COMMENTS

Comment on “Molecular Modeling Approach for Contrasting the Interaction of Ethane and Hexafluoroethane with Carbon Dioxide”

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Recently, Cece et al.[1] examined the interaction of ethane and hexafluoroethane with carbon dioxide using *ab initio* calculations in order to explain the difference solubilities of these types of molecules in supercritical carbon dioxide. They especially calculated the interaction energies between the molecules of each system at the restricted Hartree−Fock level of theory using the 6-31G* basis set while increasing the number of CO_2 molecules surrounding C_2H_6 and C_2F_6, which is summarized in Table 1. Judging from their results to show the energy differences between the C_2H_6/CO_2 and the C_2F_6/CO_2 systems, the latter has a favorable interaction.

However, it is known to require basis set superposition error (BSSE) correction in case of energy calculations for the complexes with weak intermolecular binding such like these. Moreover, it’s necessary to correct the interaction energy in these systems as the amount of that are small: −0.7 to −0.3 kcal for the C_2H_6/CO_2 systems and −3.0 to −0.8 kcal for the C_2F_6/CO_2 systems in their results. We recalculated the binding energies of two systems among the studied complexes considering the BSSE: the $C_2H_6{-}CO_2$ and the $C_2F_6{-}CO_2$. The BSSE-corrected interaction energy (ΔE) was obtained via[2,3]

$$\Delta E = E_{AB}{}^{\alpha U\beta}(AB) - E_{AB}{}^{\alpha U\beta}(A) - E_{AB}{}^{\alpha U\beta}(B) + E_{rel}{}^{\alpha}(A) + E_{rel}{}^{\beta}(B)$$

where $E_{rel}{}^{\alpha}(A) = E_{AB}{}^{\alpha}(A) - E_{A}{}^{\alpha}(A)$ and $E_{rel}{}^{\beta}(B) = E_{AB}{}^{\beta}(B) - E_{B}{}^{\beta}(B)$ are the fragment relaxation energies corresponding to the energy penalty for distorting them from their isolated geometries to the ones in the complex. In the formula, the electronic energy of a molecular system M at geometry G computed with basis set σ is defined as $E_G{}^{\sigma}(B)$.[3]

TABLE 1: Interaction Energies (kcal/mol) for Ethane/CO_2 Systems and Hexafluoroethane/CO_2 Systems at the HF Level of Theory Using 6-31G* Basis Sets

no. of CO_2’s	$E_{int}(C_2H_6/CO_2)$	$E_{int}(C_2F_6/CO_2)$
1	−0.3	−0.8
2	−0.6	−1.6
3	−0.6	−2.3
4	−0.7	−3.0

TABLE 2: BSSE Corrected Interaction Energies (kcal/mol) for Ethane−CO_2 and Hexafluoroethane−CO_2 Complexes

	method/basis	uncorrected ΔE	BSSE	corrected ΔE
$C_2H_6{-}CO_2$	HF/6-31G*	−0.31	0.39	0.08
	HF/6-311G(2d,p)	−0.31	0.35	0.04
	MP2/6-31G*	−1.27	1.05	−0.22
$C_2F_6{-}CO_2$	HF/6-31G*	−0.80	1.03	0.23

The BSSE corrected interaction energies with fragment relaxation energy terms are listed in Table 2. As the authors reported, the correction energy from the fragment relaxation are negligibly small in both cases of the $C_2H_6{-}CO_2$ and the $C_2F_6{-}CO_2$ complex. However, the BSSE corrected interaction energies show that there is no binding of two molecules in each system. When the basis set was even extended to 6-311G(2d,p) and the corrected interaction energies were calculated, the binding between them could not be also detected though the BSSE slightly decreased. The authors did not take into consideration of the BSSE so that the binding energy of the $C_2F_6{-}CO_2$ complex is more favorable than that of the $C_2H_6{-}CO_2$ in their results.

In fact, the binding energy for the $C_2H_6{-}CO_2$ complex (0.31 kcal) reported by the authors is larger than the corrected binding energy (0.22 kcal) obtained from our MP2/6-31G* calculation, which seems to show that their calculations are erroneous. They intended to compare qualitatively the difference between the binding energies of the C_2H_6/CO_2 and the C_2F_6/CO_2 systems in the paper, but the majority of their results on binding energies may originate from the BSSE, which is an artificial mathematical effect. It seems that the HF/6-31G* calculations cannot give any useful information on the interaction of hydrocarbon and fluorohydrocarbon with carbon dioxide even qualitatively.

References and Notes

(1) Cece, A.; Jureller, S. H.; Kerschner, J. L.; Moschner, K. F. *J. Phys. Chem.* **1996**, *100*, 7435.
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