

and sorbed Cr concentrations, unlike other samples. Gp and Cm, which exhibited the lowest Cr sorption capacities at both pH levels, demonstrated modifications in PSS indicative of conformational fragility and adaptation to Cr stress. Notably, at pH 2.0, Cm and Cc, with the highest sorption capacities, displayed the common feature of a substantial decrease in the proportion of unordered structures, suggesting intracellular protein proliferation to acclimate to Cr toxicity.

In summary, by combining sorption isotherms with synchrotron-related techniques, we investigated the mechanisms of Cr(VI) retention on Cyanidiales under both acidic and neutral conditions. Cm and Gp exhibited remarkable Cr(VI) sorption capacities at pH 2.0 (168.1 mg g^{-1}) and pH 7.0 (93.7 mg g^{-1}), respectively. In both cases, a significant proportion (89% for Cm at pH 2.0 and 62% for Gp at pH 7.0) of sorbed Cr occurred as Cr(III). The distribution of Cr species varied with sorption capacity, suggesting Cyanidiales employ alternative detoxification processes based on Cr stress intensity. Particularly intriguing was the intracellular formation of $\text{Cr}(\text{OH})_3$ observed only in Cm and Cc when sorbed Cr was $\geq 152 \text{ mg g}^{-1}$ at pH 2.0, highlighting Cyanidiales' unique capability to retain Cr. Apart from their sorption capability, the ability to simultaneously reduce Cr(VI) without requiring additional chemicals and partition Cr(III) intracellularly highlights the potential of Cyanidiales as innovative and sustainable remediation materials, particularly in challenging environmental conditions. (Reported by Yen-Lin Cho, National Chung Hsing University)

This report features the work of Yu-Ting Liu and her collaborators published in J. Hazard. Mater. 445, 130334 (2023).

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

TLS 01B1 X-ray Microscopy

TLS 14A1 IR Microscopy

TLS 17C1 EXAFS

- TXM, IR, XAS
- Environmental and Earth Sciences, Biological Science, Chemistry

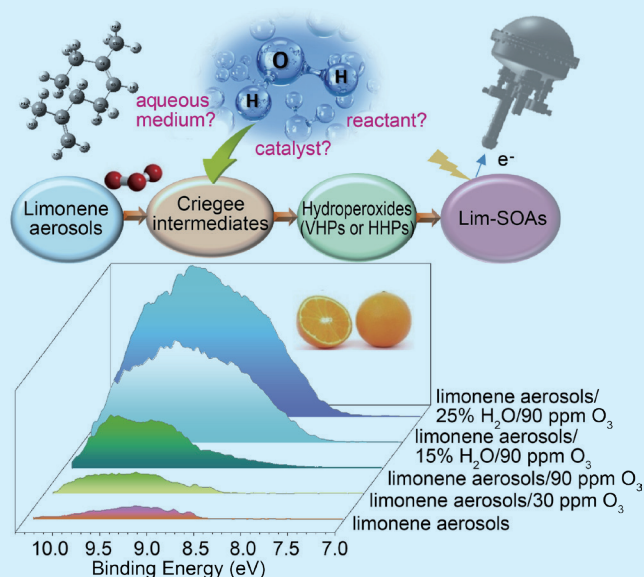
Reference

1. Y.-L. Cho, Y.-M. Tzou, C.-C. Wang, Y.-C. Lee, L.-C. Hsu, S.-L. Liu, A. Assakinah, Y. H. Chen, N. A. T. Than, Y.-T. Liu, J. Rinklebe, J. Hazard. Mater. 445, 130334 (2023).

Water Significantly Enhances Formation of Secondary Organic Aerosols in the Ozonolysis of Limonene

A combination of undulator-based aerosol vacuum ultraviolet photoelectron spectroscopy, high-resolution mass spectrometry, and density functional theory calculations revealed that water plays a multi-faceted role in enhancing the formation of secondary organic aerosols during the ozonolysis of limonene.

Atmospheric aerosols play a profound role in atmospheric chemistry, Earth's radiation budget, regional and global climates, and public health. According to planetary boundary theory,¹ atmospheric aerosol loading is one of nine major aspects that can affect the stability of Earth due to anthropogenic activities. However, the chemical composition, formation and transformation mechanisms, physical morphology, and other factors affecting atmospheric aerosol loading are not yet fully understood. A better understanding of these aspects could help with more accurate predictions of the impact of atmospheric aerosols on the climate and overall environmental ecosystem.



Chia C. Wang (National Sun Yat-sen University), Yin-Yu Lee (NSRRC), and their research team recently utilized vacuum ultraviolet (VUV) radiation at **TLS 21B2** as a photoionization source in aerosol VUV photoelectron spectroscopy to observe the valence electronic structures of limonene aerosols and the secondary organic aerosols (SOAs) generated during limonene ozonolysis for the first time.² Limonene is an important naturally occurring monoterpene with very high biogenic emission rates. About 8.6 billion kilograms of limonene are released into the atmosphere every year from natural sources alone, which accounts for about 9% of global monoterpene emissions. Limonene also has a variety of anthropogenic sources, as it

is a key component of many household cleaning products, essential oils, air fresheners, and cosmetic products. When limonene-based cleaning products are used indoors, an increase in two orders of magnitude has been reported in the indoor air concentration of limonene compared to outdoor levels. Limonene has been considered one of the most important sources of indoor secondary organic aerosols in domestic environments. The team discovered that higher concentrations of water in limonene aerosols lead to generation of more SOAs.

Wang and her research team combined VUV photoelectron spectroscopy, density functional theory quantum

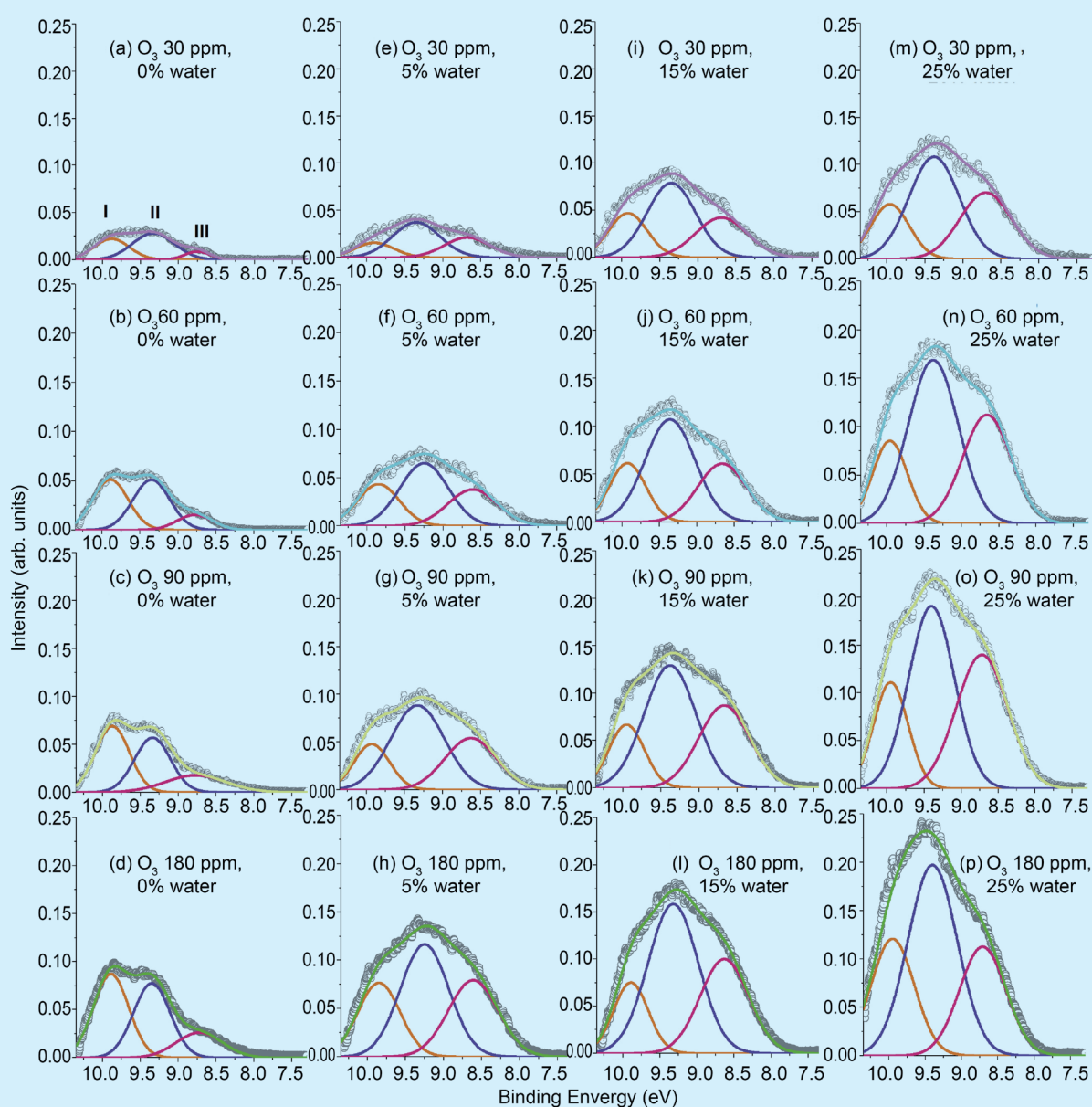


Fig. 1: VUV photoelectron spectra of Lim-SOAs formed during ozonolysis of limonene aerosols at varying levels of ozone and water. (a) O₃ 30 ppm, 0% water; (b) O₃ 60 ppm, 0% water; (c) O₃ 90 ppm, 0% water; (d) O₃ 180 ppm, 0% water; (e) O₃ 30 ppm, 5% water; (f) O₃ 60 ppm, 5% water; (g) O₃ 90 ppm, 5% water; (h) O₃ 180 ppm, 5% water; (i) O₃ 30 ppm, 15% water; (j) O₃ 60 ppm, 15% water; (k) O₃ 90 ppm, 15% water; (l) O₃ 180 ppm, 15% water; (m) O₃ 30 ppm, 25% water; (n) O₃ 60 ppm, 25% water; (o) O₃ 90 ppm, 25% water; (p) O₃ 180 ppm, 25% water. Symbol notation: experiment, -○-; spectral deconvolutions of Feature-I, orange curve; Feature-II, violet curve; Feature-III, pink curve; total fitted spectra at O₃ 30 ppm, light magenta curve; at O₃ 60 ppm, cyan curve; at O₃ 90 ppm, yellow curve; O₃ 180 ppm, green curve. [Reproduced from Ref. 2]



Ozonolysis of limonene is considered one of the most important sources of indoor SOAs. [Figure courtesy of Chia C. Wang]

mechanical calculations, and high-resolution liquid chromatography-electrospray ionization-mass spectrometry, to find that water directly intervenes in the ozonolysis of limonene and its Criegee chemistry. On the one hand, water acts as a catalyst by lowering the energy barrier during the formation of hydroperoxide through the isomerization of Criegee intermediates. On the other hand, water, especially water dimers, directly react with Criegee intermediates during limonene ozonolysis, revealing a new pathway for SOA generation. The study revealed that the chemical composition of SOAs generated from ozonolysis of water-containing limonene aerosols differs from SOAs generated by ozonolysis of dry limonene aerosols containing no water, indicating that water alters the reaction mechanisms and final products during ozonolysis.

Water is the third most abundant component in air, after nitrogen and oxygen. Traditionally water was considered only as a polar aqueous medium and its function as a catalyst or reactant was not considered. However, mounting studies have demonstrated the importance of water in atmospheric processes in regions with severe air pollution. This issue is both important and non-negligible in Asian countries, where the relative humidity is generally higher than American and European countries. For the first time, this study conducted by the Aerosol Science Research Center research team led by Wang revealed the multifunctional role played by water during the formation of SOAs by the ozonolysis of monoterpenes. Because the influential effects of water were not taken into consideration in most atmospheric chemical reaction modeling simulations, the overall yield of SOA generated in reactions where water plays a role may have been underestimated, contributing to uncertainty in predicting the impact of atmospheric aerosols on climate change.

Another important finding of this research is that ozone concentration in the air is a key factor promoting the conversion of limonene aqueous aerosols into SOAs. Environments with high ozone concentrations, such as

places where ozone-based air purifiers are frequently used, can experience enhanced production of secondary organic aerosols from ozonolysis of limonene aerosols, with numerous adverse health effects on humans and animals. To fully understand their environmental impact, it is crucially important to pay close attention to possible sources of aerosols, their chemical composition and formation routes, and their physicochemical and biochemical properties.

In summary, to fully understand the impact of aerosols on the Earth's atmosphere, climate, and health, it is crucial to understand the chemical composition, formation and transformation mechanisms, accompanying energetic information, and other physicochemical properties of SOAs, in addition to the key factors affecting them. Water, conventionally considered as an inert aqueous medium, greatly enhances SOA formation in limonene ozonolysis by serving as both a catalyst and a reactant. It is necessary to revise atmospheric and climate modeling to consider the role of water to accurately estimate the influence of atmospheric aerosols on regional and global climates. It is equally important to raise public awareness on potential sources of SOAs, both outdoors and indoors, and possible influential factors in different environmental settings to mitigate the adverse health effects of secondary organic aerosols. (Reported by Chia C. Wang, National Sun Yat-sen University)

*This report features the work of Chia C. Wang and her coworkers published in *J. Phys. Chem. Lett.* **14**, 3765 (2023). This paper was selected as a cover of the issue.*

TLS 21B2 Gas Phase

- UPS
- Aerosol Physical Chemistry, Environmental Chemistry

References

1. W. Steffen, K. Richardson, J. Rockström, S. E. Cornell, I. Fetzer, E. M. Bennett, R. Biggs, S. R. Carpenter, W. de Vries, C. A. de Wit, C. Folke, D. Gerten, J. Heinke, G. M. Mace, L. M. Persson, V. Ramanathan, B. Reyers, S. Sörlin, *Science* **347**, 1259855 (2015).
2. J.-H. Huang, F. Zhang, Y.-P. Shi, J.-R. Cai, Y.-H. Chuang, W.-P. Hu, Y.-Y. Lee, C. C. Wang, *J. Phys. Chem. Lett.* **14**, 3765 (2023).

