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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 Letter, 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.

1. 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 (scCO_2) [1–4]. In particular, efforts to develop molecules and materials that can be easily solvated in scCO_2 have led to the discovery of weak electron donor–acceptor (EDA) interactions between CO_2 (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 CO_2-philic molecules was represented by the characterization of EDA interactions between CO_2 and carbonyl groups [6]. Indeed, playing with different substituents and building polymers containing the carbonyl function has allowed tuning the solubility in CO_2 and has opened the door to a wider range of applications of this solvent in green processes. Among the carbonyl-based, CO_2-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 CO_2 with carbonyl compounds [13–25]. Former studies did confirm the existence of EDA complexes in which, as expected from simple chemical considerations, CO_2 plays 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 CO_2 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, CO_2 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.

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,

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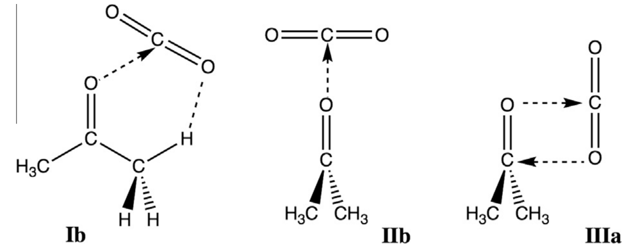

Scheme 1. Structure of the complexes (acetone–CO_2) considered in this Letter. The labeling corresponds to the one proposed in previous studies [23–25]. Electron donor–acceptor interactions are schematically represented as dashed arrows (oriented from the electron donor to the acceptor).

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

2. Computational details

The study has been carried out with different *ab initio* and DFT methods and we refer the reader to the Supplemental material (SM) section for a full bibliography on all the methods and codes used.

Full geometry optimization for the IIIa complex was attempted with the whole set of methods considered here. The nature of the stationary points found (minimum or saddle point) was inspected by a vibrational frequency analysis (except in the case of QCISD and CCSD(T) optimizations, for which frequency calculations would be too costly). Afterwards, analyses of the interaction energy were done with some selected approaches by computing the different contributions along an *ad hoc* intermolecular coordinate that links the conventional T-shaped structure IIb (CO_2 as LA) to the unconventional cyclic one IIIa (CO_2 as both LA and LB). Specifically, we carried out relaxed scan computations of the complex at the MP2/aug-cc-pVDZ level by varying the angle α (C(carbonyl)-O(carbonyl)-C(CO_2)) while keeping the C(carbonyl)-O(carbonyl)-C(CO_2)-O(CO_2) atoms coplanar. Single-point energy calculations were then carried out (same basis set) at the CCSD(T) level and using DFT methods with different exchange–correlation functionals. In agreement with our previous study [24], we checked that the increase of the basis set from aug-cc-pVDZ to aug-cc-pVTZ does not lead to significant changes in the results. The physically meaningful components of the interaction energy were obtained using symmetry-adapted perturbation theory (SAPT), which has already been successfully used to study some intermolecular complexes of carbon dioxide [30–32]. The role of basis set superposition errors (BSSE) on interaction energies and geometries was estimated using the counterpoise correction method [33] and the seven-point scheme of Dannenberg and co-workers [34,35].

3. Results

Full geometry optimization of the unconventional structure IIIa has been done with different *ab initio* and DFT methods, with and without BSSE corrections. Table 1 summarizes the results for intermolecular distances and interaction energies. The obtained values are crucially dependent on the theoretical approach. Thus, many commonly used DFT methods, such as BLYP, B3LYP or PBE0, fail to predict an energy minimum for IIIa. M11-L and LC-BLYP do predict a stationary point but the frequency analysis shows one and two imaginary frequencies, respectively. When the geometry of the complex is optimized without BSSE corrections, the best results (compared to CCSD(T)) are obtained with the range-separated functional M11 for intermolecular distances and with the M06-2X method for the interaction energy. When BSSE corrections are taken into account, the best results (the reference is now MP2) are obtained with the range-separated dispersion-corrected functional ωB97XD for both geometry and energy, although there are several other DFT methods that lead to comparable results. Dispersion 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-ωPBE fail to predict an energy minimum for IIIa.

Total energies for the acetone–CO_2 complex as functions 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),

Table 1
Interatomic C···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–CO_2 IIIa complex using different *ab initio* and DFT methods. The shortest C ··· O distance corresponds to $O_{acetone} \cdots C_{CO_2}$. 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}	**R_{CO}**		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
ωB97X	2.874	3.035	−3.26	2.893	3.076	−2.88
ωB97XD	3.010	3.100	−2.76	3.019	3.172	−2.44
HF, BLYP, B3LYP, BH and HLYP, PBEPBE, PBE0, CAM-B3LYP, LC-ωPBE	No stationary point found for IIIa structure					