Theoretical Investigation of High Pressure Phases of Carbon Dioxide

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The recent discovery of a new solid phase of carbon dioxide (CO_2-V) has made it apparent that the properties of this vital chemical species are drastically altered under high pressure conditions. The reported transition at around 40 GPa from the *Cmca* phase (CO_2-III), which is a molecular solid, into the novel phase, which was observed to be quartzlike, clearly suggests a dramatic change of the chemical, electronic, and structural properties. We here present a theoretical analysis of the implications of this metamorphosis. At even higher pressures, we predict the existence of a very hard phase of the stishovite type.

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A most striking example of a substantial change of the physical nature of a solid is provided by the recent observation [1] of a pressure induced transition of the molecular *Cmca* phase of CO_2 into a new phase, which shows evidence to have a quartzlike structure. Apart from being interesting and important from a fundamental point of view, the issue of the stability of the novel CO_2 phases has other far-reaching implications.

First, it is essential for the understanding of certain phenomena occurring in the solar system, in particular, the formation of giant planets. There are reasons to believe that these (Jupiter, Saturn, etc.) consist of a mixture of light elements. For example, a large fraction of the Jovian atmosphere consists of CO_2, NH_3, and CH_4. The comparably low density of Jupiter suggests that the same species constitute its deep interior. Therefore, the question about stability of CO_2 under high pressure is an important one for the understanding of the formation and the present state of the giant planets.

Secondly, the discovered similarity between CO_2 and SiO_2 might have significant practical importance. Stishovite, a high pressure phase of SiO_2, is presently the hardest known oxide in the rutile phase [2]. It is quenchable down to ambient conditions. The quartzlike phase of CO_2 is also quenchable. Experimental data suggest that its hardness is comparable to that of boron nitride [3]. Therefore, if CO_2 could also be synthesized in stishovite form and quenched to ambient conditions, it is possible that this phase will be the hardest material ever found.

At ambient conditions, CO_2 is stable in a cubic *Pa3*-type structure. Under high pressure, at around 10 GPa, this phase transforms to an orthorhombic *Cmca* structure [4]. In fact, the phase transformation from *Pa3* to *Cmca* was initially predicted from theory [5], based upon minimization of Gibbs free energy.

The phase transition we mainly focus on (*Cmca* → quartzlike) occurred at a pressure slightly above 40 GPa, and was observed through laser heating in a diamond anvil cell. Raman spectra were obtained, and these indicated vibration modes typical for a quartzlike structure [1].

With this clue at hand, theoretical interpretations of the experimental results became available. In an early attempt to describe the change of phase, Serra *et al.* [6] reported a theoretical phase transition in an agreeing pressure range, using first principles calculations, with the assumption that the novel phase had an α-quartz SiO_2 type of structure. However, further investigation of the subject revealed that α-quartz is not the most probable candidate among the studied SiO_2 polymorphs in CO_2 form. Dong *et al.* [7] found that out of a wide range of silica polymorphs with C substituted for Si, (quartz types, cristobalite types, coesite, and others) the β-cristobalite phase ($I\bar{4}2d$) is energetically the most favored phase, at least at zero temperature. They also report a very strong tendency for the C-O-C bond to form an angle of 124° at this pressure range, the very angle occurring in β-cristobalite. They also calculate the pressure dependent Raman shifts which agree very well with experiment. However, with the subsequent measurement of the x-ray diffraction pattern (XRD) [8] of the high pressure phase, it could readily be concluded that β-cristobalite could not, at least not on its own and at the temperature of the experiment, reproduce the correct pattern. Thus attempts were made with various polymorphs to generate XRD. Out of these, the ones falling into the group of tridymites [9] proved to give the best match, especially a constructed tridymite structure possessing an "ideal" $P2_12_12_1$ symmetry [8].

In order to gain insight into the properties of this new phase, to clarify the above issue of the different suggestions for its structure, and to investigate the high pressure properties of CO_2 in general, we have performed *ab initio* calculations of the electronic structure of different phases, using density functional theory (DFT) within the generalized gradient approximation [10]. Pressures are obtained by taking the negative derivative of the total energy as a function of volume.

The DACAPO [11] plane wave pseudopotential code was utilized together with Vanderbilt ultrasoft pseudopotentials [12]. We here refrain from giving the details of the calculations, parameters involved, etc., since they are

rather standard for the method. The procedure applies to the zero temperature case, which corresponds to the quenching of the phases examined. The atoms have been allowed to relax in order to attain their minimum energy configuration, in accordance with the constraints imposed.

In Fig. 1, we have plotted the total energies of some relevant structures as a function of volume. Since β-cristobalite attains the lowest energy after the phase change from the *Cmca* phase, we studied this transform. Using the common tangent method, the minimum transition pressure for *Cmca* $\rightarrow$ β-cristobalite amounts to 15 GPa. This is lower than the resulting corresponding pressure if CO_2-V had hypothetically been in the α-quartz phase, which would in fact have been closer to the experimental observation of a transform occurring at around 40 GPa [1]. Thus, the role of temperature for the properties of the transform seems to be an important one.

Further in the figure, we see that at volumes around 10 Å^3 per molecular unit, a polymorph analogous to the silica stishovite phase has the lowest energy. An estimate of that transition pressure gives a high value of around 400 GPa, a pressure that can be expected in the interior of the large planets. According to our calculations, this phase has a bulk modulus of 310 GPa, around twice that of CO_2 in the β-cristobalite phase, 154 GPa.

Insight into the high pressure behavior can be gained through the comparison of corresponding polymorphs of CO_2 and SiO_2. Accordingly, CO_2 in the α-quartz phase has an estimated lattice parameter of 4.20 Å, as compared to the corresponding one for SiO_2, which is 4.91 Å. The c/a ratio is virtually unchanged. The relative positions of the atoms are only slightly modified, most notably those of the oxygen atoms. The nearest neighbor C-O bond is 1.42 Å, compared to the corresponding Si-O bond in

quartz, which is 1.62 Å. As a comparison, we also present the C-O bond in a single CO_2 molecule, which is 1.18 Å, the nearest neighbor C-O distance in the *Pa3* structure, 1.18 Å, and in the *Cmca* structure, 1.17 Å. This highlights how inert the molecule really stays in the two latter phases as opposed to the case of quartz. It should be kept in mind that all of these values were obtained with the same method. It is a well-known fact that DFT slightly underestimates the length of molecular bonds.

The occurrence of a new structure clearly implicates a change of the chemical bonds and the electronic structure. To give a convenient overview of the changes at hand, we present the density of states (DOS) (Fig. 2) and valence electron density (Fig. 3) for some different relevant phases. A natural reference system is the single CO_2 molecule. Its DOS is depicted in Fig. 2a. Below the Fermi level, a characteristic peak is seen at around -2 eV representing the O $2p$ orbitals, a double peak around -7 eV, and another at about -22 eV. The molecular nature of the dimer (2b), *Pa3* (2c), and *Cmca* (2d) phases is clearly seen, since the characteristic features of the molecule are to a large extent preserved. An indication of the high pressure influence can however already be noted in the *Cmca* phase with a broadening of the peaks closest to the Fermi level. The
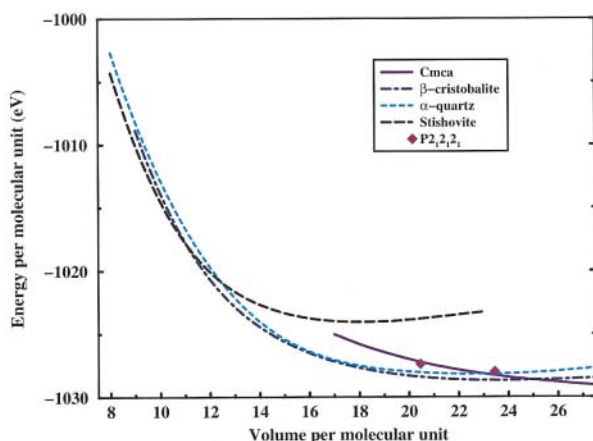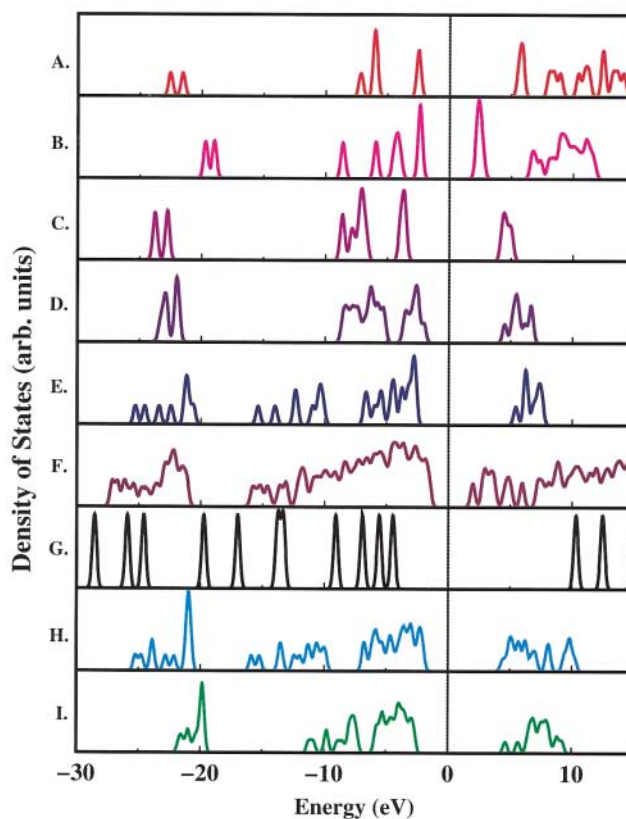

FIG. 1 (color). Phase diagram for different CO_2 crystal structures in eV/molecule. The crossover of the curve describing the quartzlike phase and the *Cmca* structure corresponds to a transition pressure of 15 GPa. Starting in the *Cmca* phase, as pressure increases, the volume per CO_2 unit decreases, until the threshold is reached at 25 Å^3.

FIG. 2 (color). Density of states (arb. units) for CO_2 in the form of a molecule (a), a dimer (b), a *Pa3* crystal (c), a *Cmca* crystal (d), a β-cristobalite crystal (e), a $P2_12_12_1$-like crystal (f), a stishovite crystal (g), an α-quartz crystal (h), and an SiO_2 α-quartz crystal (i).

big change in the high pressure phases is obvious from Figs. 2e, 2f, and 2h. New features in the range -10 to -16 eV, representing covalent bonds are now present. The peaks in the -20 eV regime take on a different shape. Further, the DOS of the $P2_12_12_1$ (2f) reveals other different features as compared to the molecular phases. A relatively small band gap of 2.2 eV is observed, and the bands are rather nestled, resulting in a continuous DOS. The DOS for β-cristobalite (2e) and α-quartz (2h) are rather similar to each other, the main difference being that the former has more states close to the Fermi level. They both display larger band gaps, around 7 and 5 eV, respectively. The substitution of C for Si in quartz seems to leave the nature of the bonds rather similar to each other. To demonstrate this, we display the DOS for the ground state of SiO_2 α-quartz (Fig. 2i). The peaks appear in similar sequences as in the quartz structures of CO_2, indicating the similarity of the chemical bonds. However, the energies of the Si orbitals differ from those of C, thus rendering peaks at different positions. In regards to our suggested phase at even higher pressure, the stishovite-type structure appears to be a very ionic compound (Fig. 2g) with very narrow bands, resulting in localized peaks associated with ionic orbitals in the DOS.

The nature of the binding mechanism is also very clearly reflected in the distribution of valence electron density (Fig. 3). For the case of the single molecule (3a), the electron cloud around the oxygen atoms shows the occupied O $2p$ states. The attraction between the two molecules in the dimer (3b) is manifested in the increase of density in the interstitial region. It is not, however, the same mechanism that binds the molecular solid, which is clear from the DOS in Fig. 2b. In 3c and 3d, the density is shown for a plane intersecting a CO_2 unit making up the phases *Pa3* and *Cmca*, respectively. Note the similarity with the isolated molecule. After the transform into covalent-type phases the change in the bonds is very clear. For example, from 3e, in which the plane intersects a nearest neighbor O-C-O constellation in a high pressure phase, electron density is transferred to the carbon atom and the interstitial region, clearly indicating the formation of covalent bonds. A substantial abundance of electron density can be observed between the CO_2 units, indicating the transition from a molecular to a covalent solid. The similarity with SiO_2-quartz (3i) is clear. However, we find that the angles in CO_2 are lower than in SiO_2, consistent with the results of Dong *et al.* [7]. This is due to the fact that the concentration of electronic charge is lower around the carbon atom than around the corresponding silicon atom reflecting the fact that the C-O bond is more covalent than the Si-O one.

In an attempt to resolve the question of the actual structure of the CO_2 crystal as seen experimentally, we consider the energy decrease involved in the relaxation of the ideal $P2_12_12_1$ structure. This results in some loss of symmetry. The typical tridymite structure, consisting of layers of
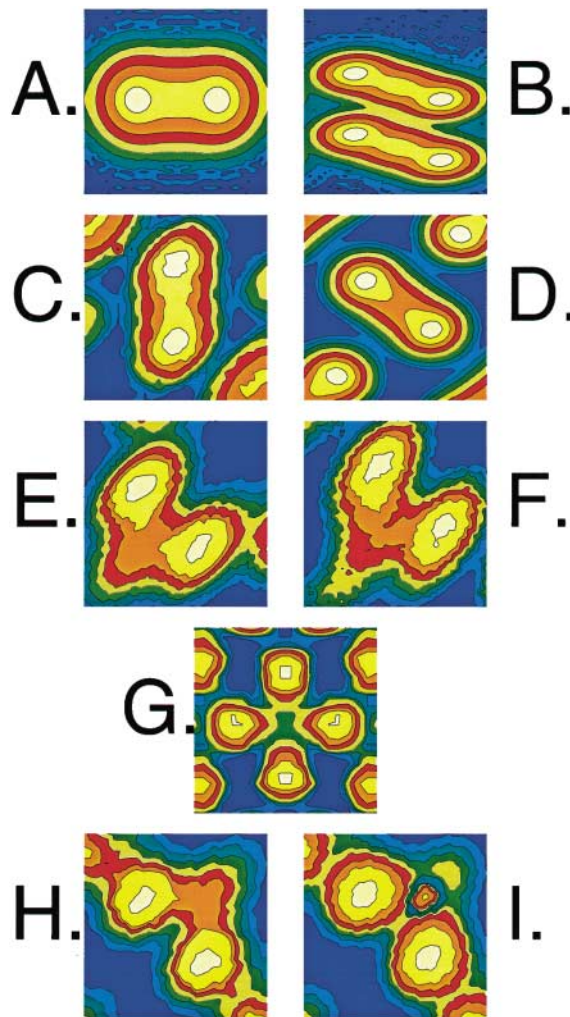

FIG. 3 (color). Density of valence electrons for CO_2 in the form of a molecule (a), a dimer (b), a *Pa3* crystal (c), a *Cmca* crystal (d), a β-cristobalite crystal (e), a $P2_12_12_1$-like crystal (f), a stishovite crystal (g), an α-quartz crystal (h), and an SiO_2 α-quartz crystal (i).

tetrahedra connected by oxygen atoms, becomes less easy to identify. It appears that the energy gain is not enough to allow this structure to attain the lowest energy among the candidates at zero temperature, neither at the experimental, nor at the theoretical volume (see Fig. 1). However, a look at the XRD (Fig. 4; Table I) clearly favors the $P2_12_12_1$ structure at the temperature of the experiment. The XRD patterns are calculated from the different structures and compared with that of the experiment of Yoo *et al.* [8]. It can clearly be seen that the β-cristobalite is too symmetric to generate the rather rich experimental pattern. Our starting $P2_12_12_1$ structure does not have the oxygen atoms placed in the ideal positions, i.e., the CO_4 tetrahedra that are the building blocks of tridymites have been deformed. The reason for this is to be able to study tendencies on the relaxation process. The peak generated at about $2\theta = 8.5°$, stemming from the 210 and corresponding planes, is absent in the theoretically ideal
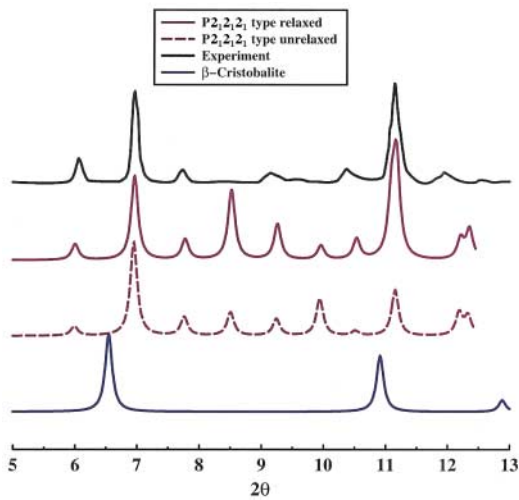
FIG. 4 (color). X-ray diffraction patterns for different candidates for the CO_2-V phase.

structure [8] and its presence can be ascribed to the deviation of the oxygen atoms from their ideal positions. As briefly indicated in Ref. [8], the relative intensity of the peak associated with the 301 planes increases, and it can be seen that apart from the peak appearing due to the initial deformation of the tetrahedra, the pattern matches the experimental one very well. It seems logical to assume that at elevated temperatures, such as that of the actual experiment, the breakdown of symmetry of the cristobalite phase due to the thermal motion of the atoms favors the $P2_12_12_1$ type tridymite structure. It would be of significant interest to learn something about the kinetics of the studied phase changes. From the present study only, this is a hard task. Normally, a phase transformation involves a transition along a path of minimum work through some intermediate structure. The nature of this structure is not evident from our investigations and requires a separate

study. However, because we deal with structures which are similar to those observed for silica, one could perhaps initially accept approximate estimates as derived from silica phase transformation experiments.

In summary, we conclude that the two previously suggested candidates for the new high pressure phase in CO_2, as seen at the conditions of the experiment by Iota *et al.* [1], have rather similar energies but very different electronic and structural properties at zero temperature. The β-cristobalite phase is a typical covalent solid, highly insulating with a large band gap. The tridymite $P2_12_12_1$-type has a small band gap and a very different nature of bands. Thus, we would expect optical properties to differ drastically between the two phases, especially the dielectric function, which has a threshold which is directly proportional to the band gap. As our results indicate that the crystal structure depends on temperature, it seems that the measurement of the dielectric function to a large extent could reveal the nature of the phase at various temperatures and pressures. Our investigations of a stishovitelike phase at very high pressures suggest that CO_2 at these circumstances is a very hard and ionic material. In analogy with the case of SiO_2, we can expect a richness of high pressure polymorphs. Thus a large amount of high quality experimental and theoretical work is needed before a complete picture of the high pressure behavior of CO_2 is obtained.

TABLE I. X-ray diffraction patterns for the CO_2-V phase.

hkl	d_{cal} (Å)	I_{cal}	d_{cal} (Å)	I_{cal}	d_{obs} (Å)	I_{obs}
011; 110	3.561	13	3.532	17	3.531	27
111; 200; 002	3.070	100	3.070	90	3.066	96
201	2.763	20	2.764	22	2.766	17
210; 012[a]	2.486	25	2.486	75		
211; 112	2.332	18	2.332	38	2.334	14
202; 020	2.168	40	2.168	15	2.161	3
120; 021	2.052	5	2.052	22	2.058	18
301; 121[b]			1.959	61		
103; 301; 310	1.921	49	1.921	100	1.923	100
311	1.786	24	1.786	19	1.793	14
122; 203	1.699	20	1.708	14	1.793	2

[a]This peak is present in the theoretical spectra because of the distortion of the CO_4 tetrahedra.
[b]The peak associated with the 301 planes gets split into two close peaks upon relaxation.

[1] V. Iota, C. S. Yoo, and H. Cynn, Science **283**, 1510 (1999).
[2] J. M. Leger, J. Haines, M. Schmidt, J. P. Petitet, A. S. Pereira, and J. A. H. da Jornada, Nature (London) **383**, 401 (1996).
[3] C. S. Yoo, in *Proceedings of the AIRAPT-17 International Conference on High Pressure Science and Technology, Honolulu, Hawaii, 1999, Abstracts.*
[4] K. Aoki, H. Yamawaki, M. Sakashita, Y. Gotoh, and K. Takemura, Science **263**, 356 (1994).
[5] B. Kuchta and R. D. Etters, Phys. Rev. B **38**, 6265 (1988); **47**, 14 691 (1993).
[6] S. Serra, C. Cavazzoni, G. L. Chiarotti, S. Scandolo, and E. Tosatti, Science **284**, 788 (1999).
[7] J. Dong, J. K. Tomfohr, and O. F. Sankey, Science **287**, 11a (2000) (in Technical Comments); Phys. Rev. B **61**, 11 979 (2000).
[8] C. S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Häusermann, and C. Mailhiot, Phys. Rev. Lett. **83**, 5527 (1999).
[9] A. K. A. Pryde and M. T. Dove, Phys. Chem. Miner. **26**, 171 (1998).
[10] See, e.g., R. M. Dreizler and E. K. U. Gross, *Density Functional Theory—An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990).
[11] B. Hammer, K. W. Jacobsen, V. Milman, and M. C. Payne, J. Phys. Condens. Matter **4**, 10 453 (1992).
[12] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).