Ultra Accelerated Quantum Chemical Molecular Dynamics Study on Mechanochemical Reaction of Micro-Bubble Induced by Shock Wave

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ABSTRACT

Mechanochemical reactions and micro-bubble formation may take place in water under strong compression/rarefaction realized by shock waves e.g. generated in collapsing process of laser-induced bubbles. The quantum chemical approach is only way to clarify such chemical reactions including production of OH radicals and so on. We have recently developed our original tight-binding quantum chemical molecular dynamics simulator to the ultra accelerated one (UA-QCMD) and successfully simulated dissociation of O-H bond of water molecule by infrared laser irradiation. In the present study, by using our UA-QCMD simulator, mechanochemical reactions of water molecules due to shock waves from the laser-induced bubble production/collapse are investigated with the aim of clarifying the secondary effect of the infrared laser irradiation to water. Combined with the bubble production analysis by our original kinetic Monte Carlo simulator, the importance of mechanical effects is suggested.

Keywords: ultra accelerated quantum chemical molecular dynamics, sonochemistry, water, infrared laser

1 INTRODUCTION

For years we have developed our original tight-binding quantum chemical molecular dynamics (TB-QCMD) simulator, "Colors [1]," which performs 5000 times faster than other conventional first-principles MD methods. Based on "Colors," combined by our original MD program "NEW-RYUDO [2]," we have recently developed the ultra accelerated quantum molecular dynamics (UA-QCMD) simulator, "New-Colors," which realizes 10 million times acceleration compared to other first-principles methods. We have also successfully optimized "New-Colors" on super-computer system to achieve an ultimate acceleration and to simulate large-scale molecular systems. In the present study, UA-QCMD is applied to the mechanochemical reaction system under the condition of high compression/rarefaction due to the formation/collapse of laser-induced bubbles.

The laser-induced bubbles have been studied by many researchers especially in the medical fields for the fine ablation of diseased biological tissues and so on [3]. In many cases shock waves are generated in collapsing phase of the bubbles, and sometimes the secondary bubbles are observed to form in the region where the shock waves propagate away [4]. The shock waves propagating in the flow field interact with the other shock waves and produce the complex compression/rarefaction waves [5]. Such compression/rarefaction causes the formation of acoustic cavitation bubbles. Another product in the collapsing process of laser-induced bubbles is "micro-jet" when the bubbles collapse near a wall boundary. The micro-jets direct away from and towards the boundary at the velocity of several hundred m/s [6,7]. To the best of author's knowledge, about the dissociation of O-H bond of water molecule by the infrared laser irradiation, an experimental study was reported once [8].

In recent years, Sonoluminescing bubble induced by an ultrasonic wave has been investigated frequently [9-12]. In addition to the light emission, shock waves are also generated [9,10] similarly to the case of laser-induced bubbles. The temperature and the pressure inside the sonoluminescing bubble at the strong collapsing stage are considered to be around several thousand K and several hundred atm, respectively [11,12]. As a result, water molecules are dissociated and chemical products such as OH radicals are created inside the bubble, and some products dissolve into the surrounding liquid [12].

We have recently succeeded to compute the dissociation of O-H bond of water molecule directly due to the infrared laser irradiation by using our UA-QCMD simulator "New-Colors," and the resulting formation of a jet flow by using CFD simulator. Based on these simulations, first we develop the kinetic Monte Carlo (KMC) simulator to analyze the bubble formation, coalescence and collapse process in water and to estimate the generation of shock waves. Then, by using our UA-QCMD simulator, we

investigate the secondary mechanochemical reactions in water due to compression/rarefaction waves under infrared laser irradiation, different from the sonochemical process under ultrasonic wave irradiation.

2 COMPUTATIONAL METHODS

2.1 Kinetic Monte Carlo Method

KMC method is used for the simulation of the phase change of water, especially of the bubble formation and coalescence process. The water molecules and H and OH radicals are moved in random direction at a distance of $(D\Delta t)^{1/2}$. Here, D is the diffusion coefficient given by $D = a \cdot d^{-n}$ where d is the particle diameter and a and n are free parameters, and Δt is the time step. When the distance of two particles is sufficiently close, they coalesce based on the theory of the probability. The KMC simulator enables us to analyze any diffusion process very fast.

2.2 Ultra-Accelerated Quantum Chemical Molecular Dynamics Method

The main concept of UA-QCMD method is as follows. By using our accelerated TB-QCMD program "Colors," the total energy can be divided into the kinetic energy of nuclei, molecular orbital energy, coulomb energy, and exchange-repulsion energy.

$$E = \sum_{i=1}^{N} m_i v_i^2 + \sum_{k=1}^{\mathrm{occ}} n_k \varepsilon_k + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} E_{ij}^{\mathrm{repul}}(r_{ij}) \quad (2)$$

The total electron energy can be divided linearly into each molecular orbital (MO), and the electron energy of each MO can be also divided into the binding energy between two atomic orbitals (AO) in the form

$$E_{MO} = \sum_{\mathrm{k=1}}^{\mathrm{occ}} n_k \varepsilon_k = \sum_{k=1}^{\mathrm{occ}} \sum_{r} n_k (C_{kr})^2 H_{rr} + \sum_{k=1}^{\mathrm{occ}} \sum_{r} \sum_{s \neq r} n_k C_{kr} C_{ks} H_{rs} \quad (3)$$

where n_k is a number of occupied electrons in the k-th MO, ε_k is an energy level of the k-th MO, C_{kr} is a coefficient of the r-th AO in the k-th MO, and H_{rr} and H_{rs} is the diagonal and the off-diagonal element of Hamiltonian, respectively. The off-diagonal element is determined from the diagonal ones by using the corrected distance-dependent Wolfsberg-Helmholz formula as follows [13].

$$H_{rs} = \frac{K}{2} S_{rs} (H_{rr} + H_{ss}) \quad (1)$$

Here, S_{rs} is the overlap integral between r-th AO and s-th AO. The first and the second term on the right-hand side of the equation (3) represent contribution of one atom and between two atoms, respectively. At this end, the decomposed binding information can be reflected as parameters of Morse and Coulomb potentials used in our original, very fast MD program "NEW-RYUDO." The MO energy is given by

$$\sum_{s} H_{rs} C_{sk} = \varepsilon_k \sum_{s} S_{rs} C_{sk} \ . \quad (4)$$

To solve this matrix eigenvalue problem is most expensive procedure in UA-QCMD. The matrix size is determined by the total number of orbitals and the number of AO is limited to several thousands for standard PC. In the present study, by use of vector-type supercomputer system (NEC SX-8), large-scale molecular system having over 10 thousand orbitals can be simulated.

3 RESULTS AND DISCUSSION

At first, in order to estimate the shock wave radiation due to the bubble formation and coalescence, the KMC simulation is run. Figure 1 shows the time development of the bubble coalescence. The parameters are set as follows: time step Δt = 1 ns, the temperature T = 315 K, the cell size = 200 Å × 50 Å × 50 Å, the diffusion coefficients of H_2O, H radical, OH radical are 3.45×10^{-9} m^2/s, 1.0×10^{-8} m^2/s, 3.45×10^{-9} m^2/s, respectively. When the energy of the laser irradiation is set to the suitable level, the rapid expansion of bubbles for 100 ns is simulated and the result is consistent with the production of the laser-induced cavitation bubbles observed experimentally [6,7,10]. The generation of the shock waves is expected by this simulation result.

In order to investigate the dependency of chemical reactions on the mechanical condition such as compressed or expressed, the two different models of water molecules are simulated by using UA-QCMD. Figure 2 shows the snapshot after the UA-QCMD simulation of 60 water molecules at 300 K with external energy added at the initial steps. This condition corresponds that the energy is injected by the laser irradiation but the density doesn't change ($1.0 g/cm^3$) because of some mechanical compression. In the figure we can see the formation of H_3O and OH species. This means that the mechanochemical reaction may be possible under the compression condition. Figure 3 shows the snapshot of the configuration of 48 water molecules at 300K under laser irradiation condition computed by the UA-QCMD. At the initial computation stage, O-H bond of water molecules was excited by giving the additional

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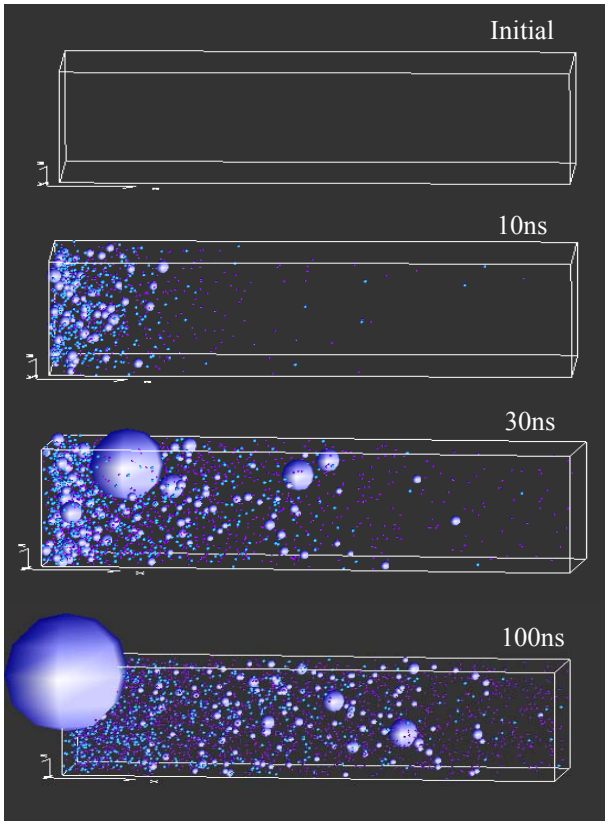

Figure 1: Formation and coalescent of bubbles computed by KMC simulator. The cell size is 200 Å × 50 Å × 50 Å.

velocities on a H atom of each water molecules. In this case the density is controlled to be 0.8g/cm^3 so as not to be compressed mechanically. At this time the formation of three H_3O was occurred. This fact may indicate that the easy dissociation of O-H bond if the system is subjected by the rarefaction condition. In consideration for the result of the macro KMC simulations, further computations for more appropriate conditions may be needed.

For the computation of the mechanical properties more accurately, the model of a large number molecules is meaningful to run. Our UA-QCMD program is remarkably matched to the vector-type supercomputer system on which the equation (4) is solved very fast. The equation (4) is most expensive calculation when the model size comes to be large more than several thousand AOs. Table 1 shows the atomic charges, bond populations, and binding energies of O-H bond of the water molecules obtained by our UA-QMCD method for the 1620 molecules model on super-computer and 1 molecule on PC in comparison with those by the first-principles program DMol^3. The value of the 1620 molecules is averaged over all atoms and bonds. It is found that both the electronic states and the binding energy of the water molecules obtained from the large system

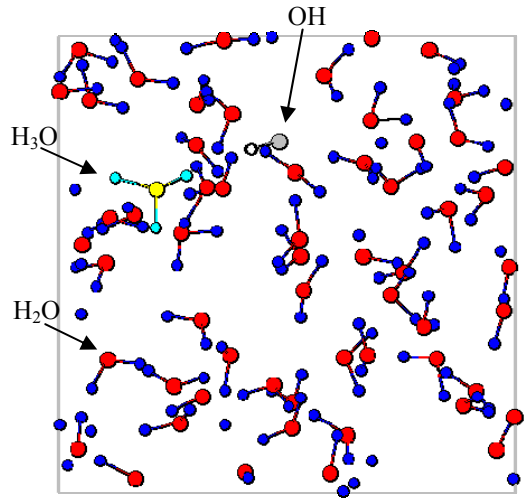

Figure 2: Snapshot of the UA-QCMD simulation of 60 H_2O at 300 K with external energy added.

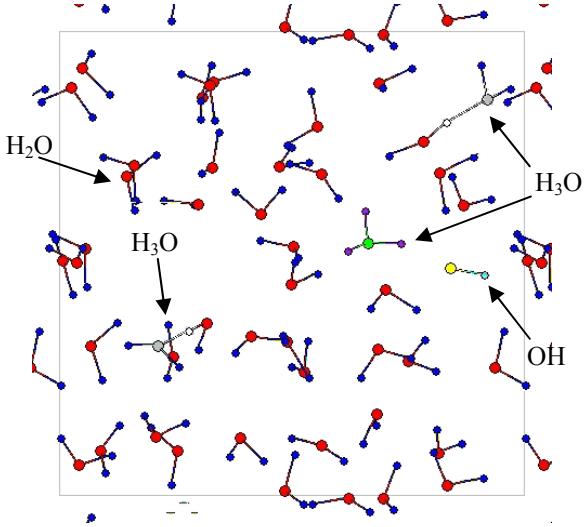

Figure 3: Snapshot of the UA-QCMD simulation of 48 H_2O at 300 K under laser irradiation condition.

simulated by supercomputer represent well those of the first-principles method. Figure 4 shows snapshot of the large-scale H_2O system simulated by UA-QCMD on the supercomputer. The total number of atoms is 4860 and the total number of AOs is 9720. The cell size is 36.42 Å^3 and the influence of the cyclic boundary condition may be neglected and the high accurate computation is realized. More details will be presented at the conference.

	UA-QCMD		First-principles
	1620 molecules	1 molecule	1 molecule
Atomic charge			
H	0.16	0.16	0.15
O	-0.32	-0.32	-0.30
Bond population			
H-O	0.69	0.68	0.51
Binding energy / kcal mol^{-1}			
H-O	-122.6	-122.2	-122.0

Table 1: Comparison of phsycochemical property of H_2O molecule. The values of 1620 molecules are calculated on supercomputer system and averaged over all atoms/bonds.

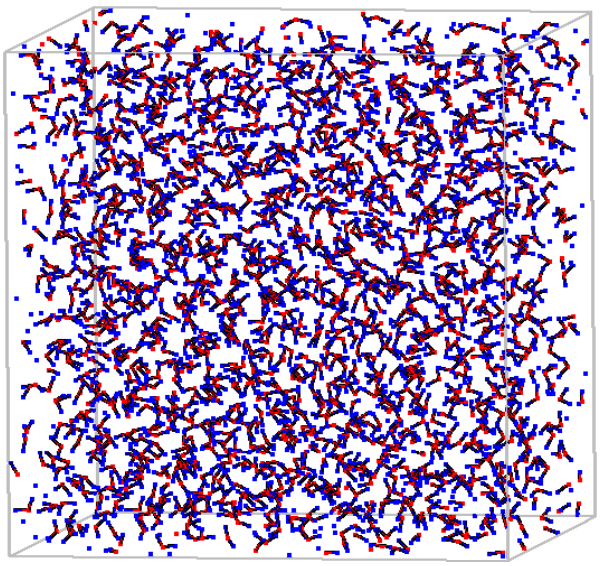

Figure 4: Snapshot of the large-scale simulation of 1620 H_2O molecules by UA-QCMD on supercomputer system. Blue circles represent hydrogen atoms and red ones represent oxygen atoms. The cell size is 36.42 $Å^3$.

4 CONCLUDING REMARKS

In the present paper, we applied our original UA-QCMD simulator to the mechanochemical reactions in water under strong compression/rarefaction realized by shock waves generated in formation process of laser-induced bubbles which was simulated by using KMC simulator. We successfully simulated dissociation of O-H bond of water molecule under both of the compression condition and the infrared laser irradiation, and the importance of mechanical effects was suggested. For more accurate computation, UA-QCMD simulation with the large number of water molecules was run on the supercomputer system successfully.

The computations were partially performed on the NEC SX-8 at the Advanced Fluid Information Research Center, Institute of Fluid Science, Tohoku University.

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