

Molecular Dynamics Simulation of Hydrocarbon Reflection and Dissociation Coefficients from Fusion-Relevant Carbon Surfaces

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Abstract

Reflection coefficients for carbon and hydrocarbon atoms/molecules on carbon-based surfaces are critically needed for plasma-surface interaction analysis in fusion devices, as carbon will continue to be used in next step devices like ITER. These have been calculated at different energies and angles with a molecular dynamics code using the Brenner hydrocarbon potential. Hydrogen saturated graphite was prepared by bombarding a graphite lattice with hydrogen, until a saturation at ~ 0.42 H:C. Carbon at 45° has a reflection coefficient (R) of 0.64 ± 0.01 at thermal energy, decreasing to 0.19 ± 0.01 at 10 eV. Carbon dimers ($R_{\text{thermal}} = 0.51$, $R_{>1\text{eV}} \sim 0.10$) tend to stick more readily than carbon trimers ($R_{\text{thermal}} = 0.63$, $R_{10\text{eV}} = 0.16$). Hydrocarbons reflect as molecules at thermal energies and break up at higher energies. The total reflection via these fragments decreases with energy, the number of unpaired electrons, and changing hybridization from sp^3 to sp^2 to sp . The results compare reasonably well with binary collision modeling for higher energies and experimental sticking data at thermal energies. A second surface, representing a “soft” redeposited carbon layer formed by the deposition of hydrocarbons onto a graphite surface, is also analyzed. In general, reflection is lower from the “soft” surface by 0.1–0.2. This reflection data can and has been incorporated in erosion/redeposition codes to allow improved modeling of chemically eroded carbon transport in fusion devices.

1. Introduction

Carbon has been considered as the ideal plasma-facing material for the divertor surfaces of future magnetic fusion experiments due to the extremely high heat and particle loads [1,2]. It has a low atomic number, does not melt, and has an extremely high sublimation temperature. However, carbon surfaces are susceptible to chemical erosion by hydrogenic species. Hydrocarbons such as CH_4 , C_2H_4 , C_2H_6 and even C_3H_8 are formed and then released into the plasma [3]. If the molecules were quickly ionized, the carbon would be redeposited and little net erosion would result. However, in a detached plasma, or other expected regimes with low electron temperatures and densities, the hydrocarbon molecules may have a significant penetration depth into the plasma [4]. In that case their break-up products, once ionized, could re-strike the divertor, reflect, and thereby migrate across the entire machine. Indeed, this was seen in the JET experiment where a large amount of carbon was found on small louvers that were far from the plasma [5]. Redeposited carbon is a strong sink for hydrogen. In a device using tritium the existence of such redeposited layers could trap a significant fraction of the allowed tritium inventory. To be able to predict the behavior of hydrocarbon erosion and transport, the

reflection coefficients and surface dissociation coefficients must be known.

Scant experimental data exists on such parameters for the energy range of interest (thermal to 20 eV). Binary collision codes such as TRIM [6] or even VFTRIM-3D [7] are not reliable at such low energies and do not treat molecules. This leaves molecular dynamics as the most appropriate tool to determine this data and is the focus of this work [8] and paper.

2. Model

Molecular Dynamics (MD) is a method of computer simulation which calculates the evolution of a system of particles over time by solving the equations of motion over many discrete time steps. At each step forward in time, the forces on all atoms due to all other atoms are calculated, and the velocities and positions are updated. The physical input to such a model is a potential energy function, which gives the potential energy between atoms as a function of interatomic distances.

The MolDyn code [9] was the starting point for this work. It uses the Brenner hydrocarbon potential [10] with the second parameter set, as is used in related plasma-surface interaction studies [11]. It is based on Tersoff’s covalent bonding formalism [12] with additional terms that correct for over bonding of radicals. The key to this type of potential is a “bond-order” term that accounts for many-body and chemical effects by modifying the magnitude of the attractive potential according to the atom’s local environment (e.g. coordination numbers, bond angles, and conjugation). The cut-off distance for the potential is 2 Å. The Brenner potential has been well benchmarked against known physical data [13–17]. The second parameter set was chosen because it gives more accurate bond stretching constants and is an updated parameterization [11]. To extend the potential to slightly higher energies, the ZBL universal potential [18] was splined to the Brenner potential for short interatomic distances.

For comparison purposes the AIREBO potential [19] was implemented in the code. It simulates a torsional potential energy and longer-ranged intermolecular van der Waals forces, and therefore must use a much longer cut-off distance (10 Å). The longer range is needed, for example, to simulate interactions between the planes of single crystal graphite. Even after parallelization of the code, the AIREBO potential was found to be too slow for this work. These simulations were conducted using distributed

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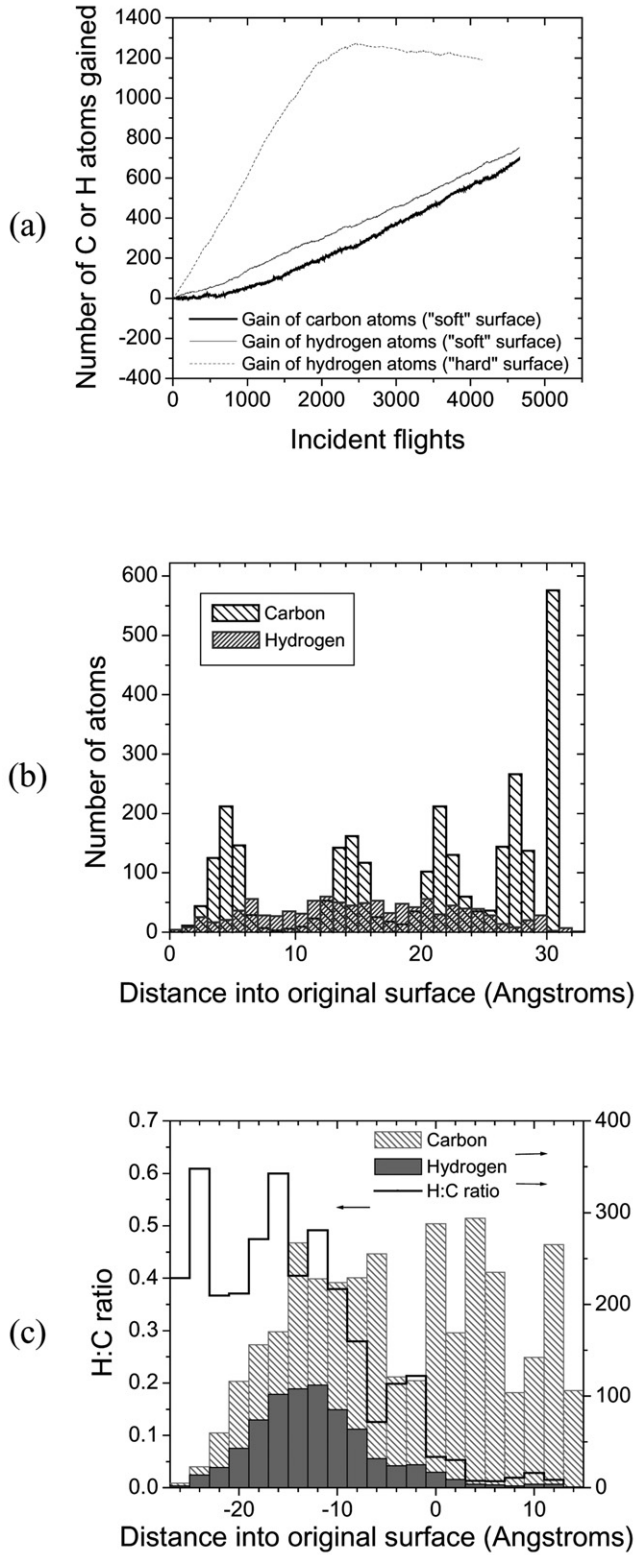


Fig. 1. Preparation of the surfaces, showing (a) Gain of carbon or hydrogen atoms with time. (b) Depth profile of carbon and hydrogen atoms on "hard" surface. (c) Depth profile of carbon and hydrogen atoms on "soft" surface.

computing [20] of approximately 20 PCs running at an average speed of 800 MHz. Each desktop computer in the group ran individual flights while idle from other tasks. With this set-up approximately 1000 flights could be run in a given day. When using the AIREBO potential the calculations took 17,000 times longer. Due to its slow speed and the fact that amorphous H:C surfaces rather than

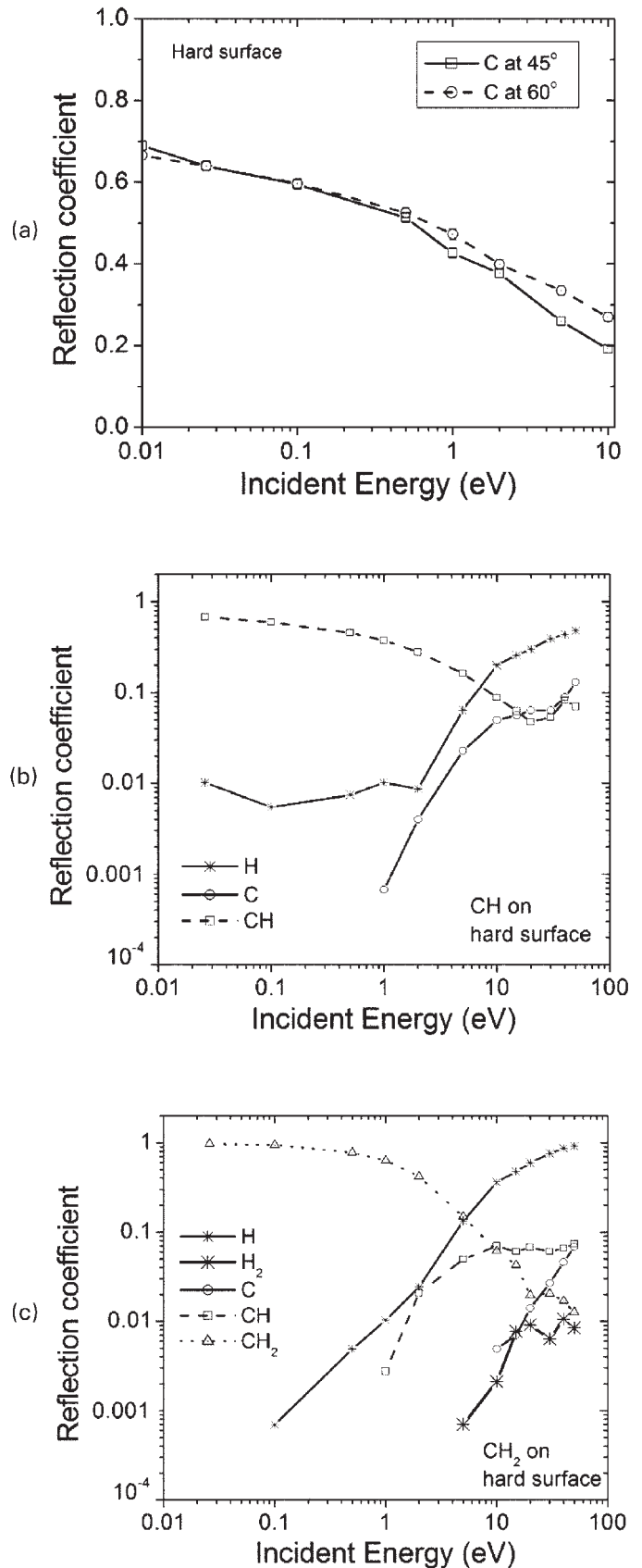


Fig. 2. Reflected species on the "hard" surface for (a) Carbon at 45° and 60°, (b) CH at 45°, (c) CH₂ at 45°, (d) CH₃ at 45°, (e) CH₄ at 45°.

crystalline were used in the work, the AIREBO potential was not used to obtain reflection data.

A unit cell approximately 40 Å × 40 Å and 25 Å deep was used. Periodic boundary conditions were used on the sides. The bottom of the surface was fixed. Smaller and

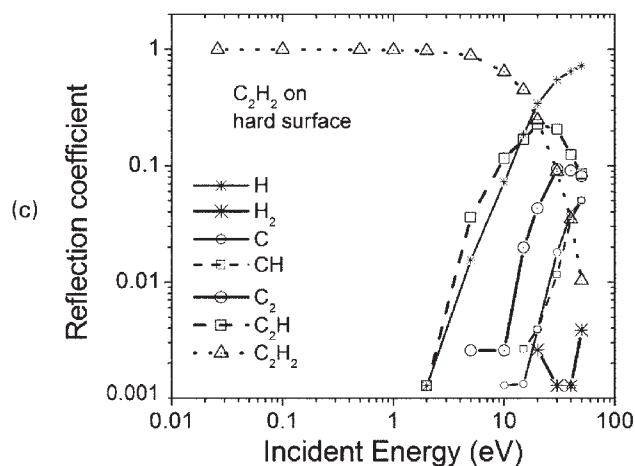
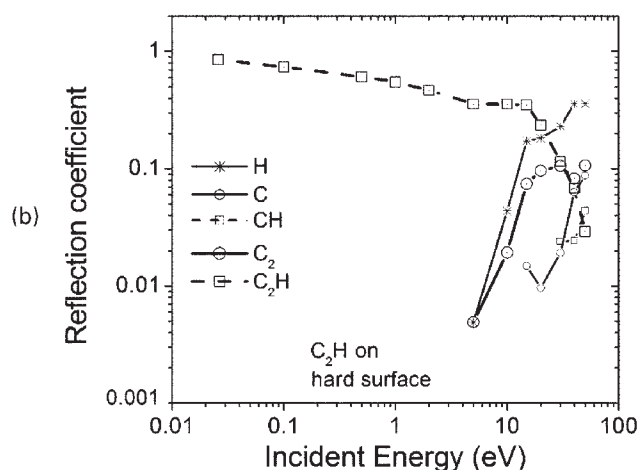
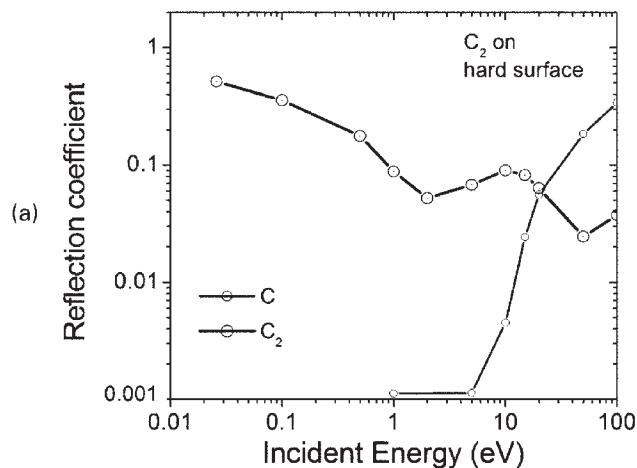
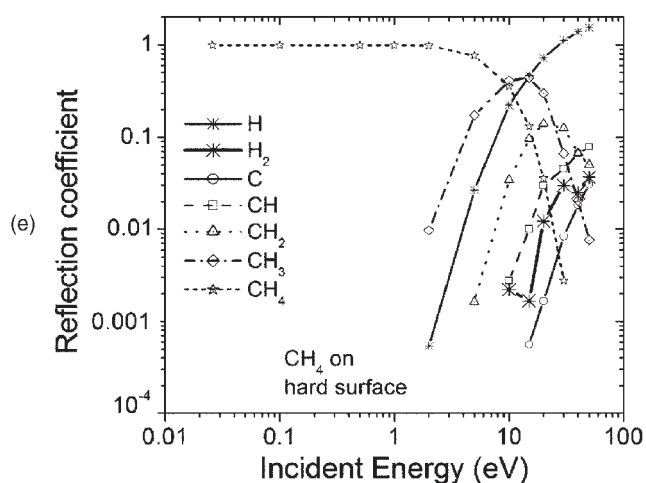
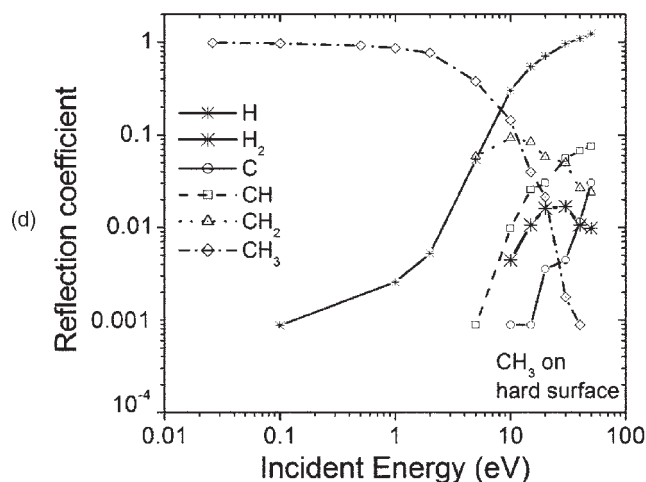


Fig 2. continued.

larger lattices were checked to insure the size was adequate. Generally a 0.2 fs timestep was used, however a routine was added to use a variable time step based on the algorithm of Nordlund [21]. A timestep of 0.2 fs was found to accurately reproduce the trajectories and conserve energy. Termination, molecule detection, visualization and molecule generation schemes were added to the code too. In addition a graphical user interface was developed.

3. Results

To create the first fusion-relevant carbon surface for this work, a graphite lattice was sequentially bombarded with thousands of 20 eV H atoms incident at 45°. After each H was incident the surface was allowed to relax for 5000 fs. After about 2500 incident flights the rate of H addition and rate of H evolution balanced. Figure 1(a) shows the time evolution of the H to C ratio with incident flights. Saturation occurred at a ratio of 0.42 H:C. This compares favorably with tokamak data which shows an approximate 0.4 H:C ratio in plasma-exposed surfaces [22]. Figure 1(b) shows that the Hydrogen bombardment amorphized the graphite. While the lattice planes are still visible, they are broadened and C as well as H can be found at every depth. However, relative to the second surface studied this surface remained fairly planar, and will be referred to as “hard”.

A “soft” hydrocarbon surface was also created. This is designed to simulate redeposited layers in a fusion system

 Fig. 3. Reflected species for 45° incidence on the “hard” surface of (a) C₂, (b) C₂H, (c) C₂H₂, (d) C₂H₃, (e) C₂H₅.

and was created by sequentially bombarding graphite with 3 eV H and 0.0259 eV C, CH and CH₂ all at 45°. The addition of these species caused the original surface to grow as shown in Fig. 1(c). After 3000 flights the rate of addition of H and of C both leveled out (Fig. 1(a)) and the surface building stage was terminated at 4500 flights. The outermost layers have an average H to C ratio of approximately 0.4.

Figure 2(a) gives the reflection coefficients for C at 45° and 60° incident on the hard surface. At thermal and hyperthermal energies there is no difference in reflection as incident angle is altered. At higher energies, more glancing

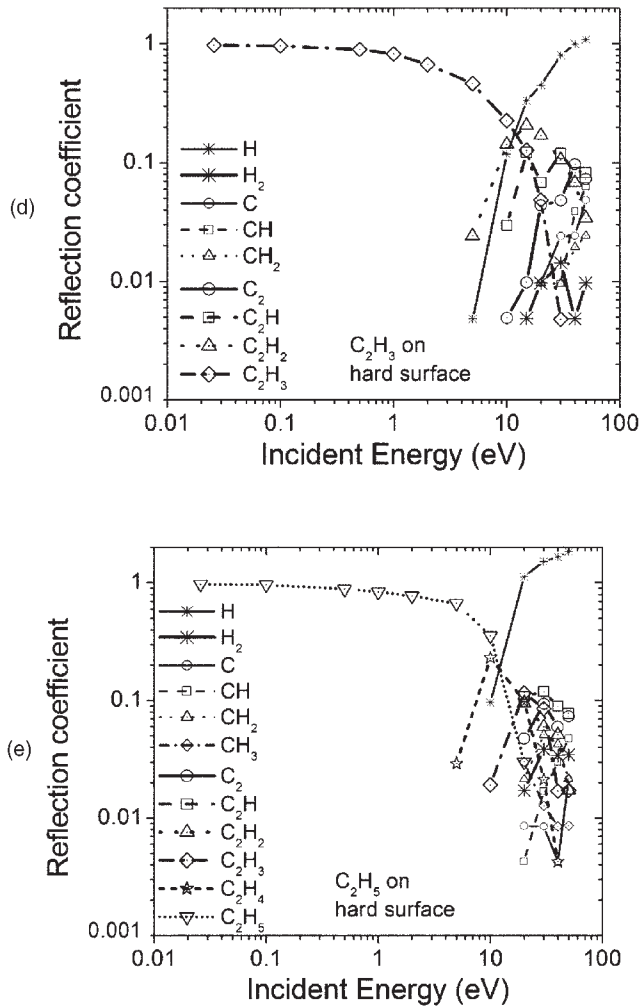


Fig. 3. Continued.

angles (60°) have a slightly higher chance of reflecting. In both cases, the reflection coefficient decreases with incident energy, due to the deeper penetration of the atom into the surface.

Figures 2(b) through 2(d) show the reflection and surface impact dissociation coefficients of CH, CH_2 , CH_3 , and CH_4 as a function of incident energy. As expected, room temperature CH_4 has a 100% chance of reflection. As the CH_4 's energy is increased there begins to be some probability for a single H atom to be broken off the molecule and emitted, leaving the CH_3 on the surface. The converse is also true. For example, there is a 0.01 chance of an incident CH_4 at 2eV to reflect as a CH_3 . That probability climbs and then falls again as emission of a CH_2 species becomes more likely. Emission of CH_2 , CH and finally C follow the same pattern as energy is increased.

The mechanisms for why certain fragments are emitted more often than others can be complicated, and may not be completely clear. For example the CH_3 molecule is more likely to be emitted than the H atom during CH_4 breakup (Fig. 2(e)), while the H atom is emitted more often than the C atom during CH breakup (Fig. 2(b)). However it is clear that carbon, when incident on the surface itself, sticks much more readily than an incident CH_3 molecule. It is probably safe to assume then that a CH_3 formed by methane breakup would tend to reflect more than a carbon atom formed during CH breakup.

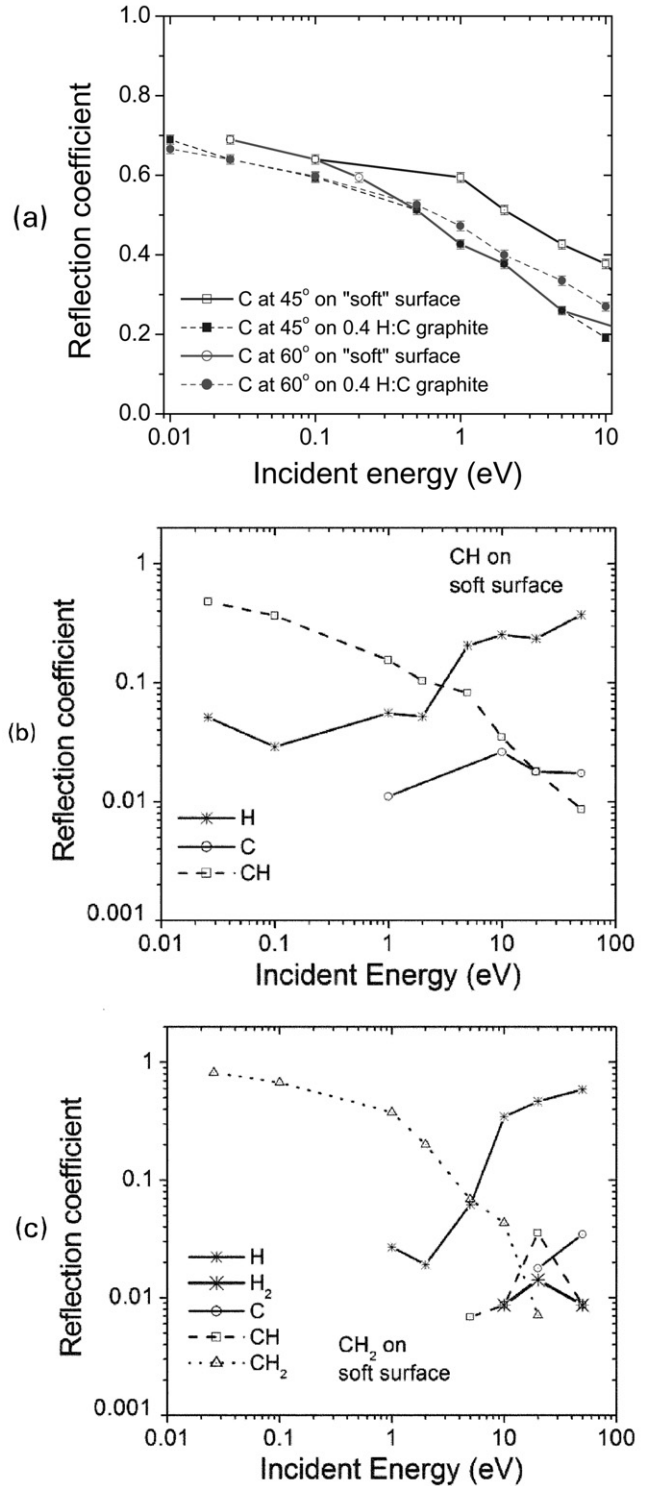


Fig. 4. Reflected species on the "soft" surface for (a) Carbon at 45° and 60° , (b) CH at 45° , (c) CH_2 at 45° , (d) CH_3 at 45° , (e) CH_4 at 45° .

The C_2H_x species exhibit the same breakup behavior with energy. Figure 3 shows the breakup pattern and reflection characteristics for C_2 , C_2H , C_2H_2 , C_2H_3 and C_2H_5 incident at 45° on the hard surface as a function of energy. C_2H_4 was not modeled because of its known stability. Of special note is that other than straight reflection, the most likely break-up pattern of C_2H_x is to simply lose a H atom to the surface and to reflect as C_2H_{x-1} . Reflection coefficients above one for H atom production simply mean that more than one H is released.

Figure 4 shows the reflection and break-up characteristics for CH_x species incident on the soft surface. Carbon

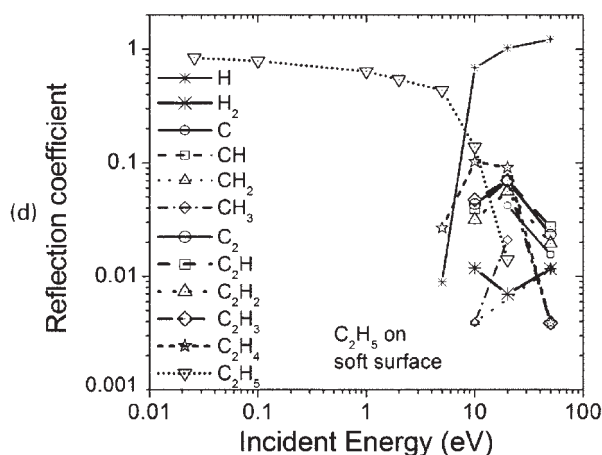
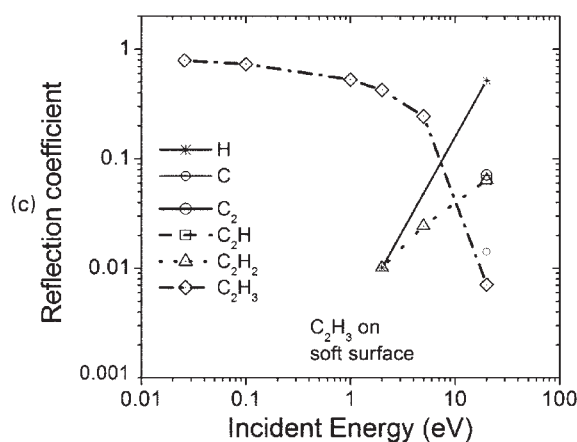
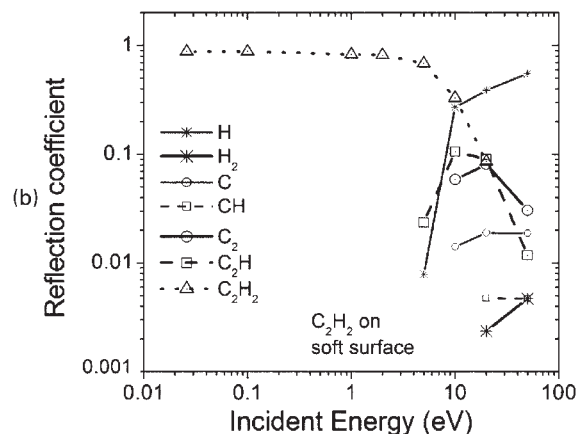
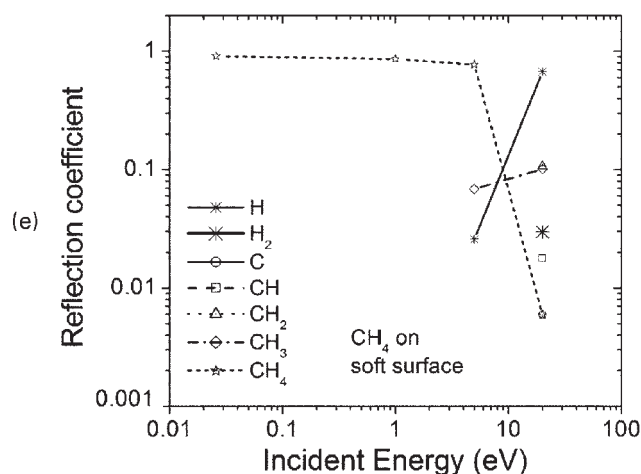
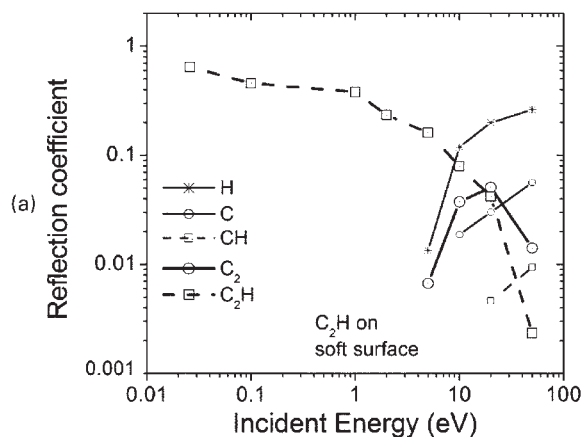
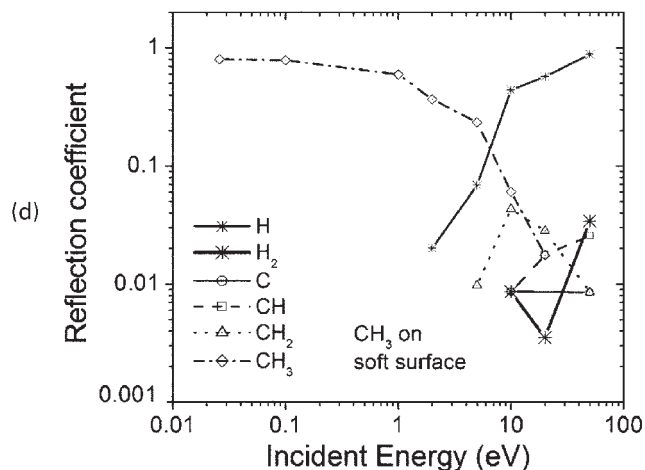


Fig 4. Continued

atoms have about the same chance of reflecting from the soft surface compared to the hard surface, while the chance of molecules reflecting is *decreased* even at thermal energies. From movies of the interactions this appears to be due to the large number of hydrogenated chains extending above the surface. The increased roughness of the “soft” surface introduces an angular dependence in the carbon reflection coefficients. Additionally, the bonding environment is more conducive to sticking on the “soft” surface, as illustrated by the decreased reflection coefficients for hydrocarbon molecules in Fig. 4.

Again the C_2H_x species shown in Fig. 5 act in a similar manner and do not reflect as easily from the soft surface as they do from the hard surface. C_2H_2 is particularly stable and tends to remain in tact until higher energies than the other C_2H_x species modeled.

Figure 6 shows the energy dependence of the reflection coefficient for three different angles of incidences for C_2H_2 on the soft surface. At low energies the larger angles of incidence tend to reflect less, probably due to the rough nature of the surface. A particle incident at a glancing angle with respect to the surface as a whole impacts a particular hydrocarbon chain extending from the surface more normally.

The energy reflection coefficient also showed a remarkable difference between the two surfaces. For the hard surface the reflected species had on average 32% of the incident energy. For the soft surfaces the reflected species possessed a mere 7% of their energy. The large difference

Fig. 5. Reflected species for 45° incidence on the “soft” surface of (a) C_2H , (b) C_2H_2 , (c) C_2H_3 , (d) C_2H_5 .

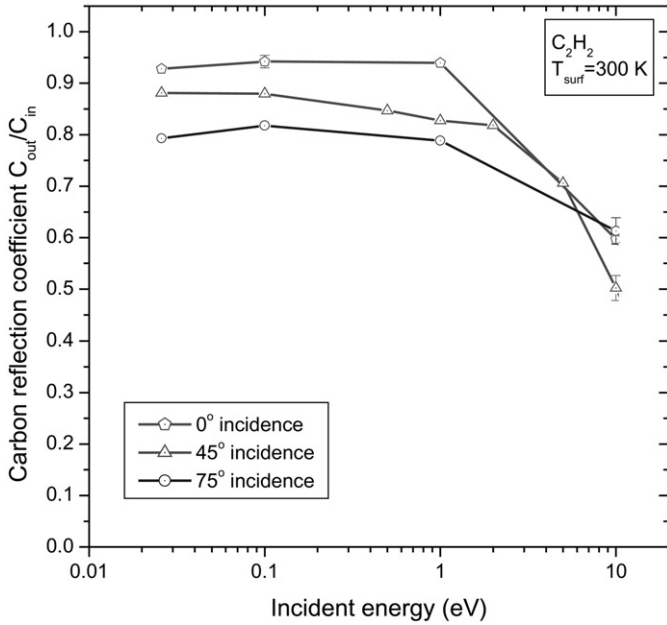


Fig. 6. Reflection of C_2H_2 incident at 0° , 45° , and 75° on the "soft" surface at 300 K.

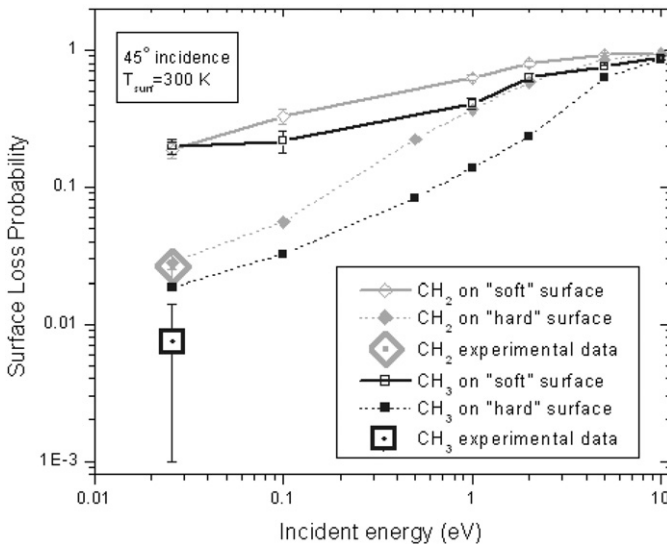


Fig. 7. Comparison to experimental data for CH_2 [23] and CH_3 [23–24] on both the "hard" and "soft" surfaces.

in the average reflected energy is primarily due to the structure of the surfaces. The soft surface has more "give" to it, because incident energy can be absorbed by movement of the surface atoms in the lower density, more hydrocarbon chain-like structure. The angular distribution of reflected particles from both surfaces was largely cosine with a small amount of specular reflection which was more pronounced on the hard surface.

4. Discussion

On both surfaces, the trend is that sticking of hydrocarbons increases with the number of unpaired electrons (in CH_x molecules) and as the hybridization of the carbon atom changes from sp^3 to sp^2 to sp (in C_2H_x hydrocarbons).

Experimental data has previously been obtained for a few of the molecules of interest [23–27]. The data for CH_2 and CH_3 were obtained in decay in the afterglow or radical

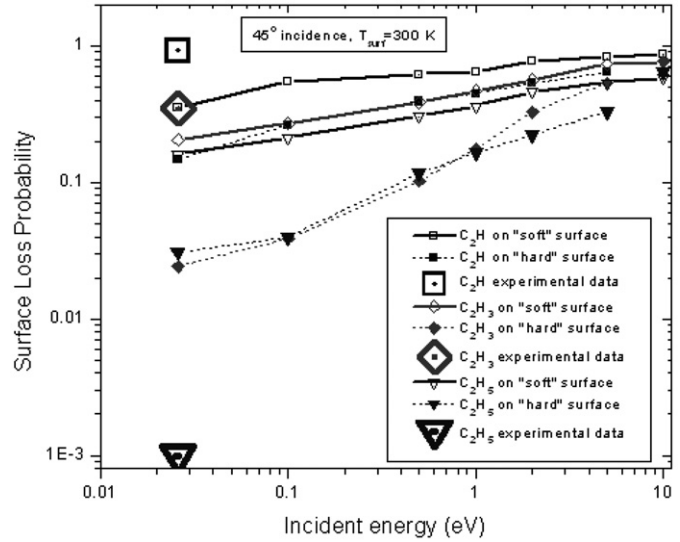


Fig. 8. Comparison to experimental data for C_2H [23], C_2H_3 [26], and C_2H_5 [27] on both the "hard" and "soft" surfaces.

beam experiments, where the surfaces experienced direct plasma bombardment and will most closely resemble the hard saturated graphite surface studied here. The C_2H_x data, however, comes from cavity experiments, in which the deposition profiles inside a remote cavity were matched to a surface loss probability (β) value. β is defined as the sum of the sticking coefficient and the probability of a surface reaction resulting in a non-reactive volatile molecule [26]. Deposition concentrated opposite the slit in the cavity would give a very high β value, while even deposition throughout the cavity indicates that radicals bounce many times before sticking. In cavity experiments, the surface studied is not in contact with the plasma and is better represented by a soft redeposited layer.

Figures 7 and 8 show the comparison of the present modeling results to the known experimental data at thermal energies. The CH_2 and CH_3 points shown in Fig. 7 are in fair agreement with the hard surface results. This is likely due in part to the similar structure ("harder" and more graphite-like) to those used in the experiments [23,24], which have direct contact with the plasma. The comparisons to the experiments in Fig. 8 are for C_2H_x species. Here the model reproduces the trend with incident molecule, but not the magnitudes. This is again likely an effect of the nature of the surfaces used in the experimental work [25–27]. The cavity experiments actually use an even "softer" surface than the one that was developed for this work, with an H to C ratio near 1:1. The error in the experimental points was not explicitly given, but the authors warn of large uncertainties in the data due to numerous factors. The surface loss probabilities measured (which are an upper bound on the sticking coefficient) assume no dependence on incident angle. They also assume that the species which make it to the collector plates are the same ones and in the same ratios as those measured in the plasma by a QMS.

5. Conclusions

Critical reflection data for many of the hydrocarbon species of importance to studying the erosion/redeposition

of chemically sputtered hydrocarbons has been obtained using molecular dynamics modeling of the molecule-surface interactions at a range of incident energies and angles. It was found that the number of unpaired electrons and hybridization of the incident molecule effected which species would stick most readily. Reflection went down with incident energy (up to 10 s of eV at least), and was higher on the hard saturated graphite surface than on the soft redeposited carbon surface.

The data presented in this paper has made an impact on the modeling of the carbon in the JET louvers mentioned in the introduction to this work. It was found [28,29] that using the calculated higher reflection coefficients and treating carbon deposits that experienced very different plasma conditions in different manners (e.g. soft vs. hard) can explain the magnitude of the carbon present.

Acknowledgements

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