

Ab Initio Quantum Mechanical Description of Noncovalent Interactions at Its Limits: Approaching the Experimental Dissociation Energy of the HF Dimer

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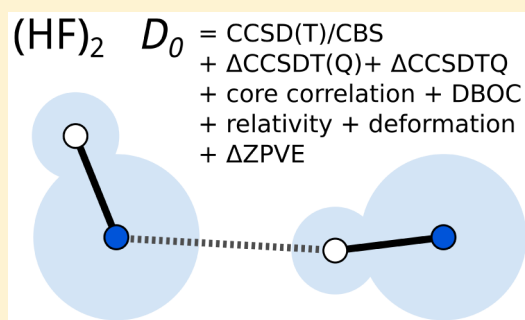
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S Supporting Information

ABSTRACT: Hydrogen fluoride dimer is a perfect model system for studying hydrogen bonding. Its size makes it possible to apply the most advanced theoretical methods available, yet it is a full-featured complex of molecules with nontrivial electronic structure and dynamic properties. Moreover, the dissociation energy of the HF dimer has been measured experimentally with an unparalleled accuracy of $\pm 1 \text{ cm}^{-1}$ (Bohac et al. *J. Chem. Phys.* **1992**, *9*, 6681). In this work, we attempt to reproduce it by purely ab initio means, using advanced quantum-mechanical computational methods free of any empiricism. The purpose of this study is to demonstrate the capabilities of today's computational chemistry and to point out its limitations by identifying the contributions that introduce the largest uncertainty into the result. The dissociation energy is calculated

using a composite scheme including large basis set CCSD(T) calculations, contributions of higher excitations up to CCSDTQ, relativistic and diagonal Born–Oppenheimer corrections and anharmonic vibrational calculations. The error of the calculated dissociation energy is 0.07 kcal/mol (25 cm^{-1} , 2.5%) when compared to the experiment. The major part of this error can be attributed to the inaccuracy of the calculations of the zero-point vibrational energy.



INTRODUCTION

Hydrogen fluoride dimer is a prototypical example of a hydrogen bond. As a tetra-atomic system, it is also the smallest possible noncovalent complex consisting of two molecules, which results in more complex geometry (C_s symmetry), electronic structure and other properties when compared to di- and triatomic complexes. It has a unique position among noncovalent complexes as it has been experimentally characterized with the highest precision—the dissociation energy was determined using a combination of high-resolution infrared spectroscopy and photofragment detection method with an unparalleled accuracy of $\pm 1 \text{ cm}^{-1}$ (0.09%).¹ The dissociation energy of the hydrogen bond is 1062 cm^{-1} , which converts to 3.036 kcal/mol.

The small size of the hydrogen fluoride dimer makes it possible to study it theoretically using the most advanced quantum mechanical methods. However, the accuracy of the experimental dissociation energy is still higher than that of the best calculations, which makes the HF dimer a very useful test case even for the most accurate computational methods. In this work, we employ the best methods applicable to a system of this size with the goal of reproducing the dissociation energy (D_0) of the complex by purely ab initio means, using no empirical parameters or experimental data. The final result comparable to the experimental value has to be composed of

multiple calculations; for each of them, we attempt to estimate its uncertainty in order to identify the components which contribute most to the overall error of the calculated dissociation energy; this allows us to point out both the strong and weak points of the computational approach.

It is not easy to compare calculations to an experiment even in the most favorable case of an isolated system (gas-phase experiment) at very low temperature. The main reason is that the experimentally observable dissociation energy (D_0), more exactly the interaction enthalpy at zero temperature (ΔH^0_0), consists of interaction energy (ΔE^{int} or D_e) and the change of zero-point vibrational energy (ΔZPVE), which can not be separated in the experimental measurement.

The first term, interaction energy, can be calculated rather accurately. The most efficient ab initio method to describe all types of noncovalent interactions accurately is the coupled-cluster method with perturbative inclusion of triple excitations, CCSD(T).² When it is extrapolated to the complete basis set limit (CBS), it is possible to achieve an accuracy of 1–2% even in larger systems (up to ~ 30 atoms). This method is now widely recognized as the “gold standard” of computational chemistry. When more accurate results are needed, further

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corrections beyond the CCSD(T)/CBS level can be calculated. The recent development in methodology, software, and hardware enabled these calculations even in molecular complexes.^{3–9} Recently, we have studied the contributions beyond the CCSD(T)/CBS level in a set of 24 diverse complexes.⁸ The most important is the inclusion of higher-order excitations, followed by core correlation and relativistic effects, but all of these effects are very small (less than 1% of the interaction energy).

While the calculation of the interaction energy is relatively straightforward, a comparably accurate ab initio evaluation of the ZPVE requires complex and computationally intensive calculations of vibrational frequencies. These calculations must be performed at a very high level in order to ensure an accurate description of the potential energy surface (PES). Additionally, it is necessary to go beyond the harmonic approximation. As a result, the calculation of the ZPVE is the step limiting the accuracy of the calculated dissociation energy. This is also the reason why the interaction energy is the only quantity used in most theoretical studies where the calculations are compared with each other (e.g., when evaluating the accuracy of an approximate method against more accurate calculations). We have attempted accurate variational vibrational calculations on a CCSD(T) PES constructed around the minimum, but the limited number of points that can be calculated at this level was not sufficient for obtaining accurate results. We had to resort to the second-order vibrational perturbation theory (VPT2),¹⁰ which covers the anharmonic effects more approximately but can be combined with accurate calculation of the potential. For advanced vibrational calculations, we refer the reader to the studies employing empirical potentials which allow accurate vibrational analysis^{11–14} within a given parametrization of the potential. For HF dimer, these potentials still rely on fitting to experimental data, there is no accurate potential constructed solely from ab initio calculations available.

In this work, we construct the dissociation energy from the following calculations at the accurate CCSD(T)/CBS geometry: The interaction energy is extrapolated to the complete basis set limit from all-electron CCSD(T) calculations in large basis sets. The effect of higher-order excitation is covered by additional CCSDT(Q)¹⁵ and CCSDTQ¹⁶ calculations. Relativistic effects are added from accurate CCSD(T) calculations with Dirac-Coulomb Hamiltonian.¹⁷ Diagonal Born–Oppenheimer correction is calculated at the CCSD level.¹⁸ Deformation energy is calculated from CCSD(T)/CBS optimizations. The Δ ZPVE term is calculated at the CCSD(T)/aug-cc-pVQZ level, anharmonicity is included by the means VPT2. This scheme is similar to the composite methods used in computational thermochemistry; from these, for example, the recent HEAT¹⁹ and W4²⁰ protocols are based on calculations at a comparable level. Finally, it must be emphasized that the calculations described here are applicable only to small systems such as HF dimer and would not be possible in larger systems because of the steep scaling of the computational complexity of the methods. We are working on reproducing experimental dissociation energies in larger noncovalent complexes as well; nevertheless, more approximate methodology must be used.

We focus mainly on the dissociation energy, but we discuss also other quantities obtained from our calculations. To validate our anharmonic vibrational calculations, we compare the calculated frequencies with the experimentally measured ones. Other data that can be used for comparison have been obtained

from the experiments indirectly, via empirical potentials fitted to experimental data. From these potentials, it is possible to obtain structural data and ZPVE from more advanced vibrational calculations (which cannot be combined with accurate ab initio calculations of the potential energy surface).

Previously, accurate theoretical studies of the HF dimer relied on the use of empirical potentials fitted to experimental data. A reliable six-dimensional potential, named SQSBDE, was built by Quack and Suhm.²¹ Through a combination of spectroscopic data and ab initio quantum mechanical calculations, the authors obtained an analytical potential surface which describes well all the available experimental evidence on the HF dimer. The authors have also shown that a PES based purely on ab initio data (i.e., without adjustment of the PES parameters) is less accurate and unable to reproduce experimental results reliably. However, the accuracy of the calculations used was limited because very large number of points has to be calculated for the construction of a complete PES. In a more recent work, the same authors developed a new semiempirical potential, SO-3.¹¹ It is based on a six-dimensional ab initio potential energy surface (counterpoise-corrected explicitly correlated CCSD(T) and MP2 calculations with extended basis sets) and it contains 61 freely adjustable parameters fitted to the experimental results. Using the SO-3 potential, the authors estimated the interaction energy (subtracting the calculated Δ ZPVE from experimental D_0) to be -4.57 ± 0.05 kcal/mol; this is the best estimate available in the literature. The error arises from the uncertainty of the potential itself; the ZPVE on the (semi)empirical potentials can be calculated very accurately.^{22,23,12–14} Similarly, the dimer geometry, which is not known experimentally, was estimated from the best available empirical and ab initio calculations.¹¹

A similar work has been done already on water dimer. Because of its general importance, water dimer was studied thoroughly in the past, even though its dissociation energy (3.159 ± 0.03 kcal/mol) was accurately determined only recently.²⁴ This experiment confirmed the accuracy of theoretical predictions,^{25,26} most notably the work of Shank et al.²⁶ who used a potential fitted to ab initio calculations and adjusted to reproduce the best benchmark calculations available.²⁷ The resulting D_0 , 3.15 ± 0.01 kcal/mol agrees very well with the experiment (however, the small error bar given describes only the convergence of the calculation of ZPVE and does not include the uncertainty of the underlying ab initio calculations of the D_e).

■ COMPUTATIONAL METHODS

The correlation-consistent basis sets of Dunning²⁸ with diffuse functions²⁹ are used thorough this study. In the all-electron calculations, the corresponding polarized-core basis sets³⁰ were used. The geometry of the complex was optimized at the composite CCSD(T)/CBS level, where Hartree–Fock energy and gradient were calculated in the aug-cc-pVQZ basis set, the MP2 correlation term was extrapolated from the aug-cc-pVTZ and aug-cc-pVQZ basis sets and the CCSD(T) correction was calculated in the aug-cc-pVDZ basis set. Optimization on this potential was carried out using gradients obtained by numerical differentiation of the CCSD(T)/CBS energy. Although larger basis sets can be used for this system, we decided to use the same geometry as in our previous work for consistency.⁸ In the original paper, we had shown that improving the method of optimization leads to an only negligible change in the interaction energy. To justify this further, we have optimized

the HF dimer while utilizing a better setup using the aug-cc-pVTZ basis set for the CCSD(T); this geometry is used for the calculation of the deformation energy. As an alternative to this composite, counterpoise-corrected scheme, we optimized the geometry also at the CCSD(T)/aug-cc-pV5Z level.

The dissociation energy is built from multiple components. Here, we will discuss the methods used to obtain each of them as well as the calculations used to estimate the error associated with them. All the interaction energy components (points 1–4 and 6) were calculated using the counterpoise correction.³¹

- (1) **Hartree–Fock energy.** The complete basis set value was extrapolated from calculations in aug-cc-pCVXZ basis sets ($X = Q, 5, 6$) using a parameter-free three-point extrapolation described in our earlier work.⁸ The error of this component is estimated as the difference between the extrapolated value and the result obtained in the largest basis set (aug-cc-pCV6Z).
- (2) **CCSD(T) correlation energy.** The CCSD(T) correlation energy was extrapolated analogously to HF energy from the same basis sets. All electrons were correlated. The error was estimated as the difference between this extrapolation and a two-point extrapolation from the two largest basis sets using the formula of Helgaker.³² The HF and CCSD(T) calculations were carried out in MOLPRO version 2010.³³
- (3) **Perturbative quadruples.** The effect of quadruples was calculated at the CCSDT(Q) level¹⁵ in the aug-cc-pCVTZ basis set as the difference to CCSD(T). All electrons were correlated. We have found that at least a triple- ζ basis set is necessary for a reliable treatment of this term. We decided not to extrapolate this term; our experience with CCSD(T) calculations suggests that extrapolation from double- and triple- ζ basis set may introduce larger error. Because we do not have any reference at this level, the estimate of the error is based on analogy with CCSD(T): we assume that the convergence of the correction term with basis set size is similar to the convergence of the CCSD(T) correlation energy. We evaluate the relative error of CCSD(T)/aug-cc-pCVTZ correlation energy compared to CCSD(T)/CBS and the error of the Δ CCSDT(Q) term is estimated from the magnitude of this term, multiplied by the relative error of CCSD(T).
- (4) **Iterative quadruples.** The difference between a full, iterative CCSDTQ calculation¹⁶ and a perturbative CCSDT(Q) treatment was calculated in aug-cc-pVDZ. The accuracy of this term was estimated analogously to the previous one. Although the uncertainty of the result obtained with a double- ζ basis is large, it introduces only a negligible error, because this term is very small. All the CCSDT(Q) and CCSDTQ calculations were performed using the MRCC program^{34,35} coupled to the CFOUR package.³⁶
- (5) **Diagonal Born–Oppenheimer correction.** While the effect of the Born–Oppenheimer approximation on the electronic energy is very small, it cannot be neglected in the most accurate calculations. We used the diagonal Born–Oppenheimer correction (DBOC) as implemented in CFour.³⁶ At the CCSD level used here, it covers a large part (95%) of the DBOC contribution to the correlation energy.¹⁸ We performed the calculation in

the aug-cc-pVTZ basis set; the error was evaluated as the difference to the calculation in the aug-cc-pVDZ basis.

- (6) **Relativity.** The relativistic effects were calculated using a four-component Dirac–Coulomb Hamiltonian with the Gaunt correction and explicit calculation of the (SSIS) small-component Coulomb integrals. The calculation was performed in the DIRAC11 program³⁷ at the CCSD(T)/aug-cc-pCVTZ level (the Gaunt correction is calculated at the SCF level); the basis set was decontracted as recommended (a relativistic basis set is not available for light elements). The error due to the incompleteness of the basis set was assessed from a comparison with an identical calculation in the decontracted aug-cc-pCVDZ basis set.
- (7) **Deformation energy.** The deformation energy was evaluated as the difference between the energy of fully optimized monomers and monomers in the geometry taken from the dimer. The structures were optimized at the CCSD(T)/CBS level with the CCSD(T) correction calculated in an aug-cc-pVTZ basis set; counterpoise correction was used in the optimization of the dimer. The deformation energy was calculated at the same level. The same procedure was applied to the CCSD(T)/aug-cc-pV5Z geometry. The uncertainty of this term was evaluated as the difference between these two calculations.
- (8) **Zero-point vibrational energy.** The Δ ZPVE term is calculated at the CCSD(T)/aug-cc-pVQZ level. Anharmonicity is treated by means of the second-order vibrational perturbation theory¹⁰ (VPT2) as implemented in CFOUR package.³⁶ In this case, the error reported here is only the one with respect to the basis-set size. The error of the VPT2 method itself cannot be quantified easily, because a better calculation using the same potential is not possible. In the discussion, we compare our calculations with experimental vibrational frequencies and the results of more advanced calculations based on empirical potentials.

■ RESULTS AND DISCUSSION

Monomer Properties. Before we move to the dimer, we must discuss the properties of the HF molecule and how our calculations reproduce them. The optimization of the monomer is carried out twice in our computational protocol: first in the calculation of the deformation energy and second in the calculation of the Δ ZPVE. The deformation-energy calculation uses CCSD(T)/CBS optimization with the CCSD(T) term calculated in the aug-cc-pVTZ basis set. This calculation yields a bond distance of 0.91689 Å, which is in perfect agreement with the experimental value of 0.91690 Å. In the calculation of vibrational properties, we use CCSD(T)/aug-cc-pVQZ calculations without the extrapolation. This method yields the HF bond distance of 0.91769 Å, which is 0.0008 Å (0.09%) longer than in the experiment.

The calculated vibrational properties of the monomer, ν_0 and ZPVE, can also be compared with experimental data. The VPT2 fundamental vibrational frequency calculated at the CCSD(T)/aug-cc-pVQZ level is 3962.76 cm^{−1}; this value is overestimated by 4.4 cm^{−1} (0.11%) when compared to the experiment (3958.34 cm^{−1}). This error comes mainly from the potential used because the harmonic calculation overestimates a harmonic frequency derived from the experiment³⁸ by a similar

Table 1. Geometrical Parameters of the Hydrogen Fluoride Dimer As Optimized by the Methods Used in This Work^a

method	$r_{\text{HF},d}$ (Å)	$r_{\text{HF},a}$ (Å)	r_{FF} (Å)	θ_d (deg)	θ_a (deg)	r_{hb} (Å)
best estimate ^b	0.923 ± 0.001	0.920 ± 0.001	2.735 ± 0.010	7.0 ± 1	68.0 ± 2	
SO-3 empirical potential ^b	0.923	0.920	2.750	8.0	65.0	1.821
CCSD(T)/CBS(aug-cc-pVDZ) ^c	0.923	0.920	2.745	6.9	68.5	1.833
CCSD(T)/CBS(aug-cc-pVTZ) ^c	0.923	0.920	2.742	6.9	68.4	1.829
CCSD(T)/aug-cc-pVQZ ^d	0.924	0.921	2.732	6.8	68.8	1.818
CCSD(T)/aug-cc-pV5Z ^d	0.923	0.920	2.735	6.9	68.8	1.822

^aThe best estimate and the SO-3 empirical potential values are listed for comparison. ^bFrom ref 15. ^cCounterpoise-corrected composite calculations, the basis set listed was used for the CCSD(T) correction. ^dWithout counterpoise correction.

amount, 3.4 cm^{-1} . The calculated ZPVE of 2052.46 cm^{-1} agrees comparably well with the experimentally derived³⁸ value of 2050.77 cm^{-1} .

Geometry of the HF Dimer. Here, we will compare the calculated geometries used in this work with the best estimate based on theoretical and experimental data which was compiled by Quack and Suhm and their empirical potential SO-3.¹¹ We will discuss four geometries: The first two were optimized using the counterpoise-corrected composite CCSD(T)/CBS scheme. The one based on CCSD(T) correction calculated in the aug-cc-pVDZ basis set was used for interaction-energy calculations in order to maintain compatibility with our earlier work;⁸ exactly the same geometry is used. A CCSD(T)/CBS geometry using a larger aug-cc-pVTZ basis set was used for the evaluation of the deformation energy in this paper. This was the best level we were able to achieve within the CCSD(T)/CBS approach; counterpoise-corrected optimizations using composite schemes with a larger basis set did not converge due to numerical instability.

Additionally, we discuss two geometries obtained at CCSD(T) level without any corrections. First, a CCSD(T)/aug-cc-pVQZ geometry was used in the calculation of vibrational properties, because the implementation of this calculation is not compatible with the counterpoise-corrected composite scheme. Second, we add the CCSD(T)/aug-cc-pV5Z as a benchmark for discussion of the accuracy of the optimizations in smaller basis sets and the effect of the counterpoise correction. The optimized internal coordinates, the bond length in the molecule which acts as a proton acceptor $r_{\text{HF},a}$, the bond length of the HF proton donor molecule $r_{\text{HF},d}$, the fluorine–fluorine distance r_{FF} , and the angles between these vectors θ_a and θ_d are listed in Table 1 (the optimum geometry is planar, the out-of plane torsion τ is not listed). The internal coordinates along with their best values calculated in this work are also shown in Figure 1. Additionally, Table 1 lists also the length of the hydrogen bond r_{hb} (the H–F distance).

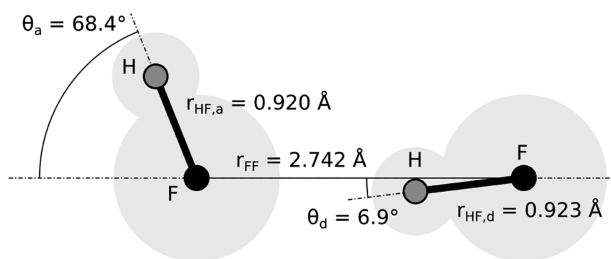


Figure 1. Internal coordinates for the HF dimer and their values optimized at CCSD(T)/CBS level with the CCSD(T) contribution calculated in aug-cc-pVTZ basis set.

It is clear that the counterpoise-corrected composite CCSD(T)/CBS optimization yields a very good geometry even when a smaller basis set is used for the CCSD(T) correction. The most obvious trend is the shortening of the intermolecular distance r_{FF} with the size of the basis set due to the decrease of the magnitude of the counterpoise correction. On the other hand, without this correction the intermolecular distance increases with basis set size as expected (due to the decrease of the artificial attraction caused by the BSSE). Therefore, the true CCSD(T)/CBS value is bound by these results and should lie in the interval 2.735 to 2.742 Å .

The geometry used for the calculations of the interaction energy is not the best one available because we prefer consistency with our earlier work where the CCSD(T)/CBS geometry optimizations with the CCSD(T) correction in aug-cc-pVDZ basis set was applied to a large set of complexes.⁸ This brings only negligible error because the interaction energy is not very sensitive to such small changes in the geometry. Within the composite CCSD(T)/CBS scheme, enlarging the basis set to aug-cc-pVTZ changes the interaction energy by only 1 cal/mol and the transition to the CCSD(T)/aug-cc-pV5Z geometry leads to difference of 3 cal/mol . This value is added to the estimate of the uncertainty of the final interaction energy. The CCSD(T)/aug-cc-pVQZ geometry used for the vibrational calculations is probably the least accurate one considered, although it is still within the error bars of the best estimate from the literature. Nevertheless, this is the best level at which the vibrational calculation was possible; our tests also show that CCSD(T) calculation in a smaller basis set would not be sufficient.

Interaction Energy in the HF Dimer. All the components of the interaction energy are listed in Table 2. Electrostatic interaction, which is the most important contribution to a

Table 2. Components of the Calculated Dissociation Energy (D^0 , ΔH_0^0) of HF Dimer and the Estimated Uncertainty of the Calculations Due to Basis Set Incompleteness

dissociation energy components (kcal/mol)	
uncertainty of the geometry	± 0.003
HF energy	-3.822 ± 0.000
CCSD(T) correlation energy	-0.786 ± 0.003
$\Delta \text{CCSDT}(\text{Q})$	-0.009 ± 0.003
ΔCCSDTQ	0.001 ± 0.001
relativistic effects	0.016 ± 0.001
diagonal B–O correction	-0.012 ± 0.000
deformation energy	0.028 ± 0.001
harmonic ZPVE	1.805 ± 0.017
ZPVE anharmonicity	-0.185 ± 0.019
sum, calcd. D_0	-2.964 ± 0.047
sum, exptl. D_0	-3.036 ± 0.003

Table 3. Error of Composite CCSD(T)/CBS Calculations Employing Basis Sets Applicable to Larger Systems, with respect to the Best Estimate of the Interaction Energy Obtained in This Work^a

HF	MP2	$\Delta\text{CCSD(T)}$	ΔE (kcal/mol)	error	
				(kcal/mol)	(%)
aug-cc-pVQZ	aug-cc-pV(T,Q)Z		−4.382	0.23	5.3
aug-cc-pVQZ	aug-cc-pV(T,Q)Z	aug-cc-pVDZ	−4.421	0.19	4.3
aug-cc-pVQZ	aug-cc-pV(T,Q)Z	heavy-aug-cc-pVTZ	−4.466	0.15	3.3
aug-cc-pVQZ	aug-cc-pV(T,Q)Z	aug-cc-pVTZ	−4.488	0.12	2.8
aug-cc-pV(Q,5,6)Z	aug-cc-pV(Q,5,6)Z	aug-cc-pV(Q,5,6)Z	−4.590	0.02	0.5

^aAdditionally, the first line features the MP2/CBS result in the same basis sets and the last line represents the best CCSD(T)/CBS value obtained with frozen-core approximation.

hydrogen bond, is described already at the Hartree–Fock level, which makes this component the largest one. The interaction energy calculated in an aug-cc-pCV6Z basis set is practically converged, the difference to the aug-cc-pCV5Z calculation is about 1 cal/mol, and the extrapolation to the CBS changes the result only negligibly to -3.8220 ± 0.0004 kcal/mol.

The major part of the contribution of the correlation energy is captured at the CCSD(T) level, at which it is possible to use large basis sets. Extrapolation from very large basis sets is needed as the correlation energy converges more slowly than the HF energy. To include the core–core and core–valence correlation, we have performed all-electron calculations in polarized-core basis sets. We have studied the contribution of the core correlation separately in our previous work,⁸ in HF dimer, it amounts to -0.025 kcal/mol. The best estimate of the CCSD(T) correlation energy at the CBS limit, -0.786 ± 0.003 kcal/mol, is obtained from a three-point extrapolation from aug-cc-pCVXZ ($X = Q, 5, 6$) basis sets. The uncertainty of this term was evaluated as the difference to a two-point extrapolation ($X = 5, 6$); we do not base the error estimate on a nonextrapolated value, because even in basis sets as large as these, the results are known to be rather far from the CBS limit (0.023 kcal/mol in an aug-cc-pCV6Z basis set). The interaction energies used in the extrapolations are listed in Table S1 in Supporting Information.

The effect of higher excitations has to be taken into account if the highest accuracy is sought. These calculations must be carried out in a sufficiently large basis set as well; we have performed the best calculations possible with our computational resources. To capture the effect of quadruples, we have used CCSDT(Q) in an aug-cc-pCVTZ basis set. The results in this as well as selected smaller basis sets is listed in the Supporting Information in Table S2. To evaluate the difference between the perturbative and full iterative calculation, we have calculated the CCSDTQ interaction in a smaller basis set, aug-cc-pVDZ. The remaining contribution of pentuple and higher excitations is very small and can be safely neglected. In our recent work,⁷ we have shown that the error of CCSDT(Q) and CCSDTQ, compared to coupled clusters up to pentuples (CCSDTQP) and full configuration interaction (FCI), is smaller than 1 cal/mol in multiple model complexes. When combined, the higher-order excitations contribute with 0.008 kcal/mol to the interaction energy. The accuracy of this term is not very high—the error was estimated to be ± 0.003 in the CCSDT(Q)/aug-cc-pCVTZ calculation and ± 0.001 in CCSDTQ/aug-cc-pVDZ. It should be noted that the transition from CCSD(T) to CCSDT(Q) could be divided into two steps, calculating the difference between CCSD(T) and CCSDT first. This calculation can be done in slightly larger basis set than the final evaluation of the quadruples. We have

calculated the CCSDT correction in up to aug-cc-pVQZ basis (with frozen core), what allows sufficiently reliable extrapolation to the CBS (aug-cc-pVTZ to aug-cc-pVQZ, using the method of Helgaker).³² The results can be found in Table S3 in the Supporting Information. However, the resulting difference (CCSDT – CCSD(T) at CBS) is only 0.7 cal/mol at the CBS. This would change the result only negligibly so we decided to omit this step to keep our computational protocol simple.

The relativistic effects were calculated using a four-component Dirac–Coulomb Hamiltonian at the CCSD(T) level. Among the interaction-energy components, this is the most important destabilizing one with an energy of 0.016 kcal/mol. The error due to the basis-set size is very small (0.001 kcal/mol); the error with respect to an exact treatment of the relativistic effects cannot be evaluated; in such an advanced model, however, it should be negligible.

The effect of the Born–Oppenheimer approximation on the interaction energy is surprisingly strong. In the HF dimer, the Born–Oppenheimer correction, the leading term in the correction to Born–Oppenheimer approximation amounts to -0.012 kcal/mol. This is a feature shared by all hydrogen bonds; the DBOC correction is based on the nuclear kinetic-energy operator, and therefore, its contribution to the interaction energy is proportional to the changes in vibrations upon the formation of the dimer. This includes the red shift of the vibrational frequency of the covalent bond in the donor. The accuracy of this term with respect to the basis-set size is very good, about 0.0001 kcal/mol.

In hydrogen bonds, the deformation energy is an important contribution destabilizing the complex because of the lengthening of the covalent X–H bond involved in the hydrogen bond. However, in the case of HF dimer, the deformation energy is rather small, 0.028 kcal/mol, because the change in the geometry is small. The estimate of the error, calculated as a difference between two setups, a composite CCSD(T)/CBS scheme and CCSD(T)/aug-cc-pVSZ optimizations, is only 0.001 kcal/mol.

The interaction energy is a sum of the contributions discussed so far; it amounts to -4.584 kcal/mol. It can be calculated very accurately; if we assume that additional contributions, such as the effect of pentuple and higher excitations, are negligible (as other evidence suggests), the error of the calculated interaction energy can be estimated as a sum of the errors of the components, which is 0.011 kcal/mol (0.25%). This error is lower than the best estimate based on the potential fitted to the experimental data, which yields an interaction energy of -4.565 ± 0.048 kcal/mol (the value calculated in this work falls into this uncertainty interval). This comparison suggests that the ab initio calculations at this level

are more accurate than the best results obtained by fitting experimental data of even higher accuracy.

The best estimate of the interaction energy (without the deformation energy) is -4.612 kcal/mol. This value can serve as the most accurate benchmark for more approximate calculations. We will use it for the evaluation error of the best method used as a benchmark in a larger systems, the composite CCSD(T)/CBS scheme (with frozen-core approximation). We have examined the setups that we use in the generation of the most recent benchmark data sets, which are based on the extrapolation of MP2 correlation energy from calculations in aug-cc-pVTZ and aug-cc-pVQZ basis sets and the CCSD(T) correction, Δ CCSD(T), calculated in up to triple- ζ basis sets. Additionally, we list also MP2/CBS interaction energy and the best result obtained at the frozen core CCSD(T)/CBS level. The results are summarized in Table 3. The source data used in the extrapolations are provided in Table S4 in the Supporting Information.

MP2 is known to describe hydrogen bonds well; the MP2/CBS interaction energy extrapolated from aug-cc-pVTZ and aug-cc-pVQZ basis sets has an error of 0.23 kcal/mol when compared to the best estimate. When the Δ CCSD(T) correction calculated in aug-cc-pVDZ is added, the improvement is rather small. This is consistent with the recent findings³⁹ that show that the Δ CCSD(T) in double- ζ basis sets is not sufficient for an accurate description of hydrogen bonds (although it brings a very important improvement in dispersion-dominated complexes). The use of a triple- ζ basis sets improves the accuracy more significantly (in addition to the aug-cc-pVTZ basis set, we list also the results obtained with the cc-pVTZ basis set with diffuse functions on all but hydrogen atoms, denoted as heavy-aug-cc-pVTZ, because this is the setup used in our S66⁴⁰ and X40⁴¹ data sets). Finally, to test the limits of a frozen-core CCSD(T) calculation, we list the interaction energy extrapolated to the complete basis-set limit from aug-cc-pVXZ ($X = Q, 5, 6$) basis sets. Here, the error drops to 0.02 kcal/mol, and this value can be viewed as the inherent error of the frozen core CCSD(T)/CBS approach caused by the neglect of all the contributions included in the best estimate. This result also indicates that the largest source of error in the current benchmark data sets is the limited basis-set size rather than the neglect of the core correlation, higher-order excitations and other corrections.

Vibrational Properties of the HF Dimer. Passing from the interaction energy to the interaction enthalpy (dissociation energy, D_0) is the most difficult step of the calculation, because it requires an accurate calculation of the zero-point vibrational energy of the dimer. Advanced methods of vibrational analysis require a wide coverage of the multidimensional potential-energy surface, what makes accurate ab initio calculations of the potential prohibitively expensive. Therefore, we must resort to a more approximate treatment of the vibrational problem if we want to couple it with accurate nonempirical calculations of the PES. To achieve a reasonable accuracy, a simple harmonic approximation is not sufficient and anharmonicity must be taken into account. We use the second-order vibrational perturbation theory (VPT2), which requires the evaluation of the third and some fourth derivatives of the potential energy. These derivatives are calculated numerically from a series of analytical calculations of the second derivatives. Such a calculation is tractable at the CCSD(T) level in a rather large (aug-cc-pVQZ) basis set.

In Table 4, we list our results along with available experimental data and an accurate six-dimensional vibrational

Table 4. Vibrational Frequencies and Zero-Point Vibrational Energy of the HF Dimer (in cm^{-1})^a

mode	experiment	SQSBDE	this work
1	3931	3941	3928
2	3868	3896	3869
3		425	464
4	~ 160	161	180
5	~ 125	126	135
6	~ 380	379	414
ZPVE		4593	4672

^aThe experimental data available, the results of an accurate vibrational analysis based on an empirical potential, and our VPT2 results calculated on the CCSD(T)/aug-cc-pVQZ potential.

calculation based on an empirical potential. Comparison of harmonic and VPT2 vibrational frequencies and ZPVE is available in Table S5 in the Supporting Information. Only the two HF stretching modes (1, 2) can be measured directly, the experimental frequencies for the low-lying intermolecular modes listed in Table 4 are mere estimates based on the observation of combination bands.⁴² This incomplete characterization of the vibrational spectrum also means that there is no experiment-derived estimate of the ZPVE. As an example of an accurate vibrational calculation possible on an empirical potential, we list the results of an accurate full-dimensional calculation¹² using the widely adopted SQSBDE potential.²¹ The difference between the experimental data and the results of the calculation on the empirical potential can be attributed to the limitations of the SQSBDE potential, the vibrational calculations on it are well converged as confirmed by multiple independent studies using different methodologies such as Monte Carlo.¹³

The VPT2 calculation based on the CCSD(T)/aug-cc-pVTZ potential describes the HF stretches very well, with errors of only 3 and 1 cm^{-1} . Similarly, the red shift in the second vibrational mode caused by the formation of the hydrogen bond is reproduced well—the calculated value of 94 cm^{-1} is close to the experimental one of 90 cm^{-1} . This quantity is important, because it directly contributes to the Δ ZPVE. It should also be highlighted that, despite its being a relative quantity where some errors cancel out, the harmonic approximation (which at the CCSD(T)/aug-cc-pVQZ level predicts a red shift of 120 cm^{-1}) does not yield a satisfactory result.

It is difficult to judge the quality of the frequencies of the intermolecular modes as there is no definitive reference. However, the agreement between the indirect experimental evidence and the empirical potential suggest that the SQSBDE potential works well for the intermolecular modes and that our VPT2 calculation has errors in the order of tens of reciprocal centimeters. The accuracy of our ZPVE is even harder to quantify, because the (otherwise well-converged) calculations are based on the empirical potentials, which introduce some non-negligible error.

Another possibility of assessing the quality of the ZPVE calculations is to compare the calculated Δ ZPVE with the one derived from the experimental D_0 by subtracting the interaction energy, which we have calculated with an accuracy 1 order of magnitude better. The Δ ZPVE derived in this way is $1.548 \pm$

0.011 kcal/mol. When the error bar of the experiment (1 cm^{-1}) is added, the error of this estimate of the ΔZPVE should be about 5 cm^{-1} , which is less than in the case of accurate vibrational calculations based on empirical potentials. The ΔZPVE calculated using VPT2 is 1.620 kcal/mol. This implies that the error of the ΔZPVE is no larger than 0.07 kcal/mol (25 cm^{-1}), which is lower than a comparison with the SQSBDE results suggests. We are aware of the fact that the agreement between VPT2 and the experiment or accurate calculations most probably a result of an error compensation but we have not found a more rigorous, empiricism-free approach that would yield better results and is tractable at CCSD(T) level in a sufficiently large basis.

Formally, it is only possible to evaluate the uncertainty of our calculations with respect to the size of the basis set used (comparing the results to the ones obtained in a smaller basis set). The estimated error of the harmonic calculation is 0.017 kcal/mol; the anharmonic correction introduces another error of 0.019 kcal/mol.

The ab initio calculations of accurate ZPVE are clearly the step limiting the overall accuracy of the calculations of the dissociation energy of noncovalent complexes. It is a topic that deserves further attention. First, it would be very useful to quantify the accuracy of the description of intermolecular vibrations by VPT2 on the model systems where an accurate reference is available. We are working on this topic, but we do not have any conclusions applicable to the HF dimer yet. Second, we feel that there is room for the development of new methods for vibrational analysis beyond VPT2 that would require only a limited sampling of the PES for them to be coupled with accurate ab initio calculations but would not require any empirical information on the form of the potential for a particular system.

Dissociation Energy of the HF Dimer. Finally, we construct the calculated dissociation energy as the sum of the interaction energy and ΔZPVE , the difference of the ZPVE of the dimer and two monomers. The final value of D_0 is -2.964 kcal/mol and its overall uncertainty with respect to the basis-set size is 0.047 kcal/mol.

A comparison to the experimental value of -3.036 ± 0.003 kcal/mol yields an error of 0.072 kcal/mol (25 cm^{-1} , 2.5%). This is very good agreement, but it is obvious that this is partially caused by an error cancellation, because the sum of the errors of the calculations of the components of D_0 , most importantly the unknown uncertainty of the anharmonic contribution to the ΔZPVE , is larger than the difference between our calculation and the experimental D_0 . However, the calculated uncertainties of all the calculated components and the empirical analysis of the accuracy of the ΔZPVE term allow us to make a conclusion that the error of the computational protocol used here is below 0.1 kcal/mol (35 cm^{-1}).

Although it is possible to combine our accurate interaction energy with the best ΔZPVE obtained using an empirical potential available in the literature, it does not improve the results significantly. The empirical potentials were fitted to reproduce experimental data and therefore yield value of D_0 very close to the experiment. However, the decomposition of this variable into D_e and ΔZPVE is not as accurate. Such a calculation based on our interaction energy and vibrational contribution taken from the work on the SO-3 potential¹¹ yields D_0 of -3.010 kcal/mol, which is closer to the experimental value than our ab initio result, but the uncertainty is almost as large, 0.06 kcal/mol. Much more valuable result

would be obtained if the analytical potential, needed for accurate vibrational calculation, was fitted only to ab initio calculations (including very accurate calculations in the important points on the PES). Unfortunately, such potential does not exist yet.

CONCLUSIONS

In this study, we have calculated the dissociation energy of the hydrogen fluoride dimer by purely ab initio means.

The geometry of the dimer, optimized at the CCSD(T)/CBS level, is in perfect agreement with previous studies. Moreover, the interaction energy is not very sensitive to the geometry used; our calculations indicate that the error in the final result arising from the geometry is negligible.

The interaction energy was calculated at CCSD(T) level and extrapolated to the complete basis set limit from a series of basis sets up to aug-cc-pCV6Z. Further corrections were made to account for higher-order excitations (up to CCSDTQ), relativistic effects, Born–Oppenheimer approximation and deformation energy. The resulting interaction energy, which amounts to -4.584 kcal/mol, can be considered very accurate—the estimated error caused by the incompleteness of the basis set in all the components of the calculation is below 0.011 kcal/mol (0.25%). This result should be more accurate than the previously published best estimate constructed by subtracting the ΔZPVE calculated using the semiempirical potential SO-3 from the experimental dissociation energy.

A direct comparison of the calculation and experiment is more challenging. The calculation of the dissociation energy D_0 requires the calculation of the change of the ZPVE upon dimer formation. Such a calculation, combining an accurate treatment of the anharmonicity of the vibrations with the accurate ab initio potential, is the step limiting the accuracy of the final result. We have used the second-order vibrational perturbation theory at the CCSD(T)/aug-cc-pVQZ level. The calculated ΔZPVE amounts to 1.620 kcal/mol, which leads to a D_0 of -2.964 kcal/mol. The error of this result with respect to the accurate experimental value is 0.072 kcal/mol. A complete estimation of the uncertainty of the calculated value was not possible, because we were not able to quantify the error introduced by the approximations in the VPT2 vibrational calculations, but the evidence that we have collected suggests that the error of the D_0 obtained with the protocol described here is below 0.1 kcal/mol (35 cm^{-1}).

This study demonstrates the capability of computational chemistry to reproduce a complex quantity, the dissociation energy of a noncovalent complex, with a very high accuracy. All the computational methods used are fully nonempirical and generally applicable, as they contain no adjustable parameters and have not been developed for this particular problem. The analysis of the uncertainty implies that the overall accuracy of such a computational protocol combining state-of-the-art methods is better than 0.1 kcal/mol.

ASSOCIATED CONTENT

Supporting Information

Optimized geometries of the complexes used in this work, calculated interaction energies, and vibrational frequencies. 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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