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

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 sub-thermal 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-/physisorptions 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, j)/graphite and O$_2$(v, j)/graphite, where v, and j, 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 ro-to-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, j) 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) is reported as a function of E$_{kin}$ for molecules initially in two different initial vibrational (v) 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, 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 T$_S$ values [10K and 100K]. Instead, some selectivity in the final rotational states can be highlighted: molecules with j$_f$ = 0 have the peak of final distribution on j$_f$ = 1, while molecules with j$_f$ ≠ 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, j) from a graphite surface, while results for its isotopologue molecules can be found in Ref. [11].
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$_{\text{kin}}$=0.01eV and E$_{\text{kin}}$=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. 1. Final rotational distributions for H$_2$(v$_i$,1). The cases of v$_i$ = 0 and v$_i$ = 1 are considered.

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$_{\text{kin}}$ 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$_f$ = j$_i$ [12]. The relationship between motion type and final rotational states emerges clearly by a careful examination of trajectories.

Fig. 2. Surface processes probability for oxygen molecule in v$_i$ = 0 and j$_i$ = 1, 5, 15.
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 $E_{\text{kin}}$, but with a helicopter-type motion, is displayed in Fig. 4.

Looking at Fig. 3 a) panel (a) 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 (b)) decreases (both atoms decelerate) and simultaneously the rotation state, defined by $j(t)$ (panel (b)), 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 ($E_{\text{kin}}$) of the molecule, for the fact that the $E_{\text{kin}}$ component of one of two atoms increases and that of the other decreases (panel (d)). 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 increment 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 (d) and (e) of Fig. 3 a) show the time evolution of energy transferred to the surface and the behaviour of $V_{\text{eff}}$. Moreover, $V_{\text{eff}}$ 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 $E_{\text{kin}}$ 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 ($t \approx 750$ fs), a decrement of kinetic energy [Fig. 4 panel (b)] of both atoms occurs with a simultaneous small increment of the rotational number [Fig. 4 panel (b)] and with a small fraction of the energy transferred to the surface [Fig. 4 panel (b)].

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...
E$_{\text{kin}}$; 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$_{\text{kin}}$, 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.

**REFERENCES**


