

in unaligned SF₆ molecules by an elliptically polarized infrared driving field. The observed fingerprints of the elliptically polarized harmonics include the first direct determination of the complete s_1 , s_2 , s_3 Stokes vector, equivalent to (ψ, ε, P) , the orientation and the signed ellipticity of the polarization ellipse, and the degree of polarization P . They are compared to so far incomplete results of XUV optical polarimetry. We finally discuss the comparison between the outcomes of photoionization and high harmonic spectroscopy for the description of molecular photodynamics.

1. Introduction

Photoionization (PI) is one of the basic processes that allows direct investigation of molecular structure and dynamics; therefore it is often used as a probe of the relaxation of transient excited molecular states involved in gas-phase photochemical dynamics. Resulting from the intimate anisotropic interaction between the light field and a molecule, molecular frame photoelectron angular distributions (MFPADs) are the most sensitive observables of the electronic/nuclear photodynamics induced by photoionization, and they simultaneously encode the polarization state of the ionizing light. Consequently, the determination of MFPADs gives access to the complex dipole matrix elements describing the photoionization transition, as well as to the three normalized Stokes parameters s_1 , s_2 , s_3 (ref. 1) characterizing the complete polarization state of the ionizing light. In particular, the ability to derive s_3 , whose sign reflects the light helicity, is a result of the circular dichroism in the molecular frame, *i.e.*, the difference in photoemission when the molecule is exposed to left- or right-handed circularly polarized light. In this work we discuss two ways that the MFPADs can be combined with the use of ultrafast XUV/VUV pulses to contribute to the tool box of ultrafast imaging of photochemical dynamics.

MFPADs can be accessed using different techniques,^{2,3} such as photoelectron spectroscopy (PES) applied to rotationally resolved excited molecules or to laser-aligned and oriented molecules, or electron-ion coincidence momentum spectroscopy. In the work presented here we use the latter approach, taking advantage of dissociative photoionization (DPI) of small molecules induced by XUV radiation to determine fully differential MFPADs. On the one hand, this method has provided a wealth of results on the photoionization dynamics following inner-valence shell^{4–6} or inner-shell^{7–10} ionization of linear molecules or small polyatomic systems most often induced by synchrotron radiation, whose high repetition rate is appropriate for coincidence measurements, *i.e.*, in the weak field regime. On the other hand, the use of MFPADs as a probe of the complete polarization state of ionizing light, known as molecular polarimetry (MP),¹¹ has been benchmarked recently by comparing data relying on coincident electron-ion 3D momentum spectroscopy and on VUV optical polarimetry¹² available on the DESIRS beamline (SOLEIL) which delivers fully controlled VUV elliptically polarized light.¹³ This development is part of the substantial effort performed, in particular in the XUV and X-ray domains at large scale facilities such as synchrotrons^{12,14} and free electron lasers,^{15,16} to characterize and control the polarization state of the light source, a key parameter for numerous experiments addressing fundamental topics such as chiral properties of matter,^{17,18} ranging from biomolecules to magnetic materials. To our knowledge, with the use of