Computational Chemistry in the Troya Group

Environmental gas/surface dynamics (OH collisions with surfactants)
Scattered species
(E, j, v, v')
Atom or Molecule
We investigate the dynamics of collisions between atmospheric gases and surfactant surfaces to shed light into heterogeneous environmental chemistry.

Lindqvist Hexaniobates

Reaction mechanism
CS8-Nb6O19
GB
R-F
Binding
Addition
TS-F
PS
Elimination
PONb+MPFA+iPOH

Zr-based MOFs

Pros:
- High surface area
- Fast solution hydrolysis rate

Cons:
- Product inhibition

UiO-66, UiO-67

Experimental probe for DMMP reaction (IR, UHV)

Experimental probe of terminal products (DMMP reaction)

Summary:
We have used electronic structure calculations to reveal the hydrolysis mechanism of nerve agents and simulants on two materials: polyniobates (PONb), and Zr-based metal organic frameworks (Zr-MOFs). The M06-L functional, in combination with the 6-31G**, 6-31+G**, and Lanl2dz basis sets have been used to characterize key stationary points for reactions on all materials at the gas-surface interface. The reaction mechanism proceeds along the following steps: i) reagent binding to the active site, ii) nucleophilic addition of hydroxide to the phosphorous center, iii) P-X (X=O,F,CI) bond breakage (elimination), and iv) product desorption. Both the polyniobate and Zr-MOF materials exhibit low reaction barriers. However, the energy profiles are characterized by strong binding of products to the metal oxide, which inhibits catalysis. Experimental probes further demonstrate product inhibition. The Zr-POM materials ameliorate product binding, warranting further experimental studies.