Totally *ab Initio* Prediction of the Structures of CO_2 Molecular Crystal

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We have succeeded in predicting a molecular crystal structure from first principles. The potential parameters and geometry for CO_2 molecule were determined by *ab initio* molecular orbital calculations. The experimentally observed CO_2 crystal structures at low and high pressures have been reproduced by molecular dynamics method without any *a priori* assumptions on lattice constants nor space group symmetry. With extra pressure of 1 GPa in [010] direction, the structural change observed at about 10 GPa has also been reproduced.

Seven years ago an article appeared in *Nature*[1] charging the "scandalous" situation of the theoretical prediction of a crystal structure. The challenge therein was to calculate from first principles the crystal structure of a compound of which nothing is known except chemical composition. Prediction of crystal structure has been done, as Hawthorne discussed,[2] by starting with a list of candidate structures and/or by assuming the space group symmetry and cell-size. Nose and Klein[3] successfully simulated the phase change of N_2 molecular crystal without these constraints, but they employed empirically determined potential functions. Gavezzotti[4] answered "definitely 'no'" to the question "Are crystal structures predictable?", reviewing many efforts in paving the way in "static" and "dynamic" approaches.

Recently, Aoki *et al.* found that the CO_2 crystal changes its structure from $Pa3$ to $Cmca$ upon placing the system under pressure at about 10 GPa at 295 K.[5] As a test example of our newly coded program MDCP (Molecular Dynamics for Crystal Packing),[6,7] we examined the polymorphs of CO_2 molecular crystal. MDCP consists of a heuristic molecular dynamics (MD) search[7] (shaking process) based on the lattice-variable constant pressure MD, proposed by Parrinello and Rahman,[8] Andersen,[9] and Nose and Klein,[3] and of the steepest-descent method (quenching process). Details of the MDCP program with some examples have been described in our previous report.[7]

Regarding the potential functions and parameters for the CO_2 molecule assembly, many empirically determined atom-atom type potentials, including those of Cox *et al.*[10] and Kuchta and Etters,[11] are already known. However, for potentials to be employed at high pressure region where property data to calibrate the potentials have not yet been reported, we thought it better to rely on potentials derived from high quality *ab initio* molecular orbital (MO) calculations. First, we determined the geometry and electric charge (CHELPG net charge[12] based on the electrostatic potential method) of the CO_2 molecule at the MP2/6-311G* and MP2/6-311G(2d) level *ab initio* MO calculations,[13] respectively. Then, potential energies for 40 dispositions in total for four different types of coordination structures of the CO_2 dimer were calculated at the MP2/6-311G(3d) level with correction for the basis set superposition error by the counter-poise method,[14] and were fitted to the exp-6 potential functions by the least square method.

$$E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6} + 1389.4\,q_i q_j r_{ij}^{-1} \quad (1)$$

The thus determined geometry, partial charges, and potential parameters are listed in Table 1. It should be noted that first and second terms in eq. 1 thus determined have no physical meaning as van der Waals (VDW) interaction term for each *i-j* atom pair, but, instead, only the total sum, not each, of these exp-6 terms for the interacting CO_2 molecule pair has meaning as the best fit to the VDW component of the potential energies calculated by the *ab initio* MO method.

Table 1. Geometry, partial charges, and intermolecular potential parameters for CO_2 molecule determined by *ab initio* MO calculations[a]

- Geometry of CO_2 molecule: $r_{CO} = 1.169$ Å
- Point charges, and potential function and parameters[b]

$E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6} + 1389.4\,q_i q_j r_{ij}^{-1}$

$q_C = 0.68$, $q_O = -0.34$

$A_{CC} = 1.95 \times 10^3$, $B_{CC} = 7.16 \times 10^2$, $C_{CC} = 2.14$

$A_{OO} = 1.48 \times 10^3$, $B_{OO} = 1.48 \times 10^6$, $C_{OO} = 4.40$

$A_{CO} = 1.70 \times 10^3$, $B_{CO} = 3.25 \times 10^4$, $C_{CO} = 3.07$

[a] E_{ij} and r_{ij} are the potential energy and interatomic distance between atoms i and j, respectively, and q_i is the partial charge on the atom i. Units: E_{ij} in kJ mol^{-1}, r_{ij} in Å, and q_i in e (elementary charge). See text for the methods and basis sets employed in the *ab initio* MO calculations. [b] Point charges are located on the corresponding atoms, and VDW potential centers for oxygen atoms are offset by 0.105 Å toward the carbon atom.

The MDCP run was started with eight CO_2 molecules randomly disposed in a roomy unit cell under a periodic boundary condition. Search for the 8 molecules per unit-cell covers those cases of 1, 2, 4, and 8 molecules per unit-cell which amount to 84.6 % of the known organic molecular crystals.[15] A set of shaking (5000 steps of heuristic MD search[7] with 2.0 fs intervals at a given temperature) and quenching processes was repeated. Note that we did not impose any constraint on space group symmetry nor lattice constants throughout the shaking and quenching process, taking advantage of the lattice-constant variable MD method in MDCP. We selected the structure showing the lowest energy as the predicted structure to be located at the global energy minimum. By additional entropy calculations based on the harmonic approximation, we also checked if the samples thus picked up have the lowest free energy. In these energy calculations, all the VDW contributions from atom pairs within 14 Å were summed up for exp-6 terms, and the Coulombic term was evaluated by the Ewald method[16] with the convergence parameter $\alpha = 0.221$.

As shown in Table 2, the observed packing structure ($Pa3$) and the lattice constants at 1 atm have successfully been reproduced by our *ab initio* determined potential functions.

Next, we searched for the most stable structures at the high

Table 2. Gibbs free energies at 100 K and lattice constants of CO_2 crystal structures predicted by our *ab initio* potentials

		Predicted symmetry	Free energy / kJ mol^{-1}	Z^a	Lattice constants at 0 K					
					a /Å	b /Å	c /Å	α / °	β / °	γ / °
At 1 atm	**1**	*Pa*3	-25.32	4	5.64	5.64	5.64	90.0	90.0	90.0
	2	$P2_1/c$	-24.26	4	7.09	4.07	6.76	90.0	112.15	90.0
	3	$Pca2_1$	-24.20	4	6.79	4.03	6.60	90.0	90.0	90.0
	Exp.[b]	*Pa*3		4	5.54	5.54	5.54	90	90	90
At 20 GPa	**1**	*Cmca*	375.64	4	4.62	4.23	5.78	90.0	90.7	90.0
	2	*Pnnm*	376.13	2	3.62	3.68	4.23	90.1	90.1	90.0
	3	*Pnnm*	376.25	2	4.18	4.82	2.80	90.7	90.0	90.0
	Exp.[c]	*Cmca*		4	4.46	4.17	5.92	90	90	90

[a]Number of molecules in a unit cell. [b]Experimental values extrapolated to 0 K.[17] [c]Experimentally observed values at 20.30 GPa at 295 K.[18]

pressure region by using the MDCP program. In agreement with experimental observation,[5] a *Cmca* structure (Table 2), instead of the *Pa*3 structure at low pressure, was predicted to become the most stable packing structure for the external pressure higher than 9 and 5 GPa by our *ab initio* and Kuchta[11] potentials, respectively. However, at pressure higher than 10 GPa, MDCP calculations with our *ab initio* potentials and the Kuchta potentials[11] predicted different symmetries for the most stable crystal structure, *Cmca* and *Pnnm*, respectively. At the moment, whether *Cmca* is the most stable in this pressure range as is predicted by our *ab initio* potentials, or the barrier for the transition from the low-pressure phase *Pa*3 to *Cmca* is the lowest, is unknown. Which of these predictions is correct is open to experimental observation.

Since the shaking process in MDCP is based on the MD algorithm, another application of MDCP was made to simulate the reported phase-transition[5] at about 10 GPa at room temperature. We studied the assembly of 108 CO_2 molecules in a unit cell. When the isotropic pressure for the simulation system was increased by 10 GPa intervals from 10 GPa to 50 GPa at 298 K for 5000-step duration each, no phase transition from *Pa*3 was observed for our *ab initio* and the Kuchta potentials. However, when we applied extra pressure of 1 GPa in [010] direction at 12 GPa, experimentally observed phase transition from the *Pa*3 to the *Cmca* structures occurred, as shown in Figure 1, in the simulation at 298 K using our *ab initio* potentials (with extra 2 GPa the same phase transition to *Cmca* was observed also for the Kuchta potentials). The reason for the necessity of an anisotropic pressure is unclear. The number of the CO_2 molecules in an MD cell, 108 in this case, may be too small for dynamic simulation of phase-transition. Or, anisotropic forces concentrated at lattice defects, for example, may be necessary for the nucleation process in the phase-transition.

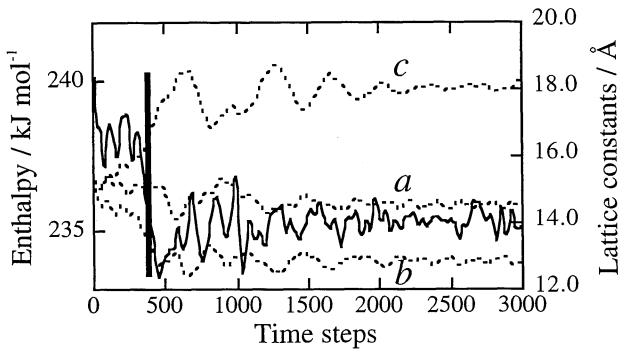

Figure 1. Changes in enthalpy and lattice constants during the simulation (108 CO_2 molecules / MD cell) of the phase-change at 12 GPa under anisotropic pressure (1 GPa excess in [010] direction) at 298 K. Interval of the time step is 1 fs. Solid line and dotted lines represent the enthalpy of the system and the lengths of the MD cell, *a*, *b*, and *c*, along *a*-, *b*-, and *c*-axes, respectively. The initial MD cell was cubic, consisting of 27 (= 3 × 3 × 3) *Pa*3 unit cells, and began to deform into 27 orthorhombic cells of *Cmca* at about the 300th time step over the following 200 time steps.

Thus, in response to the challenge, we believe we present here an example of totally *ab initio* prediction of the structure, as well as the pressure-induced structural change, of molecular crystal for a given chemical species.

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