Ab-Initio Description of Phase Transitions in TiO_2 and Ab-Initio Molecular Dynamics Simulations of Ultrafast Excited Graphene and Amorphous Carbon

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Additional Software
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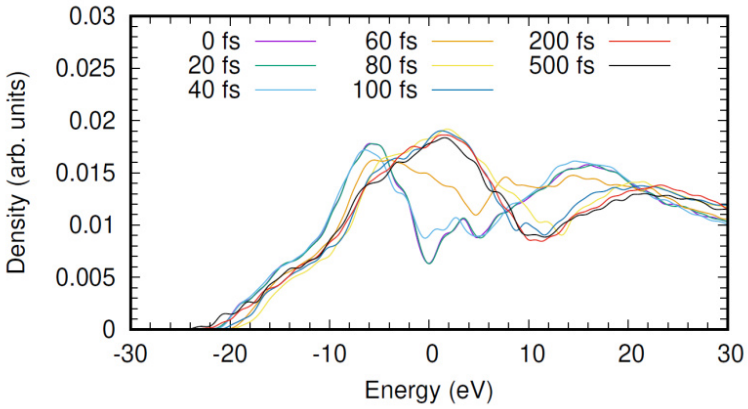

Introduction

The understanding of the interaction of ultrashort light pulses with solids and nanostructures is important for both applications and science. Because of that more and more big dedicated facilities like XFEL in Hamburg or LCLS in Stanford are constructed. The availability of better light sources enables scientists to analyze the interaction of ultrashort laser pulses with solids in increasingly greater detail. Our group belongs to the few theoretical teams worldwide able to explain experimental results and make predictions on the problem of laser-induced ultrafast structural changes in solids and nanostructures. In particular, we focus on the description of ultrafast phenomena using ab-initio molecular dynamics simulations. With our work we cover a broad range of possible phenomena, like coherent phonons, thermal phonon squeezing, laserinduced phase transitions or non-thermal melting.

Methods

We have used our in-house Code for Highly excIted Valence Electron Systems (CHIVES) for our calculations. For the optimization of the minimal energy pathways for TiO_2 we have used the generalized solid-state nudged elastic band method (G-SSNEB).

Results

Laser-excited graphene: We have found the time-evolution of

the (100) and (110) Bragg peaks of graphene after ultrafast laser excitation for a supercell with 96 atoms. As for the larger supercell, we see a fast initial decay within the first 50 fs due to the generation of strongly coupled optical phonon modes (SCOPs) and a considerably slower decay afterwards. Also for the smaller supercell the decay starts to accelerate after about 2-3 ps. Furthermore, we have started similar simulations with a supercell of 384 atoms, which were not finished yet.
Laser-excited amorphous carbon: We have calculated the response of amorphous carbon to an ultrafast laser excitation without considering incoherent electron-phonon coupling. We see that above a threshold excitation a non-thermal melting is visible. The non-thermal melting is accompanied by a drastic change of the coordination number of the atoms and more importantly by a change of the electronic density of states. Furthermore, we have included the electron-phonon coupling into the simulations. Thus, we are able to simulate the timedependent evolution of the electronic temperature and the heating of the ions due to the laser pulse. Our results are very similar to the simulation without electron-phonon coupling. However, the threshold temperature for the non-thermal melting becomes smaller because the ions have a higher kinetic energy to surpass the energy barrier for the melting.
Phase transitions TiO_2: We were able to obtain the laser-excited minimal energy pathways between the three titanium dioxide polymorphs, rutile, anatase and brookite in the laser excited case. Furthermore, we have calculated the number of broken bonds during the phase transition.

Discussion

Laser-excited graphene: The accelerating decay of the Bragg peaks after about 2-3 ps is also present for the smaller supercell. We assume that this is caused by the change of the electronic temperature and the subsequent change of the phonon frequencies. Since the sums of the phonon frequencies of the annihilated and generated phonons have to be zero, implied by energy conservation, the decay pathways need to change. Although this also happens in real system, our systems are small and the change can be considered discrete. We have submitted a manuscript to Phys. Rev. B containing the results with a supercell with 180 atoms.
Laser-excited amorphous carbon: Our results show, similar to experimental results, that a drastic change of the electronic density of states occurs after intense ultrafast laser excitation. The high electronic temperature of the sample leads to a new liquid phase, which differs from the liquid phase obtained by heating. This can be shown by the calculation of the coordination number. In our calculation the percentage of sp2 and sp3 bonded carbon atoms are considerably different than in non-excited cases. We are preparing a manuscript for publication. However, since the timescale of the simulations are faster than in the experiment we need further calculations. In these we want to calculate the influence of pulses with a duration of 50 and 75 fs, respectively. Furthermore, we plan to adapt the electron-phonon coupling to the experiment. Note, that we use the electron-phonon coupling as a free parameter to adapt to

experimental results. The ab-initio calculation of the electron-phonon coupling parameter for an amorphous system is problematic due to the needed size of the supercell.
Phase transitions TiO_2: Our results show that the phase transition pathways do not change considerably after ultrafast laser excitation. In particular, we see that the energy barrier between the anatase-rutile and brookite-rutile phase transitions are similar and are considerably smaller than that of the brookite-anatase phase transition. This is consistent with experimental results in the non-excited case. Furthermore, we see that, in comparison to the other two titanium dioxide polymorphs, rutile becomes more stable. Thus, our results suggest that the rutile phase is stabilized by the laser excitation. We have already submitted the paper to Phys. Rev. B.

Figures

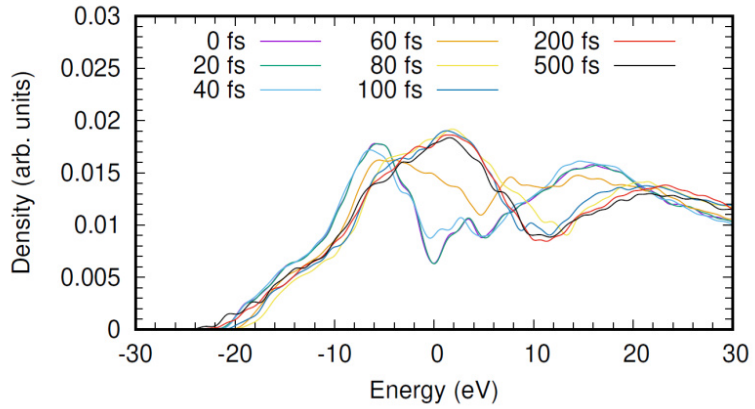

Figure1: Electronic density of states after laser excitation at different times for a supercell of 512 atoms.

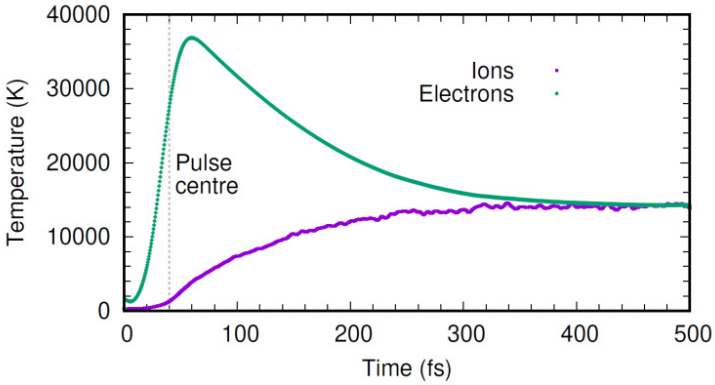

Figure2: Time-evolution of the electronic and ionic temperature after laser excitation.

Publications

Krylow, S.; Hernandez, F.; Bauerhenne, B.; Garcia, M. E.: Ultrafast structural relaxation of laser-excited graphene: ab-initio MD simulations including electron-phonon interactions

Krylow, S.; Garcia, M. E.: Ab-initio study of temperature and laser induced phase transitions in Bulk TiO2, 2019
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