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CFEL – Building 99, seminar room I and II (ground floor)

Chia Chen Wang

National Sun Yat-sen University, Kaohsiung, Taiwan, R.O.C

Valence Electronic Properties and Interfacial Solvation of Phenolic Aqueous Nanoaerosols Probed via Aerosol VUV Photoelectron Spectroscopy

An in-depth understanding of the fundamental energetic and structural properties at or near the interface of nanoscaled aqueous aerosols is of fundamental and crucial importance in understanding the impacts of organic species, either of biogenic or anthropogenic origins in intervening the cloud formation microphysics and the intrinsic nature of clouds. To address these issues, we applied the recently-developed aerosol VUV photoelectron spectroscopy [1,2] to investigate the valence electronic structures and interfacial characteristics of several organic-containing aqueous nanoaerosols that are of atmospheric significance. Phenol and phenolic compounds represent a major resource of secondary organic aerosols (SOA) in the atmosphere. We applied the recently constructed aerosol VUV photoelectron spectroscopy to investigate for the first time the valence photoelectron spectroscopy of phenol and three dihydroxybenzene (DHB) isomers in the aqueous nanoaerosol form, using the synchrotron-based VUV radiation as the ionization source [3]. By evaluating two photoelectron features of the lowest vertical ionization energies (VIE) originated from the $b_1(\pi)$ and $a_2(\pi)$ orbitals for phenolic aqueous nanoaerosols, their pH-dependent valence electronic structures and interfacial solvation characteristics are unraveled. Both phenol and phenolate are highly surface-active. On the aqueous aerosol interface, they appear only partially solvated, with the hydrophilic $-\text{OH}/-\text{O}-$ group better immersed in water and the hydrophobic aromatic ring remaining above the interface of aqueous aerosols. Deprotonations of phenolic species accompanying with increasing pH appear to enhance the hydration extent, likely due to the stronger solute-solvent interactions between the negatively charged $-\text{O}-$ group and water solvent molecules. A significant fraction of neutral phenol is observed along with phenolate at pH of 12.0, indicating that the chemical composition and surface pH at the aqueous aerosol interface deviate from the bulk. It reveals that the hydration extents, pH values, deprotonation status, and numbers/relative arrangements of $-\text{OH}$ groups are crucial factors affecting the ionization energies of phenolic aqueous nanoaerosols and thus their redox-based activities. The multi-faceted implications of the present study in the aerosol science, atmospheric/marine chemistry, and biological science will be addressed.

References

- [1] C.-C. Su, Y. Yu, P.-C. Chang, Y.-W. Chen, I. Y. Chen, Y.-Y. Lee, C. C. Wang, *J. Phys. Chem. Lett.* 2015, 6, 817.
- [2] P.-C. Chang, Y. Yu, W.-R. Chen, C.-C. Su, M.-S. Chen, Y.-L. Li, T.-P. Huang, Y.-Y. Lee, C. C. Wang, *J. Phys. Chem. B*, 2016, 120, 10181.
- [3] P.-C. Lin, Z.-H. Wu, M.-S. Chen, Y.-L. Li, W.-R. Chen, T.-P. Huang, Y.-Y. Lee and C.C. Wang*, *J. Phys. Chem. B*, 2017, 121, 1054.