

Coupled Cluster in Condensed Phase. Part I: Static Quantum Chemical Calculations of Hydrogen Fluoride Clusters

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ABSTRACT: A multiscale approach with roots in electronic structure calculations relies on the good description of intermolecular forces. In this study we lay the foundations for a condensed phase treatment based on the electronic structure of hydrogen fluoride on a very high level of theory. This investigation comprises cluster calculations in a static quantum chemical approach employing density functional theory, second order Møller–Plesset perturbation theory (MP2) and the coupled cluster singles, doubles with perturbative triples method in combination with several basis sets as well as at the complete basis set limit. The clusters we considered are up to 12 monomer units large and consist of ring and chain structures. We find a good agreement of the intramolecular distance obtained from the MP2 approach and the largest basis set. The binding energy of the hydrogen fluoride dimer calculated from coupled cluster at the basis set limit agrees excellently with experiment, whereas the calculated frequencies at all levels agree reasonably well with different experimental values. Large cooperative effects are observed for the ring structures as compared to the chain clusters. The energy per monomer unit indicates the most stable structures to be the ring clusters.

1. INTRODUCTION

Cluster structure calculations of associated compounds in terms of quantum chemical first principles methods are an established concept for gaining detailed information about the intermolecular interactions between the constituting molecules and the identification of local ordering patterns possibly relevant for the condensed phase as well.^{1–3} Thus, such calculations can constitute a scale-transferring approach if something about the condensed phase should be learned. Typical objectives addressed by such an ab initio treatment of isolated cluster structures are the analysis of hydrogen bonding and cooperative effects on the basis of sophisticated electronic structure methods.

Small- to medium-sized hydrogen fluoride (HF) clusters constitute a particular suitable system for such studies due to the small size of the molecule and the generic character of the $\text{FH} \cdots \text{F}$ hydrogen bond.^{3–7} The methods employed in many of these studies are often based on density functional theory (DFT) approaches or second order Møller–Plesset perturbation (MP2) theory, whereas a more elaborate treatment of electron correlation is rarely applied for systems larger than the HF monomer or dimer.^{3,4,8–15}

An extensive study by Maerker et al. demonstrates that many structural quantities are well reproduced by DFT methods (particular hybrid functionals), but in general these approaches are not capable to obtain the accuracy of a post Hartree–Fock treatment in combination with large basis sets.³ A good agreement between structural results obtained from hybrid DFT calculations and experimental data was also reported by Guedes et al., but the interaction energies calculated for larger clusters were found to overestimate the experimental references.⁷ Additional examinations of cooperative effects in HF clusters have been carried out in terms of a simple relation between computed interaction energies and the cluster size. The largest cooperative effects were found for the cyclic trimer and tetramer structures.⁷

Similar results were also reported for MP2 computations on small- to medium-sized HF clusters, and it has been stated that such nonadditive contributions in the intermolecular interactions are important for a proper treatment of HF in the condensed phase as well.^{5,16}

In addition, isolated cluster calculations (and the corresponding energies) are frequently employed for the generation or modification of analytical force fields used in sampling methods, like traditional molecular dynamics simulations or Monte Carlo studies.^{16–26} In the case of liquid HF, the design of such force fields on the basis of ab initio calculations (or experimental data) proved to be difficult, which is not necessarily to be expected due to the putative simplicity of this molecule.^{16,20,23} Several experimental and first principles molecular dynamics studies indicate that there is an abundance of staggered linear chains in the liquid phase of HF and that the distance between these chains is relatively large.^{27,28} It has been stated that this local inhomogeneity in the intermolecular interactions (i.e., the difference between F–F intrachain and F–F interchain distances) largely contributes to the difficulties arising in the force field design.²⁰ The local bend structure found in the HF dimer (and also in the staggered chains) is known to be a result of the permanent multipole interactions between the hydrogen-bonded monomer units.²⁹ Such interactions are expected to be well captured in isolated cluster calculations and can be easily accounted for in analytical force fields. However, the weak interactions arising between HF molecules from different chains have been found to influence the density of the liquid phase to a considerable extent, which is the reason why these medium-range forces also have to be considered in the design of a force field and for the computational treatment of liquid HF in general. In the case of isolated

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cluster studies such effects are only partly accounted for, but a more extended treatment of such intercluster effects is possible in the frame of the quantum cluster equilibrium (QCE) approach.^{30,32} The QCE method is in principle a multilevel or multiscale approach, because it combines static isolated molecule, i.e., quantum chemical, calculations with basic statistical mechanics in order to predict thermodynamics of the condensed phase. Therefore, it is possible to apply high-level electronic structure methods to the condensed phase.

The present study gives a detailed analysis of small- to medium-sized isolated cluster structures (HF)_n ($n \leq 12$) on the basis of high-quality coupled cluster methods, which have not been applied to HF clusters of this size before. The effect of the basis set size is investigated in terms of a complete basis set (CBS) extrapolation and compared to numbers obtained from DFT calculations.

The question whether ring structures play a significant role in liquid HF besides chain structures has been previously addressed in several experimental as well as theoretical studies.^{16,19,20,27,28,33–36} Whereas ab initio molecular dynamics simulations indicate a predominance of chain-like structures in liquid HF at ambient as well as supercritical states,^{16,35,36} experimental studies do not definitely attest this observation but rather assume an equality between the structure of the solid (parallel zigzag chains) and the structure of the liquid.³³ A recent first principles Monte Carlo study of the HF vapor phase indicates that for smaller aggregates (between three to six monomers) the cyclic arrangement is of increased importance and that the bulk vapor phase also contains a considerable amount of noncyclic structures.^{26,37} These findings are in contrast to earlier measurements in which the vapor phase was found to consist solely of cyclic clusters.^{38,39} In addition, experimental investigations of the liquid phase explicitly discuss the occurrence of cyclic species and highlight that cooperative effects, which are assumed to play only a minor role in the liquid as compared to the gas phase, could as well seriously affect the liquid phase structures of strongly associated liquids, such as water or HF.²⁷ In order to account for both structural motifs, clusters of chain- and ring-like geometry have been calculated for a subsequent QCE application.

The results of this study form the ab initio part of a multiscale approach toward the determination of (macroscopic) thermodynamic properties of liquid HF in terms of the QCE model over a large temperature domain, which will be presented in the second part of this study. In this way, a sophisticated post Hartree–Fock treatment of the condensed phase is possible, and the effect of electron correlation on thermodynamic properties of the condensed phase can be investigated in detail.

The study is organized as follows. First, the computational details of the cluster calculations are summarized with special regard to the coupled cluster calculations and the incremental scheme applied for the larger cluster structures. The following section introduces the set of investigated clusters and summarizes the results obtained for geometries and energies. A comparison between calculated harmonic frequencies and anharmonic as well as experimental frequencies is presented next. The paper closes with a discussion of the results and a conclusion.

2. THEORY

2.1. Computational Details. In order to evaluate molecular properties of the different clusters their geometries, harmonic frequencies, and interaction energies have to be computed. The

intracluster interaction energies $E_{\mathcal{P}}^{\text{intra}}$ are obtained according to the supramolecular approach:

$$E_{\mathcal{P}}^{\text{intra}} = E_{\mathcal{P}} - i(\mathcal{P})E_1 \quad (1)$$

where $E_{\mathcal{P}}$ and E_1 denote the total energies of the clusters containing $i_{\mathcal{P}}$ monomers and the corresponding monomer in its relaxed geometry, respectively (adiabatic interaction energy). For the determination of cluster interaction energies according to eq 1, structure optimizations were performed employing DFT as well as MP2 theory with the resolution of identity (RI) procedure.⁴⁰ Interaction energies have not been corrected for the zero-point energy. The program packages used for the actual ab initio calculations were TURBOMOLE 5.91 and associated programs.⁴¹ For DFT calculations, the gradient-corrected functionals B-P86 and PBE were employed in combination with the TZVP basis set as well as the RI technique, whereas MP2 calculations were carried out for the TZVP and QZVP basis sets.^{42–48} In order to obtain accurate structures for the CCSD(T) single point calculations (see Section 2.2), the convergence criterion for the MP2/QZVP optimization was set to 10^{-5} atomic units for the norm of the Cartesian gradient. These data will be abbreviated as MP2/QZVP* or as the basis set QZVP* only. The retrieved cluster interaction energies were counterpoise (CP) corrected by the generalization of the Boys and Bernardi scheme as introduced by Wells and Wilson.^{49,50} The other binding energies being relevant for the QCE calculations are the binding energy per hydrogen bond:

$$E_{\mathcal{P},\text{hbond}}^{\text{intra}} = E_{\mathcal{P}}^{\text{intra}} / n_{\text{hbond}} \quad (2)$$

with n_{hbond} being the number of hydrogen bonds in the cluster.

For the determination of the harmonic frequencies, the SNF program package was employed after the electronic structure calculations were carried out.⁵¹ The SNF program computes frequencies on the basis of the harmonic approximation as numerical derivatives of the analytic gradients provided by the structure optimization. All harmonic frequencies entered the vibrational partition function unscaled. We neglected anharmonic effects. Such effects, for example, nuclear quantum effects for the proton transfer or isotope effects, have been broadly studied by the group of Hammes-Schiffer.^{52–54}

2.2. Computational Details of Coupled Cluster Calculations. The coupled cluster singles and doubles with perturbative triples CCSD(T) energies were calculated with the MOLPRO quantum chemistry package^{55–57} using the aug-cc-pVXZ (X = T, Q, 5) basis sets.^{58,59} For the larger clusters the incremental scheme⁶⁰ had to be applied in order to keep the calculations in the aug-cc-pVQZ basis feasible (756, 1008, 1512 basis functions in C_1 symmetry). Here the total correlation energy is obtained from correlation calculations in small domains. In order to account for the nonadditive effects, one has to calculate correlation contributions from pairs, triples, and so on, of domains until the desired accuracy is reached. The total correlation energy is then obtained by the incremental series:

$$E_{\text{corr}} = \sum_i \Delta \varepsilon_i + \frac{1}{2!} \sum_{ij} \Delta \varepsilon_{ij} + \frac{1}{3!} \sum_{ijk} \Delta \varepsilon_{ijk} + \dots \quad (3)$$

$$\Delta \varepsilon_i = \varepsilon_{ii} \quad \Delta \varepsilon_{ij} = \varepsilon_{ij} - \Delta \varepsilon_i - \Delta \varepsilon_j$$

Table 1. CCSD(T) and MP2 Adiabatic Interaction Energies $E_{\mathcal{P}}^{\text{intra}}$ for the HF Dimer Using Different Basis Sets of the aug-cc-pVXZ Series^a

basis	SCF		MP2		CCSD(T)	
	$E_{\mathcal{P}}^{\text{intra}}$	CP	$E_{\mathcal{P}}^{\text{intra}}$	CP	$E_{\mathcal{P}}^{\text{intra}}$	CP
TZVP	−17.52	1.02	−20.10	3.11		
QZVP*	−14.85	0.30	−19.65	1.84		
aug-cc-pVDZ	−15.44	1.05	−19.58	2.96	−20.15	3.40
aug-cc-pVTZ	−14.81	0.50	−19.69	2.06	−20.21	2.18
aug-cc-pVQZ	−14.76	0.23	−19.38	1.10	−19.77	1.00
aug-cc-pVSZ	−14.57	0.03	−19.15	0.68	−19.46	0.53
aug-cc-pV6Z	−14.54	0.00	−18.95	0.40	−19.27	0.27
cc-pVDZ-F12 ^b	−14.64	0.18	−18.55	1.09	−18.71	1.33
cc-pVTZ-F12 ^b	−14.63	0.10	−18.80	0.40	−19.18	0.55
cc-pVQZ-F12 ^b	−14.57	0.02	−18.77	0.14	−19.16	0.19
extrapolation						
CBS(23)			−19.99		−20.50	
CBS(34)			−19.19		−19.48	
CBS(45)			−19.12		−19.35	
CBS(56)			−18.71		−19.05	

^aCP denotes counterpoise correction. All energies in kJ/mol.^bSCF+CABS singles, MP2-F12, and CCSD(T)(F12) energies.

where ε_i is the correlation energy of the i -th domain and $\Delta\varepsilon_{ij}$ is the two-body correction to the correlation energy for the domains i and j together.

The calculations were performed with the fully automated implementation of the incremental scheme^{61,62} using the domain-specific basis set approach.^{63,64} The incremental expansion was truncated at third order, the domain size parameter was set to 4 orbitals, and the connectivity parameter was set to 3 Bohr in order to obtain whole HF molecules as one-site domains. The order-dependent energy convergence threshold⁶⁵ for the accuracy of the coupled cluster calculations in the domains was set to $10^{-6} E_h$. The parameter to determine the environment of a domain (t_{main})^{63,64} was set to 3 Bohr. In the environment of a domain the basis set of the hydrogens was reduced to STO-3G and to 6-31G⁶⁶ for fluorine. In all calculations the frozen core approximation was applied to the 1s orbitals of fluorine. For R8a and R₂6 (see Figure 2) an order-dependent distance screening with $t_{\text{dist}} = 30/(\mathcal{O}_i - 1)^2$ Bohr was applied for the two- and three-body increments, where \mathcal{O}_i is the order of the increment.^{63,62}

The extrapolation to the basis set limit was performed with the two point scheme of Halkier and Helgaker et al.⁶⁷ For the small clusters we performed additional explicitly correlated MP2 and CCSD(T) calculations with the TURBOMOLE 6.2 package^{68,69} using the cc-pVQZ-F12 basis set of Peterson et al.⁷⁰ with the corresponding CABS⁷¹ and the aug-cc-pwCVSZ basis set for density fitting.⁷² Furthermore the Ansatz 2 was employed together with the approximation B and the fixed amplitudes formulation.⁷³ The exponent of the correlation factor⁷⁴ that determines the F12 basis was set to the recommended value of $1.1a_0^{-1}$. The Hartree–Fock energies were corrected with the CABS singles.⁷⁵

3. RESULTS

3.1. Benchmarking the Accuracy. The CCSD(T) adiabatic interaction energies have to be calculated using large basis sets,

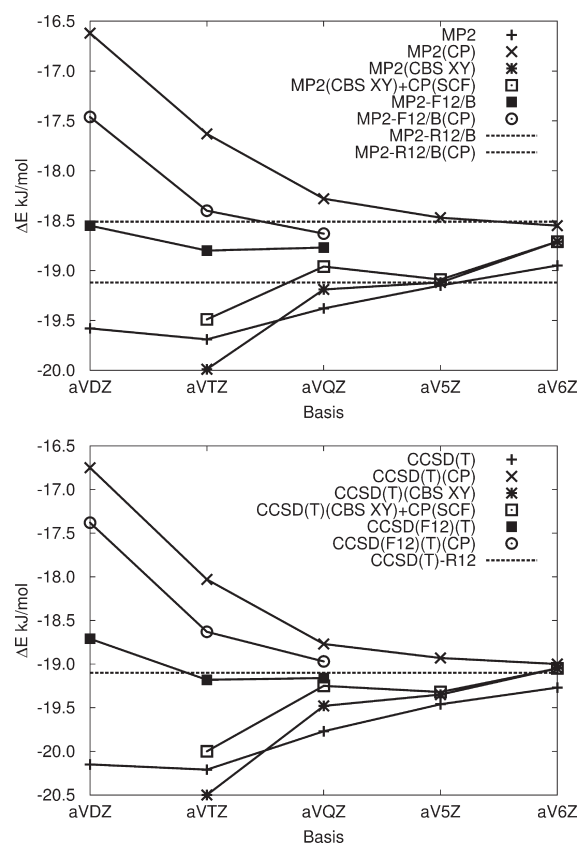


Figure 1. Convergence of the adiabatic interaction energies $E_{\mathcal{P}}^{\text{intra}}$ for MP2 and CCSD(T) with respect to the basis set. The explicitly correlated MP2-R12 and CCSD(T)-R12 values were taken from ref 4. The CCSD(T)(F12) and MP2-F12 energies were calculated with the cc-pVXZ-F12 basis sets using the recommended γ of 0.9, 1.0, and 1.1 a_0^{-1} , respectively. Additionally the CABS singles correction has been included.

including diffuse functions, to obtain the required accuracy. On the other hand the calculations still have to be feasible for the large clusters, which limits the basis set to aug-cc-pVQZ. In order to improve the accuracy of the coupled cluster energies, we use the 34 extrapolation to the basis set limit. This procedure was recently used to benchmark interaction energies for hydrogen bonds in DNA base pairs.⁷⁶ However, to validate this procedure for HF clusters, we investigate the HF dimer with the aug-cc-pVXZ basis set series ($X = D, T, Q, 5, 6$) in combination with two point extrapolations^{67,77,78} from 23 to 56 (Table 1). Such extrapolations using extended basis sets are frequently used to benchmark the explicitly correlated F12 methods.^{68,79} To obtain a further theoretical reference, we calculated the MP2-F12 and CCSD(T)(F12) adiabatic interaction energies for the cc-pVXZ-F12⁷⁰ ($X = D, T, Q$) basis set series including counterpoise correction. Since the HF dimer was intensively studied in the past,^{3,4,80–82,83} we can furthermore use the adiabatic interaction energies of the dimer to validate the accuracy of the 34 extrapolation.

The convergence of the adiabatic interaction energies with respect to the basis set is given in Figure 1. The non-CP-corrected curve converges from below to the CBS limit and the CP-corrected curve converges from above for MP2 and for CCSD(T), as expected from theory. Furthermore the two-point extrapolated adiabatic interaction energies are in between the two bounds

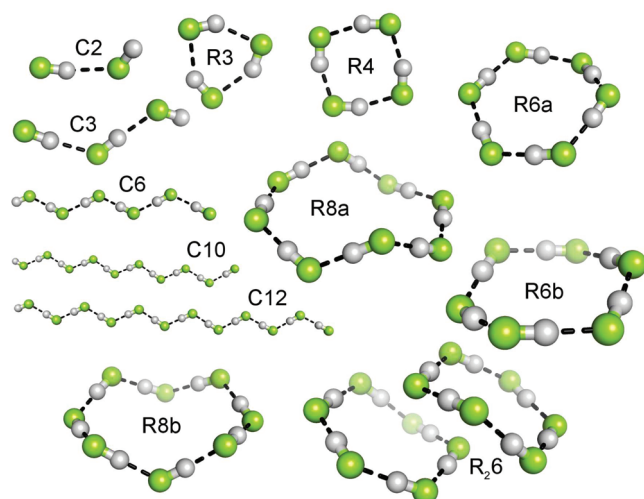


Figure 2. HF clusters investigated in the present study. Depicted are the MP2/TZVP optimized structures. First character R denotes a ring structure and first character C a chain structure. Please note that there is a boat-like (R6a) and a chair-like (R6b) conformation of the hexamer ring cluster.

except for the 23 extrapolated MP2 and CCSD(T) energies. Comparing the non-CP-corrected interaction energies in Table 1 with the R12 results of Kloppe et al.⁴ (MP2-R12/A, -18.89 kJ/mol; MP2-R12/B, -19.12 kJ/mol; CCSD(T)-R12, -19.26 kJ/mol), we find a good agreement with our calculations using the quintuple- or hexuple- ζ basis sets. Also the estimate for the complete basis set limit of -19.1 kJ/mol for CCSD(T) agrees very well with our 56-extrapolated value of -19.05 kJ/mol. Furthermore this value compares very well to the value extracted from the experimental D_0 of Miller⁸⁴ (-19.1 kJ/mol) and is consistent with the previous work of Pine and Howard (-19.08 kJ/mol).⁸⁵ Considering the calculations of Boese et al.,⁸⁶ we find a good agreement to the nonrelativistic frozen core interaction energies of -19.11 kJ/mol. However, the interaction energy changes by a few tenths of a kJ/mol (0.29 , -0.33 kJ/mol) by correlating all electrons and by including relativistic effects.⁸⁶ Since these effects have the same order of magnitude but different signs it is evident that the good agreement of the nonrelativistic 56-extrapolated frozen core CCSD(T) energy with the experimental result is due to a cancellation of both effects. On the other hand both effects are small, and therefore they are neglected. Comparing the 34-extrapolated energies with the best estimate of this work we find a difference of only 0.43 kJ/mol, which is an error on the same order of the frozen core approximation or relativistic effects. This error is smaller than the error of the applied DFT methods with -1.11 and 3.35 kJ/mol for B-P86 and PBE, respectively. Please note that the results of the explicitly correlated MP2 and CCSD(T) using the cc-pVQZ-F12 basis set agree very well to our CBS(56). Since the CP correction is small (0.14 kJ/mol for MP2, 0.19 kJ/mol for CCSD(T)) this holds for the CP-corrected and the uncorrected adiabatic interaction energy. To obtain higher accuracy one has to include other effects, like core correlation or relativistic effects as well, which is beyond the scope of this work. Based on the considerations above, we conclude that the 34-extrapolated energies are sufficiently accurate for our purposes.

3.2. Systems Investigated. The present cluster sizes (HF)_{*n*} vary from $n = 1$ for the monomer to $n = 12$ for the dimer of the cyclic hexamer as the largest cluster similar as in previous studies.^{3,21,35,87}

Table 2. Average Interatomic Distances r and Angles a of All Investigated Clusters for the MP2 Electronic Structure Methods^a

cluster	MP2							
	TZVP				QZVP			
	$r(\text{HF})$	$r(\text{H}\cdots\text{F})$	$r(\text{FF})$	$a(\text{FHF})$	$r(\text{HF})$	$r(\text{H}\cdots\text{F})$	$r(\text{FF})$	$a(\text{FHF})$
C2	92.7	184.8	276.5	169.8	92.2	181.2	272.6	170.7
C3	92.9	176.4	269.3	175.7	92.5	173.8	266.4	175.8
C6	93.7	165.9	259.8	179.3	93.2	164.5	258.0	179.0
C10	94.3	160.6	255.0	179.0	—	—	—	—
C12	94.5	159.2	253.8	178.9	—	—	—	—
R3	93.6	181.5	262.9	143.9	93.4	175.6	259.1	147.3
R4	94.8	161.1	252.9	161.7	94.5	158.8	251.2	164.7
R6a	95.4	153.4	248.6	175.7	94.9	152.8	247.6	177.6
R6b	95.4	153.4	248.6	175.7	95.0	152.7	247.6	176.7
R8a	95.5	152.2	247.6	176.4	95.0	152.2	247.1	177.8
R8b	95.5	152.3	247.8	176.5	95.0	152.1	247.1	177.6
R ₂₆	95.5	153.7	248.9	174.9	95.5	153.6	248.8	174.9

^a All distances in pm and angles in degrees.

For a complete overview of the investigated clusters cf. Figure 2. In order to characterize the stationary points illustrated in Figure 2, the eigenvalues of the Hessian were examined. From these it is found that all structures are true minima on the corresponding potential energy surfaces (PES) with the exception of R6a (transition state per B-P86/TZVP) and C6 (third-order saddle point per MP2/QZVP). The C10 cluster is a minimum only for the MP2/TZVP method, and C12 is found to be a minimum in case of the MP2/TZVP and B-P86/TZVP calculations. It should be noted that in contrast to the finite-temperature first principles Monte Carlo sampling of ref 37, no branched cluster structures were investigated in the zero Kelvin cluster optimizations of the present study.

3.3. Geometries. The geometric parameters (hydrogen bond) for all examined clusters are given in Tables 2–4.

The $r(\text{HF})$ distance of the monomer amounts 91.627 pm for MP2/QZVP, 91.627 pm for MP2/QZVP*, 92.159 pm for MP2/TZVP, 93.270 pm for B-P86/TZVP, and 93.246 pm for PBE/TZVP. Obviously both MP2/QZVP results compare best to the experimental value 91.680 pm given in ref 20. There are some values for the HF monomer equilibrium distance based on high-level quantum chemical calculations in the literature, yielding values of 91.69 ,⁸⁸ 91.70 ,⁸⁹ and 91.708 pm.⁹⁰ The authors of the first two studies point out that in the case of HF, the good performance of the CCSD(T) approach in combination with medium-sized basis sets stems from an error cancellation between basis set truncation and truncation of the excitation level in the applied coupled cluster methodology. A similar situation is found for the MP2 equilibrium distances listed in ref 89. Whereas many values obtained from the conventional MP2 calculation in combination with medium-sized basis sets are within ~ 0.1 pm of the experimental result, somewhat larger discrepancies are found for the MP2-R12 approach, i.e., for taking a substantial step toward basis set saturation. Thus, the best estimate of 91.627 pm (MP2/QZVP) from our calculations could benefit from a similar error cancellation as well and thereby approach the experimental reference as close as 0.06 pm.

Table 3. Average Interatomic Distances r and Angles a of All Investigated Clusters for MP2/QZVP*^a

cluster	MP2/QZVP*			
	$r(\text{HF})$	$r(\text{H}\cdots\text{F})$	$r(\text{FF})$	$a(\text{FHF})$
C2	92.1	181.2	272.6	170.7
C3	92.5	173.9	266.4	175.6
C6	93.2	164.5	258.0	179.0
R3	93.4	175.6	259.1	147.3
R4	94.5	158.8	251.2	164.7
R6a	94.9	152.7	247.6	177.2
R6b	95.1	152.7	247.5	176.7
R8a	95.1	152.1	247.1	177.7
R8b	95.0	152.1	247.0	177.7
R ₂ 6	95.0	152.9	247.7	176.8

^a All distances in pm and angles in degrees.**Table 4.** Average Interatomic Distances r and Angles a of All Investigated Clusters for the DFT Methods^a

cluster	DFT							
	B-P86/TZVP				PBE/TZVP			
	$r(\text{HF})$	$r(\text{H}\cdots\text{F})$	$r(\text{FF})$	$a(\text{FHF})$	$r(\text{HF})$	$r(\text{H}\cdots\text{F})$	$r(\text{FF})$	$a(\text{FHF})$
C2	93.9	180.0	272.3	165.7	93.9	180.0	271.6	163.5
C3	94.5	171.2	267.2	173.8	94.4	171.2	265.5	173.4
C6	95.8	159.4	255.5	178.3	95.7	159.5	255.6	178.3
C12	97.4	150.6	248.3	179.3	—	—	—	—
R3	96.4	167.1	253.9	147.8	96.2	168.3	254.7	147.5
R4	98.9	147.8	244.7	165.1	98.6	148.7	245.3	165.0
R6a	100.2	140.5	240.6	177.8	100.0	140.8	240.7	176.7
R6b	100.2	140.4	240.5	176.8	100.1	140.7	240.6	176.3
R8a	100.4	139.5	239.9	177.8	100.2	140.0	240.1	177.3
R8b	100.4	139.4	239.8	177.8	100.3	139.6	239.8	177.5
R ₂ 6	100.2	140.4	240.5	176.8	100.0	141.2	241.1	177.1

^a All distances in pm and angles in degrees.

For all methods we observe an increase in the intramolecular HF distance the larger the clusters are, which is also found in finite-temperature first principles calculations.³⁷ Furthermore, this bond elongation is stronger for the cyclic structures than for the linear geometries. The hydrogen-bond distances become smaller the larger the clusters are, and they are smaller in cyclic structures than in linear geometries. Both of these observations point to the fact that the hydrogen bonds are stronger with increasing number of monomers in the clusters and in comparing cyclic with linear structures. Chaban and Gerber calculated for the cyclic trimer R3 values of $r(\text{HF}) = 93.0$ pm and $r(\text{H}\cdots\text{F}) = 185.7$ pm using MP2 in combination with a TZP basis set.⁹¹ For the cyclic tetramer the authors obtained $r(\text{HF}) = 94.0$ pm and $r(\text{H}\cdots\text{F}) = 165.9$ pm using the same method and basis set combination, thus these authors find the same trend as apparent in our data.⁹¹

Comparing the different methodologies, we find shorter distances with increasing the basis set for MP2 and a more linear arrangement of the hydrogen-bond angle indicating stronger hydrogen bonds, see Table 2. The changes with the tighter convergence criterion are marginal on average, see Table 3. The

hydrogen-bond distances are even shorter (B-P86 < PBE), and the intramolecular $r(\text{HF})$ distance is shorter (B-P86 > PBE) for DFT than for MP2. However, the MP2 data provide more linear hydrogen bonds; compare the $a(\text{FHF})$ angles in Tables 2 and 3 with those in Table 4.

3.4. Energies. The adiabatic interaction energies were computed by DFT as well as the MP2 method according to eq 1. Please note that the obtained geometries vary with regard to the applied quantum chemical methodology, for a discussion see Section 2.1. As an exception the CCSD(T)/CBS(34) and MP2/CBS(34) values are obtained at the QZVP* geometries. The results of the adiabatic interaction energies $E_{\text{int}}^{\text{intra}}$ are listed in Table 5. In order to validate the accuracy of the CBS(34) energies, we compare these results with explicitly correlated methods at MP2 and CCSD(T) levels. At the MP2 level the largest deviation between the explicitly correlated result and the CBS(34) is 2.53 kJ/mol for the tetramer. At the CCSD(T) level the largest deviation is 2.17 kJ/mol. As a further benchmark we calculated the CBS(45) for the C2, C3, and R3 clusters. The CCSD(T)/CBS(45) adiabatic interaction energies agree within 0.65 kJ/mol or better with the results from the explicitly correlated CCSD(T). Due to this good agreement of the two benchmarks, we conclude that the deviation of the CBS(34) to the CBS(45) is similar to the deviations from explicit correlation (vide supra).

Comparing CCSD(T)/CBS(34) with the CP-corrected results from Klopper et al.⁸² [$(\text{HF})_2 = 19.0$, $(\text{HF})_3 = 62.8$, and $(\text{HF})_4 = 113.5$] we find a maximum deviation of 4.9 kJ/mol for the tetramer. Comparing to the best estimate of Klopper et al.,⁸² the deviation drops down to 2.4 kJ/mol and is within the provided error bars of 3 kJ/mol. Comparing Kloppers values to our CCSD(T)(F12)/cc-pVQZ-F12 results, we find the largest deviation to be 3.3 kJ/mol with respect to the CP corrected energies and a deviation of 0.8 kJ/mol with respect to the best estimate (tetramer). Please note that the geometries of Klopper et al. are slightly different from those of this work. Therefore this comparison of the adiabatic interaction energies cannot be rigorously made. On the other hand the agreement is good and demonstrates the applicability of our computational approach.

Comparing the data for B-P86 functional and the MP2 results, a reasonable agreement is found in case of the smaller clusters, whereas the values obtained from the PBE functional are significantly larger in magnitude. The coupled cluster values are in between the MP2 and the DFT values. Concerning the larger cluster structures, a strong overbinding of the DFT methods as compared to the CCSD(T) and MP2 results is observed, which was already discussed by Maerker et al.³ Although all numbers are BSSE-corrected according to the counterpoise method, a relatively strong basis set dependence for the MP2 calculations is still apparent, which amounts to a difference of up to 44 kJ/mol for the R8a cluster. It should be noted here that a better adjusted basis set for MP2 was not considered for the sake of computational applicability, because all cluster structures are optimized in the chosen basis set. Comparing our DFT values to the ones previously published, we generally find a satisfactory agreement in the range of ± 10 kJ/mol in most cases.^{5,7,21} This is also true for the estimated dimer and trimer aggregation energies from the DFT Monte Carlo calculations of the HF vapor phase at finite temperatures.³⁷ Remaining differences can possibly be attributed to the smaller double- ζ basis sets employed for the geometry optimizations in some of the previous calculations.^{7,5}

Table 5. Adiabatic Interaction Energies $E_{\mathcal{P}}^{\text{intra}}$ for All Investigated Clusters and Different Electronic Structure Methods^a

cluster	$i(\mathcal{P})$	CCSD(T)			MP2				B-P86		PBE
		cc-pVQZ-F12	CBS(45)	CBS(34)	cc-pVQZ-F12	CBS(34)	QZVP*	QZVP	TZVP	TZVP	TZVP
C2	2	−19.16	−19.12	−19.48	−18.77	−19.19	−17.81	−17.81	−16.99	−17.94	−21.40
C3	3	−44.32	−44.32	−45.13	−43.58	−44.60	−41.50	−41.49	−39.31	−43.12	−50.13
R3	3	−63.94	−63.29	−65.12	−62.68	−63.99	−59.15	−59.14	−50.52	−64.40	−72.57
R4	4	−116.84	—	−119.01	−115.90	−118.43	−109.77	−109.77	−94.98	−124.50	−136.49
C6	6	—	—	—	—	—	—	—	−118.32	−137.85	−154.94
R6a	6	—	—	−198.72	—	−198.85	−184.29	−184.28	−165.10	−212.36	−231.69
R6b	6	—	—	−199.05	—	−199.19	−184.59	−184.58	−165.19	−212.92	−232.40
R8a	8	—	—	−268.81	—	−269.00	−249.43	−248.98	−225.06	−288.93	−314.42
R8b	8	—	—	−269.11	—	−269.40	−250.06	−249.95	−225.55	−290.31	−316.41
C10	10	—	—	—	—	—	—	—	−231.00	—	—
C12	12	—	—	—	—	—	—	—	−288.31	−351.06	—
R ₂ 6	12	—	—	−415.07	—	−412.41	−377.83	−377.84	−331.07	−421.55	−465.95

^a All energies in kJ/mol. Some results are missing because the corresponding geometries are not minimum structures or the computation was infeasible on our hardware (CCSD(F12)(T), CCSD(T)/aug-cc-pV5Z).

Table 6. Adiabatic Interaction Energies $E_{\mathcal{P}, \text{hbond}}^{\text{intra}}$ per Hydrogen Bond for All Investigated Clusters and Different Electronic Structure Methods^a

cluster	$i(\mathcal{P})$	CCSD(T)		MP2			B-P86	PBE
		CBS(34)	CBS(34)	QZVP*	QZVP	TZVP	TZVP	TZVP
C2	2	−19.48	−19.19	−17.81	−17.81	−16.99	−17.94	−21.40
C3	3	−22.57	−22.30	−20.75	−20.75	−19.66	−21.58	−25.07
R3	3	−21.71	−21.33	−19.72	−19.71	−16.84	−21.47	−24.19
R4	4	−29.75	−29.61	−27.44	−27.44	−23.75	−31.13	−34.12
C6	6	—	—	—	—	−23.66	−27.57	−30.99
R6a	6	−33.12	−33.14	−30.72	−30.71	−27.52	−35.38	−38.62
R6b	6	−33.18	−33.20	−30.77	−30.76	−27.53	−35.49	−38.73
R8a	8	−33.60	−33.63	−31.18	−31.12	−28.13	−36.12	−39.30
R8b	8	−33.64	−33.68	−31.26	−31.24	−28.19	−36.29	−39.55
C10	10	—	—	—	—	−25.67	—	—
C12	12	—	—	—	—	−26.21	−31.91	—
R ₂ 6	12	−34.59	−34.37	−31.49	−31.49	−27.59	−35.13	−38.83

^a All energies in kJ/mol. Some results are missing because the corresponding geometries are not minimum structures.

The examination of interaction energies per hydrogen bond (see Table 6) gives a comparison of the relative stability of the different cluster structures and sizes. There are several approaches for measuring the degree of cooperativity in cluster structures, and some of them have been applied to HF clusters previously. Rincón et al. correlated cooperative effects obtained from bond distance and interaction energies to the critical point of the hydrogen bond in the topology of the electron density and found a linear relationship between these measures.⁵ By analyzing the interaction energy per hydrogen bond of cyclic HF clusters as well as the reaction energy for adding one HF monomer to a cluster of given size, these authors report considerable cooperative effects for the ring sizes $n = 3$ and 4. Similar observations can be found in a cluster study by Guedes et al. in which larger clusters of up to $n = 10$ monomer units are considered.⁷ Both studies also indicate a saturation of cooperative effects for cyclic HF clusters of size $n = 6$ and larger. If one considers the interaction energy per hydrogen bond (see

Table 6) as a measure for cooperativity, then it is immediately apparent that all clusters larger than the dimer are stabilized by cooperative effects. The largest stabilization can be found in case of the large cyclic clusters R6a/b and R8a/b for all investigated methods. If, however, one is interested in the variation of cooperativity with cluster size (i.e., in the difference in interaction energy per hydrogen bond for a given pair of n and $n - 1$), then it is seen from Table 6 that the largest change in hydrogen bond stabilization of ≈ 7 – 10 kJ/mol occurs for the transition $R3 \rightarrow R4$. Comparing the cooperativity between chain and ring structures for a given cluster size, it is apparent that the stabilization of the cyclic compounds is larger than those of the chain clusters for larger n , whereas the situation is reversed in the case of the trimer structures. This can be understood by considering a possible destabilization of the small trimer ring R3 in terms of ring strain.^{5,7}

As already discussed in the Introduction, the main motif of liquid HF predicted by ab initio simulations as well as recent

Table 7. Calculated Harmonic Frequencies from Different Quantum Chemical Methods, Comparison to Experimental Values, and Frequencies from Theoretical Investigations

cluster	MP2	B-P86	PBE	B3LYP	lit.	
	QZVP*	TZVP	TZVP	TZVP	aug-cc-pVDZ	
C1	4185	4159	3964 3956 ⁸⁹	3970	4073 ⁸⁹	expt 4138 ^{89,95} CC 4141, ⁹⁶ 4139, ⁸⁸ 4137, ⁸⁹ 4152 ⁸¹ MP2-R12 4138 ⁸⁹
C2	169	157	166	166	167 ⁹⁷	MP2-R12 155 ⁸⁹
C2	236	219	221	218	233 ⁹⁷	MP2-R12 209 ⁸⁹
C2	486	455	469	463	465 ⁹⁷	MP2-R12 467 ⁸⁹
C2	588	552	598	600	578 ⁹⁷	MP2-R12 547 ⁸⁹
C2	4049	4050	3772	3780	3882 ⁹⁷	MP2-R12 4030 ⁸⁹
C2	4140	4122	3921	3924	4016 ⁹⁷	MP2-R12 4090 ⁸⁹

experiments are linear zigzag chains.^{16,28,35} In the case of the small- to medium-sized clusters investigated in the present study, it is apparent that this predominance of chain structures is not reflected in the calculated interaction energies (see Table 5) or the cooperative effects (see Table 6). However, earlier studies by Karpfen et al. have shown that on lower theoretical levels the hydrogen-bond stabilization in cyclic structures approaches that of an infinite HF zigzag chain with increasing ring size.^{92–94}

Thus, the energetic preference of ring clusters as seen in Tables 5 and 6 is apparently rooted in the finite chain length considered here and in the fact that rings have an additional hydrogen bond.

Two additional aspects can be expected to contribute to the stability of chain structures in the case of the liquid phase of HF. First, open chain arrangements will be entropically favored at finite temperatures over closed cyclic structures, which in turn are stabilized by an additional hydrogen bond in isolated molecule calculations. However, in the real liquid there will be no completely isolated chain endings, and medium-range interactions from neighboring chains are expected to stabilize the loose tails, thereby partly accounting for the enthalpic penalty which these structures are subject to in the isolated quantum chemical calculation. The consideration of these effects via a finite temperature and a meanfield intercluster interaction will be covered in the second part of this study in terms of the QCE model.

3.5. The Accuracy of the Spectra. Besides the cluster interaction energies discussed in Section 3.3, the accuracy of the vibrational frequencies for the examined cluster structures have been found to be of crucial importance for a successful application in the frame of the QCE model.^{30,31}

Table 7 presents the vibrational frequencies of HF and the HF-dimer at MP2, DFT, and CC levels.^{81,88,89,96} The quantitative calculation of the harmonic wavenumber of HF was the objective of several investigations in the past,^{81,88,89,96} and it was demonstrated that the amazingly high accuracy of 1 cm^{−1} can be obtained if relativistic effects, core and core–valence correlation effects, and higher excitations in coupled cluster as well as large basis sets are used in the calculations.^{88,96} Since these effects may have different signs, they might cancel to a large extent. This is the reason why the MP2-R12 result from ref 89 (4138 cm^{−1}) agrees perfectly with the experimental value from ref 95 (4138 cm^{−1}). Since the MP2-R12 calculation is close to the MP2 basis set limit it is a good reference for the quality of the

basis set in our MP2 calculations. Comparing the harmonic MP2/TZVP wavenumber, we find a difference of 21 cm^{−1}. The increase of the basis set from TZVP to QZVP shifts the MP2 harmonic wavenumber further away from the basis set limit (error 47 cm^{−1}). This effect is not surprising since a similar behavior was observed at the CC-level before.^{98,99} For the MP2/QZVP harmonic wavenumbers of the dimer we find similar errors as compared to those in ref 80, which were obtained from an empirical refinement of the MP2-R12 potential energy surface (14–50 cm^{−1}).

4. CONCLUSION

We presented an extensive electronic structure study of hydrogen fluoride (HF) clusters containing 1–12 monomers, applying density functional theory and second-order Møller–Plesset perturbation theory as well as the coupled cluster method. As basis sets we chose the Ahlrichs basis sets for the optimization (TZVP and QZVP), and for the coupled cluster calculations we applied Dunning basis sets and extrapolated them to the complete basis set (CBS) limit. For all methods we optimized the structures except for the MP2/CBS(34) and for the coupled cluster results at the complete basis set limit. These calculations are based on MP2 structures with the combination of a tight optimization criterion denoted as MP2/QZVP*.

For the geometry of the monomer we found *r*(HF) distances of 91.627 pm for MP2/QZVP, 91.627 pm for MP2/QZVP* (higher convergence criterion), 92.159 pm for MP2/TZVP, 93.270 pm for B-P86/TZVP, and 93.246 pm for PBE/TZVP. Thus the MP2/QZVP structures compare best to the experimental value of 91.680 pm as well as to previous computations (91.69 pm) based on high-level coupled cluster approaches and large basis sets.^{20,88,89} For all methods the intramolecular HF distance was observed to become larger with increasing cluster size. Furthermore, this bond elongation was stronger for the cyclic structures than for the chain geometries. The hydrogen bonds became shorter with increasing cluster size, and they were shorter in cyclic structures than in the linear geometries. Both of these observations indicate stronger hydrogen bonds with increasing number of monomers in the clusters and comparing cyclic with linear structures. Stronger hydrogen bonding of clusters also manifested in shorter distances for MP2 with increasing basis set and a more linear arrangement of the hydrogen-bond angle as compared to the DFT results.

For the energies we observed excellent agreement of the 34 extrapolated complete basis set results with both the coupled cluster (−19.48 kJ/mol) as well as with the MP2 (−19.19 kJ/mol) calculations to the experimental binding energy of the dimer. In the case of the MP2 method the well-known large basis set dependency was observed. For example, the R8a cluster values obtained with TZVP (−225.06 kJ/mol) and QZVP (−248.98 kJ/mol) deviate by 24 kJ/mol from each other. For obvious reasons we found that in general ring structures are energetically preferred over chain structures in isolated molecule calculations for all methods and cluster sizes. Similar conclusions can be drawn for the frequencies. The best agreement is found for the MP2/QZVP* calculations. Comparing ring structures with chain structures, we find that cooperativity is more important in the ring structures than in chain clusters from the indicator of interaction energy.

As mentioned in the Introduction, we want to apply the highly accurate electronic structure results for our small- to medium-sized cluster set obtained in this article to determine thermodynamic properties of the condensed phase over a large temperature interval. The first step in a multiscale condensed phase description based on the resolution of the electronic structure consists of the accurate treatment of the underlying electronic structure problem, which has been accomplished in the present study. In the subsequent article we will show that this is a necessary prerequisite in order to obtain accurate and consistent results for the condensed phase of HF.

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