Attosecond Dynamics of Hydrogen Migration in Ultrafast Intense Laser Fields

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In an ultrashort intense laser fields, molecules exhibit a variety of characteristic dynamics. Among our recent experimental findings, ultrafast migration processes of hydrogen atoms within a polyatomic molecule are noteworthy. The discovery of the ejection of triatomic hydrogen molecular ions, H_3^+, from CH_3OH was the beginning of the series of our studies on ultrafast hydrogen migration [1,2]. The H_3^+ synthesis in an intense laser field was, of course, a very interesting issue, and indeed, this H_3^+ formation was found to be a common phenomenon for hydrocarbon molecules having more than two hydrogen atoms. However, the finding having more significance was the formation of D_2H^+ from CD_3OH in an intense laser field, which indicated the existence of ultrafast hydrogen migration occurring prior to the formation of the triatomic hydrogen molecular ion.

By paying attention to the C-O bond breaking, the Coulomb explosion processes of doubly charged methanol, CH_3OH^{2+}, in an intense laser field were investigated by the coincidence momentum imaging method [3,4]. The angular distributions of the CH_3^+ and OH^+ pair, the CH_2^+ and H_2O^+ pair, and the CH^+ and H_3O^+ pair were found to exhibit almost the same extent of anisotropy, indicating that the three different precursor states; CH_3^+ --- OH^+, CH_2^+ --- H_2O^+, and CH^+ --- H_3O^+, are prepared when the interaction with an intense ($\sim 10^{14}$ W/cm^2) ultrashot laser pulse ceases, indicating that one or two hydrogen atoms move from the carbon site to the oxygen site within the laser pulse duration of ~60 fs. It was also confirmed that the hydrogen atom migration proceeds even when sub-10 fs laser pulses are employed.

These findings clearly show that hydrogen atoms move with the extremely fast speed whose magnitude is only 0.1 % of the velocity of light. This can be regarded as a conspicuous appearance of quantum mechanical nature of light-weighted hydrogen atoms. When we try to describe the separation between the carbon and oxygen atoms in methanol in the course of the bond breaking, we have to introduce a new-type description beyond the Born-Oppenheimer approximation. This is because the hydrogen atoms move rapidly around the C---O core and the adiabatic picture in which molecular electronic structure is calculated by fixing the positions of all the nuclei within a molecule could not be applied anymore.

A new theoretical treatment in which hydrogen atoms are described in terms of a many-body wave function spreading over the entire molecule similar to electrons needs to be developed. Indeed, it seems that the hydrogen atom wave function spreads very rapidly immediately after an ultrashort intense laser pulse starts interacting with a molecule. For probing this ultrafast spread, it will be necessary to introduce attosecond pulses whose pulse duration is below 1 fs. The ultrafast hydrogen migration is now guiding us to the new experimental frontiers of attosecond chemistry as well as to the new theoretical frontiers beyond the BO approximation.

References

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