

Determination of Barrier Heights for Proton Exchange in Small Water, Ammonia, and Hydrogen Fluoride Clusters with G4(MP2)-Type, MP n , and SCS-MP n Procedures—A Caveat

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Supporting Information

ABSTRACT: Calculation of accurate water–water interaction energies is of fundamental importance in computational modeling of many biological and chemical phenomena. We have obtained benchmark barrier heights for proton-exchange reactions and complexation energies in water clusters (H₂O) _{n} ($n = 1–6$) by means of the high-level W1-F12 procedure. We find that lower-cost composite procedures (e.g., G4(MP2) and G4(MP2)-6X), as well as MP2 and SCS-MP2, exhibit surprisingly poor performance for the barrier heights of reactions involving multiple proton exchanges. Moreover, the performance significantly deteriorates with increasing size of the clusters. Similar observations apply to complexation energies in water clusters, and to barrier heights for proton exchange in ammonia and hydrogen fluoride clusters. We propose a modified version of G4(MP2)-6X (denoted G4(MP2)-6X+) that includes sp- and d-diffuse functions in the CCSD(T) term, which gives excellent proton-exchange barrier heights at a computational cost only slightly greater than that of standard G4(MP2). G4(MP2)-6X+ also leads to a substantial improvement over G4(MP2) and G4(MP2)-6X for the calculation of electron affinities.

1. INTRODUCTION

Water is vital for life and is of fundamental importance in many chemical and physical processes. Proton exchanges in water and water–solute clusters are known to play key roles in chemical phenomena such as the dynamic structure of water, solvation of molecules, and water-assisted catalysis.¹ Studying the detailed energetic properties of these processes using experimental techniques is likely to be challenging. On the other hand, computational chemistry provides an attractive alternative for such investigations.² Thus, it is imperative that we have theoretical methods that accurately describe barrier heights for proton-exchange reactions in water clusters. In the present work, we show that several commonly used standard and composite ab initio procedures give surprisingly poor performance for proton-exchange barrier heights in small water clusters, which significantly deteriorate with increasing size of the clusters. We propose a new method, G4(MP2)-6X+, which effectively removes these shortcomings.

The Gaussian-4 (G4)³ protocol and its computationally more economical variant G4(MP2)⁴ are widely used for the calculation of thermochemical and kinetic properties, and these are of particular value for the practical computational chemist. Specifically, they are applicable to relatively large systems (of up to 20–30 non-hydrogen atoms), and promise accurate predictions with mean absolute deviations (MADs) from reliable experimental thermochemical data below the threshold of “chemical accuracy” (arbitrarily defined as 1 kcal mol^{−1} \approx 4.2 kJ mol^{−1}).⁵ It has generally been found that G4(MP2) affords thermochemical and kinetic predictions that are not much worse than those of the computationally more-expensive G4 procedure.^{4–9} For example, for the 454 experimental thermochemical determinations of the G3/05 test set¹⁰ (including heats of formation, ionization energies, and electron

affinities), G4 and G4(MP2) attain MADs of 3.5 and 4.5 kJ mol^{−1}, respectively. For the computation of barrier heights, G4 and G4(MP2) also offer generally good performance. For example, both procedures give similar MADs (2.4 and 2.9 kJ mol^{−1}, respectively) when evaluated against the 24 barrier heights in the DBH24/08 database (which includes barriers for heavy-atom transfer, nucleophilic substitution, and hydrogen-transfer reactions).^{7,9} Similarly, for the set of 76 barrier heights in the “hydrogen-transfer barrier heights” (HTBH), and “non-hydrogen-transfer barrier heights” (NHTBH) datasets,¹¹ G4 and G4(MP2) attain MADs of 3.0 and 3.7 kJ mol^{−1}, respectively.⁸ A recent modification of G4(MP2), known as G4(MP2)-6X,⁹ has been shown to generally yield even better performance than G4(MP2) for thermochemistry and barrier heights.^{6,9}

Given the broader applicability of the lower-cost G4(MP2) and G4(MP2)-6X procedures, compared with G4, it is important to (i) identify cases for which these procedures do not perform well, and, if possible, (ii) arrive at guidelines with regard to when this might occur. Identifying such cases will not only help us understand the limitations of these procedures, but it might also suggest pathways for improvement.

We have recently carried out a systematic study on the performance of a variety of ab initio and density functional theory procedures in predicting barrier heights for a diverse set of proton-transfer tautomerization reactions, known as the water-catalyzed proton-transfer (WCPT) dataset.¹² The WCPT dataset contains 27 accurate barrier heights (obtained at the W2.2²⁵ or W1¹³ levels) for a set of nine proton-transfer tautomerization reactions that are either uncatalyzed, catalyzed

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by one water molecule, or catalyzed by two water molecules. We were intrigued to find that the performance of G4(MP2) and G4(MP2)-6X gradually deteriorates as the number of water molecules involved in the catalysis is increased.

In the present work, we proceed to investigate the broader ramifications of these findings for proton-exchange barrier heights in small water clusters $(\text{H}_2\text{O})_n$ ($n = 2-6$). We show that, relative to reliable benchmark barrier heights obtained using the high-level W1-F12 thermochemical protocol,¹⁴ G4 gives reasonably good performance, irrespective of the size of the cluster. However, G4(MP2) and G4(MP2)-6X perform poorly, and their performance deteriorates as the number of water molecules involved in the proton exchange is increased. The G4(MP2)-type procedures also perform poorly for complexation energies of small water clusters, and again their performance deteriorates with the size of the cluster. These findings indicate that standard G4(MP2)-type procedures should be applied with caution when modeling systems that involve explicit water molecules. We show that a modified version of G4(MP2)-6X (denoted G4(MP2)-6X+), in which the CCSD(T) base energy is obtained with extra sp- and d-diffuse functions on heavy atoms and p-functions on H, overcomes these limitations. Finally, we show that similar observations apply to $(\text{NH}_3)_n$ and $(\text{HF})_n$ clusters.

2. COMPUTATIONAL PROCEDURES

The geometries of all structures have been obtained at the B3-LYP/A'VTZ level of theory, where A'VnZ indicates the combination of standard correlation-consistent cc-pVnZ basis sets¹⁵ on H, and aug-cc-pVnZ basis sets¹⁶ on first-row elements. Harmonic vibrational analyses have been performed to confirm each stationary point as either an equilibrium structure (i.e., all real frequencies) or a transition structure (TS) (i.e., with one imaginary frequency). All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.¹⁷

In order to obtain benchmark energies with which to make comparisons, calculations have been carried out using the high-level ab initio W1-F12¹⁴ thermochemical protocol with the Molpro 2010.1 program suite.¹⁸ W1-F12 combines explicitly correlated F12 methods¹⁹ with extrapolation techniques in order to approximate the CCSD(T) basis-set-limit energy. Because of the drastically accelerated basis-set convergence of the F12 methods,^{20,21} W1-F12 is superior to the original W1 method, not only in terms of performance but also in terms of computational cost.¹⁴ In brief, the Hartree–Fock component is extrapolated from the VDZ-F12 and VTZ-F12 basis sets, using the $E(L) = E_\infty + A/L^\alpha$ two-point extrapolation formula, with $\alpha = 5$ (where VnZ-F12 denotes the cc-pVnZ-F12 basis sets of Peterson et al.,²⁰ which were specifically developed for explicitly correlated calculations). The valence CCSD-F12 correlation energy is extrapolated from the same basis sets, using the same two-point extrapolation formula but with $\alpha = 3.67$. The (T) valence correlation energy is obtained in the same way as in the original W1 protocol, i.e., extrapolated from the A'VDZ and A'VTZ basis sets using the above two-point extrapolation formula with $\alpha = 3.22$. The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent aug'-cc-pwCvTZ basis set of Peterson and Dunning,²² while the (T) inner-shell contribution is calculated with the cc-pwCvTZ(no f) basis set (where cc-pwCvTZ(no f) indicates the cc-pwCvTZ basis set without the f functions). The scalar relativistic contribution (in the second-order Douglas–Kroll–

Hess approximation)²³ is obtained as the difference between nonrelativistic CCSD(T)/A'VDZ and relativistic CCSD(T)/A'VDZ-DK calculations.²⁴

W1-F12 shows excellent performance for systems containing only first-row elements (and H). Specifically, for the 97 first-row systems in the W4-11 dataset,⁶ W1-F12 attains a root-mean-square deviation (rmsd) of 0.79 kJ mol⁻¹ from all-electron, relativistic CCSD(T) reference atomization energies at the infinite-basis-set limit. When considering reference atomization energies at the full-configuration-interaction (FCI) basis-set limit, an rmsd of 1.9 kJ mol⁻¹ is obtained. Essentially, this is equivalent to evaluating the performance of the W1-F12 procedures against experimental reference values.

Since W1-F12 represents layered extrapolations to the all-electron CCSD(T) basis-set-limit energy, it is of interest to estimate whether the contributions from post-CCSD(T) excitations are likely to be significant for the molecular clusters considered in the present work. The percentage of the atomization energy accounted for by parenthetical connected triple excitations, %TAE_c[(T)], has been shown to be a reliable energy-based diagnostic indicating the importance of non-dynamical correlation effects. It has been suggested that %TAE_c[(T)] < 2% indicates systems that are dominated by dynamical correlation, while 2% < %TAE_c[(T)] < 5% indicates systems that include mild nondynamical correlation.²⁵ Table S1 of the Supporting Information gathers the %TAE_c[(T)] values for the TSs for the proton-exchange reactions and for the molecular clusters considered in the present study. The %TAE_c[(T)] values for the TSs for the proton-exchange reactions lie in the range 1.8%–3.2%. The molecular complexes are characterized by slightly lower %TAE_c[(T)] values, in the range 1.3%–1.8%. These values suggest that our benchmark barrier heights should, in principle, be within $\pm 1-3$ kJ mol⁻¹ of the barrier heights at the FCI basis-set limit.⁶

In Section 3, we use our W1-F12 benchmark barrier heights and complexation energies to evaluate the performance of standard ab initio procedures (MP2, MP3, and MP4), modified ab initio procedures (spin-component-scaled SCS-MP2,²⁶ SCS-MP3,²⁷ scaled-opposite-spin SOS-MP2,²⁸ and MP2.5²⁹),³⁰ composite procedures (G4, G4(MP2), and G4(MP2)-6X), and modified versions of the G4(MP2)-type procedures. For the sake of making the article self-contained, we will briefly outline the various steps in the G4(MP2) method (for further details, see ref 4).

For isogyric reactions, the electronic G4(MP2) energy is given by

$$E[\text{G4(MP2)}] = E[\text{CCSD(T)/6-31G(d)}] + \Delta E(\text{MP2}) + \Delta E(\text{HF}) \quad (1)$$

where the MP2 basis-set-correction term is given by

$$\Delta E(\text{MP2}) = E[\text{MP2/G3MP2LargeXP}] - E[\text{MP2/6-31G(d)}] \quad (2)$$

and the $\Delta E(\text{HF})$ term corrects for the HF/CBS (complete-basis-set) limit energy extrapolated from truncated versions of the aug-cc-pVTZ and aug-cc-pVQZ basis sets.⁴ The G4(MP2)-6X procedure⁹ uses the same formalism but employs six additional empirical scaling factors in order to improve the performance for general thermochemistry.^{6,9}

3. RESULTS AND DISCUSSION

3.1. Performance of Theoretical Procedures for Barrier Heights of Proton-Exchange Reactions in Water Clusters. Figure 1 shows the cyclic transition structures

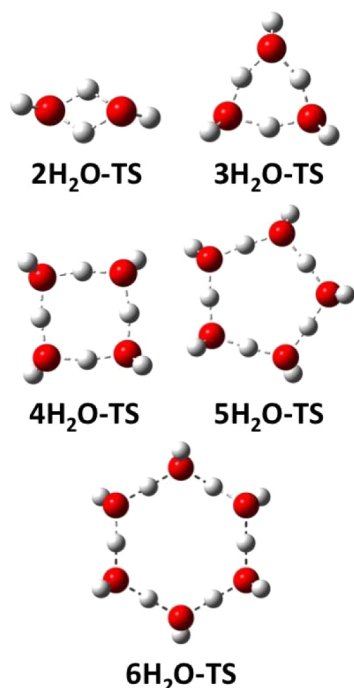


Figure 1. Transition structures obtained at the B3-LYP/A'VTZ level of theory for proton-exchange reactions in cyclic water clusters. The O–H bonds being broken and formed in the transition structures are represented by dashed lines.

that were located for proton exchange in the $(\text{H}_2\text{O})_n$ clusters ($n = 2–6$), while Table 1 reports the deviations from the W1-F12 benchmark barrier heights for these systems for G4 and G4(MP2) (and variants thereof), as well as for standard ab initio procedures (MP2, MP3, and MP4), and modified ab initio procedures (SCS-MP2, SCS-MP3, SOS-MP2, and MP2.5). We can see that G4 performs moderately well for all of the barrier heights, with deviations ranging from 4.5 kJ mol^{−1} (2H₂O-TS) to 5.8 kJ mol^{−1} (5H₂O-TS). However, even in the simplest case of the barrier height for proton exchange in the water dimer, G4(MP2) deviates from W1-F12 by 9.1 kJ mol^{−1}. Furthermore, the situation deteriorates substantially upon moving to the larger clusters, with deviations increasing almost linearly with the number of water molecules involved in the transition structures. Specifically, the deviations are 15.3 kJ mol^{−1} (3H₂O-TS), 20.3 kJ mol^{−1} (4H₂O-TS), 25.0 kJ mol^{−1} (5H₂O-TS), and 29.2 kJ mol^{−1} (6H₂O-TS). Deviations with G4(MP2)-6X are similar to those for G4(MP2) (see Table 1).

To better account for a description of the partial O⋯H bonds involved in the proton-exchange transition structures, we examine the effect of adding diffuse functions to the 6-31G(d) basis set used in the CCSD(T) and $\Delta E(\text{MP2})$ calculations. Modifications of this type in the G2+ and G2(DD) procedures were shown to yield better performance for proton transfers involving anionic species.³¹ Using the 6-31+G(d) basis set in place of 6-31G(d) in eqs 1 and 2 (labeled G4(MP2)(+)) in Table 1) reduces the deviations, but they remain large. For example, the deviation for 2H₂O-TS is reduced from 9.1 kJ

Table 1. Deviations from W1-F12 Values of Barrier Heights for Proton-Exchange Reactions in Water Clusters Obtained by Standard and Composite Ab Initio Procedures^a

	Deviation (kJ mol ^{−1})				
	2H ₂ O-TS	3H ₂ O-TS	4H ₂ O-TS	5H ₂ O-TS	6H ₂ O-TS
G4	4.5	5.4	5.6	5.8	5.6
G4(MP2)-6X	9.0	15.3	20.4	25.0	29.1
G4(MP2)	9.1	15.3	20.3	25.0	29.2
G4(MP2)(+) ^b	8.0	12.3	15.7	18.7	21.4
G4(MP2)(p) ^c	6.9	11.3	14.5	17.8	20.6
G4(MP2)(+p) ^d	5.9	8.5	10.2	11.9	13.4
G4(MP2)(+d,p) ^e	5.5	7.1	7.9	9.1	9.9
G4(MP2)-6X+ ^f	3.0	3.2	2.6	2.6	2.2
G4(MP3) ^g	7.1	9.9	11.6	13.9	16.1
G4(MP4) ^h	3.7	5.5	6.0	6.7	7.3
MP2 ⁱ	−10.2	−11.4	−14.0	−16.9	−20.1
MP2.5 ⁱ	3.1	2.0	1.8	1.7	1.7
MP3 ⁱ	16.4	15.5	17.6	20.4	23.4
MP4 ^j	−6.3	−6.7	−8.7	−10.2	−11.5
SCS-MP2 ⁱ	5.8	11.7	15.8	19.6	23.4
SCS-MP3 ⁱ	12.5	18.4	23.7	28.9	34.3
SOS-MP2 ⁱ	13.8	23.3	30.7	37.9	45.2

^aThe transition structures are shown in Figure 1 (barrier heights are calculated relative to the separated H₂O molecules). ^bThe base CCSD(T) energy and $\Delta E(\text{MP2})$ term in G4(MP2) are calculated with the 6-31+G(d) basis set, see text and eqs 1 and 2. ^cSame as footnote b, but with the 6-31G(d,p) basis set. ^dSame as footnote b, but with the 6-31+G(d,p) basis set. ^eSame as footnote d, but with an additional set of diffuse d-functions from the aug-cc-pVDZ basis set on oxygen. ^fSame as footnote e, but for the G4(MP2)-6X procedure. ^gSame as G4(MP2), but with $n = 3$ rather than $n = 2$ in the $\Delta E(\text{MP}n)$ term, see text and eq 2. ^hSame as G4(MP2), but with $n = 4$ rather than $n = 2$ in the $\Delta E(\text{MP}n)$ term, see text and eq 2. ⁱCalculated with the A'VQZ basis set. ^jCalculated with the A'VTZ basis set.

mol^{−1} to 8.0 kJ mol^{−1}, while the deviation for 6H₂O-TS is reduced from 29.2 kJ mol^{−1} to 21.4 kJ mol^{−1}. Adding a set of polarization p-functions on H, i.e., using the 6-31G(d,p) basis set in place of 6-31G(d) in eqs 1 and 2 (labeled G4(MP2)(p)), has a similar effect (e.g., the deviations obtained for 2H₂O-TS and 6H₂O-TS are 6.9 and 20.6 kJ mol^{−1}, respectively). The combination of diffuse sp-functions on O and polarization p-functions on H (labeled G4(MP2)(+p)) results in an almost additive effect. For example, the deviation for 2H₂O-TS is reduced to 5.9 kJ mol^{−1}, and that for 6H₂O-TS is reduced to 13.4 kJ mol^{−1}.

As the inclusion of diffuse sp-functions on O leads to a significant improvement in performance, we thought it worthwhile to examine the effect of the further addition of diffuse d-functions. Augmenting the 6-31+G(d,p) basis set with a set of diffuse d-functions from the correlation-consistent aug-cc-pVDZ basis set¹⁶ (labeled G4(MP2)(+d,p) in Table 1) indeed results in a further reduction in the deviations. For example, the deviation for 6H₂O-TS is reduced from 29.2 kJ mol^{−1} to 9.9 kJ mol^{−1}. A more striking result is that application of the same modifications to the G4(MP2)-6X procedure (labeled G4(MP2)-6X+), which has the same computational cost as G4(MP2)(+d,p), results in a significantly better performance. The deviations for G4(MP2)-6X+ range from 2.2 kJ mol^{−1} (6H₂O-TS) to 3.2 kJ mol^{−1} (3H₂O-TS). This remarkable improvement in the performance of G4(MP2)-6X+, compared with that of G4(MP2)(+d,p), is attributed to the

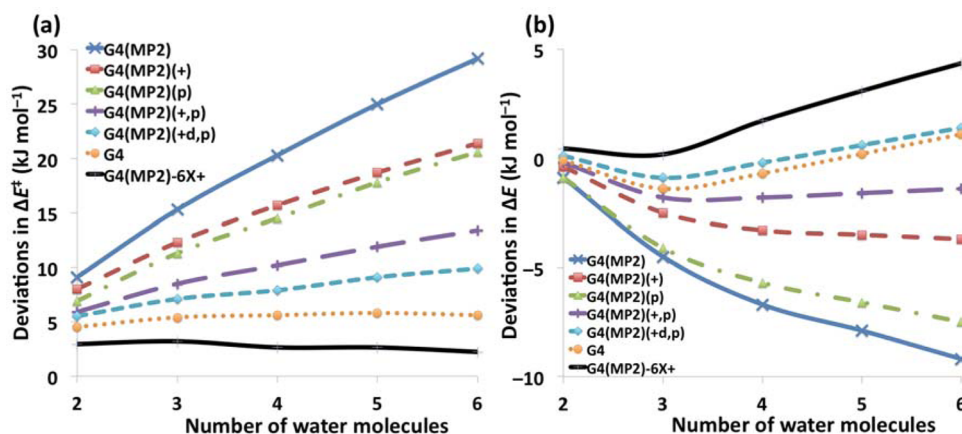


Figure 2. Deviations (in kJ mol^{-1}) from W1-F12 benchmark values of G4 and G4(MP2)-type results for (a) barrier heights (ΔE^\ddagger) of proton-exchange reactions, and (b) complexation energies (ΔE) in monocyclic water clusters ($(\text{H}_2\text{O})_n$ ($n = 2-6$)).

fact that, although G4(MP2)(+d,p) becomes nonempirical for isogyric reactions (as the empirical higher-level-correction term is the same for reactants and products), the G4(MP2)-6X+ procedure benefits from the six extra scaling parameters. A striking result is that G4(MP2)-6X+ performs even better than the computationally more expensive G4 procedure (see Table 1). The improvements in performance in the sequence $\text{G4(MP2)} \rightarrow \text{G4(MP2)(+)} \approx \text{G4(MP2)(p)} \rightarrow \text{G4(MP2)(+,p)} \rightarrow \text{G4(MP2)(+d,p)} \rightarrow \text{G4} \rightarrow \text{G4(MP2)-6X+}$ are displayed in Figure 2a.

Another strategy for attempting to improve the performance of the G4(MP2) procedure is to calculate the $\Delta E(\text{MP2})$ basis-set-correction term in eq 2 at higher-orders of perturbation theory. Using MP3 rather than MP2 in eq 2 results in a substantial improvement, e.g., the deviation for $6\text{H}_2\text{O-TS}$ is reduced from 29.2 kJ mol^{-1} to 16.1 kJ mol^{-1} , while using fourth-order perturbation theory results in deviations that are only slightly worse than those obtained for G4 (see Table 1). These results are consistent with our previous findings for the barrier heights in water-catalyzed proton-transfer tautomerization reactions.¹²

We turn now to the performance of standard and spin-component-scaled Møller–Plesset perturbation theory for the proton-exchange barrier heights (see Table 1). We note to begin that MP2 and MP3 perform poorly, and their performance significantly deteriorates with the number of water molecules involved in the proton exchanges. Furthermore, whereas MP2 systematically underestimates the barrier heights (with deviations ranging from $-10.2 \text{ kJ mol}^{-1}$ ($2\text{H}_2\text{O-TS}$) up to $-20.1 \text{ kJ mol}^{-1}$ ($6\text{H}_2\text{O-TS}$)), MP3 systematically overestimates the barrier heights (with deviations ranging from $+16.4 \text{ kJ mol}^{-1}$ ($2\text{H}_2\text{O-TS}$) up to $+23.4 \text{ kJ mol}^{-1}$ ($6\text{H}_2\text{O-TS}$)). In this situation, MP2.5, which is an average of MP2 and MP3 proposed by Hobza and co-workers for weak interactions,²⁹ gives good performance that does not deteriorate with the size of the cluster (the largest deviation being 3.1 kJ mol^{-1} for $2\text{H}_2\text{O-TS}$). Scaling the same-spin and opposite-spin components of the MP2 correlation energy in the SCS-MP2 procedure seems to overcorrect the deficiencies of MP2 and leads to a systematic overestimation of the barrier heights (up to $+23.4 \text{ kJ mol}^{-1}$ for $6\text{H}_2\text{O-TS}$). We found similar behavior for predictions of the barrier heights in water-catalyzed proton-transfer tautomerization reactions.¹²

It is instructive to consider in detail the contributions from the same-spin and opposite-spin components of the MP2 and SCS-MP2 correlation energies. In the case of the $6\text{H}_2\text{O-TS}$ transition structure, for example, the barrier height is overestimated by $176.3 \text{ kJ mol}^{-1}$ at the Hartree–Fock level but the MP2 correlation energy reduces the barrier by $196.3 \text{ kJ mol}^{-1}$ (with contributions of -95.5 and $-100.8 \text{ kJ mol}^{-1}$ from the same-spin and opposite-spin components, respectively), resulting in an overall underestimation of the barrier by MP2 by $-20.1 \text{ kJ mol}^{-1}$ (Table 1). In SCS-MP2, the correlation energy reduces the barrier by a smaller amount of $152.8 \text{ kJ mol}^{-1}$ (-31.8 and $-121.0 \text{ kJ mol}^{-1}$ from the scaled same-spin and opposite-spin components, respectively) because of the scaling. This leads to an underestimation of the correlation correction to the HF barrier and, hence, an overestimation of the barrier by $+23.4 \text{ kJ mol}^{-1}$ at the SCS-MP2 level. In a similar manner, complete neglect of the same-spin correlation, as in the SOS-MP2 procedure, results in even poorer performance, with a deviation for $6\text{H}_2\text{O-TS}$ of $+45.2 \text{ kJ mol}^{-1}$ (Table 1).

3.2. Performance of Theoretical Procedures for Complexation Energies in Water Clusters. For our assessment of the performance of the theoretical procedures for complexation energies in small water clusters ($(\text{H}_2\text{O})_n$ ($n = 2-6$)), we examined the eight water clusters shown in Figure 3. Before proceeding to a detailed discussion of the performance of the various theoretical procedures, we note that the MP2/CBS and estimated CCSD(T)/CBS reference values reported by Bryantsev et al.^{2c} are in reasonably good agreement with our W1-F12 reference values, the deviations, in absolute value ranging between $0-2 \text{ kJ mol}^{-1}$. Table 2 reports the deviations of the various theoretical procedures from W1-F12 benchmark complexation energies. We start by making the following general observations:

- With the exception of G4(MP2)-6X, G4(MP2), G4(MP2)(p), SCS-MP2, SCS-MP3, and SOS-MP2, the theoretical procedures give reasonably good to excellent performance for all of the clusters, with little or no deterioration in performance with the size of the cluster.
- Apart from MP2, MP4, and G4(MP2)-6X+, all the procedures tend to systematically underestimate the complexation energies.

The performance of G4(MP2) and G4(MP2)-6X gradually deteriorates with the size of the water cluster. For example, for G4(MP2) the following deviations are obtained for the cyclic

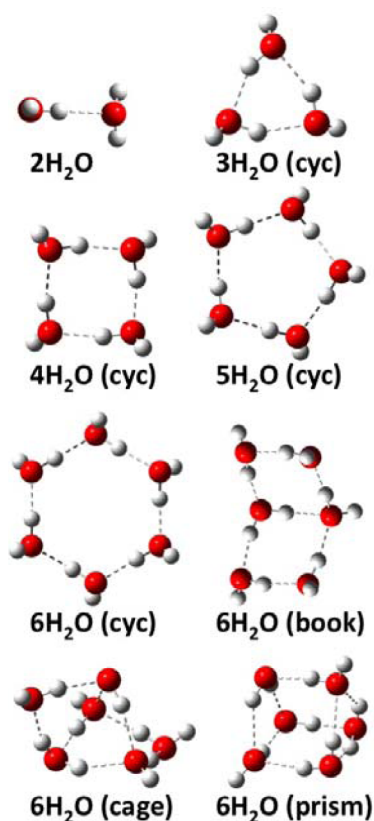


Figure 3. Structures obtained at the B3-LYP/A'VTZ level of theory for water complexes $(\text{H}_2\text{O})_n$, $n = 2-6$. The hydrogen bonds are represented by dashed lines.

clusters: -0.9 kJ mol^{-1} ($2\text{H}_2\text{O}$), -4.5 kJ mol^{-1} ($3\text{H}_2\text{O}$), -6.7 kJ mol^{-1} ($4\text{H}_2\text{O}$), -7.9 kJ mol^{-1} ($5\text{H}_2\text{O}$), and -9.2 kJ mol^{-1} ($6\text{H}_2\text{O}$) (with the largest deviation of $-12.8 \text{ kJ mol}^{-1}$ being obtained for $6\text{H}_2\text{O}(\text{prism})$).

Adding a set of polarization p-functions on H (i.e., G4(MP2)(p)) results in relatively small improvements. However, the addition of diffuse sp-functions on O, (i.e., G4(MP2)(+p)) leads to significant improvements, namely, the deviations range from -0.2 ($2\text{H}_2\text{O}$) to -4.2 ($6\text{H}_2\text{O}(\text{prism})$) kJ mol^{-1} . In addition, augmenting the oxygen with a set of diffuse d-functions (i.e., G4(MP2)(+d,p)) results in excellent performance, with deviations ranging between $+0.1$ ($2\text{H}_2\text{O}$) to -1.7 ($6\text{H}_2\text{O}(\text{prism})$) kJ mol^{-1} , which are considerably better than those for G4. Finally, we note that G4(MP2)-6X+ gives somewhat larger deviations, but still acquires itself reasonably well, with a largest deviation of 4.4 kJ mol^{-1} ($6\text{H}_2\text{O}(\text{cyc})$). The performance of the G4 and G4(MP2)-type procedures for the complexation energies of the cyclic water clusters is illustrated schematically in Figure 2b.

Examination of the performance of the MP_n and SCS- MP_n procedures for the complexation energies shows that MP2 gives only small deviations from the W1-F12 values, ranging from -0.1 kJ mol^{-1} ($2\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$) to $+1.9 \text{ kJ mol}^{-1}$ ($6\text{H}_2\text{O}(\text{cyc})$). However, SCS-MP2 and SCS-MP3 show substantially poorer performance for the complexation energies, with deviations reaching -20.7 and $-22.4 \text{ kJ mol}^{-1}$, respectively ($6\text{H}_2\text{O}(\text{prism})$). These results are in accord with the good performance of MP2 and the poor performance of SCS-MP2 for complexation energies of hydrogen-bonded complexes.³²

3.3. Performance of Theoretical Procedures for Barrier Heights of Proton-Exchange Reactions and Complexation Energies in Ammonia and Hydrogen Fluoride Clusters. The cyclic transition structures for the proton-exchange reactions for ammonia and hydrogen fluoride clusters are shown in Figures 4 and 5, while the complexes themselves are shown in Figures S1 and S2 in the Supporting Information. Table S2 in the Supporting Information gives the W1-F12 benchmark reference data for the barrier heights for proton exchange in these clusters, while the deviations from the W1-F12 barrier heights of the more-approximate theoretical procedures are summarized in Tables 3 and 4, respectively.

Table 2. Deviations from W1-F12 Values of Complexation Energies in Water Clusters Obtained by Standard and Composite Ab Initio Procedures^{a,b}

	Deviation (kJ mol^{-1})							
	$2\text{H}_2\text{O}$	$3\text{H}_2\text{O} (\text{cyc})$	$4\text{H}_2\text{O} (\text{cyc})$	$5\text{H}_2\text{O} (\text{cyc})$	$6\text{H}_2\text{O} (\text{cyc})$	$6\text{H}_2\text{O} (\text{book})$	$6\text{H}_2\text{O} (\text{cage})$	$6\text{H}_2\text{O} (\text{prism})$
G4	-0.1	-1.4	-0.7	0.2	1.1	-0.8	-2.1	-2.9
G4(MP2)-6X	-1.1	-4.8	-7.1	-8.5	-9.7	-11.6	-12.9	-13.6
G4(MP2)	-0.9	-4.5	-6.7	-7.9	-9.2	-10.9	-12.1	-12.8
G4(MP2)(+)	-0.4	-2.5	-3.3	-3.5	-3.7	-4.9	-5.6	-6.2
G4(MP2)(p)	-0.9	-4.1	-5.7	-6.6	-7.5	-9.4	-10.9	-11.7
G4(MP2)(+,p)	-0.2	-1.8	-1.8	-1.6	-1.4	-2.6	-3.5	-4.2
G4(MP2)(+,d,p)	0.1	-0.9	-0.2	0.6	1.4	-0.1	-1.1	-1.7
G4(MP2)-6X+	0.5	0.2	1.7	3.1	4.4	3.1	2.1	1.4
G4(MP3)	0.1	-0.7	-0.4	-0.1	0.2	-0.5	-0.9	-1.1
G4(MP4)	0.0	-1.3	-0.7	0.0	0.6	-1.0	-2.2	-2.9
MP2	-0.1	-0.1	0.8	1.5	1.9	1.0	0.1	-0.7
MP2.5	-0.3	-1.2	-1.6	-1.6	-1.7	-2.9	-3.8	-4.2
MP3	-0.5	-2.4	-3.9	-4.7	-5.4	-6.8	-7.7	-7.8
MP4	0.2	0.4	1.3	1.6	1.9	2.3	2.3	2.1
SCS-MP2	-1.9	-6.8	-10.8	-13.6	-16.4	-18.5	-20.1	-20.7
SCS-MP3	-2.0	-7.4	-12.0	-15.2	-18.2	-20.4	-22.1	-22.4
SOS-MP2	-2.9	-10.1	-16.6	-21.2	-25.5	-28.2	-30.2	-30.7

^aThe water complexes are shown in Figure 3. ^bFootnotes b–j of Table 1 apply.

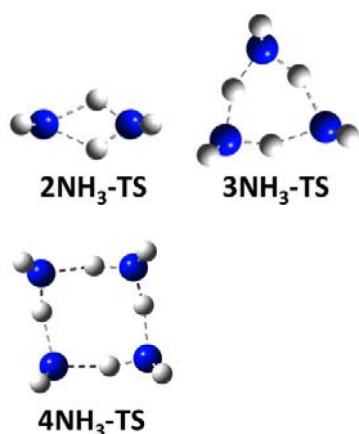


Figure 4. Transition structures obtained at the B3-LYP/A'VTZ level of theory for proton-exchange reactions in cyclic ammonia clusters $(\text{NH}_3)_n$, $n = 2-4$. The N–H bonds being broken and formed in the transition structures are represented by dashed lines.

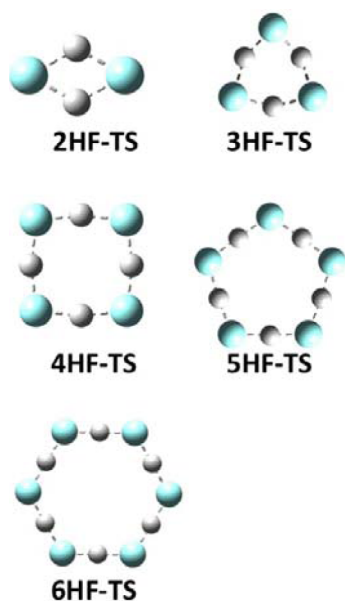


Figure 5. Transition structures obtained at the B3-LYP/A'VTZ level of theory for proton-exchange reactions in cyclic hydrogen fluoride clusters $(\text{HF})_n$, $n = 2-6$. The H–F bonds being broken and formed in the transition structures are represented by dashed lines.

Inspection of Tables 3 and 4 reveals that the performance of G4 for predicting the barrier heights of proton-exchange reactions in ammonia and hydrogen fluoride clusters is similar to that for the water clusters (see Table 1). However, the performance of G4(MP2) and G4(MP2)-6X for both the $(\text{NH}_3)_n$ and $(\text{HF})_n$ clusters is somewhat better than for the water clusters. For example, in the case of G4(MP2), a deviation of 23.4 kJ mol^{-1} is obtained for the 6HF-TS cluster while the deviation for the 6H₂O-TS cluster is 29.2 kJ mol^{-1} . For the $(\text{NH}_3)_n$ clusters, we optimized the transition structures up to 4NH₃-TS, for which the deviation for G4(MP2) is 13.6 kJ mol^{-1} , compared with a deviation of 20.3 kJ mol^{-1} for 4H₂O-TS. In a manner similar to the case of the water clusters, the G4(MP2)-6X+ procedure gives excellent performance for the $(\text{NH}_3)_n$ and $(\text{HF})_n$ clusters, the largest deviation being 3.8 kJ mol^{-1} for 3NH₃-TS. Finally, we note that the performance of the standard and modified MP n procedures for the ammonia

Table 3. Deviations from W1-F12 Values of Barrier Heights for Proton-Exchange Reactions in NH₃ Clusters Obtained by Standard and Composite Ab Initio Procedures^{a,b}

	Deviation (kJ mol^{-1})		
	2NH ₃ -TS	3NH ₃ -TS	4NH ₃ -TS
G4	3.6	6.3	6.2
G4(MP2)-6X	5.7	13.5	14.9
G4(MP2)	5.5	12.7	13.6
G4(MP2)(+)	5.7	11.0	10.8
G4(MP2)(p)	4.4	9.8	11.1
G4(MP2)(+,p)	4.9	8.5	8.8
G4(MP2)(+,d,p)	4.7	8.1	8.2
G4(MP2)-6X+	2.5	3.8	3.4
G4(MP3)	6.3	11.3	12.1
G4(MP4)	2.5	4.8	4.0
MP2	−7.6	−12.3	−11.7
MP2.5	2.1	1.3	2.6
MP3	11.8	15.0	16.8
MP4	−1.8	−2.5	−3.9
SCS-MP2	6.8	13.2	16.7
SCS-MP3	11.6	20.0	23.9
SOS-MP2	13.9	25.9	31.0

^aThe transition structures are shown in Figure 4 (barrier heights are calculated relative to the separated molecules). ^bFootnotes b–j of Table 1 apply.

Table 4. Deviations from W1-F12 Values of Barrier Heights for Proton-Exchange Reactions in HF Clusters Obtained by Standard and Composite Ab Initio Procedures^{a,b}

	Deviation (kJ mol^{-1})				
	2HF-TS	3HF-TS	4HF-TS	5HF-TS	6HF-TS
G4	4.7	7.0	7.5	6.3	5.5
G4(MP2)-6X	7.6	13.7	17.3	19.7	22.4
G4(MP2)	8.3	14.5	18.1	20.6	23.4
G4(MP2)(+)	6.4	9.4	10.8	11.5	12.4
G4(MP2)(p)	6.6	11.3	13.6	14.9	16.6
G4(MP2)(+,p)	4.8	6.3	6.3	5.9	5.8
G4(MP2)(+,d,p)	4.4	5.7	5.5	4.8	4.7
G4(MP2)-6X+	2.0	2.3	1.3	−0.2	−1.5
G4(MP3)	6.8	7.7	7.9	8.2	8.9
G4(MP4)	4.0	7.4	8.4	8.6	9.1
MP2	−7.0	−6.7	−8.3	−10.3	−12.3
MP2.5	5.0	3.5	2.6	2.0	2.0
MP3	16.9	13.6	13.5	14.3	16.2
MP4	−7.5	−7.6	−9.9	−11.8	−13.7
SCS-MP2	6.5	11.3	14.2	17.1	20.3
SCS-MP3	12.5	16.4	19.7	23.2	27.4
SOS-MP2	13.2	20.3	25.5	30.8	36.5

^aThe transition structures are shown in Figure 5 (barrier heights are calculated relative to the separated molecules). ^bFootnotes b–j of Table 1 apply.

and hydrogen fluoride clusters is very similar to that for the water clusters (see Tables 1, 3, and 4). In particular, only MP2.5 gives good performance, with deviations ranging between 1.3 and 5.0 kJ mol^{-1} .

The performance of the theoretical procedures for the complexation energies in $(\text{NH}_3)_n$ and $(\text{HF})_n$ clusters is summarized in Tables S3 and S4 in the Supporting Information. Generally speaking, the performance of the theoretical procedures for the ammonia clusters is somewhat

better than that for the water clusters, whereas the performance for the hydrogen fluoride clusters is similar to that for the water clusters. For example, for the $(\text{NH}_3)_n$ clusters both G4(MP2) and G4(MP2)-6X show reasonably good performance, with the largest deviations of -4.5 and -5.6 kJ mol^{-1} , respectively, being obtained for $6\text{NH}_3(\text{book})$. However, the deviations of these procedures obtained for the $(\text{HF})_n$ clusters are similar to those obtained for the water clusters, e.g., the deviations for 6HF-TS are -13.6 kJ mol^{-1} (G4(MP2)) and -13.0 kJ mol^{-1} (G4(MP2)-6X). The G4(MP2)-6X+ procedure shows excellent performance (with sub- kJ mol^{-1} deviations) for all of the ammonia clusters. However, larger deviations are obtained for the hydrogen fluoride clusters, with a largest deviation of $+4.0$ kJ mol^{-1} being obtained for 6HF-TS .

We now turn to the performance of the standard and modified MP n procedures. As was also the case with the water clusters, SCS-MP2 and SCS-MP3 give unacceptably large deviations of up to -15.8 kJ mol^{-1} (for the HF clusters) and -19.3 kJ mol^{-1} (for the NH_3 clusters). It is worth noting that the remainder of the procedures give good to excellent performance for both the $(\text{NH}_3)_n$ and $(\text{HF})_n$ clusters (with the exception of MP3, for which the deviations reach up to -6.6 kJ mol^{-1}).

3.4. Performance of the G4(MP2)-6X+ Procedure for General Thermochemistry and Barrier Heights. Table 5

Table 5. Overview of the Performance of the G4(MP2)-6X+ Procedure Introduced in the Present Work for the G2/97 and DBH24 Test Sets^a

	Mean Absolute Deviation, MAD (kJ mol^{-1}) ^a			
	G4 ^b	G4(MP2) ^c	G4(MP2)-6X ^c	G4(MP2)-6X+ ^d
G2/97	3.3	4.5	4.1	3.7
$\Delta_f H$	2.9	3.9	3.4	3.6
IE	3.8	4.9	4.7	4.4
EA	3.5	5.8	5.3	3.2
PA	4.2	2.4	2.8	2.9
DBH24/08	2.4	2.9	3.0	1.7

^aMADs computed from benchmark values. ^bThe MADs for the G2/97 test set are taken from ref 3, and the MAD for the DBH24/08 test set is taken from ref 7a. ^cTaken from ref 9. ^dThis work.

gives an overview of the performance of G4, G4(MP2), G4(MP2)-6X, and G4(MP2)-6X+ for the G2/97 and DBH24 test sets. The G2/97 set consists of 302 experimental determinations, including heats of formation ($\Delta_f H$), ionization energies (IEs), electron affinities (EAs), and proton affinities (PAs).³³ For the full G2/97 set, G4(MP2)-6X+ outperforms both G4(MP2)-6X and G4(MP2) (MADs = 3.7, 4.1, and 4.5 kJ mol^{-1} , respectively), although it is not quite as good as the computationally more expensive G4 procedure (MAD = 3.3 kJ mol^{-1}). For the $\Delta_f H$, IE, and PA subsets, G4(MP2)-6X+ performs slightly better than or on par with G4(MP2)-6X and G4(MP2). However, for the EA subset, G4(MP2)-6X+ (MAD = 3.2 kJ mol^{-1}) represents a substantial improvement over G4(MP2)-6X and G4(MP2) (MADs = 5.3 and 5.8 kJ mol^{-1} , respectively). Notably, for the EA subset, G4(MP2)-6X+ performs slightly better than G4 (MAD = 3.5 kJ mol^{-1}). Similarly, for the DBH24 test set, the MAD for G4(MP2)-6X+ is considerably better than that for G4(MP2)-6X, G4(MP2), and even G4 (MADs = 1.7, 3.0, 2.9, and 2.4 kJ mol^{-1} , respectively).

The G4(MP2)-6X+ procedure also shows excellent performance for the barrier heights for the uncatalyzed and water-catalyzed proton-transfer tautomerization reactions in the WCPT dataset,¹² e.g., MADs of 1.0 kJ mol^{-1} (uncatalyzed), 1.8 kJ mol^{-1} (one H_2O catalyst), and 1.8 kJ mol^{-1} (two H_2O catalysts) are obtained. For comparison, MADs of 1.9 kJ mol^{-1} (uncatalyzed), 7.4 kJ mol^{-1} (one H_2O catalyst), and 12.4 kJ mol^{-1} (two H_2O catalysts) are obtained for the G4(MP2) procedure. Moreover, G4(MP2)-6X+ outperforms the computationally more-expensive G4 procedure, for which the following MADs are obtained: 1.8 kJ mol^{-1} (uncatalyzed), 3.4 kJ mol^{-1} (one H_2O catalyst), and 4.2 kJ mol^{-1} (two H_2O catalysts).

4. CONCLUDING REMARKS

We have obtained benchmark proton-exchange barrier heights and complexation energies in small water, ammonia, and hydrogen fluoride clusters by means of the high-level W1-F12 composite thermochemistry protocol. We use these benchmark values to evaluate the performance of a variety of G4-type and MP n procedures. With regard to the performance of the theoretical procedures for the proton-exchange barrier heights, we draw the following conclusions:

- G4 shows reasonably good performance, the largest deviations being 5.8 kJ mol^{-1} ($5\text{H}_2\text{O-TS}$), 6.3 kJ mol^{-1} ($3\text{NH}_3\text{-TS}$), and 7.5 kJ mol^{-1} (4HF-TS).
- G4(MP2) shows surprisingly poor performance, the largest deviations being 29.2 kJ mol^{-1} ($6\text{H}_2\text{O-TS}$), 13.6 kJ mol^{-1} ($4\text{NH}_3\text{-TS}$), and 23.4 kJ mol^{-1} (6HF-TS). (Note that $4\text{NH}_3\text{-TS}$ is the largest ammonia cluster that was investigated.) Similar deviations are obtained for the G4(MP2)-6X procedure.
- The deterioration in performance when going from G4 to G4(MP2) or G4(MP2)-6X appears to be associated with the inadequacy of the basis-set-correction term used in G4(MP2) and G4(MP2)-6X for a description of the partial $\text{X}\cdots\text{H}$ bonds ($\text{X} = \text{O}, \text{N}, \text{F}$) involved in the proton-exchange transition structures.
- We propose a modified version of G4(MP2)-6X (denoted G4(MP2)-6X+) that overcomes these limitations by including diffuse sp- and d-functions on heavy atoms and p-functions on H in the basis-set-correction term. G4(MP2)-6X+ gives excellent proton-exchange barrier heights, the largest deviations being 3.2 kJ mol^{-1} ($3\text{H}_2\text{O-TS}$), 3.8 kJ mol^{-1} ($3\text{NH}_3\text{-TS}$), and 2.3 kJ mol^{-1} (3HF-TS).
- G4(MP2)-6X+ also leads to a substantial improvement over G4(MP2) and G4(MP2)-6X for the calculation of electron affinities. The following MADs are obtained for the EA subset of the G2/97 set: 5.8 kJ mol^{-1} (G4(MP2)), 5.2 kJ mol^{-1} (G4(MP2)-6X), 3.5 kJ mol^{-1} (G4), and 3.2 kJ mol^{-1} (G4(MP2)-6X+).
- We have also evaluated the performance of MP2, MP2.5, MP3, SCS-MP2, SCS-MP3, SOS-MP2, and MP4. MP2 systematically underestimates the barrier heights, whereas MP3 systematically overestimates them. MP2.5, which is an average of MP2 and MP3, shows excellent performance, the largest deviations being 3.1 kJ mol^{-1} ($2\text{H}_2\text{O-TS}$), 2.6 kJ mol^{-1} ($4\text{NH}_3\text{-TS}$), and 5.0 kJ mol^{-1} (2HF-TS). We note that the computationally more-expensive MP4 procedure shows significantly poorer performance for the water and hydrogen fluoride

clusters, the largest deviations being $-11.5 \text{ kJ mol}^{-1}$ ($6\text{H}_2\text{O-TS}$), -3.9 kJ mol^{-1} ($4\text{NH}_3\text{-TS}$), and $-13.7 \text{ kJ mol}^{-1}$ (6HF-TS).

With regard to the performance of the theoretical procedures for the complexation energies, we draw the following conclusions:

- With the main exceptions of G4(MP2)-6X+ and MP4, all of the theoretical procedures tend to systematically underestimate the complexation energies.
- The performance of G4(MP2) deteriorates as the size of the clusters increases. For example, for the water clusters, the deviations range from -0.9 kJ mol^{-1} ($2\text{H}_2\text{O}$) to $-12.8 \text{ kJ mol}^{-1}$ ($6\text{H}_2\text{O-TS}(\text{prism})$). Similar observations apply to G4(MP2)-6X.
- G4 shows good performance, the largest deviations being -2.9 kJ mol^{-1} ($6\text{H}_2\text{O}(\text{prism})$), -2.7 kJ mol^{-1} ($6\text{NH}_3(\text{book})$), and -3.4 kJ mol^{-1} ($3\text{HF}(\text{cyc})$).
- G4(MP2)-6X+ also shows good performance, the largest deviations being 4.4 kJ mol^{-1} ($6\text{H}_2\text{O}(\text{cyc})$), 0.9 kJ mol^{-1} ($6\text{NH}_3(\text{prism})$), and 4.0 kJ mol^{-1} ($6\text{HF}(\text{cyc})$).
- The performance of the SCS-MP2 and SCS-MP3 methods deteriorates with increasing size of the clusters; in both cases, the largest deviation is obtained for $6\text{H}_2\text{O}(\text{cyc})$, specifically $-20.7 \text{ kJ mol}^{-1}$ (SCS-MP2) and $-22.4 \text{ kJ mol}^{-1}$ (SCS-MP3).
- With the exception of the SCS-MP n and SOS-MP2 procedures, all the standard and modified MP n procedure show reasonably good to excellent performance. MP2 is the best performer, with the largest deviations being 1.9 kJ mol^{-1} ($6\text{H}_2\text{O}(\text{cyc})$), -0.2 kJ mol^{-1} ($6\text{NH}_3(\text{book})$ and $6\text{NH}_3(\text{prism})$), and -1.2 kJ mol^{-1} ($3\text{HF}(\text{cyc})$).

■ ASSOCIATED CONTENT

● Supporting Information

Script for running G4(MP2)-6X+ calculations with Gaussian 09 (text); diagnostics for the importance of nondynamical correlation effects in the transition structures and molecular clusters considered in the present study (Table S1); components of the W1-F12 barrier heights for the proton-exchange reactions and complexation energies, and final W1-F12 data at 0 and 298 K (Table S2); performance of theoretical procedures for the complexation energies in $(\text{NH}_3)_n$ clusters (Table S3); performance of theoretical procedures for the complexation energies in $(\text{HF})_n$ clusters (Table S4); performance of the modified G4(MP2)-type procedures introduced in the present work for the G2/97 and DBH24 test sets (Table S5); optimized HLC parameters for the modified G4(MP2)-type procedures introduced in the present study (Table S6); B3-LYP/A'VTZ optimized geometries for all the species considered (Table S7); full details for refs 17 and 18 (Table S8); structures for the ammonia complexes (Figure S1); and structures for the hydrogen fluoride complexes (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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