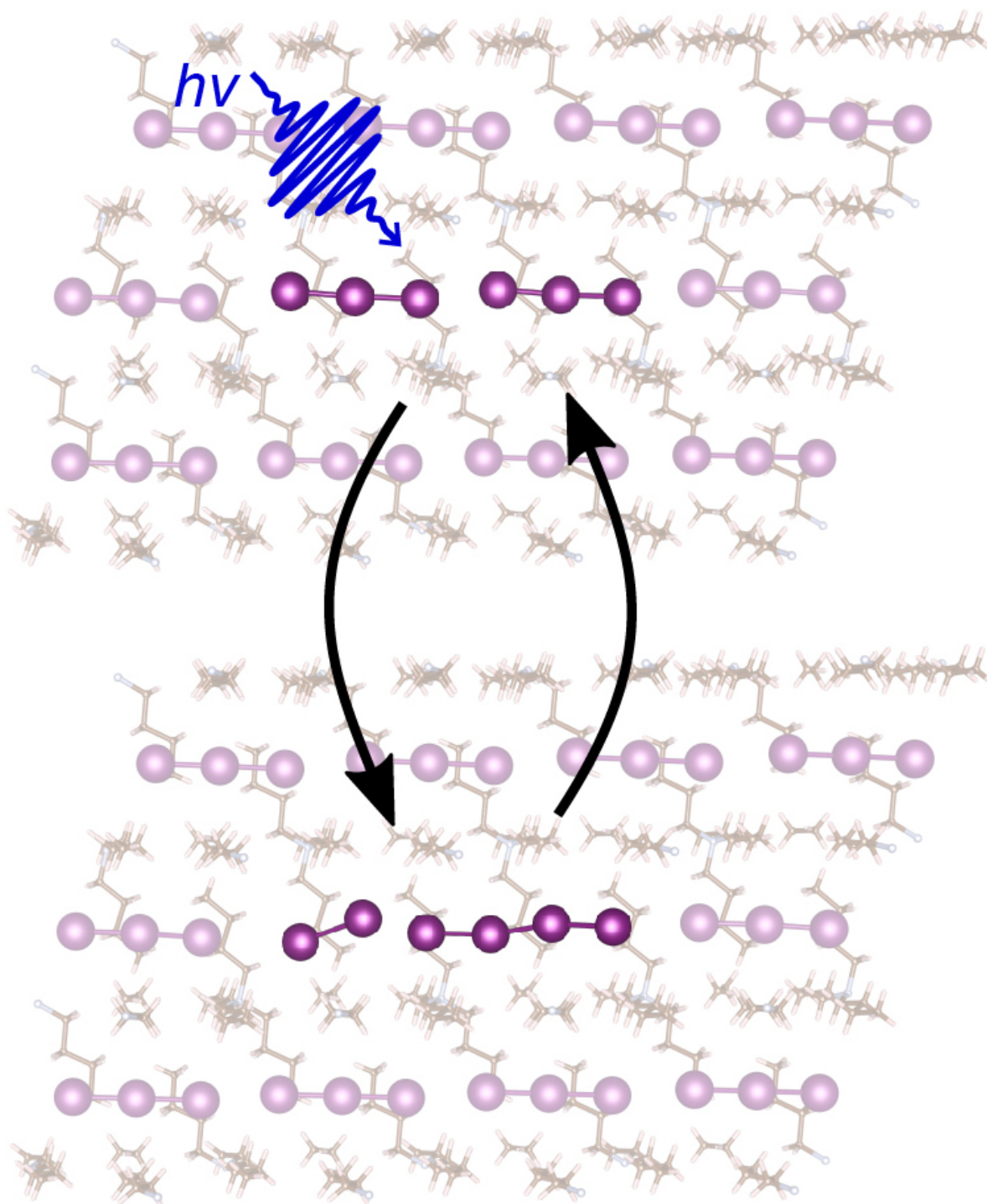


# **New intermediate discovered for the photodissociation of triiodide anion, a classic textbook reaction**

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The picture illustrates the photodissociation of triiodide initiated by a laser pulse and the secondary reaction leading to the novel 4-atom intermediate, followed by the recombination reaction. Credit: Image from R. Xian et al. *Nat. Chem.* (2017),

The photodissociation of triiodide anion ( $I_3^-$ ) is a classic textbook reaction that has been extensively studied both in solution and in gas phase. However, probing the ultrafast dynamics of this reaction in the solid state is challenging due to partial reversibility of the reaction and its sensitivity to experimental conditions. Now, a team of scientists have discovered a new reaction intermediate, the tetraiodide radical anion ( $I_4^{\bullet-}$ ), formed as a result of the unique ordering of in the crystal lattice to direct the dissociating I atom in a process reminiscent of a quantum Newton's cradle. They have published their results in *Nature Chemistry*.

In the solution phase, the triiodide anions photodissociates predominantly into iodine radical ( $I^\bullet$ ) and diiodide ( $I_2^{\bullet-}$ ) radicals. The surrounding solvent plays a passive role in the inertial confinement of the [reaction](#) products that ultimately undergo geminate and non-geminate recombination. In contrast, a dramatically different behavior was found in the ordered ionic [lattice](#) of tetra-n-butylammonium triiodide crystals. Here, the local geometry constrains the reaction and, hence, the primary photoproduct, iodine radical ( $I^\bullet$ ), is guided by the lattice to form a bond with an adjacent ( $I_3^-$ ), giving rise to a secondary reaction product, the tetraiodide radical anion ( $I_4^{\bullet-}$ ), not described before for this reaction. As shown in in the figure, the reactants are literally aligned in the lattice to form this four-atom intermediate.

"The dissociated iodine atoms collide in a quantum type of a Newton's cradle with other triiodide molecules to form this novel reaction product," explains Dwayne Miller. "Most importantly, we have demonstrated that the lattice can coherently direct the [reaction pathway](#) of solid-state photochemistry on femtosecond to picosecond time scales."

This phenomenon was only observable thanks to new sample-handling, data collection and analysis techniques developed at the MPSD together with theoretical calculations carried out at the University of Edinburgh to support the electronic and vibrational assignments of the various reaction participants, which enabled the most detailed resolution to date of the reaction intermediates, as well as the coherent modes driving the triiodide photodissociation reaction. "These observations provide a different conceptual framework to think about reaction processes and may point the way in how to couple chemical systems to a bath as a means to increase the length scales under chemical control," concludes Miller.

**More information:** Coherent ultrafast lattice-directed reaction dynamics of triiodide anion photodissociation, Rui Xian, Gastón Corthey, David M. Rogers, Carole A. Morrison, Valentyn I. Prokhorenko, Stuart A. Hayes and R. J. Dwayne Miller, *Nature Chemistry* (online), [DOI: 10.1038/nchem.2751](https://doi.org/10.1038/nchem.2751)

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