reaction pathway. Consequently, the addition reactions of BH_3 may be divided into (at least) two categories: those in which the substrate is a Lewis acid with vacant or electron-deficient p orbitals (in hydroboration, this would correspond to the ylid resonance form of ethylene), and others in which the substrate must undergo significant nuclear rearrangement to form a donation–backdonation interaction. In the former case, which only involves polarization of the electron cloud (a relatively low-energy process), the associated activation energies are likely to be very small, while the latter class of additions would typically have higher barriers. Future studies in boron hydride chemistry, both theoretical and experimental, should served to judge the propriety of this operational classification.

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A Theoretical Investigation of the Structure and Properties of BH_5

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Abstract: The intermolecular complex between borane (BH_3) and molecular hydrogen is studied with methods based on many-body perturbation theory and the coupled-cluster approximation. Calculations with very large Gaussian basis sets indicate that BH_5 is particularly stable, with the minimum of the intermolecular potential roughly 6 kcal/mol below that of the separated monomers. A pronounced basis set dependence is observed; highly correlated CCSD+T(CCSD) calculations with an unpolarized [3s2p]/[2s] basis set suggest a totally repulsive intermolecular interaction, while the singly polarized [3s2p1d]/[2s1p] basis predicts a binding energy of 2.7 kcal/mol. Continued expansion of the basis is found to systematically increase the stability of this system. The structures of four isomers are optimized at the MBPT(2)-[3s2p1d]/[2s1p] level and are compared with results of previous theoretical studies of BH_5 and its organic analogue CH_5^+ Of these isomers, only a C_s structure with the H_2 subunit eclipsing one of the B–H bonds of BH_3 is found to be a minimum—another C_s and a C_{2v} structure are found to be transition states for internal rotation and hydrogen scrambling, while a C_{4v} isomer is a second-order saddle point on the potential surface. MBPT(2) vibrational frequencies and infrared band intensities are also evaluated for the equilibrium structure and are analyzed in terms of interacting molecular subunits. The theoretical enthalpic barriers for dissociation and internal rearrangement at 298 K are 2.4 and 6.6 kcal/mol, respectively. Rate calculations using a modified RRKM model which permits an approximate inclusion of quantum effects suggest that proton tunneling may play a significant role in the experimentally observed hydrogen scrambling process. Overall, the results are qualitatively consistent with the participation of BH_5 in the aqueous hydrolysis of tetrahydroborate anion.

I. Background

Early studies of the aqueous hydrolysis of the borohydride anion[1] led to general agreement that (1) molecular hydrogen was evolved stepwise, with the release of the first mole representing the rate-determining step; (2) mixed hydroxyborohydide intermediates $[BH_{4-n}(OH)_n]^-$ were involved; and (3) the reaction was catalyzed by acid. Initially, it was believed that the rate-determining formation of borane (BH_3) was a single elementary process involving a formally neutral activated complex between hydronium ion and BH_4^-. This view was eventually challenged by Mesmer and Jolly[2], who found that although most of the hydrogen evolved from hydrolysis of BH_4^- in D_2O is HD, a statistically significant amount of H_2 is released as well. To account for this observation, these authors proposed an intermediate with stoichiometry BH_4D, which principally decomposes to yield HD but also produces small quantities of H_2. Further evidence against the simple one-step mechanism was produced 10 years later by Kreevoy and Hutchins,[3] who studied BH_4^- hydrolysis over a pH range from 10.7 to 13.6. A plot of the pseudo-first-order rate constant vs pH was highly nonlinear, implicating a process with a qualitatively different rate law. Also confirmed was a previous observation that borohydride takes up deuterium when hydrolysis is carried out in strongly basic D_2O. Although this finding could account for evolution of D_2 during hydrolysis via the postulated one-step mechanism, it does not satisfactorily explain the small amount of H_2 seen by Mesmer and Jolly.[2] To explain the experimental observations, Kreevoy and Hutchins postulated the following mechanism for the production of borane. The rate law derived

$$H^+ + BH_4^- \rightleftharpoons H_2BH_3 \tag{1}$$

$$H_2O + BH_4^- \rightleftharpoons H_2BH_3 + OH^- \tag{2}$$

$$H_2BH_3 \rightarrow H_2 + BH_3 \tag{3}$$

from these elementary reactions is successful in fitting the observed pH dependence: in acidic or weakly basic solutions, the simple pseudo-first-order rate law is recovered, but the exchange with solvent [the reverse of reaction (2)] competes at high pD, and the slope d(rate)/d(pD) decreases dramatically, in excellent qualitative

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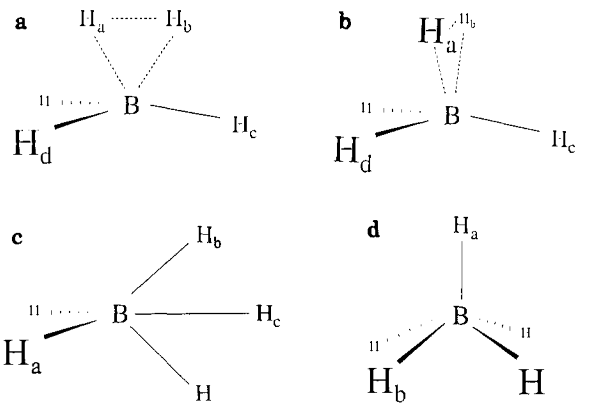

Figure 1. Isomers of BH_5 studied in this paper: (a) C_s(I); (b) C_s(II); (c) C_{2v}; (d) C_{4v}.

agreement with experiment. Thus, the mechanism above is able to account for the kinetic and isotopic observations, provided one assumes that the proton accepted by borohydride in the initial step becomes equivalent to at most one of the other hydrogens in BH_5. Relatively slow rearrangement of the BH_4D intermediate could then account for the observed evolution of H_2.

If the mechanism proposed by Kreevoy and Hutchins is correct, the pentacoordinate BH_5 intermediate is an unusually stable complex between two neutral and nonpolar molecules, and its structure is of great theoretical and practical interest. The isoelectronic complex between methyl radical and hydrogen is responsible for the ubiquitous $m/e = 17$ signal in mass spectroscopy of hydrocarbons and has been subjected to considerable theoretical investigation over the past two decades.[4] Even the earliest studies were successful in predicting the existence of two rotamers of a stable adduct having C_s symmetry (see Figure 1). On the basis of these results, Hutchins and Kreevoy suggested the C_s(I) structure for BH_5. At roughly the same time, the first theoretical study of BH_5 was presented in the literature.[5] Using the semiempirical CNDO/2 scheme, Olah and co-workers investigated a number of possible structures for BH_5, of which the C_s(II) conformation was found most stable. Unfortunately, the documented binding energy of 961 kcal/mol is unrealistic,[6] casting doubt over the validity of their conclusions.

It was not until 3 years later that the first ab initio results appeared for BH_5. The three studies which were reported in 1975 and 1976[7-9] unanimously predicted that the C_s(I) structure was the most stable form of BH_5 but suggested only slight stability with respect to dissociation. Significantly, none of the structures canvassed were bound with respect to BH_3 and H_2 at the SCF level of theory, even when an extensive double-ζ plus polarization Slater basis was used.[9] Configuration interaction (CI),[7] coupled and independent electron pair approximation (CEPA and IEPA),[7] and many-body perturbation theory (MBPT) calculations[8] showed that electron correlation effects favored the molecular complex relative to the monomers by 5–10 kcal/mol, indicating a weak ($\approx$2 kcal/mol) minimum on the vibrationless electronic potential energy surface. Another interesting finding was that correlated calculations using minimal and split-valence basis sets failed to lead to a significant stabilization of BH_5, prompting speculation that "the bonding between BH_3 and H_2 subunits is primarily due to the inclusion of polarization functions in CI calculations".[9]

By today's standards, however, any reliance on the stabilization energy of $\approx$2 kcal/mol obtained in these early studies could be objectively criticized on a number of grounds. First, due to computational limitations, complete unconstrained geometry optimizations at the correlated level of theory were not usually feasible at the time, and it was necessary to invoke certain approximations. In ref 8 and 9, optimizations were carried out at the SCF level with a constrained intermolecular distance, and correlation energies were evaluated at these partially optimal geometries. Hoheisel and Kutzelnigg[8] optimized the structure of the preferred C_s(I) isomer at the correlated CEPA level but varied only four of the eight available degrees of conformational freedom and used an unpolarized basis set. Since electron correlation appears to play a principal role in determining the stability of BH_5, calculations of any quality based on a low-level geometry are prone to systematic error, and it is likely that these approximations resulted in an underestimation of the electronic binding energy. Furthermore, no basis sets containing more than a single shell of polarization functions were used in any of the SCF or correlated calculations in these studies. The corresponding expansion of the virtual space could be important in describing the electron distribution in BH_5, and a very large basis might produce significantly different results. Second, although the CI, CEPA, and MBPT calculations indicated the presence of a critical point on the BH_5 electronic potential surface, no efforts were made to calculate the harmonic force field. Such information can be used to determine whether the structural candidate is a true local minimum on the potential surface and serves as a means to estimate the vibrational zero-point contribution to the binding energy. Dissociation of BH_5 to BH_3 and H_2 results in the loss of five vibrational degrees of freedom, and zero-point effects will likely lower the dissociation energy by a few kcal/mol.[10] Finally, a number of studies of the methyl cation–hydrogen complex have demonstrated a consistent deficiency of theory in determining the (experimentally known) binding energy;[4a-c] relatively sophisticated SDQ-MBPT(4)/6-31G**[4b] and SDTQ-MBPT(4)/6-311G**[4c] calculations yielded heats of dissociation of 34.7 and 34.8 kcal/mol, respectively. Both of these are substantially lower than the experimental result of $\approx$42 kcal/mol, suggesting that these basis sets are able to account for only ~75% of the dissociation energy of CH_5^+. Any skepticism concerning the accuracy of experimentally determined value was recently removed by Komornicki and Dixon, who presented a thorough theoretical paper on this system.[4a] Using an extensive [5s3p2d1f]/[3s2p1d] basis and CI calculations incorporating single, double, and quadruple substitutions (CISDQ), ΔH_{diss} was calculated to be 39.7 kcal/mol, roughly 2 kcal/mol below experiment. The inclusion of triple excitations, which have an established importance in chemical systems,[11] would probably have improved the agreement. Interestingly, the highest angular momentum basis functions (f on C; d on H) were responsible for approximately 8% of the theoretical binding energy, a truly remarkable effect.

Regretably, theoretical studies of BH_5 have not kept pace with those dealing with CH_5^+, and little effort has been made to deterimine the stability of the preferred C_s forms since the three studies discussed above.[12] In this paper, we report the most

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[10] In the unimolecular dissociation of diborane, the zero-point correction favors the products by roughly 6.5 kcal/mol. See: Stanton, J. F.; Bartlett, R. J.; Lipscomb, W. N. *Chem. Phys. Lett.* **1987**, *138*, 525.

[11] See, for example: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

extensive theoretical investigation of BH_5 carried out to date. First, we present structures of four isomers which have been fully optimized at the MBPT(2) level of theory with a fully polarized basis set and determine the nature of the stationary points. We then proceed to study the correlation and basis set dependence of the theoretical binding energy of the equilibrium BH_5 structure and explore possible pathways for molecular rearrangement and decomposition. We conclude with a brief summary and a discussion of this unusual chemical species.

II. Computational Details

Most of the calculations reported in this paper used the ACES program system, developed by Bartlett and collaborators.[13] Geometry optimizations were performed at the MBPT(2) level with the [3s2p1d]/[2s1p] basis described in ref 14. Newton-Raphson optimizations using a default diagonal internal coordinate Hessian were convergent for the C_{4v} and C_{2v} isomers but failed for both C_s structures. For these, the Hessian was computed analytically, and the subsequent optimizations converged rapidly. Optimization of structures along the symmetric dissociation pathway, in which the intermolecular distance was constrained, was performed with Gaussian 86.[15] At the stationary points, harmonic force fields were calculated at the MBPT(2) level both analytically[16] (for the C_{2v} and both C_s forms) and by finite difference of analytic energy derivatives (for the C_{4v} isomer). More advanced correlation corrections were computed at the optimized MBPT(2) geometries by means of higher order MBPT[17] and various levels of the coupled-cluster approximation (CC).[18] Many-body methods like MBPT and the CC approximations are ideally suited for studies of intermolecular interactions because they are size-extensive and ensure correct separation in the present application. CC theory is an infinite order generalization of MBPT and is based on an exponential transformation relating an approximate reference function with an exact solution to the Schrodinger equation

$$|\Psi_{CC}\rangle = \exp(T)|\Phi_0\rangle \tag{4}$$

The reference wave function ($|\Phi_0\rangle$) in the present case is the SCF determinant. The cluster excitation operator (T) is usually expressed as $T = T_1 + T_2 + ... + T_n$, with T_j being a j-particle excitation operator. If $n = n_{electrons}$, the CC wave function is exact in the space spanned by the basis functions. Such calculations are rarely possible for chemically interesting systems, however, and one typically works with a truncated excitation operator. If the reference function is a reasonable approximation to the exact ground-state wave function, excellent approximations to the correlation enery can be made with judiciously chosen approximations to T. To this end, we employ two well-studied models: CCSD ($T = T_1 + T_2$)[19] and CCSD+T(CCSD),[20] in which the effects of T_3 are approximated in a computationally efficient manner. Model calculations have shown that CCSD+T(CCSD) correlation energies calculated at or near equilibrium geometries are typically within a few percent of the full CI (exact) basis set results,[21] showing that this method can provide a nearly quantitative accounting of the molecular correlation energy. In most nonpathological cases, properties and energies calculated with the CCSD and CCSD+T(CCSD) models are close to their fourth-order MBPT counterparts [SDQ-MBPT(4) and MBPT(4), respectively].

In order to assess the basis set dependence of the binding energy, we have extended the [5s3p]/[3s] contracted basis of Dunning[22] to produce larger [5s4p3d]/[4s2p] and [5s4p3d1f]/[4s2p1d] basis sets. For the former, the most compact polarization functions on boron are the same as those in the [4s3p1d] basis of ref 14. The exponent for this function was then multiplied by 0.4 and 0.16, and the resulting functions were added to the basis. The [4s2p] hydrogen set is the same as that used in ref 23 and 24. To form the largest basis set, higher angular momentum functions were added to all atoms. The exponent for the d functions on H (0.6) was the same as that used by Komornicki and Dixon,[4a] and an exponent of 0.5 was used for the f functions on boron. In addition, to improve the flexibility of this basis, the innermost d function on boron was replaced by a STO-2G fit to a Slater orbital with exponent 1.80.[25] Large basis sets formed according to similar rules were found to adequately predict the higher polarizabilities and infrared intensities of water and HF,[23,24,28] suggesting that they are sufficiently versatile to accurately describe the molecular charge distribution.

Infrared intensities for the equilibrium C_s(I) structure of BH_5 were calculated at the MBPT(2) level with the [3s2p1d]/[2s1p] basis using an external point charge implementation[26] of the finite-field scheme of Komornicki and McIver.[27] A recent paper[28] has shown that this method is numerically reliable and that MBPT(2) intensities obtained with similar basis sets are usually within 30% of experimental values. Dipole moments were obtained by numerical differentiation of total energies calculated in the presence of electric fields explicitly incorporated in the one-electron Hamiltonian.

III. Results

A. Structures. Optimized MBPT(2) internal coordinates for the structures in Figure 1 are documented in Table I, along with geometries used by previous workers. It should be stressed that the cited C_s(I) parameters were only crudely optimized, while ours correspond to a true stationary point on the correlated potential surface. For the C_{2v} and C_{4v} isomers, the present results do not differ significantly from those found in extended basis set SCF studies; structures optimized with the minimal STO-3G basis[8] and with the nonempirical PRDDO method[9,29] have somewhat shorter B-H bonds. Most interesting are the results for the two C_s forms, particularly those parameters which qualitatively characterize the intermolecular interaction. Notably, the MBPT(2) minimum energy structure obtained with the [3s2p1d]/[2s] basis (which does not contain polarization functions on hydrogen) is similar to the unpolarized double-ζ CEPA structure of Hoheisel and Kutzelnigg.[7] While these workers made certain assumptions about the structure of BH_5, it is unlikely that relaxation of these constraints would have led to appreciable differences in their structure. When a shell of p polarization functions is added to the hydrogen atoms, distances between the boron and the hydrogens of H_2 are reduced by approximately 0.05 Å, with a concomitant increase of 0.013 Å in the H_a–H_b distance. These differences are easily rationalized as follows: the factors leading to a stabilized complex likely involve polarization of the H_2 charge cloud toward the boron atom. The difference between H-H distances in the monomer and in BH_5 (0.7401 and 0.7929 Å, respectively) as well as the vibrational redshift and dipole moment (see section IIIC) support this contention. Consequently, polarization functions are required

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(12) At least two subsequent papers have reported calculations on BH_5 isomers, but neither contains a serious attempt to calculate the binding energy. In ref 4b, the C_{2v} and an even less stable trigonal bipyramidal D_{3h} structure were compared with the analagous silicon and carbon isomers. In another paper [*J. Am. Chem. Soc.* **1981**, *103*, 4673], McKee and Lipscomb used the C_{2v} and C_s(I) structures as test cases for their additivity approximation but took the geometries of ref 8 and did not perform higher level calculations. Their binding energy did not differ significantly from that found in the earlier studies. Recently, Bauer [Bauer, S. H. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; p 399] quotes this paper as reporting that BH_5 is unstable relative to dissociation products by 6 kcal/mol. This statement is incorrect, however, as this was the calculated binding energy of the C_{2v} form and not of the acknowledged C_s(I) minimum.

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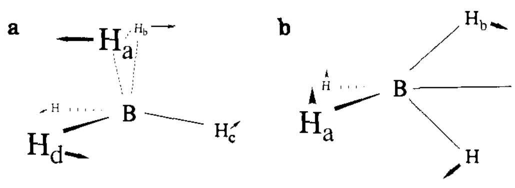

Figure 2. Transition vectors for the C_s(II) and C_{2v} saddle points. The arrows are drawn approximately to scale and correspond to the Cartesian (mass-weighting has been removed) displacements.

to provide a realistic picture of the perturbed electron distribution. By themselves, the s-type functions on the hydrogens are unable to describe any feature of the nearby electron density which is not cylindrically symmetric about the H–H axis. In this case, the only functions which can contribute to the description of the distorted density are the p and d orbitals on boron, and the magnitude of the intermolecular interaction is underestimated.

In both C_s structures, the small departure from local C_{3v} symmetry (as characterized by differences in the B–H bond lengths and the parameter Δ) is consistent with a relatively weak intermolecular interaction. The B–H bond lengths in the BH_3 subunits are larger than those found at this level in the monomer (r_e = 1.196);[30] the most distorted bonds [about 0.01 Å longer than in BH_3] are those which are eclipsed [C_s(I)] or nearly eclipsed [C_s(II)] by the H_2 unit. This could be attributed to a backdonation of electron density from the BH_3 toward the H_2 or simply to repulsion between nonbonded hydrogen atoms. The latter also effectively rationalizes the differences in the inequivalent H–B–H bond angles, as described by the asymmetry parameter, Δ (see Table I). Entirely analogous differences were noted by Komornicki and Dixon in their investigation of the corresponding CH_5^+ structures.[4a]

Although all of the isomers discussed above are local minima within their respective point groups (all eigenvalues of the totally symmetric part of the block-factored Hessian are positive), this does not guarantee that they represent local minima within the full nuclear configuration space. In order to completely characterize the stationary points, MBPT(2) harmonic force fields were determined for each of the four isomers. As expected, the eclipsed C_s(I) structure was found to be a local (and, in all likelihood, the global) minimum on the BH_5 potential surface. The diagonalized Hessian matrices (in internal coordinates) corresponding to the C_s(II) and C_{2v} structures contain one negative element; consequently, these structures represent transition states. Examination of the corresponding eigenvectors (see Figure 2) reveals that the former structure corresponds to the saddle point for internal rotation, while the C_{2v} isomer is a transition state for hydrogen scrambling. The Hessian matrix for the C_{4v} conformer contains a degenerate set of eigenvalues, and this structure appears to be a point on a (chemically uninteresting) pathway between two equivalent forms of the C_{2v} transition state.

B. Binding Energy of BH_5. Using the MBPT(2) geometries presented in Table I, high-level MBPT and CC calculations were carried out with a number of basis sets, ranging from an unpolarized split-valence [3s2p]/[2s] set to an extensive [5s4p3d1f]/[4s2p1d] basis. The latter basis should be able to provide a qualitatively correct description of the electron density in BH_5. In all correlated calculations, determinants involving excitation from the K shell molecular orbital (chiefly the boron 1s AO) were neglected. Calculations using the [4s3p1d]/[3s1p] and larger basis sets also did not consider determinants in which the highest virtual function ($\epsilon > 18$ au) was occupied. While such simplications are often made without justification in theoretical studies, the practice could be challenged in studies of lighter first-row atoms, where the core-valence energy separation is relatively small. To address this point, we computed association energies with the [4s3p1d]/[3s1p] basis, using all occupied and virtual functions in the correlated calculations. Differences between these results and those computed with the constrained configuration space ranged from +0.10 kcal/mol [MBPT(3)] to +0.13 kcal/mol [MBPT(4) and CCSD+T(CCSD)]. Thus, it seems that correlation effects involving the core electrons are slightly more significant in BH_5 than in BH_3. However, the magnitude of this preference is quite small, suggesting that omission of determinants involving excitation to and from these functions does not lead to significant systematic error in the binding energy.

Table I. Optimized Geometrical Parameters for BH_5 Isomers[h]

C_s Isomer[a,b]

	[3s2p1d]/[2s1p] MBPT(2)	[3s2p1d]/[2s] MBPT(2)	[4s2p]/[2s][c] CEPA	6-31G**[d] MBPT(2)
$r(H_a–H_b)$	0.793 (0.791)	0.780	0.783	0.751
$r(B–H_a)$	1.470 (1.466)	1.520	1.535	1.498
$r(B–H_b)$	1.454 (1.466)	1.509	1.535	1.498
$r(B–H_c)$	1.206 (1.197)	1.208	1.191	1.189
$r(B–H_d)$	1.198 (1.203)	1.202	1.191	1.189
$\angle(XBH_c)$	95.6 (101.8)	96.5	98.0	99.4
$\angle(XBH_d)$	100.7 (97.5)	99.9	98.0	99.4
Δ^e	−3.9 (3.5)	−3.3	0.0	0.0

C_{2v} Isomer

	[3s2p1d]/[2s1p] MBPT(2)	[4s2p]/[2s][c]	3-21G[f]	PRDDO[g]
$r(B–H_a)$	1.190	1.191	1.184	1.159
$r(B–H_b)$	1.277	1.270	1.274	1.254
$r(B–H_c)$	1.259	1.270	1.259	1.318
$\angle(H_bBH_c)$	50.8	51.0	50.2	56.0
$\angle(H_aBH_a)$	128.9	120.0	127.5	123.0

C_{4v} Isomer

	[3s2p1d]/[2s1p] MBPT(2)	[4s2p]/[2s][c]	4-31G[d]	PRDDO[g]	STO-3G[d]
$r(B–H_a)$	1.183	1.191	1.174	1.149	1.141
$r(B–H_b)$	1.220	1.243	1.215	1.210	1.185
$\angle(H_aBH_b)$	122.8	120.0	120.4	117.3	118.8

[b] C_s(II) internal coordinates in parentheses [$r(B–H_a) = r(B–H_b)$ by symmetry]. [c] From ref 7. [f] From ref 12. [g] From ref 9. [h] Atomic designations are consistent with those in Figure 1. All bond lengths in Å, angles in deg.

Vibrationless binding energies calculated at various theoretical levels are documented in Table II. Consistent with previous studies of this system,[7-9] BH_5 is not found to be stable at the SCF level. Incorporation of polarization functions in the basis reduces this destabilization by approximately a factor of two for this geometry, but the repulsive nature of the SCF surface persists even when the 125-GTO [5s4p3d1f]/[4s2p1d] basis is used. On the basis of our results, we believe that the Hartree–Fock ΔE_e at this geometry is probably 6.0 ± 0.5 kcal/mol. Introduction of electron correlation at the simple MBPT(2) level successfully predicts a minimum in the intermolecular potential for all basis sets except the unpolarized [3s2p]/[2s] set. The dependence of the binding energy on polarization functions, which is clearly illustrated in the table, is striking and clearly shows the importance of angular correlation. The unpolarized basis is unable to account for the stabilization of BH_5 at all levels of theory, principally because there is inadequate overlap between the available virtual space and the intermolecular binding region. Only marginal binding is predicted when the relatively diffuse d-type functions are included on the boron atoms, even though this basis is better suited to describe the stabilizing cloud of "electron glue". Only when hydrogen polarization functions are included on hydrogen atoms is the extent of the virtual space sufficient to account for significant association between BH_3 and H_2. The results obtained with the [3s2p1d]/[2s1p] basis are in good agreement with the CEPA and MBPT(2) results of ref 7 and 8, in which comparable basis sets were used.

Additional expansion of the bais within the spd/sp space appears to have only a small influence on the theoretical value of ΔE_e. When f and d functions are placed on boron and hydrogen, however, the binding energy is lowered by approximately 1.5 kcal/mol at all correlated levels of theory, approximately twice that achieved when the spd/sp basis is expanded beyond the singly

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(30) A fully optimized geometry for BH_3 at this level is given in the following: Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J.; McKee, M. L. *Inorg. Chem.*, in press. The optimum MBPT(2)-[3s2p1d]/[2s1p] bond length of H_2 is 0.7401 Å.

Table II. Binding Energies (ΔE_e) of C_s(I) BH_5 Calculated at Various Correlated Levels with the Basis Sets Described in the Text[b]

	[3s2p]/ [2s]	[3s2p1d]/ [2s]	[3s2p1d]/ [2s1p]	[4s3p1d]/ [3s1p]	[5s4p3d]/ [4s2p]	[5s4p3d1f]/ [4s2p1d]
SCF	12.0	8.5	6.5	6.4	6.6	6.2
MBPT(2)	6.3	−0.7	−3.4	−3.8	−4.2	−5.7
MBPT(3)	6.4	−0.3	−2.9	−3.3	−3.6	−5.1
SDQ-MBPT(4)	6.6	0.1	−2.2	−2.7	−2.9	−4.4
SDTQ-MBPT(4)	6.4	−0.4	−2.9	−3.6	−3.9	−5.6
CCSD	6.9	0.4	−1.8	−2.3	−2.5	−4.0[a]
CCSD+*T*(CCSD)	6.5	−0.1	−2.7	−3.3	−3.7	−5.4[a]

[a] Estimated. See text. [b] All calculations were performed at the [3s2p1d]/[2s1p] MBPT(2) minimum energy geometries of BH_5, BH_3, and H_2.

Table III. Electronic,[a] Zero-Point, and Thermal Contributions to the Enthalpy and Free Energy at 298 K for the Unimolecular Dissociation of BH_5 ($BH_5 \rightarrow BH_3 + H_2$)[b]

ΔE_e	+5.4	ΔE (298 K)	+1.8
ZPC	−4.5	ΔH (298 K)	+2.4
ΔE_0	+0.9	ΔG (298 K)	−4.1

[a] The estimated CCSD+*T*(CCSD) binding energy calculated with the [5s4p3d1f]/[4s2p1d] basis set. [b] All quantities in kcal/mol.

polarized [3s2s1p]/[2s1p] set. The importance of these functions, which account for about 30% of the theoretical binding energy, is in qualitative agreement with the recent study of CH_5^+.[4a]

The most sophisticated calculations performed with the [5s4p3d1f]/[4s2p1d] basis were carried out at the MBPT(4) level. The CC energy differences presented in Table II for this basis have been estimated from the MBPT(4) results by assuming that the differences between these values of ΔE_e and their infinite order CC counterparts [SDQ-MBPT(4) and CCSD; SDTQ-MBPT(4), and CCSD+*T*(CCSD)] are the same as those obtained with the [5s4p3d]/[4s2p] basis. In view of the nearly systematic differences between the fourth-order MBPT and CC binding energies, this approximation is probably in error by no more than 0.5 kcal/mol. Regardless, it is clear that fifth and higher order contributions of the important singly and doubly excited determinants to the correlation energy are not significant importance in determining the binding energy of BH_5. Similar behavior has been observed in our previous studies of the boranes:[10,30,31] in all of the systems we have studied to date, the standard SCF determinant makes the only major contribution to the correlated molecular wave function. The correlation effects which are so important in the boron hydrides arise from relatively weak mixing of a large number of configurations into Ψ. Such "dynamic" correlation problems, which usually can be treated effectively with single-reference MBPT methods, are to be distinguished from cases in which certain non-SCF configurations *individually* make sizable contributions to the wave function. For these systems, which are said to involve "nondynamic" correlation effects, the infinite order terms included in the various CC approximations can be very important.[32]

In Table III, we present values of the binding energy corrected for zero-point vibrations (ΔE_0) as well as the enthalpy (ΔH) and standard Gibbs free energy (ΔG) at 298 K. All corrections to ΔE_e were computed with the standard methods of statistical thermodynamics in the ideal gas–rigid rotor–harmonic oscillator approximation. The vibrational partition functions were calculated from [3s2p1d]/[2s1p]-MBPT(2) harmonic frequencies listed in Table IV, scaled by a factor of 0.9. This empirical scaling approximately accounts for deficiencies in the theoretical force field as well as differences between the actual fundamental frequencies and those of the idealized multidimensional harmonic oscillator. As expected, the vibrational energy of the BH_5 complex is larger than that of the isolated monomers. After application of the zero-point correction of −4.5 kcal/mol, we find a dissociation energy (ΔE_0) of +0.9 kcal/mol. Consequently, only the [5s4p3d1f]/[4s2p1d] calculations predict that the gas-phase association of BH_3 and H_2 is exothermic at low temperature! All of the other spd/sp and unpolarized basis sets fail in this regard. At room temperature, the significantly larger entropy of the separated monomers results in an unfavorable Gibbs free energy for association, corresponding to an equilibrium constant of $\approx 10^{-3}$ M.

Table IV. MBPT(2) Harmonic Frequencies, Infrared Intensities, and Approximate Mode Descriptions for the C_s(I) Isomer of BH_5, BH_3, and H_2[b]

symmetry			harmonic frequency ω(cm^{-1})	intensity (km/mol)	mode description
BH_5	A′	ν_1	3774 (3886)	13.5	H_2 str
		ν_2	2686 (2679)	72.7	BH_3 deg str
		ν_3	2578 (2559)	12.6	BH_3 sym str
		ν_4[a]	1670 (1493)	4.9	H_2 rock
		ν_5	1207 (1181)	7.5	BH_3 deg bend
		ν_6	1199 (1205)	31.2	BH_3 bend
		ν_7[a]	932 (932)	44.7	skeletal rock
		ν_8[a]	693 (567)	51.7	interm. breathing
	A″	ν_9	2730 (2717)	97.4	BH_3 deg str
		ν_{10}	1194 (1178)	1.6	BH_3 deg bend
		ν_{11}[a]	1020 (1017)	0.0	skeletal rock
		ν_{12}[a]	181 (132)	3.2	H_2 twist
BH_3	A_1'	ν_1	2609		sym str
	A_2''	ν_2	1185	67.5	out-of-plane bend
	E′	ν_3	2756	252.4	deg str
		ν_4	1226	24.7	deg bend
H_2	Σ_g	ν_1	4572		sym str

[a] Modes in BH_5 which strongly couple the BH_3 and H_2 units. [b] All frequencies were calculated with the [3s2p1d]/[2s1p] basis except those in parentheses for BH_5, which are those from the [3s2p1d]/[2s] harmonic force field. Frequencies in cm^{-1}, intensities in km/mol.

A few comments regarding the accuracy of our calculations are warranted at this point. First, due to the apparently rapid convergence of the MBPT contribution to the binding energy and the dynamic nature of the electron correlation in BH_5, we do not believe that an even more extensive treatment of correlation would result in a significant change in the theoretical binding energy. Considering the performance of the CCSD+*T*(CCSD) and MBPT(4) approximations in model studies,[21] we believe that our CCSD+*T*(CCSD) binding energies are within 1 kcal/mol of the full CI (i.e., exact) results *for the respective basis sets*. The unusual dependence of ΔE_e on the more diffuse regions of the space spanned by the basis sets, however, suggests that further expansion of the basis (multiple ζ for spdf/spd and possibly even the inclusion of g functions on B and f on H) could be important. Since the nature of the electron distribution in BH_5 places greater demands on the basis than in BH_3 or in H_2, it is almost certain that augmentation of the basis will continue to favor the complex. Also, the structures used in our calculations may differ somewhat from the minimum energy geometries at a high level of theory, such as CCSD+*T*(CCSD) using a very large basis set. Again, this would be most important for BH_5, where a more compact structure would probably result from a more sophisticated optimization. The differences in binding energies calculated at the MBPT(2) level with the various basis sets, coupled with the magnitude of the force constant corresponding to the "dissociation"

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(31) Stanton, J. F.; Bartlett, R. J.; Lipscomb, W. N. In *IMEBORON VI Proceedings*; World Scientific: Singapore, 1988.

(32) For a recent review of chemical applications of CC methods, see: Bartlett, R. J. *J. Phys. Chem.*, in press.

mode (see next section), leads us to believe that this would make only a modest difference (<1 kcal/mol). An uncertainty of comparable magnitude (in the opposite direction) is associated with the so-called basis set superposition error (BSSE). This nonphysical contribution to the binding energy arises from a lowering of the monomer energies *in the complex* by virtue of their exploitation of basis functions centered on the other constituent. Although this effect cannot be removed systematically, the counterpoise (CP) method of Boys and Bernardi[33] can be used to obtain an upper bound to the BSSE. With the [3s2p1d]/[2s1p] basis, the CP correction to the SCF binding energy is a mere 0.1 kcal/mol, while values of 1.2 ± 0.1 kcal/mol are obtained at all correlated levels. Since the BSSE necessarily vanishes in the limit of a complete basis, the magnitude of this contribution to the binding energy obtained with the largest basis sets is very likely <1 kcal/mol. It is also difficult to judge the accuracy of the zero-point correction, where two competing effects must be considered. First, because of the tighter binding predicted at high levels of theory, the harmonic frequencies of some of the vibrational modes are probably underestimated at the [3s2p1d]/[2s1p]-MBPT(2) level of theory. On the other hand, the soft internal rotation mechanism in BH_5 is undoubtedly very anharmonic, and the MBPT(2) harmonic frequency of 181 cm^{-1} certainly overestimates the zero-point energy of this mode by a considerable margin. With regard to the considerations above, we sepculate that the true values of ΔE_e and ΔH(298 K) are 6.0 ± 2.0 and 3.0 ± 2.0 kcal/mol, respectively.

C. **Vibrational Spectra and Dipole Moment.** Harmonic vibrational frequencies, infrared band intensities, and approximate mode descriptions for the normal vibrations of BH_5 are presented in Table IV; predicted spectra of BH_3 and H_2 are also included for comparison. The normal modes of BH_5 can be logically grouped in two distinct categories: those which correspond to perturbed vibrations of the monomers and the intermolecular coupling modes. Most interesting among those in the former category is the "H_2" stretching vibration. Due to the lengthening of the H–H internuclear distance and small but nonnegligible coupling with the heavier and more sluggish boron atom, the predicted MBPT(2) frequency for this mode is 798 cm^{-1} below that calculated for the isolated H_2 stretch. The magnitude of the redshift is approximately half the calculated for CH_5^+,[4a] which is consistent with the considerably stronger binding energy of the latter. The extent of intermolecular interaction is also seen in the splitting of the degenerate stretching and bending frequencies of BH_3 upon complexation. Again, these values [44 cm^{-1} for the stretch, 13 cm^{-1} for the bend] are smaller than those in CH_5^+ (76 and 15 cm^{-1}). All of the "BH_3" frequencies in BH_5 are lower than those computed for BH_3, except for the out-of-plane bending mode, which occurs 9 cm^{-1} above the free BH_3 mode. This result is easily understood on steric grounds; the presence of the H_2 above the apex of the umbrella acts to impede this motion, which is unfettered in the free monomer. At this level of theory, infrared intensities for the allowed transitions in the BH_3 monomer are considerably larger than those in the complex. While this could again be taken as evidence for $BH_3 \rightarrow H_2$ charge redistribution, it can also be rationalized by changes in the BH_3 geometry and by differences between corresponding normal coordinates in the free and complexed borane units. Modes which most closely correspond to the infrared-forbidden totally symmetric vibration of BH_3 and the stretch of H_2 in BH_5 have comparable intensities (12.6 and 13.5 km/mol, respectively), which again are smaller than those found in CH_5^+ (67.6 and 24.8 km/mol).

In BH_5, five of the normal vibrations are best described as coupling between the two subunits. The most interesting of these are ν_8 and ν_{12}. The former is the breathing mode of the complex—the symmetric dissocation pathway—and occurs at 693 cm^{-1}. The form of ν_{12} is dominated by internal rotation of the H_2 monomer about the H_a–B–H_b bisector, and the predicted frequency is 181 cm^{-1}. The low barrier for internal rotation [17 cm^{-1} at MBPT(2)] indicates that the actual fundamental frequency for this mode is probably much lower. The other intermolecular modes are ν_6 (a rocking of the H_2 subunit about an axis perpendicular to the symmetry plane), and the less interesting ν_7 and ν_{11}, which involve complicated coupling of skeletal rocking modes. Note that while deletion of hydrogen polarization functions has only a small effect on the predicted frequencies of the intramolecular features (other than the expected reduction of the H_2 redshift and of the degeneracy splittings), the frequencies of the intermolecular vibrations are quite sensitive. The contribution to the binding energy made by these functions is directly reflected here, especially for the breathing mode, ν_6. Significantly, the theoretically determined harmonic frequency for ν_6 in CH_5^+ is much higher (1665 cm^{-1}), again because of the much stronger binding on the organic analogue of BH_5.

Table V. Dipole Moment of the C_s(I) Equilibrium Structure of BH_5[a]

	μ (Debye)	
	[4s3p1d]/[3s1p]	[5s4p3d]/[4s2p]
SCF	1.97	1.81
MBPT(2)	1.97	1.79
MBPT(3)	1.96	1.78
SDQ-MBPT(4)	1.96	1.78
MBPT(4)	1.96	1.78
CCSD	1.95	1.78
CCSD+*T*(CCSD)	1.95	1.77

[a] Calculated with the [4s3p1d]/[3s1p] and [5s4p3d]/[4s2p] basis sets at the MBPT(2)-[3s2p1d]/[2s1p] minimum energy geometry.

Table VI. Total MBPT(2)-[3s2p1d]/[2s1p] Energy of BH_5 at Various Points Along the Symmetric Dissociation Pathway[a]

D_{B-X} (Å)	*E* (kcal/mol)	D_{B-X} (Å)	*E* (kcal/mol)
−0.2	2.52	0.9	2.52
0.0	0.00	1.2	2.71
0.2	0.84	2.0	3.21
0.4	1.76	inf	3.64
0.6	2.23		

[a] Distances between the center of mass of the H_2 and the boron atom (D_{B-X}) were constrained, and the remaining seven geometrical degrees of freedom optimized. Quoted energies are relative to the C_s(I) minimum.

Equilibrium dipole moments of BH_5 were calculated at various levels of theory with the [4s3p1d]/[3s1p] and [5s4p3d]/[4s2p] basis sets and are presented in Table V. Calculations on HF and H_2O with comparable basis sets[23,24] suggest that the MBPT(4) and CCSD+*T*(CCSD) dipole moments obtained with the larger basis are within 5% of the actual value at this geometry. The magnitude of μ is somewhat larger than we had expected and suggests that there is indeed significant distortion of the electron density when the BH_3–H_2 "bond" is formed. The weak dependence of μ to the level of correlation is remarkable and implies that the static charge distribution, unlike the stability, is relatively insensitive to correlation effects. The basis set dependence of μ is noticeable, however, in accord with the qualitative trends found in the binding energy calculations.

D. **Pathways for Dissociation and Rearrangement.** Since the symmetric decomposition of BH_5 into BH_3 and H_2 is an electronically allowed process,[9] one expects only a small barrier to dissociation. Indeed, Hoheisel and Kutzelnigg[7] presented a plot of calculated energies along the reaction pathway which suggested that there was no *kinetic* barrier at all. In order to address this question in detail, we have optimized internal coordinates for a number of structures along the reaction pathway at the MBPT(2) level, holding the B–X (X is the center of mass of the H_2) distance fixed. The results of these calculations are displayed in Table VI and clearly show that dissociation occurs with at most a slight barrier at this level of theory.[34]

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(33) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *18*, 553.

(34) Although our calculations suggests that there is no barrier to association on the electronic potential energy surface, the increase in zero-point vibrational energy along the reaction coordinate raises the possibility of a small hump on the (more meaningful) vibrationally adiabatic reaction profile. We thank the referee for mentioning this point in the review.

Table VII. Theoretical Barrier Heights for the Hydrogen Scrambling Mechanism in BH_5, via the C_{2v} Transition State Pictured in Figure 1[a]

	bare barrier height [ΔE_e(act)]	
	[4s3p1d]/[3s1p]	[5s4p3d]/[4s2p]
SCF	12.6	13.1
MBPT(2)	5.6	6.6
MBPT(3)	6.0	7.2
SDQ-MBPT(4)	6.5	7.7
SDTQ-MBPT(4)	5.9	7.0
CCSD	6.7	7.8
CCSD+*T*(CCSD)	6.0	7.2

Zero-Point Correction: −0.2 kcal/mol

ΔH_{298}(act) − ΔE_e(act) = −0.7 kcal/mol

[a] Zero-point and thermal corrections calculated from the MBPT(2)-[3s2p1d]/[2s1p] theoretical structures and the corresponding harmonic frequencies, which are listed in Table VII. All values in kcal/mol.

As mentioned in section IIIA, the C_{2v} isomer of BH_5 was found to be a transition state for hydrogen scrambling. This transition state interconverts the C_s(I) structure pictured in Figure 1 to an equivalent minimum, in which H_b and H_c comprise the H_2 subunit. In order to account for the isotopic effects in BH_4^- hydrolysis,[2] the barrier for this process must be small enough to allow for scrambling on the time scale for dissociation but large enough so that the evolved hydrogen gas is not a statistical mixture of products. On the basis of the experiments, which indicate that the probability of scrambling before dissociation is roughly 0.03,[35] it can be inferred that the effective barrier probably lies 1–2 kcal/mol above the $BH_3 + H_2$ asymptote. In order to estimate the activation energy for this process, we have carried out calculations on the optimized MBPT(2) structure with the [4s3p1d]/[3s1p] and [5s4p3d]/[4s2p] basis sets. Results are reported in Table VII. After corrections for zero-point vibrations and thermal effects, an activation enthalpy (ΔH_{298}(act)) of 6.6 kcal/mol is obtained. This value is 4.2 kcal/mol above the theoretical dissociation enthalpy at this temperature for BH_5 and is outside the range expected from the experimental isotopic studies.

Here again, a few comments regarding the interpretation of our calculations are in order. For reasons similar to those discussed in section IIIA, it is probable that a larger basis would favor the BH_5 equilibrium structure relative to the activated complex for rearrangement, leading to a somewhat higher barrier. The true barrier height is probably somewhere between 7 and 9 kcal/mol, and it is unlikely that the transition state lies only 1–3 kcal/mol above the separated BH_3 and H_2 molecules. Furthermore, simple considerations of transition-state theory[36] suggest that for a given activation energy, the unimolecular decomposition will proceed at a greater rate than the rearrangement. Finally, the Δ(PV) correction we have made to the dissociation energy is not appropriate for the solvated reaction. All of these factors argue against the involvement of the C_{2v} transition state in hydrogen scrambling. Before one too glibly dismisses this possibility, however, two factors need to be considered.

Table VIII. MBPT(2) Harmonic Frequencies for the Three Isotopomers of the Equilibrium Structure and Transition State Used in the Rate Calculations[a]

ground state			transition state		
BH_5	BH_4D	BD_4H	BH_5	BH_4D	BD_4H
3774	3270	3294	2803	2803	2349
2730	2730	2043	2684	2683	2106
2686	2686	2003	2547	2526	1964
2578	2577	1833	2350	2331	1799
1670	1485	1421	2331	1740	1710
1207	1200	907	1402	1274	1243
1199	1183	874	1212	1175	1003
1194	1165	870	1168	1161	874
1020	1008	784	1163	1132	853
932	839	777	1142	1056	846
693	621	549	891	787	712
181	153	159	1101i	1071i	841i

[a] Frequencies are in cm^{-1}.

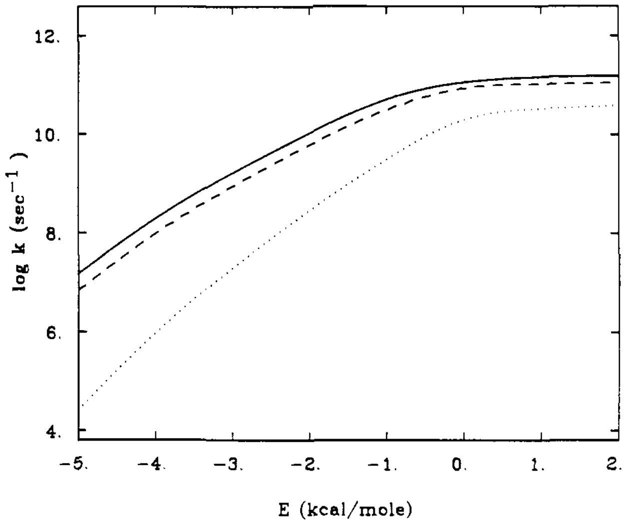

Figure 3. Microcanonical rate of hydrogen scrambling in BH_5 (solid line), BH_4D (broken line), and BD_4H (dotted line) along the pathway discussed in the text. The zero of energy refers to the ground vibrational level of the transition state. The calculations neglect rotation and are averaged over A′ and A″ vibrational states. Plotted curves are cubic spline functions fitted to rates calculated at integral values of the scaled internal energy.

1. **Solvent Effects.** In our calculations, the sometimes profound effects of solvation are not considered at all, and the results are strictly applicable only to the gas-phase species. Taken at face value (see 2. below, however), the results of our calculations suggest that negligible scrambling occurs in the gas phase. Nevertheless, BH_5 may be trapped in a solvent cage in solution, and many dissociations and subsequent reassociations may occur for every molecule of hydrogen which is evolved. Roughly 25 of these events would be compatible with the observed isotopic distribution if $\Delta H_{act} - \Delta H_{diss}$ = 4 kcal/mol.

2. **The Role of Quantum Tunneling.** Since the normal coordinate corresponding to the scrambling mechanism largely involves motion of hydrogen atoms, it is logical to speculate that proton tunneling might make an appreciable contribution to the rate. To investigate this possibility, we have used a modified RRKM model due to Miller,[37] which allows for tunneling through the classical barrier. In our calculations, the tunneling probabilities were calculated for a one-dimensional generalized Eckart barrier,[39] which was parameterized by the MBPT(2) harmonic force fields of the equilibrium and transition structures (see Table VIII) and the [5s4p3d]/[4s2p] activation energy. The quantum rate constants were calculated by explicit summation over enough vibrational levels of the transition state to achieve reasonable convergence[38] (only a few hundred states make nonnegligible contributions at the highest energy studied). The results of the microcanonical rate calculations, which indicate the tunneling is indeed important in this case, are presented in Figure 3. As

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[35] Approximately 1.5% of the evolved gas is H_2. If it is assumed that half of the rearrangements lead to scrambling (the two weakly bound hydrogen positions are not equivalent) and that the frequency factors for the two processes are roughly equivalent, the difference in effective activation energies is on the order of 2 kcal/mol.

[36] Smith, I. W. M. *Kinetics and Dynamics of Elementary Gas Reactions*; Butterworths: London, 1980.

[37] Miller, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 6810. Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem.* **1979**, *83*, 1079.

[38] Following ref 37, we have used the empirical semiclassical Whitten–Rabinovitch formula Whitten, G. Z.; Rabinovitch, B. S. *J. Chem. Phys.* **1963**, *38*, 2466 to estimate the number of internal quantum states at the various energies. Even at the lowest energies included in the plot, differences between the exact number of available states and the Whitten–Rabinovitch approximation are only ≈10%. Effects of rotation have been neglected.

expected, the greatest degree of nonclassical behavior is seen for interconversion of the BH_5 isotopomer, where a significant rate ($>10^6$ s^{-1}) persists at an energy 5 kcal/mol below the classical threshold. While interesting, this particular process does not give rise to the observed effect—the more relevant results are those obtained for BH_4D and BD_4H, with the unique isotope geminal to the hydrogen which lies on the C_2 symmetry axis. Calculations for these systems also show significant tunneling effects. Since the largest displacement in the transition vector is for the hydrogen on the rotation axis, the barrier for BH_4D scrambling is not much wider (as characterized by the imaginary barrier frequency) than that for BH_5, and the rate of leakage through the classically forbidden region is only marginally lower. In BD_4H, the barrier frequency is much softer, and the rate of tunneling is correspondingly reduced. We should point out, however, that models of tunneling which do not couple the reaction coordinate with the remaining 3N-7 vibrational modes can lead to large errors.[40] Regardless, in previous studies of the isomerization and unimolecular decomposition of HCN[41] and formaldehyde,[42] separable models gave results in good agreement with more sophisticated reaction-path Hamiltonian calculations,[43] which explicitly allow for coupling between the various degrees of freedom. Thus, we believe that it is *possible* that the C_{2v} transition state is involved in the observed hydrogen scrambling and that proton tunneling *might* play a significant role in this process.

IV. Conclusions

We have demonstrated that BH_3 and H_2 can combine to form an unusually stable molecular complex. Sophisticated calculations have predicted a binding energy nearly 3 times larger than those obtained previously, and a striking basis set dependence has been observed. One of the most interesting results of the present research is the surprisingly large exothermicity of association at room temperature. Consequently, it is possible that this molecule could be observed experimentally in the gas phase. It is our hope that some of the results reported in this paper will aid those who choose to follow this line of research. Although the actual infrared spectrum of BH_5 will undoubtedly be broadened and otherwise complicated by the facile internal rotation mechanism, our MBPT(2) band positions and intensities should serve as a guide to interpreting the gross features of the spectrum, and the theoretical dipole moment and molecular structure should be good enough to help assign the microwave spectrum.

Although we cannot make any definitive conclusions regarding the mechanism of BH_4^- hydrolysis proposed by Kreevoy and Hutchins,[3] it appears that all of our results are in accord with expectations based on the mechanism. In addition to finding that BH_5 represents a fairly secure minimum on the intermolecular potential surface, we have also shown that the C_{2v} structure is a transition state on a relatively low-energy pathway for molecular rearrangement. The predicted gas-phase activation energy for this process is somewhat higher than expected from the observed distribution of hydrogen isotopes in deuterolysis of BH_4^-, but hydrogen scrambling in solution might be due to solvation effects. Furthermore, we have produced results which suggest that proton tunneling may play an important role in this process. In conclusion, we find no significant inconsistencies between the results of our work and expectations based on the proposed mechanism.

It is interesting to speculate on the nature of bonding in BH_5. In view of the rather large association energy, it is inappropriate to classify this system as a van der Waals molecule with the subunits interacting through an induced dipole–induced dipole mechanism. Following Hoheisel and Kutzelnigg,[8] we prefer to view BH_5 as being stabilized by chemical bonds. The theoretical structure and force field of the molecule is consistent with the formation of a central (closed) three-center bond connecting the two weakly bound hydrogens with the boron atom. Any interpretation of the bonding, however, is complicated by the entirely repulsive nature of the SCF potential surface. Hence, a model based on the molecular orbital approximation may not be a satisfactory description of the interaction mechanism. The physical source of the stabilization is, as correctly pointed out 13 years ago,[9] involved with electron correlation effects in regions far removed from the boron and hydrogen nuclei. Perhaps the cause of the incorrect qualitative prediction of the SCF model is that the out-of-plane π orbital of BH_3 is unoccupied in the independent-particle wave function. The density which is "stolen" from the in-plane framework when correlation effects are included may be important in inducing the perpendicular polarization of the H–H density and the resultant formation of the stabilizing interaction. In the near future, we plan to use newly developed theoretical methods[44] to study electron distributions in the boron hydrides. At that time, we hope that a physically useful picture of the association mechanism of BH_5 will emerge.

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(39) The relevent formula for the tunneling probability is given explicitly in ref 37.

(40) For a discussion of this subject, see: Miller, W. H. *Acc. Chem. Res.* **1976**, *9*, 306.

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