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An ab initio Investigation of the dipole moment of the $CO_2 \ldots CO$ complex

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Abstract

The dipole moment of the $CO_2 \ldots CO$ van der Waals complex has been studied by highly correlated ab initio methods in the region of the experimental equilibrium geometry. Calculations at the CCSD(T) level of approximation combined with a basis of at least Pol(ANO) + f quality are needed to provide a reliable value of the dipole moment. The large amplitude motion in the van der Waals modes reduces the expectation value of the μ_z by $\sim 7\%$. The enhanced dipole is not primarily due to the field-induced bending of the CO_2 partner, which increases the effective dipole by $\sim 20\%$, but to electronic polarization. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The dipole moment of the $CO_2 \ldots CO$ van der Waals complex has been measured [1] and found to be over twice as large as that of CO (0.2439 and 0.1098 D, respectively). At least three effects may contribute to such a large enhancement of a dipole on complexation: (i) the dipole induced in each component by the electric field of the charge distribution in the partner (at long range these are described by the dipole moment of CO and the quadrupole moment of CO_2, (ii) the distortion of CO_2 from linearity to C_{2v} symmetry under the influence of the field of the CO dipole (i.e. arising from the so-called atomic polarizability of CO_2 and, no doubt, a smaller contribution from the perturbation of the higher-frequency stretch in the CO partner), and (iii) the charge transfer effects which, to enhance the existing dipole of CO (polarity C^-O^+), would have to be from the HOMO of CO (5σ) to the LUMO of CO_2 ($5\sigma_g$).

In this Letter, ab initio studies of the $CO_2 \ldots CO$ complex are presented using a high-quality basis set and taking the basis set superposition error (BSSE) [2] into account. The calculations have been performed at the MP2 [3] and CCSD(T) [4] levels of approximation. The dipole moment of the complex is studied as a function of the geometry of the van der Waals complex (bends and stretches) in order to elucidate the sources of the dipole moment changes. In comparing with the experimental value, account is taken of the fact that the measurement refers to the complex in its zero-point motion which, for low

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intermolecular modes, may be of sufficient amplitude to affect the expectation value of a vector property such as the dipole.

2. Electronic structure calculations

2.1. Methods and computational details

The choice of the basis set plays one of the key roles in ab initio calculations. Several bases have been used in this study. (i) The Pol(ANO) basis set [5] which has the uniform shape of generalized contractions and is a modification of the Sadlej Pol basis set [6] with the segmented contraction scheme for occupied shells. The range of the GTOs in the POL(ANO) basis is the same as in the original Pol basis. The generalized contractions refer essentially to the core region whereas the valence region is fully uncontracted. This modification of the Pol basis bring about only marginal changes in the results for first- and second-order properties [5]. This basis has been extended by one set of f-functions with the exponent equal to the second smallest d-exponent. The basis set used has the contraction [5s3p2d1f] and is labeled Pol(ANO) + f. (ii) The ANO basis sets of Widmark et al. [7] in the contractions [4s3p2d1f] and [5s4p3d2f] labeled ANO4321 and ANO5432, respectively. (iii) The Dunning aug-cc-pVTZ and aug-cc-pVQZ sets [8] in the contractions [5s4p3d2f] and [6s5p4d3f2g], respectively.

At all levels of approximation for the electron correlation, all 1s orbitals have been kept frozen and thus only valence electron correlation has been accounted for. For the present calculations the MOLCAS-4 quantum-chemistry program package [9] combined with the TITAN code for coupled-cluster calculations has been used [10].

The BSSE for the subsystem A is defined as

$$\mathrm{BSSE_A} = E_\mathrm{A}(\mathrm{A}) - E_\mathrm{A}(\mathrm{AB})\,, \tag{1}$$

where the subscript indicates the subsystem considered and the basis set used is given in parentheses. Thus, e.g., $E_\mathrm{CO}(\mathrm{CO})$ means the energy of the CO subsystem calculated in the basis set of CO, while $E_\mathrm{CO}(\mathrm{CO_2}\ldots\mathrm{CO})$ is the energy of CO calculated in the basis set of the $\mathrm{CO_2}\ldots\mathrm{CO}$ complex in its given geometry. The total BSSE of the complex is the sum of $\mathrm{BSSE_A}$ and $\mathrm{BSSE_B}$. The 'counter-poise' [11] corrected interaction energy is written as

$$\Delta E^\mathrm{CP} = \left[E_\mathrm{AB}(\mathrm{AB}) - E_\mathrm{A}(\mathrm{AB}) - E_\mathrm{B}(\mathrm{AB})\right] - \left[\mathrm{BSSE_A} + \mathrm{BSSE_B}\right] = \Delta E - \mathrm{BSSE}\,. \tag{2}$$

The values of the BSSE and interaction energy of the $\mathrm{CO_2}\ldots\mathrm{CO}$ complex calculated in a series of different bases are presented in Table 1. The systems have been studied in their experimental geometries. The bond lengths of CO and linear $\mathrm{CO_2}$ were kept equal to 1.128 and 1.160 Å, respectively [12]. The $\mathrm{CO_2}\ldots\mathrm{CO}$ complex is T-shaped with the $\mathrm{C}\ldots\mathrm{C}\equiv\mathrm{O}$ axis forming the $\mathrm{C_2}$ axis in C_{2v} symmetry. The subsystems CO and $\mathrm{CO_2}$ retain their original bond lengths and the CC distance is 3.277 Å [1,13,14]. It is seen from Table 1 that the biggest aug-cc-pVQZ basis set has the smallest BSSE, as would be expected; however, the BSSE of the aug-cc-pVTZ basis set is still acceptable. The relatively large BSSE of the ANO4321 and ANO5432 basis sets is quite surprising. Recently, Lee and Wright [15] explored the very weak $\mathrm{He}\ldots\mathrm{NO}$ complex (about one order of magnitude weaker than $\mathrm{CO_2}\ldots\mathrm{CO}$) using the aug-cc-pVTZ and aug-cc-pVQZ bases and concluded that only with the latter does the BSSE correction become small enough to make the potential surface meaningful. Our results in Table 1 seem to show little difference between these two basis sets. The $\Delta E^\mathrm{CP}_\mathrm{MP2}$ values of Table 1 demonstrate that the 'counter-poise' corrections nicely damp down the initial difference between the ΔE_MP2 aug-cc-pVQZ and Pol(ANO) + f values from +4.4 to −0.2 mHartree. There is a change of about 0.1 mHartree in ΔE^CP going from the MP2 to CCSD(T) approximation for the Pol(ANO) + f or ANO4321 basis. Based on the results presented in Table 1 it has been decided that the 'work horse' in the calculations of the $\mathrm{CO_2}$–CO energy surface to be the MP2 method and the aug-cc-pVTZ basis set. We believe that the difference between the $\Delta E^\mathrm{CP}_\mathrm{MP2}$ values obtained in the aug-cc-pVTZ basis set and the fully saturated one is well under 10%.

Table 1
BSSE and the interaction energy of the $CO_2 \ldots CO$ complex[a] (all in 10^{-3} a.u.)

Basis	$BSSE_{CO}$	$BSSE_{CO_2}$	BSSE	ΔE	ΔE^{CP}
SCF					
Pol(ANO) + f	0.679	0.291	0.970	−1.035	−0.064
ANO4321	0.983	0.150	1.133	−1.237	−0.104
ANO5432	0.252	0.087	0.339	−0.431	−0.093
aug-cc-pVTZ	0.130	0.033	0.163	−0.239	−0.075
aug-cc-pVQZ	0.032	0.018	0.050	−0.140	−0.090
MP2					
Pol(ANO) + f	2.347	2.448	4.795	−6.454	−1.659
ANO4321	1.996	1.521	3.517	−5.211	−1.694
ANO5432	0.640	0.421	1.061	−2.866	−1.805
aug-cc-pVTZ	0.320	0.142	0.463	−2.260	−1.797
aug-cc-pVQZ	0.128	0.090	0.218	−2.093	−1.876
CCSD					
Pol(ANO) + f	2.208	2.314	4.522	−5.860	−1.338
ANO4321	1.845	1.391	3.236	−4.579	−1.343
CCSD(T)					
Pol(ANO) + f	2.439	2.527	4.966	−6.551	−1.585
ANO4321	1.942	1.541	3.483	−5.070	−1.586

[a] See the text.

All calculations of the dipole moments have been carried out by using the finite-field numerical perturbation scheme [22] with electric properties evaluated as the finite difference approximations to the energy derivatives with energies calculated for the electric field strength equal to ± 0.001 a.u.

It is well known that electric properties of the CO molecule are extremely sensitive to the electron cor-

Table 2
Energetics of the $CO_2 \ldots CO$ complex calculated in the aug-cc-pVTZ basis set as a function of the interatomic separation R_{CC}

R_{CC} (Å)	E_{SCF} (a.u.)	E_{MP2} (a.u.)	ΔE_{MP2} (10^{-3} a.u.)	ΔE^{CP}_{MP2} (10^{-3} a.u.)
2.600	−300.48272981	−301.46121810	2.17272	
2.700	−300.48555156	−301.46309889	0.29193	
2.800	−300.48755606	−301.46431519	−0.92437	
2.900	−300.48895862	−301.46505762	−1.66680	
3.000	−300.48992324	−301.46546870	−2.07788	
3.100	−300.49057299	−301.46565383	−2.26301	
3.150	−300.49080937	−301.46568651	−2.29569	−1.75740
3.200	−300.49099922	−301.46568968	−2.29886	−1.79184
3.250	−300.49115020	−301.46566951	−2.27869	−1.80089
3.277	−300.49121790	−301.46565079	−2.25997	−1.79711
3.300	−300.49126881	−301.46563121	−2.24039	−1.78981
3.400	−300.49143009	−301.46551678	−2.12596	
3.600	−300.49155514	−301.46521533	−1.82451	
4.000	−300.49147915	−301.46462021	−1.22939	
4.500	−300.49129346	−301.46410695	−0.71613	
5.000	−300.49116437	−301.46381225	−0.42143	
6.000	−300.49104589	−301.46355232	−0.16149	
8.000	−300.49099238	−301.46342897	−0.03815	
12.000	−300.49098005	−301.46339602	−0.00519	

Table 3
Energetics of the $CO_2 \ldots CO$ complex calculated in the aug-cc-pVTZ basis set as a function of the CO_2 bond angle at an intermolecular separation $R_{CC} = 3.277$ Å

θ (deg)	E_{SCF} (a.u.)	E_{MP2} (a.u.)	ΔE_{MP2} (10^{-3} a.u.)	ΔE^{CP}_{MP2} (10^{-3} a.u.)
−10.0	−300.47686680	−301.45396040	9.43042	9.93873
−5.0	−300.48742944	−301.46262804	0.76278	
−1.0	−300.49098993	−301.46548462	−2.09380	−1.63006
0.0	−300.49121790	−301.46565079	−2.25997	−1.79711
1.0	−300.49118231	−301.46559872	−2.20790	−1.74532
5.0	−300.48838766	−301.46318681	0.20401	
10.0	−300.47875904	−301.45500495	8.38587	8.86703

relation approximation used [16–18]. The MP2 approximation is insufficient and we are forced to use the best available one which in this case is the CCSD(T) method. The Sadlej Pol basis [6] proved to be very good in calculations of electric properties [18–20]. Therefore the Pol(ANO) + f basis set, which is an extension of the Pol basis set, has been used in the calculations of the dipole moment surface. Using this basis, we obtained $\mu_e = 0.1530$ D for the CO molecule, calculated at the experimental bond distance in the CCSD(T) approximation correlating 10 electrons. Taking into account the value of vibrational averaging −0.0152 D [18] it reduced to 0.1378 D, a value that agrees reasonably well with the experimental value of 0.1222 D [21].

2.2. Calculations of the potential energy and dipole moment curves

The variation of the energy with the CO_2–CO distance around the potential energy minimum using the aug-cc-pVTZ basis set is given in Table 2.

The part of the C_{2v} potential energy surface governing the departure from the linearity of CO_2 is listed in Table 3, where θ is $(\pi-\alpha)/2$ and α is the OCO bond angle and $\theta > 0$ corresponds to the CO_2 dipole created by bending having the same sign as the CO dipole.

The change in the dipole moment at various levels of electron correlation using the Pol(ANO) + f basis set is shown in Table 4. The SCF value of the dipole moment has even the opposite sign compared to the correlated values similar as it is the case for the CO molecule [16]. The MP2 values differ by about 50 per cent from the CCSD(T) values. It can be seen that the effect of triples is not negligible and thus the CCSD approximation cannot be used for the calculation the CO_2–CO dipole moment. The MP2 dipole moment value for the equilibrium geometry calculated in the aug-cc-pVTZ basis set is 0.43214 D that is by 0.02953 D smaller than the Pol(ANO) + f value. It is rather difficult to estimate an error in calculated values of the dipole moment due to the basis set truncation. Urban et al. [19] published a detailed study of the accuracy assessment in calculations of dipole moments of small molecules. From their study follows that the average error of the POL

Table 4
The dipole $\mu(R)$ as a function of the interatomic separation R_{CC} (in Debye)

R_{CC}/Å	μ_{SCF}	μ_{MP2}	μ_{CCSD}	$\mu_{CCSD(T)}$
2.800	−0.08666	0.51260	0.29873	0.34633
2.900	−0.09663	0.50230	0.28935	0.33713
3.000	−0.10644	0.49166	0.27959	0.32737
3.100	−0.11612	0.48080	0.26958	0.31723
3.200	−0.12562	0.46993	0.25944	0.30691
3.277	−0.13274	0.46167	0.25171	0.29901
3.400	−0.14369	0.44881	0.23961	0.28658

basis set versus saturated one for the investigated set of molecules was 0.033 D. We can expect that the Pol(ANO) + f basis set has a little bit better behaviour than the original POL basis set.

A plot the dipole moment versus R over the range 2.8–3.4 Å is almost linear with only a slight point of inflection. A polynomial fit of the form

$$\mu(R) = a_0 + a_1(R - 3.277) + a_2(R - 3.277)^2 + a_3(R - 3.277)^3 \quad (3)$$

over this range of separations has given the following parameter values: $a_0 = 0.2988$, $a_1 = -0.10264$, $a_2 = 0.00877$, $a_3 = 0.03278$, (the dipole in Debye, the lengths in Å).

3. Analysis of the results

First it is noted that the computed dipole moment of the complex at the equilibrium geometry (R_{CC} = 3.277 Å) is fairly close to the observed value, but higher by 20%. The calculated enhancement of the dipole in the static complex, $\mu_{CO\ldots CO_2}(R_e) - \mu_{CO}$, is 0.146 D, 9% greater than the observed change of 0.134 D on complexation. This level of agreement is only achieved with the largest basis set and at the CCSD(T) level of treatment (Table 4) and casts some doubt on the use of MP2 methods for calculating dipole moment changes accompanying molecular association as was done, for instance, by Bunte et al. [23] for $CO\ldots Cl_2$. The change in the potential as a function of the OCO angle (CO_2 bend) indicates that there is only a very small displacement in the equilibrium angle from 180°. The potential along the bending coordinate of the complex does become anharmonic and below the effect of this on the expectation value of the dipole moment is examined, which will turn out to be small.

The primary source of the enhanced dipole moment is the dipole moment induced in the CO molecule by the local field of the CO_2 molecule. As Muenter and Bhattacharjee [1] have pointed out, the local field at the C atom of CO (the more polarizable end) is 3×10^7 V/cm; using the value $\alpha_{zz}/\pi\epsilon_0 = 2.298$ Å^3 for the polarizability of CO, the value of 0.23 D is obtained for the induced dipole moment, falling to 0.18 D if distributed polarizabilities on the C and O atoms are used. To this value must be added the dipole induced in the CO_2 molecule by the field of the CO. The order of magnitude of this contribution, estimated using the point dipole moment of the CO dipole placed it its centre of mass and $\alpha_\perp = 1.9 \times 10^{-30}$m^3 for CO_2 is +0.013 D.

These model-based dipole moments are certainly of the right order of magnitude, though somewhat too large. However, a simple point quadrupole model gives an inverse fourth-power dependence of the induced dipole,

$$\mu(R_{CC}) - \mu(\infty) \propto (R_{CC} + \delta)^{-4} \quad (4)$$

where δ is the distance of the centre of polarizability from the C atom in CO. This, in turn, predicts that the ratio of the quadratic coefficient to the linear term in an expansion of $\mu(R)$ about R_e as in Eq. (3) should be $-5/(R_e + \delta)$, approximately 1.3 Å^{-1} with $\delta = 0.5R_{CO}$. The ratio a_2/a_1 from the ab initio plot based on Eq. (3) is 0.085 Å^{-1}. This is a much less steep dependence on R_{CC} than the simple polarizability model would predict, wherever the centre of the CO polarizability is located. As Muenter pointed out [1], with decreasing R_{CC}, an increasing portion of the π electron density of the CO molecule lies in regions of space where the major component of the electric field arising from the CO_2 charge distribution is perpendicular to the C ≡ O axis and does not contribute to the induced moment in the z direction. is located.

This weak dependence of the dipole of the complex on R_{CC} does mean that the change in $\langle \mu_z \rangle$ from μ_e produced by averaging over the van der Waals intermolecular stretching mode is less than 0.01 D. Furthermore, charge transfer effects from the σ HOMO of CO to the LUMO of CO_2 also seem to be ruled out as a major cause of the enhanced dipole, at least at these separations. They would depend on the overlap of the relevant orbitals and thus cause a rapid variation of μ with R_{CC}.

3.1. The effect of perturbation of the zero-point motion of the bending mode of CO_2

Fitting the potential as a function of the CO_2 bending angle θ at constant R_{CC} by a quadratic in θ (Table 3),

$$V(\theta) = b_0 + b_1\theta + b_2\theta^2 \quad (5)$$

gives $b_1 = 0.05358$ mH deg^{-1}, $b_2 = 0.11202$ mH deg^{-2}, corresponding to a change in θ_e of 0.48° from linearity in the complex. The reliability of the quadratic term can be checked by calculating the frequency of the bending mode, ν_2, which is found to be 676 cm^{-1}, close to the observed value for free CO_2 of 667 cm^{-1} [24]. Using a harmonic basis of the unperturbed oscillator, the effect of the linear term in $V(\theta)$ arising from the interaction is to slightly mix the $v = 0$ and $v = 1$ states and hence to induce a small dipole. For small displacements of the CO_2 from linearity, we can use $\Delta\mu \approx \Delta\theta_e \times \partial\mu_{CO_2}/\partial\theta$. This correction must be added to the ab initio computed dipole at the fixed equilibrium geometry to give the observed dipole $\langle \mu_z \rangle$. Taking $\partial\mu_{CO_2}/\partial\theta = 3.3$ D rad^{-1} gives the correction $\Delta\mu = +0.03$ D, a small but not negligible contribution.

3.2. Effect of the CO libration

There are three internal rocking modes of the CO and CO_2 units. If the motion of the two molecules can be regarded as uncoupled, two of these modes are the in- and out-of-plane twist of the CO. These large amplitude modes directly affect the measured dipole by reducing the average component of μ_{CO} along the C_{2v} axis. With β the angle between the CO axis and the C_{2v} axis of the equilibrium geometry, the energy of the complex at $\beta = 0°$ and 30° was calculated, giving $k_\beta = 1114$ cm^{-1} rad^{-2} for the in-plane rocking mode of CO. The change in dipole moment from μ_e in C_{2v} symmetry when executing simple harmonic motion in this mode is then

$$\Delta\mu = \mu_{CO}\langle 0 \mid (1 - \cos\beta) \mid 0\rangle \approx \tfrac{1}{2}\mu_{CO}\langle 0 \mid \beta^2 \mid 0\rangle . \quad (6)$$

Substituting the estimated value of k_β gives $\Delta\mu = 0.004$ D. The r.m.s. value of β is 15°. A similar reduction in the observed dipole compared with the calculated equilibrium value can be expected from out-of-plane twisting of CO.

4. Conclusions

Ab initio electronic structure calculations using a basis of a least Pol(ANO) + f quality at the CCSD(T) level give a good account of the dipole moment of $CO_2 \ldots CO$ van der Waals complex. Both the SCF and MP2 treatments are inadequate, the latter predicting a dipole that is less than half the observed value.

The large amplitude zero-point motion in the CO twist and the inter-molecular stretch are taken into account and shown to reduce the vibrationally averaged dipole from the equilibrium value by slightly less than 10%. The perturbation of the bending mode in the CO_2 is slightly more significant and is probably responsible for an enhancement in the cluster dipole of ≈ 0.03 D.

The primary cause of the enhanced dipole moment is the electronic polarization of the CO molecule. However, although the simple polarization model for the dipole induced by the field of the charge distribution in CO_2 accounts fairly well for the enhancement in the moment if the free-molecule value of α_{zz} is used for CO, a plot of μ versus R(CO_2–CO) reveals that this is due to a cancellation of higher-order effects. Although the field on the CO axis rapidly rises as R_{CC} decreases beyond the van der Waals minimum, this is not matched by the calculated increase in the dipole moment of the complex, which remains almost constant.

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