Entanglement and Electronic Coherence in Attosecond Molecular Photoionization

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Electronic coherences resulting from molecular photoionization underlie the process of attosecond charge migration, widely investigated as a possible route towards controlled charge-directed reactivity. However, photoionization intrinsically produces entangled ion-photoelectron states, and this entanglement can compromise the ability to observe and interpret coherent ultrafast electron dynamics in either subsystem. Here we present combined experimental and theoretical investigations of attosecond photoionization in molecular hydrogen, in which ionization is driven by a phase-locked pair of isolated attosecond pulses in combination with a few-cycle near-infrared (NIR) field. This approach enables the preparation of coherent superpositions of ionic states while simultaneously providing a means to manipulate the continuum electron dynamics. We demonstrate that the electronic coherence in the dissociating H_2^+ ion is strongly influenced by the degree of ion-photoelectron entanglement, and that this entanglement can be actively controlled by varying both the delay between the attosecond pulses and their timing relative to the NIR probe pulse.

The measurements reveal pronounced oscillations in the fragment asymmetry, reflecting the formation of coherent superpositions of the $1s\sigma_g$ and $2p\sigma_u$ electronic states. The amplitude of these oscillations depends sensitively on the delay between the attosecond pulses, showing maxima when the delay corresponds to integer multiples of the NIR optical period and minima at half-integer values. This behavior is reproduced by full-dimensional simulations of the time-dependent Schrödinger equation, which further show a clear anticorrelation between the degree of electronic coherence and the von Neumann entropy of the reduced ionic density matrix. These results demonstrate that quantum entanglement plays a central role in limiting and enabling the observation of electronic coherences in attosecond experiments. More broadly, they establish a route towards the control of many-particle quantum dynamics in photoionization and highlight the importance of accounting for entanglement in the interpretation of ultrafast spectroscopy. This work opens new perspectives for the development of multidimensional attosecond spectroscopy and for exploiting entanglement as a resource in ultrafast molecular science.