Attosecond probing electron delocalization in water clusters

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Abstract: We report the realization of attosecond timing of local electron emission in water clusters. Ultrafast delocalized hole electron dynamics on attosecond temporal scale, which correlates to different cluster size, is observed in water clusters by a new developed attosecond coincidence metrology.

Main text:

To bridge the ultrafast electron dynamics between gas and condensed phase has been a long-standing challenge both in experiment and theory. Previous works using RABBITT and attosecond streaking have successfully revealed the photoionization time delay of atoms, molecules, and solids in time and frequency domain. Recently, these techniques have been extended to the liquid phase, which is of particularly interest in bridging the fundamental and applied sciences. The role of electron delocalization, photoelectron elastic/inelastic scattering, and the mean free path of low-energy electrons in liquid water are of fundamental importance in elucidating the photoionization dynamics and radiation damage. Clusters serve as an useful bridge between the well-known gas phase and the complex condense phase. However, attosecond time-resolved measurements on clusters have not been reported yet. Here, we report the first experimental observation and theoretical interpretation of the photoionization dynamics in small, size-resolved water clusters [1] by using a new developed attosecond coincidence metrology [2].

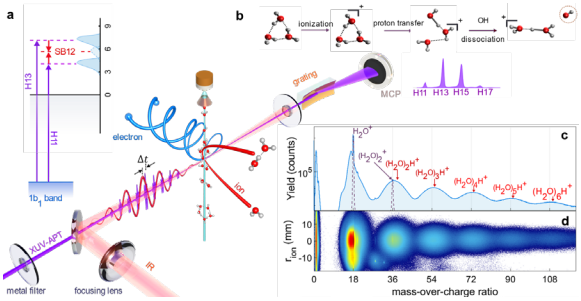

Fig. 1 Attosecond Size-resolved Cluster Spectroscopy. (**ASCS**)

Experimentally, we obtain a unique RABBIT trace for each measured water-cluster unit as presented in Fig.1(c) and 1(d). The sharp peak with a mass-over-charge ratio (MOC) of 18 is the H_2O^+ cation state generated via the photoionization of the H_2O monomer. The underlying broad distribution with the most probable value of MOC of 17 belongs to the dissociation pathway of H_2O^+. The progression of broad maxima at higher MOCs is assigned to protonated water clusters $(H_2O)_nH^+$, which mainly originate from the dissociative ionization of the next higher water clusters $(H2O)_{n+1}$. On this basis, it is possible to resolve water clusters with sizes up to n=6 in our data. The photoionization time delay increases as a function of the cluster size and saturated over pentamer and hexamer. We compare these experimental results to accurate ab-initio calculations of photoionization time delays using a recently developed scattering calculation method to extract the two-photon ionization time delay. Fig. 2 shows the measured and calculated photoionization time delay of SB12 of 1b1 electron from monomer to hexamer. A detailed analysis of the dependence of the time delays on the spatial extension of the ionized orbitals suggests that the observed increase in photoionization time delay is correlated with the increasing spatial extension of the electron hole created upon ionization.

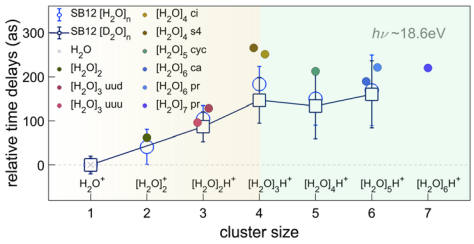

Fig. 2 Size-resolved photoionization time delays in water clusters

In summary, we have bridged the gas-to-liquid phase gap by realizing the first attosecond cluster spectroscopy on the prototype system of water clusters. A 120 as photoelectron emission time delay is observed between the pentamer and monomer in the sideband 12 of the HOMO. Our results demonstrate the novel ability to initiate and observe attosecond electronic dynamics in water clusters, which represents a crucial step forward in attosecond science and will help to progressively bridge the understanding gap between the gas and liquid phases. Furthermore, the angular resolved ability in our attosecond coincidence interferometer also helps us to move into the attosecond time resolved photoionization dynamics in molecular frame [3].

References

[1] X. Gong et al., submitted (2020).
[2] X. Gong et al., Phys. Rev. Lett. 118, 143203 (2017).
[3] X. Gong et al., submitted (2021).