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Fundamental Energy Transfer Mechanisms in High Temperature Phonon-Mediated Gas-Surface Interactions

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2019 AFOSR Annual Report: Desorption kinetics of O and CO from Graphitic Carbon Surfaces

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Abstract.

The desorption of O/CO from graphitic carbon surfaces is investigated using a one-dimensional model describing the adsorbate interactions with the surface phonon bath. The kinetics of desorption are described through the solution of a master equation for the time-dependent population of the adsorbate in an oscillator state, which is modified through thermal fluctuations at the surface. The interaction of the adsorbate with the surface phonons is explicitly captured by using the computed phonon density of states (PDOS) of the surface. The coupling of the adsorbate with the phonon bath results in the transition of the adsorbate up and down a vibrational ladder. The adsorbate-surface interaction is represented in the model using a Morse potential, which allows for the desorption process to be directly modeled as a transition from bound to free (continuum) state. PDOS is an important input within the phonon-induced desorption (PID) model, which is a property of the material and the lattice and is highly sensitive to the presence of defects. The effect of random surface defects, etch pits, and adsorbates on the PDOS is considered in the present work. The presence of defects systematically shifts the phonons to lower frequencies and broadens the distribution which changes the phonon frequency modes available for adsorbate coupling at the surface. This PDOS including defects will be used within the PID model to predict the desorption rate constant.

Nomenclature

D	Diameter
E	Energy
g	Phonon density of states
H	Hamiltonian, Height
P	Probability
Ph	Phonons
k	Rate constant
t	Time
V	Potential
v	Velocity
ω	Frequency
θ	Surface coverage
ρ	Density matrix, Density of defects
τ	Characteristic time
\hbar	Planck's constant
des	Desorption
MD	Molecular Dynamics
$PDOS$	Phonon density of states

PID Phonon induced desorption
TPS Thermal protection system

Introduction

Thermal protection systems (TPS) of space vehicles are exposed to extreme environments during hypersonic (re)entry. Extreme heat loads as well as the reactive interactions of the materials with the partially dissociated atmospheric gases of N_2 , O_2 , NO , N , and O lead to the alteration of the surface and the boundary layer flow surrounding the vehicle. Accurate modeling of ablation processes and prediction of the heat loads and recession of the TPS materials are critical to the space vehicle design. Precise knowledge of the gas-surface interactions and chemical reactions at the surface of the TPS materials is required.

Many commonly used TPS materials consist of a carbon-based substrate such as FiberForm[1] and carbon weaves.[2] The primary source of carbon ablation at lower temperatures is through oxidation, specifically due to dissociated atomic oxygen.[3] Recent studies have elucidated that the oxidation products CO and CO_2 are formed as a result of thermal processes on the surface.[4, 5, 6, 7] Desorption of thermal products from the substrate occur through the interaction with the phonon bath on the surface. Several finite-rate reaction models exist for the air-carbon system,[3, 8, 9, 10, 7] developed using results from numerous experimental studies.[11, 12, 13, 14, 15, 16, 4] However, all of these models characterize the rate of desorption only as a function of temperature. mesoscale description of the surface energetics which participate in, and promote, the desorption of surface adsorbates and oxidation products is currently lacking.

The density and energy of phonons present at the surface is described using the phonon density of states (PDOS). The phonon density of states (PDOS) is a fundamental property of the material and the lattice, which characterizes the distribution of allowed vibrational modes. The PDOS can provide information regarding heat storage (heat capacity), energy transport (lattice thermal conductivity), gas-surface interactions,[17] and surface chemistry. The PDOS shows significant variation in the presence of adsorbates, random surface defects, and etch pits (formed due to oxidation). Thus, the surface phonon density of states (PDOS) is expected to evolve during the course of ablation.

In this study, a rigorous theoretical model is used to describe the desorption of adsorbed atoms/molecules due to interaction with the surface phonons.[18] The adsorbate-surface interaction (oscillator) is coupled with the phonon bath leading to excitations and de-excitations along the vibrational 'ladder'. This process can be described as a random walk using the Markoffian approximation and first order master equation for the probability in a given state. This random walk continues till the interaction energy becomes sufficient to break the adsorbate-surface bond leading to desorption. Traditionally simple harmonic oscillators (SHO) are used to describe the vibrational bond.[19] However, within the harmonic approximation, the bond breaking is not inherently captured and has to be imposed, typically as a vibrational threshold beyond which desorption is assumed. In addition, the energy spacing between the oscillator levels are constant within the SHO approximation, which becomes a poor approximation particularly at the higher energy levels. Furthermore, the SHO allows only mono-quantum jumps, which again breaks down at higher energy levels. The Morse potential provides a much better approximation to the adsorbate surface bond with decreasing energy gaps at higher levels, finite probability of multi-quantum transitions and a clear threshold between the free and bound states. Thus, the Morse potential is employed within this framework to describe the adsorbate-surface interaction potential.[18]

The transition matrix describing the probability of transition between the oscillator energy levels accounts for the PDOS present at the surface. The coupling of the oscillator jump with each of the phonon modes is summed to give the final transition rate. Thus, introducing a realistic PDOS within the calculation of the transition matrix ensures the accurate description of the transition rates and thereby the desorption rate. The time between successive transitions (jumps) of a particular surface-adsorbate oscillator within the vibrational ladder is known to be much higher than the characteristic vibrations of the adsorbate and surface atoms.[20] This fact allows us to treat these transition processes as rare events and use Markoffian random walks to analyze them. The desorption process is treated as first order and a Master equation is used to derive the final rate constant.[18]

The PDOS is an important input within the phonon-induced desorption (PID) model. The vibrational modes present in the system is greatly altered when the distribution of the substrate atoms is changed. Molecular Dynamics (MD) is used to investigate the effect of the presence of (i) adsorbates, (ii) random surface defects, and (iii) etch pits (formed due to oxidation) on the PDOS of the system.

Phonon-induced Desorption Model

In order to describe the desorption of adsorbed atoms/molecules from the surface due to the interaction with the phonon bath, we use the theory by Efrima *et al.*[18] Within this theory, we start by describing the Hamiltonian of the system which consists of three parts: lattice (l), particle (p) and interaction (I).[18]

$$H = H_l + H_p + H_I \quad (1a)$$

$$H_l = \hbar \sum_{\lambda} \omega_{\lambda} b_{\lambda}^{\dagger} b_{\lambda} \quad (1b)$$

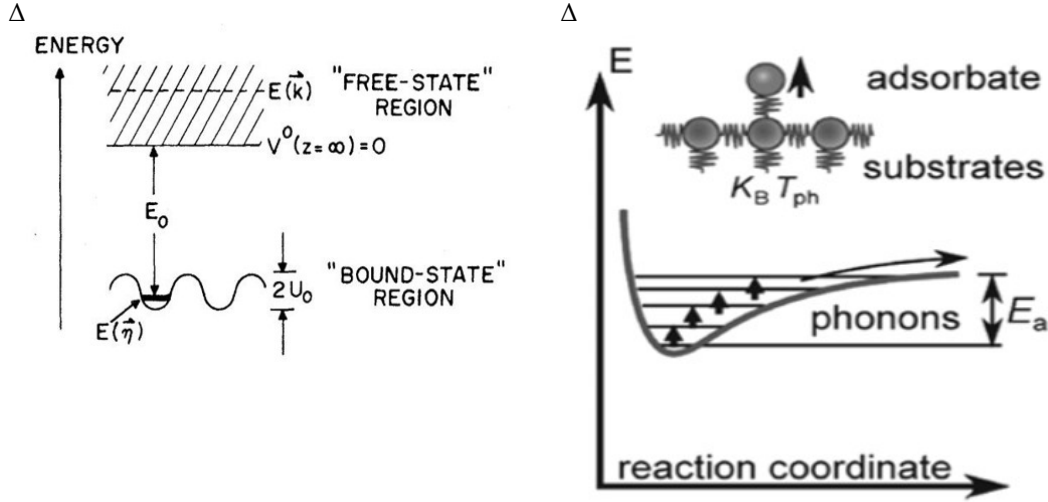
$$H_p = K_p + \langle V(\mathbf{Q}; z) \rangle \quad (1c)$$

$$H_I = V(\mathbf{Q}; z) - \langle V(\mathbf{Q}; z) \rangle \quad (1d)$$

The lattice Hamiltonian is described over the phonons (λ) in the system. ω is the phonon frequency while b and b^{\dagger} are the corresponding creation and annihilation operators. K_p is the kinetic energy of the particle, $V(\mathbf{Q}; z)$ is the interaction potential between the adsorbate and the surface atom, and $\langle V(\mathbf{Q}; z) \rangle$ is the thermal average of the lattice-particle interaction over an equilibrium phonon distribution. \mathbf{Q} is a 3N dimensional denoting the position of the N lattice atoms and z is the position of the adsorbed particle. $H_l + H_p$ is the zero-order part of the Hamiltonian while H_I describes the fluctuations in the system. The reason for the addition of the average quantity $\langle V(\mathbf{Q}; z) \rangle$ is to ensure that the average of the interaction Hamiltonian is zero which avoids the buildup of secular terms in the subsequent derivation.[18] The adsorbate-surface interaction potential is described using a Morse potential:

$$V(\mathbf{Q}; z) = D \left\{ e^{-2\alpha(z - \mathbf{Q}_0 - \mathbf{u} - r_0)} - 2e^{-\alpha(z - \mathbf{Q}_0 - \mathbf{u} - r_0)} \right\} \quad (2)$$

where \mathbf{Q}_0 is the equilibrium lattice position and \mathbf{u} is the displacement of the atoms. α and r_0 are the Morse potential parameters. The Morse potential is an excellent approximation for the adsorbate-particle interaction since it captures bond breaking (desorption), multi-quantum jumps, and decreasing energy spacing at higher energies. Thus, the definition of the bound states and free state within the model is straightforward and the ladder climbing pathway of desorption can be captured along with multi-quantum jumps (Fig. a).



The rate coefficients for desorption are ultimately obtained through the generalized master equation describing the time evolution of the probability of the adsorbates being present in a particular state $|n\rangle$ at time t : [18]

$$\frac{\partial P_n}{\partial t} = - \sum_m W_{n \rightarrow m} P_n(t) + \sum_m W_{m \rightarrow n} P_m(t) - \int W_{n \rightarrow \epsilon} P_n(t) d\epsilon \quad (3)$$

The first term on the right side of the equation describes the transitions from state n to all other states, while the second term represents the all the transitions leading to the state n . The last term denotes the depletion from state n to the continuum state ϵ (desorption). Expressing $P_n(t)$ in terms of the reduced density matrix:[18]

$$P_n(t) = \langle n | \rho_r(t) | n \rangle. \quad (4)$$

Here, $\rho_r(t)$ is the reduced density matrix of the particle which is defined as summation over all phonon state $|Ph\rangle$:

$$\rho_r(t) = \sum_{Ph} \langle Ph | \rho(t) | Ph \rangle. \quad (5)$$

The density matrix $\rho(t)$ of the lattice-particle system satisfies the Liouville equation:[18]

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H, \rho(t)] \quad (6)$$

Now substituting the Hamiltonian and $\rho(t)$ from the previous equations, we get the following expression for rate of probability:[18]

$$\begin{aligned} \frac{\partial P_n(t)}{\partial t} &= \int_0^t \sum_m K_{nm}(s) P_m(t-s) \\ K_{nm}(s) &= \frac{-2}{\hbar^2} \text{Re} \left\{ \sum_k e^{i\omega_{mk}} \langle (H_I(s))_{mk} (H_I)_{km} \rangle \delta_{nm} - e^{-i\omega_{nm}s} \langle (H_I(s))_{mn} (H_I)_{nm} \rangle \right\} \end{aligned} \quad (7)$$

Using a Markoffian approximation, the $K_{nm}(s)$ is assumed to decay on a time scale that is small enough such that the value of $P_n(t)$ is constant, resulting in[18]

$$\int_{-\infty}^t K_{nm}(s) P_m(t-s) ds \cong P_m(t) \int_{-\infty}^{\infty} K_{nm}(s) ds \cong W_{nm} P_m(t) \quad (8)$$

with

$$\begin{aligned} W_{nm} &= -\delta_{nm} \sum_k W_{m \rightarrow k} + W_{m \rightarrow n} \\ W_{n \rightarrow m} &= \frac{2}{\hbar^2} \text{Re} \left\{ \int_0^{\infty} \langle (H_I(s))_{mn} (H_I)_{nm} \rangle \right\} \end{aligned} \quad (9)$$

Assuming a first order master equation, $P(t)$ can be expressed as:[18]

$$P(t) = e^{Wt} P(0) \quad (10)$$

Using this, the average time between two successive desorption events can be calculated as:[18]

$$\langle \tau \rangle = \sum_n \int_0^{\infty} P_n(t) dt = \sum_n (W^{-1} P(0))_n \quad (11)$$

The desorption rate is given by the inverse of the average time.

$$k_{des} = \langle \tau \rangle^{-1} \quad (12)$$

Phonon Density of States (PDOS) of Defective Carbon Surfaces

The PDOS is calculated using the LAMMPS Molecular Dynamics (MD) software[21] through the determination of the velocity autocorrelation function.

$$g(\omega) = \int \frac{\langle v(t) \cdot v(0) \rangle}{\langle v(0)^2 \rangle} e^{i\omega t} dt \quad (13)$$

The ReaxFF inter-atomic potential is used to describe the C-C, C-O, and C-N interactions. ReaxFF potential is an empirical potential with a general form for various types of forces.[22]

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaal} + E_{Coulomb}. \quad (14)$$

The various parameters within this form are parameterized against an extensive quantum chemical database. The value of the parameters used in this study are taken from Shin *et al.*[23] The C-C bond parameters used in this work were recently re-parameterized to better capture the properties of the solid carbon phase.[24] The ReaxFF potential and the corresponding set of parameters were chosen because they can capture both short and long range bonds within solid carbon[25] as well as the reactive interaction between the carbon and adsorbate atoms.[26]

Surface and bulk PDOS

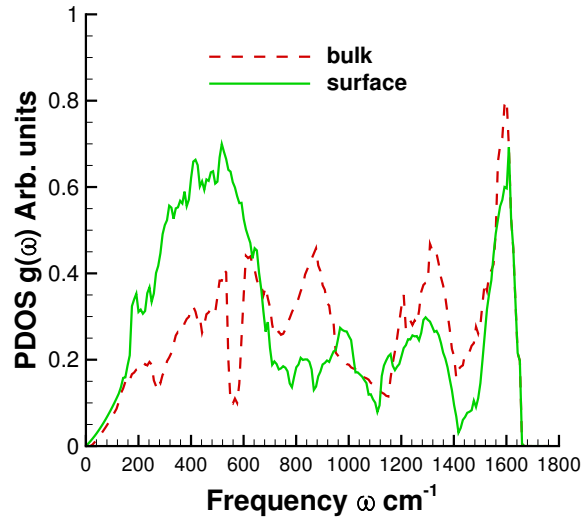


FIGURE 1: PDOS of surface and bulk carbon graphite lattice.

Before investigating the effect of surface defects on the PDOS, first the difference between the surface and bulk PDOS is analyzed. Atoms at the surface have higher energies and can move more freely due to the absence of atoms above them. Fig. 1 presents the PDOS for surface and bulk carbon graphite lattice. The difference between them is predominantly along the surface normal (lower energies). The surface PDOS has increased concentration of phonons at the lower energies and decreased concentration at higher energies compared to the bulk. Other characteristics such as the final peak are preserved in the surface PDOS.

Effect of adsorbates

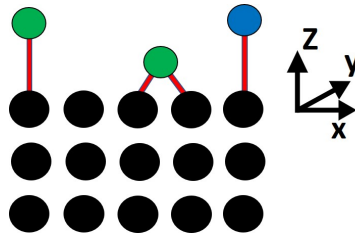


FIGURE 2: Schematic illustration of the side view of the lattice with adsorbates.

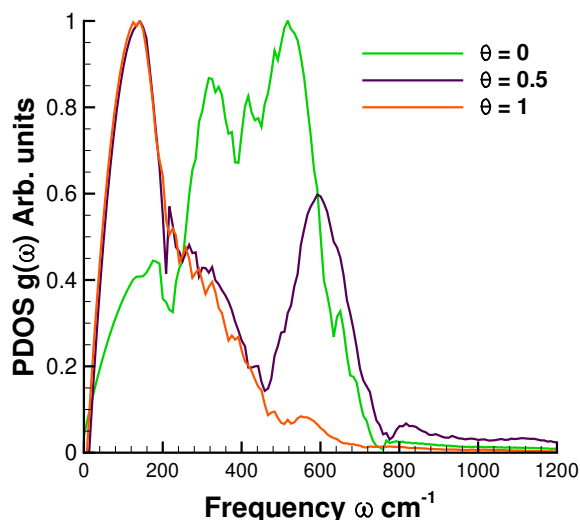


FIGURE 3: PDOS along the surface normal (z-direction) of carbon graphite surface with surface coverage of (θ) of 0, 0.5, and 1.

Next, the effect of adsorbates on the PDOS is investigated. The adsorbates (oxygen atoms) are randomly placed on a pristine graphite surface at the top sites (exactly on top of the carbon atoms), and allowed to relax before the PDOS is computed (Fig. 2). The PDOS of surface covered with adsorbates is characterized as a function of the surface coverage at three values of 0 (empty), 0.5, and 1 (full monolayer). The presence of adsorbates will alter the vibrations predominantly along the z-direction. The adsorbates are expected to have a significant effect on the PDOS since the inter-layer bonding between the carbon graphite layers is weak. The results of this study is shown in Fig. 3 which plots the PDOS along the surface normal (z-direction). First we observe that the presence of adsorbates shifts the PDOS modes towards lower frequencies. In addition, we notice that the PDOS peaks of the adsorbate covered lattice are also broad compared to the PDOS of empty surface.

Effect of random surface defects



FIGURE 4: Schematic illustration of the side view of the lattice with random surface defects.

The effect of random defects present at and near the surface on the PDOS is investigated next. The random surface defects are created on the graphite carbon by irradiation with low energy ions. The surface defects are characterized based on the depth (height H) of the defective region and the areal density (number of defects per unit area ρ) as shown in Fig. 4. Pristine graphite lattice is bombarded with ions of different energies to obtain the desired defect configurations of different depths and densities. The effect of varying both the depth and density of the defective region on the PDOS is studied (as shown in Fig. a). It is observed that the presence of defects broadens the peak within the PDOS. Additional modes at very low energies are also observed for the defective surfaces. In general, the presence of surface roughness systematically shifts the PDOS modes from higher frequencies to lower frequencies. However, additional densities at frequencies greater than the final peak of the pristine system is also observed. This is most likely a result of the close packing of defects at certain regions.

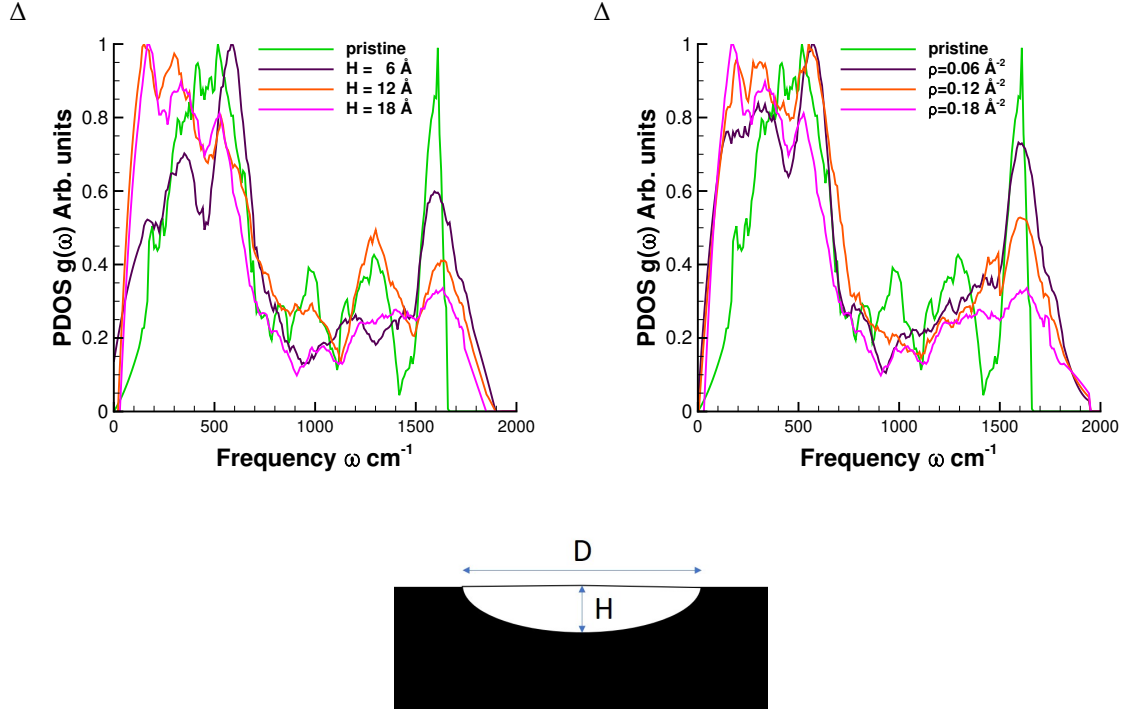


FIGURE 5: Schematic illustration of the side view of the lattice with an etch pit.

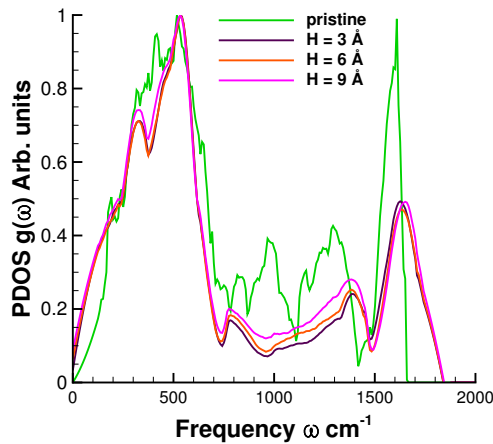
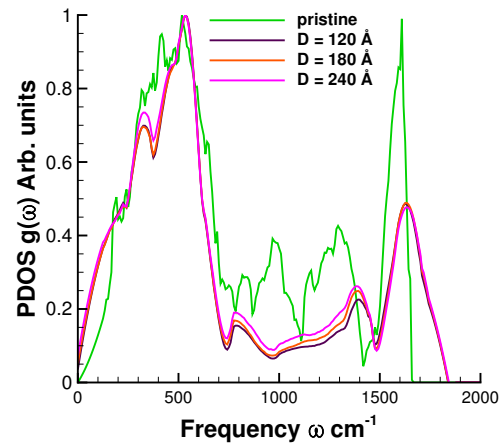
Effect of etch pits

Finally, the variation in PDOS due to the presence of etch pits is analyzed. The etch pits are formed due to oxidation processes and are ellipsoidal in shape.[27] These etch pits are characterized based on the depth (or height H) and diameter of the ellipsoid as shown in Fig. 5. The diameter of these etch pits are usually much higher than the height (or depth). This is because the oxidation along the lateral direction is much faster than along the normal direction.[27] These etch pits are directly obtained in MD by removing the atoms within the ellipsoidal region of pristine graphite lattice. The effect of varying height and diameter of the etch pit on the surface PDOS is presented in Fig. a). The values of D and H are chosen such that the ratio of $D:H$ is of the same range as found in the experiments.[27, 28, 29] Similar to the case of random surface defects, the presence of etch pits tend to broaden the PDOS modes and more rounded peaks are observed. Also the PDOS modes are shifted towards lower frequencies due to the etch pits. Again, additional densities at frequencies greater than the final peak of the pristine system is observed similar to the case of random surface defects. However, the PDOS is found to be insensitive to the geometry of the etch pits resulting in very similar density of states for a wide range of D and H values.

Conclusions and Future Work

A rigorous theoretical model based on the interaction of the adsorbed atoms/molecules with the phonon bath at the surface is used to describe the desorption process of the adsorbates. The interaction of the adsorbate with the surface phonons is explicitly captured by using the PDOS of the surface. The adsorbate-surface interaction is represented using a Morse potential, which allows for the desorption process (transition from bound to free state) to be directly modeled as the interaction energy reaches beyond a threshold level described by the potential. This model is one-dimensional and considers the interaction only along the surface normal direction. The coupling of the adsorbate with the phonon bath results in adsorbate-surface bond to jump within the interaction energy ladder. Both mono and multi-quantum jumps are considered within this framework. The desorption process is treated as a Markoffian process and a first order Master equation is used to derive the final rate constant.

The surface PDOS is an important input within the PID model. The results of the detailed MD study suggests

Δ  Δ 

that the PDOS varies widely as a result of defects present within the system. In general any kind of defect tends to broaden the phonon distributions resulting in rounded peaks. Further, the PDOS is consistently observed to be shifted towards lower frequencies leading to lower densities at higher energies. The effect of the adsorbates is predominantly along the surface normal direction. In the case of random surface defect, the PDOS was found to be sensitive both the presence and configuration of the defects. However, for the etch pits, the PDOS is observed to be only dependent on the presence of the etch pit and insensitive to the exact configuration.

As part of the future work, the PID model described here will be used to compute the desorption rate of O and CO from realistic carbon surface for a variety of different defect configurations. The PDOS will be calculated using MD for the particular type of bonding (surface-adsorbate) and defect configuration. The type of bonding will be determined based on the carbon-oxygen functional groups that are most stable on the surface which desorb from the surface in the form of O and CO.[7] Currently the PID model describes the adsorbate as a single particle and does not account for the internal structure of the adsorbate (in the case of a molecule). The internal degrees of freedom will be included as a part of the particle Hamiltonian to accurately describe the energy transfer processes, which in turn affects the transition and desorption rates. Furthermore, it is observed that the peak of the carbon PDOS occurs at a frequency of 1600 cm^{-1} , which is very close to the vibrational frequency of the CO bond (2000 cm^{-1}). This could result in resonant transfer of energy from the surface phonons directly to the vibrational model of CO leading to excited vibrational states in the desorbing molecules. The current model will be extended to characterize and provide the final internal energy distribution of the desorbing molecule.

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