Nonlinear Carbon Dioxide at High Pressures and Temperatures

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A nonlinear molecular carbon dioxide phase IV was discovered by laser heating CO_2-III (*Cmca*) between 12 and 30 GPa, followed by quenching to 300 K. The Raman spectrum of quenched CO_2-IV exhibits a triplet bending mode $\nu_2(O{=}C{=}O)$ near 650 cm^{-1}, suggesting a broken inversion symmetry because of bending. The 650 cm^{-1} bending modes soften with increasing pressure, indicating an enhanced intermolecular interaction among neighboring bent CO_2 molecules. At 80 GPa, the low-frequency vibron collapses into high-frequency phonons, and CO_2-IV becomes an extended amorphous solid.

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Simple molecules such as CO_2, N_2, O_2, H_2O, and CH_4 are fundamental building blocks in chemistry to which many chemical reactions of C, N, H, and O containing molecules converge by various intermediate states controlled by thermodynamic and kinetic principles. This is due to the high stability and chemical inertness of these molecules, stemming from strong intramolecular covalent bonds and weak intermolecular interactions. Given their presumed stability over wide ranges of pressures and temperatures, these simple molecules are considered to be the major constituents of giant planets [1] and common products of energetic processes in explosions [2]. However, the molecules with electrons localized within intramolecular bonds become less stable with increasing pressure because repulsive electron kinetic energy effects dominate the relatively weak volume dependence of electrostatic quadrupole-quadrupole interaction at high density. Supporting this thesis are an increasing number of recent theoretical and experimental results that suggest transitions of simple molecules to dimeric [3,4], polymeric [5–7], and metallic [8,9] phases at high pressures and temperatures.

Carbon dioxide is a linear, centrosymmetric molecule (D_{2h} symmetry group). At high pressures and temperatures, it undergoes several interesting phase transitions, accompanied by modifications of the intermolecular interactions, molecular configuration, and crystal structure. At ambient temperature, it crystallizes into cubic ($Pa3$) CO_2-I at 0.5 GPa, a typical linear-molecular solid with weak intermolecular quadrupole-quadrupole interactions among neighboring molecules. The low bulk modulus of this phase, 12 GPa, is evidence of weak intermolecular interactions [10]. At 11 GPa, CO_2-I transforms into another linear-molecular phase, orthorhombic (*Cmca*) CO_2-III [11]. Intermolecular interactions in phase III increase with pressure. At pressures above 20–30 GPa, CO_2-III can support large pressure gradients (up to 1 GPa/μm), typical of strained high strength solids [10]. CO_2-III has a large bulk modulus (87 GPa), which is unusual for a molecular solid but is consistent with its high lattice strain. It is stable (or, at least metastable) to 70 GPa at ambient temperature. Above 40 GPa and 1800 K, CO_2-III transforms into a polymeric solid, CO_2-V [8,10]. The structure of this extended network solid is based on CO_4 tetrahedra linked in an orthorhombic ($P2_l2_l2_l$) structure, analogous to SiO_2 tridymite, but with stronger covalent bonds. It is also a strongly optically nonlinear solid with a large bulk modulus of 365 GPa, similar to *cubic* BN. The CO_2-III to CO_2-V transition does not occur below 40 GPa or at ambient temperature, indicating a large kinetic barrier in the polymerization. In this Letter, we present the discovery of a new nonlinear CO_2 phase (denoted as CO_2-IV [12]) that links the twofold coordinated linear molecular phases (I and III) to the fourfold coordinated extended phase (V).

CO_2 samples were loaded in a diamond-anvil cell (DAC) from liquid, by condensing CO_2 gas at 233 K and 10 MPa. A few micrometer-sized ruby chips were scattered inside the cell for *in situ* pressure measurements. The CO_2 samples were heated to high temperatures by using a Nd:YLF laser at 1053 nm. Because CO_2 is transparent at this wavelength, the samples were heated indirectly by heating the rubies. The temperature of the sample was estimated by measuring thermal radiation from a laser-heated area and fitting its profile to a two-parameter gray-body radiation formula. The 514-nm line of an Ar ion laser was used to measure Raman spectra inside the DAC before and after laser heating. All Raman spectra were recorded at room temperature, using a 0.65-m triple monochromator with a liquid-N_2 cooled charge-coupled device (CCD) detector.

No transition has been observed from cubic CO_2-I below 10 GPa, even at temperatures as high as 3000 K. However, at pressures between 12–30 GPa and estimated temperatures of about 1000–1500 K, the linear CO_2-III (*Cmca*) transforms to a bent-molecular phase. The transformation has often been observed without notable incandescent light, presumably below 1000 K and the melting temperature of CO_2 [13]. In Fig. 1, the Raman spectrum of CO_2-III before heating at 25.5 GPa shows broad peaks because of the strained CO_2-III and large pressure gradient (about 1 GPa/μm). As a result, only a part of four Raman-active bands is resolved (Fig. 1); this is

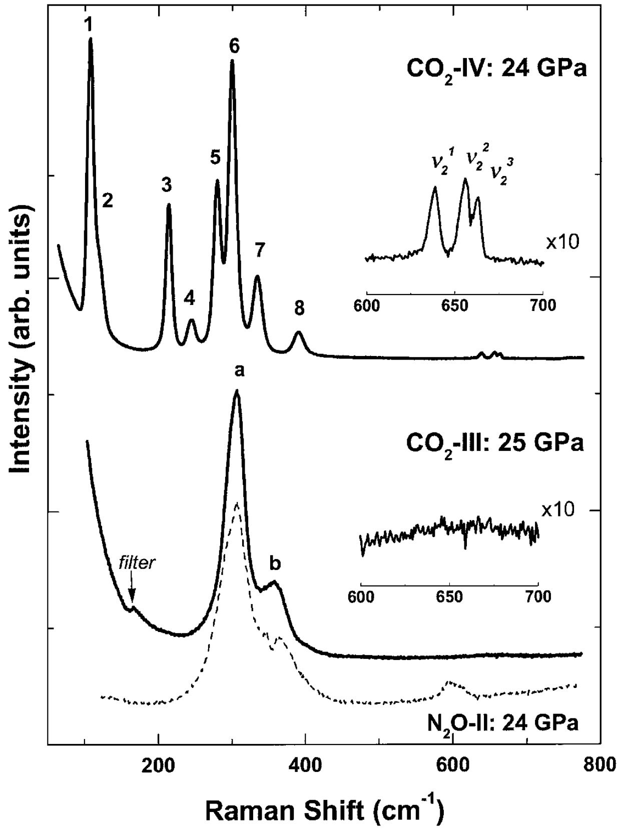

FIG. 1. Raman spectra of CO_2-III before heating at 25.5 GPa (bottom) and CO_2-IV after heating at 24 GPa (top). The Raman spectrum of N_2O-II (the dashed spectrum below CO_2-III) has also been shown for comparison. The triplet near 650 cm^{-1} after heating is due to the symmetric bending mode $\nu_2(O{=}C{=}O)$, which suggests a broken inversion symmetry because of bending of CO_2 molecules. The numbers and the symbol ν_2's respectively characterize the external and internal vibration modes and are also used in Figs. 2 and 3.

typical for the *Cmca* phase above 20 GPa. However, after heating CO_2-III between 12 and 30 GPa, the Raman spectrum changes. A new phonon spectrum appears below 500 cm^{-1} consisting of at least eight well-resolved bands. Especially important is a new triplet that appears near 650 cm^{-1}, the onset frequency of the infrared-active bending mode ν_2 of molecular CO_2. The Raman activation of these normally infrared active modes indicates a loss of inversion symmetry of the linear CO_2 molecules by bending. The ν_2 intensity is relatively weak. Nevertheless, it is comparable with that of the ν_2 mode in N_2O-II, a noncentrosymmetric molecular analog for CO_2. The increase in the number of Raman-active phonon modes indicates that the new phase IV has a lower symmetry structure than either phase I ($Pa3$) or the c-axis centered CO_2-III (*Cmca*) [14].

The room temperature CO_2-I to -III transition is sluggish and typically results in mixtures of CO_2-I and III (or, distorted III) [12]. In contrast, the transition to CO_2-IV occurs sharply even at pressures between 12 and 20 GPa. No features characteristic of either CO_2-I or -III remain after heating the mixtures between 12 and 20 GPa.

The quenched CO_2-IV is stable between 12 and 80 GPa, bypassing the entire stability field of CO_2-III (Fig. 2). In contrast to the broad and poorly resolved spectral characteristics of CO_2-III, Raman lines of CO_2-IV are relatively sharp and well resolved to 40 GPa. The pressure gradients in phase IV also remain insignificant in this pressure range. Upon pressure downloading, CO_2-IV reverts to *cubic* CO_2-I at about 8 GPa. Above 40 GPa, several phonons and vibrons split into multiple lines and become a few broader bands extending over 250 to 500 cm^{-1} above 50 GPa (Fig. 2). At 60 GPa, the tail of the 550-cm^{-1} phonon starts to overlap with the tail of the lowest energy bending mode, indicating that the intermolecular and intramolecular bond strengths become comparable. The Raman spectrum of CO_2-IV deteriorates above 60 GPa and nearly disappears at 80 GPa.

The pressure dependence of the CO_2 Raman bands in Fig. 3 suggests enhanced interaction among the bent molecules in phase IV above 40–60 GPa. All the low frequency modes shift toward higher wave numbers with pressure (blueshift). In contrast, the ν_2 bending modes shift toward lower wave numbers (redshift). This is in contrast to the blueshift of the comparable ν_2 mode observed in linear N_2O molecules at high pressures [15]. The splitting and subsequent smearing of the phonons above 40–60 GPa also reflects restrictions of

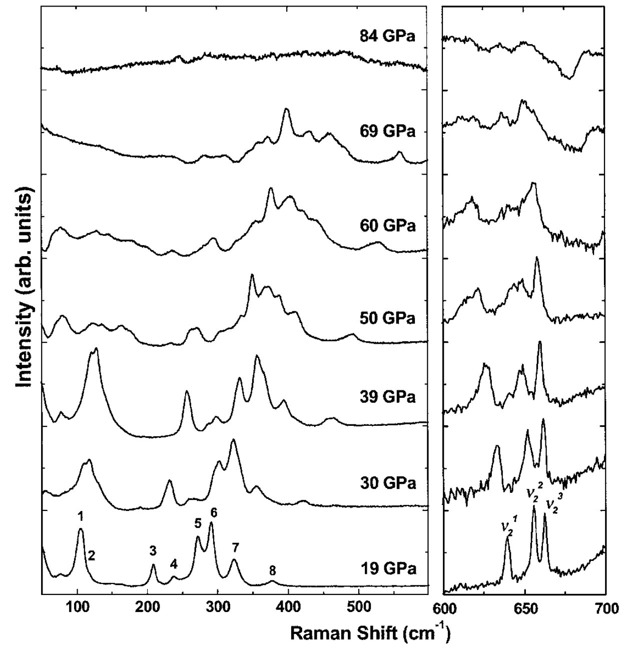

FIG. 2. Raman spectra of quenched CO_2-IV at several pressures, suggesting its high stability over the entire stability field of CO_2-III. The splitting and subsequent broadening of phonon peaks above 40 GPa may be due to enhanced intermolecular $C\cdots O$ interactions. No Raman features are apparent above 80 GPa.

the librational and translational motions by the enhanced intermolecular interactions. Furthermore, below 40 GPa, there is a substantial separation between the translational (likely 1 and 2 near 100 cm^{-1}) and librational (likely 3 to 8 above 200 cm^{-1}) modes. However, above 60 GPa this separation is practically eliminated and the two modes are indistinguishable energetically. This suggests that above 40–60 GPa, CO$_2$-IV may be considered as a pseudoextended phase consisting of threefold carbon atoms in a layer structure. Such a threefolded carbonate phase has been suggested in recent *ab initio* quantum molecular dynamics calculations [16].

The frequency of the lowest-lying ending mode (ν_2^1) approaches that of the highest-lying phonon (mode 8); the extrapolations intersect about 590 cm^{-1} and 80 GPa. The convergence of the external and internal modes at 80 GPa (Fig. 3) signals the transformation of CO$_2$-IV to a three-dimensional extended solid such as the fourfold coordinated CO$_2$-V. This transition is accompanied by the abrupt extinction of all Raman bands above 80 GPa (Fig. 2). The sample, however, remains transparent and optically isotropic, suggesting that it is still nonmetallic. No Raman lines were recovered during unloading pressures from 85 to 11 GPa, where the sample starts to revert to CO$_2$-I. A few weak but detectable Raman bands appear from the mixed phase boundary at 551 and 720 cm^{-1}, together with a broad feature peaking at 120 cm^{-1} from poorly developed crystallites of CO$_2$-I (Fig. 4, top). Recall that the ν_1(C—O—C) stretching mode of CO$_2$-V should occur at 720 cm^{-1} at 11 GPa [7], whereas the 551 cm^{-1} band is probably from the ν_2 bending of a carbonatelike structure (Fig. 3). This suggests that the extended solid formed from CO$_2$-IV at 80 GPa is amorphous and its structure is based on a mixture of fourfold and threefold coordinated carbon atoms. The transition from a threefold carbonatelike structure in CO$_2$-IV to a fourfold tetrahedral structure may introduce the disorder in the lattice near 80 GPa. Our x-ray data of CO$_2$-IV [17] reveal no distinctive diffraction lines above 60 GPa, consistent with the present Raman result. Similar pressure-induced amorphization has been observed previously in other fourfold, open structures including α-SiO$_2$(quartz) and α-AlPO$_4$(berlinite) [18,19].

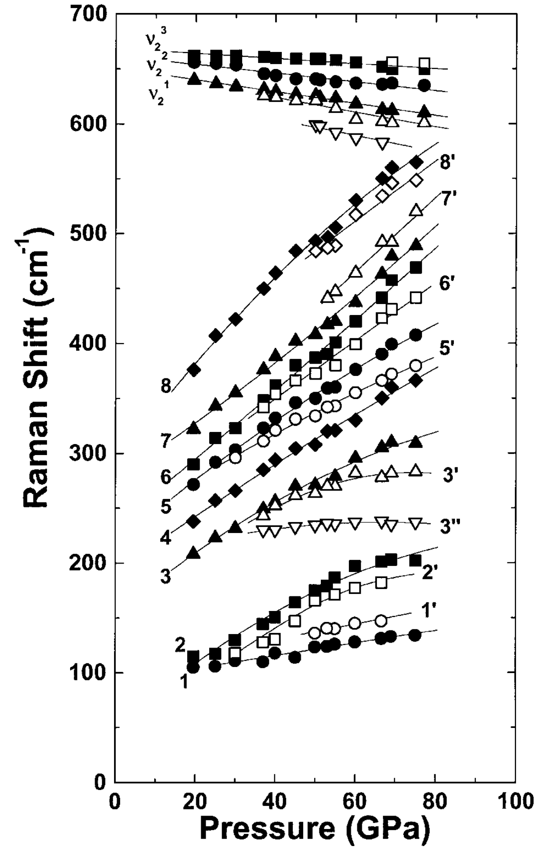

FIG. 3. Pressure dependence of the Raman bands in CO$_2$-IV, showing the redshifts of the ν_2 bending modes and the blueshifts of phonons below 600 cm^{-1}. Note that the vibron meets the phonon at 80 GPa, resulting in the transition of CO$_2$-IV to an amorphous extended phase (see text). The solid and open symbols are for illustrating the splittings of the bands between 40 and 60 GPa.

Upon heating above 30 GPa, CO$_2$-IV transforms into polymeric CO$_2$-V (Fig. 4). Again, the strong 780 cm^{-1} band at 33 GPa is characteristic for the ν_1(C—O—C) stretching mode of CO$_2$-V. The transformed material also exhibits second-harmonic-generating behavior, analogous to CO$_2$-V synthesized from CO$_2$-III [5]. The IV-to-V transition requires a lower threshold (30 GPa) than the III-to-V transition (40 GPa). The molecular bending and strong intermolecular C$\cdots$O bonds in CO$_2$-IV will lower the kinetic barrier for breaking C$=$O bonds to facilitate forming the CO$_4$ tetrahedra and, thereby, the transition threshold to the extended phases of CO$_2$ polymer and glass. Therefore, CO$_2$-IV can be considered as a precursor to these extended phases.

CO$_2$-IV is stable thermodynamically, whereas CO$_2$-III probably is metastable, formed by the martensitic compression of *cubic* CO$_2$-I. The fact that CO$_2$-V transforms to CO$_2$-IV (not to CO$_2$-III) by heating at pressures below 30 GPa supports this conclusion. The high strain and stiffness of CO$_2$-III indicates the presence of a large potential barrier for molecular displacement, precluding the transition to other structures like CO$_2$-IV at ambient temperature. As a result, CO$_2$-III may be frozen in a local energy minimum. Conversely, the transition to CO$_2$-IV occurs at high temperatures; the atomic motion is enhanced and large atomic displacements are possible (as evident from its bent molecular configuration). Such a diffusive transition certainly probes a larger number of configurations to minimize the total energy.

In summary, we have reported the discovery of a new form of CO$_2$ based on nonlinear molecules. This result challenges the presumed stability of "linear-molecular" CO$_2$ at high pressure and temperature. Our results show

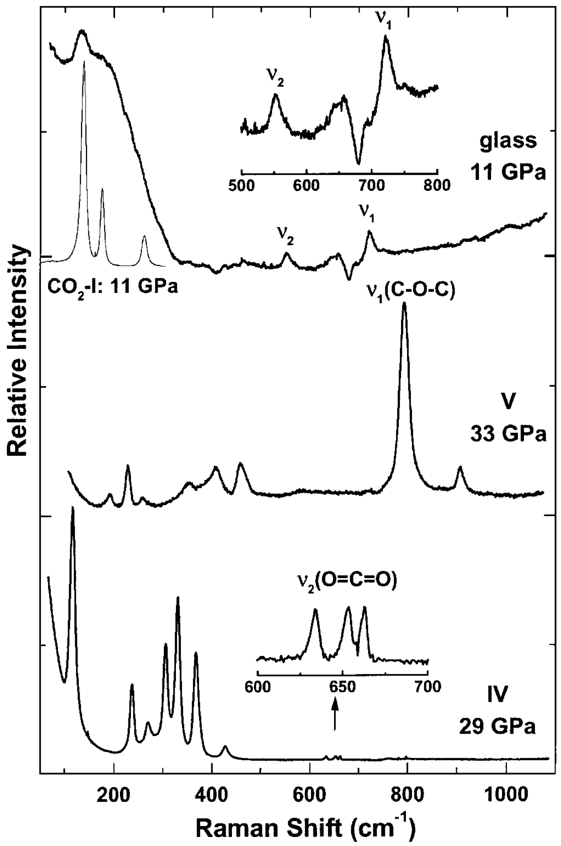

FIG. 4. Raman spectra of CO_2 phases: (bottom) quenched CO_2-IV after laser-heating CO_2-III to ~1000 K at 29 GPa, (middle) quenched CO_2-V after laser-heating CO_2-IV to ~1500 K at 34 GPa, and (top) CO_2 glass downloaded to 11 GPa after compressing CO_2-IV to 85 GPa. The strong 780-cm^{-1} band at 33 GPa and the relatively weak 720-cm^{-1} band at 11 GPa are characteristic for the ν_2(C — O — C) stretching mode in fourfold coordinated carbon atoms in polymeric CO_2-V and amorphous CO_2 glass, respectively. For comparison, the Raman spectrum of CO_2-I at 11 GPa is also included (an inset of the top).

that the linear-molecular structure in CO_2-I and III becomes unstable at high pressures and temperatures as it transforms to a bent-molecular structure in phase IV and eventually to a network structure in extended polymer and glass. The local density (or, coordination number of the carbon atom) also increases with increasing pressure: from two in linear molecular CO_2-I and III, to most likely three in highly interacting bent CO_2-IV, and to four in the extended phase V and glass. Intermolecular electron delocalization greatly increases to overcome what otherwise would be a rapidly increased repulsive potential at high pressures, and the bonding changes from weak quadrupole-quadrupole in CO_2-I and III, to likely dipole-dipole in CO_2-IV, and to strong covalent in the extended phases. This partial delocalization of the bonding electrons can also be expected to retard the insulator-metal transition in CO_2.

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