Effects of a Nonrigid Graphene Surface on the LH Associative Desorption of H Atoms and on the Deexcitation of Nascent H_2 Molecules Colliding with Model Walls of Carbonaceous Porous Material

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A planar slab of 200 C atoms bound by the Brenner potential is used to study the Langmuir–Hinshelwood (LH) recombination of two physisorbed H atoms on a graphene sheet and to simulate afterward successive collisions of the nascent H_2 molecule with pore walls of a carbonaceous dust grain of the interstellar medium. The study is based on successive propagations of classical trajectories for the 200 C + 2 H atoms. The characteristics of H_2 molecules formed by the LH reaction on the flexible surface are found to differ but negligibly from those formed on a rigid one. Collisions of those H_2 molecules with graphitic pore walls are studied next. Reflection from and "trapping" onto the surface is observed and discussed. The most important energy transfer is from the molecule vibration to its rotation. This conversion mediates the transfer of the molecule internal energy to its translation or to surface heating. It is found that a single H_2–surface impact has little effect on the internal energy of the molecules. The grain absorbs on the average but a very weak energy. Several impacts are required to appreciably cool the molecule. The molecule cooling is accompanied by a significant increase of its translational energy. The swifter the molecules are or get, the larger the number of their impacts on the surface they undergo per unit time and the more efficiently cooled they get.

1. Introduction

1.1. Astrophysical Incentive.

1.1. Astrophysical Incentive. The formation of very large amounts of molecular hydrogen from the recombination of H atoms in the interstellar medium (ISM) is a crucial issue in the understanding of the birth and evolution of prestellar clouds in the universe. It is now well accepted by the astrophysical community that, in the low temperature (10–100 K) and low density (<1000 atoms per cm^3) conditions of the ISM, H_2 formation in interstellar clouds takes place via H atom adsorption and recombination on the surface of dust grains, i.e., a heterogeneous catalysis process. There is also consensus on the dust grain composition: in diffuse clouds and PDR's (photon dominated regions) they are thought to be made of carbonaceous and/or silicaceous material; in dense molecular clouds these grain cores are most probably covered by ice mantles. It is conjectured that the sizes of the grains are in the range 1 nm to 0.1 μm with a size distribution favoring the smallest grains.[1] The structure and morphology of the grains are still matters of exciting and stimulating debate.

H_2 formation on the surface of dust grains may proceed via different mechanisms:[2,3] Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) or "hot atom" (HA) reactions. Most theoretical studies to date have considered carbonaceous dust grains which were modeled as graphitic surfaces[4,5] or large PAH (Polycyclic Aromatic hydrocarbon) platelets.[6,7] The H–H recombination reaction at the surface turns out to be quite exothermic. This is mainly due to the strong H_2 binding energy which is larger, by 3 to 4.5 eV, than the H atom adsorption energies (physisorption or chemisorption). All theoretical studies of the two main mechanisms, namely: LH, for physisorbed H atoms on a rigid surface,[8–11] or ER, with or without surface relaxation, for a chemisorbed[5,12–15] or physisorbed[5] H atom, have shown that the nascent H_2 molecule has substantial internal energy especially in the form of vibration. Experiments on dust grain analogues in which the internal energy of the product H_2 (HD) molecules is measured have been undertaken recently. In the most recent ones[16–18] significant vibrational excitation is reported, albeit not as high as those predicted by theory. Such a vibrational excitation is at variance with what is usually inferred from astrophysical observations.[19,20] Let us point out however that a high energy vibration–rotation excitation tail of H_2 emission extending up to quite high rotational levels (e.g., $v = 0$, $j = 30$ and $v = 3$, $j = 7$) has been reported in ref 21. Though the origin of the observed lines is uncertain, newly formed H_2 molecules have been tentatively proposed among the possible candidates.

With these pieces of information in mind two tracks of investigation are open: (i) to conceive new H–H recombination scenarios that are able to produce internally cold (or colder) H_2 molecules; (ii) to investigate processes that could quench the internal excitation of the nascent H_2 molecule. An example of an attempt along track (i) is provided by the complementary works of refs 22–24 for the ER recombination reaction in presence of a surface impurity, actually taken as a spectator H atom. The present work goes along track ii. It concerns the study of energy conversion in the molecule and energy flow out of it near the surface. This is done in two ways; on the one hand, with reference to the work of Morisset et al.,[8,9] we investigate the effect of *freeing the substrate* during the LH recombination

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of two *physisorbed and mobile* H atoms on a graphitic surface, and, on the other hand, we endeavor to explore the effect of a succession of vibrationally rotationally inelastic collisions of an internally hot H_2 molecule with nonrigid walls of a porous dust grain.

1.2. Physisorption versus Chemisorption. The reason why we favor physisorption in the present study as done in refs. [8−11] is that H atoms with energies well below 2000 K, as is the case in the ISM, cannot chemisorb on a graphitic surface owing to the presence of a ≈0.2 eV (2400 K) activation barrier at a distance ≈2 Å from the surface. This has been established in refs 4, 6, 7, and 25 and has been confirmed in several subsequent works. Recent work[22,23,26−29] has put in evidence and discussed in some depth the existence of chemisorption pairing on graphene. Yet, aside from the existence of chemisorption barriers of few tenths of an eV in all cases but one, namely that of the so-called para pair with singlet spin,[22,23,29] a prerequisite condition for the discussed pairing is that one H atom is already chemisorbed on the surface; but this already requires the overcoming of the abovementioned ≈0.2 eV activation barrier; again an energy which is not available in the ISM conditions. An additional argument[11] for putting chemisorption aside is that when H atoms are chemisorbed, they are quite tightly bound to the carbon atoms of the surface; in order to hop from site to site and diffuse on the surface until their encounter according to the LH mechanism, they have to overcome barriers whose heights are huge (>0.5 eV) compared to the available energies in the ISM (see, e.g., ref. 30). Hence, at present we do not consider the possibility that the hydrogen adsorption is dominated by defects without barriers leading to chemisorbed states with properties very different from the physisorbed states considered here.[22,23,31−33]

For similar reasons, we consider at present that H_2 scattering from a graphitic surface at ISM temperatures is likely to be governed exclusively by physisorption type interactions.[34]

1.3. Framework of the Present Study. In the work of Morisset et al.[8,9] the LH mechanism involves two physisorbed and mobile H atoms on a *rigid surface (i.e., without any energy accommodation to the surface)*. The recombination process occurs as a result of *momentum transfer* in the H + H collision and scattering near the surface. The H−H scattering causes one atom to be sent toward the vacuum and the other atom toward the surface; the latter atom thus rebounds and finally moves toward the vacuum too. This gives rise to a quite stretched H_2 molecule that contains substantial vibrational and rotational energy: the vibrational distribution lies in the range $5 < v < 15$ and peaks near $v \approx 11-13$; the rotational distribution covers the range below $j = 20$ and has a maximum at $j \approx 10-11$. In the simplest case, the translational energy of the nascent H_2 molecule is large enough to lead to a direct desorption. Otherwise, the H_2 molecule is trapped in a quasi stationary state where it oscillates in the physisorption well with a significant amount of vibrational and rotational energy. As these H_2 motions are hindered by the surface there is a coupling between them and the H_2 translation relative to the surface; this allows for the escape of the molecule. One may thus wonder whether consideration of a non rigid surface is likely to modify the energy balance of LH reaction and in particular to significantly reduce the vibration−rotation excitation of the nascent H_2 molecule.

The porosity of ISM dust grains is invoked in many contexts: coagulation of protoplanetary disks,[35] optical properties of the ISM,[36] H_2 formation on icy grains[37−42] and on dust analogues,[43] etc. The possibility of having pores (crevices, cavities, vesicles, etc.) in the grain material provides the means of having a nascent hot H_2 molecule interact several times with the walls of the pore and cooled down. Here we also endeavor to shed some light on the efficiency of this quenching process.

The outline of the study is as follows. First we study the LH recombination of two H atoms physisorbed on a *nonrigid* surface. This allows us to quantify the percentage of reacting events and to determine the sharing between the internal energy of the nascent molecule in rotation and vibration, its translational energy and the energy put into surface excitation as a function of the temperature of the medium. Then we simulate the reflections of this nascent molecule on walls of a pore until its release. This is done by making the molecule undergo a succession of collisions at random incidence angles on a *nonrigid* surface. This simulation allows us to assess if and how the molecule, trapped in a porous material, is able to convert and relax its energy (especially its vibrational energy).

Throughout this study the dust grain is assumed to be composed of carbonaceous and locally graphitic material, that is: the LH reaction and each H_2−surface collision involve a slab of 200 carbon atoms forming a piece of a graphene layer. The above presented simulation scenarios involving unconstrained motions of so many atoms are presently conceivable and tractable only in a classical molecular dynamics framework. We discuss below why we believe such an approach is permissible.

1.4. Features of the Considered Problem Allowing the Use of Classical Mechanics. Let us consider first the LH recombination reaction. It has been shown by Morisset et al.[8,9] that quasiclassical trajectory calculations (i.e., classical calculations with conditions simulating the initial quantal H−surface zero point energy) yield results in general good agreement with full 4D quantal calculations. Such a success was not expected for light atoms (H) interacting and reacting at very low energies. In fact, this is the consequence of a few favorable conditions. First, since the H_2 formation reaction is barrier-less, there is no tunneling to worry about. Moreover, the reaction is highly exothermic: it involves the strongly attractive H−H interaction which is 100 times greater than the H−surface interaction. As recalled above this produces the H_2 molecule in quite high vibration−rotation (v,j) states close to the dissociation limit. Actually, the spectrum obtained by gathering all v,j levels of the H_2 molecule in its ground electronic state is rather dense (see e.g. ref. [10]) especially for high v,j pairs. Thence, owing to the large number and close spacing of the vibration−rotation v,j states (not merely separate vibration or rotation states) the dynamics of vibrational−rotational-translational transitions near a rigid surface is actually described correctly enough by classical mechanics.

We may next wonder whether allowance of the surface vibrations in the LH reaction and in the subsequent H_2−surface collisions is likely to change the situation in a manner that severely invalidates the use of classical mechanics.

It is clear that if the H_2 interaction with the vibrating surface were solely of the vibration-vibration ($v_{\text{molecule}} - V_{\text{surface}}$) type then worrying problems would indeed arise. These problems are related to the large energy spacings of the H_2 vibrational energy levels (from 0.1 eV for the largest v's up to 0.5 eV for the lowest ones). For comparison, the phonon density of states (PDOS) of the graphene surface is essentially continuous and extends from 0 to 0.2 eV.[44,45] So in general, the quenching of one quantum of H_2 vibration requires the simultaneous excitations of a few or several surface phonons. If such events are susceptible of taking place they should involve resonant multiphonon excitation which might not have a classical counterpart. However, one soon realizes that, owing to the small mass ratio of the H atoms to the C atoms of the surface, most H_2 impacts with the surface, except the very impulsive ones, should release less than 0.2 eV into the surface in pure $v_{\mathrm{molecule}} - V_{\mathrm{surface}}$ transfers[46] In as much as vibrational jumps with continuous small bits of energy are classically allowed but quantally forbidden, because of the large spacing of the discrete H_2 vibrational quantum levels, the quenching of the molecule by pure vibrational energy transfer to the surface would be overestimated by classical mechanics.

Nevertheless, one should keep in mind that the problem actually involves altogether the vibration−rotation−translation of the molecule and the vibrations (all sorts of phonons[44,45]) of the surface. In as much as (i) vibrational−rotational−translational transitions near a rigid surface are likely to be properly described by classical mechanics as argued above and (ii) the majority of energy transfers between an H_2 molecule and a carbonaceous non rigid surface is likely to occur by small bits of energy, the problem is likely to be consistently and properly described by classical mechanics if vibrational−rotational transitions $v,j \rightarrow v',j'$ with $v > v'$, $j < j'$ and with small internal energy changes occur prior to or even simultaneously with comparable energy transfers to the molecule translation or surface vibrations. Anticipating on the presentation of the results let us mention that this is indeed what actually happens.

The next sections successively describe the interaction potentials, the LH calculations of H_2 formation and the multiple H_2−surface collision calculations.

2. Interaction Potentials

The model consists of two H atoms interacting with the C atoms of a graphene sheet (one layer of a graphite (0001) surface). The H atoms individually or bound in an H_2 molecule are assumed to interact with the surface via physisorption-type interactions.

In the case of physisorption we can assume that the interaction potential can be written as the sum of three terms. The first one concerns the carbon atoms of the surface, the second one the interaction of each H atom with the surface atoms and the third one the H−H interaction potential.

2.1. The Graphite Potential. In our model, the graphite (0001) surface is reduced to its outer layer: a graphene sheet spreading along the *XY* plane. This model surface is further represented as a rectangular slab of 200 carbon atoms arranged in a hexagonal mesh with a C−C bond distance of 1.45 Å. Periodic boundary conditions are applied in the *X* and *Y* directions. The number of atoms constituting the slab is directly related to the H−surface potential (section 2.2 below); it is chosen in such a way that the H−surface potential at the center of the slab is insensitive to any further addition of C atoms at the slab borders.

We use the empirical bond-order potential due to Brenner[47] to represent the interactions of the C atoms of the surface. This potential is quite popular and is widely and satisfactorily used for miscellaneous hydrocarbon structure and dynamics calculations. In particular, it was found to satisfactorily reproduce the phonon density of states (PDOS) of graphene and graphite.[45] It is basically a sum of nearest neighbor interactions but it includes a many-body term reflecting the local environment of each bond. Thus, the potential is short ranged and determines the forces between the C atoms within and about the graphene sheet.

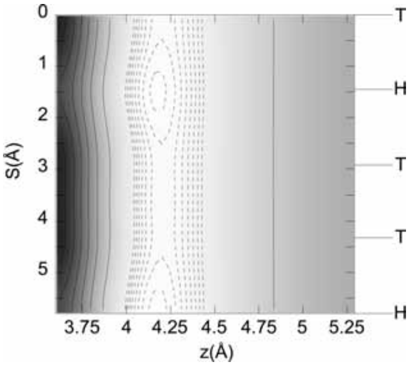


Figure 1. Cut of the model potential used in the present work to describe the interaction between an H atom and a graphite surface. The potential is plotted as a function of the H−surface distance *z* and the distance along a line S passing through two opposite C atoms (para sites) of a hexagonal carbon ring of the surface. In this figure the carbon atoms are in the same plane at their equilibrium position. The symbols T and H respectively indicate the positions of the top and hollow sites respectively. Contour lines are plotted every 10^{-2} eV from 0.02 eV to −0.04 eV (solid lines) and every 5×10^{-4} eV between −0.04 eV and −0.0435 eV (dashed lines).

2.2. The H-Surface Potential. As recalled in section 1.2, for low energy H atoms (well below 0.2 eV, that is: $T \ll 2400$ K) interacting with a graphite (0001) surface the H-graphite interaction potential is of the physisorption-type and is characterized by a relatively small corrugation.[6,7,48] As indicated above, we represent the H−surface interaction as a sum over all C atoms in the slab (section 2.1) of pairwise C−H potentials:

$$V_{\mathrm{H-Surface}}(x, y, z, \{\vec{\rho}_i\}) = \sum_{i=1}^{n} V_{\mathrm{H-C}}(r_i) \qquad (1)$$

where r_i is the distance between the H atom and the *i*th C atom of the surface; $\{\vec{\rho}_i\}$; represents the coordinates of the C atoms collectively, z is the distance of the H atom from the surface and x,y are its coordinates in the plane parallel to the surface:

$$V_{\mathrm{H-C}}(r_i) = D\left[\left(1 + \frac{\Lambda(r_i - r_{\mathrm{eq}})}{p}\right)^{-2p} - 2\left(1 + \frac{\Lambda(r_i - r_{\mathrm{eq}})}{p}\right)^{-p}\right] \qquad (2)$$

The parameters of this formula given by Ghio and used for the H−C potential were fitted in order to reproduce the equilibrium H−surface distance ($z_{\mathrm{eq}} = 4.13$ Å) taken from the DFT calculations of Sidis et al.[7] and the experimental physisorption energy ($D_{\mathrm{eq}} = 43$ meV) taken from Ghio et al.[49] In this way the present calculations may unambiguously be compared with those of Morisset et al.[8,9] The parameters of the potential are thus as follows: $n = 200$, $D = 2.42$ meV, $\Lambda = 1.48$ Å^{-1}, $r_{\mathrm{eq}} = 4.6$ Å, and $p = 4.9$.

A cut of the resulting potential, when all C atoms lie in the $z = 0$ plane at their equilibrium graphite distance $\{\vec{\rho}_{i,0}\}$, is shown in Figure 1 along a line $S(x,y)$ passing through two opposite C atoms of a hexagonal carbon ring of the surface (para sites). It presents a large corridor almost independent of the position in the *XY* plane with a well of −0.043 eV at the distance $z = 4.13$ Å. A faint corrugation is observed, namely: slightly deeper minima occur at the center of the rings (H sites) than on top of the C atoms (T sites) or on the C−C bonds (2.9 Å < S < 4.35 Å). However, the energy gap between the minima at these positions is less than 1 meV (12 K) which means that the physisorbed atoms are free to diffuse along the surface at rest; this is consistent with the calculations of ref 48.

The $V_{\mathrm{H-Surface}}$ potential is smaller than 10^{-5} eV for z distances larger than 9.5 Å; the latter value was taken as the range z_{M} of this potential.

2.3. The H−H Potential. This interaction potential is given by a simple Morse function of the H−H separation R:

$$V_{\mathrm{H-H}}(R) = D_{\mathrm{e}}\{\exp[2\beta(R_{\mathrm{e}} - R)] - 2\exp[\beta(R_{\mathrm{e}} - R)]\} \quad (3)$$

with the parameters: $D_e = 4.75$ eV, $\beta = 1.95$ Å^{-1}, $R_e = 0.74$ Å deduced as usual from the spectroscopic data of the vibrational levels of the molecule.[50] This potential is smaller than 10^{-10} eV for $R > 8$ Å; the latter value was taken as the range R_M of this potential in the LH calculations of section 3.

3. Dynamical Calculations: H−H Associative Desorption

The present simulation using the above-described potential makes use of a home-built computer code whose the main aspects are presented below.

3.1. Initial Conditions and Propagation. The initial conditions are defined for a system made of the above-defined surface and two physisorbed H atoms at temperature T. The calculations are undertaken in a classical framework; they are thus marred by the *zero-point energy* problem of the bound atoms.

The initial conditions for the surface are chosen by first assigning to each degree of freedom of the C atoms velocities corresponding to random kinetic energies in the range (0, k_BT). The atoms are then equilibrated for 24 fs after which the velocities are scaled in order that their total kinetic energy sum corresponds to $^3/_2k_BT$ per atom.

Each degree of freedom of each H atom is ascribed a mean kinetic energy of $^1/_2k_BT$. This is done separately, on the one hand, for the free motions parallel to the surface plane *XY* and, on the other hand, for the bound vibrations along the Z direction.

For the H *motions parallel to the surface plane* we attribute an energy k_BT to each of the relative and center of mass (CM) motions. The procedure to fix the initial conditions is as follows. The two atoms are first placed along an arbitrary axis $S(x,y)$ at a mutual relative distance R_M. The initial direction $D_\alpha(x,y)$ of their relative motion *toward each other* is taken to make an angle α with the $S(x,y)$ axis such that $\sin\alpha = b^*/R_M$; b^* is thus a sort of projected impact parameter (associated with R_M) in the *XY* plane. The actual initial x,y positions and direction of relative motion are thereafter fixed by a random overall rotation of $S(x,y)$ and $D_\alpha(x,y)$ about the CM and a random displacement of the x and y coordinates of the CM. The randomly oriented CM velocity vector is finally added to the relative atom velocities to yield the individual atom velocities parallel to the surface.

For each H atom the position and the velocity along the Z direction are chosen for a total energy k_BT in the potential $V_{\mathrm{H\text{-}Surface}}(x,y,z,\{\vec{\rho}_{i,0}\})$ which essentially depends on z (section 2.2): the initial z positions are picked at random from the bound oscillatory motion between the two classical turning points in such a way that on the average there is $\approx ^1/_2k_BT$ in each of the kinetic and potential energies.

The propagation of the trajectories for the 200 C + 2 H atoms is done in the microcanonical ensemble; this implies energy conservation even though the initial conditions are made to sample an initial temperature. Each b^* characterizes a trajectory. The b^* values are evenly distributed in the (0, $b^*_{\max}(T)$) range. $b^*_{\max}(T) < R_M$ is determined beforehand, by coarse exploratory scans, as the b^* value for which the reaction probability drops below 2×10^{-3}. For each trajectory, the classical equations of motion are propagated using the velocity Verlet algorithm[51] with a time step of 0.12 fs. The maximum duration of one trajectory is $t_{LH} = 12$ ps.

A dilemma arises upon choosing the temperature range of the study. The astrophysical literature on the diffuse ISM incites one to choose temperatures in the 10−100 K range.[1] However, in our classical trajectory framework, selecting this range does not allow to account for the zero point energy (ZPE) motions of the H atoms in their physisorption wells. This is actually a crucial issue. Indeed, the previous study of the LH recombination reaction[8,9] indicated that fluctuations of the z positions of the physisorbed H atoms as allowed at least by their ZPE motions are essential for an adequate description of the reaction and for making classical calculations agree with the reference quantal ones. In as much as the ZPE of the physisorbed H atoms is 11.8 meV (correponding to 136 K) we have decided to carry out our calculations at $T \geq 200$ K. Thus for the bound atom motions T is clearly a *pseudo temperature* which is used to set up an initial albeit reasonable degree of disorder in the system. However, one should be aware that a *pseudo temperature* $T \geq 200$ K is pretty large in view of the temperatures of astrophysical relevance for the considered LH mechanism. It may lead to processes which do not occur in a quantum calculation. In adsorption processes of light particles at low temperatures this may lead to strong differences between classical and quantum calculations.[52,53] Compared with the work of Morisset et al.[8,9] the C atom vibrations at temperature T introduce a sort of *dynamical corrugation* of the surface that may influence the course of the reaction. Moreover, the possibility of energy exchange between the H atoms and the flexible surface introduces some probability of H atom desorption in the incoming stage of the collision.

From the Arrhenius−Polanyi−Wigner law the probability $P_{\mathrm{survival}}(T)$ of having *both* H atoms still physisorbed on the surface after an incoming encounter time t_{in} may be estimated as follows:

$$P_{\mathrm{survival}}(T) = p(T)^2 \quad (4)$$

$$p(T) = \exp[-\Gamma(T)t_{\mathrm{in}}] \quad \Gamma(T) = \nu\exp[-E_{\mathrm{d}}/(k_BT)] \quad (5)$$

ν is the vibration frequency of a physisorbed H atom relative to the surface and E_d is the physisorption well depth. t_{in} is also a function of T; it may be roughly estimated as the time it takes for the H−H internuclear distance to decrease from R_M to 1 Å. Values of P_{survival} are respectively 0.74, 0.58, and 0.49 at 200, 300, and 400 K. The latter values are but estimates, the computed reaction probabilities contain in effect the actual thermal leakage of the reactants in the course of the encounter.

3.2. Final Conditions. During the trajectory propagation two tests are done to determine whether it should be stopped before the maximum propagation time. In the first test, the distance of the two H atoms is controlled to evaluate if they are still interacting ($R < R_M$). This condition eliminates non reactive trajectories. The second test determines for each H atom whether it has desorbed ($z > z_M$) or not. Trajectories for which both H atoms still interact ($R < R_M$) and have not desorbed ($z_{1,2} < z_M$) before the maximum integration time are still able to react; trajectories of this kind that have still not desorbed when the maximum integration time has elapsed ($t_{LH} = 12$ ps) are considered as "trapped".

For trajectories in which both H atoms have desorbed with $R < R_M$ the reaction has taken place. One then defines the properties of the nascent molecule: angular momentum j and internal energy E_{int}. Any molecule with an internal energy larger than D_e is considered as dissociative even though it may be bound by a rotational barrier (quantally metastable); these are referred to as metastable-dissociative.

The reactive trajectories are thus separated in three categories: (i) stable, desorbed, (ii) metastable-dissociative desorbed and (iii) "trapped" at $t_{LH} = 12$ ps. For the first category one can

TABLE 1: Characteristics of the H_2 Recombination Reaction via the LH Mechanism on a Flexible Graphene Surface as a Function of T^a

T (E_{rel})	efficient length (Å)	mean E_{tr} (eV)	stable desorbed (%)	metastable-dissociative desorbed (%)	trapped t_{LH} = 12 ps (%)
200 K (0.0172 eV)	0.765	0.078	96.1	0.3	3.5
300 K (0.0259 eV)	0.39	0.091	95.7	2.6	1.7
400 K (0.0345 eV)	0.115	0.114	83.5	15.9	0.5

[a] The initial relative energy E_{rel} of H−H motion is given in parentheses in the first column. The efficient length and mean translational energy of the stable desorbed molecules are given. The percentages of stable, metastable, and trapped trajectories among reactive events are also given. As mentioned in the text, the metastable species are ultimately considered as dissociated.

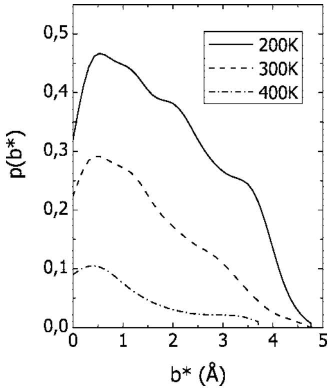


Figure 2. Reaction probability for the H−H associative desorption via the Langmuir−Hinshelwood mechanism on a flexible graphene sheet as a function of the impact parameter b^* for three surface temperatures.

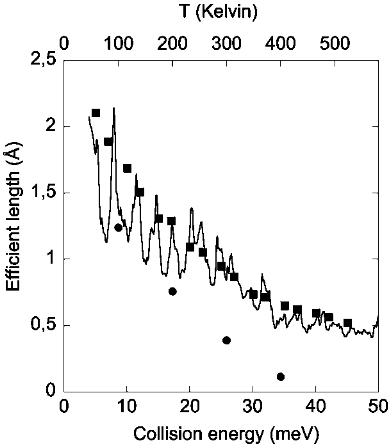


Figure 3. Efficient length for the H−H associative desorption via the Langmuir−Hinshelwood mechanism. Line and squares: quantal and quasiclassical results of ref 9 respectively for a flat rigid surface at 0 K as functions of the H−H collision energy measured in eV or in Kelvin (bottom and top axes respectively). Dots: present results using a flexible graphene sheet at temperature T (top axis).

determine the energy partitioning between the molecule internal energy E_{int}, its translational energy E_{tr} and the energy exchanged with the surface. Moreover, the internal vibration and rotation energies of the molecule can be put in correspondence with v and j quantum numbers respectively.

3.3. Results. Ensemble of trajectories were run for temperatures T = 200, 300, and 400 K. The number of trajectories is 20000 except for 400 K where 50000 trajectories were launched.

The gross characteristics of the computed LH reaction as functions of T for a flexible graphene surface are presented in Table 1. The percentage of “trapped” trajectories at t_{LH} is generally much smaller than the desorbed ones ($\leq 3.5\%$). Therefore, we have not deemed it worth to extend the integration time limit t_{LH} to higher values to inquire about their further development.

The reaction probability $p(b^*)$ for the stable desorbed molecules is shown in Figure 2 for the three values of T. By integration of this probability over b^*, we may deduce an estimate of the so-called “efficient length”[9] λ though strictly speaking such a quantity may not be defined for H atoms evolving on a shaky surface:

$$\lambda = f\int_{-\infty}^{+\infty} p(b^*)\, \mathrm{d}b^* \approx 2f\int_{0}^{b^*_{\max}} p(b^*)\, \mathrm{d}b^* \qquad (6)$$

$f = {}^1/_4$ is the statistical weight for singlet spin coupling of the electrons when dealing with electronic spin-unpolarized H atoms.[9,10] The integration boundaries in the first integral take into account the fact that the reduced particle may pass to the right or to the left of the scattering center in the considered quasi-2D world when the atoms are migrating on the surface. The efficient lengths for the three T values are displayed and compared in Table 1.

On the whole, one observes an appreciable decrease of the reaction probability and efficient length with the system temperature (Figures 2 and 3). This effect is partly due to reasons already identified in ref 8. Indeed, as recalled in section 1, the considered LH reaction may be viewed as an H + H collision in front of the surface. During this encounter, one H atom is deflected toward the vacuum and the other one toward the surface; the latter atom thus rebounds and finally moves toward the vacuum too. The formation of a bound H_2 molecule requires that the latter rebound occurs on the surface with a substantial amount of kinetic energy. This occurs only when the deflection angle of the H + H collision significantly differs from 0° (and incidentally 180°). Raising the temperature increases both the relative energy of the H + H encounter and the vibration energy of each H atom relative to the surface. For a given H−H impact parameter the increase of the relative collision energy has the effect of reducing the discussed deflection angle. Moreover, the increase of the H−surface vibration energies widens the z-range of the two H−surface motions thereafter spreading the z-range of impact parameters of the H + H encounter. This reduces the efficiency of the LH reaction too (Figure 3). This latter effect is a quite prominent one that did not exist in the quasi classical calculations of refs 8 and 9 since in the later work the only available H−surface energy was the zero point energy (11.8 meV).

Other effects contributing to the reduction with temperature of the reaction probability and of the efficient length (Figures 2 and 3) are, as pointed out above, the increasing disorder and thus corrugation of the surface when T increases as well as the increasing leakage of reactants owing to thermal desorption (section 3.1). Pursuing this digression, it is clear that the systematic increase in T will ultimately lead to the breakage of the H−surface bond (desorption) thereby rendering the discussed LH reaction off the subject. Anyhow, Figure 3 shows that as k_BT approaches the surface–H zero point energy ($T \approx 136$ K)

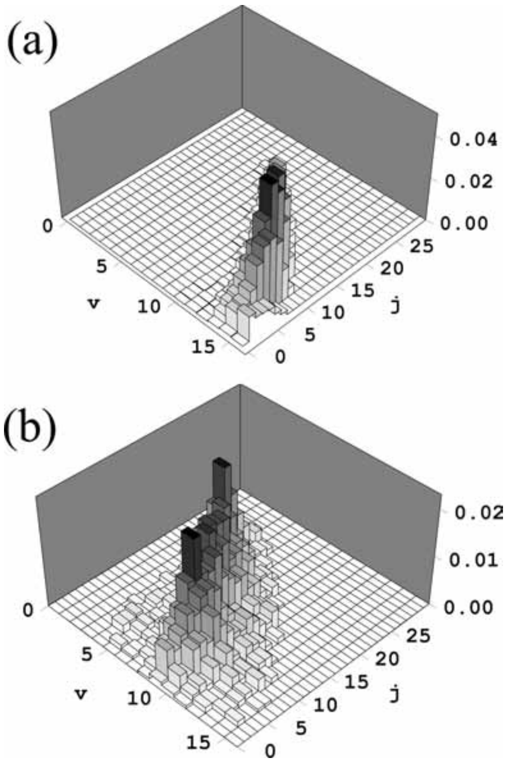


Figure 4. Rovibrational distribution of H_2 molecules emerging from a flexible graphene surface at $T = 200$ K: (a) nascent molecules issuing from the Langmuir−Hinshelwood reaction; (b) reflected molecules after one collision with the surface.

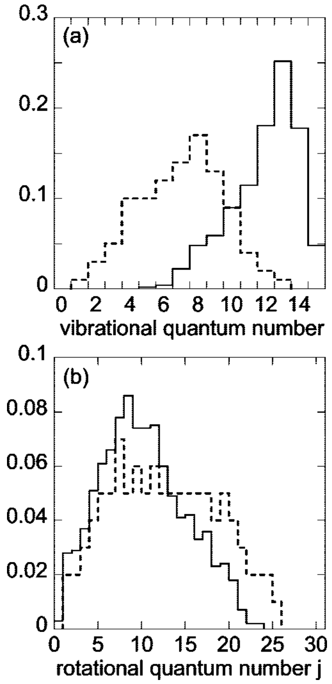


Figure 5. (a) Vibrational distribution summed over rotations of the H_2 molecules emerging from a flexible graphene surface at $T = 200$ K. Thin solid line: nascent molecules issuing from the Langmuir−Hinshelwood reaction. Dashed line: after one collision with the surface. (b) Same caption and symbols as in part a but for the rotational distribution summed over vibrations.

the present calculations yield an efficient length consistent with the quantal result of ref 9.

Of particular concern in the present work is the effect on the LH reaction, and especially on the internal energy of the molecule, of freeing the surface atom motions. Without entering into detailed comparisons let us just mention that we find that whether the surface is rigid or not plays a minor role in the molecule formation and in the energy balance of the LH reaction. In particular the energy transfer to the surface is less than 0.1 eV and is on the average around 0.05 eV. This is quite small compared to the exothermicity of the reaction.

Figures 4a and 5 show the vibrational and rotational distributions of the nascent H_2 molecule at $T = 200$ K. In as much as very little amounts of energy are transferred to the surface (≤ 0.1 eV, see above) or go into the molecule translation away from the surface (≤ 0.15 eV, Table 1) the internal energy of the molecule lies very close to the maximum energy allowed. As found by Morisset et al.[9] for a rigid surface, the vibrational distribution spans the range $5 < v < 15$ with a maximum around $v \approx 12-14$; moreover the rotational distribution is rather broad: it extends up to $j = 20$ and is largest around $j \approx 10$. The distributions at $T = 300$ and 400 K have nearly the same characteristics as those just discussed. Following the discussion of section 1.4, the above results come in support of our classical trajectory approach.

To conclude this section, we may say that the allowance given in the present work to the surface atoms to freely move according to the laws of classical mechanics during the LH associative desorption does not change in any significant way the earlier rigid surface findings of Morisset et al.[9] as concerns the very high internal energy content of the nascent H_2 molecule. These theoretical results are thus still in disagreement with the available experimental data.[16−18] Though recent measurements extending the previous ones have been reported[18] v and j levels beyond $v = 7$ and $j = 6$ have not been detected in these experiments.

In what follows we use the results of this section as starting points for the study of a succession of $H_2(v,j)$−surface collisions.

4. Dynamical Calculations: Successive $H_2(v,j)$−Surface Impacts

As stated above, the set of trajectories yielding stable desorbed molecules from the LH reaction constitute a good representative sampling when proceeding to set up initial conditions for the subsequent $H_2(v,j)$−surface collisions simulating interactions with walls of carbonaceous porous material.

4.1. Single H_2−Surface Impact. H_2 molecules issued from the LH reaction at temperature T (section 3) are directed toward a graphene surface representing a pore wall. This is conveniently achieved in practice by keeping the same surface, properly reset at temperature T, and randomly reorienting the CM velocity vector of the molecule motion; if still necessary, the Z component of the reoriented vector is made negative to have the molecule move toward the surface. Of course, the CM velocity vector reorientation lets the characteristics of the H_2 internal motion intact. The set of reoriented trajectories of the molecules are subsequently propagated using the same method as in section 3. The maximum duration of a trajectory is $t_{max} = 12$ ps.

As a result of an H_2−surface impact the molecules can be reemitted from the surface as bound (cooled, $\Delta E_{int} < 0$, or heated, $\Delta E_{int} > 0$) molecules. Molecules heated above D_e are considered as dissociated (metastable-dissociative). There is also a possibility that after a time interval t_{max} from the impact some molecules have not yet been reemitted from the surface; these are called “trapped” molecules.

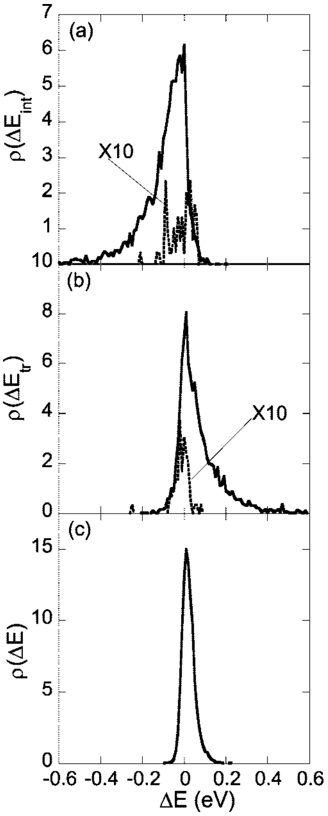


Figure 6. Energy distributions ρ of H_2 molecules emerging from the surface. Solid lines: molecules reflected after a time interval t_{max} from a single impact; dashed lines: molecules released between t_{max} and $2t_{max}$. (a) internal energy of the molecules; (b) translational energy of the molecules; (c) energy transferred to the surface.

4.1.1. Molecules Reflected from a Single H_2–Surface Impact. Figures 4b and 5 show the vibrational (v) and rotational (j) distributions of the bound molecules reflected after one impact onto the surface at $T = 200$ K. The comparison between the v,j distributions before (Figures 4a and 5) and after (Figures 4b and 5) the impact readily shows an appreciable vibration to rotation conversion: the vibrational distribution peak is displaced to lower v values by 5 quanta and the rotational distribution broadens and extends to higher j values by 5–10 quanta. As discussed in section 1.4 this is in agreement with our expectations and thus comes in support of our use of a classical molecular dynamics description.

Parts a–c of Figure 6 show respectively the distributions of the molecule internal energy change (ΔE_{int}), that of its translational energy change (ΔE_{tr}) and that of the surface energy gain (ΔE_{surf}) as a result of a single H_2–surface impact. These plots convey the following information: (i) the percentage of cooled molecules is much larger than that of heated ones (Figure 6a); (ii) the molecule cooling ($\Delta E_{int} < 0$) occurs to the benefit of its translational energy ($\Delta E_{tr} > 0$) and much less to that of energy transfer to the surface (Figures 6b,c). Thus statistically, the molecules are accelerated and little energy is imparted to the surface ($\Delta E_{surf} < 0.15$ eV).

4.1.2. "Trapped" Molecules Resulting from the First H_2–Surface Impact. 7% of the molecules that are fired at the surface at $T = 200$ K get trapped. Molecules that are likely to be "trapped" are actually those that have small translational energy before the impact. This is illustrated in Figure 7 which compares, the translational energy distributions before the H_2–surface impact of the molecules that get reflected from the surface with that of the molecules that end "trapped" within the t_{max} time interval. The latter molecules have initial translational energies smaller than ≈0.1 eV; this is comparable with the H_2–surface physisorption well depth.

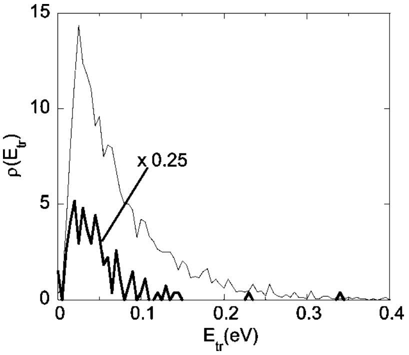


Figure 7. Translational energy distributions before the H_2–surface impact of the molecules that get reflected from the surface (thin line) and of the molecules that end "trapped" (bold line) within the t_{max} time interval. Each distribution is normalized separately.

TABLE 2: Probabilities for internal energy variations of an H_2 molecule after one collision on a flexible graphene surface at temperature T. ΔE_m is the mean $|\Delta E_{int}|$ value

T (K)	cooled $\Delta E_{int} <$ 0 (%)	warmed $\Delta E_{int} >$ 0 (%)	metastable-dissociative	trapped (%)	ΔE_m (eV) cooled	ΔE_m (eV) warmed
200	78.0	10.0	5%	7	0.12	0.02
300	72.5	12.4	13.5%	2.6	0.12	0.03
400	67.5	11.3	21%	0.2	0.12	0.04

In order to examine what happens to the "trapped" molecules we have allowed them to evolve further from t_{max} to $2t_{max}$. In so doing, nearly 25% of the "trapped" molecules succeed in desorbing. Thenceforth, the half-lifetime of the "trapped" molecules amounts to ≈29 ps. Moreover, parts a and b of Figure 6 show that, when the "trapped" molecules succeed in desorbing, their internal and translational energies upon desorption are but very little different from their values prior to the impact; the average ΔE_{int} and ΔE_{tr} values are very close to -0.02 eV and -0.008 eV respectively.

From the above, we may infer that most of the molecule's internal energy conversion essentially occurs when the molecule hits the surface and is reflected back. If the translational energy is large then efficient energy transfer ensues. On the other hand, energy exchange with the grain during the stay of "trapped" molecules near the surface is not very efficient.

4.1.3. Results as Functions of Temperature. Table 2 summarizes the information on the internal energy variation of the excited H_2 molecule after a single H_2–surface impact at temperature T. The percentages of cooled, heated, metastable-dissociative (heated above D_e) and trapped molecules are given together with the mean internal energy variations in one or the other direction.

As shown above, the percentage of cooled molecules dominates that of heated ones. Also, the change in the internal energy of the molecule is not sensitive to the temperature. The molecule internal energy reduction is on the average close to 0.12 eV whereas its increase is much smaller ≈0.03 eV. These figures are not predictable using simple kinematic models[54] and are not readily interpretable using the much more evolved theory of multiphonon excitation in molecule–surface collisions[55,56]

4.2. Successions of H_2–Surface Impacts. Multiple Collisions with Pore Walls. To simulate multiple collisions with pore walls we iterate the procedure adopted in the preceding section for one collision: the nth H_2–surface impact utilizes as

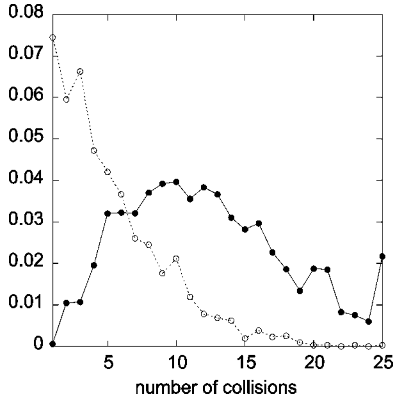


Figure 8. Probabilities of the 3200 trajectories issuing from the initial Langmuir−Hinshelwood reaction that undergo within 12 ps the indicated number of collisions with a flexible graphene sheet at 200 K and lead to trapped (dashed line) or reflected (solid line) H_2 molecules.

initial input H_2 molecules with internal and translational energies as formed at completion of the $(n - 1)$th step. We let each trajectory propagate and undergo successive impacts for $t_{prop} =$ 12 ps; the number of impacts is limited to 25. Actually this latter limitation concerns only 2% of the trajectories (see below). The next discussions focus mainly on the results obtained at T $= 200$ K.

After the above-described iteration procedure, among the 3200 initial trajectories issued from the LH reaction on the surface that produced H_2, 56% are reflected from the surface and 44% are "trapped". Figure 8 shows the percentages of the molecules that undergo a given total number of impacts with reflections ($\leq$25) during t_{prop}. For the 1800 reflected trajectories the average number of impacts is $\approx$12. Figure 8 also shows the percentages of the molecules that undergo a given total number of impacts and are finally "trapped" during t_{prop}. The latter percentages are seen to rapidly decrease with the number of impacts; molecules that have undergone more than 15 impacts have negligible chances of being "trapped".

4.2.1. Molecules Reflected from the Succession of H_2−Surface Impacts. Figure 9 shows the evolution of the molecule vibrational−rotational distributions for different numbers of H_2−surface impacts at $T = 200$ K. Along with Figures 4 and 5 it clearly shows, up the 15th impact, a conversion of vibration into rotation: the vibration gets cooled (down to the range $0 < v < 10$) while the rotation gets heated (up to j values as high as $j = 28$). After the 15th impact the v range gets narrower, $0 < v < 5$, and a "backward surge" of the molecule rotation appears.

Figures 10 and 11 show the evolution of the internal (E_{int}) and translational (E_{tr}) energies of the molecules for different numbers of impacts. Comparison is also made with the results obtained for the nascent molecule and after a single H_2−surface impact. The effect of the succession of impacts appears as displacements and broadenings of the E_{int} and E_{tr} distributions together with their prolongation by tails extending toward 0 and beyond 1.5 eV respectively. These figures clearly show that the molecules are more and more accelerated with the number of impacts. Their analysis also shows that the swifter the molecules the stronger their E_{int} reduction. These results depict a "virtuous circle" in which the molecules are cooled to the benefit of their translational energy which in turn favors their cooling.

Figure 12 shows the distribution of the cumulated energy brought by the successions of impacts to the grain heating (E_{surf}). As expected these distributions move to larger energies with the number of impacts. On the average, typical bits of 0.05 eV per impact are imparted to the surface.

4.2.2. Molecules "Trapped" During the Succession of H_2−Surface Impacts. As pointed out above, at the end of our calculations on the succession of H_2−surface impacts, 44% of the molecules are found "trapped". Figure 8 shows that, among the successive collisions, the contribution of the first one to this percentage ($\approx$7%) is the largest. This figure also shows that the percentage of trapped trajectories progressively diminishes with the number of collisions; this is because at each impact the mean translational energy of the molecules increases. The average number of impacts leading to "trapping" is $\approx$ 6.

Since the "trapping" duration is finite (section 4.2.1), when "trapped" molecules are at last released into the vacuum only a fraction of them is susceptible of being trapped again in subsequent impacts. The complementary fraction thus enters into the above-described "virtuous circle" (section 4.2.1) and gets more and more accelerated; this increases their chance of escaping any further "trapping".

The results of section 4.2.1 for the single H_2−surface impact have also established that the "trapped" molecules ultimately desorb with very little changes of the internal and translational energies they had before being "trapped". Thus it is plausible that a molecule that gets "trapped" m times will have after n impacts an internal energy close to that of a molecule having undergone $n - m$ impacts without being trapped. In other words, *"trapping" slows down the cooling*.

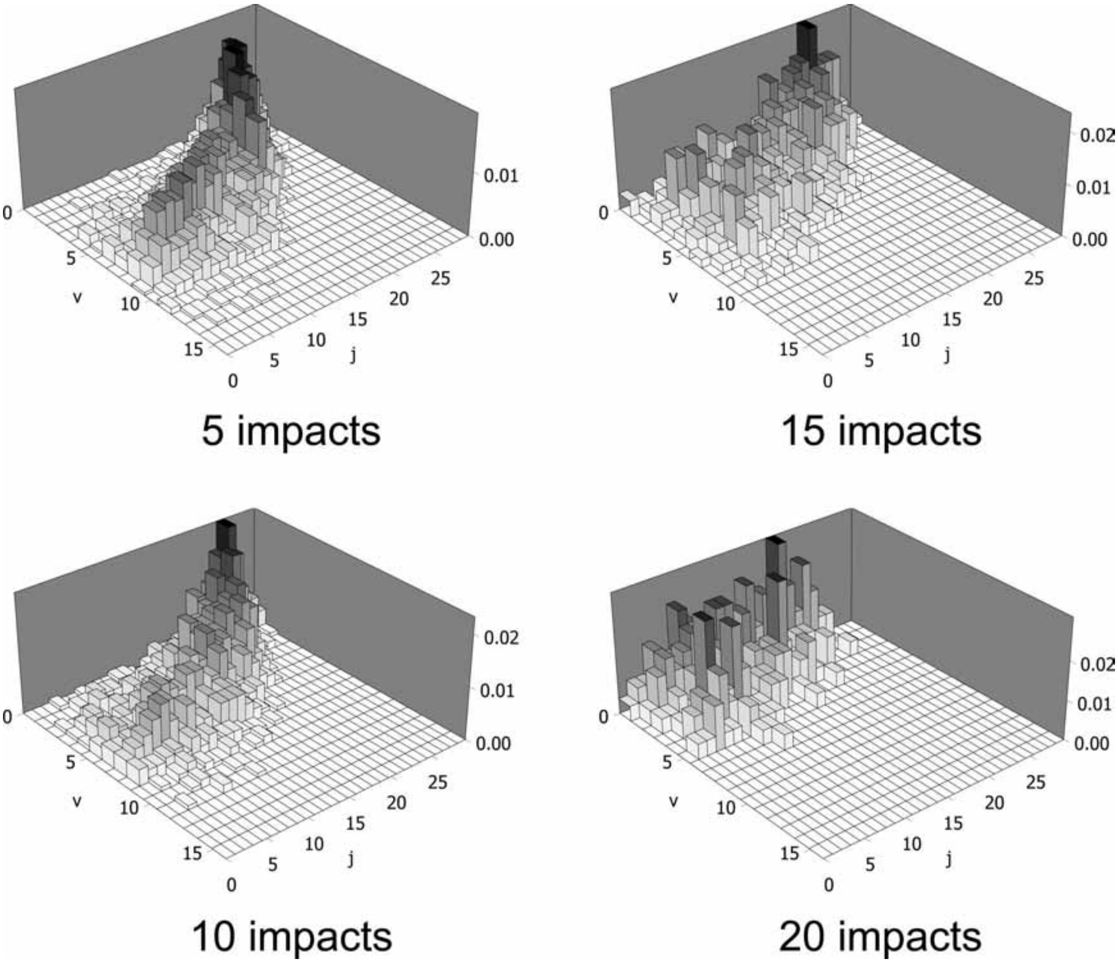
5. Summary and Conclusions

Using a nonrigid graphene sheet to model the surface of carbonaceous dust grains of the ISM we have investigated the LH associative desorption of physisorbed H atoms and have thereafter simulated collision successions of the resulting H_2 molecules with pore walls of the grain.

Concerning the LH reaction, we find quite similar results to those obtained by Morisset et al.[9] using a rigid surface: the nascent H_2 molecules have quite high internal energies ($v \approx$ 12−14 and $j \approx 10$). Thus very little energy (typically $\approx$0.05 eV) is imparted to the surface during the reaction. This conclusion casts doubts on the adequacy of the mere LH mechanism to explain the H−H recombination mechanism that takes place in the experiments of refs 16−18.

In a single collision of the nascent H_2 molecule with the graphene surface (intended to represent a pore wall) the molecule may be reflected back from, or get "trapped" onto, the surface. The reflected molecules are in a majority; their probability of having got cooled down increases (from 68% to 80%) when temperature decreases (from 400 to 200 K, respectively). One observes a significant conversion from the vibration to the rotation of the molecule but its mean internal energy reduction remains small $\sim$0.12 eV. Here too, typically 0.05 eV of the molecule internal energy loss flows on the average into the surface; the remainder goes into the molecule translational energy: the reflected molecules are thus statistically cooled and accelerated. "Trapped" molecules have a half-lifetime of $\approx$29 ps. Contrary to the reflected molecules they show, when released into the vacuum, insignificant changes of the internal and translational energies they had before being "trapped": trapping neutralizes the cooling process.

As a result of our simulation of several collisions with graphitic pore walls we may say that a sample of H_2 molecules issuing from an LH reaction may undergo immediate successions of roughly 12 impacts with reflections and 6 impacts with trapping during 12 ps. Actually, 56% of the sample is reflected and 44% is trapped.



5 impacts

15 impacts

10 impacts

20 impacts

Figure 9. Rovibrational distributions of H_2 molecules reflected from a flexible graphene surface at $T = 200$ K after the indicated numbers of impacts since their formation by the LH reaction.

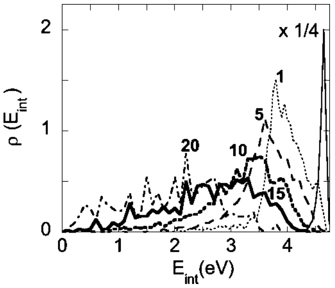


Figure 10. Internal energy distributions of H_2 molecules reflected from a flexible graphene surface at $T = 200$ K after the indicated numbers of impacts since their formation by the LH reaction: (full thin line) nascent molecules, (dotted line) 1 impact, (dashed line) 5 impacts, (thick short dashes) 10 impacts, (bold line) 15 impacts, (dashed dotted line) 20 impacts. Each distribution is normalized separately.

The reflected molecules show in the first 5 to 15 impacts a substantial conversion of their vibrational energy into rotation. This conversion actually mediates the flow of the molecule internal energy into its translational energy and surface heating. The molecules are cooled but the internal energy change is slow. Indeed, compared to the initial internal energy of the molecule $\approx$4.6 eV, on the average only 0.10 eV is lost per impact. The cooling of the reflected molecules benefits in part to their translational energy, on the average: 0.03 eV per impact. However, this average value is an underestimation and it imperfectly reflects what actually happens: the swifter the molecules are or get the larger the number of impacts on the surface they undergo and the more efficiently cooled they get.

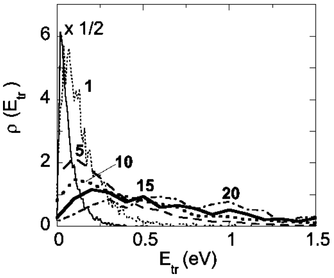


Figure 11. Same as Figure 10 for the translational energy of the H_2 molecules.

A "virtuous circle" of acceleration−cooling thus sets up for the reflected molecules. Impacts with reflections also impart energy to the surface heating; on the average bits of 0.05−0.06 eV per impact flow into the surface.

As concerns the fraction of "trapped" molecules, cooling is neutralized for the "trapping" duration: trapping thus slows down the already slow cooling process. Nevertheless, it is most plausible that, upon their release, previously "trapped" molecules progressively enter into the abovementioned "virtuous circle" and thus get accelerated−cooled.

In conclusion we have shed some light on how the quite important internal energy content of the nascent H_2 molecules issued from the LH reaction between physisorbed H atoms on a graphitic grain surface is possibly converted by a succession of collisions with pore walls of a carbonaceous dust grain. A substantial vibration-to-rotation conversion takes place prior to

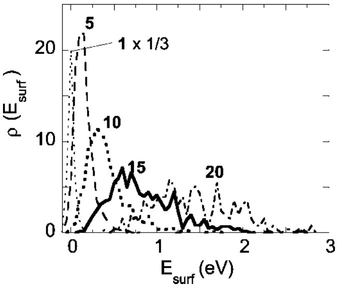


Figure 12. Same as Figure 10 for the cumulated energy imparted to the surface as a result of the indicated numbers of impacts.

or simultaneously with the reduction of the molecule internal energy; this extends the already high rotational distribution of the nascent molecules $5 < j < 20$ upward by 5 to 10 quanta. The cooling of the molecules is relatively slow but a clear displacement of the nascent vibrational distribution from the $5 < v < 15$ range down to the $0 < v < 10$ range is observed after a succession of impacts (typically 10−15). It is tempting to relate these findings to the ISO−SWS (infrared space observatory−short-wavelength-spectrometer) observations of high v,j ($v \leq 4$, $j \leq 30$) values in the H_2 emission from the Orion OMC-1 cloud,[21] but this is admittedly too early of an association. While the bits of energy transferred to the surface or to the translation per collision are small compared to the total internal energy of the molecule they constitute quite important energy inputs into such a cold medium as the ISM. This should stimulate the investigation of the astrophysical implications of the present findings.

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