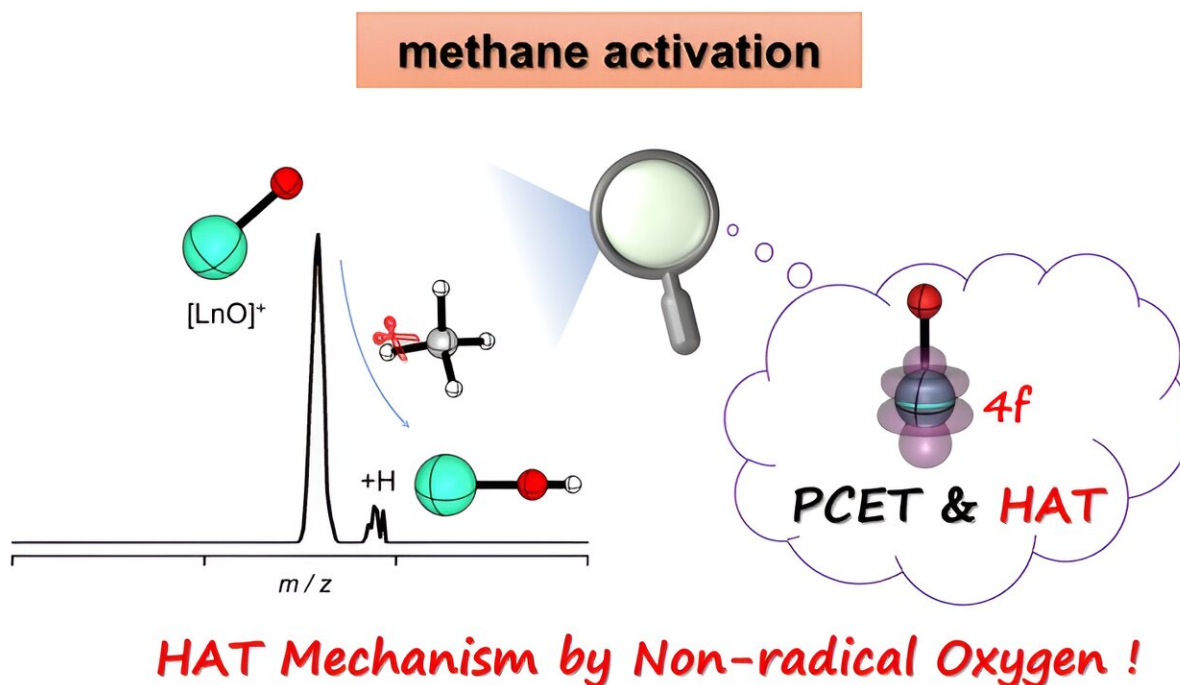


Methane activation by $[\text{LnO}]^+$: The 4f orbital matters

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By adjusting the occupancy of the 4f orbitals, it is possible to induce the HAT mechanism for the activation of C-H bonds. Credit: Science China Press

As the "holy grail" in the field of chemistry, the catalytic activation of methane has been a topic of great interest in the field of heterogeneous catalysis. Gas-phase experiments provide an ideal platform for exploring

catalytic reaction mechanisms and gaining in-depth understanding of electronic structures.

Over the past few decades, a large number of substances capable of activating [methane](#) in the gas phase have been discovered, and even complete catalytic cycles for methane conversion have been established. The mechanism of initial C-H bond activation in methane can be divided into hydrogen atom transfer (HAT), proton-coupled electron transfer (PCET), and hydride transfer (HT), and the construction of low-energy activation sites has become a recent research hotspot.

Recently, the research group led by Professor Shao-Dong Zhou reported on the reaction of $[\text{LnO}]^+$ [ions](#) ($\text{Ln} = \text{Sm-Lu}$) with methane, and experimental results showed that $[\text{LnO}]^+$ ions can extract a hydrogen atom from methane, with $[\text{EuO}]^+$ and $[\text{YbO}]^+$ exhibiting the highest reactivity.

Quantum chemical calculations revealed that $[\text{LnO}]^+$ ions are triply bonded ions with unpaired electrons occupying the 4f orbitals. In the reactions of $[\text{EuO}]^+ / [\text{YbO}]^+$ with methane, one of the Ln-O bonds undergoes homolytic cleavage, forming an oxygen radical, thus activating methane through the HAT mechanism.

In other systems, methane activation occurs via the PCET mechanism through heterolytic cleavage of Ln-O bonds. It is worth noting that upon formation of the [transition state](#), the occupancy of the 4f orbitals in $[\text{EuO}]^+ / [\text{YbO}]^+$ changes from $4f^6 / 4f^{13}$ to $4f^7 / 4f^{14}$, resulting in a half-filled or fully-filled state of the 4f orbitals, stabilizing the transition state and lowering the reaction barrier.

This differs from previous studies, where the interaction between lanthanide metals and oxygen ligands led to the degeneracy of the 4f orbitals, reducing the reaction barrier rather than the 5d-4f electron

transition. This paper's experimental and computational results indicate that rational modulation of the occupancy of the 4f orbitals may be beneficial for the design of radical reactions.

The findings are [published](#) in the journal *Science China Chemistry*.

More information: Bowei Yuan et al, Methane activation by [LnO]⁺: the 4f orbital matters, *Science China Chemistry* (2023). [DOI: 10.1007/s11426-023-1801-4](https://doi.org/10.1007/s11426-023-1801-4)

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