Researcher finds that on water's surface, nitric acid is not so tough

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Nitric acid is a notoriously strong and chemically destructive compound found in water on earth and in our atmosphere. However, a team of researchers have found that its punch is much weaker when it sits on the top of a water surface.

The discovery of the weaker and more highly exposed nature of nitric acid on the surface of water requires us to re-evaluate how we think about its reactive role in our world, said Geraldine Richmond, the Richard M. and Patricia H. Noyes Professor of Chemistry at the University of Oregon.

Richmond, who was named a Guggenheim Fellow for 2007 earlier this year, described her lab's exploratory research involving chemical reactions at the surface of water in a talk today at the 234th national meeting of the American Chemical Society in Boston. Her address was one of six scheduled talks on "Recent Advances in Studies of Molecular Processes at Interfaces."

Richmond is the principal investigator on this and many recent papers that examine unique properties of water surfaces using a combination of computer modeling and laser based experiments.

Nitric acid, a commonly used strong acid in the laboratory, is most notable for its widespread use in the manufacture of fertilizers and explosives. In our environment it is an important player in the atmosphere, where it concentrates in clouds and is one of the primary

components of acid rain. Once dissolved in water, its reactive acidic and oxidizing properties can become unleashed. The water causes it to break apart into hydrogen and nitrate ions, creating a highly acidic solution – hence its designation as a "strong acid" – that is very reactive to plants, soils and other matter. At high acid concentrations it can react explosively with other compounds, often releasing highly toxic gases.

Richmond and colleagues have found that when nitric acid swims to the top of a water surface, it tends to tread water – with part of its molecular structure in the air and the rest surrounded by water. Under these conditions they find that it is much less likely to dissociate into its ionic parts – giving the surface of nitric acid solutions very different reactive properties than its well-known reactive and acidic behavior in the bulk of the acid solution.

"Our combined laser experiments and computer simulations provide a rich picture of how nitric acid behaves on a water surface, the way it dances around on the top layer of the water surface in a way that significantly reduces its ability to shed its acidic hydrogen compared to when it is submerged in the liquid," Richmond said. "Hydrogen bonding to surface solvating water molecules plays a key role in this altered molecular behavior."

The exposed nature of nitric acid at the surface, Richmond said, makes it more readily available for reaction with immediate surroundings. But as a consequence of this exposure, it acts as a much weaker acid. The results have important implications for understanding the role of nitric acid in our environment, particularly in the many instances where the chemistry in our atmosphere occurs on the surface of nitric acid containing droplets and particulates.

Source: University of Oregon