of the excited state of each monomer moiety as is clear from the observation that the DPTR rate of heterodimer is by 3 orders of magnitude smaller than that of the 7-AI dimer. To explain this large difference, it seems to be necessary to carry out an elaborate calculation of the energy barrier in the excited-state surface. However, an ab initio calculation for these many electron system with high accuracy may be beyond our scope, at the present stage, and is an subject to be solved in the future.

The most significantly feature of the DPTR for these dimers is that the rate is promoted dramatically by the excitation of the symmetric stretching vibration in the hydrogen bond. This finding unveiled the microscopic aspect of proton-transfer dynamics.

The 7-AI tautomer, which is the product of DPTR, was also trapped and characterized in a jet. The fluorescence excitation and dispersed fluorescence spectra of tautomer exhibit an extensive progression of the symmetric stretching mode, indicating that this vibration plays a key role in DPTR.

In order to explain the present results, we considered a two-dimensional model potential. Using this potential surface, the mechanism of the promotion is explained as the enhancement of the classical detour pathway overtaking the quantum mechanical (tunneling) pathway as the result of the dynamical coupling of proton motion with the intermolecular vibrational motion.

Ab Initio Energy and Structure of H⁻(H₂)₂

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The structure and energy of the H⁻(H₂)₂ complex have been investigated by using the restricted Hartree–Fock (RHF) and Møller–Plesset perturbation theory (MPPT) methods. The geometries were optimized at the RHF and second-order MPPT (MP2) levels of theory, and energies were calculated at the RHF through fourth-order MPPT (MP4) levels. The predicted equilibrium geometry of the complex changes drastically when correlated methods are used. The RHF results predict the complex to be linear with the hydride between the two H₂ moieties and yields an interaction energy of −1.76 kcal/mol relative to H⁻, H₂, and H₂. The correlated results show the complex to be V-shaped with the hydride at the base of the V and give interaction energies of −2.79 and −2.75 kcal/mol at the MP2 and MP4 levels of theory, respectively. The nonadditive contribution to the interaction energy is found to be large and to cause the geometry of the complex to be nonlinear. The in-phase bending motion of the two H₂ species about the central hydride is found to be an extremely low frequency mode; in fact, the energy difference between the linear complex and the V-shape complex is −0.24 kcal/mol at the correlated level. The thermodynamic stability of the H⁻(H₂)₂ anion cluster is predicted to be unlikely, but a few of the isotopically substituted complexes are predicted to be thermodynamically stable.

Introduction

Recently, there has been considerably interest in lightly solvated anions.[1-28] New developments in various types of anion sources and anion spectroscopy have opened this field to be a wide variety of experimental avenues of study.[29-42] These techniques are used to probe isolated anions and those that are interacting with one or more solvent molecules. We believe it is important for these systems to be studied theoretically as well, because the interactions among the various species are unusual whenever anions are involved. Anions associate more intimately with solvent molecules than do neutral species due to both the charge and the diffuse electron distribution of the anion. In turn, the solvent molecules more strongly affect the loosely bound electrons of an anion. Thus, the anion can strongly polarize the solvent and the polarized solvent can back-polarize the anion. Because of these facts, it is likely that investigations of solvated anions will produce results that are somewhat different from observations of solvated neutral or cationic species.

There has been much interest in hydride anions solvated by various species. In particular, solvation by H₂ molecules to form hydrogen anion clusters has generated substantial attention.[19-28] This work is important to researchers interested in anion–molecule interactions and to atmospheric, combustion, and interstellar

chemistry.[20,27,28] Most of the previous work has been confined to H₃⁻, the smallest of the hydrogen anion clusters. To date, only

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(1) Chalasinski, G.; Kendall, R. A.; Simons, J. *J. Chem. Phys.* **1987**, *87*, 2965.
(2) Hirao, K.; Kawai, E. *J. Mol. Struct.* (THEOCHEM) **1987**, *149*, 391.
(3) Simons, J.; Jordan, K. D. *Chem. Rev.* **1987**, *87*, 535.
(4) Wetzel, D. M.; Brauman, J. I. *Chem. Rev.* **1987**, *87*, 607.
(5) Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1987**, *87*, 4302.
(6) Ortiz, J. V. *J. Chem. Phys.* **1987**, *87*, 3557.
(7) Bowen, K. H.; Eaton, J. G., to be published in *Proceedings of the International Workshop on the Structure of Small Molecules and Ions.*
(8) Griffiths, W. J.; Harris, F. M. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, R7.
(9) Griffiths, W. J.; Harris, F. M. *Org. Mass Spectrom.* **1987**, *22*, 812.
(10) Cremer, D. C.; Kraka, E. *J. Phys. Chem.* **1986**, *90*, 33.
(11) Rohlfing, C. M.; Allen, L. C.; Cook, C. M.; Schlegel, H. B. *J. Chem. Phys.* **1983**, *78*, 2498.
(12) Dacre, P. D. *J. Chem. Phys.* **1984**, *80*, 5677.
(13) Rao, B. K.; Kester, N. R. *J. Chem. Phys.* **1984**, *80*, 1587.
(14) Kalcher, J.; Rosmus, P.; Quack, M. *Can. J. Phys.* **1984**, *62*, 1323.
(15) Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1985**, *83*, 3169.
(16) Squires, R. R. In *Ionic Processes in the Gas Phase*; Amoster Ferreira, M. A., Ed.; Reidel: Dordrecht, 1984.
(17) Paulson, J. F.; Henchman, M. J. In *Ionic Processes in the Gas Phase*; Amoster Ferreira, M. A., Ed.; Reidel: Dordrecht, 1984.
(18) Viggiano, A. A.; Arnold, F. In *Ionic Processes in the Gas Phase*; Amoster Ferreira, M. A., Ed.; Reidel: Dordrecht, 1984.
(19) Rayez, J. C.; Rayez-Meaume, M. T.; Mass, L. J. *J. Chem. Phys.* **1981**, *75*, 5393.
(20) Sapse, A. M.; Rayez-Meaume, M. T.; Rayez, J. C.; Massa, J. L. *Nature (London)* **1979**, *278*, 332.

two other studies have investigated larger anion clusters.[20,23] Sapse et al.[20] studied H_n^- (n = 3, 5, 7, 9, 11, 13) clusters at the Hartree–Fock (HF) level of theory. Hirao and Yamabe[23] investigated the same anion clusters at the HF and the configuration interaction (CI) (with single and double excitations from a single reference configuration (SDCI)) levels of theory. Our earlier work[22] on H_3^- indicated that such SCF and even SDCI calculations may *not* yield reliable results.

Our purpose here is to examine the $H^-(H_2)_2$ cluster anion in its ground electronic state and to add to the knowledge of anion–molecule interactions with more than one solvent molecule. Large basis sets optimized at the correlated level of theory are used to accurately determine these weak interactions. The size-consistent Møller–Plesset perturbation theory[44] (MPPT) through fourth order (MP4) as implemented in GAUSSIAN 82[45–48] was used to treat polarization and electron correlation effects. The effects of basis set superposition errors (BSSE) are corrected for by using the "counterpoise" (CP) method of Boys and Bernardi.[49] RHF treatments of $H^-(H_2)_2$ yield results very similar to those of Sapse et al.[20] and Hirao and Yamabe.[23] When correlation effects are included, the predicted geometry is drastically altered. The possibility of the thermodynamic stability of $H^-(H_2)_2$ and larger clusters of the same series (i.e., for odd values of n) is also discussed. RHF vibrational frequencies are reported for the $H^-(H_2)_2$ cluster and for various isotopically substituted clusters.

Method

MPPT Intermolecular Interactions. The use of MPPT to calculate intermolecular interactions has several advantages when compared to other methods. As shown by Diercksen et al.[50] on

the Be_2 system, a complete fourth-order MPPT calculation can obtain an adequate approximation to the correlation effects, with size-consistent results. In fact, very extensive calculations of Handy et al.[51,52] confirmed that, unless multiconfigurational bond breaking or curve crossing occurs, the MPPT series converges well and is very reliable. Moreover, it has been shown that many valuable qualitative and some quantitative results may be obtained at levels of theory beneath fourth-order MPPT (MP4). As shown by Kestner et al.[53,54] and by Szczesniak and Scheiner,[55] the MP2 and MP3 approximations with BSSE corrections can be used to study hydrogen-bonded systems. Furthermore, second-order and third-order corrections to the interaction energy can be related to physically meaningful contributions to the interaction energy derived from the classic Rayleigh–Schrödinger perturbation theory of intermolecular forces.[56] It should also be pointed out that the functional form of the correlation energy terms allows the pertinent computer codes to be easily vectorized to give high performance on supercomputers. This aspect of MPPT has permitted various researchers to investigate such systems as $H^-(H_2O)_2$,[1] the water dimer,[57] and the nitromethane dimer,[58,59] with quite large basis sets.

The complete fourth-order MPPT, as implemented in the GAUSSIAN 82 computer codes,[47,48] is used in the calculations of this paper. All contributions to the total energy through fourth order in the electron correlation perturbation series are calculated. This includes single (S), double (D), triple (T), and quadruple (Q) substitutions relative to the reference HF determinant. The interaction energy for a general system is outlined in detail in ref 1. The interaction energy, for a three-monomer system, *at* the ith order is defined as

$$\Delta E_{ABC}^{(i)} = E_{ABC;G_{ABC}}^{(i)} - E_{A;G_A}^{(i)} - E_{B;G_B}^{(i)} - E_{C;G_C}^{(i)} \quad (1)$$

where $E_{ABC}^{(i)}$, $E_A^{(i)}$, $E_B^{(i)}$, and $E_C^{(i)}$ are the ith-order MPPT energies of the ABC, A, B, and C moieties, respectively (e.g., $H^-(H_2)_2$, H^-, H_2, and H_2), and where G_{ABC} and G_X indicate the energy of the species should be evaluated at the geometry of complex ABC and the geometry of the monomer X, respectively. The interaction energy *through* the ith order is defined in a similar manner:

$$\Delta E_{ABC}(i) = E_{ABC;G_{ABC}}(i) - E_{A;G_A}(i) - E_{B;G_B}(i) - E_{C;G_C}(i) \quad (2)$$

where $E_{ABC}(i)$, $E_A(i)$, $E_B(i)$, and $E_C(i)$ are the MPPT energies through the ith order of the ABC, A, B, and C moieties, respectively. Also, the relationship between these two equations is given by

$$\Delta E(i) = \sum_{j=0}^{i} \Delta E^{(i)} \quad (3)$$

The Hartree–Fock (HF) interaction energy is given in terms of the zeroth-order and first-order energies as

$$\Delta E_{ABC}^{SCF} = \Delta E_{ABC}^{(0)} + \Delta E_{ABC}^{(1)} = \Delta E_{ABC}(1) \quad (4)$$

At the ith order of MPPT, it is useful to express the total interaction energy of the three-monomer complex in terms of a many-body expansion

$$\Delta E_{ABC}^{(i)} = \sum_X \tilde{\Delta} E_X^{(i)} + \sum_{X>Y} \tilde{\Delta} E_{XY}^{(i)} + \tilde{\Delta} E_{ABC}^{(i)} \quad (5)$$

where X and Y are the monomers A, B, or C. Each element of

(21) Bae, Y. K.; Coggiola, M. J.; Peterson, J. R. *Phys. Rev. A* **1984**, *29*, 2888.

(22) Chalasinski, G.; Kendall, R. A.; Simons, J. *J. Phys. Chem.* **1987**, *91*, 6151.

(23) Hirao, K.; Yamabe, S. *Chem. Phys.* **1983**, *80*, 237.

(24) Aberth, W.; Schnitzer, W.; Anbar, M. *Phys. Rev. Lett.* **1975**, *34*, 1600.

(25) Hurley, R. E. *Nucl. Instrum. Methods* **1974**, *118*, 307.

(26) Macias, A. *J. Chem. Phys.* **1968**, *48*, 3464.

(27) Michels, H. H.; Montgomery, J. A., Jr. *Chem. Phys. Lett.* **1987**, *139*, 535.

(28) Watson, W. D. *Rev. Mod. Phys.* **1976**, *48*, 513.

(29) Ghoroghchian, J.; Sarfarazi, F.; Dibble, T.; Cassidy, J.; Smith, J. J.; Russel, A.; Dunmore, G.; Fleischmann, M.; Pons, S. *Anal. Chem.* **1986**, *58*, 2278.

(30) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. *Gas Phase Ion Chem.* **1984**, *3*, 213.

(31) Haberland, H.; Schindler, H.-G.; Worsnop *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 270.

(32) Gudeman, C. G.; Saykally, R. J. *Annu. Rev. Phys. Chem.* **1984**, *35*, 387.

(33) Corderman, P. R.; Lineberger, W. C. *Annu. Rev. Phys. Chem.* **1979**, *30*, 347.

(34) Herzberg, G.; Lagerquist, A. *Can. J. Phys.* **1968**, *46*, 2363.

(35) Zheng, L. S.; Karner, C. M.; Brucut, P. J.; Yang, S. H.; Pettiette, C. L.; Craycroft, M. J.; Smalley, R. G. *J. Chem. Phys.* **1986**, *85*, 1681.

(36) Lykke, K. R.; Mead, R. D.; Linberger, W. C.; Marks, J.; Brauman, J. I. *J. Chem. Phys.* **1984**, *81*, 4883.

(37) Andersen, T.; Lykke, K. R.; Neumark, D. M.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *86*, 1858.

(38) Lykke, K. R.; Neumark, D. M.; Anderson, T.; Trapa, V.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *87*, 6842.

(39) Owrutsky, J. C.; Rosenbaum, N. H.; Tack, L. M.; Saykally, R. J. *J. Chem. Phys.* **1986**, *84*, 5308.

(40) Tack, L. M.; Rosenbaum, N. H.; Owrutsky, J. C.; Saykally, R. J. *J. Chem. Phys.* **1985**, *83*, 4364.

(41) Al-Za'al, M.; Miller, H. C.; Farley, J. W. *Phys. Rev. A* **1987**, *35*, 1099.

(42) Cosby, P. C.; Mosely, J. T. *Phys. Rev. Lett.* **1975**, *34*, 1603.

(43) Freidhoff, C. B.; Snodgrass, J. T.; Coe, J. V.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1986**, *84*, 1051.

(44) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(45) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(46) Krishnan, R.; Frishch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(47) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegal, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1983**, *No. 13*, program 406.

(48) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Ragharachri, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82; Carnegie-Mellon University: Pittsburgh, PA, 1986.

(49) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(50) Diercksen, G. H. F.; Kello, V.; Sadlej, A. *J. Chem. Phys.* **1985**, *96*, 59.

(51) Handy, N. C.; Knowles, P. J.; Somasundram, K. *Theor. Chim. Acta* **1985**, *68*, 87.

(52) Knowles, P. J.; Somasundram, K.; Handy, N. C. *Chem. Phys. Lett.* **1986**, *113*, 8.

(53) Newton, M. D.; Kestner, N. R. *Chem. Phys. Lett.* **1983**, *94*, 198.

(54) Kestner, N. R.; Newton, M. D.; Mathers, T. L. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1983**, *17*, 431.

(55) Szczesniak, M. M.; Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 6328.

(56) Chalasinski, G.; Szczesniak, M. M. *Mol. Phys.* **1988**, *63*, 205.

(57) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.

(58) Cole, S. J.; Szalewicz, K.; Bartlett, R. J. *Int. J. Quantum Chem.* **1986**, *30*, 695.

(59) Cole, S. J.; Szalewicz, K.; Purvis, G. D. III; Bartlett, R. J. *J. Chem. Phys.* **1986**, *84*, 6833.

eq 5 has a unique physical interpretation. The one-body term is related to the geometrical relaxation of the monomer X and is defined as

$$\tilde{\Delta E}_X^{(i)} = E_{X;G_{ABC}}^{(i)} - E_{X;G_X}^{(i)} \qquad (6)$$

The two-body term is the pairwise interaction between two relaxed monomers and is defined as

$$\tilde{\Delta E}_{XY}^{(i)} = E_{XY;G_{ABC}}^{(i)} - E_{X;G_{ABC}}^{(i)} - E_{Y;G_{ABC}}^{(i)} \qquad (7)$$

The three-body term is the nonpairwise additive interaction of the three relaxed monomers and is defined as

$$\tilde{\Delta E}_{ABC}^{(i)} = E_{ABC;G_{ABC}}^{(i)} - \sum_{X=A,B,C} E_{X;G_{ABC}}^{(i)} - \tilde{\Delta E}_{AB}^{(i)} - \tilde{\Delta E}_{AC}^{(i)} - \tilde{\Delta E}_{BC}^{(i)} \qquad (8)$$

It is also useful to investigate the change in energy for the dissociation of the complex into its various fragments. For the dissociation of ABC → AB + C, the change in energy is defined as

$$-\Delta E_{ABC \rightarrow AB+C}^{(i)} = \tilde{\Delta E}_{AC}^{(i)} + \tilde{\Delta E}_{BC}^{(i)} + \tilde{\Delta E}_{ABC}^{(i)} + \tilde{\Delta E}_C^{(i)} + DE_{AB}^{(i)} \qquad (9)$$

where $DE_{AB}^{(i)}$ is relaxation energy of the AB fragment due to the removal of the C monomer from the ABC complex:

$$DE_{(AB)}^{(i)} = E_{AB;G_{ABC}}^{(i)} - E_{AB;G_{AB}}^{(i)} \qquad (10)$$

The dissociation energy of a two-body system, AB → A + B, is simply the additive inverse of the interaction energy of that system.

If the energies of ABC, A, B, and C are calculated with finite basis sets ($\chi_A \cup \chi_B \cup \chi_C$, χ_A, χ_B, and χ_C, respectively), the use of eq 1 and 2 introduces BSSE. This basis set inconsistency can be corrected by using the counterpoise (CP) method of Boys and Bernardi[49] generalized for the interaction of many distortable molecules.[1] The generalized CP method requires that the interaction energy is calculated from eq 5 rather than from eq 1 in order to correct for the BSSE. Then, two-body and three-body interaction terms are calculated with energies of the appropriate moieties obtained with the *full* basis set of the complex (e.g., $\chi_A \cup \chi_B \cup \chi_C$). Each one-body term is calculated with only the respective monomer basis set. The BSSE at the ith order of MPPT for monomer A is given by

$$\delta_A^{(i)} = E_{A;G_{ABC}}^{(i)}(\chi_A \cup \chi_B \cup \chi_C) - E_{A;G_{ABC}}^{(i)}(\chi_A) \qquad (11)$$

The total BSSE effect is given by

$$\delta^{(i)} = \sum_X \delta_X^{(i)} \qquad (12)$$

where X ranges over all "monomers" (e.g., H^-, H_2, and H_2). This method has proven to be useful in our earlier anion complex studies on $H^-(H_2O)_{1,2}$ and $H^-(H_2)$.[1,22]

Basis Sets. The contracted Gaussian type orbital (GTO) basis sets used in this investigation are based on the Lie and Clementi[60] s basis set. To form the so-called "N basis" used in our work, this s set is augmented with one diffuse s-type and four p-type polarization functions. This basis was optimized by Adams[61] for the electron correlation energy of both the H_2 molecule and H^- anion to arrive at the final N basis. The so-called "N(3d) basis" set is formed by the addition of three higher polarization d basis functions to the N basis; the higher polarization functions were selected to reproduce the electric moments of H_2 and long-range interaction coefficients of H_2–H_2 and H_2–He.[22] These two basis sets have been used previously to determine the intermolecular interactions of $H^-(H_2)$ and gave reliable results with very little BSSE. The N and N(3d) basis sets are tabulated explicitly in Table VI of ref 22.

Results and Discussion

Optimization of Geometry. The geometry of the lowest $^1A'$ state of the $H^-(H_2)_2$ anion cluster was optimized at the SCF and

(60) Lie, G. C.; Clementi, E. *J. Chem. Phys.* **1974**, *60*, 1275.
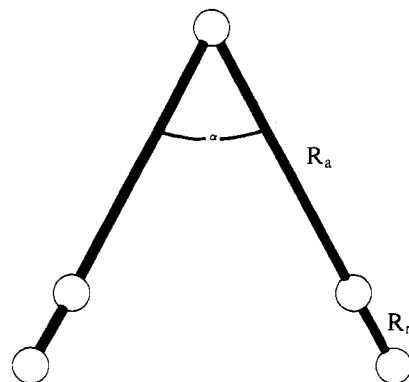(61) Adams, N., unpublished results.

Figure 1. Geometrical parameters for the $H^-(H_2)_2$ anion.

MP2 levels of theory by using the analytic energy derivative algorithm implemented in the GAUSSIAN 82 suite of programs.[47,48] Although some distortions that break the C_{2v} symmetry were examined, none were found that led to lower energies. The parameters optimized in this work are R_m, R_a, and α (see Figure 1). R_m is the distance between the two hydrogens in each of the H_2 molecules, R_a is the distance between each of the two H_2 molecules and the H^- anion, and α is the angle made from one H_2 molecule, through the H^- anion, and to the other H_2 molecule. The resultant optimal SCF and MP2 geometries were found to be very different.

At the SCF level of theory, the $H^-(H_2)_2$ complex is predicted to have a linear geometry (i.e., $\alpha = 180°$). With the N basis, R_m was found to be 0.7382 Å and R_a was found to be 3.1801 Å. With the N(3d) basis, we obtained $R_m = 0.7384$ Å and $R_a = 3.1719$ Å. These two SCF results are very similar to each other and are analogous to distances found by Chalasinski et al.[22] and Michels and Montgomery[27] in $H^-(H_2)$. These results differ from the previous SCF studies of $H^-(H_2)_2$ by Sapse et al.,[20] who found $R_a = 2.10$ Å with a constrained $R_m = 0.74$ Å. Hirao and Yamabe[23] obtained $R_a = 3.275$ Å with a constrained $R_m = 0.739$ Å, which is closer to our prediction. The Sapse et al.[20] result can be explained by the fact that an inadequate basis set was used.[22] In our work, the SCF surface was probed at many bent configurations. The surface was found to be extremely flat for α between 70° and 180°, where differences in energy are on the order of 10^{-3} kcal/mol!

A complete optimization of the three geometrical parameters at the MP2 level was done for the N basis. The optimized geometry at the MP2 level of theory was found to be $R_m = 0.7441$ Å, $R_a = 2.6806$ Å, and $\alpha = 62.2°$. Optimization for the much larger N(3d) basis set is prohibitively expensive and therefore was not performed. However, it is known from our $H^-(H_2)$ work that the smaller N basis set can give reliable geometries.[22] The use of symmetry, however, allows us to optimize the linear complex at the MP2 level of theory with the N(3d) basis. The difference between the optimal linear geometry and the optimal V-shaped geometry for the N basis was used to scale the optimal linear geometry of the N(3d) basis to obtain an arbitrary V-shaped geometry for the N(3d) basis. The resultant geometrical parameters for the N(3d) basis were $R_m = 0.7458$ Å, $R_a = 2.63$ Å, and $\alpha = 62°$.

The optimal MP2 geometry is drastically different from the SCF geometry. The R_a distance shortens from 3.1801 Å (SCF) to 2.6806 Å (MP2). This is partially due to the fact that, at the HF level of theory, the H^- moiety is not bound. Only the optimal MP2 R_m distance (0.7441 Å) is similar to the optimal SCF result (0.7382 Å). Moreover, both these results are close to the internuclear distance for the isolated H_2 molecule (0.7354 Å, MP2 result for the N basis). Hence, the H_2 geometry is only moderately relaxed upon formation of the anion complex and inclusion of the correlation effects.

It is important to note that the potential energy surface is quite flat in the α degree of freedom. Thus, we feel that at most two digits of the optimized geometrical parameters should be considered as significant. Moreover, the difference in energy between

TABLE I: Interaction Energy and BSSE at the Equilibrium SCF Geometry[a]

basis	$\Delta E(1)$	δ_{H_2}	δ_{H^-}
N	-1.757	-1.7 (-5)	-0.03
N(3d)	-1.759	-5.1 (-4)	-0.06

[a] Energies are in kilocalories per mole, and the interaction energies are the BSSE corrected energies.

TABLE II: Correlated Interaction Energy and BSSE at the Equilibrium MP2 Geometry[a]

	N basis			N(3d) basis[b]		
(i)	$\Delta E^{(i)}$	$\delta_{H_2}^{(i)}$	$\delta_{H^-}^{(i)}$	$\Delta E^{(i)}$	$\delta_{H_2}^{(i)}$	$\delta_{H^-}^{(i)}$
SCF	-1.348	-3.5 (-5)	-0.022	-1.234	-0.001	-0.029
2	-1.136	-0.004	-0.242	-1.559	-0.011	-0.120
3	-0.045	+0.001	+0.176	-0.046	+0.004	+0.145
4DQ[c]	+0.222	-2.2 (-4)	+0.034	+0.267	+2.5 (-4)	-0.022
4SDQ[d]	+0.246	-1.5 (-4)	+0.037	+0.295	+2.2 (-4)	-0.021
4	+0.089	-1.5 (-4)	+0.037	+0.089	+2.2 (-4)	-0.021
sum	-2.440	-0.003	-0.052	-2.750	-0.009	-0.025

[a] Energies are in kilocalories per mole, and the interaction energies are the BSSE corrected energies. [b] This geometry for the N(3d) basis set is not fully optimized. See text for details. [c] Fourth-order MPPT with double and quadruple excitations only. [d] Fourth-order MPPT with single, double, and quadruple excitations only (i.e., no triples).

the MP2 optimized linear and V-shaped complexes is only 0.24 kcal/mol or about 10% of the total binding energy. Such a flat bending potential was also observed for the analogous distortional mode of $H^-(H_2O)_2$.[1] Also, large differences between the SCF and MP2 optimal R_a bond distances were observed for the $H^-(H_2)$[22,27] and $H^-(H_2O)$[1] anion complexes. Moreover, these previous studies show that the MP2 optimal geometries are very close to the MP4 optimal geometries. Therefore, we have chosen to calculate the MP4 intermolecular interactions at the MP2 geometries in order to avoid the prohibitive cost of a pointwise geometrical optimization at the MP4 level of theory.

As mentioned above, the change in geometry from the RHF level to the MP2 level is quite substantial (N basis set result). There was concern that this change in geometry was a basis set effect and not a physical one, since the difference in energy between the optimal linear geometry and the optimal V-shaped geometry (-0.24 kcal/mol) is roughly the same as the MP2 BSSE correction at the V-shaped geometry (-0.25 kcal/mol). However, the BSSE in the linear complex (-0.20 kcal/mol) is similar to the V-shaped result. Thus, we conclude that the change in geometry due to the treatment of the correlation effects is truly a physical effect and not a basis set effect.

Interaction Energy between H^- and Two H_2 Molecules. The components of the interaction energy, $\Delta E^{(i)}$, the total interaction energy, $\Delta E(4)$, and the associated BSSE effects, as per eq 11 and 12, are given in Tables I and II, for the SCF and MP4 results, respectively. Both basis sets yield interaction energies within a few tenths of a kcal/mol of one another. The total interaction energy amounts to -2.44 kcal/mol for the N basis and -2.75 kcal/mol for the N(3d) basis. Each basis set yields very small BSSE's, with the largest error at -0.05 kcal/mol.

The values of the one-, two-, and three-body interaction terms and the dissociation energy for the linear and V-shaped $H^-(H_2)_2$ complexes calculated with the N basis are given in Table III. The same quantities for the V-shaped $H^-(H_2)_2$ complex calculated with the N(3d) basis are also given in this table. One important fact to notice from Table III is that the sum of the MP4 one- and two-body terms for the linear complex (-2.15 kcal/mol) is more attractive than for the V-shaped complex (-2.04 kcal/mol) and would predict a linear geometry. On the other hand, the three-body interaction goes from -0.04 kcal/mol at the linear geometry to -0.40 kcal/mol for the V-shaped geometry. Thus, the bent configuration is more stable largely because of the three-body interaction. This three-body interaction is dominated by the SCF contribution and originates from the first-order exchange and second-order induction factors. One might ask why the complex

TABLE III: Many-Body Terms and Dissociation Energy[a]

(i)	one-body $\Delta E_{H_2}^{(i)}$	two-body $\Delta E_{H^-,H_2}^{(i)}$	two-body $\Delta E_{H_2,H_2}^{(i)}$	three-body $\Delta E_{H^-,H_2,H_2}^{(i)}$	dissociation $\Delta E_{H_5^- \rightarrow H^-(H_2)+H_2}^{(i)}$
		N Basis Bent Geometry			
SCF	0.0476	-0.6680	0.2567	-0.3635	0.6066
2	-0.0148	-0.4643	-0.1766	-0.0015	0.7617
3	-0.0201	0.0149	-0.0283	-0.0064	0.0356
4DQ[b]	-0.0112	0.1303	0.0051	-0.0215	-0.1204
4SDQ[c]	-0.0128	0.1476	0.0074	-0.0309	-0.1307
4	-0.0128	0.0710	-0.0035	-0.0240	-0.0403
sum	-0.0002	-1.046	0.0481	-0.3954	1.3636
		N Basis Linear Geometry			
SCF	0.0372	-0.7876	0.0037	-0.0396	0.7913
2	-0.0127	-0.3681	-0.0034	0.0164	0.3626
3	-0.0173	0.0201	-0.0006	-0.0113	0.0094
4DQ[b]	-0.0097	0.1107	8 (-5)	-0.0117	-0.0883
4SDQ[c]	-0.0110	0.1266	0.0001	-0.0139	-0.1006
4	-0.0110	0.0623	-0.0001	-0.0102	-0.0403
sum	-0.0039	-1.0732	-0.0003	-0.0447	1.1230
		N(3d) Basis Bent Geometry			
SCF	0.0606	-0.6192	0.3077	-0.4246	0.5430
2	-0.0254	-0.6455	-0.2286	0.0110	1.0058
3	-0.0206	0.0203	-0.0354	-0.0100	0.0408
4DQ[b]	-0.0119	0.1550	0.0069	-0.0258	-0.1416
4SDQ[c]	-0.0134	0.1740	0.0106	-0.0364	-0.1539
4	-0.0134	0.0756	-0.0054	-0.0298	-0.0342
sum	0.0011	-1.1687	0.0383	-0.4534	1.5554

[a] Energies in kilocalories per mole. [b] Fourth-order MPPT with double and quadruple excitations only. [c] Fourth-order MPPT with single, double, and quadruple excitations only (i.e., no triples).

is not also bent at the RHF level of theory if the three-body interaction is dominated by the SCF contribution. The answer is that the sum of the SCF one- and two-body terms is 0.51 kcal/mol higher for the bent geometry than for the linear geometry. Only the correlation effects suppress this difference by affecting for instance the H_2–H_2 repulsion and allowing the three-body contribution to favor the bent configuration.

The energy change for the reaction $H^-(H_2)_2 \rightarrow H^-(H_2) + H_2$ is 1.36 kcal/mol for the N basis and 1.56 kcal/mol for the N(3d) basis. The next sequential loss of H_2 (e.g., $H^-(H_2) \rightarrow H^- + H_2$) requires 1.07 kcal/mol for the N basis and 1.19 kcal/mol for the N(3d) basis.[62] This result is contrary to those obtained for $H^-(H_2O)_2$,[1] where loss of the first solvent molecule required less energy than loss of the second H_2O. This trend in $H^-(H_2)_2$ can be understood by comparing the two-body and three-body interactions of these two cases. In the $H^-(H_2)_2$ complex, the three-body term is quite large and represents 28.9% of the first solvation energy. At the same time, the H_2–H_2 repulsive interaction represents only 0.4%. In the water case the three-body term has a much smaller contribution (3.6%), and the water–water interaction has a strong repulsive effect (8.6%). The N(3d) basis gives similar results, with the three-body term yielding 16.5% of the total interaction energy. The complicated interplay of the two-body and the three-body interaction terms is responsible for the V-shaped geometry and the counterintuitive sequential solvation energies of the $H^-(H_2)_2$ complex.

Finally, the results presented in Table III clearly illustrate that the use of a correlated theoretical treatment is essential to obtain reliable interaction energies for such weakly bound species.

Comparison with Previous Results. Two previous studies of the $H^-(H_2)_2$ anion cluster were performed by Sapse et al.[20] and Hirao and Yamabe.[23] Sapse et al.[20] used a very small basis set: four Gaussian orbitals per hydrogenic s-type orbital. Hirao and Yamabe[23] used a better, but still relatively small, basis set: a 4-31G basis with two diffuse s-type and one polarization p-type orbitals added.[23,63]

(62) The $H^-(H_2)$ interaction energies used here are not those from our previous work but interaction energies from the fully optimized complex (e.g., R_m is not fixed at 0.739 Å); see ref 22.

TABLE IV: Comparison with Previous Results[a]

	SCF			
	R_m	R_a	α	ΔE_{int}
Sapse et al.[20]	0.74	2.10	180.0	-7.30
Hirao and Yamabe[23]	0.739	3.275	180.0	-1.69
N basis	0.7382	3.1801	180.0	-1.757[b]
N(3d) basis	0.7384	3.1719	180.0	-1.759[b]

	correlated level of theory				
	R_m	R_a	α	ΔE_{int}	method
Hirao and Yamabe[23]	0.739	3.275	180.0	-1.41	SDCI
N basis	0.7441	2.6806	62.2	-2.44[b]	MP4
N(3d) basis	0.7458	2.63	62.0	-2.75[b]	MP4

[a] Energies in kilocalories per mole, angles in degrees, and distances in angstroms. [b] BSSE corrected interaction energy.

TABLE V: SCF Vibrational Frequencies for the N(3d) Basis

freq, cm⁻¹	sym of vibration	freq, cm⁻¹	sym of vibration
26, 26	π_u	407, 407	π_u
82	σ_g	4493	σ_u
186	σ_u	4494	σ_g
396, 396	π_g		

The results of these two groups are tabulated with the present work in Table IV. The optimized geometries of the three studies are very similar at the SCF level. The Sapse et al.[20] work was limited to the SCF level of theory. Hirao and Yamabe[23] imply that the geometry was reoptimized at the correlated level of theory, but they do not report any geometrical parameters for the hydrogen anion clusters and their SCF geometry is quite different from our MP2 geometry. Our SCF interaction energies and the well depths for the H⁻(H₂)₂ cluster agree with the Hirao and Yamabe[23] result and are very different from the results of Sapse et al.[20] (see Table IV). However, the correlated interaction energy reported by Hirao and Yamabe[23] is approximately one-half of our MP4 value. These differences between the previous results and our need to be explained. The previous studies used basis sets that are simply incapable of adequately describing correlation effects, used the inherently size-inconsistent SDCI method, and/or suffered from large BSSE's. In fact, the Hirao and Yamabe[23] calculations obtained a repulsive contribution from the effect of electron correlation, as was also observed in their H⁻(H₂) calculations. This is most likely due to the use of the non-size-extensive SDCI method and is in conflict with our findings.

SCF Vibrational Frequencies. The harmonic vibrational frequencies for the N(3d) basis at the linear SCF equilibrium geometry are given in Table V. These frequencies are typical for anion complexes held together by intermolecular forces of charge-quadrupole, charge–induced dipole, etc., nature. The SCF vibrational frequencies for the N basis are given in Table VI. This SCF force constant matrix was obtained from the Bartlett and Fitzgerald ABINITIO code, and the vibrational frequencies were calculated by using the UTAH MESS KIT code.[64] The frequencies vary as expected upon isotopic substitution. The MP2 vibrational frequencies were not calculated with these large basis sets due to their relative expense.

Conclusions

Our calculations show that the H⁻(H₂)₂ complex is bound by approximately 3.0 kcal/mol and has a V-shaped equilibrium geometry with a very soft bending mode along which linear geometries are easily accessible to the zero-point vibration. To predict the thermodynamic stability of this anion cluster, we will use our N basis SCF frequencies and the MP4 interaction energy,

TABLE VI: SCF Vibrational Frequencies for the N Basis[a,b]

mode	H_5^-	D_5^-	H^- $(D_2)_2$	D^- $(H_2)_2$	$(D_2)H^-$ (H_2)	H^- $(HD)_2$
1	4503	3185	3186	4503	3902	3903
2	4502	3184	3185	4502	3897	3902
3	413	292	298	408	366	348
4	412	291	298	407	365	347
5	400	283	283	400	339	335
6	399	282	282	399	338	334
7	184	130	175	143	178	178
8	81	57	57	81	66	66
9	27	19	25	21	25	26
10	26	18	24	20	25	25

[a] Frequencies in wavenumbers. [b] Monomer frequencies: H₂, 4592 cm⁻¹; HD, 3997 cm⁻¹; D₂, 3248 cm⁻¹. Relative error for monomer frequencies is 4% from values quoted in: Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.

as well as our previous H⁻(H₂) energy and harmonic vibrational frequency results.[22] Proper accounting for the zero-point vibrational energies[65] shows that the H⁻(H₂)₂ anion complex is predicted to be thermodynamically unstable relative to H⁻ and two H₂ molecules (e.g., H⁻ + H₂ + H₂ → H⁻(H₂)₂; ΔH = +0.1 kcal/mol at 0 K). The complex is even more likely to dissociate to H₃⁻ and H₂ (e.g., H⁻(H₂) + H₂ → H⁻(H₂)₂; ΔH = +0.7 kcal/mol at 0 K). The isotopically substituted anion clusters (D₂)H⁻(H₂) and D⁻(H₂)₂ are also predicted to be thermodynamically unstable relative to the three isolated monomers H₂, D₂, and H⁻. On the other hand, we predict that the D₅⁻, H⁻(D₂)₂, and H⁻(HD)₂ anion clusters are thermodynamically stable at 0 K (relative to their three respective monomers) and thus would be more viable experimental candidates than H⁻(H₂)₂. At higher temperatures, ΔG is no longer equal to ΔH and the entropy change involved in the formation of the cluster must be considered. For the formation of the H⁻(H₂)₂ cluster, the entropy change will undoubtedly favor dissociation of the cluster. For the isotopically substituted clusters the change in entropy contribution may cause them to dissociate as well. The larger H_n^- ($n \geq 7$ and odd) clusters are not likely to exist because of the instability of the H⁻(H₂)₂, although larger clusters of the isotopically substituted species might be stable.

These results together with our previous results on H⁻(H₂)[22] and H⁻(H₂O)₁,₂[1] add to our knowledge base of anion–molecule interactions. We have consistently shown that the effects of electron correlation are vital for achieving reliable predictions of equilibrium geometries and interaction energies (with the correlation corrections amounting to 40–55% of the total interaction energy for these types of anion clusters). We have also shown it to be important to carry out the many-body analysis of the interaction energy in order to gain a physical understanding of this energy. Finally, we have demonstrated the importance of removing BSSE for obtaining quantitative interaction energy results.

(63) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(64) The UTAH MESS KIT system of programs was programed in 1986–1988 by J. A. Nichols, M. R. Hoffmann, R. A. Kendall, H. L. Taylor, D. W. O'Neal, E. Earl, R. Hernandez, and J. Simons.

(65) Del Bene, J. E.; Mette, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. *J. Phys. Chem.* **1983**, *87*, 3279.