

# Equilibrium structure of the carbon dioxide–water complex in the gas phase: an ab initio and density functional study

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## Abstract

High-level ab initio (MP2/6-311++G(2d,2p) geometry, Gaussian-2, MP4(SDTQ) and QCISD(T) binding energies) and density-functional (Becke3LYP/6-311++G(2df,2pd)) calculations have been performed on the charge-transfer complex between water and carbon dioxide. The complex appears to have two equivalent non-planar minima of  $C_s$  symmetry. Minima are separated by transition states with  $C_1$  symmetry, whereas the totally planar structure with  $C_{2v}$  symmetry is a second-order transition state. All the critical points lie at approximately the same energy (less than  $0.05 \text{ kJ mol}^{-1}$  difference). Therefore, the experimentally observable structure should be planar. The best equilibrium intermolecular distance for this complex calculated at the MP2/6-311++G(2d,2p) level is  $2.800 \text{ \AA}$ . Our best estimate of the observable intermolecular distance (corrected for anharmonicity) is  $2.84 \text{ \AA}$ , in agreement with the experimentally derived value of  $2.836 \text{ \AA}$ . Our best estimate of the binding energy at the QCISD(T) level, taking into account the variation of the distance owing to anharmonicity and the use of more sophisticated theoretical treatments, is  $-12.0 \pm 0.2 \text{ kJ mol}^{-1}$ . Our best estimate of the barrier to internal rotation, also at the MP2/6-311++G(2d,2p) level, is  $4.0 \text{ kJ mol}^{-1}$ , outside the error limits of the experimental determination ( $3.64 \pm 0.04 \text{ kJ mol}^{-1}$ ). Density functional theory at the level employed here gives an equilibrium intermolecular distance that is too large ( $2.857 \text{ \AA}$ ), a binding energy that is too small ( $8.1 \text{ kJ mol}^{-1}$ ), attributable neither to geometry nor to the basis set, and also a barrier to internal rotation that is slightly too small ( $3.39 \text{ kJ mol}^{-1}$ ). The overall picture is, however, reasonably good.

**Keywords:** Ab initio; Carbon dioxide; Density functional; Van der Waals complex; Water

## 1. Introduction

The interaction of water with carbon dioxide is a topic of interest in many areas of research, such as biochemistry, geochemistry and atmospheric chemistry. Consequently, the structure of this complex has recently been the subject of many experimental and theoretical studies. Matrix-isolation IR experiments [1–3] as well as gas-phase molecular beam electric resonance (MBER) [4] and optothermal IR [5] deter-

minations suggest that  $\text{CO}_2\cdot\text{H}_2\text{O}$  is a T-shaped, planar charge transfer (electron-donor–acceptor; EDA) complex with a  $\text{O}\cdots\text{C}$  distance of  $2.836 \text{ \AA}$  [4]. The complex presents hindered internal rotation of the water monomer with respect to carbon dioxide. The barrier was derived experimentally from a microwave study by Peterson and Klemperer [4], who found a value of  $V_b = 3.59 \pm 0.84 \text{ kJ mol}^{-1}$ . The most recent and more accurate determination, by Block et al. [5], is  $V_b = 3.64 \pm 0.04 \text{ kJ mol}^{-1}$ . No accurate experimental determination of the binding energy of this complex exists at present.

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Theoretical ab initio [5–9] and density functional theory (DFT) calculations have been made at several levels of theory. In general, these studies agree in favoring the EDA planar complex over other possibilities, in particular the hydrogen-bonded structure. However, there is still disagreement on the exact value of the binding energy of the complex (calculated values range from  $-9.06$  to  $-33.05$   $\text{kJ mol}^{-1}$ ) [5,7–15] and on the intermolecular distance at the equilibrium structure [5,7–15]. The most accurate calculations present in the literature are MP2/6-31 G(*d,p*) performed by Cox et al. [6,7], MP2/6-31+G(2*d,2p*) by Block et al. [5] and MP2/6-31++G(*d,p*) by Makarewicz et al. [8]. In the first case, the authors of this most recent work on the subject concluded that water and carbon dioxide appear not to form stable 1:1 EDA or hydrogen-bonded complexes, because they were not able to find true minima (i.e. all-positive eigenvalues of the Hessian matrix) on the potential energy surface (PES). This conclusion is at variance with experiment and with the previous more exact calculations. Moreover, their binding energy corrected by basis set superposition error (BSSE) is  $-9.06$   $\text{kJ mol}^{-1}$ , suggesting that the minimum on the PES exists and was simply not found. Block et al. [5] found a planar minimum at the MP2/6-31+G(2*d,2p*) level of theory with a C $\cdots$ O equilibrium distance of 2.792 Å and a binding energy of  $-12.6$   $\text{kJ mol}^{-1}$ . Makarewicz et al. [8], on the other hand, found that the complex has two equivalent, slightly non-planar, equilibrium configurations, but behaves like a quasiplanar molecule. Their optimum C $\cdots$ O bond length is about 2.771 Å, 0.02 Å shorter than that of Block et al. [5], and they found a stabilization energy of  $-14.2$   $\text{kJ mol}^{-1}$ , larger than that of Block et al. [5] and congruent with the smaller intermolecular distance. In the only available DFT calculation [10], the researchers obtained intermolecular distances from 2.502 to 2.858 Å and binding energies from  $-12.1$  to  $-23.7$   $\text{kJ mol}^{-1}$  (depending on the details of the calculation). As to the calculations of the barrier for internal rotation, the most recent theoretical values are those obtained by Block et al. [5] at the ab initio level (4.04  $\text{kJ mol}^{-1}$ ) and by Abashkin et al. [10] at the DFT level (5.23  $\text{kJ mol}^{-1}$ ). Both of them are clearly outside the experimental error limits, but by small amounts (about 0.4  $\text{kJ mol}^{-1}$  and 1.6  $\text{kJ mol}^{-1}$ , respectively, i.e. less than 0.5  $\text{kcal mol}^{-1}$ ).

In view of the discrepancies existing among the different theoretical calculations on the one hand and between them and the available experimental information on the other, we deemed it necessary to perform a more precise and systematic determination of the CO<sub>2</sub>–H<sub>2</sub>O equilibrium structure, using better theoretical methods than those employed up to now. The questions we want to answer in this paper are: (1) what is the reason for the discrepancies among the theoretical methods, which at least in one case [8] precluded the location of a minimum? (2) What are the most precise theoretical values of the important geometrical and energetical parameters of the dimer (intermolecular distance, binding energy and barrier to rotation)? (3) How well do conventional ab initio and DFT calculations compare between themselves and with respect to experiment, in the determination of those parameters?

## 2. Methods

Both ab initio [16] and DFT [17] calculations are reported in this paper. First, we used Møller–Plesset perturbation theory [18] at second order (MP2) [19] and the 6-31 G(*d,p*) [16] basis set to obtain results of the same quality as those reported in the most recent work on the subject [6,7]. The 6-311++G(2*d,2p*) basis set [16] was used also to obtain more exact optimized geometries and binding energies at the MP2 level. With respect to the more exact calculations performed up to now (Block et al. [5] MP2/6-31+G(2*d,2p*)), this basis set adds diffuse functions also on the hydrogens and has a larger valence space. Finally, we performed even more exact calculations of the binding energy of the complex in two different ways. On the one hand, we used the Gaussian-2 (G2) level of theory [20]. Results obtained at this level are approximations to a full QCISD(T)/6-311+G(3*df,2p*) treatment, but have the drawback that geometry optimizations are performed only at the MP2/6-31 G(*d*) level. Moreover, the G2 method has not been calibrated for Van der Waals (VdW) systems. On the other hand, we used the MP2/6-311++G(2*d,2p*) optimum geometries and calculated MP4(SDTQ) [19] and QCISD(T) [21] energies. These calculations are, respectively, approximations to full MP4(SDTQ)/6-311++G(2*d,2p*) and QCISD(T)/6-311++G(2*d,2p*) treatments, with the

advantage that optimum geometries do not, in general, change excessively on going from MP2 to MP4 or QCISD(T) (although this statement may not be accurate for VdW systems).

DFT calculations were performed using the Becke three-parameter semiempirical potential [22] (Becke3) as the exchange part of the energy functional and Lee–Yang–Parr (LYP) potential [23] for the correlation part. This method is referred to below as B3LYP and seems to be the most exact of those currently available [22]. A word of caution is needed, because Becke3 as coded in G92/DFT (the computer program [24] used to perform the calculations) is not identical with Becke's original formulation [22], although this difference is not significant. On the other hand, several DFT methods have been employed for the study of the Cl<sub>2</sub>–ethylene charge-transfer (C-T) complex by Ruiz et al. [31], and the conclusion of those workers was that C-T complexes represent a stringent and important testing ground for new functionals. In particular, they pointed out that hybrid methods are promising but do not represent a panacea. For instance, the optimum B3LYP distance between the Cl atom and the ethylene plane was calculated as 2.835 Å whereas the experimental value is 3.128 Å. However, anharmonicity was not considered in that paper and, therefore, these results should not be regarded as ruling out the application of B3LYP to C-T complexes. Moreover, it should also be

mentioned that B3LYP was parametrized on systems completely different from the one under study in this paper.

Initially, the same basis set as with MP2, 6-31G(*d,p*), was used in the DFT calculations. Then calculations were performed, increasing steadily the basis set in the following way: (I) 6-31G(*d,p*), (II) 6-311G(*d,p*), (III) 6-311+G(*d,p*), (IV) 6-311++G(*d,p*), (V) 6-311+G(2*d*,2*p*) and (VI) 6-311++G(2*df*,2*pd*). Full geometry optimization was performed in all cases, imposing very stringent convergence criteria of  $4 \times 10^{-6}$  Hartrees Å<sup>-1</sup> (or per radian),  $3 \times 10^{-6}$  Å (or radians) and  $1 \times 10^{-15}$  Hartrees in gradients, coordinate displacements and total energies, respectively. These tight limits were imposed because the complex is very floppy, as noted already by Damewood et al. [15]. Frequency calculations were performed as usual [16] employing analytical second derivatives. The calculations were performed on a cluster of IBM RS/6000 workstations and a Cray Y-MP.

### 3. Results and discussion

The optimum geometrical parameters obtained using the 6-31G(*d,p*) basis sets are shown in Table 1. As reported already [6,7], the MP2/6-31G(*d,p*) critical point on the PES corresponding to the structure with C<sub>2v</sub> symmetry is not a minimum (structure A, Fig. 1)

Table 1  
Optimum geometrical parameters of the complex and the fragments using the 6-31G(*d,p*) basis sets

	MP2				B3LYP		
	Complex A <sup>a</sup>	Complex B	CO <sub>2</sub>	H <sub>2</sub> O	Complex B	CO <sub>2</sub>	H <sub>2</sub> O
Δ <i>E</i> (kJ mol <sup>-1</sup> )	-12.9	-14.3			-15.2		
rCO <sub>1</sub> (Å)	1.1691	1.1678	1.1691		1.1771	1.1787	
rCO <sub>2</sub> (Å)	1.1691	1.1709	1.1691		1.1797	1.1787	
rCO <sub>w</sub> (Å)	2.7609	2.7900			2.7849		
rO <sub>w</sub> H <sub>1</sub> (Å)	0.9646	0.9656		0.9653	0.9615		0.9608
rO <sub>w</sub> H <sub>2</sub> (Å)	0.9646	0.9654		0.9653	0.9611		0.9608
θO <sub>1</sub> CO <sub>w</sub> (deg)	(90.00)	85.89			85.60		
θO <sub>2</sub> CO <sub>w</sub> (deg)	(90.00)	96.91			96.75		
θO <sub>1</sub> CO <sub>2</sub> (deg)	(180.00)	-2.80	180.00		-2.35	180.00	
θH <sub>1</sub> O <sub>w</sub> C (deg)	127.59	90.08			92.86		
θH <sub>2</sub> O <sub>w</sub> C (deg)	127.59	115.76			125.02		
θH <sub>1</sub> O <sub>w</sub> O <sub>2</sub> (deg)	104.82			103.74			103.87
φH <sub>1</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	(0.00)	9.86			11.93		
φH <sub>2</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	(0.00)	115.97			121.93		

<sup>a</sup> Values in parentheses were fixed during geometry optimization.

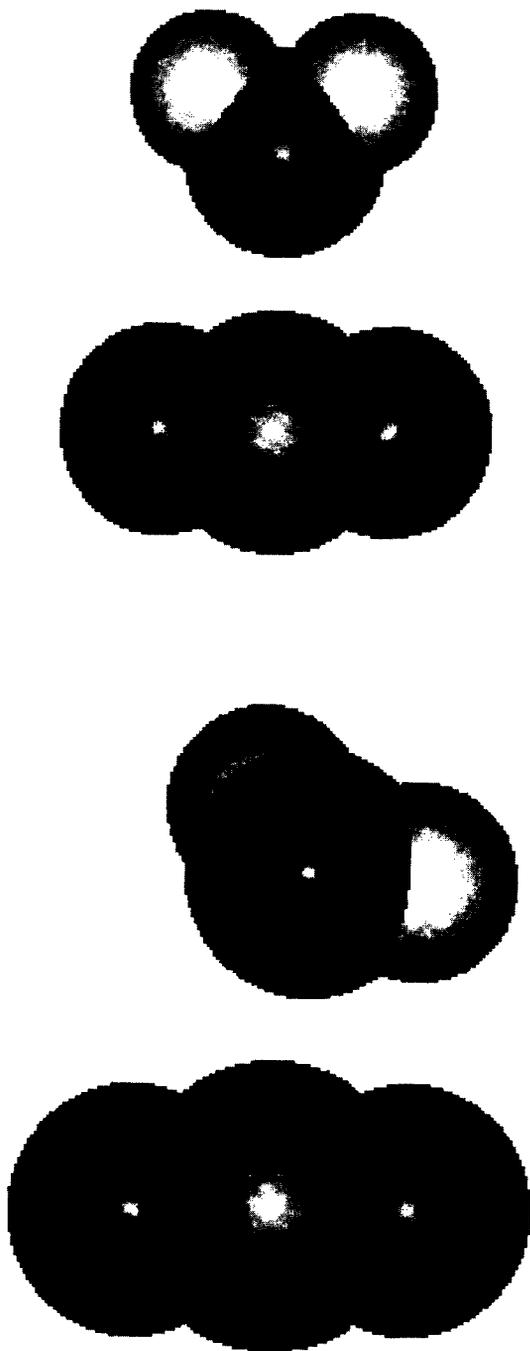


Fig. 1. (a) Planar  $C_{2v}$  conformation of the  $\text{CO}_2\text{H}_2\text{O}$  complex, a transition state at the MP2/6-31G(*d,p*) and B3LYP/6-31G(*d,p*) levels, and a minimum or second-order transition state with larger basis sets. (b) Non-planar  $C_1$  structure, a minimum at the MP2/6-31G(*d,p*) and B3LYP/6-31G(*d,p*) levels, and a transition state with larger basis sets.

but a transition state. At this level of calculation, however, there exists a stable equilibrium structure for the dimer with  $C_1$  symmetry (structure B, Fig. 1), which was not reported before. This is a true minimum (i.e. all the eigenvalues of the analytically determined Hessian are positive) on the MP2/6-31G(*d,p*) PES, lying only  $1.4 \text{ kJ mol}^{-1}$  below the transition state (structure A). It is characterized by almost parallel and coplanar C=O and O–H bonds. The other hydrogen in water lies significantly away from that plane. The energy of the transition state A ( $-12.9 \text{ kJ mol}^{-1}$ ) is higher than that found before at this level ( $-14.9 \text{ kJ mol}^{-1}$ ) [6,7]. This is probably due to the much tighter limits imposed here for the optimization procedure on the complex and its fragments. Thus, our result should be considered as the most precise of the two. In any case, the energy of the true minimum structure B is lower than that found before [6,7] for structure A.

The geometry optimization done using DFT at the B3LYP/6-31G(*d,p*) level affords a structure closely similar to that found with MP2/6-31G(*d,p*). It should be noted, for instance, that the  $\text{C}\cdots\text{O}$  distances obtained with these methods are within  $5 \times 10^{-3} \text{ \AA}$  of each other. The most noticeable difference is an increased deviation of the second hydrogen in water from the  $\text{O}=\text{C}-\text{O}\cdots\text{H}$  plane, without any significance owing to the floppiness of this complex. It is concluded from this experiment that B3LYP calculations are providing essentially the same information as MP2. Therefore we performed a study of the influence of the basis set employing only the B3LYP method. This is reported in Table 2. It must be mentioned that these data do not provide information about the convergence of MP2 calculations with the amelioration of the basis set. In fact, in the case of DFT methods, the basis set has only to describe the density, whereas for traditional correlated methods, the electro–electron correlation cusp has to be described, and this is much more demanding (we are grateful to the referee for pointing out this argument to us). The basis set requirements of DFT are more likely to be similar to those of Hartree–Fock than to those of highly correlated methods. Therefore, one can expect that the basis set influence on MP2 calculations would be larger than that reported in Table 2 for B3LYP.

Several findings are immediately obvious. First, the deep minimum obtained with 6-31G(*d,p*) is spurious,

Table 2

Optimum geometrical parameters of the CO<sub>2</sub>:H<sub>2</sub>O complex using the B3LYP method with several basis sets

	(II) <sup>a</sup>	(III) <sup>a</sup>	(IV) <sup>a</sup>	(V) <sup>a</sup>		(VI) <sup>a</sup>
				Non-planar	Planar <sup>b</sup>	
$\Delta E$ (kJ mol <sup>-1</sup> )	-14.3	-10.9	-10.8	-7.95	-7.95	-8.12
rCO <sub>1</sub> (Å)	1.1607	1.1609	1.1609	1.1603	1.1603	1.1595
rCO <sub>2</sub> (Å)	1.1607	1.1609	1.1609	1.1603	1.1603	1.1595
rCO <sub>w</sub> (Å)	2.7415	2.7825	2.7838	2.8647	2.8630	2.8574
rO <sub>w</sub> H <sub>1</sub> (Å)	0.9619	0.9620	0.9620	0.9609	0.9608	0.9609
rO <sub>w</sub> H <sub>2</sub> (Å)	0.9619	0.9620	0.9620	0.9609	0.9608	0.9609
$\theta$ O <sub>1</sub> CO <sub>w</sub> (deg)	91.42	91.18	91.18	90.95	90.95	90.95
$\theta$ O <sub>2</sub> CO <sub>w</sub> (deg)	91.42	91.18	91.18	90.95	90.95	90.95
$\theta$ O <sub>1</sub> CO <sub>2</sub> (deg)	-2.84	-2.36	-2.36	-1.90	-1.90	-1.90
$\theta$ H <sub>1</sub> O <sub>w</sub> C (deg)	118.82	127.08	127.08	125.71	127.14	127.09
$\theta$ H <sub>2</sub> O <sub>w</sub> C (deg)	118.82	127.08	127.08	125.71	127.14	127.09
$\theta$ H <sub>1</sub> O <sub>w</sub> O <sub>2</sub> (deg)		105.84	105.84		105.72	105.82
$\varphi$ H <sub>1</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	25.24	0.00	0.00	11.02	(0.00)	2.06
$\varphi$ H <sub>2</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	154.76	180.00	180.00	168.98	(180.00)	177.87

<sup>a</sup> The definition of the basis sets is as follows: (II) 6-311G(*d,p*); (III) 6-311+G(*d,p*); (IV) 6-311++G(*d,p*); (V) 6-311++G(2*d*,2*p*); (VI) 6-311++G(2*df*,2*pd*).

<sup>b</sup> Values in parentheses were fixed during geometry optimization.

and is due only to the incompleteness of the basis set. Second, the true minimum has a coplanar arrangement of the four 'heavy' atoms, whereas both hydrogens lie symmetrically away to the same side of that plane. Third, finding this true minimum is extremely difficult and strongly dependent on the size and internal balance of the basis set. Extending the valence part of the basis set from 6-31 (used in the most precise geometry optimizations up to now) to 6-311 already causes a symmetrization of the complex. A plane containing the C···O bond and the bisectrix of the HOH angle appears in the equilibrium structure at the 6-311G(*d,p*) level. This same effect was obtained in other calculations extending the 6-31G(*d,p*) basis with diffuse functions. Further extension of the 6-311G(*d,p*) basis adding diffuse functions while maintaining the same number of polarization functions causes convergence toward a planar equilibrium structure. Extension of the polarization part of the basis again stabilizes the non-planar structure, although the introduction of higher angular-momentum polarization functions tends to give a structure of higher planarity. In this sense, it is instructive to notice that Block et al. [5] at the MP2/6-31+G(2*d*,2*p*) level obtained a planar complex, whereas Makarewicz et al. [8] at the MP2/6-31++G(*d,p*) level found a non-planar structure. Also in Table 2 we provide a comparison of the fully planar

(constrained) structure and the true minimum using only the 6-311++G(2*d*,2*p*) basis set. The planar structure has two negative eigenvalues, one of which connects the planar critical point with the true minimum whereas the other leads from this second-order transition state to a first-order one, whose structure resembles the 6-31G(*d,p*) minimum (structure **B**). These three critical points are remarkably similar in energy, implying that the water molecule is able to perform high-amplitude motions, as already reported [5,8]. The averaged structure is then, probably, planar.

It is important to notice two methodological points with respect to these DFT calculations. On the one hand, the importance of the composition and balance of the basis set found in this work is in contrast with the insensitivity noticed by Hertwig and Koch [25] in their study of the dependence of equilibrium structure, energies and frequencies of 21 homonuclear diatomics from Li<sub>2</sub> to Br<sub>2</sub> with respect to the basis set. The reason for the discrepancy is obviously related to the differences in the respective PES. Whereas for the diatomics the well is relatively deep, in the CO<sub>2</sub>:H<sub>2</sub>O complex the PES for the large-amplitude motion of the water monomer is exceedingly flat. Therefore, in this case a minor variation in the basis set leads to a qualitative difference in the equilibrium structure of the complex (planar vs. non-planar). The second

methodological point concerns the previous DFT study of this same complex. There are three essential differences between our work and the previous study. First, the method employed by Abashkin et al. [10], using the deMon program [26], requires that the charge density and the exchange–correlation potential be fitted using auxiliary sets of basis functions, in addition to the orbital ones, using the algorithm of Sambe and Felton [30]. This fact introduces an extra factor to be considered for the precision of the calculations. In the second place, the orbital basis sets used were of TZVP (triple zeta valence + polarization) on carbon and oxygen, and DZP on hydrogen. This set is roughly equivalent to 6-311G(*d,p*), with no diffuse functions and only one set of polarization functions. Finally, they used the Becke functional [28] for exchange, and the Perdew [27] one for correlation. This combination is known to produce larger bond lengths than experiment and therefore it is increasingly being replaced by functionals using LYP for correlation. A consequence of all these facts is, for example, that depending on the combination of functionals and grid points, Abashkin et al. [10] reported minima in which the water monomer is rotated up to 28° with respect to the all planar configuration. Their best result, however, is a planar configuration with an intermolecular distance surprisingly close to experiment (2.831 Å vs. experimental 2.836 Å). Because, on the one hand, there is no information about second derivatives and, on the other, there is no hint as to whether the calculations are converged with respect to the number of grid points, it is difficult to appreciate whether their result is truly significant for the potential of DFT in the study of Van der Waals complexes. The results presented in Table 2 are completely converged with respect to grid points, basis sets and optimization parameters and, therefore, clearer with respect to the true achievements of DFT in this respect. In any event, to have a more complete comparison, we performed a Becke–Perdew optimization of the geometry of the complex in the same conditions as for performing the B3LYP (6-311++G(2*d*,2*p*) basis set, very tight convergence thresholds, extrafine grid). We obtained a planar minimum, with an intermolecular distance of 2.9281 Å and a binding energy of  $-4.37 \text{ kJ mol}^{-1}$ . Therefore, until better calculations are performed, one can guess that the good results obtained by Abashkin et al. [10] were an artifact of

the computational conditions. Moreover, one can see clearly that the difficulty is associated mostly with the exchange part of the potential. In fact, if instead of using Becke3 (a linear combination of several exchange potentials including the exact one [22]) one uses the pure Becke 1988 potential [28] together with the LYP correlation functional (i.e. BLYP instead of B3LYP) the optimization using 6-311++G(2*d*,2*p*) leads to an optimum distance of 2.9768 Å, even larger than Becke–Perdew result.

Although the results obtained at the MP2 and B3LYP levels using the small 6-31G(*d,p*) basis set are fairly coincident, and there is a reasonable convergence of the results with the extension of the basis set, one can doubt whether it is valid to rely completely on DFT for the study of the geometry of this complex. Therefore, we also performed a full MP2 geometry optimization of the non-planar and planar critical points obtained with the 6-311++G(2*d*,2*p*) basis set at the B3LYP level. These results are reported in Table 3 together with the other two more precise calculations available in the literature. One can see that the B3LYP and MP2 calculations using this basis set (Table 2 and Table 3, respectively) agree on the presence of these two very close critical points, one planar and one non-planar. Furthermore, both of them agree also in that the non-planar structure is the actual minimum and the planar one is a second-order transition state. Moreover, one can see that our MP2 calculation is the one giving the best agreement with experiment up to now. On the other hand, there is a discrepancy in the intermolecular distances (DFT longer than *ab initio*). Although both of them have the same absolute discrepancy with experiment, the experimental determination incorporates the effect of anharmonicity, whereas the theoretical ones do not. Including this effect would tend to elongate the theoretical intermolecular distances, from which one can conclude that the MP2 result is more in agreement with experiment than the DFT. On the other hand, the variation of the geometrical parameters with respect to the basis sets (Table 2 and Table 3) is the same, and is important at both the DFT and *ab initio* levels. Makariewicz et al. [8] calculated that anharmonicity implies an enlargement of around 0.040 Å in the intermolecular distance, from which we can estimate an (*ab initio*) intermolecular separation of 2.84 Å, which is in perfect

Table 3

Comparison of the optimum geometrical parameters of the CO<sub>2</sub>:H<sub>2</sub>O complex available in the literature

	6-31++G( <i>d,p</i> )	6-31+G(2 <i>d,2p</i> )	6-311++G(2 <i>d,2p</i> )	
	Makarewicz et al. [8]	Block [5]	Non-planar	Planar <sup>a</sup>
$\Delta E$ (kJ mol <sup>-1</sup> )	-14.2	-12.6	-11.7	-11.7
rCO <sub>1,2</sub> (Å)	1.1689	1.1698	1.1680	1.1680
rCO <sub>w</sub> (Å)	2.7710	2.7917	2.8003	2.7974
rO <sub>w</sub> H <sub>1,2</sub> (Å)	0.9595	0.9595	0.9576	0.9576
$\theta$ O <sub>1,2</sub> CO <sub>w</sub> (deg)	90.98	90.83	90.87	90.86
$\theta$ O <sub>1</sub> CO <sub>2</sub> (deg)	-1.96	-1.66	-1.74	-1.72
$\theta$ H <sub>1,2</sub> O <sub>w</sub> C (deg)		127.62	125.96	127.54
$\varphi$ H <sub>1</sub> O <sub>w</sub> H <sub>2</sub> (deg)	104.14	104.76		104.92
$\varphi$ H <sub>1</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	14.65	0.01	11.62	(0.00)
$\varphi$ H <sub>2</sub> O <sub>w</sub> CO <sub>1</sub> (deg)	165.35	179.99	168.38	(180.00)

<sup>a</sup> Values in parentheses were fixed during geometry optimization.

agreement with the 2.836 Å separation obtained experimentally.

A further observation is that our most precise determinations of the optimum geometries lead to complexation energies (-8.12 kJ mol<sup>-1</sup> at the B3LYP/6-311++G(2*df,2pd*) level or -11.7 kJ mol<sup>-1</sup> at the MP2/6-311++G(2*d,2p*) level) that are much lower than other estimates in the literature (ranging from -11.91 to -33.05 kJ mol<sup>-1</sup>, uncorrected for BSSE). Cox et al. [6,7] determined a BSSE correction at the MP2/6-31G(*d,p*) level of 5.81 kJ mol<sup>-1</sup>, leading them also to a low interaction energy (-9.06 kJ mol<sup>-1</sup>). Their result, however, is not very reliable because their structure is not a minimum at the level employed and, moreover, we saw already that this level is not precise enough. Block et al. [5] calculated a value of -12.6 kJ mol<sup>-1</sup> at the MP2/6-31+G(2*d,2p*) level, whereas our more exact calculation at the MP2/6-311++G(2*d,2p*) gives a smaller value (-11.7 kJ mol<sup>-1</sup>).

A Gaussian-2 estimation of the complexation energy was attempted, the energies necessary for the calculation being reported in Table 4. With these values, one can find that the binding energy at the Gaussian-2 level is -12.7 kJ mol<sup>-1</sup>. This result is in reasonable agreement with that of Block et al. [5], and is larger than our MP2/6-311++G(2*d,2p*) result. Gaussian-2 theory has, however, an important drawback, which concerns the geometry optimization. This is done, according to Pople's prescription, at the MP2/6-31 G(*d*) level. The intermolecular separation in the dimer at this level is 2.711 Å, much shorter than our best result. Thus, one can guess that even if the corrections owing to higher levels of correlation and extension of the basis set are introduced in the Gaussian-2 theory, the geometry is not properly corrected. Therefore, we made calculations of the correlation energy at several levels using both the MP2 and B3LYP optimum geometries obtained with

Table 4

Energies (in Da) necessary for the Gaussian-2 calculation of the binding energy of H<sub>2</sub>O·CO<sub>2</sub>, obtained at the MP2(Full)/6-31G(*d*) optimum geometries

Basis	Correlation	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub> O·CO <sub>2</sub>
6-311G( <i>d,p</i> )	QCISD(T)	-76.2760664	-188.2153228	-264.4970168
	MP4	-76.2760657	-188.2250664	-264.5065383
	MP2	-76.2636520	-188.1987694	-264.4679485
6-311+G( <i>d,p</i> )	MP4	-76.2868993	-188.2327526	-264.5251481
	MP2	-76.2745453	-188.2062732	-264.4861919
6-311G(2 <i>df,p</i> )	MP4	-76.3134580	-188.3253915	-264.6446705
	MP2	-76.2989412	-188.2945728	-264.5994810
6-311+G(3 <i>df,2p</i> )	MP2	-76.3181073	-188.3114402	-264.6340675

Table 5

Total (in Da) and binding (in  $\text{kJ mol}^{-1}$ ) energies of the  $\text{CO}_2\cdot\text{H}_2\text{O}$  complex at different levels of computation of the correlation energy using the 6-311++G(2d,2p) basis set and optimum geometries at the B3LYP or MP2 level

Level	At the optimum geometry obtained with							
	Becke3LYP				MP2			
	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub> O·CO <sub>2</sub>	$\Delta$	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub> O·CO <sub>2</sub>	$\Delta$
HF	-76.0561377	-187.694632	-263.7539565	-8.36	-76.0559027	-187.6926185	-263.7521245	-9.45
B3LYP				-7.95				
MP2	-76.3173572	-188.3072513	-264.6289748	-11.5	-76.3173122	-188.3074928	-264.6714263	-11.7
MP3	-76.3197725	-188.2884135	-264.6126132	-11.6	-76.3196724	-188.2876295	-264.6119990	-12.3
MP4(SDQ)	-76.3229651	-188.3024282	-264.6296940	-11.3	-76.3229022	-188.3022656	-264.6296283	-11.7
MP4(SDTQ)	-76.3306582	-188.3356410	-264.6707683	-11.7	-76.3306219	-188.336232	-264.6714263	-12.0
QCISD	-76.3231432	-188.3017936	-264.6292814	-11.4	-76.3230824	-188.301593	-264.6291428	-11.6
QCISD(T)	-76.3298834	-188.326441	-264.6608657	-11.9	-76.3298415	-188.3265690	-264.6610883	-12.2

the 6-311++G(2d,2p) basis set. The results obtained are collected in Table 5. No calculations were attempted with more extended basis sets, because of the long time needed for them (more than 7 h of single-processor CPU time in the Cray Y-MP for each calculation). One immediate conclusion is that the geometry at which the calculations are performed does not greatly affect the results: the difference is of the order of  $0.3 \text{ kJ mol}^{-1}$ . A second conclusion is that the main level of correlation is already introduced by MP2, the difference from full MP4 calculations or QCISD(T) ones being less than  $0.5 \text{ kJ mol}^{-1}$  in each case. Finally, although the MP4 and QCISD(T) calculations at the 6-311++G(2d,2p) geometry give a lower binding energy than the Gaussian-2 estimation, the three of them are still in reasonable agreement. Considering the different results, one can say that the best estimation of the binding energy of this complex is  $12.0 \pm 0.2 \text{ kJ mol}^{-1}$ , a little larger than the MP2 result. Thus, the discrepancy of the B3LYP binding energy with the MP2 one cannot be explained on the grounds of different geometries or better levels of correlation energy. Using better basis sets (as can be seen in the last column of Table 2) does increase marginally the binding energy, but there continues to be a 30% difference between the DFT and conventional correlated ab initio values. In fact, the B3LYP value is more similar to the Hartree–Fock one (at the B3LYP geometry) than to any of the correlated ones. It must then be concluded that the density functional method is underestimating the binding energy of this complex (it is not inappropriate at this moment to

remind the reader that the B3 exchange is not parametrized to reproduce binding energies of C-T or VdW complexes). A final interesting consideration in this table is that the variation of the binding energy with distance is much more marked at the Hartree–Fock level than at any of the correlated levels. This implies that in the range of distances we are talking about, exchange and correlation energies are counterpoising each other. The maximum Hartree–Fock

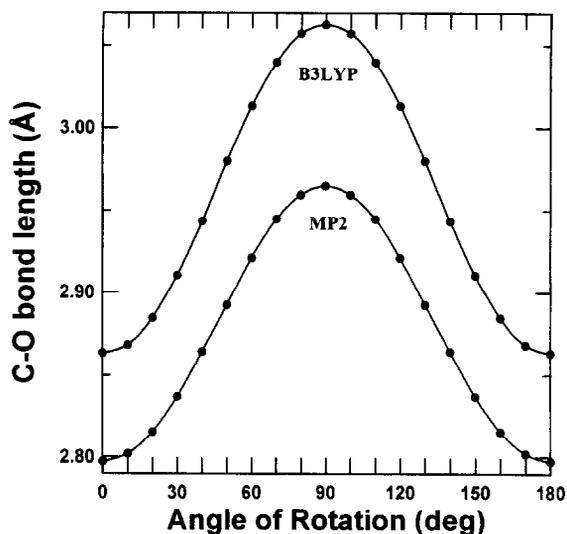


Fig. 2. Variation of the intermolecular C...O distance with the internal rotation angle of  $\text{H}_2\text{O}$  with respect to  $\text{CO}_2$  at the MP2/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) levels. All parameters except the rotation angle were optimized at each point. The points at  $0^\circ$  and  $180^\circ$  represent the two equivalent planar conformations of the complex.

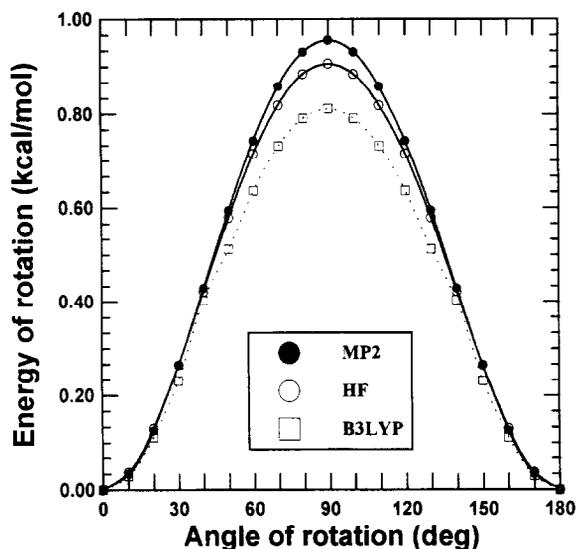


Fig. 3. Barrier to internal rotation of  $\text{H}_2\text{O}$  with respect to  $\text{CO}_2$  obtained at the Hartree–Fock, MP2 and B3LYP levels with the 6-311++G(2d,2p) basis set. All parameters except the rotation angle were optimized at each point (except for Hartree–Fock, for which the optimum MP2 geometries were used). The points at  $0^\circ$  and  $180^\circ$  represent the two equivalent planar conformations of the complex.

(exchange) binding energy is at larger distances, where correlation energy is smaller, and vice versa.

To test the accuracy of previous calculations and test further the performance of DFT with respect to MP2 theory, we made the calculation of the energy curve for the internal rotation of the  $\text{H}_2\text{O}$  monomer around the  $\text{C}\cdots\text{O}\text{C}_2$  axis in steps of  $10^\circ$ . Two interesting results are produced by these calculations: the dependence of the intermolecular distance (Fig. 2) and the dependence of the energy (Fig. 3) on the angle of rotation. What one appreciates in Fig. 2 is that there is

a strong coupling between the intermolecular distance and the rotation angle. Both DFT and MP2 behave in a similar way, although the distance is larger in DFT, and its variation between the minimum ( $\theta = 0$ ) and the transition state ( $\theta = 90$ ) is also larger in DFT ( $0.199 \text{ \AA}$ ) than in MP2 ( $0.167 \text{ \AA}$ ). These results can only be compared with those obtained by Block et al. In our case, we not only used a better basis set, but also allowed geometry relaxation of the monomers at each step in the rotation. Consequently, our value for the intermolecular separation at  $90^\circ$  is significantly larger than theirs ( $2.965 \text{ \AA}$  vs.  $2.937 \text{ \AA}$ ) whereas the difference at equilibrium is not significant ( $2.797 \text{ \AA}$  vs.  $2.791 \text{ \AA}$ ). This better representation of the structure at  $\theta = 90$  has as a consequence that the energy barrier we found for the internal rotation ( $4.01 \text{ kJ mol}^{-1}$ ) is marginally lower than theirs ( $4.04 \text{ kJ mol}^{-1}$ ). Neither of them is in quantitative agreement with experiment ( $3.64 \pm 0.04 \text{ kJ mol}^{-1}$ ). Interestingly, the Hartree–Fock barrier obtained at the MP2 geometries ( $3.79 \text{ kJ mol}^{-1}$ ) gives better agreement with the experimental barrier than the MP2 calculations themselves. DFT provides too low a result (a consequence of the much larger intermolecular distance) of  $3.39 \text{ kJ mol}^{-1}$ , also outside the experimental error limits. The discrepancy between the theoretical values and the experimental one can probably be explained by the fact that the experimental intermolecular distance is midway between the MP2 and the DFT ones. Thus, the MP2 barrier (shorter distance) is larger and the DFT barrier (larger distance) is shorter than the experimental value.

Finally, we consider the IR spectrum of this complex. The frequencies and intensities of the transitions, calculated with the 6-311++G(2d,2p) basis sets at the B3LYP

Table 6  
Theoretical and experimental vibrational frequencies (in  $\text{cm}^{-1}$ ) for the  $\text{CO}_2\cdot\text{H}_2\text{O}$  complex

		Experimental		This work 6-31G(d,p) MP2	Block 6-31+G(2d,2p) MP2	This work 6-311++G(2d,2p) B3LYP
		$\text{N}_2$ Matrix	$\text{O}_2$ Matrix			
$\text{H}_2\text{O}$	$\nu_1$	3632.1	3633.5	3889.5	3845.1	3820.6
	$\nu_2$	1598.1	1588.8	1675.3	1647.4	1637.1
	$\nu_3$	3724.8	3731.3	4028.7	3979.5	3923.6
$\text{CO}_2$	$\nu_2$	665.3	666.9	649.2	693.7	678.4
	$\nu'_2$	656.3	654.2	632.7	679.8	663.7
	$\nu_3$	2351	2344.3	2456.6	2396.9	2401.2

Table 7

Theoretical and experimental dimerization shifts in the vibrational spectrum of the CO<sub>2</sub>:H<sub>2</sub>O complex (in cm<sup>-1</sup>)

		Experimental			This work 6-31G(d,p) MP2	Block 6-31+G(2d,2p) MP2	This work 6-311++G(2d,2p) B3LYP
		N <sub>2</sub> Matrix	O <sub>2</sub> Matrix	Gas			
H <sub>2</sub> O	$\nu_1$	-2.4	-3.2		+4.9	+0.4	-1.4
	$\nu_2$	+0.5	-2.4		+8.5	-4.9	-1.2
	$\nu_3$	-2.1	-1.0	-3.0	+4.4	-4.7	-0.1
CO <sub>2</sub>	$\nu_2(op)$		+4.1		+7.1	+3.2	+2.6
	$\nu_2(ip)$		-8.6		-9.4	-10.7	-12.1
	$\nu_3$		+3.7		-2.4	+3.7	+1.2
	$\Delta\nu_2$	+9.0	+12.7		+16.5	+13.9	+14.2

and MP2 levels of theory and measured experimentally in O<sub>2</sub> and N<sub>2</sub> matrices, are shown in Table 6. B3LYP and MP2 calculations behave in a very similar way, giving harmonic frequencies in reasonable agreement among the different theoretical levels. As the experimental frequencies are anharmonic, direct comparison is of little help. One can resort instead to the frequency shifts upon dimerization which, as we showed for various dimers [29], are much less affected by anharmonicity. The experimental and theoretical dimerization shifts are collected in Table 7. Almost all of them are very small, making difficult the analysis of the quality of different theoretical levels. However, the splitting of the degenerate  $\nu_2$  mode of CO<sub>2</sub> upon dimerization is relatively large. Experimentally, the value of 12.7 cm<sup>-1</sup> in the O<sub>2</sub> matrix is more accurate than the value in the N<sub>2</sub> matrix. This is due to the sample being more diluted and the peaks sharper, making measurements more precise. The theoretical values are in reasonable agreement with the experimental determination, and improvement of the basis set causes a lowering of the splitting. There is agreement between the DFT and MP2 methods on the magnitude of this splitting. Tso and Lee [2,3] suggested that it would be of interest to know whether it is the in-plane or the out-of-plane degenerate vibration that is shifted downwards. Analysis of the vectors corresponding to those frequencies in our calculations shows that it is the in-plane vibration that is shifted about 10 cm<sup>-1</sup> toward lower frequencies.

#### 4. Conclusions

High-level ab initio and DFT calculations have been performed on the charge-transfer complex

between water and carbon dioxide. The complex appears to have two equivalent non-planar minima of C<sub>s</sub> symmetry. The minima are separated by transition states with C<sub>1</sub> symmetry, whereas the totally planar structure with C<sub>2v</sub> symmetry is a second-order transition state. All the critical points lie at approximately the same energy (less than 0.05 kJ mol<sup>-1</sup> difference). Therefore, the experimentally observable structure should be planar, lending theoretical support to the interpretation of the experimental microwave spectrum. The best intermolecular distance for this complex, uncorrected for anharmonicity, calculated at the MP2/6-311++G(2d,2p) level is 2.800 Å. Our best estimate of the observable intermolecular distance (corrected for anharmonicity) is 2.84 Å, in agreement with the experimentally derived 2.836 Å. Our best estimate of the binding energy at the QCISD(T) level, taking into account the variation of the distance owing to anharmonicity and the use of more sophisticated theoretical levels, is 12.0 ± 0.2 kJ mol<sup>-1</sup>. Our best estimate of the barrier for internal rotation, also at the MP2/6-311++G(2d,2p) level, is 4.0 kJ mol<sup>-1</sup>, just outside the experimental error limits.

Density functional theory at the level employed here, B3LYP/6-311++G(2df,2pd), gives an intermolecular distance that is too large (2.857 Å), a binding energy that is too small (8.1 kJ mol<sup>-1</sup>), attributable neither to geometry nor to basis set, and also a barrier to internal rotation that is too small (3.39 kJ mol<sup>-1</sup>). The behavior of B3LYP (with a semiempirically corrected exchange potential) is, however, much better than BLYP or BP in the estimation of the geometry of this complex. It must be pointed out, moreover, that B3LYP behaves much better in the description of this

complex than as reported by Ruiz et al. [25] with respect to the O<sub>2</sub>–ethylene complex. In fact, they found a discrepancy of 0.29 Å between the B3LYP and experimental intermolecular distances, whereas in the CO<sub>2</sub>–water complex the disagreement is much smaller (0.02 Å). With respect to the binding energy and the barrier to internal rotation, the errors of the B3LYP method (about 4 kJ mol<sup>-1</sup> and 0.2 kJ mol<sup>-1</sup>) are well within chemical accuracy, and also are better than the discrepancy found in the Cl<sub>2</sub>–ethylene complex (more than 1 kcal mol<sup>-1</sup>).

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