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A comparison of *ab initio* Quantum-Mechanical and Experimental D_0 Binding Energies for Eleven H-Bonded and Eleven Dispersion-Bound Complexes

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Abstract

Dissociation energies (D_0) of 11 H-bonded and 11 dispersion-bound complexes were calculated as the sum of interaction energies and the change of zero-point vibrational energies ($\Delta ZPVE$). The structures of H-bonded complexes were optimized at the RI-MP2/cc-pVTZ level, at which also deformation and harmonic $\Delta ZPVE$ energies were calculated. The structures of dispersion-bound complexes were optimized at the DFT-D3 level, and harmonic $\Delta ZPVE$ energies were determined at the same level as well. For comparison, CCSD(T)/CBS D_0 energies were also evaluated for both types of complexes. The CCSD(T)/CBS interaction energy was constructed as the sum of MP2/CBS interaction energy, extrapolated from aug-cc-pVTZ and aug-cc-pVQZ basis sets, and $\Delta CCSD(T)$ correction, determined with the aug-cc-pVDZ basis set. The $\Delta ZPVE$ energies were determined for all complexes at the harmonic level and for selected complexes, these energies were also calculated at second-order vibration perturbation (VPT2) theory. For H-bonded complexes, the harmonic CCSD(T)/CBS D_0 energies were in better agreement with the experimental values (with the mean relative error (MRE) of 6.2%) than the RI-MP2/cc-pVTZ D_0 (the MRE of 12.3%). The same trend was found for dispersion-bound complexes (6.2% (MRE) at CCSD(T)/CBS and 7.7% (MRE) at the DFT-D3 level). When the anharmonic $\Delta ZPVE$ term was included instead of harmonic one, the agreement between theoretical and experimental D_0 deteriorated for H-bonded as well as dispersion-bound complexes. Finally, the applicability of “diagonal approximation” for determining the anharmonic $\Delta ZPVE$ was shown. For the Phenol...H₂O complex, the $\Delta ZPVE$ energy calculated at the VPT2 level and on the basis of “diagonal approximation” differed by less than 0.1 kcal/mol.

Introduction

In recent years, computational chemistry has made enormous progress in determining the binding energies of noncovalently bound complexes, and the wide application of the CCSD(T)/complete basis set (CBS) method^{1,2} has dramatically increased the accuracy of calculated stabilization energies. How accurate are these stabilization energies? Answer to this question is surprisingly not straightforward. It can be relatively easily estimated by making “theory to theory” comparison.³ For example, the accuracy of about 1–2% was reached for stabilization energies of 66 noncovalently bound complexes from the S66 database⁴ by comparing the stabilization energies calculated at two different levels: First, based on the composite scheme of determining CCSD(T)/CBS interaction energies from MP2/CBS⁵ interaction energies, extrapolated from aug-cc-pVTZ and aug-cc-pVQZ basis sets, and CCSD(T) correction terms evaluated as a difference between CCSD(T) and MP2 interaction energies, calculated with a smaller basis set (aug-cc-pVDZ), and second, based on the same scheme but using aug-cc-pVTZ and aug-cc-pVQZ basis sets for extrapolation and the aug-cc-pVTZ basis set for the evaluation of the CCSD(T) correction term.^{6,7} Such a comparison is straightforward and can be extended for example to higher-electron excitations (Q, P, ...) or to the role of relativistic and Born-Oppenheimer corrections.⁸ On the other hand, a comparison of theory to experiment⁹ is not straightforward even in the simplest case represented by the isolated gas-phase complex at very low temperature. Under such conditions, the binding free energy (ΔG) can be identified with binding energy, which means that entropy, whose calculation is tedious, can be neglected. Nevertheless, the experimental binding energy, D_0 , consists of stabilization energy, D_e , and the change of zero-point vibrational energy ($\Delta ZPVE$), which cannot be separated in experimental measurements. The former term can be accurately calculated by e.g. the above-mentioned CCSD(T)/CBS method, whereas the comparably accurate evaluation of the ZPVE requires complex and computationally intensive calculations of vibrational frequencies. The calculations must be performed at a very high level in order to ensure an accurate description of the potential energy surface (PES). Further, it is inevitable to go beyond the harmonic approximation, which is the main problem. As a result, the determination of the $\Delta ZPVE$ is the step limiting the accuracy of the calculated D_0 .

Recently, we have studied the dimerization of the HF molecule.⁸ One of the reasons for completing this study was the fact that the D_0 of this process (1062 cm^{-1} , which converts to 3.036 kcal/mol) had been measured with an unprecedented accuracy of $\pm 1 \text{ cm}^{-1}$. Our aims were to demonstrate the capability of current computational chemistry but also to show its limits.^{10,11} The D_0 was constructed as the sum of CCSD(T)/CBS D_e , deformation energy and the anharmonic $\Delta ZPVE$. Corrections to T- and Q-electron excitations, and relativistic and Born-Oppenheimer effects were also included. The final error of D_0 , when compared to experiment, was 25 cm^{-1} (0.07 kcal/mol), which is about 2.5%. The $\Delta ZPVE$ anharmonicity (–0.19 kcal/mol) itself is larger than the sum of higher-electron excitation contributions (iterative T and Q), relativistic and Born-Oppenheimer contributions and deformation energies, and its inclusion was *conditio sine qua non* for obtaining such a close

agreement with experiment. The assessment of the $\Delta ZPVE$ at the harmonic CCSD(T)/CBS level will dramatically increase the final error.

The aim of the present study is to determine D_0 for 11 H-bonded complexes (having from 7 to 23 atoms) and 11 dispersion-bound complexes (from 12 to 23 atoms) and to compare these values with the experimental ones. The structures of these complexes were determined by gradient optimization at the RI-MP2¹²/cc-pVTZ and B97D3/def2-QZVP¹³ levels of theory for the H-bonded and dispersion-bound complexes, respectively. The D_e energies were calculated with the CCSD(T)/CBS method. Finally, the harmonic $\Delta ZPVE$ term was calculated with the same methods as those used for optimization; on the other hand for the anharmonic $\Delta ZPVE$ term, the VPT2 theory¹⁴ was applied along with the respective methods used for optimization. The use of the VPT2 method for larger complexes is limited. Therefore, we are trying to find an efficient method for the assessment of the $\Delta ZPVE$, which goes beyond the harmonic level, and consider diagonal approximation,¹⁵ where only one-dimensional non-coupled anharmonic frequencies are taken into account for the construction of $\Delta ZPVE$ term.

Computations

The System Investigated

Altogether 11 H-bonded complexes, depicted in Fig. 1, have been investigated. In seven of them (complexes 1–7), the aromatic chromophore containing the polar group (OH, NH) acts as a proton donor while water (H_2O), ammonia (NH_3) and methanol (CH_3OH) act as an electron donor. In three complexes (8–10), water acts as a proton donor while oxygen, fluorine and nitrogen in the aromatic chromophore act as an electron donor. Finally in complex (11), the double bond in ethylene (C_2H_4) acts as an electron donor while H in HCl acts as a proton donor. The set of 11 H-bonded complexes was augmented by 11 dispersion-bound stacked complexes, which are visualized in Fig. 2. They all possess an aromatic chromophore and an inert gas (Ne, Ar, Kr). The structures of all the complexes were manually prepared using Molden.¹⁶

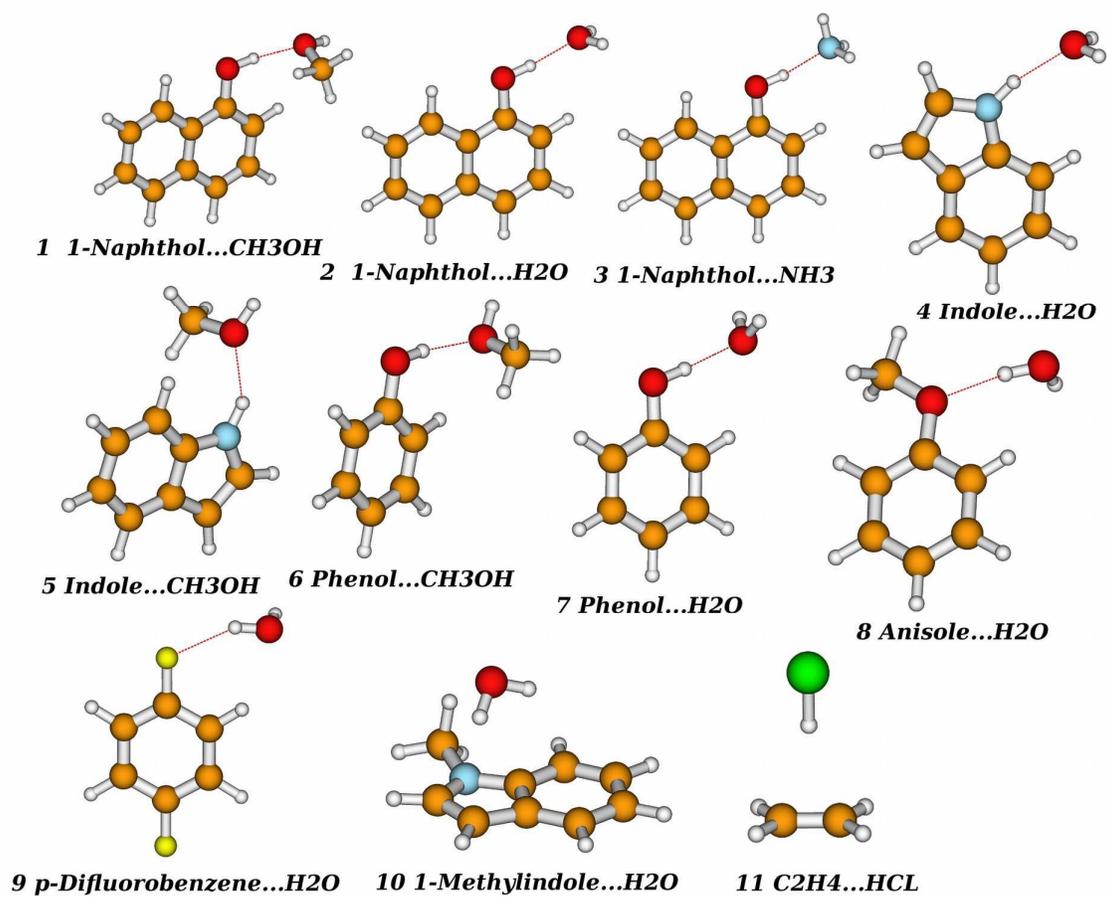


Figure 1: A list of all the 11 H-bonded complexes investigated.

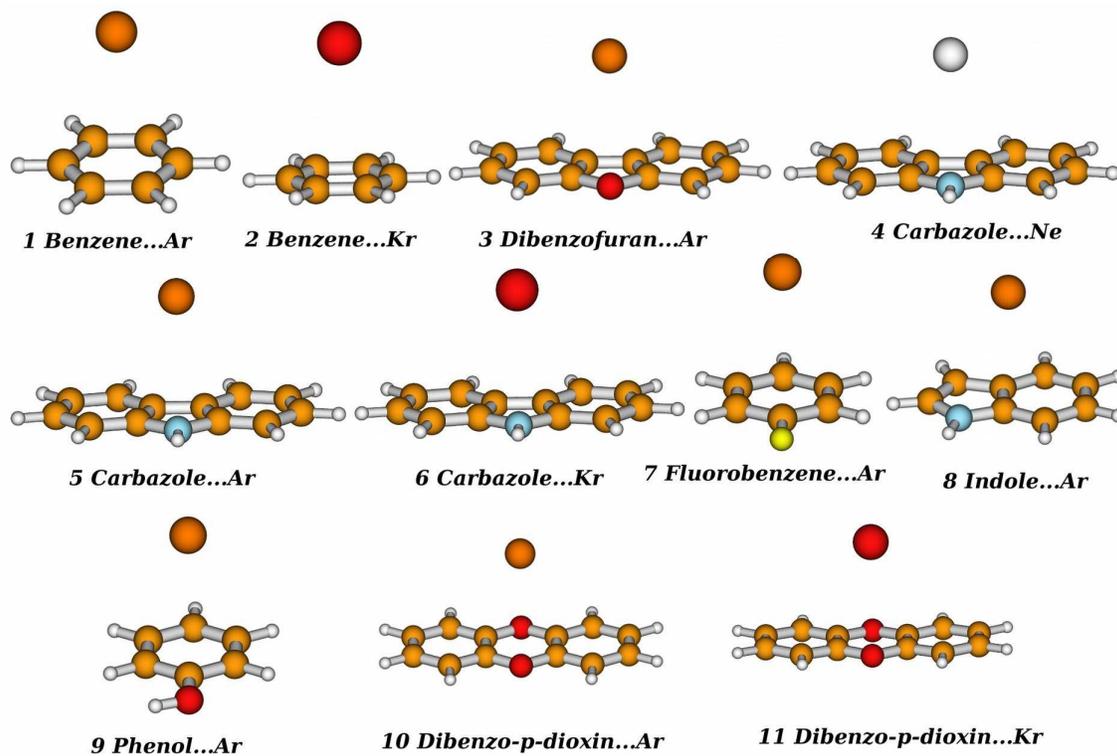


Figure 2: A list of all the 11 dispersion-bound complexes investigated.

The Structure and Interaction Energy

The structures of H-bonded and dispersion-bound complexes were obtained by gradient optimization at the RI-MP2/cc-pVTZ and B97D3/def2-QZVP levels of theory, respectively. Harmonic vibration analysis was done at the same level, and the resulting vibration frequencies were not scaled.

The interaction energies of all the complexes were defined as follows,

$$\Delta E^{(RT)} = E^{(RT)} - E^{(R)} - E^{(T)}, \quad (1)$$

where $E^{(RT)}$ stands for the total electronic energy of the complex and $E^{(R)}$, and $E^{(T)}$ denotes the electronic energies of the corresponding subsystems R and T, respectively. Throughout the study, the basis set superposition error was eliminated by using the function counterpoise (CC) procedure introduced by Boys and Bernardi.¹⁷ Interaction energies of H-bonded and dispersion-bound complexes were calculated at the same level as that used for gradient optimization. The relaxation of interacting subsystems is important and the deformation energy defined as a difference between the energy of subsystems in the dimer- and monomer-optimized geometries was considered. Deformation energy is important for H-bonded complexes but not for dispersion-bound systems, and it was thus considered only for the former complexes. Finally, the accurate interaction energies were determined for all complexes at the CCSD(T)/complete basis set (CBS) limit level of theory. Here a composite scheme¹⁸ was used, and the CCSD(T)/CBS interaction energy was defined as follows,

$$\Delta E^{\text{CCSD(T)}} = \Delta E^{\text{MP2/CBS}} + (\Delta E^{\text{CCSD(T)}} - \Delta E^{\text{MP2}})_{\text{small-basis-set}} \quad (2)$$

The MP2/CBS interaction energy was determined by extrapolation (aug-cc-pVTZ \rightarrow aug-cc-pVQZ basis sets) and the Helgaker et al. scheme^{19,20,21} was utilized. The second term in Eq. 2, called the $\Delta\text{CCSD(T)}$ correction term, evaluated as the difference between CCSD(T) and MP2 interaction energies, was calculated in the smaller basis set (aug-cc-pVDZ). It should be added that the same composite scheme has been used in the S66 database recently introduced in our laboratory.⁴ All the MP2, DFT and VPT2 calculations were performed in the Gaussian09 suite of programs²² with RI approximation (RI-MP2¹²) and CCSD(T) calculations in the Molpro package.²³

Theoretical and Experimental Dissociation Energies

Stabilization energy (the absolute value of interaction energy (eq. 1)), which is also denoted as D_e , is not observable. What is observable is D_0 energy, which corresponds to stabilization enthalpy, defined as

$$D_0 = D_e + \Delta ZPVE, \quad (3)$$

where the $\Delta ZPVE$ term denotes the difference in the zero-point vibrational energies of the complex and the subsystems. The RI-MP2/cc-pVTZ and B97D3/def2-QZVP levels have been applied to perform the harmonic $\Delta ZPVE$ calculations for all H-bonded and dispersion-bound complexes, respectively. We are aware that anharmonicity plays an important role and its inclusion is essential for reproducing the experimental values of D_0 (see our recent paper on the HF dimer⁸). We were able to estimate the anharmonic $\Delta ZPVEs$ for several complexes using the second-order perturbation method (VPT2), which approximately covers the anharmonic effects. The use of the VPT2 method especially for larger complexes is limited; here we have tested the use of the diagonal approach, where only the diagonal one-dimensional anharmonic vibrational frequencies are considered (see below).

Diagonal Approach

One-dimensional anharmonic vibration frequencies were calculated for all six intermolecular vibration modes and for the X–H intramolecular stretching mode, which participates in the H-bonding (X–H...Y). For each mode, we performed a scan using curvilinear valence coordinates and fitted the potential with Morse, sine and cosine functions, for which the vibrational energy levels can be expressed analytically. For more details, see the reference.^{15, 24, 25}

Results and Discussion

Stabilization energies

H-bonded complexes

Optimized structures of all 11 H-bonded complexes are shown in Fig. 1. Table 1 presents stabilization and deformation energies determined at the RI-MP2/cc-pVTZ level (the level used for optimization) as well as the benchmark CCSD(T)/CBS stabilization energies. Evidently, deformation energies are not negligible and should be considered. Their main contribution comes from X–H bond lengthening upon the formation of X–H...Y H-bond. Deformation energy correlates with the strength of the H-bond and is the largest for the strongest complex, 1-Naphthol...NH₃ (0.39 kcal/mol). The CCSD(T)/CBS stabilization energies are mostly larger than the RI-MP2 ones and the differences are not negligible. The largest difference (–0.82 kcal/mol) was found for the Anisole...H₂O complex, which was more than twice the average difference (–0.37 kcal/mol). For reaching an agreement with experiment, it is thus recommendable to work at the CCSD(T)/CBS level. As expected, the largest stabilization energies were found for 1-Naphthol and Phenol acting as a proton donor and NH₃ and CH₃OH acting as an electron donor. The strongest H-bond close to 10 kcal/mol was detected in the 1-Naphthol...NH₃ complex.

As already mentioned, the CCSD(T)/CBS De energies are to be preferred. How accurate are these values, or, in other words, are they already converged? The accuracy of the present composite scheme also used in the S66 database has recently been tested. It was shown that passing to the larger basis

sets for MP2 as well as Δ CCSD(T) energies changes the resulting CCSD(T)/CBS interaction energies by less than 2%.⁶ We have investigated the convergence of the present CCSD(T)/CBS composite scheme, specifically of the Δ CCSD(T) correction term, for one of the strongest H-bonded complexes, the Phenol...H₂O complex. Passing from the aug-cc-pVDZ basis set to the much larger aug-cc-pVTZ basis set, its absolute value increased from 0.56 to 0.64 kcal/mol, which changed the final CCSD(T)/CBS D_e by less than 1%. We can thus conclude that the present CCSD(T)/CBS D_e energies are accurate enough with the error not exceeding 1%.

Complexes ^a	D_e (RI-MP2/c-c-pVTZ)	D_e (CCSD(T)/CBS)	ΔE^b	D_f^c	ΔZPV E (harm) ^d	D_0 ((RI-MP2/cc-pVTZ))	D_0 (CCSD(T)/CBS)	EXPT ^e
1 1-Naphthol...CH ₃ OH	8.02	8.58	- 0.55	0.22	1.31	6.49	7.05	7.56 ²⁶
2 1-Naphthol...H ₂ O	6.79	7.07	- 0.27	0.10	1.53	5.16	5.44	5.82 ²⁶
3 1-Naphthol...NH ₃	9.23	9.57	- 0.33	0.39	1.67	7.18	7.51	7.66 ²⁶
4 Indole...H ₂ O	5.75	5.70	0.05	0.06	1.09	4.59	4.55	4.66 ²⁷
5 Indole...CH ₃ OH	6.78	7.02	- 0.24	0.11	0.91	5.75	5.99	5.60 ²⁸
6 Phenol...CH ₃ OH	7.65	8.21	- 0.56	0.18	1.33	6.14	6.71	6.11 ²⁹
7 Phenol...H ₂ O	6.54	6.82	- 0.28	0.09	1.55	4.91	5.18	5.43 ²⁹
8 Anisole...H ₂ O	4.07	4.89	- 0.82	0.06	1.53	2.48	3.30	3.69 ²⁸
9 p-difluorobenzene...H ₂ O	3.04	3.66	- 0.62	0.05	1.08	1.91	2.53	2.79 ³⁰
10 C ₂ H ₄ ...HCl	2.99	3.01	- 0.02	0.01	1.16	1.83	1.85	3.18 ³¹
11 1-Methylindole...H ₂ O	5.21	5.63	- 0.41	0.22	1.43	3.57	3.98	4.10 ²⁷

Table 1: Stabilization energies (D_e) and dissociation energies (D_0) of 11 H-bonded complexes calculated at the RI-MP2/cc-pVTZ and CCSD(T)/CBS levels. ^acf. Fig. 1, ^bthe difference in the stabilization energy (D_e (RI-MP2/cc-pVTZ) - D_e (CCSD(T)/CBS)), ^cthe deformation energy, ^dthe Δ ZPVE calculated at the harmonic level, ^eexperimental values.

Dispersion-bound complexes

The structures of all 11 dispersion-bound complexes optimized at the B97D3/def2-QZVP level are

visualized in Fig. 2 and their stabilization energies are collected in Table 2. The present stabilization energies are much smaller than those of previously discussed H-bonded complexes, and the Dibenzo-*p*-dioxin...Kr complex was found to be the strongest one (DFT-D3 level) with a D_e of 2.32 kcal/mol. At the CCSD(T) level the strongest complex is the Carbazole...Kr one with a D_e of 2.15 kcal/mol. Contrary to the previous case, the CCSD(T)/CBS stabilization energies are smaller than the DFT-D3 values (on average by 0.08 kcal/mol), with the difference not exceeding 0.24 kcal/mol or 10%. The difference in D_e between lower- and higher-level calculations is not as large as with H-bonded complexes, and the use of the DFT-D3 level especially for large dispersion-bound complexes can thus be recommended here.

complexes ^a	D_e (DFT-D3)	D_e (CCSD(T)/CBS)	ΔE^b	$\Delta ZPVE$ (harmonic) ^c	D_0 (DFT-D3)	D_0 (CCSD(T)/CBS)	EXPT ^d
1 Benzene...Ar	1.20	1.13	0.07	0.21	0.99	0.92	0.97 ³²
2 Benzene...Kr	1.59	1.42	0.17	0.21	1.38	1.21	1.15 ³²
3 Dibenzofuran...Ar	1.58	1.57	0.01	0.11	1.47	1.46	1.49 ³³
4 Carbazole...Ne	0.58	0.51	0.07	0.08	0.49	0.42	0.61 ³⁴
5 Carbazole...Ar	1.68	1.68	0.00	0.14	1.53	1.54	1.52 ³⁴
6 Carbazole...Kr	2.29	2.15	0.13	0.09	2.19	2.06	1.97 ³⁴
7 Fluorobenzene...Ar	1.19	1.13	0.07	0.19	0.99	0.93	0.92 ³⁵
8 Indole...Ar	1.48	1.48	0.0	0.16	1.32	1.33	1.29 ³⁶
9 Phenol...Ar	1.24	1.19	0.05	0.23	1.01	0.96	1.04 ⁹
10 Dibenzo- <i>p</i> -dioxin...Ar	1.72	1.65	0.07	0.21	1.51	1.44	1.51 ³⁷
11 Dibenzo- <i>p</i> -dioxin...Kr	2.32	2.08	0.24	0.23	2.09	1.85	1.83 ³⁷

Table 2: Stabilization energies (D_e) and Dissociation energies (D_0) of 11 dispersion-bound complexes calculated at the DFT-D3 and CCSD(T)/CBS levels. ^acf. Fig. 2, ^bthe difference in the stabilization energy (D_e (DFT-D3) – D_e (CCSD(T)/CBS)), ^cthe $\Delta ZPVE$ calculated at the harmonic level, ^dexperimental values.

D_0 Binding Energy

H-bonded complexes

D_0 energies (covering deformation energies) utilizing the harmonic $\Delta ZPVE$ are presented in Table 1, also showing experimental D_0 values. For H-bonded complexes, the harmonic vibration analysis was performed at the same level as that used for gradient optimization, i.e. at the RI-MP2/cc-pVTZ level.

D_0 values based on D_e energies determined at the RI-MP2 and CCSD(T)/CBS levels will be discussed separately. However, in both cases the deformation energy as well as $\Delta ZPVE$ terms were calculated at the same level, i.e. the RI-MP2/cc-pVTZ one. The $\Delta ZPVE$ term is important and its average value is 1.32 kcal/mol (462 cm^{-1}). Since it forms a non-negligible part of D_0 energies (about 29% of the CCSD(T)/CBS D_0), its neglect will make the agreement with the experimental D_0 value much worse (see below).

The mean relative error (MRE) and the mean absolute error (MAE) for RI-MP2 D_0 energies were 15.1% and 0.63 kcal/mol, respectively. Passing to the CCSD(T)/CBS level, both errors were reduced – to 9.4% and 0.41 kcal/mol, respectively. The best agreement between the calculated and experimental D_0 values was found for Phenol...CH₃OH surprisingly at the RI-MP2/cc-pVTZ level (MRE, 0.5%). Passing to the more reliable CCSD(T)/CBS level, the MRE error slightly increased. At the CCSD(T)/CBS level, the best agreement with experiment was found for the 1-Naphthol...NH₃ complex (MRE, 2.0%). On the other hand, the worst agreement (the MRE of about 42% at both theoretical levels) was found for the C₂H₄...HCl complex. The very large error clearly indicates that the experimental value is not reliable and should be considered with caution. When this complex is omitted, the agreement between theoretical and experimental D_0 values considerably improves: the MREs at the RI-MP2 and CCSD(T) levels are 12.3% and 6.2%, respectively. This implies the need to include the $\Delta ZPVE$ term. Without considering the $\Delta ZPVE$, both of the above-mentioned errors dramatically increased to 18.0% and 26.8% at the RI-MP2 and CCSD(T) levels, respectively. In order to approach the experimental D_0 value, it is inevitable to include the $\Delta ZPVE$ term.

Dispersion-bound complexes

D_0 energies based on DFT-D3 as well as on CCSD(T)/CBS D_e energies are summarized in Table 2. In both cases, the harmonic DFT-D3 $\Delta ZPVE$ s were added. The deformation energy is systematically neglected. The $\Delta ZPVE$ energies are now considerably smaller than in the previous case and the average $\Delta ZPVE$ is only 0.17 kcal/mol (60 cm^{-1}). This energy forms only about 13% of the D_0 energy, which is less than one half of that contribution for H-bonded complexes (see above). The MRE and MAE amount to 7.7% and 0.09 kcal/mol, respectively, at the DFT-D3 level and to 6.2% and 0.06 kcal/mol, respectively, at the CCSD(T)/CBS level. The lower- and higher-level D_0 for the dispersion-bound complexes differ much less than in the case of H-bonded complexes. The best agreement between theoretical and experimental D_0 was found for the Dibenzo-*p*-dioxin...Ar complex (MRE, 0.3%) at the DFT-D3 level; passing to the more reliable CCSD(T)/CBS level, both errors slightly increased. At the CCSD(T)/CBS level, the best agreement was found for the Dibenzo-*p*-dioxin...Kr complex (MRE, 1.4%).

For dispersion-bound complexes, the $\Delta ZPVE$ plays a less important role. If omitted, the calculated errors between the theoretical and experimental values were found to be 18.8% (MRE) and 0.24 kcal/mol (MAE) at the DFT-D3 level and 14.5% (MRE) and 0.17 (MAE) at the CCSD(T)/CBS level,

which is considerably less than in the case of H-bonded complexes. Nevertheless, also here it is essential to include the $\Delta ZPVE$ term in order to reach agreement with experiment.

Anharmonicity

H-bonded complexes. The perturbation VPT2 calculations are CPU-time intensive and, further, they frequently have problems with convergence, especially, to predict the coupled low frequency modes associated with Fermi resonance. We were able to perform the VPT2 method for only four strong H-bonded complexes: Phenol...H₂O, *p*-Difluorobenzene...H₂O, Phenol...CH₃OH, and the HF...HF dimer.⁸ As mentioned above, VPT2 calculations were performed at the RI-MP2 level. Table 3 presents D_0 energies for these four H-bonded complexes based on RI-MP2 and CCSD(T)/CBS D_e energies. First, the HF dimer will be discussed, because accurate $\Delta ZPVE$ energies based on CCSD(T)/CBS values are available there.⁸ The anharmonic $\Delta ZPVE/CCSD(T)$ calculation amounts to 1.81 kcal/mol while the present value calculated similarly but based on RI-MP2 calculations is smaller (1.69 kcal/mol). The difference between both values is about 0.1 kcal/mol and the present theoretical level makes the $\Delta ZPVE$ smaller. Consequently, the D_0 values based on RI-MP2 $\Delta ZPVE$ and CCSD(T)/CBS D_e energies represent the upper limit of the real value.

Further, we compare D_0 energies for the remaining three H-bonded complexes (Phenol...H₂O, *p*-Difluorobenzene...H₂O and Phenol...CH₃OH), for which the $\Delta ZPVE$ term was evaluated at harmonic as well as VPT2 anharmonic levels (in both cases based on RI-MP2 calculations). First, the VPT2 anharmonic term is smaller for all three complexes (like for the HF dimer⁸) than the harmonic one, with this difference being practically negligible for the first complex. However, contrary to our expectation, the relative error for these three complexes did not change systematically when passing from the harmonic to the VPT2 anharmonic $\Delta ZPVE$ term. Specifically for the first and second complex, it increased from 4.6 to 5.5% and from 9.3 to 18.8%, respectively, and only for the third one it decreased from 9.8 to 6.8%. For the Phenol...H₂O complex, harmonic D_0 is closer to the experimental value, which evidently arises from the quality of the $\Delta ZPVE$ term, because the D_e energy is already converged (as demonstrated by increasing the basis set for the calculation of the CCSD(T) correction term from aug-cc-pVTZ to aug-cc-pVQZ). Evidently, the anharmonic $\Delta ZPVE$ terms determined by the perturbation VPT2 method are not reliable enough and the use of the method cannot be recommended for this purpose.

Complexes	H-bond			EXPT
	$\Delta ZPVE^a$ RI-MP2/cc- pVTZ	D_0 (RI- MP2/cc- pVTZ)	D_0 (CCSD(T)/CB S)	
Phenol...H ₂ O	1.59	4.86	5.14	5.43
Phenol...CH ₃ OH	1.51	5.96	6.52	6.11

<i>p</i> -Difluorobenzene...H ₂ O	1.35	1.65	2.27	2.79
HF...HF ⁸			2.96	3.04
Dispersion				
Benzene...Ar	0.26		0.88	0.97
Benzene...Kr	0.21		1.21	1.15
Phenol...Ar	0.14		1.05	1.04
Fluorobenzene...Ar	0.15		0.98	0.92

Table 3: The dissociation energy (D_0) calculated at the anharmonic VPT2 level for 4 H-bonded and 4 dispersion-bound complexes. ^athe anharmonic $\Delta ZPVE$ is calculated at the RI-MP2/cc-pVTZ//VPT2 level for both H-bonded and dispersion-bound complexes.

Dispersion-bound complexes. CCSD(T)//VPT2/DFT-D3 calculations were applied for four complexes shown in the lower part of Table 3. As expected, the harmonic as well as anharmonic $\Delta ZPVE$ terms are small and do not exhibit any systematic behavior. The calculated D_0 based on both harmonic and anharmonic $\Delta ZPVE$ terms are in reasonable agreement with experiment. When D_0 was constructed from the harmonic $\Delta ZPVE$ term, the mean relative error for the complexes shown in Table 3 was 5%. Passing to the anharmonic $\Delta ZPVE$ term, this error slightly increased to 5.6%. Evidently, both approaches for determining the $\Delta ZPVE$ term provide similar values of theoretical D_0 , which agree reasonably well with experimental values. The inclusion of the $\Delta ZPVE$ is, however, essential. When the $\Delta ZPVE$ term was not considered, the mean average error dramatically increased to 19.4%.

Diagonal approximation. From the previous paragraphs, it becomes evident that a routine calculation of anharmonic $\Delta ZPVE$ terms at the perturbation VPT2 level is impractical. The inclusion of the harmonic $\Delta ZPVE$ term improves the agreement between theoretical and experimental D_0 , but especially for H-bonded complexes, anharmonicity plays an important role. Is there any (simple) way to go beyond the harmonic level? A possible solution is to use diagonal approximation, where the $\Delta ZPVE$ term is determined using only one-dimensional (i.e. non-coupled) anharmonic vibrational frequencies. The evaluation of all $3n-6$ vibrational frequencies, where n equals the number of atoms of a complex, could be tedious, but it can be simplified by considering only six intermolecular degrees of freedom. We have shown that for dispersion-bound complexes, the deformation energy is negligible, which clearly indicates that intramolecular coordinates are not affected by complexation. On the other hand for H-bonded complexes, this energy is not negligible and its main contribution comes from the elongation/shortening of the X–H bond upon the formation of the H-bond. The applicability of the diagonal approximation was tested for the strong H-bonded complex, Phenol...H₂O. Here we considered all six intermolecular vibration frequencies plus the Phenol O–H intramolecular one. The $\rho 1$, $\beta 1$ and $\sigma(O..O)$ are the three hindered translational modes whereas τ , $\rho 2$ and $\beta 2$ are the three

hindered rotational modes, respectively (cf. Fig. 3).³⁸ The Δ ZPVE term based on these seven one-dimensional anharmonic vibrational wavenumbers equals to 497 cm^{-1} (1.41 kcal/mol), which surprisingly well agrees with the respective VPT2 value (460 cm^{-1} , 1.31 kcal/mol). The close agreement between both values could be, however, caused by the compensation of errors, and further verification of this very promising simple technique for the estimation of the anharmonic Δ ZPVE term is needed.

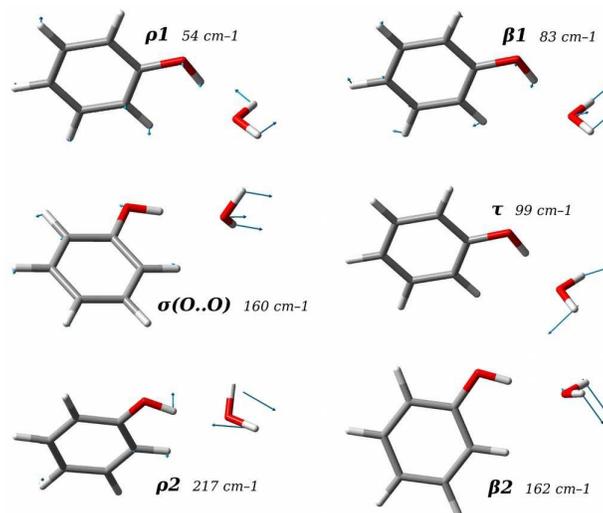


Figure 3. Pictorial representation of all the low-vibrational intermolecular modes of Phenol...H₂O.

Phenol...H ₂ O	Full-dimensional VPT2 calculation	Diagonal approximation
$\rho 1$	54	40
$\beta 1$	58	83
$\sigma(O..O)$	145	160
τ	98	99
$\rho 2$	235	217
$\beta 2$	162	162
$\sigma(O..H)$	3492	3451
free(O...H)	3660	3683

Table 4: The anharmonic fundamental wavenumbers calculated at the standard full-dimensional VPT2 RI-MP2/cc-pVTZ level and applying the 1-dimensional diagonal approximation for the Phenol...H₂O complex.

Conclusions

i) A comparison of theoretical and experimental D_0 for 11 H-bonded complexes has revealed that the experimental D_0 for the C₂H₄...HCl complex is unrealistically high and should be omitted. The

agreement between theoretical D_0 , based on the harmonic $\Delta ZPVE$ term, and the experimental D_0 for the remaining 10 H-bonded complexes is reasonable (12.3% and 6.2% at the RI-MP2 and CCSD(T) levels, respectively) and, as expected, it is considerably better at the CCSD(T) level. When the harmonic $\Delta ZPVE$ was ignored, the error dramatically increased to 18.0% and 26.8%, respectively. This clearly demonstrates the importance of considering the $\Delta ZPVE$ term. When passing to the anharmonic $\Delta ZPVE$ term, the agreement did not improve, which indicates that the applicability of the perturbation VPT2 technique for H-bonded complexes is limited.

ii) Theoretical D_0 , based on the harmonic $\Delta ZPVE$ term, agree with experimental D_0 for 11 dispersion-bound complexes comparably well and the relative error at the DFT-D3 and CCSD(T) levels amounts to 7.7% and 6.2%, respectively. Also here, the inclusion of the $\Delta ZPVE$ term is important (although less than for H-bonded complexes), and when the term was omitted, the error at the DFT-D3 and CCSD(T) levels increased to 18.8% and 14.5%, respectively. When the anharmonic $\Delta ZPVE$ term was included instead of the harmonic one, the agreement between theoretical and experimental D_0 slightly deteriorated.

iii) The applicability of diagonal approximation for the estimation of the $\Delta ZPVE$ term was investigated for the Phenol...H₂O complex, for which the perturbational VPT2 technique converged. The agreement between the $\Delta ZPVE$ term determined using the diagonal approximation and the VPT2 method has been excellent (within 0.10 kcal/mol).

Acknowledgements

This work was part of the Research Project RVO: 61388963 of the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic. This work was also supported by the Czech Science Foundation [P208/12/G016]. The authors gratefully acknowledge the support by the project LO1305 of the Ministry of Education, Youth and Sports of the Czech Republic. We would like to thank Prof. Vladimír Špirko for the helpful discussion and his kind guidance.

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