface. The experimental value for the optical measurement is derived from Ref. 6.

Transition	$T^{o} + V^{o}$	$T^0 + V^0 + V^1$	$T^0 + T^1 + V^0 + V^1$	Optical
		BH <sub>3</sub>		
1°20	1181	1180	1159	1141
10 <sup>2</sup> 20	2363	2359	2289	
1 <mark>0</mark> 20	2630	2602	2607	
		BD,		
1021	921	920	908	
10 <sup>22</sup>	1842	1835	1762	•••
$1_0^1 2_0^0$	1859	1851	1884	

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potential was generated by an MP4 calculation using a 6-31 + G(d,p) basis set. This is not the same basis set as was used for the BH<sub>3</sub> vibrations. However, since we are not comparing total energies but only the shape of the potential around the minimum, this is not a problem. The coordinates  $S_1$  and  $S_2$  were not varied simultaneously and this greatly reduces the computational effort; since we only require the ground state, this was not considered a deficiency. The BH<sub>3</sub><sup>-</sup> potential was expanded in a form where terms which couple the symmetric stretch and the out-of-plane bend are not included:

$$V(S_1,S_2) = \sum_{i=2}^{8} a_i S_1^i + \sum_{j=1}^{4} b_j S_2^{2j}.$$
 (11)

The coefficients from this fit are given in Appendix C in Table VIII.

Franck-Condon factors for detachment from the ground vibrational state of the ion to a number of vibrational states of the neutral have been calculated. This has been done for the fully anharmonic  $BH_3$  wave functions, i.e., those with kinetic and potential coupling. These are shown in Table V



FIG. 10. (a) BH<sub>3</sub><sup>-</sup> Franck–Condon simulation with anharmonic  $v_1 = 1$  and  $v_2 = 2$ . (b) BD<sub>3</sub><sup>-</sup> Franck–Condon simulation with anharmonic  $v_1 = 1$  and  $v_2 = 2$ .

and Figs. 10(a) and 10(b). It can be seen that the agreement is quite reasonable.

## **V. DISCUSSION AND CONCLUSION**

We return to the question of the identity of peak **B** in the experimental photoelectron spectrum. Does the detachment process excite (A) the symmetric B-H stretch  $(v_1)$ , (B) an overtone of the umbrella-like mode  $(2v_2)$ , or (C) some complicated coupling mode? We are inclined to favor assignment (C).

The Franck–Condon factors of the previous section show that both assignments (A) and (B) can reproduce our experimental findings (Figs. 8 and 9). Both of these assignments rely on empirical fits to the data; we always choose the frequencies of the active modes to fit our data [viz.  $\omega_1$  in case (A) and  $2\omega_2$  for (B)]. To force a fit to the experimental data, we must have  $\delta r_{eq}$  of 0.035 Å for case (A) while interpretation (B) insists on a nonplanar BH<sub>3</sub><sup>-</sup> ion with  $\delta\theta = 7^{\circ}$ . Both (A) and (B) geometry changes contradict our *ab initio* calculations and are at variance with the experimental facts for the isoelectronic species, CH<sub>3</sub>.

The third set of Franck-Condon factors, corresponding to interpretation (C), have been obtained from a totally ab initio calculation. A variational calculation of a coupled oscillator basis over a high quality potential energy surface has produced vibrational wave functions from which Franck-Condon factors have been extracted. Thus these Franck-Condon factors have no adjustable parameters; Figs. 10(a) and 10(b) suggest that there is a close match with the experimental detachment spectra. These Franck-Condon factors show that excitation is going into both  $v_1 = 1$  and  $v_2 = 2$  and that these levels are in fact mixed by a 2:1 Fermi resonance. In the BH<sub>3</sub><sup>-</sup> spectrum peak **B** is thus broadened since  $v_1 = 1$ and  $v_2 = 2$  are split by over 300 cm<sup>-1</sup>. For the case of BD<sub>3</sub><sup>-1</sup> peak B is not so broadened since the two levels fall within 120  $cm^{-1}$  of each other. The deficiency of these Franck-Condon factors is that the area under these peaks is somewhat lower than in the experiments. However the accuracy of these variational calculations is shown by the good agreement of the fundamental of  $v_2$  with experiment: 1159 cm<sup>-1</sup> calculated vs the laser diode value of 1141 cm<sup>-1</sup>.

The *ab initio* Franck-Condon factors show the best agreement with the experiment and we conclude that detachment is taking place to a pair of states which are mixed by a 2:1 Fermi resonance. We believe that both BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> are planar species. None of the models considered here admit the BH<sub>3</sub><sup>-</sup> ion to be pyramidal by more than  $\theta_0 = 7^\circ$ .

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TABLE VI. G matrix elements and derivatives.<sup>a</sup>

	General	Equilibrium
<b>g</b> <sub>s1 s1</sub>	$\mu_{\rm H} + 3\mu_{\rm B}\cos^2(\Theta)$	
<b>8</b> 5152	$-3\sin(2\Theta)\mu_{\rm B}/2R$	0
<b>g</b> <sub>s2s2</sub>	$[\mu_{\rm H} + 3\mu_{\rm B} \sin^2(\Theta)]/R^2$	$(\mu_{\rm H} + \mu_{\rm B})/r_{\rm eq}^2$
$\partial g_{s1s2} / \partial s2$	• • •	$\mu_{\rm B}/r_{\rm eq}$
$\partial g_{s2s2}/\partial s1$	•••	$-2(\mu_{\rm H}+3\mu_{\rm B})/r_{\rm eq}^{3}$

<sup>a</sup> All entries calculated for an AB<sub>3</sub> molecule of a minimum symmetry of  $C_{3\nu}$ . The symmetry coordinates are defined as in Table III. The variables are defined in analogy with those of Ref. 39;  $\mu_a = 1/m_a$  and  $S_1 = (r_1 + r_2 + r_3)/\sqrt{3}$  while  $S_2 = (\theta_1 + \theta_2 + \theta_3)/\sqrt{3}$  and the bond lengths/bond angles are  $r_1 = r_2 = r_3 = (R - r_{eq})$  and  $\theta_1 = \theta_2 = \theta_3 = (\Theta - \pi/2)$ .

## APPENDIX A: SYNTHESIS OF BH<sub>3</sub>CO

Borane carbonyl (BH<sub>3</sub>CO) was prepared<sup>34</sup> by mixing 10 psi of B<sub>2</sub>H<sub>6</sub> with 100 psi of CO in a stainless steel lecture bottle and heating to 90 °C for 30 min; diborane is in equilibrium with borane monomer and the large excess of CO allows appreciable formation of the BH<sub>3</sub>CO adduct. To separate BH<sub>3</sub>CO from the starting materials (B<sub>2</sub>H<sub>6</sub> and CO),<sup>35</sup> the contents of the lecture bottle were cooled to liquid nitrogen temperature and the carbon monoxide pumped off. The remaining volatile material was transferred to a U-tube trap held at -196 °C. While this trap was slowly warmed with a methylcyclohexane/liquid nitrogen slush at -125 °C, the reaction products were pumped through two more traps, one at -155 °C (isopentane/liquid nitrogen slush) to trap the borane carbonyl, and one at -196 °C to trap the excess diborane. Diborane was prepared<sup>36</sup> by condensing 1 part BF<sub>3</sub> (Scientific Gas Products) into 2 parts NaBH<sub>4</sub> or NaBD<sub>4</sub> (Aldrich) and allowing the mixture to stir for 24 h. The identity of both  $BH_3CO$  and  $B_2H_6$  was established by their infrared spectra.37,38

## **APPENDIX B: COORDINATES OF VIBRATIONS**

The calculations of vibrational frequencies which are reported in this paper have used two coordinates. One describes the symmetric stretching motion of the BH<sub>3</sub> and BH<sub>3</sub><sup>-</sup> species and the other describes their out-of-plane bending (umbrella) motion. Since these are the only motions away from the equilibrium geometry which are consid-

TABLE VIII. Potential parameters of BH3-.ª

a2	1.1871( - 1)	<i>b</i> <sub>1</sub>	5.4537(-2)
$a_3$	-6.0119(-2)	<i>b</i> <sub>2</sub>	4.3285(-1)
$a_{A}$	2.1157(-2)	<b>b</b> <sub>3</sub>	- 9.1469( - 1)
a.	-5.1221(-3)	<i>b</i> <sub>4</sub>	1.0532
$a_6$	-1.0518(-3)		
a7	6.4054( - 4)		
$a_8$	1.7213(-3)		

<sup>a</sup> All units are atomic units. The potential is defined in Eq. (11).  $A(B) = A \times 10^{B}$ .

ered, it is implicit that the molecules always have a minimum of  $C_{3v}$  symmetry. Consequently, the B-H bond lengths are always equal; likewise the three angles which the B-H bonds make with the threefold axis of symmetry are also equal to each other. As given in Eq. (7) the two symmetry coordinates  $S_1$  and  $S_2$ , which describe these vibrations, are defined as follows<sup>39</sup>:

$$S_1 = 3^{-1/2}(r_1 + r_2 + r_3)$$
, (B1a)

$$S_2 = 3^{-1/2} (\theta_1 + \theta_2 + \theta_3)$$
. (B1b)

The figure in Table III describes  $r_i$  as the change in the *i*th bond length from its equilibrium value while  $\theta_i$  is the change in the angle which the *i*th bond makes with the threefold axis of symmetry from its equilibrium value. Table VI lists the inverse masses or G matrix elements together with the nonzero derivatives which are necessary for the variational calculation of the vibrational energy levels. In Table VI, R refers to the length of the B-H bonds and not its change from equilibrium; similarly  $\Theta$  refers to the angle between the B-H bonds, not its change from equilibrium. Thus for a planar species  $\Theta = \pi/2$ . Finally in our paper when we report the planarity of any species we use  $\theta$  which we define to be the complement of  $\Theta$ :

$$\theta \equiv \Theta - \pi/2$$
 (B2)

This is the angle which is implied when any reference is made to the out-of-plane angle. Thus for a planar species the outof-plane angle  $\theta$  is zero.

#### APPENDIX C: VIBRATIONAL POTENTIALS

The data for the potentials which were used in the vibrational Hamiltonians are given in Table VII for neutral BH<sub>3</sub>

TABLE VII. BH<sub>3</sub> potential parameters.<sup>a</sup>

<i>a</i> <sub>2</sub>	1.3189(-1)	<i>b</i> <sub>1</sub>	3.1547(-1)	<i>c</i> <sub>11</sub>	- 5.5967( - 2)	<i>c</i> <sub>41</sub>	2.2376(-4)
$a_3$	- 6.5557( - 2)	$b_2$	1.2622(-2)	$c_{12}$	- 5.7222(-3)	$c_{42}$	- 1.1435( - 2)
$a_4$	2.1449(-2)	$b_3$	4.4995( - 2)	<i>c</i> <sub>13</sub>	2.2579(-2)	C43	3.0864(-2)
a.	-6.1549(-3)	$b_{4}$	-2.8027(-2)	$c_{21}$	-7.6668(-3)	C51	-9.2534(-3)
a,	1.7556(-3)			c22	1.0120(-2)	C57	8.0496(-3)
a,	-5.5312(-4)			C23	-4.3346(-2)	C53	-2.5407(-2)
a,	1.1801(-4)			C 11	2.1229(-3)	C61	4.5576(-3)
0				C 17	-1.7661(-3)	C67	-7.0760(-4)
				C 3 3	2.0785(-2)	C63	1.3620(-3)
				35		05	

<sup>a</sup> All units are atomic units. The potential is defined in Eq. (10).  $A(B) = A \times 10^{B}$ .

and in Table VIII for the anion  $BH_3^-$ . All the units in these tables are atomic units.

- <sup>1</sup>F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1962).
- <sup>2</sup>W. S. Koski, Adv. Chem. Ser. **32**, 78 (1961); M. Hillman, D. J. Mangold, and J. H. Norman, *ibid*. **32**, 151 (1961).
- <sup>3</sup>J. H. Wilson and H. A. McGee Jr., J. Chem. Phys. 46, 1444 (1967).
- <sup>4</sup>O. Herstad, G. A. Pressley, Jr., and F. E. Stafford, J. Phys. Chem. 74, 874
- (1970).
- <sup>5</sup>A. Kaldor and R. F. Porter, J. Am. Chem. Soc. 93, 2140 (1971).
- <sup>6</sup>K. Kawaguchi, J. E. Butler, C. Yamada, S. H. Bauer, T. Minowa, H. Kanamori, and E. Hirota, J. Chem. Phys. 87, 2438 (1987).
- <sup>7</sup>R. C. Catton, M. C. R. Symons, and H. W. Wardale, J. Chem. Soc. A **1969**, 2622.
- <sup>8</sup>E. D. Sprague and F. Williams, Mol. Phys. 20, 375 (1971).
- <sup>9</sup>J. R. M. Giles and B. P. Roberts, J. Chem. Soc. Perkin Trans. 2 1983, 743.
- <sup>10</sup>R. D. Mead, A. E. Stevens, and W. C. Lineberger, in *Gas Phase Ion Chem-istry*, edited by M. T. Bowers (Academic, London, 1984), Vol. 3, Chap. 22.
- <sup>11</sup>M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, J. Phys. Chem. Ref. Data 8, 631 (1979).
- <sup>12</sup>H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 14, 731 (1985).
- <sup>13</sup>T. Koenig, T. Balle, and W. Snell, J. Am. Chem. Soc. 97, 662 (1975).
- <sup>14</sup>J. Dyke, N. Jonathan, E. Lee, and A. Morris, J. Chem. Soc. Faraday Trans. 2 72, 1385 (1976).
- <sup>15</sup>G. Herzberg, Proc. R. Soc. London Ser. A 262, 291 (1961).
- <sup>16</sup>The electron affinity of the amino radical has been measured a number of times: R. J. Celotta, R. A. Bennett, and J. L. Hall, J. Chem. Phys. **60**, 1740 (1974) find EA(NH<sub>2</sub>) = 0.779  $\pm$  0.037 eV while K. C. Smyth and J. L. Brauman, J. Chem. Phys. **56**, 4620 (1972) report EA(NH<sub>2</sub>) = 0.744  $\pm$  0.022 eV. To remove the experimental discrepancy between these values, this binding energy was remeasured and EA(NH<sub>2</sub>) = 0.772  $\pm$  0.005 eV. An account of these studies will be published by C. T. Wickham-Jones, K. M. Ervin, and W. C. Lineberger and this more precise number, 0.772  $\pm$  0.005 eV, is the value we have used in these experiments.
- <sup>17</sup>H. B. Ellis Jr., Ph.D. thesis, University of Colorado, 1983; H. B. Ellis, Jr. and G. B. Ellison, J. Chem. Phys. **78**, 6541 (1983).
- <sup>18</sup>S. Moran, Ph.D. thesis, University of Colorado, 1988.

- <sup>19</sup>R. D. Srivastava, O. M. Uy, and M. Farber, Trans. Faraday Soc. 67, 2941 (1971).
- <sup>20</sup>P. C. Engelking, J. Phys. Chem. 90, 4544 (1986).
- <sup>21</sup>B. Ruscic, C. A. Mayhew, and J. Berkowitz, J. Chem. Phys. 88, 5580 (1988).
- <sup>22</sup>JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. Ref. Data Vol. 14, Supplement No. 1 (American Chemical Society, Washington, D.C., 1985).
- <sup>23</sup>E. Fermi, Z. Phys. **71**, 250 (1931); D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).
- <sup>24</sup>GAUSSIAN 86, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, S. Topiol, and J. A. Pople, Carnegie-Mellon Quantum Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213.
- <sup>25</sup>T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, J. Comp. Chem. 4, 294 (1983).
- <sup>26</sup>C. Yamada, E. Hirota, and K. Kawaguchi, J. Chem. Phys. **75**, 5256 (1981).
- <sup>27</sup>G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1945).
- <sup>28</sup>D. J. DeFrees and A. D. Maclean, J. Chem. Phys. 82, 337 (1985).
- <sup>29</sup>B. A. Hess, Jr., L. J. Schaad, P. Carsky, and R. Zahradnik, Chem. Rev. 86, 709 (1986).
- <sup>30</sup>G. Herzberg, Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1966).
- <sup>31</sup>P. Botschwina, J. Flesch, and W. Meyer, Chem. Phys. 74, 321 (1983).
- <sup>32</sup>P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, London, 1979), p. 121.
- <sup>33</sup>E. L. Sibert III, J. T. Hynes, and W. P. Reinhardt, J. Phys. Chem. **87**, 2032 (1983).
- <sup>34</sup>T. P. Fehlner and G. W. Mappes, J. Phys. Chem. 73, 873 (1969).
- <sup>35</sup>S. H. Bauer, G. Herzberg, and J. W. C. Johns, J. Mol. Spectrosc. 13, 256 (1964).
- <sup>36</sup>M. A. Toft, J. B. Leach, F. L. Himspl, and S. G. Shore, Inorg. Chem. 21, 1952 (1982).
- <sup>37</sup>T. Shimanouchi, J. Phys. Chem. Ref. Data 6, 993 (1977).
- <sup>38</sup>T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. 39 (U.S. GPO, Washington, D.C., 1972), Vol. 1.
- <sup>39</sup>E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (Dover, New York, 1955).