



Energy decomposition analysis of organic pollutants in water: a way for finding plasma degradation routes ?

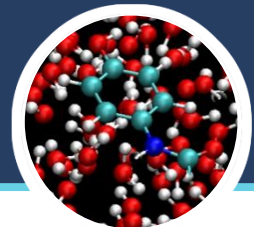
P. Brault¹, M. Magureanu², C. Bradu³, F. Bilea²

¹*GREMI CNRS - Université d'Orléans, BP6744, 45067 Orléans cedex 2, France*

²*National Institute for Lasers, Plasma and Radiation Physics, Department of Plasma Physics and Nuclear Fusion, Atomistilor Str. 409, P.O. Box MG-36, Magurele, 077125 Bucharest, Romania*

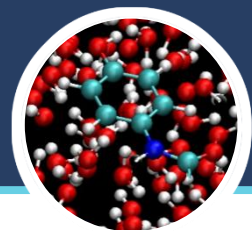
³*University of Bucharest, Faculty of Biology, Department of Systems Ecology and Sustainability, Splaiul Independentei 91-95, 050095 Bucharest, Romania*





Outline

- Plasma (NTPA) degradation of organic pollutants in water
- Molecular simulation principles
- Study of reactivity of sulfamethoxazole with OH in water: experiments and molecular simulations
 - Experiments
 - Energy Decomposition Analysis in IQA frame
 - Quantum chemistry coupled with Molecular Dynamics
- Conclusions



Plasma (NTPA) degradation of organic pollutants in water

- Within the scope of plasma-liquid interactions

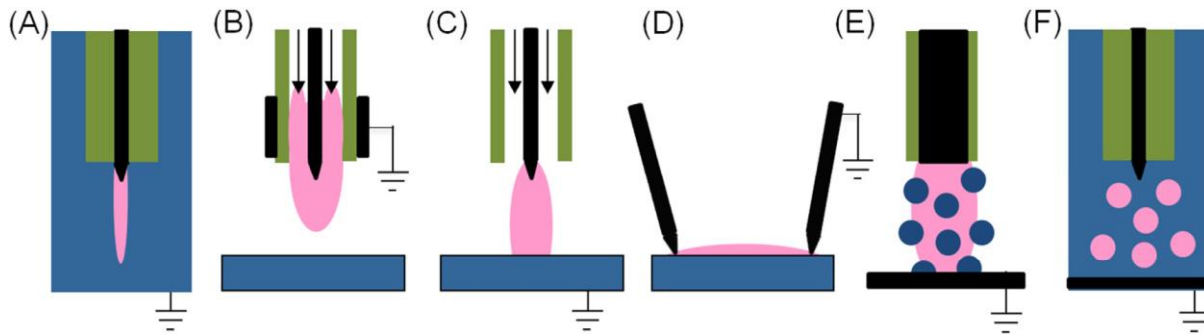
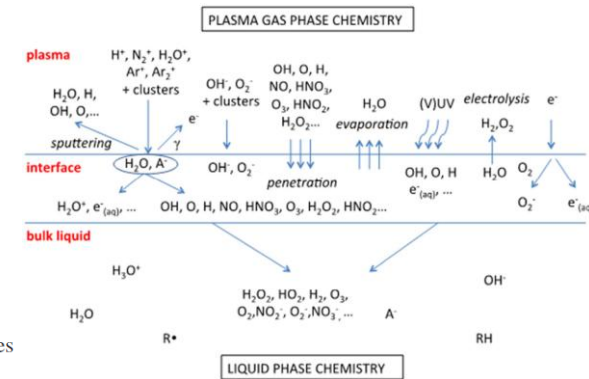


Figure 2. Schematic of different discharges used in plasma-liquid interactions: (A) direct discharge in liquid, (B)–(D) gas phase discharges and (E) and (F) multiphase discharges. In more detail: (B) plasma jet without direct contact with liquid, (C) gas phase plasma with liquid electrode, (D) surface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



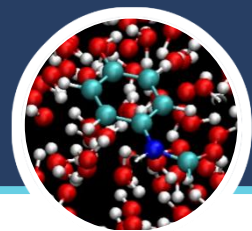
- Non Thermal Plasma at Atmospheric Pressure (NTPA) is creating oxidizing species (RONS) expected to interact with organic pollutant in water

- 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 ?

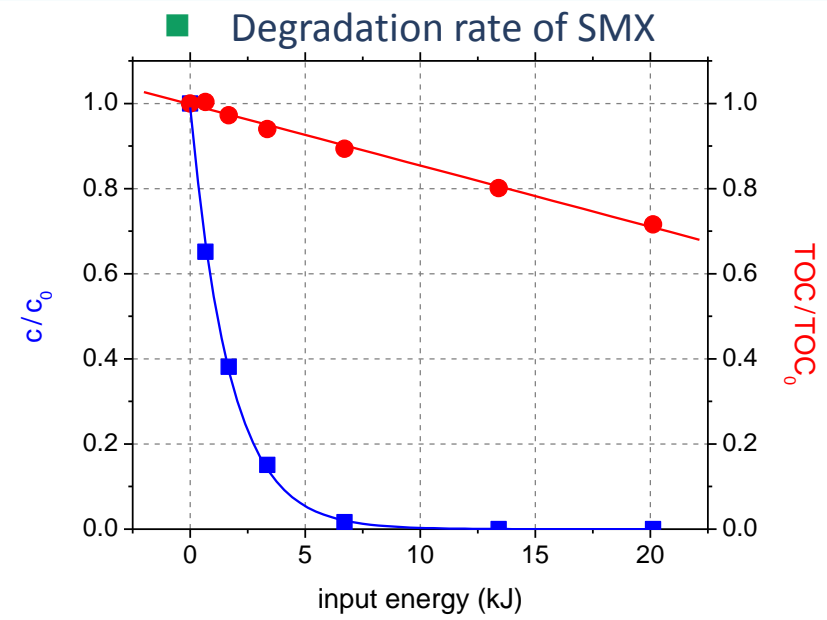
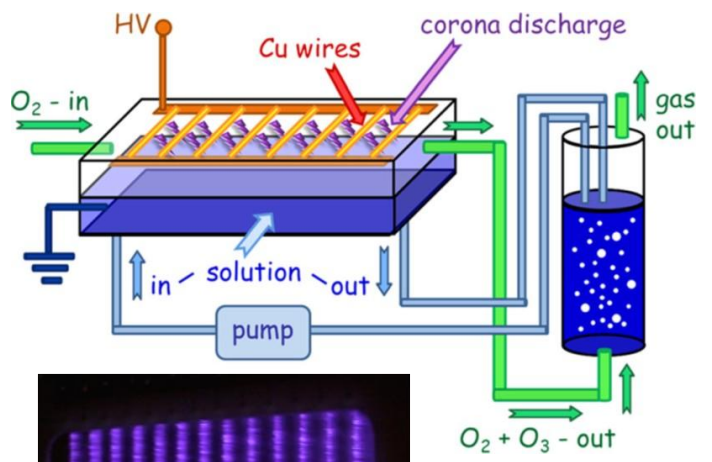
Samukawa S et al, The 2012 plasma roadmap, *J. Phys. D: Appl. Phys.* 45 (2012) 253001

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

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



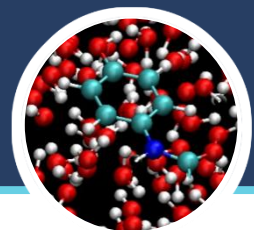
Plasma (NTPA) degradation of organic pollutants in water: INFLPR experiment



- High voltage electrode: array of 20 Cu wires ($F = 100 \mu\text{m}$, $L = 36 \text{ mm}$, $d_{i-i+1} = 6 \text{ mm}$)
- Ground electrode: Al tape ($46 \times 160 \text{ mm}$)
- Discharge gap $\sim 5 \text{ mm}$
- Liquid depth $\sim 5 \text{ mm}$
- Gas: oxygen, flow rate 300 mL/min
- Solution: volume 330 mL , conductivity $300 \mu\text{S/cm}$, pH 7.1, solution flow rate 160 mL/min

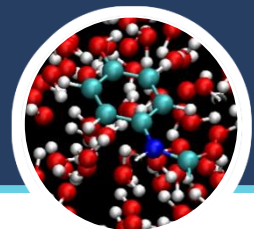
- Almost complete degradation after 20 min treatment
- Degradation efficiency
 - 67 g/kWh at 50% degradation
 - 33 g/kWh at 90% degradation
- Slow mineralization: TOC decrease 28.4% after 60 min treatment
- N-containing and S-containing organic products still present in the treated solution after 60 min

F Bilea, C Bradu, M Magureanu, Potential of plasma treatment as water reclamation process for irrigation, Journal of Physics D: Applied Physics 53 (2020) 224002



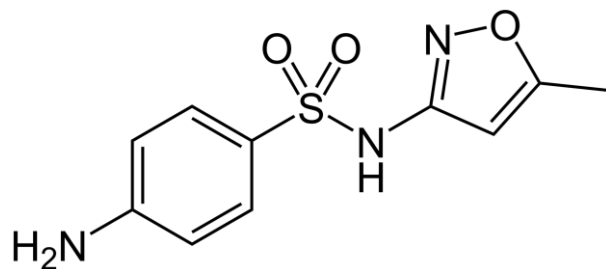
Molecular simulations: Quantum Chemistry (+ MD)

- For geometry optimization of pollutants molecules and basic data (Mulliken charges, bond lengths and angles, electronic levels, IR frequencies, etc)
- For calculating and sorting all internal bond energies of pollutant molecules
 - identifying weak 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
 - Take account of electron processes (charge transfer, etc)
 - But at the expense of increasingly computing time



Pollutant molecule of interest: SMX

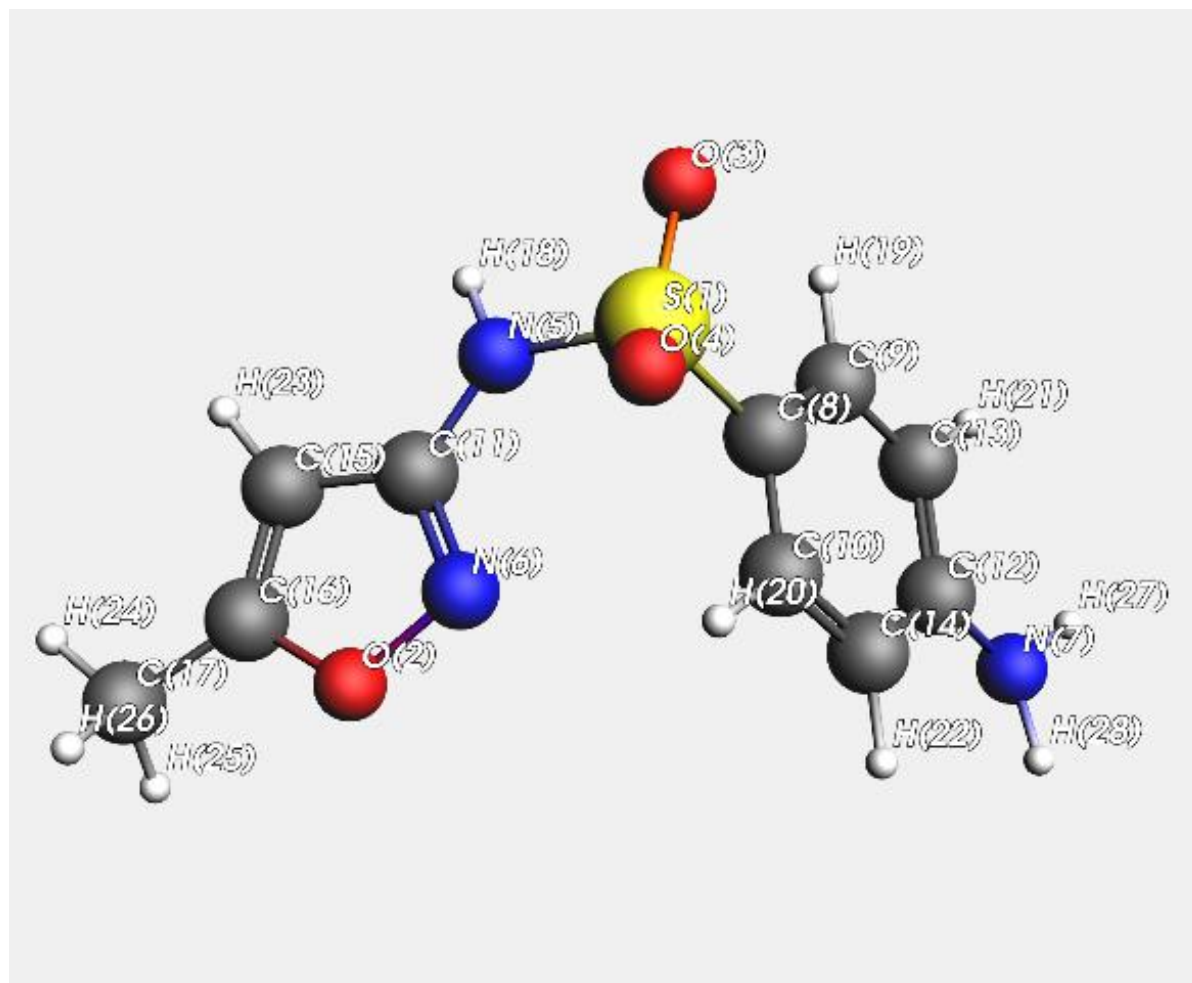
■ Sulfamethoxazole

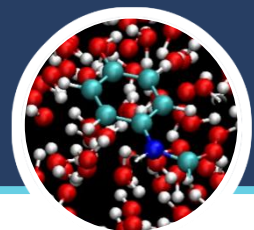


■ Antibiotics

Widely used for
animal breedings and
human care

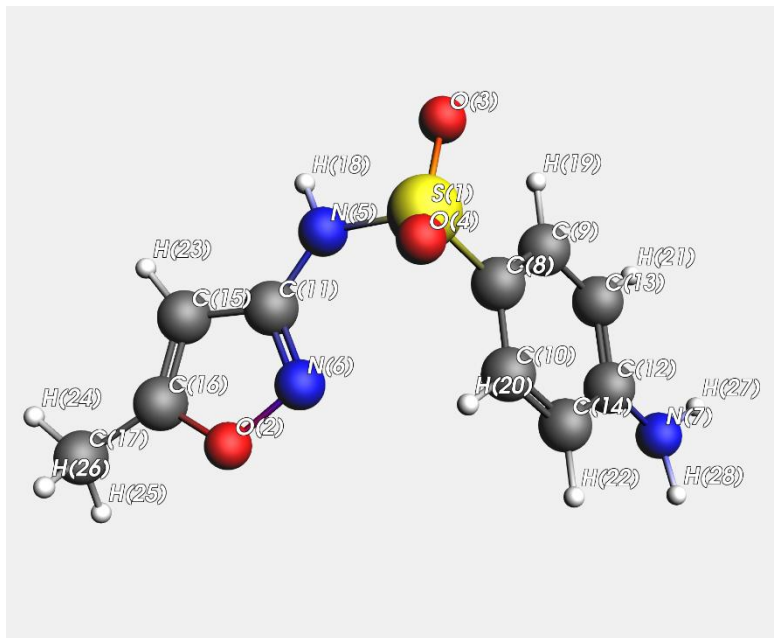
No reactive FF (S-N bond)
-> DFTB - MD





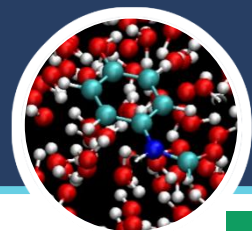
Energy Decomposition Analysis

- Calculation of all bond energies in a molecule. 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)



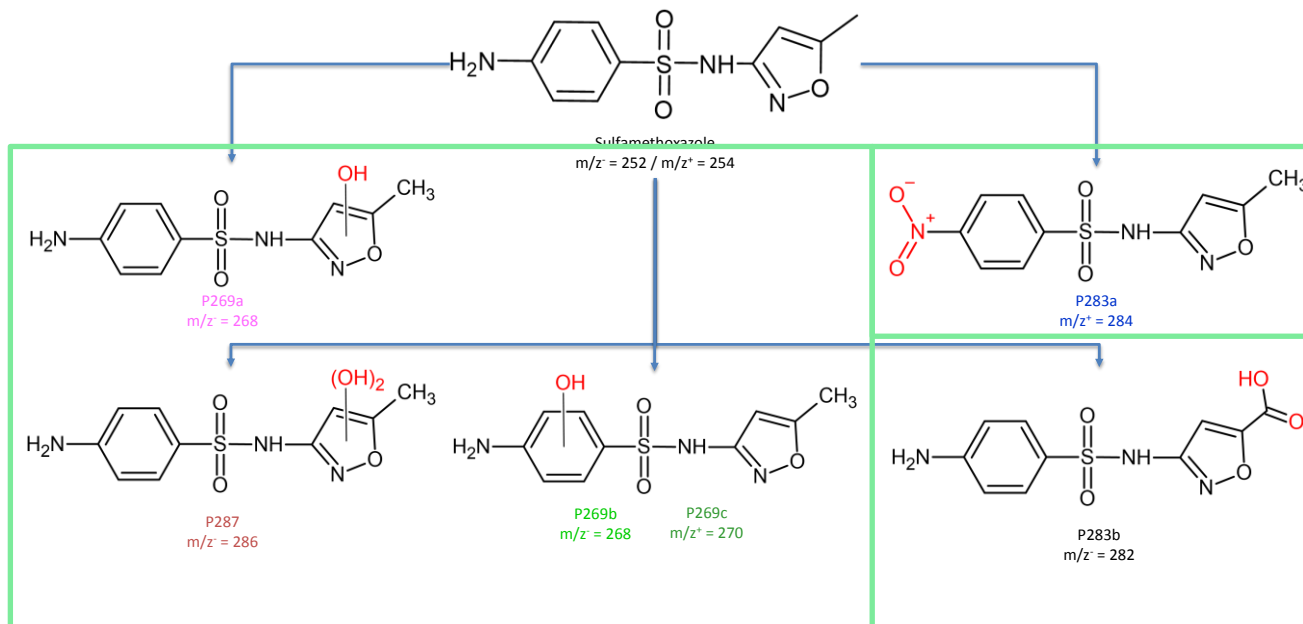
bond	No H2O	With H2O	Variation (%)
S1-O3	-2.046	-1.993	-2.6
S1-O4	-2.053	-1.97	-4.0
S1-N5	-1.352	-1.588	17.5
S1-C8	-0.38	-0.37	-2.6
N5-C11	-0.711	-0.726	2.1
N5-H18	-0.455	-0.291	-36.0
N6-C11	-0.576	-0.586	1.7
N6-O2	-0.304	-0.289	-4.9
N7-C12	-0.59	-0.539	-8.6
N7-H28	-0.427	-0.419	-1.9
C15-C16	-0.379	-0.378	-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)

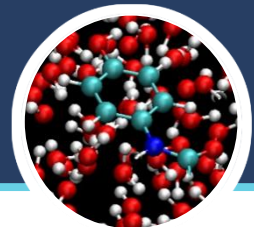


Sulfamethoxazole degradation in NTPA experiment (at short time)

- electrospray ionization tandem mass spectrometry (+/- ESI-MS/MS) experiment (M. Magureanu, F. Bilea, C. Bradu)

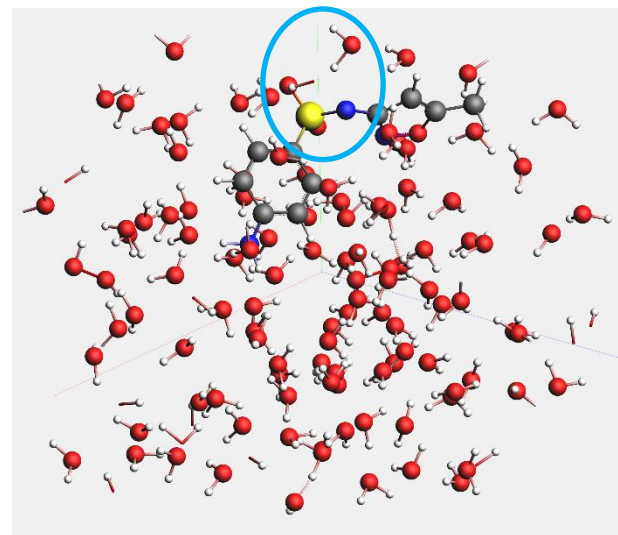
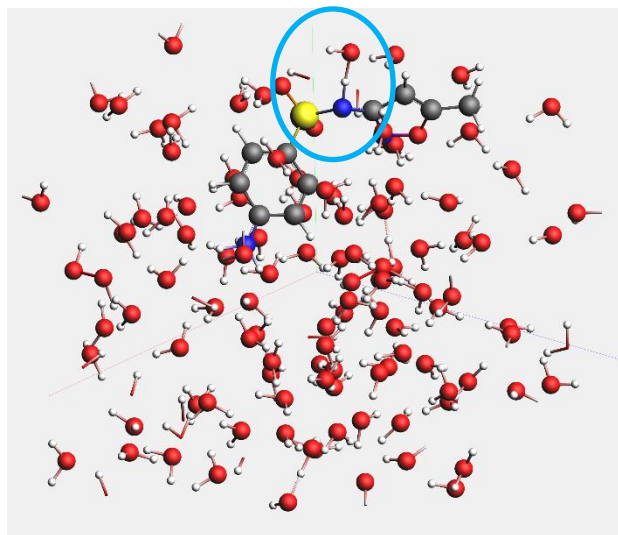
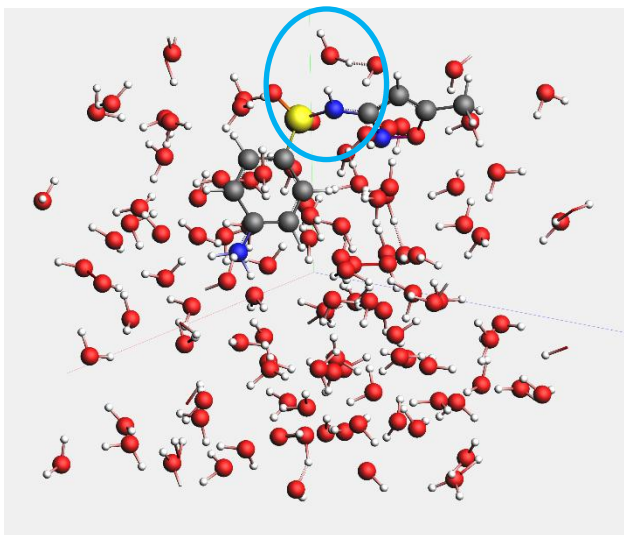


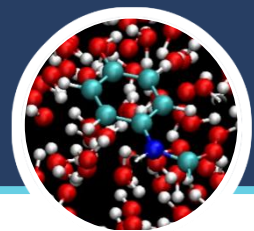
- OH interaction places consistent with EDA calculations
→ Weaker bonds



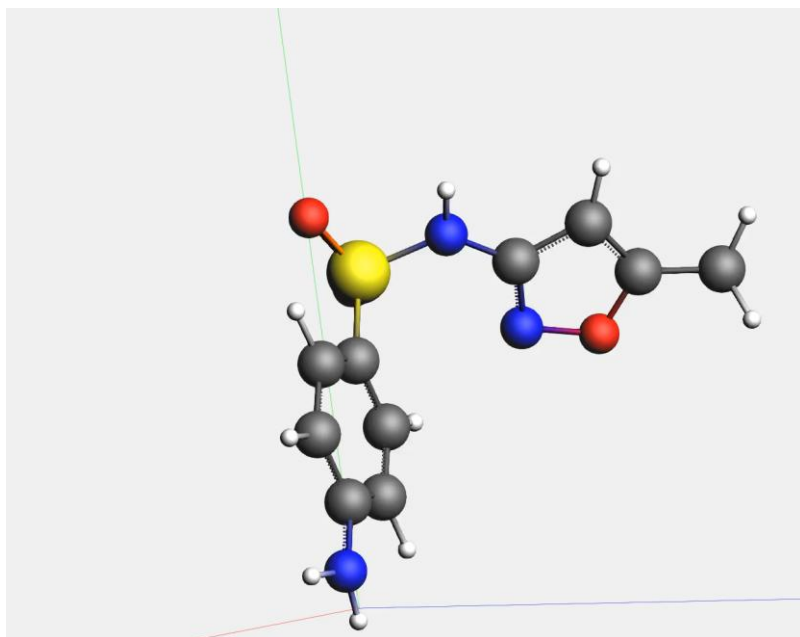
Quantum Chemistry + MD

- 100 H₂O + 10 OH + SMX → what is it in reality ?
- Calculating interaction potentials using DFTB - SCC scheme
- T = 300 K





Quantum Chemistry + MD



- SMX (+ 10 OH + 100 H₂O), 6 ps elapsed time
OH and H₂O have been removed for clarity

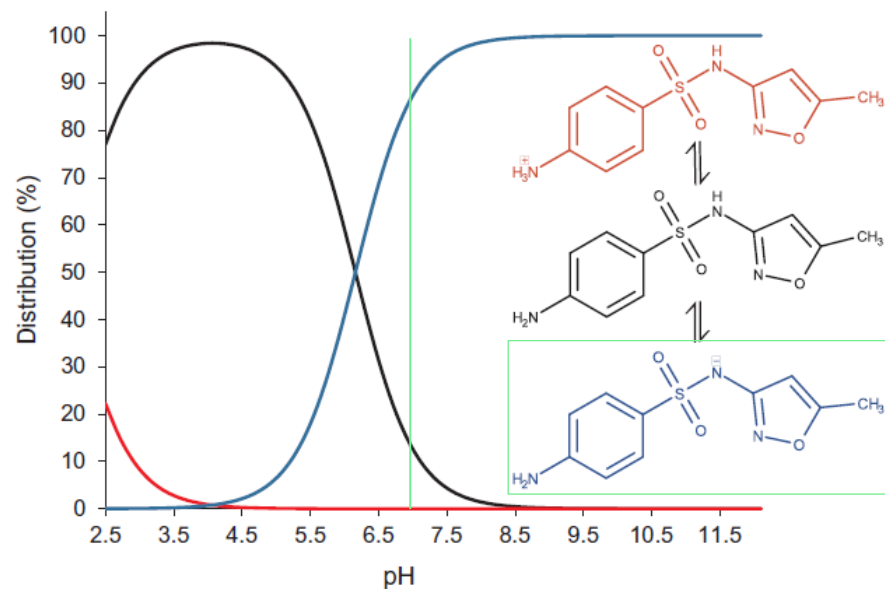
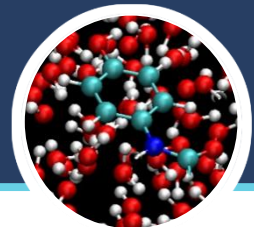


Fig. 6. Distribution of SMX as a function of pH. Made in MarvinSketch 18.4 (ChemAxon). [H. Milh et al, Chem Eng J. 379 \(2020\) 122234](#)

- For use of semi-empirical reactive variable charge potential (reaxFF family)

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



Conclusions

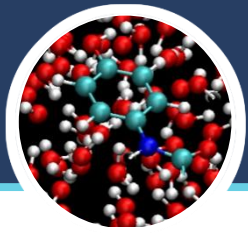
Conclusions

- Molecular simulations can provide insights into oxidation process of plasma degradation of organic pollutants in water
- High throughput simulations are required for scanning a wide range of pollutants and active species.
- NTPA is a valuable technique for organic pollutant degradation.
- Availability of high-resolution analysis of degradation products allows comparison with simulation predictions.

Future work

- High throughput reactive molecular dynamics for unravelling reaction pathways of a large set of pollutants and direct comparison to NTPA experiments -> Amoxicillin, glyphosate and Endocrine Disruptor Chemical (EDCs).

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GREMI, Orléans

- *D. Hong, O. Aubry, H. Rabat*

INFLPR / Faculty of Biology, University of Bucharest

- *M. Magureanu, C. Bradu, F. Bilea*

And warm greetings to other friends at INFLPR

- *M. and G. Dinescu, F. Gherendi, M. Nistor*

Thank you for your attention