The CO_2 Trimer: Between Gas and Fluid Phase

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Dedicated to Prof. *Edgar Heilbronner* on the occasion of his 80th birthday

A random search for CO_2 trimers by means of *ab initio* pair potentials in an additive manner yields, in addition to the two experimentally known isomers, three new ones. This result is independent of the potential applied for four different potentials. A model process for trimer formation is simulated and predicts a reasonably high frequency of formation for at least one of the new isomers, making a new experimental search worthwhile. Elsewhere, these potentials are applied in the same manner to calculate bulk properties of fluids. Their performance in reproducing the experimental structures of trimers gives useful hints of what accuracy can be expected for fluid structures.

Introduction. – The structure of a CO_2 trimer was reported for the first time in 1987, by *Fraser et al.* [1]. It has C_{3h} symmetry, with a $C \cdots C$ separation of 403.2 pm. In 1995, *Weida et al.* [2] also observed this trimer in a slit-jet supersonic expansion, by high-resolution infrared-diode laser spectroscopy. Calculations with empirical models confirmed its stability, but also predicted an asymmetric top isomer of similar energy. A year later, *Weida* and *Nesbitt* [3] reported spectroscopic and structural information about the second isomer.

Only two corresponding *ab initio* studies have so far been reported. *Tsuzuki et al.* [4] studied the two experimentally detected isomers and found the asymmetric top molecule to be more stable by 0.38 kJ/mol. *Bukowski et al.* [5] calculated a pair potential using the symmetry-adapted perturbation method (SAPT). Applying this potential to the trimer, under an assumption of pair-additivity, they predicted the two known isomers and found, in addition, a third stable trimer where the three monomers lie staggered in a plane. Full trimer calculations showed that the differences in magnitude of the three-body interactions for the different trimers are of the same order as the overall energy differences, making it very difficult to confirm the relative energies.

Spectroscopists often like to interpret dimers and trimers as a 'conceptual bridge' to the fluid. For simulators such as ourselves, accurate models of dimers and trimers form the very foundation of our studies of fluids. A common methodology is to model bulk fluids as a periodically repeated collection of a few hundred molecules, considering only pair interactions. It is assumed that many-body interactions have a negligible effect on the properties of the bulk. We and other groups have recently used this approach to study fluid CO_2. First, quantum-chemical techniques are used to densely sample the potential-energy surface describing the interactions of pairs of rigid monomers. An analytical function is then fitted to these points. Such functions have been efficiently applied in Monte Carlo [6] and molecular-dynamics simulations [7–10] of the fluid to obtain bulk properties.

In this work, we set out to show with what accuracy these various *ab initio* pair potentials predict the trimer structures. This should provide a reliable indication of the accuracy with which they are able to model the microscopic structure of fluids without the inclusion of many-body interactions. The effect of neglecting such interactions varies with density and system composition. In the case of Ne, we were able to study it directly through the application of a quantum-chemical *ab initio* three-body potential in molecular dynamics simulations [11] [12]. The results showed that the liquid structure is hardly influenced by the three-body interaction. However, an atomic fluid is of little predictive power for the present molecular system.

In addition, we will model the formation of the isolated trimer. This leads to the prediction of additional isomers, and an approximate probability of their formation. Hopefully these predictions will initiate an experimental search for the additional stable trimers.

Computational Method. – Spectroscopists investigate trimers in the supersonic expansion of a gas jet. In our model of trimer formation, we assumed that three monomers are found in a random configuration, in close-enough proximity to one another to interact, with virtually no (relative) kinetic energy, and rotationally cold. The attractive interaction leads then either to a metastable trimer, which might have a lifetime long enough to allow it to be observed, or the excess energy is dissipated through additional soft interactions with surrounding monomers and a stable trimer is formed. The model is realized by a two-step application of Monte Carlo techniques.

To start with, the Monte Carlo method is used to produce the initial random arrangements of three monomers. To this end, we form triangles and place C-atoms at the three vertices. The shortest side of the triangle is selected, with uniform probability, from a range $(A \pm 1)\ a_0$. The parameter A is adjustable, set in such a way that the molecules are not yet too close, but that it does not take too long to form a trimer. Several runs with different values of A were performed to study its impact on the results (see below). Next, the vertex angles are randomly determined. The first (α) is uniformly distributed between 0° and 180°, the next between 0° and $(180° - \alpha)$, and the third is then the complement of the first two. This scheme also allows for linear arrangements. To exclude configurations where the monomers are too far apart to interact, only triangles with a perimeter smaller than a second parameter B (typically $30 a_0$, see *Table 2*) are included. With the triangle fixed in this way, the axes of the monomers are determined, with a uniformly distributed out-of-plane angle between 0° and 90°, and an in-plane angle between 0° and 360°.

The Monte Carlo method is then used in the standard way to find the minimal energy, *i.e.*, to optimize the geometry of the trimer, starting with the configuration chosen in the first step. This two-step process is repeated in a loop a few thousand times to find how often each isomer is formed. In this way, one finds not only other stable trimers, if they exist, but also their relative energies and the approximate probability of formation and, hence, the chance to find them experimentally.

The four *ab initio* pair potentials applied in this study will henceforth be designated WSSH, SDKH, BBV, and SAPT-s. WSSH is an older potential from our group [13] (note that the simulation results in the original paper were not equilibrated; corrections were published in [9][10]). SDKH is a newer, improved potential from our group [9]. Both of these potentials have been applied in fluid simulations [9][10]. The BBV potential was published recently by *Bock et al.* [14], the SAPT-s potential is that of *Bukowski et al.* [5]. The latter two potentials have not yet been applied in simulations. All four pair potentials have rigid monomers.

Results and Discussion. – In addition to the two experimentally known isomers **1** (C_{3h}) and **2** (asymmetric top), we found three other stable isomers (see *Fig. 1*). Isomer **3** consists roughly of a slipped-parallel dimer with the third monomer perpendicular to the plane of the first two, forming roughly a T-shaped dimer with one of the other two monomers, it is only little higher in energy compared to the two most stable trimers. Isomer **4** is the staggered linear arrangement already studied by *Bukowski et al.* [5], which is much higher in energy. In isomer **5**, the monomers are also in a plane, with the outer monomers slipped parallel in relation to the central one, and with the C-atoms forming an isosceles triangle.

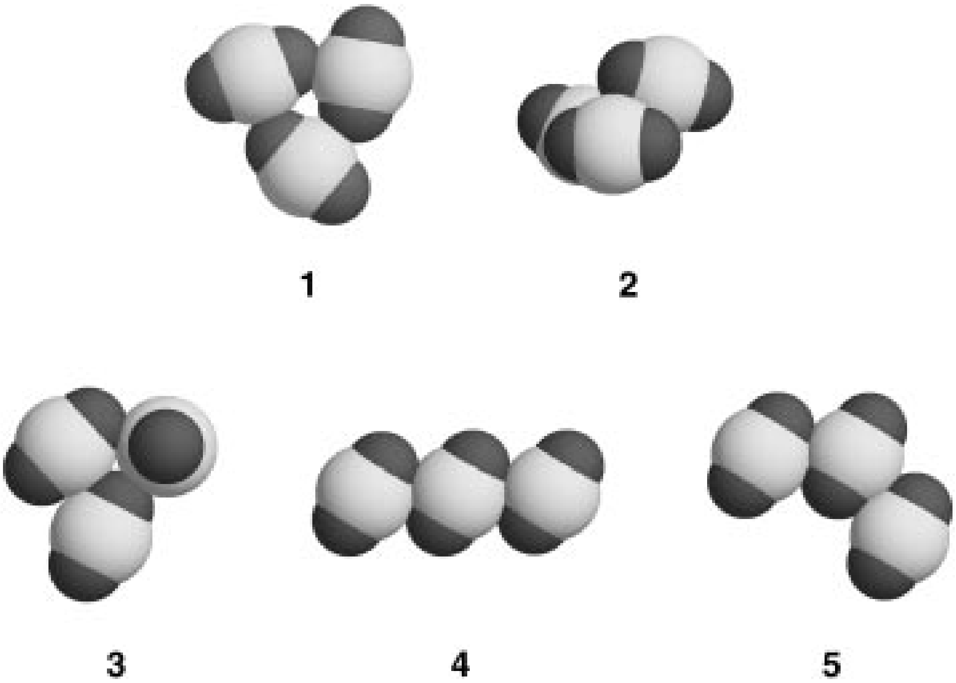

Fig. 1. *The five stable isomers of the* CO_2 *trimer found in this investigation*

Table 1 shows the absolute and relative energies obtained with the different potentials. The two experimentally known trimers are the most stable with all potentials, but, with the SDKH and the SAPT potentials, the order is exchanged. The absolute energies decrease with the quality of the potentials. Interestingly, isomer **3**,

Table 1. *Absolute and Relative Energies of the Five Isomers from Different Potentials*

Isomer	Absolute energies/kJ mol^{-1}					
	WSSH[a])	TUTKTH[b])	SDKH[c])	BBV[d])	SAPT-a[e])	SAPT-s[f])
1	– 11.54	– 13.60	– 13.07	– 15.34	– 15.13	– 14.95
2	– 11.32	– 12.43	– 13.51	– 14.68	– 15.71	– 15.27
3	– 10.92		– 12.75	– 14.51		– 14.40
4	– 8.49		– 10.02	– 10.96	– 11.77	– 11.43
5	– 8.23		– 9.76	– 10.63		– 11.12
Isomer	Relative energies/kJ mol^{-1}					
	WSSH	TUTKTH	SDKH	BBV	SAPT-a	SAPT-s
1	0	0	0.44	0	0.58	0.32
2	0.22	1.17	0	0.66	0	0
3	0.62		0.76	0.83		0.87
4	3.05		3.05	4.38	3.94	3.84
5	3.31		3.31	4.71		4.15

[a]) This work with the potential from [13].
[b]) From [5] with the potential from [8].
[c]) This work with the potential from [9].
[d]) This work with the potential from [14].
[e]) From [5] with the angular fit.
[f]) From [5] and this work with the site-site fit.

which has not yet been observed, is only a little higher in energy than isomers **1** and **2**. There is a marked gap between the first three isomers and the last two, the gap being larger with the better potentials.

Table 2 and *Fig. 2* show the statistics of our computer experiments. Although the details differ for different potentials and different choices of starting parameters A and B, the results clearly demonstrate that the barrel-like isomer **2** has the highest probability of formation, independent of its relative stability. Evidently, also the not-yet-observed isomer **3** is quite likely to be formed. Depending on the potential and the value chosen for the parameter B (the maximum allowed perimeter of starting triangle), its likelihood is similar to or a little lower than that of isomer **1**. Whereas isomer **5** always has a low probability for $B = 30\ a_0$, it is similar to that of isomers **1** and **3** when B is $40\ a_0$.

The linear staggered isomer **4** has some probability to be formed with $A = 7\ a_0$, but the probability is negligible for larger A, if B is kept at $30\ a_0$. This, however, is an artifact. As isomer **4** has a linear conformation, it is far more likely to be formed if the starting configuration is close to linear. Such configurations have a triangle perimeter of at least four times the shortest side length. With a B/A ratio of 30 : 7, most such flat triangles are rejected by the selection criteria, thus disadvantaging the formation of linear isomers. Similar arguments are valid for isomer **5**. We, therefore, ran some simulations with an increased value of B (see the last two entries of the *Table 2*). This led to the surprising result that the probability of formation of isomer **4** became very large, despite its much higher energy. Our model does not take into account that the shape of isomers **4** and **5** makes them very vulnerable to hits by other molecules, which would both diminish their chance of formation and reduce their lifetime. We think an

Table 2. *Relative Frequencies of Formation of the Different Isomers in the Monte Carlo Simulation*

Potential	Parameter		Number of Simulations	Frequency [%] for isomers **1**–**5**				
	A	*B*		**1**	**2**	**3**	**4**	**5**
WSSH	7 a_0	30 a_0	1857	14	70	8.7	6.0	1.5
SDKH	7 a_0	30 a_0	1990	10	73	7.4	6.5	2.4
BBV	7 a_0	30 a_0	2353	17	62	14	5.9	0.4
	9 a_0	30 a_0	3061	22	61	16	0.2	0.1
	10 a_0	30 a_0	3761	24	60	16	0.0	0.0
SAPT-s	7 a_0	30 a_0	1819	9.5	75	5.7	6.9	3.1
	9 a_0	30 a_0	1828	15	76	7.7	0.4	1.4
	7 a_0	40 a_0	1826	4.5	61	4.6	25	4.5
	9 a_0	40 a_0	1804	3.4	56	4.4	32	3.9

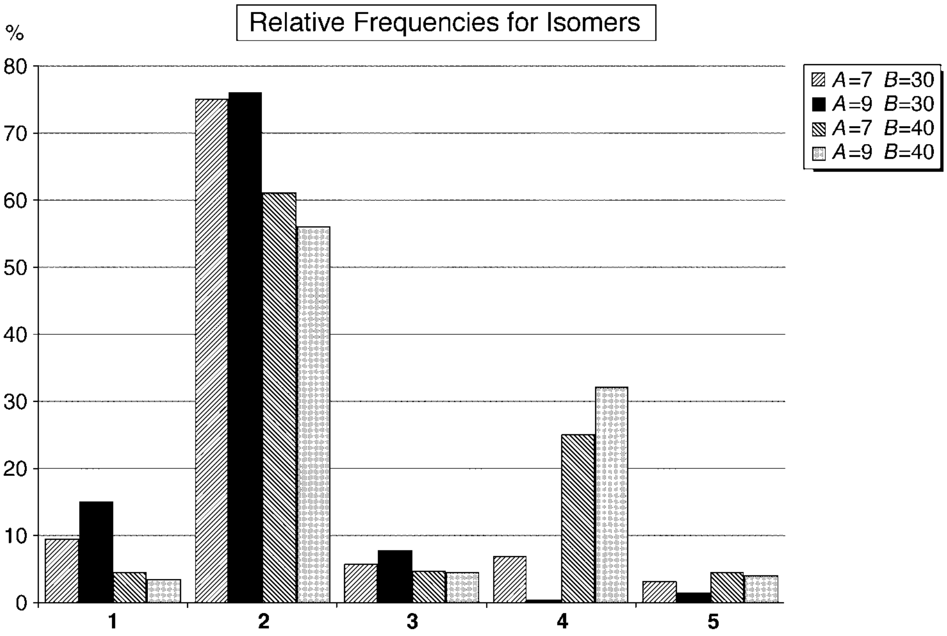

Fig. 2. *The relative frequencies of formation of the isomers obtained from the SAPT-s potential as a function of parameters* A *and* B (see text)

experimental search should concentrate on isomer **3**, but there is also some chance to find **4** and perhaps even **5**.

Finally, we discuss some structural features. In a comparison with the experimental structures, one should keep in mind that all calculated structures are equilibrium structures, whereas the experimental ones are time-averaged. Due to the weak and anharmonic intermolecular potentials, the differences between the two structures are expected to be several pm, *i.e.*, exact agreement should not be expected. This applies particularly to the angles. Further discrepancies may be due to the neglect of three-body interactions. The structural parameters of the different isomers are defined in *Fig. 3*.

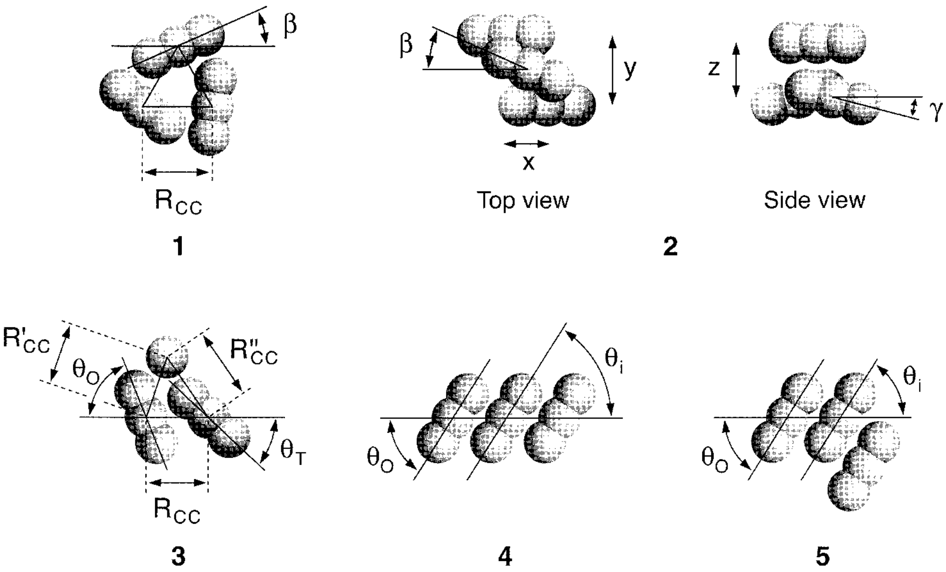

Fig. 3. *Definition of the structural parameters for the isomers*

Isomer **1** is characterized by the C ··· C distance and the angle β, between the axis of the monomers and the opposite side of the equilateral triangle connecting the centres of mass. Calculated and experimental values are shown in *Table 3*. The distance changes with increasing quality of theory, but the angle remains relatively constant. This suggests that the deviation of the angle is due to the fact that calculated and experimental angles are different physical observables, as discussed above. A similar conclusion for the distance is not possible, as the changes with potential quality are still too large. Calculations of *Tsuzuki et al.* [4] have, however, shown that the inclusion of three-body interactions shorten it by only 2 pm. That this change is so small indicates that our results for liquid Ne [12], where three-body terms hardly changed the liquid structure, also apply to this molecular arrangement.

Weida et al. reported that isomer **2** has C_2 symmetry. However, the WSSH and the BBV potentials yield a similar isomer of lower symmetry. For the potential of *Tsuzuki et al.* (TUTKTH), the situation is unclear. *Bukowski et al.* [5] claimed that this potential yields also an isomer of lower symmetry, whereas *Tsuzuki et al.* [4] reported the C_2 conformation described by us. The first five structural parameters shown in the *Table 3* are those reported by the original authors [3][5]; x and y give the parallel displacements of the two nearly planar isomers, and z is the displacement of the C-atom of the third monomer from the point midway between the C-atoms of the two former monomers. As we saw for isomer **1**, the calculated angles are very consistent, but differ from experiment. This is probably a further hint that equilibrium and averaged values are indeed different. But the distances x, y, and z give a somewhat fluctuating pattern. As this could be due to their strong dependence on the angular orientation of the monomers, we calculated, in addition, the three C ··· C distances. These show a more consistent pattern, although the shortest calculated distance is *ca.* 10 pm shorter than

Table 3. *Structures of the Different Isomers from* ab initio *Pair Potentials and Experiment*

	WSSH[a])	TUTKTH[b])	SDKH[c])	BBV[d])	SAPT-s[e])	SAPT-a[f])	ai[g])	Exp.
Isomer **1**								
R_{CC}/pm	417	414	411	396	404	404	401	403.76 ± 0.02
β/°	40.0	41.4	39.8	39.2	39.3	39.6	39.1	33.8 ± 0.5
Isomer **2**								
x/pm	[h])	265.7	213.7	[h])	219.3	214.9	208.7	238.0 ± 4.3
y/pm		311.1	311.2		305.3	307.4	[i])	291.3 ± 4.3
z/pm		314.0	297.6		291.9	289.4		301.7 ± 2.8
β/°		23.1	22.9		25.0	22.4		27.1 ± 6.9
γ/°		13.3	11.9		11.9	10.9		5.8 ± 4.0
R_{CC}/pm	402.6	409	378	386	376	375		376
R'_{CC}/pm	363.4	375	353	348	347	345		356
R''_{CC}/pm	359.3	375	353	344	347	345		356
Isomer **3**								
R_{CC}/pm	368		360	356	355			
R_{CC}'/pm	385		377	371	371			
R_{CC}''/pm	430		425	408	417			
θ_T/°	52.6		55.0	49.0	53.8			
θ_O/°	65.1		63.5	69.0	63.5			
Isomer **4**								
R_{CC}/pm	368		361	349	353	356		
θ_O/°	57.1		57.7	57.7	58.4	57.0		
θ_i/°	58.9		59.1	60.6	59.7	58.4		
Isomer **5**								
R_{CC}/pm	369		362	349	357			
θ_O/°	57.5		58.2	58.6	57.4			
θ_i/°	58.6		58.7	59.8	58.0			

[a]) This work with the potential from [13].

[b]) From [5] and [4] with the potential from [8]. *Bukowski et al.* [5] claim that isomer **2** with this potential has no C_2 symmetry.

[c]) This work with the potential from [9].

[d]) This work with the potential from [14].

[e]) From [5] with the angular fit.

[f]) From [5] and this work with the site-site fit.

[g]) *Ab initio* calculation including three-body interactions [4].

[h]) No C_2 symmetry.

[i]) Only x was optimized.

the experimental one. This suggests again that the equilibrium and averaged lengths are in fact different, which would perhaps point to a floppy isomer. That some potentials fail to show the expected symmetry, but are close to it, as is seen from the C ⋯ C distances in the *Table 3*, could be a further confirmation. The isomer from the BBV potential, shown in *Fig. 4*, appears somewhat like a transition state towards isomer **3**. As isomers **2** and **3** are close in energy, their structures might be very sensitive to the potential. It could even be possible that exact calculations would yield the result that isomer **3** is only a transition state between two isomers **2**, similar to the well-known situation in the dimer.

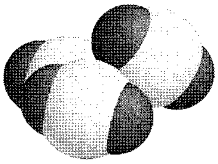

Fig. 4. *Isomer* **2** *from the BBV potential*

Isomer **3** consists of two monomers that form very roughly a slipped parallel conformation. One of them forms nearly a T-shaped conformation with the third monomer, whereas the other is slipped forward towards the T-bar C-atom. The difference between the angles θ_T and θ_O is the deviation from parallel. It changes markedly between the different potentials, in contrast to the angles in isomers **1** and **2**.

Isomers **4** and **5** show again quite constant angles. The distances behave similarly as for the other isomers, with a convergence to *ca.* 350 pm.

Conclusion. – Monte Carlo-type model calculations were performed using several *ab initio* pair potentials from the literature, to find all stable trimers of CO_2, and to estimate the probability of their formation in a supersonic jet expansion. In addition to the two experimentally known isomers, we found two novel trimers and observed a third one that had already been found in calculations by other authors [5]. Some of the novel trimers show a frequency of formation large enough that it should be possible to find them experimentally. Quantum-chemical *ab initio* calculations will be performed to confirm the present results.

The relatively accurate confirmation of the experimental structures from pair potentials in this work, and the only literature results from *ab initio* trimer calculations [4], suggest that pair potentials should be able to model the liquid structure fairly well. However, a quantitative simulation of the radial distribution functions, as obtained experimentally in diffraction studies, suffers from the nearly equal energies of the different dimer and trimer arrangements.

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