COMMENTS

Comment on "Strength of the N−H···O=C Bonds in Formamide and *N*-Methylacetamide Dimers"

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Cis-amides are common in biologically important molecules. They provide neighboring hydrogen bonding N−H donor and C=O acceptor sites, thereby significantly influencing the structures of nucleic acids, proteins, and peptides. The formamide dimer, $(FA)_2$, is the simplest cis-amide dimer and has therefore been widely studied experimentally and theoretically in the gas and liquid phases.[1−5] The results obtained are essential for understanding and modeling the structures and interactions between more extended biopolymers.

Vargas et al. calculated the binding energies of five different H-bonded $(FA)_2$ dimers at the MP2 level of theory, using the aug-cc-pVXZ (X = D, T, and Q) basis sets and extrapolated them to the complete basis set (CBS) limit.[1] The aug-cc-pVXZ series of basis sets was designed[6] for frozen-core MP2 calculations; i.e., the 1s electrons should not be correlated. However, Vargas et al. employed the aug-cc-pVXZ basis sets for fully correlated calculations.[1] We address several points, comparing their CBS limit binding energy of the most stable $(formamide)_2$ isomer with values obtained using frozen-core MP2 calculations. The binding energies D_e and the counterpoise (CP) corrected binding energies D_e^{CPC} obtained by frozen-core and fully correlated[1] calculations are compared in Table 1 and plotted in Figure 1.

First, in ref 1 only half of the necessary CP correction was applied to the aug-cc-pVDZ binding energy, giving rise to a CBS extrapolation curve with an unusual shape. The correctly calculated D_e^{CPC}, marked by a diamond in Figure 1b, is given in parentheses in Table 1 and leads to a monotonically decreasing CBS extrapolation curve, as is usually found. Second, the CBS binding energy $D_{e,CBS} = -14.35$ kcal/mol given in ref 1 corresponds to an extrapolation[7] of the CP-uncorrected D_e values *only*. No CBS limit binding energy for the CP-corrected D_e^{CPC} energies was given in ref 1, which is unusual, given that both extrapolations should, in principle, lead to nearly the same value. It is also a priori unclear why the uncorrected and not the corrected binding energies should be extrapolated. We calculated the CP-corrected value to be $D_{e,CBS}^{CPC} = -14.82$ kcal/mol (using the correct aug-cc-pVDZ CP-corrected binding energy). This value is about 0.5 kcal/mol larger than the $D_{e,CBS}$ value; see also Figure 1b. This rather large difference can be traced to the use of the fully correlated calculation: Extrapolation[8] of the *frozen core* corrected and uncorrected binding energies result in $D_{e,CBS}(FC) = -14.86$ kcal/mol and $D_{e,CBS}^{CPC}(FC) = -14.72$ kcal/mol. The much smaller difference between these two extrapolated binding energies shows that the CBS procedure works reliably if the basis sets are used as intended.[7] The average frozen core CBS value $D_e^{\infty}(FC) = -14.79$ kcal/mol is shown as a dashed line in Figure 1a. This binding energy is 0.51 kcal/mol larger than that reported in ref 1.

TABLE 1: Calculated Frozen Core and Fully Correlated MP2 Binding Energies of $(formamide)_2$ (kcal/mol), Using the aug-cc-pVXZ (X= D, T, Q) Basis Sets. the Fully Correlated Binding Energies in Parentheses Are Recalculated

	fully correlated		frozen core	
	D_e	D_e^{CPC}	D_e	D_e^{CPC}
aug-cc-pVDZ	−15.80[a]	−14.68[a] (−13.39)[b]	−15.598[b]	−13.388[b]
aug-cc-pVTZ	−16.83[a]	−13.98[a]	−15.362[b]	−14.109[b]
aug-cc-pVQZ	−15.37[a]	−14.49[a]	−15.073[b]	−14.482[b]
CBS limit	−14.35[a,c]	(−14.82)[b,c]	−14.86[b,d]	−14.72[b,d]

[a] Values from ref 1. [b] This work. [c] Extrapolation to the complete basis set limit according to ref 7. [d] Extrapolation to the complete basis set limit according to ref 8.

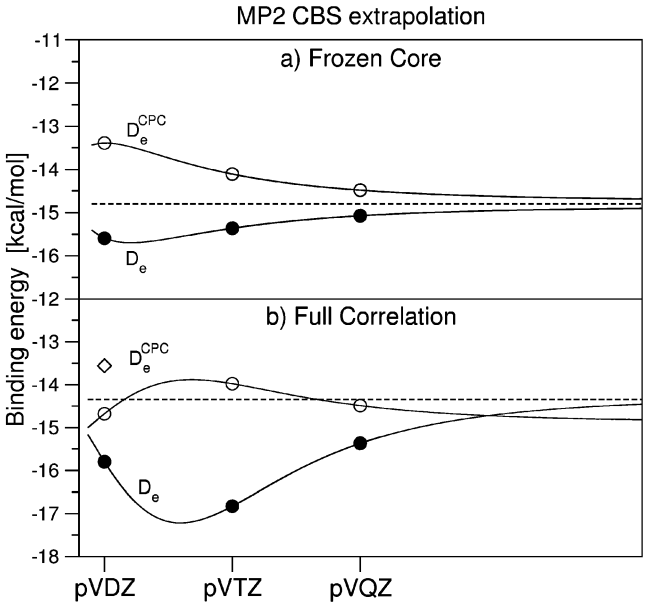

Figure 1. Complete basis set (CBS) extrapolations of the binding energies D_e (●) and counterpoise-corrected binding energies D_e^{CPC} (○) of the most stable isomer of $(formamide)_2$ using (a) frozen core, this work, and (b) fully correlated MP2 calculations, reported in ref 1. The aug-cc-pVDZ point in (b) labeled by ○ should be corrected to the value ◇; see Table 1 and the text. The dashed lines correspond to the CBS limits: (a) frozen core, this work; (b) fully correlated, reported in ref 1.

References and Notes

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