Supplementary information
for paper

Ab initio quantum mechanical description of noncovalent interactions at its limits: approaching the experimental dissociation energy of the HF dimer

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1) Optimized geometries of HF dimer

1a) CCSD(T)/CBS(aug-cc-pVDZ), counterpoise-corrected

Composite scheme: HF/aug-cc-pVQZ + MP2/aug-cc-pV(T,Q)Z + ΔCCSD(T)/aug-cc-pVDZ

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4

H    0.000000000   0.802677096   1.695289760
F    0.000000000  -0.045966169   1.340340769
H    0.000000000  -0.120404367  -0.490816810
F    0.000000000   0.009768180  -1.404250429
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1b) CCSD(T)/CBS(aug-cc-pVTZ), counterpoise-corrected

Composite scheme: HF/aug-cc-pVQZ + MP2/aug-cc-pV(T,Q)Z + ΔCCSD(T)/aug-cc-pVTZ

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4

H    0.000000000   0.801914870   1.695044410
F    0.000000000  -0.045951140   1.338500700
H    0.000000000  -0.120363250  -0.489162780
F    0.000000000   0.009792140  -1.402477460
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1c) CCSD(T)/aug-cc-pVQZ

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4

H    0.000000000   0.805520090   1.683468580
F    0.000000000  -0.046108440   1.333655500
H    0.000000000  -0.118280260  -0.482737710
F    0.000000000   0.009647660  -1.397359000
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1c) CCSD(T)/aug-cc-pV5Z

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4

H    0.000000000   0.805189040   1.684994240
F    0.000000000  -0.046057430   1.335435640
H    0.000000000  -0.119663150  -0.485179930
F    0.000000000   0.009687590  -1.399090500
```

2) Interaction energies and their components

The following tables summarize the individual calculations of interaction energy used to obtain the final (e.g. extrapolated) results presented in the paper. All the results were calculated on the CCSD(T)/CBS(aug-cc-pVDZ) geometry. Values are in kcal/mol.

Table S1. *Interaction energies used in the extrapolation of the CCSD(T)/CBS contribution*

Basis set	Frozen core	SCF energy	CCSD(T) correlation
aug-cc-pCVDZ	no	-3.76172	-0.22772
aug-cc-pCVTZ	no	-3.74442	-0.58170
aug-cc-pCVQZ	no	-3.81531	-0.71611
aug-cc-pCV5Z	no	-3.82048	-0.75555
aug-cc-pCV6Z	no	-3.82158	-0.76276

Table S2. *CCSD(T) and CCSDT(Q) interaction correlation energies used for the evaluation of the contribution of quadruples.*

Basis set	Frozen core	CCSD(T)	CCSDT(Q)
aug-cc-pVDZ	no	-0.22417	-0.21726
cc-pVTZ	no	-0.27829	-0.27896
heavy-aug-cc-pVTZ	no	-0.53005	-0.53581
heavy-aug-cc-pCVTZ	no	-0.54147	-0.54852
aug-cc-pVTZ	no	-0.57299	-0.58047
aug-cc-pCVTZ	no	-0.58172	-0.59043

Table S3. *Interaction correlation energies used for the evaluation of the difference between perturbative and iterative treatment of triples.*

Basis set	Frozen core	CCSD(T)	CCSDT
aug-cc-pVTZ	yes	-0.55813	-0.55554
aug-cc-pVTZ	yes	-0.69261	-0.69113
CBS	yes	-0.79074	-0.79008

Table S4. *The source data used in the evaluation of more approximate composite CCSD(T)/CBS schemes.*

Basis set	Frozen core	SCF	MP2 correlation	CCSD(T) correlation
aug-cc-pVDZ	yes	-3.75580	-0.18193	-0.22130
aug-cc-pVTZ	yes	-3.74225	-0.45189	-0.55813
heavy-aug-cc-pVTZ	yes	-3.74739	-0.43221	-0.51636
aug-cc-pVQZ	yes	-3.81600	-0.56563	-0.69261

3) Vibrational frequencies and ZPVE

Table S5. *Harmonic and anharmonic (VPT2) CCSD(T) vibrational frequencies and ZPVE calculated in aug-cc-pVTZ and aug-cc-pVQZ basis sets. Values in* cm^{-1}.

Dimer

	aug-cc-pVTZ		aug-cc-pVQZ	
Mode	Harmonic	VPT2	Harmonic	VPT2
1	4088	3919	4103	3928
2	4009	3865	4021	3869
3	575	457	572	464
4	219	170	220	180
5	161	133	163	135
6	471	408	467	414
ZPVE	4762	4655	4773	4672

Monomer

	aug-cc-pVTZ		aug-cc-pVQZ	
Mode	Harmonic	VPT2	Harmonic	VPT2
1	4125	3950	4142	3963
ZPVE	2062	2044	2071	2052