Exploring CO$_2$-Philicity: Effects of Stepwise Fluorination

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It is well-known that, in general, fluorocarbons are highly soluble in liquid and supercritical CO$_2$ and fluorine substitution has been widely utilized as a method to make otherwise insoluble organic compounds more CO$_2$-philic. In this work, we investigate the CO$_2$-philicity of fluorinated compounds with varying numbers of fluorine atoms in the system by using simple quantum chemical calculations. We explore the fundamental nature of fluorocarbon and hydrocarbon interactions with CO$_2$ by examining the effects of stepwise fluorination on methane using correlated ab initio calculations. The results suggest an optimum density of fluorine atoms that can be viewed as a maximum CO$_2$-philicity. As a charge-separated molecule, CO$_2$ is observed to act as a weak Lewis acid as well as a weak Lewis base in intermolecular interactions. In this work, we present evidence that CO$_2$−fluorocarbon and CO$_2$−hydrocarbon interactions are fundamentally different, although energetically comparable. Fluorocarbons interact through the carbon atom of CO$_2$, while hydrocarbons interact through the oxygen atoms. The results indicate that in the case of *partially* fluorinated hydrocarbons, there is a specific fluorine atom−CO$_2$ interaction. In these systems, the C−H bonds may also contribute to CO$_2$-philicity through weak C−H···O interactions. The effect of fluorine substitution on the CO$_2$-philicity of carbonyl containing CO$_2$-philes is also investigated.

1. Introduction

The high miscibility and solubility of fluorocarbons[1−10] with liquid and supercritical (sc) CO$_2$ has motivated many experimental and theoretical studies and is still a subject of active debate among the supercritical fluid research community.[11−17] Fluorocarbons are currently employed as CO$_2$-philic functionalities in many chemical and analytical applications utilizing supercritical or liquid CO$_2$ as a "green" alternative to conventional organic solvents.[1−4,7−10] Substitution of hydrogen atoms by fluorine atoms in organic molecules is a generally accepted method to increase miscibility or solubility with scCO$_2$.[1,18] It is important, therefore, to investigate the extent to which fluorination can increase CO$_2$-philicity and the role played by the orientation of fluorine atoms in these systems. An important issue is whether the CO$_2$-philicity of fluorinated hydrocarbons is proportional to the density of fluorine atoms. Since fluorine has a much higher electronegativity than hydrogen, we hypothesize that stepwise fluorination will result in weak Lewis base units capable of interacting with the carbon atom of CO$_2$ due to the formation of polar C−F bonds. However, additional fluorination should result in a competition among the individual electronegative fluorine atoms, thus diminishing their Lewis base potential. Another issue is the extent to which the electron deficient hydrogen atoms on a partially fluorinated chain can contribute to CO$_2$-philicity, through weak C−H···O interactions with the CO$_2$ oxygen atoms. Recent work by our group has identified this mode of interaction as a stabilizing force in the interaction between acetate or aldehyde functionalities and CO$_2$.[19,20]

One hypothesis regarding the miscibility of fluorocarbons in CO$_2$ is the idea that there is a specific fluorine−CO$_2$ interaction. However, to date, no consensus has been reached regarding the

nature of these interactions or whether they truly exist. Dardin et al.[11] carried out density-dependent ^{1}H and ^{19}F NMR chemical shift studies on fluorocarbons and hydrocarbons in scCO$_2$ and showed there was a distinct difference in the chemical shift changes, as a function of density, for the two nuclei.[11] This work suggested a specific solute−solvent interaction between the fluorocarbons and CO$_2$.[11] Additionally, there was a site specificity for the ^{19}F shifts that was explained in terms of the surface accessibility of the individual fluorine atoms.[11] Cece et al.[12] had previously used Hartree−Fock calculations to compute the binding energies for (CO$_2$)$_n$−C$_2$H$_6$ and (CO$_2$)$_n$−C$_2$F$_6$ clusters with $n = 1−4$ and concluded that the attractive interaction between fluorocarbons and CO$_2$ is higher compared to their hydrocarbon analogues. Han and Jeong pointed out that these results were erroneous since the calculations did not take into account the basis set superposition errors.[13] Using similar calculations, at a higher level of theory and with improved basis sets, Diep et al.[14] showed that the interaction between CO$_2$ and hydrocarbons are stronger than that between fluorocarbons and CO$_2$. Yonker used experimental measurements of ^{19}F, ^{1}H, and ^{2}H relaxation times of perfluorobenzene, benzene, and perdeuteriobenzene to conclude that there was no specific interaction between CO$_2$ and fluorine that contributed to the relaxation mechanism.[17] More recently, NMR and molecular dynamics simulations were used by Yonker and Palmer[15] to investigate the nuclear shielding of ^{1}H and ^{19}F nuclei in CH$_3$F and CHF$_3$. Upon comparison to mixtures with CO$_2$, they concluded that there are no distinct or specific interactions between fluoromethanes and CO$_2$. Earlier, Yee et al.[16] reported that the polarizabilities of CF$_4$ and C$_2$F$_6$, derived from dielectric constant measurements, are larger than those for CH$_4$ and C$_2$H$_6$ and noted that this would lead to a proportional difference in the magnitudes of the induced dipole-induced dipole interactions. On the bases of these results they suggested that there is a greater repulsion of CO$_2$ for CF$_4$ than for CH$_4$. However, Diep et al.

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argued[14] that the polarizabilities cited by Yee et al. are the total polarizabilities and that only the electronic component of the polarizability is relevant for the induced dipole−induced dipole interactions between the molecules. They showed that the electronic polarizabilities of the perfluorocarbon moieties and the analogous hydrocarbon analogues are comparable. The question still remains, however, whether there is a fundamental difference in the nature of the interactions of hydrocarbons and fluorocarbons with CO_2.

In this work, we address these issues computationally in an effort to understand the effect of stepwise fluorination on the CO_2-philicity of methane. We present ab initio calculations on the complexes of CO_2 with CH_nF_m, where $n = 4 - m$ with m ranging from 0 to 4. We also investigate the effects of fluorination on the CO_2-philicity of carbonyl-based CO_2-philes. It is of interest to examine how the CO_2-philicity of carbonyl functionalities are affected by fluorination since fluorine substitution on carbon atoms adjacent to functional groups results in the withdrawal of electron density, making the carbonyl a weaker Lewis base.

2. Computational Methods

Ab initio calculations were performed on the complexes of CO_2 with CH_4, CH_3F, CH_2F_2, CHF_3, CF_4, CH_3CHO (AcH), and CF_2HCHO (DFAcH) using Gaussian98[21] at the second-order Møller−Plesset (MP2)[22] level of theory to include the effects of electron correlation. Optimizations were carried out at the MP2 level using Dunning's polarized, correlation consistent aug-cc-pVDZ basis set,[23] augmented by diffuse functions. Dissociation energies were calculated using the "supermolecule" method[24] as the difference between the energy of complex and the sum of the isolated energies of the monomers. Basis set superposition errors (BSSE) were applied using the counterpoise method of Boys and Bernadi.[25] The depth of the potential energy well for the complexes at the optimized geometries were further examined by carrying out single point calculations at the MP2/aug-cc-pVQZ level. Vibrational frequencies were also calculated to ensure that the optimized geometries are at actual minima of the potential energy surface. Molden[26] was used to visualize the results of the calculations. Partial charges on individual atoms were calculated by fitting the electrostatic potential using the CHELPG subroutine of Gaussian98.

3. Results and Discussion

The solvent properties of CO_2 have been studied extensively, however, there is still only a very basic view of the nature of this system.[27−34] An understanding of the molecular properties of CO_2 is essential for the rational design of CO_2-philic materials. Historically, CO_2 was considered as a nonpolar solvent, owing primarily to the absence of a dipole moment and its low dielectric constant. It was commonly assumed that supercritical CO_2 should be comparable to hexane in its solvent properties. However, this notion was discarded in later years as many materials that are miscible with hexane were reported to be insoluble in $scCO_2$ and vice versa. CO_2 possesses a large quadrupole moment and its presence is responsible for the solvation of other molecules.[30] From an interaction stand point, CO_2 is considered as a Lewis acid (LA) since the electron deficient carbon atom can interact with a Lewis base (LB) group such as a carbonyl group.[35−37] Recently, we presented evidence suggesting that CO_2 can act as both a Lewis acid and a Lewis base by showing that in the interaction between CO_2 and a carbonyl functionality, such as an acetate group, while the carbon atom of CO_2 interacts as a Lewis acid with the carbonyl

TABLE 1: Comparison of the Partial Charges on the Individual Atoms of H_2O and CO_2 with the Mulliken Charges as Well as the Charges Derived by Fitting the Electrostatic Potentials (CHELPG charges) in Electrons (e) Calculated at the MP2/aug-cc-pVDZ Level

	H_2O			CO_2	
atom	Mulliken (e)	CHELPG (e)	atom	Mulliken (e)	CHELPG (e)
H(1)	0.16	0.36	O(1)	−0.18	−0.36
O	−0.32	−0.72	C	0.36	0.72
H(2)	0.16	0.36	O(2)	−0.18	−0.36

group of the acetate moiety, one oxygen atom of CO_2 can interact as a Lewis base with one of the electron deficient α-hydrogen atoms[19,20] through a cooperative C−H···O hydrogen bond.[38−43] This latter interaction provided approximately 0.5 kcal/mol additional stabilization energy.[19,20]

The quadrupolar charge separation present in CO_2 results in a partial positive charge on the carbon atom and partial negative charges on the oxygen atoms. Thus, CO_2 can act as either an electron donor or as an electron acceptor. The situation is somewhat analogous to the case of H_2O, which can act both as a Lewis acid and a Lewis base. For a comparison, the Mulliken, as well as the CHELPG charges (calculated by fitting the electrostatic potentials) on the individual atoms of CO_2 and H_2O are presented in Table 1. It is observed that the charge separation is similar for CO_2 and H_2O except for the reversal of the sign in the charges of the end versus central atoms.

Although charges are only an abstract representation of a more complex electron density picture, at this point it is pertinent to pose the question of whether CO_2 behaves more like H_2O as a solvent, at least when compared to a nonpolar solvent like hexane. It is well-known that the intermolecular associations in water are unique due to the extended network of cooperative hydrogen bonds.[44] The ability of water to act as a proton donor and a proton acceptor makes water a unique solvent for polar materials. Although much less efficient, CO_2 also may take part in similar interactions. In fact, similar partial charges on the atoms of water and CO_2 do not make them comparable in terms of their strength of interaction. However, this still predicts that one may consider the polarization of electron density in CO_2 and the corresponding implications in its interaction with polar groups. Also, since the double bonds of CO_2 are easily polarizable, CO_2 can participate in relatively strong LA−B interactions with strong LB groups. Such strong LA−LB interactions will make the oxygen atoms of CO_2 better LB units. In fact, we have observed that the interaction between CO_2 and the sulfonyl group of dimethyl sulfoxide is about 83% as strong as that for the water dimer.[19]

Thus, we began our calculations with the hypothesis that the polar C−F bonds on a fluoromethane should be able to participate in a weak LA−LB interaction with CO_2. Another important difference in our approach compared to the previous calculations[14] on the interaction of CO_2 with CH_4 and CF_4 is that our results indicate that the hydrogen atoms on CH_4 are carrying partial positive charges, while the fluorine atoms on CF_4 carry partial negative charges (Table 2). Thus, regarding the CO_2–CH_4 interaction, the probability of the hydrogen atoms interacting with the LB oxygen atoms of CO_2 are greater while in the CO_2−CF_4 complex, the fluorine atoms tend to interact with the carbon atom of CO_2. Also, one would expect a repulsive interaction between the fluorine atoms of CF_4 and the oxygen atoms of the CO_2 molecule. Table 2 also shows the partial charges on individual atoms in CH_3F, CH_2F_2, and CHF_3. All of these interactions are rather weak, but do need to be considered when addressing the fundamental nature of solvation

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TABLE 2: Comparison of the Partial Charges on CH₄, CH₃F, CH₂F₂, CHF₃, and CF₄[a]

CH₄		CH₃F		CH₂F₂		CHF₃		CF₄	
atom	CHELPG	atom	CHELPG	atom	CHELPG	atom	CHELPG	atom	CHELPG
C(1)	−0.36	C	0.11	C	0.36	C	0.55	C	0.69
H(2)	0.09	H	0.04	H	0.06	H	0.08	F	−0.17
H(3)	0.09	H	0.04	H	0.04	F	−0.21	F	−0.17
H(4)	0.09	H	0.04	F	−0.23	F	−0.21	F	−0.17
H(5)	0.09	F	−0.25	F	−0.23	F	−0.21	F	−0.18

[a] The charges in electrons (e) are derived by fitting the electrostatic potentials (CHELPG charges) calculated at the MP2/aug-cc-pVDZ level.
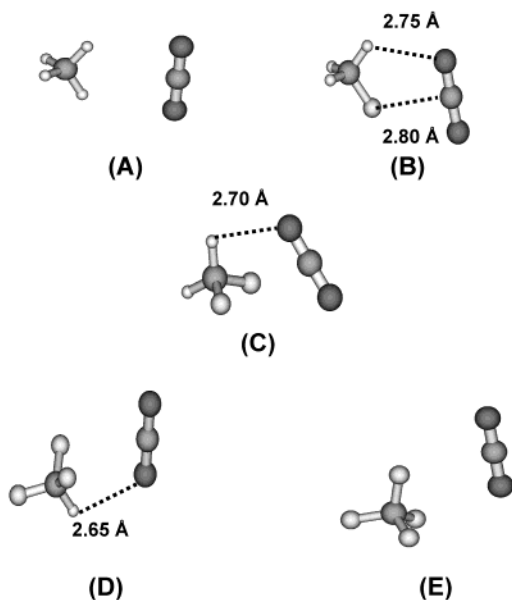
Figure 1. Optimized geometries of the complexes of CO_2 with (A) CH_4, (B) CH_3F, (C) CH_2F_2, (D) CHF_3, and (E) CF_4.

TABLE 3: BSSE-Corrected Dissociation Energies (kcal/mol) for the Complexes of CO₂ with CH₄, CH₃F, CH₂F₂, CHF₃, and CF₄ Calculated at the MP2 Level Using the aug-cc-pVDZ and aug-cc-pVQZ Basis Sets (Optimizations of the Complexes Performed Using the aug-cc-pVDZ Basis Set) Along with the Dissociation Energies at Both the SCF (D_e^c(SCF)) and MP2 (D_e^c(MP2) Levels
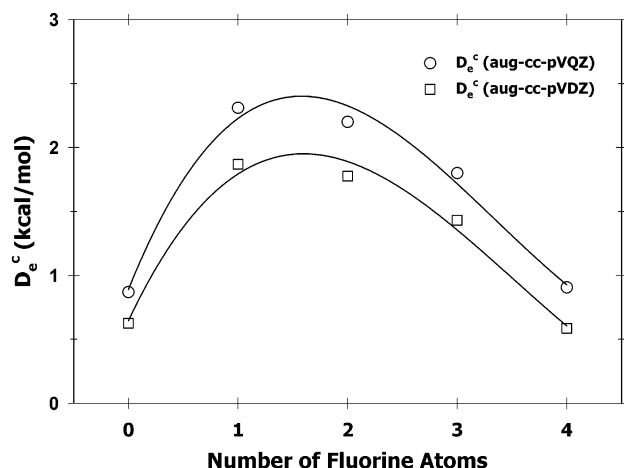
	aug-cc-pVDZ		aug-cc-pVQZ	
species	D_e^c(SCF)	D_e^c(MP2)	D_e^c(SCF)	D_e^c(MP2)
CH₄+CO₂	−0.45	0.63	−0.43	0.87
CH₃F+CO₂	1.02	1.87	1.00	2.31
CH₂F₂+CO₂	0.49	1.78	0.41	2.20
CHF₃+CO₂	0.26	1.43	0.19	1.80
CF₄+CO₂	−0.70	0.58	−0.70	0.90

in CO_2. These issues deserve greater attention when considering partially fluorinated alkanes since the charge separations due to atom-specific electron withdrawal and partial charges on these atoms are more significant leading to increased site-specific interactions.

The optimized geometries for the complexes of CO_2 with CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 are presented in Figure 1. It is seen that as predicted, for the CO_2−CH_4 interaction geometry, the oxygen atoms of CO_2 are directed toward the hydrogen atoms of CH_4 indicating a very weak electrostatic interaction, or possibly a very weak C−H···O interaction. A careful analysis of the optimized geometries reported by Diep et al.[14] also reveals this. The interaction is rather weak (D_e^c = 0.63 kcal/mol) compared to the interaction of the CO_2 dimer (D_e^c = 1.1 kcal/mol) at the MP2/aug-cc-pVDZ level.[19]

For the CO_2−CH_3F complex, however, the C−F bond should be considerably polarized. This enables the fluorine atom of CH_3F to act as a potential LB for interaction with the carbon atom of CO_2. Also, the hydrogen atoms now have an increased partial positive charge and may interact with the oxygen atom of CO_2. These interactions are reflected in the optimized geometry presented in Figure 1B. On further fluorination, the fluorine atoms will compete with each other resulting in each being a less effective electron donor and at the same time results in the hydrogen atoms on the fluoromethanes becoming more electron deficient (Table 2). This is clearly demonstrated in the dissociation energies of the complexes of CO_2 with CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 which are 0.63, 1.87, 1.78, 1.43, and 0.58 kcal/mol, respectively, at the MP2/aug-cc-pVDZ level. The single point calculations using aug-cc-pVQZ basis set yield higher dissociation energies, but the trend remains the same (Table 3). As was reported in the previous calculations, there

is a sizable component of electron correlation in the dissociation energies of these complexes at this level of calculation. It is important to note that the electron correlation component of the dissociation energy mostly represents dispersive interactions and in the case of CH_4−CO_2 and CF_4−CO_2 complexes, there is no binding at the Hartree−Fock level of theory. Discussion of the directional nature of interactions, based on what may apparently be the result of dispersive interactions, may be out of place. However, we feel that in the case of CH_4 and CF_4 it still makes sense to consider these issues due to the differences in the nature of the polarization of the C−H and C−F bonds.

It is of interest to observe that, as expected from our initial hypothesis, the interaction between the oxygen of CO_2 and the hydrogen of the fluoromethane becomes stronger and the H···O distance decreases systematically (2.75, 2.70, and 2.65 Å for the respective CO_2-complexes of CH_3F, CH_2F_2, and CHF_3,) on increased fluorine substitution indicating that the hydrogen atoms of a partially fluorinated hydrocarbon may also contribute to increased CO_2-philicity (Figure 1). Also, it is noteworthy from the optimized structures that the repulsion between fluorine and oxygen is another factor that determines the optimized geometries of these complexes.

The dissociation energies reveal that, at least in the case of partially fluorinated hydrocarbons, there is clearly a specific interaction between the fluorine atoms and CO_2, the fluorine atoms acting as weak Lewis base moieties. Also, it appears that even though the interaction energies of the complexes of CO_2 with fluorocarbons and hydrocarbons are comparable, the fundamental nature of their interactions is different. While CO_2 acts as a weak Lewis acid in CO_2−fluorocarbon interactions, it acts as a weak Lewis base in CO_2−hydrocarbon interactions (or one may consider these as weak electrostatic interactions). The variation of the strength of the CO_2-philic interactions with a stepwise increase in the number of fluorine atoms for fluoromethane is presented in Figure 2. Thus, as far as the enthalpic contribution to the solute−solvent interaction cross-section is concerned, the present results indicate that there is a limit to the optimum number of fluorine atoms for maximum CO_2-philicity and a turn over thereafter. This model may be extended to larger fluorocarbons since in those systems each C−F bond has an antiparallel C−F bond that results in a
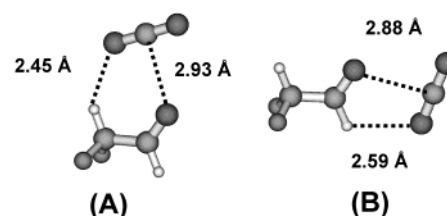
Figure 2. Plot of the dissociation energies (D_e^c) of the complexes of CO_2 with fluoromethanes versus the number of fluorine atoms (varying from 0 to 4), at MP2 level using the MP2/aug-cc-pVDZ and the MP2/aug-cc-pVDZ basis sets.

Figure 3. Optimized geometries for the (A) methyl-side and (B) proton-side complexes of difluoroacetaldehyde.

competing electron withdrawal. In larger fluorohydrocarbons, the orientation of these fluorine atoms also will play a significant role in determining the solute−solvent interaction.

Fluorine Substitution of Carbonyl Compounds. It is of interest to compare the CO_2-philicities of fluorocarbons and carbonyl-based CO_2-philes. It was shown previously that the interactions between carbonyl compounds and CO_2 are rather strong compared to fluorocarbons. For example, the highest dissociation energies for the complexes of CO_2 with methyl acetate and acetaldehyde are 2.82 and 2.63 kcal/mol, respectively[19] (compared to the solvent−solvent interaction of 1.1 kcal/mol), with potential to contribute to an enthalpy driven solvation. This led us to investigate this approach for the development of CO_2-philes and we have recently reported the unparalleled miscibility and solubility of peracetylated sugars in scCO$_2$ (>30 wt %).[20] Since fluorination as well as the introduction of carbonyl containing functionalities are currently employed as methods for enhancing the CO_2-philicity of organic compounds, we are interested in understanding how the fluorination of carbonyl compounds affects their CO_2-philicity due to the significant electron withdrawal effects of the fluorine atoms. We have chosen acetaldehyde as the model carbonyl system for this investigation. As was mentioned previously,[19] there are two interaction configurations between acetaldehyde and CO_2, namely, the methyl- and the proton-side approaches, respectively. In the first case, the in-plane hydrogen atom of the methyl group is involved in a C−H···O hydrogen bond with one of the oxygen atoms of the CO_2 molecule, while in the other it is the aldehyde proton that is involved in the C−H···O hydrogen bond.[19] Also, in both cases there is a relatively strong LA-LB interaction between the carbonyl oxygen and the carbon atom of CO_2. The effect of substituting two of the hydrogen atoms of the methyl group (that are not involved in the C−H···O hydrogen bonds) with fluorine atoms were investigated to examine the changes to the enthalpic contribution to CO_2-philicity. The optimized geometries (at the MP2/aug-cc-pVDZ level) of the interaction of difluoroacetaldehyde in the methyl- and proton-side interactions are presented in Figure 3A and 3B, respectively.

It is useful to make a comparison between the interaction energies of acetaldehyde and difluoroacetaldehyde in the two interaction geometries. The BSSE-corrected dissociation energies for the acetaldehyde−CO_2 complexes in the methyl- and proton-side configurations at the MP2/aug-cc-pVDZ level are 2.42 and 2.63 kcal/mol, respectively. For the methyl- and proton-

side approaches of the difluoroacetaldehyde−CO_2 complexes, the BSSE-corrected dissociation energies are 2.10 and 2.11 kcal/mol. These results reveal that even though the carbonyl electron density is affected in the same way by fluorination for the methyl- and proton-side approaches of CO_2, the proton-side approach is more affected by the fluorine substitution. This points to the role of the C−H···O interaction in the stabilization of the CO_2 complexes of both acetaldehyde and difluoroacetaldehyde. The fluorine substitution of the methyl group affects the electron density of the remaining methyl hydrogen more significantly than the aldehyde hydrogen, rendering the former more suitable for a C−H···O interaction with the CO_2 oxygen. This can partially compensate for the weakening of the Lewis base potential of the carbonyl group. This result supports the hypothesis that the oxygen of CO_2 can act as a Lewis base and needs to be considered when addressing the design of CO_2-specific interactions into a molecular system.

These effects are also reflected in the geometric parameters of the CO_2 complexes of acetaldehyde and difluoroacetaldehyde. For example, the distances between the carbonyl oxygen and the carbon atom of CO_2 (C=O···C) for the methyl- and proton-side configurations with acetaldehyde are 2.87 and 2.82 Å, respectively. For the same configurations in the difluoroacetaldehyde-CO_2 complexes, the C=O···C distances are 2.93 and 2.88 Å, respectively. In both the CO_2 approaches fluorination has caused an increase in the C=O···C distance by 60 mÅ showing that the LA-LB interaction is weakened to the same extent in both configurations. The distances between the oxygen of the CO_2 molecule and the hydrogen atom involved in the C−H···O interaction for the methyl- and the proton-side configurations of the acetaldehyde−CO_2 complexes are 2.54 and 2.62 Å, respectively. The corresponding distances for the methyl- and proton-side configurations of difluoroacetaldehyde−CO_2 complexes are 2.45 and 2.59 Å, respectively, showing that while contraction of the O···H distance is 90 mÅ for the methyl-side approach, it is only 30 mÅ for the proton-side configuration, upon fluorine substitution.

4. Conclusions

We had several goals for carrying out these simple quantum chemical calculations. The first is to understand the fundamental molecular attributes of CO_2, which is essential for the rational design of CO_2-philic materials. The results reveal that despite being a molecule with zero dipole moment, CO_2 can act as both a Lewis acid (through the electron deficient carbon atom) as well as a Lewis base (through the electron rich oxygen atoms) by virtue of the quadrupolar charge separation in the molecule. CO_2 is a versatile molecule and can interact with LA and LB systems with a range of interaction energies, facilitated by the easily polarizable π-electron system. Another goal was to determine the existence or nonexistence of a specific interaction between CO_2 and the fluorine atoms of fluorinated organic compounds. A comparison of the results for methane and perfluoromethane indicate that the interactions of CO_2 with

fluorocarbons and hydrocarbons are of a fundamentally different nature, even though they are energetically comparable. The results also show that in the case of the partially fluorinated systems there is a clear, specific interaction between CO_2 and the fluorine atoms. The calculation of the dissociation energies as a function of the number of fluorine atom substitutions on a hydrocarbon, varying from 0 to 4, indicate that there may be an optimal density of fluorine atoms in a fluorocarbon chain that yields a maximum CO_2-philicity. In these systems the results highlight the fact that CO_2 can act as both a weak Lewis acid and a Lewis base. Both the fluorine atoms in these complexes as well as the electron deficient C−H bonds (through C−H··⋅O interactions) do contribute to the overall CO_2-philicity. Lastly we have investigated the effect of fluorine substitution in carbonyl compounds on the strength of their interaction with CO_2. As expected, fluorination weakens the carbonyl groups as potential Lewis base units and thereby decreases the carbonyl CO_2-philicity.

In concluding, we would like to caution the reader that the solubility-miscibility of a solute in scCO_2 is an issue decided by a number of parameters including the enthalpic and entropic contributions from the solute−solute, solute−solvent, and the solvent−solvent interactions and in this work we are only discussing the enthalpic contributions to the solute−solvent interactions. However, the results are of importance in obtaining a better understanding of CO_2 as a solvent and indicate that there are interactions that deserve attention in formulating the principles for the design of CO_2-philes. In fact the trends observed in the present calculations are in agreement with recent Monte Carlo results obtained by Lee and Sanchez which indicate that the Henry's law solubility in CO_2 passes through a maximum.[45] This lends credence to the idea that the solute-CO_2 interaction energy is the most important factor in determining solubility. These results also conclusively show the fundamental differences between the CO_2−hydrocarbon and CO_2−fluorocarbon interactions.

References and Notes

(1) (a) Laintz, K. E.; Wai, C. M.; Yonker, C. R.; Smith, R. D. *J. Supercrit. Fluids* **1991**, *4*, 194−198. (b) Hoefling, T. A.; Enick, R. M.; Beckman, E. J. *J. Phys. Chem.* **1991**, *95*, 7127−7129.

(2) (a) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *267*, 945−947. (b) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; Combes, J. R.; McClain, J. B.; Romack, T. *Science* **1994**, *265*, 356−359.

(3) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. *Science* **1996**, *271*, 624−626.

(4) Wells, S. L.; DeSimone, J. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 518−527. (b) Oakes, R. S.; Clifford, A. A.; Rayner, C. M. *J. Chem. Soc., Perkin Trans.* **2001***, 1*, 917−947.

(5) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extractions: Principles and Practice*, 2nd ed.; Butterworth-Heinerman: Boston, MA, 1994.

(6) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *J. Phys. Chem.* **1996**, *100*, 15581−15587.

(7) McClain, J. B.; Londono, D.; Combes, J. R.; Romack, T. J.; Canelas, D. A.; Betts, D. E.; Samulski, E. T.; Wignal, G.; DeSimone, J. M. *Science* **1996**, *274*, 2049−2052.

(8) Ji, M.; Chen, X.; Wai, C. M.; Fulton, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2631−2632.

(9) Ohde, H.; Wai, C. M.; Kim, H.; Kim, J.; Ohde, M. *J. Am. Chem. Soc.* **2002**, *124*, 4540−4541.

(10) Consani, K. A.; Smith, R. D. *J. Supercrit. Fluids* **1990**, *3*, 51−65.

(11) Dardin, A.; DeSimone J. M.; Samulski, E. T. *J. Phys. Chem. B* **1998**, *102*, 1775−1780.

(12) Cece, A.; Jureller, S. H.; Kerschner, J. L.; Moschner, K. F. *J. Phys. Chem.* **1996**, *100*, 7435−7439.

(13) Han, Y.; Jeong, H. Y. *J. Phys. Chem. A* **1997**, *101*, 5604.

(14) Diep, P.; Jordan, K. D.; Johnson, J. K.; Beckman, E. J. *J. Phys. Chem. A* **1998**, *102*, 2231−2236.

(15) Yonker, C. R.; Palmer, B. J. *J. Phys. Chem. A*, **2001**, *105*, 308−314.

(16) Yee, G. G.; Fulton, J. L.; Smith, R. D. *J. Phys. Chem.* **1996**, *96*, 6172−6182.

(17) Yonker, C. R. *J. Phys. Chem. A* **2000**, *104*, 685−691.

(18) Laitinen, A.; Jauhiainen, O.; Aaltonen, O. *Org. Process Res. Dev.* **2000**, *4*, 353−356.

(19) (a) Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 12590−12599. (b) Blatchford, M. A.; Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14818−14819.

(20) Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7274−7275.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−624. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1−19.

(23) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358−1371. (b) Dunning, T. H. *J. Phys. Chem. A* **2000**, *104*, 9062−9080.

(24) Morokuma, K.; Kitaura, K. In *Molecular Interactions;* Ratajczak, H., Orville Thomas, W. J., Eds.; Wiley: New York, 1980; Vol. 1, pp 21−87.

(25) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−556.

(26) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123−134.

(27) Illies, A. J.; McKee, M. L.; Schlegel, H. B. *J. Phys. Chem.* **1987**, *91*, 3489−3494.

(28) Nesbitt, D. J. *Chem. Rev.* **1988**, *88*, 843−870.

(29) Jucks, K. W.; Huang, Z. S.; Miller, R. E.; Fraser, G. T., Pine, A. S.; Lafferty, W. J. *J. Chem. Phys.* **1988**, *88*, 2185−2195

(30) Kauffman, J. F. *J. Phys. Chem. A* **2001**, *105*, 3433−3442.

(31) Bukowski, R.; Szalewicz, K.; Chabalowski, C. F. *J. Phys. Chem. A.* **1999**, *103*, 7322−7340.

(32) Salaniwal, S.; Cui, S.; Cochran, H. D.; Cummings, P. T. *Ind. Eng. Chem. Res.* **2000**, *39*, 4543−4554.

(33) Rice, J. K.; Niemeyer, E. D.; Dunbar, R. A.; Bright, F. V. *J. Am. Chem. Soc.* **1995**, *117*, 5830−5839.

(34) Ngo, T. T.; Bush, D.; Eckert, C. A.; Liotta, C. L. *AIChE. J.* **2001**, *47*, 2566−2572.

(35) Nelson, M. R.; Borkman, R. F. *J. Phys. Chem. A* **1998**, *102*, 7860−7863.

(36) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729−1736.

(37) Meredith, J. C.; Johnston, K. P.; Seminario, J. M.; Kazarian, S. G.; Eckert, C. A. *J. Phys. Chem.* **1996**, *100*, 10837−10848.

(38) Sutor, D. J. *Nature* **1962**, *193*, 68−69.

(39) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

(40) Scheiner, S. *Hydrogen Bonding: A Theoretical Perspective*; Oxford University Press: Oxford, 1997.

(41) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (b) Hozba, P., Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253−64.

(42) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750−4755.

(43) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411−9422.

(44) Xantheas, S. S.; Dunning, T. H. *J. Chem. Phys.* **1993**, *99*, 8774−8792.

(45) Lee, K. M.; Sanchez, I. C. personal communication, NSF Science and Technology Center for Environmentally Responsible Solvents and Processes.