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Complexes Containing CO$_2$ and SO$_2$.  
Mixed Dimers, Trimers and Tetramers

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ABSTRACT  
Mixed dimers, trimers and tetramers composed of SO$_2$ and CO$_2$ molecules are examined by $ab$ $initio$ calculations to identify all minimum energy structures. While AIM formalism leads to the idea of a pair of C···O bonds in the most stable heterodimer, bound by some 2 kcal/mol, NBO analysis describes the bonding in terms of charge transfer from O lone pairs of SO$_2$ to the CO $\pi^*$ antibonding orbitals. The second minimum on the surface, just slightly less stable, is described by AIM as containing a single O···O chalcogen bond. The NBO picture is that of two transfers in opposite directions: one from a SO$_2$ O lone pair to a $\pi^*$ antibond of CO$_2$, supplemented by CO$_2$ O$_{lp} \rightarrow \pi^*(SO)$. Decomposition of the interaction energies points to electrostatic attraction and dispersion as the dominant attractive components, in roughly equal measure. The various heterotrimers and tetramers generally retain the dimer structure as a starting point. Cyclic oligomers are favored over linear geometries, with a preference for complexes containing larger numbers of SO$_2$ molecules.

KEYWORDS: chalcogen bonds; C···O bonds; O···O bonds; CO$_2$–philicity; SO$_2$–philicity
INTRODUCTION

Noncovalent interactions between molecules are central to condensed phases and to our understanding of the structures adopted by a wide range of single molecules such as proteins and nucleic acids. There is an assortment of different noncovalent forces, among which the hydrogen bond (HB) has been intensively studied over a long period of time.\textsuperscript{1-14} Earlier ideas about the nature of HBs in which the proton donor and acceptor atoms are F, O, or N has slowly been modernized to a more generalized scheme which includes less electronegative atoms like Cl, S, or C,\textsuperscript{5-9} and the idea that the bridging proton interacts with a lone electron pair has been extended to π and σ bonds,\textsuperscript{10-14} and even to a hydridic H atom within the context of dihydrogen bonds.\textsuperscript{12, 15-18}

A different but related class of noncovalent bond is associated with the attraction between a pair of electronegative atoms. Depending upon the nature of the bridging atom, these interactions are commonly designated as halogen,\textsuperscript{19-24} chalcogen,\textsuperscript{25-31} or pnicogen\textsuperscript{23, 32-41} bonds. The attractive force has been attributed to an anisotropic distribution of electron density around the bridging X atom, characterized by a crown of positive electrostatic potential along the extension of the Y–X bond (σ–hole) or in areas perpendicular to it (π–hole).\textsuperscript{42-46} This latter region is attracted to the partial negative charge of a neighboring molecule. Like HBs, the electrostatic attractions within these bonds are supplemented by charge transfer from the lone pair(s) of the acceptor atom into the σ* or π* antibonding Y–X orbitals, respectively, which tends to weaken and lengthen the latter Y–X bond. Attractive London (dispersion) forces further supplement the overall binding energy.

Attractive forces between stacked aromatic systems served as a springboard to examine other noncovalent bonds which are dominated by π→π* charge transfers. As an example, it was recently shown\textsuperscript{47} that a pair of amide units can arrange themselves in a stacked configuration with almost the same binding energy as the standard NH···O HBs that are a hallmark of α-helices and β-sheets in proteins. A dominant contributor to this stacked geometry is the transfer of charge from the CO π bond of one amide to the CO π* antibond of its neighbor, an idea that has been reinforced by others.\textsuperscript{48} There are other related systems which have been proposed to be held together in part by transfers into a π* antibond, with the charge originating in a lone pair of the partner molecule.\textsuperscript{49-52}

We have recently examined the interesting sorts of interactions that arise when SO\textsubscript{2} is paired with H\textsubscript{2}CO and H\textsubscript{2}CS, not only as dimers, but also in larger aggregates.\textsuperscript{53} These molecules were bound together by surprisingly strong forces, exceeding 5 kcal/mol. The
noncovalent bonds were identified as CH···O HBs and S···O chalcogen bonds, the latter of which was characterized by charge transfer from an O lone pair to a S–O π* antibonding orbital. An even more unusual sort of bond arose from the charge transfer from a SO$_2$ oxygen lone pair to the C–S π* antibonding orbital of H$_2$CS.

In the present work, we consider the interactions between CO$_2$ and its SO$_2$ congener. The first molecule is of particular interest in that its linear geometry imbues it with a zero dipole moment, which cuts down on Coulombic interactions. The absence of H atoms also precludes the presence of any HBs, even in a secondary role. The binding here is thus reduced, but is nonetheless substantial, in the neighborhood of 2 kcal/mol. The analysis reveals the attraction is due primarily to transfers from the O lone pair to the antibonding π* orbitals, of both CO and SO type. Analysis of trimers and tetramers provides an estimate of the influence of cooperative effects in stabilizing larger aggregates, and in determining the origin of the attractive forces, some of which are not present in the simpler dimers.

From a more practical standpoint, both CO$_2$ and SO$_2$ have relevance in a number of fields such as biological, industrial and environmental chemistry. CO$_2$ is a main product of cellular respiration and also of the carbon combustion that contributes so heavily to the greenhouse effect.$^{54}$ In that sense, its role in climate change is a topic of current and growing interest. Furthermore, supercritical carbon dioxide (sc-$\text{CO}_2$) has been the subject of research involving so-called green solvents,$^{55}$ i.e., solvents that have minimal environmental impact (cost, safety and health issues). Experimental work has been aimed toward greater understanding of the behavior of sc-$\text{CO}_2$ as solvent with organic compounds.$^{56}$ From another direction, computational efforts have added to understanding the role of the CO$_2$–philicity with different solutes, as for example, peracetylated β-cyclodextrins,$^{57}$ and carbonyl$^{58}$ and carbamides$^{59}$ (as simple models of aminoacids) derivatives. SO$_2$ is a principal cause of acid rain,$^{60}$ due to its ability to form SO$_3$ which in combination with water, leads to the formation of sulfuric acid. The reaction of carbonyl oxides with SO$_2$ is also relevant, due to the possible contribution of this reaction to acid rain, which was experimentally studied in the 1980s by Calvert et al.$^{61}$

**COMPUTATIONAL METHODS**

The geometries and properties of the CO$_2$:SO$_2$ heterodimers, the CO$_2$:(SO$_2$)$_2$ and (CO$_2$)$_2$:SO$_2$ heterotrimmers, and the CO$_2$:(SO$_2$)$_3$ and (CO$_2$)$_3$:SO$_2$ heterotetramers were optimized and analyzed through the use of the second-order Møller-Plesset perturbation theory (MP2)$^{62}$ with the aug-cc-pVDZ basis set.$^{63-66}$ In all cases, vibrational frequencies were
calculated in order to confirm that the structures correspond to true minima and to obtain the zero point vibrational energy (ZPE). Also, single-point CCSD(T)/aug-cc-pVTZ calculations were performed for the CO$_2$:SO$_2$ heterodimers, using MP2/aug-cc-pVDZ optimized geometries so as to obtain more accurate values. All these calculations were performed with the GAUSSIAN09 program.

Interaction energies, $E_{int}$, were computed as the difference in energy between the binary complex on one hand, and the sum of the energies of the two monomers on the other, using the monomer geometries from the optimized complex. Interaction energies for the heterodimers were corrected by the counterpoise procedure. In addition, binding energies, $E_b$, were computed as the difference in energy between the complex on one hand, and the sum of the energies of the optimized monomers on the other, taking into account also the ZPE. The multi-body procedure was applied to trimers (eq. 1) and tetramers (eq. 2), whereby the interaction energy can be expressed as:

$$E_{int} \text{ (trimer)} = \Sigma \Delta^2 E + \Delta^3 E \quad (1)$$
$$E_{int} \text{ (tetramer)} = \Sigma \Delta^2 E + \Sigma \Delta^3 E + \Delta^4 E \quad (2)$$

where $\Delta^n E$ is the $n^{th}$ complex term (2 = for dimers, 3 = for trimers, etc.) and the largest value of $n$ represents the total cooperativity in the full complex.

Further analysis was carried out via the Atoms in Molecules (AIM) approach at the MP2-level using the AIMAll program, and Natural Bond Orbital (NBO) treatment with the oB97XD functional, using the NBO6.0 program. The interaction energy of each CO$_2$:SO$_2$ heterodimer was decomposed via DFT-SAPT calculations at the PBE0/aug-cc-pVTZ level with the MOLPRO program. The DFT-SAPT interaction energy, $E_{DFT-SAPT}$, is obtained as the sum of five components (eq. 3): electrostatic ($E_{ele}$), exchange ($E_{exc}$), induction ($E_{ind}$), dispersion ($E_{dis}$) and higher-order contributions ($\delta_{HF}$).

$$E_{DFT-SAPT} = E_{ele} + E_{exc} + E_{ind} + E_{dis} + \delta_{HF} \quad (3)$$

For the monomers, the experimental ionization potentials were taken from NIST. They are 13.778 ± 0.002 eV for CO$_2$ and 12.5 ± 0.1 eV for SO$_2$. 
RESULTS AND DISCUSSION

The first section below presents the Molecular Electrostatic Potentials (MEP) of the monomers, which play an instrumental role in guiding the complexes into their optimized geometries. The succeeding sections detail the results first for the CO\textsubscript{2}:SO\textsubscript{2} heterodimers, next for the CO\textsubscript{2}:\(\text{SO}_2\)\textsubscript{3} and (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} heterotrimers, and finally, for the CO\textsubscript{2}:\(\text{SO}_2\)\textsubscript{3} and (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} heterotetramers.

Molecular Electrostatic Potential (MEP) of the Monomers

Carbon dioxide (CO\textsubscript{2}) and sulfur dioxide (SO\textsubscript{2}) monomers adopt \(D_\infty h\) and \(C_2v\) optimized geometries, respectively. MEP at the ±0.020 au contour of each molecule is illustrated in the top of Fig. 1, where red regions correspond to negative potentials and blue regions to positive. This potential is negative along the extensions of the C=O bonds of CO\textsubscript{2}, and a cylinder of positive potential encircles the central C atom. The potential around the SO\textsubscript{2} molecule is also largely positive with a negative lobe along the extension of each S=O bond. There is a prominent lobe of positive potential above and below the S atom, perpendicular to the molecular plane. The regions of positive potential in CO\textsubscript{2} and SO\textsubscript{2} can be described as π–holes about the central atom, which has its maximum of 37.5 kcal/mol for CO\textsubscript{2} and 31.2 kcal/mol for SO\textsubscript{2}. These areas represent candidate-binding sites for interactions with the negative potentials of partner molecules. Another perspective on the MEP is that computed on an isodensity surface, displayed in Fig. S1 of the Electronic Supplementary Information (ESI), calculated by the WFA-SAS program.

CO\textsubscript{2}:SO\textsubscript{2} Heterodimers

CO\textsubscript{2} and SO\textsubscript{2} engage in two different minima, illustrated in Fig. 2. The first and more stable one, A\textsubscript{1} with \(C_2v\) symmetry, has been previously described in the literature by experimental techniques.\textsuperscript{79} The second one, A\textsubscript{2} with \(C_1\) symmetry, has not been noted in the past even though its energy is very similar to that of A\textsubscript{1}: within around 0.3 kcal/mol at both the MP2 and CCSD(T) computational levels. As can be seen in Table 1, the interaction energies (\(E_{int}\)) at the MP2/aug-cc-pVDZ level are equal to −1.71 and −1.44 kcal/mol, respectively for A\textsubscript{1} and A\textsubscript{2}, following counterpoise correction of Basis Set Superposition Error (BSSE). These quantities rise slightly to −2.14 and −1.88 kcal/mol when the CCSD(T) approach is applied to the MP2 geometries. Very similar values can be seen in Table 1 for the binding energies (\(E_b\)), indicating very little deformation of the monomer geometries within the complex. Table 2 gathers the various thermodynamic quantities for the association
reactions in the CO$_2$:SO$_2$ heterodimers at room temperature (298 K). In both cases, $\Delta S^\circ$ is negative, as expected for an association reaction. When combined with a slightly negative $\Delta H^\circ$, the free energy of formation becomes positive at 298 K. It is interesting that the less negative value of $\Delta S^\circ$ for A2 as compared to A1 overrides its less negative $\Delta H^\circ$, leading to a less positive $\Delta G^\circ$ at 298 K. A similar stability reversal was observed previously for complexes of SO$_2$ with H$_2$CO and H$_2$CS.

In order to check the reliability of the aug-cc-pVDZ basis set, the structures of A1 and A2 were reoptimized with the larger aug-cc-pVTZ set. Only very minor changes in geometry were observed: The R(C··O) distances in A1 were slightly elongated by 0.040 Å, and R(O··O) in A2 contracted by 0.008 Å.

Both A1 and A2 are consistent with simple Coulombic interactions. A1 permits the negative regions about the SO$_2$ O atoms to approach the positive belt that encircles the CO$_2$ molecule. One of the SO$_2$ O atoms again overlaps with this positive CO$_2$ belt in A2, but a second attraction, albeit less direct, occurs between the negative potential of the CO$_2$ O atom and the positive region around the S of SO$_2$.

Within the context of AIM theory, A1 presents two symmetrical interactions with bond paths that link the C atom of CO$_2$ and the O atoms of SO$_2$, with R(C··O) = 3.047 Å. A2 is stabilized by a bond path between two O atoms, one on each molecule. These two O atoms are separated by 3.121 Å.

An alternate description of the bonding pattern arises from NBO analysis which emphasizes interorbital interactions. Table 3 and Fig. 3 summarize the important contributions via second-order perturbation energies $E(2)$. The pair of symmetrical interactions in A1 are described in terms of charge transfers from the lone pairs of the O atom to a $\pi^*$ antibonding CO orbital of CO$_2$. Each such interaction amounts to a value of $E(2)$ equal to 0.83 kcal/mol. The O···O bond that AIM predicts for A2, appears in NBO as a pair of different sorts of interactions. In the first, and stronger interaction, charge is transferred from the SO$_2$ O lone pair to a $\pi^*$ antibond of CO$_2$. This contribution of 1.41 kcal/mol is supplemented by a transfer in the opposite direction, from the O lone pair of CO$_2$ to a $\pi^*$ antibond of SO$_2$, which amounts to 0.37 kcal/mol. The specific shapes of the involved orbitals are illustrated in Fig. 3, which also partitions the totals in Table 3 into contributions from individual lone pairs and $\pi^*$ orbitals.

Decomposition of the total interaction energy into individual components opens another window into the nature of the interaction. These components, displayed in Table 4, show that
the repulsive exchange term is largest, in absolute terms, with values of 3.89 and 3.65 kcal/mol for $A_1$ and $A_2$, respectively. The attractive electrostatic and dispersion terms are quite similar to one another, between –2.44 and –2.88 kcal/mol. Induction energy is an order of magnitude smaller, and $\delta_{HF}$ even smaller. The two configurations have nearly identical electrostatic and induction energy, so the slightly greater stability of $A_1$ vs $A_2$ may be traced to its larger dispersion energy.

As two molecules begin to approach and interact with one another, they perturb one another’s electron clouds. The shifts in total electron density that occur as a result of the formation of each complex are illustrated in Fig. 4, where purple and yellow regions indicate respective gains and losses of density, relative to the isolated monomers. In both heterodimers, there is a loss of density near the C atom, facing SO$_2$. This pattern is consistent with the NBO interpretation of involvement of O lone pairs with CO $\pi^*$ antibonds. The O atoms of SO$_2$ that interact with CO$_2$ show a density gain, as does the O atom of CO$_2$ in $A_2$ that interacts with SO$_2$.

The redistribution patterns in Fig. 4 provide an interesting alternative view of the electron density to the AIM picture in Fig. 2. In the case of $A_1$, the two AIM C···O bonds are reflected by a shift of density from C to O, C losing density and O gaining. In contrast, both of the O atoms involved in the AIM O···O bond of $A_2$ gain density. The latter may perhaps be explained in part by the NBO view of the bonding which is dual in nature. There is first of all the transfer from the O lone pair of SO$_2$ to $\pi^*$ of CO$_2$, chiefly involving the O atom of SO$_2$ which is involved in the AIM bond. (Notably, the O atom from CO$_2$ which participates in this bond is not involved in the recipient CO$_2$ $\pi^*$ orbital, see Fig. 3.) As a second component, there is also a transfer in the reverse direction, from an O lone pair of CO$_2$ to a $\sigma^*$ orbital of SO$_2$. This transfer involves the O atom of CO$_2$ that does participate in this same AIM bond (but not the participating O atom from SO$_2$). So, the density shift in Fig. 4 may be thought of as the sum of two separate processes, each of which separately account for the change observed in the two O atoms involved in the AIM O···O bond of $A_2$.

**Heterotrimers**

Minimum-energy configurations for the mixed (CO$_2$)$_2$:SO$_2$ and CO$_2$:SO$_2$? heterotrimers were identified following a dual strategy: i) inserting the third molecule (CO$_2$ and SO$_2$ in each case) in various locations around the aforementioned CO$_2$:SO$_2$ optimized dimers, taking into account their MEP; and ii) fresh starting points, with no prejudice toward the heterodimer structures.
i. (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} Heterotrimers

The structures of the (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} heterotrimers optimized at the MP2/aug-cc-pVDZ computational level are gathered in Fig. 5. A total of 4 unique minima have been obtained (B1 to B4), with all of them derived in some sense from the A1 or A2 heterodimers, i.e., a principal geometrical disposition between the CO\textsubscript{2} and the SO\textsubscript{2} monomers noted in the heterodimers remains in these (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} structures. Specifically, in B1, B2, and B3, the SO\textsubscript{2} molecule is poised with its two O atoms roughly symmetrically disposed around CO\textsubscript{2}(1). One difference appears in the AIM analysis of B1 and B2, which places bonds between O atoms, not the C⋯O of A1. The O⋯O interaction that characterizes A2 is present in B2 and B3 in terms of CO\textsubscript{2}(2). The noncyclic B4 geometry places the SO\textsubscript{2} in the center, such that the two CO\textsubscript{2} molecules are situated very similarly to A2, although the AIM treatment of the electron density topology describes O⋯S bonds, rather than the O⋯O of A2. The second CO\textsubscript{2} molecule in noncyclic B3 also interacts with the central SO\textsubscript{2} much as it does in A2.

It is notable that there are no minima present in which the two CO\textsubscript{2} monomers interact directly with one another. This absence can be attributed to the weak forces between CO\textsubscript{2} molecules: the most stable T-shape CO\textsubscript{2} dimer\textsuperscript{80} has an interaction energy of –1.11 kcal/mol at the counterpoise-corrected CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ level, roughly half of that for the mixed CO\textsubscript{2}:SO\textsubscript{2} heterodimer.

The interaction energies and the pairwise energies derived from the multi-body analysis of these heterotrimers are reported in Table 5. The first point to note is that the pairwise terms are little changed from the interactions in the dimers. Specifically, the MP2/aug-cc-pVDZ interaction energies for A1 and A2 in Table 1 are –2.81 and –2.54 kcal/mol, respectively. The former value is nearly duplicated for \( E_{12} \) in B1, B2, and B3, where the SO\textsubscript{2} and CO\textsubscript{2}(1) molecules are disposed much as in A1. Likewise, \( E_{23} \), which reflects the interaction between SO\textsubscript{2} and CO\textsubscript{2}(2), is rather close to –2.54 kcal/mol in all four cases, as is \( E_{12} \) in B4, reflecting the similar configuration as in A2. As B3 and B4 are noncyclic, the two CO\textsubscript{2} molecules are far apart, which results in a near zero value of \( E_{13} \). In contrast, the closer approach of these two molecules in B1 and B2 results in a pairwise attraction of –1.56 and –1.35 kcal/mol, respectively. It is this latter CO\textsubscript{2}⋯CO\textsubscript{2} attraction which is primarily responsible for the greater stability of these two cyclic trimers, along with a small cooperative \( \Sigma^3E \) attraction up to –0.23 kcal/mol.

Table S1 summarizes the NBO analysis for the (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} heterotrimers. The O\textsubscript{lp}→\( \pi^* \)(CO) interactions of A1 remain in B1, B2, and B3, and in roughly equal measure.
Similarly, the O_\text{lp} \rightarrow \pi^*(\text{CO}) transfer of A2 is reproduced in B3 and B4, also with little diminution in its value. New interactions arise in B1 and B2. Both of these structures contain an O_\text{lp} \rightarrow \pi^*(\text{CO}) transfer involving the two CO_2 molecules, consistent with the O···O AIM bond in Fig. 5, with R(O···O) \sim 3.15 \text{ Å}. The attractive force between SO_2 and CO_2(2) can be traced to an O_\text{lp} \rightarrow \pi^*(\text{SO}) transfer, an interaction that is not seen in any dimers. It is interesting that this same O_\text{lp} \rightarrow \pi^*(\text{SO}) transfer, and in equal amounts, is characterized by AIM as an O···S bond in B1, but an O···O bond in B2.

ii. CO_2:(SO_2)_2 Heterotrimers

The 11 unique minima of the CO_2:(SO_2)_2 heterotrimer optimized at the MP2/aug-cc-pVDZ computational level are gathered in Fig. 6. C1 to C8 may all be classified as cyclic, and the three higher-energy trimers are linear. In order to understand the reasons underlying their geometries, it must first be pointed out that (SO_2)_2 dimers\(^{81}\) are more strongly bound than are the mixed SO_2:CO_2 heterodimer. There are three different (SO_2)_2 configurations, displayed in Fig. S2, and as reported in Table S2, their interaction energies vary between 2.52 and 3.02 kcal/mol, larger than the 1.88-2.14 kcal/mol range of the heterodimer at the same CCSD(T) level. It is thus the preferred SO_2···SO_2 intermolecular arrangements which play a dominant role in the CO_2:(SO_2)_2 heterotrimers. For example, the most stable C1 structure resembles the lowest energy (SO_2)_2 dimer in terms of the arrangement of the two SO_2 molecules, as does C2-C4. Nonetheless, one can see remnants of the preferred heterodimer arrangements within the structures of Fig. 6. For example, the A1 configuration is evident within C1 and C2, and C9-C11 are reminiscent of A2.

The interaction energies and the pairwise energies derived from the multi-body analysis of these heterotrimeric are reported in Table 6. The cyclic structures C1-C8 are bound by between 7.44 and 8.60 kcal/mol, and the remaining linear geometries by between 5.16 and 6.35 kcal/mol. Consistent with the strong binding between SO_2 molecules, it is \(E_{23}\) which is generally the largest term in Table 6. \(E_{12}\), comprising the interaction between CO_2 and a SO_2 molecule, is equal to \(-2.83\) kcal/mol for C1 and C2, the same as in the simple CO_2:SO_2 A1 dimer. Similarly, this same quantity is 2.51-2.56 kcal/mol in C9-C11 which is equal to \(\Delta E\) for A2. Structures C1-C6 exhibit the most negative three-body \(\Delta^3E\) term, corresponding to the strongest cooperativity. This quantity is much smaller in the linear geometries C9-C11.

Table S3 of the ESI contains the NBO analysis for the CO_2:(SO_2)_2 heterotrimers. The SO_2 molecules interact with one another primarily via O_\text{lp} \rightarrow \pi^*(\text{SO}) and \pi(\text{SO}) \rightarrow \pi^*(\text{SO}) transfers,
although C5 contains elements of an O\textsubscript{lp}→π*(SO) transfer. Interactions between SO\textsubscript{2} and CO\textsubscript{2} are largely a repeat of those seen in the SO\textsubscript{2}:(CO\textsubscript{2})\textsubscript{2} heterotrimers, namely O\textsubscript{lp}→π*(CO), and some of the reverse O\textsubscript{lp}→π*(SO). There is a new transfer, only in C6, from the O lone pair of SO\textsubscript{2} to a “lone vacant” C orbital of CO\textsubscript{2}. \(E(2)\) for this transfer is surprisingly large, at 2.02 kcal/mol. It is notable that this C···O interaction is not reflected by a corresponding bond in the AIM analysis of this structure.

**Heterotetramers**

Minima for 1:3 and 3:1 heterotetramers were searched taking as starting points the optimized heterotrimer structures. An exhaustive search yielded 16 (D1-D16) and 38 (E1-E38) different minima for the (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} and CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3} heterotetramers, respectively. The 16 (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} heterotetramers span an energy range of 4.98 kcal/mol, with total interaction energies between –6.98 and –11.95 kcal/mol. The CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3} structures span a slightly wider range of 6.64 kcal/mol, and are more strongly bound, varying between –9.12 and –15.76 kcal/mol.

Figs. S3 and S4 display the most stable minima of each type, with energies within 1 kcal/mol of one another. As reported in these figures and Tables S4 and S5, there are 3 such structures for (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} with similar energies and 10 for CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3}. Examination of these structures reveals that the D1 and D3 minima may be thought of as combining elements of the A1 CO\textsubscript{2}:SO\textsubscript{2} heterodimer and the B1 and B2 (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} heterotrimers, respectively. D2, on the other hand, has little resemblance to the prior dimer and trimer structures. All ten of the lowest-energy CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3} heterotetramers have one feature in common. The three SO\textsubscript{2} molecules form a ring, a sort of “SO\textsubscript{2}-wheel”, to which the CO\textsubscript{2} is attached.

Examination of Tables S4 and S5 reveals that the cooperativity effects are minimal at the four-body level, with \(\Delta^4E\) less than 0.06 and 0.11 kcal/mol for (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} and CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3} heterotetramers, respectively. Three-body effects are much larger in these complexes than in the heterotrimers, with \(-\Delta^3E\) as high as 0.59 and 1.29 kcal/mol for (CO\textsubscript{2})\textsubscript{3}:SO\textsubscript{2} and CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{3}, respectively, in comparison to only 0.23 and 0.45 kcal/mol for their (CO\textsubscript{2})\textsubscript{2}:SO\textsubscript{2} and CO\textsubscript{2}:(SO\textsubscript{2})\textsubscript{2} trimer counterparts. It is tempting to speculate that this cooperativity will continue to grow as the system approaches the situation approximating CO\textsubscript{2} dissolved in SO\textsubscript{2} solvent, or vice versa.

**SUMMARY AND CONCLUSIONS**
The CO$_2$:SO$_2$ heterodimer exists in two stable structures, both bound by about 2 kcal/mol. The more stable of the two belongs to the $C_2v$ point group, with the two O atoms of SO$_2$ symmetrically disposed above and below the C atom of CO$_2$. While AIM analysis leads to the idea of a pair of C···O bonds, NBO treatment describes the bonding in terms of charge transfer from O lone pairs to the CO $\pi^*$ antibonding orbitals. The geometry of the slightly less stable structure places one of the S–O bonds parallel to the OCO molecule. The AIM model of an O···O chalcogen bond contrasts with the NBO version which retains the O$_{lp}$→$\pi^*(CO)$ transfer of the global minimum, supplemented by transfer in the opposite direction from the O lone pair of CO$_2$ to a $\pi^*$ antibond of SO$_2$. Electron redistribution patterns are supportive of the NBO interpretation of the bonding. Both structures are consonant with attractions between oppositely charged regions of the molecular electrostatic potentials of the two monomers. Decomposition of the interaction energies point to electrostatic attraction and dispersion as the dominant attractive components, in roughly equal measure.

The various heterotrimers derived by adding either a CO$_2$ or SO$_2$ molecule to the heterodimer generally retain the dimer structure as a starting point. Due to the stronger interaction between pairs of SO$_2$ as compared to CO$_2$ molecules, the (SO$_2$)$_2$:CO$_2$ trimers are more strongly bound than (CO$_2$)$_2$:SO$_2$. In general, the most stable of the various heterotrimer structures are cyclic in that all three molecules interact directly with one another. In the case of the less stable linear trimers, it is SO$_2$ rather than CO$_2$ that tends toward the central position. The trimers present an interaction not observed in the dimers, the charge transfer from the lone pairs of a CO$_2$ O atom to the $\pi^*$ S–O antibonding orbital. Multi-body analysis suggests that cooperativity is fairly small in these heterotrimmers, less than 0.5 kcal/mol. The number of minima continues to increase as a fourth molecule is added, with 16 structures identified for (CO$_2$)$_3$:SO$_2$ and 38 for CO$_2$:(SO$_2$)$_3$. The most strongly bound, of the latter category, has a total interaction energy of 16 kcal/mol. Four body effects are quite small, although the total three-body energies are as large as 1.3 kcal/mol.

SUPPLEMENTARY MATERIAL

Electronic Supplementary Information (ESI) associated with this article can be found via Internet at http://rsc.com/. See DOI: 10.1039/XXXXXXXXXX.

ACKNOWLEDGMENTS
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REFERENCES

Table 1. Interaction ($E_{\text{int}}$) and binding ($E_b$) energies in kcal/mol for the CO$_2$:SO$_2$ heterodimers at MP2/aug-cc-pVDZ and at CCSD(T)/aug-cc-pVTZ (single point) computational levels.

<table>
<thead>
<tr>
<th>Complex</th>
<th>MP2</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{int}}$ (CC)$^a$</td>
<td>$E_b$ (ZPE)$^b$</td>
</tr>
<tr>
<td>A1</td>
<td>$-2.81$ ($-1.71$)</td>
<td>$-2.80$ ($-2.34$)</td>
</tr>
<tr>
<td>A2</td>
<td>$-2.54$ ($-1.44$)</td>
<td>$-2.52$ ($-2.12$)</td>
</tr>
</tbody>
</table>

$^a$In parenthesis, counterpoise correction of the Basis Set Superposition Error (BSSE).
$^b$In parenthesis, Zero Point Energy (ZPE) addition.

Table 2. Entropy ($S$) in cal/mol K, enthalpy and Gibbs free energies ($H$ and $G$) in kcal/mol, for the association reactions in the CO$_2$:SO$_2$ heterodimers at the MP2/aug-cc-pVDZ computational level at room temperature (298 K).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta S$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$-20.04$</td>
<td>$-1.88$</td>
<td>$4.09$</td>
</tr>
<tr>
<td>A2</td>
<td>$-17.60$</td>
<td>$-1.61$</td>
<td>$3.63$</td>
</tr>
</tbody>
</table>

Table 3. Second-order perturbation NBO energy $E(2)$, in kcal/mol, for the CO$_2$:SO$_2$ heterodimers at the oB97XD/aug-cc-pVDZ computational level.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Donor/Acceptor</th>
<th>Type</th>
<th>$E(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>SO$_2$/CO$_2$</td>
<td>O$_{lp}$→$\pi^*$ (CO)</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>SO$_2$/CO$_2$</td>
<td>O$_{lp}$→$\pi^*$ (CO)</td>
<td>0.83</td>
</tr>
<tr>
<td>A2</td>
<td>SO$_2$/CO$_2$</td>
<td>O$_{lp}$→$\pi^*$ (CO)</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>CO$_2$/SO$_2$</td>
<td>O$_{lp}$→$\sigma^*$ (SO)</td>
<td>0.37</td>
</tr>
</tbody>
</table>
**Table 4.** Interaction energy terms in kcal/mol for the CO$_2$:SO$_2$ complexes, calculated using the DFT-SAPT (PBE0/aug-cc-pVTZ) methodology.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{ele}}$</th>
<th>$E_{\text{exc}}$</th>
<th>$E_{\text{ind}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$\delta_{\text{HF}}$</th>
<th>$E_{\text{DFT-SAPT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>-2.68</td>
<td>3.89</td>
<td>-0.24</td>
<td>-2.88</td>
<td>-0.13</td>
<td>-2.03</td>
</tr>
<tr>
<td>A2</td>
<td>-2.55</td>
<td>3.65</td>
<td>-0.33</td>
<td>-2.44</td>
<td>-0.15</td>
<td>-1.82</td>
</tr>
</tbody>
</table>

**Table 5.** Multi-body energy terms in kcal/mol for the (CO$_2$)$_2$:SO$_2$ heterotrimer at MP2/aug-cc-pVDZ computational level. Subscripts 1, 2 and 3 refer to CO$_2$(1), SO$_2$ and CO$_2$(2) molecules in the heterotrimer complexes (see Fig. 5).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{12}$</th>
<th>$E_{13}$</th>
<th>$E_{23}$</th>
<th>$\Sigma\Delta^2E$</th>
<th>$\Sigma^3E$</th>
<th>total $E_{\text{int}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
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<td>-1.56</td>
<td>-2.23</td>
<td>-6.62</td>
<td>-0.23</td>
<td>-6.85</td>
</tr>
<tr>
<td>B2</td>
<td>-2.82</td>
<td>-1.35</td>
<td>-2.44</td>
<td>-6.61</td>
<td>-0.21</td>
<td>-6.82</td>
</tr>
<tr>
<td>B3</td>
<td>-2.83</td>
<td>-0.06</td>
<td>-2.57</td>
<td>-5.46</td>
<td>0.02</td>
<td>-5.44</td>
</tr>
<tr>
<td>B4</td>
<td>-2.54</td>
<td>-0.05</td>
<td>-2.55</td>
<td>-5.14</td>
<td>0.05</td>
<td>-5.09</td>
</tr>
</tbody>
</table>
Table 6. Multi-body energy terms in kcal/mol for the CO$_2$(SO$_2$)$_2$ heterotrimers at MP2/aug-cc-pVDZ computational level. Subscripts 1, 2 and 3 refer to CO$_2$(1), SO$_2$ and CO$_2$(2) molecules in the heterotrimer complexes (see Fig. 6).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{12}$</th>
<th>$E_{13}$</th>
<th>$E_{23}$</th>
<th>$\Sigma \Delta^2 E$</th>
<th>$\Delta^3 E$</th>
<th>total $E_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-2.83</td>
<td>-2.17</td>
<td>-3.15</td>
<td>-8.15</td>
<td>-0.45</td>
<td>-8.60</td>
</tr>
<tr>
<td>C2</td>
<td>-2.83</td>
<td>-1.78</td>
<td>-3.48</td>
<td>-8.09</td>
<td>-0.37</td>
<td>-8.46</td>
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<tr>
<td>C3</td>
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<td>C4</td>
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<td>-7.64</td>
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</tr>
<tr>
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<td>-7.86</td>
</tr>
<tr>
<td>C6</td>
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<td>-2.16</td>
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<td>-7.74</td>
</tr>
<tr>
<td>C7</td>
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<td>C8</td>
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<td>-7.44</td>
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<tr>
<td>C9</td>
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<td>-5.27</td>
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</tr>
<tr>
<td>C11</td>
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<td>-2.55</td>
<td>0.10</td>
<td>-4.99</td>
<td>-0.17</td>
<td>-5.16</td>
</tr>
</tbody>
</table>
**Figure 1.** Molecular Electrostatic Potential (MEP) for the monomers CO$_2$ and SO$_2$ at the $\pm 0.020$ au contour at the MP2/aug-cc-pVDZ computational level. Lefthand diagram represents molecular plane, and the normal plane is shown on the right. Red and blue regions indicate negative and positive regions, respectively.

**Figure 2.** CO$_2$:SO$_2$ heterodimers optimized at the MP2/aug-cc-pVDZ computational level. Blue dotted lines link atoms which present interatomic AIM BCPs, with interatomic distances in Å. Complexes are arranged in ascending order of energy.
**Figure 3.** Orbital interactions (NBO, isovalue ±0.020 au) for the CO$_2$:SO$_2$ heterodimers at DFT $\omega$B97XD/aug-cc-pVDZ computational level. $E(2)$ in kcal/mol.

<table>
<thead>
<tr>
<th>A1</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Diagrams" /></td>
<td><img src="image2" alt="Diagrams" /></td>
</tr>
<tr>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.09$</td>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.09$</td>
</tr>
<tr>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.61$</td>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.61$</td>
</tr>
<tr>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.13$</td>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.13$</td>
</tr>
<tr>
<td><img src="image3" alt="Diagrams" /></td>
<td><img src="image4" alt="Diagrams" /></td>
</tr>
<tr>
<td>CO$_2$/SO$<em>2$ $O</em>{lp} \rightarrow \sigma^*(SO)$ $E(2) = 0.37$</td>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 0.09$</td>
</tr>
<tr>
<td><img src="image5" alt="Diagrams" /></td>
<td><img src="image6" alt="Diagrams" /></td>
</tr>
<tr>
<td>SO$_2$/CO$<em>2$ $O</em>{lp} \rightarrow \pi^*(CO)$ $E(2) = 1.32$</td>
<td></td>
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</tbody>
</table>
Figure 4. Electron Density Shifts (EDS) occurring within CO$_2$:SO$_2$ heterodimers at MP2/aug-cc-pVDZ level. Purple and yellow colors refer to gain and loss of density in complex, respectively, relative to isolated monomers. Isosurface value ±0.0005 au.

Figure 5. (CO$_2$)$_2$:SO$_2$ heterotrimers optimized at MP2/aug-cc-pVDZ computational level. Broken blue lines link atoms which present interatomic AIM BCPs, with interatomic distances in Å. Complexes are arranged in ascending order of energy.
Figure 6. $\text{CO}_2(\text{SO}_2)_2$ heterotrimers optimized at the MP2/aug-cc-pVDZ level. Blue broken lines link atoms which present interatomic AIM BCPs, with interatomic distances in Å. Complexes are arranged in ascending order of energy.
Two stable minima for the 1:1 heterodimer of CO$_2$:SO$_2$, both bound by about 2 kcal/mol. Binding is dominated by charge transfer from O lone pairs of SO$_2$ to CO $\pi^*$ antibonding orbitals.