Theoretical Studies for Lewis Acid−Base Interactions and C−H···O Weak Hydrogen Bonding in Various CO_2 Complexes

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Comprehension of the basic concepts for the design of CO_2-philic molecules is important due to the possibility for “green” chemistry in supercritical CO_2 of substitute solvent systems. Lewis acid−base interactions and C−H···O weak hydrogen bonding were suggested as two key factors in the solubility of CO_2-philic molecules. To isolate the stabilization energy of weak hydrogen bonding from the overall binding energy, high-level quantum mechanical calculations were performed for the van der Waals complexes of CO_2 with methane, methylacetate, dimethylether, acetaldehyde, and 1,2-dimethoxyethane. Structures and energies were calculated at the MP2 level of theory using the 6-31+G(d) and aug-cc-pVDZ basis sets with basis set superposition error corrections. In addition, the single-point energies were calculated using recently developed multilevel methods. This study shows that the Lewis acid−base interaction has a significant impact on the complex stability compared to the C−H···O weak hydrogen bond. The additional stabilization energy of the cooperative weak hydrogen bond with α-proton of the carbonyl group was negligible on the enhancement of supercritical CO_2 solubility. However, the stabilization energy was larger for the ether group, such that it may have an important role in increasing the supercritical CO_2 solubility. Additional formation of cooperative weak hydrogen bonds may not further increase the solubility due to the stability reduction by steric hindrance.

Introduction

Extensive theoretical and experimental studies on supercritical carbon dioxide ($scCO_2$) have been performed.[1−4] $scCO_2$ has many advantages as a process solvent in that it is inexpensive, abundant, and environmentally genial. As a result, for the past decade, $scCO_2$ has been treated as a “green” processing solvent. The usage of $scCO_2$ as a solvent has serious limitations due to the poor solubility of the majority of polar and ionic materials. To this end, it was hypothesized that polar materials could be added to the solution via various surfactants. Many research groups have attempted to design CO_2-philic materials and increase the solubility of the CO_2-based organic solvent. The most widely applied method to increase the solubility is to use a fluorocarbon.[5−7] The fluorocarbon-based CO_2-philes are very soluble in liquid and $scCO_2$, but these “successful CO_2-philes” are very expensive. Thus, it is necessary to design inexpensive hydrocarbon-based CO_2-philes, i.e., carbonyl oxygen complexes, ether oxygen complexes, and amine complexes. To choose the possible molecules that have a high solubility in the CO_2 complexes, it is necessary to recognize the specific interactions between these CO_2-philes and CO_2. As a result, the basic concepts for the chemical state of CO_2 need to be elucidated.

Two possible major interactions of CO_2 complexes are the Lewis acid−base (LA−LB) interaction and cooperative C−H···O weak hydrogen bonding. Even though the dipole moment for carbon dioxide is zero, the quadrupole moment is not. It is clear that there is charge separation between carbon and oxygen, such that the electron density has been polarized and the electrons migrate toward the oxygen atoms. As a result, the carbon atom has a partial positive charge acting as a Lewis acid (LA) and the two oxygen atoms have partial negative charges acting as a Lewis base (LB), resulting in the carbon atom acting as an electron acceptor in an LA−LB interaction with carbonyl groups. The oxygen atoms with partial negative charges can be involved in weak electrostatic interactions with properly placed electron-deficient C−H bonds, which form a cooperative weak hydrogen bond (H-bond).

Recently, a number of groups have performed quantum mechanical calculations to estimate the energies of the LA−LB interactions and weak H-bonds. Diep et al.[5] have investigated the interactions of CO_2 with small hydrocarbons and fluorocarbons (CH_4, C_2H_6, CF_4, and C_2F_6) using the Hartree−Fock and Møller−Plesset second-order perturbation theory (MP2) methods. They reported binding energies of the CO_2−hydrocarbon clusters ranging from 0.79 to 1.17 kcal/mol at the MP2 level after basis set superposition error corrections. Although the solubility of perfluorocarbons is greater than the hydrocarbons in CO_2, the binding energies for the CO_2−hydrocarbon complexes are slightly larger than the corresponding CO_2−perfluoro-carbon clusters. As a result, they were unable to discern the reason for greater solubility of perfluorocarbons in CO_2 from their calculations on the small clusters. Raveendran and Wallen[8] have studied the role of a cooperative C−H···O interaction as an additional stabilizing interaction with the LA−LB interaction between CO_2 and carbonyl compounds and their implications for solvation in $scCO_2$. Ab initio calculations were performed on complexes of CO_2 with model carbonyl systems such as HCHO, acetaldehyde, and methylacetate. Among the carbonyl systems investigated, methylacetate had the strongest interaction with CO_2 and provided evidence for the existence of the C−H···O H-bond, although the relative contribution of the C−H···O interaction to the overall stabilization was questionable. Saharay and

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Balasubramanian have performed an ab initio MD study for ethanol−CO_2 complexes and shown that the LA−LB interaction is energetically more favorable than hydrogen bonding.[9] Kilic et al.[10] have also performed extensive quantum mechanical calculations for the CO_2−methylacetate complex and determined that the binding energies for CO_2 interacting with the ether oxygen were very close to the energy with the carbonyl oxygen. They suggested that ether oxygens should be just as effective as carbonyl oxygens at increasing the solubility of polymers in CO_2. The influence of LA−LB interaction on the $\nu_2(CO_2)$ vibrational mode was studied for various CO_2 complexes at the HF/3-21G(d) level.[11]

It has been suggested that the C−H···O weak H-bonds play an important role in structure chemistry and crystal packing,[12−16] molecular recognition processes,[17,18] and possibly the structure of biological macromolecules.[13,19−21] Additionally, it is important to investigate whether the CO_2 oxygen atoms can form a weak H-bond with electron-deficient hydrogen atoms in a CO_2-phile. Raveendran and Wallen's ab initio calculations have shown that the CO_2 oxygen participates in a cooperative C−H···O H-bond with the electron-deficient hydrogen atoms attached to the carbonyl carbon atoms.[8,22,23] NMR, IR, and Raman spectroscopic studies of acetaldehyde and CO_2 mixtures provided experimental evidence for the presence of both the LA−LB interaction between CO_2 and the carbonyl group, as well as a weak C−H···O H-bond.[22,24] Although the cooperative C−H···O H-bond is formed with CO_2, the role it plays in enhanced solubility is not certain.[10] Part of the reason is that it is very difficult to isolate the cooperative weak H-bond energy from the overall stabilization energy of complexes. Therefore, more systematic studies are necessary.

Most of the electronic structure calculations for the complexes use a supermolecular approach where the interaction energy of the complex is obtained as the energy difference between the complex and monomers. However, this approach is sensitive to the basis set superposition error (BSSE). In some cases where the interaction energies are small, the BSSEs are as large as the interaction energies.[5,10] A conceptually simple way of accounting for BSSE is the counterpoise (CP) correction method, in which the energies of the fragments are calculated on the full basis of the complex. When computing the interaction energy, these CP-corrected energies are used for the energies of the fragments but occasionally cause overestimation of the actual correction.[25−27] Recently, Truhlar and co-workers have suggested elaborate schemes that combine scaling, extrapolation to an infinite basis set, and fitting to a set of experimental data.[28−32] In these methods, the total energy is written as a linear combination of energy terms with different basis sets, and coefficients are adjusted to fit experimental data (atomization energies). The BSSE correction is included in some of the coefficients, although not completely.[33] These linear combination methods are called multilevel methods, and some multilevel methods show very good agreement with experiments of the interaction energies of water and HF dimers.[34]

A systematic study was performed to isolate the stabilization energy of a weak C−H···O H-bond using a high-level quantum mechanical method, including the multilevel method. The role of C−H···O H-bonds as a CO_2-philic stabilization factor and the LA−LB interactions were elucidated. The interactions of CO_2 complexes with methylacetate (MA), acetaldehyde (AL), dimethylether (DE), and 1,2-dimethoyethane (DME) were studied.

Computational Methods

All ab initio electronic structure calculations were performed using the Gaussian03 pakages.[35] Geometry optimization was performed at the MP2 level using the 6-31+G(d), aug-cc-pVDZ basis sets. The vibrational frequencies were also calculated to confirm that the structures were at the real potential energy minimum. The interaction energies (ΔE) of these complexes are defined as

$$\Delta E = E_{AB} - (E_A + E_B) \tag{1}$$

where E_{AB} is the energy of the optimized CO_2 complex and E_A and E_B represent the energies of the optimized monomers. Zero-point energies (ZPEs) were also included in the interaction energies using the MP2 frequencies scaled by 0.95.[36]

The BSSE were calculated using the CP method of Boys and Bernadi.[37]

$$E_{BSSE} = [E_m(M_1) - E_d(M_1{}')] + [E_m(M_2) - E_d(M_2{}')] + E_{rel} \tag{2}$$

$$E_{rel} = [E_m(M_1{}') - E_m(M_1)] + [E_m(M_2{}') - E_m(M_2)] \tag{3}$$

where $E_m(M)$ and $E_d(M')$ are the energies of the monomer in its own basis set and the basis set of the CO_2 complex, respectively. The M and M' indicate the optimized geometry of the monomer and the monomer in the optimized complex, respectively. The fragment relaxation energy (E_{rel}), the energy associated with the transition from the optimized geometry of monomer to the geometry in the complex, should be included in the BSSE correction. The corrected interaction energy is determined as follows:

$$E_{corr} = E_d(D) - [E_m(M_1) + E_m(M_2)] + E_{BSSE} \tag{4}$$

$$= E_d(D) - [\mathrm{E}_d(M_1{}') + \mathrm{E}_d(M_2{}')] + E_{rel} \tag{5}$$

where $E_d(D)$ is the energy of the CO_2 complex in its own basis set. The binding energy or dissociation energy is defined as the negative value of the interaction energy of the complexes.

The multicoefficient correlated quantum mechanical methods (MCCMs) were used to calculate interaction energies of the complexes. This method has been described elsewhere in detail, and only a short description of each method will be provided.[28−32] These methods involve differences between energies at different basis sets and theory levels, and a short notation has been used to concisely write the equation for a multilevel energy. In this notation, the pipe "|" is used to represent the energy difference between either two one-electron basis sets $B1$ and $B2$, or two levels of electronic structure theory $L1$ and $L2$. The energy difference between two basis sets is denoted as

$$\Delta E(L/B2|B1) = E(L/B2) - E(L/B1) \tag{6}$$

where L is a particular electronic structure method and $B1$ is smaller than $B2$. The energy change that occurs upon improving the treatment of the correlation energy is represented by

$$\Delta E(L2|L1/B) = E(L2/B) - E(L1/B) \tag{7}$$

where $L1$ is a level of theory lower than $L2$ and B is a common, one-electron basis set. Finally, the change in energy increment due to the increasing level of treatment of the correlation energy with one basis set compared to an increment from a smaller basis set is represented as

$$\Delta E(L2|L1/B2|B1) = E(L2/B2) - E(L1/B2) - [E(L2/B1) - E(L1/B1)] \quad (8)$$

The Utah form of MCCM methods are written as

$$E(\text{MCCM-UT-L}) = c_1E(\text{HF/cc-pVDZ}) + c_2\Delta E(\text{HF/cc-pVTZ|cc-pVDZ}) + c_3\Delta E(\text{MP2|HF/cc-pVDZ}) + c_4\Delta E(\text{MP2|HF/cc-pVTZ|cc-pVDZ}) + c_5\Delta E(\text{L|MP2/cc-pVDZ}) + E_{\text{SO}} + E_{\text{CC}} \quad (9)$$

where E_{SO} and E_{CC} represent the spin−orbit and core-correlation energies, respectively, and L = CCSD for the MCCM-UT-CCSD method. The multicoefficient G3(MCG3) method is written as

$$E(\text{MCG3}) = c_1E(\text{HF/6-31G(d)}) + c_2\Delta E(\text{HF/MG3|6-31G(d)}) + c_3\Delta E(\text{MP2|HF/6-31G(d)}) + c_4\Delta E(\text{MP2|HF/MG3|6-31G(d)}) + c_5\Delta E(\text{MP4SDQ|MP2/6-31G(d)}) + c_6\Delta E(\text{MP4SDQ|MP2/6-31G(2df,p)|6-31G(d)}) + c_7\Delta E(\text{MP4|MP4SDQ/6-31G(d)}) + c_8\Delta E(\text{QCISD(T)|MP4/6-31G(d)}) + E_{\text{SO}} + E_{\text{CC}} \quad (10)$$

The multilevel energies are calculated using the MULTILEVEL 4.0 program, which uses the Gaussian03 packages to obtain the energy, gradient, and Hessians components to calculate the corresponding multilevel values.[38]

Results and Discussion

The solubility of organic molecules in $scCO_2$ fluid depends on the interaction between CO_2 and the CO_2-philic functional group and their relative strength compared to the solvent−solvent and solute−solute interactions. The structure and binding energies of the CO_2 dimer have been extensively studied.[39−43] It is well-established that there are two favored geometrical configurations for the CO_2 dimer: slipped parallel (C_{2h} symmetry) and T-shaped (C_{2v} symmetry). In the gas phase, the CO_2 dimer with the slipped parallel geometry is preferred. Tsuzuki et al.[43] have reported that the binding energies of the CO_2 dimer with the slipped parallel and T-geometries are 1.36 and 1.14 kcal/mol, respectively, at the MP2 level with the complete basis sets. CO_2 complexes with larger binding energies would have significant roles in $scCO_2$ solubility.

TABLE 1: Binding Energies for the CO_2–Methane Complex Calculated at the MP2 and Multilevels[a]

	energies
MP2/aug-cc-pVDZ	0.62 (0.16)/0.76[b]
MP2/aug-cc-pVTZ[c]	0.88/0.19
MP2/aug-cc-pVQZ//MP2/aug-cc-pVDZ	0.92 (0.45)/0.14, 0.87[d]
MCCM-UT-CCSD	0.93 (0.46)
MCCM-CO-CCSD(T)	1.12 (0.66)
MCG3	0.86 (0.39)

[a] Energies in kcal/mol. Numbers in parentheses include ZPE corrections. [b] The BSSE using the CP correction. [c] Reference 5. [d] Reference 44.

In order for it to be meaningful to the $scCO_2$ solubility, although the weak hydrogen bonding is expected to be very weak, its energy should be still larger than the van der Waals energy between CO_2 and nonpolar molecules, such as methane and ethane. Binding energies between CO_2 and hydrocarbons, such as methane and ethane, were calculated by Diep et al.[5] at the MP2/aug-cc-pVTZ level with the BSSE corrections to be 0.88 and 1.17 kcal/mol, respectively. They have shown that there is a sizable component of electron correlation in the binding energy, which represents dispersive interactions. Recently, Raveendran and Wallen[44] have also reported that the binding energy of the CH_4−CO_2 complex is 0.87 kcal/mol at the MP2/aug-cc-pVQZ level with CP correction. The structure of the CO_2−CH_4 complex at the MP2/aug-cc-pVDZ level was recalculated to obtain the binding energies at the MP2/aug-cc-pVQZ and MCCM levels, as listed in Table 1. It should be noted that the BSSE using the CP correction was much larger than the binding energy including ZPEs at the MP2/aug-cc-pVDZ level. The MP2/aug-cc-pVQZ energy in this study was 0.92 kcal/mol without the ZPE corrections, which was slightly different from previous results found in studies by Raveendran and Wallen. The CP correction often overestimates the BSSE,[25−27] which may lead to an incorrect conclusion, particularly when the binding energies are very small. To this end, it is potentially better to use the largest basis sets affordable without the CP correction. Recently, dimerization energies for $(H_2O)_2$ and $(HF)_2$ have been reproduced with chemical accuracy using an MCCM with good empirical parameters and without CP correction.[33,34] Three multilevel methods, the MCCM-UT-CCSD, MCG3, and MCCM-CO-CCSD(T), were used in this study. The best estimates of the van der Waals energy for CH_4−CO_2 complex were 0.66 and 1.12 kcal/mol with and without ZPE corrections at the MCCM-CO-CCSD(T) level, respectively. These binding energies were approximately 0.2 kcal/mol greater than the other two multilevel methods. In order to test the geometrical sensitivity, the MCCM-CO-CCSD(T) energies were calculated using the structures optimized at the MP2/6-31+G(d) level and resulted in nearly the same values. Therefore, the weak H-bond energies calculated from MP2/6-31+G(d) structures were assumed to be as correct as those from MP2/aug-cc-pVDZ structures. The van der Waals energy for the CH_4−CO_2 complex at the MCCM-CO-CCSD(T) level was slightly smaller than the binding energy of the slipped parallel CO_2 dimer but similar to the T-shaped dimer.

Theoretical studies for the CO_2−MA complexes have been performed previously by other research groups to elucidate the effect of LA−LB interactions and the cooperative weak hydrogen bonding of $scCO_2$ solubility.[8,10] Three CO_2−MA complexes were calculated depending on the location of CO_2, as shown in Figure 1. In the optimized structures of MA-A and MA-B, CO_2 is bound to the carbonyl oxygen with C−H···O weak H-bonds to α- and methoxy protons, respectively. In the complex MA-C, CO_2 is bound to the methoxy oxygen with two concomitant types of weak H-bonds. The LA−LB distances (C···O distances) of these complexes were very similar: 2.839, 2.872, and 2.861 Å for MA-A, MA-B, and MA-C, respectively. The geometrical parameters for MA-A are identical to those of previous studies,[8] but those for MA-B show small differences, namely, in the distance of the weak H-bond to the methoxy protons. It is interesting to note that the dihedral angle of O═C−C−H containing the weakly H-bonded proton in MA-A was 11.7°. A structure with 0° has one imaginary frequency, and the energy is only 0.003 kcal/mol higher. These results

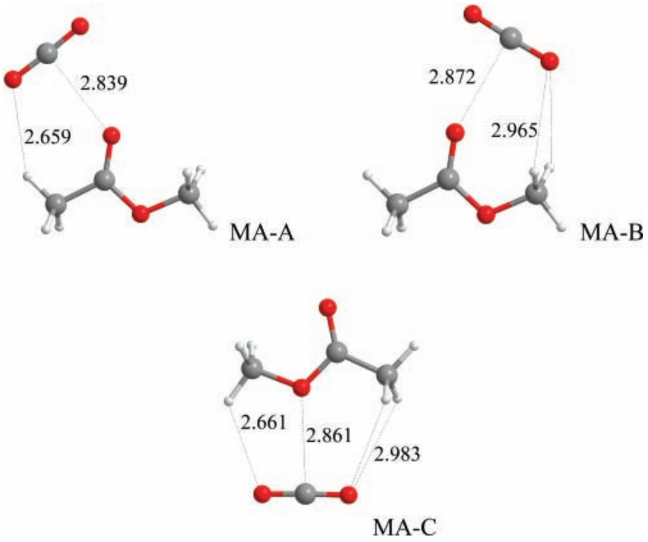

Figure 1. Geometric parameters for CO_{2}–methylacetate complexes. Lengths are in angstroms.

reveal that the potential energy surface of methyl rotation along the C−C bond was very flat and the hydrogen bonding was very weak.

The binding energies for each complex at the MP2 and MCCM levels are listed in Table 2 along with previous results. The binding energies for MA-A, MA-B, and MA-C complexes at the MP2 level were 2.25, 2.09, and 2.16 kcal/mol before the ZPE correction and 1.81, 1.76, and 1.71 kcal/mol after the correction, respectively. The BSSEs, which should be considered in the calculation of the binding energies of the complexes, are approximately 1.4 kcal/mol for MA-A and MA-B and 1.8 kcal/mol for MA-C. These values were comparable to the binding energies of corresponding complexes including ZPEs. Fragment relaxation energies, which are part of the BSSE corrections, are negligible in most cases and not listed in this table. Multilevel calculations at the MCCM-CO-CCSD(T) level, which is the most accurate and extensive calculations among the multilevel methods, predicted 3.05, 3.14, and 3.05 kcal/mol for the binding energies of MA-A, MA-B, and MA-C complexes including ZPEs, respectively. All multilevel methods predict larger binding energies than the CP-corrected MP2 values, which is probably attributed to the electron correlation involved in the binding energy. It is interesting to note that the binding energies of CO_2 bound to the methoxy oxygen is quite similar to those of the other two complexes where CO_2 is bound to the carbonyl oxygen and agrees very well with previous results.[10] The energy variations among the complexes at each level of theory were very small. These results provide strong evidence that methoxy oxygen should be just as effective as carbonyl oxygen in acting as an LB and can increase the $scCO_2$ solubility.[10]

There are one, two, and three weak H-bonds in MA-A, MA-B, and MA-C complexes, respectively. It is difficult to determine any correlation between binding energies or the number (or distances) of weak H-bonds. Recently, Wallen and co-workers have extensively studied the cooperative effect of weak H-bonds on the solubility of CO_2-philes in supercritical CO_2 fluid.[8,22−24,44,45] However, the role of the enhanced solubility is not certain.[10] In order to elucidate the cooperative effect of the weak hydrogen bonding on the $scCO_2$ solubility of CO_2-philic molecules, it is necessary to understand how much binding energy of the complex originates from the weak hydrogen bonding, compared to nonspecific interactions such as the van der Waals interaction between CO_2 and CO_2-philes, and possibly show an additive effect, such as more weak H-bonds or larger binding energy, which may lead to larger $scCO_2$ solubility. However, it is not possible to isolate the energetic contribution of weak H-bonds from overall binding energies, thus requiring a careful and systematic study.

The CO_2−acetaldehyde (AL) complex is a small molecular system containing an LA−LB interaction between CO_2 and carbonyl groups with cooperative weak hydrogen bonding. As shown in Figure 2, five different CO_2−AL complexes were calculated depending on the position of the CO_2. In AL-A and AL-B, CO_2 is bound to the carbonyl oxygen with concomitant weak H-bonds, and their geometrical parameters were quite similar to previous studies except for the smaller C−H···O and C···O distances.[8] Binding energies at various computational levels are listed in Table 3. The binding energies for AL-A and AL-B including ZPEs at the MP2/aug-cc-pVDZ level were 1.82 and 1.94 kcal/mol, respectively, with quite large BSSEs. The binding energies at the MCCM-CO-CCSD(T) level were 2.61 and 2.84 kcal/mol with ZPE corrections, respectively.

In order to evaluate the correct weak H-bond energy without any complication from the LA−LB interaction, two weakly H-bonded complexes, AL-C and AL-D, were calculated, as shown in Figure 2. There was no LA−LB interaction in these structures, but weak H-bonds with α- and aldehyde protons were formed. Note that the CO_2 molecule in AL-D is located perpendicular to the aldehyde plane. The weak H-bond distances of AL-C and AL-D were approximately 2.98 and 2.92 Å, respectively. The distances between C and O in the weak H-bonds were smaller than the limiting *D*-values (4 Å) for the weak C−H···O bond.[12] There was no cooperative effect involved, suggesting that the binding energies were for pure weak hydrogen bonding between CO_2 and α-protons. The binding energies at the MP2 level were very small, even smaller than the corresponding CP-corrected BSSEs. Multilevel values were much larger than the MP2 values, which indicate that there was also a sizable component of electron correlation in the binding energy. The binding energy of AL-C including ZPEs was 0.67 kcal/mol at the MCCM-CO-CCSD(T) level, which was nearly the same as the van der Waals energy of CO_2−CH_4 at the same level. This suggests that noncooperative weak hydrogen bonding may not have a special role on $scCO_2$ solubility, although weak H-bonds can be formed. The smaller binding energy of AL-D indicates that this type of complex did not have any advantages compared to the CO_2−CH_4 complex in the $scCO_2$ solubility.

One possible way to estimate the energetic contribution of cooperative weak H-bonding is to calculate the binding energy without weak H-bonds and compare it to that of AL-A. Since α-protons cannot be removed, the CO_2 molecule was relocated to remove the weak H-bond. One way to relocate the CO_2 molecule is to rotate it 90° along the C···O axis of AL-A. In this case, the change in the energetic contribution of LA−LB interaction needs to be considered. When the carbon of CO_2 was linearly located with the C═O bond of formaldehyde, two conformers were formed: in-plane T-complex, where CO_2 is in the plane of formaldehyde, and out-of-plane T-complex, where CO_2 is perpendicular to the plane.[8] Both in- and out-of-plane conformers were not in the potential energy minimum at the MP2/aug-cc-pVDZ level but were at stationary points with two and one imaginary frequencies, respectively. Interestingly, the out-of-plane T-complex was more stable (0.5 kcal/mol) than the in-plane complex, which suggests more favorable LA−LB interaction in the former. If CO_2 is a quadrupolar solvent that has only solvent quadrupole−solute dipole interaction (i.e.,

TABLE 2: Binding Energies for the CO_2−Methylacetate (MA) Complexes Calculated at the MP2 and Multilevels[a]

	MA-A	MA-B	MA-C
MP2/6-31+G*	2.25 (1.81)/1.42[b]	2.09 (1.76)/1.40	2.16 (1.71)/1.76
MP2/6-31+G*[c]	2.34/1.25	2.18/1.25	2.26/1.54
MP2/aug-cc-pVDZ//MP2/6-31+G*[d]	2.82	2.64	
MCCM-UT-CCSD	3.32 (2.87)	3.30 (2.97)	3.29 (2.84)
MCCM-CO-CCSD(T)	3.49 (3.05)	3.47 (3.14)	3.49 (3.05)
MCG3	3.35 (2.91)	3.26 (2.92)	3.36 (2.91)

[a] Energies in kcal/mol. Numbers in parentheses include ZPE corrections. [b] The BSSE using the CP correction. [c] Geometry was optimized with the CP correction (ref 10). [d] Reference 8.

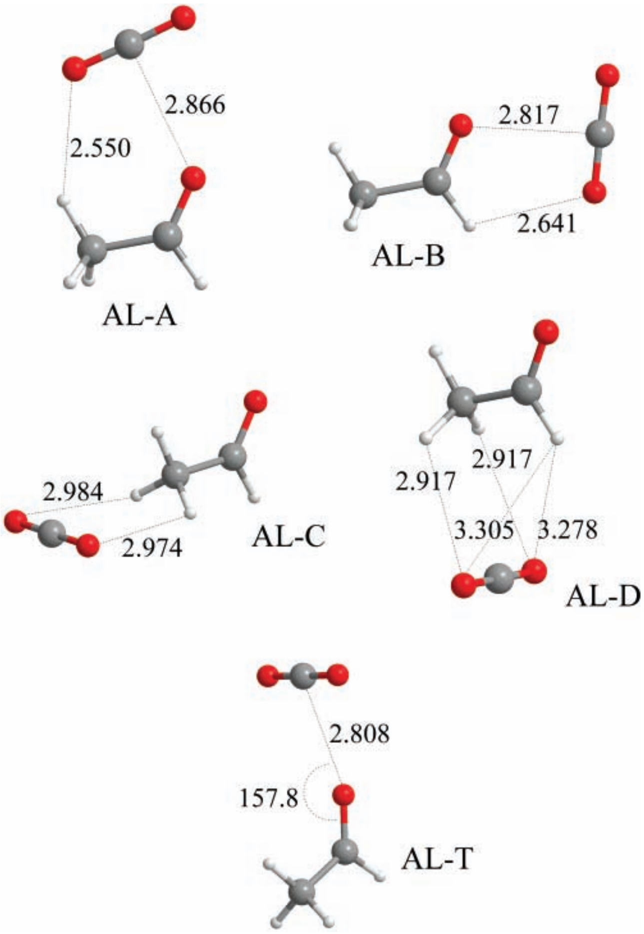

Figure 2. Geometric parameters for CO_2–acetaldehyde complexes. Lengths are in angstroms and angles in degrees.

electrostatic interactions) as suggested by Kauffman, there would be no difference in the binding energies. In the LA−LB interaction there is also an interaction between the highest occupied molecular orbital (HOMO) of LB and lowest unoccupied molecular orbital (LUMO) of LA. As shown in Figure 3, there are two lobes in the HOMO of carbonyl oxygen and LUMO of the carbon atom in CO_2, and because of their relative orientation the overlap of HOMO and LUMO is better in the out-of-plane T-complex. When C═O and the C atom of CO_2 has an angle as shown in the AL-A geometry, only one lobe of each orbital will overlap with each other. Both electrostatic and orbital interactions play an important role in the binding of CO_2 on the carbonyl group. This trend would hold for the AL molecule. When the CO_2 molecule of AL-A is rotated 90° along the C⋯O axis to remove the cooperative weak hydrogen bonding, the LA−LB interaction energy would be increased slightly, but not as much as that of linear T-complexes in formaldehyde. AL-T is the stationary point with out-of-plane T-geometry optimized at the MP2/aug-cc-pVDZ level. Note that the rotation of the CO_2 molecule results in the larger C═O⋯C angle and the shorter C⋯O distance as this is the way to enhance the quadrupole−dipole interaction and HOMO−LUMO overlap (an LA−LB interaction). The driving force of the transition from AL-T to AL-A is the cooperative weak hydrogen bonding, and the contribution to the overall binding energy would be approximately 0.2 kcal/mol, which was the energy difference between AL-T and AL-A. It is of interest that the additional stabilization energy by the formation of the cooperative weak H-bond was quite small, and even smaller than the thermal energy provided at the supercritical temperature of CO_2. The small energy was attributed to the unfavorable orientation of CO_2 for the quadrupole−dipole interaction and HOMO−LUMO overlap.

In order to study the LB capacity of bidentate oxygen and estimate the strength of weak H-bonds, CO_2 complexes with DE were calculated, as shown in Figure 4. Depending on the location of CO_2 bound to DE, there are four different configurations, DE-A, DE-B, DE-C, and DE-T. The DE-A complex has been studied experimentally and theoretically by Van Ginderen et al.[46] The experimental binding enthalpy was 1.92 kcal/mol in liquid argon. The binding potential energy was 3.94 kcal/mol that is estimated with theoretical corrections from ab initio and Monte Carlo calculations. Table 4 lists the binding energies for the CO_2−DE complexes at the MP2 and multilevels. The distance between C and ether oxygen (O_E) was 2.66 Å, and the weak H-bond distance was 2.92 Å for the DE-A complex. The MCG3 binding energy without ZPE is apparently the same as the estimated experimental binding energy by Van Ginderen et al.[46] The MCCM-UT-CCSD and MCCM-CO-CCSD(T) level seem to slightly overestimate the binding energy of DE-A. The binding energies at the MCCM-UT-CCSD, MCCM-CO-CCSD(T), and MCG3 levels were 3.73, 3.84, and 3.39 kcal/mol with ZPE corrections, respectively. These values were, on average, 0.71 kcal/mol larger than those of the MA-C complex, which has the same type of LA−LB interaction. The CO_2 molecule of the DE-A complex was rotated 90° along the C⋯O_E axis to remove the cooperative weak hydrogen bonding and form the DE-T complex. The complex had one imaginary frequency for the rotational motion of CO_2 along the C⋯O_E axis, indicating that this structure was at the top of the potential energy curve along the rotational coordinate. The C⋯O_E distance increased to 2.82 Å, and the weak hydrogen bonding was removed. Unlike the case of the AL complex, there was an additional solvent quadrupole−solute quadrupole interaction that became unfavorable by the rotation of the CO_2 molecule. The overlap between the HOMO of DE and LUMO of CO_2 was also reduced by the rotation. The difference in energy at the MCCM-CO-CCSD(T) level between the DE-A and DE-T was 1.33 kcal/mol with ZPE corrections. This value includes the loss of the energetic contribution from LA−LB interactions, the quadrupole−quadrupole interaction, and the overlap between HOMO and LUMO, and therefore it should be regarded as the upper limit of the cooperative weak H-bond energy.

TABLE 3: Binding Energies for the CO_2−Acetaldehyde (AL) Complexes Calculated at the MP2 and Multilevels[a]

	AL-A	AL-B	AL-C	AL-D	AL-T
MP2/aug-cc-pVDZ	2.36 (1.82)/1.04[b]	2.54 (1.94)/1.03	0.44 (0.21)/0.82	0.39 (0.16)/0.83	2.08 (1.68)/0.79
MP2/aug-cc-pVDZ//MP2/6-31+G*[c]	2.52	2.69			
MCCM-UT-CCSD	2.93 (2.39)	3.23 (2.63)	0.67 (0.44)	0.58 (0.28)	2.67 (2.27)
MCCM-CO-CCSD(T)	3.15 (2.61)	3.44 (2.84)	0.90 (0.67)	0.87 (0.56)	2.77 (2.38)
MCG3	2.85 (2.31)	3.12 (2.52)	0.76 (0.52)	0.71 (0.40)	2.50 (2.11)

[a] Energies in kcal/mol. Numbers in parentheses include ZPE corrections. [b] The BSSE using the CP correction. [c] Reference 8.

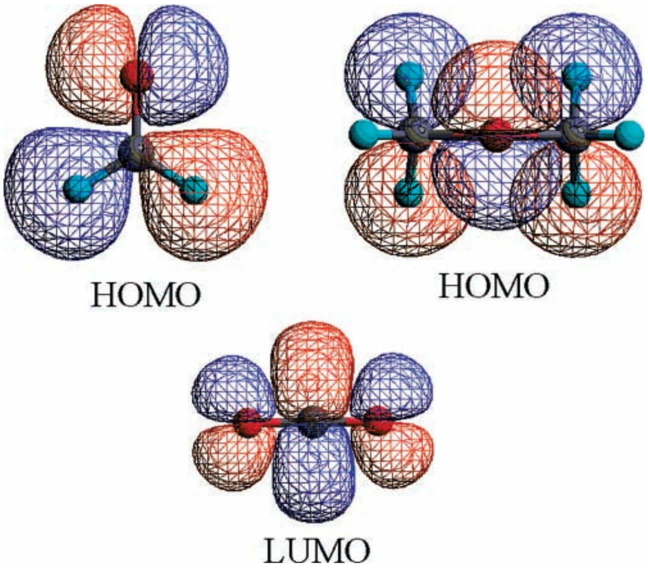

Figure 3. The HOMOs of formaldehyde and dimethylether and the LUMO of CO_2.

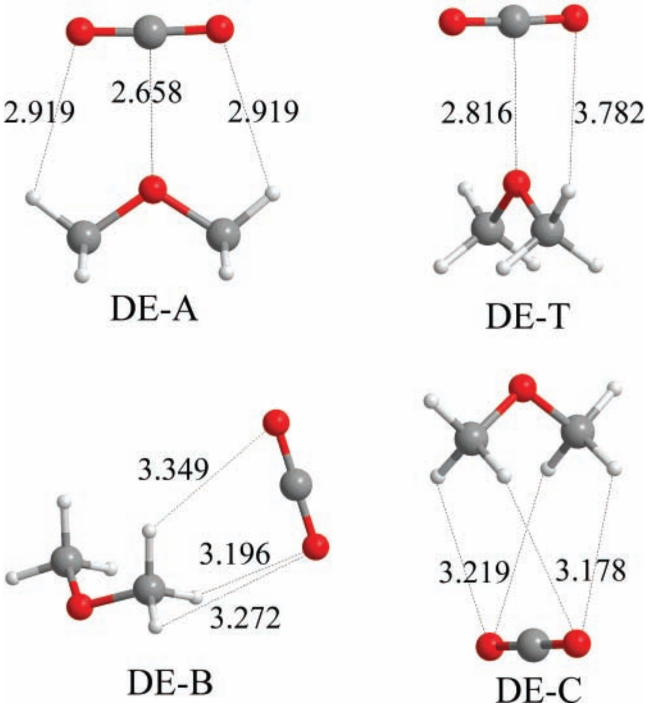

Figure 4. Geometric parameters for CO_2–dimethylether complexes. Lengths are in angstroms.

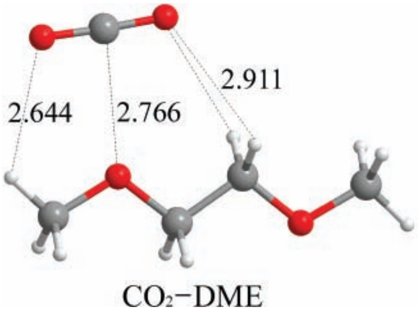

Figure 5. Geometric parameters for the CO_2–1,2-dimethoxyethane complex. Lengths are in angstroms.

In order to evaluate noncooperative weak H-bond energy, two complexes of CO_2 H-bonded to a methyl group, DE-B and DE-C, were calculated, as shown in Figure 4. The weak H-bond lengths were approximately 3.2 Å. There was no LA−LB interaction in these complexes but rather only C−H···O weak H-bonds. The binding energies for DE-B and DE-C including ZPEs were −0.07 and −0.18 kcal/mol at the MP2/6-31+G(d) level with the BSSE corrections, respectively. This is unrealistic since negative binding energy creates unstable complexes, which can be attributed to the overestimated BSSEs. With the use of the larger basis sets, 6-311+G(2d,2p), the negative binding energy was slightly remedied, resulting in positive binding energies with smaller BSSEs. The MCCM-CO-CCST(T) binding energies for DE-B and DE-C including ZPEs were 0.80 and 1.04 kcal/mol, respectively, which were larger than the corresponding MP2 values. These results indicate that electron correlation as well as the accurate BSSE correction is very important in evaluating the weak H-bond energy correctly. The weak H-bond energies larger than the van der Waals energy of CO_2-CH_4 suggested that these H-bonds were formed as one of the specific solute−solvent interactions and had an important role in increasing the $scCO_2$ solubility. It is of interest that the ratio of the binding energies for DE-B to DE-C was approximately 3:4 for the multilevel methods, which corresponds to the ratio of the H-bonds in these two complexes. As there are two weak H-bonds in DE-T, the cooperative weak H-bond energy would be between 0.6 and 1.3 kcal/mol.

The CO_2 complexes with polyether, 1,2-dimethoyethane (DME), were calculated, and the optimized structure and binding energies are shown in Figure 5 and Table 5, respectively. There are two types of weak H-bonds, one with the α-proton and β-proton from the oxygen acting as an LB, and the distances were 2.66 and 2.91 Å, respectively. These distances were shorter and similar compared to the weak H-bond distances in DE-A and DE-B, respectively, but the $C\cdots O_E$ distance (2.77 Å) was longer than that of DE-A. The binding energies at the MCG3 and MCCM-UT-CCSD levels were approximately 3.8 kcal/mol including ZPEs. There was some discrepancy in the energy difference between the DME−CO_2 and DE-A complexes, depending on the multilevel methods. Among the multilevel methods, the MCCM-UT-CSD method was superior to MCG3 in the prediction of the H-bond energy,[33,34] and the binding energies for DE-A and DE-T were closer to those at the MCCM-CO-CCSD(T) level. The energy difference at the MCCM-UT-CCSD level was only 0.1 kcal/mol, which suggests that the additional weak H-bond and shorter bond distance did not significantly increase the binding energy. Conceivably, the longer $C\cdots O_E$ distance caused by steric hindrance reduced the LA−LB interaction, which was compensated for by the ad-

TABLE 4: Binding Energies for the CO_2−Dimethylether (DE) Complexes Calculated at the MP2 and Multilevels[a]

	DE-A	DE-T	DE-B	DE-C
MP2/6-31+G*	3.08 (2.50)/1.94[b]	1.56 (1.27)/1.73	0.09 (−0.07)/0.62	0.16 (−0.18)/0.83
MP2/6-311+G(2d,2p)			0.41 (0.25)/0.5	0.63 (0.39)/0.57
MP2/6-311++G(3df,2pd)//MP2/6-311++G(d,p)	3.72 [*3.94*][c]			
MCCM-UT-CCSD	4.32 (3.73)	2.72 (2.42)	0.82 (0.66)	1.08 (0.83)
MCCM-CO-CCSD(T)	4.42 (3.84)	2.80 (2.51)	0.96 (0.80)	1.28 (1.04)
MCG3	3.97 (3.39)	2.30 (2.01)	0.85 (0.68)	1.11 (0.87)

[a] Energies in kcal/mol. Numbers in parentheses include ZPE corrections. [b] The BSSE using the CP correction. [c] Reference 46. The number in brackets is an estimated experimental value without ZPE.

TABLE 5: Binding Energies for the CO_2−1,2-Dimethoxyethane Complexes Calculated at the MP2 and Multilevels[a]

	energies
MP2/6-31+G*	2.91 (2.42)/1.98[b]
MCCM-UT-CCSD	4.31 (3.81)
MCG3	4.29 (3.79)

[a] Energies in kcal/mol. Numbers in parentheses include ZPE corrections. [b] The BSSE using the CP correction.

ditional weak H-bond formation. To this end, additional weak H-bond formation may not necessarily increase $scCO_2$ solubility.

Conclusions

High-level quantum mechanical calculations for the CO_2 complexes of various organic molecules were performed to investigate the role of the LA−LB interactions and the cooperative weak hydrogen bonding in $scCO_2$ solubility. The binding energy of CO_2−MA was approximately 3.1 kcal/mol at the MCCM-CO-CCSD(T) level, which was the most accurate and extensive calculation. The binding energies for the CO_2−AL and CO_2−DE complexes including cooperative weak hydrogen bonding with α-protons were 2.5 and 3.8 kcal/mol, respectively.

Depending on the functional groups to which CO_2 was bound, two types of cooperative weak hydrogen bonding were observed. The additional stabilization energy of cooperative weak hydrogen bonding in the CO_2−AL complex was estimated to be very small, approximately 0.2 kcal/mol. The energy was smaller than the thermal energy provided at the supercritical temperature of CO_2. The relatively small energy was attributed to the unfavorable orientation of CO_2 for the quadrupole−dipole interaction and HOMO−LUMO overlap, where most of the binding energy originates. The additional stabilization energy in the CO_2−DE complex was between 0.6 and 1.3 kcal/mol, which may have some impact on the solubility. This study shows that cooperative weak hydrogen bonding in ether molecules can provide a considerable amount of stabilization energy that may increase $scCO_2$ solubility. However, additional cooperative weak H-bonds may not have a significant impact on the solubility because steric hindrance reduces stability.

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