



ISTITUTO
PER LA SCIENZA
E TECNOLOGIA
DEI PLASMI

Molecule interactions with surfaces

Maria Rutigliano

CNR-ISTP, Bari, Italy

Online Low Temperature Plasma (OLTP) seminar, November 21, 2023



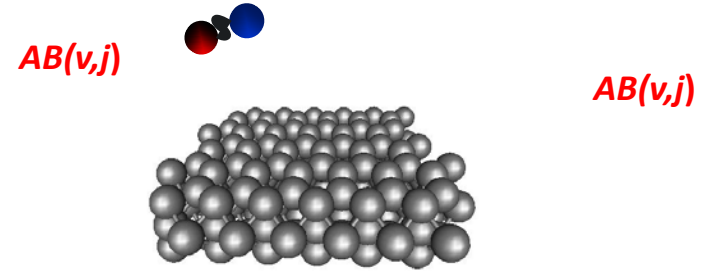
maria.rutigliano@cnr.it

OUTLINE

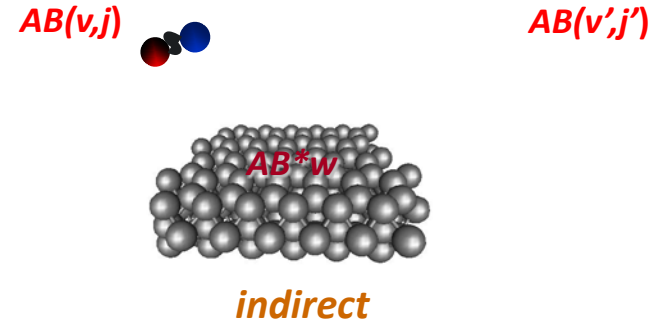
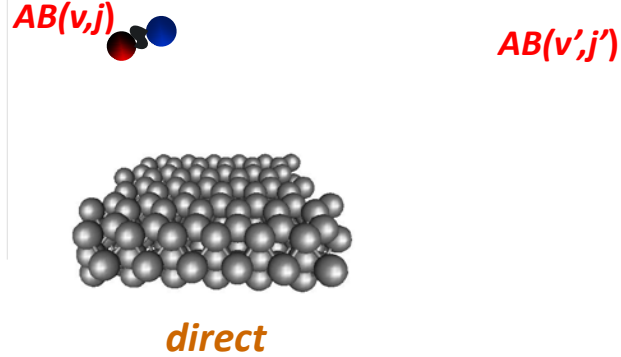
- Plasma-Surface Processes
- Surface Activity
- Surface reactions modelling
- Molecular Dynamics Approach
- Collisional Database
- Some Results
- Final Remarks

PLASMA SURFACE PROCESSES: I. MOLECULE SCATTERING

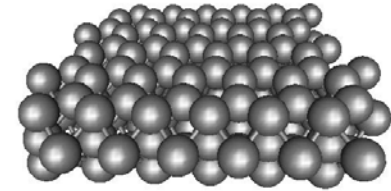
Elastic Scattering



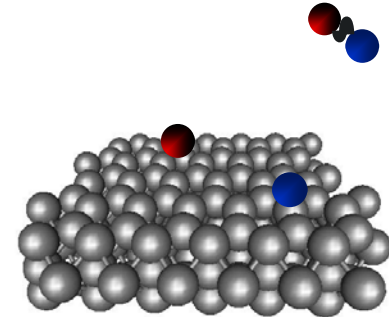
Inelastic Scattering



Molecule Adsorption

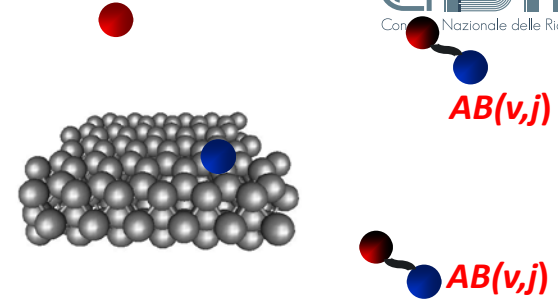


Molecular Dissociative Adsorption

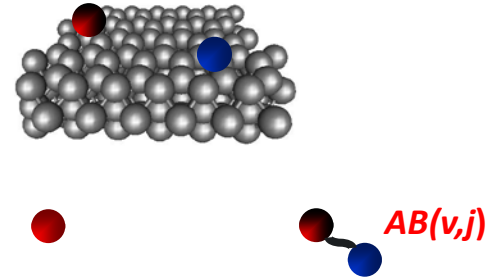


PLASMA SURFACE PROCESSES: II. ATOM RECOMBINATION

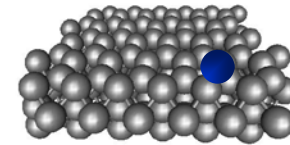
Eley-Rideal mechanism



Langmuir-Hinshelwood mechanism



Hot atom mechanism

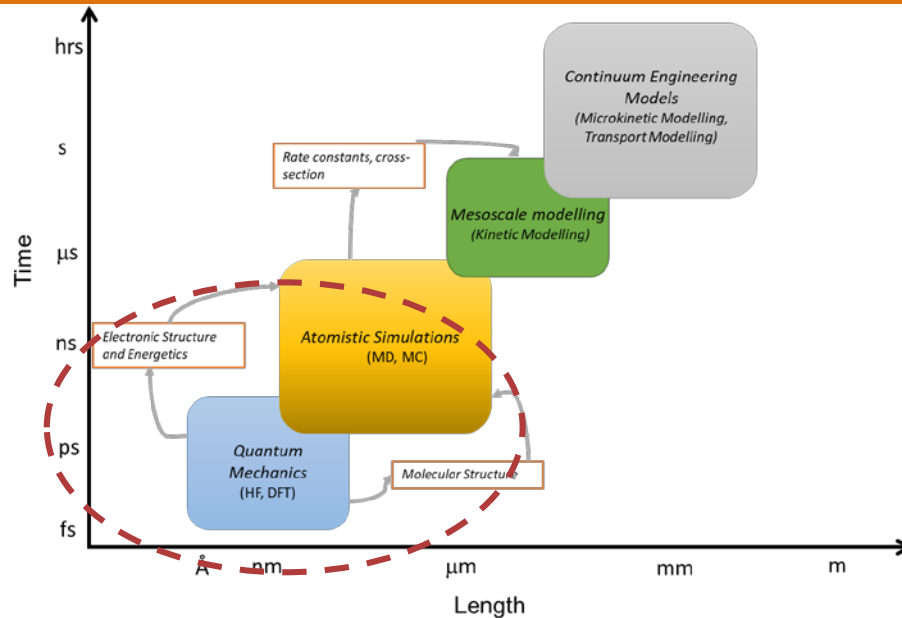


PLASMA SURFACE PROCESSES: SUMMARY

$A_{\text{gas}} + w$		
	$A_{\text{gas}} + w$	<i>atomic elastic/inelastic scattering</i>
	$A_{\text{ads}} + w$	<i>atomic adsorption</i>
	$A^{\pm} + w$	<i>ion formation/scattering</i>
$[AB(v_i; j_i)]_{\text{gas}} + w$		
	$[AB(v_i; j_i)]_{\text{gas}} + w$	<i>molecule elastic/inelastic scattering</i>
	$[AB(v_i; j_i)]_{\text{gas}} * w$	<i>molecule adsorption</i>
	$A_{\text{ads}} * w + B_{\text{ads}} * w$	<i>molecule dissociative adsorption</i>
	$A_{\text{ads}} * w + B_{\text{gas}}$	<i>atom adsorption/desorption</i>
	$A_{\text{gas}} + B_{\text{gas}} + w$	<i>atom scattering</i>
$A_{\text{gas}} + B_{\text{ads}} * w$	$[AB(v; j)]_{\text{gas}} + w$	<i>Eley-Rideal atom recombination</i>
	$[AB(v; j)]_{\text{ads}} + w$	<i>molecule adsorption</i>
	$A_{\text{gas}} + B_{\text{ads}} * w$	<i>atom adsorption/desorption</i>
	$A_{\text{ads}} * w + B_{\text{gas}}$	<i>atom adsorption/desorption with exchange</i>
	$A_{\text{ads}} * w + B_{\text{ads}} * w$	<i>atom adsorption</i>
	$A_{\text{gas}} + B_{\text{gas}} + w$	<i>atom scattering</i>
$A_{\text{ads}} * w + B_{\text{ads}} * w$	$[AB(v; j)]_{\text{gas}} + w$	<i>Langmuir-Hinshelwood atom recombination</i>
	$[AB(v; j)]_{\text{ads}} + w$	<i>molecule adsorption</i>
	$A_{\text{gas}} + B_{\text{ads}} * w$	<i>atom adsorption/desorption</i>
	$A_{\text{gas}} + B_{\text{gas}} + w$	<i>atom scattering</i>

HIERARCHICAL APPROACH TO MODELING SURFACE REACTIONS

The modelling of surface reactions can be described accurately by a hierarchy approach including different computational methods at different time and length scales that may be linked together to answer questions spanning from the atomic to the macroscopic level.



By solving Schrödinger equation enables to obtain:

- ❖ *molecular properties*
- ❖ *adsorption energies*
- ❖ *activation barriers for individual elementary reaction steps*

Methods

- *semiempirical*: ZINDO, MINDO
- *accurate*: Hartree-Fock(HF), Configuration Interaction (CI), Møller-Plesset perturbation method (eg. MP2), Density Functional Theory(DFT)

Choice of method is dictated by the competition between speed and accuracy

Models

Cluster: small atom number to represent local environment around the active site

Embedding: a small region is treated QM while classical approach is used for long range interactions

Slab: periodic boundary conditions to simulate infinite solids

Molecular Dynamics

numerical solution of motion equation in the framework of different collision methods

Input

Chemical composition and structure of the heterogeneous system

Interaction Potential Function between the species involved in the reaction

most critical aspect of
surface reactions

Usually pairwise additive potential computed from accurate ab-initio data or empirical potential functions, which have been parametrized to reproduce experimental data.

Output

Surface processes probabilities, Energetics reactions, Diffusion coefficients, Activation energies for diffusion

The number and complexity of the effects and phenomena to account for MD simulations of particle collisions with surfaces is high .

CLASSICAL

Newton motion equations

Computationally heavy for the high number of atoms of the solid to take into account

→ [GLE approach](#)

SEMICLASSICAL

methods that are neither fully classical nor fully quantum. Many approaches have been proposed in literature (see e.g. [H.-D. Meyer, S. C. Park, G. D. Billing](#))

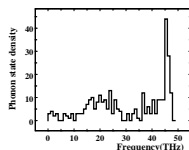
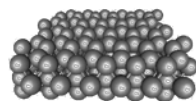
QUANTUM

Schrödinger motion equation

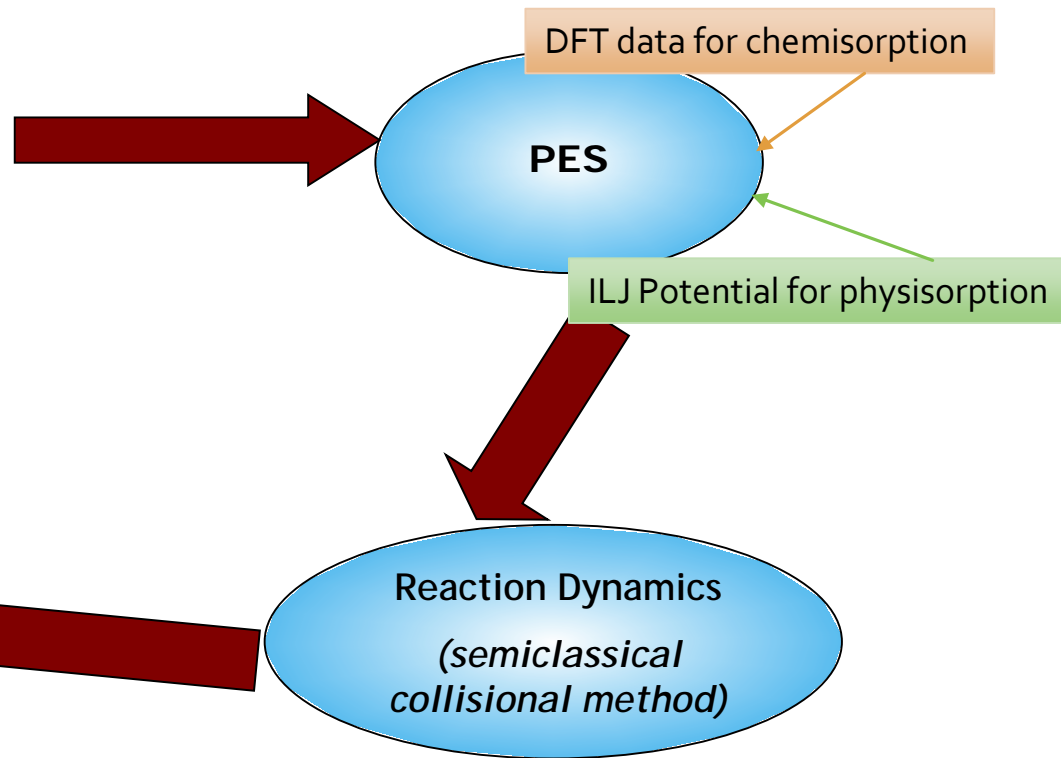
Molecule-surface interaction the number of coupled equation increases for the inclusion of molecule internal degrees of freedom.

Today with modern supercomputers and parallelisation techniques a full dimensional quantum treatment of molecule/surface interaction can be affordable.

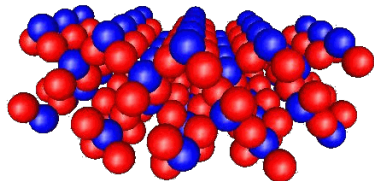
3D 'model'
Surface
&
Lattice dynamics



Collisional Data

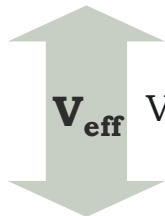


THE SEMICLASSICAL COLLISIONAL METHOD



*Classical system
gas-phase particles*

Hamilton 's equations



V_{eff}

$$V_{\text{eff}}(r, R | t, T_S) = \langle \Psi_{\text{ph}}(t, T_S) | V_{\text{int}}(r, R) | \Psi_{\text{ph}}(t, T_S) \rangle$$



*Quantum system
phonons*

TdS equations

$$H = \frac{1}{2} \sum_{i,\alpha} \frac{P_{i\alpha}^2}{m_i} + V(r) + V_{\text{eff}}(r, R, t, T_S) + \Delta E_{\text{ph}}$$

G.D.Billing "Dynamics of molecules surface interaction", Wiley 2000

IMPROVED LENNARD-JONES POTENTIAL

$$V_{ILJ}(R) = \varepsilon \left[\frac{m}{n(R) - m} \left(\frac{R_m}{R} \right)^{n(R)} - \frac{n(R)}{n(R) - m} \left(\frac{R_m}{R} \right)^m \right]$$

size repulsion

dispersion attraction

$$n(R) = \beta + 4 \left(\frac{R}{R_m} \right)^2$$

ε potential well depth, R_m potential well location, β depends on the “hardness” of the two partners. $m=6$ for the neutral-neutral interactions.

$$C_6 = \varepsilon \cdot R_m^6$$

$$C_3 = \frac{\pi C_6 \rho}{6}$$

understanding

the dynamics pathways underlying
atom/molecule-surface interactions

predicting

the surface activity as a function of
molecular properties and
behaviours of the solid substrate

determining

accurate **database of collisional coefficients** *to be used*
in continuum engineering modelling

COLLISIONAL DATA FOR SURFACE PROCESSES

- ◆ $S_0(E_{\text{kin}} | \{.\} | v, j | T_s)$ *state-selected sticking probability*
- ◆ $\gamma(v, j | T_s)$ and $\gamma(T_s)$ *state-to-state and global recombination coefficient*
- ◆ $\beta(T_s)$ *energy accommodation coefficient*
- ◆ $N(v, j)$ *roto-vibrational distribution in the final states*
- ◆ $I(\vartheta, \varphi / T_s)$ *angular distribution in intensity and energy*
- ◆ τ_{ad} *lifetime and probability for ads. and ad./des.*

Molecule interactions with surfaces:
the role of long-range interactions

H_2 , O_2 , N_2 , CO interaction with graphite

DISPERSION COEFFICIENTS

Chemical species	Surface	C_6 (eVÅ ⁶)	C_3 (meVÅ ³)	C_3 (meVÅ ³) ¹
H ₂	CARBON	9016	535	520 ± 30
H	CARBON	6384	379	380 ± 17
O ₂	CARBON	10228	1213	1157
O	CARBON	10327	612	
N ₂	CARBON	11333	1344	1259
N	CARBON	13502	801	
C (in CO)	CARBON	14271	846	
O (in CO)	CARBON	8955	531	
C	CARBON	17553	1041	
O	CARBON	10396	616	

¹ G. Vidali, G. Ihm, H. Y. Kim, M. W. Cole, Surf. Sci. Rep. 1991, 12, 133

M.R. and F. Pirani, 2023 *submitted*

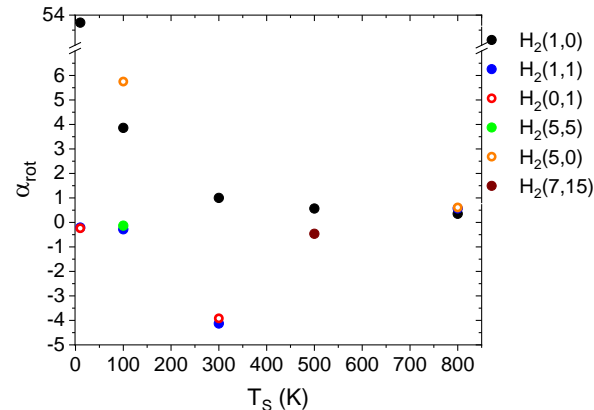
H₂/GRAPHITE

- ✓ Reaction mechanism: **direct**
- ✓ v_i is preserved for low initial vibrational states
- ✓ Reaction Dynamics determined by T-R coupling and controlled j_i that determine the fate of trajectories
- ✓ Selectivity in the final rotational states ($j_i = 0$ peak on $j_f = 1$, $j_i \neq 0$ peak in $j_f = j_i$)
- ✓ No surface temperature effect

✓ $\alpha_{\text{vib}} = 0$ *except for*

H₂(5,5) at $T_S = 100\text{K}$ $\alpha_{\text{vib}} = -1.56 \cdot 10^{-2}$

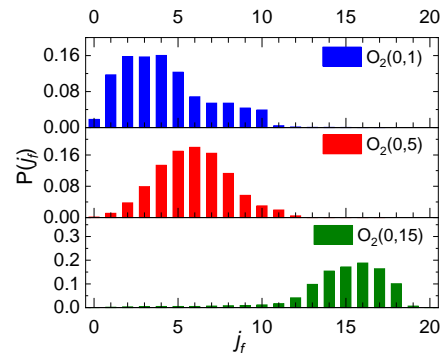
H₂(7,15) at $T_S = 500\text{K}$ $\alpha_{\text{vib}} = 0.27$



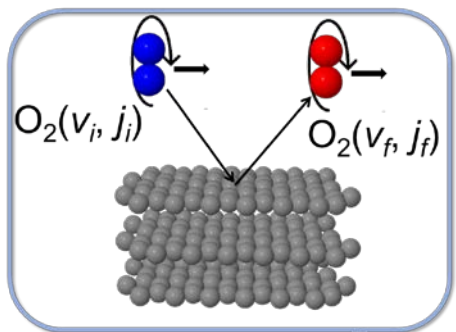
O₂, N₂ /GRAPHITE

- ✓ Reaction mechanism: direct indirect
- ✓ v_i is preserved, except for high initial vibrational states
- ✓ Surface temperature effect appreciable at very low collision energy
- ✓ Reaction dynamics dominated by T-R coupling
 - ↳ for low-medium E_{coll} is also triggered by the energy exchange with the surface phonons

- ✓ Final rotational states exhibit non-Boltzmann distributions

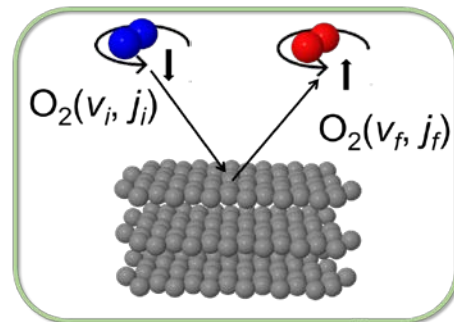


Trajectory analysis reveals that there is an important **SELECTIVITY** with regard the excitation/de-excitation of rotational levels which is controlled by the initial orientation of the molecular rotation axis (or rotation plane) with respect to the surface.



cartwheel-type motion

$$j_f > j_i$$



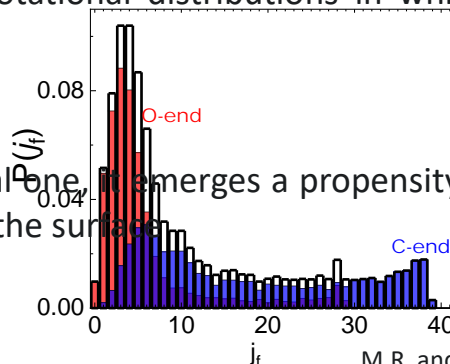
helicopter-type motion

$$j_f \approx j_i$$

For **NITROGEN**, the motion selectivity with respect to the initial rotational configuration, no longer exists under thermal collision energy conditions.

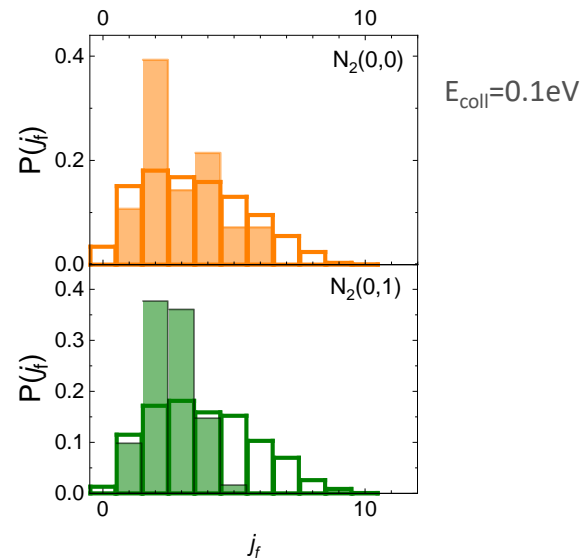
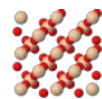
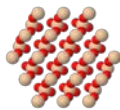
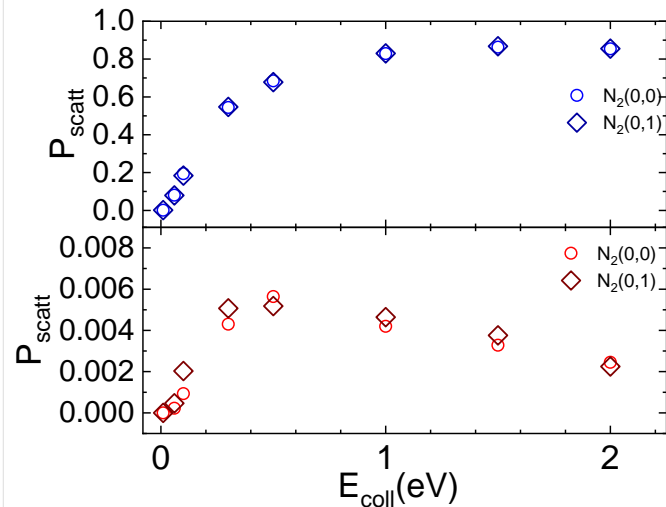
M.R. and F. Pirani, *J. Phys. Chem. C* **2019**, 123, 11752; *J. Phys. Chem. C* **2020**, 124, 10470

- ✓ Reaction mechanism: direct
indirect
- ✓ v_i is preserved
- ✓ **SELECTIVITY** with regard the excitation/de-excitation of rotational levels controlled by the initial orientation of the molecular rotation axis
- ✓ molecule C-end bends toward the surface while approaching this latter, due to the anisotropic physisorption attraction
- ✓ heteronuclear character produces final rotational distributions in which the contribution of O,C-end molecules is well distinguishable
- ✓ for collision energy lower than the thermal one, it emerges a propensity to the scattering for molecules approaching with O-end closer and facing the surface



N_2 interaction with silica and tungsten

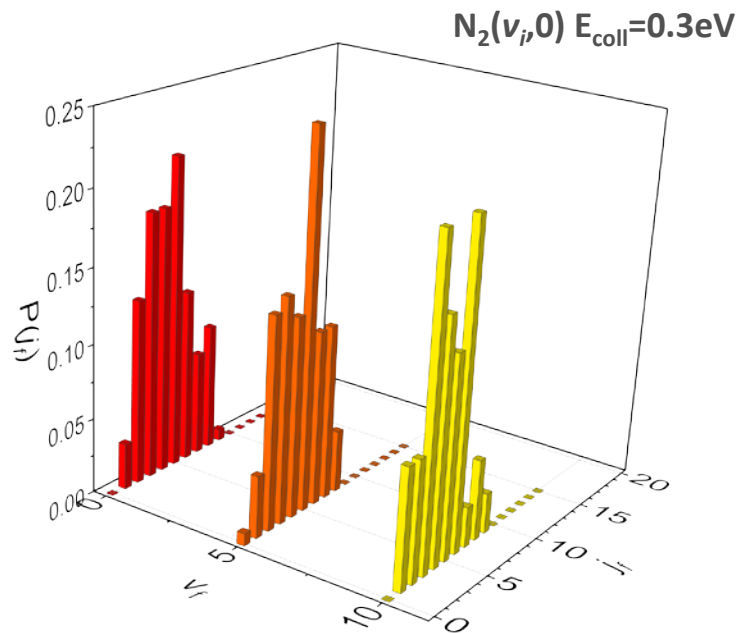
- ✓ Inelastic scattering probability and final rotational distributions depend on the crystallographic structure



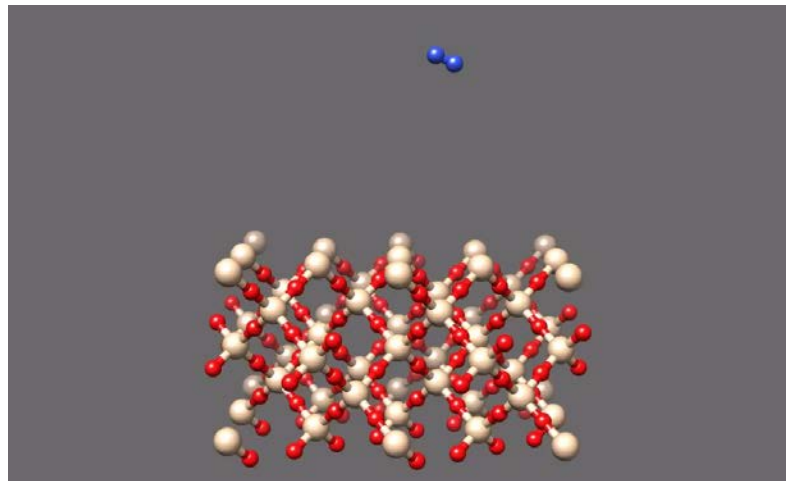
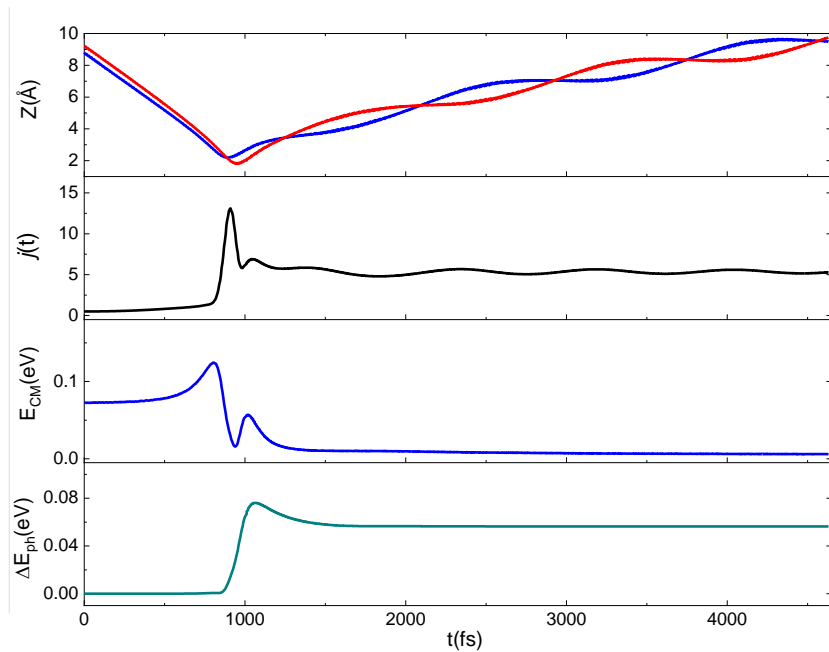
- ✓ Surface temperature effect on the inelastic scattering probability predicted only for cristobalite and for N₂ in the ground-state and for low collision energies ($E_{coll} \leq 1.0$ eV)

The interaction of the N₂ molecule with the surface triggers the **T-R** energy transfer. Molecules inelastically scattered from the surface are more rotationally but less translationally excited than the incident ones.

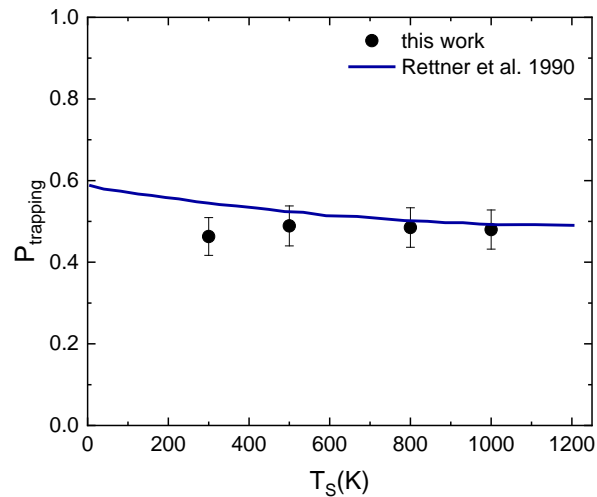
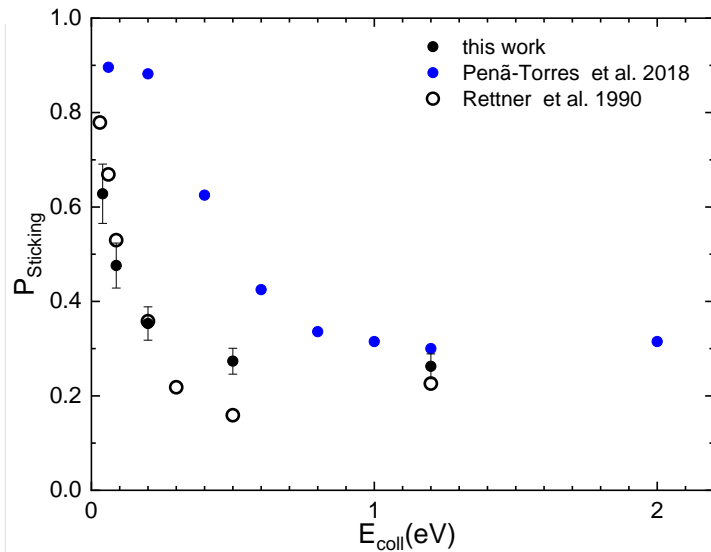
Non-equilibrium condition between T_{rot} and T_{tr} due to the silica surface. This result contradicts the equilibrium condition between these two temperatures often assumed in LTP.



N₂(5,0)----> N₂(5,5) E_{coll}=0.3eV, T_S=100K



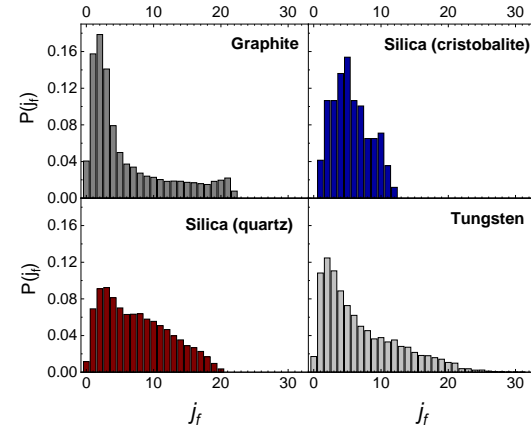
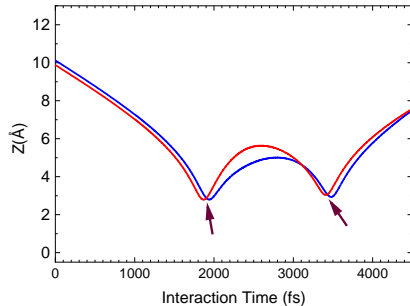
N₂/TUNGSTEN: STICKING



M.R. and F. Pirani *Molecules* **2023**, *28*, 7546

N₂ scattering from different surfaces

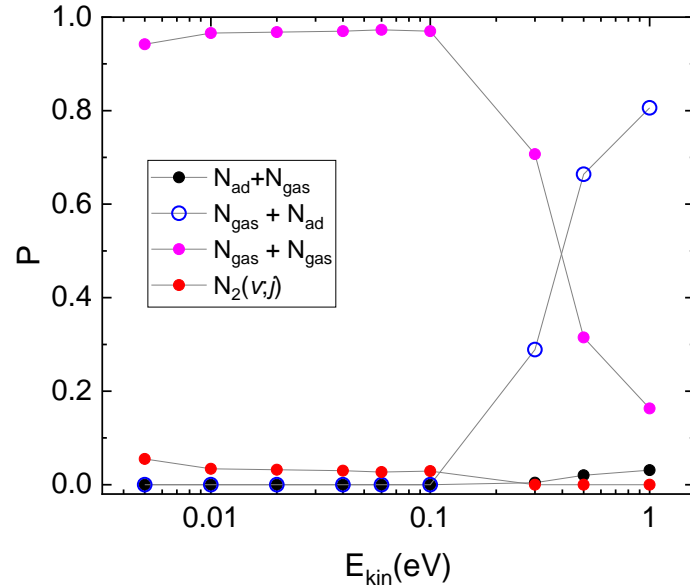
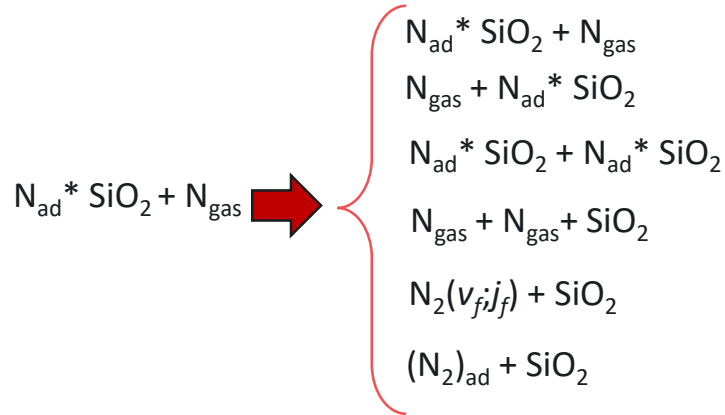
- Mechanism underlying collision events is essentially based on the exchange between rotational and translational molecular internal degrees of freedom as N₂ approaches the surface.
- The efficiency of this exchange at promoting inelastic scattering depends on the topology and energy put into play by the phonons participating in the interaction and manifests in the rotational inelasticity exhibited by the final rotational distributions.



- Synchronization-desynchronization in the relative movement of the two N atoms in the molecule observed for interaction on graphite and tungsten

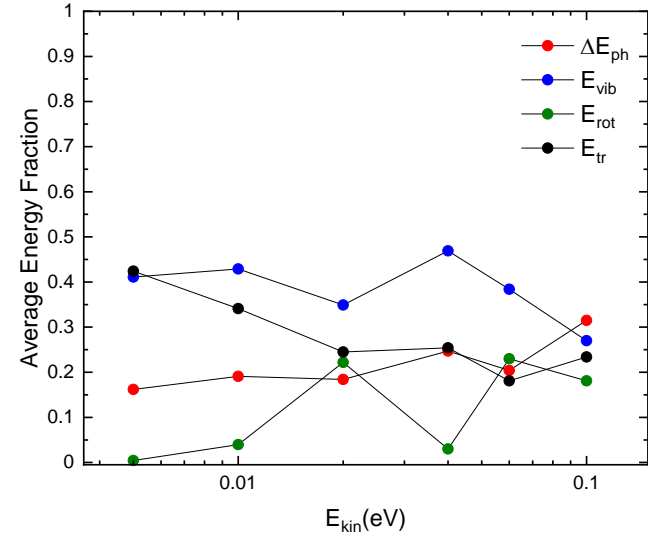
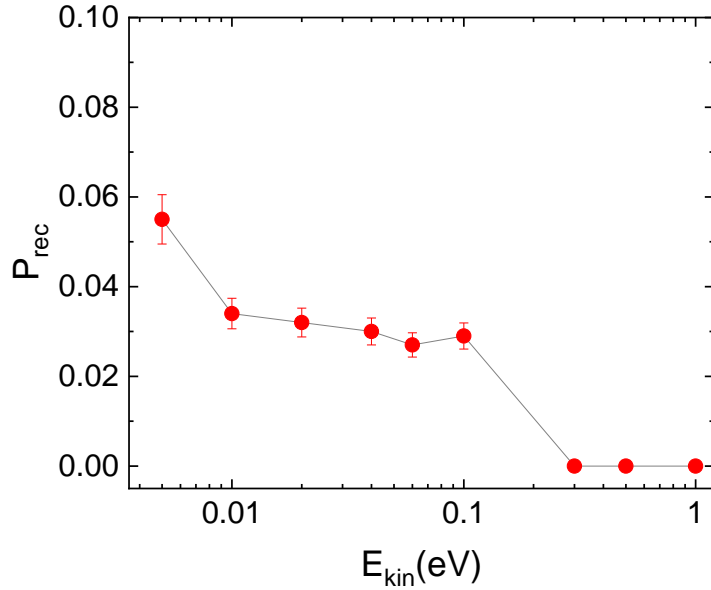
**Recombination at surfaces:
a source of roto-vibrational excited molecules**

NITROGEN ATOM INTERACTION ON CRISTOBALITE



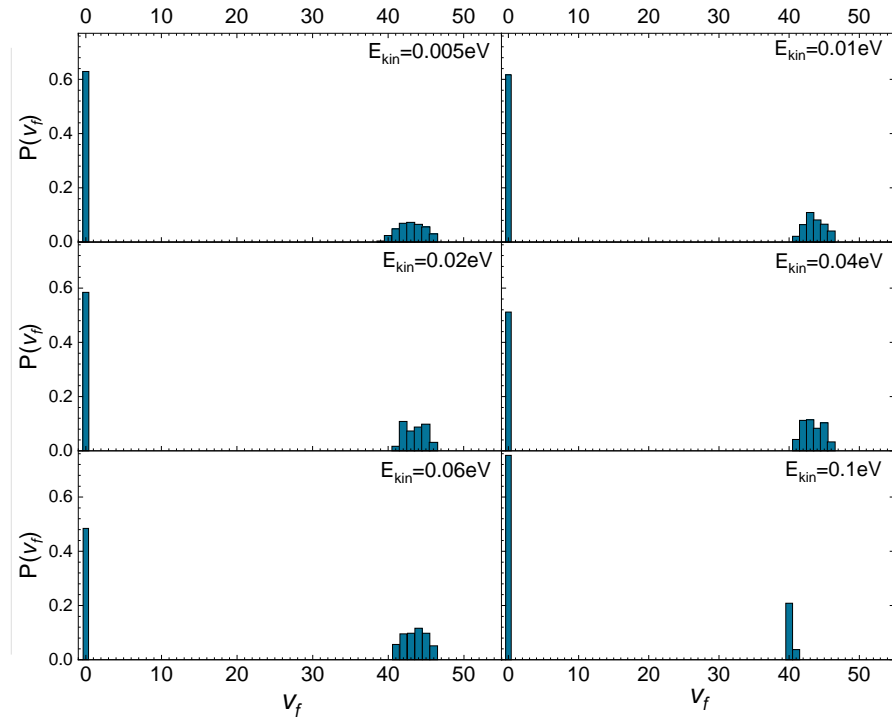
M.R. and F. Pirani *Plasma Sources Sci. Technol.* **2022**, 31, 094006

NITROGEN ATOM RECOMBINATION ON CRISTOBALITE



M.R. and F. Pirani *Plasma Sources Sci. Technol.* **2022**, 31, 094006

NITROGEN ATOM RECOMBINATION ON CRISTOBALITE



	$T_g=100\text{K}$	$T_g=300\text{K}$
$\gamma(T_g)$	$4.45 \cdot 10^{-2}$	$3.65 \cdot 10^{-2}$
	$\gamma(v, T_g)$	
v	$T_g=100\text{K}$	$T_g=300\text{K}$
0	0.627	0.589
39	$0.117 \cdot 10^{-2}$	$0.539 \cdot 10^{-3}$
40	$0.789 \cdot 10^{-2}$	$0.138 \cdot 10^{-1}$
41	$0.345 \cdot 10^{-1}$	$0.337 \cdot 10^{-1}$
42	$0.729 \cdot 10^{-1}$	$0.838 \cdot 10^{-1}$
43	$0.769 \cdot 10^{-1}$	$0.834 \cdot 10^{-1}$
44	$0.821 \cdot 10^{-1}$	$0.820 \cdot 10^{-1}$
45	$0.749 \cdot 10^{-1}$	$0.794 \cdot 10^{-1}$
46	$0.2745 \cdot 10^{-1}$	$0.315 \cdot 10^{-1}$

M.R. and F. Pirani *Plasma Sources Sci. Technol.* **2022**, 31, 094006

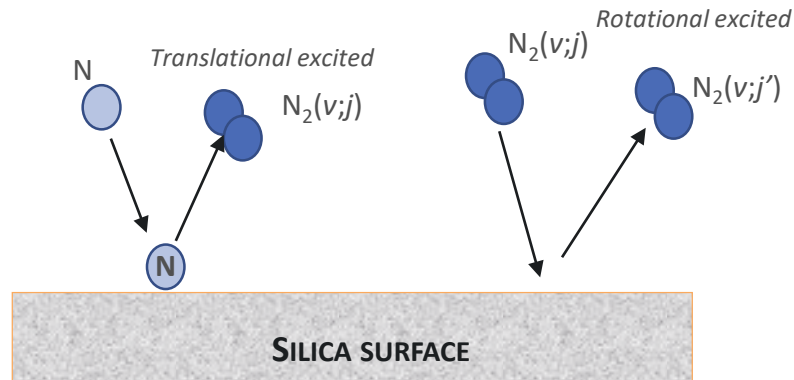
EFFECT ON NITROGEN PLASMA OF SILICA SURFACE PROCESSES

N_2 molecules nascent from the atomic recombination on the surface have a fair probability of forming at very high vibrational levels, with a consistent part of reaction exothermicity transferred to the translational energy.

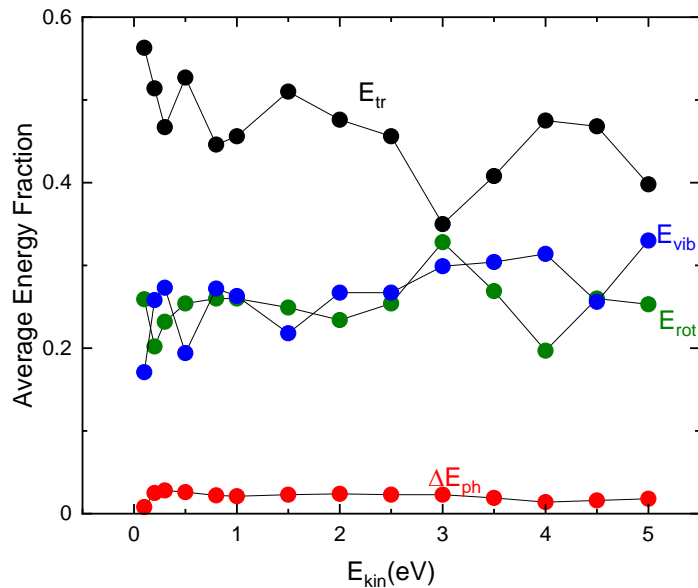
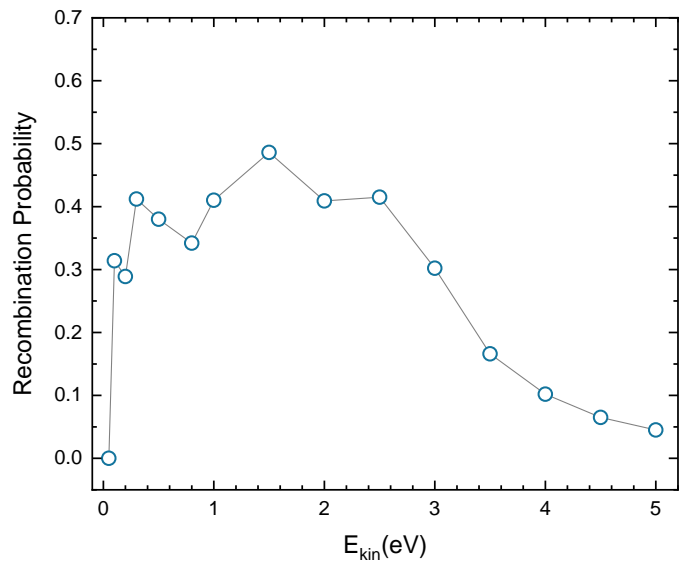
The appearance of the band, in correspondence of high vibrational levels, indicates that molecules do not form close to the surface but at separation distances for which the long-range forces are still active. For this reason, the population of levels starts from the top of the vibrational ladder.

Silica surface contributes both to the production and retention of vibrationally excited molecules as a result of energy exchanges involving both the surface and the internal degrees of freedom of N_2 molecules.

*These molecules diffuse in the plasma bulk and inelastically colliding with other plasma species can ultimately influence the **eedf**.*

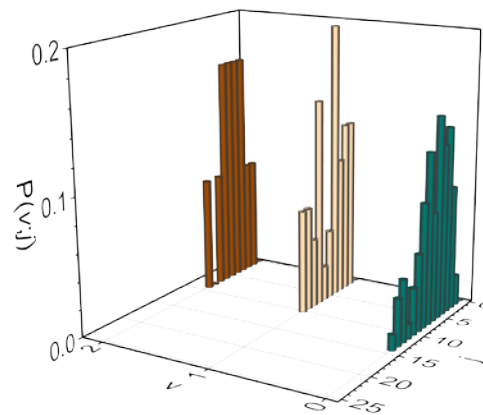
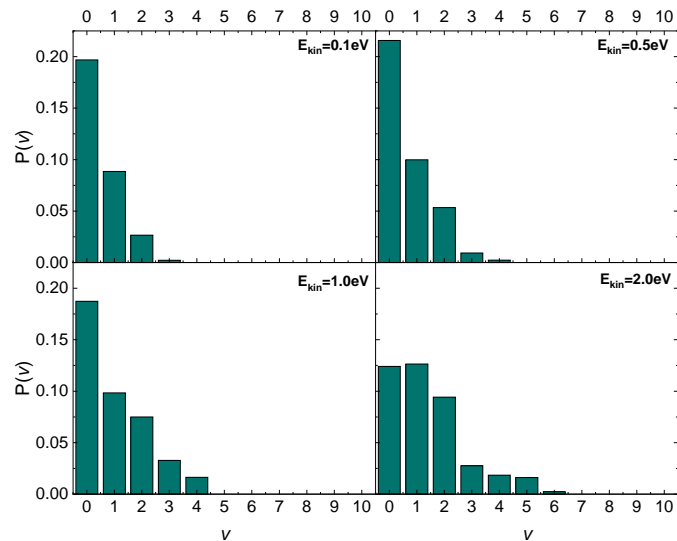


HYDROGEN ATOM RECOMBINATION ON W(100)

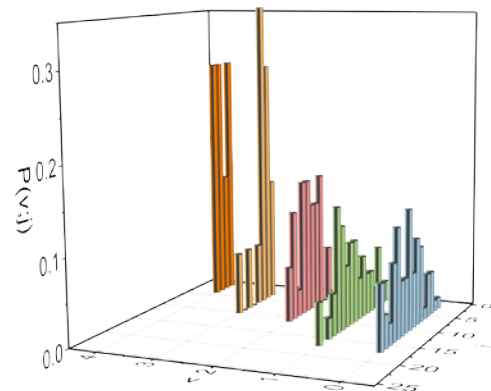


M.R. and M. Cacciatore Phys. Chem. Chem. Phys., **2011**, 13, 7475

HYDROGEN ATOM RECOMBINATION ON W(100)



$E_{kin}=0.1\text{eV}$



$E_{kin}=1.0\text{eV}$

M.R. and M. Cacciatore Phys. Chem. Chem. Phys., **2011**, 13, 7475

TAKE HOME MESSAGE

Molecular Dynamics calculations, in our approach, can give possible answers, both at a predictive and interpretative level, to different problems related to processes occurring at surfaces.

Basic steps of molecules-surface interactions can be simulated at atomic level.

The impact of surface and bulk properties as well as of impinging species on the reaction dynamics can be determined.

The used ILJ potential model has proved suitable to describe the interaction of molecules with different surfaces and to characterize relevant features of the inelastic collision dynamics.

Some important selectivities in the molecules scattered/formed from the surfaces can be properly characterized.

Inelastic scattering and atom recombination at the surfaces are source of roto-vibrational excited molecules.

Collisional coefficients relevant to kinetic modeling, dynamic MC etc. can be determined for different surface processes.

The accuracy of the calculated coefficients mostly relies on the accuracy of the interaction potential assumed in the dynamics, rather than to the approximations made in the collisional model.

A quite good agreement has been obtained with available experiment measurements.