INTERMOLECULAR INTERACTIONS IN THE $(CO_2)_2$, N_2–CO_2 AND CO–CO_2 COMPLEXES

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Received July 15, 2003
Accepted August 29, 2003

Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

Interaction energies of the most stable structures of the title complexes are calculated using the supermolecule CCSD(T) and MP4 methods and aug-cc-pV*X*Z (*X* = D, T, Q) basis sets extended by a set of midbond functions centered in the middle of the intermolecular bond. Geometrical parameters for these structures are in very good agreement with experimental data.

Keywords: Van der Waals complexes; Interaction energy; $(CO_2)_2$, N_2–CO_2 and CO–CO_2 complexes; Potential energy surfaces; CCSD(T); *Ab initio* calculations.

While the carbon dioxide dimer belongs to the most experimentally and theoretically studied van der Waals (vdW) molecules, little attention has been paid to the N_2–CO_2 and CO–CO_2 complexes. The long unresolved debate concerning the shape of the CO_2 dimer was settled conclusively in favour of the slipped parallel (C_{2h}) geometry[1–5]. The structures of slightly polar N_2–CO_2 and CO–CO_2 complexes were determined to be the T-shaped configurations (C_{2v}) with N pointing towards the C atom[6] and the T-shaped C–C bonded arrangement[7,8], respectively. In contrast to these five-atomic dimers, the T-shaped structure of $(CO_2)_2$ corresponds to the transition state[3,4]. With respect to the fact that CO is isoelectronic with N_2 and has similar electric properties, the CO–CO_2 species should be isostructural to the N_2–CO_2 complex.

Molecular deflection studies[1] of $(CO_2)_2$ indicated a nonpolar molecule which is incompatible with the T-shaped geometry. Also the vibrations in a slipped parallel $(CO_2)_2$ obey the mutual exclusion rule required by the

doi:10.1135/cccc20040177

ground state C_{2h} symmetry[4,5]. Structural parameters of the CO_2 dimer were determined spectroscopically by Walsh *et al.*[2] and Jucks *et al.*[3,4] A number of *ab initio* studies were also reported[9–16]. Intermolecular bond lengths for the N_2–CO_2 and CO–CO_2 vdW complexes were obtained from analyses of the fully rotationally resolved infrared spectra[6–8]. To our knowledge, there are no high-level *ab initio* calculations on these two mixed dimers. Their interaction energies were only estimated[6,8] by using the distributed multipole analyses (DMA)[17,18]. The aim of our study is to calculate the energetic and geometrical data for some selected structures of the title complexes on the same footing as it has been done for the isoelectronic triad of CO–N_2, $(N_2)_2$ and $(CO)_2$ clusters studied recently[19,20], and to interrelate the results.

COMPUTATIONAL

With the monomers held rigid, the intermolecular potentials in the $(CO_2)_2$, N_2–CO_2 and CO–CO_2 complexes can be expressed as a function of four variables R, θ_A, θ_B and ϕ. $R = |\boldsymbol{R}|$ is the intermolecular bond length with the vector $\boldsymbol{R}$ pointing from the centre of mass of the monomer A to that of B. θ_A and θ_B are the angles between $\boldsymbol{R}$ and the vectors $\boldsymbol{r}_A$ and $\boldsymbol{r}_B$ which are oriented from C to O^1, N^1 to N^2 and C to O in the CO_2, N_2 and CO subunits, respectively. ϕ is the dihedral angle between the two planes defined by the pair of vectors $\boldsymbol{R}$, $\boldsymbol{r}_A$ or $\boldsymbol{R}$, $\boldsymbol{r}_B$; all three angles are taking on values between 0 and 180°. Bond lengths in the N_2 and CO monomers are kept fixed at their experimental values[21] 1.0977 and 1.1283 Å, respectively. The C–O bond length in CO_2 was kept at 1.161 Å, in accord with experimental values[22,23] 1.160 and 1.162 Å.

As in our previous studies on the CO–N_2, $(N_2)_2$ and $(CO)_2$ complexes[19,20], for the calculation of the interaction energies ΔE, the CCSD(T) and MP4 methods have been used in conjunction with the full Dunning aug-cc-pV*X*Z basis sets[24] (denoted av*x*z), extended by 3s3p2d1f1g midbond functions (MB) centered in the middle of the intermolecular bond, with frozen core orbitals. The exponents of the MB functions were the same as those used for the above-mentioned four-atomic triad of the dimers[19,20]. For each selected dimer structure, the intermolecular distance R was varied in the vicinity of the minimum with a step size of 0.02 a_0 (a_0 is the Bohr radius). The angular step sizes were fixed at 1, 1 and 3° for θ_A, θ_B and ϕ, respectively. The interaction energies were corrected for the basis set superposition error (BSSE) using the counterpoise method[25]. In order to assure, whether the presumed minima really correspond to minima on the interaction energy surface, analyses of two- and three-dimensional fits were performed.

Interaction energies were extrapolated to the complete basis set (CBS) limit by a procedure based on the formula proposed by Helgaker *et al.*[26,27]

$$E(X) = E(\infty) + A/X^3 , \qquad (1)$$

which employs energies from the sequence of correlation consistent basis sets. X is the cardinal number (2, 3 and 4 for the DZ, TZ and QZ basis set, respectively). $E(\infty)$, representing the estimated CBS limit, is determined by solving the system of two linear equations[28] for $E(\infty)$ and the parameter A. The same formula was applied also for the basis sets comprising bond functions even though its application is lacking additional justification. All supermolecule calculations were carried out with the MOLPRO 2000.1 program package[29].

RESULTS AND DISCUSSION

CO_2–CO_2

Most of the theoretical studies[9–16] on interactions within the CO_2 dimer were based either on the supermolecule calculations or on the symmetry adapted perturbation theory (SAPT)[30–32]. Recently, four complete BSSE-corrected potential energy surfaces (PES) for $(CO_2)_2$ have been published. Three studies[13–15] were performed at the MP2 level of theory, Bukowski *et al.*[16] have used the SAPT method. All these *ab initio* calculations confirmed that the slipped parallel (SP) dimer ($\theta_A = \theta_B = \theta$; $\phi = 0$) was more stable than the T-shaped one.

Our structural $(CO_2)_2$ parameters for the global minimum and the saddle point on the potential energy surface (PES), computed within the CCSD(T) and MP4/av$x$z(+MB), x = d, t models, are collected in Table I. This Table shows that the CCSD(T) and MP4/av$x$z series converge to the CBS limit from above and for av$x$z+MB from below. A similar behaviour was found also for both mixed vdW dimers. The final CBS limit for individual structures is taken simply as an arithmetic mean of $\Delta E_{\mathrm{av}x\mathrm{z}}(\infty)$ and $\Delta E_{\mathrm{av}x\mathrm{z+MB}}(\infty)$. The CBS limits, in addition to geometrical parameters, are compared with theoretical predictions of some other authors and available experimental data in Table II. As far as the global minimum on the PES is concerned, the CCSD(T)/avtz geometrical data are very close to experimental values and near to the SAPT results. The CCSD(T) interaction energy is the highest in

Table I
Interaction energies ΔE (in cm^{-1}) and intermolecular bond lengths R (in Å) for the slipped parallel (SP) structure ($\theta_A = \theta_B = \theta$, $\phi = 0°$), and the T-shaped configuration of the carbon dioxide dimer

Method	Basis set	SP		T	
		ΔE	R	ΔE	R
CCSD(T)	avdz	–407.5	3.65	–353.5	4.22
	avdz+MB	–517.1	3.55	–433.4	4.15
	avtz	–469.4	3.57	–398.2	4.16
	avtz+MB	–507.5	3.54	–424.1	4.14
MP4	avdz	–426.2	3.61	–371.3	4.21
	avdz+MB	–550.1	3.51	–456.9	4.12
	avtz	–492.8	3.53	–414.8	4.14
	avtz+MB	–534.0	3.50	–442.2	4.13

[a] R is determined for the fixed value of θ optimized at the CCSD(T)/avtz and MP4/avtz levels, respectively; θ[CCSD(T)] = 58.6°, θ[MP4] = 59.0°.

Table II
Interaction energies ΔE (in cm^{-1}), intermolecular C–C bond lengths R (in Å) and the C–C–O angles θ (in °) for the global minimum (slipped parallel (SP) structure), and the saddle point (T) of the CO_2 dimer

Method and basis set	SP			T		References
	ΔE	R	θ	ΔE	R	
CCSD(T)/CBS[a]	–499.5	3.57	58.6	–418.6	4.16	This work
MP4/CBS[a]	–523.5	3.53	59.0	–434.6	4.14	This work
SAPT/5s3p2d1f	–484.0	3.54	59.0	–412.0	4.14	Ref.[16]
MP2/CBS	–482.8	3.47	59.8	–411.9	4.10	Ref.[15]
MP2/8s6p4d1f	–412.8	3.61	58.4	–360.4	4.21	Ref.[14]
MP2/6-311+G(2df)[b]	–451.2	3.58	66.5	–374.9	4.20	Ref.[13]
Experiment	–	3.602	57.9	–	–	Ref.[2]
Experiment	–	3.599(7)	58.2(8)	–	–	Ref.[4]

[a] The final CBS limit is taken as an arithmetic mean of the CBS limits extrapolated by using the av*x*z and av*x*z+MB basis sets (x = d, t). The R values are obtained by optimization with the avtz basis set. [b] With the monomer geometry optimized at the MP2/6-311G(3d) level.

magnitude among all the data and the closest to the SAPT value. There is also very good agreement between the CCSD(T) and SAPT results for the saddle point. From all approaches, the MP4/CBS model leads to the highest magnitude of the interaction energies for both stationary points on the PES.

The BSSE-corrected energy profiles for the model energy paths connecting the slipped parallel and the T-shaped dimers are displayed in Fig. 1. They are calculated at the CCSD(T)/avtz level for three fixed C–C intermolecular bond lengths, and specified by the varying angles θ_A and $\theta_B = 2(90° - \theta_A)$. The energy difference between the two structures is about 71 cm^{-1}, *i.e.*, nearly the same as that obtained by the SAPT. Both the CCSD(T) and MP4/CBS models give better geometrical parameters (in comparison with experimental data) than the MP2/CBS approach[15] which was based on the cc-pV*X*Z (*X* = D, T, Q) series alone. It should be noted that there is the highest degree of agreement between experimental and MP2 results of Steinebrunner *et al.*[14] However, their corresponding interaction energy for the SP structure seems to be underestimated in magnitude.

N_2–CO_2

We have considered four configurations of the N_2–CO_2 complex: Two T-shaped structures with the N–N bond axis pointing towards the carbon atom (T_N) and with the O–C–O axis pointing to the centre of the N–N bond

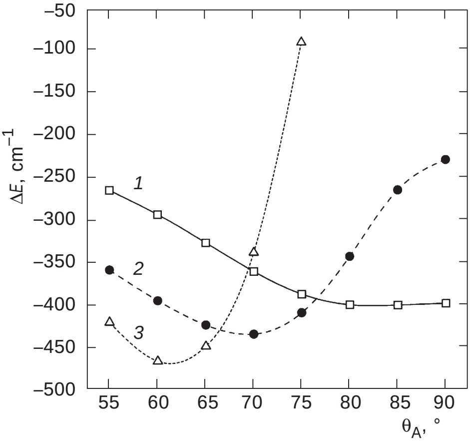

FIG. 1

Cuts of the $(CO_2)_2$ potential energy surface at three different intermolecular distances *R* (in Å): 4.16 (*1*), 3.86 (*2*) and 3.57 (*3*) as a function of the angle θ_A ($\theta_B = 2(90° - \theta_A)$), calculated within the CCSD(T)/avtz model. All curves correspond to the dihedral angle equal to zero

(T_O), the SP structure with the angle $\theta_A = \theta_B = \theta = 54°$ optimized at the CCSD(T)/avtz level, and finally the X-shaped structure. Some structural data (ΔE, R) for these configurations are summarized in Table III. The CCSD(T)/avqz vdW bond length 3.714 Å agrees very well with the spectro-

TABLE III
Interaction energies (in cm^{-1}; the top number in each cell) and intermolecular bond lengths (in Å; the bottom number in each cell) for the two T-shaped, slipped parallel (SP), and X-shaped structures of the N_2–CO_2 complex

Method	Basis set	T_N[a]	T_O[b]	SP[c]	X
CCSD(T)	avdz	–261.6	–125.2	–149.2	–103.6
		3.79	4.56	4.03	3.57
	avdz+MB	–338.6	–163.1	–200.5	–172.3
		3.70	4.47	3.94	3.40
	avtz	–300.6	–147.0	–176.1	–139.8
		3.71	4.51	3.96	3.45
	avtz+MB	–326.4	–158.7	–192.6	–161.6
		3.68	4.47	3.93	3.41
	avqz	–316.7	–152.3	[d]	–152.5
		3.71	4.51	–	3.45
MP4	avdz	–287.8	–141.1	–169.3	–115.2
		3.77	4.52	3.99	3.49
	avdz+MB	–372.3	–180.3	–225.5	–194.0
		3.67	4.45	3.89	3.38
	avtz	–331.5	–164.0	–199.0	–156.8
		3.68	4.47	3.92	3.42
	avtz+MB	–358.8	–176.2	–217.1	–180.6
		3.66	4.45	3.88	3.37
	avqz	–348.2	–169.5	[d]	–170.2
		3.68	4.47	–	3.42

[a] T-shaped structure with N–N forming a “leg” of the T. [b] T-shaped structure with O–C–O forming a “leg” of the T. [c] The structure with θ = 54°; the angle was optimized at the CCSD(T)/avtz level. [d] The data could not be calculated because of exceedingly large requirements for the disk space of our computer facilities.

scopic value[6] of 3.731 Å. The final CCSD(T)/CBS limit for the binding energy of the T_N configuration amounts to 319.2 cm^{-1}. The MP4/avqz model leads to a shorter intermolecular bond length (3.68 Å) and higher absolute value of the interaction energy (348 cm^{-1}). It is worth mentioning that Walsh *et al.*[6] modelled the electrostatic interaction in the complex using the distributed electrostatic multipole analysis including dispersion interaction of the form $-C_6/R^6$. For the T_N structure with the experimentally determined configuration and with the value of 118 a.u. for the C_6 coefficient determined by Pack[33], this approach gave much higher binding energy (453 cm^{-1}) than the CCSD(T)/avqz value (317 cm^{-1}). The energy difference between both T-shaped dimers calculated at the same level is about 164 cm^{-1} in favour of the T_N structure, the difference between the T_N and SP structures calculated within the CCSD(T)/avtz model is about 125 cm^{-1}, *i.e.* by 54 cm^{-1} larger than that in the CO_2 dimer.

CO–CO_2

Computed energetic and geometrical data for five selected structures of the dimer (two T-shaped, two slipped parallel and X-shaped) are displayed in Table IV. The T-shaped C-bonded configuration (T_C) was found to be the most stable. The intermolecular bond length calculated at the CCSD(T)/avqz level (R = 3.89 Å) is in very good agreement with the experimental value[8] of 3.9066 Å. The interaction energy for the T_C arrangement is markedly higher in magnitude (by more than 100 cm^{-1}) compared to the other ones. For example, the energy difference between the two T-shaped structures, *i.e.* the C- and O-bonded complexes, is about 110 cm^{-1} within the CCSD(T)/avqz model.

Similarly to the N_2–CO_2 mixed dimer, the DMA model was applied by Randall *et al.*[8] to the estimation of the CO–CO_2 binding energies using the same C_6 coefficient as for N_2–CO_2. The authors determined two potential minima of about –410 and –459 cm^{-1} for the T_C structure, and –313 and –252 cm^{-1} for the T_O structure, respectively. Our CCSD(T)/avqz values (see Table IV) are –394 cm^{-1} (T_C) and –284 cm^{-1} (T_O), respectively.

The same T-shaped structure of both isostructural vdW molecules can be understood on grounds of the fact that quadrupole–quadrupole interactions prevail over all other intermolecular interactions, and that the N_2 and CO subunits possess similar electric properties[36–39] and dispersion coefficients[40].

TABLE IV
Interaction energies (in cm^{-1}; the top number in each cell) and intermolecular bond lengths (in Å; the bottom number in each cell) for the two T-shaped, two slipped parallel (SP), and X-shaped structures of the CO–CO_2 complex

Method	Basis set	T_C[a]	T_O[b]	SP_1[c]	SP_2[d]	X
CCSD(T)	avdz	–331.9	–230.0	–163.1	–194.4	–97.6
		3.98	3.65	3.78	4.18	3.58
	avdz+MB	–423.7	–293.9	–215.4	–248.9	–167.0
		3.88	3.56	3.67	4.05	3.41
	avtz	–375.4	–269.0	–195.6	–218.8	–136.8
		3.89	3.58	3.69	4.10	3.45
	avtz+MB	–404.2	–291.4	–213.5	–238.4	–157.3
		3.87	3.55	3.66	4.06	3.42
	avqz	–393.9	–283.5	[e]	[e]	[e]
		3.89	3.58	–	–	–
MP4	avdz	–373.2	–226.3	–155.3	–224.2	–112.4
		3.96	3.63	3.78	4.13	3.55
	avdz+MB	–476.4	–292.5	–211.0	–287.6	–193.1
		3.84	3.56	3.65	4.01	3.37
	avtz	–423.2	–261.5	–185.4	–254.1	–158.5
		3.85	3.58	3.69	4.04	3.41
	avtz+MB	–454.5	–284.6	–204.1	–276.2	–181.8
		3.84	3.55	3.66	4.02	3.37
	avqz	–442.9	–275.7	[e]	[e]	[e]
		3.85	3.58	–	–	–

[a] T-shaped structure with the C^2–O^3 monomer forming a “leg” of the T. [b] T-shaped structure with O^1–C^1–O^2 forming a “leg” of the T. [c] The structure with θ = 62° and the C^1–C^2 bond longer than the intermolecular C^1–O^3 bond; the angle was optimized at the CCSD(T)/avtz level. [d] The structure with the θ = 50° and the C^1–C^2 bond shorter than the intermolecular C^1–O^3 bond; the angle $\theta_A = \theta_B = \theta$ was optimized at the CCSD(T)/avtz level. [e] Exceedingly large requirements for the disk space.

Basis Set Superposition Errors and Assessment of Interaction Energies of Mixed Dimers

As seen from Table V, for all three dimers the BSSE significantly decreases with an improvement of the basis set. Also, the basis set dependence is rather similar for both methods used. The difference in the BSSE, for a given structure and basis set, calculated by CCSD(T) and MP4 is lower than 3% of the binding energy. It may be of interest that in the case of $(CO_2)_2$, the MP4 value is somewhat larger than the CCSD(T) one, while the opposite is true for both mixed dimers. For higher energy structures, the BSSE's are larger than those for the ground states species, *e.g.*, for the T_O configuration of CO–CO_2, the BSSE calculated within the CCSD(T) or MP4/avqz model amounts to around 14% of the binding energy.

Before concluding, one other point should be mentioned. Since the early days of the theory of intermolecular interactions and its application in statistical thermodynamics, many combination rules (*e.g.*, Lorentz–Berthelot rule[34]) for parameters in model potentials of interacting atoms or molecules A and B were proposed. These parameters (well depth (ε) and zero potential location) were estimated from quantities related to the A–A and B–B interactions. Recently, we have shown that a harmonic mean rule[35]

$$\varepsilon_{AB} = 2\, \varepsilon_A \varepsilon_B / (\varepsilon_A + \varepsilon_B) \qquad (2)$$

TABLE V
Basis set dependence of the BSSE[a] for the most stable structures of the $(CO_2)_2$, N_2–CO_2 and CO–CO_2 vdW complexes

Complex	Method	Basis set		
		avdz	avtz	avqz
$(CO_2)_2$	CCSD(T)	52	22	[b]
	MP4	54	23	[b]
N_2–CO_2	CCSD(T)	71	29	13
	MP4	68	27	12
CO–CO_2	CCSD(T)	63	28	11
	MP4	59	25	10

[a] BSSE is expressed in per cent of the binding energy. [b] Exceedingly large requirements for the disk space.

can be successfully applied to the family of the isoelectronic four-atomic dimers CO–N_2, $(N_2)_2$ and $(CO)_2$ (ref.[20]). More specifically, we found that the BSSE-corrected interaction energy of the most stable structure of the CO–N_2 complex calculated at the CCSD(T)/CBS (or, *e.g.*, avqz) level was nearly the same as that assessed by using the harmonic mean rule together with the data (ΔE) for the CO and N_2 dimers. Making use of Eq. (*2*) and the final CBS limits for homomolecular complexes collected in Table VI enabled us to assess the binding energies also for the N_2–CO_2 and CO–CO_2 complexes. However, these estimates of 173 and 204 cm^{-1}, obtained by the harmonic

TABLE VI
Comparison of binding energies (in cm^{-1}) for the most stable structures of the $(CO_2)_2$, N_2–CO_2, CO–CO_2, $(CO)_2$ and $(N_2)_2$ vdW complexes

Method	Basis set	$(CO_2)_2$	N_2–CO_2	CO–CO_2	$(CO)_2$[a]	$(N_2)_2$[a]
CCSD(T)	avdz	407.5	261.6	331.9	110.5	83.6
	avtz	469.4	300.6	375.4	121.0	98.2
	avqz	–	316.7	393.9	127.8	102.6
	CBS[b]	495.5	317.0	393.7	125.4	104.3
	avdz+MB	517.1	338.6	423.7	139.4	114.6
	avtz+MB	507.5	326.4	404.2	132.9	108.1
	avqz+MB	–	–	–	132.8	107.4
	CBS(+MB)[b]	503.5	321.3	396.0	130.2	105.4
	Final CBS[c]	499.5	319.2	394.9	127.8	104.9
MP4	avdz	426.9	287.8	373.2	137.9	90.7
	avtz	492.2	331.5	423.2	151.8	106.4
	avqz	–	348.2	442.9	159.3	110.6
	CBS[b]	519.7	349.9	444.3	157.7	113.0
	avdz+MB	550.1	372.3	476.4	171.8	122.7
	avtz+MB	534.0	358.8	454.5	165.6	116.4
	avqz+MB	–	–	–	165.1	115.7
	CBS(+MB)[b]	527.2	353.1	445.3	163.0	113.7
	Final CBS[c]	523.5	351.5	444.8	160.4	113.4

[a] Taken from our previous work[20]. [b] Calculated using Eq. (*1*). [c] The final CBS limit is taken as an arithmetic mean of the CBS and CBS(+MB) limits extrapolated using the av*x*z and av*x*z+MB basis sets (x = d, t).

mean rule, amount to only 54 or 52% of the binding energy calculated directly by the CCSD(T) method and extrapolated to the final CBS limits. The corresponding percentages for the MP4 approach are by 1–3% larger. These findings confirm that the validity of the combination rule (*2*) for the above-mentioned triad of four-atomic dimers represents a special case which may be viewed as a manifestation of the isoelectronic principle.

CONCLUSIONS

The CCSD(T) and MP4 methods, in conjunction with the aug-cc-pV*X*Z (X = D, T, Q) basis sets extended by a set of bond functions, have been used to calculate some structural and energetic parameters of the triad $(CO_2)_2$, N_2–CO_2 and CO–CO_2 vdW complexes. All the geometrical parameters for the most stable structures are in very good accord with available experimental data. The deviations between experiment and theory (CCSD(T)) was lower than 0.03 Å. In all the dimers, the aug-cc-pV*X*Z results converged to the CBS limit from above and aug-ccpV*X*Z+MB from below. The final CBS limit for interaction energies were calculated as an arithmetic mean of both av*x*z and (av*x*z+MB) CBS limits, x = d, t. In the case of the global minimum and saddle point structures of the carbon dioxide dimer, our CCSD(T)/CBS interaction energies are rather close to the SAPT ones. On the basis of the CBS energy data one can expect a somewhat stronger intermolecular bond for CO–CO_2 than for the isostructural N_2–CO_2 complex.

This work was supported by the long-term Project MSM 113100001 of the Ministry of Education, Youth and Sports of the Czech Republic and by the Grant Agency of the Czech Republic (Grant No. 203/00/0600). The time allocation in the Czech Academic Supercomputer Centre is greatly acknowledged.

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