

Ab Initio Investigation of the Hyperfine Structure in the $1^2\Pi_u(X^2A_1, A^2B_1)$ System of BH_2

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The results of pure ab initio calculations of the hyperfine coupling constants for the vibronic levels of the $1^2\Pi_u(X^2A_1, A^2B_1)$ system of the BH_2 molecule are presented. Computations are performed for various isotopomers of BH_2 in the energy range 0–15 000 cm^{-1} . The study shows that even for the lowest vibronic states reliable hfcc's can be obtained only if the nuclear motion is taken into account. Comparisons with NH_2 and CH_2^+ are made. © 1994 Academic Press, Inc.

1. INTRODUCTION

The BH_2 radical represents the smallest triatomic molecule whose electronic spectrum has been analyzed thus far (1, 2). Because BH_2 has only seven electrons it should be expected that the results of ab initio calculations for this species would be in very good agreement with their experimental counterparts. However, the early theoretical studies (3–7) have not been able to explain the structure of the BH_2 spectrum. Only by taking into account the vibronic coupling in the $X^2A_1-A^2B_1(1^2\Pi_u)$ system (Renner-Teller effect) (8, 9) has it been possible to interpret unambiguously the observed spectrum. On the basis of the ab initio studies (8, 9) a reassignment of the progressions reported in Ref. (1) has been proposed. Very recently, a very extensive theoretical study on BH_2 was published by Brommer *et al.* (10). An AO basis involving *s*, *p*, *d*, *f*, and *g* species on B and *s*, *p*, *d*, and *f* on H (140 Gaussian groups) was used and the complete three-dimensional potential surfaces for the two lowest lying electronic states were computed by the complete active space self-consistent field (CASSCF) method. About a hundred CSF's for both symmetries in question (A' and A'' of the C_s point group) were employed as the reference species in the MRCI calculations. The rovibronic levels were computed by a fully coupled variational approach. While confirming the reassignment proposed in the previous, much simpler theoretical work (8), the results of this benchmark study improved the quantitative agreement between the calculated and the observed vibronic band positions.

The present paper is devoted to the theoretical analysis of the hyperfine structure in the $X^2A_1-A^2B_1$ system of BH_2 observed recently in an ESR experimental study (11). With this work we continue our investigation of the interplay between the hyperfine and the vibronic couplings previously performed on a number of such similar species as C_2H (12, 13), NH_2 (14, 15), and CH_2^+ (16). Thus we want to go beyond the framework of, to our knowledge, the only ab initio studies concerning the hyperfine structure of the BH_2 spectrum (11, 17) in which the electronic mean values of the hyperfine coupling constants (hfcc's) were published.

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2. TECHNICAL DETAILS

The isotropic and anisotropic hfcc's describe the interaction between a nuclear spin \mathbf{I} and the electron spin \mathbf{S} . They are determined by the net unpaired electron-spin density at the position of the given nucleus and the spatial distribution of the electron-spin density. The isotropic hfcc, A_{iso} , being the proportionality factor between the scalar product $\mathbf{I} \cdot \mathbf{S}$ and the corresponding part of the Hamiltonian (see, for example, Ref. (18)) is defined for a nucleus N as

$$A_{\text{iso}}^N = \frac{8}{3} \pi g_N g \beta_N \beta_e \frac{1}{S} \langle \Psi | \sum_k \delta(r_{kN}) s_{ak} | \Psi \rangle, \quad (1)$$

where β_N and g_N are the nuclear magneton and nuclear g factor, respectively. The term g is the g value for the electrons in the free radical, while β_e is the Bohr magneton. In the present work, a value of 2.0 is used for g . The sum on the right-hand side of Eq. (1) runs over all electrons of the molecule; $\delta(r_{kN})$ indicates that only the spin density at the position of the nucleus under consideration is taken into account. In a normal definition of A_{iso} the spin part is given as s_{zk} ; here the abbreviation s_{ak} is taken to show that we use the I' representation (19) ($x \leftrightarrow b$ $y \leftrightarrow c$ $z \leftrightarrow a$). This is important for comparing the calculated elements of the anisotropic hyperfine tensor with experimental data (20). Ψ generally represents the total molecular wavefunction.

The anisotropic part of the hf operator for the atom N is represented by a traceless tensor whose Cartesian coordinates with respect to a molecule-fixed frame are given by

$$A_{ij}^N = g_N g \beta_N \beta_e \frac{1}{S} \left\langle \Psi | \sum_{n=1}^n \left(\frac{3ij - r^2 \delta_{ij}}{r^5} \right)_{kNS_{ak}} | \Psi \right\rangle, \quad (2)$$

with $i, j = a, b, c$, again using the I' representation (see above).

In the present study, the interpretation in the expressions (1) and (2) is preformed in two steps. The total wavefunctions Ψ is represented by

$$\Psi = \psi^{A_1} \Phi^{A_1} + \psi^{B_1} \Phi^{B_1}, \quad (3)$$

where ψ^{A_1} and ψ^{B_1} are the electronic wavefunctions for the states X^2A_1 and A^2B_1 , respectively, computed in the framework of the Born–Oppenheimer approximation, and Φ^{A_1} and Φ^{B_1} are the corresponding rovibrational functions. Thus the electronic mean values of A_{iso} and A_{ij} , corresponding to the expressions obtained from (1) and (2) upon replacing the total wavefunction Ψ by the electronic species ψ^{A_1} , ψ^{B_1} , are first calculated as functions of the molecular geometry. We call these quantities “electronic hfcc’s.” These functions are then integrated over the rovibrational coordinates, resulting in “vibronic hfcc’s.”

The atomic orbital (AO) basis employed in the present study for the boron atom consists of the (13s, 8p) Gaussians in the [8s, 5p] contraction as proposed by van Duijnefeldt (21); it is augmented by three d functions with exponents $\alpha_d = 1.110$, 0.405, and 0.145 (22) for a better description of the polarization effects, as well as by two additional d species ($\alpha_d = 8.0, 0.1$) which are known to improve the computation of the isotropic hfcc (23, 24). For the hydrogen centers the (9s) set of van Duijnefeldt (21) in a [7s] contraction is augmented by one s function [$\alpha_s = 0.01$] and three p functions ($\alpha_p = 1.848, 0.649$, and 0.228) (22). To both basis sets an s function with a very high exponent ($\alpha_B = 166801$, $\alpha_H = 8510.53$) was added, because it was found that such functions improve the description of isotropic hfcc's of electronic states

possessing σ character. Thus, the AO basis set consists of 90 Gaussian groups and is therefore appreciably smaller than that employed by Brommer *et al.* (10). It has been shown, however, that the addition of higher order functions (particularly f species) does not influence significantly either the description of the two lowest lying electronic states of BH₂ or the calculation of hfcc's (23).

All calculations are performed within the C_{2v} point group. The electronic mean values of the isotropic hfcc and the electronic Cartesian components of the anisotropic hyperfine tensor are computed employing the multireference single and double excitation configuration interaction (MRD-CI) method (25) in connection with a modified B_K correction (26). In these calculations all electrons are correlated and no virtual orbitals are discarded. Approximate natural orbitals (NO's) for both of the electronic states in question are used as the one-electron basis. Twenty-six reference species for the X^2A_1 state and 16 for A^2B_1 state are employed. Their contribution (sum of squared coefficients) to the final CI wavefunctions varies between 97 and 98%. The dimension of the CI spaces generated by single and double excitations with respect to them are roughly one million and the number of the symmetry-adapted functions selected according to an energy-lowering criterion (threshold $T = 0.1 \mu\text{Hartree}$) is between 17 000 and 23 000 depending on the molecular geometry. In the framework of the B_K treatment all coefficients in the CI expansion with magnitude greater than 0.01 (roughly 400) as well as those of configurations generated by single excitations from the leading reference configuration are corrected. The calculations are performed with the B-H bond distances kept fixed at 2.211 Bohr and bond angle values of 180, 160, 140, 131, 120, 100, 80, and 60°. To estimate the influence of the symmetric stretch vibration for the bond angle of 131° three different B-H distances were calculated (see below).

The approach employed for computation of the vibronic hfcc's has been described in detail elsewhere (15). The Hamiltonian derived by Bunker and co-workers (27, 28), allowing for treatment of the large-amplitude bending vibrations and incorporating (if necessary) the leading part of the bend-stretch interaction, is adjusted to the problem of two electronic states coupled via the Renner-Teller effect (29, 30). It is assumed that the stretching vibrations, as well as the rotations around the axes orthogonal to the smallest moment of inertia axis a , can be separated. The projection of the total angular momentum (excluding spin) onto the a axis, coinciding at the linear molecular geometry with the molecular axis, is assumed to be conserved; the corresponding quantum number is denoted by K . The remaining *degrees* of freedom (electronic motion, bending, and a axis rotation) are treated simultaneously. In the present study, we neglect the effect arising from spin-orbit coupling, because it can be assumed that it will influence the hfcc's only to a very small extent, as found for the CH₂ molecule (16). The corresponding Schrödinger equation is solved variationally, with the vibronic wavefunctions represented by expansions in the eigenfunctions of a two-dimensional harmonic oscillator. The vibronic hfcc's are computed as integrals over the vibronic wavefunctions. The nonvanishing vibronic matrix elements involving the components of the hf tensor correspond to the selection rules

$$\langle K | A_{\text{iso}} | K \rangle \quad (4a)$$

$$\langle K | A_{aa} | K \rangle = -\langle K | A_{bb} + A_{cc} | K \rangle \quad (4b)$$

$$\langle K | A_{ab} \pm iA_{ac} | K \pm 1 \rangle \quad (4c)$$

$$\langle K | A_{bb} - A_{cc} \pm 2iA_{bc} | K \pm 2 \rangle, \quad (4d)$$

where A_{iso} , A_{aa} , etc., denote electronic hfcc's. The relation (4b) holds because the anisotropic part of the hf Hamiltonian represents a traceless tensor. In the present study, we neglect the term $A_{bc}(\epsilon B_1)$, which has a nonvanishing value between 2B_1 and 2A_1 electronic wavefunctions for both B and H atoms, as well as $A_{ac}(\epsilon A'')$ for the H atoms connecting the states ${}^2A'$ and ${}^2A''$ which correlate in the lower C_s point group to 2A_1 and 2B_1 of C_{2v} , respectively. These neglected terms connecting vibronic states with energy differences of generally at least several hundred cm^{-1} are expected to have nonsignificant effects on the hyperfine structure of the spectra. The terms $A_{ac}(\epsilon A_2)$ and $A_{ab}(\epsilon B_2)$ for the boron atom vanish by symmetry.

In the present study, we calculate only those vibronic hfcc's which can be extracted from experimental findings, i.e., the diagonal (in v and K) matrix elements (4a) and (4b) and the off-diagonal elements (4d) between the vibronic states v , $K = -1$ and v , $K = +1$ which are degenerate in the framework of the approximation assumed (no K -doubling). The latter quantities are formally computed as the diagonal $\langle K = 1 \parallel K = 1 \rangle$ matrix elements of the $A_{bb}-A_{cc}$ linear combination in the 2A_1 and $A_{cc}-A_{bb}$ in the 2B_1 state as explained in detail in Ref. (15).

3. RESULTS AND DISCUSSION

The bending potential curves for the X^2A_1 and A^2B_1 states computed in the present study at a B-H distance kept fixed at 2.211 Bohr are displayed in Fig. 1. They are

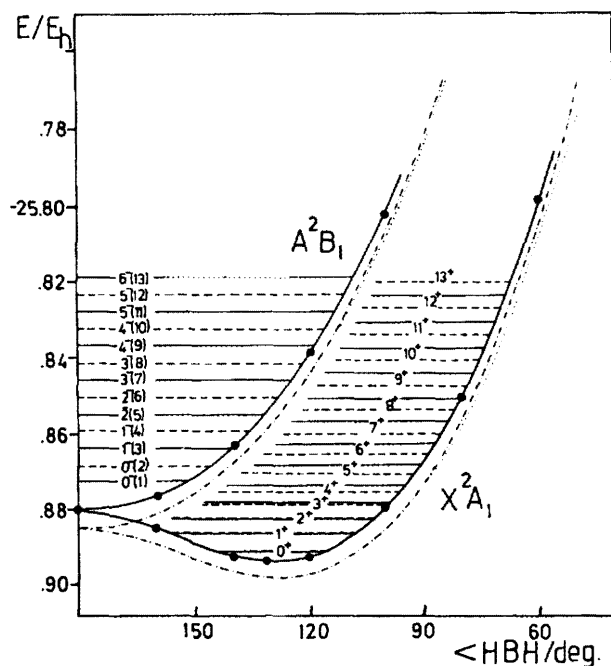


FIG. 1. Bending potentials for the X^2A_1 and A^2B_1 electronic states of BH_2 . The points denote the energy values computed in the present study at the B-H bond length kept fixed at 2.211 Bohr. Dashed-dotted line, Bending potentials corresponding to the same B-H bond length, calculated by Brommer *et al.* (10); dotted line, effective bending potentials by Brommer *et al.* corresponding to the optimized bond lengths. Positions of the $K = 0$ (full lines) and $K = 1$ (dashed lines) vibronic levels are indicated. The levels belonging predominantly to the X^2A_1 electronic state are assigned by v_2^{vib} , and those of the A^2B_1 state by both v_2^{vib} and v_2^{vib} (in parentheses).

very similar to those published in our previous work (8), where a slightly different AO basis set and CI treatment were employed. For comparison, the bending curves corresponding to the same bond length value published by Brommer *et al.* (10) are presented, too. The latter ones, generated in computations in which an appreciably larger AO basis (140 AO's compared to the 85 in the present study), and a much larger-scale CI treatment was employed, are lower by about 0.0045 Hartree, but their shapes differ insignificantly from those of the present work, the relative differences in the whole range of bond angles considered ($180 < \text{HBO} < 60$ degree) being less than 0.01 eV. Effective bending curves, corresponding to optimized B–H bond lengths, computed employing the expansion coefficients given in Ref. (10) are also shown. It can be seen that relaxation of the bond length upon bending has as a consequence only a slight change in the bending potential curves.

The positions of the $K = 0$ and $K = 1$ vibronic levels computed in the present study are also indicated in Fig. 1. The corresponding numbers are given in Table I, together with those published by Brommer *et al.* Since the form of the bending potentials is, as stated above, practically identical, the differences between both sets of results should be ascribed to different vibrational treatments. While Brommer *et al.* (10) carried out full three-dimensional calculations, our approach is based on the use of the essentially one-dimensional semi-rigid bender model by Bunker and Landsberg (28) which enables only an indirect account of the bend–stretch coupling. A consequence of this is that the differences in positions of the corresponding levels become continuously larger with increasing v_2 quantum number (particularly for the levels belonging to the X^2A_1 electronic state), reaching roughly 500 cm^{-1} in the energy region at about $15\,000 \text{ cm}^{-1}$ (with respect to the lowest vibronic level). This is in accordance with our experience applying the present approach to similar systems; for a detailed analysis see Refs. (29, 30).

The symmetric stretching potential curve, corresponding to the bond angle value of 131° , computed in the present study is compared in Fig. 2 with the corresponding one constructed employing the data published in Ref. (10). The agreement is again very good. The position of the lowest two stretching levels is indicated. The dependence of the isotropic hfcc's on a variation of the B–H distance is also given in Fig. 2.

The electronic hfcc's for ^{11}B and ^1H are displayed as functions of the bond angle value in Figs. 3–5. Besides the Cartesian components of the anisotropic hf tensor, the irreducible component $A_{bb}-A_{cc}$ (Eq. (4d)) is also presented. All results correspond to the B_K corrected wavefunctions. The forms of the curves given in Figs. 3–5 are very similar to those of the isoelectronic ion CH_2^+ (16). It can be noted that the absolute values for the electronic hfcc's of boron are roughly smaller than for the carbon atom in CH_2^+ by a factor of two. The difference in the spin density in both molecules is even larger because the g_N value of ^{13}C is smaller than the g_N value of ^{11}B (6728.0 rad/G sec vs 8584.1 rad/G sec). As already found for analogous systems (NH_2 (14, 15), H_2O^+ (28), CH_2^+ (16)), the bond angle dependence of the electronic hfcc's for the 2A_1 state is generally much stronger than that of their 2B_1 counterparts. This is a direct consequence of the fact that the $2b_1$ orbital, singly occupied in the 2B_1 state, is predominantly built of the out of plane p_x orbital of the boron atom, and thus does not change appreciably upon bending. On the other hand, the $3a_1$ orbital (partially populated in the 2A_1 state) is of π character at the linear molecular geometry and gains continuously more from the σ character upon bending. Particularly dramatic is the change of the value for A_{iso} of the hydrogen atom in the X^2A_1 state by bending, accompanied with reversing of the sign not far from the equilibrium geometry of this

TABLE I
Results of Calculations of the Vibronic Energy Levels and Vibronic Mean Values for the Hyperfine Coupling Constants in the $1^2\Pi_u(X^2A_1, A^2B_1)$ System of $^{11}\text{BH}_2$ and a Comparison to the Vibronic Energies Computed by Brommer *et al.* (10)

v_2	K=0						v_2	K=1							
	Energy [cm ⁻¹]		¹¹ B		H			Energy [cm ⁻¹]		¹¹ B		H			
	present work	Brommer et al.	A_{100} (MHz)	A_{00} (MHz)	A_{100} (MHz)	A_{00} (MHz)		present work	Brommer et al.	A_{100} (MHz)	A_{00} (MHz)	$A_{100}-A_{00}$ (MHz)	A_{100} (MHz)	A_{00} (MHz)	$A_{100}-A_{00}$ (MHz)
0*	0	0	341.30	-40.7	32.766	15.5	0*	43	47	343.57	-40.6	126	33.364	15.4	27.0
1*	991	986	319	-41.2	21.8	15.7	1*	1046	1044	321	-41.2	128	22.3	15.7	27.8
2*	1942	1930	305	-41.6	12.5	15.9	2*	1974	1977	285	-42.1	131	5.33	16.2	28.8
3*	2910	2879	310	-41.5	10.2	15.7	3*(0)	2740	2765	236	-43.5	135	-16.3	16.9	30.0
4*	3957	3888	330	-40.9	13.0	15.2	4*	3520	3485	283	-42.2	132	-2.51	16.0	29.4
0(1)	4108	4216	62.4	-48.1	-80.8	18.5	5*	4523	4422	320	-41.2	129	7.19	15.2	28.9
5*	5098	4975	354	-40.3	16.6	14.7	0(2)	5011	5097	91.0	-47.3	147	-71.6	17.5	31.3
1(3)	6054	6115	64.9	-48.0	-81.5	17.0	6*	5729	5599	354	-40.3	127	14.3	14.6	28.7
6*	6324	6124	376	-39.7	19.7	14.2	7*	6899	7091	236	-43.4	136	-26.9	15.0	29.3
7*	7662	7302	396	-39.1	22.1	13.8	1(4)	7066	7023	220	-43.8	138	-32.9	15.1	29.4
2(5)	8007	8006	67.5	-47.9	-82.2	15.4	8*	8303	7952	400	-39.0	124	21.3	13.6	28.7
8*	8981	8749	415	-38.6	24.2	13.3	2(6)	8957	8927	77.9	-47.5	149	-79.6	14.7	28.6
3(7)	9968	9890	69.9	-47.7	-82.9	14.0	9*	9695	9429	419	-38.4	122	23.6	13.1	28.8
9*	10392	10165	432	-38.0	26.1	12.9	3(8)	10912	10780	101	-46.9	148	-74.1	13.2	27.3
10*	11849	11490	448	-37.5	27.8	12.5	10*	11142	10879	412	-38.5	123	18.3	12.7	28.9
4(9)	11937	11768	72.4	-47.6	-83.6	12.6	11*	12594	12226	443	-37.5	121	25.2	12.2	29.1
11*	13345	12900	462	-36.9	29.5	12.1	4(10)	12914	12702	86.5	-47.2	150	-80.2	11.9	25.9
5(11)	13917	13640	74.7	-47.5	-84.4	11.2	12*	14115	13609	467	-36.8	119	29.5	11.9	29.4
12*	14876	14299	47.6	-36.4	31.1	11.7	5(12)	14893	14566	80.1	-47.3	151	-83.5	10.6	24.5
6(13)	15906	15507	77.0	-47.4	-85.1	9.96	13*	15664	15021	481	-36.2	118	31.0	11.5	29.6

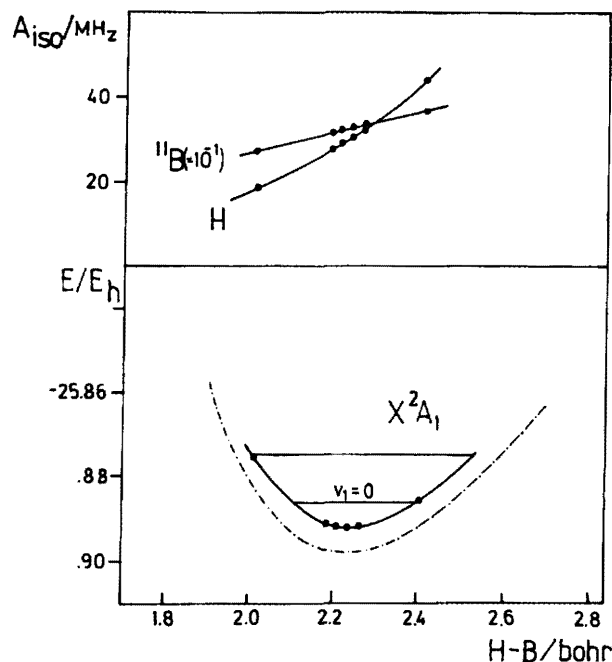


FIG. 2. (Bottom) Stretching potential curve for the X^2A_1 state computed at the bond angle of 131° . Position of the two lowest lying vibrational levels is indicated. For comparison the corresponding potential curve calculated by Brommer *et al.* (10) (dashed-dotted line) is also given. (Top) Symmetric stretching dependence (with the bond angle kept fixed at 131°) of the isotropic hfcc's for ^{11}B and H in the ground electronic state X^2A_1 of BH₂.

state. This can be explained by the interplay between the direct contribution from the $3a_1$ orbital (positive sign) and negative contributions arising from the spin polarization of the doubly occupied shells by the unpaired electron, as already pointed out for the NH₂ molecule (14). The dependence of the anisotropic tensor elements on the bond angle is similar to the behavior found for CH₂⁺ (16) or NH₂ (14, 15).

The vibronically averaged values for the hfcc's in the $K = 0$ and $K = 1$ states of the $1^2\Pi_u(X^2A_1, A^2B_1)$ system of $^{11}\text{BH}_2$ are presented in Table I. The isotropic hfcc's for other isotopomers involving ^{11}B , ^{10}B , H, and D are given in Tables II–VI. The values for the lowest $K = 0$ and $K = 1$ level are given with five significant figures to show the expected isotopic shifts. The values for deuterium in ^{11}BHD and ^{10}BHD can be obtained by multiplying those for the lighter isotope (H) by the factor $g_{\text{D}}/g_{\text{H}} = 0.153506$.

As already stressed in our previous studies (14–16), the variation of the vibronic hfcc's from one vibronic level to another in electronic states coupled via the Renner–Teller effect generally reflects three effects, connected more or less with each other: (i) geometry dependence of the electronic hfcc's; (ii) composition of the vibronic wavefunctions, particularly the amount of the various coupled electronic states in them; and (iii) strong local coupling between (accidentally) close lying vibronic levels belonging in the zeroth-order approximation to different electronic states. Note that especially the last two effects are intimately connected with one another because a near degeneracy of the levels with $K \neq 0$ has dramatic consequences for the composition of the corresponding wavefunctions. For these reasons, a reliable comparison of the

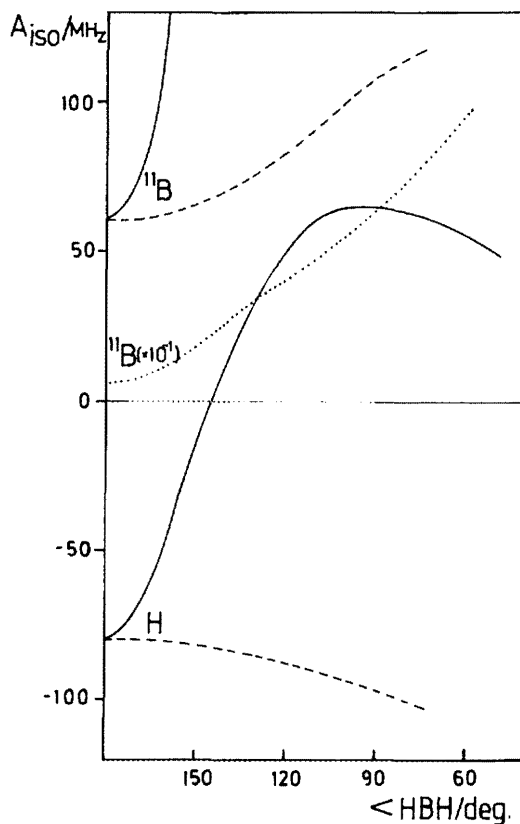


FIG. 3. Bond angle dependence (computed at the B–H bond length kept fixed at 2.211 Bohr) of the electronic mean values for the isotropic hfcc's of ^{11}B and H in the X^2A_1 ground state (full lines) and the A^2B_1 state (dashed lines). Dotted line, the results for ^{11}B in the X^2A_1 state multiplied by factor of 0.1.

results of calculations with the experimental findings can generally not be achieved if the proper vibronic averaging has not been carried out. An important exception often represents the lowest lying vibronic levels of a strongly bent lower electronic state (as, for example, the $v_2 = 0$ level in the X^2B_1 states of NH_2 and H_2O^+) where the electronic hfcc's computed at the equilibrium geometry of the ground state do not differ significantly from the vibronically averaged values for the zeroth vibronic level (14, 15, 31).

In the present case, however, vibronic averaging plays an important role even in the lowest vibronic states. Let us analyze the situation for the example of the isotropic hfcc's for ^{11}B and ^1H in the $v_1, v_2, v_3 = 0, K = 0$ and 1 levels of the X^2A_1 electronic state. For the boron atom the electronic isotropic hfcc calculated at the experimentally estimated bond angle value of 131° (1) and the bond length of 2.211 Bohr (1.17 Å) is 325 MHz. At the same angle and the experimentally determined equilibrium bond length (1) of 2.230 Bohr (1.18 Å) the value of 330 MHz is obtained. It compares fairly well with the computations by Fernandez *et al.* (17) performed at the same geometry. However, at the equilibrium geometry determined in the *ab initio* calculations of Brommer *et al.* (10), being essentially the same as that published in our previous work (8) ($\text{HBH} = 128.68^\circ, R_{\text{HB}} = 2.2373$ Bohr (1.184 Å)), we obtain for

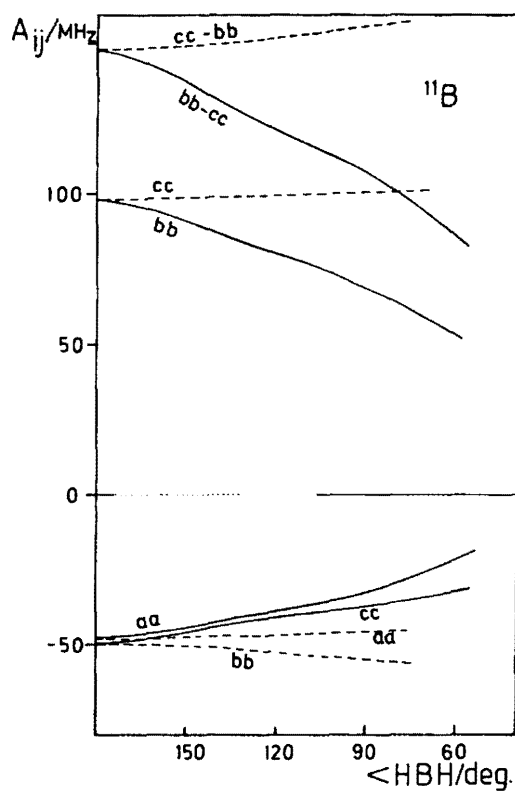


FIG. 4. Bond angle dependence ($B-H = 2.211$ Bohr) of the electronic mean values for the components of the anisotropic hf tensor for ¹¹B. Full lines, X^2A_1 electronic state; dashed lines, A^2B_1 state.

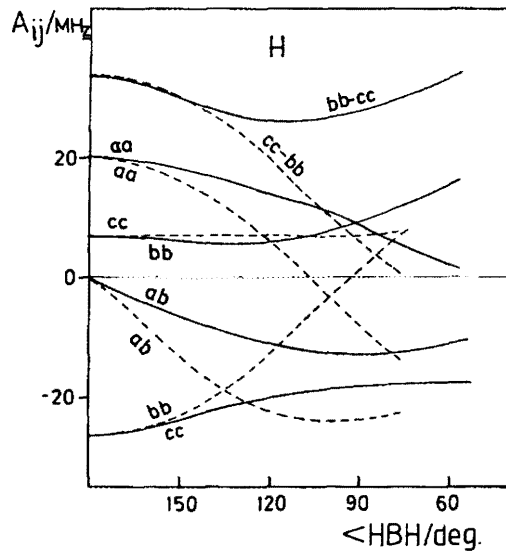


FIG. 5. Angular dependence of the electronic mean values for the components of the anisotropic hf tensor of the hydrogen centers. Full lines, X^2A_1 state; dashed lines, A^2B_1 electronic state.

TABLE II

Results of Calculations of the Vibronic Energy Levels and the Vibronic hfcc's for ^{11}BHD

K=0				K=1			
v_2	E cm ⁻¹	"B	H	v_2	E cm ⁻¹	"B	H
		A _{iso} (MHz)	A _{iso} (MHz)			A _{iso} (MHz)	A _{iso} (MHz)
0*	0	342.22	33.296	0*	34	344.03	33.772
1*	876	322	23.4	1*	984	325	24.1
2*	1713	304	13.6	2*	1758	299	11.4
3*	2539	302	8.89	3*	2486	247	-10.7
4*	3412	316	10.4	4*	3117	253	-11.6
0(1)	3955	62.1	-80.7	5*	3913	308	5.24
5*	4363	338	14.0	0(2)	4700	134	-56.3
6*	5387	359	17.3	6*	4934	283	-6.91
1(3)	5680	64.4	-81.3	7*	5933	360	15.8
7*	6477	378	20.0	1(4)	6506	79.4	-77.0
2(5)	7409	66.6	-82.0	8*	7060	379	18.5
8*	7621	396	22.2	9*	8173	276	-16.8
9*	8812	413	24.1	2(6)	8298	199	-41.6
3(7)	9143	68.8	-82.6	10*	9430	417	23.5
10*	10045	429	25.8	3(8)	9993	76.7	-80.8
4(9)	10882	71.0	-83.2	11*	10686	433	25.5
11*	11313	443	27.4	4(10)	11730	88.4	-78.6
12*	12614	456	28.9	12*	11978	435	23.6
5(11)	12628	73.2	-83.9	13*	13276	447	25.1
13*	13943	469	30.4	5(12)	13497	90.8	-79.4
6(13)	14380	75.2	-84.5	14*	14625	472	30.3
14*	15298	481	31.8	6(14)	15246	79.9	-83.8

$A_{\text{iso}}(^{11}\text{B})$ the value of 347 MHz. This value rises slightly (by about 1%) upon averaging over the symmetric stretching coordinate in the zeroth ($v_1 = 0$) vibrational state, becoming 351 MHz. Finally, the integration over the bending coordinate results in the value of 341.3 MHz (i.e., a lowering of about 3%). This result is in good agreement with the experimental finding by Knight *et al.* (11), 358 ± 2 MHz. For the comparison between experiment and our study one has to keep in mind that the influence of the asymmetric stretch motion is missing in our treatment. Assuming a similar effect for that found for the symmetric stretch motion the agreement would be improved (345 MHz vs 358 ± 2 MHz). In the lowest $K = 1$ level of $^{11}\text{BH}_2$ the isotropic hfcc for the boron atom is computed to be 343.6 MHz. In this case, in addition to the above effect a small admixture of the upper electronic species contributes nonnegligibly to the vibronic mean value.

TABLE III
 Vibronic Energies and Vibronic hfcc's in the
 $1^2\Pi_u(X^2A_1, A^2B_1)$ System of $^{11}\text{BD}_2$

v_2	K=0			v_2	K=1		
	E (cm ⁻¹)	¹¹ B	D		E (cm ⁻¹)	¹¹ B	D
		A_{iso} (MHz)	A_{iso} (MHz)			A_{iso} (MHz)	A_{iso} (MHz)
0*	0	343.48	5.2124	0*	24	344.79	5.2653
1*	745	326	3.93	1*	776	329	4.04
2*	1457	308	2.52	2*	1496	310	2.58
3*	2143	296	1.38	3*	2164	278	0.332
4*	2836	301	1.15	4*	2722	233	-2.59
5*	3577	318	1.57	5*	3277	272	-0.897
0(1)	3779	61.8	-12.4	6*	3983	310	0.923
6*	4379	337	2.12	0(2)	4451	90.2	-10.9
7*	5236	355	2.58	7*	4828	329	1.42
1(3)	5252	63.7	-12.5	8*	5680	347	1.95
8*	6141	373	2.96	1(4)	5967	84.8	-11.5
2(5)	6726	65.6	-12.5	9*	6619	376	2.87
9*	7086	389	3.29	2(6)	7426	103	-10.8
10*	8068	404	3.56	10*	7596	362	1.75
3(7)	8201	67.6	-12.6	11*	8573	405	3.36
11*	9081	418	3.81	3(8)	8926	77.0	-12.2
4(9)	9679	69.4	-12.7	12*	9605	422	3.78
12*	10122	431	4.02	4(10)	10400	81.1	-12.2
5(11)	11159	71.3	-12.8	13*	10664	428	3.68
13*	11189	444	4.24	14*	11728	431	3.48
14*	12277	455	4.44	5(12)	11895	92.0	-11.9
6(13)	12642	73.1	-12.9	15*	12834	458	4.42
15*	13386	466	4.64	6(14)	13374	77.7	-12.8
7(15)	14128	74.9	-13.0	16*	13954	469	4.64
16*	14514	476	4.84	7(16)	14859	84.2	-12.6

For A_{iso} (H) the values of 29.7 and 30.9 MHz are computed at the bond angle of 131° and the B-H bond lengths of 2.211 and 2.230 Bohr, respectively. The latter result should be compared with those published by Fernandez *et al.* (17) lying between 27.5 and 33.4 MHz, depending on the AO basis and the CI treatment employed. At the equilibrium geometry determined in the ab initio calculations of Brommer *et al.* (10) (see above) a value of 35.3 MHz is obtained for A_{iso} (H). Averaging over the stretching coordinate now has a more dramatic effect—the value for A_{iso} (H) increases by about 6%, becoming 37.4 MHz. This is a consequence of nonlinearity of the

TABLE IV
 Vibronic Energies and Vibronic hfcc's for $^{10}\text{BH}_2$

v_2	K=0			v_2	K=1		
	E (cm^{-1})	^{10}B	H		E (cm_1)	^{10}B	H
		A_{iso} (MHz)	A_{iso} (MHz)			A_{iso} (MHz)	A_{iso} (MHz)
0*	0	114.29	32.750	0*	44	115.06	33.356
1*	997	107	21.7	1*	1053	107	22.2
2*	1955	102	12.6	2*	1986	95.4	5.04
3*	2931	104	10.4	3*	2754	79.0	-16.3
4*	3987	111	13.2	4*	3544	95.1	-2.01
0(1)	4120	20.9	-80.8	5*	4557	107	7.12
5*	5139	119	16.8	0(2)	5031	30.7	-71.4
1(3)	6080	21.8	-81.5	6*	5774	119	14.6
6*	6375	126	19.9	7*	6942	72.0	-33.7
7*	7683	133	22.3	1(4)	7111	81.0	-25.9
2(5)	8047	22.6	-82.2	8*	8368	134	21.4
8*	9052	140	24.4	2(6)	9004	26.2	-79.6
3(7)	10021	23.4	-82.9	9*	9771	141	23.8
9*	10473	145	26.3	3(6)	10973	32.3	-75.5
10*	11940	150	28.0	10*	11227	140	19.9
4(9)	12004	24.3	-83.7	11*	12689	148	24.9
11*	13446	155	29.7	4(10)	12988	29.6	-79.7
5(11)	13996	25.0	-84.4	12*	14221	157	29.7
12*	14986	160	31.3	5(12)	14979	26.9	-83.5
6(13)	15998	25.8	-85.2	13*	15779	162	31.2

stretching dependence of the electronic isotropic hfcc for H (see Fig. 2, top). The same holds for the averaging over the bending coordinate: it results in a decrease of roughly 15%, the final result for $A_{\text{iso}}(\text{H})$ in the lowest vibronic level becoming 32.8 MHz. This value is in reasonable agreement with the experimental result of 38 ± 1 MHz published by Knight *et al.* (11). Similar to the case of ^{11}B , the agreement is further improved if the asymmetric stretch motion is taken into account, assuming that it has a similar effect as the symmetric stretch vibration. With this, a final value of $A_{\text{iso}}(\text{H}) \approx 35$ MHz is calculated in our study. For the interpretation of the isotropic hfcc of the hydrogen center one has to take into account that two large effects, the direct contribution from the singly occupied $3a_1$ orbital and the indirect contribution arising due to the polarization of the doubly occupied shells by the unpaired electron, cancel each other. As already found for the NH_2 molecule (14, 15) both effects have the same sign for the heavier center, where the direct contribution is dominant. The computed isotropic hfcc's for both the boron and the hydrogen centers underestimate

TABLE V

Vibronic Energy Levels and Vibronic hfcc's for ¹⁰BHD

K=0				K=1			
v ₂	E (cm ⁻¹)	¹⁰ B	H	v ₂	E (cm ⁻¹)	¹⁰ B	H
		A ₁₀₀ (MHz)	A ₁₀₀ (MHz)			A ₁₀₀ (MHz)	A ₁₀₀ (MHz)
0*	0	114.60	33.277	0*	34	115.22	33.762
1*	883	108	23.3	1*	928	109	24.1
2*	1726	102	13.6	2*	1771	99.8	11.2
3*	2561	101	9.06	3*	2502	82.7	-11.2
4*	3444	106	10.7	4*	3140	85.4	-11.0
0(1)	3967	20.8	-80.7	5*	3948	103	5.66
5*	4404	114	14.3	0(2)	4726	42.2	-59.3
6*	5440	121	17.5	6*	4976	98.1	-3.56
1(3)	5709	21.6	-81.4	7*	5991	121	16.0
7*	6541	127	20.2	1(4)	6544	26.6	-77.0
2(5)	7454	22.3	-82.0	8*	7129	128	18.9
8*	7696	133	22.4	9*	8241	79.7	-28.7
9*	8898	139	24.3	2(6)	8363	79.7	-29.5
3(7)	9202	23.1	-82.6	10*	9522	140	23.7
10*	10142	144	26.0	3(8)	10060	25.8	-80.7
4(9)	10957	23.8	-83.3	11*	10788	146	25.8
11*	11421	149	27.6	4(10)	11812	28.7	-79.4
5(11)	12717	24.5	-83.9	12*	12090	147	24.7
12*	12733	153	29.2	13*	13399	149	24.0
13*	14073	158	30.7	5(12)	13594	32.0	-78.0
6(13)	14483	25.2	-84.6	14*	14760	159	30.6
14*	15437	162	32.0	6(14)	15356	26.8	-83.8

slightly the experimental findings, in accord with our experience with most similar systems (12-16).

According to the above analysis, it can be concluded that in the case of the BH₂ molecule it is dangerous to judge the reliability of the calculated hfcc's solely on the basis of their electronic mean values, even if the comparison is made with the experimental findings for the lowest vibronic levels. The reasons are: (i) the ground electronic state is of A₁ symmetry with the singly occupied MO strongly changing with geometry variations, which results in strong dependence of the electronic hfcc's on the geometry; (ii) the lower electronic state is of quasilinear character with a consequence that the corresponding bending curve is highly anharmonic and the bending wavefunctions in low vibronic levels are significantly asymmetric with respect to the equilibrium bond angle value; (iii) the upper electronic state lies only 2700 cm⁻¹ above the minimum

TABLE VI
Vibronic Energies and Vibronic hfcc's for $^{10}\text{BD}_2$

K=0				K=1			
v_2	E (cm^{-1})	^{10}B	D	v_2	E (cm^{-1})	^{10}B	D
		A_{100} (MHz)	A_{100} (MHz)			A_{100} (MHz)	A_{100} (MHz)
0*	0	115.02	5.2091	0*	25	115.47	5.2633
1*	753	109	3.91	1*	784	110	4.02
2*	1472	103	2.50	2*	1512	104	2.55
3*	2165	99.5	1.40	3*	2184	92.8	0.241
4*	2868	101	1.19	4*	2744	78.4	-2.59
5*	3621	107	1.63	5*	3312	92.1	-0.657
0(1)	3794	207	-12.4	6*	4031	104	0.959
6*	4435	114	2.18	0(2)	4477	29.9	-11.0
1(3)	5286	21.4	-12.5	7*	4889	112	1.58
7*	5305	120	2.64	8*	5753	116	1.81
8*	6222	126	3.02	1(4)	6012	29.7	-11.3
2(5)	6778	22.0	-12.5	9*	6706	127	2.93
9*	7180	131	3.35	2(6)	7490	31.2	-11.3
10*	8174	136	3.61	10*	7693	126	2.29
3(7)	8271	22.7	-12.6	11*	8684	136	3.36
11*	9208	141	3.85	3(8)	9005	26.3	-12.2
4(9)	9765	23.3	-12.7	12*	9730	142	3.82
12*	10253	145	4.07	4(10)	10496	26.6	-12.3
5(11)	11262	23.9	-12.8	13*	10800	145	3.82
13*	11331	149	4.28	14*	11875	141	3.02
14*	12432	153	4.48	5(12)	12010	34.8	-11.4
6(13)	12762	24.5	-12.9	15*	12995	154	4.47
15*	13553	157	4.68	6(14)	13502	26.1	-12.8
7(15)	14264	25.1	-13.0	16*	14127	158	4.70
16*	14692	160	4.88	7(16)	15004	27.7	-12.7

of the lower one, thus contributing appreciably for all $K \neq 0$ vibronic states, including those lying below the barrier to linearity.

The results for vibronic hfcc's in $K = 0$ levels of the $1^2\Pi_u(X^2A_1, A^2B_1)$ system of BH_2 presented in Tables II–VI reflect the geometry variations of the corresponding electronic mean values accompanied by the change of the shapes of the bending wavefunctions with the bending quantum number. It is not easy to estimate the error limits for the vibronic hfcc's for excited vibronic states predicted in the present study; it is difficult even to state which of the two possible error sources, namely the inaccuracy of the electronic hfcc functions or the inaccuracy of the vibronic wavefunction, plays

a more important role. However, some light on this problem can be shed by the analysis performed in our study of the $1^2\Pi_u(X^2B_1, A^2A_1)$ system of NH₂ (15). In this case accurate potential surfaces derived by fitting the experimental data were available (32), which made it possible to investigate the effect of inaccuracy of the ab initio calculated vibronic levels on the vibronic mean values for the hfcc's. It was shown that, despite the fact that the differences between the positions of the corresponding $K = 0$ vibronic levels, employing two sets of potentials (ab initio and experimentally derived) in the energy range between 0 and 20 000 cm⁻¹ amounted to as much as 1000 cm⁻¹, the discrepancies between the values of the vibronic hfcc's were generally smaller than 3%. Furthermore, the computed values for the isotropic hfcc's in a vibronic level lying about 12 000 cm⁻¹ above the lowest one were in very good agreement with the corresponding experimental findings. Since in the present case the discrepancies between the computed and the observed term values are substantially smaller than those for NH₂, we expect that our results for vibronic hfcc's in higher $K = 0$ levels are of comparable accuracy with those of the lowest vibronic state. In the case of the isotropic hfcc's, particularly for that of the hydrogen atom, the relative error in higher vibronic levels is expected to be even smaller than that in the ground vibronic state because of the much less dramatic dependence of the electronic hfcc's on the bending angle in the geometry region far from the equilibrium geometry at the X^2A_1 electronic state.

In the $K = 1$ states vibronic mixing plays an additional role. The effects of the vibronic coupling might be divided into two categories: (i) by approaching the energy region where both component electronic states touch one another (corresponding to the linear molecular geometry), each of these states "feels" more strongly the presence of the other one with a consequence that the $K \neq 0$ vibronic levels are continuously more shared between both electronic species, and (ii) if two $K \neq 0$ levels lie accidentally close to one another their vibronic wavefunctions are of strongly mixed A_1/B_1 electronic character, independent of whether these levels lie close to the barrier to linearity or not. A consequence of such local interactions is that the corresponding vibronic levels cannot be attributed unambiguously to a particular electronic state. An example of this kind is represented by the $K = 1$ levels assigned to $v_2 = 7^+$ and 1^- (4) (Table I), calculated to lie only 167 cm⁻¹ from one another. For the levels belonging predominantly to the X^2A_1 electronic state we use in the present paper the "bent" notation, the superscript + indicating the totally symmetrical character of the electronic species; the levels of the A^2B_1 state are assigned by both bent and "linear" (in parentheses) bending quantum numbers. The connection between the bent and linear notation is given by $v_2^{\text{lin}} = 2v_2^{\text{bent}} + K + \Lambda (=1)$. The mixed character of the corresponding vibronic wavefunctions is reflected in all properties of these states. So, for example, the values for $A_{\text{iso}}(^1B)$ in these two vibronic species are computed to be 236 and 220 MHz, respectively, whereas the values for the same quantity for the levels lying in the same energy region but belonging unambiguously to the X^2A_1 electronic state ($K = 0$) are roughly 400 MHz, and for those of the A^2B_1 state, 60–70 MHz. One of the greatest difficulties in pure ab initio calculations of the vibronic hfcc's is reliable description of these local interactions because the amount of mixing depends dramatically on the position of the interacting vibronic states. In the absence of corresponding experimental finding we can try to estimate the reliability of the values for vibronic hfcc's calculated for the levels 7^+ and 1^- (4) only by comparing our results for the vibronic term values with those published by Brommer *et al.* (10). If the results of the latter study are really as accurate as the authors claim (errors smaller than 6 cm⁻¹)

the energy difference between the $K = 1$ levels 7^+ and $1^- (4)$ should be 68 cm^{-1} . Comparing that value with the present work, in which the energy distance of these levels is calculated to be around 167 cm^{-1} , an even stronger mixing of the two electronic states can be expected. Thus it can be concluded that our values for hfcc's in these two states are quite reliable.

Let us note that we assign the 6899 cm^{-1} feature to 7^+ and the 7066 cm^{-1} one to $1^- (4)$, whereas Brommer *et al.* (10) prefer to assign the lower energy level (7023 cm^{-1}) to $1^- (4)$ and the higher one (7091 cm^{-1}) to 7^+ . As already stated, in the cases of such strong mixing of the electronic states an unambiguous assignment of the vibronic levels to one particular electronic species is not possible—ours is based on a slightly closer similarity of the values for hfcc's computed for the level at 6899 cm^{-1} with those for the levels belonging predominantly to the X^2A_1 electronic state, but as already pointed out, the mixing of both electronic states should change.

4. CONCLUSION

In this study, we present the results of pure ab initio calculations of the hyperfine coupling constants for the vibronic levels of the $1^2\Pi_u(X^2A_1, A^2B_1)$ system in various isotopomers of the BH_2 molecule, in the energy range $0\text{--}15000 \text{ cm}^{-1}$. The computational strategy applied is very economical, using a moderately large AO basis set and a truncated CI method in which smaller effects are included by perturbation theory. For a description of the nuclear motion, effectively a one-dimensional bending problem is solved variationally whereby the potentials and the electronic hfcc's computed at only 7–8 points are used. In spite of the very modest computational efforts, many quantities are calculated which could be of use in future experimental works.

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