High-pressure-activated carbon tetrachloride decomposition*

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The pressure-induced molecular dissociation as one of the fundamental problems in physical sciences has aroused many theoretical and experimental studies. Here, using a newly developed particle swarm optimization algorithm, we investigate the high-pressure-induced molecular dissociation. The results show that the carbon tetrachloride (CCl_4) is unstable and dissociates into C_2Cl_6 and Cl_2 under approximately 120 GPa and more. The dissociation is confirmed by the lattice dynamic calculations and electronic structure of the *Pa*3 structure with pressure evolution. The dissociation pressure is far larger than that in the case of high temperature, indicating that the temperature effectively reduces the activation barrier of the dissociation reaction of CCl_4. This research improves the understanding of the dissociation reactions of CCl_4 and other halogen compounds under high pressures.

Keywords: crystal structure prediction, decomposition, carbon tetrachloride, high pressure

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1. Introduction

The molecular crystal exhibits a highly developed polymorphism in a wide pressure or temperature range. Carbon tetrachloride (CCl_4), a typical molecular crystal under pressure, was known to have polymorphism several decades ago. Extensive experimental measurements, including x-ray diffraction and Raman spectra, have been carried out to reveal CCl_4 crystal structures.[1–4] At room temperature, the CCl_4 crystallizes into a disordered face-centered cubic $Fm3m$ structure at 0.13 GPa,[2,3] which transforms into a monoclinic $C2/c$ structure at a higher pressure (0.4 GPa) and then continuously transforms into another monoclinic structure $P2_1/c$ symmetry at 0.7 GPa.[2–5] In compression up to 2.3 GPa, it transform into a cubic *Pa*3.[6–9]

A dimerization reaction of CCl_4 ($2CCl_4 \rightarrow C_2Cl_6+Cl_2$) under pressure in ranges of 7 GPa–17 GPa has been reported[10,11]. However, using an *ab initio* method[12], no dissociation behavior was detected within 0–20 GPa at room temperature, which is unambiguously in disagreement with previously measured results.[6,8,13] Recently, Yukio reported that the dimerization reaction ($2CCl_4 \rightarrow C_2Cl_6+Cl_2$) occurred at higher temperatures ranging from 1500 K to 2350 K in nearly the same pressure range 10.1 GPa–16 GPa,[14] based on the heat capacity $C_V(T)$ investigations. These discrepancies motivated us to investigate the decomposition of CCl_4 under high pressure.

Here, we explore the decomposition pressure of CCl_4 at 0 K by the newly developed particle swarm optimization (PSO) algorithm for crystal structure prediction,[15] which has been implemented in the CALYPSO code[15] and successfully benchmarked on a number of different systems.[16–20] It is found that the CCl_4 molecule became unstable at approximately 120 GPa and dissociated completely into C_2Cl_6 and Cl_2. The dynamical instability of its *Pa*3 structure showing some imaginary phonons at above 120 GPa have supported the dissociated action. The result also reveals that the temperature has a significant effect on the dissociation of CCl_4 compared with the previously reported result.

2. Methods

The crystal structure prediction is based on a global minimization of free-energy surfaces combined with *ab initio* total-energy calculations via the PSO technique as implemented in the crystal structure analysis by the particle swarm optimization (CALYPSO) code.[15] We carry out the CCl_4 structural simulations with simulation cell sizes ranging from one to four formula units at 0, 50, 100, and 150 GPa. The detailed structural search can be divided into three steps. The first step of the structure simulation is to generate random structures (named as the first generation) symmetrically constrained within 230 space groups. Once a particular space group is selected, the lattice parameters are then confined within the chosen symmetry. The corresponding atomic coordinates are generated by the crystallographic symmetry operations. The second step is to realize the local optimization process for the previously determined crystal structures in order to obtain their

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most stable geometries. After all of such structural optimizations, only those structures with the lowest-enthalpy (the best 70% of previous generation), which are in the most promising area of the configuration spaces, are selected to produce the next generation; random structures (30% of the population of each generation) are also generated with symmetrically constrained within 230 space groups. For all of the generations, a symmetry checking technique is applied in order to remove the identical symmetric structures. This allows the generation of diverse structures, which is actually crucial for increasing the efficiency of global minimization. To analyze the produced results, we select a number of distinct structures with the lowest enthalpies for optimizing their most stable geometries by using VASP code.[21] The underlying *ab initio* structural relaxations and electronic calculations are performed by density functional theory within the framework of Perdew–Burke–Ernzerhof (PBE) functional, as implemented in the VASP code. The PAW pseudopotentials with $2s^2 2p^2$ and $3s^2 3p^5$ electrons are adopted as valences for C and Cl, respectively. The energy cutoff 800 eV and appropriate Monkhorst–Pack k meshes are chosen to ensure that the enthalpy calculations are well converged to better than 1 meV/atom. The phonon calculations are carried out by using a supercell approach, as implemented in the PHONOPY code.[22]

3. Result and discussion

Variable-cell structure predictions by the CALYPSO technique are performed for CCl_4 with the cell sizes containing 1–4 formula units at 0, 50, 100, and 150 GPa, respectively. The three known structures, with corresponding space groups of $C2/c$, $P2_1/c$ and $Pa3$, are successfully uncovered in our predictions. These reproduced structures all contain completely well-separated CCl_4 molecules.

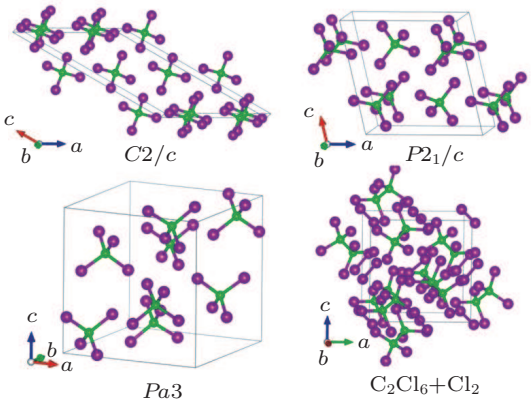


Fig. 1. (color online) Predicted $C2/c$, $P2_1/c$ and $Pa3$ structures of CCl_4 (well-separated molecules). The low-enthalpy structure made of C_2Cl_6 mixed with Cl_2 molecules at 150 GPa. The large and small spheres represent Cl and C atoms, respectively.

At 150 GPa, our structural simulations reveal, surprisingly, a low-enthalpy structure consisting of hexachloroethane (C_2Cl_6) mixed with chlorine (Cl_2) molecules (Fig. 1). It suggests a possibility of decomposition of CCl_4, so in the next step, we investigate the stable structures of C_2Cl_6 and Cl_2 in such a pressure range by performing additional evolutionary structural searches. The most stable structures for C_2Cl_6 (P-1) and Cl_2 ($C2/c$) at 150 GPa are supplemented by our searches. Further, the decomposition enthalpy on the basis of the C_2Cl_6 (P-1) + Cl_2 ($C2/c$) reaction pathway is calculated. All the obtained enthalpies relative to the predicted $C2/c$ structure are shown in Fig. 2. It shows that the CCl_4 is decomposed into C_2Cl_6 and Cl_2 at above 120 GPa.

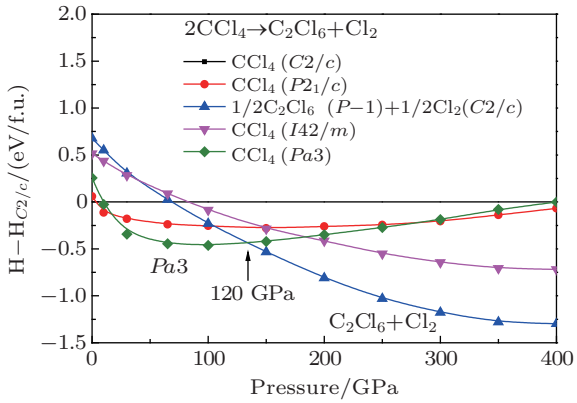


Fig. 2. (color online) Enthalpy curves (relative to the predicted $C2/c$ phase) for CCl_4 as a function of pressure.

For the decomposition phenomenon of CCl_4, the previous experimental results showed its decompositions at 10.1 GPa–16 GPa, but these measurements were conducted at above 1500 K.[12,23–25] Note that here our structural searches and enthalpy calculations are performed actually at 0 K temperatures in our work. Obviously, the calculated dissociation pressure (120 GPa) is far larger than the previous value 10.1 GPa–16 GPa (1500 K–2350 K). The reason for this significant discrepancy can be attributed to the large temperature effect. Since the dissociation is an endothermic reaction, the existence of high temperature leads to the need for a much lower pressure for the dissociation reaction. Therefore, the decomposition reaction can be sufficiently activated at 1500 K–2350 K at much lower pressures (10.1 GPa–16 GPa). Also, it is easily understandable that the temperature is closely related to the molecular kinetic energy: the lower the temperature, the larger the activation barrier will be. It means that at relatively low temperatures, a large kinetic barrier exists and prevents CCl_4 from decomposing. An accurate evaluation of the decomposition kinetic barrier is needed to give a precise conclusion, but a major challenge remains, which is beyond the scope of this study.

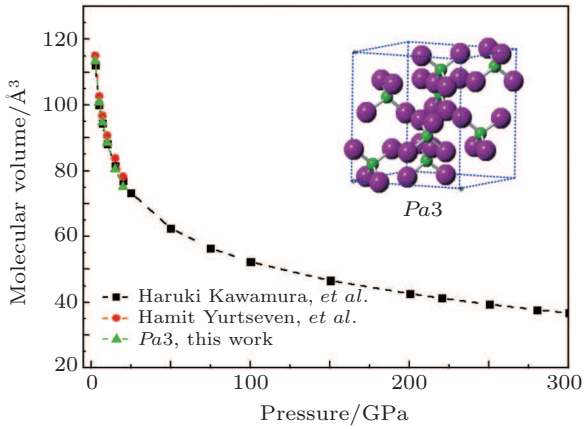


Fig. 3. (color online) Comparisons between the calculated results (green triangles) from the equation of state (*Pa*3) and the experimental data (black squares from Ref. [6] and red solid circles from Ref. [25].)

Considering the equation of state (EOS), we calculate the EOS of *Pa*3 in a large pressure range, as seen in Fig. 3 and the available experimental data.[6,26] Satisfactorily, the results are in good agreement with the measured data. We perform the lattice dynamic calculations of the *Pa*3 structure for further discussion. Dynamical structural stabilities in the relevant pressure range of this *Pa*3 structure are investigated (Fig. 4). As expected, the *Pa*3 phase is stable in the whole studied pressure ranges of 2.5 GPa–100 GPa due to the absence of the phonon vibrational imaginary frequency. However, with pressure increasing up to 120 GPa, the structure turns unstable due to the phonon softening and broadening of *G* with a negative value (−4.5 eV) at 120 GPa, which in turn supports the foregoing idea about the decomposition of CCl_4 at above 120 GPa.

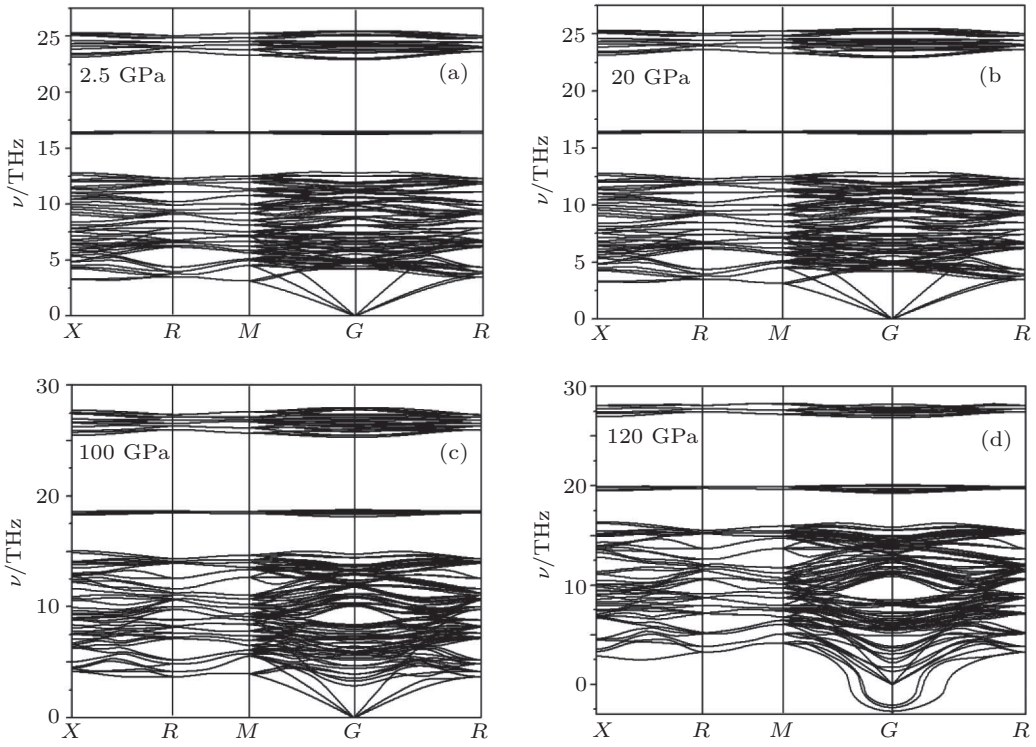


Fig. 4. Phonon dispersion curves of the predicted *Pa*3 at 2.5 GPa (a), 20 GPa (b), 100 GPa (c), and 120 GPa (d).

Further, the band structures of *Pa*3 along the high-symmetry points of the Brillouin zone are calculated; the results are shown in Figs. 5(a)–5(c). The Fermi level E_F is set at zero energy. Analyses of the energy band structures of *Pa*3 reveal a direct band gap with a value of about 3.8 eV at 20 GPa, which decreases to 1.6 eV at 100 GPa. At above 120 GPa, the energy gap vanishes at point *G*, implying that the *Pa*3 phase has been metalized at 120 GPa. As is well known, both the local density approximation (LDA) and generalized gradient approximation (GGA) methods usually underestimate the bandgap values of insulator and semiconductor.[27–29] Therefore, the metallization of *Pa*3 should occur at above 120 GPa. However, the metallic formation of the C–Cl covalent bonds is very unusual for these relevant materials; to our knowledge, there has been no relevant research report on this phenomenon. It in turn reflects that the existence of a metallic *Pa*3 phase should not be reasonable at above 120 GPa and the CCl_4 structure should have changed in such a pressure range.

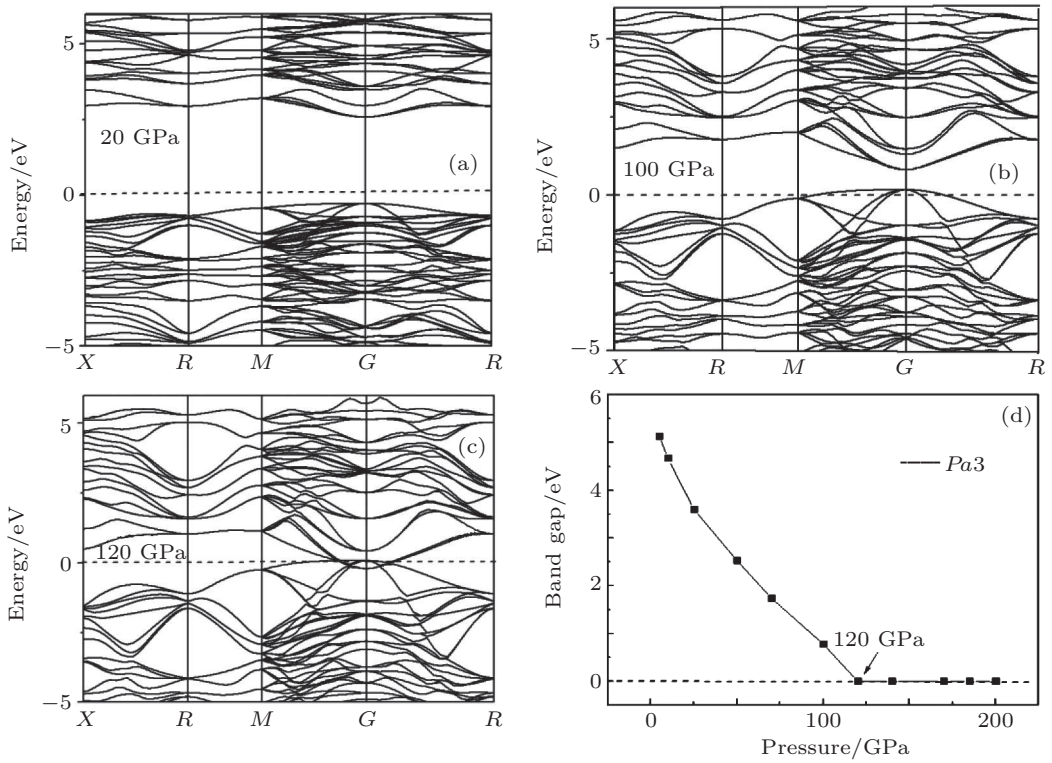


Fig. 5. Electronic band plots along high-symmetry directions for *Pa*3 at 20 GPa (a), 100 GPa (b), and 120 GPa (c); the band gap for *Pa*3 structure as a function of pressure panel (d).

4. Conclusion

In this paper, we explore the CCl_4 high-pressure structures using a newly developed particle swarm optimization algorithm for crystal structure prediction. The results reveal that the CCl_4 becomes unstable and dissociates into C_2Cl_6 and Cl_2 at above 120 GPa. The dissociation pressure is far larger than the previously reported value; the discrepancy between them is mainly due to the significant temperature effect. The lattice dynamic behaviors and the variations of the electronic structure of the *Pa*3 phase with pressure are extensively studied; the results indicate the phonon softening and broadening of point *G* and the unreasonable metallic *Pa*3 phase at above 120 GPa, confirming the decomposition of the CCl_4 structure at above 120 GPa.

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