Chemistry Triggered by Infrared Vibrational Excitation in Cryogenic Matrices

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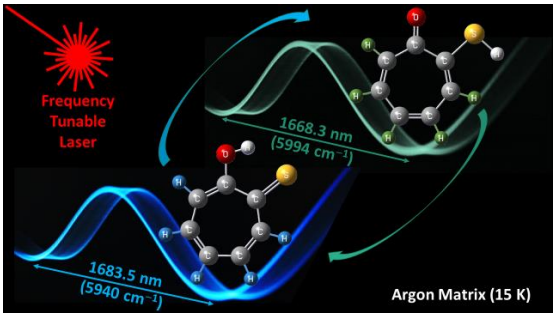
Infrared vibrational excitation is a promising approach to achieve molecular transformations in an exceptional highly-selective and controlled manner. In this context, the precise manipulation of specific molecular conformations, even in distinct environments, has been demonstrated using vibrational excitation in conjugation with matrix-isolation technique.[1] However, until recently, this methodology has been essentially limited to induce conformation isomerizations, with most examples reporting the manipulation of an OH fragment by narrowband irradiation at its first stretching overtone frequency.

In recent breakthrough investigations, we have shown that besides conformation isomerizations,[2] bond-breaking/bond-making reactions can also be triggered by near-IR vibrational excitation under matrix-isolation conditions. Here, we will highlight such pioneer results, which comprise: the activation of a H-shift tunneling reaction;[3] the bidirectional activation of a thione-enol ↔ thiol-keto tautomerization (figure below);[4] and the activation of an electrocyclic ring-expansion by excitation of a remote vibrational antenna.[5]



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