

Molecular Dynamics simulations of low temperature plasma processes

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E. Neyts, P. Brault, Molecular dynamics simulations for plasma surface interactions, *Plasma Processes and Polymers* 14 (2017) 1600145

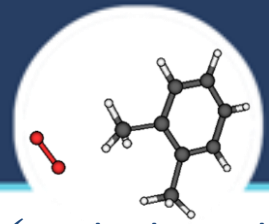
D. B. Graves, P. Brault, Molecular dynamics for low temperature plasma-surface interaction studies, *J. Phys. D* 42 (2009) 194011



The image shows a circular icon containing two molecular models. On the left is a small diatomic molecule with one red and one white atom. On the right is a larger, more complex organic molecule with a central ring and several substituents.

Outline

- Molecular Dynamics principles and practical issues
- Insights into hydrocarbon plasma reactivity
 - Soot precursor formation using REBO potential
- Insights into plasma oxidation processes of organic pollutant in water
 - Case study #1: Paracetamol degradation using reactive FF
 - Case study #2: Sulfamethoxazole degradation using DFTB-MD
- Conclusions



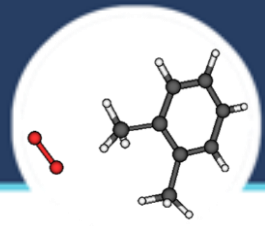
Molecular Dynamics: Principles

- ✓ Calculate all trajectories of a set of atoms, molecules, etc via the Newton equations of motion
→ Suitable for processes at nanoscale (up to 10^9 atoms)
- ✓ A rigorous approach requires the use of robust interaction potentials if comparison with experiments is looked for.
 - If necessary running DFT, i.e. electronic calculations → *ab-initio* or *first-principles* MD and/or Machine Learning methods
 - Availability of FF including electrons (eFF, eReaxFF) for basic mechanism in plasmas
- ✓ and initial conditions (positions, velocities) preferably matching experimental conditions
→ appropriate kinetic energy or velocity distribution functions can be obtained/deduced from experiments (MS, laser spectroscopy, etc) or plasma-kinetic models.
- ✓ Proper energy dissipation:
 - Energy release during deposition, allowing bond formation/breaking
 - Annealing
 - via friction term(s), thermostat(s)

$$\vec{F}_i = m_i \vec{a}_i = m_i \frac{d\vec{v}_i}{dt} = m_i \frac{d^2 \vec{r}_i}{dt^2}$$

and

$$\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$$



Molecular Dynamics: Practical issues

Relevance/significance of MD Simulations

Fluxes:

Exp. $10^{15} \text{cm}^{-2} \text{s}^{-1} = 10 \text{ species} / \text{nm}^2 / \text{s}$ - **MD** $1 \text{ specie} / 10 \times 10 \text{ nm}^2 / 2 \text{ ps}$

Prohibits long time diffusion, except if including specific acceleration strategies (fbMC, CVHD, hyperdynamics, ...)

Pressure/simulation box size:

Solid density : Pt 65 nm^{-3}

Liquid density: water 33 nm^{-3}

If box size is in the range $10 \times 10 \times 10 \text{ nm}^3 \rightarrow 65\,000 \text{ Pt atoms}$ or $33\,000 \text{ water molecules}$

\rightarrow Statistical quantities (diffusion coeff, reaction rates, etc) can be directly calculated

Gas density: $1 \text{ atm} = 2.4 \cdot 10^{-2} \text{ nm}^{-3}$

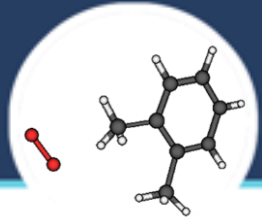
\rightarrow Not enough species in box of size d at pressure P

\rightarrow Chemistry and reactivity in the gas phase require scaling law between simulation box and reactor size \rightarrow

Solution: relevant parameter = Collision number $\propto P \cdot d \rightarrow \uparrow P \downarrow d$

P. Brault, *Multiscale Molecular Dynamics Simulation of Plasma Processing: Application to Plasma Sputtering*, Front. Phys. 6 (2018) 59

P. Brault, *Multiscale Molecular Dynamics Simulations of Fuel Cell Nanocatalyst Plasma Sputtering Growth and Deposition*, Energies 3 (2020) 3584



Molecular Dynamics: Practical issues

■ Plasma surface interactions (solid/liquid)

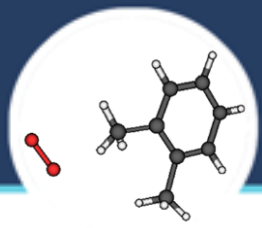
- Density differences → high MD fluxes → significance of resulting deposition/etching rates
- Solution: Growth or etching probability provided energy dissipation through the condensed medium is properly addressed → scaling with experimental flux

Φ_{MD}

Φ_{exp}

$$\Rightarrow \tau_{E,G}^{exp} = \frac{\Phi_{exp}}{\Phi_{MD}} \cdot \tau_{E,G}^{MD}$$

Solid or liquid



Insights into hydrocarbon plasma reactivity → Building simulations

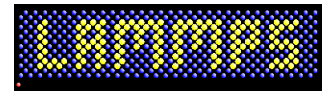
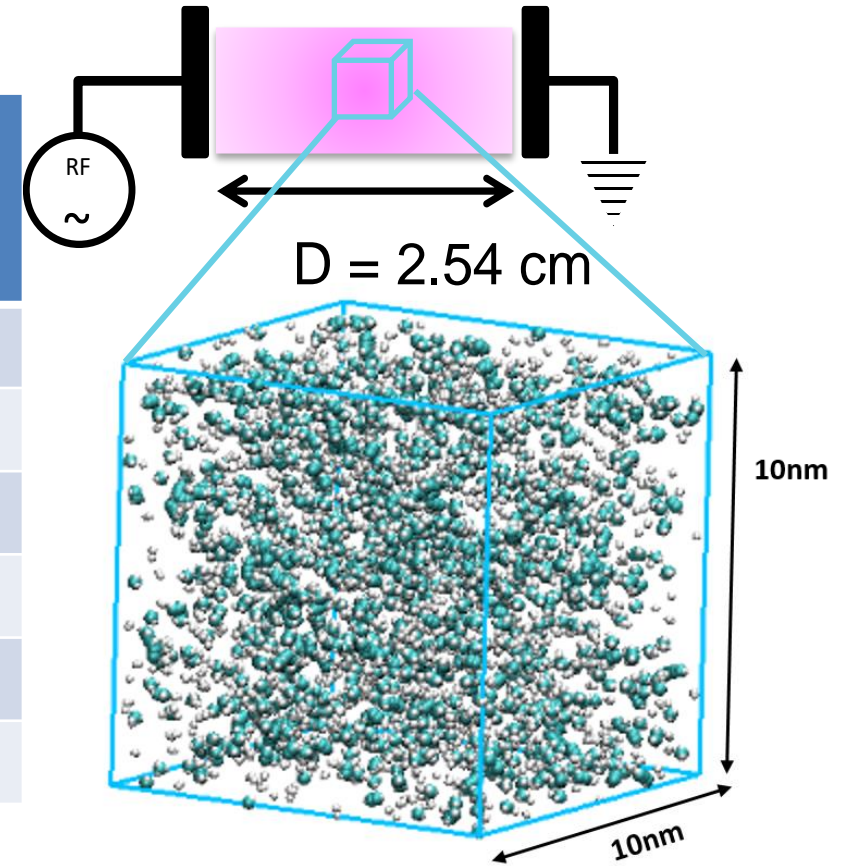
■ Initial conditions issued from 1D fluid model of Ar/4% CH₄ → RF plasma, P = 70 Pa, V_b = 100 V (*)

■ Simulation box size and total number of molecules issued from $P_{exp} \cdot d_{exp} = P_{sim} \cdot d_{sim}$
 → 10 x 10 x 10 nm³ and N= 2683

■ Temperatures: 300, 400, 500 and 1000 K

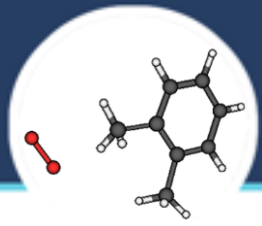
■ Glenn Otakandza's PhD work, Uni Orléans

Neutral species	Molar ratio	Molecule number in sim box
CH ₄	1.4 10 ⁻²	630
H ₂	3.2 10 ⁻²	1440
C ₂ H ₄	5.3 10 ⁻³	243
C ₂ H	3.2 10 ⁻³	144
C ₂ H ₂	2.7 10 ⁻³	122
CH ₃	2.3 10 ⁻³	104



(*) G. Têtard et al, Discharge dynamics, plasma kinetics and gas flow effect in argon-acetylene discharges, PSST (2021) <https://doi.org/10.1088/1361-6595/ac2a17>

S. Prasanna et al, Self-consistent simulation studies on effect of methane concentration on microwave assisted H₂-CH₄ plasma at low pressure, Plasma Sources Sci. Technol. 26 (2017) 097001



Insights into hydrocarbon plasma reactivity → Interaction potential

- The Reactive Empirical Bond Order (2ndG-REBO) forcefield is suitable for describing hydrocarbon interactions, including high energy impacts.

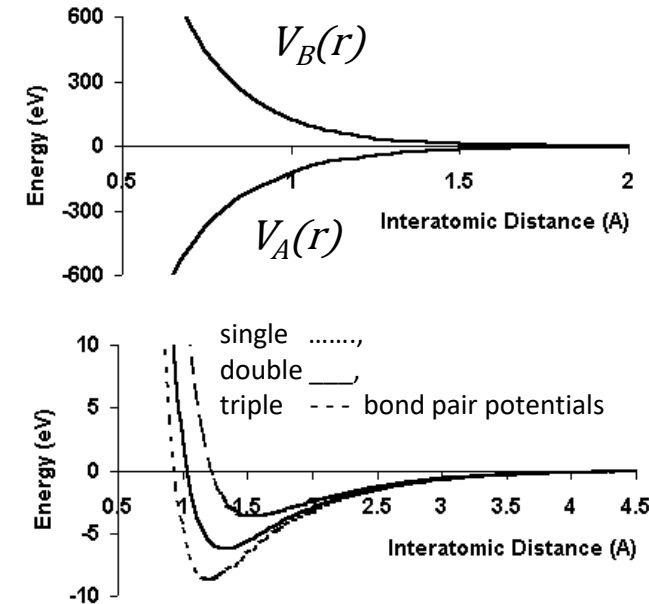
- REBO total energy reads

$$E_b = \sum_i \sum_{j>i} [V_R(r_{ij}) - b_{ij}V_A(r_{ij})]$$

$$V_R(r) = f_c \left(1 + \frac{Q}{r} \right) A e^{-\alpha r}$$

$$V_A(r) = f_c \sum_{n=1}^3 B_n e^{-\beta_n r}$$

- The bond order term b_{ij} allows capturing the local coordination behavior and thus can reproduce the reaction with the correct bond breaking/formation.



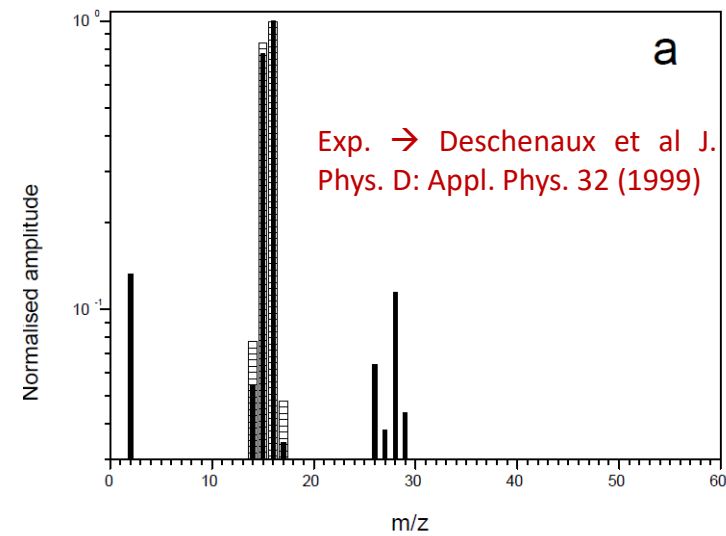
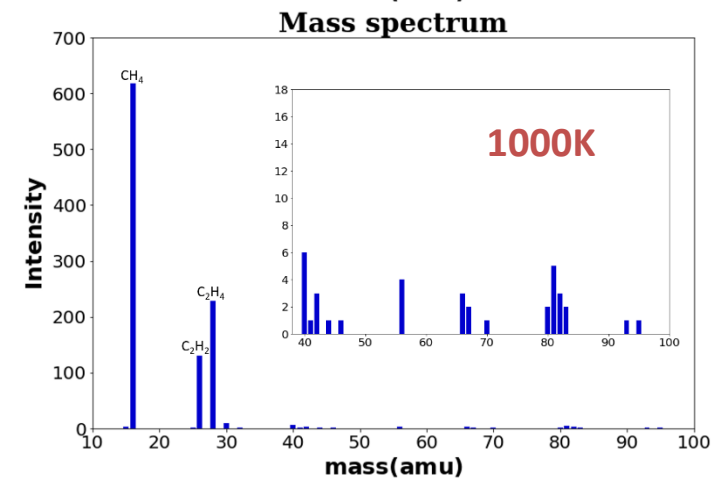
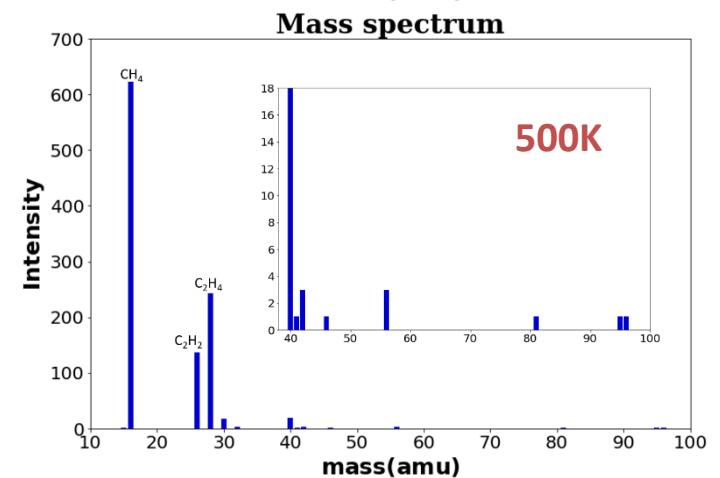
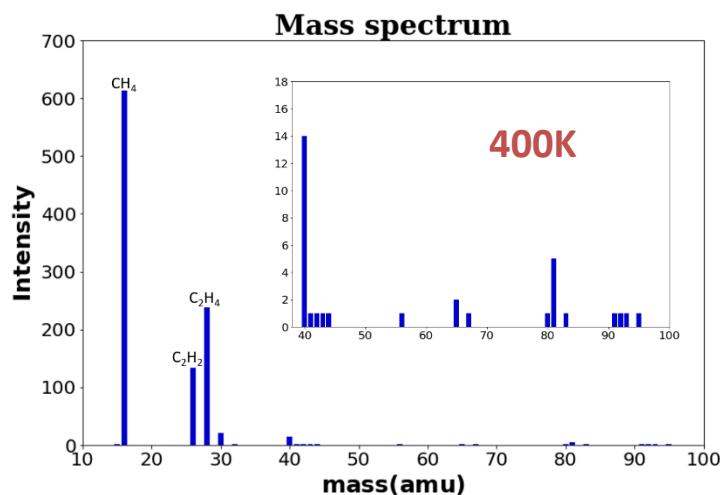
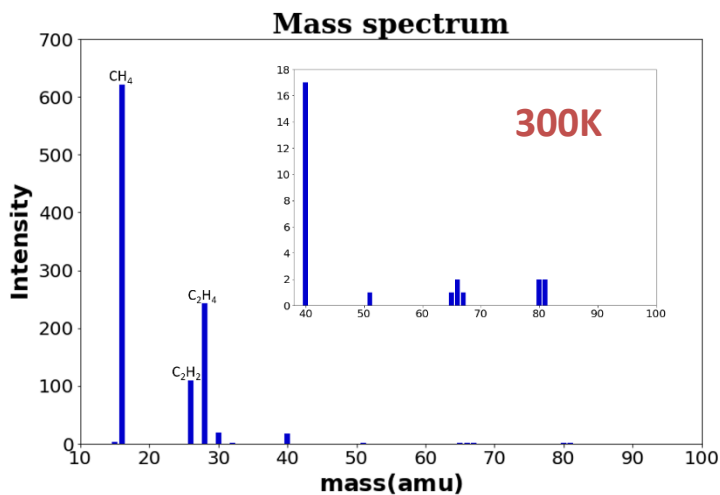
D. W. Brenner et al, A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons, J Physics: Condensed Matter 14 (2002) 783

S. J. Stuart et al, A reactive potential for hydrocarbons with intermolecular interactions, J. Chem. Phys. 112 (2000) 6472

M. Zarshenas et al, Molecular dynamics simulations of hydrocarbon film growth from acetylene monomers and radicals: Effect of substrate temperature, J. Phys. Chem C 122 (2018) 15252

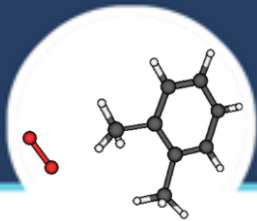
Insights into hydrocarbon plasma reactivity → mass spectra

- MD simulations in NVT ensemble at the desired temperatures. Damping time 100 fs.
- Timestep = 0.1 fs; total integration time : 40 ns (4. 10⁸ timesteps)



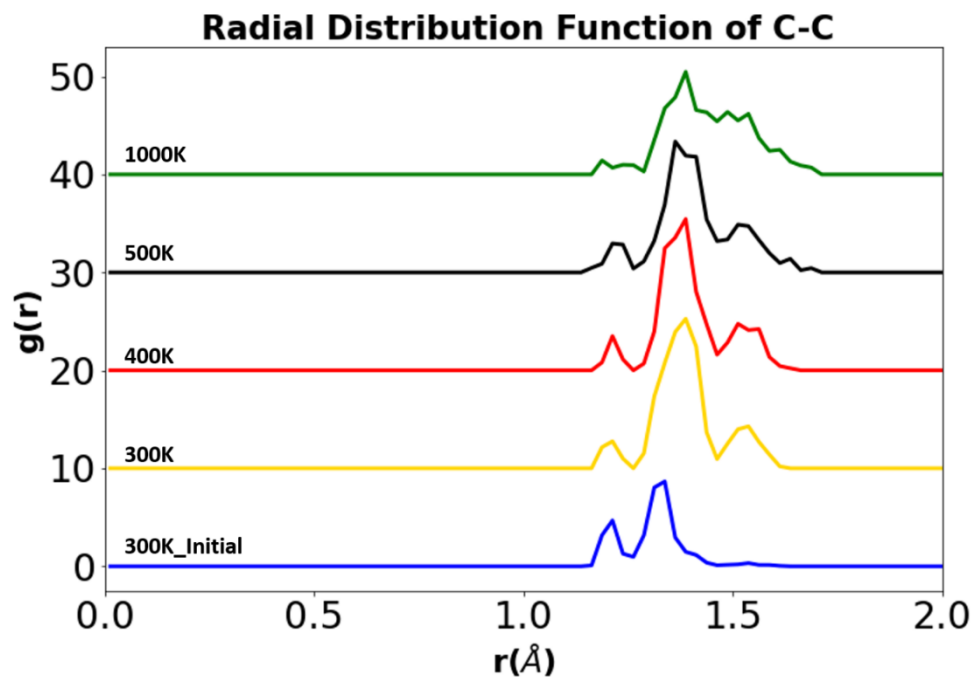
- The species CH₄, C₂H₂, C₂H₄, are the more abundant.
- Higher mass C_nH_m, n > 3 have been identified. Among them aromatic compounds are growing above t= 500K

Insights into hydrocarbon plasma reactivity → Bond order



- RDFs account for ratio of single/double and triple bonds, for $n_C > 3$

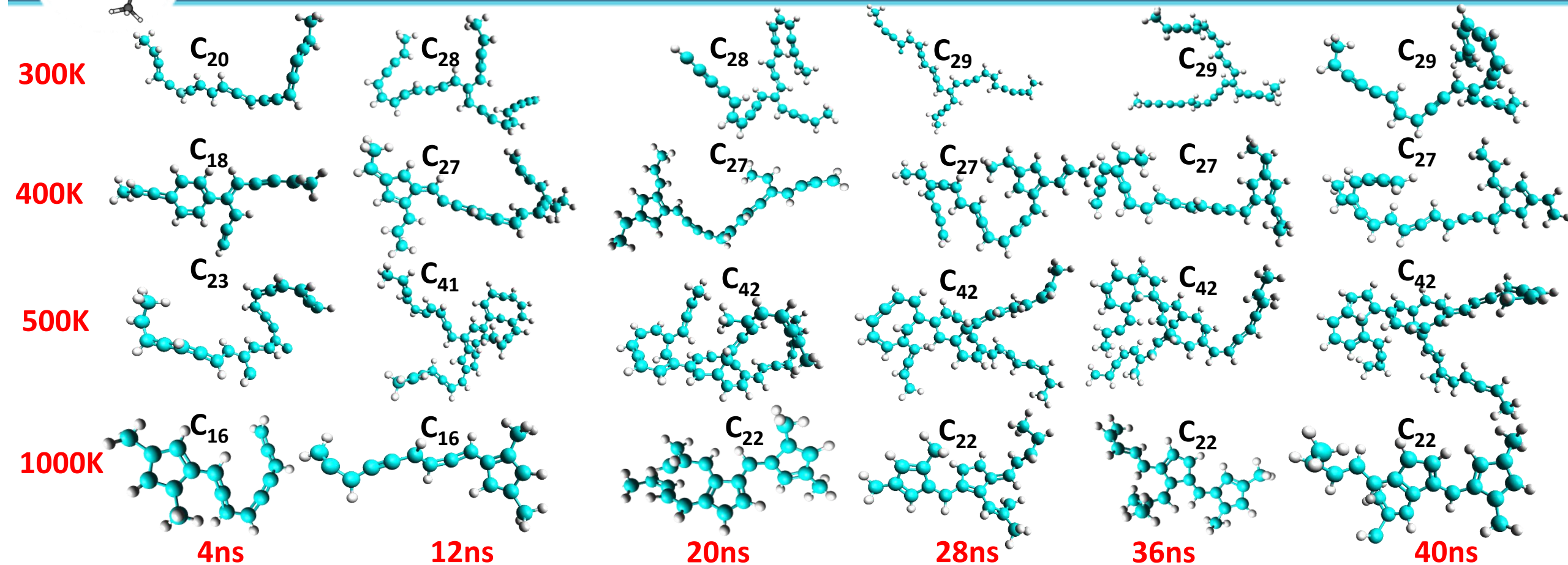
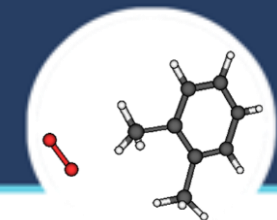
$$g(r_{ij}) = \frac{V}{N_i \cdot N_j} \left\langle \sum_{i=1}^{N_i} \sum_{j=1}^{N_j} \delta(r - \|r_{ij}\|) \right\rangle$$



Bond type fraction	300 K initial	300 K	400 K	500 K	1000 K
Single (%)	0	19	22	19	8
Double (%)	82	74	70	71	87
Triple (%)	12	7	8	10	5

- C=C double bonds predominate in soot precursors.

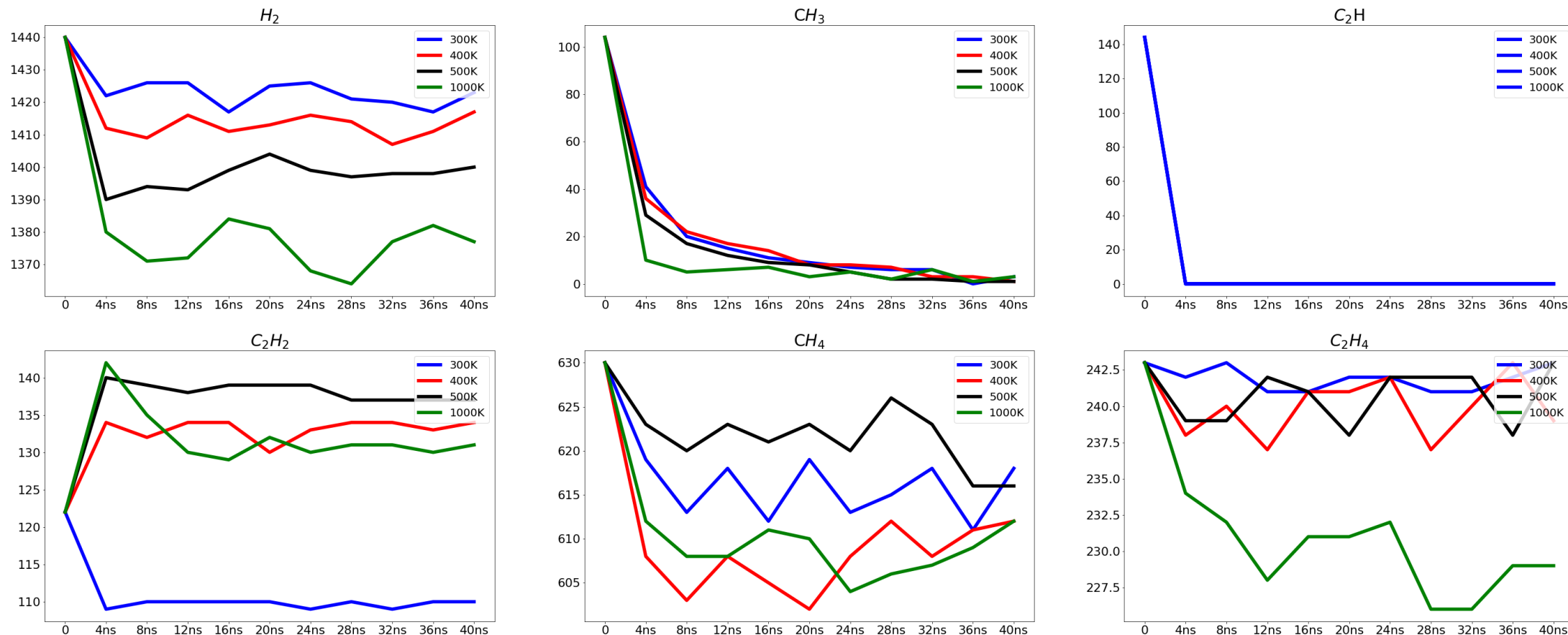
Insights into hydrocarbon plasma reactivity → species



- The largest carbon cluster contains **42** carbon atoms and is observed at the 500k temperature.
- Carbon cluster size increases with time and begins to stabilize at **20ns**
- Mainly linear branched molecules, From 400K, mixture of cyclic and branched molecules

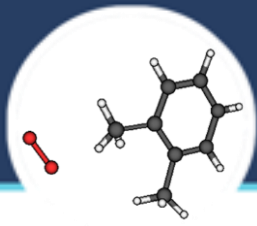
Insights into hydrocarbon plasma reactivity → kinetics

Evolution of the initial neutral species as a function of time

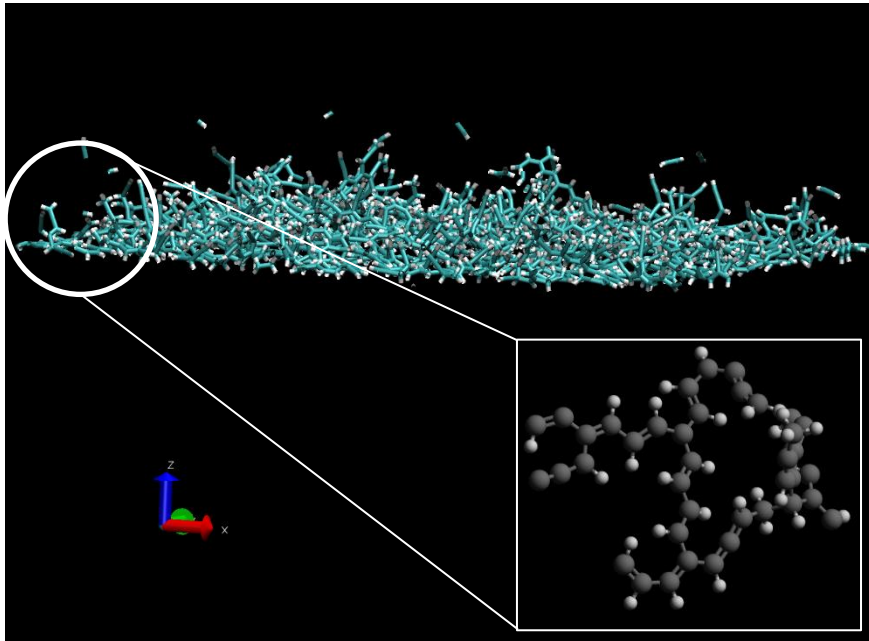


- CH_3 , C_2H are the most consumed radicals → main precursors of larger molecules.
- C_2H_2 is created as an intermediate precursor

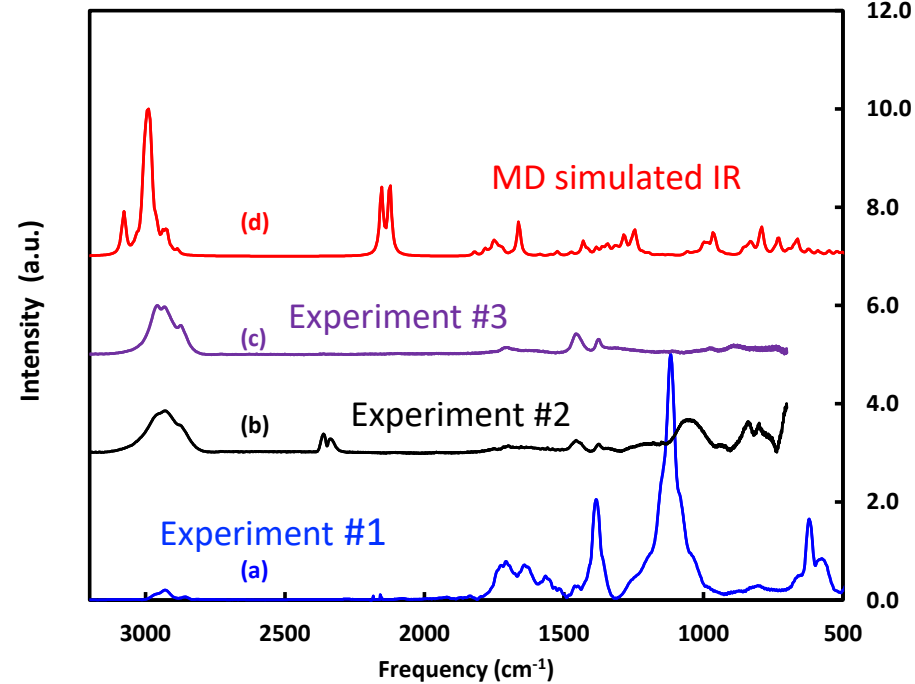
Insights into hydrocarbon plasma reactivity → acetylene plasma polymer IR spectra



■ Pure acetylene plasma deposition



Experiment	C ₂ H ₂ flow (sccm)	Pressure (mbar)	Support electrode
#1	10	0.01	grounded
#2	10	0.2	powered
#3	10	0.2	grounded

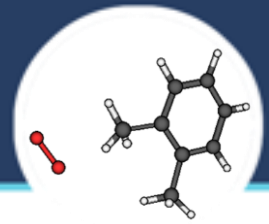


Wavenumber (cm ⁻¹)	pp-Ac experiments	pp - Ac simulated
2965	v(asym) CH ₃	yes
2925	v(asym) CH ₂	yes
2856	v(sym) CH ₂	yes
1720	v C=O	no
2160	disubstituted C-C alkyne spectrum (a)	yes
1645	v C=C	yes
1463	δ CH ₂	yes
1387	δ (sym) CH ₃	yes
1084/1120	v C-C (only A)	no
659	δ C-H from C=C	yes

P. Brault, M. Ji, D. Sciacqua, F. Poncin-Epaillard, J. Berndt, Eva Kovacevic, Insight into acetylene plasma deposition using molecular dynamics simulations, Plasma Processes and Polymers (2021) <https://onlinelibrary.wiley.com/doi/full/10.1002/ppap.202100103>

Insights into plasma oxidation processes of organic pollutant in water

→ Plasma (NTPA, CAP) degradation of organic pollutants in water



■ Within the scope of plasma-liquid interactions

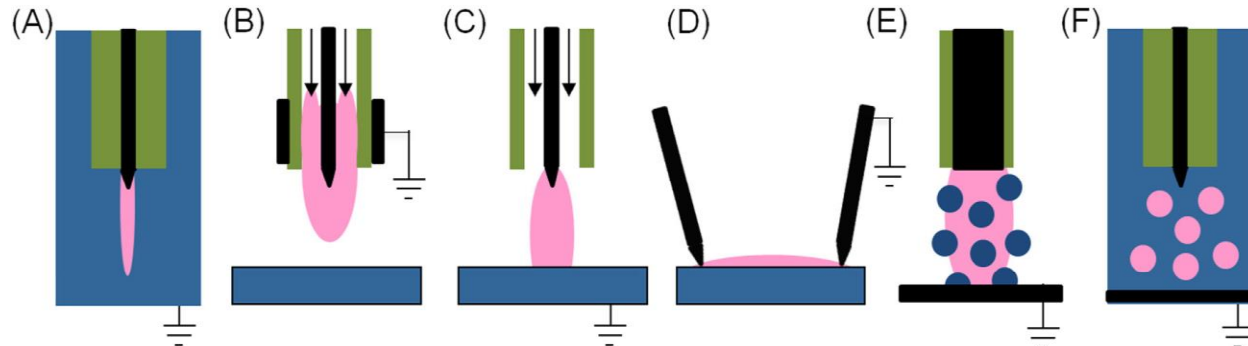
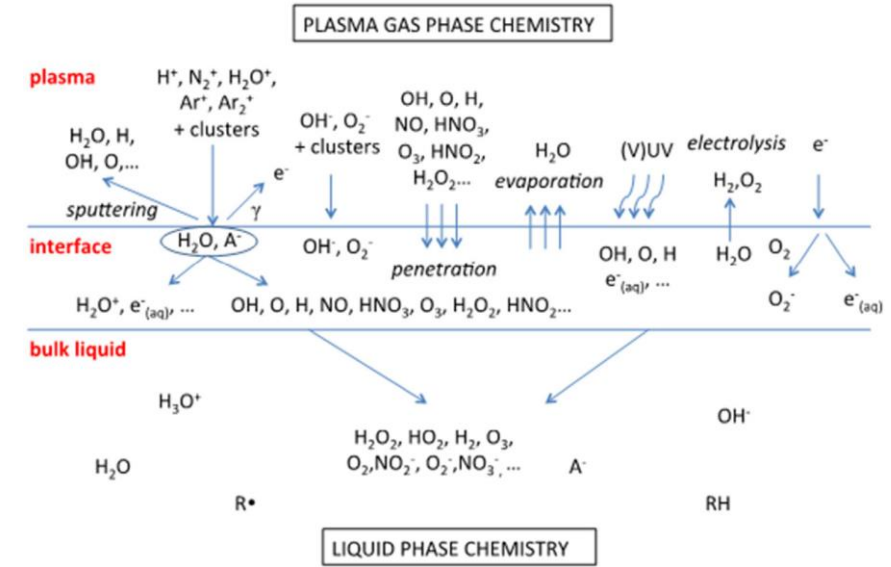


Figure 2. Schematic of different discharges used in plasma–liquid interactions: (A) direct discharge in liquid, (B)–(D) gas phase discharges and (E) and (F) multiphase discharges. In more detail: (B) plasma jet without direct contact with liquid, (C) gas phase plasma with liquid electrode, (D) surface discharge, (E) gas phase plasma with dispersed liquid phase (aerosols) and (F) discharges in bubbles. Blue = liquid, pink = plasma, green = dielectric, black = metal electrodes.



■ Non Thermal Plasma at Atmospheric Pressure (NTPA) is creating oxidizing species (RONS) expected to interact with organic pollutant in water

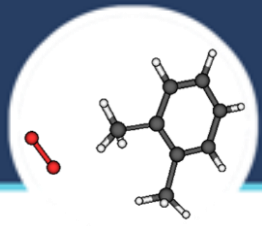
- Efficiently degrade the parent molecule to non-toxic products
 - Optimize (plasma) process: requires knowledge of oxidation chemistry in water : reactants, reaction products, pathways and selectivity
- molecular simulations ?

M Magureanu et al, A review on non-thermal plasma treatment of water contaminated with antibiotics, *J Haz. Mat.* 417 (2021) 125481

P Vanraes and A Bogaerts, “Plasma physics of liquids—A focused review”, *Appl. Phys. Rev.* 5, 031103 (2018).

P J Bruggeman et al, Plasma–liquid interactions: a review and roadmap, *Plasma Sources Sci. Technol.* 25 (2016) 053002

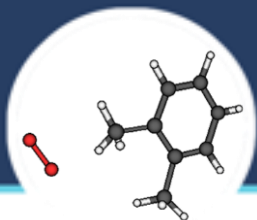
Samukawa S et al, The 2012 plasma roadmap, *J. Phys. D: Appl. Phys.* 45 (2012) 253001



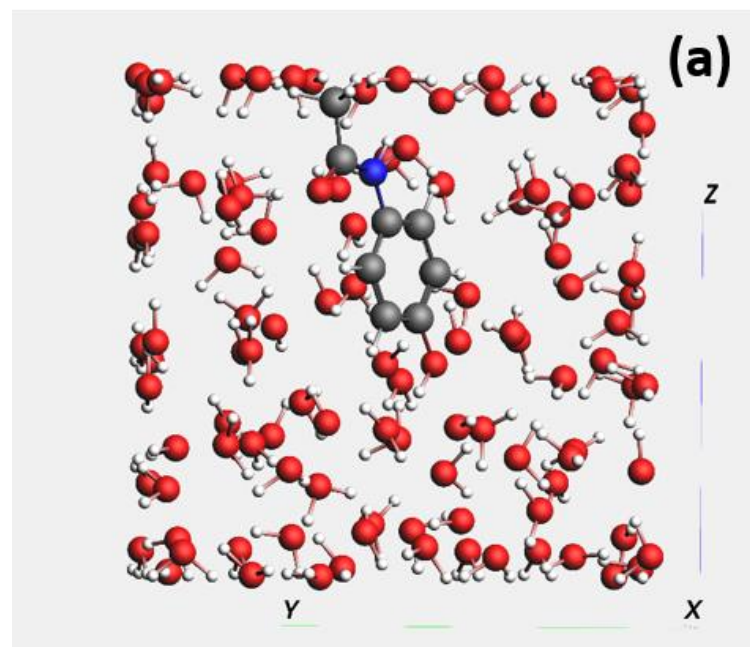
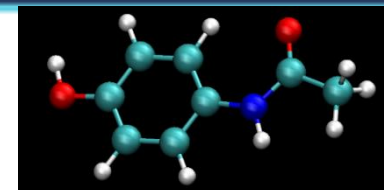
Insights into plasma oxidation processes of organic pollutant in water → Molecular dynamics implementation

- Water + oxidant molecules/radicals + organic pollutant
 - But which composition since pollutant fraction is ranging from 1 ng/L to 100 mg/L ?
 - Which ratio of oxidant radicals ?
- Finding possible products
 - Temperature ramp: 300 K - 3500 K → hierarchy of product formation
 - Conversely → Product prediction and associated energetics
- Major drawback: no electron → role of solvated electron → the hope of electron FF
- Lack of reactive forcefields for complex organic pollutants.
 - Help of quantum chemistry

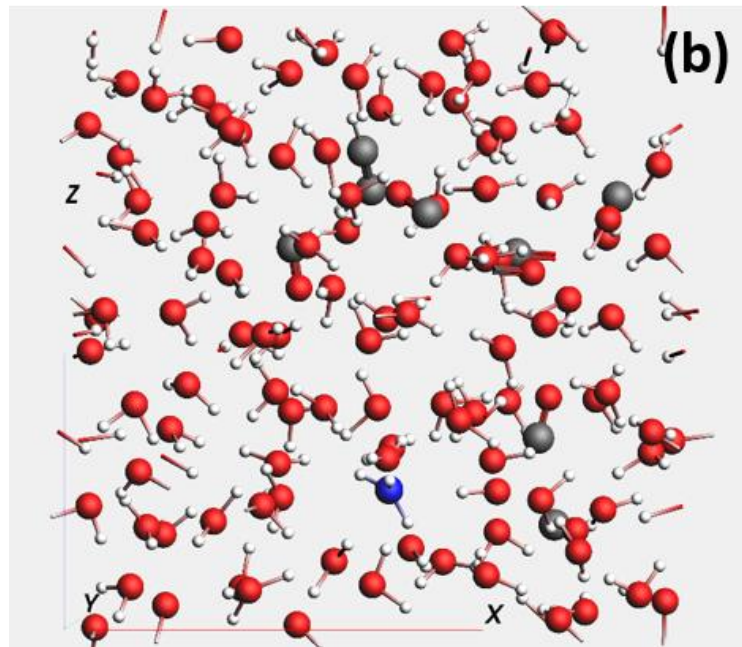
Insights into plasma oxidation processes of organic pollutant in water → Case study #1: Paracetamol



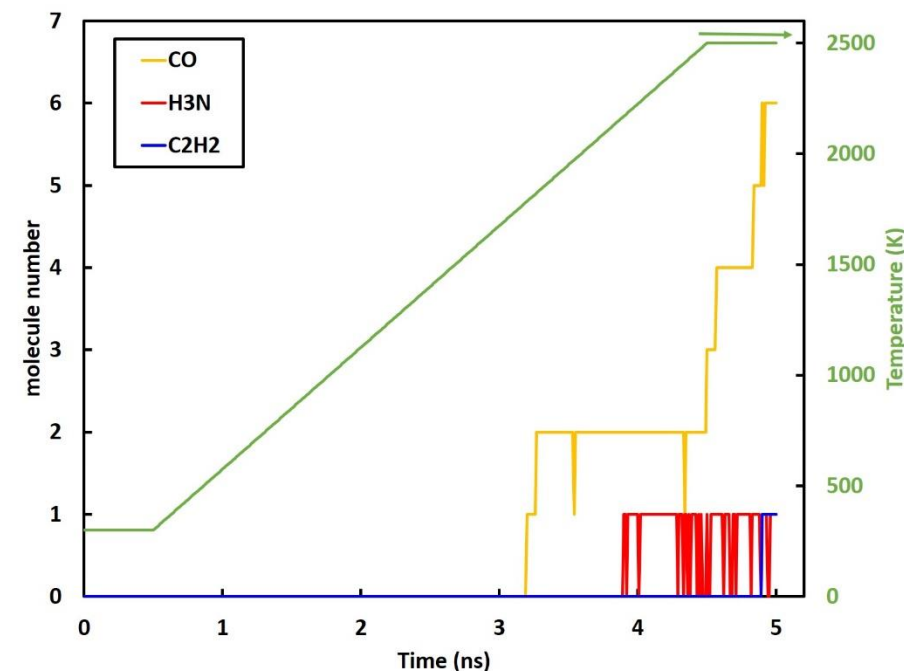
- $100 \text{ H}_2\text{O} + 10 \text{ HO}^\cdot + 1 \text{ C}_8\text{H}_9\text{NO}_2$ Exp. → $6 \cdot 10^{16} \text{ paracetamol cm}^{-3} / \text{HO}^\cdot 10^{18} \text{ cm}^{-3}$
- Reactive force field ReaxFF: O. Rahaman et al, J. Phys. Chem. B 115, 249 (2011)
- dt = 0.1 fs; Nit = $5 \cdot 10^7$ itérations; Nosé-Hoover Thermostat $\tau = 100$ fs; Temperature ramp : 0.55 K.ps^{-1}



Initial configuration

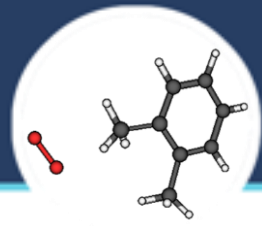


Final configuration (5 ns)



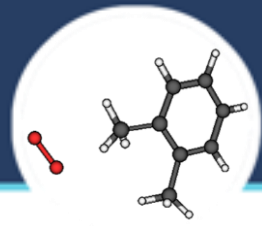
Final products: 6 CO, 1 C₂H₂, 1 NH₃, 103 H₂O, 1 H₂, 1 H₃O

P. Brault, M. Abraham, A. Bensebaa, O. Aubry, D. Hong, H. Rabat, M. Magureanu, Insight into plasma degradation of paracetamol in water using a reactive molecular dynamics approach, J. Appl. Phys 129 (2021) 183304



Insights into plasma oxidation processes of organic pollutant in water → Quantum Chemistry and MD

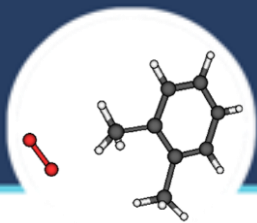
- For geometry optimization of pollutants molecules and basic data (Mulliken charges, bond lengths and angles, electronic levels, IR frequencies, ionization potential, electron affinity, etc)
- For calculating and sorting all internal bond energies of pollutant molecules
 - Identifying weakest bonds thus able to break efficiently
 - When surrounded with water and active species, checking bond energy evolution: weakening vs tightening.
- Ab-Initio Molecular Dynamics → for solving Newton equations of motion, the interaction potentials can be calculated using quantum methods, such as Hartree-Fock, Hückel, DFT(B), etc
 - Necessary if bond-order reactive semi-empirical potentials are not available for MD simulations
 - Taking account of electron processes (charge transfer, etc)
 - **But at the expense of increasingly computing time → Relevant Modeling**



Insights into plasma oxidation processes of organic pollutant in water → Quantum Chemistry and MD

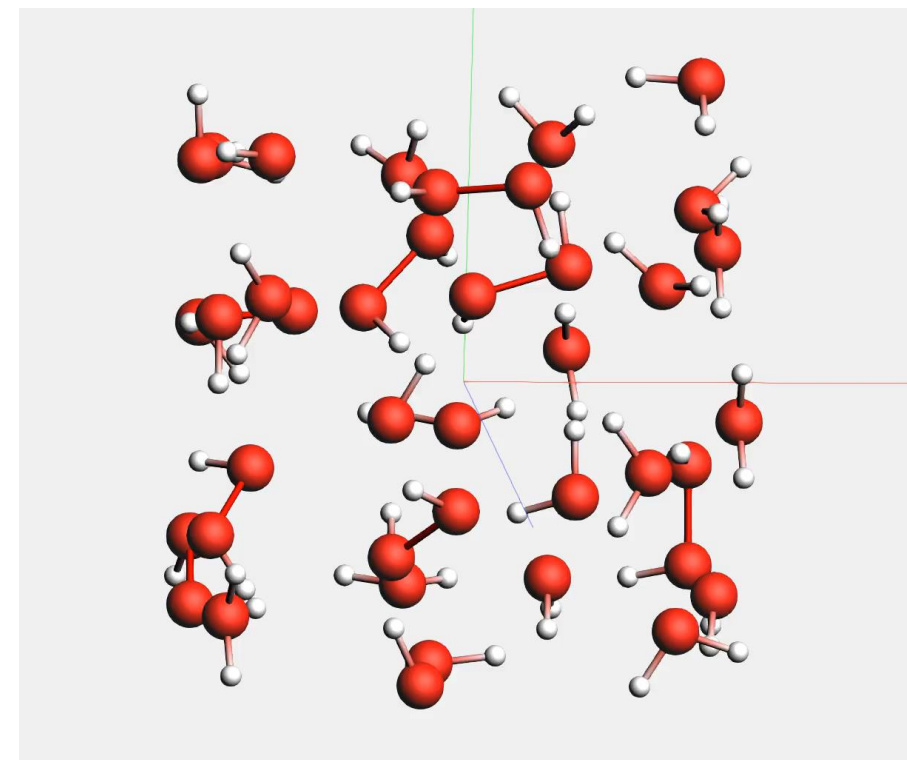
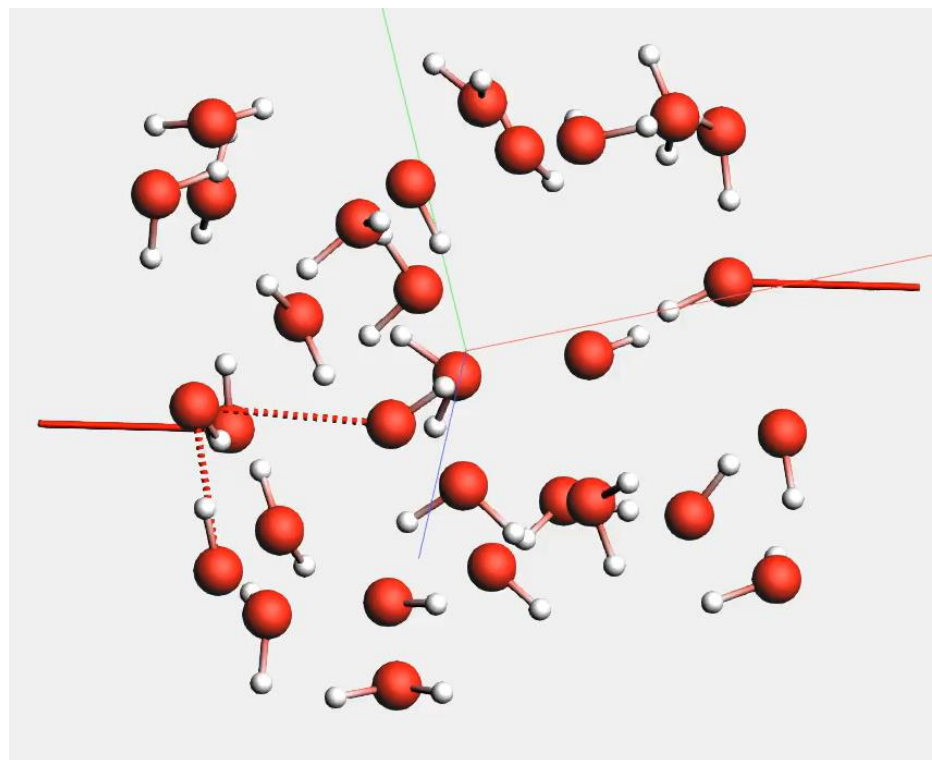
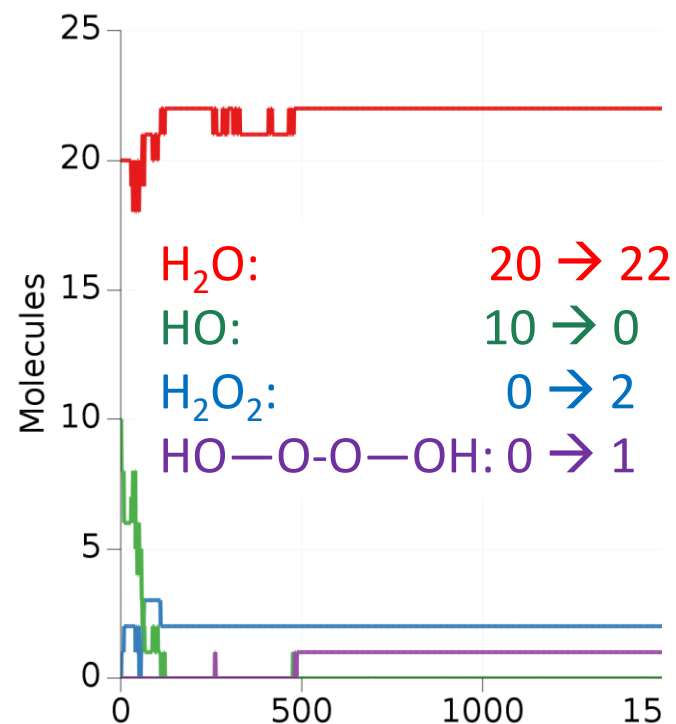
- What is the goal of quantum chemistry ?
 - Classical MD → atoms are points subjected to forces possibly included charge effects through Coulomb forces
 - Solving Schrödinger equation including electrons
 - But 1 nucleus = 1 electron for H but 6 for C, 7 for N, 8 for O, and 16 for S
 - So full electrons calculations of the interaction potentials becomes almost unfeasible
- Thus, Density Functional Theory (DFT) comes into play
 - Hohenberg-Kohn theorem: The full many-particle ground state is a unique functional of $n(\mathbf{r})$
 - There are many assumptions leading to improving computational but more complicated approximations solve more specific problems
 - Here Density Functional Theory in the Tight-Binding approach → DFTB (Computationally efficient DFT scheme) → GFN1-xTB parameterization, which is optimized for geometries, frequencies and non-covalent interactions and covers all elements of the periodic table up to radon.

Insights into plasma oxidation processes of organic pollutant in water → DFTB-MD (GFN1-xTB parameterization): preliminaries



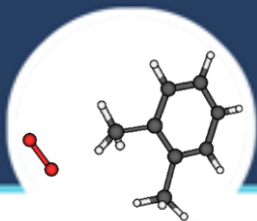
■ 10 HO + 20 H₂O
→ HO quickly reacts

■ 5 H₂O₂ + 20 H₂O
→ very stable

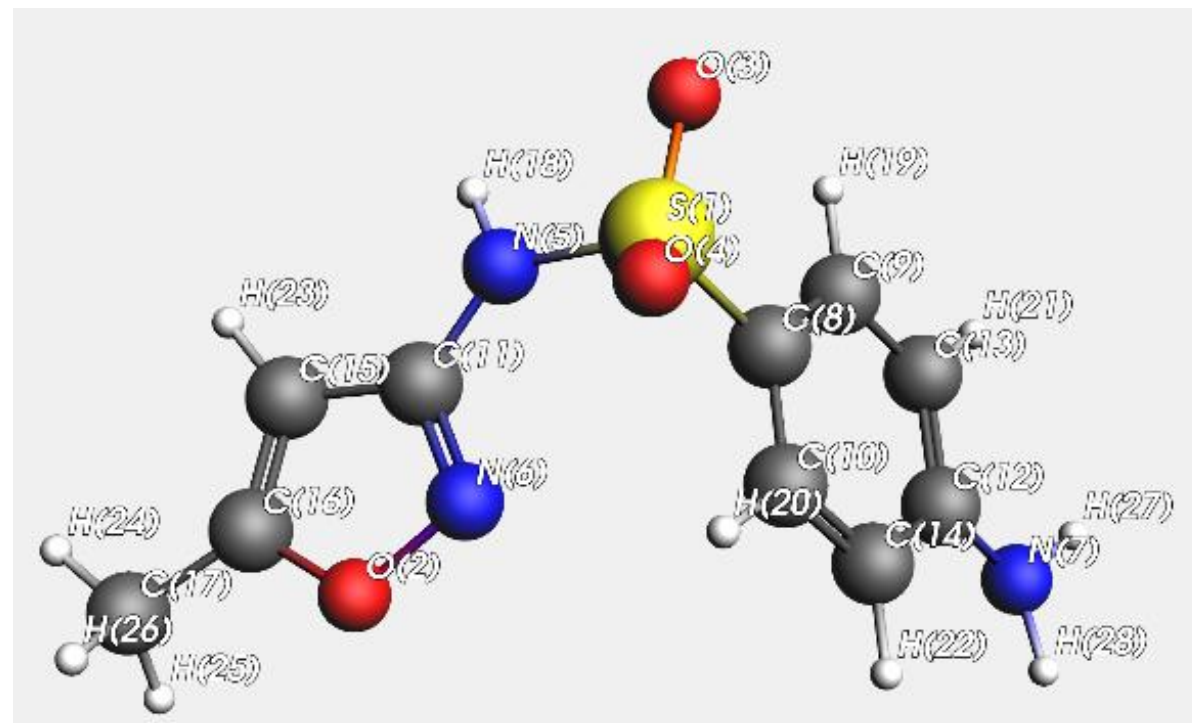
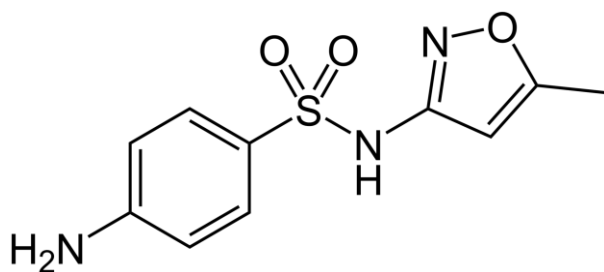


■ 300K, dt = 0.25 fs; Nosé-Hoover thermostat

Insights into plasma oxidation processes of organic pollutant in water → Case study #2: Sulfamethoxazole (SMX)



■ Sulfamethoxazole

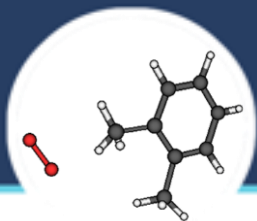


■ Antibiotics → Widely used for animal breedings and human care

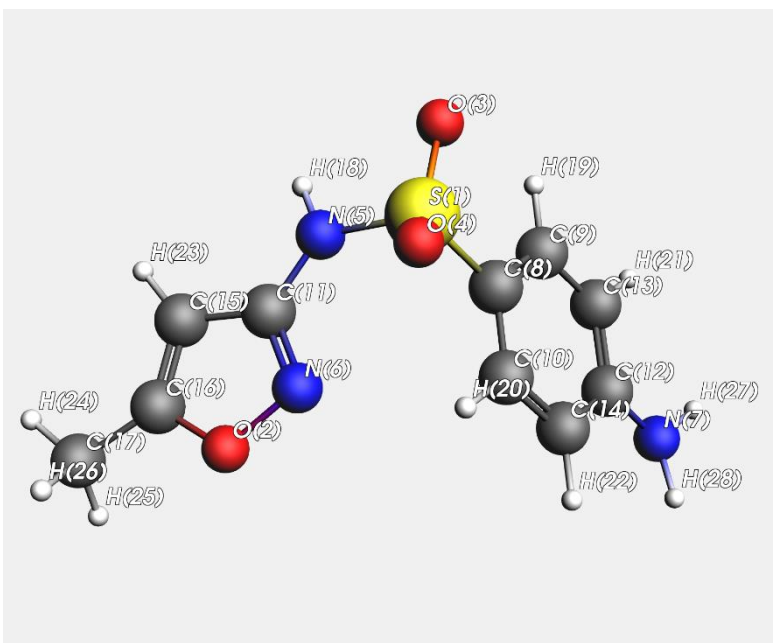
■ No reactive FF (S-N bond) → DFTB - MD

Collaboration Uni Bucharest/INFLPR)

Insights into plasma oxidation processes of organic pollutant in water → Case study #2: Sulfamethoxazole (SMX)



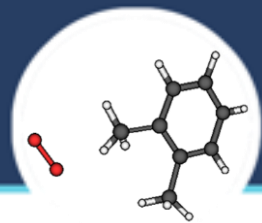
- **Energy Decomposition Analysis (EDA):** Calculation of all bond energies in a molecules. Using Internal Quantum Atom (IQA) method, it is now possible to establish, if the interaction between two atoms is energetically stabilizing or not, and to conclude about its nature (electrostatic, covalent, etc.).
- Sulfamethoxazole isolated and with H₂O (1g.cm⁻³)



- IP = 7.747 eV
- EA = -0.968 eV

bond	No H ₂ O	With H ₂ O	Variation (%)
S1-O3	-2.046	-1.993	-2.6
S1-O4	-2.053	-1.97	-4.0
S1-N5	-1.352	-1.588	17.5
S1-C8	-0.38	-0.37	-2.6
N5-C11	-0.711	-0.726	2.1
N5-H18	-0.455	-0.291	-36.0
N6-C11	-0.576	-0.586	1.7
N6-O2	-0.304	-0.289	-4.9
N7-C12	-0.59	-0.539	-8.6
N7-H28	-0.427	-0.419	-1.9
C15-C16	-0.379	-0.378	-0.3
C15-H23	-0.241	-0.231	-4.2
C16-C17	-0.286	-0.286	0.0
O2-C16	-0.587	-0.584	-0.5

V. Tognetti and L. Joubert, On the physical role of exchange in the formation of an intramolecular bond path between two electronegative atoms, *Journal of Chemical Physics* 138, 024102 (2013)

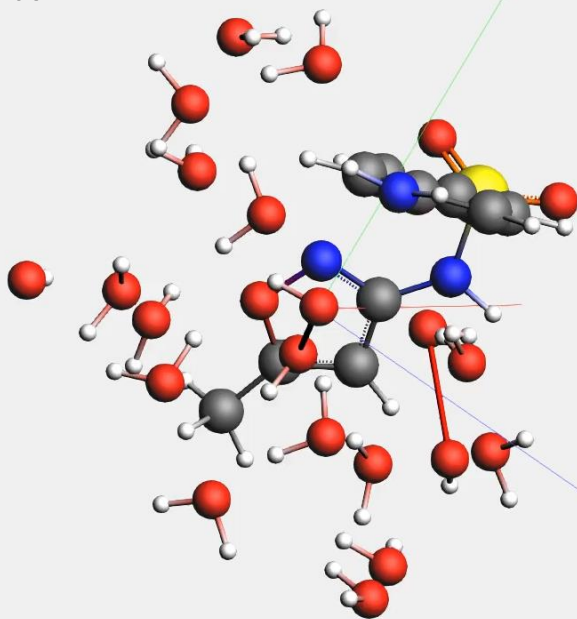


Insights into plasma oxidation processes of organic pollutant in water → Case study #2: Sulfamethoxazole (SMX)

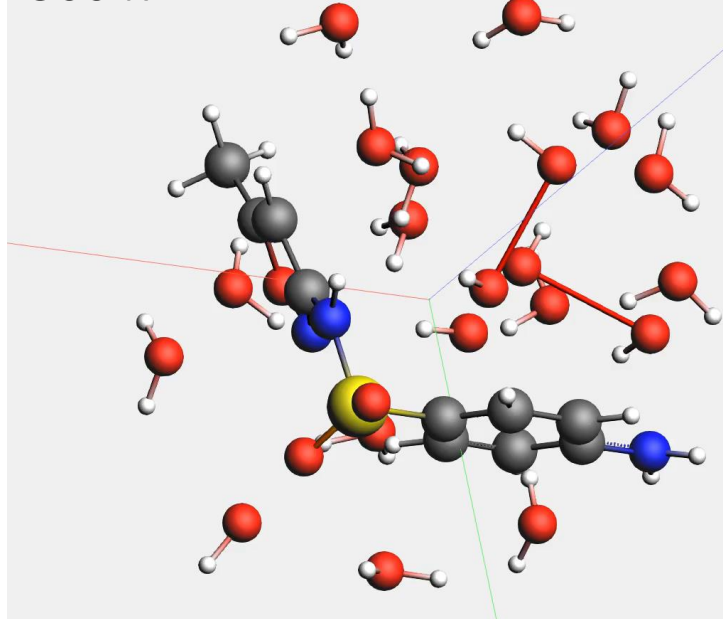
15 H₂O + 5 HO + 1 SMX (1g.cm⁻³)

15 H₂O + 4 H₂O₂ + 1 SMX (1g.cm⁻³)

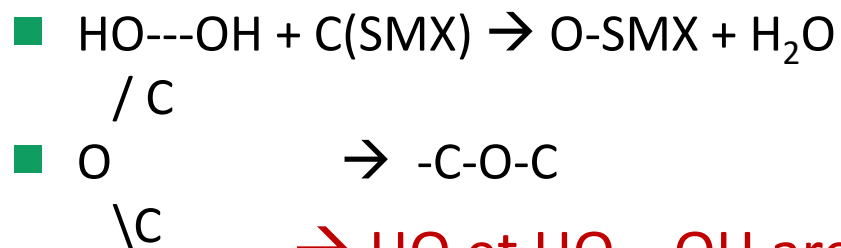
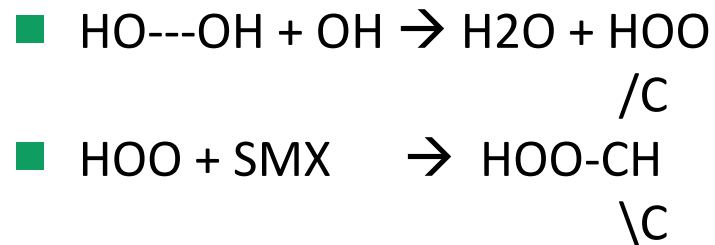
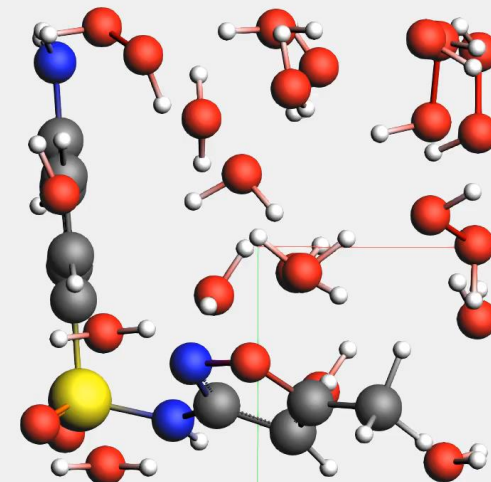
300 K



500 K



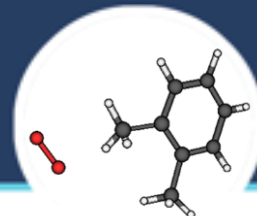
300 K & 500 K



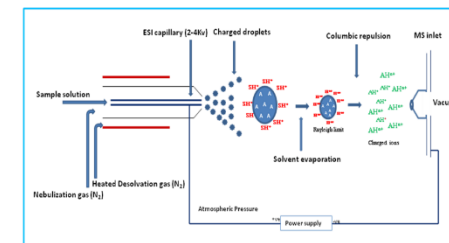
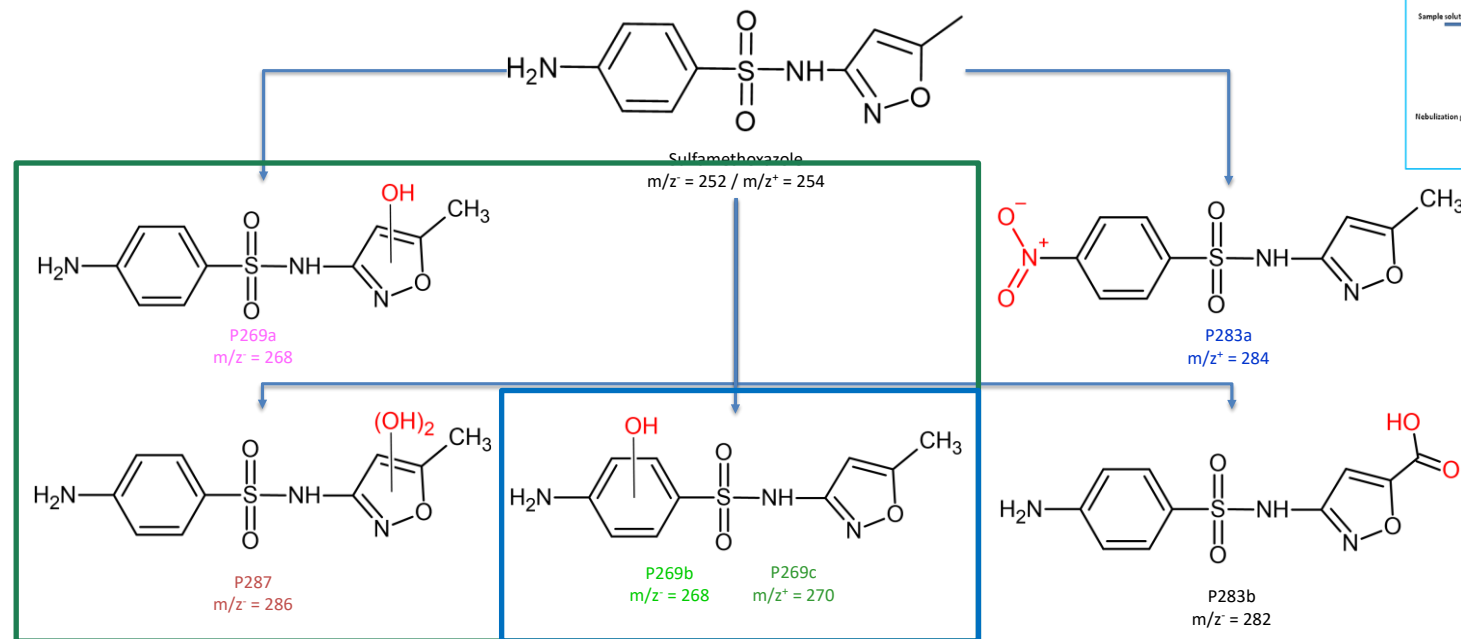
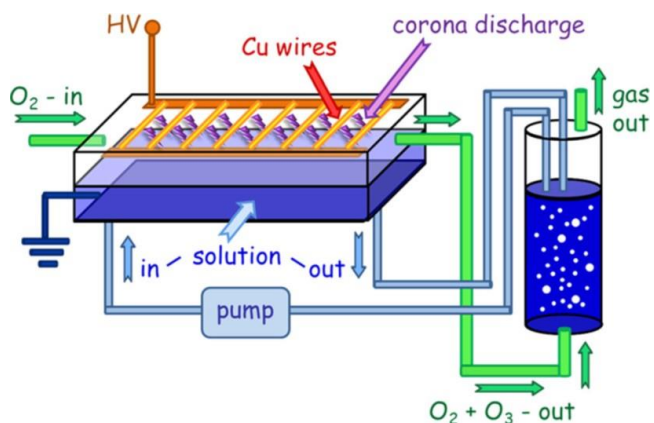
■ Nothing happens

→ HO et HO---OH are responsible of bond formation

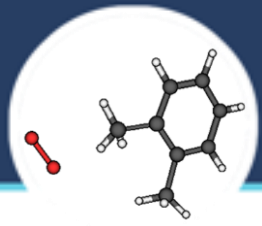
Insights into plasma oxidation processes of organic pollutant in water → Case study #2: Sulfamethoxazole (SMX)



- Sulfamethoxazole degradation in NTPA experiment (at short time)
 - Electrospray ionization tandem mass spectrometry (+/- ESI-MS/MS) experiments (M. Magureanu, C. Bradu, F. Bilea)



- EDA calculations consistent with OH interaction places → Weaker bonds
- DFTB-MD products at 300K (?) and 500K consistent with P269b/c (+/- ESI) products



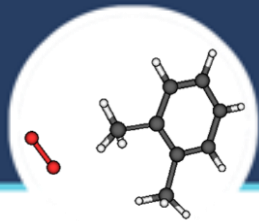
Conclusion

- YES, we can use molecular dynamics to address/solve plasma issues
- NO, it does not fully treat a plasma problem as do the "fluid" methods
- Provided that we are rigorous about the initial conditions and the interaction potentials, relevant comparisons with the experiments and predictions are possible
- There are some ways for including electrons in MD for a better approach

As a matter of fact,

Molecular Dynamics Simulation is really a Digital Microscope

It is able to supply Monte-Carlo and fluid/kinetic models with suitable data



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