J. Phys. Chem. A **2005,** *109,* 6991−6992 **6991**

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

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Received: April 18, 2005; In Final Form: May 13, 2005

We appreciate the comments of Frey and Leutwyler[1] on our previous work.[2] We agree that we made a mathematical error in the calculation of the BSSE corrected binding energy for the dimerization energy of formamide dimer structure **1** with the aug-cc-pVDZ basis set and appreciate that Frey and Leutwyler[1] have corrected this error. We also agree that our previous calculations were done with all electrons correlated instead of just the valence electrons and that the work presented by Frey and Leutwyler[1] represents a better approximation to the electronic component of the valence electrons to the dissociation energy of the formamide dimer than did our previous work.

To better understand the role of correlating the 1s electrons with the aug-cc-pVnZ basis sets and extrapolating to the complete basis set (CBS) limit, we have performed two sets of calculations.[3,4] We first calculated the electronic contribution to the dissociation energy of the water dimer as shown in Table 1. The calculations were done with the geometry optimized at the frozen core MP2/aug-cc-pVTZ level.[5,6] The calculations show that at the complete basis set (CBS) limit,[7] the results with the core correlated give a well-depth 0.4 kcal/mol deeper than when the core is not included, similar to the difference of 0.5 kcal/mol (out of ~15 kcal/mol) that Frey and Leutwyler[1] find for the electronic contribution for the formamide dimer. We also note the hump in the dissociation energy curve for the all electron correlation calculations just as found for the formamide dimer. This hump represents a basis set superposition error (BSSE) that presumably arises because the introduction of more functions with the larger basis sets helps to correlate the core electrons better. We note that the fully correlated and frozen core results for the electronic energy contribution to the dimer dissociation energy when the counterpoise correction is included are the same for the H_2O dimer just as found by Frey and Leutwyler[1] for the formamide dimer after correcting our mathematical mistake. It is clear that inclusion of the counterpoise correction[8] does allow one to minimize errors if the core electrons are included in a calculation without core−valence correlation functions. We note that calculations including the core electrons with only the aug-cc-pVnZ basis sets are not recommended.

TABLE 1: Electronic Energy Components to the Dissociation Energy, D_e, of the Water Dimer in kcal/mol

	frozen core (FC)		full		FC − full	
basis set	D_e	D_e^{CPC}	D_e	D_e^{CPC}	ΔD_e	ΔD_e^{CPC}
aug-cc-pVDZ	5.22	4.39	5.50	4.39	−0.28	0.00
aug-cc-pVTZ	5.24	4.72	6.22	4.74	−0.98	−0.02
aug-cc-pVQZ	5.09	4.86	5.74	4.87	−0.65	−0.01
CBS	4.99	4.94	5.39	4.95	−0.40	−0.01

TABLE 2: Electronic Energy Contributions to the Dissociation Energy, D_e, of the Formamide Dimer 1 in kcal/mol

basis set *n*	D_e(full) aug-cc-pwCVnZ	D_e(FC) aug-cc-pwCVnZ	D_e(full) aug-cc-pVnZ
D	15.67	15.51	15.80
T	15.19	15.13	16.83
Q	15.01	14.96	15.37
CBS limit	14.90	14.85	14.35

To further assess the role of the core electrons, we have also calculated the dimerization energy for the formamide dimer with the effects of the 1s electrons included in a basis set that treats core−valence interactions properly.[9] We used the tight core functions together with the augmented correlation-consistent basis sets (aug-cc-pwCVnZ, for n = D, T, Q) and the geometries previously reported by us.[2] We calculated the dissociation energies with all electrons correlated and with only the valence electrons correlated. These results are shown in Table 2 together with our previous results with the aug-cc-pVnZ basis set.[2] The calculations show that there is a more regular convergence behavior when the core−valence interactions are included with a basis set appropriate for such interactions. We also note that there are very small differences between the valence electron-only, frozen core dissociation energy (FC) and the dissociation energy with core−valence interactions (full) included. The core−valence correction is 0.05 kcal/mol at the CBS limit, and the best value for the electronic dissociation energy of the formamide dimer is 14.90 kcal/mol, in excellent agreement with the values of Frey and Leutwyler.[1] The core−valence correction of 0.05 kcal/mol is smaller than the value of 0.1 kcal/mol obtained by Frey and Leutwyler with just the aug-cc-pVnZ basis set. (Neither of the two groups advocate the practice of using the valence aug-cc-pVnZ basis sets to obtain core−valence corrections.)

These calculations were done on the Cray XD-1 computer in the Alabama Supercomputer Center and the HP Linux computer in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. The EMSL is a DOE sponsored national user facility.

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10.1021/jp0520042 CCC: $30.25

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