We describe a mechanism that explains the formation of hydrocarbons and hydrocarbyls from hydrogenated graphene/graphite; hard C–C bonds are weakened and broken by the synergistic effect of chemisorbed hydrogen and high temperature vibrations. Total energies, optimized structures, and transition states are obtained from Density Functional Theory simulations. These values have been used to determine the Boltzmann probability for a thermal fluctuation to overcome the kinetic barriers, yielding the time scale for an event to occur. This mechanism can be used to rationalize the possible routes for the creation of small hydrocarbons and hydrocarbyls from etched graphene/graphite in stellar regions.

Recent technological advances providing improved sensitivity in radio-astronomical receivers, and through the usage of large (sub)millimeter radio telescopes, have permitted to find numerous new chemical species in outer space. Several chemical processes lead to the formation of these molecules in gas-phase in space; e.g. ion-neutral, neutral-neutral, and radical-neutral reactions. In addition, reactions at the surface of the grains can also enhance the gas-phase abundance of these species when the temperature of dust grains increases above a critical value. Heating processes of dust grains can occur due to shocks, UV photon absorption from external sources, or by the proximity of a newly formed star. Nevertheless, the presence of complex molecules in photodissociation regions requires a continuous production mechanism that so far is not fully understood, although understanding these chemical processes is crucial to study the chemical evolution of the interstellar gas in galaxies. Therefore, there is an increasing interest in detailed microscopic calculations leading to models that can explain the relative abundance of these molecules.

Carbonaceous particles are usually terminated on graphene/graphite-like layers or amorphous carbon, which may transform under heating to other stable forms of carbon. Clouds rich on silicates or carbonaceous dust grains are covered with ices (H₂O, NH₃, CH₃, CH₂OH, CO, ...) providing support for the formation of different species. A paradigmatic example is the formation of the hydrogen molecule from atomic hydrogen; due to the presence of ices it is produced even at temperatures as low as 10 K, as demonstrated by laboratory experiments on circumstellar grain analogs and by Density Functional Theory (DFT) simulations. On the other hand, in low-density clouds (diffuse) these particles are known to be clean of contaminants like ice, and a similar mechanism is lacking since the thermally activated process of molecular hydrogen formation would require temperatures T > 250 K to achieve a reasonable yield in times ranging between a few years to some thousands years.

The opposite problem is the effect of atomic hydrogen on carbonaceous particles. It has recently attracted attention because of its potential to explain the formation of hydrocarbon molecules and all sort of radicals in space. These authors have described the high-temperature etching of SiC grains in a hydrogen-rich atmosphere in the laboratory. The main experimental observation is the formation of holes on a graphene surface. This is surprising since the typical energy stored in a C–C bond on graphene is ≥ 4 eV, and such a process would only happen on a time-scale of several years in pristine graphene at the temperature of the experiment (1000 K), cf. Fig. 1. Indeed, graphene is one of the known toughest materials in Nature, with a very large in-plane Young modulus of ≈ 1 TPa, which arises from the extraordinary efficiency of the sp² and π-like hybrid orbitals bonding C atoms on a honeycomb topology. Furthermore, bonding between C atoms is very versatile, resulting in a range of strengths from triple to single bonds, ≈ 10 eV to 4 eV per bond, respectively. Characteristic energies for the simple (S), double (D) and triple (T) C–C bonds are represented by vertical dashed lines. The top dashed horizontal line represent the total time since the big-bang (∼ 10¹⁰ years), and the middle horizontal line represents 1 year. Around the blue 3500 K line the breaking of C–C bonds in the solid-liquid phase transition takes place in about ms.

![Graphene formation mechanism](image-url)
exponential dependence with temperature of the Boltzmann factors such a process at 500 K would take an amount of time equivalent to the Age of the Universe and would not happen, while at the same time the solid-liquid phase-transition starting around 3500 K is correctly predicted to take place in about a few minutes. We notice that a reduction of the barrier below 3 eV would be enough to allow such a process to happen on about a few nanoseconds. Experiments run on heavily hydrogenated graphene make it clear that the presence of hydrogen does not eliminate these kinetic barriers, but we find that it acts to reduce their values so it can happen on a reasonable laboratory time scale, between milliseconds and minutes. Here we search for detailed mechanisms that can explain the catalytic-like activity of atomic hydrogen leading to the reported formation of holes in the graphene layer, as well as the nature of the fragments formed at the same time, i.e. hydrocarbons and radicals of various sizes.

In the ab-initio atomistic simulations, total energies, forces and stresses were minimized by using DFT as implemented in the plane-waves package QUANTUM ESPRESSO. A perturbative van der Waals (vdW) correction was used to check for the effect of long-range interactions on the different configurations analyzed. For this purpose, we have used an empirical vdW R−6 correction to add dispersive forces to conventional density functionals within the DFT+D formalism. This vdW contribution to the total energy is almost negligible around the transition states; it only becomes significant (∼15%) when distances between the expelled fragments and graphene increases > 4 Å, which only matters for a good description of energies at asymptotic distances. The Local Density Approximation (LDA) has been used for the exchange and correlation potential. It describes fairly well both the C–C and C–H bonds, and at the same time offers a most simple and clear conceptual frame. Similar conclusions have been reached by checking a few selected cases with a Generalized Gradient Approximations (GGA) to the exchange and correlation potential. Norm-conserving scalar-relativistic pseudopotentials have been used to model the ion-electron interaction.

Models having from tens to hundreds of atoms have been considered to construct both finite-size clusters (labeled as C) and extended periodic-cell models (labeled as e). A k-space mesh of Δk ≤ 0.01 Å−1, and an energy cutoff of 500 eV yielded total energies with an accuracy of ΔE ≈ ±0.05 eV (converged to a precision better than 10−6 eV). Optimized geometries were obtained with residual forces lower than 0.01 eV/Å, and stresses below 0.1 GPa. Besides enthalpies of formation, H, for a particular process the all important feature to ascertain its feasibility is the height of the barrier at the transition state (TS), ΔE. These TSs have been investigated within the climbing-image nudge elastic band (CI-NEB) approach, implemented in the QUANTUM ESPRESSO package, where the initial, the final and all the intermediate image-states were free to fully relax. At this point, it is important to remark that the underlying chemistry of these systems is well represented by all the approximations adopted here, and we expect a good correlation with experimental data, as it is usually attained.

A plausible mechanism that would allow the breaking of the strong in-plane C–C bonds should involve a transition state low enough to get from the initial to the final state in a meaningful time on the experiment time scale. Our simulations show that atomic hydrogen plays a dual role in this job. On the one hand, it chemisorbs on the graphene layer with an adsorption energy of ≈ 1 eV, and a small initial sticking barrier of ≈ 0.15 eV. This small barrier appears as a result of the induced deformation upon adsorption of H on the stiff planar graphene layer, where the sp2 acquires a partial sp3 character. On the other hand, hydrogen can adsorb on the edges of the newly created holes saturating the dangling bonds very effectively. That kind of C–H bond can store as much as 5 eV and it is characterized by vibrational frequencies that match the phonons of the graphene layer. Therefore, the C–H bond can effectively compete with the C–C bond making it possible to reduce transition barriers for various processes to reasonable amounts (see Fig. 2). Fig. 1 gives in a logarithmic scale the typical time in seconds of having a process with a transition barrier of ΔE (eV) at a temperature T (K). At the temperatures of interest (T > 500 K) we can safely neglect tunneling contributions and we assume that the probability for a thermal fluctuation to overcome the TS barrier is determined by the canonical Boltzmann factor:

$$
\Gamma = \Gamma_0 e^{-\frac{\Delta E}{k_B T}}.
$$

Since the exponential dominates the behaviour of this probability as a function of T we take the prefactor as a temperature-independent value, which can be estimated via a typical C–C or C–H phonon, $\Gamma_0 \approx 1000$ cm−1. Due to the Boltzmann factor, variations on $\Gamma_0$ by even a few orders of magnitude are quickly overcome by the effect of the temperature. By propagation of errors, we find for typical temperatures of ≈ 1000 K, and typical energy barriers of ≈ 1 eV that uncertainties in the calculation of barriers of ≈ ±0.05 eV, and in the values of temperatures of ≈ ±10 K, result in Fig. 1 in fractional errors < 35%. These errors bars, even much bigger values, are quite acceptable to draw conclusions since the rates change so quickly with the values of the barriers.
ment and other hydrogens left in the layer. Instead, we find to steric impediments from hydrogens in the extracted frag-
mental to saturate this ring with H atoms to directly obtain
It would be desirable from the point of view of the formation
to weaken first, and then to passivate the broken C–C bonds.

Take as an example the extraction of a six C ring (see Fig. 3).
which now may take place
in less than a second at 1000 K. The mechanism involves C–
C stretching so a wagging mode of a nearby chemisorbed H
can place the H closer to the middle of the C–C bond and can
help to break it while forming at the same time a new C–H
bond, cf. Fig. 2. The formation of a favourable configuration
of chemisorbed hydrogen atoms depends on the available den-
sity of atoms impinging on the surface; the reference experi-
ments have been performed under conditions where atomic H
has been admitted in the UHV chamber up to a $10^{-6}$ mbars
($\approx 10^{10}$ atoms/cm$^3$), and temperature has been raised up
to 1000 K. These conditions imply hydrogen saturation condi-
tions, making likely to reach a favourable configuration, that
then determines the shape of the hole. These experiments have
been designed to mimick regions near red-giant stars between
3 to 15 stellar radii, where temperature ranges from 1500 K
to 200 K, and hydrogen densities take values between $10^{11}$ to
$10^6$ atoms/cm$^3$. We remark that the enthalpy of formation
for this particular C$_6$ hole is negative ($-1.12$ eV), therefore
making the hole saturated with hydrogen and the fragment,
C$_6$H$_3$, stable. A similar pattern follows for a large cluster la-
belled C in Table II, with values of $+2.81$ and $-0.82$ eV for the
barrier and the enthalpy of formation, respectively. The main
difference between the periodic and finite-size simulations re-
sides in the barriers to stick the hydrogen initially near the
region to be etched. This is mainly due to the different elastic
constants for a continuous layer and a small chunk of material
that may be supported by some substrate or not. Finally, we
analyze, for the case of the periodic system, the upstart of the
scaling with the size of the hole formed, i.e. with the number of
C atoms to be extracted, by considering 10 and 14 C atoms.
These holes have been labeled in Fig. 3 with A, B and C, and
in the continuous lines marked with empty circles, squares and
diamonds, respectively. Enthalpies of formation grow slowly
with the size of the fragment tending to the saturation value to
be found on very large systems. Interestingly enough, how-
ever, the transition state barriers tend to be nearly the same, in-
dicating that the main difficulty to extract large fragments re-
sides with the configurational statistical complexity more than
with the chemistry. This can be fixed by introducing an abun-
dant amount of hydrogen favoring the appearance of many
different configurations; the holes observed would then corre-
respond to the particular configuration realized on the graphene
layer. Finally, we notice that in an elegant experiment Xie et al.
have recently measured the etching of single graphene
layer edges by hydrogen plasma at a rate of approximately 0.3
nm/min. According to our model, to create a C$_6$ hole with a
perimetral length of approximately 9 Å at the measured rate
it would require a barrier of $\approx 2.85$ eV, which is remarkably
close to the values in Table I taking into account that our fo-
cus is on the general mechanism using arguments based in the
order of magnitude of rates, not on the detailed values that we
cannot expect to obtain with such accuracy.

Second, we focus on the small molecules formed on the
internal edges of the holes left on the surface, and in the ex-
ternal edges of the ejected fragments following the creation
of a large defect on the layer. Table II shows a comparison
between enthalpies and transition state barriers for a variety
of small molecules. Formation of CH$_2$ and CH$_3$ involves the
We have studied the formation of large holes on graphene byls, and other polyaromatics from hydrogenated graphene. The proposed mechanism also sheds light into possible routes for opposite reasons. In the first case, the H chemisorbed on top position (continuous circle) finds it too favorable to bond to the second C (dashed circle) and cannot participate in the breaking of the C–C bond. In the second case, the second carbon atom cannot support the interaction with four H plus the first carbon atom. Nevertheless, CH₂ and CH₃ fragments detached from hydrogenated graphene/graphite will capture environmental H atoms to spontaneously form CH₄. Other fragments with higher C content, such as C₂H₂, C₂H₄, and C₂H₆, are not exothermic, but display reasonable formation barriers too. The inverse process, where the fragment joins the edge, is hindered by entropic orientational considerations and does not play an important role. The transition barriers for these molecules having two C atoms are higher than for those having just one C atom, but still reasonable if compared with typical times in the circumstellar medium. To complement the scenario, since these particles may be bombarded by charged particles in a realistic situation located near a star we have considered the breaking of C₂H₂ on a charged surface, leading to the anion C₂H₂⁻. The barrier for this case is of +2.20 eV, i.e. very similar to the one found on the inner side of the hole for the periodic system. The presence of the extra charge on the surface does not significantly alter the mechanism of breaking the relevant C−C bonds, and indicates that the abundance of anions and neutral species should be similar.

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