

Neutron diffraction study of crystal structure and temperature driven molecular reorientation in solid α -CO

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ABSTRACT

Neutron diffraction studies have been carried out on carbon monoxide (CO) in the temperature range of 14–68 K. From the data of the temperature dependent crystal parameters, the volume thermal expansion β (T), C–O bond length, and intermolecular distance of CO have been determined and compared with calculations. The volume evolution of cubic CO solids indicates a normal thermal expansion. However, the bond length of CO molecules contracts with the increase in temperature. Correspondingly, the distance between CO molecules increases much faster with an increase in the temperature. We find that intermolecular and intramolecular interactions account for these abnormal temperature behaviors of CO molecular crystals. The abnormal change observed in the curve β (T), evolution of C–O bond length, and distance between two CO molecules indicate an order–disorder phase transition induced by head-to-tail reorientations of CO dipoles.

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INTRODUCTION

Carbon monoxide (CO) is the second most abundant gas after H₂ in the universe and is a common solid molecule found in the interstellar medium and solar system ice.¹ It has been reported that more than half of the atmospheric CO came from anthropogenic sources.² Disturbance in the CO amount will perturb tropospheric chemistry, resulting in global warming and other climatic changes.³ Recently, the Planck space telescope made available the first-ever all-sky map of carbon monoxide in the cosmos, which can help spot star-forming regions where carbon monoxide glows brightly. CO occurs in mixed gas hydrates (CO₂, H₂, N₂, etc.), and the formation of these phases may play an important role in comets and the outer planets in the solar system.^{4,5}

The CO molecule is isoelectronic with N₂, in which C and O atoms are connected by a triple bond. It consists of two

regular covalent bonds and one dative covalent bond, which is also known as a dipolar bond or coordinate bond. At low temperature, CO condenses into liquid and then freezes at triple points of 68.15 K, forming a disordered hexagonal solid β -phase. When cooled down to 61.6 K, the solid β -phase will transform to a molecular ordered α -phase.⁶ The primitive structure of α -CO is cubic, with a basis of four molecules per unit cell, and belongs either to the space group $P2_13$ or to the space group $Pa3$ (similarly to N₂); the evidence is conflicting.^{7–12} According to Refs. 7–9, solid α -CO occupies centrosymmetric positions and has been assigned a disordered structure in the space group $Pa3$ (analogous to the structure of α -N₂). Its molecular axes are aligned parallel to the cell diagonals. These authors reject the space group $P2_13$ of a lower symmetry in which the molecular axes are directed along the four cube body diagonals and α -CO only slightly shifts from the $Pa3$ arrangement.¹⁰ It is worth noting here that CO is a polar molecule. The

crystal structure of the location of the molecules and the end-to-end ordering^{13–15} in α -CO are related to dipolar ordering. In other words, α -CO in its equilibrium state is bound to have the $P2_13$ structure, which differs from the $Pa3$ structure in which α -CO molecules are in end-to-end ordering. Until now, by x-ray diffraction experiments, there is no strong evidence to confirm the structure of α -CO belonging to $P2_13$ or $Pa3$. More accurate measurements would be desirable.

In this study, in order to resolve the ambiguity about the low-temperature modification structure of solid CO, we performed a neutron diffraction experiment by condensing CO gas in a vanadium gas cell under a pressure of 20 MPa at the beamline of High-Pressure-Preferred Orientation (HIPPO),^{16,17} Los Alamos Neutron Science Center (LANSCE). The temperature dependence of lattice parameters, bond length of carbon and oxygen, and intermolecular distance have also been investigated, which allow for the calculation of the thermal expansion coefficient and analysis of intermolecular and intramolecular interactions.

EXPERIMENTS

The neutron diffraction experiment was performed using Displex¹⁸ in a low-temperature environment, the whole chamber of which was vacuumed to 10^{-5} Pa; the CO gas was loaded in a high-pressure vanadium cell, which was previously flushed by pure CO gas (from Alpha Asia) and vacuumed 3–4 times. Then, the CO was pressurized up to 20 MPa at room temperature and cooled down to the lowest temperature of 10 K. At each temperature point, for every 1–2 h, neutron exposure was collected for a better signal/noise ratio. The neutron diffraction patterns under different temperatures were analyzed with Rietveld refinement using the GSAS program.¹⁹

Based on density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package,^{20–22} first-principles calculations were performed by using the projector augmented wave

(PAW) method.^{23,24} The electronic exchange-correlation effects were described by local-density approximation (LDA).^{25,26} We chose LDA instead of GGA because the C–O bond length in the CO gas phase calculated by LDA (1.1351 Å) was closer to the experimental value (~ 1.13 Å), and the GGA result (1.1433 Å) was observably larger. The energy cutoff of 500 eV was used for the plane wave basis set, and a Monkhorst–Pack k -point of $6 \times 6 \times 6$ was used for Brillouin zone sampling. In structural relaxations, the convergence criteria of energy and force were set to 1×10^{-5} eV and 0.02 eV/Å, respectively. α -CO is a molecular crystal, so van der Waals (vdW) interaction may play an important role. Here, we have used van der Waals correction of the DFT-D3 method.²⁷ Besides, all the calculations were carried out below 20 MPa, which was consistent with the experimental conditions.

For molecular dynamics (MD) simulations, we have used an NPT ensemble established in a supercell of $3 \times 3 \times 3$ α -molecular crystal with 216 atoms in total, and only gamma point was used in the MD simulations. During simulations, we have increased the temperature from 1 K to 60 K with a step of 5 K. The time step at each temperature was 1 fs, running for a period of 6 ps. After reaching equilibrium, the volume and C–O bond length were averaged for the last 3000–6000 structures at each temperature, and the error bars were estimated by the standard deviations during statistics.

RESULTS AND DISCUSSION

Low-temperature neutron diffraction studies have been carried out on carbon monoxide in the temperature range of 14–68 K. Figure 1 shows the refined neutron diffraction patterns selected at different temperatures. It is observed that the neutron diffraction peaks could be well indexed with the cubic $P2_13$ unit cell in the temperature range from 14 K to 60 K and with $a = 5.6341(1)$ Å at 30 K [as shown in Fig. 1(a)] and the hexagonal $P6_3/mmc$ unit cell with $a = 4.1132(1)$ Å and $c = 6.7118(3)$ Å at 65 K [as shown in Fig. 1(b)].

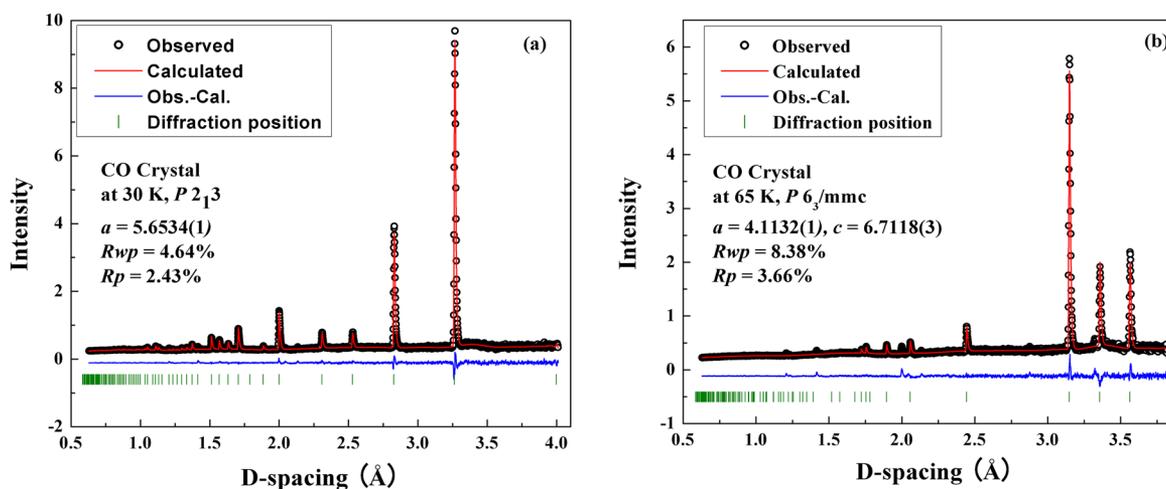


FIG. 1. Rietveld refinement of CO neutron diffraction data, (a) at 30 K with space group $P2_13$; (b) at 65 K with space group $P6_3/mmc$. The observed and calculated data points are marked by symbols and red solid lines, respectively. Tick marks indicate the positions of Bragg reflections. Difference curves are also shown.

The analysis of neutron diffraction patterns has shown that the α -CO structure belongs to the space group $P2_13$ instead of the conflictual $Pa3$. It is reasonable that CO has a molecular dipole compared with the N_2 molecule, so a slightly lower symmetric space group can be adopted for CO. More specifically, if we make a relative shift ($1/4, 1/4, 1/4$) of the two-unit cell of CO and N_2 , along the (111) direction, the intermediate N_2 and CO have the same orientation and almost overlapped with each other, while the upper and lower three-fold molecule rotated about 70° (as shown in Fig. 2). Another feature is that the CO molecule in the middle is with oxygen downward and the rest of the upper and lower CO molecules is with oxygen upward, in the purpose of minimizing electric polarization and total energy.

The temperature depending lattice parameter of α -CO is permitted to estimate the thermal expansion coefficients of the crystal in a wide temperature range. The values of volume and volume

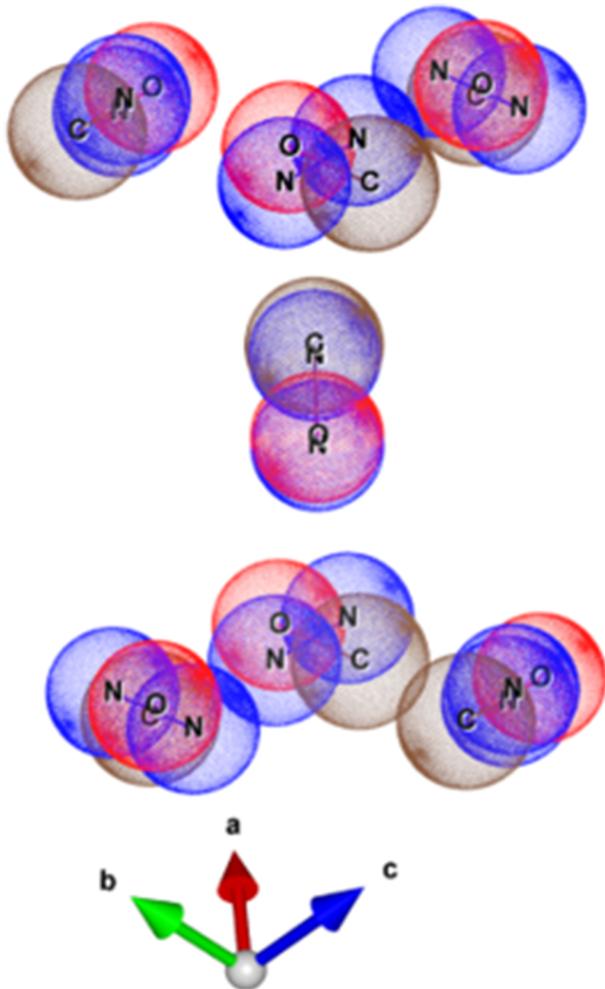


FIG. 2. Two unit cells of CO in $P2_13$ and N_2 in $Pa3$ crystal structures, the CO layer was shifted ($1/4, 1/4, 1/4$) relatively to the N_2 layer. The balls in blue, in soil color and in red represent nitrogen atoms, carbon atoms and oxygen atoms respectively.

TABLE I. The lattice parameter, volume, and volume thermal expansion of α -CO as a function of temperature.

Temperature (K)	a (Å)	V (Å ³)	Volume thermal expansion ($\times 10^{-4} \text{ K}^{-1}$)
14	5.635 7	178.996	...
20	5.640 21	179.426	4.0038
25	5.646 09	179.988	6.2644
30	5.653 37	180.685	7.7449
35	5.665 98	181.897	13.4156
40	5.676 58	182.919	11.2371
45	5.683 94	183.632	7.7958
50	5.697 02	184.903	13.8429
52.5	5.703 9	185.573	14.4941
55	5.711 82	186.347	16.6834
57.5	5.720 35	187.184	17.9665
60	5.729 78	188.111	19.8094
62.5	5.740 99	189.217	23.5180

thermal expansion are given in Table I and are shown in Fig. 3. The profile of the temperature dependence curve $\beta(T)$ is quite typical of the ordered phase for many molecular crystals.²⁸ It can be seen that the curve $\beta(T)$ undergoes an abnormal change at around 35 K, which may be related to an order-disorder phase transition induced by head-to-tail reorientations of CO dipoles.²⁹ The mechanism of reorientation involves 180° reorientation (head-tail flips). As Li^{29,30} suggested, the CO molecules are in a disordered state for $T \geq 37$ K, in which there are head-tail disordering motions. The disordering motions are fast in the temperature range above 37 K. Below this temperature, the motions were gradually frozen as thermal fluctuation decreased. Therefore, the curve $\beta(T)$ shows a dome shape in the disordered state due to the influence of head-tail orientational disordering on the expansion.

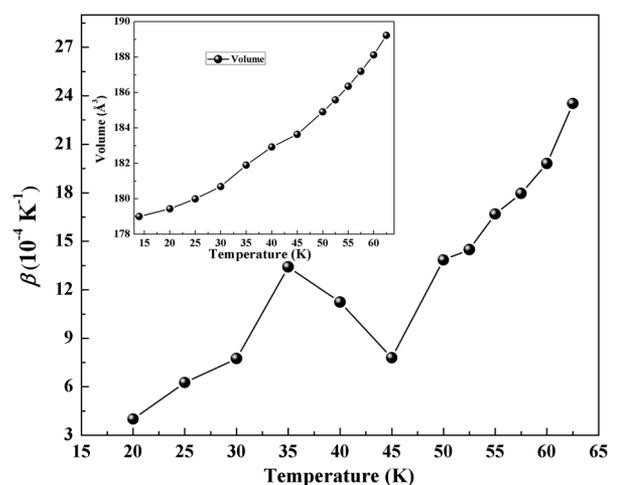


FIG. 3. Temperature dependence of volume thermal expansion coefficient and volume of α -CO.

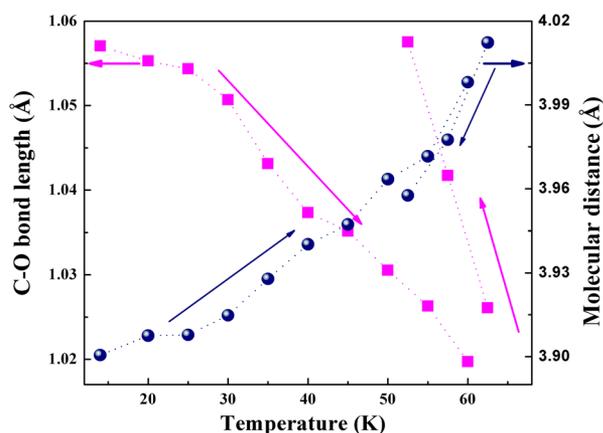


FIG. 4. Evolutions of CO bond length and inter molecular distance as function of temperature.

Figure 4 shows evolutions of the CO bond length and intermolecular distance of solid CO as a function of temperature. It is found that the distance between CO molecules increases with rising temperature, which can be interpreted as volume thermal expansion (as shown in Fig. 3). However, the bond length of CO is contrary to the trend in intermolecular distance with increasing temperature, which indicates the decrease in intermolecular interaction between carbon and oxygen atoms. Intermolecular and intramolecular interactions play important roles in the abnormal temperature behavior of CO molecular crystals. In solid α -CO, there are three primary interactions between two carbon monoxide molecules: an attractive van der Waals interaction, a repulsive short-range interaction, and a quadrupole–quadrupole electrostatic interaction. These three intermolecular interactions were weakened due to thermal expansion; correspondingly, the interaction between C and O atoms should be

enhanced to equilibrium. Therefore, intermolecular and intramolecular interactions play important roles in the abnormal temperature behavior of CO molecular crystals. It is worth mentioning that in the temperature range above 30 K, both C–O bond length and intermolecular distance show a fast change, which may be attributed to head–tail orientational disordering.

To further understand the abnormal temperature behavior of α -CO, DFT calculations were performed. As shown in Figs. 5(a) and 5(b), the average of volume and C–O bond length with the change in temperature are fluctuating, but the trend agrees well with our experiment. The reason for the fluctuation might be related to the size limitation of the supercell used in our MD simulations. From the two black solid curves shown in Fig. 5, we can see that their overall trends are consistent with the experimental results, where the volume increases as there is an increase in temperature, but the C–O bond length decreases with increasing temperature. The reason for volume expansion is easy to be understood. As for the decrease in the C–O bond length, we infer that as the temperature increases, the volume increases, leading to a weaker intermolecular van der Waals interaction. As a result, the C–O bond in the molecular crystal evolves toward the gas phase (the bond length is 1.1351 Å using LDA), so the intramolecular C–O bond length will gradually decrease.

CONCLUSIONS

In conclusion, the neutron diffraction experiment on solid CO molecules was investigated in the temperature range of 14–68 K. The structure of solid α -CO has been identified as $P2_13$, which differs from the $Pa3$ structure in which CO has a molecular dipole compared with N_2 molecules. The lattice parameter, volume, volume thermal expansion β (T), temperature dependence of C–O bond length, and intermolecular distance were obtained by refined high quality neutron diffraction data. The abnormal change appearing at around 30–35 K in β (T) indicates that the crystal α -CO undergoes an order–disorder phase transition induced by head-to-tail

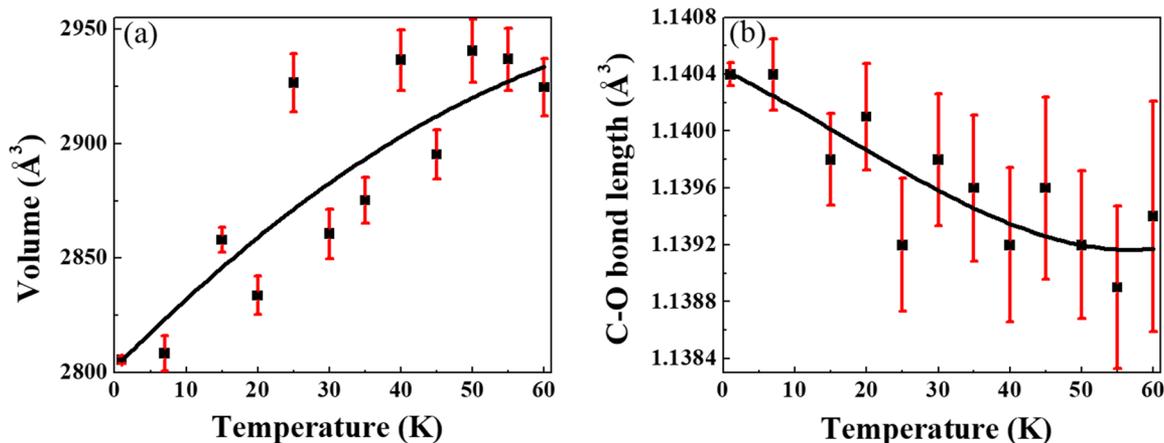


FIG. 5. Volume (a) and C–O bond length of the molecular crystal (b) as a function of temperature in MD simulations. The solid black lines are polynomial fitting of the filled squares. Error bars are denoted with red line-segment.

reorientations of the CO dipoles. According to experimental data and theoretical calculation, as the temperature increases, the volume increases, but the C–O bond length decreases. This anomalous behavior of the C–O bond length with respect to increase in temperature attributes to the equilibrium between the intermolecular van der Waals interaction and intramolecular interaction between C and O atoms in CO molecular crystals.

AUTHOR'S CONTRIBUTIONS

L.W. and C.S. contributed equally to this work.

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