

Rendiconti Accademia Nazionale delle Scienze detta dei XL *Memorie di Scienze Fisiche e Naturali* 136° (2018), Vol. XLII, Parte II, Tomo II, pp. 35-46

## D. CATONE\* – N. ZEMA\* – T. PROSPERI\* – L. AVALDI\* S. TURCHINI\*,\*\*

# PhotoElectron Circular Dichroism: a versatile probe for chirality

**Abstract** – The use of circularly polarised light in PhotoElectron Spectroscopy enhances the response to conformational effects in chiral systems. PhotoElectron Circular Dichroism (PECD) provides a rich and detailed dynamics with respect to tiny changes of the electronic and structural properties by means of the dispersion of the intensity of the circular dichroism as a function of photoelectron kinetic energy. This is due to the interference of the outgoing partial waves of the photoelectron in the transition matrix element. Due to this particular interference term in the dipole allowed matrix element, PECD is the chiroptical spectroscopy with the highest asymmetry ratio. State of the art Density Functional Theory (DFT) is an important tool to interpret conformational effects in PECD spectra and to achieve quantitative information.

In this *rendiconto* examples of PECD studies of chiral molecular systems will be presented. They prove that PECD is a versatile tool with high sensitivity to group substitution, isomerism, conformer population, vibrational modes.

#### Introduction

Chiroptical spectroscopies represent the cornerstone for the stereochemical analysis. Optical Rotatory Dispersion (ORD), Electronic Circular Dichroism (ECD), Vibrational Circular Dichroism (VCD), Raman Optical Activity (ROA) along with Density Functional Theory calculations provide the basis to determine the absolute enantiomer configuration. Chirality affects a wide variety of scientific fields such as

\* Istituto Struttura della Materia-CNR (ISM-CNR), Via del Fosso del Cavaliere 100 - 00133 Roma, Italy.

\*\* E-mail: stefano.turchini@ism.cnr.it

enantioselective reactions, chiral recognition in biological processes, homochirality in terrestrial life. The analysis of conformers represents a challenge for spectroscopy; Boltzmann averages over different geometries should be performed in order to reproduce data and the need of a set of independent data is crucial to significantly retrieve the correct weights in the analysis. At variance with, photoabsorption, photoelectron spectroscopy is characterized by two independent quantum labels namely the photon energy and the electron kinetic energy, and provides for each electronic state an electron kinetic energy distribution. The drawback is that the photon energy dependence of the photoelectron cross section of different conformers is faible. In the language of quantum scattering theory this is reflected in a dependence of the photoelectron cross section on the interference of partial waves with the same angular momentum without phase effect. To display the full sensitivity of the electron kinetic distribution to conformer geometry one should select terms with a strong interference. PhotoElectron Circular Dichroism (PECD) presents interference of the  $l, l \pm 1$  outgoing partial waves of the photoelectron in the transition matrix element [1] and this is the origin of the extreme sensitivity in electronic and structural properties of chiral molecules [2].

#### PECD primer

Ritchie [3] pointed out that the PECD appears in the transition matrix element already in the electron dipole term, whereas circular dichroism in absorption is present at the second order perturbation level in the electric dipole/magnetic dipole and electric dipole/electric quadrupole interference terms. Consequently, the detected asymmetries are in the range 10<sup>-1</sup>-10<sup>-2</sup> for PECD and 10<sup>-3</sup>-10<sup>-4</sup> for CD in absorption. PECD is the chiroptical spectroscopy with the highest asymmetry value. Moreover the variety of spectroscopies and experimental methods based on photoemission can find a specific application to the study of chiral molecules. PECD has found application in valence band [4], core levels [5], resonant photoelectron spectroscopy [6], Auger-photoelectron coincidence spectroscopy [7], multiphoton photoelectron spectroscopy [8], ion-photoelectron coincidence [9], above threshold and tunnel ionization [10], time resolved PES [11].

The photoelectron angular distribution for a circularly polarized radiation and unoriented molecules is written:

$$I_m(\theta) = \frac{\sigma}{4\pi} \left( 1 + mDP_1(\cos(\theta)) - 2\beta P_2(\cos(\theta)) \right)$$
(1)

where  $P_{1_{2}}$  and  $P_{2}$  are Legendre polynomials,  $\theta$  is the scattering angle,  $\sigma$  is the total integrated cross section,  $\beta$  is the classical anisotropy parameter and D is the dichroism parameter, which describes the dynamics of the photoionization,  $m = \pm 1$  for left and right circularly polarized light. The parameter D is defined for each molecular state and is a function of the electron kinetic energy.

PECD is efficiently modeled by Continuum Multiple Scattering-Xa [12, 13] and B-spline-Linear Combination of Atomic Orbitals (LCAO) - Density Functional Theory (DFT) [14, 15, 16]. PECD has been exploited to study several facets which affect molecular chirality such as isomerism, group substitution, conformer population, clustering, vibrational effects, transient chirality and chiral self-assembled monolayers. Since the early days of the interpretation of PECD conformational geometries were recognized as crucial for the comparison between experiments and theory. A theoretical study on methyl-oxirane derivatives [15] reveals the sensitivity of the D parameter to the changes in the electronic structure due to group substitution also for very localized orbitals. This behavior is associated to the sensitivity of the photoelectron to the whole molecular potential; small variations in the molecular geometry change the molecular potential and could dramatically vary the sine of the phase difference in the D parameter, even for tiny phase differences around zero. Moreover the sine function allows the dichroism to change intensity and sign. At variance the  $\beta$  asymmetry parameter depends on the cosine of the phase difference and is not sensitive to small phase differences. In PECD the final state character plays the most important role; this immediately results from the PECD of the core levels, which are achiral orbitals with localized character. It is worth noticing that also in the case of core levels, despite the local origin of the excitation, PECD displays sensitivity to the absolute enantiomer configuration, as a true chiroptical spectroscopy. Although the first PECD spectra measured with synchrotron radiation were obtained by means of bending magnets, the development of the circular dichroism in photoemission has been associated to the employment of insertion devices fully dedicated to the delivery of photon beams with high flux and large degree of circularly polarization. These insertion devices induce elliptical trajectories of the electron beam in the storage ring, that result in the production of circularly polarized radiation on the central axis of the elliptical path. The two helicity branches are produced by the clockwise/anticlockwise direction of rotation of the elliptical motion. The measurements reported in this *rendiconto* were performed at the Circularly Polarised beamline (CiPo), built and managed by the Istituto di Struttura della Materia – CNR, of the synchrotron radiation facility ELETTRA (Trieste, Italy). The CiPo insertion device is an electromagnetic wiggler that spans the 5-900 eV energy range. PECD measurements are normally taken reversing the photon helicity at 0.05 Hz, recording the two polarity branches of the spectrum. The beamline [17, 18] is equipped with a normal incidence monochromator in the range 5-35 eV (resolving power ~10000 at 16 eV, ~ 6000 at 21 eV) and a grazing incidence spherical grating monochromator in the range 35-900 eV. The polarization ratio is 60% at 15 eV, 90% in the range 40-120 eV in guasi-undulator mode and 80% in the range 120-900 eV in wiggler regime. The electron analyser is a 150 mm electron hemispherical analyser.

#### Vibrational effects in PECD

The Born-Oppenheimer approximation suggests that the adiabatic coupling between electronic and nuclei allows us to express a molecular state as a product between a vibrational wavefunction depending on the nuclei coordinates and an electronic wavefunction of the electronical coordinates with nuclear coordinates as parameters.

The photoionization matrix element is written as follows:

$$M_{i,f,\nu,\nu'} = \left\langle \chi_{f,\nu'}(\boldsymbol{R}) \middle| \chi_{f,\nu}(\boldsymbol{R}) \middle| \psi_{f,k}(\boldsymbol{r},\boldsymbol{R}) \middle| \mu_{el} \middle| \psi_{i}(\boldsymbol{r},\boldsymbol{R}) \middle\rangle \right\rangle$$
(2)

where  $\mathbf{r}$  and  $\mathbf{R}$  are representative of the electronic and the nuclei coordinates,  $\mu_{el}$  is the electric dipole,  $\psi_{f,k}^{(-)}(\mathbf{r}, \mathbf{R})$  and  $\psi_i(\mathbf{r}, \mathbf{R})$  are the final and initial electron state, respectively, with the corresponding vibrational function  $\chi_{f,v}(\mathbf{R})$  and  $\chi_{i,v'}(\mathbf{R})$ . Franck-Condon (FC) approximation considers the electric dipole matrix element independent on the molecular geometry sampled by the vibrations and allows us to factorize the electronic and nuclear contribution.

Violations of the FC approximation are reported due to the influence of shape resonances [19] or of the Cooper minimum [20]. It is worth noting that if the FC approximation holds then PECD should be independent on vibronic effects. D parameter is apt to change as a function of molecular conformation, hence the integral over the electronic coordinates is expected to vary significantly with R, making impossible the separation of the electronic and vibrational contribution. The vibrational intensity of PECD could also display different signs, that is equivalent to a forward-backward asymmetry associated to an opposite sign of the vibronic transitions. Vibrationally resolved K shell circular dichroism in oriented CO [21] is explained in terms of a transition matrix element that employs the integration of the dipole moment over the internuclear distance. A theoretical study on a selected enantiomer of H<sub>2</sub>O<sub>2</sub> [22], which is a chiral molecule that interconverts enantiomers and displays lack of optical activity, clearly points out that in the average over the vibrational matrix the vibrational phase effects play a key-role in forward-backward asymmetry; the matrix element is a complex quantity and the difference is dramatically affected by small change of the phase between the different contributions. The PECD of the HOMO of the methyl-oxirane, measured at 21 eV of photon excitation [23], clearly displays a variation of about 40% of the D parameter across the HOMO vibrational envelopes. PECD on the same molecule [24, 25] with photon energy excitation close to the HOMO ionization potential shows a sign inversion in the PECD of different vibrational terms.

It is worth noticing that the tiny changes in the electronic structure due to vibronic effects is highly reflected in the intensity and sign of PECD enlightening the role of the phase difference of the different contributions in the transition matrix element. Figures 1 and 2 report high resolution PECD spectra, together with the PES



Fig. 1. HOMO PhotoElectron spectrum of S-methyl-oxirane (blue line) measured at 16.6 eV of photon energy together with D parameter (red line).



Fig. 2. HOMO PhotoElectron spectrum of S-methyl-oxirane (blue line) measured at 21.4 eV of photon energy together with D parameter (red line).

spectra, of the vibrationally resolved HOMO of methyl-oxirane measured at photon energy 16.6 and 21.4 eV, respectively. Distinct values of D parameter in the vibrational structure are observed as a function of photon energy and vibrational structure.

#### Conformer Population studied by PECD

To establish on firm grounds the interpretation of PECD it is desirable to compare the experimental PECD of molecules that are structural isomers and molecules presenting different group substitutions. Alaninol and isopropanolamine are linear saturated bifunctional molecules and are structural isomers with swapped functional groups (-OH,-NH<sub>2</sub>). For HOMO and HOMO-1 [26, 27, 28] the DFT theory displays a good agreement in the shape of the dispersion, but it is shifted in kinetic energy toward lower energies for HOMO and toward positive D values in HOMO-1. A better quantitative accord is reported for HOMO-2 and HOMO-3. In the case of the isopropanolamine the comparison with theory improves for HOMO and HOMO-1 with respect to the alaninol case, while it is poor for HOMO-2 and HOMO-3. Theory should give the same level of agreement with respect to the experiments in molecules with the same functional groups and similar skeleton structure. The answer to this issue is clearly important for the interpretation of PECD. From the comparison of the experimental D parameters of the two molecules a similar dichroism dispersion for HOMO and HOMO-1 is found. The difficulty of the theory to represent HOMO and HOMO-1 dichroic dispersion relies in the assignment of the character of the orbitals. For alaninol and isopropanolamine the LB94-DFT method [29] calculates as the main contribution to the HOMO the one of the O 2p and for the HOMO-1 the one of the N 2p, while Hartree-Fock (HF) and OVGF calculations predict a reverse situation. The good agreement of the DFT predicted dichroism with the experiments for isopropanolamine points out that the electronic assignment is O 2p for the HOMO and N 2p for the HOMO-1. On the basis of the topological similarity of the orbitals with respect to the skeleton structure, the good agreement of the experimental dichroism parameter for HOMO and HOMO-1 of the two molecules indicates that the DFT assignment for the HOMO and HOMO-1 of alaninol should be reversed. By means of the PECD dispersion, it is also possible for both molecules to individuate states in the PES spectrum belonging to the minority conformer in the energy range predicted by the OVGF calculations.

Conformational effects in 3-Methylcyclopentanone were observed by PECD varying the conformer population in vapor target at thermal equilibrium [30]. PECD experiment was performed at two different temperature  $T_1=300$  K and  $T_2=370$  K. Assuming a prevailing two conformer population (equatorial and axial conformers) the population at 300 K is  $P_{eq}=0.9$  and  $P_{ax}=0.1$ , the population at 370 K is  $P_{eq}=0.85$  and  $P_{ax}=0.15$ . Using a Boltzman average for the PECD dispersion at the two temperatures, a 2x2 linear system is formed to retrieve the experimental dichroism parameter of the two conformers. The HOMO experimental dispersions, obtained

solving the linear systems, corresponding to the  $P_{eq}$  and  $P_{ax}$  show a good agreement with the calculated ones. On the other hand the agreement between the experimental data and the Boltzmann average is good as far as the shape and sign are con-

tal data and the Boltzmann average is good as far as the shape and sign are concerned, but it is only qualitative. These findings directly point out to the contribution of rotations not accounted for in the calculation. PECD is an oscillating signal and sum over conformer contribution in general decreases the intensity. This simple argument explains why the calculated PECD at the equilibrium geometry is usually more intense than the experimental one. However in a great number of experiments calculation at equilibrium geometry reproduces at least qualitatively the experimental data. The above result may suggest that the effect of the average on free rotations results in a superimposed slow varying signal that can shift and distort the shape of the signal of equilibrium geometry. Since PECD strongly depends upon tiny structural variations, the above results pave the road for a quantitative and structural analysis of the conformer population in equilibrium and non-equilibrium states.

### Future experimental developments at Elettra

In order to continue the activity described in the previous sections as well as to address other outstanding questions connected with the understanding of the physical mechanism behind the electronic chiral response, the formation of aerosol particles in the atmosphere, the role of spatial and anisotropic properties in biological structure recognition and drug design and the mechanisms of radiation damage and protection in DNA and RNA strands, a project to develop a synchrotron radiation based chemical-physics laboratory at Elettra is under development. The core of the project is a new beamline named MOST (Molecular Science and Technology). The technical specifications of this new beamline are: a wide photon energy range (8 - 1500 eV), full polarization control (horizontal or vertical linear polarization, left or right circular polarization), high flux, (one order of magnitude or more higher than the actual beamline at Elettra), high spectral purity (around a few percents of harmonic content) and superior resolution, taking advantage of the lower emittance of planned Elettra 2.0 source and the lower slope errors of the new optical elements.

The source will consist of two variable polarization undulators, for low and high energy. This configuration has proven to give optimal flux when a wide photon energy range is required, and the most recent soft x-ray beamlines at Elettra are designed like this. The low energy insertion device will be aperiodic to reduce the harmonic content and provide greater spectral purity [31]. The full polarization control will allow an easy determination of asymmetry and dichroic parameters.

The beamline will consist of two branches (figure 3), a low energy branch and a main line where up to three end-stations can be located. The beam emerging from the undulator will be incident on the first optical element, which has the function of absorbing the heat load, deflecting the beam so that gamma rays can be blocked by suitable shielding, and it may also focus the beam. This optical element will deflect



Fig. 3. Schematic layout of the MOST beamline.

the beam either to the main line equipped with a plane grating monochromator or to the low energy branch equipped with a normal incidence monochromator.

As for the main line a design without entrance slits is proposed, an approach widely used for modern beamlines, because since the introduction of top-up operation, Elettra has become a very stable machine, and Elettra 2.0 is expected to be even more stable This shortens the beamline, providing more space after the monochromator for branch lines and experimental stations. Also it may reduce the number of optical elements, increasing flux and reducing cost. The adoption of Variable Line Space (VLS) and Variable Groove Depth (VGD) plane gratings [32] in the monochromators will allow the optimisation of either spectral purity (suppression of higher orders) or flux. The beam will emerge from the exit slit horizontally, and enters a deflection chamber with mirrors to deflect the beam left or right, or allow it to pass straight through. All three branches will have refocusing optics, which provide a small spot in the experimental station. The central branch will provide the full range of energy, and the left and right branches will have lower cut-off energies, depending on the deflection angle chosen for the mirrors. A laser hutch will be constructed, to allow pump-probe experiments with optical laser plus synchrotron light.

The low energy branch line will be equipped with a normal incidence monochromator (refurbishing of the existing one at CIPO beamline which can host two gratings) and cover an energy range 8-35 eV. This branch will serve a permanent end-station devoted to mass spectrometric studies of biomolecules, proteins and ionmolecule reactions. The gratings and focusing optics will be chosen in order to achieve a high flux and optimal suppression of higher orders. The typical resolving power will be at least 10000 over all the energy range.

#### Conclusions

In the last decade PECD has been established as a promising chiral spectroscopy; it displays the highest chiroptical asymmetry  $(10^{-1} - 10^{-2})$  and benefits from the steep development of circularly polarized VUV sources, such as synchrotron insertion devices and laser high harmonics generation, and from state of the art photoelectron spectroscopy experimental methods. The odd/even interference term of the angular momentum outgoing wavefunction gives rise to the sensitivity to both electronic and structural properties of chiral molecules. DFT-theory is suitable to reproduce experiments and analyzes the experimental signal in terms of conformer population. The future challenge for PECD will be to manage the extreme conformational sensitivity of PECD by means of reliable time consuming calculation approaches.

#### REFERENCES

- [1] Powis I. 2008, Photoelectron circular dichroism in chiral molecules *Adv. Chem. Phys.* 138 267-329.
- [2] Turchini S. 2017, Conformational effects in photoelectron circular dichroism J. Phys. Condens. Matter 29 503001.
- [3] Ritchie B. 1976, Theory of the angular distribution of photoelectrons ejected from optically active molecules and molecular negative ions *Phys. Rev. A* **13** 1411-5.
- [4] Böwering N., Lischke T., Schmidtke B., Müller N., Khalil T., Heinzmann U. 2001, Asymmetry in Photoelectron Emission from Chiral Molecules Induced by Circularly Polarized Light *Phys. Rev. Lett.* 86 1187-90.
- [5] Hergenhahn U., Rennie E.E., Kugeler O., Marburger S., Lischke T., Powis I., Garcia G. 2004, Photoelectron circular dichroism in core level ionization of randomly oriented pure enantiomers of the chiral molecule camphor J. Chem. Phys. 120 4553-6.
- [6] Catone D., Stener M., Decleva P., Contini G., Zema N., Prosperi T., Feyer V., Prince K.C., Turchini S. 2012, Resonant Circular Dichroism of Chiral Metal-Organic Complex *Phys. Rev. Lett.* 108 83001.
- [7] Alberti G., Turchini S., Contini G., Zema N., Prosperi T., Stranges S., Feyer V., Bolognesi P., Avaldi L. 2008, Dichroism in core-excited and core-ionized methyloxirane *Phys. Scr.* 78 058120.
- [8] Lux C., Wollenhaupt M., Bolze T., Liang Q., Köhler J., Sarpe C., Baumert T. 2012, Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses *Angew. Chemie - Int. Ed.* 51 5001-5.
- [9] Fanood M.M.R., Ram N.B., Lehmann C.S., Powis I., Janssen M.H.M. 2015, Enantiomer-specific analysis of multi-component mixtures by correlated electron imaging-ion mass spectrometry *Nat. Commun.* 6 7511.
- [10] Beaulieu S., Ferré A., Géneaux R., Canonge R., Descamps D., Fabre B., Fedorov N., Légaré F., Petit S., Ruchon T., Blanchet V., Mairesse Y., Pons B. 2016, Universality of photoelectron circular dichroism in the photoionization of chiral molecules *New J. Phys.* 18 102002.
- [11] Comby A., Beaulieu S., Boggio-Pasqua M., Descamps D., Légaré F., Nahon L., Petit S., Pons B., Fabre B., Mairesse Y., Blanchet V. 2016, Relaxation Dynamics in Photoexcited Chiral Molecules Studied by Time-Resolved Photoelectron Circular Dichroism: Toward Chiral Femtochemistry J. Phys. Chem. Lett. 7 4514-9.

- [12] Powis I. 2000, Photoelectron circular dichroism of the randomly oriented chiral molecules glyceraldehyde and lactic acid J. Chem. Phys. 112 301.
- [13] Powis I. 2000, Photoelectron Spectroscopy and Circular Dichroism in Chiral Biomolecules: I-Alanine J. Phys. Chem. A 104 878-82.
- [14] Turchini S., Zema N., Contini G., Alberti G., Alagia M., Stranges S., Fronzoni G., Stener M., Decleva P., Prosperi T. 2004, Circular dichroism in photoelectron spectroscopy of free chiral molecules: Experiment and theory on methyl-oxirane *Phys. Rev. A - At. Mol. Opt. Phys.* 70 014502.
- [15] Stener M., Fronzoni G., Di Tommaso D., Decleva P. 2004, Density functional study on the circular dichroism of photoelectron angular distribution from chiral derivatives of oxirane J. *Chem. Phys.* **120** 3284-96.
- [16] Giardini A., Catone D., Stranges S., Satta M., Tacconi M., Piccirillo S., Turchini S., Zema N., Contini G., Prosperi T., Decleva P., Di Tommaso D., Fronzoni G., Stener M., Filippi A., Speranza M. 2005, Angle-resolved photoelectron spectroscopy of randomly oriented 3-hydroxytetrahydrofuran enantiomers *ChemPhysChem* 6 1164-8.
- [17] Derossi A., Lama F., Piacentini M., Prosperi T., Zema N. 1995, High flux and high resolution beamline for elliptically polarized radiation in the vacuum ultraviolet and soft x-ray regions *Rev. Sci. Instrum.* 66 1718-20.
- [18] Desiderio D., Difonzo S., Dlviacco B., Jark W., Krempasky J., Krempaska R., Lama F., Luce M., Mertins H.C., Placentini M., Prosperi T., Rinaldi S., Soullie G., Schäfers F., Schmolle F., Stichauer L., Turchini S., Walker R.P., Zema N. 1999, The elettra circular polarization beamline and electromagnetic elliptical wiggler insertion device *Synchrotron Radiat. News* **12** 34-8.
- [19] Dittman P.M., Dill D., Dehmer J.L. 1982, Shape-resonance-induced non-Franck-Condon effects in the valence-shell photoionization of O2 J. Chem. Phys. 76 5703.
- [20] Rao R.M., Poliakoff E.D., Wang K., McKoy V. 1996, Global Franck-Condon Breakdown Resulting from Cooper Minima Phys. Rev. Lett. 76 2666-9.
- [21] Jahnke T., Foucar L., Titze J., Wallauer R., Osipov T., Benis E.P., Alnaser A., Jagutzki O., Arnold W., Semenov S.K., Cherepkov N.A., Schmidt L.P.H., Czasch A., Staudte A., Schöffler M., Cocke C.L., Prior M.H., Schmidt-Böcking H., Dörner R. 2004, Vibrationally Resolved K -shell Photoionization of CO with Circularly Polarized Light *Phys. Rev. Lett.* **93** 083002.
- [22] Powis I. 2014, Communication: The influence of vibrational parity in chiral photoionization dynamics J. Chem. Phys. 140 111103.
- [23] Contini G., Zema N., Turchini S., Catone D., Prosperi T., Carravetta V., Bolognesi P., Avaldi L., Feyer V. 2007, Vibrational state dependence of B and D asymmetry parameters: The case of the highest occupied molecular orbital photoelectron spectrum of methyl-oxirane *J. Chem. Phys.* **127** 124310.
- [24] Garcia G.A., Nahon L., Daly S., Powis I. 2013, Vibrationally induced inversion of photoelectron forward-backward asymmetry in chiral molecule photoionization by circularly polarized light *Nat. Commun.* 4 3132.
- [25] Garcia G.A., Dossmann H., Nahon L., Daly S., Powis I. 2017, Identifying and Understanding Strong Vibronic Interaction Effects Observed in the Asymmetry of Chiral Molecule Photoelectron Angular Distributions *ChemPhysChem* 18 500-12.
- [26] Catone D., Turchini S., Contini G., Zema N., Irrera S., Prosperi T., Stener M., Di Tommaso D., Decleva P. 2007, 2-amino-1-propanol versus 1-amino-2-propanol: Valence band and C 1s core-level photoelectron spectra J. Chem. Phys. 127 144312.
- [27] Turchini S., Catone D., Contini G., Zema N., Irrera S., Stener M., Di Tommaso D., Decleva P., Prosperi T. 2009, Conformational effects in photoelectron circular dichroism of alaninol *ChemPhysChem* 10 1839-46.
- [28] Catone D., Turchini S., Contini G., Prosperi T., Stener M., Decleva P., Zema N. 2017, Photoelectron circular dichroism of isopropanolamine *Chem. Phys.* 482 294-302.

- [29] Van Leeuwen R., Baerends E.J. 1994, Exchange-correlation potential with correct asymptotic behavior *Phys. Rev. A* 49 2421-31.
- [30] Turchini S., Catone D., Zema N., Contini G., Prosperi T., Decleva P., Stener M., Rondino F., Piccirillo S., Prince K.C., Speranza M. 2013, Conformational sensitivity in photoelectron circular dichroism of 3-methylcyclopentanone *ChemPhysChem* 14 1723-32.
- [31] Diviacco B., Bracco R., Millo D., Walker R.P., Zalateu M., Zangrando D. 1999, Development of elliptical undulators for ELETTRA *Proceedings of the IEEE Particle Accelerator Conference* vol 4 pp. 2680-2.
- [32] Polack F., Lagarde B., Idir M., Cloup A.L., Jourdain E. 2007, Variable Groove Depth Gratings and their Applications in Soft X-ray Monochromators *AIP Conference Proceedings* vol. 879 (AIP) pp 639-42.