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# Electron asymmetries in the photoionization of chiral molecules: possible astrophysical implications

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## ABSTRACT

Photoelectron circular dichroism (PECD) is an intense orbital-specific chiroptical effect observed as asymmetries in the angular distribution of photoelectrons produced by photoionization of randomly oriented pure enantiomers with circularly polarized light. After a broad introduction placing this effect in the context of new physical chiral-sensitive methods, we review the main characteristics of PECD in terms of molecular photoionization dynamics. We stress also the analytical capabilities of PECD to retrieve enantiomeric excesses (e.es.) and to probe subtle details of the whole molecular potential, some of them exemplified by the showcase camphor and fenchone molecules. We then present the case of the amino acid alanine for which an interplay between PECD and conformer population is rationalized. Based on this study, we propose a photophysical astrophysical scenario for the origin of life's homochirality, relying upon the asymmetry of the associated recoiling alanine parent ion that could lead at the relevant Lyman- $\alpha$  energy to an e.e. of up to 4% in a given line of sight, which appears independent of the temperature. In an attempt to generalize this scenario to other amino acids, new data on proline showing an e.e. of 12%, of the same sign as alanine, are also presented.

**Abbreviations** ARPES: Angle-resolved photoemission; CMS-Xa: Continuum multiple scattering with Xa local-exchange potential; CPL: Circularly polarized light; CD: Circular dichroism; CSM: Circumstellar medium; DPI: Dissociative ionization; HHG: High harmonics generation; HOMO: Highest occupied molecular orbital; ISM: Interstellar medium; KE: Kinetic energy; MS: Mass spectrometry; MW: Microwave; PAD: Photoelectron angular distribution; PECD: Photoelectron circular dichroism; PECD-PICO: Photoelectron circular dichroism / photoion coincidence; PEPICO: Photoelectron / photoion coincidence; PES: Photoelectron spectrum; PV: Parity Violation; REMPI: Resonance-enhanced multi-photon ionization; RH: Resistive heating; TD: Thermodesorption; UV:

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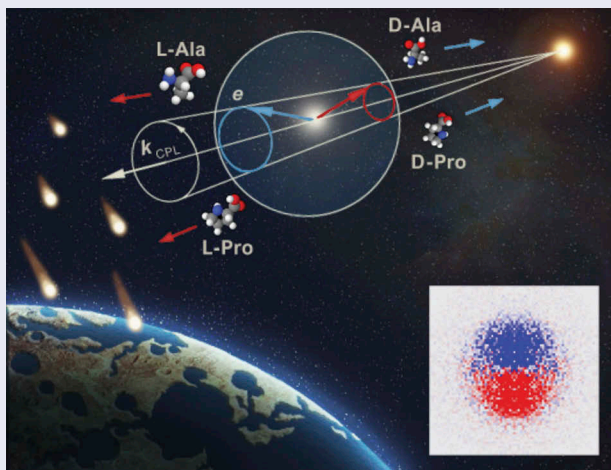
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Ultra-violet; VMI: Velocity map imaging; VUV: Vacuum ultra-violet.



## 1. Introduction

Chirality, the property for an object not to be superimposable onto its mirror image as defined by Lord Kelvin in 1904, is ubiquitous in science (mathematics, particles physics, or nanoscience, for instance) and around us, in nature, at the macroscopic level: snail shells, fluid swirls, some mineral surfaces, etc. At the molecular level, chirality is a major 3D structural property of considerable importance in chemistry and life sciences. In particular, elementary bricks of life such as amino acids, the building blocks of proteins, and sugars of nucleic acids are chiral species. Furthermore, these biomolecules are found as homochiral species in the biosphere [1], and their handedness imposes that of the corresponding biopolymers such as protein alpha helixes and DNA.

The two nonsuperimposable enantiomers of a given chiral system possess the same physicochemical properties, except for tiny energy differences between enantiomers due to parity violation (PV) in the weak interaction [2,3], but will exhibit their ‘chiral’ behavior when they are themselves embedded into a chiral medium. This medium can be constituted by other chiral molecules leading to the so-called chiral recognition process [4], which is a central mechanism involved in metabolism, including odor perception and drug action. In the gas phase, where fundamental molecular processes can be studied in a solvent- and substrate-free environment, and on which we will focus from now, chiral recognition, also described as a pure ‘molecular handshake’, is used to probe the chirality of a given molecule by another chiral system leading to

the formation of homo- and hetero-chiral complexes, the structure of which may be deciphered and unraveled by UV-REMPI (resonance-enhanced multiphoton ionization) techniques [5] or by absorption in the micro-waves (MW) via the emerging chiral tagging method [6].

In physics, a chiral medium may be provided by the true chiral nature of circularly polarized light (CPL) [7], leading to various chiral recognition processes between a 'chiral photon' and a chiral molecule. A typical example is the well-established circular dichroism (CD) in absorption [8]. Because of symmetry considerations, CD in absorption, an integral probe, is forbidden in the electric dipole approximation and therefore relies on weaker terms in the expansion of the light-matter interaction Hamiltonian, such as  $E1.M1$ , leading to small relative CD signals, typically in the  $10^{-3}$  to  $10^{-5}$  range. CD, and its related counterpart phenomenon optical rotation, is however a very useful structural probe, widely used in biochemistry [9] but, except for a few studies performed via cavity-ring down polarimetry [10,11], mainly restricted to the liquid phase, because of its poor sensitivity. Recent extensions to gas-phase samples have been performed with the background-free-related technique of total ion yield associated with a REMPI excitation process [12–15], which in some cases allows the retrieval of conformer-specific CD [16,17]. All these approaches provide 2D information (CD vs photon energy).

Other enantio-sensitive methods on dilute targets have been recently proposed making this field very lively nowadays [18], including high harmonic generation (HHG) from a chiral gaseous medium [19]. It is worth mentioning recent experiments on the Coulomb explosion induced by either laser [20,21], synchrotron radiation [22], or beam foil [23], which allowed direct imaging and deciphering of the absolute configuration of a racemic (50% left/50% right) mixture of a chiral species in the gas phase for the first time. New innovative and very sensitive chiroptical spectroscopic methods based on non-coplanar bound-bound transition dipoles in the MW by three wave-mixing [24,25] and in the UV by use of CPL fs-pulses creating a coherent helical motion of bound electrons [26] appear very promising especially for their potential ability to separate enantiomers [27], which is still a challenge in stereochemistry and asymmetric catalysis.

Another chiroptical effect, called photoelectron circular dichroism (PECD), and the main subject of this review, is based upon photoionization, i.e. bound-continuum transitions, such that the chiral information is encoded into the scattering off by a chiral molecular potential of the outgoing photoelectron. More precisely, PECD manifests itself by a forward/backward asymmetry (with respect to the photon propagation axis) in the photoelectron angular distribution (PAD), resulting from the CPL ionization of randomly oriented pure enantiomers. PECD was predicted by Ritchie decades ago [28], but was the object of dedicated calculations on

actual molecular systems only in 2000 by Powis [29,30]. Since its first experimental evidence by one-photon ionization [31,32] and multiphoton ionization [33], PECD has been the subject of a large array of experimental and theoretical work showing that PECD is an intense, orbital-specific, continuum sensitive chiroptical effect, providing rich 3D data (PECD vs photon energy and vs Kinetic Energy) of high physical and analytical relevance, i.e. a priori much richer than conventional CD (for recent reviews, see [34] and [35]). Besides, unlike CD, mostly used in the condensed phase, the intensity of PECD allows the study of dilute compounds in the gas phase. This provides a solvent- and substrate-free medium to template fundamental chiral processes on isolated molecules, and in some cases in a controlled manner when associated with molecular beams, offering the opportunity to study chiral complexes and clusters. Finally, unlike bound-bound transition, photoionization is a universal probe that does not suffer from any selection rules, nor does it need any chromophore, which permits the use of sensitive, background-free technique such as Photoelectron Spectroscopy (PES), sometimes associated in coincidence with mass spectrometry (MS).

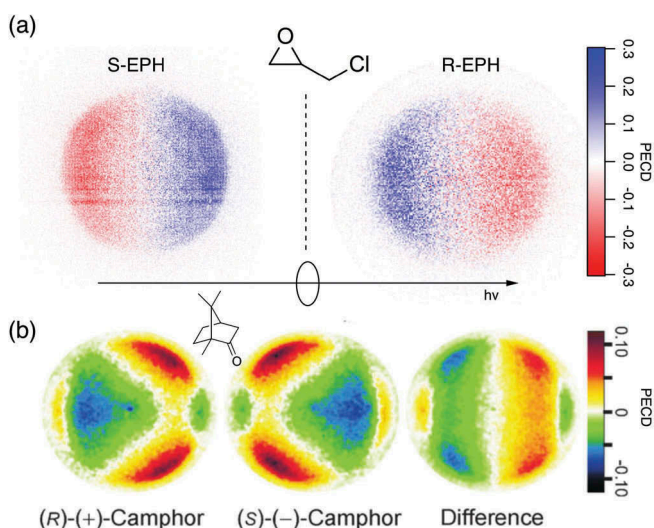
PECD on randomly oriented chiral species should not be confused with circular dichroism in the angular distribution as observed in molecular frame-PADs from fixed-in-space achiral species [36,37]. This effect, unlike PECD, leads to electron asymmetries in the plane perpendicular to the photon axis. However, it is worth to mention that a recent study showed the interplay between the two effects, i.e. between intrinsic chirality and the extrinsic chirality provided by a chiral experimental arrangement [38].

In the next section, we will expand on the presentation of PECD, provide some experimental details, and illustrate one-photon VUV-PECD showcasing the camphor and fenchone molecules. Then in the last section, we will present the case of PECD on amino acids, alanine in particular, showing how PECD could have a link with the origin of life's homochirality, a cornerstone in astrobiology, directly connected to the origin of life itself.

## **2. Overview on PECD: case of fenchone and camphor**

### **2.1 Formalism and properties**

As opposed to the widely known and commonly used CD in absorption, which is an integral effect that necessitates non-orthogonal electric and magnetic dipole transitions (such as E1.M1), PECD is a differential effect that relies on electric dipole transitions alone and is therefore fully developed within the electric dipole approximation [30,39]. In this context, the



**Figure 1.** Antisymmetric properties of PECD.

Notes: Difference raw electron images for the two different enantiomers measured on (a) epichlorohydrin in the one-photon ionization case at  $h\nu = 11.0$  eV, and (b) camphor in the 3-photon ( $2 + 1$ ) ionization case. For (b), the extra step of subtracting the enantiomers (third column) is needed to remove the asymmetric artifacts seen in the individual enantiomers. (b) Reproduced from [33], with permission.

normalized photoelectron angular distribution is given by the simple expression [40]:

$$I^{\{m_p\}}(\theta) = 1 + \sum_{l=1}^{l=2N} b_l^{\{m_p\}} P_l(\cos\theta) \quad (1)$$

where  $N$  is the number of absorbed photons,  $P_l(\cos\theta)$  are the Legendre polynomials of order  $l$  with their respective angular parameters  $b_b$  and  $m_p$  describes the polarization state of the light (0 for linear polarization, +1 for left and -1 right circular polarization). The polar angle  $\theta$  is measured with respect to the propagation direction of the light. Symmetry considerations provide the following restrictions to the odd angular parameters:  $b_{l=\text{odd}}^{\{m_p\}} = 0$  if the target is not chiral or if  $m_p = 0$ ; and  $b_{l=\text{odd}}^{(+1)} = -b_{l=\text{odd}}^{(-1)}$ . Also note that  $b_2^{(\pm 1)} = -\frac{1}{2}b_2^{(0)}$ , where  $b_2^{(0)}$  is commonly known as  $\beta$ , or anisotropy parameter. Apart from changing sign when switching the light helicity, the odd terms will change sign if the mirror molecule (opposite enantiomer) is ionized (see Figure 1 (a)). The above properties lead to an equivalent Photoelectron CD (PECD) obtained, for a given enantiomer, as the difference between the angular distributions recorded with left and right CPL, normalized over the average signal:

$$\text{PECD} = I^{\{+1\}}(\theta) - I^{\{-1\}}(\theta) = 2 \sum_{l=\text{odd}} b_l^{\{+1\}} P_l(\cos\theta) \quad (2)$$

In the particular, and so far most commonly studied case of one-photon PECD, the above equation simplifies to  $\text{PECD} = 2b_1^{(+1)}\cos\theta$ , and the PECD is conveniently given as the forward/backward ( $\theta = 0^\circ, 180^\circ$ ) difference,  $2b_1$ , corresponding to the maximum asymmetry (expressed in %). In the multiphoton case, on the other hand, the direction that maximizes the PECD depends on the final linear combination of odd Legendre polynomials (see [Figure 1\(b\)](#)). Therefore, an alternative definition has been described as the difference between the forward and backward integrated asymmetries, normalized by the average signal per hemisphere [41,42]:

$$\text{MP - PECD} = 2b_1^{\{+1\}} - \frac{1}{2}b_3^{\{+1\}} + \frac{1}{4}b_5^{\{+1\}} - \frac{5}{32}b_7^{\{+1\}} + \frac{7}{64}b_9^{\{+1\}} + \dots \quad (3)$$

Note that because multiphoton PECD is now a sum of various terms that can have opposite signs, some works quote a quadratic PECD to avoid cancellation effects and have a better measure of the overall chiral effect [43].

From the first valence-shell calculations [29,30] and experimental measurements [31] of PECD for a one-photon direct ionization process, it became evident that PECD was orders of magnitude larger than absorption CD, and nowadays measured experimental asymmetries of up to 32% of the mean signal have been recorded [44]. Another very interesting feature is the fact that the dichroic chiral parameter ( $b_1$ ) was strongly dependent on the ionized orbital (initial state), as well as on the kinetic energy of the outgoing photoelectron (final state). The chirality of the initial orbital, however, is not a necessary requirement to observe PECD as demonstrated in the core-shell ionization of the spherical C(1s) and O(1s) orbitals [45–51], where only the photoelectron scattering process by a chiral potential can be responsible for the appearance of an asymmetry. Other dynamical effects affecting  $b_1$  have been described in the case of continuum resonances, such as shape [29,52,53] or autoionization resonances [54].

Furthermore, it was rapidly established by comparing the first measurements on the valence shell of bromo-camphor [31] and camphor [32,55], where marked differences in PECD were observed between both isomers, that the dichroic chiral parameter ( $b_1$ ) was also distinctly tied to the molecular structure, a fact already predicted theoretically on the different conformers of glyceraldehyde [30] and alanine [29]. Further experiments have shown that this sensitivity to molecular structures is more pronounced for slow photoelectrons, i.e. having kinetic energies in the first few eVs, and in all cases below  $\sim 10$  eV [56–58]. This is especially the case of supramolecular assemblies, for which PECD appears to be a long-range



probe of the overall potential, as revealed by its high sensitivity to clustering [56,59,60].

The marked structural dependence also yields interesting dynamical effects, in which the PECD is dramatically affected by the nuclear motion. This breakdown in the Franck–Condon approximation leads to forward/backward asymmetries depending on the cation final vibrational state, including in some cases a reversal of the asymmetry's sign [61–65].

The theoretical description and quantitative calculations of PECD have been critical in advancing our understanding of this effect. For one-photon ionization, two methods have been routinely used: continuum multiple scattering with an X $\alpha$  local-exchange potential (CMS-X $\alpha$ ) [66], and B-spline linear combination atomic orbital density functional theory [67]. Both methods have had comparable success in reproducing the experimental data and agree well with each other especially for core-shell PECD, while there are some divergences for valence-shell ionization, where the influence of the initial electronic structure surfaces [52]. In addition to these popular multicenter approaches, a single-center method [68] has been recently applied to core-shell PECD with excellent results [51].

The high sensitivity of the chiral parameter to the molecular potential can be traced to the partial waves interference pattern associated with the outgoing photoelectron. Indeed, it has been shown that  $b_1$  depends on the sinus of the phase between two adjacent partial waves [48,69,70], while  $b_2$  depends on the cosine of the phases between every other waves, and  $b_0$  has no phase dependence. The enhanced sensitivity to subtle changes in the partial wave composition, and therefore to the molecular potential throughout the scattering process, with respect to the even terms has been demonstrated in various theoretical [45,49,63,71–73] and experimental works [56]. However, and somewhat ironically, it is this property that presents a computational challenge, so that quantitative agreement is difficult to achieve in the valence-shell region which in turn reduces the amount of structural information that can be obtained by comparing experiments and theory. The experimental region that is expected to provide the most detailed structural information, low kinetic energy photoelectrons, are the ones that are most difficult to model, and both the CMS-X $\alpha$  and B-spline methods have had mixed success [52,57,58]. The quantitative agreement, however, is improved for faster photoelectrons ( $h\nu > 6$  eV) so that absolute configurations can be regularly retrieved [34,35], even in the case of floppy molecules [72,74], by comparing the calculated and experimental sign of the asymmetry as is the case with reference CD/OR methods [75,76].

Moreover, theory has been able to rationalize conformer populations from experimental PECD data [35,44,65,71,72,74,77–80]. Again, although the agreement is enough to confirm expectations, quantitative conformer



populations cannot be accurately derived due to theoretical limitations in the modeling of the electronic and molecular structure, and the current lack of experimental data on conformer-selected PECD that would help benchmarking current theoretical methods. Despite these shortcomings, interesting conformational information can still be obtained, such as the interplay observed between conformational and configurational enantiomerism in 1,3-butanediol, where two quasi-isoenergetic conformers coexist as near enantiomers but possess equal absolute configuration [73].

Another example where our understanding of PECD has advanced with only qualitative theoretical trends involves its vibrational dependence. Here, a full model on the experimentally studied systems is not yet feasible due to the amount of vibrational degrees of freedom, but its origin and general trends have been established through the use of a simple model such as  $\text{H}_2\text{O}_2$  [63].

All of the general properties outlined above can be directly applied to the more recent but active field of laser-based multiphoton PECD, or MP-PECD, except here the intermediate state is added to the initial and final states to affect the final asymmetry observed, which is now expressed as a linear combination of odd Legendre polynomials, as expressed in Equation (3). As with the case of one-photon ionization, the first experiments were performed in model systems such as bicyclic ketones like camphor, fenchone, and norcamphor [33,41,43] via a 2 (CPL)+ 1(CPL) REMPI at 398–400 nm going through either 3s or 3p Rydberg intermediate states, and comparable forward/backward asymmetry intensity with respect to the one-photon case was obtained. The presence and chiral antisymmetry of the higher order odd Legendre coefficients was also confirmed. Subsequent works have focused on the effect of the intermediate state. Fanood et al. [81] reported that although one would expect the nature of the intermediate resonance to affect the value of the PECD, in the case of limonene, the PECD was surprisingly insensitive to the pump laser wavelength, a fact also corroborated by Beaulieu et al. on the same target [82]. Kastner et al. however have measured the 2 + 1 REMPI MP-PECD on fenchone and reported distinct differences between the three possible Rydberg intermediate states, and between one-photon PECD for the same electron kinetic energy [83].

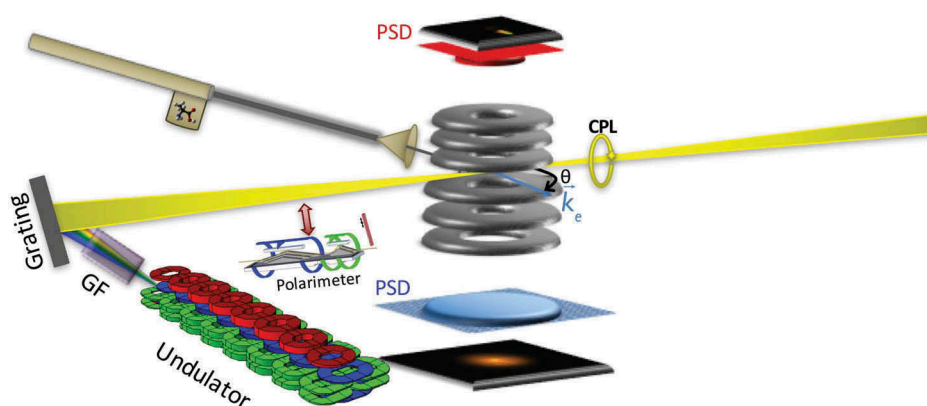
Extensions to other photon/matter interaction schemes such as above threshold ionization [82,84,85] and high-field tunneling ionization [82,85] have shown the universality of PECD for all photonic regimes.

Time-resolved PECD using femtosecond multiphoton ionization offers the possibility of using  $b_{l=\text{odd}}$  as very sensitive supplementary observables to probe molecular processes involved in femtochemistry, and has been recently achieved in fenchone with a 1(linear polarization)+ 1'(CPL) REMPI scheme, going through the 3s Rydberg intermediate states [86].

In this pioneering experiment, PECD was used as a probe of the dynamics of the initial electronic wavepacket created in the 3s state. Two different relaxation behaviors were observed in the  $b_1$  and  $b_3$  terms, with the former being related to vibrational relaxation dynamics on a sub-ps timescale, confirming the sensitivity to the intermediate state reported by Kastner et al. [83], and the latter dominated by a depolarization effect due to molecular rotation. In terms of electron dynamics, the PECD forward/backward asymmetries have been recently associated with tiny differences in the Wigner time (photoemission duration), below 10 as, between the forward and backward electron emissions [87].

Theoretically, CMS-X $\alpha$  calculations have been applied to interpret MP-PECD experiments with qualitative results [41,42], while other methods are being developed to match the pace of recent experimental breakthroughs [26,88,89]. Note that recent advances in high harmonic generation now allow for table-top laser-based one-photon PECD experiments that would remove the contribution from intermediate states, greatly simplifying the data interpretation and theoretical treatment while keeping the advantages of a table-top fs system, as demonstrated in fenchone [90].

Finally, the sensitivity to the molecular potential and the large asymmetry values measured in both one-photon and multiphoton schemes render PECD a useful analytical tool to determine enantiomeric excesses (e.es.), i.e. the degree of enantio-purity of a given chemical substance. This is a grand challenge in the broad field of chirality, and probably one of the driving forces of the development of MP-PECD, with major fundamental and applied implications (for instance in asymmetric synthesis and catalysis), where gas-phase measurements offer the possibility to provide direct *in situ* measurements, as demonstrated by MW 3-wave mixing [25,91] and more recently by chiral tagging associated with rotational spectroscopy [6]. Indeed, the sign and amplitude of the odd terms driving the PECD can be used to determine e.es. if these terms are known for the enantiopure samples, as shown by several groups in the one-photon [58] and multiphoton regimes [92,93], where e.es. have been derived with a precision down to 1%. Even more interesting from the analytical point of view is the combination of angle-resolved photoemission (ARPES) with ion mass spectrometry or full momentum imaging. In the past years, single- and double-imaging coincidence techniques have been used to determine the composition of complex media, such as flames [94–96], smog chambers [97], or planetary aerosols [98], by mass-selected multiplex photoelectron spectroscopy to determine the isomeric composition of a given compound having a signature in the mass spectrum. One could easily add the PECD information so that, apart from the structure, e.es. could be given for chiral mixtures, as demonstrated by Fanoood et al. [99] on a prepared chiral mixture of limonene and camphor. Such a technique, PECD-PICO, can



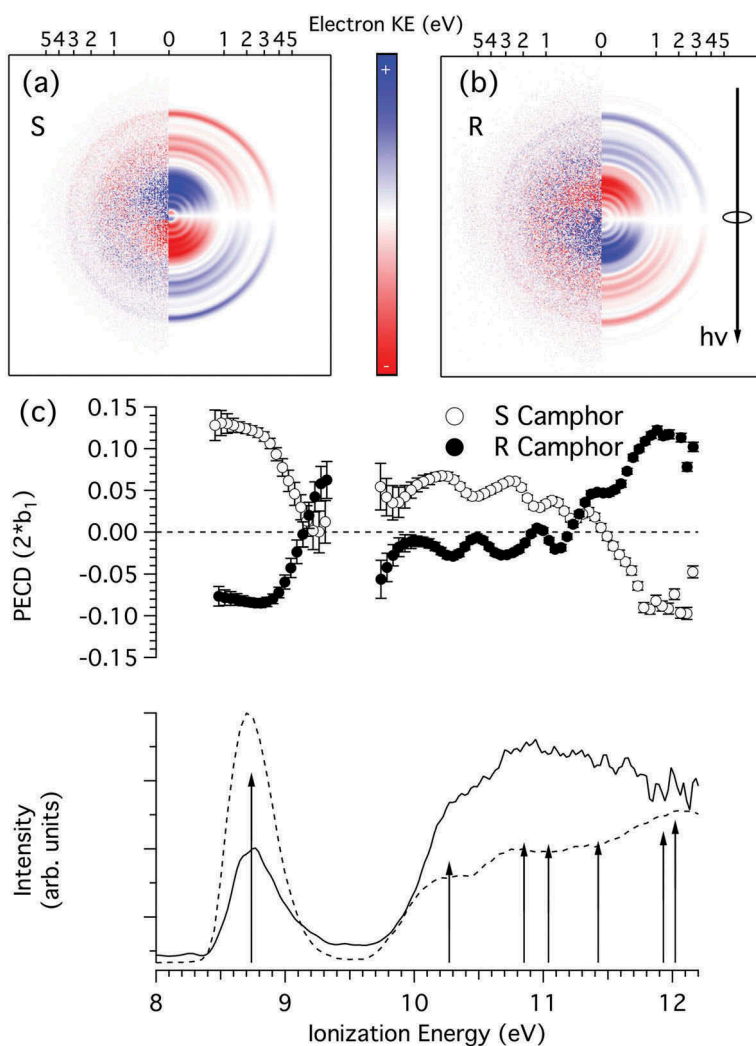
**Figure 2.** Experimental setup showing the coupling of the DESIRS beamline to the DELICIOUS3 i<sup>2</sup>PEPICO spectrometer.

Notes: PSD stands for position sensitive detectors and GF for gas filter. Figure adapted from [133] with permission.

be applied even in cases where several structural isomers contribute to the same given mass channel providing their photoelectron spectra are structured and separated enough in energy. It is important to point out, however, that since theoretical calculations are not yet quantitative, one needs to measure first the PECD for the probable enantiopure components of a given mixture before being able to determine e.es., continually building up a database for future reference. The analytical potential of this PECD-PICO method, especially with the availability of table-top laser systems, is now starting to be realized but has already been acknowledged by the analytical community as a mean to determine enantiomeric compositions in the gas phase [100,101].

## 2.2 Experimental methods and examples: the case of camphor and fenchone

The various experimental approaches, as well as computational methods, used in PECD experiments by several groups have been reviewed in [34]. Briefly, all the data presented in this paper have been obtained using the variable polarization undulator-based VUV beamline DESIRS delivering a high flux and tunable quasi-perfect CPL [102]. Solid or liquid chiral samples are usually brought into the gas phase by resistive heating (RH) in a dedicated oven coupled to an adiabatic expansion in the so-called SAPHIRS setup. The corresponding molecular beam is then doubly skimmed [103] before reaching the ionization region, located at the center of DELICIOUS3, a double-imaging PEPICO spectrometer [104] combining a velocity map imaging (VMI) [105] spectrometer on the electron side to a 3D momentum imaging on the ion side (see Figure 2). This setup



**Figure 3.** PECD of the showcase camphor molecule.

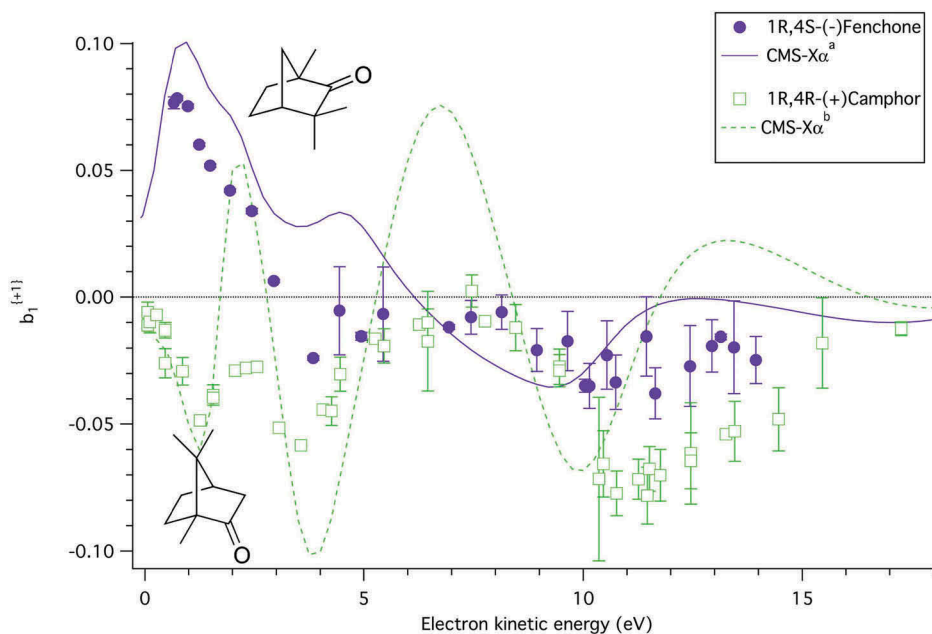
Notes: (a) VMI difference images (LCP-RCP) recorded at  $h\nu = 12.3$  eV for 1S,4S-camphor and (b) 1R,4R-camphor enantiomers. The left-half images show raw 2D projections, and the right half the corresponding Abel inverted image. (c) PECD (open and filled circles) and PES (solid line) extracted from inversion of the total and difference images. A higher resolution PES obtained at  $h\nu = 95$  eV is also represented (dashed line) along with the calculated values (arrows), both taken from [154]. (a)–(c) taken from [58] with permission.

allows ARPES to be performed on mass-selected and kinetic energy release-selected samples, discarding any background or spurious compounds. In targets where specific orbitals correlate with specific dissociative ionization channels, mass selection leads to orbital selection even if orbitals overlap due to their natural or instrument-induced width. This is often the case for ionization from the Highest Occupied Molecular Orbital (HOMO), which tends to be the only stable electronic state of the cation.

Therefore, the photoelectrons corresponding to ionization from this orbital can be isolated by selecting only the correlated parent ion mass [57].

In the case of fragile thermolabile molecules, such as amino acids, we use as a complementary vaporization method the so-called thermodesorption (TD) method in which aerosols are formed via nebulization in an atomizer from a solution of enantiopure amino acid diluted in water. These aerosols are dried and then guided into the experimental chamber via an aerodynamic lens where they impinge onto a hot tungsten tip located inside the VMI interaction region [106], which vaporizes the aerosol and releases a plume of intact neutral parent molecules. For both vaporization methods and when PECD experiments are performed, mass-tagged electron images are recorded for alternate left- and right-handed CPL, with a typical helicity switch every 15 min. After normalization to the total electron counts, the image differences are Abel-inverted with the pBasex algorithm [107] providing  $b_1$  parameters for a given electron KE according to a procedure described elsewhere [53], while the sum of the left- and right-handed CPL images provides the PES and  $b_2$ . For a given photon energy and orbital, the  $b_1$  parameter is given as a PES-weighted average over the full width half maximum of the band

$\hat{b}_1 = \frac{\sum_{\text{FWHM}} b_1(\text{KE}) b_0(\text{KE})}{\sum_{\text{FWHM}} b_0(\text{KE})}$ . When plotted, the error bars assume individual



**Figure 4.** Sensitivity of PECD to isomerism.

Notes: Chiral parameter ( $b_1^{(+1)}$ ) for ionization from the HOMO orbital of R-fenchone and R-camphor (S enantiomers negated). The points represent all the available experimental data in the literature, including the present work, while the lines correspond to CMS-Xα calculations. <sup>a</sup>From Powis et al. [155]. <sup>b</sup>From Nahon et al. [53]. Figure adapted from [58] with permission.

Poisson distributions for each image pixel whose associated error is then propagated using standard formulas throughout all the algebra operations.

An example of the experimental data that can be obtained with the spectrometer described above is presented in [Figure 3](#) for the showcase of camphor. The image shows the photoelectron spectrum and associated PECD recorded at a fixed photon energy a few eVs above its ionization threshold, and encapsulates various general properties that have been introduced in the previous subsection, namely the sign reversal when swapping enantiomers, the high sensitivity to chirality with up to 12% asymmetry, and the strong dependence on the orbital being ionized. The latter is worth commenting upon, first because sign changes can be seen depending on the orbital, and second because  $b_1$  is more sensitive to the initial state than  $b_0$  (= PES), thus changing rapidly from band to band so that structures that are invisible in the PES can be easily discerned in the PECD and correlated with the calculated positions of the electronic states, as seen in panel 3c.

[Figure 4](#) shows the asymmetry parameter as a function of the electron kinetic energy, i.e. the final state dependency, for the same orbital (HOMO) and absolute configuration of camphor and fenchone which are structural isomers differing by the position of two methyl groups. Two striking effects can be inferred from this image, the rich variation of PECD with electron kinetic energy (continuum effect), and the dramatic change in sign and magnitude when moving from one isomer to the other for electrons with kinetic energies below 5 eV showing a spectacular sensitivity to isomerism. Also plotted along with the experimental data are the curves predicted with the CMS-X $\alpha$  method for both molecules. Although the agreement cannot be considered quantitative, it nevertheless matches remarkably the experimental trend considering the challenges posed by these relatively big molecules lacking any symmetry, even in the difficult low-KE region. Furthermore, these comparisons help benchmarking available methodologies and drive future developments, such as the inclusion of electron correlation or vibrational motions which will close the gap between current experiments and models.

### 3. Case of amino acids Ala and Pro: possible implications for the origin of life's homochirality

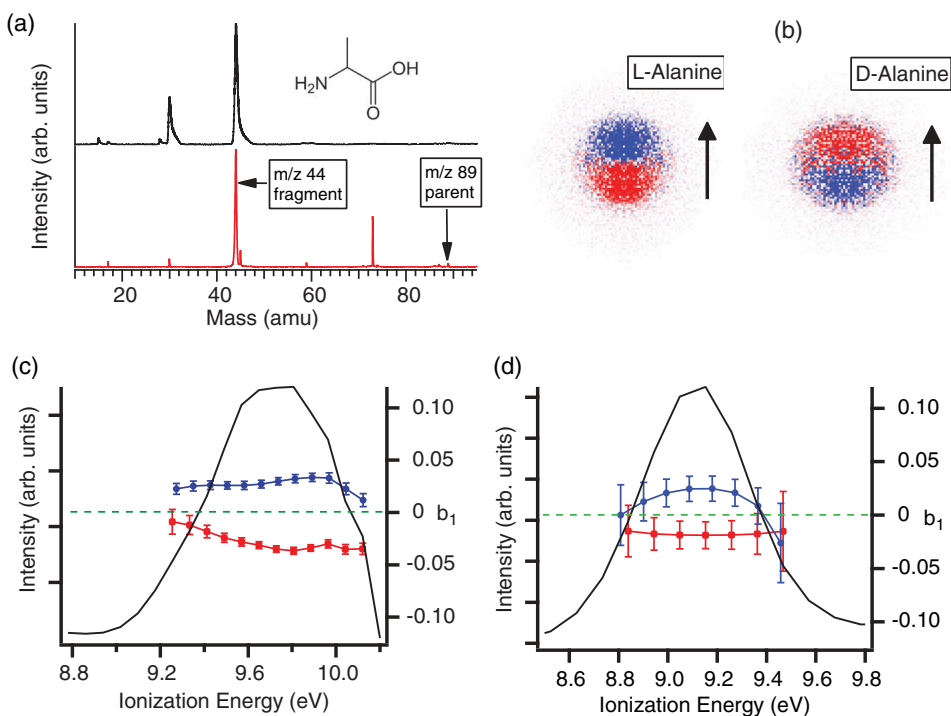
Within a bottom-up approach of biomolecular complexity, the study of gas-phase, isolated, elementary bricks of life [108] such as amino acids aims at shedding light on their molecular and electronic structures, chemical reactivity, and chiroptical properties. In the next section, we will focus onto alanine (Ala), the simplest chiral proteogenic amino acid, for which not much is known in terms of VUV chiroptics, except for a gas-

phase study that reported on the total ion yield providing CD upper values [109], as well as another study on thin films [110]. We will show how PECD of alanine may be of interest in terms of structure (conformational analysis) and, most of all, we will stress a possible link between PECD and the origin of life's homochirality.

Homochirality of life, also called biomolecular asymmetry, refers to the fact that only L-amino acids and D-sugars of nucleic acids are found in the biosphere [1]. Since its first inference by Pasteur in the mid-nineteenth century, who clearly saw in this asymmetry a signature of life (unlike the symmetric 'inert' matter), the origin of such a major asymmetry has been puzzling scientists and remains a fundamental open question and a central issue in the broad field of astrobiology, probably directly linked to the origin of life itself. This origin of this symmetry breaking has been the subject of a very broad range of scenarios (for reviews see [111,112]), most of which are abiotic, i.e. suggesting that the asymmetry, or at least some e. e., was existing prior to life and was a necessary condition for its development [113]. Deterministic scenarios, based upon the consequences of chemical and physical laws, include tiny energy differences between enantiomers induced by the so-called PV effect in the electroweak interaction [2,114], as well as photochemistry under the influence of chiral fields: magnetic fields, responsible for the magneto-chiral effect [115,116], and those associated with CPL on which we will focus from now.

Since the discovery of a partially CPL in heavy star forming regions [117,118], such as the one from which the Sun was formed, and together with the fact that L-enriched amino acids have been found in carbonaceous meteorites, such as the Murchison meteorite [119–121], CPL-induced processes have been proposed as a chiral bias to which amino acids, formed in the interstellar medium/circumstellar medium (ISM/CSM), would have been subjected to during their journey toward Earth, via meteorites and comets delivery. This could lead to significant e.e. that would be, later on, amplified on Earth toward full homochirality via autocatalytic reactions [122]. So far, most of recent laboratory experiments have been focused on *photochemical* asymmetric processes in the condensed matter, using in particular the synchrotron radiation in the UV/VUV as a soft continuous photon source to mimic the UV/VUV ISM spectrum [123,124]. Such processes include the asymmetric photolysis from initially racemic thin films of leucine [125] and alanine [126], induced by non-vanishing absorption anisotropy factors  $g$  [127], as well as asymmetric photochirogenesis of Ala [128] and other amino acids [129] from achiral precursors in ISM ice analogs – and ongoing research is aiming now toward the photochirogenesis of sugars [130] and their precursors [131].





**Figure 5.** Characterization and PECD of alanine at Ly- $\alpha$  radiation (10.2 eV).

Notes: (a) Time-of-flight spectra of alanine photoionized at 10.2 eV and produced by the TD (black line) and RH methods (red line), (b) raw difference images, filtered on all alanine-related ions, (c) corresponding PES and  $b_1$  dichroic parameter distribution over the HOMO band. The blue (resp. red) data correspond to the D- (resp. L-) enantiomer, (d) parent-filtered ( $m/z$  89) PES and  $b_1$  measurement on oven-produced D-(blue curve) and L-alanine (red curve). (a)–(d) adapted from [133] with permission.

In this context, one could wonder if the asymmetry induced by PECD could lead to an asymmetric *photophysical* process on gas-phase amino acids, in connection with life's homochirality. We focus first on Ala, the simplest chiral amino acid which is the second one, after the non-chiral amino acid glycine, to have been recruited by life [132]. Ala has been the subject of a thorough VUV PECD study [72] with a specific focus onto the PECD recorded at the Lyman- $\alpha$  radiation wavelength (121.6 nm = 10.2 eV) [133], of major astrophysical relevance, since it dominates by far the UV/VUV ISM/CSM spectrum [129,134,135].

### 3.1: production of gas-phase Ala and its PECD at the Lyman- $\alpha$ radiation

Because of their very low vapor pressure and thermolabile character, amino acids are quite challenging to bring in the gas phase. This led us to use and benchmark two complementary vaporization methods (see Sec. 2.2): the RH in an oven coupled to an adiabatic expansion and the method of aerosol TD. The former would a priori produce a denser and colder

molecular beam, but may lead to the formation of spurious decomposition products, while the latter method only produces intact parent neutrals but because of the presence of the TD in the ionization region of DELICIOUS3 might be associated with degraded performances in terms of mass and electron resolutions.

Figure 5(a) shows, for two methods, the mass spectra of Ala photoionized at 10.2 eV, an energy located well above the adiabatic ionization energy of 8.82 eV [136] and leading to the ejection of an electron from the HOMO orbital [137]. As previously documented [136], the spectrum is dominated by the fragment ( $m/z$  44) corresponding to the loss of COOH via a dissociative photoionization (DPI) process. In the TD-mass spectrum, the parent peak ( $m/z$  89) barely visible because of the poor resolution amounts to  $0.7 \pm 0.4\%$  of the total Ala signal. Peaks at masses 28 and 30 are linked to the nebulizing gas of the aerosols. The RH-mass spectrum, in addition to the parent ( $m/z$  89 representing about 0.9% of the total Ala signal) and the broad (i.e. hot) DPI fragment ( $m/z$  44), shows a series of sharp (i.e. cold) peaks ( $m/z$  17, 59, 73) corresponding to thermal decomposition products in the oven prior to the supersonic expansion which are not related to nascent neutral Ala since they are not present on the TD-mass spectrum. Owing to the PEPICO scheme, when treating the RH-data we can discard their spurious contribution to the electron images and therefore to PECD, via the so-called filtered asymmetry multiplex approach PECD-PICO. Note that by analyzing, via a statistical model, the appearance energy onset of the  $m/z$  44 fragment produced by unimolecular dissociation of a hot ground-state parent ion [72,138], we could estimate the internal temperature of the nascent neutral species:  $\sim 310$  K for the RH-method and  $\sim 350$  K for the TD-method.

The PECD-PICO treatment has been applied to the RH-raw data to produce the difference images shown in Figure 5(b), whose radial and angular analysis leads to the PES and  $b_1$  profiles of Figure 5(c). Despite the presence of several conformers a priori, the PECD is significant and clearly visible on the raw difference images, with an average value for the HOMO orbital of 6% (i.e.  $b_1 = 0.03$ ). The nice mirroring between the L- and D-Ala images and corresponding  $b_1$  profiles shows the high quality of the data. The filtering on the parent mass ( $m/z$  89) leads to the PES and  $b_1$  profile presented in Figure 5(d), showing that the parent alanine only survives when a little amount of vibrational energy is imparted into the cation and undergoes an unimolecular fragmentation above  $\sim 9.5$  eV binding energy. Across the parent-filtered PES band, the average  $b_1$  value is 0.02, corresponding to a PECD of 4%, slightly lower than the 6% found over the full HOMO band. Such a 4% asymmetry is orders of magnitude greater than any classical CD signal (see for instance [109]).

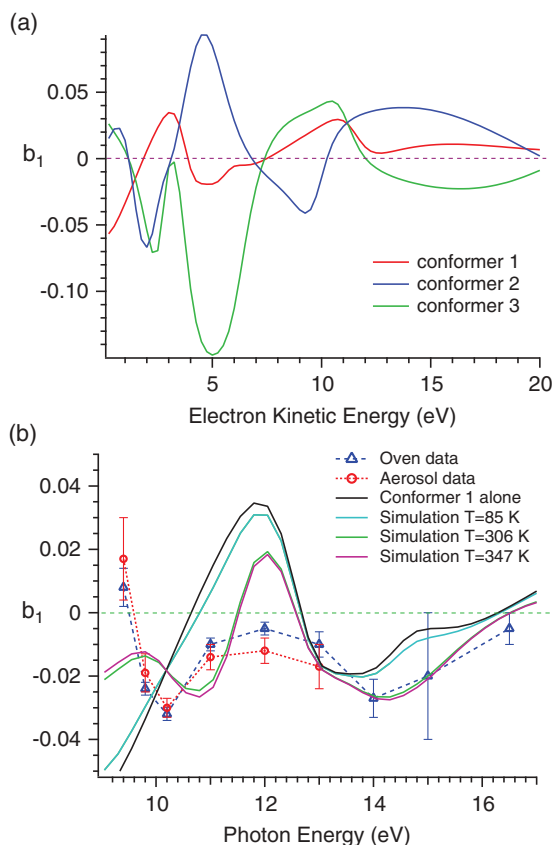
### 3.2 Possible implications for the origin of life's homochirality

Let us consider that gas-phase alanine is present in the ISM/CSM as racemate, likely produced by evaporation in hot cores [139], photon or energetic beam-impact desorption from molecules synthesized on icy grains, or by ion-neutral reactions in the gas phase surrounding icy grain mantles [140]. Note that although the discovery of gas-phase glycine in the ISM is still controversial [140,141], this basic amino acid has been observed in the gas phase in the coma of the 67P/Churyumov–Gerasimenko comet [142], a pristine ancestor and witness of the early solar system [143], via the airborne COSINA mass spectrometer on the Rosetta mission orbiter. In addition, complex and quite large gas-phase molecules, including the chiral species methyloxirane [144], have been detected in the ISM, although not via an enantio-specific method. Therefore, large gas-phase amino acids are probably also present in the ISM/CSM but difficult to detect because of their congested IR/MW signature due to their size and the possible existence of several conformers.

Let us further consider that this racemic mixture of gas-phase alanine is embedded into a partially CPL field with a given and constant helicity over a large region of space, as in the Orion Nebulae, similar to the one from which the Sun was formed, as discussed in [128]. Then the fact that  $b_1$  is anti-symmetric with the swapping of enantiomers means that the PECD-induced electron asymmetry at the Lyman- $\alpha$  radiation (10.2 eV) will be opposite for the two enantiomers. Because of momentum conservation, the corresponding recoiling ions will also have opposite asymmetries, i.e. opposite directions of propagation. This process leads therefore to an asymmetry in the flux of non-fragmented alanine parent ions in a given line of sight, which may reach a maximum value of  $2b_1$ , i.e. 4% in the limit of pure CPL. In other words, along the photon axis direction, the expanding sphere of recoiling ions presents an asymmetry of up to 4%, which corresponds to a net e.e. of the same value. This enantio-enriched gas-phase alanine ion cloud of a given handedness, separating from its enantio-opposite counterpart, may then be captured, neutralized, and embedded into comets and meteorites seeding Earth with an exogenous organic matter presenting an initial e.e. (see graphical abstract figure as an illustration of this process).

### 3.3. Alanine conformer analysis and temperature effects

Amino acids are floppy molecules – a crucial property in biological activity involved in folding processes [145] and in the building up of supra-molecular assemblies and peptides [146]. The associated conformational landscape, governed by inter-molecular interactions, is best captured in the



**Figure 6.** PECD of alanine over the full VUV range for the HOMO orbital.

Notes: (a) Calculated  $b_1$  values for L-alanine obtained by (CMS-X $\alpha$ ) for the three lowest lying conformer of alanine, (b) calculated  $b_1$  values for L-alanine obtained by applying a Boltzmann conformer distribution as a function of the photon energy for three temperatures:  $T = 85$  K (blue curve),  $T = 306$  K (green curve), and  $T = 347$  K (purple curve). Experimental points related to the TD experiment are in red and those related to the RH experiment are in blue. (a) and (b) adapted from [72] with permission.

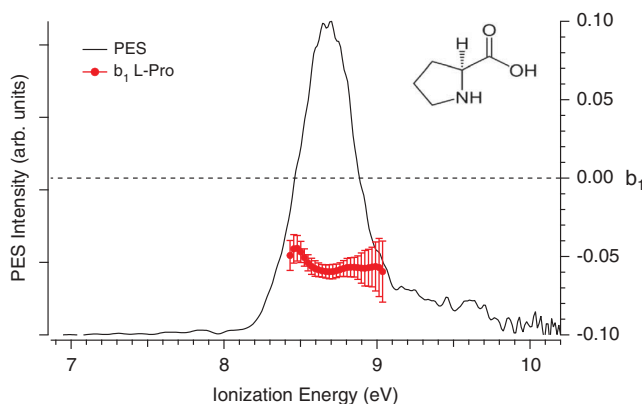
solvent-free gas phase. Because of its high sensitivity to the whole molecular potential, PECD is a subtle probe of such molecular structures (see Sec. 2). This was illustrated by the comprehensive PECD-based conformer analysis of Ala [72], which we will hereafter summarize in the context of a possible link between PECD and the origin of life's homochirality.

We will consider the three low-lying energy conformers (separated by 24 meV) susceptible to be populated in our experimental conditions [29,137,147]. In Figure 6(a), we present CMS-X $\alpha$  calculated  $b_1$  values as a function of the electron KE for the HOMO orbital, showing strong dynamical oscillations and, most of all, a very strong conformer sensitivity (especially for slow electrons), much more so than the conventional  $\beta$  parameter [72]. The same calculated  $b_1$  values, Boltzmann averaged for different temperatures, are plotted as a function of photon energy in Figure 6(b) together with experimental data recorded over a broad VUV range

with the two vaporization methods RH (310 K) and TD (350 K). Despite an over-predicted  $b_1$  value around 12 eV due to the presence of a shape resonance and a clear discrepancy in the challenging very slow electron range, the agreement between the experimental and modeled data is satisfactory with most of the experimental features reasonably well reproduced by the 310 K and 350 K theoretical curves that consider the contributions of the three conformers.

Beyond the case of the Lyman- $\alpha$  photon energy, the extended experimental and theoretical PECD data over a large VUV range bring some interesting additional clues regarding the PECD-based asymmetric astrophysical scenario developed above. First, we notice the clear temperature insensitivity of the PECD asymmetry around 10.2 eV for which the experimental  $b_1$  values obtained via both vaporization methods, and therefore at different temperatures, are very similar. This is very well reproduced by the theoretical modeling, with the high- and low-temperature average conformer PECD theoretical curves crossing exactly around 10.2 eV. This can be rationalized by the fact that, as we can observe in [Figure 6\(a\)](#), the individual PECD curves of the three main conformers cross at  $\sim 1.1$  eV KE, i.e. around 10.2 eV for the part of the HOMO band leading to the parent alanine ion (see [Figure 5\(d\)](#)). This temperature independence around the Lyman- $\alpha$  radiation energy strengthens the astrophysical scenario by not setting any temperature constraint on the precise type of ISM/CSM environment in which the CPL/amino acid interaction may have taken place, and for which the temperature may vary from 10's to 300 K or more in hot cores [128].

Besides, an important point for this astrophysical scenario is the fact that the  $b_1$  parameter keeps a constant sign over the whole studied VUV range, except for the very limited range between the ionization energy and 9.6 eV, for which  $b_1$  has an opposite sign compared to the rest of the spectrum, and for which the photoionization cross section and  $m/z$  89 absolute yields are quite small, one order of magnitude below the corresponding one at 10.2 eV (Lyman- $\alpha$  radiation energy) [148]. Overall, by integrating over the whole UV/VUV spectrum encountered either in the ISM/CSM or close to the solar system [135], largely dominated by the Lyman- $\alpha$  radiation, and taking into account the ionization cross sections reaching a plateau around 18 eV and then decreasing [148], and the fact that the PECD effect vanishes in general in the 10's eV above the ionization energy, there is no way, at least in the case of alanine, that the asymmetry would cancel out because of the alternating sign of  $b_1$ , nor because of a possible blurring out due to the various conformer contributions.



**Figure 7.** PECD of L-proline at Lyman- $\alpha$  radiation (10.2 eV).

Notes: Parent-filtered ( $m/z$  115) PES and  $b_1$  measurements on TD-produced L-proline (red curve).

### 3.4 Case of proline photoionized at Lyman- $\alpha$ radiation

In order to strengthen this scenario, we recently extended our studies toward other amino acids, including proline (Pro). Pro is relevant in terms of astrochemistry since it belongs to the first five amino acids to have been recruited into the genetic code [132] and has been as well detected in the Murchison meteorite in large quantity and with an L-excess [119,120]. Pro possesses a very specific and unique structure based upon a pyrrolidine ring including a secondary amine. This feature provides proline-rich proteins and peptides with specific structural properties. Despite the increased structural rigidity provided by the pyrrolidine ring compared to the very flexible aliphatic amino acids, Pro can adopt many conformers, four of which are calculated with low-lying energies such that they have to be considered in our experimental conditions [149,150]. These four conformers can be divided into two categories, I and II, differing by the carboxylic group orientation and containing each two conformers with different pyrrolidine ring puckering geometries [149,150]. These two families are, respectively, associated with two different bands centered around 8.9 and 9.5 eV ionization energy as observed from the experimental HOMO PES [150,151].

As for the Ala case, the main experimental difficulties for studying Pro reside in its low vapor pressure and possible thermal decomposition. Therefore, for this very first study on Pro we used the aerosol TD method, heated here at 140°C. Note that a new high-throughput aerodynamic lens was used for Pro, the description of which will be provided in a forthcoming dedicated paper.

In Figure 7, we present new data on L-Pro showing the associated PES and  $b_1$ , filtered on the parent cation mass ( $m/z$  115), recorded at the

Lyman- $\alpha$  radiation. Indeed, as for the Ala case, the parent-filtered data are the only meaningful contribution for our scenario aiming at rationalizing e.e.s. on parent Pro molecules. Interestingly, the parent filtering leads to a relatively narrow band in the PES, centered around 8.8 eV, and therefore associated with only type I conformers, an apparent conformer-specific fragmentation that will be discussed in a dedicated future article. Even more interesting is the fact that the  $b_1$  dichroic parameter associated with the parent-filtered cation possesses a PES-averaged absolute value of 0.06, corresponding to a PECD asymmetry of 12%, i.e. three times larger than the corresponding result on Ala. Besides this striking intensity, which may lead in a given line of sight to a 12% e.e. of the recoiling parent Pro ion, the crucial point is that at Ly- $\alpha$ , the  $b_1$  parameter for Pro is of the same sign as the one for Ala, leading to an associated e.e. of the same sign, which strengthens our hypothesis of a possible link of PECD to the origin of life's homochirality.

#### 4. Conclusions and outlooks

PECD is a recently established very intense chiroptical effect which might be observed by using various sources in the VUV/XUV such as synchrotron radiation [34] and HHG [90] and probably very soon free-electron lasers for one-photon ionization PECD, and in the UV range for laser-based REMPI-PECD. As we reviewed in the present paper, PECD possesses a wide range of interest from fundamental molecular physics to quantum chemistry, stereochemistry, and molecular dynamics up to purely analytical chemistry for e.e. determination. Such a broad array of applications explains the blooming of the field with the worldwide quick development of table-top laser-based setups to perform both frequency- and time-resolved PECD experiments.

We also show, by the use of soft continuous VUV synchrotron radiation, how PECD could be connected, along with other processes, to the origin of biomolecular asymmetry, in the showcase of amino acids Ala and Pro. This abiotic scenario is based upon an asymmetric emission of recoiling parent ions which would have been embedded into comets and meteorites delivering on the early Earth an enantio-enriched material. Future work on Pro for which a full conformer analysis is currently ongoing, based upon the use of several sample temperatures and a benchmarking with conformer-specific PECD calculations, should allow the study of the Pro-PECD temperature dependence and therefore possibly provide new ISM environment constraints for the validity of our scenario. Such a study appears very timely with the ongoing analysis of the Rosetta mission data and especially the first identification of several organic molecules by the COSAC instrument of the Rosetta mission Philae lander [152],



and the still possible analysis, despite the brutal landing of Philae onto the comet, of e.es. with a dedicated chiral sensitive *in situ* chromatographic probe [143,153]. The detection in the 67P/Churyumov–Gerasimenko comet of L-enriched amino acid molecules, as observed in meteorites, would support the assumption that chiral organic molecules were indeed delivered to early Earth during the late heavy-bombardment phase by comets and/or other small interplanetary bodies whose organic content may be of interstellar/presolar origin, tracing back to the molecular cloud from which our solar system was formed.

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## Disclosure statement

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