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Rotational Inelastic Scattering of H_2 and O_2 Molecules from Graphite

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Abstract – State-to-state Molecular Dynamics simulations have been performed, in a wide range of temperatures and collision energies, in conjunction with new Potential Energy Surfaces formulated in terms of the Improved Lennard-Jones model. Such simulations have been exploited to investigate the scattering of H_2 (and its isotopologue molecules, D_2 and HD) and O_2 with graphite. Impinging molecules are considered in their ground and excited roto-vibrational levels. Selectivity and peculiarities have been highlighted for the scattered molecules which are of crucial importance for the rationalization of phenomena occurring at the gas-surface interfaces and of interest in astrochemical kinetics.

Keywords: Inelastic scattering; Gas-surface interaction; Molecular Dynamics simulations; Roto-Vibrational Distributions

Riassunto – Simulazioni di Dinamica Molecolare stato-a-stato sono state eseguite in un ampio intervallo di temperature ed energie collisionali, utilizzando nuove superfici di energia potenziale formulate in termini del modello Improved Lennard-Jones. Tali simulazioni hanno permesso di studiare la riflessione di H_2 (e dei suoi isotopologhi, D_2 e HD) e O_2 con la grafite. Le molecole incidenti sulla superficie sono considerate tanto nei loro livelli roto-vibrazionali fondamentali quanto in quelli eccitati. Le selettività e le peculiarità evidenziate per le molecole riemesse sono di fondamentale importanza per la razionalizzazione dei fenomeni che si verificano all'interfaccia gas-superficie e di interesse per la cinetica astrochimica.

Parole chiave: Riflessione inelastica; Interazione Gas-Superficie; Simulazioni di Dinamica Molecolare; Distribuzioni Roto-Vibrazionali

Introduction

The interaction of atom/molecules with cold surfaces is strictly related to the astronomical observations. In fact, molecules represent excellent probes of chemical-physics conditions in Interstellar Medium (IM) through quantities such as pressure, density and temperature. Furthermore, atoms/molecules are mainly physisorbed, with adsorption energy around 100meV, on dust grains, whose temperature is lower than 100 K. The grains act as catalyst for the forma-

tion or de-activation of molecules. A paradigmatic example of this statement is given by the hydrogen molecule case. In fact, H_2: 1) is the precursor of more complex molecules; 2) is dissociated by cosmic rays and UV radiation; 3) is abundant in IM and in particular a high ratio H_2/H is observed in dense cloud. To explain these concomitant observations since many years it has been supposed that H_2 is produced on the surface of cold carbonaceous grains. Starting from one of pioneering work of one of us [1], many studies, both experimental and theoretical, have been performed by different groups in the last twenty years on this subject, with different methods and then at different degrees of accuracy (see for example Ref.s [2-5] and references therein). Note again that collisions at low energy and involving ground-state molecules with cold surfaces are of great interest for subthermal phenomena, as those occurring in cold environments of IM [6].

Among the different elementary processes storing energy in molecular roto-vibrational states, those occurring at the gas-surface interface certainly play a primary role. In fact, chemi-/physi-sorptions of diatomic molecules can lead to their dissociation as well as to their backscattering in the gas-phase. The dynamics of elementary processes involved directly controls the energy exchange mechanism between the surface and the internal degrees of freedom of incident molecules. Furthermore, molecular dissociation at the surface produces two atoms that, if trapped on the surface, modify its chemical and thermal properties, or if diffused into the gas phase, they can act as very effective collision quenchers [7].

In light of these considerations, we studied the interaction $H_2(v_i, j_i)$/graphite and $O_2(v_i, j_i)$/graphite, where v_i and j_i are the number defining, respectively, the initial vibrational and rotational state of molecules. The effects of these interactions have been studied by performing Molecular Dynamics (MD) simulations, in a wide collisional energy range, that in our approach consist mainly of three different steps: I) building-up of a 3D crystal lattice of graphite for which we determined the phonons dynamics; II) determination of the Potential Energy Surface (PES) driving the reaction. In particular, for the part relating to the chemisorptions, we used results derived by Density Functional Theory (DFT) calculations, while for that relating to long range interactions, where the failure of the DFT is well known, we used the Improved Lennard-Jones Potential recently proposed in literature [8]; III) characterization of thousands of trajectories, in the framework of semiclassical collisional methods [9], to cast light on the reaction dynamics. Therefore, from the trajectories analysis we are able to determine reaction mechanism, probabilities of elementary surface processes and roto-vibrational distributions of the final products.

Here, we will give insights for some of the main results obtained in the investigation of the scattering of H_2 and O_2, in their ground and in excited roto-vibrational levels, with a graphite surface for collisional energies and surface temperatures of interest for astrochemical kinetics. Moreover, the complete study done on these heterogenous systems, includes also higher values of collisional energy (E_{kin}), of surface temperature (T_S) and of initial roto-vibrational states [10-12].

Results and Discussion

The main results obtained for the inelastic scattering of hydrogen and oxygen molecules in well-defined initial roto-vibrational states will be presented and discussed in the two following subsections.

Hydrogen

When $H_2(v_i, j_i)$ molecules impinge on the graphite surface, they are reflected in the gas-phase following a direct mechanism, in the sense that each molecule immediately scattered after the interaction with the surface, preserving its initial vibrational state. On the other hand, the reaction dynamics is mostly controlled by rotational excitation that determines the fate of trajectories, as shown in Fig. 1.

In this Figure, the probability of the first four final rotational states (j_f) is reported as a function of E_{kin} for molecules initially in two different initial vibrational (v_i) states, but in the same initial rotational level (j_i =1). From the figure it appears that, except for j_f=0, that for very low collisional energy exhibits a different behaviour, for the other values of j_f the result is the same, irrespective of v_i and of E_{kin} values considered.

Furthermore, from MD simulations it appears that the reaction is independent of the value of the surface temperature T_S, and this has been stated by propagating the same bunches of trajectories for different Ts values [10K and 100K]. Instead, some selectivity in the final rotational states can be highlighted: molecules with j_i= 0 have the peak of final distribution on j_f=1, while molecules with $j_i \neq 0$ have peak in $j_f = j_i$. The interested reader can refer to Ref. [10] for the complete set of results concerning the scattering of $H_2(v_i, j_i)$ from a graphite surface, while results for its isotopologue molecules can be found in Ref. [11].

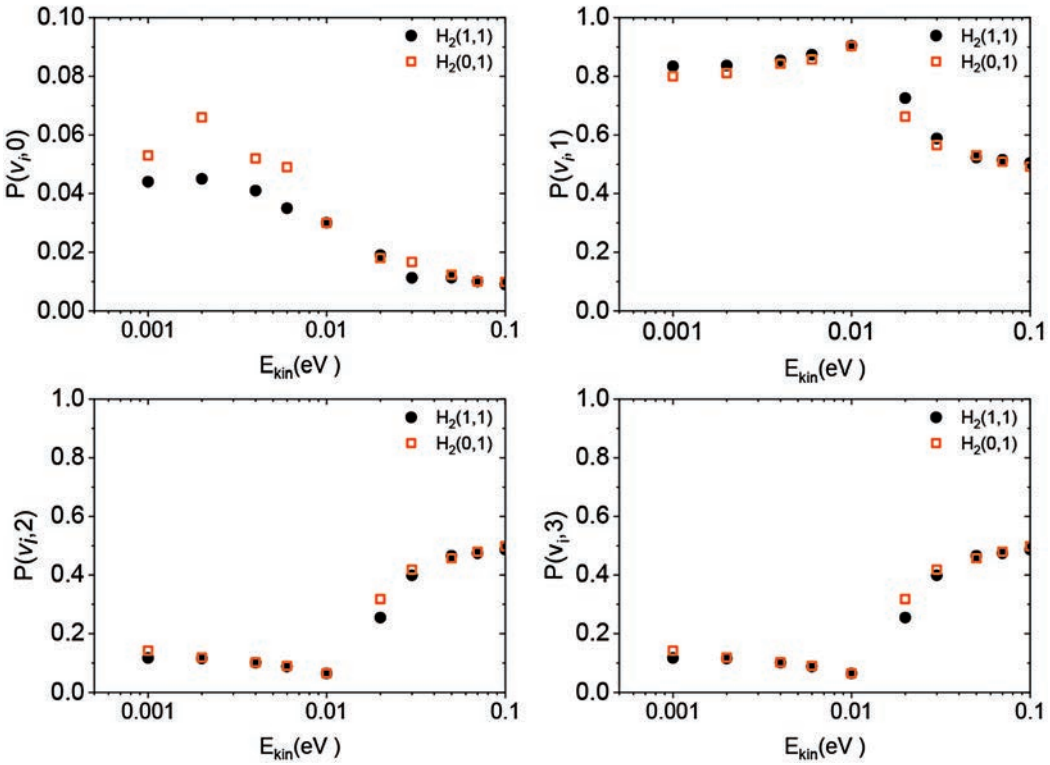

Fig. 1. Final rotational distributions for $H_2(v_i,1)$. The cases of $v_i = 0$ and $v_i = 1$ are considered.

Oxygen

For the interaction of $O_2(v_i, j_i)$ with a graphite surface, we found that for the ground vibrational state and for the lowest collisional energies (E_{kin}=0.01eV and E_{kin}=0.1eV) an appreciable percentage of trajectories is affected by the molecular physisorption. This is shown in Fig. 2, where the probability for scattering and physisorption for three different values of j_i is reported.

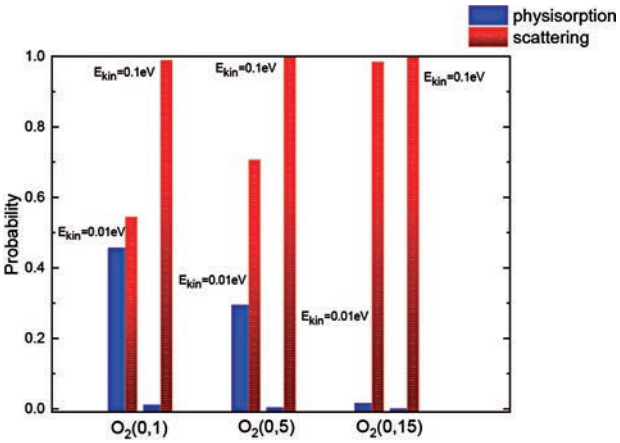

Fig. 2. Surface processes probability for oxygen molecule in $v_i = 0$ and $j_i = 1, 5, 15$.

For oxygen molecules, the reaction mechanism can be direct, as that described in the case of hydrogen, or indirect in the sense that the molecule remains trapped close to the surface for a certain time lapse before to be reflected in gas-phase. In this case also, low v_i values, involved in the astrochemistry, are preserved in the interaction, that is molecules are reflected with $v_f = v_i$ and it is not predicted any surface temperature effect [12].

The interaction dynamics, for O_2 molecule, is dominated by the translational (T)–rotational (R) coupling, and for low-medium E_{kin} values is also triggered by the energy exchange with the surface phonons.

A very accurate trajectory analysis reveals that there is an important selectivity with regard to the excitation/de-excitation of rotational levels which is controlled by the orientation of the molecular rotation axis (or rotation plane) with respect to the surface. In fact, molecules approaching the surface with a *cartwheel* – type motion undergo a pronounced rotation excitation and are backscattered with $j_f > j_i$, while molecules moving with *helicopter* – type motion are elastically backscattered with $j_f \approx j_i$ [12]. The relationship between motion type and final rotational states emerges clearly by a careful examination of trajectories.

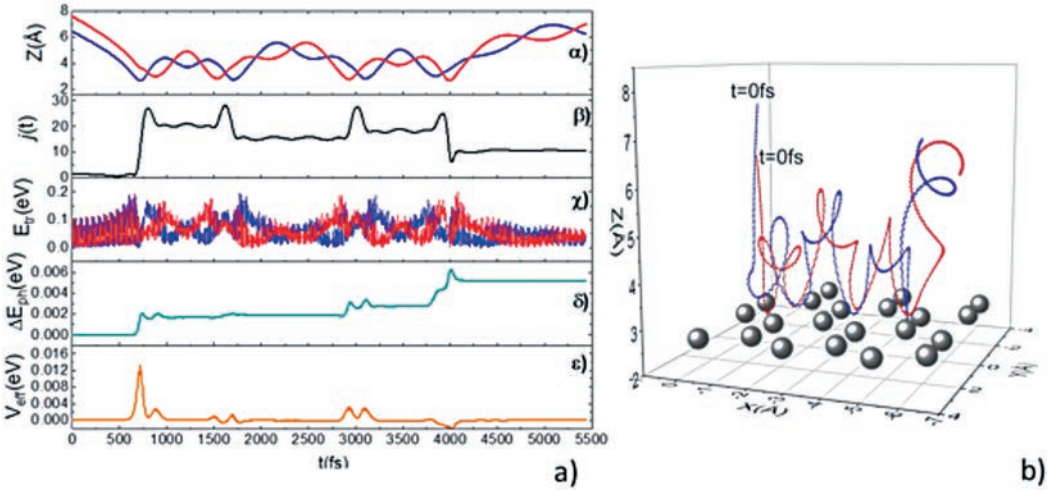

Fig. 3. Trajectory for O_2 (0, 1) at E_{kin} = 0.1 eV backscattered in gas phase as O_2 (0, 11). a) Panel (α): dependence on the time t and on Z, the normal coordinate, for the two atoms in the O_2 molecule; a) panel (β): rotational state evolution along the trajectory; a) panel (χ): kinetic energy of two O atoms in the molecule; a) panel (δ): energy exchanged with the surface phonons along the trajectory; a) panel (ε): $V_{eff}(t)$ potential. b) 3D trajectory in which the cartwheel-type motion is depicted. The C atoms on the surface first-layer (an up-shift has been made from their position Z = 0) are also reported (dark grey spheres).

In Fig. 3 an example of trajectory (1D and 3D) associated with the scattering occurring at medium-low collision energy and leading to a remarkable final rotational excitation, together with rotational state and energetic terms evolution, is shown. In this case, the O_2 (0,1) molecule impinges on the surface with a *cartwheel*-type motion, while, for useful comparison, an example of trajectory (1D and 3D) for O_2 (0,1) molecule colliding at the same E_{kin}, but with a *helicopter*-type motion, is displayed in Fig. 4.

Looking at Fig. 3 a) panel α) and at Fig. 3 b), we observe that up to the first bounce on the surface, one of O atom in the molecule (blue line) is closer to the surface because the rotational motion is slow and of *cartwheel*-type. After the first jump the kinetic energy of both atoms in the molecule (panel χ)) decreases (both atoms decelerate) and simultaneously the rotation state, defined by j(t) (panel β)), jumps to a value higher than j=20. This impact causes then an excitation of the molecule that continues to move close to the surface maintaining an excited rotational motion of *cartwheel*-type. In particular, j(t) remains constant as well as, on average, the kinetic energy (E_{kin}) of the molecule, for the fact that the E_{kin} component of one of two atoms increases and that of the other decreases (panel (χ)). At about t = 1500 fs, that is when the other atom in the molecule (red line) comes close to the surface, j(t) undergoes another little increase but within a few tens of fs it undergoes a decrease in conjunction with the approach of the other atom (blue line) to surface. This sequence of events repeats again before the molecule has enough energy to leave the surface and to go in gas-phase, with a strong decrement of rotational number. Panels (δ) and (ε) of Fig. 3a) show the time evolution of energy transferred to the surface and the behaviour of V_{eff}. Moreover, V_{eff} is an additive term to the T–R exchange when the atoms come close to the surface.

Fig. 4 demonstrates the fact that a molecule, impinging on the surface at the same E_{kin} of trajectory in Fig. 3, but moving with a *helicopter*-type motion, does not change or changes slightly its rotational number and is scattered by a direct mechanism. In this case when both atoms come close to the surface (t ≈ 750 fs), a decrement of kinetic energy [Fig. 4 panel (χ)] of both atoms occurs with a simultaneous small increment of the rotational number [Fig. 4 panel (β)] and with a small fraction of the energy transferred to the surface [Fig. 4 panel (δ)].

Therefore, we can affirm that the microscopic mechanisms determining observed stereo-dynamical effects can be related to the conjectures introduced to rationalize the molecular alignment in seeded supersonic Molecular Beam (MB) [13]. This finding arises from the fact that the mechanisms of both phenomena, must be complementary for the following reasons: 1) the rotational relaxation in gaseous expansions occurs at low collision energies, when rotational excitations are not much probable, while the O_2 molecule excitations at graphite surface are well evident at intermediate-high

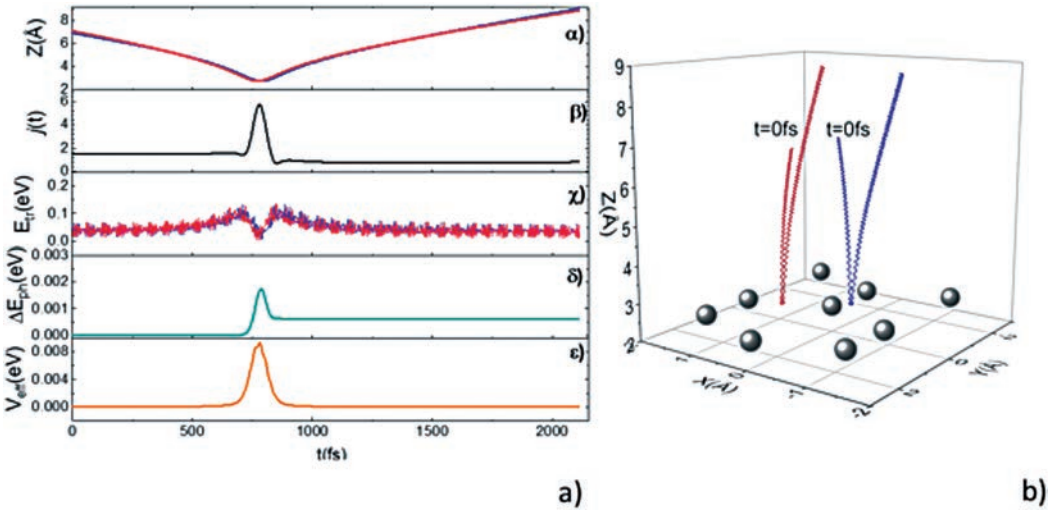

Fig. 4. Trajectory for $O_2(0, 1)$ at E_{kin} = 0.1 eV backscattered in the gas phase in $O_2(0, 1)$. a) The physical quantities shown in the panels are the same as in Fig. 3a); b) 3D trajectory in which the *helicopter*-type motion is depicted. The C atoms on the surface first-layer (an up-shift has been made from their position Z = 0) are also reported (dark grey spheres).

E_{kin}; 2) several carrier gas-seeded molecule collisions, promoting many rotational jumps each one with small changes in *j*, are necessary to observe the phenomenon in MB because the anisotropic intermolecular forces at play are weak and then less efficient, and collisions can occur with different impact parameters.

It appears that in molecule-surface scattering, the selectivity is favoured by the stronger anisotropic interaction and by the higher collision energies involved. However, what it is found is that both in the MB alignment as in the scattering by surface, the cartwheel molecules show the highest propensity to give rotation inelastic events.

Conclusions

The recent ILJ potential model has been used to formulate and to study the interaction of H_2, O_2 with a graphite surface and to characterize relevant features of the inelastic collision dynamics for E_{kin}, ranging from sub-thermal up to hyper-thermal conditions, where the role of the long-range forces, specifically their strength range and anisotropy, play a crucial role. The interaction dynamics of H_2, O_2 molecules with graphite surface is dominated by the T–R coupling, to which the contribution of surface phonons is added mainly for low collision energies, the energy range of interest in astrochemistry. MD simulations enable us to properly characterize some important selectivities in the inelastic scattering for H_2 -/O_2- graphite.

Therefore, we can affirm that the molecule-surface scattering, driven by stronger and more anisotropic force fields, appears to be an important tool to emphasize relevant stereo-dynamics effects controlling a myriad of elementary processes occurring both in gaseous and condensed phase.

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