Photoelectron-photoion coincidence momentum imaging of intense-laser induced dissociative ionization of polyatomic molecules

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When molecules are exposed to intense laser fields, photoelectron emission, electronic excitation and dissociation are induced. We investigate multichannel dissociative ionization of polyatomic molecules in intense laser fields using photoelectron-photoion coincidence momentum imaging with a Ti:Sapphire laser system. Fundamental wavelength (800 nm) and frequency-doubled wavelength (400 nm) are used in our study. Three-dimensional momenta of a photoelectron and an ion produced from the same molecule are measured in coincidence. Ethanol and methanol are adopted as sample molecules.

Energy correlation between a photoelectron and a fragment ion tells us how much internal energy is gained in the respective channels. Photoelectron spectra allow us to know the electronic states prepared at photoelectron emission. Kinetic energy distributions of fragment ions indicate how much internal energy is gained by cations just before dissociation. Correlation between them clarifies the pathway in photoelectron emission and subsequent photoexcitation [1-3]. When ethanol and methanol cations are formed in their electronic ground state at photoelectron emission, electronic excitation takes place subsequently for dissociation and causes the large internal energy. Subsequent electronic excitation becomes more decisive as the laser intensity increases to 23 TW/cm^2 at 783 nm and to 17 TW/cm^2 at 400 nm.

Angular correlation between the momentum vectors of a photoelectron and a fragment ion also enables us to gain an insight into electronic dynamics in ionization. In the case of ethanol in a linearly polarized NIR laser field with 23 TW/cm^2, photoelectrons are dominantly emitted along the laser polarization. The photoelectron angular distribution (PAD) is not influenced by the orientation direction of ethanol with respect to the laser polarization direction. In a circularly polarized laser field with 80 TW/cm^2, the PAD of CH_3CD_2OH in the recoil frame of the CD_2OH^+ channel exhibits a preference for photoelectron emission from the CH_3 moiety at the moment of photoelectron emission. Using the density functional theory, we calculate the ionization probability as a function of the orientation direction. The comparison between the experimental and theoretical recoil-frame PADs suggests that the inner valence 10a′ molecular orbital of ethanol is deformed by the laser field prior to photoelectron emission [4, 5].

References:

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