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Molecular dynamics simulations of CH_3 sticking on carbon surfaces, angular and energy dependence

P. Träskelin [a,*], E. Salonen [a,1], K. Nordlund [a], J. Keinonen [a], C.H. Wu [b]

[a] *Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Helsinki, Finland*
[b] *EFDA, Max-Planck-Institut für Plasmaphysik, D-85748 Garching bei München, Germany*

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Abstract

Sticking cross-sections for CH_3 radicals at different angles of incidence and different energies were calculated using molecular dynamics simulations, employing both quantum-mechanical and empirical force models. The chemisorption of a CH_3 radical at 2100 K onto a dangling bond is found to be highly dependent on the angle of incidence of the incoming radical. The sticking cross-section decreases from (10.4 ± 1.2) to (1.4 ± 0.3) $Å^2$ when the angle of incidence of the methyl radical increases from 0° to 67.5°. A simple geometrical model is presented to explain the angular dependence. In the sticking process of CH_3 radicals with higher kinetic energies (1, 5, and 10 eV) both a fully hydrogen-terminated surface and a surface with dangling bond were studied. The sticking probability is enhanced as the radical energy increases. We observed sticking onto the fully hydrogen-terminated surface for all cases except for the case when the methyl radicals had energies corresponding to a temperature of 2100 K.

1. Introduction

The selection of plasma facing materials for present and next-generation fusion devices is still an open question. Diamond and materials with diamond-like structures are important in many technological applications because of their unique mechanical, chemical and optical properties [1,2]. Diamond-like hydrocarbon films have attracted particular attention in fusion research [3–5] since carbon is a major candidate as a plasma-facing material. The plasma-facing component lifetime and the contamination of the plasma will be determined by the erosion mechanisms and their rates, but also by the transport and re-deposition of eroded material. Hydrocarbon species are released via physical and chemical sputtering when deuterium as well as and tritium ions and neutrals which have escaped from the fusion core plasma interact with carbon-based first walls. These radicals may later be re-deposited onto the divertor tiles but also in other regions of the vacuum chamber which are not in direct contact with the fusion plasma [6,7]. Due to the fact that tritium bound in these hydrocarbon films, is highly radioactive and cannot be easily recycled, fundamental understanding and control of the deposition and erosion processes relevant to re-deposited C:H films is of great importance. In experiments carried out at ASDEX Upgrade [7], both soft polymer-like C:H films (H/C∼1) and hard C:H films (H/C∼0.4) were formed. Hence detailed knowledge about such film growth, especially about the fundamental erosion and re-deposition processes of hydrocarbon species, is needed in order to successfully model and predict the performance of the next-step device.

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[*] Corresponding author. Tel.: +358-9 191 50088; fax: +358-9 191 50042.

E-mail address: petra.traskelin@helsinki.fi (P. Träskelin).

[1] Present address: Helsinki Institute of Physics and Laboratory of Physics, P.O. Box 1100, FIN-02015 Helsinki University of Technology, Finland.

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The C:T film formation in fusion devices might be controlled by using a liner in the divertor pump duct [8] where neutral hydrocarbon radicals will be trapped or transformed before they can deposit in remote areas of the vacuum vessel. One of the most abundant sputtered radical species is the CH_3 radical [9,10] which is also known to be an important growth species in chemical vapor deposition growth of carbon films [11,12]. Experimental investigations on surface processes between polymer-like C:H films and simultaneous methyl and atomic hydrogen beams, performed by von Keudell and coworkers [13,14], have provided valuable information on the individual film growth mechanisms. Since chemisorption of the impinging methyl radicals predominantly takes place on dangling bonds, the film growth can be characterized with a CH_3 sticking cross-section to these sites. The sticking cross-section can be thought of as the effective area to which the CH_3 radical always chemisorbs upon impact.

Using molecular dynamics (MD) simulations we have examined the sticking process of methyl radicals impinging onto a surface with one carbon dangling bond. The angle of incidence of the incoming radical was varied. By using both a fully hydrogen-terminated surface and a surface with one dangling bond, we have also examined how the sticking probability is affected by incoming radicals at higher kinetic energies.

2. Simulation method

Both tight-binding (TB) [15,16] and empirical [17] hydrocarbon force models have been employed in our simulations of methyl radicals impinging onto diamond (1 1 1) surfaces. The chemistry in C–H systems is well described by either one of these models. The empirical Brenner potential [17], with the carbon–carbon cutoff 2.46 Å, is computationally less expensive which allows one to achieve more comprehensive statistics in MD simulations, while maintaining a correct description of bond formation and breaking. TB is based on a second order expansion of the Kohn–Sham total energy in density functional theory with respect to charge density fluctuations. This method provides a quantum mechanical description.

In our simulations, we have used a diamond lattice with two layers of carbon atoms, a total of 120 atoms, as a chemisorption substrate. Both (1 1 1) surfaces were hydrogen terminated and an unsaturated carbon site was created by removing one hydrogen atom from the surface (see Fig. 1). In the study of CH_3 radicals impinging at normal angle of incidence and larger energies, we used both a fully hydrogen terminated surface and a surface with one unsaturated carbon site. The surface temperature prior to the radical bombardment was 0 K in all our simulations. For a more detailed description, see Ref. [18].

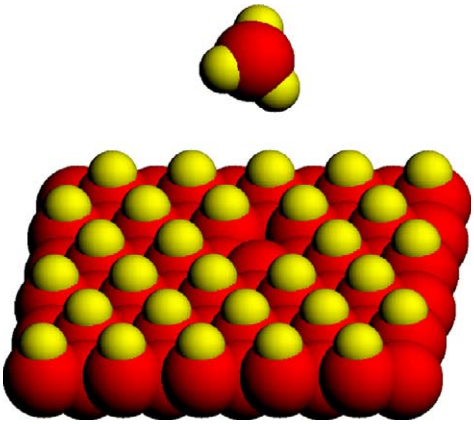

Fig. 1. Diamond (1 1 1) surface with one dangling bond. The CH_3 radical can be seen above the surface.

A CH_3 radical was placed above the diamond surface at a distance larger than the effective interaction range of the model. The radical, having translational velocity, rotational and vibrational motion corresponding to a selected temperature, was directed at a certain angle of incidence to a randomly chosen point on the surface. According to a stratified Monte Carlo (MC) strategy, the impact points on the surface were chosen randomly inside circular segments with a radial width of $\Delta r = 0.1$ Å each and centered at the dangling bond site (see Fig. 2). This has been shown to give accurate results more efficiently than conventional MC (i.e., completely arbitrary impact points on the whole surface) [19,20]. The impact points were chosen at a distance of 0.6 Å above

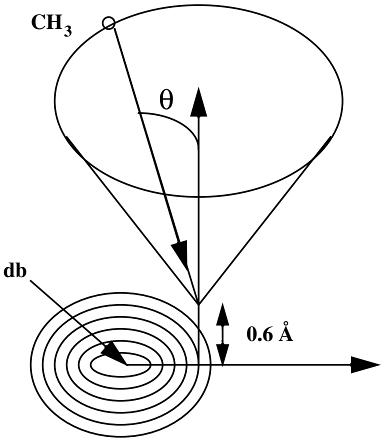

Fig. 2. Determination of the impact point for the CH_3 radical with angle of incidence, θ. The impact point is chosen randomly inside a circular segment centered on the dangling bond site, with a radial width $\Delta r = 0.1$ Å.

the surface, since test simulations had revealed that with this distance the obtained sticking cross-sections for direct impingement onto the dangling bond are at a maximum.

The maximum distance of an impact point from the dangling bond site was 3.0 Å. By running series of impact simulations for each segment and integrating over the corresponding sticking probabilities, the sticking cross-section was obtained.

Radicals which were bound to the dangling bond by covalent bonds at the end of the simulation were considered chemisorbed. The simulations were run for 500 fs after which the final bonding configuration was examined. Previous tests with longer simulation times had verified that 500 fs were adequate to determine the chemisorption of an incoming radical.

3. Results

3.1. Tight-binding simulations

In the simulations with varying angle of incidence of the incoming CH_3 radical, the most common reaction processes for the radical were

1. chemisorption of the radical onto the dangling bond,
2. formation of a volatile methane (CH_4) molecule by capturing a surface hydrogen which thereafter drifted away from the surface,
3. chemisorption of one hydrogen of the CH_3 radical onto the dangling bond after which the remaining CH_2 radical drifted away.

For increasing angles of incidence the number of cases in which CH_2 radicals were formed increased. At 67.5° angle of incidence this process dominated over the formation of CH_4 molecules. In the simulations in which the angle of incidence was 55° or larger, we also observed a few bonding configurations in which the incoming CH_3 radical fragmentated as one or two of its hydrogen atoms reacted with a surface hydrogen atom or the dangling bond. These bonding configurations were probably metastable, but the time scale of the simulations did not allow us to determine the lifetime of these states. Since these bonding configurations are scarce, they have no significant effect on the sticking cross-sections reported below within the statistical uncertainties.

The sticking cross-sections obtained vary between (10.4 ± 1.2) and (1.4 ± 0.3) Å^2 for normal and 67.5° angle of incidence, respectively (see Fig. 3). In these simulations the incoming methyl radical had an energy corresponding to 2100 K. The reason for this angular dependence can be partly explained by a simple geometric argument: the dangling bond is more exposed to the incoming radical at normal angle of incidence than at larger angle of incidence. If a methyl radical impinges at a large angle of incidence, it will more readily react with a surface hydrogen atom and form a volatile methane molecule than in the case of a normal angle of incidence.

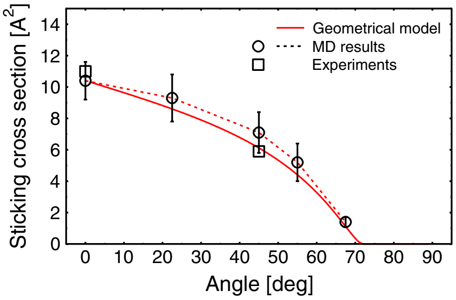

Fig. 3. Sticking cross-sections obtained when employing the tight-binding model in the simulations for the case with one dangling bond at the surface and different angles of incidence of the incoming methyl radical. The methyl gas temperature was 2100 K in all cases. The results are compared with sticking cross-sections obtained with the simple geometrical model, and with experimental data [13,14,21].

3.2. Classical simulations

The results of the classical model differ from those obtained with TB. The values obtained are a factor of 2–7 smaller depending on the angle. With the classical model we can, however, analyze the sticking profiles in more detail since, although the absolute values differ, better statistics can be achieved. The results of the classical model are plotted in Fig. 4.

For CH_3 radicals with higher energies, i.e., 1, 5, and 10 eV, we observed sticking even if we used the fully hydrogen-terminated surface. The sticking probability is

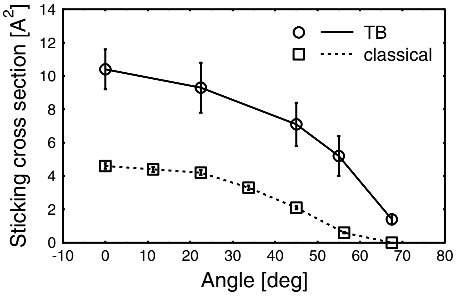

Fig. 4. Profiles of sticking probabilities obtained with the tight-binding model and the classical Brenner hydrocarbon potential for the case with one dangling bond at the surface and different angles of incidence for the incoming methyl radical. The methyl gas temperature was 2100 K in all cases.

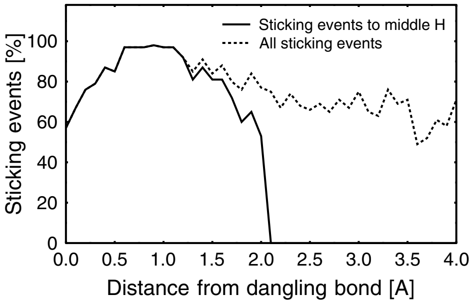

Fig. 5. Sticking events obtained with the classical Brenner hydrocarbon potential when using a fully hydrogen terminated surface and methyl radicals with energies of 10 eV. The line represents sticking events onto the middle hydrogen atom on the surface, while the dashed line represents all sticking events on the fully hydrogen terminated surface.

generally enhanced at higher energies. For radicals with energies corresponding to 2100 K we observed no sticking when using the fully hydrogen-terminated surface. Fig. 5 shows the number of sticking events obtained for a fully hydrogen-terminated surface and methyl radicals with energies of 10 eV.

4. Discussion

Our results show that the angle of incidence of the incoming methyl radical has a dramatic effect on the chemisorption probability. Depending on the angle of incidence, the sticking cross-section was observed to decrease from (10.4 ± 1.2) to (1.4 ± 0.3) Å^2 when the angle of incidence increased from 0° to 67.5°. This angular dependence can be explained by a simple radially symmetric geometrical model, in which the dangling bond is approximated by a cylinder with the surrounding hydrogen atoms at its edges. The incoming radical is assumed to move in a straight path, and it can only change its direction by scattering off the surface. Radicals which reach the bottom of the cylinder are assumed to stick always. The area of the bottom of this cylinder, on which the incoming radical is able to chemisorb onto the dangling bond, decreases with increasing angle of incidence. However, at oblique angles radicals scatter from the surface, shadowing part of the cylinder.

The sticking cross-section $\sigma(\theta)$ is thus the total area, A, that the radical can reach at the bottom of the dangling bond cylinder. This area, $A(r,h,\theta)$, will due to simple geometry become (see Figs. 6 and 7),

$$A(r,h,\theta) = 2vr^2 - 2ab, \tag{1}$$

where

$$v = \tan^{-1}\left(\frac{b}{a}\right), \tag{2}$$

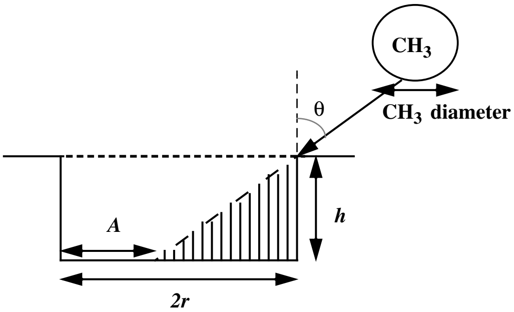

Fig. 6. Simple geometrical model for the sticking cross section at a certain angle θ of incidence of the CH_3 radical. The cross-section is calculated as the total area A at the bottom of the cylinder, where the incoming radical is able to chemisorb onto the dangling bond. The dangling bond is approximated to be surrounded by a cylinder with radius r and height h.

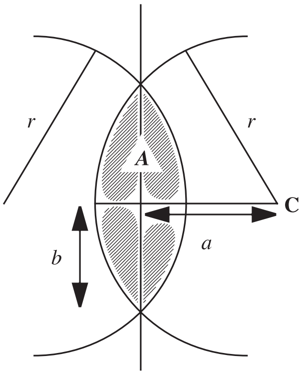

Fig. 7. Calculation of the total area A (shaded) at the bottom of the dangling bond cylinder, in which radicals are able to chemisorb onto the unsaturated carbon atom. This area consists of two segments of two circles. a is defined as the distance from the center of the cylinder, C, to the point of intersection in the middle of the two circle segments. b is defined as the distance from this intersection to the point of intersection between the two circles.

$$a = r - \frac{2r - h\tan(90-\theta)}{2} \tag{3}$$

and

$$b = \sqrt{r^2 - a^2}. \tag{4}$$

The height, h, and the radius, r, of the dangling bond cylinder (see Fig. 6) are chosen as follows. We first obtain an effective radius for the CH_3 radical by calculating the total volume of one carbon and three hydrogen atoms from their covalent radii (0.77 Å for C and 0.35 Å for H) and then computing the radius of a sphere with this volume. [2] The parameter h is then chosen as the sum of the effective radius of the CH_3 radical (≈0.85 Å) and the covalent radius of a hydrogen atom (0.35 Å). This choice has a reasonable physically motivation: if the carbon atom in the methyl radical gets down to the same level as the hydrogen atoms surrounding the unsaturated carbon site, there is nothing which prevents it from sticking. Otherwise it is assumed to be reflected. The parameter d, defined as $d = 2r$, is simply a fit to the sticking value for $\theta = 0$. This gives $r = 1.82$ Å and $h = 1.20$ Å.

The geometrical model yields excellent agreement with the sticking coefficients observed in our TB MD simulations (see Fig. 3). In particular, it gives a natural explanation why the sticking coefficient drops to zero below 90° angle of incidence.

We note that there are several processes related to the sticking for which our simple geometrical model does not account. First, the angle of rotation of the radical with respect to the surface has an effect on the sticking probability: a radical rotated such that its hydrogen atoms face the surface will react more easily with the surface as observed in our simulations. In the opposite case the methyl radical will more likely stick to the dangling bond. Second, some of the radicals that in the simple geometrical model would react with the dangling bond, can also react with the surface before this. For example, they can react with a surface hydrogen, resulting in the formation of a CH_4 molecule. Third, radicals have also been observed to chemisorb onto the unsaturated carbon atom when impinging at a rather large distance from the dangling bond due to a steering effect [18], contributing to a larger sticking cross-section. However, the fact that our radially symmetric model fits well the angular dependence, indicates that all these complications can be averaged out as a first approximation.

The values of sticking cross-sections obtained in our simulations compare well with experimentally determined values. In experiments by von Keudell et al. [13,14,21], sticking cross-sections of $\sigma = 11$ Å^2 for normal angle of incidence, and 5.9 ± 1 Å^2 for 45° angle of incidence were obtained from complex rate equations, employing various experimentally determined parameters. In these experiments the sample was not diamond-like carbon, but polymer-like hydrogenated carbon, for which the average number of neighboring carbon atoms is smaller and the shielding of the unsaturated carbon site can therefore be assumed to be quite low. Both of the experimental values agree well with our results for normal and 45° angle of incidence, (10.4 ± 1.2) and (7.1 ± 1.3) Å^2, respectively. Thus our findings strongly support the experimental evidence that the sticking process is angle dependent.

In the simulations with different kinetic energies of the incoming radical, we observed an increasing sticking cross-section for increasing energy of the CH_3 radical. Even for a fully hydrogen-terminated surface, 1 eV radicals stuck to the surface. When radicals had an initial energy corresponding to a temperature of 2100 K, no sticking was observed. In Ref. [22] no sticking was observed for fully hydrogen-terminated surfaces even when the incoming radical had energies of 1, 5, and 10 eV. The surface was diamond (1 0 0). One explanation for the increased sticking probability for radicals with higher energies is that the original molecule can break up, allowing the fragments to stick to the surface more easily. Hydrogen atoms at the surface are more likely to be sputtered when the radicals are impinging with higher energies, which also renders it easier for the radicals to chemisorb to the surface. These results imply that for different coordination of the surface one may have to use different values for the sticking cross section.

Often a single value for the sticking cross-section is used in the literature [23,24]. Our results suggest that several different values should be used depending on the angles of incidence and energies of the incoming radicals.

5. Conclusions

In the modeling of erosion and re-deposition for future fusion devices, the angle at which particles are impinging and reflected, is of great importance. Methyl radical chemisorptions on a single dangling bond on a diamond (1 1 1) surface was studied, employing both tight-binding and empirical hydrocarbon force models in molecular dynamics simulations. Our results show that the CH_3 radical chemisorption is affected by the angle of incidence of the radical and that the sticking of CH_3 at higher energies (1, 5, and 10 eV) occurs also in the case of a fully hydrogen-terminated (1 1 1) surface. The dependence of the sticking cross section on the angle of incidence can be described by a simple geometrical model.

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[2] While the exact values of the covalent radii used are somewhat arbitrary, we note that the quality of the fit is still good within the uncertainties even for values of the radii differing by some tens of percents.

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