Explicit correlation and intermolecular interactions: Investigating carbon dioxide complexes with the CCSD(T)-F12 method

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We have optimized the lowest energy structures and calculated interaction energies for the CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 dimers with the recently developed explicitly correlated coupled cluster singles doubles and perturbative triples [CCSD(T)]-F12 methods and the associated VXZ-F12 (where X = D,T,Q) basis sets. For a given cardinal number, we find that results obtained with the CCSD(T)-F12 methods are much closer to the CCSD(T) complete basis set limit than the conventional CCSD(T) results. The relatively modest increase in the computational cost between explicit and conventional CCSD(T) is more than compensated for by the impressive accuracy of the CCSD(T)-F12 method. We recommend use of the CCSD(T)-F12 methods in combination with the VXZ-F12 basis sets for the accurate determination of equilibrium geometries and interaction energies of weakly bound electron donor acceptor complexes. © *2011 American Institute of Physics*. [doi:10.1063/1.3526956]

I. INTRODUCTION

The painfully slow convergence of electron correlation energy with increasing basis set size is considered one of the great challenges in modern computational chemistry. In the last few years, significant advancements have been made to accelerate this convergence by including a small number of terms to the wavefunction that depend explicitly on the interelectronic distance r_{12}.[1–4] These so-called explicitly correlated methods have been shown to give correlation energies using a triple-ζ basis set that are better than conventional coupled cluster singles doubles and perturbative triples [CCSD(T)] with a quintuple-ζ basis set.[5–8]

Recently, we determined equilibrium geometries and interaction energies for a series of hydrogen bonded complexes, including H_2O–H_2O, H_2O–H_2S, H_2O–NH_3, and H_2O–PH_3, with conventional CCSD(T) and the Dunning-type correlation consistent basis sets and with explicitly correlated CCSD(T)-F12 and the corresponding VXZ-F12 (where X = D,T,Q) basis sets.[9] We found that the CCSD(T)-F12 intermolecular distances and interaction energies were in impressive agreement with the CCSD(T) complete basis set (CBS) limit and recommended use of this explicitly correlated method for the accurate description of hydrogen bonded complexes. This initial work[9] was restricted to relatively strong hydrogen bonded complexes, and so the conclusions drawn are not necessarily generalizable to other types of more weakly bound complexes that display different intermolecular interactions. Recently, Marchetti *et al.* calculated CCSD(T)-F12a interaction energies[10] for the S22 benchmark set of complexes using the RI-MP2 geometries from the original investigation.[11]

In the present investigation, we consider a series of weakly bound complexes involving carbon dioxide, namely CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. These complexes exhibit weak electron donor acceptor and more general van der Waals-type intermolecular interactions and hence are representative of more weakly bound complexes. We investigate the optimized geometries, harmonic vibrational frequencies, and interaction energies for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 and their constituent monomer with both conventional and explicitly correlated CCSD(T)–F12 theory. The related MP2-F12 explicitly correlated method has been recently found to accelerate basis set convergence of interaction energies for a series of weakly bound electron donor acceptor complexes involving CO_2 and nitrogen-containing heterocycles.[12] With exception of CO_2–NH_3, the lowest energy structure of each complex possesses C_{2v} symmetry, which allows benchmark quality conventional CCSD(T) results to be calculated. We compare intermolecular distances and interaction energies obtained with both conventional CCSD(T) and explicitly correlated CCSD(T)-F12 to the CCSD(T)/CBS limit and, where possible, to experiment.

Results from this investigation are useful not only for the purpose of assessing the accuracy of the recently developed CCSD(T)-F12 methods but also provide high quality equilibrium geometries and interaction energies for a series of atmospherically relevant molecular complexes. The equilibrium constant of formation (k_{eq}) for a weakly bound complex depends exponentially on the interaction energy (at a given temperature). It follows that accurately determining the interaction energies of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 is crucial in order to estimate their abundance and potential role in the atmosphere.

II. THEORETICAL METHODS

We have fully optimized the geometries of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 and their constituent monomers with the CCSD(T) *ab initio* theory using

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Dunning-type correlation consistent basis sets. The CCSD(T) method is considered the "gold-standard" of modern electronic structure theory, and with a suitably large basis set it has been shown to give accurate geometries of small systems that are in excellent agreement with experiment.[13–15] We have used the aug-cc-pVXZ basis sets (where X = D,T,Q,5,6) for hydrogen and all the first row elements and the aug-cc-pV(X+d)Z basis sets (where X = D,T,Q,5,6) for the second row element Ar.[16–18] For brevity, we refer to these basis sets as AVXZ (where X = D,T,Q,5,6), whereby it is assumed that Ar has the additional tight d basis functions. We have optimized the geometry of the complexes using both a standard optimization scheme and a full counterpoise (CP) corrected optimization scheme to reduce the effects of basis set superposition error (BSSE) on our optimized geometries.[19]

We have also optimized the geometries of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 and their constituent monomers with the recently developed explicitly correlated CCSD(T)-F12 methods, as implemented in MOLPRO 2009.1.[6,20] We have used the VXZ-F12 orbital basis sets (where X = D,T,Q) of Peterson *et al.* that have been specifically optimized for use with explicitly correlated F12 methods.[21] For a given cardinal number, the VXZ-F12 basis sets have been designed to be of a similar size to the equivalent aug-cc-pVXZ and aug-cc-pV(X+d)Z basis sets but have fewer diffuse basis functions. Density fitting approximations[22,23] were used in all explicitly correlated calculations using the VXZ/JKFIT (where X = D,T,Q) and the AVXZ/MP2FIT (where X = D,T,Q) auxiliary basis sets.[24,25] We have used the resolution of the identity (RI) auxiliary basis sets of Yousaf and Peterson for all RI approximations.[26] The complementary auxiliary basis set singles correction was applied in all explicitly correlated calculations,[6] which substantially improves the accuracy of the Hartree–Fock contributions, particularly, with smaller orbital basis sets.[10] The diagonal, fixed amplitude 3C(FIX) *ansatz* was used, which is orbital invariant, size consistent, and free of geminal basis set superposition error.[3,27,28] Two different approximations are available for solving the CCSD(T)-F12 energies in MOLPRO 2009.1, denoted CCSD(T)-F12a and CCSD(T)-F12b.[8,23] Unless specified when we refer to CCSD(T)-F12 we mean both the CCSD(T)-F12a and CCSD(T)-F12b methods. The default CCSD-F12 correlation factor ($1/\beta e^{-\beta r_{12}}$, where $\beta = 1$) was used in all explicitly correlated calculations.

We have extrapolated the CCSD(T) energies to the CBS limit with the following two parameter extrapolation for the correlation energy

$$E_{XY}^{\text{corr}} = \frac{X^3 E_X^{\text{corr}} - Y^3 E_Y^{\text{corr}}}{X^3 - Y^3}, \tag{1}$$

where X and Y are the cardinal numbers of the two basis sets and E_X^{corr} and E_Y^{corr} are the corresponding correlation energies.[29,30] The extrapolated correlation energy, E_{XY}^{corr}, is added to the Hartree–Fock energy obtained with the larger basis set to give an estimate of the CCSD(T)/CBS limit energy.

We estimate the intermolecular distance of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 at the CCSD(T)/CBS limit by numerically determining the minimum of a CBS intermolecular potential obtained using Eq. (1). The potential used extends from −0.40 to +0.50 Å in 0.05 Å steps about the equilibrium value of either the standard optimized or CP optimized CCSD(T)/AV5Z intermolecular distance. All other geometric parameters are kept fixed at the corresponding CCSD(T)/AV5Z values. In principle, all of the geometric parameters of the complexes could be optimized at the CCSD(T)/CBS limit[31] but this is unfortunately prohibitive with the AV5Z/AV6Z basis sets and our current computational resources.

Unless specified all coupled cluster calculations assume a frozen core (C:1s; N:1s; O:1s; Ar:1s,2s,2p) and were performed using MOLPRO 2009.1.[20] The optimization threshold criteria was set to gradient = 1×10^{-6} a.u., stepsize = 1×10^{-6} a.u., and energy = 1×10^{-8} a.u. All single point energies were converged to 1×10^{-9} a.u.

To confirm the nature of stationary points we calculated harmonic vibrational frequencies with conventional CCSD(T), and the AVDZ and AVTZ basis sets and with explicitly correlated CCSD(T)-F12 with the VDZ-F12 and VTZ-F12 basis sets. These results are included in Tables SI-SVI of the supplementary material.[32] For some of the complexes with particularly flat potential energy surfaces, we had difficulty in identifying true minima using numerical second derivatives in MOLPRO 2009.1. Hence, we reoptimized and calculated harmonic frequencies of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 with conventional CCSD(T)/AVTZ using the analytical gradients available in CFOUR.[33] The optimization and single point convergence threshold criteria for these calculations were set to SCF_CONV = 1×10^{-10} a.u., CC_CONV = 1×10^{-11} a.u., LINEQ_CONV = 1×10^{-11} a.u., and GEO_CONV = 1×10^{-10} a.u.

The intermolecular potential energy surface of a weakly bound complex is highly anharmonic and hence ground state vibrational averaging can signficantly increase the intermolecular distance from its equilibrium value (R_e). We have calculated the average intermolecular distance in the vibrational ground state (R_g) and the intermolecular distance between average nuclei positions in the vibrational ground state (R_a) using the ANHARM = VIBROT vibrational perturbation routine in CFOUR.[33] The necessary cubic force constants were evaluated with the CCSD(T)/AVTZ method.

To quantify the extent of charge transfer in the weakly bound electron donor acceptor complexes, we have calculated atomic charges using the natural bond orbital analysis in GAUSSIAN 09 (Ref. 34) and have included these in Table SVII of the supplementary material.[32] For this analysis, we have calculated single point CCSD/AVQZ energies obtained at the CCSD(T)-F12b/VQZ-F12 optimized geometry.

III. RESULTS AND DISCUSSION

A. Monomer geometry

In Table I we present the geometric parameters of N_2, CO, CO_2, H_2O, and NH_3 optimized with the CCSD(T) method and the explicitly correlated CCSD(T)-F12 methods

TABLE I. Optimized geometric parameters (in angstrom and degrees) of N_2, CO, CO_2, H_2O, and NH_3.

	N_2	CO	CO_2	H_2O		NH_3	
	R_{NN}	R_{CO}	R_{CO}	R_{OH}	θ_{HOH}	R_{NH}	θ_{HNH}
CCSD(T)							
AVDZ	1.1209	1.1473	1.1775	0.9665	103.94	1.0237	105.94
AVTZ	1.1040	1.1360	1.1670	0.9616	104.18	1.0149	106.41
AVQZ	1.1005	1.1318	1.1631	0.9590	104.37	1.0128	106.54
AV5Z	1.0996	1.1309	1.1622	0.9584	104.43	1.0123	106.59
AV6Z	1.0993	1.1306	1.1620	0.9584	104.45	1.0122	106.62
CBS	1.0990	1.1302	1.1616	0.9583	104.48	1.0121	106.64
CCSD(T)-F12a							
VDZ-F12	1.1000	1.1317	1.1630	0.9588	104.36	1.0123	106.59
VTZ-F12	1.0995	1.1309	1.1623	0.9588	104.40	1.0124	106.59
VQZ-F12	1.0990	1.1305	1.1618	0.9584	104.46	1.0121	106.64
CCSD(T)-F12b							
VDZ-F12	1.0997	1.1310	1.1625	0.9585	104.34	1.0122	106.58
VTZ-F12	1.0993	1.1306	1.1620	0.9586	104.40	1.0124	106.60
VQZ-F12	1.0989	1.1303	1.1617	0.9583	104.45	1.0121	106.64
Expt.[a]	1.094	1.1281	1.1615	0.958	104.27	1.014	106.47
Expt.[b]	1.0977	1.1284	1.1601	0.9579	104.40	1.0139	107.17

[a] Equilibrium bond distances (R_e) from Ref. 35.

[b] Equilibrium bond distances (R_e) derived from experimental rotation constants using *ab initio* calculated vibration–rotation interaction constants from Ref. 39.

as well as the experimentally determined values. As expected, the conventional CCSD(T) optimized geometric parameters converge uniformly toward the CBS limit as the cardinal number of the basis set increases. We find that the bond lengths progressively shorten and the bond angles steadily increase from AVDZ to AV6Z. With the exception of the H_2O and NH_3 bond lengths, the explicitly correlated CCSD(T)-F12 optimized geometric parameters also systematically converge toward the CBS limit as the cardinal number of the basis increases.

In agreement with earlier work,[37] we find that geometric parameters optimized at the CCSD(T)/CBS limit are in excellent agreement with experiment. For a given cardinal number, geometric parameters optimized using the explicitly correlated methods are found to be in much better agreement with CCSD(T)/CBS limit and hence with the experiment than geometric parameters optimized with conventional CCSD(T). In general, CCSD(T)-F12 geometric parameters obtained with a given basis set are of comparable accuracy to conventional CCSD(T) results obtained with a Dunning basis set two cardinal numbers higher.

B. Complex geometry

In Fig. 1 we show the optimized geometries of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. We find that the lowest energy structure of all five complexes is "T-shaped," with the electron deficient carbon atom of the CO_2 subunit acting as an electron acceptor and the adjacent heavy atom of the other subunit acting as an electron donor. All five complexes and the corresponding six monomers are uncharged. We determine the magnitude of charge transfer for each complex from the net difference in natural atomic charges for the two constituent monomers. At the CCSD/AVQZ level of theory, we find charge transfer of 0.0031 for CO_2–Ar, 0.0005 for CO_2–N_2, 0.0021 for CO_2–CO, 0.0019 for CO_2–H_2O, and 0.0033 for CO_2–NH_3. The magnitude of charge transfer in all five complexes is small as CO_2 is only a weak electron acceptor (weak Lewis acid). For comparison, charge transfer in BH_3–NH_3 (a strong electron donor acceptor complex) is 0.3774, calculated with the same level of theory.

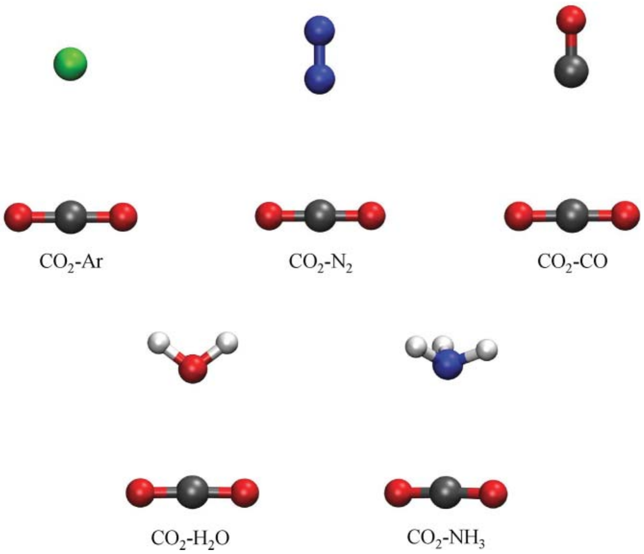

FIG. 1. CCSD(T)-F12b/VQZ-F12 optimized geometries. From left to right, top to bottom: CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.

The CO_2–Ar complex has been the subject of several experimental investigations that have utilized molecular beam techniques to record spectra in the radio frequency, microwave, and infrared regions.[38–42] The potential energy surface and vibrational–rotational spectra have also been investigated theoretically by several groups, with the most recent calculations completed with the CCSD(T)/aug-cc-pVTZ method.[43–45] The results of all these previous investigations are pleasingly concordant, with the only minimum found to be a symmetric "T-shaped" structure of C_{2v} symmetry, in agreement with the present work.

The geometry of the CO_2–N_2 complex has been experimentally determined as a planar symmetric "T-shaped" structure of C_{2v} symmetry by rotationally resolved FTIR spectroscopy using a pulsed molecular beam.[46] This structure has also been shown to be consistent with recent matrix isolation FTIR spectra.[47] The optimized geometry of the CO_2–N_2 complex has been reported with the MP2/aug-cc-pVDZ and MP2/6-311+G(d) methods, and the potential energy surface has been explored using fixed monomer geometries at the MP4 and CCSD(T) levels of theory.[47–49] Our present CCSD(T) and CCSD(T)-F12 calculations are consistent with these previous investigations and find the global minimum of CO_2–N_2 to be a planar symmetric "T-shaped" structure of C_{2v} symmetry.

The CO_2–CO complex is isoelectronic with the CO_2–N_2 complex. The geometry of CO_2–CO has been investigated using microwave spectroscopy and infrared spectroscopy and corresponds to a planar symmetric "T-shaped" structure of C_{2v} symmetry.[50–52] The electric dipole moment of the CO_2–CO complex has been experimentally measured, and this is also consistent with a C_{2v} structure.[53] The potential energy surface of CO_2–CO has been explored using fixed monomer geometries at the MP4 and CCSD(T) levels of theory.[49] Our present CCSD(T) and CCSD(T)-F12 global minimum structures are consistent with these earlier experimental and theoretical investigations.

The lowest energy structure of CO_2–H_2O has been determined in a number of experimental investigations to be a planar symmetric "T-shaped" structure of C_{2v} symmetry.[54–57] However, a recent matrix isolation FTIR experiment has suggested that a second asymmetric tilted C_s structure exists.[58] This C_s structure is corroborated by the authors own *ab initio* calculations with the MP2/aug-cc-pVTZ method,[58] by previous MP2/aug-cc-pVTZ calculations by Danten *et al.*,[59] and by subsequent MP2 triple-ζ calculations by Altmann *et al.*[60] However in contrast, Chaban *et al.* were unable to identify the asymmetric tilted C_s structure as a minimum using the MP2/aug-cc-pVTZ method.[61] Very recently, the potential energy surface of CO_2–H_2O was more thoroughly investigated with the MP2 method and aug-cc-pVDZ to aug-cc-pVQZ basis sets using both standard and counterpoise optimization schemes.[62] Makarewicz found that the asymmetric tilted C_s structure was only a minimum with the standard optimization scheme using the aug-cc-pVDZ and aug-cc-pVTZ basis sets, indicating that this structure is an artefact of basis set superposition error with the MP2 level of theory. This result corroborates earlier CCSD(T) investigations by Garden *et al.* using standard and counterpoise optimization schemes with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.[63] In the present work, only the symmetric C_{2v} structure of CO_2–H_2O was found to be a minimum with both conventional CCSD(T) and the AVDZ-AV6Z basis sets and explicitly correlated CCSD(T)-F12 and the VDZ-F12, VTZ-F12, and VQZ-F12 basis sets. The asymmetric tilted C_s structure was found to be a first order saddle point in all our CCSD(T) and CCSD(T)-F12 results and was not considered further.

The CO_2–NH_3 complex has received surprisingly little attention in the literature with only a few experimental investigations[64–66] and low level calculations.[66–68] The structure has been experimentally determined by matrix isolation FTIR spectroscopy and microwave spectroscopy to be "T-shaped," with an assumed symmetric C_{2v} CO_2–N framework.[64–66] Two staggered structures are possible for CO_2–NH_3, corresponding to one of the hydrogen atoms being either in plane with (C_s symmetry) or perpendicular to (C_s symmetry) the CO_2 group. The energetic barrier to convert between these two structures is expected to be very small, permitting almost free rotation around the sixfold potential about the principal rotation axis.[65] Our present CCSD(T) and CCSD(T)-F12 calculations show that the energy of the in plane and perpendicular structures is almost degenerate, with the in plane structure $\sim$0.1 cm^{-1} lower in energy with all basis sets. However, both structures appear to be first order saddle points when the harmonic frequencies are calculated using numerical gradients, with a single imaginary frequency corresponding to rotation of the NH_3 subunit. The harmonic frequencies of both structures were also calculated using analytical gradients in CFOUR,[33] and only the in plane structure was found to be a minimum. This result highlights the difficulty in calculating accurate second order energy derivatives for flat potential energy surfaces via numerical gradients. For comparison, we present CCSD(T)/AVTZ harmonic frequencies of all five complexes obtained using both the numerical and analytical gradients in Table SVIII of the supplementary material.[32]

C. Intermolecular distance

In Table II we present the standard and CP optimized CCSD(T) intermolecular distances of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. We limit discussion in the manuscript to consider only the intermolecular distances of the complexes, with the full optimized geometries given in Tables SIX–SXVIII of the supplementary material.[32] The accuracy of the intermolecular distance can be considered a guide to how well a particular *ab initio* method and basis set describes the intermolecular interactions between two monomers in a complex.

Unlike the monomer geometries in Table I, the standard optimized intermolecular distances do not necessarily systematically and uniformly converge toward the CBS limit as the cardinal number of the basis set increases. This apparent oscillation in some of the intermolecular distances with increasing basis set is attributed to a cancellation of basis set incompleteness error and basis set superposition error. The magnitude of BSSE and its effect on intermolecular distances is the largest for small basis sets. Hence, if we exclude the AVDZ results of CO_2–CO and the AVDZ and AVTZ results of CO_2–Ar, we find that the optimized intermolecular distances of the three more weakly bound complexes (CO_2–Ar, CO_2–N_2, CO_2–CO) progressively shorten and converge to the CBS limit as the cardinal number of the basis set increases. For CO_2–H_2O, the standard optimized intermolecular distance contracts from AVDZ to AVQZ, lengthens from AVQZ to AV5Z, and then contracts from AV5Z to the CBS limit. For CO_2–NH_3, the oscillation in the optimized intermolecular distance is worse still. In contrast, the CP optimized intermolecular distances of all five complexes systematically and uniformly converge to the CP corrected CBS limit as the cardinal number of the basis set increases. It is worth noting that the CBS limits obtained with the standard and CP corrected 1D potential energy curves are generally in very good agreement with each other, with the CP values 0.001–0.002 Å smaller. Hence, comparison to either the standard CBS limit or the CP corrected CBS limit yields largely the same conclusions.

The systematic and uniform basis set convergence of the CP optimized intermolecular distances is clearly more satisfying than the sometimes oscillatory basis set convergence of the standard optimized intermolecular distances. However for a given basis set, the absolute difference between the CP optimized intermolecular distances and the CP CBS limit is actually larger than the absolute difference between the standard optimized intermolecular distance and the CBS limit. For example, the average absolute error between the AVDZ CP optimized distances and the CP CBS limit is ~0.14 Å whereas, the average absolute error between the AVDZ standard optimized distances and the CBS limit is ~0.013 Å. This perhaps surprising behavior, whereby CP correction increases the discrepancy with the CBS limit, was also noted in our previous work on hydrogen bonded complexes,[9] indicating that this is a systemic problem with CP correction of CCSD(T) intermolecular distances. As expected, the difference between the standard and CP optimized intermolecular distances becomes smaller as the cardinal number of the basis set increases due to a decrease in the magnitude of BSSE.

TABLE II. CCSD(T) intermolecular distances (in angstrom) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
Standard					
AVDZ	3.4392	3.1020	3.2038	2.7628	2.9208
AVTZ	3.4461	3.1147	3.1889	2.7577	2.9224
AVQZ	3.4208	3.1169	3.2080	2.7557	2.9181
AV5Z	3.4217	3.1251	3.2136	2.7566	2.9205
AV6Z	3.4221	3.1270	3.2150	2.7565	—
CBS[b]	3.4224	3.1293	3.2167	2.7562	2.9193
Counterpoise					
AVDZ	3.6448	3.2494	3.3463	2.8521	3.0254
AVTZ	3.5055	3.1683	3.2535	2.7902	2.9529
AVQZ	3.4504	3.1440	3.2300	2.7681	2.9318
AV5Z	3.4362	3.1354	3.2223	2.7615	—
CBS[c]	3.4205	3.1275	3.2146	2.7552	2.9174

[a] The intemolecular distance is between the carbon atom of CO_2 and the closest atom of the other monomeric substituent, i.e., $R_{C\cdots Ar}$, $R_{C\cdots N}$, $R_{C\cdots C}$, $R_{C\cdots O}$, and $R_{C\cdots N}$.

[b] Extrapolation to the complete basis set limit utilizes the AV5Z and AV6Z results.

[c] Extrapolation to the complete basis set limit utilizes counterpoise corrected AV5Z and AV6Z results.

TABLE III. CCSD(T)-F12 intermolecular distances (in angstrom) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
CCSD(T)-F12a					
VDZ-F12	3.4178	3.1371	3.2241	2.7610	2.9259
VTZ-F12	3.4205	3.1296	3.2157	2.7578	2.9197
VQZ-F12	3.4237	3.1288	3.2155	2.7558	2.9187
CCSD(T)-F12b					
VDZ-F12	3.4327	3.1453	3.2328	2.7650	2.9314
VTZ-F12	3.4251	3.1319	3.2184	2.7590	2.9216
VQZ-F12	3.4242	3.1295	3.2168	2.7563	2.9194

[a] The intemolecular distance is between the carbon atom of CO_2 and the closest atom of the other monomeric substituent, i.e., $R_{C\cdots Ar}$, $R_{C\cdots N}$, $R_{C\cdots C}$, $R_{C\cdots O}$, and $R_{C\cdots N}$.

In Table III we present the CCSD(T)-F12a and CCSD(T)-F12b optimized intermolecular distances of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. Unlike our previous work with hydrogen bonded complexes,[9] we find that the CCSD(T)-F12 optimized intermolecular distances of the present weakly bound electron donor acceptor complexes systematically converge as the cardinal number of the basis set increases. With exception of the CCSD(T)-F12a results for CO_2–Ar, we find that the intermolecular distances become progressively smaller from VDZ-F12 to VQZ-F12. In general, the explicitly correlated intermolecular distances are in very good agreement with the CBS limits in Table II. We find that for a given cardinal number, the CCSD(T)-F12 intermolecular distance is in much better agreement with the CBS limit than the conventional CCSD(T) result obtained either with or without CP correction. The impressive performance of the explicitly correlated results is particularly pronounced for the VTZ-F12 and VQZ-F12 results. For example, the average absolute error (with respect to the CBS limit) of the VQZ-F12 intermolecular distances is smaller than the corresponding error in the conventional CCSD(T)/AV6Z results.

Overall, we find that the CCSD(T)-F12a intermolecular distances obtained with the VDZ-F12 and VTZ-F12 basis sets are in slightly better agreement with the CCSD(T)/CBS limit than the corresponding CCSD(T)-F12b results. However, this situation reverses for the VQZ-F12 basis set, where the CCSD(T)-F12b method appears to slightly outperform the CCSD(T)-F12a method. The observed relative performance of the CCSD(T)-F12a and CCSD(T)-F12b methods is consistent with previous investigations.[8,9]

Comparison of the calculated intermolecular distances in Table II and Table III to experiment is not trivial. The calculated intermolecular distance represents the minimum energy equilibrium structure (R_e) and allows all geometric parameters allowed to relax. In contrast, the experimental intermolecular distance corresponds to an effective structure (R_0) that is fitted to rotational constants measured in the vibrational ground state (B_0), with fixed geometric parameters for the monomeric units.[39,46,50,57,65] The intermolecular

TABLE IV. Calculated and experimental intermolecular distances (in angstrom) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
Calc. R_e[b]	3.446	3.115	3.189	2.758	2.921
Calc. R_a[c]	3.528	3.192	3.263	2.844	2.972
Calc. R_g[d]	3.529	3.198	3.269	2.846	2.973
Best Est. R_a[e]	3.507	3.206	3.291	2.842	2.970
Best Est. R_g[f]	3.507	3.212	3.297	2.844	2.971
Expt. R_0[g]	3.504[h]	3.182[i]	3.277[j]	2.838[k]	2.988[l]

[a] The intemolecular distance is between the carbon atom of CO_2 and the closest atom of the other monomeric substituent, i.e., $R_{\mathrm{C\cdots Ar}}$, $R_{\mathrm{C\cdots N}}$, $R_{\mathrm{C\cdots C}}$, $R_{\mathrm{C\cdots O}}$, and $R_{\mathrm{C\cdots N}}$.

[b] CCSD(T)/AVTZ equilibrium intermolecular distance.

[c] CCSD(T)/AVTZ intermolecular distance between average nuclear positions in the vibrational ground state obtained using vibrational perturbation theory.

[d] CCSD(T)/AVTZ average intermolecular distance in the vibrational ground state obtained using vibrational perturbation theory.

[e] Sum of CCSD(T)-F12b/VQZ-F12 equilibrium distance and $R_a - R_e$ anharmonic vibrational-rotational "correction".

[f] Sum of CCSD(T)-F12b/VQZ-F12 equilibrium distance and $R_g - R_e$ anharmonic vibrational–rotational "correction."

[g] Effective intermolecular distance fitted to ground state rotational constants. See text for details.

[h] Reference 39.

[i] Reference 46.

[j] Reference 50.

[k] Reference 57.

[l] Reference 65.

potential energy surfaces of the present complexes are highly anharmonic. It follows that determining the intermolecular distance from B_0 rotational constants will result in a value for R_0 that is significantly longer than that would be obtained for R_e if equilibrium rotational constants (B_e) were used. It is also important to note that assuming the geometric parameters of the monomers remain frozen upon complexation becomes less valid for the more strongly bound complexes. For example, the OCO angle of CO_2 in the five complexes deviates from linearity proportional to the interaction energy (*vide infra*) and is 179.99° for CO_2–Ar, 179.71° for CO_2–N_2, 179.53° for CO_2–CO, 178.14° for CO_2–H_2O, and 177.46° for CO_2–NH_3 with the CCSD(T)-F12b/VQZ-F12 method.

In Table IV we present the CCSD(T)/AVTZ calculated equilibrium R_e intermolecular distances and experimental R_0 intermolecular distances for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. To facilitate a more fair comparison between theory and experiment, we also show the CCSD(T)/AVTZ intermolecular distance between average nuclei positions in the vibrational ground state (R_a) and the average intermolecular distance in the vibrational ground state (R_g) determined from the vibrational perturbation theory. The suitability of vibrational perturbation theory to describe vibrational–rotational coupling in weakly bound complexes is not obvious as intermolecular potential energy surfaces are generally very flat and anharmonic. However, at least pragmatically, this approach appears to perform well, with our previous vibrationally averaged intermolecular distance for water dimer (H_2O–H_2O) found to be in good agreement with results obtained using more specialized approaches.[9]

For all five complexes, the difference between R_a and R_g is small, with R_a 0.001–0.006 Å smaller. As expected, vibrational averaging appreciably increases the CCSD(T)/AVTZ calculated intermolecular distances, with R_a and R_g calculated to be as much as 0.09 Å larger than the $\boldsymbol{R_e}$ equilibrium values. As demonstrated in Tables II and III, the CCSD(T)/AVTZ intermolecular distances differ from the CCSD(T)/CBS limit by up to ~0.03 Å. Hence, we obtain our best estimate of $\boldsymbol{R_a}$ or $\boldsymbol{R_g}$ by adding the difference between $\boldsymbol{R_a}$ and $\boldsymbol{R_e}$ or $\boldsymbol{R_g}$ and $\boldsymbol{R_e}$ respectively, to the CCSD(T)-F12b/VQZ-F12 equilibrium intermolecular distances. For CO_2–Ar and CO_2–H_2O, the agreement between our estimated R_a/R_g intermolecular distances and the experimental R_0 distance is exceptionally good. For the other three complexes, the variation between our estimated R_a/R_g results and the experimental effective R_0 intermolecular distances is not quite as impressive with an average remaining variation of ~0.02 Å.

D. Interaction energy

In Table V we present the standard and counterpoise corrected CCSD(T) interaction energies for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. The monomer and complex energies have been determined using CCSD(T)-F12b/VQZ-F12 optimized geometries, as this method demonstrated closest agreement to the CCSD(T)/CBS limit (Tables I–III). It is interesting to note that the magnitude of the interaction energy appears largely uncorrelated to the magnitude of charge transfer (*vide supra*). For example, the CO_2–Ar complex has the weakest interaction energy and yet demonstrates the second largest amount of charge transfer.

If we first consider the nonextrapolated results, we find that both the standard and CP corrected CCSD(T) interaction

TABLE V. CCSD(T) interaction energies (in kcal mol^{-1}) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
Standard					
AVDZ	−0.63	−1.31	−1.57	−3.21	−3.46
AVTZ	−0.63	−1.11	−1.37	−2.99	−3.09
AVQZ	−0.61	−1.03	−1.25	−2.97	−3.09
AV5Z	−0.60	−0.96	−1.18	−2.93	−3.05
AV6Z	−0.58	−0.95	−1.17	−2.93	−3.04
CBS AVDZ/AVTZ	−0.65	−1.05	−1.35	−3.01	−3.08
CBS AVTZ/AVQZ	−0.60	−0.99	−1.21	−2.97	−3.10
CBS AVQZ/AV5Z	−0.60	−0.91	−1.14	−2.91	−3.02
CBS AV5Z/AV6Z	−0.57	−0.94	−1.16	−2.92	−3.04
Counterpoise					
AVDZ	−0.27	−0.70	−0.88	−2.39	−2.50
AVTZ	−0.45	−0.85	−1.06	−2.71	−2.84
AVQZ	−0.53	−0.91	−1.12	−2.84	−2.97
AV5Z	−0.55	−0.92	−1.14	−2.88	−3.00
AV6Z	−0.57	−0.93	−1.15	−2.90	−3.02
CBS AVDZ/AVTZ	−0.53	−0.90	−1.13	−2.84	−2.98
CBS AVTZ/AVQZ	−0.58	−0.94	−1.16	−2.92	−3.05
CBS AVQZ/AV5Z	−0.58	−0.94	−1.17	−2.93	−3.04
CBS AV5Z/AV6Z	−0.58	−0.94	−1.17	−2.93	−3.05

[a] All calculations are carried out at the CCSD(T)-F12b/VQZ-F12 optimized geometry.

energies systematically and uniformly converge as the cardinal number of the basis set increases from AVDZ to AV6Z. As expected, the standard CCSD(T) interaction energies are largest with the AVDZ basis set and converge downward whereas the CP corrected interaction energies are smallest with the AVDZ basis set and converge upward. The decrease in the standard CCSD(T) interaction energies with increasing basis set size is attributed to BSSE, which is largest for the modest AVDZ basis set and becomes progressively smaller for the AVTZ–AV6Z basis sets. The increase in the CP corrected CCSD(T) interaction energies with increasing basis set size is attributed to an overestimate of the magnitude of BSSE in the CP correction, which becomes less pronounced for the AVTZ–AV6Z basis sets.

In general, the standard and CP corrected CBS interaction energies also converge as the cardinal number of the two basis sets involved increases from AVDZ/AVTZ to AV5Z/AV6Z, although there is some oscillation, particularly in the standard results. The difference between the standard and CP corrected AVDZ/AVTZ CBS interaction energies is appreciable, and it is notable that the CP results are much more accurate. As expected, this difference decreases as the basis set size increases, and consequently, the CBS AV5Z/AV6Z interaction energies obtained either with or without CP correction are in very good agreement with each other, with the CP values 0.01 kcal mol^{-1} more negative. Hence, like the corresponding standard and CP corrected CBS intermolecular distances, comparison to either the standard CBS interaction energies or CP corrected CBS interaction energies yields the same conclusions.

For a given basis set, we find that the standard interaction energies of CO_2–Ar, CO_2–H_2O, and CO_2–NH_3 appear to be in better agreement with the CBS AV5Z/AV6Z limit than the CP corrected interaction energies, whereas for CO_2–CO and CO_2–N_2 the opposite is true. This indicates that BSSE may be more significant in the CO_2–CO and CO_2–N_2 complexes, particularly with the smaller AVDZ–AVQZ basis sets. For the larger AV5Z and AV6Z basis sets, the relative error in the standard and CP corrected CCSD(T) interaction energies of all five complexes is comparable and both approaches lead to results in good agreement with the CCSD(T)/CBS limit. The computational cost of the present CP corrected interactions energies is approximately three times longer than the corresponding standard interaction energies. While this additional cost is not prohibitively large, it is also not clear from the present results whether CP correction necessarily "improves" the accuracy of the CCSD(T) interaction energies.

In Table VI we present the CCSD(T)-F12 calculated interaction energies for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3. Consistent with our previous work with hydrogen bonded complexes,[9] we find that the explicitly correlated interaction energies of these weakly bound electron donor acceptor complexes systematically converge as the cardinal number of the basis set increases from VDZ-F12 to VQZ-F12. However, unlike this earlier work, the interaction energies of some complexes converge downward to the CCSD(T)/CBS limit, whereas others converge upward to the CCSD(T)/CBS limit. Nonetheless, the basis set convergence of the explicitly correlated interaction energies is excellent, with the largest variation between all basis sets just 0.05 kcal mol^{-1}.

The VXZ-F12 basis sets contain fewer diffuse basis functions than the corresponding AVXZ basis sets and include only the diffuse s and p augmenting functions of the AV(X+1)Z basis sets. This absence of diffuse functions with higher angular momentum in the VXZ-F12 basis sets was noted as being potentially insufficient for the rapid convergence of van der Waals interaction energies.[21] However, results from both the present investigation and our earlier hydrogen bonded work exhibit impressive convergence in both the optimized intermolecular distance and interaction energies with the VXZ-F12 basis sets.

For a given cardinal number, we find that the explicitly correlated CCSD(T)-F12 interaction energies in Table VI are in much closer agreement to the CCSD(T)/CBS AV5Z/AV6Z limit than the conventional CCSD(T) results obtained either with or without CP correction in Table V. The average absolute error in the CCSD(T)-F12a and CCSD(T)-F12b VDZ-F12 interaction energies is ~0.03 kcal mol^{-1}, which is an order of magnitude smaller than the corresponding error in the standard (~0.3 kcal mol^{-1}) or CP corrected (~0.4 kcal mol^{-1}) conventional CCSD(T)/AVDZ interaction energies. In general, we find that explicitly correlated CCSD(T)-F12 interaction energies obtained with a given basis set are equal to or better than the conventional CCSD(T) results obtained with a cardinal number two higher. For example, the average absolute error in the CCSD(T)-F12/VTZ-F12 results is ~0.01 kcal mol^{-1}, whereas the corresponding error in the conventional CCSD(T)/AV5Z interaction energies is ~0.02 kcal mol^{-1}.

It is also instructive to compare the accuracy of the CCSD(T)-F12 interaction energies in Table VI to the accuracy of the CBS extrapolated interaction energies in Table V obtained using basis sets of comparable size. We find that the standard and CP corrected AVDZ/AVTZ CBS interaction energies have an average absolute error of ~0.1 and ~0.05 kcal mol^{-1}, respectively, whereas the CCSD(T)-F12/VDZ-F12 and CCSD(T)-F12/VTZ-F12 results have a much smaller average absolute error of ~0.03 and ~0.008 kcal mol^{-1}, respectively. The average absolute error of the standard AVTZ/AVQZ CBS extrapolated interaction energies is ~0.05 kcal mol^{-1}, whereas the average absolute errors in the CP

TABLE VI. CCSD(T)-F12 interaction energies (in kcal mol^{-1}) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
CCSD(T)-F12a					
VDZ-F12	−0.60	−0.93	−1.14	−2.97	−3.07
VTZ-F12	−0.57	−0.93	−1.15	−2.93	−3.05
VQZ-F12	−0.57	−0.94	−1.16	−2.92	−3.04
CCSD(T)-F12b					
VDZ-F12	−0.57	−0.91	−1.11	−2.94	−3.02
VTZ-F12	−0.57	−0.93	−1.14	−2.92	−3.04
VQZ-F12	−0.57	−0.93	−1.16	−2.92	−3.04

[a] All calculations are carried out at the CCSD(T)-F12b/VQZ-F12 optimized geometry.

TABLE VII. CCSD(T) and CCSD(T)-F12 ZPVE corrections (in kcal mol^{-1}) for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3.[a]

	CO_2–Ar	CO_2–N_2	CO_2–CO	CO_2–H_2O	CO_2–NH_3
CCSD(T)					
AVDZ	+0.12	+0.35	+0.37	+0.80	+0.89
AVTZ	+0.11	+0.30	+0.38	+0.79	+0.72
CCSD(T)-F12a					
VDZ-F12	+0.11	+0.29	+0.37	+0.79	+0.78
VTZ-F12	+0.11	+0.29	+0.37	+0.77	+0.78
CCSD(T)-F12b					
VDZ-F12	+0.11	+0.29	+0.36	+0.81	+0.78
VTZ-F12	+0.11	+0.30	+0.36	+0.77	+0.82

[a] All calculations are carried out at their respective optimized geometry.

corrected AVTZ/AVQZ and CCSD(T)-F12/VQZ-F12 results are all less than 0.01 kcal mol^{-1}. It is worth noting that correlation energies obtained with the CCSD(T)-F12a are unable to be extrapolated to the CBS limit.[69] While such extrapolation is possible for the CCSD(T)-F12b method,[67] the results of the present investigation indicate that this may not be necessary for routine determination of accurate interaction energies.

Overall, we find that the CCSD(T)-F12a and CCSD(T)-F12b interaction energies are in excellent agreement with each other, with the CCSD(T)-F12a results consistently equal to or slightly larger than the CCSD(T)-F12b results. The computational cost of the present explicitly correlated CCSD(T)-F12 interaction energies is approximately 4, 2, and 1.5 times longer than conventional CCSD(T) interaction energies obtained with double-ζ, triple-ζ, and quadruple-ζ basis set, respectively. This relatively modest increase in the computational cost between explicit and conventional CCSD(T) is more than compensated for by the impressive accuracy of the CCSD(T)-F12 method. To achieve similarly accurate interaction energies, the cumbersome approach of extrapolating CP corrected energies to the CBS limit with at least AVTZ/AVQZ basis sets is required. Hence, we highly recommend use of the explicitly correlated CCSD(T)-F12 methods in combination with the VXZ-F12 basis sets for the accurate determination of interaction energies in weakly bound electron donor acceptor complexes.

In Table VII we present CCSD(T), CCSD(T)-F12a, and CCSD(T)-F12b zero point vibrational energy (ZPVE) corrections for CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3, obtained with double-ζ and triple-ζ basis sets. The corresponding harmonic frequencies are included in Tables SI– SVI of the supplementary material.[32] As expected, the ZPVE correction for all five complexes is positive and reduces the magnitude of the corresponding interaction energy. This is largely due to the conversion of rotational and translational modes of the constituent monomers upon complexation into low frequency intermolecular vibrational modes. The magnitude of ZPVE correction appears reasonably well correlated to the raw interaction energy of the complex and is the smallest for CO_2–Ar and the largest for CO_2–NH_3.

In general, we find that the variation in the conventional CCSD(T) ZPVE corrections obtained with the AVDZ and AVTZ basis sets is much smaller than the corresponding variation in the raw interaction energies obtained with the same basis sets (Table V). We attribute this small variation in ZPVE with basis set to a cancellation of error between the vibrational frequencies of the complex and the vibrational frequencies of its constituent monomers. It follows that ZPVE corrections obtained with explicitly correlated CCSD(T)-F12 vibrational frequencies also demonstrate relatively small variation with basis set and are in good agreement with the conventional CCSD(T) results. It is important to note that a 0.01 kcal mol^{-1} change in ZPVE is equivalent to a net change of just ~3.5 cm^{-1} in the corresponding vibrational frequencies. As noted earlier, the intermolecular vibrational frequencies of a complex are notoriously difficult to determine accurately and variations of up to 9 cm^{-1} (or even the incorrect sign) were found when comparing vibrational frequencies obtained with either analytical or numerical gradients (Table SVII of supplementary material[32]).

IV. CONCLUSIONS

We have optimized the lowest energy structures and calculated interaction energies for the CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 complexes as well as their constituent monomers with both conventional and explicitly correlated CCSD(T) theory. We find that the bond lengths and angles of the CO_2, N_2, CO, H_2O, and NH_3 monomers optimized with the CCSD(T)-F12a and CCSD(T)-F12b methods are in impressive agreement with the CCSD(T)/CBS limit and with the experiment.

We find that the lowest energy structure of CO_2–Ar, CO_2–N_2, CO_2–CO, CO_2–H_2O, and CO_2–NH_3 is "T-shaped," with the electron deficient carbon atom of the CO_2 subunit acting as an electron acceptor and the adjacent heavy atom of the other subunit acting as an electron donor. With exception of CO_2–NH_3, this lowest energy structure is symmetric and has C_{2v} symmetry. For CO_2–H_2O, we were unable to identify the recently proposed asymmetric tilted "T-shape" structure of C_s symmetry with either CCSD(T) or CCSD(T)-F12.

For a given cardinal number, we find that intermolecular distances and interaction energies obtained with the CCSD(T)-F12 methods and VXZ-F12 basis sets are much closer to the CCSD(T)/CBS limit than conventional CCSD(T) results with the AVXZ Dunning-type correlation consistent basis sets. The increased computational cost of CCSD(T)-F12 compared to the conventional CCSD(T), as implemented in MOLPRO 2009.1, is relatively modest, particularly given the impressive basis set convergence of the explicitly correlated results. In general, CCSD(T)-F12 geometric parameters and interaction energies obtained with a given basis set are of comparable accuracy to conventional CCSD(T) results obtained with a basis set two cardinal numbers higher. It follows that we highly recommend the use of the CCSD(T)-F12 methods in combination with the VXZ-F12 basis sets for the accurate determination of equilibrium geometries and interaction energies of molecular complexes that display weak electron donor acceptor type intermolecular interactions.

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