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Rigid intertetrahedron angular interaction of nonmolecular carbon dioxide solids

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We have theoretically investigated several polymeric (nonmolecular) CO_2 solids analogous to various phases of SiO_2. Our calculations reveal that CO_2 differs dramatically from SiO_2 because of its rigid intertetrahedron angular interaction. Because of this, we find that a β-cristobalitelike phase is energetically the favored polymeric CO_2 phase rather than quartz, which is preferred in SiO_2. The calculated Raman spectrum of β-cristobalite CO_2 shows a dominant A_1 peak at about 780 cm^{-1} at 40 GPa which shifts down to about 640 cm^{-1} at 1 GPa. This is consistent with the recent high-pressure experiments of Iota *et al.* [Science **283**, 150 (1999)].

Carbon dioxide (CO_2) is a linear molecule which contains strong double bonds between carbon and oxygen, and is an unreactive gas at room temperature and pressure. At low temperature and pressure it crystallizes into its ''dry-ice'' *molecular* phase ($Pa3$). This phase is familiar to all and has many uses since it is inexpensive, nontoxic, nonflammable, and under ambient conditions it sublimes directly into the vapor phase. This solid is a true molecular solid since the C=O double bonds remain intact with concomitant high frequency intramolecular vibrational modes quite similar to those of the gas phase molecules. These frequencies can be tuned somewhat with pressure,[2] including the Fermi resonance between the bending modes and the symmetric stretching modes of the CO_2 molecule, showing quite clearly that the solid is a weakly bound array of CO_2 molecules.

New chemistry can exist under extreme conditions such as under the application of very high pressure. The four bonds sought by carbon and the two bonds sought by oxygen can alternatively be obtained in solid CO_2 by forming just single bonds and doubling the number of bonds compared to that found in a double-bonded molecular solid. Such a polymeric solid for CO_2 ought then to have similarities with the polymorphs of SiO_2. There is an extraordinary richness of polymorphism diversity in the SiO_2 system and even modest pressures and temperatures give α- and β-quartz, tridymite, α- and β-cristobalite, coesite, and stishovite; in addition there are over one hundred officially recognized expanded aluminosilicate zeolites,[3] with zeosils being the pure SiO_2 analogs of these.

Recently, it has been reported by Iota *et al.*[1] that at high pressure ($\sim$40 GPa in the diamond anvil cell) and high temperature ($\sim$1800 K), CO_2 transforms from a molecular solid to a polymeric solid. They refer to this new phase as phase V, but its structural motif remains speculative since diffraction measurements have not yet been achieved. They probe this new phase with optical spectroscopy, including Raman spectroscopy and the detection of second harmonic generation (SHG) of the light from the Nd:YLF laser used to heat the samples to high temperatures. The large SHG efficiency ($\sim$0.1%) indicates that the unknown crystal structure is noncentrosymmetric. Iota *et al.* have made careful measurements of the Raman modes from $\sim$50 GPa on down to only $\sim$1 GPa where, unfortunately, the new polymeric phase reverts back to a molecular phase. The experimental Raman lines of the polymeric phase are fairly sharp, indicating that the material is not amorphous. These Raman modes and their pressure dependence give important clues to the structure and bonding of this newly synthesized material, and theory can be used to follow these clues further and extract new information not yet available from experiments. From their Raman frequencies and the existence of SHG, Iota *et al.* suggest the polymeric phase is similar to the quartz or coesitelike phase of SiO_2; this suggestion can be further explored by theory.

In the present work, we perform calculations of the total energies, and phonon vibrational modes at the center of the Brillouin zone, which are the appropriate modes for Raman spectroscopy (and infrared absorption). Our calculations give strong support to the hypothesis that the new CO_2 polymeric phase is indeed an SiO_2 analog; however it is not the quartz or coesite phase, but rather a cristobalitelike phase. Specifically our calculations point to a structure similar to the $I\bar{4}2d$ β-cristobalite phase as the most likely structural candidate. The key new feature that we find for the CO_2 system is that the C-O-C bond angle is very stiff, severely limiting structural candidates.

The theory we use is density functional theory (DFT) in the local density approximation (LDA) implemented in a planewave basis,[4] using ultrasoft pseudopotentials.[5] All the structures we consider are found to be insulators. A generalized gradient approximation[6] (GGA) was also used to evaluate the energies of the optimized structures. Because the densities of the structures we considered are all similar, the GGA has little effect on the relative energetics of the polymeric phases.

The polymeric phases we considered contain corner sharing CO_4 tetrahedra analogous to SiO_4; they are α-quartz ($P3_221$), β-quartz ($P6_221$), α-cristobalite ($P4_12_12$), β-cristobalite ($I\bar{4}2d$), coesite ($C2/c$), and C9 ($Fd\bar{3}m$). We optimize all structural parameters including the external and internal coordinates, and fit the results to the Birch-Murnaghan equation of state (EOS). The parameters of the fit are shown in Table I, and plots of the total energy (compared to separated atoms) *vs.* volume are shown in Fig. 1. The LDA clearly shows that the β-cristobalite phase is the

TABLE I. The parameters of the Birch-Murnaghan equation of state $[E(V)=E_0+\frac{9}{8}KV_0[(V_0/V)^{2/3}-1]^2(1+[(4-K')/2][1-(V_0/V)^{2/3}])]$ obtained from a fit of the LDA energy vs volume curve. The parameter E_0 is the minimum energy (binding energy relative to separated atoms), V_0 is the minimum energy volume, K is the bulk modulus, and $K'=dK/dP$ the volume derivative of the bulk modulus.

Phase	E_0 (eV/CO$_2$)	V_0 (Å^3/CO$_2$)	K (GPa)	K'
β-cristobalite	-24.60	22.30	149.1	3.62
α-cristobalite	-24.40	22.01	142.8	4.21
α-quartz	-24.20	20.93	205.7	3.92
β-quartz	-23.69	23.74	268.4	3.28
C9 cristobalite	-22.76	30.86	235.5	3.97

lowest energy phase of those tested by at least 0.2 eV/CO$_2$. Figure 1 also shows that there are no ''common tangents'' connecting these curves so that thermodynamically driven transitions between these phases is unlikely.

Amongst the phases we have chosen to study, why is β-cristobalite the lowest in energy? To answer this, we study the energetics of the CO$_2$ system by varying the C-O-C bond-angle ($\theta_{\text{C-O-C}}$) and the C-O bond length ($d_{\text{C-O}}$). In β-cristobalite ($I\bar{4}2d$), these two quantities can be varied completely independently of one another.[7,8] The structure contains CO$_4$ tetrahedra, with each oxygen corner shared with another tetrahedron. If we view the CO$_4$ tetrahedra as being ideal (four equal bond lengths with O-C-O angles of 109.5°[9]) and rigid (fixed bond lengths), the angle $\theta_{\text{C-O-C}}$ then is the rotation angle of one corner sharing CO$_4$ tetrahedron relative to its neighboring corner sharing tetrahedron. This rotation is quite ''floppy'' for SiO$_2$,[10] particularly for large angles, but is generally found to lie near $\sim 145-150°$. We perform calculations where we vary the bond-angle $\theta_{\text{C-O-C}}$ from linear (180°) which is the C9 cristobalite ($Fd\bar{3}m$) structure (the C9 structure is commonly, but incorrectly, assigned to the true SiO$_2$ β-cristobalite $I\bar{4}2d$ phase[11]), to the defective chalcopyrite structure ($\theta_{\text{C-O-C}}=\theta_{\text{tetrahedral}}=109.5°$).

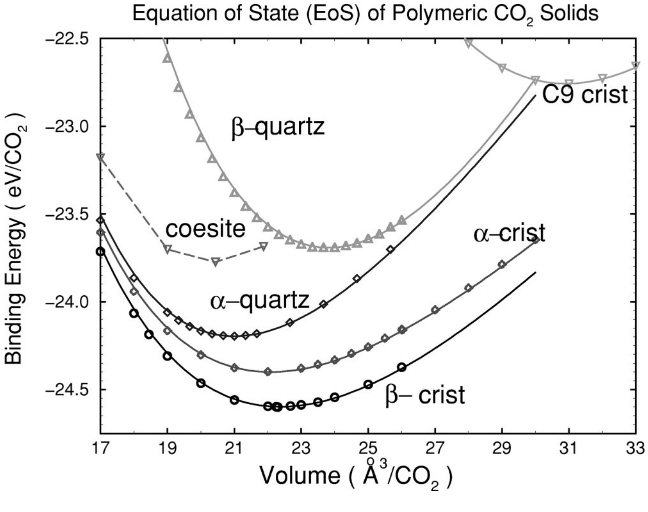
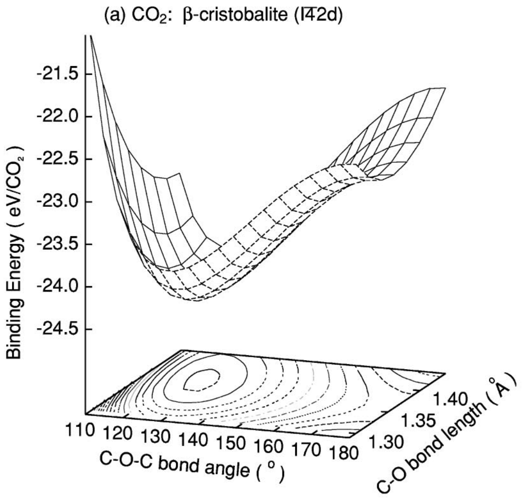


FIG. 1. LDA binding energy curves for several CO$_2$ polymeric phases analogous to those of SiO$_2$. The binding energies are relative to free atoms. The solid curves are fits to the Birch-Murnaghan EOS (Table I). All structures are fully optimized, and β-cristobalite is the $I\bar{4}2d$ structure.



(b) SiO$_2$: β-cristobalite (I$\bar{4}$2d)

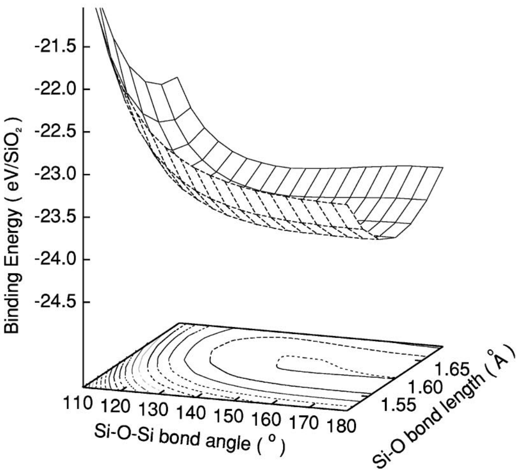


FIG. 2. Contour plots of the binding energy as a function of bond length and intertetrahedral bond angle of ideal (perfect tetrahedra) $I\bar{4}2d$ β-cristobalite phases of (a) CO$_2$ and (b) SiO$_2$. This structure allows the intertetrahedron bond angle and bond length to be varied independently. The insensitivity of the SiO$_2$ binding energy to intertetrahedron bond angle is in sharp contrast to the deep minimum observed in CO$_2$.

We show in Fig. 2(a) energy contour curves of CO$_2$ as a function of $\theta_{\text{C-O-C}}$ and $d_{\text{C-O}}$ in β-cristobalite ($I\bar{4}2d$), and for comparison similarly computed curves for SiO$_2$ in Fig. 2(b). The contours for CO$_2$ show a ''bulls-eye'' pattern, while those for the SiO$_2$ show a ''thumb-print'' pattern. This dramatically illustrates the key difference between possible new high pressure CO$_2$ polymeric phases and analogous SiO$_2$ phases; the CO$_2$ analogs of SiO$_2$ have an enormously increased rigidity of the intertetrahedral rotation angle $\theta_{\text{C-O-C}}$. The softness of the SiO$_2$ rotation angle allows SiO$_2$ to form a rich variety of polymorphs. CO$_2$ on the other hand is far more sensitive to the angle and as such ought not to be expected to form such a diverse set of structural polymorphs.

Recent theoretical calculations by Serra *et al.*[12] have also energetically ordered various phases of CO$_2$. These workers chose only the two end members of the $I\bar{4}2d$ series: defec-

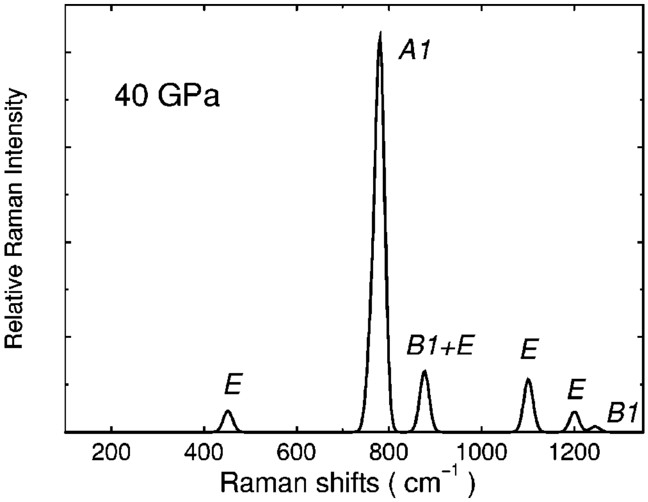


FIG. 3. The calculated Raman spectrum of β-cristobalite ($I\overline{4}2d$) CO_2 at 40 GPa.

tive chalcopyrite ($\theta_{\text{C-O-C}}=109°$), and C9 cristobalite ($\theta_{\text{C-O-C}}=180°$). They correctly concluded that these are not energetically likely structures, but did not consider intermediate angles $\theta_{\text{C-O-C}}$, and hence concluded that α-quartz is the lowest energy high pressure phase. Our calculations strongly suggest that a $I\overline{4}2d$ β-cristobalite-like phase (or perhaps another uncalculated phase with C-O-C bond-angles near 120–125°) is the likely polymeric CO_2 phase. This is because the α-quartz phase cannot adjust its geometrical configuration to capture the center of the ''bulls-eye'' in Fig. 2(a).

Calculations using DFT have been very successful in the past, but there are many known failures, so we seek confirmation of this result by comparing the observed Raman scattering peaks with our calculated Raman spectra. The Γ-point phonon modes are derived from the first principles calculation of force constant matrix,[13] using finite displacements of the atoms in the minimum energy (zero-force) structure. The calculated phonon frequencies and mode displacement patterns are in principle exact within the harmonic approximation. We carry out this procedure at various volumes which the EOS translates into pressures. The Raman intensities are not predicted from first principles, but are obtained from a bond-polarizability model, where two empirical parameters[14,15] are best fit to the experiments of Iota *et al.* at 40 GPa. The $I\overline{4}2d$ space group allows the spectrum of modes $1A_1+2A_2+2B_1+2B_2+4E$ (neglecting the $1B_2+1E$ translational modes), or 11 distinct frequencies. Our results for the Raman spectrum of CO_2 β-cristobalite at 40 GPa are shown in Fig. 3. These results can be compared with the experimental results of Ref. 1 (see their Fig. 3). By far the dominant peak in both theory and experiment is the A_1 (our assignment) peak at 781 cm^{-1} (theory) and 790 cm^{-1} (experiment). In this mode, the carbon atom does not move, and the oxygen atomic displacement is in the C-O-C plane and perpendicular to the line running between its two neighboring carbon atom. This displacement of the oxygen atom stretches the two C-O bonds, and bends the stiff C-O-C angle. Table II shows a numerical comparison between theory and experiment at 40 GPa. All the high frequency modes (452, 781, 880, 1103, and 1201 cm^{-1}) agree with experiment to within $\approx 3\%$ (except about 9% in the 452 cm^{-1} mode).

There are differences between theory and experiment with the low frequency modes (Table II). At 40 GPa theory finds no modes below 452 cm^{-1} while experiment reveals low-frequency modes of relatively small intensity. We note that modes observed at about 360 and 390 cm^{-1} (40 GPa) are from unconverted CO_2-III which is the phase existing before the laser heating has enabled the phase transition.[16] The modes which do not agree completely with theory then are the three modes at 200, 230, and 260 cm^{-1} which are absent in β-cristobalite $I\overline{4}2d$. This discrepancy in the low-frequency modes is an important issue, which we are unable to satisfactorily resolve without further structural information. There are several possible explanations why theory does not produce these modes. (i) The experimental Raman spectra shows the polymeric phase and the molecular phase simultaneously. There is no reason to rule out the possibility that another new molecular phase has also been synthesized in addition to those already known. The observed low-frequency modes then could correspond to the ''molecular'' modes of this new phase. (ii) Another possible explanation is a lattice distortion producing a pseudo-supercell effect in which the β-cristobalite structure acts as a parent structure, but the true structure has a larger unit cell of several parents cells slightly different from one another. This effectively brings in phonons at nonzero wave vectors into the parent Brillouin zone. This explanation would require that the Raman intensity of the additional high-frequency modes is small compared to that of the additional ''folded in'' low-frequency modes. (iii) We have been assuming perfect crystal structures, while the samples synthesized at high-pressure and laser-heating conditions may be highly defective. Diffraction of such samples does not always produce sharp lines due to extended defects.

We have performed some simple tests concerning (ii) by searching for low-frequency modes in larger unit cells. The β-cristobalite phase has no low-frequency modes below 450 cm^{-1} ($2CO_2$ units/cell), while α-quartz and *alpha*-cristobalite have only one low-frequency mode (near 200 cm^{-1}). The situation becomes more favorable when tridymite is considered. Tridymite is similar to β-cristobalite in that

TABLE II. A comparison of the experimentally observed Raman lines with the theoretical predictions of the β-cristobalite model at 40 GPa. The data are taken from Fig. 4 (and 3) of Ref. 1. The * indicates a mode reported in Fig. 3 but not Fig. 4 of Ref. 1. The lower portion of the table gives B_1 or B_2 modes which have either a very small Raman intensity (or outside the range of the experiment, e.g., the 1246 cm^{-1} B_1 mode), or are Raman silent (†).

Expt. (cm^{-1})	200	230	260	415	790	905	1110*	1190
Theory (cm^{-1})—seen in Raman	– –	– –	– –	452(E)	781(A_1)	880(E)	1103(E)	1201(E)
Theory (cm^{-1})—not seen			641($A_2{}^{\dagger}$)	762(B_2)	876(B_1)	1100(B_2)	1181($A_2{}^{\dagger}$)	1246(B_1)

the T atoms (tetrahedral atoms, here carbon) form a hexagonal wurtzite (or lonsdalite) network in tridymite, and a zincblende (or diamond) network in β-cristobalite. The local topologies of β-cristobalite and tridymite are similar in the same sense that zincblende is similar locally to wurtzite. Thus there is a striking similarity in the ring configurations of cristobalite and tridymite. Energetically we find that low-tridymite structures are only a little higher in energy than β-cristobalite, although we have not yet found a tridymite structure more favorable than β-cristobalite. Tridymite represents a class of SiO_2 polymorphs, and the relations among these SiO_2 polymorphs are still not completely understood. Tridymite SiO_2 has a variety of incommensurate superstructures, a high degree of stacking disorder, and intimate intergrowth with cristobalite.

Specifically for a vibrational signature, we have checked a form of low-tridymite, namely the averaged MX-1 structure[17] (monoclinic, space group Cc). Our calculated Raman spectra indeed produces three Raman active modes in the low-frequency region of the experiments at 40 GPa. Unfortunately, its high-frequency spectra (800–1200 cm^{-1}) becomes more complex and does not match the experimental spectra well. A final understanding of the low-frequency modes and synthesized structure(s) can only be resolved by further experimental studies, e.g., x-ray synchrotron studies.

The dependence of pressure on the Raman frequencies offers an independent check of our β-cristobalite assignment. In Fig. 4,[18] we show the theoretical pressure dependence of the Raman modes (solid lines) together with the experimental results (triangles) of Ref. 1. For comparison, we also show the theoretical pressure dependence of the Raman frequencies in α-quartz (dashed lines). The theoretical results for $I\bar{4}2d$ β-cristobalite are more consistent with the experiment than those of α-quartz. This is most evident in the ‘‘signature’’ A_1 mode and the E mode (near 900 cm^{-1} at 40 GPa). The A_1 mode near 790 cm^{-1} (at 40 GPa) is experimentally the signature mode of the new high-pressure phase, and both the frequency and the pressure dependence are better described by the cristobalite phase than by the quartz phase. The behavior of the E mode near 900 cm^{-1} is even more striking. For this mode, the quartz phase yields a frequency which is quite sensitive to pressure while the β-cristobalite phase exhibits the pressure insensitivity observed in the experiment. However, we note that the agreement between the cristobalite modes and the experimental data is not perfect, in particular with the E mode near 415 cm^{-1}.

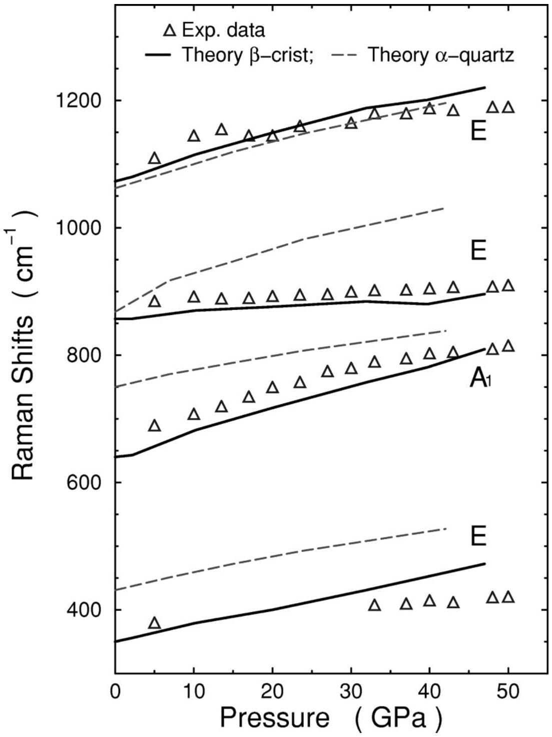


FIG. 4. The pressure dependence of high frequency Raman modes of polymeric CO_2 calculated for two candidate structures and experiment. The solid lines (theory) are those for $I\bar{4}2d$ β-cristobalite, the dashed lines (theory) are those for α-quartz, and the triangles are those of the experiment of Iota *et al.* (Ref. 1).

In conclusion, our calculations show that polymeric (non-molecular) CO_2 solids have a far more rigid intertetrahedron angular interaction than their SiO_2 analogs. Thus the energetic ordering of solid CO_2 structures does not follow trends established by SiO_2. One ramification of this is that structures similar to β-cristobalite are energetically favored. We have compared a computed Raman spectrum of β-cristobalite to the Raman spectra of the newly synthesized CO_2 samples. We find good agreement with all the high-frequency modes which are signatures of the tetrahedral bonding units of a four-connected network of T atoms. However, three low-frequency modes are not accounted for in the theoretical spectrum, and future experimental and theoretical studies are necessary to achieve a further understanding of this exciting new class of materials.

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[16] Due to a clerical error, the authors of Ref. 1 attribute modes near 200 and 230 cm^{-1} at 40 GPa in their Fig. 4 to CO_2-III, which should have been attributed to modes at 360 and 390 cm^{-1}.

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