Interaction of Dihydrogen with Small and Light Molecules

Olaf Hübner[†] **and Wim Klopper***[,†,‡]

Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany, and Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

Received: November 22, 2006; In Final Form: January 26, 2007

Second-order Møller−Plesset (MP2) calculations (using the approximate resolution of the identity, RI-MP2), explicitly correlated MP2 (MP2−R12) calculations, and coupled-cluster calculations including all single and double excitations with a perturbative estimate of triple excitations [CCSD(T)] are performed to study the interaction of molecular hydrogen with the small molecules HF, H_2O, NH_3, and LiOH. Different adsorption positions are studied. In the cases of H_2O and NH_3, the most favorable configuration places H_2 in an end-on fashion on the O or N atom, respectively. In the cases of HF and LiOH, the H_2 molecule takes a side-on position on the H atom of HF or the Li atom. With respect to MP2 calculations in a triple-ζ basis, both the enlargement of the basis set and the extension of the correlation treatment (CCSD(T) vs MP2) increase the interaction energy. The basis set limit CCSD(T) estimates of the interaction energy of H_2 with the HF, H_2O, NH_3, and LiOH molecules amount to 4.40, 2.67, 3.02, and 10.74 kJ mol^{-1}, respectively. The interaction energy for the simultaneous interaction of H_2 with two LiOH molecules does not significantly exceed the value obtained for the interaction with a single LiOH molecule. Furthermore, the interaction energies (by MP2) of H_2 with glycine, the glycine dimer, and imidazolium chloride amount to 2.78, 5.00, and 6.30 kJ mol^{-1}, respectively.

1. Introduction

In view of a possible relevance to the development of hydrogen storage materials based on physisorption, the interaction of dihydrogen with various small systems is studied. To store hydrogen, in principle different possibilities exist: pressurized hydrogen, liquified hydrogen, chemically bound hydrogen, and hydrogen bound by physisorption.[1] Physisorption materials that preserve the H_2 unit would have the advantage that no large enthalpies would be involved in loading or unloading.[2] Presently, among others, nanostructured carbon, zeolites, and metal−organic frameworks are subject to investigations.[2]

The interaction of H_2 with various systems has also been the subject of numerous theoretical investigations. The studies comprise the interaction with charged systems such as the alkali cations Li^+, Na^+, K^+, and Rb^+,[3−8] the halogenide anions F^-, Cl^-, Br^-, and I^-,[3,9−14] small molecular ions CN^- and NO^+, and charged complexes of CO with Li^+, Mg^{2+}, and Al^{3+},[3] as well as the interaction with neutral molecules such as CO,[3] H_2O,[15] C_2H_2,[16] BeO,[17,18] MgF_2, and AlF_3[19] and the complexes Li(CN), $Mg(CN)_2$, and $Al(CN)_3$[3] or 18-crown-6 ether.[20] Further studies have been concerned with organic molecules: benzene or its derivatives[3,21−27] and larger polycyclic aromatic hydrocarbons.[21−23,25−29] Other work has been concerned with the interaction of H_2 with transition metal complexes in which the interaction strength approaches more or less continuously the chemisorption range.[30] Some studies of the coordination of H_2 to transition metals have been performed, especially with respect to the hydrogen storage issue.[31−34]

The present study is performed to complement the above-mentioned work. It is divided into three parts that are concerned with (1) the small molecules NH_3, H_2O, HF, and LiOH; (2) systems that contain two NH_3 or LiOH units; and (3) finally, some organic molecules. A detailed knowledge about the interaction of H_2 with small molecules might be of value when trying to build more complex binding sites by combination of different interaction sites. Then, the question naturally arises whether it is possible to increase the interaction strength simply by combining favorable sites. Moreover, for the small systems, it is possible to obtain very accurate reference data that help to assess the accuracy of other calculations.

According to Lochan et al.,[3] for storage purposes, the ideal physisorption energy would be in the range between 20 and 40 kJ mol^{-1}. But so far, interactions that fall within this range have been realized, except for transition metal complexes, only for systems that involve isolated ions, but not for neutral systems. With isolated halogenide anions and alkali cations, interaction energies up to 25 kJ/mol^{-1} are achieved,[5,9] and the values are even larger for multiply charged ions.[3] According to Lochan et al.,[3] it is very unlikely to obtain larger interaction energies (of H_2 with other systems) solely based on van der Waals interactions. Therefore, the attempt is made to search for systems with a potentially higher interaction with H_2, referring to ionogenic compounds. But since free ions are not realistic model systems, in this work overall neutral systems are considered: the amino acid glycine and derivatives of imidazole. It is well known that amino acids exist as zwitterions in the solid state, and imidazolium ions are typical ingredients of ionic liquids.

The investigation is based on second-order Møller−Plesset (MP2) calculations.[35] MP2 is the simplest wave function-based method to take into account dispersion.[3] For the smaller systems, we rely on coupled-cluster calculations including the single and

---

[*] To whom correspondence should be addressed.
[†] Forschungszentrum Karlsruhe.
[‡] Universität Karlsruhe (TH).

10.1021/jp0677647 CCC: $37.00

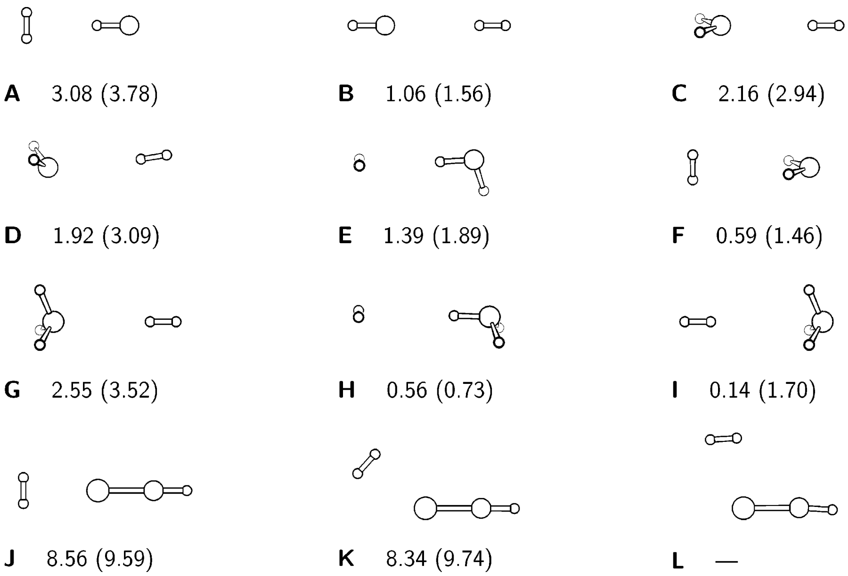


Figure 1. Structures of stationary points of $H_2\cdots HF$ (**A**, **B**), $H_2\cdots H_2O$ (**C**, **D**, **E**, **F**), $H_2\cdots NH_3$ (**G**, **H**, **I**), and $H_2\cdots LiOH$ (**J**, **K**) by MP2/TZVPP calculations (without correction for BSSE) and interaction energies (kJ mol^{-1}) with and (in parentheses) without correction for BSSE and structure of $H_2\cdots LiOH$ by CCSD(T)/aug-cc-pVQZ calculations (**L**).

double excitations with a perturbative estimate of the triple excitations [CCSD(T)].[36,37] Basis set limit estimates for the MP2 method are obtained by means of explicitly correlated MP2 (MP2-R12) calculations.[38,39] At this point it shall be stressed that MP2-R12 is not a different method compared to MP2 but only a means to improve the convergence of MP2 with respect to the size of the basis set.

2. Methods

In a first step, for the complexes of H_2 with HF, H_2O, NH_3, and LiOH, the structures of different stationary points were optimized by MP2 calculations (using the approximate resolution of the identity[40] (RI-MP2)). In a second step, selected structures were optimized by CCSD(T) calculations. Furthermore, some structures were optimized by MP2 calculations taking into account the counterpoise correction[41] for the basis set superposition error (BSSE). Those structures were obtained by explicitly calculating the counterpoise correction for the energy and the gradient at each step of the optimization and searching for the minimum on the corrected hypersurface. The MP2 optimizations used the recently developed polarized triple-ζ valence basis set[42] (def2-TZVPP) for all atoms (in the following, we shall use the label TZVPP for def2-TZVPP). The appropriate auxiliary-TZVPP basis set was used for the resolution-of-the-identity approximation.[43] The CCSD(T) optimizations used the augmented correlation-consistent polarized valence quadruple-ζ basis set[44,45] (aug-cc-pVQZ) on H, N, O, and F in combination with the correlation-consistent polarized core-valence quadruple-ζ basis set (cc-pCVQZ) on Li. The Li basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database.[46] Within the calculations, the 1s orbitals of N, O, and F were not correlated. In order to obtain complete basis set limit estimates of the interaction energy, CCSD(T) calculations were performed for the lowest-energy isomer of each complex (CCSD(T)-optimized structure) with correlation consistent basis sets of different size: on H, N, O, and F non-augmented and augmented cc-pVXZ with X = T, Q, 5, and on Li cc-pCVXZ with X = T, Q. Additionally, for the complexes of HF, H_2O, and NH_3, explicitly correlated MP2 calculations (MP2-R12) were performed (using the approximate resolution of the identity[47] (RI-MP2-R12)). These calculations used a special R12 basis set ([6s4p3d2f] on H; [8s7p5d4f2g] on N, O, F), which is a partially decontracted quadruple-ζ valence (QZV) basis set[48] with the diffuse and polarization functions from the aug-cc-pVQZ basis set and, on N, O, and F, with additional tight d and f functions: N, 8.31(d), 6.00(f); O, 11.0(d), 8.27(f); and F, 14.6(d), 11.1(f).

All interaction energies were corrected for the BSSE by the full counterpoise procedure.[41] For the CCSD(T) results, the extrapolation was made according to the expression[49] $E_{corr} = a + bX^{-3}$, with X being the cardinal number of the basis set, and by taking in each case as reference energy the Hartree−Fock energy in the largest basis set.

For the structures optimized by MP2 (without correction for BSSE), the order of the stationary points was determined by computing the harmonic vibrational frequencies, which were obtained by numerical differentiation of analytical gradients.

The RI-MP2 and RI-MP2-R12 calculations were carried out with the program TURBOMOLE.[40,50,51] The CCSD(T) calculations were performed with the program MOLPRO.[52−54]

The calculations on systems with two ammonia and two lithium hydroxide moleclules as well as on the larger systems containing glycine or imidazolederivatives used only the MP2 method in connection with the TZVPP basis set.

3. Results and Discussion

3.1. Structures of the Adsorption Complexes. First, the different positions of H_2 on the molecules as determined by the MP2 calculations are considered. Figure 1 shows stationary points of $H_2\cdots HF$ (**A**, **B**), $H_2\cdots H_2O$ (**C**, **D**, **E**, **F**), $H_2\cdots NH_3$ (**G**, **H**, **I**), and $H_2\cdots LiOH$ (**J**, **K**). These structures are obtained without correction for BSSE. For selected structures, the structural parameters are compiled in Table 1. Structure **A**, where H_2 takes a side-on position at the hydrogen atom of HF (C_{2v}), is the structure of $H_2\cdots HF$ with the largest binding energy of H_2. According to the frequency calculations, this structure is a minimum of the potential energy hypersurface. Structure **B**, where H_2 sits end-on at the fluorine atom ($C_{\infty v}$), is a second-order transition structure that lies about 2 kJ mol^{-1} higher in energy. (Configurations where H_2 sits side-on at the fluorine or end-on at the hydrogen are characterized by a repulsive interaction.) Structure **C**, where H_2 points with its axis to the

TABLE 1: Structural Parameters of the Optimized Structures of the Coordination Complexes of H_2 on HF, H_2O, NH_3, and LiOH

system	parameter[a]	$MP2^{corr.f.BSSE}$/ TZVPP	MP2/ TZVPP	CCSD(T)/ aug-cc-pVQZ
$H_2\cdots HF$ (C_{2v})	r_{H_2-HF}	206.1	201.3	198.2
	r_{H-H}	73.9	73.9	74.4
	r_{F-H}	91.9	91.9	91.9
$H_2\cdots OH_2$ (C_{2v})	$r_{H_2-OH_2}$	271.8	263.6	263.3
	r_{H-H}	73.8	73.9	74.4
	r_{O-H}	95.9	95.9	95.9
	φ_{HOH}	103.9	103.9	104.4
$H_2\cdots H_2O$ (C_s)	r_{H_2-HOH}		231.1	227.0
	r_{H-H}		73.8	74.3
	r_{O-H}		95.9	95.9
	φ_{HOH}		103.9	104.4
$H_2\cdots NH_3$ (C_{3v})	$r_{H_2-NH_3}$	287.2	276.7	280.8
	r_{H-H}	73.9	74.0	74.4
	r_{N-H}	101.1	101.1	101.3
	φ_{HNH}	106.4	106.5	106.5
$H_2\cdots H_3N$ (C_{3v})	$r_{H_2-H_3N}$		319.7	320.9
	r_{H-H}		73.7	74.3
	r_{N-H}		101.1	101.3
	φ_{HNH}		106.6	106.7
$H_2\cdots H_3N$ (C_s)	$r_{H_2-HNH_2}$		273.2	272.9
	r_{H-H}		73.7	74.3
	r_{N-H}		101.1	101.3
	φ_{HNH}		106.5	106.6
$H_2\cdots LiOH$ (C_s)	r_{H_2-LiOH}		211.2	205.8
	$\varphi_{(H_2)LiO}$		143.2	105.7
	r_{H-H}		74.1	74.9
	r_{Li-O}		158.8	158.8
	r_{O-H}		95.0	94.9
$H_2\cdots LiOH$ (C_{2v})	r_{H_2-LiOH}	214.5	213.1	211.2
	r_{H-H}	74.1	74.1	74.6
	r_{Li-O}	158.8	158.8	158.5
	r_{O-H}	95.0	95.0	94.9
HF ($C_{\infty v}$)	r_{F-H}		91.8	91.8
H_2O (C_{2v})	r_{O-H}		95.9	95.9
	φ_{HOH}		103.8	104.4
NH_3 (C_{3v})	r_{N-H}		101.1	101.3
	φ_{HNH}		106.5	106.6
LiOH ($C_{\infty v}$)	r_{Li-O}		158.5	158.1
	r_{O-H}		94.9	94.9
H_2 ($D_{\infty h}$)	r_{H-H}		73.7	74.2

[a] All r values in picometers; all φ values in degrees.

oxygen atom of H_2O and lies within the H_2O plane (C_{2v}), is the structure of $H_2\cdots H_2O$ with the strongest binding of H_2, provided the correction for BSSE is included. Frequency calculations without correction for BSSE classify structure **C** as a first-order transition structure, connecting two minima of structure **D**, where H_2 points to the oxygen but does not lie within the plane of H_2O (C_s). A structure optimization including the correction for BSSE, starting with structure **D**, leads straightforwardly to the symmetric structure **C**. Therefore, it is very likely that structure **C** represents the minimum. Structure **E**, where H_2 is coordinated side-on to one of the hydrogens of H_2O (C_s), is found to be higher in energy than structure **C** by about 0.8 kJ mol^{-1} and is a minimum, whereas structure **F** is a second-order transition structure. Structure **G**, with H_2 pointing to the nitrogen of NH_3 (C_{3v}), is the lowest-energy structure of $H_2\cdots NH_3$. Structure **H**, with H_2 sitting side-on at one of the hydrogens (C_s), lies about 2 kJ mol^{-1} higher in energy. Frequency calculations without correction for BSSE indicate structure **G** to be a minimum, but structure **H** to be a first-order transition structure, whereas structure **I**, where the H_2 points to the side of the three hydrogens (C_{3v}), is a minimum. However, including the correction for BSSE, structure **I** becomes less stable than structure **H** by 0.4 kJ mol^{-1}. Therefore, it very well might be that structure **I** is, in fact, not a minimum. According to the MP2/TZVPP calculations, structure **J**, where the H_2 molecule coordinates side-on to the lithium atom of LiOH on the axis of the molecule (C_{2v}), is the structure of $H_2\cdots LiOH$ with the strongest binding of H_2 if the correction for BSSE is included. Its energy is lower by 0.22 kJ mol^{-1} than that of structure **K**, the minimum structure without correction for BSSE, where again H_2 is coordinated side-on to the lithium atom, but the direction of coordination forms an angle of about 140° with the axis of LiOH (C_s). Without correction for BSSE, structure **J** is a first-order transition structure and higher in energy than the MP2/TZVPP minimum structure **K** by 0.15 kJ mol^{-1}. Thus, in two cases, for H_2 on H_2O and LiOH, the structures qualitatively depend on whether the correction for BSSE is applied or not.

To obtain more comprehensive information about the influence of the BSSE on the structures, optimizations of the lowest-energy complexes were performed by MP2/TZVPP calculations including the correction for BSSE, and the results are given in Table 1. In the cases of $H_2\cdots H_2O$ and $H_2\cdots LiOH$, comparison is made with respect to the more symmetrical structures that have been identified as the lowest in energy by taking into account the correction for BSSE to the energies. The inclusion of the correction for BSSE elongates the intermolecular distances by between 1 and 10 pm, while the intramolecular distances are hardly affected, by up to 0.1 pm only. At this point, it shall already be mentioned that this elongation has no large effect on the interaction energies: they are increased by less than 0.1 kJ mol^{-1}. In the case of the present complexes, one can state that, to obtain energies corrected for BSSE, it is sufficient to optimize the structures of different stationary points without correction and then to select the structures only by considering the energy values corrected for BSSE at those structures. This works only because the structures including the correction for BSSE are the more symmetrical ones, and, hence, symmetry can be imposed to obtain those structures.

To obtain a further check on the structures, for selected stationary points of the different systems, optimizations were performed by CCSD(T)/aug-cc-pVQZ calculations (see Table 1). In the case of H_2 on HF, H_2O, and NH_3, the CCSD(T)/aug-cc-pVQZ structures essentially agree with MP2/TZVPP structures (with and without correction for BSSE), referring in the case of $H_2\cdots OH_2$ to the C_{2v} results. The intramolecular distances differ by less than 1 pm. The intermolecular distances deviate by 0−4 pm from the MP2 values without correction for BSSE and by 6−9 pm from the MP2 structures that take it into account. Only in the case of LiOH a considerable difference is observed between the CCSD(T)/aug-cc-pVQZ and MP2/TZVPP results. Remember that the MP2/TZVPP structure (with correction for BSSE) is characterized by a H_2 coordination to the lithium atom of LiOH in a T-shaped fashion (H_2−Li distance 215 pm). By contrast, CCSD(T) with the aug-cc-pVQZ basis yields a structure whose angle between the coordination direction and the LiOH axis is about 106° (H_2−Li distance 106 pm). This means an almost parallel alignment of H_2 and LiOH; see structure **L** in Figure 1. The structure optimized in C_{2v} symmetry by the same method with the same basis set (H_2−Li distance 111 pm) has an energy that is higher by 1.02 kJ mol^{-1} (0.98 kJ mol^{-1} without correction for BSSE). Thus, in this case, a pronounced difference between the CCSD(T)/aug-cc-pVQZ and MP2/TZVPP stucture is observed.

The question arises whether this difference is due to the choice of the method or to the size of the basis set. Therefore, the MP2 energies with the aug-cc-pVQZ basis set at both the

C_s and the C_{2v} CCSD(T) structures of LiOH are compared. In doing so, one finds that, with the aug-cc-pVQZ basis set, even by MP2 the C_s structure (**L**) with parallel-aligned H_2 and LiOH is lower in energy, namely by 0.58 kJ mol^{-1} (with and without correction for BSSE). This is only somewhat more than half the value for the same difference by CCSD(T), but nevertheless it is a clear indication that, when using a larger basis set, also by MP2, a structure similar to the CCSD(T) one has to be expected. Hence, the pronounced differences in structure must essentially be attributed to the use of the TZVPP basis set. (The same holds for the H_2O complex in the case of the structure obtained without correction for BSSE.)

To summarize this subsection, it is found that the coordination of H_2 to the negatively polarized sites of the molecules (N, O, and F atoms) happens in an end-on fashion, but coordination to the positively polarized atoms (H, Li atoms) happens in a side-on (T-shaped) fashion. These different types of coordination are consistent with the configurations observed for the coordination of H_2 to alkali cations and halogenide anions:[5,9] H_2 coordinates side-on to the cations (T-shaped) and end-on to the anions, a fact that can be understood essentially in terms of the quadrupole and dipole-polarizability-dependent contributions.[5,9] In the case of $H_2\cdots H_2O$ and $H_2\cdots NH_3$, the end-on coordination to the electronegative site is energetically favored, whereas in case of $H_2\cdots HF$, side-on coordination to the H atom is favored. On closer inspection, it is observed that, when going from NH_3 via H_2O to HF, the stability of the complexes with H_2 coordination at the hydrogen site increases and, vice versa, the stability of the complexes with coordination at N, O, or F decreases. According to Vitillo et al.,[5,9] one important contribution to the interaction energy stems from the interaction of the quadrupole moment of H_2 with the surrounding charges. The increase in interaction strength at the H site of the molecules might be understood on the basis of the interaction of the dipole moment of the F−H, O−H, and N−H bonds with the H_2 quadrupole moment. With respect to the trend observed for the end-on coordination at the electronegative atoms, one may notice that the interaction increases with the polarizability of the adsorbing molecule, and this increasing polarizability might also be the reason for increasing dispersive interactions.

3.2. Interaction Energies with H_2.

Figure 2 presents the interaction energies for the different complexes obtained by different methods and basis sets for the adsorption position with the largest binding energy. Selected values are listed in Table 2. For the sequences of CCSD(T) calculations, the convergence to the basis set limit estimates clearly can be observed. The different estimates (without and with correction for BSSE, using augmented and non-augmented basis sets) approximately coincide. The largest difference is 0.13 kJ mol^{-1}. The values corrected for BSSE converge from below, whereas the uncorrected values mostly converge from above. In the following, reference is made only to values corrected for BSSE. The values for the augmented basis sets essentially are closer to the limit than their non-augmented counterparts. The largest difference between the estimates using augmented and non-augmented basis sets amounts to 0.07 kJ mol^{-1}.

By MP2/TZVPP calculations, values of 3.08, 2.16, 2.55, and 8.56 kJ mol^{-1} are obtained for the dissociation energies of $H_2\cdots HF$, $H_2\cdots H_2O$, $H_2\cdots NH_3$, and $H_2\cdots LiOH$, respectively. The CCSD(T) basis set limit estimates, based on the augmented basis sets, amount to 4.40, 2.67, 3.02, and 10.74 kJ mol^{-1}, respectively. They are larger by 1.32, 0.51, 0.47, and 2.18 kJ mol^{-1} than the respective MP2/TZVPP values; that is, the MP2 values account for 70, 81, 84, and 80% of the CCSD(T) basis set limit estimates. The values obtained by MP2-R12 calculations are near basis set limit MP2 results. Such calculations give values of 4.17, 2.51, and 2.79 kJ mol^{-1} for the dissociation energies of $H_2\cdots HF$, $H_2\cdots H_2O$, and $H_2\cdots NH_3$, respectively. Thus, they account for 95, 94, and 92%, respectively, of the CCSD(T) basis set limit estimates. Hence, both the step from a TZVPP basis to a nearly complete basis within MP2 and the step from MP2 to CCSD(T) basis set limit estimates increase the values for the interaction energy. This result is in contrast to the observa-

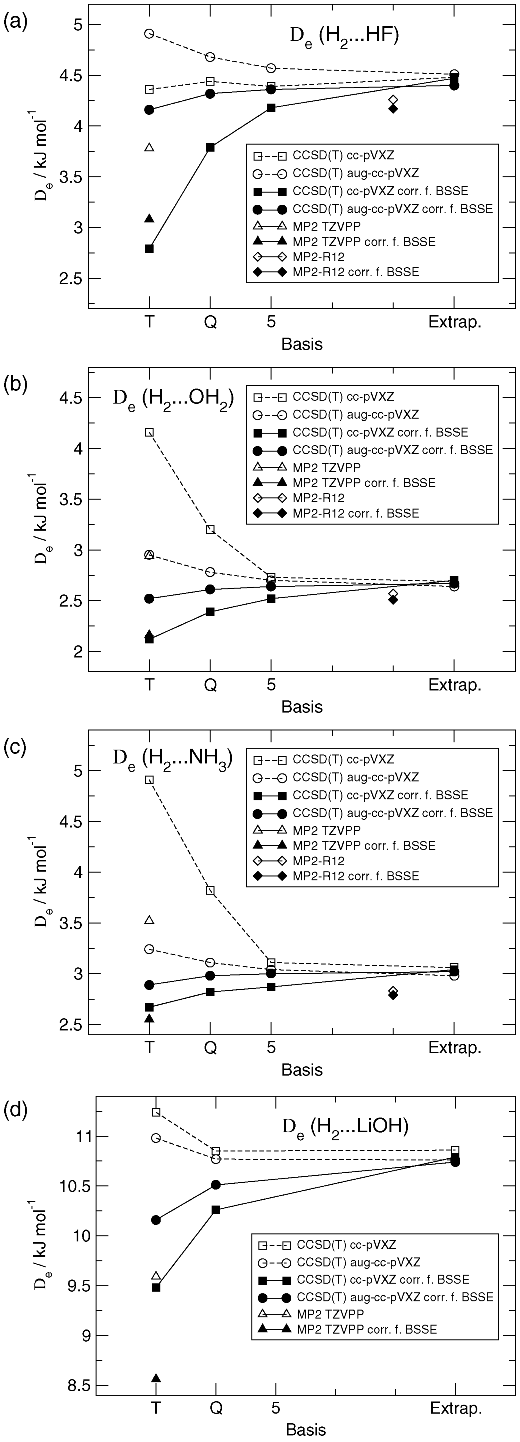


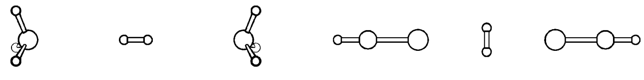
Figure 2. Interaction energies for $H_2\cdots HF$, $H_2\cdots OH_2$, $H_2\cdots NH_3$, and $H_2\cdots LiOH$ by CCSD(T) calculations with different basis sets (CCSD(T)/aug-cc-pVQZ structure) and by MP2/TZVPP and MP2-R12 calculations (MP2/TZVPP structure). For $H_2\cdots H_2O$ and $H_2\cdots LiOH$, the MP2 values refer to the C_{2v} structures, which are the lower-lying structures when including the correction for BSSE. Note that, in the case of $H_2\cdots LiOH$, it disagrees with the CCSD(T) structure.

TABLE 2: Dissociation Energies for the Detachment of H_2 from HF, H_2O, NH_3, and LiOH, Including Correction for BSSE (Uncorrected Values in Parentheses)

system	structure	method	basis	D_e/kJ mol^{-1}
$H_2\cdots HF$ (C_{2v})	MP2	MP2	TZVPP	3.08 (3.78)
		MP2-R12	R12	4.17 (4.26)
	MP2$^{\text{corr.f.BSSE}}$	MP2	TZVPP	3.11
	CCSD(T)	MP2	aug-cc-pVQZ	4.08 (4.50)
		CCSD(T)	aug-cc-pVQZ	4.32 (4.68)
		CCSD(T)	extrap.	4.40 (5.51)
$H_2\cdots OH_2$ (C_{2v})	MP2	MP2	TZVPP	2.16 (2.94)
		MP2-R12	R12	2.51 (2.57)
	MP2$^{\text{corr.f.BSSE}}$	MP2	TZVPP	2.19
	CCSD(T)	MP2	aug-cc-pVQZ	2.47 (2.68)
		CCSD(T)	aug-cc-pVQZ	2.61 (2.78)
		CCSD(T)	extrap.	2.67 (2.64)
$H_2\cdots H_2O$ (C_s)	MP2	MP2	TZVPP	1.39 (1.89)
	CCSD(T)	MP2	aug-cc-pVQZ	2.11 (2.33)
		CCSD(T)	aug-cc-pVQZ	2.31 (2.49)
$H_2\cdots NH_3$ (C_{3v})	MP2	MP2	TZVPP	2.55 (3.52)
		MP2-R12	R12	2.79 (2.83)
	MP2$^{\text{corr.f.BSSE}}$	MP2	TZVPP	2.63
	CCSD(T)	MP2	aug-cc-pVQZ	2.77 (2.95)
		CCSD(T)	aug-cc-pVQZ	2.98 (3.11)
		CCSD(T)	extrap.	3.02 (2.98)
$H_2\cdots H_3N$ (C_{3v})	MP2	MP2	TZVPP	0.14 (1.70)
	CCSD(T)	MP2	aug-cc-pVQZ	0.56 (0.65)
		CCSD(T)	aug-cc-pVQZ	0.78 (0.85)
$H_2\cdots H_3N$ (C_s)	MP2	MP2	TZVPP	0.56 (0.73)
	CCSD(T)	MP2	aug-cc-pVQZ	0.93 (1.03)
		CCSD(T)	aug-cc-pVQZ	1.07 (1.14)
$H_2\cdots LiOH$ (C_s)	MP2	MP2	TZVPP	8.34 (9.74)
	CCSD(T)	MP2	aug-cc-pVQZ	9.86 (10.22)
		CCSD(T)	aug-cc-pVQZ	10.51 (10.77)
		CCSD(T)	extrap.	10.74 (10.76)
$H_2\cdots LiOH$ (C_{2v})	MP2	MP2	TZVPP	8.56 (9.59)
	MP2$^{\text{corr.f.BSSE}}$	MP2	TZVPP	8.56
	CCSD(T)	MP2	aug-cc-pVQZ	9.28 (9.64)
		CCSD(T)	aug-cc-pVQZ	9.49 (9.79)

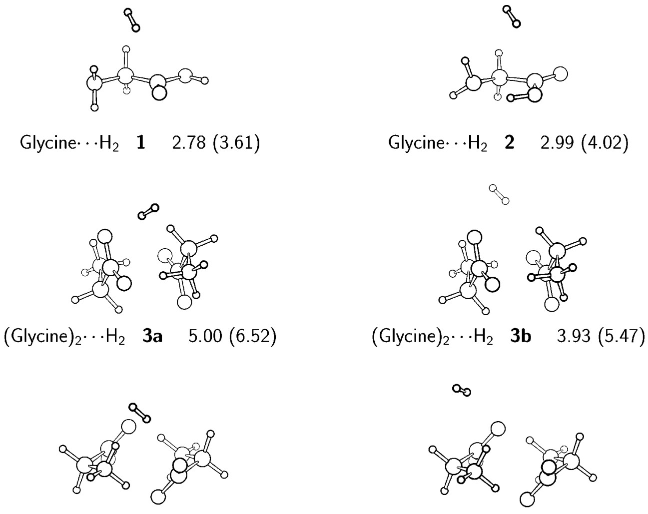
tions made in the case of the adsorption of H_2 on aromatic systems, where it was found that the enlargement of the basis set and the step from MP2 to CCSD(T) have approximatively the same effect but of opposite sign,[27] and therefore, the MP2/TZVPP results could be considered good estimates for more accurate values. Although it seems not possible to simply infer accurate estimates based on MP2/TZVPP calculations and a fortuitous cancellation of errors, the MP2/TZVPP calculations reproduce the general trends in interaction energies well and also approximately the magnitude of the interaction energy. This is an important fact, because MP2 (in connection with a basis set of moderate size like TZVPP) has a considerably broader range of applicability than the demanding CCSD(T) method. Hence, MP2 is nevertheless a very useful tool for a quick determination of the interaction energies of H_2 with a larger set of molecules.

While for the interaction of H_2 with HF, H_2O, and NH_3 the interaction potential energies lie between 2.5 and 4.5 kJ mol^{-1}, the value for the interaction with LiOH is characterized by the clearly larger value of 10.7 kJ mol^{-1}, certainly because of the more ionic character of the alkali center. Among the interactions of H_2 with different alkali cations, that with Li^+ is the strongest, at 24.3 kJ mol^{-1} (by MP2/aug-cc-pVQZ).[5] This means that, taking the LiOH molecule, this interaction is reduced by more than 50%. Similarly, among the interactions of H_2 with the



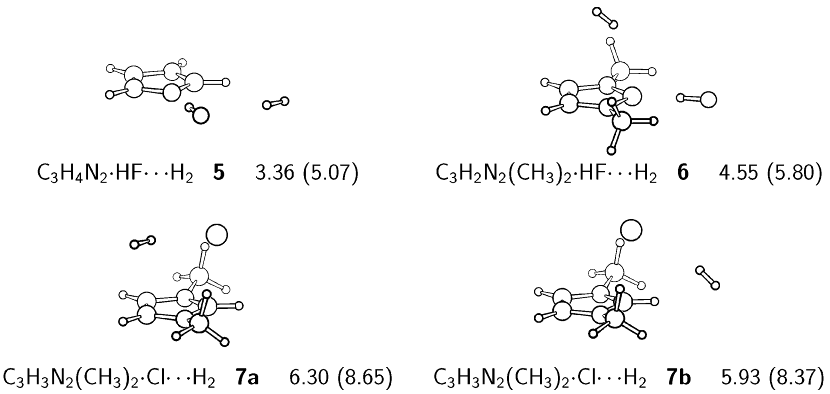
$H_3N\cdots H_2\cdots NH_3$ 4.08 (5.44) $HOLi\cdots H_2\cdots LiOH$ 9.34 (11.18)

Figure 3. Structures of $H_3N\cdots H_2\cdots NH_3$ (D_{3h}) and $HOLi\cdots H_2\cdots LiOH$ (D_{2h}) for which the interaction energy with H_2 has been determined for different fixed distances of the coordinating molecules and maximum MP2/TZVPP interaction energies with and (in parentheses) without correction for BSSE.



Glycine$\cdots H_2$ **1** 2.78 (3.61)
Glycine$\cdots H_2$ **2** 2.99 (4.02)
(Glycine)$_2\cdots H_2$ **3a** 5.00 (6.52)
(Glycine)$_2\cdots H_2$ **3b** 3.93 (5.47)
(Glycine)$_2\cdots H_2$ **4a** 4.97 (6.27)
(Glycine)$_2\cdots H_2$ **4b** 4.45 (5.73)

Figure 4. Structures of the adsorption complexes of H_2 with glycine and the glycine dimer and MP2/TZVPP interaction energies with and (in parentheses) without correction for BSSE.



$C_3H_4N_2{\cdot}HF{\cdots}H_2$ **5** 3.36 (5.07) $C_3H_2N_2(CH_3)_2{\cdot}HF{\cdots}H_2$ **6** 4.55 (5.80)

$C_3H_3N_2(CH_3)_2{\cdot}Cl{\cdots}H_2$ **7a** 6.30 (8.65) $C_3H_3N_2(CH_3)_2{\cdot}Cl{\cdots}H_2$ **7b** 5.93 (8.37)

Figure 5. Structures of the adsorption complexes of H_2 with imidazole hydrofluoride (**5**), 1,3-dimethylimidazol-2-ylidene hydrofluoride (**6**), and 1,3-dimethylimidazolium chloride (**7a**,**b**) and MP2/TZVPP interaction energies with and (in parentheses) without correction for BSSE.

halide anions, that with F^- is the strongest, at 24.8 kJ mol^{-1} (MP2/aug-cc-pVQZ),[9] and replacing F^- by HF reduces the interaction by 80%.

The CCSD(T) basis set limit value of 2.67 kJ mol^{-1} for $H_2{\cdots}OH_2$ agrees with the value of 2.646 kJ mol^{-1} from CCSD-(T)-R12 calculations reported by Faure et al.[15]

So far, the systems studied are composed of formally only singly charged atoms. But one can speculate that, by using systems with formally multiply charged ions, it might be possible to obtain a still stronger interaction, since the interaction with bare, multiply charged ions is also considerably stronger. But so far, only for the BeO molecule (and, for instance, not for MgO) a large value of about 70 kJ mol^{-1} has been found for the interaction with H_2.[17,18] And unfortunately, because of its toxicity, this system is not interesting for technical applications.

3.3. Interaction of H_2 with Two LiOH Molecules. In an attempt to see if larger interaction energies with H_2 could be achieved simply by using systems composed of two molecules, the interaction of H_2 with two NH_3 as well as two LiOH molecules was studied. For this purpose, axial structures were assumed, in which H_2 takes a central position. Within $H_3N{\cdots}H_2{\cdots}NH_3$ (D_{3h}), the NH_3 molecules lie on the axis of H_2, and within $HOLi{\cdots}H_2{\cdots}LiOH$ (D_{2h}), the two Li atoms point to the middle of the H−H bond. Then, the interaction energy is determined for different fixed distances of the coordinating molecules. In fact, the distances of the two N atoms of the NH_3's or the distances of the outer H atoms of the LiOH's are fixed, and the structures are optimized with restriction by symmetry. Corresponding optimizations are performed on systems where the H_2 is removed. For each distance, the BSSE is estimated.[41]

Figure 3 shows the structures of $H_3N{\cdots}H_2{\cdots}NH_3$ (D_{3h}) and $HOLi{\cdots}H_2{\cdots}LiOH$ (D_{2h}). The interaction energies (including the correction for BSSE) for the optimized distances of the coordinating molecules amount to 4.08 and 9.34 kJ mol^{-1}, respectively. The corresponding structures are characterized by an N−N distance of 676 pm and by an H−H distance between the outer H atoms of the LiOH molecules of 957 pm, whereas the Li−Li distance amounts to 453 pm. The value of 4.08 kJ mol^{-1} for $H_3N{\cdots}H_2{\cdots}NH_3$ is larger (after all) by 1.5 kJ mol^{-1} (or 60%) than the value for a single NH_3. But the value of 9.34 kJ mol^{-1} for $HOLi{\cdots}H_2{\cdots}LiOH$ is larger by only 0.78 kJ mol^{-1} (9%) than the value of 8.56 kJ mol^{-1} for one LiOH and H_2.

Thus, the action to replace one LiOH by two LiOH's essentially does not increase the interaction energy. Unfortunately, despite the increase of the interaction energy by 60% for the ammonia system, the final value of about 4 kJ mol^{-1} is still much too low to be interesting. Considering the structures investigated here, it can be noted that the symmetrical structures considered in this part essentially try to optimize the interactions with the quadrupole moment of H_2, whereas polarization will cancel. Therefore, there might be less symmetrical arrangements with increased interaction by polarization.

3.4. Interaction of H_2 with Some Organic Molecules. Figure 4 shows the adsorption complexes of H_2 with a glycine molecule and a glycine dimer for different conformers. All structures shown in this section have been fully optimized. The free glycine monomer in the gas phase does not exist as a zwitterion. The two most stable glycine conformations are those of structures **1** and **2**. Structure **2** of the isolated glycine is less stable by 1.44 kJ mol^{-1} than structure **1**. The interaction energies of H_2 with glycine with the structures **1** and **2** amount to 2.78 and 2.99 kJ mol^{-1}, respectively. The interaction strength is somewhat weaker than that of H_2 with HF and about 1 kJ mol^{-1} weaker than that of H_2 with benzene.[27] Ionic configurations of the glycine monomers are present within the glycine dimer. The interaction energy with H_2 is calculated for the conformations (of C_i symmetry) of the dimer shown in structures **3a**/**3b** and **4a**/**4b**. The dimer conformation in structure **3a**/**3b** is more stable by 2.03 kJ mol^{-1} than that in structure **4a**/**4b**. The interaction of H_2 with the more stable dimer conformation for the most favorable adsorption site (structure **3a**) amounts to about 5.00 kJ mol^{-1}. Thus, the interaction strength of H_2 is increased with respect to the monomer: it is now in the range of the interaction of H_2 with antracene. But values that substantially exceed those for the aromatic systems (e.g., by a factor of about 3) are not obtained.

Figure 5 shows the adsorption complexes of H_2 with imidazole hydrofluoride (**5**), 1,3-dimethylimidazol-2-yliden hydrofluoride (**6**), and 1,3-dimethylimidazolium chloride (**7a**,**b**). In order to build a simple ionic system containing imidazolium, the imidazolium structure was optimized in combination with an F^- anion. But the free imidazolium cation is not stable in the presence of F^-: the F^- abstracts a proton, resulting in the (non-ionic) hydrogen-bonded adduct of imidazole and HF. The interaction energy of this complex with H_2 amounts to only 3.36 kJ mol^{-1}. Next, we tried to saturate the nitrogen positions of imidazole with methyl groups. Then, F^- again takes a proton, but now from the carbon position between the nitrogens, resulting in an ylidene compound. The interaction with H_2 is only weakly increased in energy with respect to the former compound, to 4.55 kJ mol^{-1}. Only with a chloride anion does the dimethylimidazolium cation form a stable complex that preserves the ionic nature of the components. The interaction with H_2 for the more favorable position of H_2 leads to the somewhat larger value of 6.30 kJ mol^{-1}. This is definitely not in the range that would be interesting for a possible application in hydrogen storage media.

4. Summary and Conclusions

The energy of the interaction of H_2 with NH_3, H_2O, and HF has the quite small values of 3.02, 2.67, and 4.40 kJ mol^{-1}, respectively. The interaction with LiOH is already stronger, at 10.74 kJ mol^{-1}. On NH_3 and H_2O, the most favorable position for adsorption of H_2 is on the side of the N or O atom, whereas on HF and LiOH, it is on the H or Li atom. On the N or O atoms, H_2 takes an end-on orientation, but on the H or Li atoms it takes a side-on orientation. With respect to MP2/TZVPP results, both the step from MP2 to CCSD(T) and the enlargement of the basis set increase the interaction energy values. MP2/TZVPP results account for 70−84% of the CCSD(T) complete basis set estimates. MP2 calculations are able to efficiently yield rough interaction energy estimates, and thus they are a reasonable tool to inspect a larger set of systems.

The simultaneous interaction of H_2 with two LiOH molecules instead of one essentially does not lead to an increased interaction energy. The interaction of H_2 with ionic organic molecules (zwitterionic amino acid glycine, imidazolium) yields interaction energies (5.0−6.3 kJ mol^{-1}) that are increased by only a small amount compared to those obtained for interaction with the small molecules NH_3, H_2O, or HF.

We conclude that the interaction of H_2 with NH_3, H_2O, and HF is weak, and it is not likely to achieve clearly stronger interactions just by combination of the main characteristics of the molecules. This is in agreement with the results reported for the interaction of H_2 with the crown ether 18-crown-6.[20] Furthermore, the introduction of ionicity does not substantially strengthen the interaction. Only with the Li-containing system LiOH an interaction energy larger than 10 kJ mol^{-1} is obtained (unfortunately, the energy is not simply doubled by using two LiOH units). But even this amounts to less than half of the value obtained for interaction of H_2 and a bare Li^+ cation (about 24 kJ mol^{-1}). Thus, the attempt to provide a counterion largely reduces the interaction. Hence, also for systems with metal ions like Li^+, it will be hard to obtain an enhanced interaction.

Acknowledgment. This work has been supported by the DFG Research Center for Functional Nanostructures (CFN) under project number C3.3. It has been further supported by a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Az: 7713.14-300). We also thank the Fonds der Chemischen Industrie for additional financial support.

References and Notes

(1) Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. *Nature* **2001**, *414*, 353−358.

(2) Fichtner, M. Nanotechnological aspects in materials for hydrogen storage. *Adv. Eng. Mater.* **2005**, *7*, 443−455.

(3) Lochan, R. C.; Head-Gordon, M. Computational studies of molecular hydrogen binding affinities: The role of dispersion forces, electrostatics, and orbital interactions. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1357−1370.

(4) Nyulasi, B.; Kovács, A. Theoretical study of $F^-{-}(H_2)_n$ and $Cl^-{-}(H_2)_n$ ($n = 1{-}8$) anion complexes. *Chem. Phys. Lett.* **2006**, *426*, 26−29.

(5) Vitillo, J. G.; Damin, A.; Zecchina, A.; Ricchiardi, G. Theoretical characterization of dihydrogen adducts with alkaline cations. *J. Chem. Phys.* **2005**, *122*, 114311.

(6) Barbatti, M.; Jalbert, G.; Nascimento, M. A. C. The effects of the presence of an alkaline atomic cation in a molecular hydrogen environment. *J. Chem. Phys.* **2001**, *114*, 2213−2218.

(7) Davy, R.; Skoumbourdis, E.; Kompanchenko, T. Complexation of hydrogen by lithium: structures, energies and vibrational spectra of Li^+-$(H_2)_n$ ($n = 1{-}4$), $Li{-}H(H_2)_m$ and $Li{-}H^+(H_2)_m$ ($m = 1{-}3$). *Mol. Phys.* **1999**, *97*, 1263−1271.

(8) Bushnell, J. E.; Kemper, P. R.; Bowers, M. T. $Na^+/K^+{\cdot}(H_2)_{1,2}$ clusters: Binding energies from theory and experiment. *J. Phys. Chem.* **1994**, *98*, 2044−2049.

(9) Vitillo, J. G.; Damin, A.; Zecchina, A.; Ricchiardi, G. Theoretical characterization of dihydrogen adducts with halide anions. *J. Chem. Phys.* **2006**, *124*, 224308.

(10) Grinev, T. A.; Buchachenko, A. A.; Kłos, J.; Bieske, E. J. *Ab initio* potential energy surface, infrared spectra, and dynamics of the ion-molecule complexes between Br^- and H_2, D_2 and HD. *J. Chem. Phys.* **2006**, *125*, 114313.

(11) Lukeš, V.; Ilčin, M.; Laurinc, V.; Biskupič, S. On the structure and physical origin of the interaction in $H_2{\cdots}Cl^-$ and $H_2{\cdots}Br^-$ van der Waals anion complexes. *J. Chem. Phys.* **2004**, *121*, 5852−5859.

(12) Buchachenko, A. A.; Grinev, T. A.; Kłos, J.; Bieske, E. J.; Szczęśniak, M. M.; Chałasiński, G. *Ab initio* potential energy and dipole moment surfaces, infrared spectra, and vibrational predissociation dynamics of the $^{35}Cl^-{\cdots}H_2/D_2$ complexes. *J. Chem. Phys.* **2003**, *119*, 12931−12945.

(13) Alexander, M. H. Theoretical investigation of the lower bend-stretch states of the Cl^-H_2 anion complex and its isotopomers. *J. Chem. Phys.* **2003**, *118*, 9637−9642.

(14) Hartke, B.; Werner, H.-J. Time-dependent quantum simulations of FH_2^- photoelectron spectra on new ab initio potential energy surfaces for the anionic and the neutral species. *Chem. Phys. Lett.* **1997**, *280*, 430−438.

(15) Faure, A.; Valiron, P.; Wernli, M.; Wiesenfeld, L.; Rist, C.; Noga, J.; Tennyson, J. A full nine-dimensional potential-energy surface for hydrogen molecule-water collisions. *J. Chem. Phys.* **2005**, *122*, 221102.

(16) Chenoweth, K.; Dykstra, C. E. Pinwheel binding of hydrogen molecules to acetylene. *Chem. Phys. Lett.* **2004**, *400*, 153−157.

(17) Hwang, D.-Y.; Mebel, A. M. Theoretical study on the reversible storage of H_2 by BeO. *Chem. Phys. Lett.* **2000**, *321*, 95−100.

(18) Simandiras, E. D.; Nicolaides, C. A. Nonclassical hydrogen complexes of the alkaline earths. *Chem. Phys. Lett.* **1991**, *185*, 529−534.

(19) Nicolaides, C. A.; Simandiras, E. D. Prediction of non-transition-metal hydrogen complexes. *Chem. Phys. Lett.* **1992**, *196*, 213−219.

(20) Hübner, O.; Fichtner, M.; Klopper, W. Comment on 'a theoretical study of nanoporous organic molecules for hydrogen storage' [Microporous Mesoporous Mater. 89 (2006) 138]. *Microporous Mesoporous Mater.* **2006**, *94*, 371−372.

(21) Buda, C.; Dunietz, B. D. Hydrogen physisorption on the organic linker in metal organic frameworks: Ab initio computational study. *J. Phys. Chem. B* **2006**, *110*, 10479−10484.

(22) Sagara, T.; Ortony, J.; Ganz, E. New isoreticular metal-organic framework materials for high hydrogen storage capacity. *J. Chem. Phys.* **2005**, *123*, 214707.

(23) Sagara, T.; Klassen, J.; Ortony, J.; Ganz, E. Binding energies of hydrogen molecules to isoreticular metal-organic framework materials. *J. Chem. Phys.* **2005**, *123*, 014701.

(24) Hamel, S.; Côté, M. First-principles study of the rotational transitions of H_2 physisorbed over benzene. *J. Chem. Phys.* **2004**, *121*, 12618−12625.

(25) Sagara, T.; Klassen, J.; Ganz, E. Computational study of hydrogen binding by metal-organic framework-5. *J. Chem. Phys.* **2004**, *121*, 12543−12547.

(26) Heine, T.; Zhechkov, L.; Seifert, G. Hydrogen storage by physisorption on nanostructured graphite platelets. *Phys. Chem. Chem. Phys.* **2004**, *6*, 980−984.

(27) Hübner, O.; Glöss, A.; Fichtner, M.; Klopper, W. On the interaction of dihydrogen with aromatic systems. *J. Phys. Chem. A* **2004**, *108*, 3019−3023.

(28) Scanlon, L. G.; Balbuena, P. B.; Zhang, Y.; Sandi, G.; Back, C. K.; Feld, W. A.; Mack, J.; Rottmayer, M. A.; Riepenhoff, J. L. Investigation of corannulene for molecular hydrogen storage via computational chemistry and experimentation. *J. Phys. Chem. B* **2006**, *110*, 7688−7694.

(29) Okamoto, Y.; Miyamoto, Y. Ab initio investigation of physisorption of molecular hydrogen on planar and curved graphenes. *J. Phys. Chem. B* **2001**, *105*, 3470−3474.

(30) Kubas, G. J. *Metal dihydrogen and σ-bond complexes. Structure, theory and reactivity*; Kluwer Academic/Plenum Publishers: New York, 2001.

(31) Kiran, B.; Kandalam, A. K.; Jena, P. Hydrogen storage and the 18-electron rule. *J. Chem. Phys.* **2006**, *124*, 224703.

(32) Sun, Q.; Wang, Q.; Jena, P.; Kawazoe, Y. Clustering of Ti on a C_{60} surface and its effect on hydrogen storage. *J. Am. Chem. Soc.* **2005**, *127*, 14582−14583.

(33) Zhao, Y.; Kim, Y.-H.; Dillon, A. C.; Heben, M. J.; Zhang, S. B. Hydrogen storage in novel organometallic buckyballs. *Phys. Rev. Lett.* **2005**, *94*, 155504.

(34) Gagliardi, L.; Pyykkö, P. How many hydrogen atoms can be bound to a metal? Predicted MH_{12} species. *J. Am. Chem. Soc.* **2004**, *126*, 15014−15015.

(35) Møller, C.; Plesset, M. S. Note on an approximation treatment for many-electron systems. *Phys. Rev.* **1934**, *46*, 618−622.

(36) Purvis, G. D., III; Bartlett, R. J. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(37) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

(38) Klopper, W.; Kutzelnigg, W. Møller−Plesset calculations taking care of the correlation cusp. *Chem. Phys. Lett.* **1987**, *134*, 17−22.

(39) Klopper, W. Orbital-invariant formulation of the MP2-R12 method. *Chem. Phys. Lett.* **1991**, *186*, 583−585.

(40) Weigend, F.; Häser, M. RI-MP2: first derivatives and global consistency. *Theor. Chem. Acc.* **1997**, *97*, 331−340.

(41) Boys, S. F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys.* **1970**, *19*, 553−566.

(42) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(43) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. RI-MP2: optimized auxiliary basis sets and demonstration of efficiency. *Chem. Phys. Lett.* **1998**, *294*, 143−152.

(44) Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(45) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796−6806.

(46) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information.

(47) Manby, F. R. Density fitting in second-order linear-r_{12} Møller−Plesset perturbation theory. *J. Chem. Phys.* **2003**, *119*, 4607−4613.

(48) Weigend, F.; Furche, F.; Ahlrichs, R. Gaussian basis sets of quadruple zeta valence quality for atoms H−Kr. *J. Chem. Phys.* **2003**, *119*, 12753−12762.

(49) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. Basis-set convergence of correlated calculations on water. *J. Chem. Phys.* **1997**, *106*, 9639−9646.

(50) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic structure calculations on workstation computers: The program system TURBOMOLE. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(51) Villani, C.; Klopper, W. Explicitly correlated calculation of the second-order Møller−Plesset correlation energies of Zn^{2+} and Zn. *J. Phys. B: At. Mol. Opt. Phys.* **2005**, *38*, 2555−2567.

(52) Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J. *MOLPRO*, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2002.6.

(53) Hampel, C.; Peterson, K.; Werner, H.-J. A comparison of the efficiency and accuracy of the quadratic configuration interaction (QCISD), coupled cluster (CCSD), and Brueckner coupled cluster (BCCD) methods. *Chem. Phys. Lett.* **1992**, *190*, 1−12.

(54) Deegan, M. J. O.; Knowles, P. J. Perturbative corrections to account for triple excitations in closed and open shell coupled cluster theories. *Chem. Phys. Lett.* **1994**, *227*, 321−236.