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New insights on the non-adiabatic dynamics of the ultrafast photodissociation of the methyl iodide cation

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The development of light sources in the extreme ultraviolet (XUV) based on high harmonic generation has opened new avenues for the investigation of time-resolved photodynamics in cationic excited electronic states of polyatomic molecules. Here, an XUV pump-infrared (IR) probe scheme with femtosecond time resolution is employed to study the dynamics of dissociative ionization in methyl iodide [1].

A time-delay-compensated XUV monochromator is employed to isolate the 9th harmonic of the fundamental 800 nm (13.95 eV, 88.89 nm), which is used as a pump pulse to prepare the cation in several electronic states. A time-delayed IR probe pulse is used to probe the dissociative ionization dynamics on the first excited $\tilde{A}\ ^2A_1$ state. Photoelectrons and photofragment ions are detected by velocity map imaging. The experimental results are complemented with high-level ab initio calculations of potential energy curves (PECs) of the electronic states of CH_3I^+ as well as full-dimension on-the-fly trajectory calculations on the $\tilde{A}^2A_1$ state, considering the presence of the IR pulse. CH_3^+ and I^+ transients reflect the role of the IR pulse in probing the photodynamics of CH_3I^+ in the $\tilde{A}^2A_1$ state, mainly through the coupling to the ground state $X^2E_{3/2,1/2}$ and to the excited B^2E state manifold. Oscillatory features are observed and attributed to a vibrational wave packet prepared in the $\tilde{A}\ ^2A_1$ state. The IR probe pulse induces a coupling between electronic states leading to a slow depletion of CH_3^+ fragments after the cation is transferred to the ground $X^2E_{3/2,1/2}$ states and an enhancement of I^+ fragments by absorption of IR photons yielding dissociative photoionization.

Complementary experiments have been carried out at the synchrotron SOLEIL using double imaging photoelectron photoion coincidence (i^2 PEPICO) spectroscopy to study the valence-shell dissociative photoionization of methyl iodide. The measured threshold photoelectron spectrum for CH_3^+ reveals that the ν_5 scissors vibrational mode promotes a transfer of population from the initially populated first excited state ($\tilde{A}^2A_1$) into the ground cationic state, leading to the formation of CH_3^+. Additional high-level ab initio calculations of PECs reveal the presence of an elusive conical intersection mediating this internal conversion.

References
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