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Single Photon Photoelectron Elliptical Dichroism of Amino Acid Anions

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Abstract

Single photon photoelectron elliptical dichroism (PEELD) has been investigated in the photodetachment of electrosprayed amino acid anions, i.) tryptophan (Trp) and ii.) phenylalanine (Phe). PEELD refers to the variation of the asymmetry parameter G with the ellipticity parameter $|S_3/S_0|$. For Trp G is found to scale linearly with $|S_3/S_0|$. For Phe a small but significant deviation from linear scaling is observed in the region of $0.8 \leq |S_3/S_0| \leq 1$, i.e. approaching perfect circular polarization. Commonalities and differences to existing PEELD literature are being discussed.

Introduction

Research in the field of chirality continues to attract considerable interest. Recent work has been shining new light on different aspects of chirality ranging from molecular chirality in the synthesis and analysis of enantiomers [1] [2] [3] to helical chirality in proteins regarding suitable medical attack schemes on viruses [4] and also graphene nanostructures regarding their optical and electronic properties. [5] [6]

In the context of this work the development of chiroptical techniques has been most pertinent. While classical circular dichroism has been measured in one photon electronic absorption (ECD) [7] [8] for many decades, the measurement of circular dichroism in total ion yields (PICD) [9] [10] [11] [12] and in photoelectron angular distribution (PECD) [13] [14] [15] [16] [17] [18] [19] [20] has been demonstrated to yield inherently larger CD values compared to ECD observed in one photon absorption in the last two decades. This enhanced sensitivity has paved the way towards new analytic methods in chirality analysis ultimately leading, e.g., to the coincident detection of PICD and PECD. [21] [22]

The development of photodetachment of electrons from electrosprayed anions represents another milestone providing access to the chirality analysis of single chemical entities of biological relevance. [23] [24] [25]

For most of the history of chiroptical experiments, the focus of efforts was on achieving the highest degree of circular polarization possible. This was motivated by the perception that the largest PICD or PECD values would inherently be expected for perfect circular polarization. Recent work employing elliptically polarized light has shown, that the reality is much more colorful. By now, there is a number of published reports systematically studying the asymmetry parameter G as function of the ellipticity of the light. This ellipticity is most suitably characterized through the ratio of Stokes parameters $|S_3/S_0|$. In the limit of $|S_3/S_0|$ approaching 1 the light becomes perfectly circular polarized and the PEELD turns into the classical PECD. In particular for multiphoton ionization schemes the largest asymmetry parameters were often not observed for perfect circular polarization, i.e., $|S_3/S_0| = 1$ but for ratios $|S_3/S_0| < 1$. [26] [27] [28] [29] In early work Lux et al. reported a small deviation from linear scaling of G with the ellipticity of the light, however, with the largest G value observed for perfect circular polarization. [30] The work mentioned above all considered photoionization of neutral molecules. On the other hand, there is by now a number of reports on the PECD observed in photodetachment from anions.[24] [25] [31] [32] [33] We are not aware of PEELD studies in photodetachment from anions. It is the goal of this work to close this gap, by providing two examples for PEELD measurements, i. one for tryptophan, for which the largest PEELD is observed for perfect circular polarization and ii. one

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for phenylalanine, where the largest PEELD is observed around $|S_3/S_0| = 0.95$. In both cases photodetachment is initiated by one photon absorption.

Experimental

The PEELD measurements described in this work have been carried out in an Electrospray-Ionisation-PECD spectrometer previously described by KRÜGER and WEITZEL.[24] In brief, anions are generated in an Electrospray-Ionisation source, transferred to an octopole ion trap, before being introduced into the source of a CD spectrometer capable of analyzing electrons and also ions. Photodetachment is induced by shining laser light onto the anion beam. Detached photoelectrons are detected on a microchannel plate detector with two half-circle anodes positioned in forward and backward direction for analysis of asymmetries. Polarization of the laser light is controlled by a combination of a Glan-Taylor polarizer from TOPAG LASERTECHNIK and an achromatic Quarter-wave plate from BERNHARD HALLE NACHFL. Analysis of the polarization state is performed by use of a second set of identical polarizer and Quarter-wave plate.
Compared to our previous set up [24,32], the polarization manipulation has been optimized by implementing an enhanced gearing ratio of the quarter-wave plate (QWP) used to convert the linear polarization to elliptical polarization. The new gearing ratio enables a four times more precise setting of the QWP angle (smallest step for angle variation, $\Delta\varphi_{\min} = 0.45°$). The current precision for the determination of S_3/S_0 is $\pm$ 0.01. To analyze the polarization a turning QWP, fixed polarizer approach was used.[34] Pulse energies were ranging from 50 µJ to 100 µJ and for each recorded polarization state 200000-300000 laser shots were recorded.
All PEELD experiments have been performed employing solutions of commercially available L-Phe (MERCK KGAA), nominal purity 99%, D-Phe (FLUOROCHEM), nominal purity 98%, L-Trp (APPLICHEM GMBH), nominal purity 99%, and D-Trp (FLUOROCHEM), nominal purity 97%, were used. The purity stated refers to chemical purity. The concentrations of the analytes were 100 µmol/L for tryptophan and 50 µmol/L for phenylalanine. As a solvent pure methanol (HPLC grate) from FISHER SCIENTIFIC was used. The PECD of Phe and Trp anions had been reported previously. [32] For comparison to those former data sets the light source was kept at the same settings, as used before.[32] The Radiant Dyes NarrowScan dye laser was operated at 10 Hz at 234 nm employing Coumarin 102.

Results

For the analysis of the polarization the light intensity is described by equation 1, based on Stokes parameters.

$$I = \frac{1}{2} \cdot \{S_0 - [S_1 \cdot \cos(2 \cdot \varphi) + S_2 \cdot \sin(2 \cdot \varphi)] \cdot \cos(2 \cdot \varphi) + S_3 \cdot \sin(2 \cdot \varphi)\} \quad (1)$$

Figure 1 depicts the measured reduced Stokes Parameter for S_1, S_2 and S_3. These parameters were reproducible throughout the entire set of experiments. The measurements show nearly identical absolute values for S_3/S_0 for each ellipticity and in all cases comparable S_1/S_0 and S_2/S_0 parameters. It is therefore assumed that LEP and REP measurements for the respective ellipticity can be compared with each other and symmetrization is eventually carried out between them. Evidently, the optimized polarization setup employed in this work, allows generating both elliptical polarizations with the same value for S_3/S_0 over the whole range of S_3/S_0 $[-1{:}1]$.

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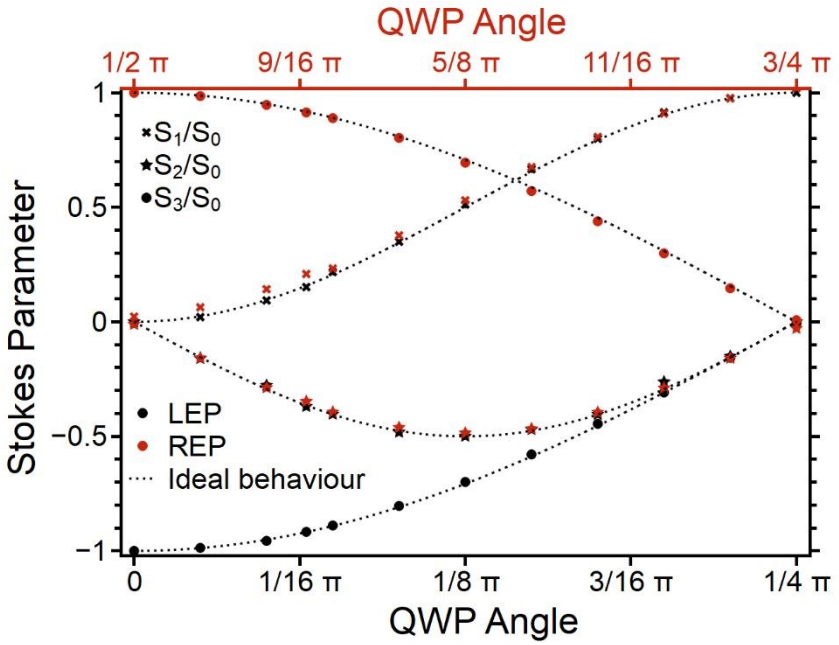

Figure 1 Characterization of polarization for the PEELD measurements of tryptophan and phenylalanine. Measured Stokes parameters S_1/S_0 (cross), S_2/S_0 (star) and S_3/S_0 (dot), ideal behavior of a quarter wave plate on linear polarization (dotted lines).

For the analysis of asymmetries G the same procedure was employed as in previous work.[32] The forward-backward-asymmetry G of the photoelectrons was calculated for single laser shots with equation 2. The resulting asymmetry G_p is depending on the polarization *p*. The electron integral signal is denoted as *Y* with forward and backward direction on the detector denoted as FWD and BWD.

Photoelectron asymmetries were always measured for two opposing elliptical polarizations in a direct sequence and symmetrized between those two measurements. To optimize the measurement versus dead time of the setup we do those measurements in bunches of laser shots, so called passes. Each pass consists of 300 laser shots LEP and 300 laser shots REP. Again, to reduce dead time we do not change the polarization between two passes. Effectively we therefore measure 600 laser shots LEP and 600 laser shots REP alternating.

These alternating measurements are usually carried out for 6-8 h, i.e. one day of operation, for one $|S_3/S_0|$ ratio and one enantiomer. For each laser shot the electron time-of-flight spectrum between 0 ns and 8022 ns is recorded and stored. The analysis of the electron asymmetry is done after the measurement. The ellipticities of our polarization were measured in advance and checked repeatedly. No significant drift was observed.

$$G_p = 4 \cdot \frac{Y_p^{FWD} - Y_p^{BWD}}{Y_p^{FWD} + Y_p^{BWD}} \qquad (2)$$

The polarization dependent asymmetry was subsequently symmetrized using equation 3

$$G = \frac{G_{LEP} - G_{REP}}{2} \qquad (3)$$

Errors given in the PEELD plots are the standard errors from the calculation of G_p that were propagated to G using equation 4.

$$\Delta G = \frac{\Delta G_{LEP} + \Delta G_{REP}}{2} \qquad (4)$$

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Tryptophan

Triggered by experience from previous work, the mono-anion of the deprotonated dimer, i.e. the $[2\mathrm{Trp}-\mathrm{H}]^-$ signal, was selected for the PEELD measurements of tryptophan. There, PECD values of ± 0.05 have been reported for the dimer anion, a factor of 5 larger than the corresponding value for the monomer anion.[32] Selection of the dimer anion provides access to better signal-to-noise ratios. Here, it is possible to exclusively photodetach the tryptophan dimer, and therefore it is also possible to isolate the PEELD of said anion. Figure 2 shows the mass spectrum of tryptophan in the mass region ranging from the monomer anion to the dimer anion. The depicted difference trace highlights the photodetachment of the dimer anion, the absence of other peaks in the trace shows that exclusively electrons from the dimer are detected.

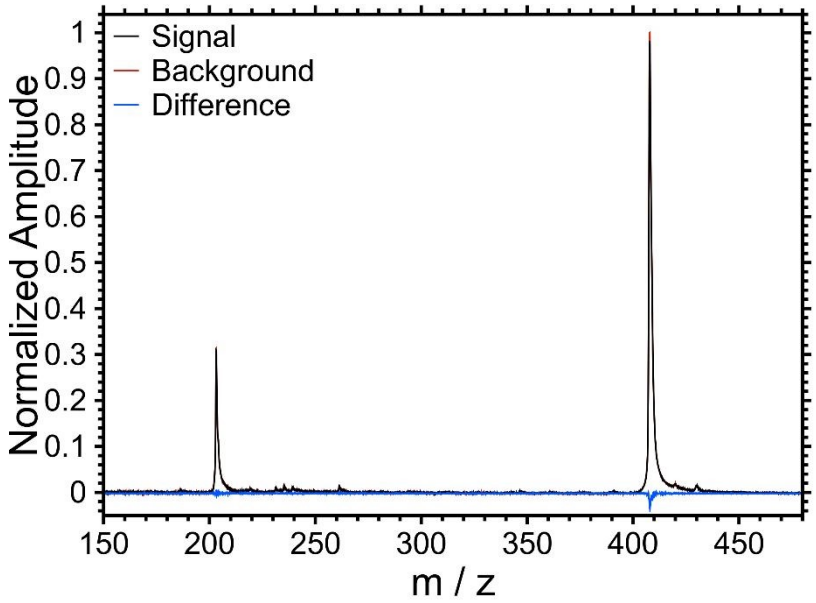

Figure 2 Mass spectrum of tryptophan with laser induced depletion. Spectrum with laser interaction, signal (black line); spectrum without laser interaction, background (red line) and difference induced by the laser interaction, difference (blue line).

For the analysis of the PEELD of Trp-dimers, the asymmetry of the angular distribution of the photoelectrons detached from said species was measured. As shown in Figure 1 the two linear reduced Stokes parameters S_1/S_0 and S_2/S_0 were kept as close to each other as possible while systematically varying the S_3/S_0 parameter. The asymmetries presented are the symmetrized values for G calculated with equation 3. The measured asymmetries are presented in Figure 3 as a function of $|S_3/S_0|$. In the limit of $|S_3/S_0| = 1$ the observed G parameter is ± 0.055. Within the error margin, this is compatible with the value of $PECD = \pm 0.05$ reported in previous work. [32]

The main conclusion from Figure 3 is, that G in good approximation scales linearly with $|S_3/S_0|$. The gradient of the increase is basically identical for both enantiomers and symmetric around $G = 0$. The observed gradient is -0.055 for L-Trp and $+0.055$ for D-Trp.

In order to elucidate the number of photons involved in the detachment process, the electron yield has been analyzed as a function of the laser intensity. The log – log plot of the electron yield versus the laser intensity exhibits a slope equal to 1 (c.f. Fig. S3 of the ESI), indicating that the detachment is predominantly induced by one photon. This appears plausible with regard to the threshold for detachment reported at 2.85 eV for the Trp monomer anion [35] compared to a photon energy at 234 nm corresponding to 5.3 eV. The threshold for detachment from the Trp dimer anion may differ slightly from the value of 2.85 eV. Evidently the photon energy employed in this work is sufficient to overcome the threshold for detachment.

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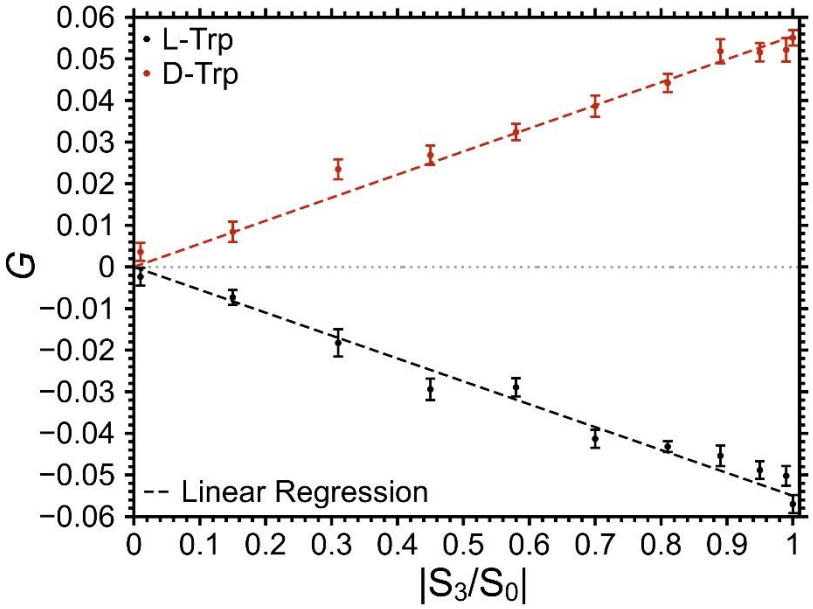

Figure 3 Measured asymmetries G of tryptophan for different ellipticities $|S_3/S_0|$ (symbols). Result of linear regression through origin employing the relation $G = a_1 \cdot |S_3/S_0|$ (dashed lines).

Phenylalanine

In the case of phenylalanine a PECD value of ± 0.037 has been reported for the monomer anion $[\mathrm{Phe} - \mathrm{H}]^-$, significantly higher than the values for the monomer anion $[\mathrm{Trp} - \mathrm{H}]^-$.[32] In this work, the mass spectrum for the Phe-monomer was remeasured to verify that the electrons are photodetached from the intended species. Figure 4 shows that we are able to isolate the Phe-monomer and photodetach only this species. This is highlighted by the difference spectrum.

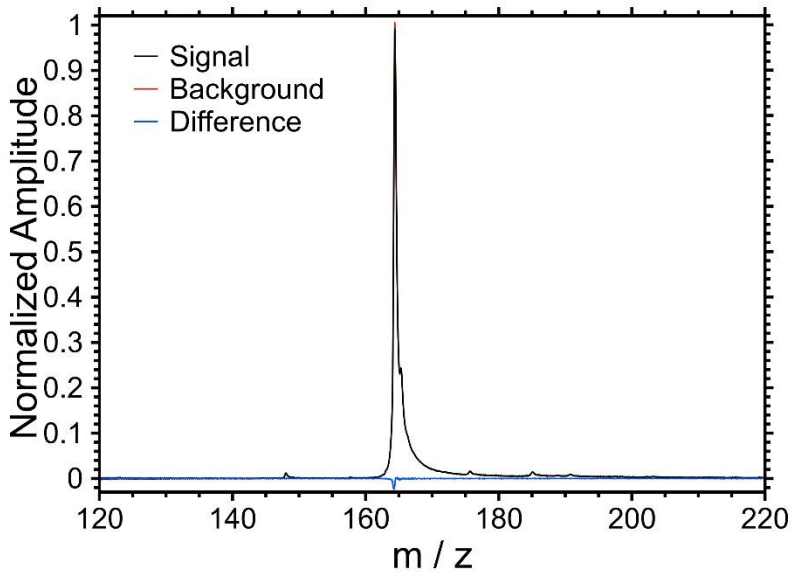

Figure 4 Mass spectrum of phenylalanine with laser induced depletion. Spectrum with laser interaction, signal (black line); spectrum without laser interaction, background (red line) and difference induced by the laser interaction, difference (blue line).

The data for the PEELD of Phe exhibit a more complex variation of G with $|S_3/S_0|$. In the range of $|S_3/S_0|$ values from $0 - 0.8$ a basically linear increase of G with $|S_3/S_0|$ is observed, but for

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higher $|S_3/S_0|$ values in the region of $0.8 - 1$ a deviation from linearity is evident. The maximum absolute value for G is observed around $|S_3/S_0| = 0.95$. Note, that the experimental data presented for D-Phe and L-Phe are almost perfectly mirror symmetric without enforcing this by the data analysis. The PECD value, i.e. the G value for $|S_3/S_0| = 1$ is ± 0.033, i.e. slightly lower than the previously reported value of ± 0.037.[32] The numbers are fully compatible within the error margins, in particular considering that the actual $|S_3/S_0|$ in that previous work was rather 0.99 than 1.

As for the Trp case, the number of photons involved in the detachment was investigated by analyzing the variation of electron yields with the laser intensity. The log – log plot of the electron yield versus the laser intensity exhibits a slope equal to 1 (c.f. Fig. S4 of the ESI), indicating that the detachment is predominantly induced by one photon. This appears again plausible with regard to the threshold for detachment reported at 3.54 eV for the Phe monomer anion [35] compared to a photon energy at 234 nm corresponding to 5.3 eV. Evidently, the photon energy employed in this work is sufficient to overcome the threshold for detachment.

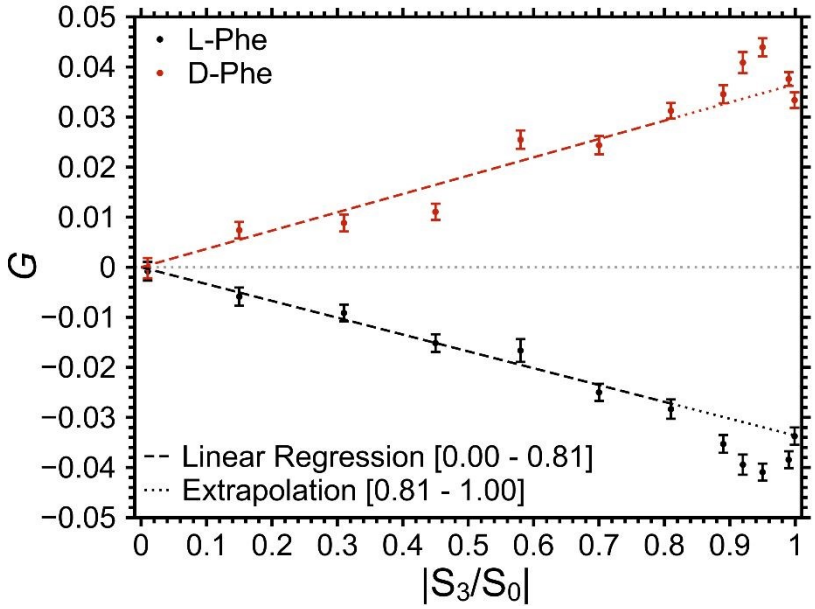

Figure 5 Measured asymmetries G of phenylalanine for different ellipticities $|S_3/S_0|$ (symbols). Linear regression employing the relation $G = a_1 \cdot |S_3/S_0|$ for $0 < |S_3/S_0| < 0.81$ (dashed lines) to highlight the linear increase of G in this range. The extrapolation to $|S_3/S_0| = 1$ (dotted lines) highlights the PECD value that closely matches the linear approximation.

Discussion

The main findings of the current work pertains to the characteristic variation of G with $|S_3/S_0|$ presented in Figure 3 and Figure 5 indicating a linear variation for Trp but a non-linear variation for Phe.

Since the PECD may be considered a special case of PEELD, i.e. the one for which $|S_3/S_0| = 1$, but much more information being available on PECD than PEELD, it is instructive to briefly recall the current view on this PECD. Here, the currently established way of modelling the PECD is based on a coefficient $b_1^{\pm 1}$ and the first Legendre polynomial, $cos\theta$, as indicated in equation 5. This representation is considered valid in the case of a single photon excitation from a single initial orbital in a case where the outgoing electron feels an isotropic potential of the chemical system left behind. The superscript ± 1 represents the direction of circular polarization.[14,17] In the following only the +1 polarization is addressed explicitly, with $b_1^{+1} = -b_1^{-1}$.

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$G = 2b_1^{+1}cos\theta$	5

Due to the use of two half plate detectors in the current setup with, the electrons detected are effectively angle integrated from 0 to 180° and from 180° to 360°. As a consequence, the full photoelectron angle distribution (PAD) is not accessible anymore and equation 5 simplifies to equation 6.

$G = 2b_1^{+1}$	6

While the use of hemispherically integrating detectors prevents us from analyzing full PAD's, the current data still provide intriguing hints at the mechanism involved. Since, as a matter of fact the PEELD data of $[\mathrm{Phe} - \mathrm{H}]^-$ cannot be presented by a linear regression function, the current data set has been modelled by the same approach as suggested by GREENWOOD et al., i.e. a power series expansion of G in $(S_3/S_0)^n$, with $n = 1, 3, 5, 7, 9$, i.e. up to.

$G = a_1 \cdot \left\lvert\frac{S_3}{S_0}\right\rvert^1 + a_3 \cdot \left\lvert\frac{S_3}{S_0}\right\rvert^3 + a_5 \cdot \left\lvert\frac{S_3}{S_0}\right\rvert^5 + a_7 \cdot \left\lvert\frac{S_3}{S_0}\right\rvert^7 + a_9 \cdot \left\lvert\frac{S_3}{S_0}\right\rvert^9$	7

This approach is presented in detail in the electronic supplementary material (ESI). For allowing a critical assessment of the analysis, fits are shown in the ESI for increasing number of non-linear terms included. Evidently and not surprisingly, the fits become better with increasing number of terms included as judged from the R^2 value observed. The pivotal question is, which terms are significant for inclusion in the analysis. In a conservative approach, the inclusion of non-linear terms would be interpreted not significant in the case of Trp but significant at least up to the 7th order for the Phe data set.

This in turn triggers the question for the reason of non-linear contributions to the PEELD. COMBI et al. reported the PEELD for a number of molecules in the (n+1) REMPI of neutral molecules including the full PAD's. They reported a linear variation of the asymmetry parameter G with $|S_3/S_0|$ for low absolute values of $|S_3/S_0|$, assuming that linear polarization dominates this region, but non-linear variation at large absolute values of $|S_3/S_0|$. In the latter case, the PEELD was concluded to be dominated by the final step of REMPI, i.e. a one photon excitation leading to the ejection of the electron. In that limiting case the non-linearity observed in G was correlated with the number of photons absorbed in the detachment, in analogy to the common approach in the analysis of PECD for multiphoton ionization of neutral molecules.[19 30 36] For a more general overview covering photoelectron angular distributions (PAD) the reader is referred to the literature .[37 38]

The situation is different for the experiment presented in this work in various respects. First, as evidenced from the laser intensity dependence of electron signals, all data presented here result from one photon excitation. Thus, a multiphoton rational is not operative in explaining the findings.

There are further possible reasons causing non-linear scaling of G with $|S_3/S_0|$.

First, the photodetachment of electrons from an anion leaves a neutral radical behind. Thus, the PECD and PEELD observed originate from the interaction of an outgoing electron wave with the potential of a neutral species. As a consequence, coulombic forces can be neglected here, in contrast to the PECD in the ionization starting from a neutral species. This is also reflected in the Wigner laws for ejection of an electron being different for ionization of a neutral and detachment from an anion.[39 40 41 42] The molecular potential of the neutral radical formed in our photodetachment is not known and it is not clear at this point, how the PEELD depends on that particular potential.

There is another, perhaps even more likely, cause of non-linearities in G. The detachment energy provided by the laser photon is more than 1.5 eV above the detachment threshold in the case of Phe anions. At this energy the electron signals detected may well contain contributions not only from the HOMO orbital of the anion but also from lower lying orbitals in the anion. For indalone anions, e.g., BRANDT et al. reported that different orbitals may

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contribute with different sign to the overall PECD.[33] That could give rise to non-linearities in an analysis as employed in this work.
Additional insight into this matter would benefit from angle resolved measurement of the PAD and from molecular orbital calculations. Both are not available to us at this point. Still, we conclude that hemispherically integrated measurements of PEELD contain subtle details of the detachment mechanism to be unraveled in future work. It is hoped that the current work triggers future efforts along this line of question.

Summary and Conclusion

The photoelectron elliptical dichroism (PEELD) has been investigated in the photodetachment of electrons from electrosprayed amino acid anions. For one example presented, the tryptophan dimer anion, the asymmetry parameter G scales predominantly linear with the ellipticity parameter $|S_3/S_0|$. For another example, the phenylalanine monomer anion the scaling of G with $|S_3/S_0|$ deviates markedly from linearity, in particular for $|S_3/S_0|$ values around 0.9. Here, the photodetachment is very likely a single photon process.
Linear and non-linear scaling of G with $|S_3/S_0|$ has also been reported by GREENWOOD et al. in the multiphoton ionization of several neutral molecules.[26] For fenchone and pinene, e.g., a non-linear scaling was observed. For several phenyl alcohols a linear scaling was observed. In addition, GREENWOOD et al. demonstrated that the characteristics of the ellipticity dependence can be influenced by changing the laser light intensity. This clearly refers to multiphoton excitation processes. While it is obvious to discuss the population of intermediate states in multiphoton ionization, such states are not involved in single photon photodetachment. Therefore, more studies are needed to further advance the understanding of the effect of ellipticity in photochemical processes. In particular, single-photon elliptical dichroism of a neutral molecule could give further insights and help with the understanding of the phenomena.
Research on the effect of elliptical polarization is highly relevant. It can give insights beyond the analysis in a closed chemical or physical setup. It is, e.g., of astrophysical importance due to the occurrence of elliptical polarization within the cosmos emitted by interstellar objects and possible implications for the origin of homochirality.[43] [44] [45] Furthermore elliptical polarization was measured in the first meters below the marine surface.[46] [47] An effect of the elliptical polarization on marine wildlife is therefore also possible.[48] [49]

Conflicts of Interest

The authors declare no conflict of interest.

Electronic Supplementary Materials

Electronic supplementary material is available providing model calculations for the PEELD data and supporting the one-photon mechanism invoked.

Acknowledgments

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