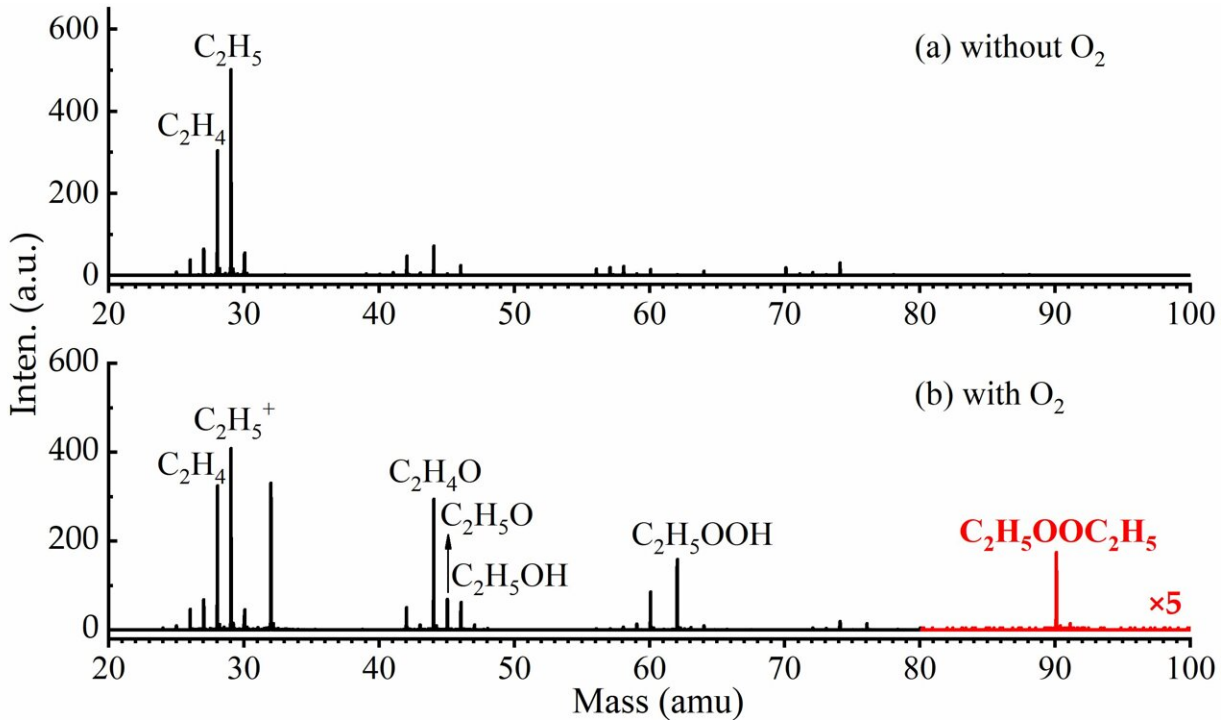
Scientists detect dimer product ROOR generated by self-reaction of ethyl peroxy radicals

March 16 2023, by Zhang Nannan



VUV lamp photoionization mass spectra measured (a) without O_2 and (b) with O_2 in the microwave discharge flow tube, with five times magnified data in red. Credit: Lin Xiaoxiao

Organic peroxy radicals (RO_2) are important intermediates in the degradation of atmospheric volatile organic compounds. It not only

participates in the cycling of atmospheric radicals and influences oxidizing capacity of the atmosphere, but also controls the formation of secondary pollutants.

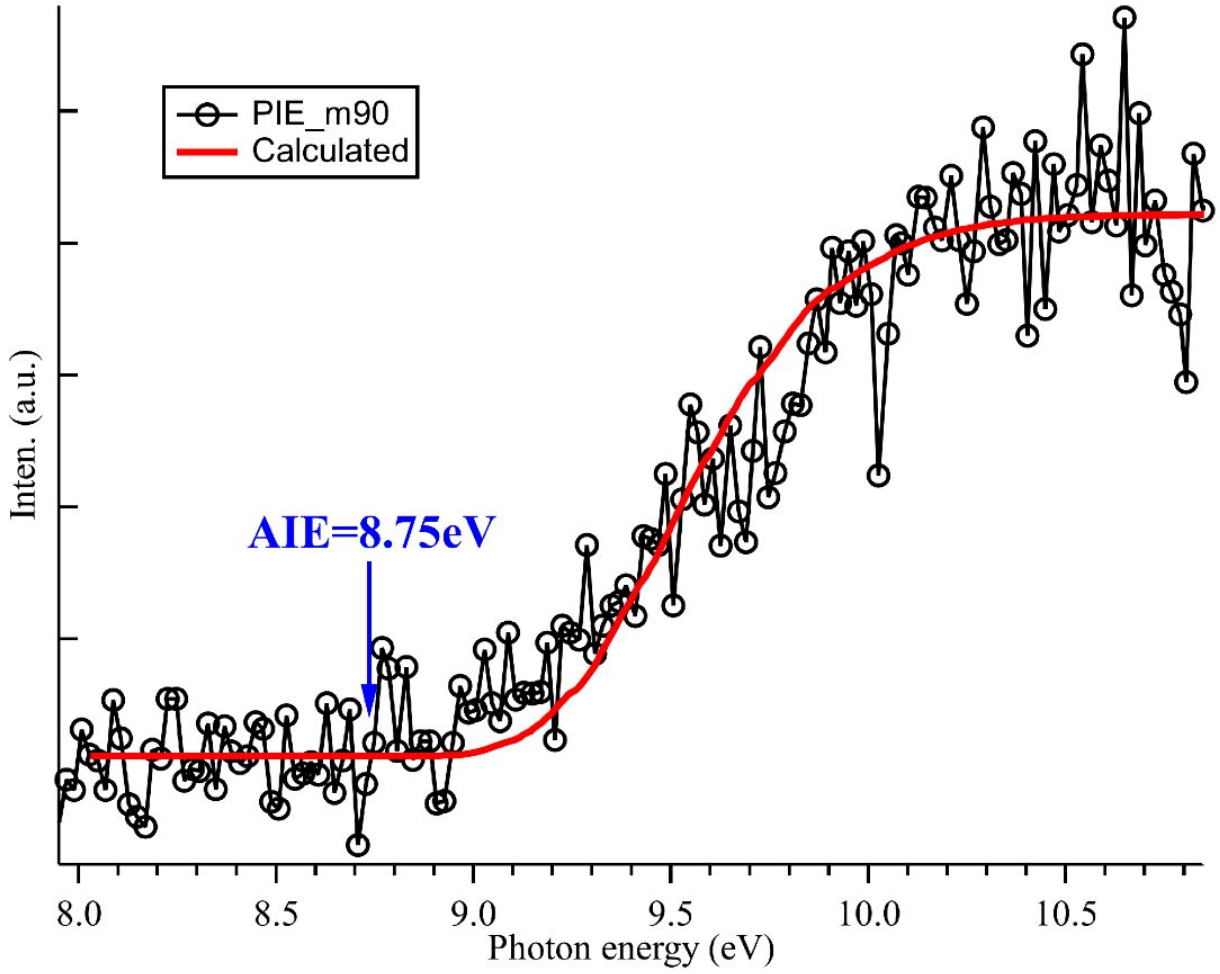
Under low NO_x conditions, peroxy radicals react mainly with HO_2 radicals, as well as with themselves, and their products tend to have low volatility and readily enter the particulate phase. However, the associated double radical reactions are complex, the chemical mechanisms are poorly understood and experimental and theoretical studies are extremely challenging.

A collaborative team led by Prof. Weijun Zhang from the Hefei Institutes of Physical Science of the Chinese Academy of Sciences studied the self-reaction of ethyl peroxy radicals ($C_2H_5O_2$). They combined advanced vacuum ultraviolet (VUV) photoionization mass spectrometry with theoretical calculations, providing a new insight into the direct measurement of the elusive dimeric product organic peroxides (ROOR).

The results have been published in the *International Journal of Molecular Sciences*.

Together with scientists from the Université de Lille, France, the researchers investigated the self-reactions of $C_2H_5O_2$. In addition to the main products CH_3CHO, C_2H_5OH, C_2H_5O and C_2H_5OOH, the dimeric product $C_2H_5OOC_2H_5$ from the self-reaction of $C_2H_5O_2$ was clearly observed for the first time in the VUV photoionization mass spectrum.

The kinetic experiments of the self-reaction of $C_2H_5O_2$ and theoretical calculations were performed to verify the reaction mechanism of the ROOR product channel. The adiabatic ionization energy of $C_2H_5OOC_2H_5$ was also determined by measuring the synchrotron photoionization efficiency spectrum.



Photoionization spectrum of $C_2H_5OOC_2H_5$ and its calculated results in red. Credit: Xiaoxiao

Combined with Franck-Condon factor simulations, the neutral and ionic structures of $C_2H_5OOC_2H_5$ were revealed.

"Our study shows that the ROOR product channel is not negligible in the small RO2 self-reactions," said Lin Xiaoxiao, a member of the team.

More information: Hao Yue et al, Dimeric Product of Peroxy Radical Self-Reaction Probed with VUV Photoionization Mass Spectrometry and Theoretical Calculations: The Case of $C_2H_5OOC_2H_5$, *International Journal of Molecular Sciences* (2023). DOI: 10.3390/ijms24043731

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