Computational Chemistry Modelling of the Oxidation of Highly Oriented Pyrolitic Graphite (HOPG)

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1 Introduction

The flow over hypersonic vehicles is characterized by extreme conditions with shock layer temperatures reaching 10,000 K and heat fluxes as high as 5 kW/cm². Thermal protection systems (TPS) consisting of carbon-based surface-ablating materials are effective structures that enable much of the heat flux to be carried away from the vehicle by the ablating material.

At these high temperatures, dissociated oxygen atoms (O) strike the TPS surface leading to several possible gas-surface chemical reactions. Specifically, the oxygen atom could chemically bond to the surface, it could recombine with another adsorbed oxygen and leave the surface as a molecule (O_2), or the impinging atom could 'oxidize' the carbon surface resulting in products such as CO and CO_2 leaving the surface and being injected into the boundary layer. Such oxidation reactions result in the recession of the surface (surface ablation). Currently, much uncertainty exists in both the dominant reactions themselves as well as the rates of these reactions. The mechanisms and rates are required as input into state-of-the-art CFD simulations of hypersonic flows. Experimental determination of the chemical mechanisms themselves under extreme hypersonic conditions is difficult and often they must be inferred from macroscopic observations such as heat flux and surface recession measurements. However, as the field of computational chemistry continues to advance in step with advances in computational power, fundamental chemistry studies may be able to provide insight into the chemical mechanisms and associated rates for such surface ablation processes.

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Figure 1: X-37B Orbital Test Vehicle

The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF force field. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments. In this work, we simulate the collision of hyperthermal (5eV) O atoms with Highly Oriented Pyrolitic Graphite (HOPG) and compare our results to the molecular beam experiments performed by Minton and co-workers[1].

2 Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single-collision events are studied on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphene (representing HOPG) with large surface area. We do this to simulate the evolution of oxidized HOPG as observed experimentally including the net removal of surface carbon atoms, the product species created, and the geometry of etch pits. Molecular Dynamics simulations are performed with the LAMMPS molecular dynamics program, using the ReaxFF potential.

2.1 ReaxFF Potential

ReaxFF is a bond order dependent potential that uses a relationship between bond distance and bond order along with bond order and bond energy to describe bond dissociation properly. This allows natural creation and destruction of bonds which is critical to our oxidation simulations. The complete energy of a system is given by a number of terms, including long range non-bonded terms such as Coulomb and Van der Waals interactions:

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{ip} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWalls} + E_{Coulomb}$$

The force field parameters used in the present simulations have already been optimized by Chenoweth *et. al* [3], and it has been demonstrated that graphene-oxygen interactions are accurately modeled with this potential.

2.2 Surface Preparation

The collision of a 5 eV O atom with the atomistic-scale HOPG surface in such MD simulations results in a significant increase in the temperature of the simulated 'slab' of HOPG. Under low pressure experimental conditions[1], any transfer of energy to the surface would be conducted into the bulk material long before the next O atom collision. In our simulations we thermostat the bottom layer of the HOPG slab to maintain a constant surface temperature. However, in addition, we also had to wait roughly 12.5 ps before the increased temperature of the top layer cooled back to the thermostated surface temperature as shown in Fig. 2. If the next gas-phase atom is injected prior to this, it hits a surface at an unphysically high surface temperature, not representative of the experiment. Colliding atoms at 1 ps intervals without temperature control results in very high surface temperatures which causes the HOPG to oxidize much faster than it would in the experiment. However, simulating the system for 12.5 ps between collisions is computationally expensive and there are no reactions over this time scale. In fact, most reactions were observed to occur at short timescales (<1 ps).
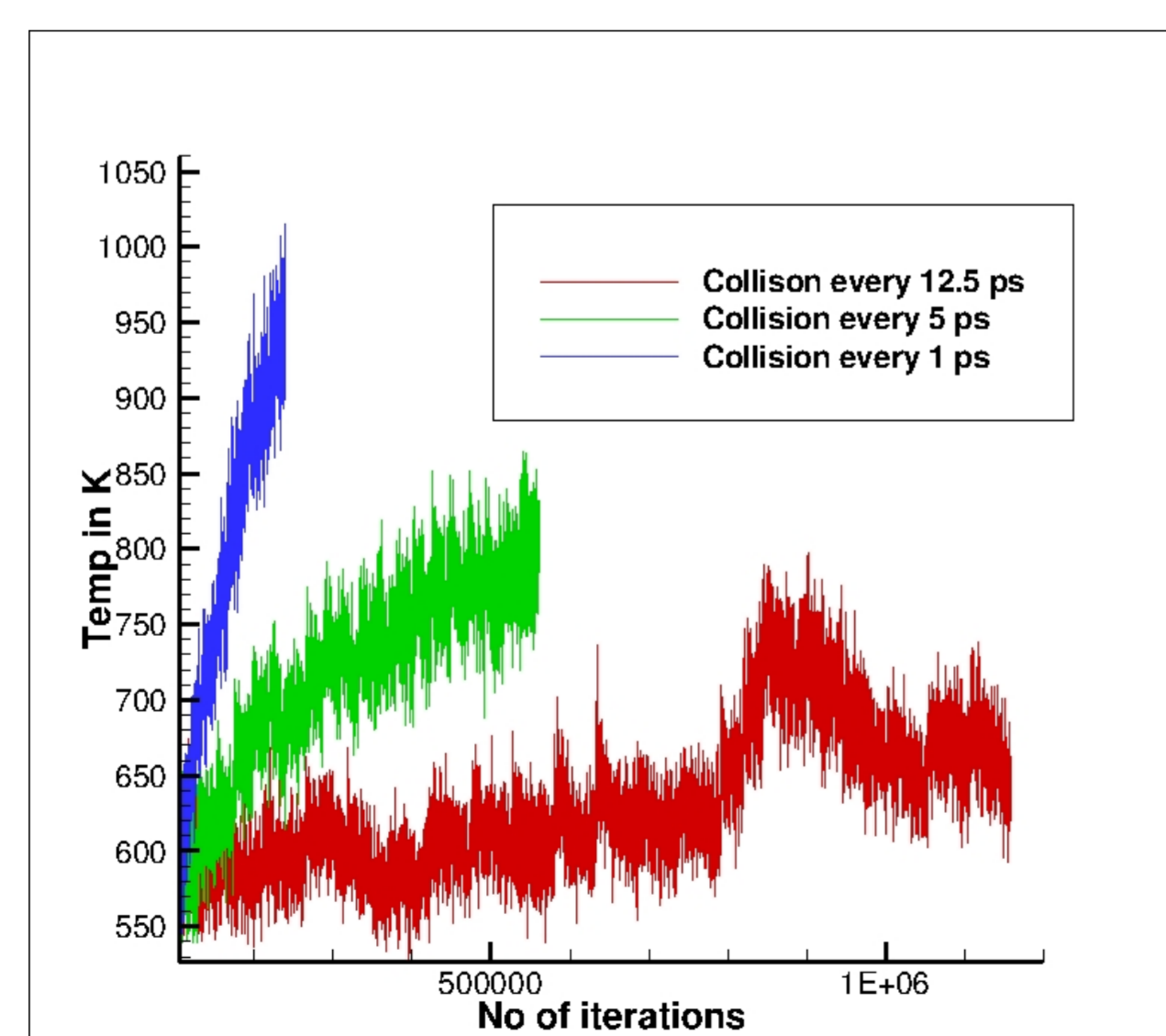

Figure 2: Figure showing temperature increase after 20 continous collisions

Thus, we simulate the collision with a NVE ensemble for 1 ps, which is sufficient to determine the outcome of the collision (reflection, adsorption, oxidation, etc.). After the reaction is over (after 1 ps), we then thermostat the *entire system* for 0.75 ps to restore the surface temperature to its proper value. This added complexity, compared to previous studies involving single isolated collisions, is essential for both physical accuracy and computational efficiency.

2.3 Surface Coverage

It is well known that pristine HOPG does not undergo oxidation due to O atom collisions even with high energy O atoms (5eV). However, the HOPG surface does become populated with adsorbed O atoms either in epoxide form(C-O-C) or C-O form, and possibly other intrinsic surface defects. Thus it is reasonable to begin our MD simulations with HOPG and this surface coverage. If we initialize our MD simulation with a complete epoxide coverage on the HOPG surface (at $t = 0$) and then integrate the system, we find that the top atomic layer of the HOPG surface buckles as shown in figure 4(b). This buckling then accelerates the oxidation of the HOPG slab in our simulations. However, we have confirmed that this buckling is an artifact of the simulation. Instead, we start with a pristine HOPG surface, thermostat it to the desired temperature, and then place oxygen atoms in the epoxide positions (at the equilibrium bond distance) with velocities sampled from a gaussian distribution at the surface temperature. The entire system is then integrated in NVE ensemble and a certain number of the oxygen atoms remain bonded to the surface in the epoxide configuration. The non bonded atoms are removed from the system and the process is repeated for a few times. If this procedure is followed, which is physically more realistic in that full oxygen coverage would not occur instantaneously, an HOPG surface with epoxide coverage is obtained without buckling. This then, is how we prepare our HOPG surfaces prior to gas-phase oxygen impacts.
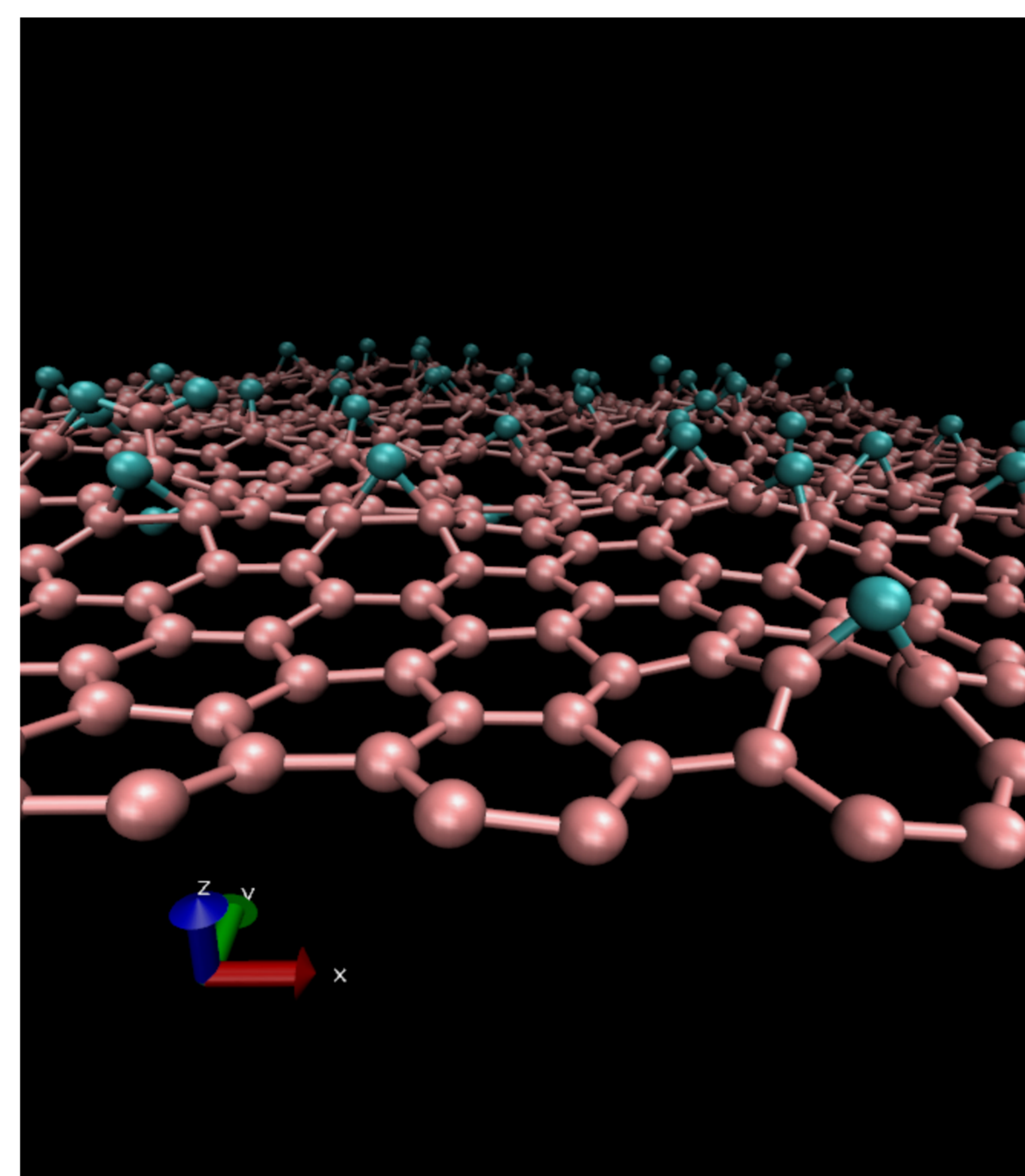

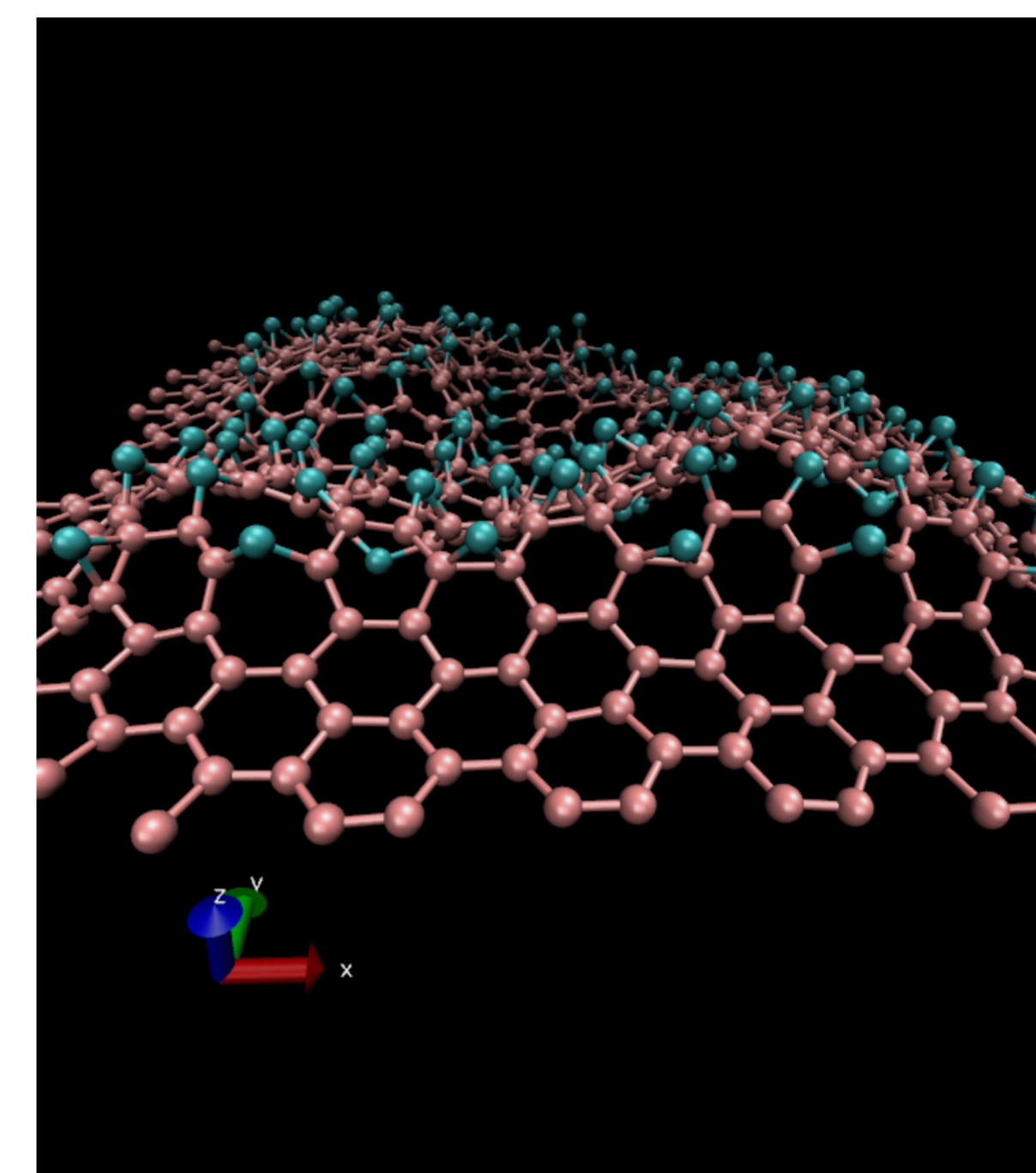**Figure 4(a)**: Flat surface populated with O atoms. Only top layer shown

Figure 4(b): Buckled surface populated with O atoms. Only top layer shown

2.4 Continuos Collisions

Oxygen atoms at 5eV are continuously injected towards the HOPG surface. A total of 1000 continuous collisions are performed. The simulations predict the pit growth in the intraplanar direction to be much more rapid than etching in the interplanar direction. This was observed experimentally[1] (Fig. 5) where shallow but wide etch pits were created. Our results predict that 1 carbon atom is approximately removed for every 6 O atoms injected. However, this ratio depends on the size of atomic beam flux compared to the size of the specific etch pit. The surface temperature was maintained at 373K. In another set of experiments[4] performed at 525 K, the experimental data predict the ratio of CO to CO_2 products as 1:2 while our simulations predict this ratio of products to be roughly 1:4. The fact that our simulations predict more CO_2 products than CO, and in a reasonable proportion compared to experiment is encouraging.
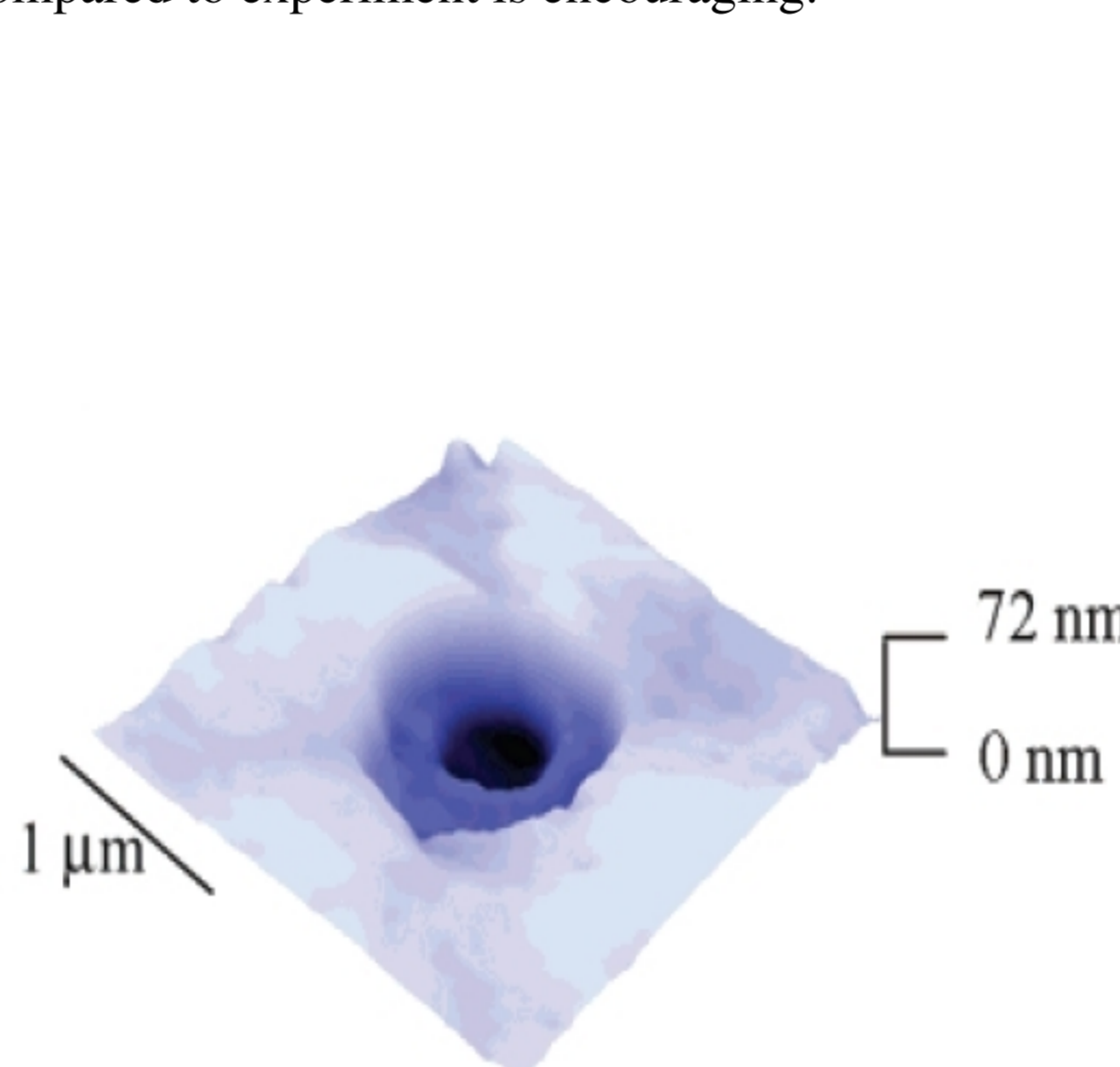

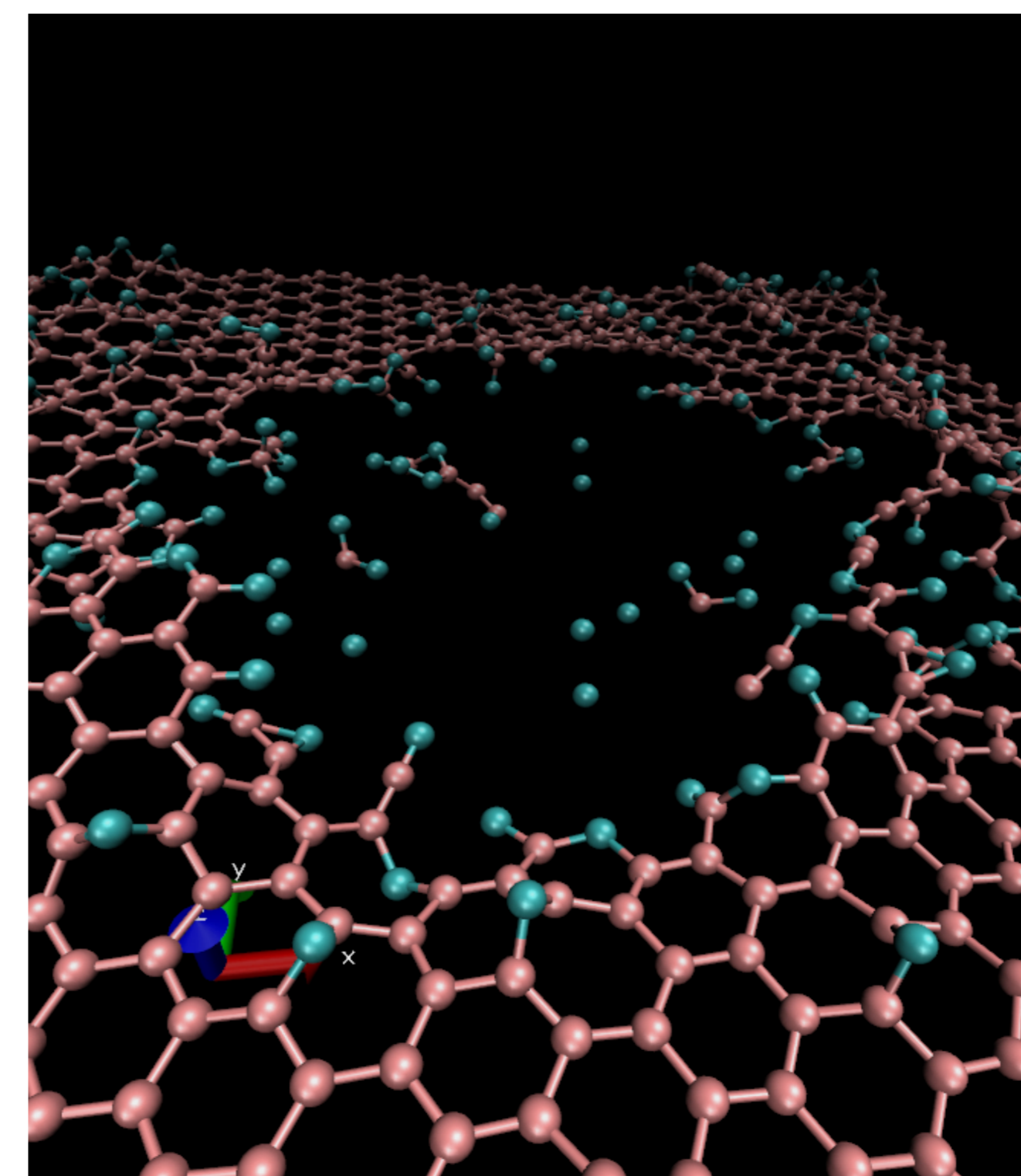**Figure 5(a)**: Pit observed in experiments[1]

Figure 5(b) : Pit observed in simulations. Only top layer shown

Figure 6 indicates the number of carbon atoms removed as a function of the number of collisions. On close observation, it is seen that the first oxidation (removal of C atom) reaction occurs after 100 collisions. The number of carbon atoms removed thereafter is steady and happens at a relatively constant rate. The steady rate also suggests that the oxidation would increase with higher flux of incoming O atom which is also observed in experiments.
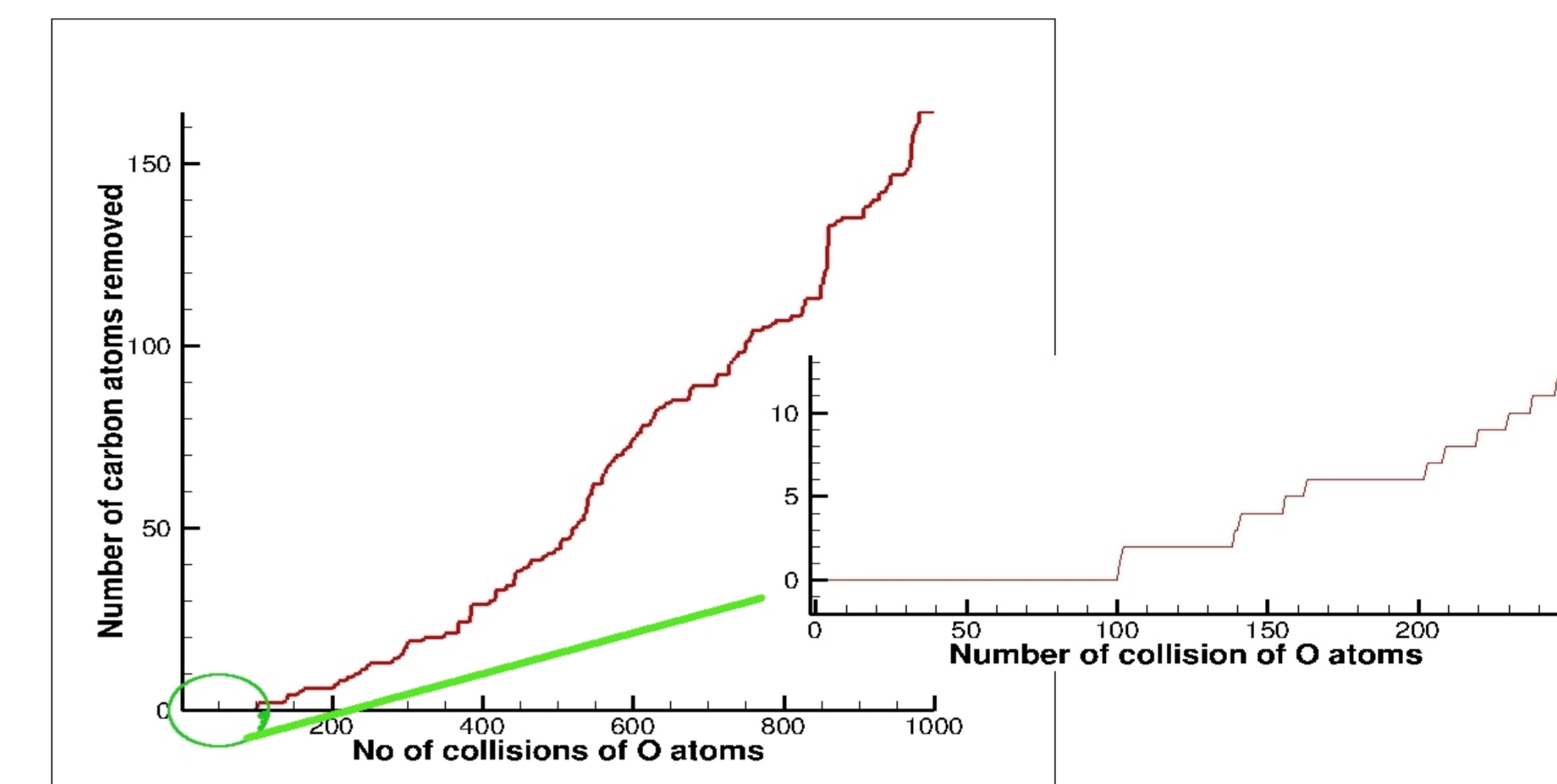

Figure 6: Number of carbon atoms removed as a function of number of collisions

2.5 Effect of surface temperature

The work in Ref. [1] also shows that the rate of oxidation increases with an increase in surface temperature. The experiments were done in the temperature range of $298K - 573K$. In Molecular Dynamics simulations, the variation in this narrow range of temperature would be difficult to capture, as a large number of ensemble averages (many simulations) may be required to reduce scatter in the results. We simulated the collisions over a much larger temperature range of 300K, 600K, 1000K and 1500K. The results are tabulated in Table 1. As seen in the Table 1, our simulations do indeed predict a higher oxidation rate as the surface temperature increases, consistent with experimental observation. Specifically, this trend with temperature should reveal the activation energies of the specific reactions that lead to oxidation. If determined, these mechanisms and activation energies could be useful for finite-rate models used in CFD simulations.

Surface Temperature(K)	Number of Carbon atoms removed
300	115
600	164
1000	224
1500	360

Table 1: Surface Temperatures vs Number of Carbon atoms removed

3 Conclusions and Future Work

In this work, we have studied the oxidation of HOPG by hyperthermal O atoms. To avoid long wait times between successive collisions, we thermostat the system to the desired target temperature. It was also observed that the pristine HOPG sheet does not oxidize even by the collision of hyperthermal O atoms. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coverage of O atoms on the surface by allowing the O atoms to bond naturally to the surface instead of placing them in epoxide form which results in buckling of the surface. Our continuous collision results are compared with the trends observed in molecular beam experiments. We observed that oxidation in the intraplanar direction is faster than in the interplanar direction as observed in experiments, and also that the oxidation rate increases with higher surface temperature. Finally, our simulations predicted higher production of CO_2 compared to CO and in similar amounts that were in agreement with experimental observations. These preliminary results are promising for the validation for our simulation techniques including the interatomic potentials and modeling assumptions.

In future work, we wish to characterize the rates quantitatively of all species formed on the surface and to run large length scale and time scale MD simulations to validate our results as close as possible to available experimental data. We could then run simulations at high surface temperatures and a variety of crystal orientations to investigate oxidation reactions present under hypersonic conditions for more realistic carbon-based surface ablator materials.

4 References

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