Paper Presentation

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Article

Spontaneous Degradation of the "Forever Chemicals" Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) on Water Droplet Surfaces

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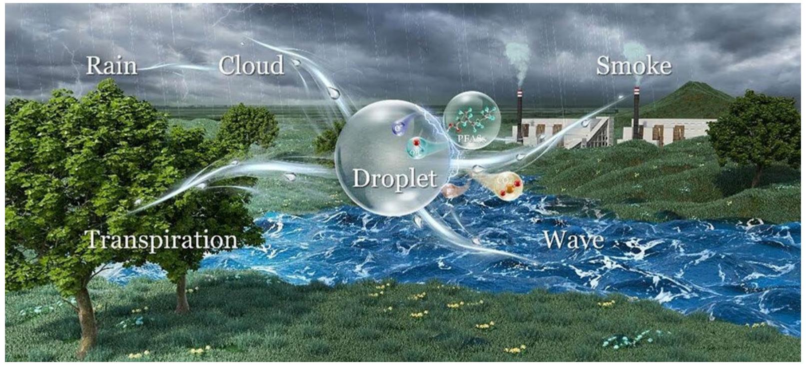
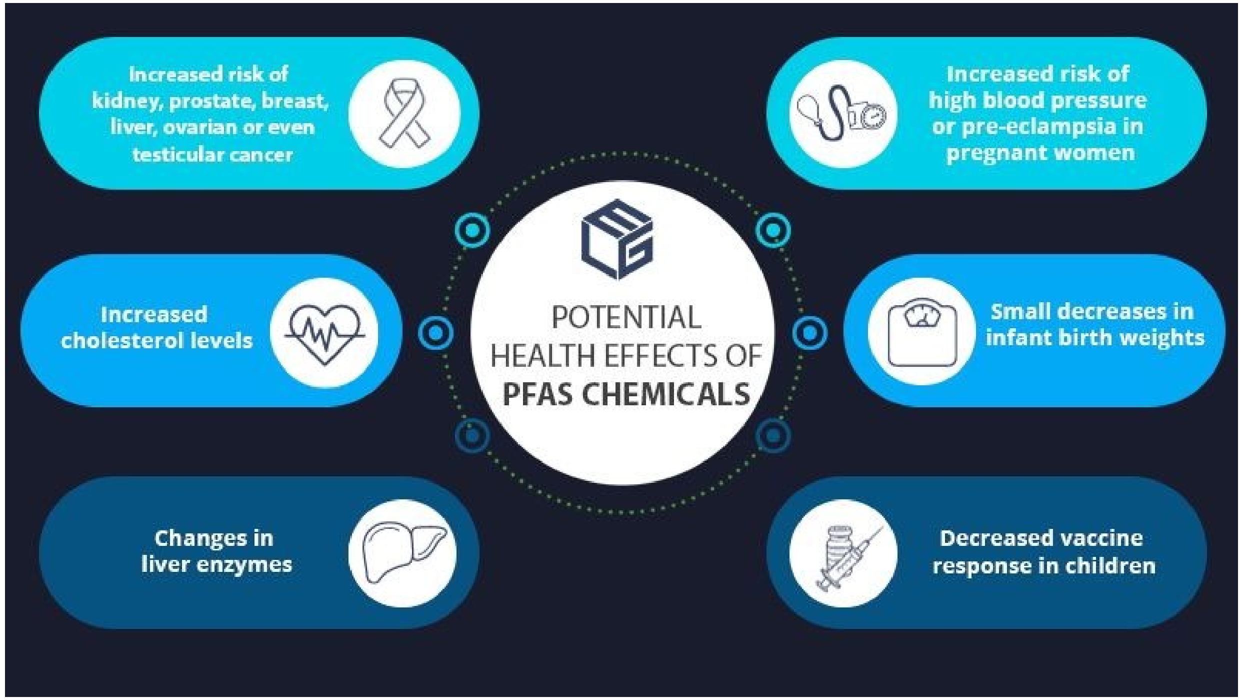


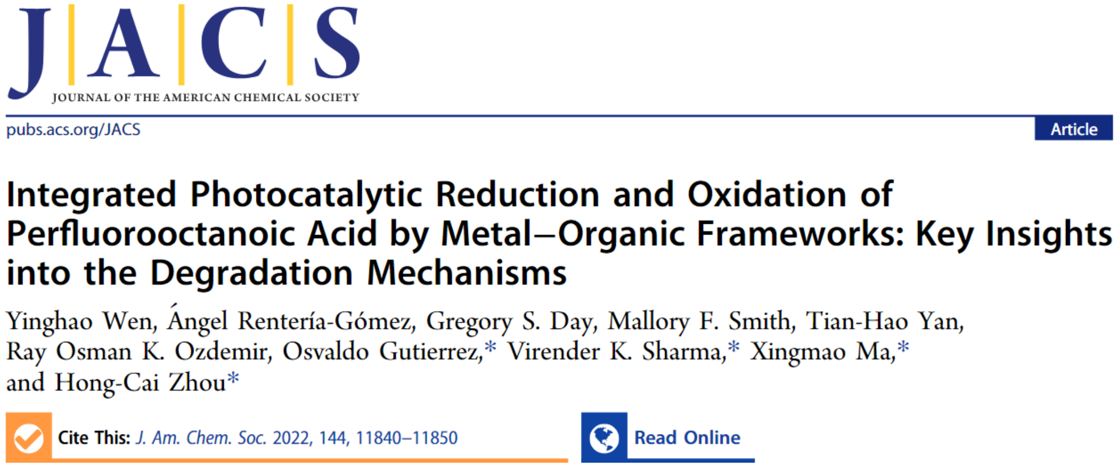
Presented by
Sinchan Mukherjee
11/5/2024



POTENTIAL HEALTH EFFECTS OF **PFAS CHEMICALS**

- Increased risk of kidney, prostate, breast, liver, ovarian or even testicular cancer
- Increased risk of high blood pressure or pre-eclampsia in pregnant women
- Increased cholesterol levels
- Small decreases in infant birth weights
- Changes in liver enzymes
- Decreased vaccine response in children

Source : Internet



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Article

Integrated Photocatalytic Reduction and Oxidation of Perfluorooctanoic Acid by Metal–Organic Frameworks: Key Insights into the Degradation Mechanisms

Yinghao Wen, Ángel Rentería-Gómez, Gregory S. Day, Mallory F. Smith, Tian-Hao Yan, Ray Osman K. Ozdemir, Osvaldo Gutierrez,* Virender K. Sharma,* Xingmao Ma,* and Hong-Cai Zhou*

Cite This: *J. Am. Chem. Soc.* 2022, 144, 11840–11850

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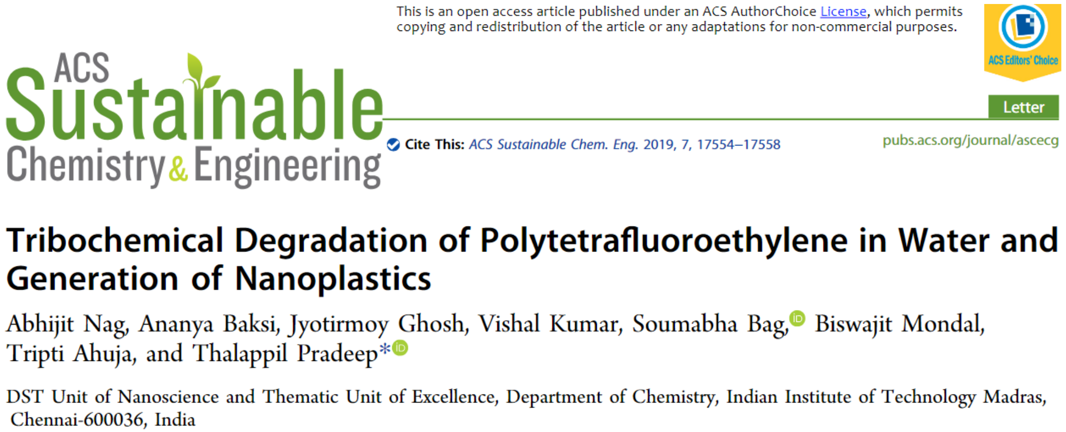

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Tribochemical Degradation of Polytetrafluoroethylene in Water and Generation of Nanoplastics

Abhijit Nag, Ananya Baksi, Jyotirmoy Ghosh, Vishal Kumar, Soumabha Bag, Biswajit Mondal, Tripti Ahuja, and Thalappil Pradeep*

DST Unit of Nanoscience and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India

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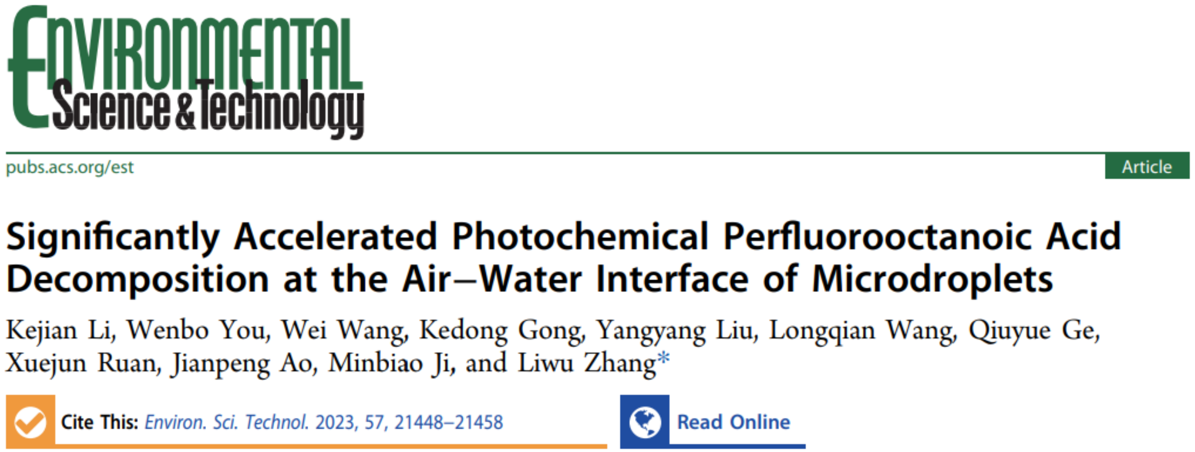

Environmental Science & Technology
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Article

Significantly Accelerated Photochemical Perfluorooctanoic Acid Decomposition at the Air–Water Interface of Microdroplets

Kejian Li, Wenbo You, Wei Wang, Kedong Gong, Yangyang Liu, Longqian Wang, Qiuyue Ge, Xuejun Ruan, Jianpeng Ao, Minbiao Ji, and Liwu Zhang*

Cite This: *Environ. Sci. Technol.* 2023, 57, 21448–21458

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Why this paper?

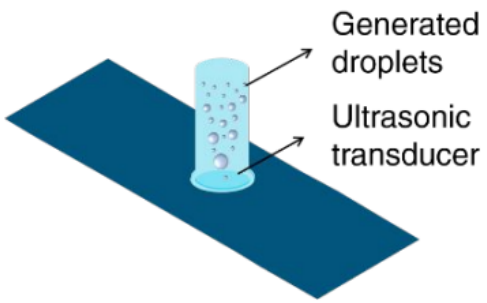
- No catalysts are being used here, $OH_{\cdot}$ Radical and e^- on the air-water interface does the job
- The degradation happens simply in water.
- Carried out at room temperature.
- The degradation process is very fast (happens in milliseconds)

Relevance to our group:

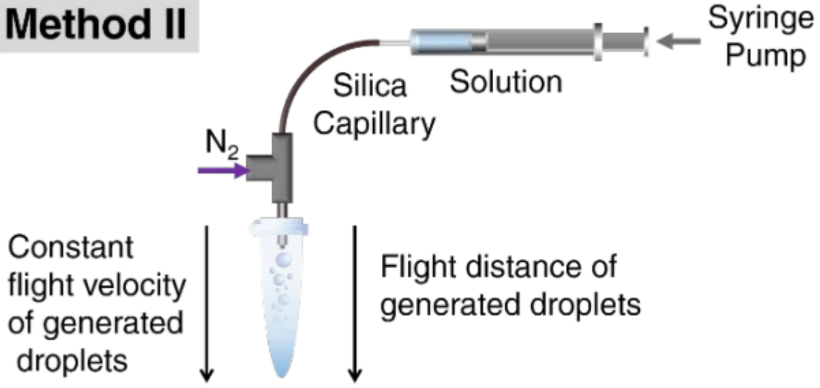
- Water microdroplets
- Electrospray ionization and deposition

Experimental setup

Method I

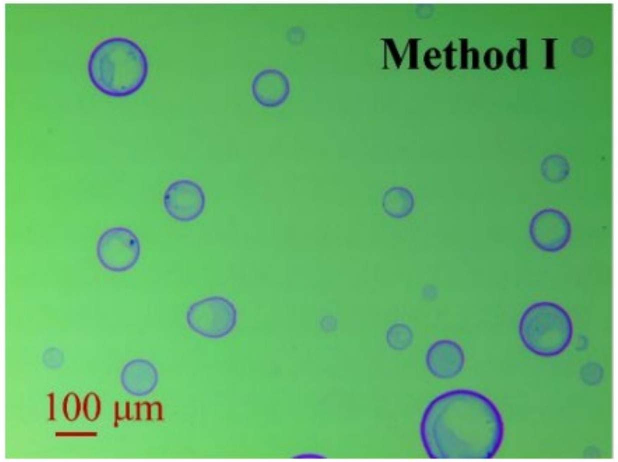


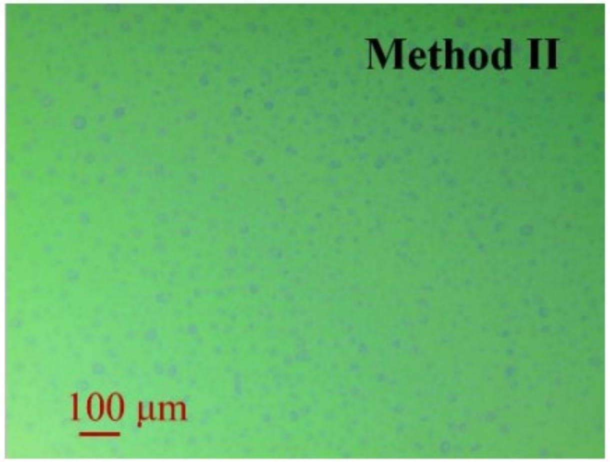
Method II



Reaction time for Method I = Time of ultrasonic atomization

Reaction time for Method II = Flight distance / Flight velocity





Experimental setup

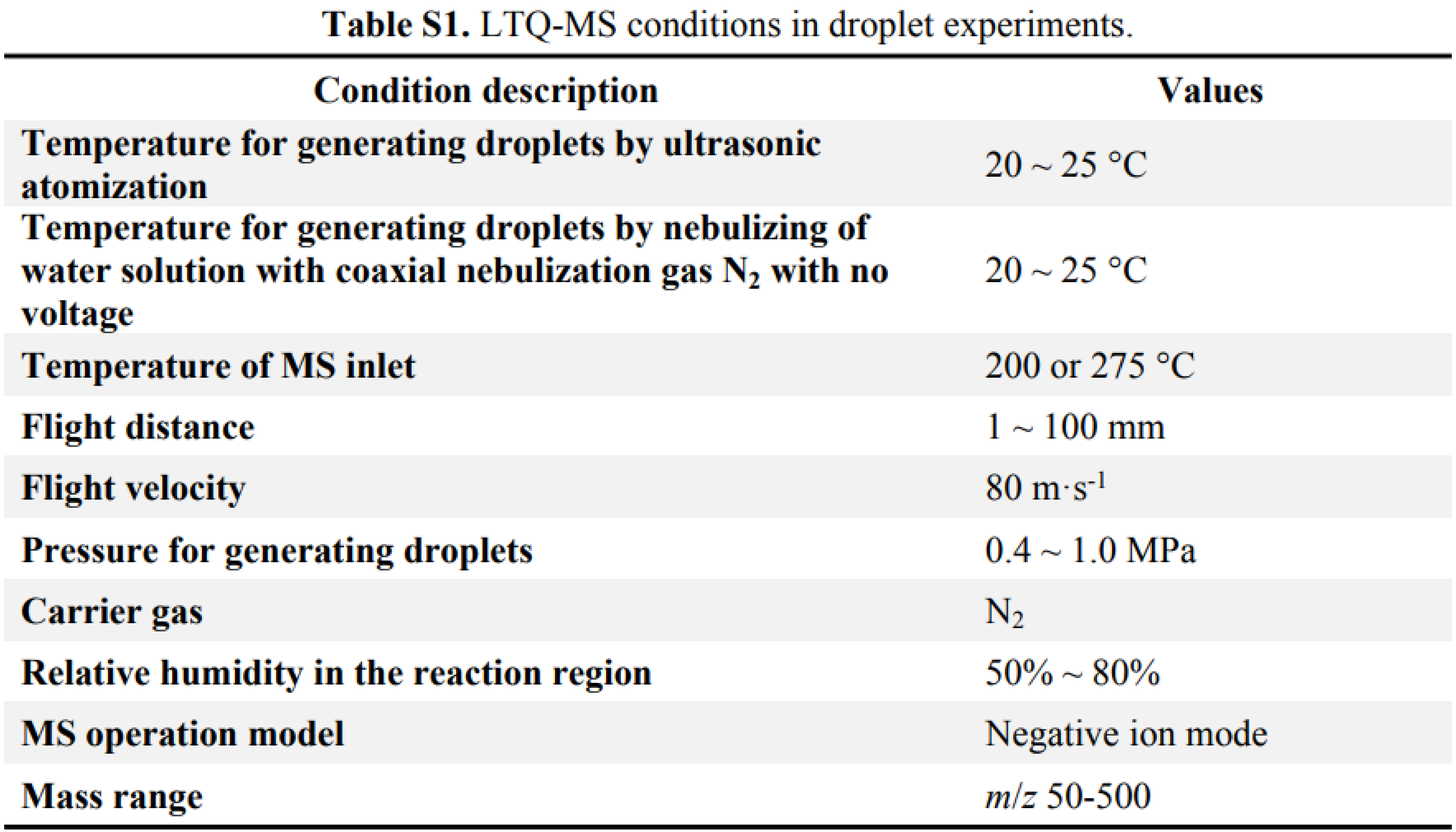
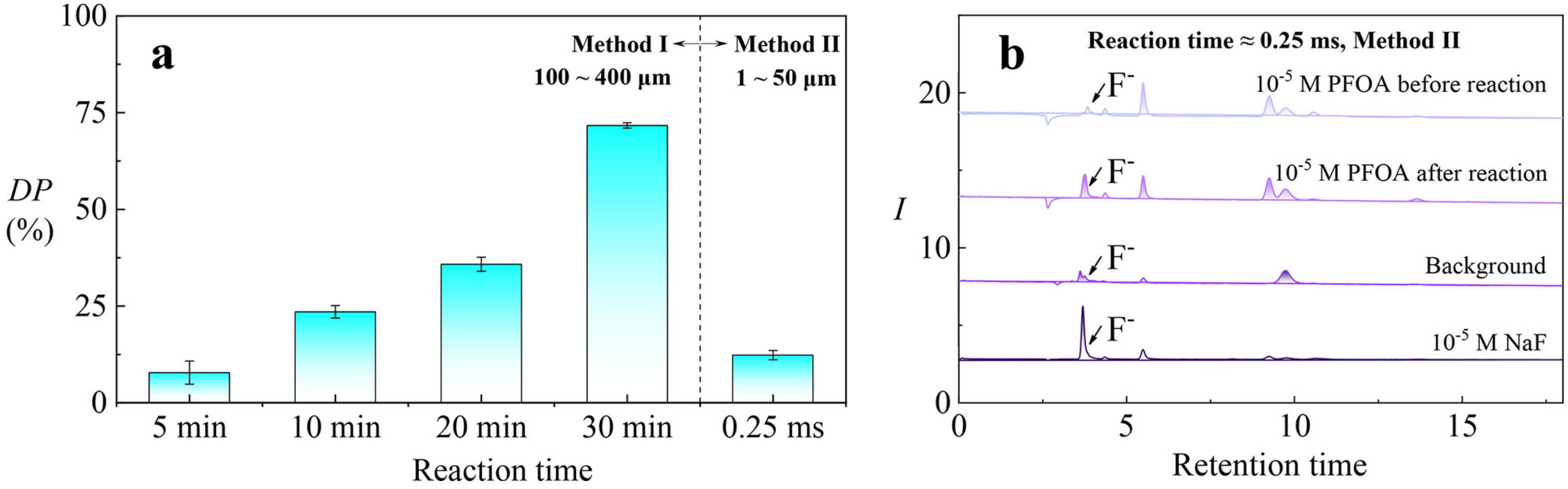
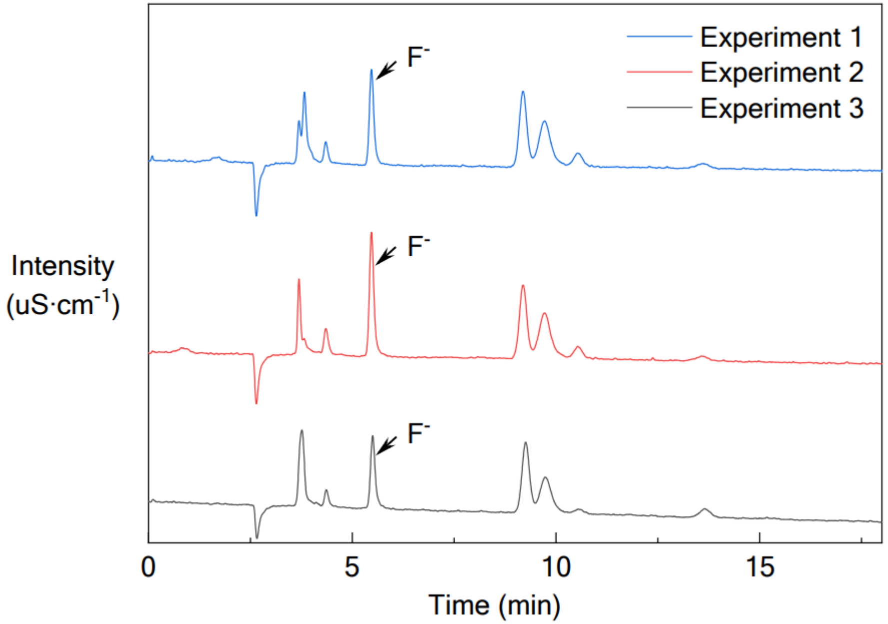


Table S1. LTQ-MS conditions in droplet experiments.

Condition description	**Values**
Temperature for generating droplets by ultrasonic atomization	20 ~ 25 °C
Temperature for generating droplets by nebulizing of water solution with coaxial nebulization gas N_2 with no voltage	20 ~ 25 °C
Temperature of MS inlet	200 or 275 °C
Flight distance	1 ~ 100 mm
Flight velocity	80 $m \cdot s^{-1}$
Pressure for generating droplets	0.4 ~ 1.0 MPa
Carrier gas	N_2
Relative humidity in the reaction region	50% ~ 80%
MS operation model	Negative ion mode
Mass range	*m*/*z* 50-500

Results and Discussion





Results and Discussion

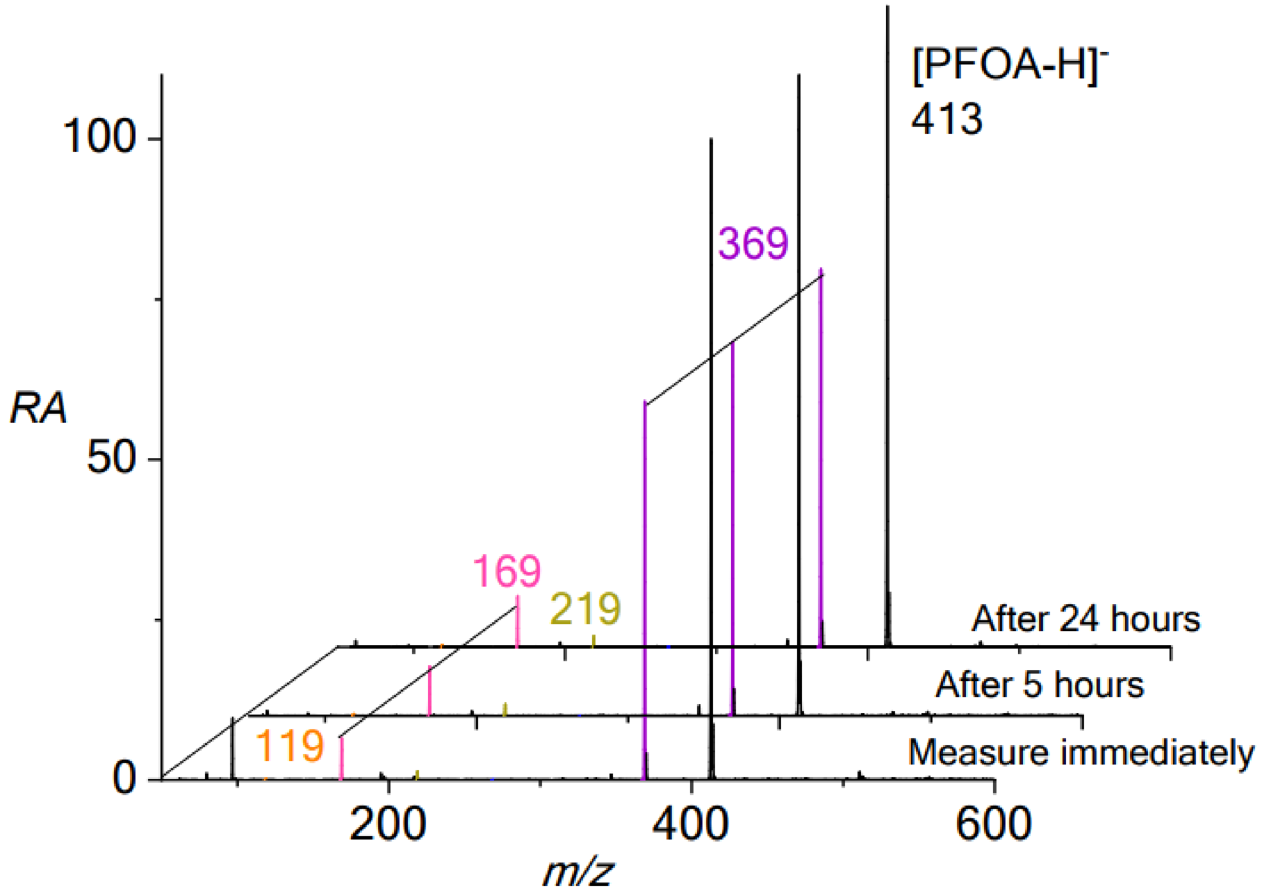


Fig. S5.
Relative abundance (*RA*) of detected species by an online LTQ XL mass spectrometer for a 250 µs microdroplet experiment, a 250 µs microdroplet experiment + 5 hours aqueous phase reaction, and a 250 µs microdroplet experiment + 24 hours aqueous phase reaction.

Results and Discussion

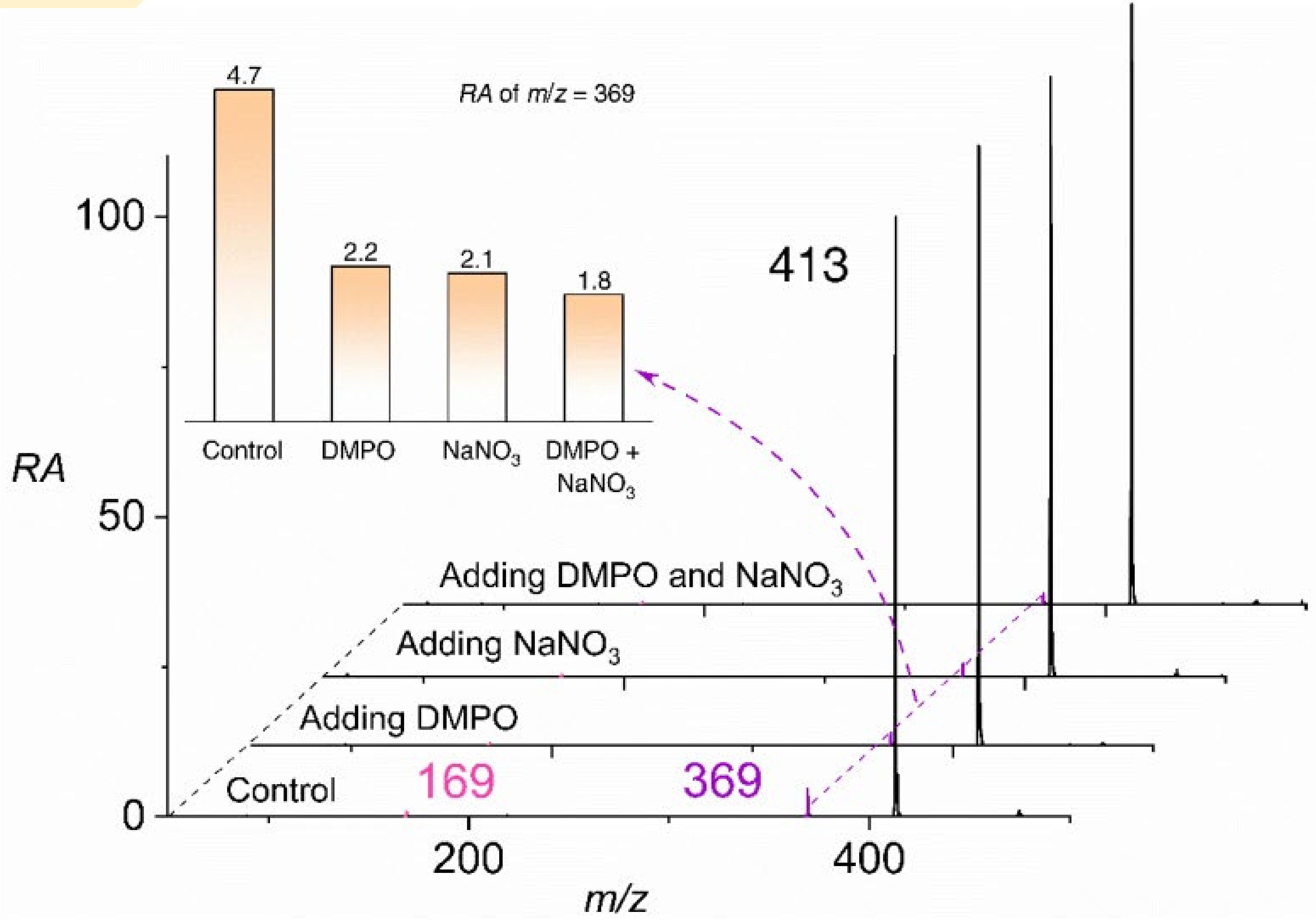


Fig. S6.

Relative abundance (*RA*) of reactant and intermediates by an online LTQ XL mass spectrometer in a 250 μs microdroplet experiment with 10^{-4} M 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 10^{-4} M $NaNO_3$, or 10^{-4} M DMPO + 10^{-4} M $NaNO_3$ under the conditions of 200 °C inlet temperature.

Results and Discussion

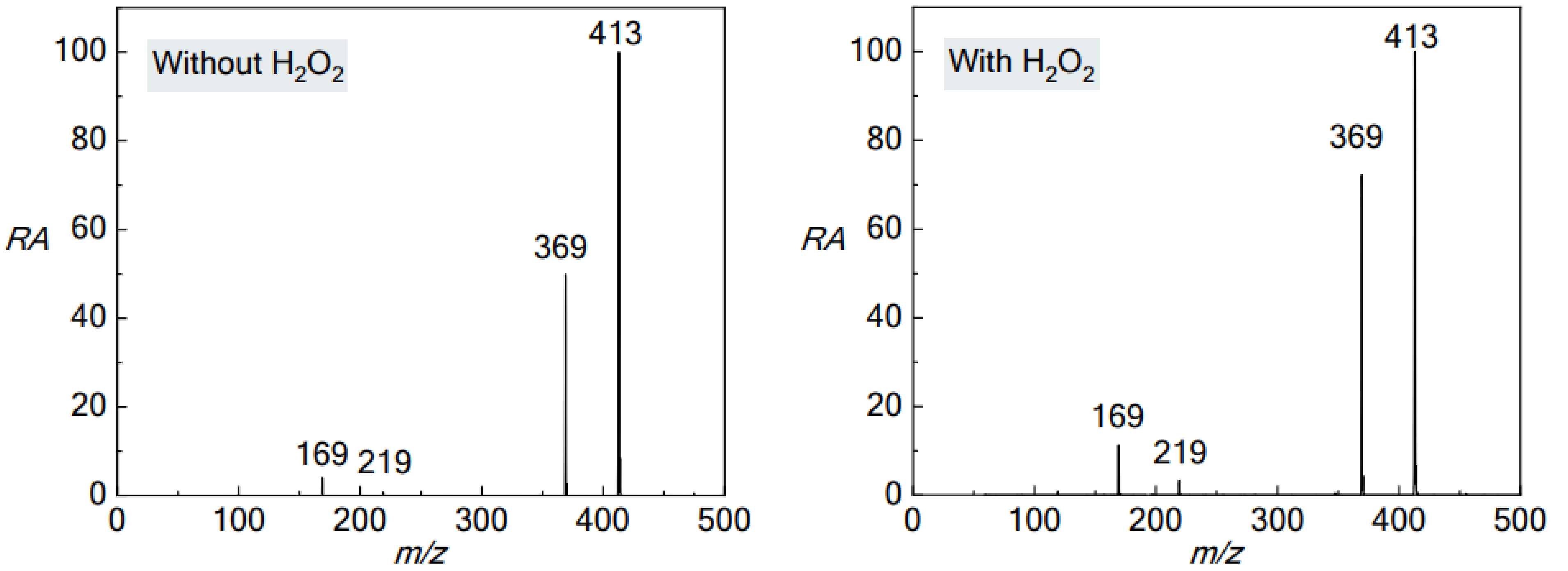


Fig. S7.
Relative abundance (*RA*) of reactant and intermediates by a LTQ XL mass spectrometer with and without H_2O_2 under the conditions of 275 °C inlet temperature.

Results and Discussion

$$H_2O\cdot^{+} + H_2O \rightarrow \cdot OH + H_3O^{+} \qquad (2)$$

$$H_2O\cdot^{+} + C_7F_{15}COOH \rightarrow \cdot C_7F_{15} + H_3O^{+} + CO_2 \qquad (3)$$

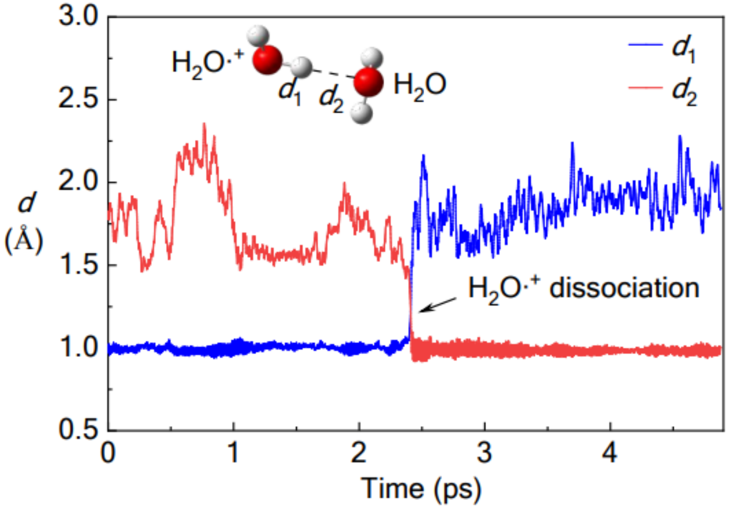


Fig. S8.
Time evolution of key distances in $H_2O\cdot^{+}$ dissociation reaction obtained by *ab initio* molecular dynamics simulation.

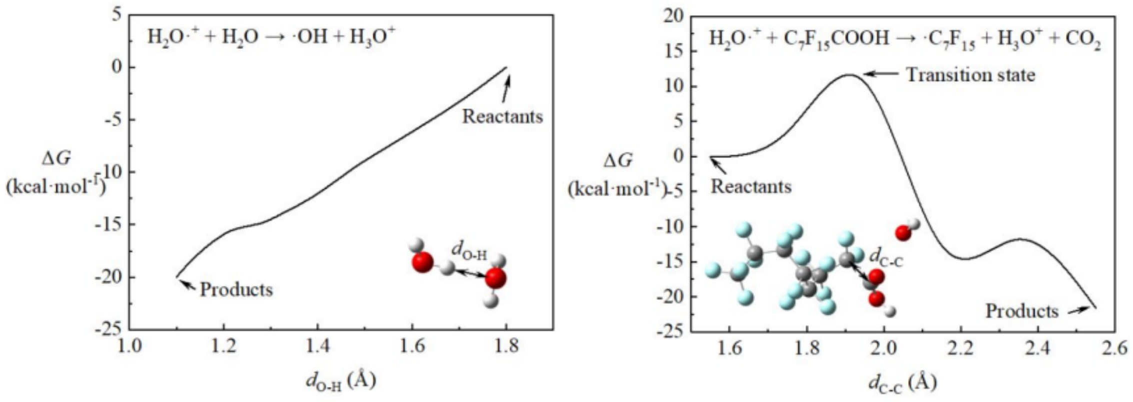


Fig. S9.
Gibbs-free-energy profile for "$H_2O\cdot^{+} + H_2O \rightarrow \cdot OH + H_3O^{+}$" (left) and "$H_2O\cdot^{+} + C_7F_{15}COOH \rightarrow \cdot C_7F_{15} + H_3O^{+} + CO_2$" (right) reactions.

Results and Discussion

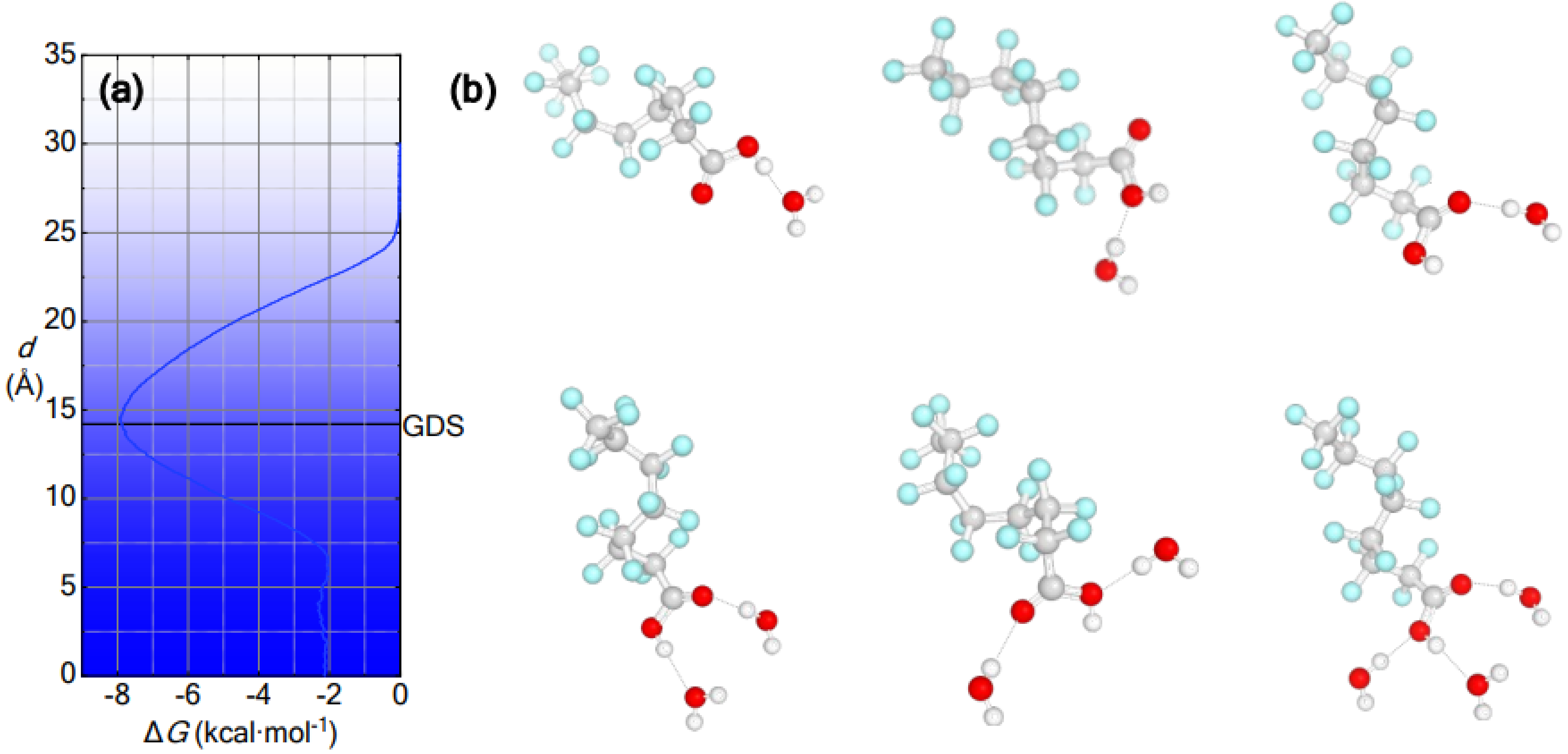
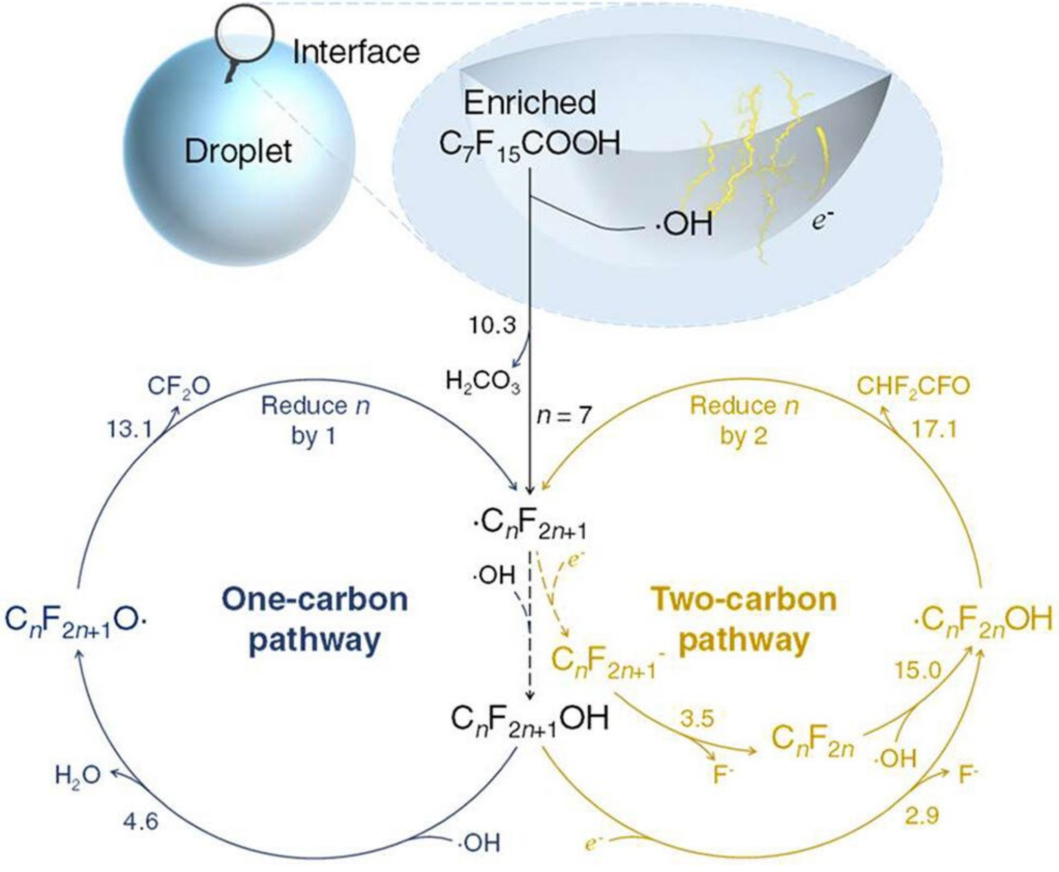


Fig. S10.

Surface preference of PFOA. **a**, Gibbs-free-energy change (Δ*G*) profile of a PFOA molecule pulled into water as a function of distance (*d*, Å) between centers of PFOA and droplet (GDS represents Gibbs division surface). **b**, Six most abundant configurations of PFOA adsorption (The dashed lines represent the hydrogen-bonds between PFOA and water molecules at air-water interfaces).

Results and Discussion



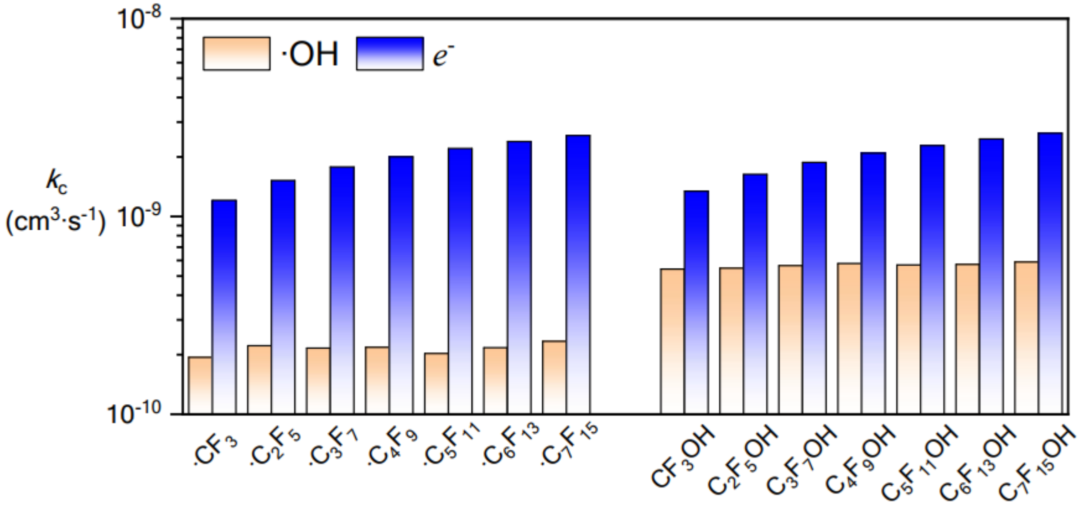


Fig. S21.
Calculated capture rate coefficients (k_C, $cm^3 \cdot s^{-1}$) of $\cdot C_nF_{2n+1}$/$C_nF_{2n+1}OH$ (n = 1−7) by ·OH and e^- based on the geometries optimized at the M06-2X/aug-cc-pVTZ level of theory.

Results and Discussion

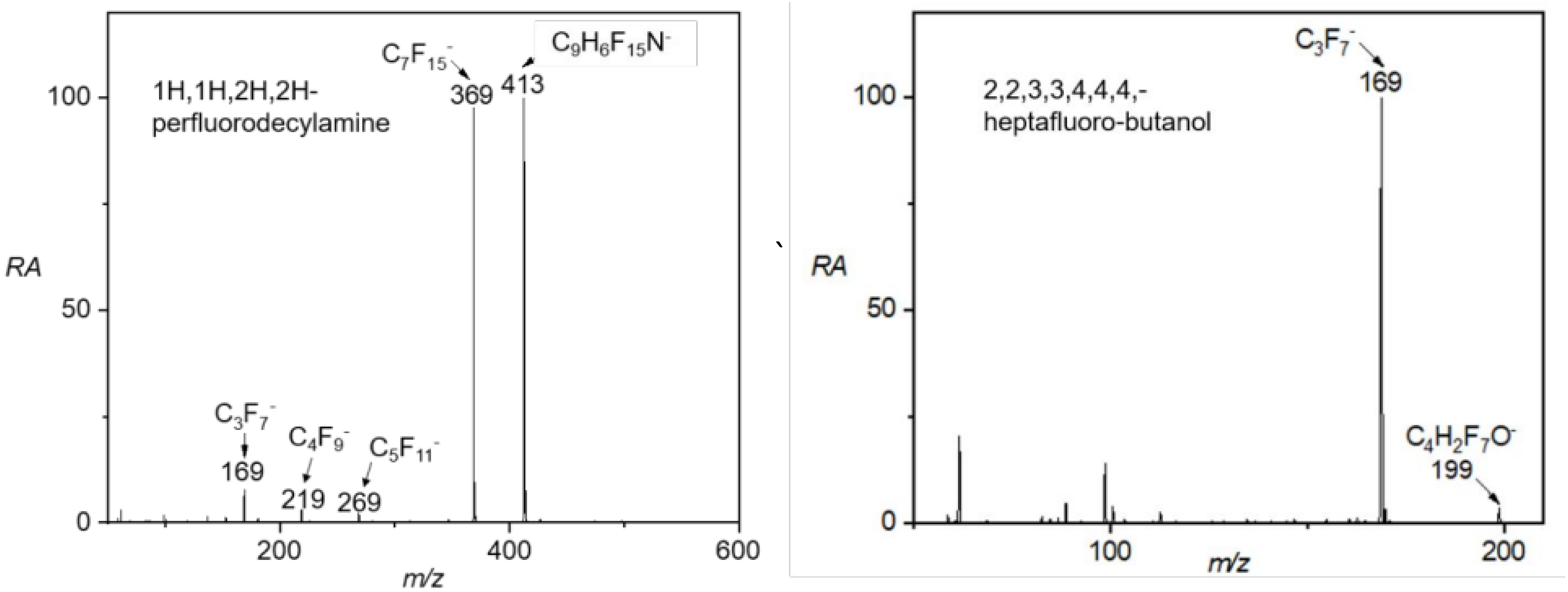


Fig. S23.
Relative abundance (*RA*) of 10 µM 1H,1H,2H,2H-perfluorodecylamine (left) and 2,2,3,3,4,4,4,-heptafluoro-butanol (right) after microdroplet experiments.

Results and Discussion

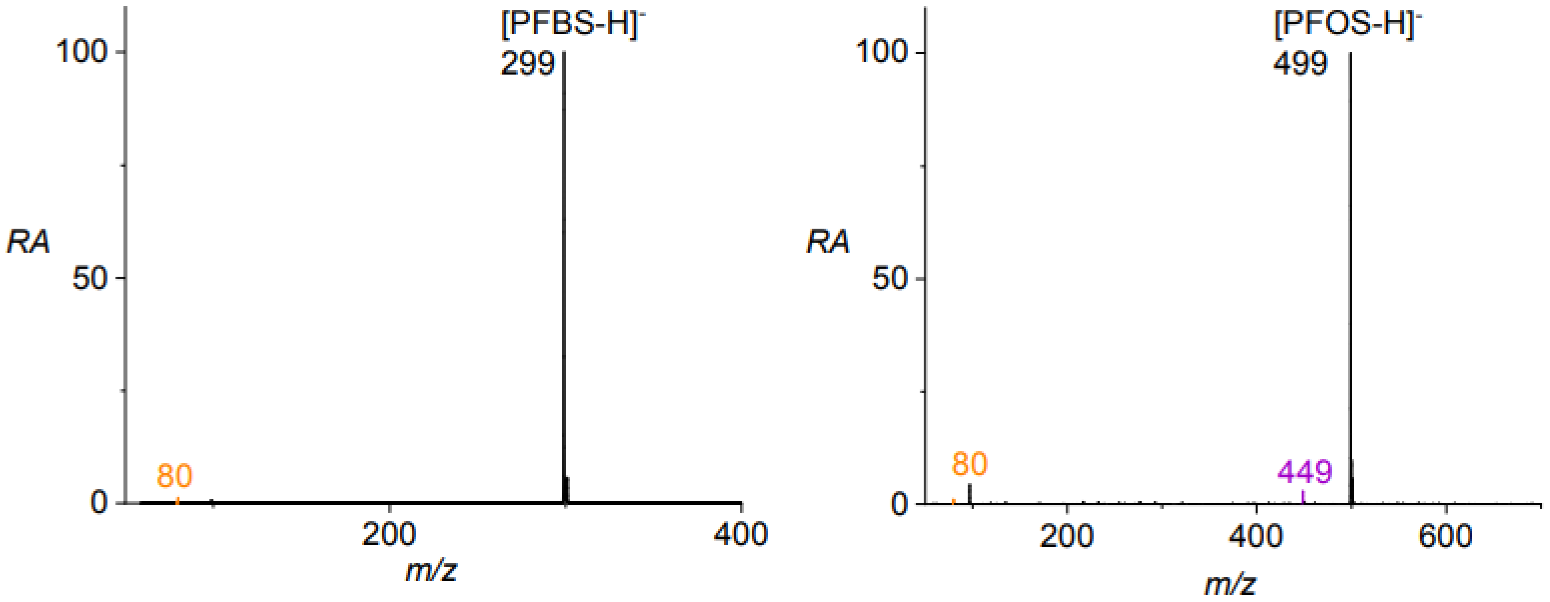


Fig. S24.
Relative abundance (*RA*) of 10 μM perfluorooctanesulfonic acid (PFBS, left) and perfluorobutane sulfonic acid (PFOS, right) after microdroplet experiments.

Results and Discussion

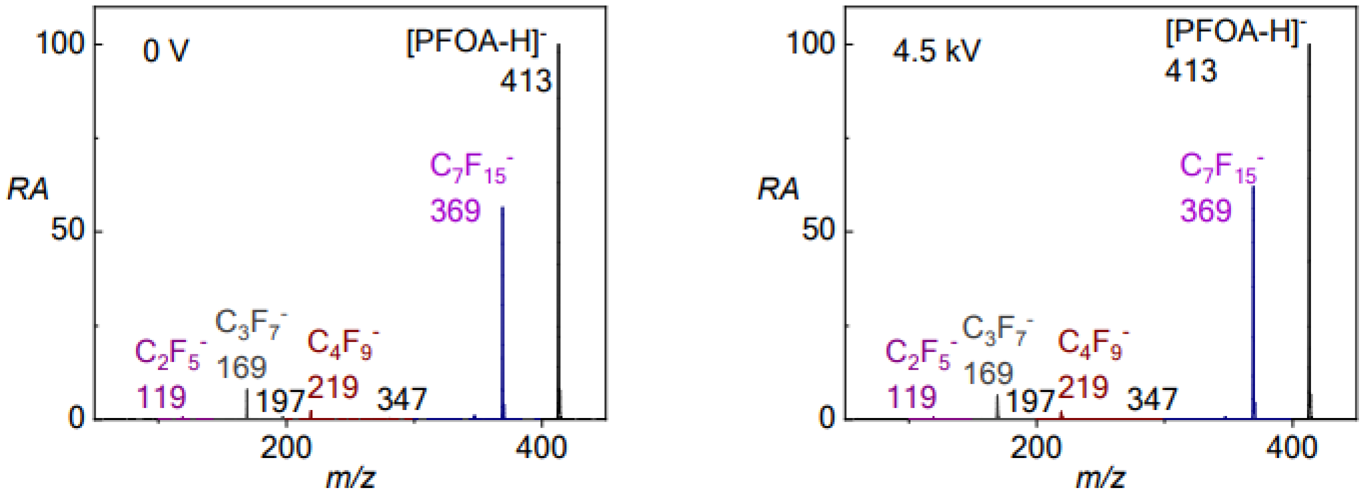


Fig. S25.
Comparison of relative abundance under the conditions of 0 (left) and 4.5 kV (right) external voltage during the nebulization using Method II.

Conclusion:

- Spontaneous degradation of PFAS has been carried out in a catalyst-free manner using water microdroplets at the air-water interface.
- OH radical and electrons at the AWI are the determining factors of the mechanism.
- The process described here is ultrafast (method II takes only 25 milliseconds to degrade the PFAS)

Thank you for listening!

Persist like PFAS and be reluctant to degradation!