The equation of state and nonmetal-metal transition of benzene under shock compression

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Abstract

We employ quantum molecular dynamic simulations to investigate the behavior of benzene under shock conditions. The principal Hugoniot derived from the equation of state is determined. We compare our first-principles results with available experimental data and provide predictions of chemical reactions for shocked benzene. The decomposition of benzene is found under the pressure of 11 GPa. The nonmetal-metal transition, which is associated with the rapid C-H bond breaking and the formation of atomic and molecular hydrogen, occurs under the pressure around 50 GPa. Additionally, optical properties are also studied.

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I. INTRODUCTION

The nature of hydrocarbons under extreme conditions is of great scientific interest and has recently attracted extensive studies. Specially, due to the possible importance in the formation of organic materials in the early solar system [1], chemical reactions of small hydrocarbon molecules, such as acetylene, ethylene, methane, and benzene have gained particular attention. A major constituent of the “ice” layer in Uranus and Neptune, where the pressure could reach 600 GPa and temperature 8000 K, is thought to be methane [2, 3], and the planetary magnetic fields are greatly influenced by the electrical conductivity of methane at these conditions. Another important source of planetary carbon is thought to be benzene, which has been found in the atmosphere of Jupiter and in carbonaceous chondrites [4, 5]. Naturally, comprehensive studies on the characteristics of benzene are indispensable for understanding the various astrophysical phenomena at high temperatures and pressures.

Researches on benzene properties under shock conditions start from the plate impact experiments [6]. As pressure increases, benzene has been found to decompose at 13 GPa along its Hugoniot [7, 8, 9, 10, 11]. At high static and dynamic temperatures and pressures, benzene mainly converts into defective carbon nanoparticles and H2, with the possible products of small concentrations of polycyclic aromatic hydrocarbons, such as alkanes [12, 13]. Such reactions have also been found to be similar to the detonation of explosive materials [14]. Nonmetal-metal transition of benzene was experimentally reported by Nellis et al. [15] and was attributed to thermal activation of defective carbon nanoparticles under the pressure between 20 and 40 GPa; further increase in pressure does not have much effect on the conductivities. To date, although a number of explanatory and predictive results in some cases have already been provided by experimental studies, less information is available for shock-introduced chemical reactions, and many fundamental questions of benzene under extreme conditions are still yet to be investigated.

Concerning the theoretical side, a tight-binding model has been applied to study the properties of liquid benzene [16]. The results agree well with the experiments in $(D, u)$ diagram (shock velocity verse particle velocity), but the calculated temperatures remain too high. The thermodynamic properties of benzene were taken into account by classical force field method [17]. While this method showed good agreement with the low-pressure experimental measurements, however, it is unsuitable in determining Hugoniot curve at higher...
pressures. Overall, due to the intrinsic approximations of these methods, the electronic structure, which is predominant in determining the nonmetal-metal transition and equation of state (EOS) for benzene under shock conditions, is out of consideration. Thus, the change in the electronic structure of benzene under extreme condition is still recommended to be presented with a full quantum-mechanical description. On the other side, quantum molecular dynamics (QMD), where electrons are fully quantum mechanically treated, has been proven particularly suitable for the study of the chemical reactions, such as dissociation, ionization, and recombination of molecules. Meanwhile, the electronic structure, thermodynamical and optical properties of warm dense matter have been successfully investigated by QMD simulations [18, 19]. According to the aspects mentioned above, the electronic structure, EOS and Hugoniot from density functional theory (DFT) are highly needed for shocked benzene.

In the present work, we apply QMD simulations to study the properties of benzene along the principal Hugoniot. The EOS and the pair correlation functions (PCF) are determined by QMD simulations. The Kubo-Greenwood formula is used as a starting point for calculating the dynamic conductivity $\sigma(\omega)$, from which the dc conductivity is determined. The dielectric function $\epsilon(\omega)$ and reflectivity are then extracted. This paper is organized as follows. The simulation details are briefly described in Sec. II. The PCF, which is used to study the dissociation of benzene, and Hugoniot curve are given in Sec. III. In Sec. IV Nonmetal-metal transition and optical properties are discussed. Finally, we close our paper with a summary of our main results.

II. COMPUTATIONAL METHOD

In this study, we perform simulations for benzene by employing the Vienna Ab-initio Simulation Package (VASP) plane-wave pseudopotential code, which is developed at the Technical University of Vienna [20, 21]. Electrons are fully quantum mechanically treated through plane-wave, finite-temperature DFT [22, 23], and the electronic states are populated according to the Fermi-Dirac distribution at temperature $T_e$. The exchange correlation functional is determined by generalized gradient approximation (GGA) with the parametrization of Perdew-Wang 91 [24]. The ion-electron interactions are represented by a projector augmented wave (PAW) pseudopotential [25, 26]. Atoms move classically according to the
forces, which originate from the interactions of ions and electrons. The system is calculated with the isokinetic ensemble (NVT). In all the simulations, the system is kept in local thermodynamical equilibrium by setting the electron (\( T_e \)) and ion (\( T_i \)) temperatures equal. The ion temperature \( T_i \) is kept constant every time step by velocity scaling.

For molecular dynamic simulations, only \( \Gamma \) point is employed to sample the Brillouin zone, while \( 4 \times 4 \times 4 \) Monkhorst-Pack \( k \) points are used for the electronic structure calculations. The plane-wave cutoff energy is set to be 600.0 eV. 48 carbon and 48 hydrogen atoms (8 benzene molecules) are calculated in a cubic cell at separate densities and temperatures. The selected densities range from 1.2 to 2.7 g/cm\(^3\) and temperatures between 500 K and 6000 K to present the principal Hugoniot. All the dynamic simulations are lasted for 4\( \sim \)6 ps, and the time step selected for the atomic motion is 2 fs. Then, the system is equilibrated 200 steps and the properties are calculated via the data from the final 300 steps.

### III. SHOCK EQUATION OF STATE AND PAIR CORRELATION FUNCTION

The accurate calculation of electrical and optical properties depends on a precise description of the materials properties, such as EOS. A crucial measurement of EOS data of benzene under shock condition is the Hugoniot \[28\], which can be derived from conservation of matter, momentum, and energy for an isolated system compressed by a pusher at a constant velocity. Rankine-Hugoniot equation describes the locus of points in \((E, P, V)\)-space satisfying the relation as follows:

\[
(E_0 - E_1) + \frac{1}{2}(V_0 - V_1)(P_0 + P_1) = 0
\]

where \( E \) is the internal energy, \( V \) is the volume, \( P \) is the pressure, and the subscripts 0 and 1 refer to the initial and shocked state, respectively. In the canonical ensemble, shock adiabat between the initial and final states is described by the principal Hugoniot, which includes the locus of states \((E, P, V)\) satisfying Eq. \[1\]. In our present calculations, the pressure \( P \) is evaluated using the forces provided by VASP. The internal energy consists of the total energy from finite-temperature DFT calculation and zero-point energy. The determination of Hugoniot points is described as follows. For a given \( V_1 \), a series of simulations have been executed for different temperatures \( T \). Then \( E_1 \) and \( P_1 \) are fitted to a cubic function of
The principal Hugoniot points \((E_1, P_1, V_1)\) are evaluated by solving Eq. (1). For the present system, the initial density \(\rho_0\) is 0.874 g/cm\(^3\), and the internal energy \(E_0= 72.83\) eV/molecule at the temperature \(T=298\) K. The initial pressure can be neglected compared to the high pressure of shocked states. Principal Hugoniot points derived from Eq. (1) are listed in Tab. I.

Agreement between our calculated Hugoniot and experimental data is revealed in Fig. 1. The region, which lies in the density range between 1.7 and 1.8 g/cm\(^3\), should be noticed. This region is accompanied with a rapid increase in pressure, which is attributed to the incipient dissociation of benzene and the formation of diamond-like nanoparticles. The transition of atomic structure results in the change of physical properties. Diamond is the hardest material, and the compression in such system will consequently lead to the rapid increase in pressure. Experiments indicate that benzene decomposes at 13 GPa [7, 8, 9, 10, 11], while our QMD simulations provide the value of 11 GPa. We further examine the EOS data at the densities ranging from 2.1 to 2.4 g/cm\(^3\) as shown in Fig. 2. The pressure shows a systematic behavior in terms of the density and temperature, except for the region \((\rho=2.3 \sim 2.4\) g/cm\(^3\), \(T=3500 \sim 4000\) K, and \(P\approx50\) GPa). Due to the rapid C-H bond breaking and the formation of atomic and molecular hydrogen, this region is featured by \((\partial P/\partial T)_V <0\).

**TABLE I: Principal Hugoniot points derived from DFT-MD simulations at a series of density \((\rho)\), pressure \((P)\), and temperature \((T)\).**

| \(\rho\) (g/cm\(^3\)) | \(P\) (GPa) | \(T\) (K) |
|----------------------|-----------|--------|
| 1.2                  | 4.3       | 598    |
| 1.4                  | 7.9       | 814    |
| 1.6                  | 10.0      | 1093   |
| 1.7                  | 10.9      | 1200   |
| 1.8                  | 19.3      | 1324   |
| 1.9                  | 19.2      | 1437   |
| 2.1                  | 33.7      | 2963   |
| 2.2                  | 43.2      | 3370   |
| 2.3                  | 54.4      | 3749   |
| 2.4                  | 67.2      | 4334   |
FIG. 1: Comparison between the previous experimental data of Refs. \cite{6, 12, 15} and the present QMD results for the principal Hugoniot.

The structural change of benzene under shock condition can be clearly reflected by PCF, which represents the possibility of finding a particle at a distance $r$ from a reference atom. Typical C-C bond length in benzene molecule is 1.40 Å, and the bond length of C-H is 1.09 Å in our calculations. In the case of diamond and H$_2$, C-C and H-H have the bond length of 1.50 and 0.75 Å, respectively. PCF, atomic structure, and charge density distribution at four densities of benzene along the principal Hugoniot are shown in Fig. 3. At $\rho=0.874$ g/cm$^3$ and $T=298$ K, one can see from Fig. 3(a) that the PCF is featured by two peaks at 1.09 and 1.40 Å, which represent the typical bond length of C-H and C-C in benzene molecule, respectively. These two peaks begin to reduce in amplitude and get broaden due to the thermal excitation at higher pressure [as shown in Fig. 3(b)]. For the densities $\rho < 1.7$ g/cm$^3$ and temperatures $T < 1200$ K, benzene turns out to retain in its molecular shape. This fact could be established through analysis of the atomic configuration and typical $\pi$ bond suggested by charge density. When $\rho > 1.7$ g/cm$^3$ and $T > 1200$ K, diamond-like nanoparticles with vacancies and H substitutions are formed in the system. At this stage,
C-C bond length changes into 1.50 Å [Fig. 3(c)], which is a typical value of diamond, and the \( \pi \) bond converts into \( sp \) hybrid bond. Benzene decomposes under the present condition, and the reference pressure is 11 GPa. With further increase in pressure, the dissociation of C-H bond becomes remarkable, and the formation of H\(_2\) molecule is suggested by the peak at \( r=0.75 \) Å, as shown in Fig. 3(d).

**IV. DYNAMIC CONDUCTIVITY AND OPTICAL PROPERTIES**

The real part of the dynamic conductivity \( \sigma_1(\omega) \) is derived from the Kubo-Greenwood formula:

\[
\sigma_1(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_k w(k) \sum_{j=1}^{N} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} [f(\epsilon_i, k) - f(\epsilon_j, k)] \\
\times |\langle \Psi_{j,k}|\nabla_\alpha|\Psi_{i,k}\rangle|^2 \delta(\epsilon_{j,k} - \epsilon_{j,k} - \hbar \omega),
\]

(2)
where $f(\epsilon_i, k)$ describes the occupation of the $i$th band, with the corresponding energy $\epsilon_{i,k}$ and the wavefunction $\Psi_{i,k}$ at $k$, and $w(k)$ is the $k$-point weighting factor. The imaginary part of the dynamic conductivity $\sigma_2(\omega)$ follows from the Kramer-Krönig relationship. Then, the real and imaginary parts of the dielectric function are given by $\epsilon_1(\omega) = 1 - \frac{1}{\epsilon_0 \omega} \sigma_2(\omega)$ and $\epsilon_2(\omega) = \frac{1}{\epsilon_0 \omega} \sigma_1(\omega)$, respectively, from which the optical constants such as the refractive index $n(\omega)$, extinction coefficient $k(\omega)$ and reflectivity $r(\omega)$ may now be derived ($\epsilon_1=\nu^2-k^2$, $\epsilon_2=2nk$, and $r=(1-n)^2+k^2$).

The behavior of $\sigma_1(\omega)$ at different Hugoniot points is summarized in Fig. 4. Overall, we find that the real part of dynamic conductivity $[\sigma_1(\omega)]$ is featured by a main peak around
FIG. 4: $\sigma_1(\omega)$ along the principal Hugoniot.

10.0 eV and approach to vanish for the energy higher than 25.0 eV. For the pressure lower than $30 \sim 40$ GPa ($\rho < 2.1 \sim 2.2$ g/cm$^3$), the dc conductivity, which could be given as: $\sigma_{dc} = \lim_{\omega \to 0} \sigma_1(\omega)$, is zero, which obviously shows the insulating nature of benzene at low pressure regime. With the increase of pressure along the principal Hugoniot ($\rho = 2.3 \sim 2.4$ g/cm$^3$), three prominent new features occur in the frequency-dependent conductivity: (i) The main peak in $\sigma_1(\omega)$ moves towards lower energies; (ii) There tends to develop an additional little peak around the energy of 2.5 eV, which again signifies the occurrence of diamond-like structure in the system; (iii) The dc conductivity is no longer zero. This indicates that nonmetal-metal transition, which is associated with the rapid C-H bond breaking, happens at the high-pressure Hugoniot points around 50 GPa ($\rho \sim 2.3$ g/cm$^3$ and $T \sim 3700$ K), consistent with the predicted value derived from experiment measurement [15]. Furthermore, the optical reflectivity of benzene along the principal Hugoniot is shown in Fig. 5. The pressure-induced change in reflectivity can be clearly indicated in the energy range of 1.0$\sim$5.0 eV (the reference wave length is correspondingly from 250 to 1250 nm). For the photon energy
FIG. 5: Optical reflectivity of benzene along the principal Hugoniot.

$E=1.0$ eV, a considerable increase in reflectivity (from 0.2 to 0.6), which is attributed to high pressure induced nonmetal-metal transition, is observed along the principal Hugoniot.

V. CONCLUSION

In summary, the QMD simulations presented here demonstrate the properties of shock compressed benzene. The EOS and principal Hugoniot are determined according to the simulated results, and the results show excellent agreement with the available experiments. Our calculations have shown that the benzene molecule begins to dissociate around 11 GPa. The considerable C-H bond breaking appears at the pressure around 50 GPa. The nonmetal-metal transition also occurs at this stage, which will lead to the increase in optical reflectivity from 0.2 to 0.6.
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