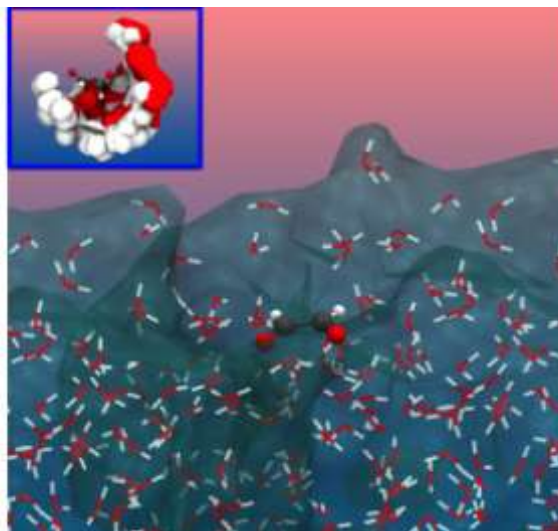


Toward a Comprehensive Picture of Heterogeneous Chemistry at Atmospheric Aerosols: The Catalyzed Isomerization of Glyoxal at the Liquid Water Interface

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Microphysical and chemical processes on aerosols surface are still poorly characterized and they greatly affect the reliability of weather and air-quality predictions. Glyoxal has been recently suggested as a possible catalyzer for aerosols growth in atmosphere. Glyoxal is the result of anthropogenic and biogenic emissions and, once hydrated, can strongly bind sulfate, which is one of the major ingredient for the aerosol nucleation. Preliminary evidences shows that glyoxal can hydrolyze even in the presence of few water molecules, suggesting that it can enhance water uptake on inorganic aerosols and, thus, aerosol growth. However, all these processes are speculative due to the lack of detail information about the physicochemical behavior of glyoxal at the interface of atmospheric aerosols.



After a brief introduction on the large-scale impact of microphysical and chemical processes occurring on aerosols surfaces, I present our results on the interaction of glyoxal at the air/liquid water interface obtained by electronic structure calculations and accurate classical and Born-Oppenheimer *ab-initio* molecular dynamics (AIMD) simulations. When glyoxal is adsorbed at the liquid water interface, the TRANS to CIS isomerization is catalyzed by the interface compared to what occur in the gas phase or in small water clusters. Moreover, molecular dynamics results show that the TRANS isomer can be absorbed more easily in the bulk than the CIS one, while the CIS form prefers more to reside at the interface. The catalytic effect of the interfacial water environment on glyoxal isomerization and the different surface propensity of the two isomers can, therefore, lead to an enhancement of glyoxal in its CIS form at the water interface.

Glyoxal is generally assumed to be in its TRANS form in the gas phase and at interfacial environments; however, the results of this work indicate that the CIS/TRANS relative concentration can be enhanced in favor of the CIS form at the interface, even if the latter is less energetically favorable. This has important implications in the experimental interpretation and modeling of glyoxal chemistry at the interface of water aerosols in the atmosphere. Moreover, these findings suggest a more general property of water interfacial environments in selecting specific stereo/chiral forms at the interface.