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Universality of photoelectron circular dichroism in the photoionization of chiral molecules

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Abstract

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

1. Introduction

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

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

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

Here we first show that PECD is rather insensitive to the electronic character and oscillator strength of resonances involved in MPI of limonene in the UV range. Switching to fenchone samples, we further demonstrate by increasing the laser intensity and wavelength that PECD exists in very high-order ATI peaks, up to the tunneling ionization regime. We interpret this universality using a classical analysis of the ionization process, which gives an intuitive picture of the ongoing electron dynamics.

2. PECD measurements

The experiments were conducted using the Aurore laser at CELIA, which provides 7 mJ-25 fs pulses at 800 nm with a 1 kHz repetition rate. The laser pulses are frequency doubled in a 200 μ m thick type I BBO crystal, whose orientation was adjusted to tune the central frequency of the pulses between 396 nm and 409 nm. For long wavelength experiments, an optical parametric amplifier (HE-TOPAS) was used to convert pulses of 4.5 mJ at 800 nm to 500 μ J ones at 1850 nm with ~100 nm FWHM bandwidth. The pulses were focused by a 50 cm focal lens into a velocity map imaging spectrometer. The chiral molecules were heated in an oven and introduced as a continuous flow through a 200 μ m capillary 7 cm away from the laser focus. The pressure in the interaction chamber was typically 2 × 10⁻⁶ mbar, with a background pressure of 5 × 10⁻⁸ mbar. The PECD was measured by recording the photoelectron spectra with left (LCP, p = +1) and right (RCP, p = -1) circular laser polarizations, defined from the point of view of the observer. In order to remove the influence of slow drifts in the experiments, the polarization state was switched every 10 seconds. Typically 7 × 10⁵ laser shots were accumulated to obtain each of the LCP and RCP images.

The velocity map imaging spectrometer measures 2D projections of the 3D photoelectron angular distributions (PADs). The PAD can be decomposed as a sum of Legendre polynomials $S_p(E, \theta) = \sum_{i=0}^{2N} b_i^p(E) P_i(\cos(\theta))$ where $p = \pm 1$ is the light helicity, *E* is the photoelectron energy, θ its ejection angle with respect to the light propagation direction, and *N* the number of ionizing photons. The even expansion coefficients $b_{i=2n}^p(E)$ fulfill $b_{i=2n}^{+1}(E) = b_{i=2n+1}^{-1}(E)$ while $b_{i=2n+1}^{+1}(E) = -b_{i=2n+1}^{-1}(E)$ for the odd ones (see e.g. [12]). The former ones are therefore obtained by least-square fitting the experimental projection of the averaged PAD, $\overline{\text{PAD}}(E, \theta) = (S_{+1} + S_{-1})/2$, while the odd coefficients are retrieved from the fit of the dichroism image $(S_{+1} - S_{-1})/2$ [17]. The PECD is then defined as PECD $(E, \theta) = 2(S_{+1} - S_{-1})/(S_{+1} + S_{-1})$, and the angular-integrated $\overline{\text{PAD}}$ provides the photoelectron spectrum (PES) $b_0(E)$.

2.1. MPI- and REMPI-PECD

2.1.1. Role of resonant enhancement in REMPI-PECD

First, we studied the photoionization of (4R)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene, referred to as (+)-limonene, by absorption of 3 photons where the central wavelength λ was varied between 409 and 396 nm, at intensity $I \sim 10^{12}$ W cm⁻². Figures 1(a)–(c) shows the measured PADs, and figures 1(d)–(f) the PECD. Using the ionization potentials IP $_{0 \rightarrow i}$ from the ground state of limonene (0) to the ground (0) and excited (i) states of the associated cation given in [18], we calculate the expected positions of the $3\hbar\omega(0 \rightarrow 1)$ and $3\hbar\omega(0 \rightarrow 0)$ ionization pathways, depicted as continuous circles. Within the Koopmans approximation, they correspond to the removal of one electron from the highest occupied molecular orbital (HOMO, outer circle) and the HOMO-1 (inner circle) respectively. The most striking feature is a strong change of the intensity of the HOMO peak as the photon wavelength decreases: the signal increases by around one order of magnitude when the wavelength changes from 409 to 396 nm. In addition, the angular distribution of the photoelectrons ejected from the HOMO is modified, with a sign change of the b_2 Legendre coefficient from positive to negative. This indicates a clear modification of the ionization scheme. Indeed, changing λ from 409 to 396 nm brings different Rydberg states of limonene into resonance with $2\hbar\omega$ absorption from the HOMO: from 3s to the lowest 3p state according to the assignment made in [18], or from the lowest 3p to the intermediate 3p state according to [11]. Comparison of figures 1(d) and (f) unambiguously shows that similar PECDs are obtained at both wavelengths for the HOMO, with the same sign and in the 4% range. Furthermore, (2 + 1)-REMPI at 420nm, involving vibrationally excited 3s state as the intermediate step, also led to $\sim 4\%$ PECD [11]. All of this proves that PECD is not sensitive to either the electronic character or the strength of the intermediate resonance involved in UV-MPI of limonene. Further investigations on different systems are required to determine whether limonene is an exceptional case or if this is a general trend of REMPI-PECD.

2.1.2. Vibrational features in MPI-PECD

A more advanced assignment of the different structures can be performed by plotting the Legendre coefficients (figures 1(g) and (h)). The lower peak in the PES is associated to the $3\hbar\omega$ (0 \rightarrow 1) pathway which involves the 3s(HOMO-1) resonance encountered around 6.1 eV [11]. As the laser wavelength increases, this peaks shifts up in energy, but not as much as expected. At 396 nm it is 0.1 eV below the expected position, which is probably a



Figure 1. MPI of (+)-limonene molecules. PADs (a)–(c) and PECD images (d)–(f) for $\lambda = 409$ (a), (d), 401 (b), (e) and 396 nm (c), (f). The light propagation axis is horizontal and the radius extends from 0 to 1.4 eV. (g), (h): PESs (shaded area) and normalized b_1/b_0 (solid line) and b_3/b_0 (dashed line) as functions of *E*, for $\lambda = 409$ nm (g) and 396 nm (h). The theoretical positions of the PES peaks are marked by k(i), as a shortcut of the notation $k/k\omega$ ($0 \rightarrow i$) employed in the text; the arrow combs refer to vibrational quanta of energy.

trace of vibrational excitation of the cation. At 409 nm the $3\hbar\omega$ (0 \rightarrow 0) pathway shows a nice maximization of the asymmetric coefficients b_1 and b_3 at the expected electron energy 0.6 eV (figure 1(g)). As the electron energy decreases, the PECD coefficients switch sign and maximize at 0.17 eV lower from the main peak (gray arrow). This 0.17 eV shifted band corresponds to one quantum of vibrational energy in the ground electronic state of the ion [18]. The detected structures are thus most likely associated to $3\hbar\omega$ (0 \rightarrow 0) ionization producing ions with some population in the $\nu = 1$ state. Signatures of vibrational excitation also show up in the $3\hbar\omega$ (0 \rightarrow 0) ionizing process at 396 nm (figure 1(h)). The PES shows a shoulder around the expected electron energy for an



Figure 2. MPI and ATI of (+)-fenchone by 402 nm pulses. PECDs for $I \sim 5 \times 10^{12}$ (a) and 4×10^{13} W cm⁻² (b). The light propagation axis is horizontal and the radius extends from 0 to 12 eV. (c): corresponding PES and MP-PECD for $I \sim 5 \times 10^{12}$ W cm⁻² (lightest shaded area) and $I \sim 4 \times 10^{13}$ W cm⁻² (darkest shaded area); the dark (blue) and light (red) thick vertical lines are the one-photon PECD values from the HOMO and HOMO-1,2, respectively, measured in [20]; the thin lines labeled k(i) indicate the positions of PES peaks expected from our calculations.

ion left in $\nu = 1$ excited state, and the associated PECD sign is again opposite to that corresponding to $\nu = 0$. The magnitude of the PECD increases to reach a maximum around E = 0.57 eV, which roughly corresponds to the electron kinetic energy release for a limonene cation in the $\nu = 2$ state. In addition electron kinetic energy effects between the $3\hbar\omega (0 \rightarrow 0)$ and $3\hbar\omega (0 \rightarrow 1)$ thresholds might also play a role. Sign reversals in PECD from vibrationally excited ions have recently been observed in one XUV-photon absorption and intepreted as a signature of non Frank-Condon transitions [5, 19]. Our present findings generalize this observation in the MPI regime and show that PECD enables resolving vibrational features invisible in PADs.

2.2. PECD in the ATI regime

We now turn to the investigation of high-order ATI by increasing the laser intensity *I* while keeping the wavelength fixed at 402 nm. We consider a different chiral species, (1S,4R)-fenchan-2-one, referred to as (+)-fenchone, in which two-photon absorption of 402 nm pulses resonantly excites Rydberg states. Figures 2(a) and (b) show the PECD images obtained at 402 nm for $I \sim 5 \times 10^{12}$ and 4×10^{13} W cm⁻², respectively. The associated PES are displayed in figure 2(c), together with the so-called multiphoton PECD defined as MP-PECD (*E*) = $\frac{1}{b_0} \left(2b_1 - \frac{1}{2}b_3 + \frac{1}{4}b_5 - \frac{5}{32}b_7 \right) [10, 12]$. This quantity corresponds to difference between electron emission in the forward and backward hemispheres, normalized by the average number of electrons per hemisphere. At low intensity, the PES presents two series of ATI peaks equally spaced by the energy of one photon, $\hbar\omega = 3.09$ eV. The two series begin at E = 0.53 and 1.57 eV, respectively. According to time-dependent

density functional theory (TDDFT) calculations of the electronic spectra of neutral and cationic fenchone⁴, these two series correspond to the ionization channels $k\hbar\omega$ (0 \rightarrow 0), with k ranging from 3 to 6, and $k'\hbar\omega$ (0 \rightarrow 1, 2), with $k' \leq 7$. Our TDDFT calculations validate the Koopmans approximation for i < 11, so that the two series can safely be interpreted as ionization from the HOMO and HOMO-1,2, respectively⁵. The angle-resolved PECD (figure 2(a)) shows that the PECD is maximum about $\theta = 0^{\circ}$ at threshold and maximizes around higher θ values as the ATI order increases. This is due to the additional absorption of photons which results in the increase of the maximum order in the Legendre decomposition. The MP-PECD from the HOMO is negative and decays from $\sim -12\%$ at threshold (k = 3) to $\sim -1\%$ for 6-photon ionization (figure 2(c)). This reflects the fact that as the electron gets more energy through sequential absorption of photons, it is less sensitive to the molecular chiral potential. The values of the PECD obtained by a single-photon XUV ionization experiments [20] are reported in the same figure. While the results are remarkably similar for the 3-photon (3 $\hbar\omega$ = 9.3 eV) and single-photon ($\hbar \omega = 9.3 \,\text{eV}$) ionization of the HOMO, the single-photon PECD switches sign above this energy, while it remains negative in the multiphoton regime. Well above threshold, the single-photon PECD is much stronger than the multiphoton one. This could be the signature of a better isolation of the HOMO contribution by coincidence electron-ion detection in the single-photon experiment, while background from other channels may decrease the multiphotonic PECD.

As the laser intensity increases, the overal value of the PECD diminishes (figure 2(b)). This is the signature of the stronger influence of the laser field on the electron dynamics compared to that of the chiral molecular potential. Deeper observation of the PECD plot reveals significant changes, especially for $E \ge 4$ eV. This can be understood by monitoring the PES in figure 2(c): it still consists of two series of ATI peaks, but they appear upshifted in energy with respect to the lower intensity case. The series that was attributed to HOMO-1,2 now maximize around the neighbor $k'' \hbar \omega (0 \rightarrow i)$ transitions, with i = 12-14 and k'' = 6-8. Interestingly, TDDFT associates i > 11 excited states of the cation to two-hole-one-particle configurations which are accessible from the ground state of the neutral through excitation + ionization processes. Similar processes, with even higher i in the range 16–20, may also come into play in the close neighborhood of the main HOMO peaks. In both cases, the juxtaposition of one-electron direct ionization and higher-order (excitation + ionization) processes leads to the observed shift of the PES peaks. It also leads to modifications of the PECD picture, inducing sign changes in the high-E range where the magnitude of the high-order ATI peaks associated to one-electron direct ionizations is low. Thus, tuning the laser intensity enables probing different responses of the molecule: the pure one-electron PECD response at low intensity, and higher order processes, beyond the Koopmans theorem, at higher intensity.

2.3. From ATI to tunnel ionization

The ionization regime is not only defined by the laser intensity but also by its wavelength. A recent study of molecular strong field ionization showed that ionization to excited cationic states was significantly suppressed if the gap between the ground and excited states was higher than the photon energy [25]. In other words, ionization from orbitals deeper than $\hbar\omega$ from the HOMO is unfavored. Since the HOMO and HOMO-1 channels are separated by ~ 2 eV, using 800 nm photons (1.55 eV energy) should enable isolating the response of the HOMO. That is what we show in figures 3(a), (b) which display the PADs obtained for $\lambda = 800$ nm and $I \sim 0.9$ and 1.2×10^{13} W cm⁻², respectively. The PADs exhibit three ATI peaks associated to 7-, 8- and 9-photon absorption, all of them leaving the fenchone cation in its ground state. The contributions of excited ionic states, mainly located about the $7\hbar\omega$ (0 \rightarrow 0) peak, are extremely weak. The peaks show a global downshift in energy with respect to the positions inferred from field-free TDDFT calculations. This is the signature of the laser-induced ponderomotive shift, which is a typical feature of non-resonant MPI. The PECD presents very significant values, reaching ~8% in figure 3(d), and exhibits repeatedly regular features associated to ionization from the HOMO in the ATI range. However, as *I* is increased to 1.2×10^{13} W.cm⁻² the PECD picture becomes blurred (see figure 3(e)). In fact these last irradiation conditions correspond to a Keldysh parameter $\gamma \sim 1.9$ which is rather close to the limiting value of 1 that signs the entrance to the tunneling regime.

2.4. PECD in the tunneling regime

This last observation led us to investigate PECD in genuine tunneling regime. We employed 1850 nm, $I \sim 4 \times 10^{13} \,\mathrm{W \, cm^{-2}}$ pulses, corresponding to $\gamma \approx 0.6$. We present in figures 3(c) and (f) the raw experimental 2D projections of the PAD and PECD. The shape of the PAD, strongly peaked about 90°, is typical of tunnel-ionized electron distributions. It extends up to energies corresponding to the absorption of more than 30

5

⁴ We have optimized the geometry of fenchone at the TDDFT level of theory, employing the GAMESS-US package [21] with a $6-311++G^{**}$ basis [22] and CAMB3LYP hybrid exchange-correlation functional [23, 24]. The same geometry has been used for the cation, yielding all necessary vetical ionization potentials IP_{0→i}. The computed IP_{0→0} is 8.74 eV, in very good agreement with the experimental one, 8.72 eV. ⁵ The penultimate (HOMO-1) and third-to-last (HOMO-2) occupied molecular orbitals of fenchone lie too close on the energy scale to be experimentally distinguished.



photons from the HOMO. There is no contribution of inner orbitals to the signal because of the exponentially decaying rate of tunnel-ionization with increasing IP. A clear PECD is observed, in the 1%–2% range. This demonstrates that PECD still persists in the tunneling regime, even high above the ionization threshold.

3. A classical outlook on PECD

In order to understand how the chiral potential succeeds in imprinting asymmetry in such a high intensity regime, we performed Classical Trajectory Monte Carlo (CTMC, [26, 27]) calculations. We focused on electron dynamics from the HOMO of fenchone, in the fixed-nuclei approximation. We used an approximate point-charges description of the ionic potential, where effective charges located on the nuclei of fenchone are set so as to reproduce the quantum mechanical potential issued from Hartree–Fock calculations [28]. For a given molecular orientation, the final (*E*, θ)-distribution of freed electrons is simply defined by counting among the $\mathcal{N} = 10^6$ independent electron trajectories those with positive energy at the end of the interaction. A typical ionizing trajectory is displayed in figure 4(a). We then mimic random alignment of the experimental gas samples by repeating the CTMC calculations for an ensemble of molecular orientations defined in terms of Euler angles with regular spacing $\Delta \alpha = \Delta \beta = \Delta \gamma = \pi/8$ rad.

Figure 4(b) illustrates the PAD and PECD obtained at the end of a half-cyle pulse with $\lambda = 800$ nm and $I = 10^{14}$ W cm⁻². Such irradiation conditions correspond to tunnel-ionization for the HOMO, with a Keldysh parameter of $\gamma \approx 0.85$. The classical simulations are in very good qualitative agreement with the experimental results of figures 3(c) and (f). In the commonly accepted picture of tunneling, the electron is freed at a distance $r \sim \text{IP}/F_0$ from the center of the target, where F_0 is the maximum strength of the pulse electric field. Using Hartree–Fock results for IP, this yields $r \sim 7$ a.u. The ionic potential still presents small chiral anisotropy beyond such distances, which can thus induces small PECD. However our CTMC calculations reveal that the electron trajectories are submitted to significant multiple scattering on chiral nuclear structure before leaving the target, as examplified in figure 4(a). This is the main source to significant PECD within CTMC.

PECD from one-photon ionization can also be described classically, in the framework of the sudden approximation. Photon absorption is assumed to give the electron a kick resulting in instantaneous modification of its momentum at fixed position. Absorption occurs randomly within one laser cycle and the magnitude of the kick, in opposite direction to the driving field, is determined so that the electron suddenly



reaches the energy $\hbar\omega$ -IP. The subsequent dynamics of the freed electron is calculated over three laser cycles, during which the electric field amplitude linearly decreases down to 0. The PAD and PECD associated to absorption of 9.3 eV photons are presented in figure 4(c). A ring structure is obtained for the PAD, as expected. The PECD is weak, of the order of ~1% at the maximum of the PES. However it reaches very significant and opposite values, of the order of ±15%, in the tail of the PES. This PECD shape shows that electrons with different kinetic energies have experienced significantly different scattering on the chiral potential. Similar features are observed in quantum mechanical descriptions [4, 29].

4. Conclusion

To sum up we have demonstrated that PECD is a universal effect in the photoionization of fenchone molecules by circularly polarized radiation. Molecular chirality is clearly encoded in the PADs whatever the ionization regime, ranging from one-photon to tunnel ionization. To what extent can these results be generalized to other chiral systems? One-photon VUV PECD has been measured in a broad range of chiral molecules. Its value varies a lot from one system to another, and depending on the photon energy. Nevertheless, PECD can be considered as a general effect in XUV photoionization. On the other hand, laser-based PECD was up to now only measured in a REMPI scheme. This sets quite a limitation on the range of systems that can be studied, and makes data interpretation challenging for example when multiple resonances are hit by the excitation process. Nevertheless, REMPI-PECD is considered as a promising technique and a great metrology tool, enabling for instance accurate determination of enantiomeric excess [30, 31]. In this work, we have bridged the gap between the generality of one-photon XUV PECD and the versatility of femtosecond laser sources by demonstrating that PECD could be observed in non-resonant multiphoton/tunnel ionization. The fact that PECD still exists in the strong-field regime is indeed not so intuitive, because this regime is often successfully described using the strong-field approximation, in which the influence of the chiral molecular potential is neglected. Our CTMC calculations have revealed that even in a strong laser field, the chiral potential was able to significantly affect the ionizing electrons, imprinting a forward/backward asymmetry. We have shown that this effect was qualitatively similar to the one at the origin of one-photon PECD. Thus, strong-field PECD should be a general effect, as XUV PECD is. Its magnitude will of course depend on the molecules, and it may be very weak in some specific cases.

The variety of ionization regimes in which PECD can be measured offers interesting perspectives to obtain complementary pictures of the chiral response. Tuning the wavelength and intensity of the driving laser in the MPI and ATI ranges enables probing different electronic ionizing states, from one-electron (Koopmans) to two-hole-one-particle configurations. Vibrationally resolved PECD is also accessible in the MPI regime. All of this opens the route to more sophisticated multi-color ionization experiments, in which the control of different laser pulses will enable coherent control of the electron asymmetry, or to reach chiral information on the attosecond dynamics underlying molecular photoionization [32].

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References

- [1] Berova N, Polavarapu P L, Nakanishi K and Woody R W (ed) 2012 Comprehensive Chiroptical Spectroscopy vol 1 (New York: Wiley)
- [2] Ritchie B 1976 Phys. Rev. A 13 1411
- [3] Böwering N, Lischke T, Schmidtke B, Müller N, Khalil T and Heinzmann U 2001 Phys. Rev. Lett. 86 1187
- [4] Powis I, Harding C J, Garcia G A and Nahon L 2008 Chem. Phys. Chem. 9 475
- [5] Garcia G A, Nahon L, Daly S and Powis I 2013 Nat. Commun. 4 2132
- [6] Tia M, Cunha de Miranda B, Daly S, Gaie-Levrel F, Garcia G A, Powis I and Nahon L 2013 J. Phys. Chem. Lett. 4 2698
- [7] Turchini S et al 2013 Chem. Phys. Chem. 14 1723
- [8] Ferré A et al 2015 Nat. Photon. 9 93
- [9] Lux C, Wollenhaupt M, Bolze T, Liang Q, Kchler J, Sarpe C and Baumert T 2012 Angew. Chem. 51 500
- [10] Lehmann C S, Ram N B, Powis I and Janssen M H M 2013 J. Chem. Phys. 139 234307
- [11] Fanood M M R, Janssen M H M and Powis I 2015 Phys. Chem. Chem. Phys. 17 8614
- [12] Lux C, Wollenhaupt M, Sarpe C and Baumert T 2015 Chem. Phys. Chem. 16 115
- [13] Fanood M M R, Powis I and Janssen M H M 2014 J. Chem. Phys. A 118 11541
- [14] Lux C, Senftleben A, Sarpe C, Wollenhaupt M and Baumert T 2016 J. Phys. B: At. Mol. Opt. Phys. 49 02LT01
- [15] Kröner D 2011 J. Phys. Chem. A 115 14510
- [16] Dreissigacker I and Lein M 2014 Phys. Rev. A 89 053406
- [17] Garcia G A, Nahon L and Powis I 2004 Rev. Scient. Instrum. 75 4989
- [18] Smialek M A, Hubin-Franskin M J, Delwiche J, Duflot D, Mason N J, Vronning-Hoffmann S, Souza G G B D, Rodrigues A M F, Rodrigues F N and Limao-Vieira P 2012 Phys. Chem. Chem. Phys. 14 2056
- [19] Powis I 2014 J. Chem. Phys. 140 111103
- [20] Nahon L et al 2016 Phys. Chem. Chem. Phys. 18 12696
- [21] Schmidt M W et al 1993 J. Comput. Chem. 14 1347
- [22] Krishnan R, Binkley J S, Seeger R and Pople J A 1980 J. Chem. Phys. 75 650
- [23] Tawada Y, Tsuneda T, Yanagisawa, Yanai T and Hirao K 2004 J. Chem. Phys. 120 8425
- [24] Yanai T, Tew D P and Handy N C 2004 Chem. Phys. Lett. 393 51
- [25] Zhao A, Sandor P, Rozgonyi T and Weinacht T 2014 J. Phys. B: At. Mol. Opt. Phys. 47 204023
- [26] Abrines R and Percival I C 1966 Proc. Phys. Soc. 88 861
- [27] Botheron P and Pons B 2009 Phys. Rev. A 80 023402
- [28] Schaftenaar G and Noordik J H 2000 J. Comput.-Aided Mol. Des. 14 123
- [29] Stener M, Fronzoni G, Di Tommaso D and Decleva P 2004 J. Chem. Phys. 120 3284
- [30] Fanood M M R, Ram N B, Lehmann C S, Powis I and Janssen M H M 2015 Nat. Commun. 67511
- [31] Kastner A, Lux C, Ring T, Zillighoven S, Sarpe C, Senftleben A and Baumert T 2016 Chem. Phys. Chem. 17 1119
- [32] Haessler S et al 2009 Phys. Rev. A 80 011404(R)
- [33] http://mcia.univ-bordeaux.fr