Partial Cross Sections of Methane from Photoemission Spectroscopy with Synchrotron Radiation

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We present partial cross section data of methane (CH_4), which serves as a prototype system to explore the capabilities of the Photoemission Orbital Tomography (POT) for molecules in gas phase. In POT, angular and photon energy-dependent photoemission measurements are used to characterize the electronic properties of ordered molecular monolayers on crystalline surfaces. Previous applications of POT have successfully quantified properties such as charge transfer, geometry, reaction intermediates, and orbitals of surface-absorbed molecules. Particularly impressive is the 2D and 3D reconstruction of molecular orbitals from momentum space measurements by a Fourier transformation, which follows from a simple plane wave assumption of the photoelectron's final state.

In this study, we extend the application of POT to the gas-phase environment focusing on CH_4, whose electron configuration $1a_{12}2a_{12}1t_{26}$ is analogous to that of atomic neon $1s^2 2s^2 1p^6$. In a previous study, we have reconstructed the radial orbital electron densities 1s, 2s and 2p of neon, by adapting the final state of the photoelectron to the central field symmetry of a free atom. Building on this success, we now aim to explore the possibilities of POT for simple molecules with also a rotational symmetry.

While partial cross section measurements with uncertainty contributions for single atoms are well-documented in the literature, the most recent data for partial cross sections of methane dates back to the 1970s. These measurements, obtained through electron coincidence techniques, provide limited or no information about the uncertainty contributions to the partial cross sections.

Here, we present the experimental determination of partial cross sections for CH_4 using photoelectron spectra (PES). The experimental setup involves monochromatized synchrotron radiation with a quantified photon flux. The PES for CH_4 were recorded in a photon energy range of 16.5 eV to 70 eV and capture the electronic states of CH_4, including the s-like orbital 2a1 and the p-like state 1t2, which are analogous to neon's 2s and 2p state. The inclusion of uncertainty contributions provides information about the reliability and accuracy of the experimental results. These uncertainties enhance the interpretation and applicability of the obtained data.

The results in this study represent a significant milestone in advancing our understanding of the photoemission processes in CH_4 and provide a solid foundation for future studies on gas-phase molecules. By bridging the gap between studies on single atoms and more complex molecular systems, our research aims to improve the description of the photoelectron's final state for the broader application in POT in general.