CO_2−Fluorocarbon and CO_2−Hydrocarbon Interactions from First-Principles Calculations

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Received: September 16, 1997; In Final Form: January 9, 1998

The interactions of CO_2 with small hydrocarbons and fluorocarbons (CH_4, C_2H_6, CF_4, and C_2F_6) are investigated using the Hartree−Fock and second-order many-body perturbation theory (MP2) methods. Hartree−Fock calculations with flexible basis sets fail to give appreciable binding for any of the four dimers. In contrast, MP2 calculations using flexible basis sets and including corrections for basis-set superposition error give binding energies of the CO_2−CH_4, CO_2−C_2H_6, CO_2−CF_4, and CO_2−C_2F_6 clusters ranging from −0.79 to −1.17 kcal/mol. The binding energies for the CO_2−hydrocarbon complexes are slightly larger in magnitude than the corresponding CO_2−perfluorocarbon clusters.

1. Introduction

The application of supercritical (SC) carbon dioxide in industrial extraction is a promising technology. In addition to being environmentally benign, nonflammable, relatively nontoxic, and inexpensive, the low viscosity of SC CO_2 allows for rapid mass transport in extraction processes. The critical point of CO_2 is readily accessible at 31 °C and 72.9 atm. The solvent power of SC CO_2 can be tuned by adjusting the density, which can be altered by over an order of magnitude with small changes in temperature or pressure. Reduction of pressure to atmospheric results in complete separation of the solutes from the solvent.

However, CO_2 is a low dielectric constant fluid that is a relatively poor solvent for polar organics and many other solutes. One strategy that has proven quite successful for overcoming this limitation is to make use of CO_2-philic functional groups. For example, standard metal-chelating agents can be made soluble in SC CO_2 by attaching CO_2-philic tails to the chelates.[1,2] This mixture can then be used to extract metal contaminants from soils and sludges. Fluorinated alkanes and ethers have proven to be particularly useful in solubilizing chelates and polymers in SC CO_2.[2−4] It has been observed that fluorinated compounds are much more soluble in CO_2 than their hydrocarbon counterparts. Unfortunately, highly fluorinated compounds are expensive. There is great incentive to design new, inexpensive CO_2-philic groups, particularly for applications that involve processing large volumes of waste, e.g., contaminated soil remediation.

To design new CO_2-philic materials, one must first understand why many fluorinated compounds are so soluble in SC CO_2. There is considerable controversy over the origin of this high solubility.[5] Several possible explanations for the enhanced solubility of fluorinated compounds in CO_2 have been forwarded. Enick has shown that the differences in phase behavior between CO_2−hexane and CO_2−perfluorohexane systems are consistent with the differences in pure-component critical parameters.[6] Brady has suggested that the enhanced solubility can be attributed to the fact that both fluoroalkanes and CO_2 have negative π^* polarizability parameters,[7] whereas π^* for a typical hydrocarbon is positive.[8] Yee et al.[9] observed that the polarizabilities of CF_4 and C_2F_6, derived from dielectric constant measurements, are larger than those of CH_4 and C_2H_6 and further noted that one would expect a proportional difference in the magnitudes of the induced dipole−induced dipole (i.e., dispersion, or van der Waals) interactions. However, these authors concluded that the enhanced polarizabilities are counterbalanced by “a large and very repulsive hard-sphere potential” for the perfluoroalkanes relative to the alkanes.[9] We will revisit this argument in Section 3.A. Yee et al. found no evidence of any special attractive interactions between CO_2 and perfluoroethane. Moreover, they claimed that CO_2 is more repulsive to perfluoroethane than to ethane, on the basis of observed frequency shifts of the ν_2 bending mode of CO_2 in perfluoroethane and ethane.[9] Finally, they concluded that the enhanced solubility of perfluorocarbons in CO_2 is due to the highly repulsive nature of fluorocarbon−fluorocarbon interactions, making the solute−solute interactions less favorable than the solute−solvent interactions.

A very different picture emerges from a recent paper by Cece et al.,[10] who used Hartree−Fock calculations in an attempt to discover the molecular-level reasons for the enhanced solubility of fluorocarbons in supercritical CO_2. These authors presented results for the $(CO_2)_n$−C_2H_6 and $(CO_2)_n$−C_2F_6 clusters, where $n = 1−4$. Their calculations, carried out using the 6-31G(d) Gaussian-type orbital basis set,[11] indicated a more attractive interaction between CO_2 and C_2F_6 than between CO_2 and C_2H_6. Their computed binding energy[12] for the CO_2−C_2F_6 cluster was −0.80 kcal/mol, compared to −0.31 kcal/mol for the CO_2−C_2H_6 cluster. Cece et al. credited the enhanced binding in the former species to the electrostatic interaction between the positively charged carbon atom of CO_2 and the negatively charged fluorine atoms in the fluorocarbon.

The lack of a consensus regarding the nature of CO_2−fluorocarbon and CO_2−hydrocarbon interactions has led us to revisit this problem. In this work, we use first-principles

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S1089-5639(97)03030-2 CCC: $15.00

methods to examine the binding energies between CO_2 and small fluorocarbons and hydrocarbons. We focus on the solvent−solute interactions as a first-order approach to describing solubility. A complete description of solvation must also include solvent−solvent and solute−solute interactions and calculation of free energies. We approach this problem using higher levels of theory than employed in the study by Cece et al. Our calculations are "higher level" in the sense that: (1) the effects of electron correlation are included through the use of MP2 perturbation theory, (2) more flexible basis sets are employed, and (3) corrections are made for basis set superposition error (BSSE).[13] BSSE results from the use of incomplete basis sets and the consequent lowering of each molecule's energy by "borrowing" basis functions centered on other molecules. The use of flexible basis sets and the inclusion of electron correlation effects are essential for properly describing inductive and dispersion interactions, the latter of which are not included at the Hartree−Fock level of theory. The systems studied—CO_2−CH_4, CO_2−C_2H_6, CO_2−CF_4, and CO_2−C_2F_6—were chosen to facilitate comparison of our results with those of Yee et al.[9] and Cece et al.[10]

2. Computational Methods

In our study of the interactions of CO_2 with CH_4, C_2H_6, CF_4, and C_2F_6, we have adopted second-order many-body perturbation theory (MP2) as the principle theoretical method. Numerous studies of other systems have shown that the MP2 method, provided that sufficiently flexible basis sets are employed, adequately describes weakly bonded clusters with significant electrostatic and inductive interactions.[14] As a check of the suitability of the theoretical approach, the polarizabilities of the various monomers are calculated and compared with experiment. For the cluster calculations, corrections for BSSE have been computed by means of the counterpoise procedure.[13] All calculations were performed using the Gaussian 94 software package.[15]

Both HF/6-31G(d) and MP2/aug-cc-pVDZ optimized geometries were used in the present study. The former were included primarily to facilitate comparison with the results of Cece et al. For the HF/6-31G(d) optimized structures, single-point MP2 calculations were carried out with the 6-31G(d) basis set as well as with the aug-cc-pVDZ and aug-cc-pVTZ correlation consistent basis sets of Dunning and co-workers.[16] For the MP2/aug-cc-pVDZ optimized structures, single-point MP2 calculations were carried out using the aug-cc-pVDZ, aug-cc-pVTZ-f, and aug-cc-pVTZ basis sets. The 6-31G(d), aug-cc-pVDZ, and aug-cc-pVTZ basis sets are contracted to (3s2p1d), (4s3p2d), and (5s4p3d2f) for heavy atoms and to (2s), (3s2p), and (4s3p2d) for hydrogen atoms, respectively. The aug-cc-pVTZ-f basis set is formed from aug-cc-pVTZ by deleting the d functions for hydrogen and the f functions for the heavier atoms. The augmented correlation consistent basis sets, unlike the 6-31G(d) basis set, include diffuse functions that are important for describing van der Waals interactions.

The MP2 results presented here were obtained with an extended frozen-core approximation, with the molecular orbitals that are nominally C, O, and F 1s as well as O and F 2s being kept doubly occupied. Comparison with the results of calculations with keeping only the nonvalence 1s orbitals frozen reveal that freezing the 2s orbitals on O and F introduces relatively small errors in the interaction energies (<0.1 kcal/mol).

For the CO_2−CF_4 dimer the interaction energy was also calculated using nonlocal density functional theory (DFT) employing the Becke3LYP functional. However, the DFT calculations were found to be inadequate in that they considerably underestimated the magnitude of the binding energy. For example, at the HF/6-31G(d) optimized geometry, the Becke3LYP calculations predict the complex to be unbound by 0.13 kcal/mol, whereas the MP2/aug-cc-pVTZ calculations with counterpoise correction predict the cluster to be bound by 0.78 kcal/mol. The failure of DFT to describe the attractive interaction between the CO_2 and CF_4 molecules may be a reflection of the fact that the Becke3LYP[17] functional does not correctly describe the dispersion interactions. In light of these results, DFT calculations were not performed on the other systems.

TABLE 1: Comparison of Calculated and Experimentally Measured Polarizability Volumes, α (10^{-24} cm^3)[a]

molecule	α(MP2)	α(RI)	α(DC)
CO_2	2.61	2.64[b]	2.91[b]
CH_4	2.42	2.60[b]	2.59[b]
CF_4	2.77	2.85[b]	3.84[b]
C_2H_6	4.16	4.50[b]	4.44[b]
C_2F_6	4.66	4.83[c]	6.82[d]

[a] Calculated polarizabilities are denoted as α(MP2), while α(RI) and α(DC) are experimental data from refractive index and dielectric constant measurements, respectively. [b] From ref 18. [c] From ref 22. [d] From ref 23.

3. Results and Discussion

3.A. Polarizabilities. Table 1 summarizes the calculated and experimental values of the polarizabilities of CO_2, CH_4, CF_4, C_2H_6, and C_2F_6. The computations were performed at the MP2/aug-cc-pVDZ level of theory. We have tested the convergence of the polarizabilities by performing calculations for the CF_4 molecule using the more flexible aug-cc-pVTZ basis set and by including higher order correlation effects by means of the MP4/aug-cc-pVDZ method. Neither of these extensions gave a value of the polarizability appreciably different from the MP2/aug-cc-pVDZ result.

The total polarizability consists of an electronic term, due to the distortion of the electronic cloud, and a nuclear relaxation term (also referred to as atomic polarizability), which is due to the distortion of the equilibrium geometry induced by an applied electric field. For most molecules the nuclear relaxation contribution to the polarizability is unimportant,[18] and this is the case for CH_4 and C_2H_6. However, the nuclear contribution is relatively large for CO_2, CF_4, and C_2F_6. This may be seen from comparison of the experimental polarizabilities from refractive index (RI) and dielectric constant (DC) measurements, both of which are reported in Table 1. RI measurements only include the electronic contribution to the polarizability, while DC measurements include both electronic and nuclear relaxation contributions. The data in Table 1 show that the total polarizabilities are larger than the electronic polarizabilities by 11%, 35%, and 41% for CO_2, CF_4, and C_2F_6, respectively. Our calculated polarizabilities, which neglect nuclear relaxation, are in good agreement with RI measured polarizabilities for all molecules listed in Table 1.

In discussing differences between perfluoroalkanes and alkanes, Yee and co-workers[9] noted that the polarizabilities of CF_4 and C_2F_6 are substantially larger than their hydrocarbon counterparts. The polarizabilities cited by Yee et al. are the total polarizabilities, derived from DC measurements. However, only the electronic part of the polarizability is relevant for the induced dipole−induced dipole (dispersion) interactions between molecules. As shown in Table 1, the electronic polarizabilities, obtained from both calculations and RI measurements, of the perfluorocarbon molecules and the analogous hydrocarbon

TABLE 2: Binding Energies (kcal/mol) of the $(CO_2)_n$−C_2H_6 and $(CO_2)_n$−C_2F_6 Clusters at HF/6-31G(d) Optimized Geometries[a]

solute	no. of CO_2 molecules	HF/6-31G(d) HF	HF/6-31G(d) BSSE	HF/6-31G(d) HF-C	MP2/6-31G(d) MP2	MP2/6-31G(d) BSSE	MP2/6-31G(d) MP2-C
C_2H_6	1	−0.31	−0.39	0.08	−0.93	−0.58	−0.35
	2	−0.59	−0.77	0.18	−1.86	−1.15	−0.71
	3	−2.86	−1.92	−0.94	−5.53	−3.05	−2.48
	4	−4.21	−2.71	−1.51	−7.43	−3.77	−3.67
C_2F_6	1	−0.80	−1.06	0.27	−2.15	−1.66	−0.48
	2	−1.56	−2.21	0.65	−4.25	−3.40	−0.85
	3	−2.32	−3.37	1.05	−6.27	−5.09	−1.17
	4	−3.12	−4.21	1.10	−7.31	−5.63	−1.68

[a] HF-C and MP2-C denote results with the counterpoise correction for BSSE.

molecules are comparable. Therefore, at comparable separations the dispersion interactions in the CO_2−fluorocarbon systems should also be comparable to those in the CO_2−hydrocarbon systems. This obviates the need to invoke the argument made by Yee et al. of larger "repulsive sizes" of the fluorocarbons to counterbalance the enhanced attractive interactions due to larger polarizabilities.

For each of the five monomers, the HF/aug-cc-pVDZ values of the polarizabilities (not tabulated) are about 10% smaller than the corresponding MP2 values. Also, both the HF and MP2 polarizability values are considerably underestimated when calculated using basis sets lacking diffuse functions (e.g., 6-31G-(d)). It follows from these considerations that the use of a flexible basis set and the inclusion of electron correlation effects are necessary for accurately describing the induction and dispersion contributions to the interactions of CO_2 with alkanes and perfluoroalkanes.

3.B. Interaction Energies. *3.B.1. Results at HF/6-31G(d) Optimized Geometries.* The only prior ab initio study of CO_2−perfluorocarbon interactions of which we are aware is that of Cece et al.,[10] who applied the HF/6-31G(d) method to the $(CO_2)_n$−C_2H_6 and $(CO_2)_n$−C_2F_6, $n = 1-4$, clusters. Table 2 summarizes the HF/6-31G(d) and MP2/6-31G(d) binding energies calculated at the HF/6-31G(d) optimized geometries for each of these clusters. Results are reported both with and without the counterpoise correction for BSSE.

With the exception of $(CO_2)_3$−C_2H_6 and $(CO_2)_4$−C_2H_6, the counterpoise corrections are larger in magnitude than the uncorrected HF binding energies. This indicates that the binding obtained from HF/6-31G(d) calculations on the $(CO_2)_n$−C_2H_6, $n = 1$, 2, and $(CO_2)_n$−C_2F_6, $n = 1-4$, clusters is an artifact of BSSE. Upon inclusion of correlation effects at the MP2/6-31G-(d) level, all the clusters are predicted to be bound even after application of the counterpoise correction. However, given the magnitudes of the correlation and counterpoise corrections, it is clear that basis sets more flexible than 6-31G(d) are required to reliably characterize these clusters.

The effects of increasing the basis set flexibility on the binding energies of the CO_2−CH_4, CO_2−C_2H_6, CO_2−CF_4, and CO_2−C_2F_6 clusters are reported in Table 3. Both HF and MP2 results are reported for each of the 6-31G(d), aug-cc-pVDZ, and aug-cc-pVTZ basis sets. As above, all result are for HF/6-31G(d) optimized geometries. As the basis set is made more flexible, the interaction energies at the HF level become more repulsive, mainly owing to the decrease in BSSE. With the aug-cc-pVTZ basis set, the uncorrected HF interaction energies range from −0.04 to 0.24 kcal/mol, and the counterpoise-corrected values range from −0.01 to 0.41 kcal/mol. These results are consistent with the finding that when the geometries of the dimers are reoptimized at the HF/aug-cc-pVTZ level, the resulting complexes are predicted to be only very weakly bound, with large separations between the CO_2 and hydrocarbon or perfluorocarbon molecules.

As is well-known, BSSE tends to be appreciably larger in calculations including electron correlation than in HF calculations.[19] Moreover, the contribution of BSSE to the correlation portion of the binding energy tends to fall off less rapidly with increasing basis-set flexibility than that in the HF contribution. These well-known trends are reflected in the results for the dimers studied here.

As the basis set is made more flexible the contribution of "true" correlation effects to the binding energy tends to increase. The "true" correlation contributions to the interaction energies are given by the difference between the MP2−C and HF−C interaction energies, where the "C" implies that the counterpoise correction for BSSE is included. Specifically, for the four dimers considered the true correlation contribution to the binding energy increases in magnitude by about 0.3−0.5 kcal/mol in going from the 6-31G(d) to the aug-cc-pVDZ basis set and then by approximately another 0.1 kcal/mol in going to the aug-cc-pVTZ basis set. With the aug-cc-pVTZ basis set, the correlation contributions to the binding energies (after the counterpoise correction) are −0.63 and −0.81 for CO_2−CH_4 and CO_2−C_2H_6, respectively, and −1.04 and −1.38 kcal/mol for CO_2−CF_4 and CO_2−C_2F_6, respectively. The BSSE contributions to the MP2 energies drop by 35−50% in going from the 6-31G(d) to the aug-cc-pVDZ basis set, and then by roughly another factor of 3 in going to the aug-cc-pVTZ basis set. With the aug-cc-pVTZ basis set, the counterpoise corrections to the MP2 interaction energies range from about 0.1 to 0.3 kcal/mol, and the corrected binding energies range from −0.64 to −0.97 kcal/mol, with the interactions being slightly more attractive for CO_2−CF_4 and CO_2−C_2F_6 than for CO_2−CH_4 and CO_2−C_2H_6. We note also that, after the application of the counterpoise corrections for BSSE, the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ interaction energies agree to within 0.2 kcal/mol, with the results of the calculations with the aug-cc-pVTZ basis set being slightly more attractive. This gives us confidence that the MP2/aug-cc-pVTZ calculations with inclusion of the counterpoise correction give interaction energies that are close to the MP2 complete-basis-set limit values.

3.B.2. Results at MP2/aug-cc-pVDZ Optimized Geometries. Because the sizable "binding" of the dimers found at the HF/6-31G(d) level of theory is an artifact of BSSE, it is important to consider the consequences of reoptimizing the geometries with inclusion of electron correlation and the use of a more flexible basis set. In this study we have opted to use the MP2 method in conjunction with the aug-cc-pVDZ basis set. One drawback to this approach is that the BSSE at the MP2/aug-cc-pVDZ level of theory is sizable, which could result in unrealistically short CO_2−hydrocarbon and CO_2−perfluorocarbon separations. To check whether this is indeed a problem, in the case of CO_2−CH_4, the geometry was also optimized at the MP2/aug-cc-pVTZ level of theory. For this dimer, the MP2 structures obtained using the aug-cc-pVDZ and aug-cc-pVTZ basis sets are nearly identical, indicating that the tendency of BSSE to lead to too short an intermonomer separation must be compensating in part for deficiencies in the aug-cc-pVDZ basis set for describing true correlation effects. We expect that a similar compensation will occur in the other dimers, although this should be explored further.

Significant differences between the MP2/aug-cc-PVDZ and HF/6-31G(d) optimized structures are found for CO_2−CH_4 and

TABLE 3: Binding Energies (kcal/mol) of the Dimers at the HF/6-31G(d) Optimized Geometries[a]

	6-31G(d)				aug-cc-pVDZ				aug-cc-pVTZ			
cluster	HF	HF-C	MP2	MP2-C	HF	HF-C	MP2	MP2-C	HF	HF-C	MP2	MP2-C
CO_2-CH_4	−0.31	0.01	−0.76	−0.28	−0.13	−0.01	−0.89	−0.58	−0.04	−0.01	−0.76	−0.64
$CO_2-C_2H_6$	−0.31	0.08	−0.93	−0.35	−0.07	0.08	−1.08	−0.65	0.04	0.09	−0.88	−0.72
CO_2-CF_4	−0.79	0.13	−1.80	−0.39	−0.07	0.24	−1.45	−0.68	0.14	0.26	−1.03	−0.78
$CO_2-C_2F_6$	−0.80	0.27	−2.15	−0.48	−0.02	0.42	−1.59	−0.80	0.24	0.41	−1.30	−0.97

[a] HF-C and MP2-C denote results with the counterpoise correction for BSSE.

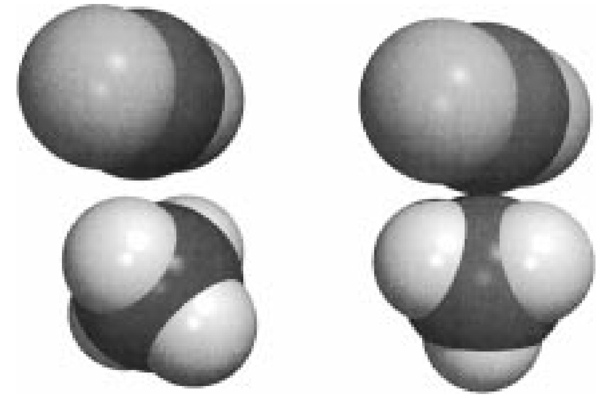

Figure 1. Geometries for the CO_2-CH_4 dimer. The HF/6-31G(d) optimized structure is shown on the left-hand side and the MP2/aug-cc-pVDZ optimized structure is on the right. The carbon−carbon distance decreases by about 0.5 Å when the geometry is optimized at the MP2/aug-cc-pVDZ level of theory.

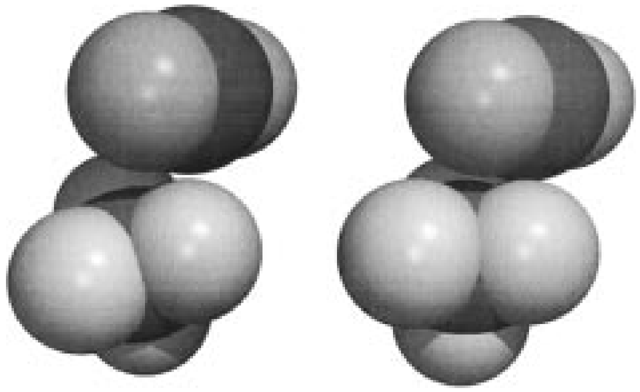

Figure 2. Geometries for the CO_2-CF_4 dimer. The HF/6-31G(d) optimized structure is shown on the left-hand side and the MP2/aug-cc-pVDZ optimized structure is on the right. The carbon−carbon distance decreases by about 0.2 Å when the geometry is optimized at the MP2/aug-cc-pVDZ level of theory. This is a much smaller change than observed for the CO_2-CF_4 cluster. Cf. Figure 1.

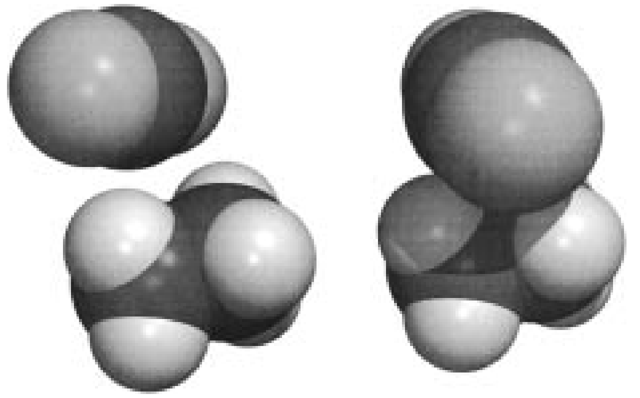

Figure 3. Geometries for the $CO_2-C_2H_6$ dimer. The HF/6-31G(d) optimized structure is shown on the left-hand side and the MP2/aug-cc-pVDZ optimized structure is on the right. The average intermolecular carbon−carbon distance decreases by about 0.7 Å when the geometry is optimized at the MP2/aug-cc-pVDZ level of theory.

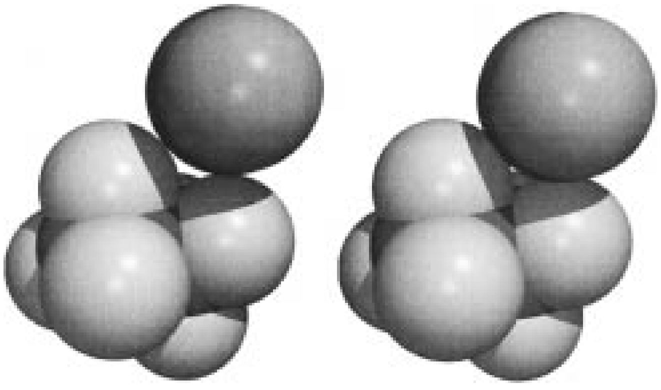

Figure 4. Geometries for the $CO_2-C_2F_6$ dimer. The HF/6-31G(d) optimized structure is shown on the left-hand side and the MP2/aug-cc-pVDZ optimized structure is on the right. The average intermolecular carbon−carbon distance decreases by about 0.16 Å when the geometry is optimized at the MP2/aug-cc-pVDZ level of theory. This is a much smaller change than observed for the $CO_2-C_2H_6$ cluster. Cf. Figure 3.

$CO_2-C_2H_6$. In contrast, the structures of the CO_2-CF_4 and $CO_2-C_2F_6$ clusters are similar at these two levels of theory. The HF/6-31G(d) and MP2/aug-cc-pVDZ optimized geometries for the four clusters are presented in Figures 1−4, with the HF/6-31G(d) and MP2/aug-cc-pVDZ optimized structures being shown in the left-hand and right-hand sides, respectively. The binding energies for each of the four dimers optimized at the MP2/aug-cc-pVDZ level of theory are given in Table 4.

For the CO_2-CH_4 dimer the distance between the monomers (as measured between the two carbon atoms) decreases by 0.5 Å upon geometry reoptimization at the MP2/aug-cc-pVDZ level. The corresponding change in the carbon−carbon distance of CO_2-CF_4 is only 0.2 Å. Moreover, in the former case, there is a greater change in the relative orientation of the two monomers. These results are consistent with the greater change in the MP2-C/aug-cc-pVTZ binding energy of CO_2-CH_4 than of CO_2-CF_4 upon reoptimization of the geometry at the MP2/aug-cc-pVDZ level (0.24 vs 0.01 kcal/mol). A similar trend is found for the $CO_2-C_2H_6$ and $CO_2-C_2F_6$ dimers. Namely, the geometry of the former changes significantly, while that of the latter dimer by much less upon reoptimization of the geometry at the MP2/aug-cc-pVDZ level. In terms of average carbon−carbon separations, the changes are 0.7 and 0.16 Å for $CO_2-C_2H_6$ and $CO_2-C_2F_6$, respectively. The associated changes in the corrected MP2/aug-cc-pVTZ binding energies are 0.45 and 0.03 kcal/mol, respectively.

One possible explanation for the observation that the CO_2−hydrocarbon geometries change significantly while the CO_2−perfluorocarbon geometries change very little in going from the HF/6-31G(d) to the MP2/aug-cc-pVDZ level of theory is that the BSSE in the HF/6-31G(d) calculations roughly compensates for the neglect of correlation for the CO_2−perfluorocarbon dimers, but not for the CO_2−hydrocarbon dimers. This

TABLE 4: Binding Energies (kcal/mol) of the Dimers at the MP2/aug-cc-pVDZ Optimized Geometries[a]

	aug-cc-pVDZ				aug-cc-pVTZ-f				aug-cc-pVTZ			
cluster	HF	HF-C	MP2	MP2-C	HF	HF-C	MP2	MP2-C	HF	HF-C	MP2	MP2-C
CO_2-CH_4	0.25	0.51	−1.26	−0.66	0.42	0.48	−0.99	−0.74	0.42	0.47	−1.07	−0.88
$CO_2-C_2H_6$	0.70	1.04	−1.77	−0.88	0.91	1.02	−1.38	−0.97	0.92	1.00	−1.48	−1.17
CO_2-CF_4	0.25	0.70	−1.36	−0.58	0.46	0.72	−1.12	−0.65	0.54	0.69	−1.12	−0.79
$CO_2-C_2F_6$	0.29	0.83	−1.69	−0.65	0.52	0.81	−1.39	−0.85	0.59	0.80	−1.41	−1.00

[a] HF-C and MP2-C denote results with the counterpoise correction for BSSE.

hypothesis is consistent with the observation from Table 3 that the corrected MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ binding energies for the CO_2−perfluorocarbon dimers are within about 0.1 kcal/mol of the uncorrected HF/6-31G(d) binding energies. On the other hand, the binding energies for the CO_2−hydrocarbon dimers increase in magnitude by 0.3−0.4 kcal/mol, which more than doubles these binding energies.

The changes in the true correlation energy contributions to the binding energies in going from the aug-cc-pVDZ to the aug-cc-pVTZ basis set range from −0.2 to −0.3 kcal/mol and are roughly three times greater in magnitude at the MP2/aug-cc-pVDZ than at the HF/6-31G(d) optimized geometries. Our best estimates of the binding energies of the clusters are provided by the MP2-C/aug-cc-pVTZ results at the MP2/aug-cc-pVDZ optimized geometries and are −0.88, −1.17, −0.79, and −1.00 kcal/mol for CO_2-CH_4, $CO_2-C_2H_6$, CO_2-CF_4, and $CO_2-C_2F_6$, respectively. At this level of theory, the CO_2−hydrocarbon dimers are predicted to be somewhat more strongly bound than the corresponding CO_2−perfluorocarbon dimers. The correlation energy contributions to these binding energies are large and are similar for CO_2-CH_4 and CO_2-CF_4 (−1.4 and −1.5 kcal/mol, respectively) as well as for $CO_2-C_2H_6$ and $CO_2-C_2F_6$ (−2.2 and −1.8 kcal/mol, respectively).

Comparison of the aug-cc-pVTZ-f and aug-cc-pVTZ binding energies in Table 4 shows that the higher angular momentum functions increase the binding by as much as 0.2 kcal/mol for these dimers. This is a significant fraction of the total binding energy and indicates that higher angular momentum functions are important for computing accurate interaction energies.

It is interesting to compare the situation for the CO_2−hydrocarbon and CO_2−fluorocarbon dimers with that for $(CO_2)_2$. Not only is the net binding of $(CO_2)_2$ (around −1.0 kcal/mol[20,21]) comparable to that found here between CO_2 and the small hydrocarbons and fluorocarbons, nearly all of the binding in $(CO_2)_2$ at its equilibrium geometry arises from electron correlation effects,[20,21] as is found for the mixed dimers studied here. A theoretical investigation of $(CO_2)_2$ has indicated that the dispersion contribution to the binding energy is about −1.9 kcal/mol,[20] which is considerably greater in magnitude than the net interaction energy. It is likely that the dispersion contributions are also larger in magnitude than the net correlation contributions to the interaction energies for the CO_2−hydrocarbon and CO_2−fluorocarbon clusters.

4. Conclusions

MP2 calculations with flexible basis sets reveal that CO_2 experiences a sizable attractive interaction with both simple hydrocarbons and their perfluorinated analogues, with the binding energies ranging from −0.79 to −1.17 kcal/mol, and being slightly more attractive in the CO_2−hydrocarbon species. These binding energies are comparable to that in the CO_2 dimer. As a result, it is not possible to discern the reason for the greater solubility of perfluorocarbons than of hydrocarbons in CO_2 from calculations on the small clusters used in this study. In contrast to the study by Cece et al.,[10] we do not find any enhanced attraction between CO_2 and perfluorocarbons relative to the analogous hydrocarbons.

At the MP2-optimized geometries, the interactions between CO_2 and simple hydrocarbons and perfluorocarbons are repulsive at the Hartree−Fock level of theory. Thus, the binding of these species is dominated by electron correlation effects. Although an energy-decomposition analysis was not carried out, we expect, by analogy with $(CO_2)_2$, that dispersion interactions are especially important.

We are unaware of any spectroscopic studies of the CO_2-CH_4, $CO_2-C_2H_6$, CO_2-CF_4, and $CO_2-C_2F_6$ species. The sizable interaction energies predicted here suggest that these species should be readily formed in mixed seeded supersonic jet conditions, and it is hoped that our theoretical results will motivate experimental studies of these mixed dimers. In addition, the present work suggests several directions for future theoretical study, including obtaining estimates of the contribution of vibrational zero-point energies to the binding energies and mapping out more complete potential energy surfaces for use in testing model potentials for describing CO_2−hydrocarbon and CO_2−perfluorocarbon interactions.

Acknowledgment. We gratefully acknowledge Dr. A. Cece for providing the Hartree−Fock geometries of the clusters described in Table 2. We thank the National Science Foundation for partial support of this work through Graduate Research Training Grant 9554576. We acknowledge NCSA and PSC for generous grants of computer time. Part of the calculations were carried out on the University of Pittsburgh Chemistry Department's workstation cluster funded in part by a grant from the NSF.

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