PECD study of a single conformer molecule: a critical comparison of experiment and theory

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Abstract

In this work we address a specific experimental and theoretical quest on the influence of a conformational population in the modeling of PhotoElectron Circular Dichroism spectroscopy. In the last two decades PECD revealed a rich and complex phenomenology in molecular processes with an unprecedented insight, especially in molecular geometry sensitivity. Since the early development of this spectroscopy, theory pointed out the importance of conformer influence on the PECD, in particular the rotation of methyl groups were surprisingly found responsible of a strong modulation of the PECD signal. Here to advance understanding the effect of rotations we chose to study norcamphor, a single conformer molecule, as a benchmark for the PECD comparison between experiment and theory at the Density Functional and Time Dependent Density Functional Theory level. The excellent agreement between experimental data and theory for norcamphor sheds light on the influence of rotations and gives a solid explanation for the just qualitative agreement in the PECD of camphor, where three methyl groups are added to the same molecular structure.

Introduction

Most organic molecules present a floppy structure amenable of interconvertible bond rotations if the local minima of the potential corresponding to the conformer configurations are populated in accordance with an equilibrium distribution. The presence of conformers is also reported for supersonic molecular beams due to non-thermodynamic fast cooling that can trap conformers in the minimum of low thermal barriers. Conformers play a role in chemical reactivity [1] due to the conformation-dependent electrostatic properties in the long-range interaction potentials. Moreover, with the rise of femtochemistry[2], the possibility of shaping the excited wavepacket to control the intramolecular dynamics opens new perspective to realize selective reaction pathways not accessible to the reaction at the molecular ground state. For this reason it would be desirable to perform a spectroscopic characterization of conformational effects in and out of equilibrium states. Nevertheless, if there is, on one hand, a steep rise in exploring new possibilities of enhancing conformational effects, on the other hand the spectroscopic characterization of a mixture of conformers lags behind. In absorption and photoelectron spectroscopy very often the effects of conformations do not significantly change the spectra features because cross sections and ionization energies[3] are scarcely affected by the conformer geometry and generally result in broadening within the total experimental resolution difficult to analyze. There are of course notable exceptions, as is the case of proline, where two sets of conformers can be distinguished by significantly different ionization energies, which has been thoroughly studied [4,5,6,7]. Resonant two-photon ionization (R2PI) is generally more successful to provide the conformational analysis and to characterize the low-energy conformers formed in the supersonic jet expansion[8]. Vibrational Circular Dichroism also displays a selective sensitivity to non-mirror image isomers[9].

In the last two decades a new approach for conformer study of chiral molecules was explored by means of PhotoElectron Circular Dichroism (PECD) that is an extension of classical UV-IR circular dichroism applied to VUV-Soft X-ray range where photoionization is present. The final state is a photoelectron with defined kinetic energy and momentum, allowing us to measure circular dichroism as a two dimensional dispersion, while circular dichroism in absorption is only measured as a function of the photon energy.

PECD has been measured in almost every sample target compatible with photoelectron spectroscopy, effusive and supersonic molecular beams in the gas phase, and thin films. The asymmetry has the same order of magnitude for valence and core PECD, and it is one order of magnitude larger than the absorption one, because the matrix element is at the electric dipole level[10]. Moreover, PECD has been measured in PhotoElectron PhotoIon Spectroscopy[11121314], photoelectron–Auger electron coincindence[15], resonant photoemission [16], multiphotonics photoelectron spectroscopy[17], femtosecond time resolved pump-probe experiments[18].

Since the beginning it was clear that PECD is extremely sensitive to conformer geometry[19,20] and this result turned out to be ambivalent. On the one hand PECD reveals itself to be a powerful spectroscopy capable of detecting elusive electronic and structural properties, on the other hand this sensitivity deeply challenges the theoretical modeling. The dependence of PECD on tiny distortion of geometry is attributed to the partial wave interference of the form $\sin(\eta_l - \eta_{l'})$ in the matrix element[21], where η_l are the generalized phase shifts of the asymptotic wave of photoelectrons for a non-central potential and *l* and *l'* are the angular momenta. For phase shift of the same order of magnitude the sine can rapidly change sign. It is worth noticing that classical photoemission depends on the cosine of the difference of the phase shifts and near zero is almost constant.

We underline that the rich and complex oscillatory behavior stemming for each state of the molecule represents a serious benchmark for theory. To better focus the aim and results of our work we summarize the results so far achieved in the study of conformers by PECD. Comparison between valence band spectra and theory in methyl-oxirane molecule showed an excellent agreement between LCAO–B spline theory[22] and experiment[23,24]. In a subsequent theoretical work it was focused the effect of conformational geometry on PECD. The most dramatic variation is related to the rotation of the methyl group of methyl-oxirane with variation of intensity and sign[25].

The same behavior is reported even for core levels, where the picture of a local character of the initial state would suggest a less intense effect. However, the work on conformation of methyl-oxirane confirms the previous result: performing a Boltzmann average over conformations, the obtained dispersion is reasonably close to that of the equilibrium geometry used for the previous work.

At this point the most urgent quest is how much is reliable the equilibrium geometry in presence of rotations? Subsequently, if the accuracy of the calculations in the case of the equilibrium geometry is not satisfactory, how to efficiently include the effect of the conformers? The cases of some organic molecules studied gave us some hints of interpretation. In the case of alaninol[26] we tried to interpret the data with the population at room temperature formed by the two conformers belonging to the most representative population at equilibrium. For some states we successful improved the agreement considering the presence of the second conformer. A PECD study of the valence band of 3-methyl-ciclopentanone[27] revealed a change in the PECD spectra heating the molecular gas at a temperature of 370 K. On the basis of a two conformers population analysis we found a good agreement in the comparison between theoretical predictions and experimental data of the difference of the PECD spectra taken at 370 K and room temperature (300 K). The agreement of the difference of the spectra taken at the above mentioned temperatures is better than that of the terms of the difference. Our interpretation was that in this case the subtraction of the PECD taken at different temperatures lifted the rotating groups contribution and the result was closer to the difference of the calculations at equilibrium geometry. Similar conformational effects were observed for alanine[11,28] and proline[29].

We planned an *experimentum crucis* choosing (+)-(1*S*,4*R*)-norcamphor (Figure 1), a molecule with a single conformational geometry. Norcamphor (2-Norbornanone, Bicyclo[2.2.1]heptan-2-one) might be thought as the structural parent compound of the large bornane family whose more versatile chiral compound is the naturally occurring bicyclic ketone (+)-(1*R*,4*R*)-camphor, differing from norcamphor by the presence of two methyl groups bonded at the C7 atom and one methyl group substituting the hydrogen bonded to C1, adjacent to the carbonyl group. The multiple site reactivity of the bornane skeleton and its rigidity has made these molecules highly useful in different fields as the introduction of chiral groups into pharmacologically active molecules[30] and in enantioselective hydrogenation[31]. Finally norcamphor has been experimented as a suitable chemical for rare functionalisations at carbon of the bornane moiety that provide an efficient approach for the preparation of important norcamphor scaffolds[32].

The experimental PECD of camphor was carefully studied [33,34] by comparison with two different state of the art theoretical methods Multiple Scattering-Xa[35,36] and LCAO B-spline. The outcome of both calculation methods is in accord and describes qualitatively the experimental dispersion for the Highest Occupied Molecular Orbital (HOMO). Our aim is to find evidence whether the average on conformational rotamer configurations distorts PECD calculation at the equilibrium geometry. The idea at the heart of the experiment is to study norcamphor to suppress the effects of the rotamers and to critical compare the outcome of the theory with the experimental results.

At last it is worth to mention that vibrations can also affect PECD via the ion displacement. Actually, a dramatic breakdown of the Franck-Condon (FC) approximation was found for the valence band of methyl-oxirane molecule[37]. Apart the obvious consideration that vibrations are related to different geometrical configurations, the complex nature of the matrix element, together with the consideration of pseudo-asymmetries, originates an outcome of the sum of the contributions extremely sensitive to tiny phase change between them. Indeed, the current landscape, supported by theoretical work[38], points out that weak FC transitions associated with small ion displacements are the transition more amenable to break the FC approximation. Consequently, since in unresolved PECD the transition with large FC factors are more weighted in the overall signal, it seems to be safe to interpret in this way the success of vibrational unrestricted PECD calculations, although it is not possible to exclude violations as a result of a more complex behavior[39]. Clearly a final goal of theoretical simulations will include accurate treatment both of conformational flexibitlity and of remaining vibrational modes.

In PECD data analysis each i-th electronic state of the molecule gives rise to a dispersion as a function of the photoelectron kinetic energy. Phenomenologically PECD is described by three dynamical parameters in the angle resolved differential cross section of the photoelectrons. In the following the equation for elliptical polarized light is reported:

$$I \propto \frac{\sigma(\omega)}{4\pi}\left[1-\frac{1}{2}\beta(\omega)P_2(\cos\theta_z)+\frac{3}{4}S_1(\omega)\beta(\omega)(\cos^2\theta_x-\cos^2\theta_y)+m_r S_3(\omega)D(\omega)P_1(\cos\theta_z)\right]$$

where $\sigma(\omega)$ is the isotropic photoelectron cross section, $\beta(\omega)$ is the asymmetry parameter and $D(\omega)$[10] is the dichroism parameter, P_i is the Legendre polynomial of i-th degree, S_1 and S_3 are the Stokes parameters related to linear and circular light polarization vector components, respectively, m_r is +1 or -1 for left and right circular polarization, θ_x, θ_y, θ_z are the angles formed by the photoelectron momentum and the axis of the polarized light, z is oriented along the wavevector of the radiation, and y and x are the major and minor axis of the elliptically polarized light, respectively. For clarity we remind that the D parameter is also named b_1[21] in the current literature.

Experimental section

The experiment was carried out at the Circular Polarization beamline (ELETTRA-Trieste (Italy))[40]. The circularly polarized light was provided by an Electromagnetic Elliptical Wiggler. We used a Normal Incidence Monochromator in the photon energy range of 15 – 32 eV for valence band and a Spherical Grazing Monochromator in the energy range of 295-345 eV for C 1s core level. In the considered energy range the circular polarization ratio varied from 60% to 80% for valence band measurements and was about 80% for C 1s core level. The PECD spectra were measured using a VG, 6-channel, 150 mm hemispherical electron energy analyzer, placed at θ_z =54.7°. The total resolution of the photoelectron spectra was about 200 meV.

(+)-(1*S*,2*R*,4*R*)-endo-2-Norborneol was purchased from Sigma-Aldrich. Optical rotations were measured on a Perkin Elmer Model 241 polarimeter. TLC's were performed on Polygram® Sil

G/UV254 silica gel pre-coated plastic sheets (eluant: light petroleum-ethyl acetate, 4 : 1). Flash chromatography was run on silica gel 230-400 mesh ASTM (Kieselgel 60, Merck).

(+)-(1*S*,4*R*)-norcamphor was synthetized by oxidation of (+)-(1*S*,2*R*,4*R*)-*endo*-2-norborneol following the procedure indicated in the literature[41]. (+)-*endo*-2-Norborneol (1.0 g, 8.9 mmol) was dissolved in 50 mL of anhydrous dichloromethane at 0 °C under Ar, 3Å molecular sieves (9 g) and pyridinium chlorochromate (6.0 g, 27.8 mmol) were added and the suspension was vigorously stirred for 3 h. Diethyl ether (100 mL) was added and after decantation, the solution was filtered through a glass filter filled with Silica Gel with 13% calcium sulphate (Fluka). The black residue was washed three times with diethyl ether and the combined filtrates were carefully concentrated at rotavapor. The resulting (+)-(1*S*,4*R*)-2-norbornanone was purified by flash chromatography (eluent: light petroleum:diethyl ether, 9:1), 40% total yield with $[\alpha]_D^{25}$ = +26.3 (c 1.0, $CHCl_3$) ($[\alpha]_D^{25}$ =+29.1 (c 1.5, $CHCl_3$)[42], $[\alpha]_D^{25}$ = + 29.8 (c 1.1, $CHCl_3$)[43], $[\alpha]_D^{25}$ = +27.2 (c 1.8 $CHCl_3$)[44]); all spectroscopic data are identical to a commercially available sample of racemic 2-norbornanone.

To acquire data in linearly polarized radiation a commercially supplied (purity 98 %, Sigma–Aldrich) racemic mixture of norcamphor was used. The norcamphor was introduced into an effusive source exploiting room temperature vapor tension.

To ease the comparison between norcamphor and camphor we reversed the sign of the dichroism of (1*S*,4*R*)-norcamphor to obtain the PECD of (1*R*,4*S*)-norcamphor enantiomer.

The pressure during the measurements was about 5×10^{-6} mbar. PECD measurements were recorded alternating the helicity of the radiation at 0.05 Hz frequency. The complete description of the experimental D extraction and analysis and the correction for the ellipticity of light present at the Circularly Polarization beamline are reported elsewhere[26].

Computational methods

The calculations of the PECD spectra were performed on the grounds of Density Functional Theory (DFT) and Time-Dependent Functional Theory (TDDFT)[22]. The LB94 exchange-correlation potential[45], which provides the correct asymptotic behavior of the Coulomb tail for continuum calculations, was chosen. The ground state density, which defines the Kohn-Sham Hamiltonian, was obtained from an SCF calculation with a DZP basis employing the ADF program[46].

The B-spline LCAO method was employed to calculate the photoelectron wave function in the continuum[47]. It is based on the use of basis functions of the type

$$\chi_{ilm} = 1/r\, B_i(r)\, Y_{lm}(\theta,\varphi)$$

products or radial B-spline functions times spherical harmonics. A single center expansion, with long range and large angular momentum is supplemented by short range functions centered on all nuclei, in the spirit of the LCAO approach. Such basis affords a numerically very accurate solution of both bound and continuum orbitals. A maximum angular momentum L_{max}=15 and an expansion up to 25 atomic units was employed in the present calculation, giving convergent results for the photoionization observables

Ionization energies were separately computed to confirm assignment of the spectrum with the OVGF approach and the Gaussian program[48].

Results and discussion

Figure 2 reports the unpolarized valence band spectrum measured at photon energy 23.2 eV together with the OVGF ionization energies. The HOMO is well resolved and is identified with the first peak. The HOMO is mainly based on O 2p lone pair with a significant contribution of 2p of C adjacent atoms. Mulliken population reports for HOMO most significant contribution 55% 2p O, 8% 2p C3 (CH_2), 10% 2p C1(CH).

The isolated HOMO peak allows us to neglect any mixing of others molecular orbitals in the experimental data analysis and, consequently, to avoid to convolve theoretical data with a poor reliable assumption about energy position, intensity and width.

Figure 3 displays the experimental valence band D dispersion of the HOMO of (-)-(1*R*,4*S*)-norcamphor as a function of kinetic energy along with the DFT and TDDFT calculated dispersion.

The theoretical D parameters are shifted 1.6 eV towards higher kinetics energy to align the minima, this phenomenological shift is justified by the attractive behavior of the LB94 functional. The D parameter is always negative and the shape of the dispersion is a valley with a marked minimum at 9 eV and the full shape presents an excellent quantitative agreement for both DFT and TDDFT. In particular, TDDFT dispersion is closer to the experimental one and displays a more structured behaviour; the calculated dispersion is also in agreement with a fine structure of the experimental dispersion in the range 12 – 14 eV. This result is of paramount importance because it straightforward addresses the issue we posed at the beginning, the absence of rotating groups has a remarkable influence on the comparison between calculation at the equilibrium geometry and the experiment.

To better understand this crucial aspect, we compare our results with those obtained in the case of the HOMO of camphor and reported in the literature[34]. Figure 4 displays a comparison between the HOMO D dispersion of (+)-(1*R*,4*R*)-camphor (data digitalized and plotted from ref. 34) and (-)-(1*R*,4*S*)-norcamphor in the energy range of 5-20 eV; to make the comparison easier, camphor data were multiplied by a factor 2 and shifted 2 eV towards lower kinetic energies to align the minima. The HOMO dispersions of the two molecules present the same sign and profile; the same asymmetric shape around the minimum is present with a longer tail towards higher kinetic energies. This result clearly proves from a phenomenological point of view that structural similarities are reflected on the PECD dispersion, and we believe that the same sign and the resemblance of the two minima are an indication of the similar molecular structure.

In the camphor HOMO study both MS-Xa and B-spline theories reproduce in a satisfactory way the shape of the experimental dispersion in the intermediate energy range, in particular the oscillation around minimum at 12.2 eV. The MS-Xa also follows the oscillations closer to thresholds. Preliminary calculation with the B-spline code shows that this behavior is strongly dependent on the choice of the local potential. At the quantitative level comparison of the sign and intensity of the theoretical and experimental dispersion fails in some region of the investigated range, in fact the sign of the experimental data is always negative while the theoretical values oscillates between positive and negative values. The different agreement of the theory of norcamphor and camphor, together with the close similarity of a region of the dispersion, directly indicates that the influence of the rotating methyl groups cannot be considered negligible in the theoretical modeling of the experimental data.

To strengthen this consideration we remind that a similar conclusion was drawn for the PECD of the structural isomers alaninol and isopropanolamine[49], where a strong resemblance between alaninol and isopropanolamine was found for the experimental HOMO and HOMO-1 dispersion, in spite of a qualitative agreement with DFT B-spline calculations. The calculations at the equilibrium geometry do not fully reproduce experimental data; nevertheless, experimental dispersion exhibit similar shapes.

Although at the present stage it is not possible to convert the line of reasoning exposed above into a quantitative one, like a data analysis procedure or a prescription in the calculation, we believe it grasps an important behavior of the PECD conformational sensitivity.

The findings of the C 1s PECD of norcamphor were also studied. Figure 5 reports the 1s core PES core levels acquired at 320 eV of photon energy. The spectrum is composed by two separate peaks that are assigned to the C 1s of the carbonyl group (IE=293.0 eV) and to the other alkylic C 1s contributions (IE=290.6 eV). The PECD measurements were performed on the carbonyl related peak to investigate a single atomic C 1s signal. Figure 6 shows the comparison between experimental data and theoretical DFT and TDDFT calculations. The calculations were shifted 1.2 eV towards higher kinetic energies. The calculations are in good agreement with the descendent part of the dispersion and also the shoulder. Although for kinetic energies greater than 20 eV the agreement is hampered by the poor signal to noise ratio, the calculated dispersion is in satisfying agreement close to the experimental error bar.

In the literature both MS-Xa and B-spline LCAO reproduce well core levels also in molecules where the valence band agreement is qualitative or not satisfactory. The prevalent atomic nature of

C 1s core level provides a sharply defined initial state, as for the valence band the theory assignment is more dependent on the chosen theoretical method. This simplification is certainly helpful in the accuracy of the theoretical calculation. Indeed, conformational geometry effects on the PECD have different origin in valence band and in core level states. Despite the local character of the core level excitation, the sensitivity is neither fully local nor fully extended, as in the case of valence band, and the balance between local excitation and the whole molecular potential probed by photoelectrons gives to the core level PECD a sufficient sensitivity to the molecule geometry. As reported above, in methyl oxirane C 1s calculations the rotations of the methyl group exert their influence also for C atoms not directly connected with methyl groups[25].

Moreover, it is important to note that the pure p-wave continuum generated by core 1s ionization limits the number of accessible angular momentum channels of the photoelectron continuum wavefunction, and PECD directly probes the rescattering generated by the neighboring atoms.

It is worth noticing that for camphor the experimental C 1s PECD dispersion of the carbonyl group is well reproduced by MS-Xa theory[50]. To qualitatively understand the different agreement of the calculations for the valence band and C 1s core of camphor, it could be likely that the methyl groups are far enough to have a tiny influence on the photoelectron wavefunction in the proximity of the C absorbing atom and the effect of the rotations could be considered negligible, although it is not possible to rule out that the Boltzmann average of the configurations approximates the equilibrium calculation. As reported in figure 4 for the HOMO dispersion, Figure 7 shows the experimental D dispersion for the C 1s of the carbonyl group for (+)-(1*R*,4*R*)-camphor and (-)-(1*R*,4*S*)-norcamphor. Camphor data are extracted and plotted from ref. 50, the reported asymmetries were divided by cos(54.7°) to obtain the D parameter. As previously reported for the HOMO, there are also similar features in the C 1s dispersion, the descendent part and the negative region of the minimum have the same shape, although the minimum is not clearly outlined for the norcamphor. The zero crossing of the norcamphor stays at higher electron kinetic energies with respect to the camphor one.

From the comparison of experiment and theory in norcamphor and camphor we outline general conclusions that help us to understand some open issues on PECD. State of the art DFT and TDDFT quantum theory at the equilibrium geometry can correctly describe PECD of molecules in absence of rotating groups. Rotamers do exert influence on PECD and the average on the configurations can sort out a theoretical dispersion different from the dispersion calculated at the equilibrium geometry. Another important result is that the comparison of camphor and norcamphor experimental HOMO dispersions shows that there are similarities, due to the identical skeleton structure. When equilibrium geometry calculations are employed in molecules where are present conformers and/or rotamers the outcome can differ from the experimental dispersion in a not predictable way. However, it is also evident from the previous studies that equilibrium geometry calculations always describe essential features, especially in determining maxima and minima of the D dispersion as a function of kinetic energy, and can be posed as a solid foundation of the PECD spectroscopy. Due to possible slight energy misalignment between experimental and calculated PECD profiles, it is important that the experimental data cover a substantial energy region, at least several eV, beyond the threshold region.

Conclusions

In conclusion our work confirmed in a straightforward way the relation between PECD dispersion and tiny conformational effects such as rotations of functional groups. State of the art method of calculations such as B-spline approximation is capable of fully reproducing the PECD dispersions of the HOMO of a mono-conformer molecule.

In this context, the future effort will be devoted to incorporate a treatment to take into account the distribution of the conformational geometries, providing an efficient choice of the ensemble of configurations to avoid the unsustainable burden of a brute-force calculation.

A fair trade off between calculation accuracy and number of configurations is desirable to avoid to waste calculation time in a not needed accuracy or oversampling the configurations. A subsequent question that cannot be ducked is the influence of the density functional on PECD calculations; in this and the previous studies performed by the authors the density functional LB94 was the preferred choice due to the correct tail for continuum calculations, but it could be of paramount importance to explore the correlation with other functionals. PECD intertwines structure and electronic properties and this is a gift and a curse because it is not easy to isolate and recognize which approximation is not corresponding to the actual description of the molecular system. In this perspective the effort of the last two decades gave a solid foundation but loose ends still remain to fully harness the power of PECD.

Given the importance of theoretical simulations to extract maximum information from experimental data, the development of predictive computational tools is mandatory. The typical size of chiral molecules, and possible conformational averaging, makes higher level treatments hardly affordable, and spurs the optimization of local and possibly nonlocal single particle potentials, especially for the lower kinetic energy region where important signatures of PECD are found. To this end a set of accurate experimental data on rigid systems, to avoid ambiguities in conformational distribution, is highly desirable to serve as benchmark for theoretical development.

Although the circularly polarized core level spectroscopy is traditionally rooted in the X-ray Magnetic Circular Dichroism, the increasing interest in PECD fosters the demand for chemical physics investigation of chiral molecules.

Exploiting the Core level PECD, profiting of the reduced number of angular momentum channels and the local nature of the excitation, could be of practical importance to access both electronic and structural properties of chiral molecules in the gas phase.

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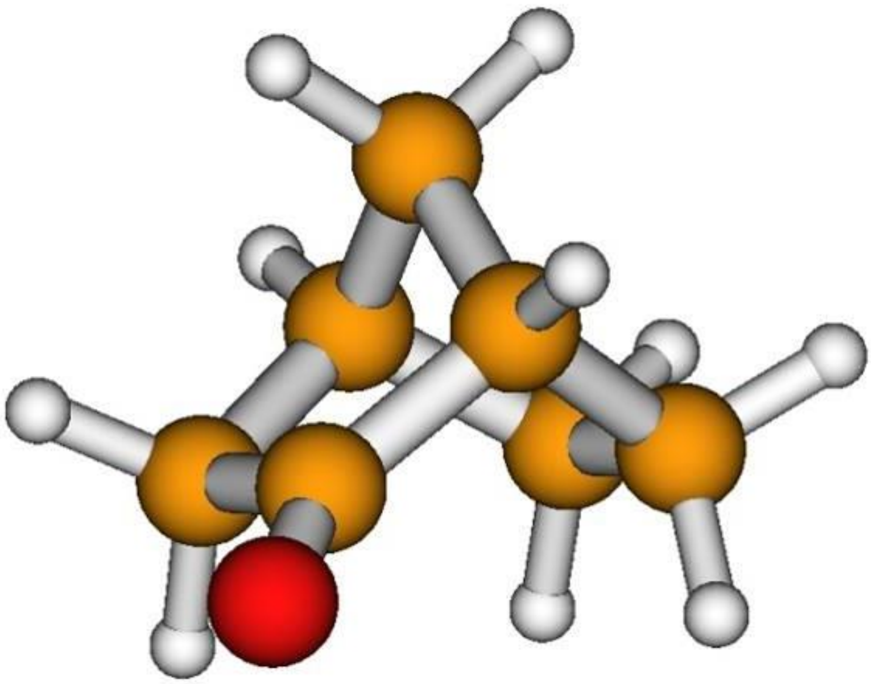

Figure 1: Sketch of the (+)-(1*S*,4*R*)-norcamphor molecule

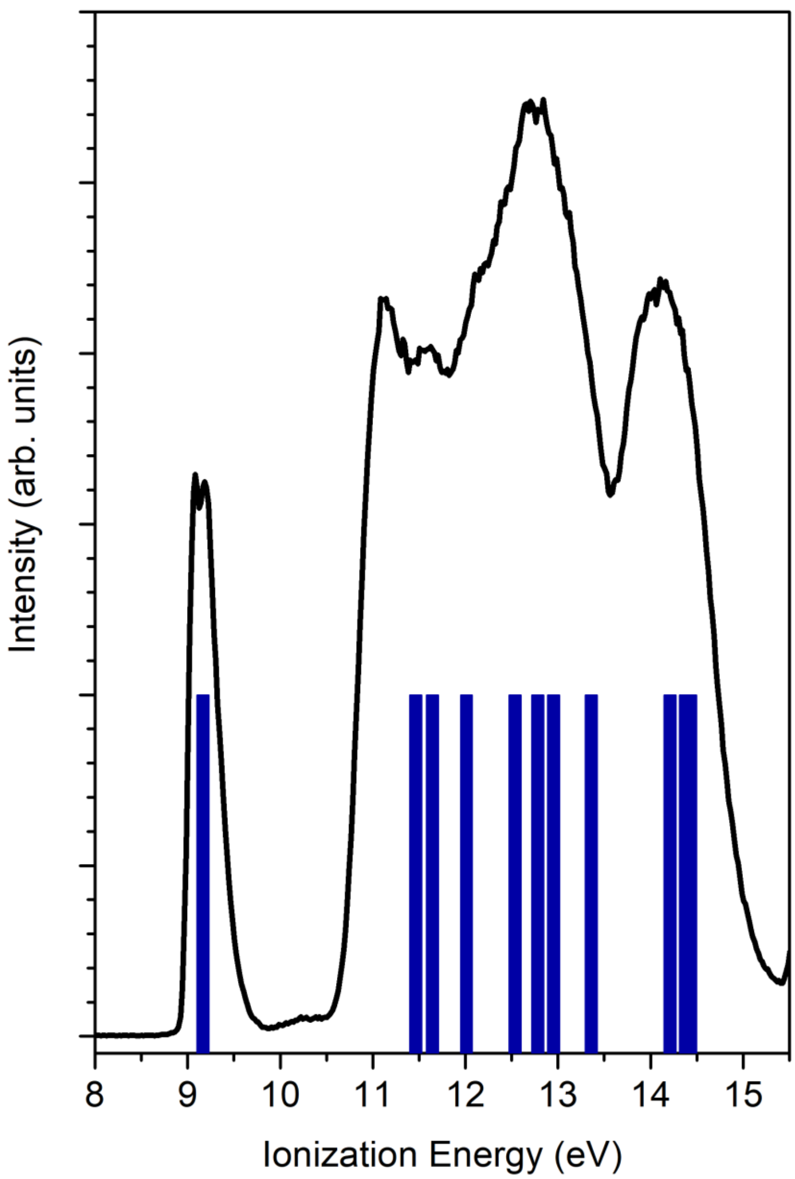

Figure 2: PES of norcamphor (black line) together with OVGF ionization energy calculation (blue sticks). The calculated energies are aligned at the experimental HOMO ionization energy (ΔE=+0.25 eV). The excitation photon energy is 23.2 eV.

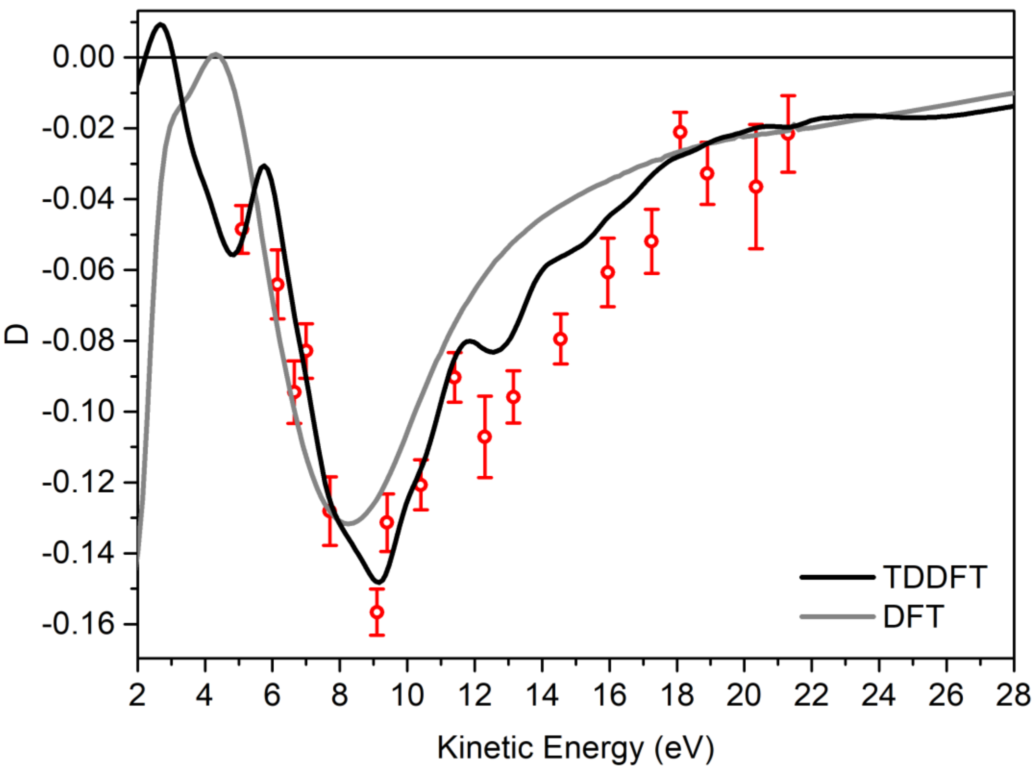

Figure 3: Experimental dichroism parameter D (red circles) for (-)-(1*R*,4*S*)-norcamphor HOMO along with the DFT (grey line) and TDDFT (black line) calculations. The theoretical data are shifted 1.6 eV toward higher kinetic energy to take into account the attractive nature of LB94. The (1*S*,4*R*)-enantiomer data have been negated to obtain (1*R*,4*S*)-enantiomer D.

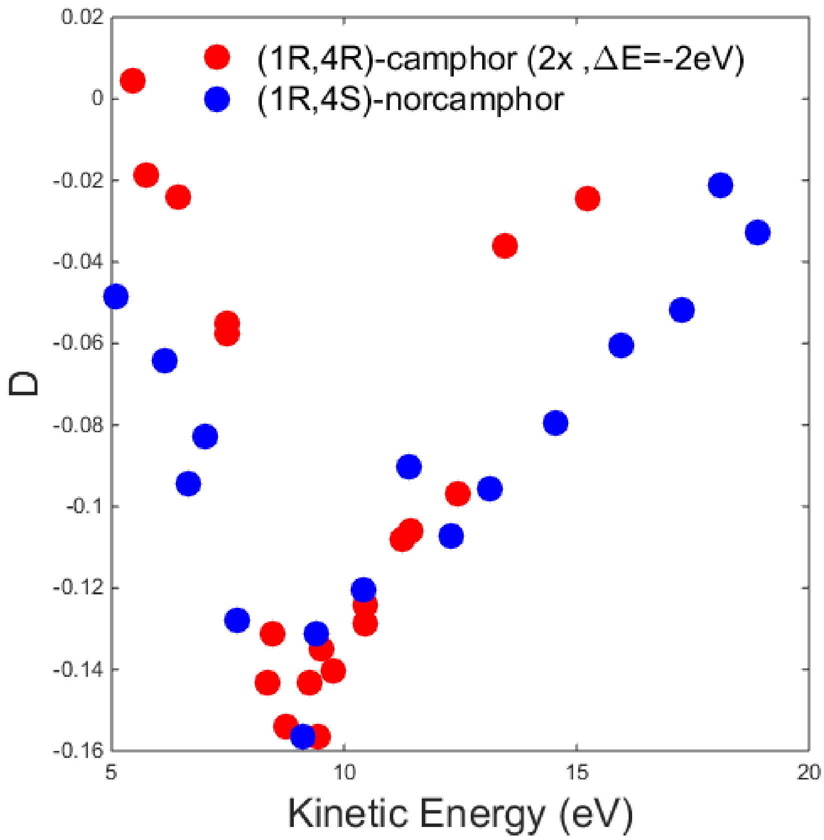

Figure 4: Experimental D dispersions of HOMO of (+)-(1*R*,4*R*)-camphor (red dots) and (-)-(1*R*,4*S*)-norcamphor (blue dots). The camphor HOMO dispersion has been multiplied by a factor 2 and shifted 2 eV toward lower kinetic energies to facilitate the visual comparison. Camphor data are digitalized and plotted from ref. 34. Error bars are omitted. The (1*S*,4*R*)-norcamphor data have been negated to obtain (1*R*,4*S*)-norcamphor D.

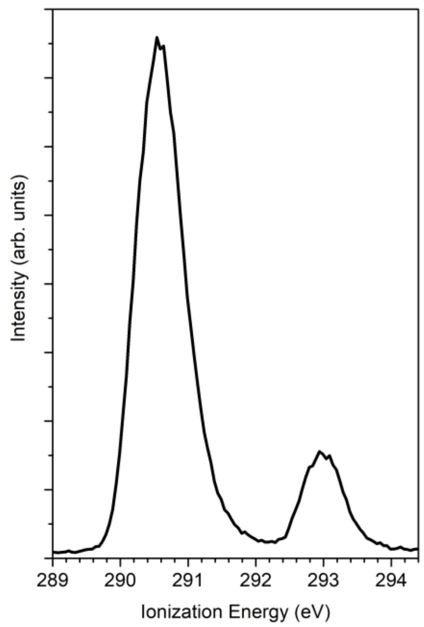

Figure 5: PES C 1s of norcamphor taken at photon energy 305 eV. The binding energy of the C atom of the carbonyl group is 293 eV.

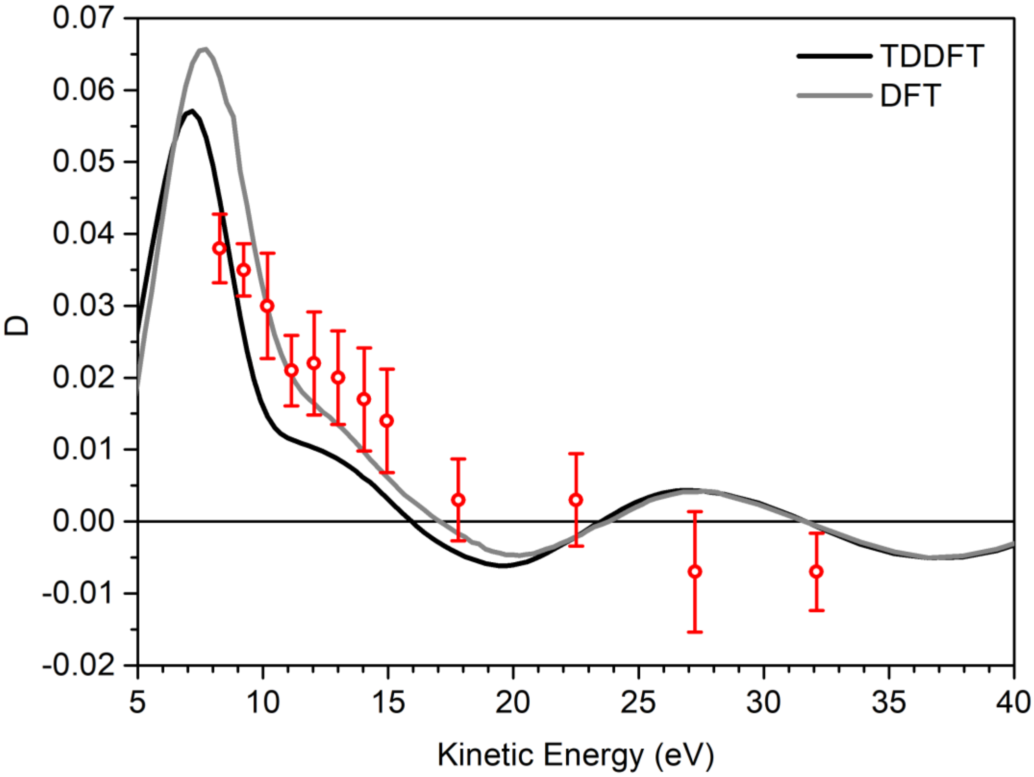

Figure 6: D experimental dispersion (red circles) of C 1s belonging to the carbonyl group of (-)-(1*R*,4*S*)-norcamphor, DFT (grey line) and TDDFT calculation (black line). To compensate the attractive nature of the LB94 a shift of 1.2 eV of kinetic energy was applied to the calculated D dispersions. The (1*S*,4*R*)-enantiomer data have been negated to obtain (1*R*,4*S*)-enantiomer D.

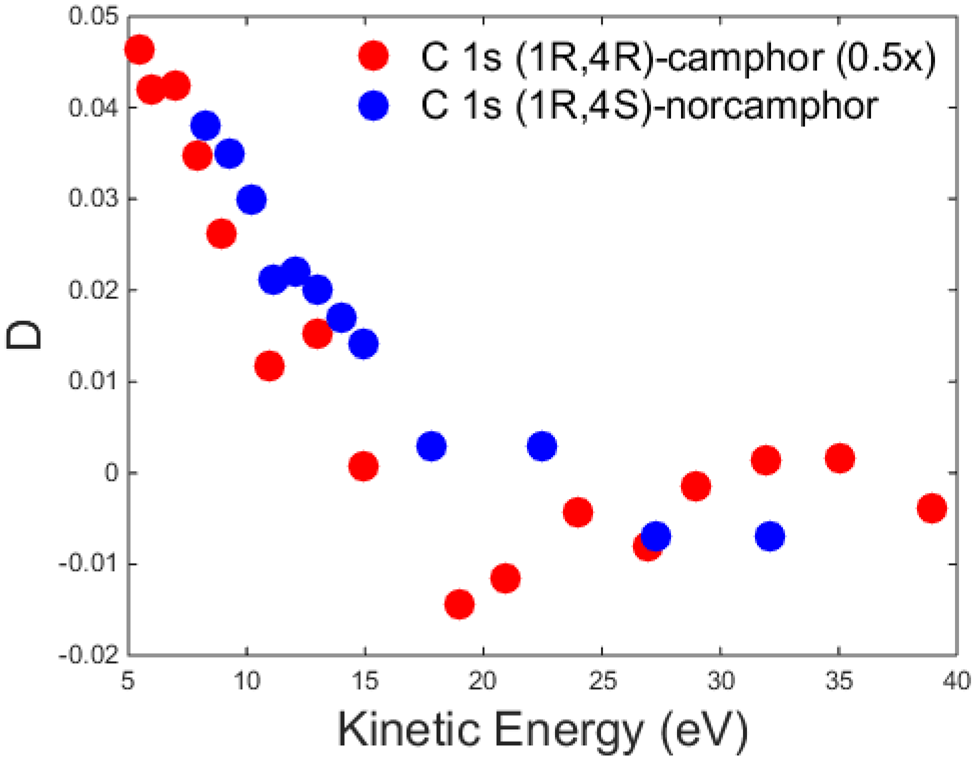

Figure 7: Experimental D dispersions of C 1s of (+)-(1*R*,4*R*)-camphor (red dots) and (-)-(1*R*,4*S*)-norcamphor (blue dots). The camphor C 1s dispersion has been multiplied by a factor 0.5 to facilitate the visual comparison. Camphor data are extracted and plotted from ref. 50, the reported asymmetries were divided by cos(54.7°) to obtain the D parameter. Error bars are omitted. The (1*S*,4*R*)-norcamphor data have been negated to obtain (1*R*,4*S*)-norcamphor D.