

Accepted Manuscript

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PII: S0009-2614(14)00251-6

DOI: <http://dx.doi.org/10.1016/j.cplett.2014.03.084>

Reference: CPLETT 32075

To appear in: *Chemical Physics Letters*

Received Date: 20 January 2014

Accepted Date: 26 March 2014

Please cite this article as: E.S. Fabián, F. Ingrosso, A. Lambert, M.I. Bernal-Uruchurtu, M.F. Ruiz-López, Theoretical insights on electron donor-acceptor interactions involving carbon dioxide, *Chemical Physics Letters* (2014), doi: <http://dx.doi.org/10.1016/j.cplett.2014.03.084>

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Theoretical insights on electron donor-acceptor interactions involving carbon dioxide

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Abstract

Electron donor-acceptor (EDA) interactions are widely involved in chemistry and their understanding is essential to design new technological applications in a variety of fields ranging from material sciences and chemical engineering to medicine. In this work, we study EDA complexes of carbon dioxide with ketones using several *ab initio* and Density Functional Theory methods. Energy contributions to the interaction energy have been analyzed in detail using both variational and perturbational treatments. Dispersion energy has been shown to play a key role in explaining the high stability of a non-conventional structure, which can roughly be described by a cooperative EDA interaction.

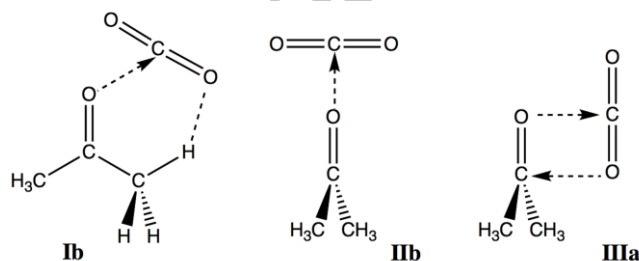
Keywords: Electron donor-acceptor interactions, carbon dioxide, *ab initio* methods, density functional theory, dispersion energy.

I. INTRODUCTION

Intermolecular interactions involving carbon dioxide have attracted increasing attention in recent years in connection with a variety of technological applications such as carbon dioxide capture and sequestration or separation and synthetic processes in supercritical carbon dioxide (scCO₂).[1-4] In particular, efforts to develop molecules and materials that can be easily solvated in scCO₂ have led to the discovery of weak electron donor-acceptor (EDA) interactions between CO₂ (Lewis acid, LA) and compounds containing fluorine atoms (Lewis base, LB), such as fluorinated polymers.[5] The next milestone for advances in the development of CO₂-philic molecules was represented by the characterization of EDA interactions between CO₂ and carbonyl groups.[6] Indeed, playing with different substituents and building polymers containing the carbonyl function has allowed tuning the solubility in CO₂ and has opened the door to a wider range of applications of this solvent in green processes. Among the carbonyl-based, CO₂-phile materials that have been developed are functionalized silicones,[7] diglycolic acid esters,[8] poly(ether-carbonate) copolymers,[9] sugar[10] and amide[11, 12] derivatives.

Theoretical studies on model systems have been carried out to analyze the interactions of CO₂ with carbonyl compounds.[13-25] Former studies did confirm the existence of EDA complexes in which, as expected from simple chemical considerations, CO₂ play the role of the electron acceptor (*i.e.*, it behaves as a Lewis acid). Recent work, however, has revealed the existence of other unconventional EDA structures. On the one hand, when the carbonyl derivative is conveniently activated (for instance through perfluorinated groups) the donor-acceptor role is inversed and CO₂ behaves as the Lewis base, the carbonyl compound playing the role of the Lewis acid. On the other hand, in ketones, esters or amides (but not in aldehydes), a dual interaction occurs.[23-25] In that case, CO₂ and the carbonyl compound behave as the electron

donor and acceptor, respectively and reciprocally. An illustrative example is shown in Scheme 1 (structure IIIa), which also shows other classical structures reported in the literature (Ib and IIb). For simplicity, we use the same labeling than in previous works. IIIa has been shown to display a comparable or even larger stability compared to Ib, which in the past had been generally considered to correspond to the global energy minimum. For example, amides and carbamides lead to IIIa complexes with interactions energies as large as 6 kcal/mol.[25] This result is particularly relevant in the context of solvation studies in $scCO_2$ and may have significant implications in terms of CO_2 -phile molecules development. However, the nature of the stabilizing energy contributions responsible for the unexpected IIIa structure still remains unclear.



Scheme 1. Structure of the complexes (acetone- CO_2) considered in this paper. The labeling corresponds to the one proposed in previous studies.[23-25] Electron donor-acceptor interactions are schematically represented as dashed arrows (oriented from the electron donor to the acceptor).

In order to get new insights on this topic, we have analyzed the potential energy surface (PES) of the acetone- CO_2 model system using different theoretical approaches. First, a decomposition of the interaction energy has been made in terms of Coulomb, exchange, correlation and electron

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4 kinetic energy contributions. The results of DFT methods are compared to those of HF, MP2 and
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6 CCSD(T) *ab initio* calculations. Through this comparison, we aimed to assess the ability of
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8 commonly used exchange-correlation functionals to describe cooperative EDA interactions (note
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10 that some previous DFT studies have already been devoted to EDA systems[26, 27]). Then,
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12 using the symmetry-adapted perturbation theory (SAPT),[28, 29] we have evaluated the
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14 electrostatic, induction, exchange and dispersion contributions to the interaction energy in order
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16 to clarify their respective role in the stabilization of conventional and unconventional complexes
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18 of carbonyl dioxide with carbonyl compounds.
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26 II. COMPUTATIONAL DETAILS

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28 The study has been carried out with different *ab initio* and DFT methods and we refer the
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30 reader to the Supplemental Material (SM) section for a full bibliography on all the methods and
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32 codes used.
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36 Full geometry optimization for the IIIa complex was attempted with the whole set of methods
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38 considered here. The nature of the stationary points found (minimum or saddle point) was
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40 inspected by a vibrational frequency analysis (except in the case of QCISD and CCSD(T)
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42 optimizations, for which frequency calculations would be too costly). Afterwards, analyses of
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44 the interaction energy were done with some selected approaches by computing the different
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46 contributions along an *ad hoc* intermolecular coordinate that links the conventional T-shaped
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48 structure IIb (CO₂ as LA) to the unconventional cyclic one IIIa (CO₂ as both LA and LB).
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50 Specifically, we carried out relaxed scan computations of the complex at the MP2/aug-cc-pVDZ
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52 level by varying the angle α (C(carbonyl)-O(carbonyl)-C(CO₂)) while keeping the C(carbonyl)-
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54 O(carbonyl)-C(CO₂)-O(CO₂) atoms coplanar. Single-point energy calculations were then carried
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4 out (same basis set) at the CCSD(T) level and using DFT methods with different exchange-
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6 correlation functionals. In agreement with our previous study,[24] we checked that the increase
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8 of the basis set from aug-cc-pVDZ to aug-cc-pVTZ does not lead to significant changes in the
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10 results. The physical meaningful components of the interaction energy were obtained using
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12 symmetry-adapted perturbation theory (SAPT), which has already been successfully used to
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14 study some intermolecular complexes of carbon dioxide.[30-32] The role of basis set
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16 superposition errors (BSSE) on interaction energies and geometries was estimated using the
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18 counterpoise correction method[33] and the seven-point scheme of Dannenberg and co-
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20 workers.[34, 35]
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28 III. RESULTS

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30 Full geometry optimization of the unconventional structure IIIa has been done with different
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32 *ab initio* and DFT methods, with and without BSSE corrections. Table 1 summarizes the results
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34 for intermolecular distances and interaction energies. The obtained values are crucially
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36 dependent on the theoretical approach. Thus, many commonly used DFT methods, such as
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38 BLYP, B3LYP or PBE0, fail to predict an energy minimum for IIIa. M11-L and LC-BLYP do
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40 predict a stationary point but the frequency analysis shows one and two imaginary frequencies,
41
42 respectively. When the geometry of the complex is optimized without BSSE corrections, the best
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44 results (compared to CCSD(T)) are obtained with the range-separated functional M11 for
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46 intermolecular distances and with the M06-2X method for the interaction energy. When BSSE
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48 corrections are taken into account, the best results (the reference is now MP2) are obtained with
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50 the range-separated dispersion-corrected functional ω B97XD for both, geometry and energy,
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52 although there are several other DFT methods that lead to comparable results. Dispersion
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corrections and long-range corrections to the non-Coulomb part of the exchange functional seem therefore important to describe the complex IIIa. However, it should be noted that some hybrid range-separated functionals such as CAM-B3LYP or LC- ω PBE fail to predict an energy minimum for IIIa.

Table 1. Interatomic C \cdots O distances (R_{CO} , Å), interaction energies (E_{int} , kcal/mol) and interaction energies corrected for BSSE (E_{int}^{CP} , kcal/mol) obtained for the acetone – CO₂ IIIa complex using different *ab initio* and DFT methods. The shortest C \cdots O distance corresponds to O_{acetone} \cdots C_{CO2}. The geometries have been fully optimized with each method. The vibrational frequency analysis shows that all optimized structures correspond to energy minima, except in the case of M11-L (one imaginary frequency) and LC-BLYP (two imaginary frequencies). In the case of QCISD and CCSD(T), frequency calculations were not attempted due to computational limitations.

Method	Geometry optimization without BSSE corrections			Geometry optimization including BSSE corrections		
	R_{CO}	E_{int}	E_{int}^{CP}	R_{CO}	E_{int}	E_{int}^{CP}
MP2	2.946	2.956	-4.01	3.040	3.114	-2.59
QCISD	2.953	3.006	-3.95			
CCSD(T)	2.931	2.963	-4.09			
M06-2X	2.821	2.940	-3.62	2.845	2.974	-3.12
M06-HF	2.813	2.971	-3.59	2.825	3.017	-3.09
M11	2.861	2.940	-3.24	2.902	3.000	-2.79
M11-L	2.859	3.157	-1.94	2.942	3.090	-1.32
LC-BLYP	2.814	3.016	-3.61	2.801	3.113	-3.17
BLYP-D	3.022	3.102	-2.42	3.026	3.177	-2.03
ω B97X	2.874	3.035	-3.26	2.893	3.076	-2.88
ω B97XD	3.010	3.100	-2.76	3.019	3.172	-2.44
HF, BLYP, B3LYP, BHandHLYP, PBEPBE, PBE0, CAM-B3LYP, LC- ω PBE	No stationary point found for IIIa structure					

Total energies for the acetone – CO₂ complex as a function of the α angle linking structures IIb to IIIa are reported in Figure 1 using some representative theoretical methods (energies are given relative to the T-shaped structure IIb). As shown, MP2, CCSD(T), M06-2X and ω B97XD calculations predict an energy minimum for $\alpha \cong 100^\circ$ (IIIa structure) and the same methods predict a flat PES around $\alpha=180^\circ$ (structure IIb). Conversely, HF, PBE0, BHandHLYP, BLYP and B3LYP do not predict an energy minimum for IIIa but they do so for IIb. It is worth noting that upon full optimization of IIb, all methods lead to a stationary point, but its nature depends on method. Thus IIb is a true energy minimum at the HF, B3LYP, ω B97XD and M06-2X levels, a first-order transition state at the PBE0, BHandHLYP and BLYP levels and a second-order saddle point in MP2 calculations.

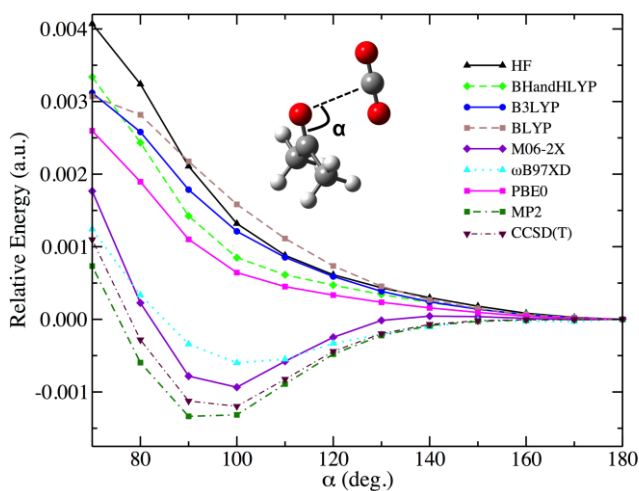


Figure 1. Potential energy of the acetone-CO₂ complex (a.u.) along the α coordinate (angle C=O...C) chosen for our study. Structures IIb and IIIa correspond to $\alpha=180^\circ$ and $\alpha \cong 100^\circ$, respectively. Energy values are given relative to T-shaped structure IIb ($\alpha=180^\circ$). Results are reported for selected quantum chemistry methods.

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7 The fact that the Hartree-Fock (HF) potential energy surface of this system does not present a
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9 minimum for the IIIa structure, in contrast to MP2 or coupled cluster approaches, emphasizes the
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11 crucial role of correlation effects for describing CO₂-carbonyl compound interactions. In the
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13 following discussion, we will focus our analysis on the variation of the relative contributions to
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15 the total interaction energy in going from structure IIb to structure IIIa trying to get a deeper
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17 insight into the origin of such interactions and the reasons that make them so dependent on the
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19 theoretical method.
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23 To start with, let us consider the HF energy. In Figure 2, we report the total potential (V) and
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25 kinetic (T) energies along the chosen coordinate (the angle α) as well as the decomposition of
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27 the potential term into Coulomb (V_C) and exchange (V_{ex}) contributions. Approaching the value
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29 of $\alpha=100^\circ$, which corresponds to the IIIa structure, the potential energy (V) has a minimum,
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31 arising from the stabilizing contribution of both Coulomb and exchange interactions. The total
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33 kinetic energy instead exhibits a maximum in this region. Qualitatively, therefore, V and T
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35 display the expected behavior for the formation of a chemical bond. The quantitative comparison
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37 between these terms, however, shows that the kinetic energy rises more rapidly than the potential
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39 energy decreases, so that the variation of the total energy T+V (black solid curve in Figure 1) is
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41 globally repulsive and does not exhibit a minimum value in the proximity of the IIIa region.
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48 Let us now consider the results from the correlated *ab initio* and DFT-based calculations. In
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50 the case of DFT-based methods, we have two series of energy calculations. In the first case, we
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52 use the HF orbitals/density so that the kinetic and Coulomb contributions are the same for all
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54 methods and the comparison can focus on the exchange-correlation terms. The corresponding
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56 results are included as supplemental material and will not be discussed hereafter in detail. In the
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second case, we use the Kohn-Sham orbitals/densities, as obtained with each specific method. The results are gathered in Figures 3 and 4, where we have plotted the exchange and correlation contributions to the interaction energy, respectively.

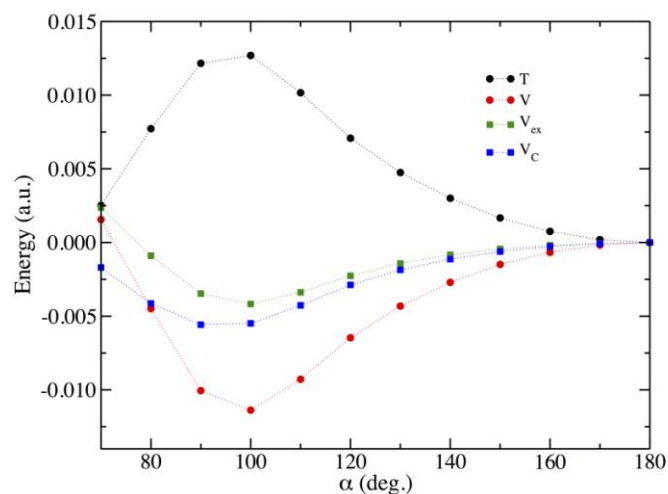


Figure 2. Relative values of the Hartree-Fock potential (V) and kinetic (T) energies along the coordinate α with respect to the T-shaped structure IIb ($\alpha=180^\circ$). The Coulombic (V_C) and exchange (V_{ex}) contributions to the potential energy are displayed as well.

As shown in Figure 3, most methods predict a minimum for the exchange energy at about $\alpha=100^\circ$ (in agreement with HF results) although significant differences are found among the different functionals and particularly with M06-2X and ω B97XD. The first method does not predict a minimum at all whereas the second predicts a very shallow one. Interestingly when the HF orbitals/densities are used (see SM), the decrease of the non-local exchange energy obtained in the HF calculations are qualitatively well reproduced by all DFT methods, including M06-2X and ω B97XD for which very different curve shapes were obtained using the Kohn-Sham orbitals/densities, as shown in Figure 3.

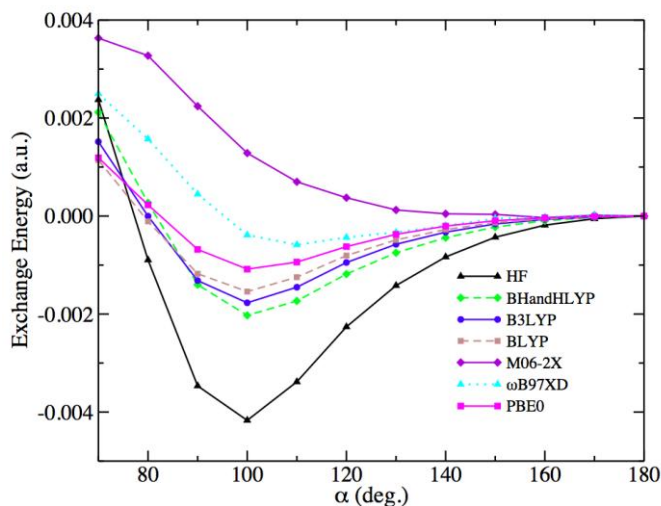


Figure 3. Relative values of the exchange energy (a.u.) for the acetone-CO₂ complex along the coordinate α with respect to the T-shaped structure IIb ($\alpha=180^\circ$). Exchange energy includes for hybrid methods, local and non-local contributions.

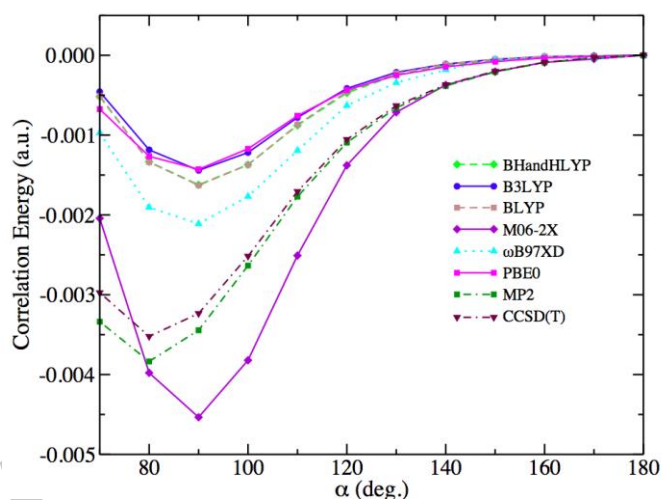


Figure 4. Relative values of the correlation energy (a.u.) for the acetone-CO₂ complex along the α coordinate with respect to the T-shaped structure IIb ($\alpha=180^\circ$).

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4 The shape of the correlation energy curves shown in Figure 4 for the MP2 and CCSD(T)
5 calculation is similar. Both display a minimum around $\alpha=80^\circ$ with comparable depth (-0.00352
6 au or -2.21 kcal/mol at the CCSD(T) level) to the exchange minimum (-0.00417 au or -2.62
7 kcal/mol at the HF level). All the DFT functionals tested here predict this correlation energy
8 minimum (using either the HF or Kohn-Sham electron densities) but the minima appear at
9 slightly larger α values (around $\alpha=90^\circ$) and their depth is very dependent on method. The M06-
10 2X functional overestimates the depth of the well (note that when the HF electron density is
11 used, M06-2X provides a reasonably good estimate of the correlation energy variation, see SM)
12 whereas other DFT methods underestimate it. A special comment is required in the case of
13 ω B97XD calculations since this method also includes an empirical dispersion correction. The
14 results for this term are shown in the SM; the shape of the curve is similar to the correlation term
15 in Figure 4 with a minimum at 80° and a well depth of 0.00153 au (0.96 kcal/mol).
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34 35 36 **IV. DISCUSSION.**

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38 According to the NBO (natural bond orbital) analysis[24, 25] the intermolecular interaction in
39 IIIa involves two donor-acceptor terms coming from: 1) the π orbital of the carbonyl compound
40 interacting with the π^* orbital of CO_2 and 2) the n orbital of CO_2 interacting with a π^* orbital of
41 the carbonyl compound. This dual LA-LB interaction is consistent with the stabilizing Coulomb
42 + exchange HF energy described above. However, the results show also that such a contribution
43 is clearly insufficient to compensate the associated increase in electronic kinetic energy. In other
44 words, the formation of a stable IIIa complex is only possible by the supplementary stabilizing
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In order to quantify in a more formal way the role of dispersion energy on the intermolecular interaction, a SAPT analysis has been carried out (for this study, we use the MP2/aug-cc-pVDZ optimized structures). In the SAPT method, the unperturbed Hamiltonian of the dimer is the sum of the Fock operators for the monomers and the perturbation Hamiltonian contains two terms: the intramonomer correlation operator and the intermolecular interaction operator. The total interaction energy is obtained as a sum of perturbative corrections corresponding to electrostatic, induction and dispersion contributions and their respective exchange counterparts. At second order:

$$E_{\text{int}}^{\text{SAPT}} = E_{\text{elec}}^1 + E_{\text{exch}}^1 + E_{\text{ind}}^2 + E_{\text{disp}}^2 + E_{\text{exch-ind}}^2 + E_{\text{exch-disp}}^2$$

For systems with polar molecules, it is usual to add a correction to this energy, δ_{HF} , that accounts for higher order terms and that is defined as:

$$\delta_{\text{HF}} = E_{\text{int}}^{\text{HF}} - E_{\text{elec}}^1 - E_{\text{exch}}^1 - E_{\text{ind}}^2 - E_{\text{exch-ind}}^2$$

where $E_{\text{int}}^{\text{HF}}$ is the counterpoise corrected supermolecular interaction energy.

First of all, we make a comparison of SAPT contributions to the interaction energy for the conventional Ib complex, usually assumed to be the global minimum, the IIIa complex, which involves a cooperative EDA interaction, and the structure IIb, which, as said above, is an energy minimum at the HF level but a second-order saddle point at the MP2 level. The results are summarized in Table 2. For all cases, the electrostatic energy is the main stabilizing factor and it decreases (in absolute value) in the order Ib>IIIa>IIb. The repulsive exchange contribution is by far the largest one in Ib and IIIa but in the case of IIb its magnitude is comparable to the absolute value of the electrostatic energy. The induction and the dispersion energies, though smaller compared to the electrostatic and the exchange terms, provide a significant contribution to the

stabilization energy for the three complexes. Note, incidentally, that the higher-order terms estimated by the δ_{HF} contribution are small, around 0.2-0.3 kcal/mol. From the comparison of the SAPT energy contributions in the three complexes, it is clear that only complex IIIa is crucially dependent on E_{disp} . In the case of Ib and IIb, the interaction energy E_{int}^{SAPT} is larger in absolute value than the dispersion energy, meaning that these complexes would be predicted to be more stable than the separated monomers even if the dispersion term was neglected, as found with the HF method. On the contrary, neglecting the dispersion contribution would lead to an unstable IIIa complex (or to a very slightly stable complex if the δ_{HF} energy correction is considered).

Table 2. Comparison between the interaction energies for acetone-CO₂ complexes as calculated with the SAPT method. In all cases, we use the MP2 optimized geometries of the complex and the aug-cc-pVDZ basis set. Deformation energy is not taken into account (*i.e.*, the monomers are taken at their geometry in the complexes). The exchange term in this table contains first and second order corrections.

Complex	E_{elec}^1	E_{exch}^{1+2}	E_{ind}^2	E_{disp}^2	E_{int}^{SAPT}	$E_{int}^{SAPT} + \delta_{HF}$
Ib	-5.19	6.42	-2.29	-2.93	-3.99	-4.27
IIb	-3.91	3.89	-1.29	-2.07	-3.38	-3.56
IIIa	-4.52	6.98	-2.36	-3.57	-3.47	-3.69

A striking result in Table 2 is the small difference between the SAPT interaction energies for IIb and IIIa complexes. This finding is consistent with the *ab initio* MP2 and CCSD(T) PES in Figure 1, although the SAPT energy difference is even smaller. To complete the analysis, we calculated the SAPT contributions along the angle α used above for constructing the PES. The results for different terms are plotted in Figure 5. Note that the total SAPT interaction energy

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4 curve corresponds to the corrected energy $E_{\text{int}}^{\text{SAPT}} + \delta_{\text{HF}}$ and does not include the deformation
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6 energy of the monomers (*i.e.*, the energy required to transform the isolated monomers optimized
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8 structures into their geometry in the optimized dimer). This last term is small and has been
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10 omitted for simplicity but it can explain part of the difference with respect to the *ab initio* PES.
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12 Indeed, the SAPT energy exhibits a similar shape to the MP2 and CCSD(T) curves represented
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14 in Figure 1, therefore confirming the existence of an energy minimum for $\alpha \approx 100^\circ$, as in the
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16 case of structure IIIa. The curves confirm the conclusions derived from the results gathered in
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18 Table 1. It appears that the three stabilizing contributions to the interaction energy in the
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20 framework of perturbation theory, electrostatic, induction and dispersion, do favor complex IIIa
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22 with respect to the standard EDA complex IIb ($\alpha=180^\circ$). The results emphasize once again the
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24 remarkable role of the dispersion contribution, as can be deduced if one compares the curves for
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26 E_{disp} and E_{Total} . Indeed, for α slightly above 90° (structure IIIa), the two curves intersect,
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28 meaning that the stabilizing role of electrostatic + induction energies is counterbalanced by
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30 exchange contributions, which reach an energy maximum in that region. The perturbation
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32 analysis confirms therefore the trends discussed above on the basis of the variational
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34 supermolecular calculations and the evaluation of the independent Hartree-Fock and correlation
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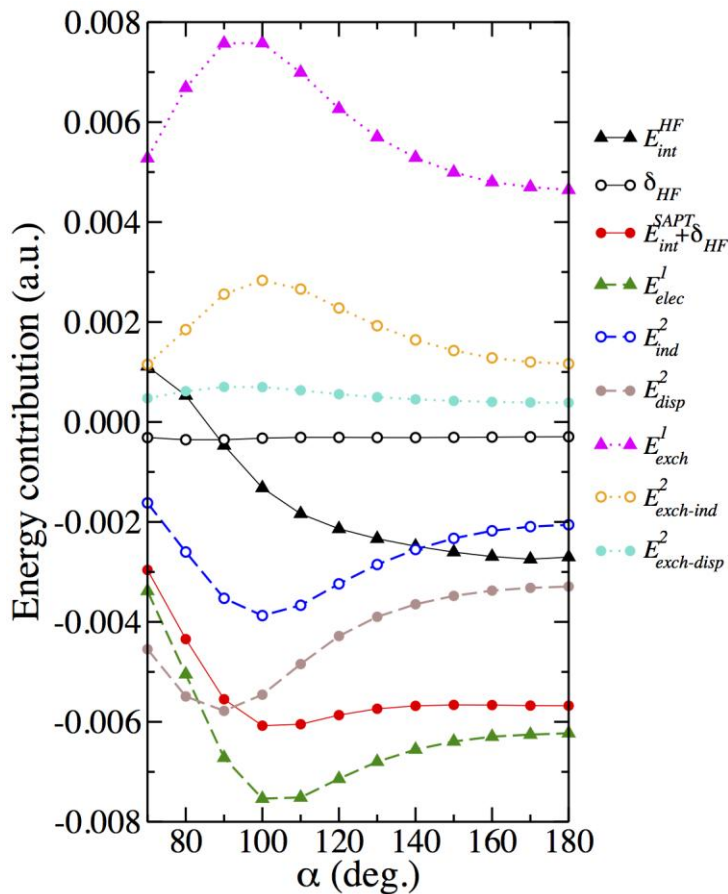


Figure 5. Contributions to the SAPT interaction energy for the acetone-CO₂ complex along the coordinate α .

IV. CONCLUSION

The reported analysis, which combines variational and perturbational molecular orbital theories, allows us to highlight the key role played by dispersion energy in the IIIa-type EDA complexes formed between carbonyl dioxide and carbonyl compounds. Accordingly, such complexes cannot be predicted by HF methods or by many commonly used DFT-based techniques. We have shown that the variations of exchange and correlation contributions moving from IIb to IIIa, though qualitatively correct in most cases, are significantly underestimated by

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4 all tested DFT methods. Clearly, the subtle combination of intermolecular interactions leading to
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6 the stabilization of IIIa, among which dispersion energy has been shown to give an important
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8 contribution, is difficult to capture by approximated DFT functionals of different type (hybrid,
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10 GGA, meta-GGA). Overall, range-separated hybrid functionals, in which the interelectronic
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12 Coulomb operator is split into a short-range and a long-range part, and those including an
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14 empirical dispersion correction of the interaction energy, appear to perform better than the
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16 others. However, this trend is not systematic and some hybrid range-separated functionals do not
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18 predict an energy minimum for IIIa (CAM-B3LYP, LC- ω PBE). In spite of these apparent
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20 inconsistencies, our findings point out possible directions to improve DFT techniques in the
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22 future. Note finally that the unconventional structures IIIa might exist in many other complexes
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24 involving CO₂ but further work will be necessary to confirm this hypothesis.
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33 SUPPLEMENTAL MATERIAL

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37 References on electronic methods used. Total, exchange and correlation energies obtained with
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39 the HF density. Dispersion energy with the ω B97XD method.
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45 ACKNOWLEDGMENTS

46
47 ESF thanks the University of Alicante, Spain, for a sabbatical grant.
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Highlights

- We study the potential energy surface of the acetone - carbon dioxide complex with ab initio methods
- We analyze the contributions to the interaction energy with variational and perturbative approaches
- We describe non-conventional structures in which dispersion energy plays a key role.
- We show that current density functional theory methods are unsuitable to describe this type of complexes.

ACCEPTED MANUSCRIPT

