



PERSPECTIVE

Photoelectron circular dichroism in different ionization regimes

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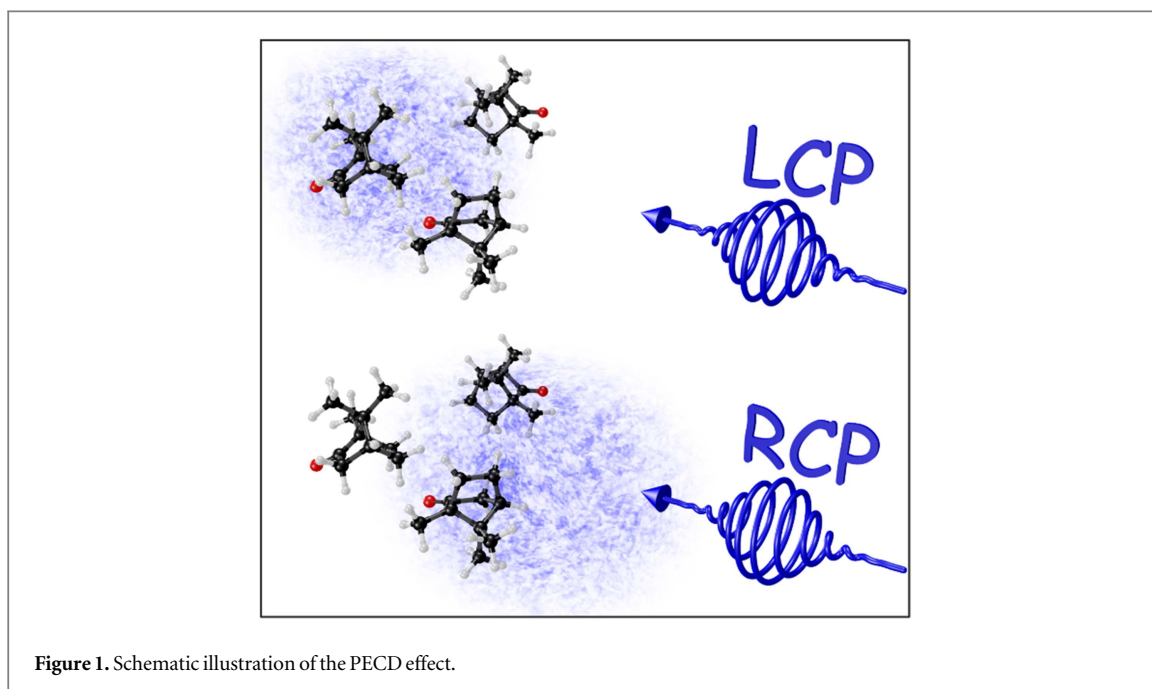
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Keywords: chirality, multiphoton ionization, circular dichroism, femtosecond, photoelectron spectroscopy**Abstract**

Photoelectron circular dichroism (PECD) describes an asymmetry in the photoelectron angular distribution (PAD) from photoionization of randomly oriented enantiomers with circularly polarized light. Baulieu *et al* present a comprehensive set of measured PADs from multiphoton ionization of limonene and fenchone in different ionization regimes (multiphoton and tunneling) and analyze the resulting PECD (Baulieu *et al* 2016 *New J. Phys.* **18** 102002). From their observations the authors conclude that the PECD is universal in the sense that the molecular chirality is encoded in the PAD independent of the ionization regime. The analysis is supplemented by a classical model based on electron scattering in a chiral potential. The paper presents beautiful data and is an important step towards a more complete physical picture of PECD. The results and their interpretation stimulate the ongoing vivid debate on the role of resonances in multiphoton PECD.

Our hands are mirror images of one another and presumably the most familiar example for chiral objects. As suggested by the word chiral—derived from $\chi\epsilon\iota\rho$, the Greek word for ‘hand’—a chiral three-dimensional object cannot be mapped to its mirror image by three-dimensional rotation and translation alone. In 1894 Lord Kelvin introduced the term chirality by defining ‘I call any geometrical figure, or group of points, ‘chiral’, and say that it has chirality if its image in a plane mirror [...] cannot be brought to coincide with itself [1]. Likewise, a molecule is called chiral if the spatial configuration of its atoms is not superimposable on its mirror image. In physical chemistry, chiral molecules and their corresponding mirror images are called enantiomers. Chiral molecules play an important role in all natural sciences [2]. One of the major unresolved questions in biology is the origin of homochirality of bio-molecules such as amino acids on earth. In pharmaceuticals chirality is a central issue because more than half of the drugs currently in use are chiral compounds with marked differences in their biological activities. Also in modern chemistry enantio-selective synthesis is one of the key processes. Physicists study the properties of chiral molecules for both fundamental and applied purposes. In applied physics, various chiroptical processes are routinely measured to characterize chiral molecules, however, the quantum physics of chiral molecules has been puzzling scientists for almost 90 years. Shortly after the discovery of quantum physics, Friedrich Hund noticed that the existence of enantiomers is hard to explain from first quantum physical principles [3]. Hund investigated why chiral molecules are found either in their left-handed or in their right-handed configuration rather than in a superposition of these chiral states. He explained ‘the paradox of the optical isomers’ by long tunneling times from one chiral configuration to the other. Later, even fundamental parity violations have been discussed in the context of molecular enantiomers [4]. More recently, employing the concept of environmental decoherence, Trost and Hornberger have studied collisional stabilization of chiral molecules [5] to unravel Hund’s venerable paradox. In essence, this approach takes into account the loss of quantum coherence due to external interactions such as collisions with surrounding gas particles. In this picture, the colliding particles ‘knock the molecule into a chiral state and keep it there before it has a chance to tunnel out to its mirror image’ [6].

Asymmetries in the interaction of polarized light with chiral molecules have been studied extensively since Pasteur’s pioneering experiments on the optical activity of sodium ammonium tartrate. The photoelectron circular dichroism (PECD) is an example of an asymmetry in the ionization of chiral molecules with light. As illustrated in figure 1, PECD describes a forward / backward asymmetry in the photoelectron angular



distribution (PAD) in the light propagation direction arising from photoionization of randomly oriented chiral molecular enantiomers with circularly polarized light [7]. The PECD is a rather remarkable physical effect—qualitatively, because the above mentioned asymmetries are observed *in spite of the random orientation* of the molecules, and quantitatively, because the magnitude of the asymmetries associated with the PECD are several orders of magnitude larger than those typically measured in conventional optical circular dichroism experiments [7].

PECD was predicted theoretically 40 years ago [8], and observed not until 25 years later experimentally in one-photon ionization of bromocamphor enantiomers by synchrotron radiation [9]. Since then, the influence of the molecular properties such as electronic structure and vibrational excitation have been studied extensively in numerous experiments using synchrotron radiation as reviewed for example in [7]. Nowadays, PECD studies have gained momentum due to the availability of ultrafast laser light sources for ionization. For instance, circularly polarized UV femtosecond pulses have been used to demonstrate multiphoton PECD (MP-PECD) of the chiral prototype molecules camphor and fenchone [10]. In addition, femtosecond MP-PECD was observed in the above threshold ionization (ATI) [11] and used as a tool to accurately determine the enantiomeric excess [12]. In order to investigate circular dichroism in one-photon ionization with ultrashort laser pulses circularly polarized high harmonic XUV radiation has been used [13]. Using different light sources ranging from the extreme ultraviolet to the mid-infrared, the PECD of fenchone has been investigated in different ionization regimes [14].

Despite the numerous experimental studies of PECD, details of the physical mechanism are still debated. In particular, the roles of the initial state, the intermediate resonances and the final continuum states are subjects of discussion. For instance, a very pronounced dependence on the initial state, from which ionization occurs, was observed for valence ionization of fenchone [15]. For resonance enhanced multi photon ionization (REMPI) it seems likely that intermediate resonances strongly affect the PECD. Evidence for the importance of resonances in multiphoton ionization was found in a theoretical study [16]. The crucial role of the continuum was emphasized in the same publication and is supported by experiments on inner shell ionization of camphor molecules [17]. In this article it was concluded that ‘since the initial state is an atomic-like spherically symmetric orbital, this strongly suggests that the asymmetry is caused by final-state effects’. The paper by Baulieu *et al* on ‘Universality of photoelectron circular dichroism in the photoionization of chiral molecules’ sheds light on the physical mechanism involved in PECD. Baulieu *et al* present an extensive experimental study on the PADs of limonene and fenchone in different ionization regimes. In particular, using a velocity map imaging spectrometer, photoelectron momentum distributions are measured in the multiphoton regime for threshold and ATI photoelectrons and in the tunnel ionization regime. From the results Baulieu *et al* conclude that molecular chirality is encoded in the PAD *independent of the ionization regime* (from one-photon to tunnel ionization). This conclusion is supplemented by a classical picture of the ionizing process in which the PECD is described as electron scattering by a chiral potential under the influence of a circularly polarized electric field.

Baulieu *et al* start by studying three-photon PADs of limonene molecules at different ionization photon energies around 3 eV (400 nm). In order to quantify the PECD, the normalized Legendre coefficients are analyzed as a function of the photoelectron kinetic energy. It is already visible in the data that the even part of the PAD changes significantly upon variation of the photon energy whereas the PECD seems to be insensitive to changes of the excitation wavelength. From these observations it is concluded that the PECD is not sensitive to the electronic character of the intermediate resonance. However, the authors point out that ‘further investigations on different systems are required to determine whether limonene is an exceptional case or if this is a general trend of REMPI-PECD’. By increasing the laser intensity Baulieu *et al* demonstrate PECD in the high-order ATI of fenchone enantiomers. Evaluation of the MP-PECD [18, 19] for two intensities differing by an order of magnitude as a function of the photoelectron kinetic energy showed—amongst other findings—that the PECD diminishes for increasing laser intensity. This observation is rationalized by the stronger influence of the laser field on the electron dynamics as compared to that of the chiral molecular potential. Finally, by changing the ionization wavelength to 1850 nm (0.67 eV) Baulieu *et al* were able to investigate the PECD of fenchone in the genuine tunneling regime at a Keldish parameter of $\gamma = 0.6$. Although the PADs change dramatically from the multiphoton to the tunneling regime, the PECD persists, albeit at a lower 1%–2% level. Again, this result is regarded a confirmation of the universal character of the PECD that reveals the chirality of the target.

Overall, this study presents a comprehensive set of PADs from chiral molecules for different excitation conditions. By variation of the laser intensity and wavelength the MP-PECD was studied in different ionization regimes. The use of tunable UV radiation allowed Baulieu *et al* to investigate the role of resonances in MP-PECD. Their contribution is an important step towards a more complete physical picture of PECD. It remains to be investigated to what extent these results can be generalized to other chiral systems. In any case, the findings underscore the need for further studies on the dependence of the Legendre coefficients on the number of absorbed photons and their energy, the laser intensity and the pulse shape. The paper highlights that the use of ultrafast light sources has opened a rich field for fundamental research on chiral molecules. Further studies on chiral molecules will include advanced detection such as electron-ion coincidence imaging [20, 21] and direct mapping of the three-dimensional PECD distribution by tomographic reconstruction [19]. More detailed information on the ionization dynamics will be obtained by refined multicolor ionization schemes such as bichromatic fields, ultra-broadband and attosecond laser pulses. Eventually it will be interesting to see coherent control of the electron dynamics in chiral molecules by shaped femtosecond laser pulses in order to manipulate the magnitude of the PECD.

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