

Physics on photoemission from oriented molecules: past, present and future

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In conventional angle-resolved photoelectron spectroscopy of gaseous molecules, detailed information on photoionization dynamics is washed out by the freely tumbling molecules. A breakthrough of the situation occurred in the middle of 1990's due to the application of angle-resolved electron-ion coincidence techniques, which allows the selection of molecules with a well-defined spatial orientation from an ensemble of the randomly oriented molecules. Photoelectron angular distributions measured by such coincidence techniques are called molecular frame photoelectron angular distributions (MFPADs). Nowadays, the MFPAD measurements are growing in importance due to their sensitivity to photoionization dynamics combined with their avoidance of deleterious averaging over the molecular orientation.

For further extension of the MFPAD studies, it is noteworthy that the principle idea of the electron-ion coincidence measurements is reminded. Namely, the scenario of such measurements is as follows: In an axial recoil dissociation process, the two fragment ions fly off exactly anti-parallel to one another. If the dissociation is initiated by the ejection of a core-level photoelectron that is followed by the Auger decay, then the photoelectron is tied to the direction of the molecular axis at the moment of photoionization. Assuming that this whole process takes place on a timescale that is short compared with a rotational period, this means that the measurement of the recoil frame PAD is equivalent to the MFPAD referenced to the direction of the breaking bond. In this scenario, the fragment ion pair detection has two roles: one is to record the molecular axis, and the other is to select a *specific dissociation channel* after the Auger decay. Although the former is necessarily used in the MFPAD measurements, the latter is not deeply considered so far, except for several works. In this context, we consider the latter as well as the former to open a new era of *dissociation channel selected* MFPADs.

As a future subject, we propose a new scheme to realize a molecular movie with femtosecond time and Angstrom spatial resolution for small- to medium-sized gas-phase molecules, combining the best of the previously reported theoretical and experimental works. It relies on the availability of XFEL, velocity map imaging of photoelectrons, control of molecular alignment or orientation by strong electric fields of optical lasers and is based on the well-developed XPD scenario for surface structure analyses. We discuss the feasibility of imaging polyatomic molecular structures, i.e., measuring their geometric parameters such as bond lengths and bond angles on a femtosecond time scale using XFEL.