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Heating of Nanosized Liquid Water in High-Intensity Terahertz Pulses *

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Non-equilibrium molecular dynamics simulations of liquid water in picosecond high-power terahertz pulses are performed by using a non-polarizable potential model. Numerical results show that the energy absorption of water molecules exhibits a pronounced resonance with THz pulses in the frequency range of 14–17 THz. With the THz pulse at resonant frequencies, the maximum temperature is about 562 K by heating the water at room temperature. Further investigation indicates that the results are independent of the size of the nanoscale water box. The efficiency of energy transfer by resonant absorption is more than seven times of microwave heating. These studies show promising applications of ultrashort THz pulses.

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Nowadays, the high-intensity THz sources have made significant progress.[1–3] Lately, Gopal *et al.* reported the observation of subpicosecond THz pulses with energies ≥460 μJ from a laser-driven ion accelerator and the experiments were performed with intense laser pulses to irradiate thin metal foil targets.[4] Similarly, Casalbuoni *et al.* created an ultrabroadband THz source covering an exceptionally broad frequency range from about 200 GHz to 100 THz producing powerful radiation.[5] The application of ultrafast laser pulses is an exciting field that has grown rapidly in the past few years.[6–8] Due to their unique characteristics of extremely high intensity, ultrashort pulse duration, ultrafast lasers show great promise for precise material processing and efficient temperature jump experiments in liquid water.[6,8] Ellen *et al.* recently introduced an infrared pump-THz probe technique to measure the thermalization dynamics of aqueous solutions with a time resolution <200 fs.[7] Recent advances in laser technology have pushed the frontier of applications in the near future.

In the last four decades, liquid water is perhaps one of the most studied chemical systems, with numerous experimental and theoretical studies.[9–11] However, some of its characteristics and properties are still not completely understood.[12] Recent investigations have increased our understanding of confined water,[13] showing that many properties of nanosized water differ drastically from those of bulk water. Boyd *et al.* used THz time-domain spectroscopy to explore very low frequency modes of reverse micelles[14] and found that dramatic resonances in the far-infrared (3–33 cm^{-1}) absorption shift with the size of confined water. Zhang *et al.* found that there is a resonant response of the in-tube water molecule to the radial breathing mode of the single-walled carbon nanotube[15] with the frequency range of 5–11 THz. In the THz frequency range, it is theoretically and experimentally indicated that some evident collective vibrational modes of water may be excited.[16,17]

Usually, the *ab initio* molecular dynamics obtains more accurate characteristic parameters, while restricts the size of simulation systems due to the large amount of calculation. Despite simplicity in theory, the classical molecular dynamics method has the advantageous computation efficiency. In this Letter, we consider the response of nanosized liquid water in high-intensity THz pulses by means of classical molecular dynamics (MD) simulations.

The nonequilibrium molecular dynamics (NEMD) simulation system built with the molecular visualization program is illustrated in Fig. 1. In our simulation, 3924 water molecules are put in the cubic box with the side length 52 Å. The MD simulations are performed by using the NAMD2[18] in a non-equilibrium ensemble and under periodic boundary conditions in all directions. The electrostatic interactions are handled by the particle mesh Ewald method[19] with a real space cutoff of 1.2 nm, the same as the cutoff for the van der Waals interaction. The CHARMM27 force field[20] and the TIP3P water model[21] are employed in all the simulations. In our simulation, the system is shone to the terahertz electric field (TEF). The frequency of the THz pulses ranges from 0.1 to 30 THz, and the intensity is taken from 6×10^8 W/cm^2 to 6×10^{10} W/cm^2. This intensity has now become achievable at labora-

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tory THz sources.[4] Since the wavelength (0.01–3 mm) is much larger than the size of the water system which is approximately 52 Å in one direction, we can safely assume that the THz pulse is spatially uniform for the motion of water molecules.

With the electric field direction parallel to the x-axis, the TEF acting on the atomic partial charges can be expressed as

$$E = (\epsilon(t)\cos(\omega t), 0, 0),$$

where $\epsilon(t)$ is a Gaussian envelope with a full width at half maximum (FWHM) of 1 ps (as shown in Fig. 2). In the calculation, we take the rms intensity 0.01–0.1 V/Å. The effect of the magnetic field is ignored in our calculation. The simulation processes are as follows: initial conditions are sampled from a 10 ps NVT trajectory of a thermally equilibrated water box at a temperature of 300 K and a density of 1 g/cm^3, followed by the non-equilibrium simulation with THz pulse (10 ps). The system is in non-equilibrium state due to the fact that the total energy of the system increases with the external electric field. Thus the multiple time-step techniques are applied: during the period of equilibrium states, 1 fs of time-step is adopted, while during the NEMD runs, 0.1 fs is used.

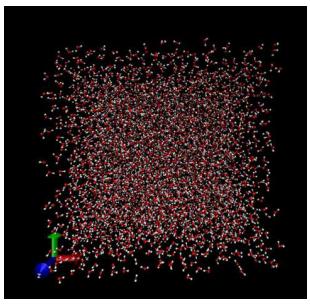

Fig. 1. (Color online) Snapshot of the simulation system. A water box of $5.2 \times 5.2 \times 5.2\,\mathrm{nm}^3$ with 3924 molecules.

The MD simulations are performed with THz pulse at different frequencies and at different intensities. For each frequency, the FWHM of Gaussian envelope is 1 ps and the simulation time is 10 ps. The results of the last 5 ps are collected for analysis. With the energy transfer from the TEF pulse, the temperature of the system increases. In the simulation, we directly measure the temperature to probe the kinetic and dynamical changes of the system. The temperature as a function of time is shown in Fig. 2, where the initial temperature is 300 K and the TEF frequency is 15 THz. We find that the temperature is dramatically enhanced during the interval of the THz pulse, and the maximum temperature is about 562 K. Shown in Fig. 3 is the temperature variation as a function of frequency for various intensities. When the pulse intensity is 6×10^{10} W/cm^2 (corresponding to 0.1 V/Å), the temperature increases rapidly in the frequency range of 4–24 THz, and the peak value, appearing in the frequency interval of 14–17 THz, is about 560 K. The absolute increase is 260 K by subtracting initial temperature 300 K. It is noticeable that the increase of temperature, at frequencies below 1 THz, is much smaller than the peak value. In the high frequency region roughly larger than 25 THz, the temperature enhancement decreases rapidly. Meanwhile, the temperature reduces rapidly with decreasing the pulse intensity. When the pulse intensity decreases to 1.5×10^{10} W/cm^2 (6×10^8 W/cm^2), the maximum temperature value reduces to 380 K (302 K) at the frequency of 15 THz. When the temperature is larger than 380 K, the NEMD runs were continued into the supercritical region.[22] The prompt heating will lead to structural modification of liquid water which could be measured by time-resolved x-ray diffraction.[23] In a recent study, Ellen *et al.* introduced an infrared pump-terahertz probe technique to measure the thermalization dynamics of aqueous solutions with a time resolution <200 fs,[7] much shorter than the Gaussian envelope which is about 1 ps in our simulation. These studies show promise for experimental verification of our numerical models.

For comparison, we also investigate the microwave heating in the frequency range of 2.45–100 GHz. We find that, however, the kinetic temperature does not change much in this frequency interval. The peak value of the temperature is 335 K (the absolute increase is 35 K), less than one seventh of the THz pulse heating. It should be mentioned here that this comparison is preliminary since the results are based on the classical MD simulation, not on *ab initio* calculation. Nonetheless, it can be inferred that the heating mechanism of THz pulse is different from the microwave heating.

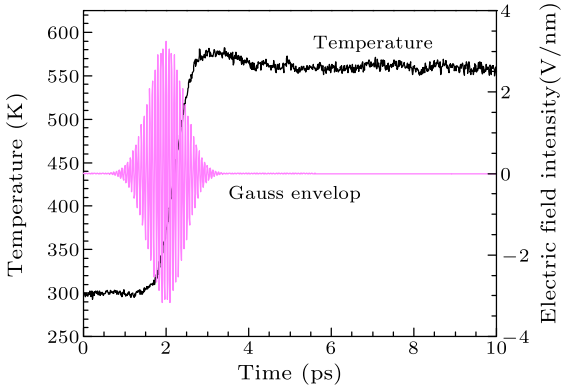

Fig. 2. Kinetic temperature of water as a function of time (black). Electric field profile of the THz pump pulse (purple).

As pointed out in Ref. [15], the energy absorption in the frequency range of 5–11 THz is explained by the resonant absorption due to the excitation of the vibration motions of water molecules. As inspired by Ref. [15], we assume that the prompt energy absorp-

tion of water in 14–17 THz EF pulses is also a resonant phenomenon, but with different mechanisms, as there should not be direct vibrational motion of charge-neutral water molecules in the presence of TEF. In this work, the polar water molecules are effected by a torque of alternating TEF. With the rotor model of different moments of inertia in different axes of rotation, we obtain that the natural frequencies of water molecules are about 14–17 THz.[24] A resulting characteristic of the resonance is the rupture of the hydrogen bonds (H-bonds) of water molecules. To diagnose the evolution in the dynamic property of the system, we count the H-bond numbers of water molecules, according to the criterion of the oxygen distance less than 3.5 Å and hydrogen-bond angle $\leq 30°$. Interestingly, the frequency range of about 4–24 THz where the number of H-bond decreases remarkably corresponds nicely to that for the temperature change, as shown in Fig. 4. The remarkable decrease of H-bond is a result of the efficient resonant energy absorption. In the whole frequency region, we can see that the correspondence between the variation of kinetic temperature and the change of H-bond is also roughly clear. The rotational resonant mechanism here plays a decisive role in heating the water molecules, while such a resonant mechanism does not exist for the microwave heating.

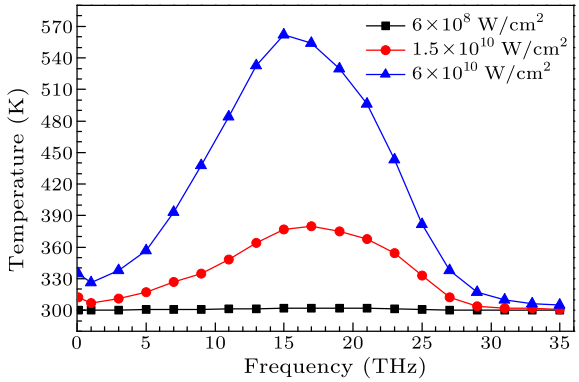

Fig. 3. Temperature of water as a function of the THz frequency at different intensities with the initial temperature of 300 K.

Furthermore, we investigate the size effect of different cubic water boxes with 128, 384, 6805 and 8265 water molecules, corresponding to the side length of 17, 25, 62, 66 Å, respectively. Despite slight statistical fluctuations, the main results are more or less the same. It is indicated that the energy absorption is independent of the size of the simulated nanoscale water box in the THz frequency range. The reason for this to occur is that the THz wave length is much larger than the nano water box. It should be noticed that the resonant mechanism, related to the intrinsic properties of water, does not depend on the size of cubic water box, i.e., the mechanism proposed here is fairly universal.

It is worth pointing out that our studies are based on the rigid-molecule nonpolarizable potential model, which is unable to describe the dissociation of water molecules.[25–27] For example, the low-frequency absorption regime governed by intermolecular vibrations continues to be a challenge to the force-field-based MD simulations.

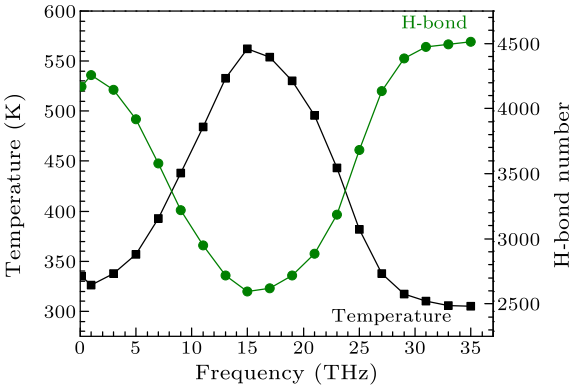

Fig. 4. Temperature of water (black) and the number of hydrogen bond (green) as a function of the THz frequency.

In summary, we have demonstrated the heating of nanosized water in the high-intensity THz pulse with the non-equilibrium MD simulation. The efficient heating is observed in the frequency range of 4–24 THz and is attributed to the rotational resonant energy absorption due to the excitation of the vortical motions of polar water molecules. With the THz pulse at resonant frequencies, high temperatures of water molecules can be obtained, and in our simulation, the maximum temperature increase is about 262 K by heating the water at room temperature. Moreover, the resonant energy absorption is associated with the intrinsics characteristics of liquid water, which is independent of the size of nanoscale water box. In the framework of classical MD simulation, we have also investigated the microwave heating, and found that the efficiency of energy absorption is just about one seventh of that with the resonant THz heating. Since the rotational resonant frequency is sensitive to the atom mass in molecules, our finding may have potential applications in isotope separation and ion transport.

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