Computational study of reaction between prebiotic molecules on surfaces

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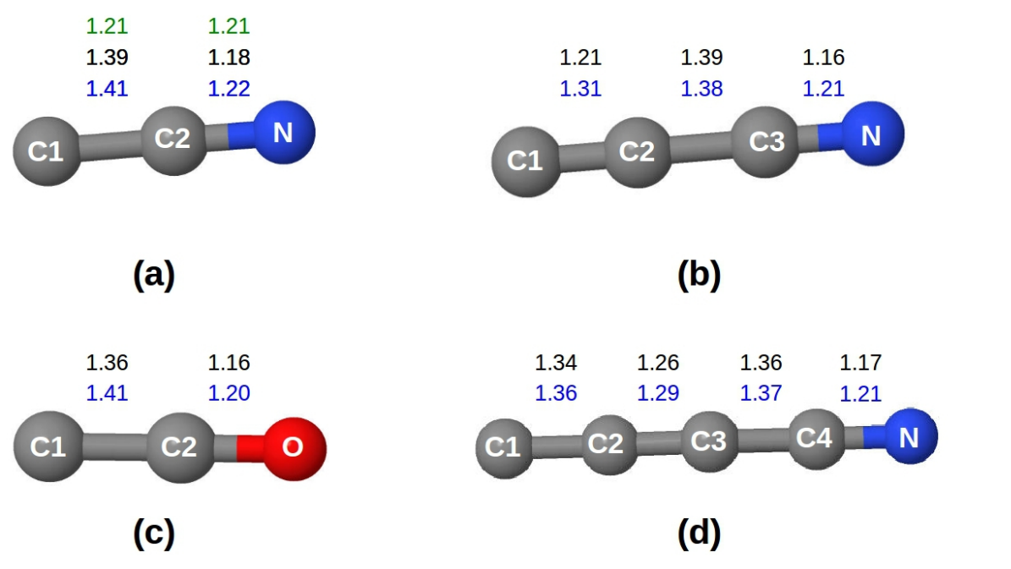
Aim of this work is the computational modeling of the reaction between carbon monoxide and the prebiotic species C_nN (n = 1, 2, 3) in a carbon-rich dense molecular cloud which produces molecules that have all the elements of the amino acids backbone.
The mentioned reactions have been investigated on two carbon surfaces: graphene, as a model of an interstellar grain covered by carbonaceous materials, and a polycyclic aromatic hydrocarbon, abundantly present in dense molecular clouds. [1-3]
Among all the reactions investigated, the one leading to the C_3NO formation is by far the most exoergic, therefore it was extensively studied and two reaction mechanisms have been suggested. The first one is a Langmuir-Hinshelwood-type, investigated by means of DFT calculations. The second one is an Eley-Rideal-type, studied by *ab initio* molecular dynamics, performed at the DFT level according to the SIESTA method. The energetic aspects of the Eley-Rideal mechanism are detailed through a velocity distribution function (VDF) analysis.

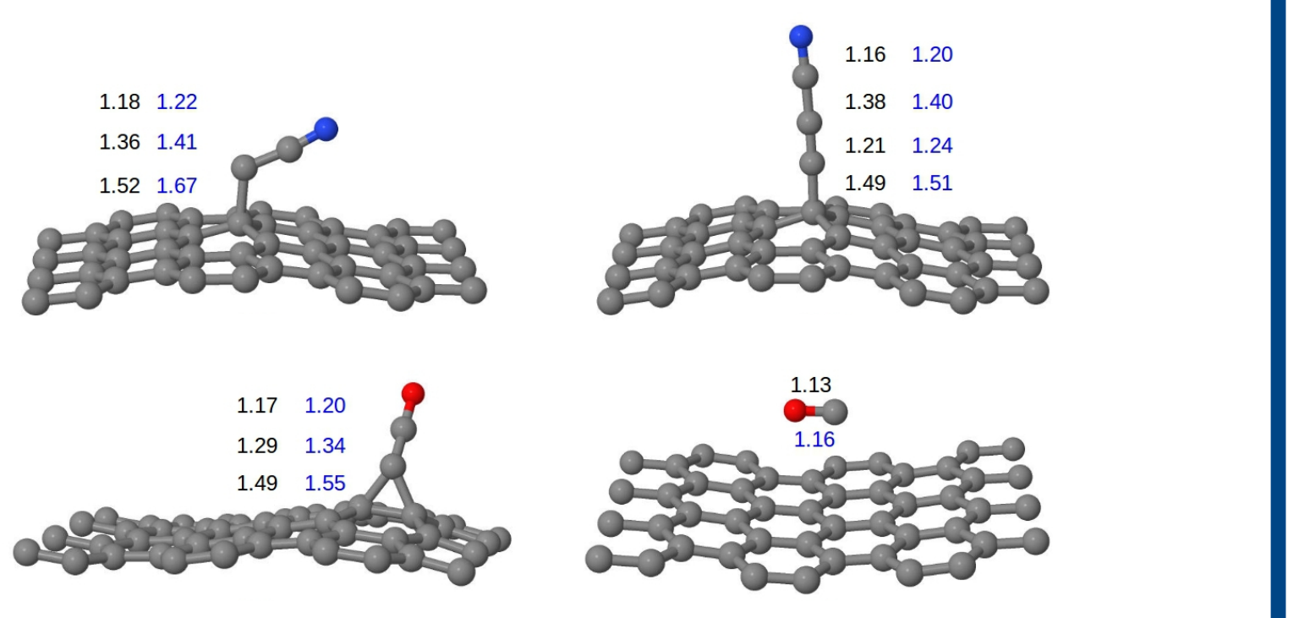
Geometry of prebiotic molecules on surfaces

The geometries of C_nN and C_2O are reported on figure (a,b,c,d). The latter was studied in order to suggest a different reaction pattern for the formation of C_3NO.

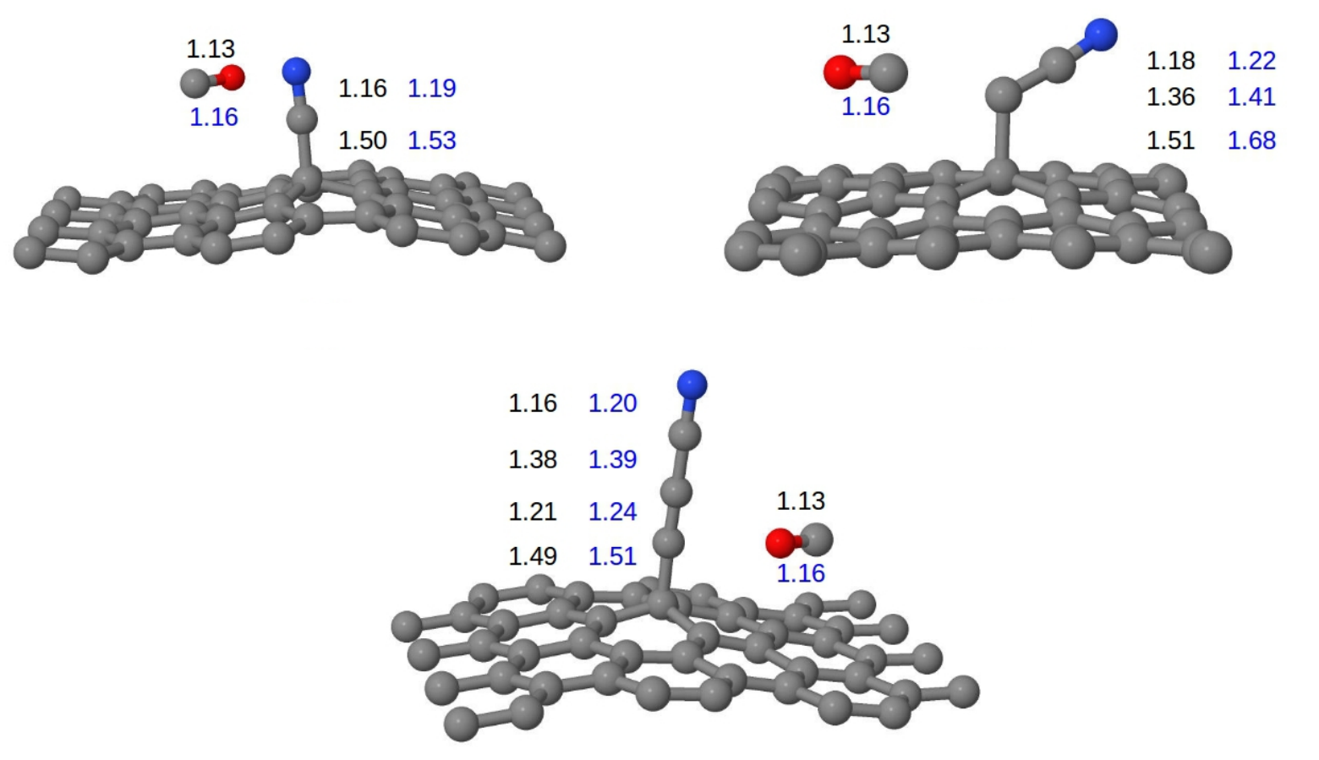


Prebiotic species adsorption produce a small distortion on the surface. In presence of a structural defect, the C1-C2 bonding is elongated by 0.10 Å, making the $-C_2N$ fragment activate.
The adsorption of C_2O is the most exoergic, due to the bridge interaction. Carbon monoxide is phisisorbed on both carbonaceous surfaces.

	SIESTA* DRSLL	M062X/cc-pvDZ*	
		ΔSCF	ΔZPE
CN / g	-140.62	-169.50	-163.10
C_2N / g	-80.52	-71.52	-65.27
C_3N / g	-159.67		
CO / g	-31.72	-12.28	-8.54
C_2O / g	-113.50	-283.94	-269.04



Coadsorption of prebiotic molecules



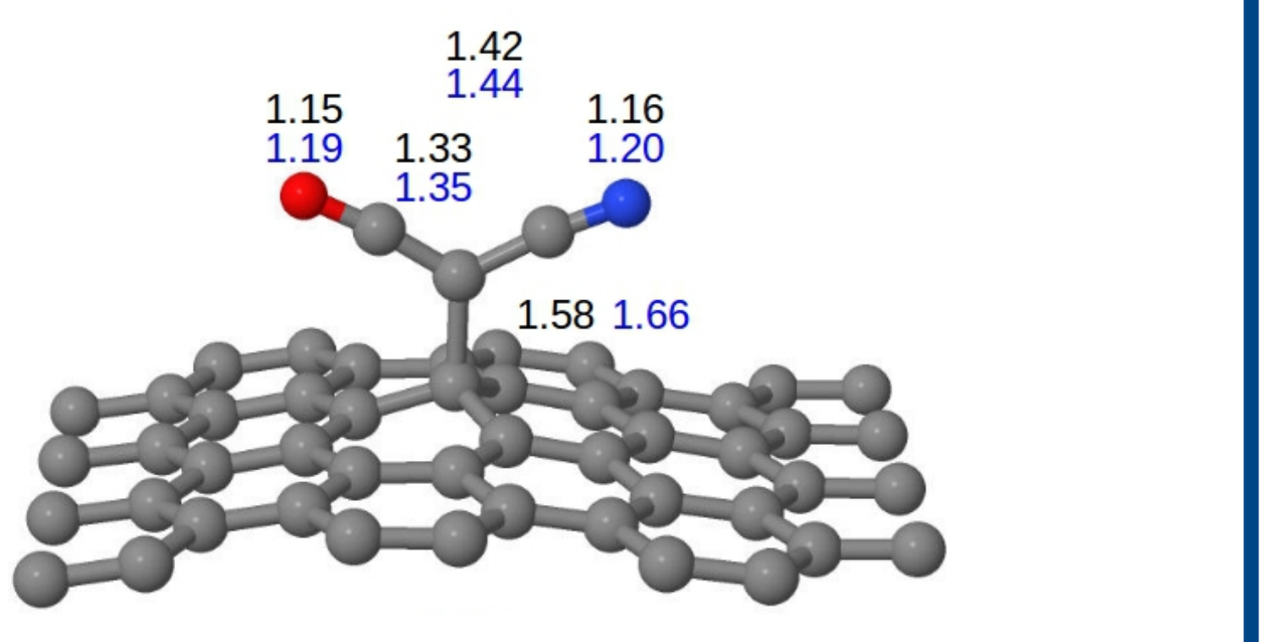
The adsorption of CO in presence of a C_nN molecule is an exoergic process, for all the prebiotic species. Co-adsorption geometry of CN in presence of C_2O converges at the product C_3NO one. The geometries of co-adsorption of C_nN and CO are almost the same of those corresponding to the adsorption of the single species.

(KJ/mol)	SIESTA* DRSLL	M062X/cc-pvDZ*	
		ΔSCF	ΔZPE
CO + CN/g	-31.56	-6.75	-2.54
CO + C_2N/g	-27.21	-16.30	-11.53
CN + C_2O/g	-410.52	-407.17	-398.44
CO + C_3N/g	-34.23	-4.17	0.07

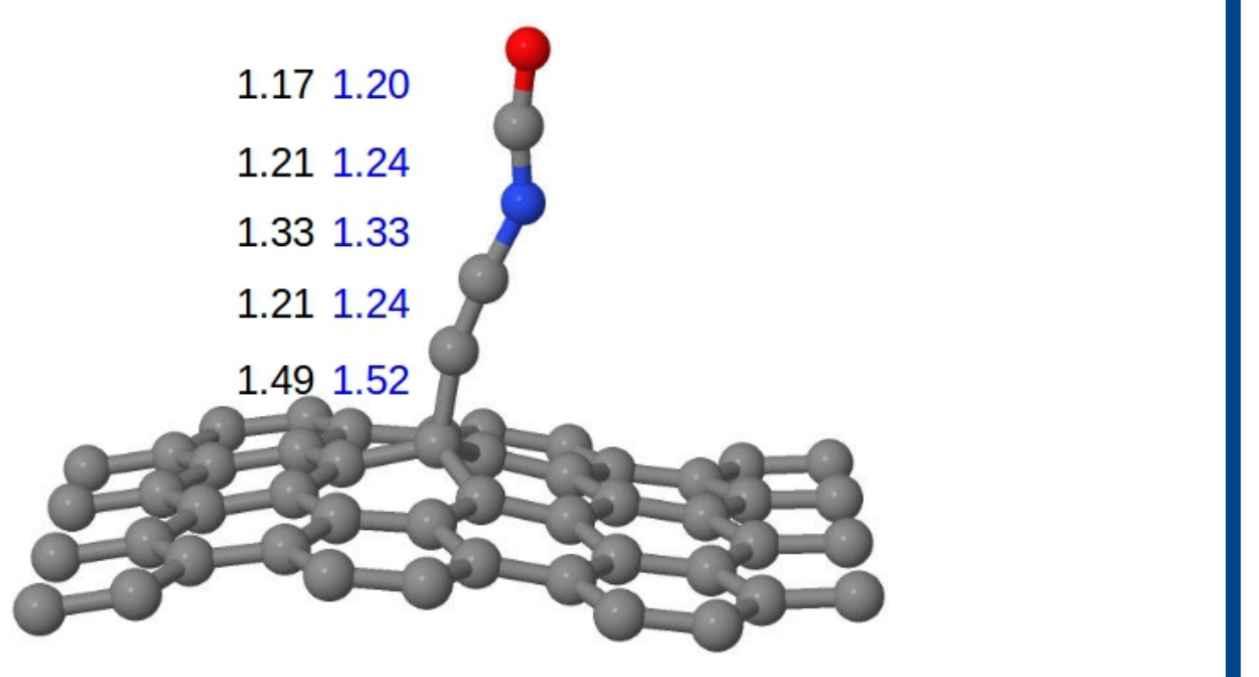
*Energies are reported in kJ/mol

Reaction product – LH and ER mechanisms

LH	SIESTA* DRSLL	M062X/cc-pvDZ*	
		ΔSCF	ΔZPE
C(CO)N/g	-0.17	4.76	10.17
C(CO)CN/g	-212.11	-253.71	-238.36
CC(CO)N/g	-104.00	-163.76	-149.89
C(CO)CCN/g	2.183	-5.51	4.55
CC(CO)CN/g	5.64	-4.52	5.09
CCC(CO)N/g	129.16	119.30	127.23



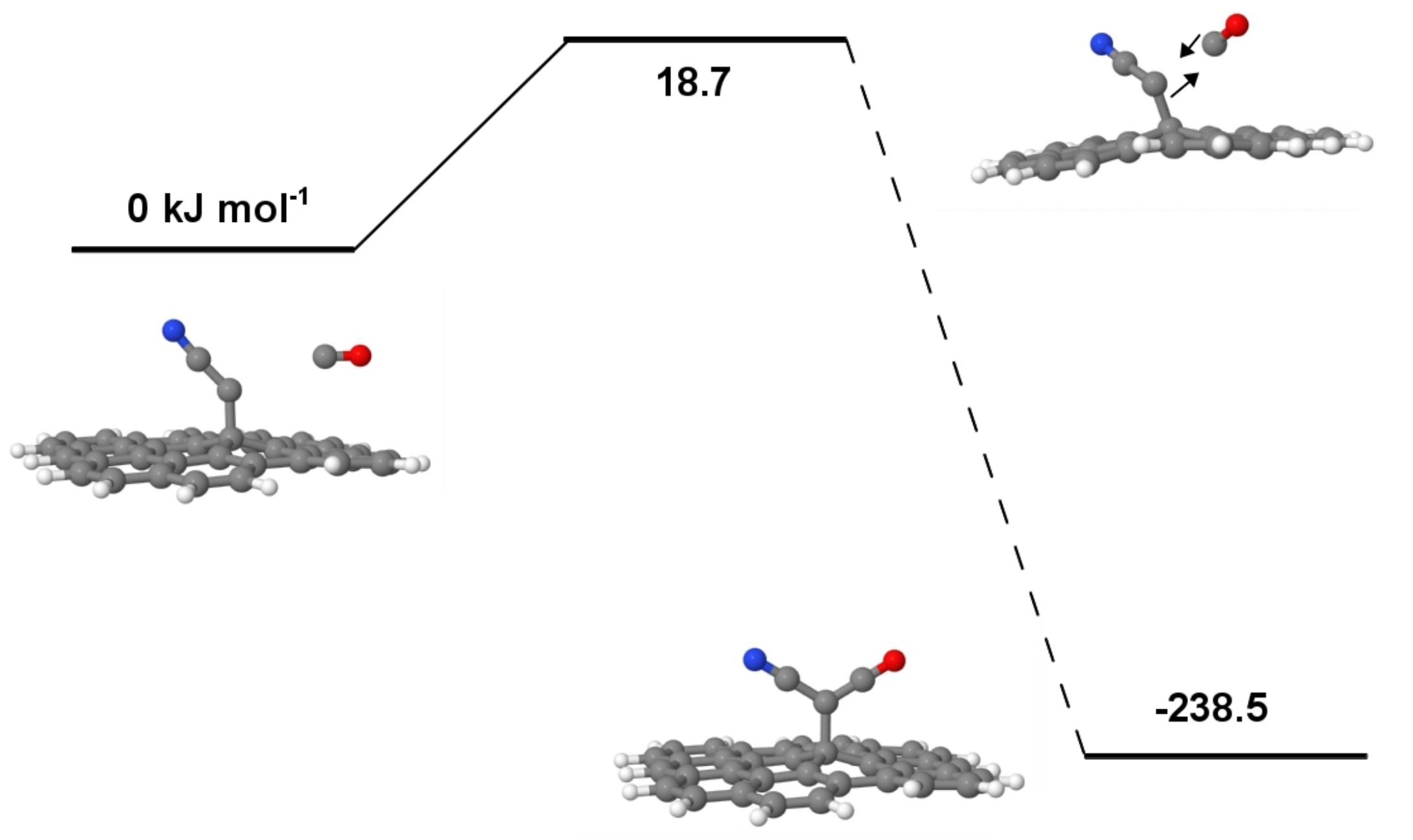
ER	SIESTA* DRSLL	M062X/cc-pvDZ*	
		ΔSCF	ΔZPE
C(CO)N/g	-31.73	-1.99	7.63
C(CO)CN/g	-239.32	-270.01	-249.88
CC(CO)N/g	-131.21	-180.06	-161.42
C(CO)CCN/g	-32.05	-9.68	4.62
CC(CO)CN/g	-28.59	-8.69	5.16
CCC(CO)N/g	94.93	115.12	127.29



*Energies are reported in kJ/mol

In order to distinguish the different isomers of the products, the attack site of CO is put on brackets. The reaction occurring between C_2N and CO is the most exoergic one (product C(CO)CN in red), thus this reaction was studied in detail and two different reaction paths have been suggested. All the other reactions between prebiotic molecules and CO are lightly exoergic or endoergic.

Langmuir-Hinshelwood mechanism



The molecule C_2N is chemisorbed, while CO is physisorbed. Thus, a first attempt to evaluate the transition state has been made scanning the energy as the bond length of the fragment -CO in the C_3NO. The geometry of transition state has been finally founded through QST3 method

Computational Details

The pseudopotentials used for the SIESTA method were generated for all atoms involved in the investigation. The Troullier-Martins parametrization was adopted and the semilocal form produced was transformed into the fully non local form proposed by Kleinman and Bylander. The pseudopotential generation process mainly involved three steps:
1) generation of DFT atomic levels for the selected atom.
2) generation of the pseudopotential
3) check of the results.

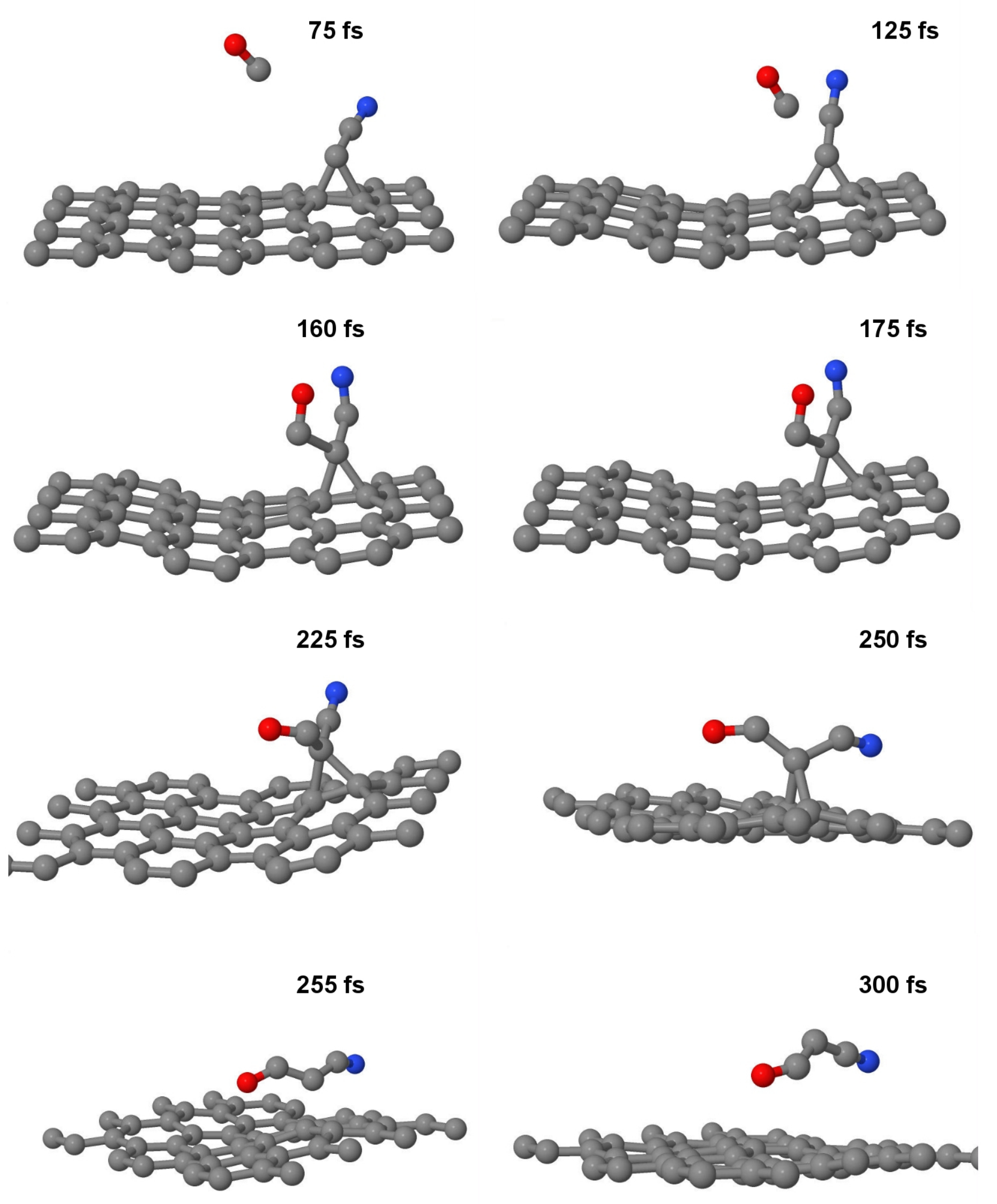
We tested the pseudopotential in two steps: we calculated the difference between the atomic eingevalues obtained with the all-electron calculations and those computed with the pseudopotential (a value of 0.01 Ry for this difference was retained optimal). Then we performed a test calculation for the transferability, to evaluate the behavior of the pseudopotential in a chemical environment different from an atom.

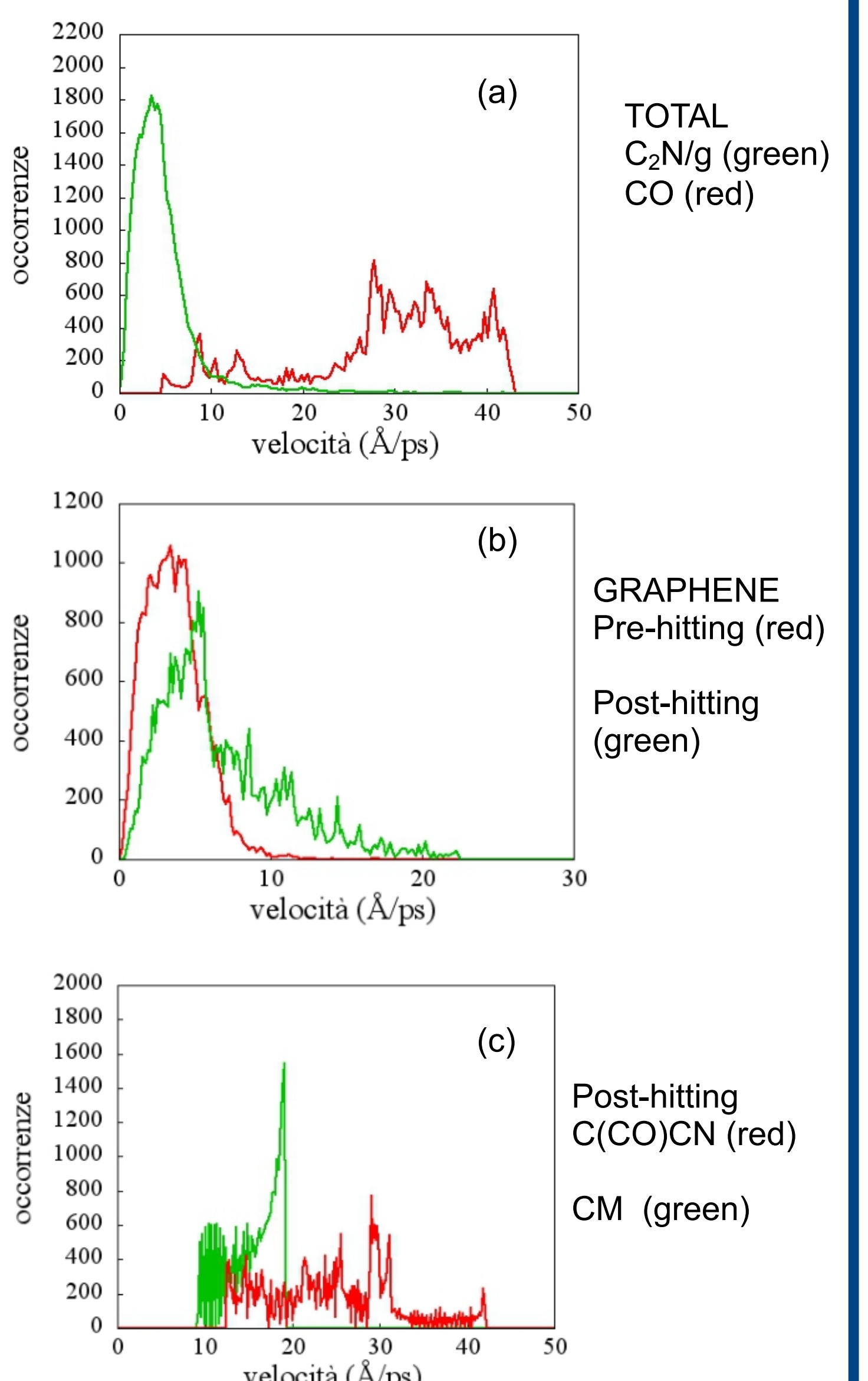
Strictly localized basis sets where optimized using the pseudopotential previously generated. Our optimized basis set are equivalent to a double zeta polarized, considered accurate in this theoretical context. We exploited SIMPLEX algorithm in order to optimized variationally all the parameters defining the basis set. The standard of acceptance of basis set were the same applied for the transferability test of pseudopotential.

In the *ab initio* molecular dynamic we used the PBE functional.

In order to evaluate correctly the van der Waals interactions we used the M06-2X functional for the investigation on PAH with the Gaussian 09 software and the DRSLL functional with the SIESTA method on graphene.

Eley-Rideal mechanism

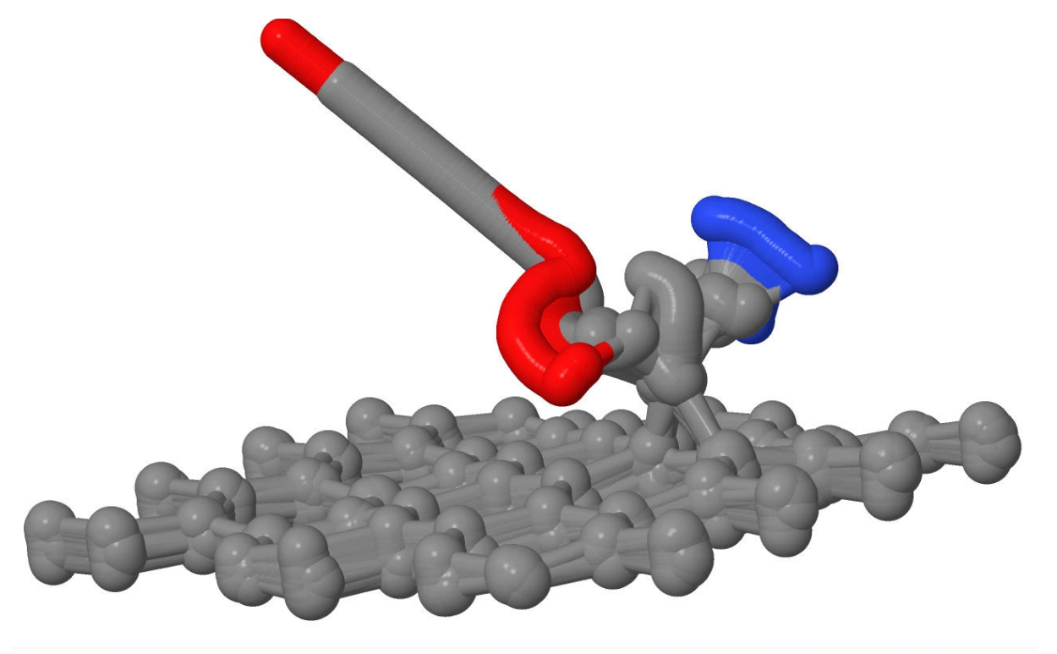




In the molecular dynamics, we considered CO as projectile and the C1 atom of C_2N as target. The hitting has been investigate starting from CO different approach directions and initial kinetic energies (between 0.2 - 3.5 eV). When CO has 2 eV and follows the direction showed in figure, the reaction happens. Structural rearrangement occurs in 125 fs after the hitting. From the VDF analysis we figure out that:

- **CO transfer energy to graphene (figure a, b)**
- **The desorbed product C_3NO is vibrationally excited (figure c, red)**
- **Desorption requires times and energy (figure c, green)**
- **The final speed of the center of mass of C_3NO is 19 Å/ps, wich corresponds to 1.2 eV.**

	Equilibration	Hitting
Ensemble	NVT	NVE
Algorithm	Nosè	Verlet
Temperature/K	100	-
Timestep/fs	0.5	0.5
Total time/fs	2500	variable



Overlap of all the simulation snapshots

References

[1] Chiar, J. E., Tielens, A. Adamson, Ricca, A. The Astrophysical Journal, 770(1), 78 - 91, **2013**

[2] Tielens, A. G. G. M. Reviews of Modern Physics, 85(3), 1021-1081, **2013**

[3] UMIST Database http://udfa.ajmarkwick.net/

Conclusion

- **We investigated two possible mechanisms of reaction for the formation of the backbone of a β-amino acid.**
- **Energy barrier calculated for the LH mechanism is relatively low.**
- **At 2 eV the Eley-Rideal reaction has been observed.**
- **The product C_3NO may continue reacting either on surface or in the void, thanks to the exoergicity of its formation.**

Astronomical complex organic molecules in different environments, 1st Italian workshop on astrochemistry - Florence 10-11 March 2016