New Journal of Physics
The open access journal at the forefront of physics

Deutsche Physikalische Gesellschaft DPG
IOP Institute of Physics

Published in partnership with: Deutsche Physikalische Gesellschaft and the Institute of Physics

OPEN ACCESS

RECEIVED
18 July 2016

REVISED
24 August 2016

ACCEPTED FOR PUBLICATION
19 September 2016

PUBLISHED
12 October 2016

FAST TRACK COMMUNICATION

Universality of photoelectron circular dichroism in the photoionization of chiral molecules

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Keywords: photoelectron circular dichroism, chirality, strong fields, multiphoton ionization

Abstract

Photoionization of chiral molecules by circularly polarized radiation gives rise to a strong forward/backward asymmetry in the photoelectron angular distribution, referred to as photoelectron circular dichroism (PECD). Here we show that PECD is a universal effect that reveals the inherent chirality of the target in all ionization regimes: single photon, multiphoton, above-threshold and tunnel ionization. These different regimes provide complementary spectroscopic information at electronic and vibrational levels. The universality of the PECD can be understood in terms of a classical picture of the ionizing process, in which electron scattering on the chiral potential under the influence of a circularly polarized electric field results in a strong forward/backward asymmetry.

1. Introduction

Chiral molecules exist as two forms—enantiomers—which are mirror images of each other but are non superimposable. The two forms can be labeled (+) and (−), and can only be distinguished through their interaction with another chiral object. For instance, circularly polarized light gives rise to many fascinating enantiospecific phenomena, referred to as chiroptical processes [1]. However most of them are forbidden within the electric dipole approximation, involving magnetic dipole or electric quadrupole effects which are extremely weak [1]. As a purely dipolar effect [2], photoelectron circular dichroism (PECD) is the exception to this rule.

PECD was predicted in 1976 [2], and observed experimentally in 2001 in single-photon ionization by extreme ultraviolet (XUV) radiation [3]. It consists of a strong (up to 20%–30%) forward/backward asymmetry in the angular distribution of electrons ionized from *randomly oriented* chiral molecules by circularly polarized light. Many studies of PECD using synchrotron radiation have shown its high sensitivity to electronic structure [4], vibrational excitation [5] and conformation [6, 7]. PECD has also been recently demonstrated in photoionization by ultrashort high-harmonics, opening the way to time-resolved studies [8].

The extension of PECD to the multiphoton ionization regime was demonstrated in 2012. Lux *et al* [9] measured a ∼15% PECD in (2 + 1) resonance-enhanced multiphoton ionization (REMPI) of fenchone and camphor where two photon absorption brings the molecule into an electronic excited state while the third photon ionizes the system. Since this pioneering experiment, REMPI-PECD has been measured in other compounds, in (2 + 1) [10–12] and (3 + 1) [13] configurations. Recently, Lux *et al* observed PECD in the first above threshold ionization (ATI) peak in a (2 + 2) scheme [14]. The role of the resonance in REMPI-PECD has however not yet been clearly studied. On one hand, resonances are known to play a determinant role in the ionization of chiral compounds by circular radiation, since they can lead to strong asymmetries in the total ionization yield beyond the dipolar approximation [15]. On the other hand, PECD was predicted to exist in dipolar MPI without any resonance [16], but with an opposite sign compared to experiments, which may be the signature of the resonance.