

# Molecular Structure Determination of Solid Carbon Dioxide Phase IV at High Pressures and Temperatures Based on MP2 Theory

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## ABSTRACT

Carbon dioxide has attracted considerable attention owing to its physics and abundant polymorphs. Despite decades of extensive experiments and theoretical simulations, the structure and properties of carbon dioxide under extreme pressures and temperatures are yet to be properly understood. Particularly, the intermediate phase IV of solid carbon dioxide, which separates the molecular phases at low pressures from the non-molecular phases at high pressures, has not been fully investigated, and its structure remains controversial. Here, based on the second-order Møller–Plesset perturbation (MP2) theory and the embedded fragment method, we study the crystal structure, equation of state, and Raman spectra of solid carbon dioxide phase IV at high pressures and temperatures. We demonstrate that the solid carbon dioxide phase IV is a molecular structure that remains in a molecular state rather than the bent state shown in other literatures, which is consistent with the experimental work by Datchi *et al.* and denies the observed results by Park *et al.* The proposed work is of great significance in determining the structure of the high-pressure phases of carbon dioxide and further exploring the new phase of molecular crystals.

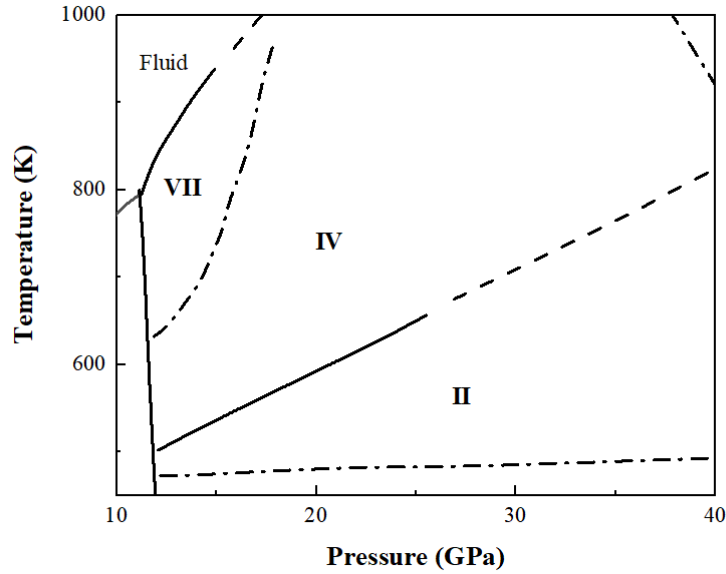
## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is the major constituent of the atmospheres of terrestrial planets, including Venus and Mars<sup>1,2</sup>; it can also be found in other planets and asteroids in ice form<sup>3</sup>. At room temperature and pressure, CO<sub>2</sub> is a gas molecule with a triatomic structure. CO<sub>2</sub> is held together by strong covalent double bonds (O=C=O) and relatively weak intermolecular interactions, making it compressible and chemically inert. At high pressures, the electronic delocalization will affect the  $\pi$  bonds and turn the gaseous CO<sub>2</sub> into a solid since the  $\pi$  bonds are less stable than the  $\sigma$  bonds. Therefore, it is interesting to find out what the structure of CO<sub>2</sub> becomes at very high pressures. At high pressures, solid CO<sub>2</sub> has been intensively investigated for decades and has been demonstrated to possess at least five molecular polymorphs with different intermolecular interactions and intramolecular bonds<sup>1,4,5</sup>, i.e., phases I, II, III, IV, VII, etc<sup>5–12</sup>. The high stability of these polymorphs make solid CO<sub>2</sub> an important product of energetic chemical reactions and a major constituent of the atmospheres of giant planets. However, the physical and chemical properties of solid CO<sub>2</sub> structures under extreme conditions are yet to be fully understood.

Phases II and IV of solid CO<sub>2</sub>, formed at similar pressure and temperature ranges, are the least cognized and explored structures, particularly as to whether or not they are molecular structures. For the two phases, the intermolecular interactions are substantially stronger than the normal quadrupole–quadrupole interactions but weaker than the covalent bonds. Such phases are considered as the intermediates between molecular and covalently bonded crystals, which could transform to extended covalent (non-molecular) phases as the pressure increases to 60 GPa. Recent experiments<sup>8</sup> and *ab initio* calculations<sup>13</sup> have confirmed that phase II is a molecular phase with straight O=C=O bonds; however, whether or not phase IV is a molecular phase remains an open question. Early experiments<sup>9</sup> demonstrated that phase IV has a space group of *Pbcn*, with a C=O bond length that is 30% higher than that of phase I, and its O=C=O angle is bent to 160°. However, theoretical calculations<sup>14</sup> and spectroscopic data<sup>15</sup> have questioned such bent and elongated structure of phase IV (*Pbcn*). Datchi *et al.*<sup>10</sup> established a new structure for phase IV with a  $R\bar{3}c$  space group, where the solid CO<sub>2</sub> molecules have C=O bond lengths and O–C–O angles similar to those in other molecular phases. In this case, the main controversial question remains whether the molecules of solid CO<sub>2</sub> phase IV are bent or linear. Further work is essential to confirm the reasonable structure of solid CO<sub>2</sub> phase IV based on the reliable experiments or accurate theories.

In this work, we perform a quantitative and effective computational research on solid CO<sub>2</sub> phase IV and determine its crystal structure within the pressure range of 10–40 GPa, via the calculation of the state equation and Raman spectroscopy. We use the second-order Møller–Plesset perturbation (MP2)<sup>16</sup> theory, which is an *ab initio* orbital theory with effective and accurate systematic simulations, along with the embedded fragment method. Compared with the density functional theory (DFT)<sup>17–19</sup> and Hartree–Fock (HF)<sup>20</sup> methods, MP2 has the ability to describe all the important interactions in a crystal, such as the covalent, ionic, and dispersion interactions. The

embedded fragment method is used to analyze large molecular systems, where the internal energy per unit cell of a crystal can be divided into a proper combination of the energies of monomers and overlapping dimers. The MP2 theory combined with the embedded fragment<sup>13</sup> method has been successfully applied to calculate and predict the physical properties and phase transitions of solid CO<sub>2</sub> phases I, II, III<sup>13,21</sup>, and ice structures<sup>22,23</sup>. Fig. 1 shows the phase diagram of solid CO<sub>2</sub> at pressure and temperature ranges of 10–40 GPa and 10–1000 K, respectively, where the phase IV is located at a pressure above 12 GPa. In this work, based on the MP2 theory, we demonstrate that the crystal structure of phase IV with a  $R\bar{3}c$  symmetry is stable, which contains linear CO<sub>2</sub> molecules and the C=O bond length is 1.1 Å. However, the solid CO<sub>2</sub> phase IV with the  $Pbcn$  space group and bending O=C=O bonds possesses an unstable structure, which becomes linear after full optimization. This work reproduces the experimental results of the equation of state and Raman spectra of CO<sub>2</sub> phase IV by Datchi *et al.*<sup>10</sup>, where the CO<sub>2</sub> phase IV is a molecular structure composed purely of linear molecules, rather than an intermediate phase with bent O=C=O bonds proposed by Park *et al.*<sup>9</sup>.



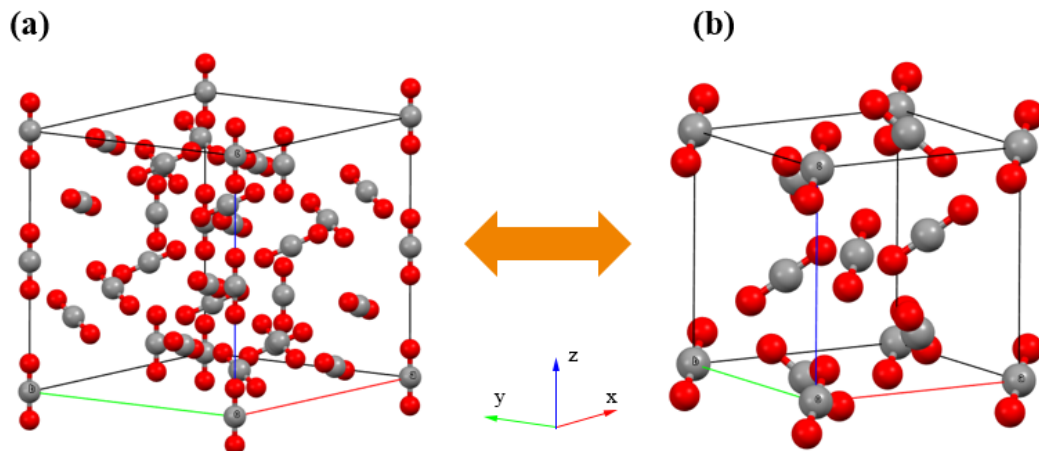
**Fig. 1** Phase diagram of solid carbon dioxide at high pressure. The experimental data are taken from Giordano *et al.*<sup>4,24</sup> and Iota *et al.*<sup>5</sup>. Solid lines are experimental phase transition lines. Dashed lines are extrapolated transition boundary of phase II-IV and the extrapolated melting curve. The dash-dotted lines are considered as kinetic boundaries.

## RESULTS AND DISCUSSION

### Crystal structure

Fig. 2 displays the crystal structures of CO<sub>2</sub> phase IV, with a space group of  $R\bar{3}c$ . The selected crystal structures for the conventional R-centered cell of the solid CO<sub>2</sub> phase IV<sup>10</sup> are as follows: ( $R\bar{3}c$ ) ( $a, b, c, \alpha, \beta, \gamma$ ) = (8.628, 8.628, 10.604, 90°, 90°, 120°), corresponding to the atomic positions of  $C_1(6b) = (0.000, 0.000, 0.000)$ ,  $O_1(12c) =$

$(0.000, 0.000, 0.108)$ ,  $C_2(18e) = (0.000, 0.249, 0.250)$ , and  $O_2(36f) = (0.142, 0.320, 0.208)$ . The primitive rhombohedral cell parameters are  $a_R = 6.108$  and  $\alpha_R = 89.87^\circ$ .

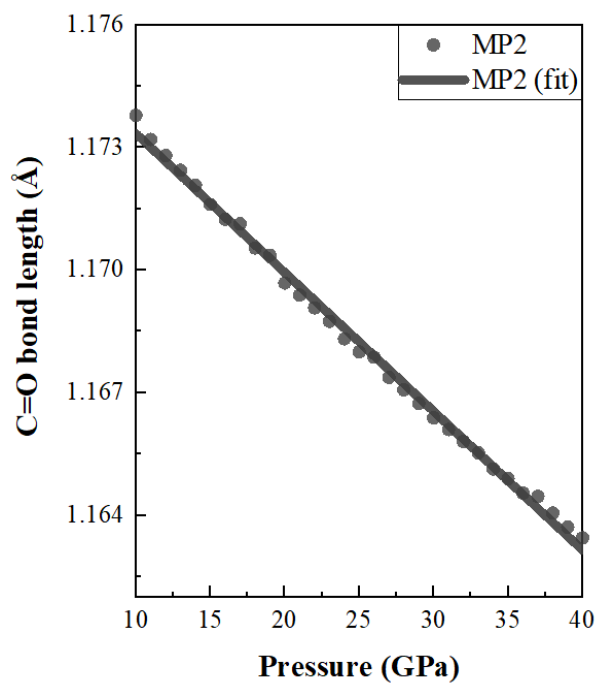


**Fig. 2** Crystal structures of carbon dioxide phase IV ( $R\bar{3}c$ ) taken from Datchi *et al.*<sup>10</sup>. (a) The conventional R-centered cell, which contains 24 molecules. (b) The primitive rhombohedral cell, which contains 8 molecules.

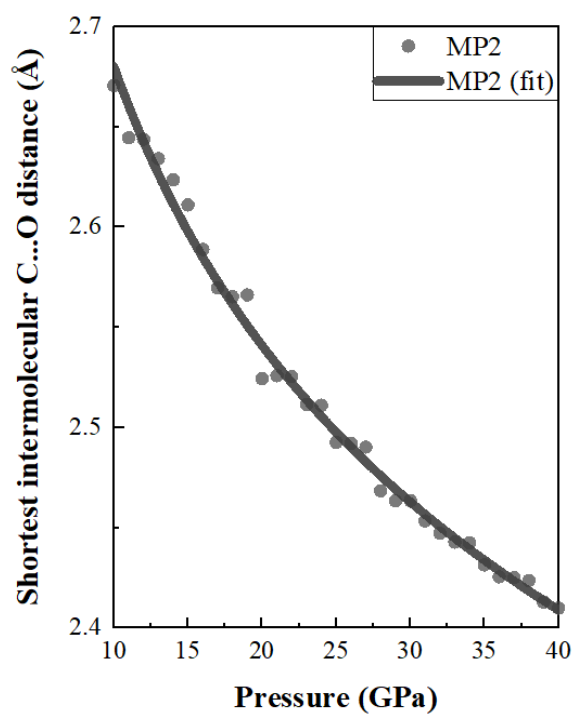
Based on the embedded fragment method and the MP2 theory, we propose an effective parallel-execution program for the energy calculation, crystal structural optimization, and vibrational analysis<sup>13</sup>, as shown in Methods. Table 1 shows the MP2/aug-cc-pVDZ calculated structural parameters (the primitive cell) of CO<sub>2</sub> phase IV at 15.2 GPa compared with the experimental results by Datchi *et al.*<sup>10</sup> at 15.2 GPa and Park *et al.*<sup>9</sup> at 15 GPa, respectively. As expected, the MP2 calculations agree considerably with the measured data from Datchi *et al.*, with a minimum deviation of 0.3% for the lattice constants.

**Table 1.** Lattice parameter of solid CO<sub>2</sub> phase IV.

Method	$a=b=c$ (Å)	Average Intramolecular C=O bond length (Å)	Shortest Intermolecular C...O distance (Å)
MP2 <sup>§</sup>	6.089	1.171	2.61(±0.02)
XRD <sup>†</sup>	6.108	1.155	2.62(±0.02)
XRD <sup>‡</sup>	N/A	1.50	2.1(±0.2)
<sup>§</sup> This work, MP2 calculation, at 15.2 GPa. <sup>†</sup> X-ray diffraction study at 15.2 GPa by Datchi <i>et al.</i> <sup>10</sup> . <sup>‡</sup> X-ray diffraction study at 15 GPa by Park <i>et al.</i> <sup>9</sup> .			



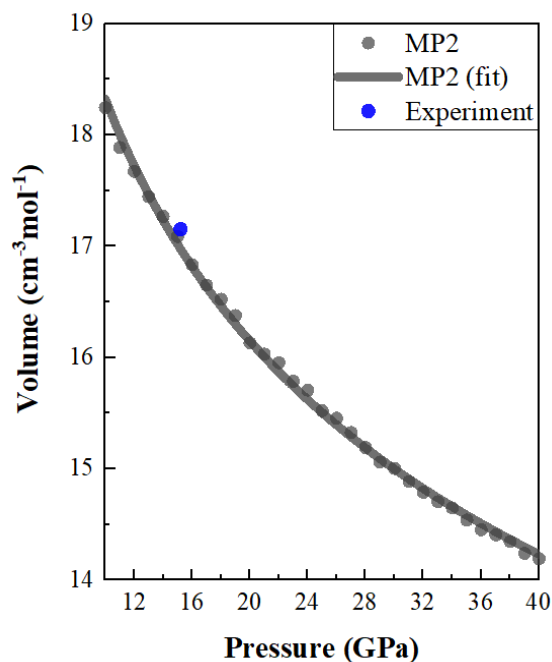
**Fig.3** The pressure dependence of intramolecular C=O bond lengths of CO<sub>2</sub> phases IV, calculated by the MP2/aug-cc-pVDZ theory.



**Fig.4** The pressure dependence of shortest intermolecular C...O distance of CO<sub>2</sub> phases IV, calculated by the MP2/aug-cc-pVDZ theory.

The most persistent debate about the solid CO<sub>2</sub> phase IV is whether it is a molecular state or an intermediate state, depending on the intramolecular C=O bond length and the intermolecular C...O distance. As early as 2003, Park *et al.*<sup>9</sup> presented the structure of solid CO<sub>2</sub> phase IV via XRD technique and demonstrated that it is an intermediate state with bent molecules ( $\angle\text{O-C-O}=160^\circ$ ). In their work, the intramolecular C-O bond displayed an increase of about 30% for the C-O single bond length (1.5 Å), while the distance of intermolecular C...O distance decreased to 2.1 Å. Based on the crystal proposed by Park *et al.*,<sup>9</sup> Bonev *et al.*<sup>14</sup> calculated the energy and structure of solid CO<sub>2</sub> phase IV via DFT theory and proposed that the measurements of the phase IV at high pressures possibly be a distorted molecular phase. For this controversy, Datchi *et al.*<sup>10</sup> reproduced the structure measurement of solid CO<sub>2</sub> phase IV in laboratory and reported that the C=O covalent bond length is 1.155 Å and the shortest intermediate C...O distance is 2.62 Å. Datchi *et al.*'s<sup>10</sup> work indicated that solid CO<sub>2</sub> phase IV has a molecular structure composed of linear O=C=O bonds. Address the controversy that whether solid CO<sub>2</sub> phase IV is a molecular structure, we perform the *ab initio* calculations based on the high-level MP2 theory combined with the embedded fragment<sup>13</sup> method in this study. After full optimization, the MP2 calculated C=O bond length is about 1.1–1.2 Å, which agrees with the results by Datchi *et al.* As shown in Fig. 3, as the pressure increases, the length of the C=O bonds of phase IV shows an almost linear decline from 10 to 40 GPa, presenting about 15% decrease (from 1.17 Å to 1.16 Å). The shortest intermediate C...O distance, as shown in Fig. 4, is about 2.60–2.62 Å (Table 1), which is also consistent with the results proposed by Datchi *et al.* Moreover, we also optimize the crystal structure of solid CO<sub>2</sub> phase IV proposed by Bonev *et al.* from 10 to 40 GPa. The results show that the CO<sub>2</sub> molecule becomes almost linear as the length of the C=O bonds decreases to 1.16 Å, indicating that the non-molecular structure of phase IV is not stable. Therefore, the proposed MP2 calculation indicates that the solid CO<sub>2</sub> phase IV is a molecular state rather than an intermediate phase, agreeing with the conclusion by Datchi *et al.*<sup>10</sup>.

## Equations of state

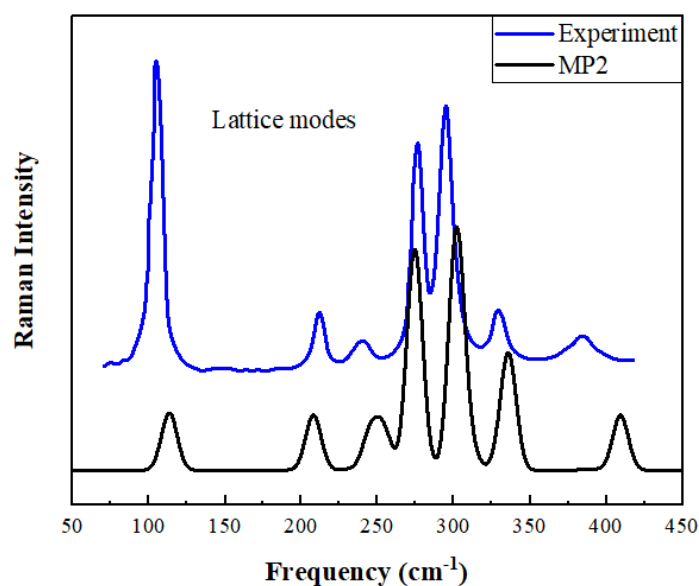


**Fig.5** Pressure-volume relationship of solid CO<sub>2</sub> phase IV, calculated by MP2/aug-cc-pVDZ theory. The blue dot is an experimental data taking from Ref. 10.

Fig. 5 presents the pressure–volume curve at 0 K of CO<sub>2</sub> phase IV by MP2 calculations compared with the measured data<sup>10</sup>. In Fig. 5, the volume progressively decreases as the pressure increases, indicating that the density of the solid CO<sub>2</sub> phase IV will increase. The main reason for this result is that as the pressure increases, the CO<sub>2</sub> atoms enter the repulsive parts of the atom–atom potential, and both the intramolecular bonds and the intermolecular interactions become stronger. Meanwhile, the intermolecular interaction is still weaker than the covalent intramolecular bonds. Such a relationship is in agreement with the C=O bond lengths and the C...O distances shown in Figs. 3 and 4.

### Vibrational spectra

Vibrational spectra are considered to be the unique fingerprint for certain materials or molecules and are often more sensitive to structural change, which can be used to effectively identify the molecules or materials. With considerable accuracy, we calculated the Raman spectra of solid CO<sub>2</sub> phase IV based on the MP2/aug-cc-pVDZ theory. The Raman spectra of the calculated and measured results of carbon dioxide phase IV at 20.9 GPa are shown in Fig. 6, where the observed curve is taken from the experimental work by Datchi *et al.*<sup>10</sup>. For the lattice modes, the Raman spectra calculated by MP2 theory from 50 to 450 cm<sup>-1</sup> are in excellent agreement with the observed data, which further confirms the accuracy of the proposed solid CO<sub>2</sub> calculations at high pressures.



**Fig.6** The observed (blue curve) and calculated (black curve) Raman spectra of phase IV from 50cm<sup>-1</sup> to 450cm<sup>-1</sup> at 15.2 GPa, based on the MP2/aug-cc-pVDZ theory.

## CONCLUSIONS

In conclusion, based on the embedded fragment–MP2 method, we investigate the solid CO<sub>2</sub> phase IV at high temperatures and pressures using *ab initio* calculations. We reproduce the equation of state, lattice constants, and Raman spectra of CO<sub>2</sub> phase IV quantitatively, which are consistent with experimental data. The results confirm that the solid CO<sub>2</sub> phase IV is a molecular structure with linear O=C=O bonds and invalidate the intermediate state proposal with nonlinear O=C=O bonds, in which the CO<sub>2</sub> molecules cannot be stable at the given pressure. This work is of great significance not only for accurately determining the physical properties of solid CO<sub>2</sub> at high pressures, but also for the further understanding of the formation process of other high-pressure phases and the exploration of exciting new structures.

## METHODS

### System energy

We combine the embedded fragment method<sup>13,21,25,26</sup> and the high-level MP2 theory for the energy calculation, which has been successfully employed for the structure, spectra and phase transition predictions of solid CO<sub>2</sub> phases I, II, and III. For a molecular crystal, the internal energy for the unit cell can be obtained by



$$\begin{aligned}
U_e = & \sum_i E_i + \sum_{i=1} \sum_{\substack{j=i+1 \\ r_{ij} < \lambda}} \Delta E_{ij} \\
& + \frac{1}{2} \sum_N (1 - \delta_{x0}) \sum_{\substack{i,j \\ r_{ij} < \lambda}} (E_{i(0)j(x)} - E_{i(0)} - E_{j(x)}) + E_{LR},
\end{aligned} \tag{1}$$

where  $x$  is the three-integer cell index,  $E_{i(x)}$  is the energy of the  $i$ th molecule in the  $x$ th unit cell, and  $E_{i(0)j(x)}$  is the interaction energy of the  $i$ th molecule in the  $0$ th unit cell and the  $j$ th molecule in the  $x$ th unit cell.  $E_i$  is the one-body energy in a unit cell, and  $\Delta E_{ij}$  is the energy of the two-body interactions for both molecules in the unit cell. All monomers and dimers at a short distance are calculated at the MP2/aug-cc-pVDZ level and are embedded in an electrostatic field represented by the electrostatic point charges of the other atoms calculated at the HF/aug-cc-pVDZ level. The interactions of long-range dimers are determined by charge–charge electrostatic interactions. The related gradient, Hessians, and Raman spectra can be calculated by summing the corresponding quantities of the monomers and dimers. After including the contribution of external pressure<sup>22</sup>, the enthalpy ( $E_e$ ) for a unit cell can be calculated by

$$E_e = U_e + PV, \tag{2}$$

where  $P$  represents the external pressure, and  $V$  is the unit cell volume.

In the present study, we use the primitive rhombohedral cell of CO<sub>2</sub> phase IV, as shown in Fig. 2(b), which contains 8 CO<sub>2</sub> molecules. The dimers at a short distance in the  $3 \times 3 \times 3$  supercell are embedded in the background charges represented by the  $11 \times 11 \times 11$  supercell and calculated by the quantum-mechanical theory. Furthermore, in a  $41 \times 41 \times 41$  supercell, the long-range contribution of the electrostatic interactions is taken into account.

### Raman spectra calculation

Using the force constant matrix ( $F_n$ ) from the  $0$ th to the  $x$ th unit cells, we can calculate the  $\mathbf{k}$ -dependent force constant matrix,  $F(\mathbf{k})$ , by the following:

$$F(\mathbf{k}) = \sum_0^N F_n e^{in\mathbf{k}a}, \tag{3}$$

where  $a$  is the translational period. For the Raman spectra calculation, only the vibrations in a zero-center ( $\mathbf{k} = 0$ ) have nonzero intensities and are Raman-active. Therefore, the Raman frequency and intensity calculations of in the  $x$ th phonon mode are calculated with the  $0$ th force constant matrix,  $F(\mathbf{0})$ , of the central cell by the following equation<sup>13</sup>:

$$R_{x0} \propto \frac{3}{2} \left( \sum_p^{a,b,c} \frac{\partial P_{ii}}{\partial Q_{x0}} \right)^2 + \frac{21}{2} \sum_i^{a,b,c} \sum_j^{a,b,c} \left( \frac{\partial P_{ij}}{\partial Q_{x0}} \right)^2, \tag{4}$$

where  $Q_{x0}$  is the corresponding normal mode, and  $\partial P_{ij}/\partial Q_{x0}$  is the polarizability derivative.

### Structure optimization

In this study, to optimize the molecular structure of CO<sub>2</sub> phase IV and obtain the most stable crystal structure under a given condition, we introduce the quasi-Newton algorithm<sup>27</sup>, which performs structural optimization by minimizing the enthalpy  $H_e$  and forces of all atoms. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm<sup>28</sup> is used to update the approximate Hessian matrix. Furthermore, we set 0.001 Hartree/Bohr of the maximum gradient as the convergence criterion. All the calculations, including the energy calculation, structural optimization, Hessian matrix calculation, and vibrational spectra determination, are performed using our in-house parallel program.

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## COMPETING INTERESTS

The authors declare no competing interests.

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