Using circular dichroism to control energy transfer in multi-photon ionization

A.H.N.C. De Silva,1 D. Atri-Schuller,2 S. Dubey,1 B.P. Acharya,1 K.L. Romans,1 K. Foster,1
O. Russ,1 K. Compton,1 C. Rischbieter,1 N. Douguet,3 K. Bartschat,2 and D. Fischer1

1Physics Department and LAMOR, Missouri University of Science & Technology, Rolla, MO 65409, USA
2Department of Physics and Astronomy, Drake University, Des Moines, Iowa 50311, USA
3Department of Physics, Kennesaw State University, Kennesaw, Georgia 30144, USA

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The response of laser-excited Li atoms prepared in the (2p, m = +1) state to circularly polarized radiation with the same or opposite helicity of the initial state is investigated. For a field frequency near the excitation energy of the polarized initial state, the photoelectron energies are significantly different for the two helicities. Good agreement between theory and experiment is obtained, and the observed energy shifts are explained by the helicity-dependent Autler-Townes splitting due to the coupling of the 2p state with the Li ground state.

Circularly polarized light exhibits handedness, a feature that gives rise to breaks in symmetry in its interaction with matter. This intriguing phenomenon is well known as circular dichroism (CD), and it unfolds, e.g., as the difference in photoelectron angular distributions (PADs) for opposite photon helicities in single-photon ionization of oriented diatomic molecules [1] and even of ground-state atomic targets [2, 3]. For these nonchiral targets, however, the systems of opposite photon handedness are merely mirror images of one another (neglecting parity-violating effects [4, 5]). This mirror symmetry is only lifted, therefore, if the target also possesses a handedness. Chiral molecules, i.e., molecules that are not superimposable with their mirror images, are a prominent example of such handed targets. Their ionization by single- [6, 7] or multi-photon [8, 9] absorption as well as strong optical fields [10] reveals significant dichroic asymmetries even for randomly oriented molecules. Such asymmetric photoreactions have far-reaching implications that could contribute to the solution of the long-standing puzzle of the homochirality of terrestrial life [11, 12].

Single atoms can also feature chirality if their orbital angular momentum is polarized along the projectile beam direction with a mean magnetic quantum number ⟨m⟩ ≠ 0 [13, 14]. Due to their comparably simple structure, polarized atomic targets represent benchmark systems for our understanding of asymmetries in the interaction of chiral light with chiral matter. Recent studies focussed, amongst other things, on fundamental aspects of magneto-optics [15] or on the details of tunneling dynamics [20, 22] and resonance-enhanced multi-photon ionization (REMPI) [17, 23, 24]. Dichroic asymmetries occurring in the total scattering yield or in PADs can be qualitatively understood in the electric dipole approximation by the change of the magnetic quantum number m, which is +1 (−1) for each absorbed photon of right-(left-)handed circular polarization, thus resulting in different partial waves for opposite helicities to contribute and interfere in the final state [23, 20]. Dichroic shifts in the photoelectron energies are either completely absent [20] or relatively small (as compared to peak widths and positions), but they can give insights into the structure of the dressed target atoms [23, 24, 27] or reveal fingerprints of atomic ring currents [21, 28].

In this Letter, we demonstrate an atomic multi-photon ionization scheme, in which circular dichroism manifests itself in strong and controllable shifts in the photoelectron energy spectrum. Alkali atoms are optically pumped to a polarized p-state and subsequently ionized by the absorption of two photons in the circularly polarized field of an intense femtosecond laser. A change of the field helicity results in relative shifts of the photoelectron energies by up to 40%. This observation is qualitatively understood by the polarization-selective Autler-Townes splitting of the initial state due to its coupling to the ground state in the intense light field. The counter-intuitive energy dependence on the photons’ polarization provides an additional dial for the quantum control of the emission of polarized electrons [29, 30], which can be used to enhance the chiral response in the analysis of handed targets.

The present study contributes also to the interesting and much-debated question whether photoionization proceeds more efficiently for the electron current density of the initial state being co-rotating or counter-rotating with the ionizing field. For low-intensity single-photon absorption, it is well-established that ionization is strongly favored in the co-rotating case [25], but the trend was found to be reversed in the nonadiabatic tunnel ionization regime [20, 28]. For multi-photon ionization, in contrast, this question was not answered unambiguously. In fact, the favored geometry swaps with increasing field intensity [23, 31]. The intensity dependence can be very strong [24] due to transient (“Freeman”) resonances [32], where quasi-energies of dressed intermediate states are moved in resonance, thereby enhancing specific REMPI channels. In the system investigated here, resonance enhancement does not significantly affect dichroic...
atoms populating the magnetic sub-level with 93% of the excited state optical pumping in the AOT results in a high degree excitation fraction of about 25%. As shown earlier [33], two non-collinear optical parametric amplifier (NOPA) stages. For the present experiment, the system was configured to emit pulses with a wavelength, duration, and repetition rate of 665 ± 5 nm, 65 fs, and 200 kHz, respectively, and a peak power of up to 10^12 W/cm^2. The femtosecond laser beam is focused and guided through the vacuum chamber with a waist of 50 μm at the target position and an angle of 10^° with respect to the polarization direction of the atoms (i.e., the z-axis). Electron and recoil ion momenta are measured in coincidence in a cold-target recoil-ion momentum spectrometer (COLTRIMS) [35].

The experimental data shown below are compared with predictions from an ab initio calculation based on the solution of the time-dependent Schrödinger equation (TDSE). For the setup considered here, lithium can be well described as an active (nℓ) valence electron above an inert He-like (1s^2) core. The latter was simulated by the static Hartree potential supplemented by phenomenological terms to simulate the core polarizability as well as exchange between the valence electron and the core. The ideas of the method were described in [36-37] and successfully used by Schuricke et al. [38]. With a few further improvements, we obtained the ionization potentials of the 2s and 2p orbitals, as well as those of the n = 3 orbitals, to better than 1 meV of the recommended data [39]. The initial state was then propagated in time by solving the TDSE numerically [40-41]. We used an updated version of the code with the necessary modifications introduced for circularly polarized light described by Douguet et al. [12].

For the conditions described above, the corresponding Keldysh parameters are always larger than about 6.5 and the ionization process is well described in a multi-photon picture. The ionization pathways are depicted in Fig. 1 according to lowest-order perturbation theory. Lithium atoms in the 2s ground state are ionized by the absorption of three photons, resulting in a final-state (orbital) angular momentum of (ℓ, m) = (3, 3). Note that the center frequency of the laser pulses is near the 2s – 2p zero-field resonance energy with a blue-shift of Δν_0 ≈ 4 THz (16 meV). For target atoms in the excited 2p state, two photons suffice to promote the valence electron to the continuum. For the co-rotating case, the final angular momentum is identical to 2s ionization and hence given by (3, 3). For the counter-rotating case, on the other hand, the final magnetic quantum number is m = 1, with the total angular momentum in a superposition of ℓ = 1 and ℓ = 3. The different angular momenta result in vastly different PADs, as illustrated in Fig. 1.

Figure 2 exhibits momentum distributions of low-energy electrons in the plane perpendicular to the laser beam propagation direction (the xy-plane) for 2s ionization as well as for co- and counter-rotating 2p ionization. All spectra feature ring structures due to the cylindrical symmetry of the systems. The diameters of the rings reflect different electron continuum energies. There is reasonable qualitative agreement between the experimental and theoretical spectra, even though the ring diameters do not perfectly align for experiment and theory.

The differential ionization probabilities as a function of the photoelectron energy are plotted in Fig. 3. The energy range shown in the figure contains more than 98% of the theoretical cross sections, i.e. contributions of higher electron energies due to above-threshold ionization (ATI) are small for the investigated field intensities. For ionization of the 2s ground state, the distributions for left- and right-handed circular polarization are expected to be identical (neglecting the spin polarization of the target atoms), which is consistent with the experimental obser-
The general features observed in the experiment are well reproduced by our model. However, some differences between experiment and calculation persist. For the initial 2s state as well as for excited-state ionization with co-rotating laser polarization, the calculated spectra exhibit two well-separated energy peaks, which are more narrow and have a larger separation than in the experimental spectra. These differences can only partly be explained by the experimental resolution, which is about 30 meV in the relevant energy regime. More significant systematic uncertainties are related to the field intensity: Generally, target atoms are not ionized at a single point in the center of the laser focus, but ionization takes place in a region around the focus at different local peak intensities. This effect can be accounted for by convoluting theoretical spectra over the intensity distribution of the reaction volume around the focal point [35], which was not done in the present study. Instead, this effect was accounted for approximately by considering a reduced average intensity, which was chosen to be 3/4 of the estimated experimental peak intensity.

The structure and shifts observed in the energy spectra for 2s ionization and for 2p ionization with co-rotating polarization can be qualitatively interpreted by the “dressing” of the initial states in the photon field. The dressed-state approach is widely used to explain structures in photoelectron energy spectra for multi-photon ionization of atoms and molecules (e.g. [24, 44]) and provides intuitive insights into the physical mechanisms at play. Particularly interesting is the situation where the photon field is at resonance and couples two atomic levels. The coupling splits the levels into Autler-Townes doublets that are well known in atomic spectroscopy [44] and multi-photon ionization [45, 49]. In the dressed-atom description, these doublets stem from avoided crossings of the combined “atom + photons” states (or Floquet states) at the resonant field frequency (e.g. [77]). Their separation depends on the strength of the coupling, i.e., on the intensity of the coupling field as well as the dipole moment of the atomic transition.

In the present system, the field frequency is close to the 2s – 2p resonance with a slight blue shift, splitting the two levels into doublets, which materialize as two lines (or one line with a shoulder) in the photoelectron energy distributions. For the counter-rotating field, the 2p state does not exhibit the Autler-Townes splitting, because the excited initial state is not coupled to the ground state by radiation of opposite helicity (see Fig. 1). Generally, the evolution of dressed states in a femtosecond laser pulse
is a time-dependent problem. Assuming the rather unrealistic case of a fully adiabatic evolution of the dressing, the blue-shifted radiation would cause an up-shift (down-shift) in energy of the initially undressed 2s (2p) state, i.e., only one level out of the respective doublet would be populated. Therefore, the observation of both lines of the doublet might generally indicate the nonadiabaticity of the process with their relative intensities even providing a quantitative measure. Additionally, the electron energies are subject to ponderomotive shifts. These are, however, rather small (≤ 21 meV) for the present field intensities.

Quantitatively, circular dichroism is given by the difference of the relative ionization yields for the two photon spins. It is defined as $CD = (P_+ - P_-)/(P_+ + P_-)$, where $P_+$ and $P_-$ are the ionization probabilities for co- (+) or counter-rotating (−) helicities, respectively. For the two peak intensities shown in Fig. 3 the measured angle-and energy-integrated $CD$ values are $0.55 \pm 0.08$ and $0.56 \pm 0.10$, respectively. Both values are in good agreement with the theoretical predictions of 0.66 and 0.53, respectively. However, the measured values have large errors, which are dominated by the uncertainty of the excited-state fraction of the atomic gas cloud which is $(25 \pm 3) \%$. Contributions due to statistical errors and the cross-normalization procedure of the spectra for co- and counter- rotating radiation are relatively small. The given errors do not account for systematic effects due to the imperfect polarization of target and laser field, which generally are expected to shift the absolute $CD$ value slightly down. The small discrepancy between theory and experiment might again be explained by the extension of the reaction volume around the focal point, as mentioned above.

It is interesting to compare the present results to other recent studies of circular dichroism in multi-photon ionization of other atomic systems. Specifically, Ichen et al. [23] and Grum-Grzhimalo et al. [24] investigated circular dichroism in the double ionization of helium in an XUV-IR two-frequency field. In this system, the absorption of two XUV photons results in the sequential and resonant ionization-excitation of the target to the polarized He$^+$ (3p) state, which is subsequently ionized by the absorption of four or more IR photons. Here, the integrated $CD$ value is close to +100% at low intensities before it drops and even changes sign for higher intensities. Interestingly, this change occurs over a very narrow intensity range. Doubling the intensity already suffices to bring the $CD$ value down to nearly zero.

For the present system, the overall intensity dependence of the dichroism is much weaker and appears to be more consistent with an earlier theoretical study considering state-prepared atomic hydrogen [31]. This different behavior can be understood by the vastly unalike preparation methods of the polarized $p$ states: In [23], the target excitation and the multi-photon ionization processes occur both on the same time scale in a two-frequency femtosecond radiation pulse. The steep drop of the dichroism is explained by the polarization-selective dynamic Stark shift of the He$^+$ (3p) state in the intense IR field shifting the XUV field and the excited target state out of resonance [24]. In the present study, in contrast, the target excitation and the multiphoton ionization processes are largely disentangled, as the lithium atoms are excited in the quasi-continuous, low-intensity (in the order of $10^{-2}$ W/cm$^2$) resonant field of the AOT cooling lasers on a much longer time scale given by the lifetime of the excited state (about 27 ns). Therefore, dynamic Stark shifts of the excited 2p state in the femtosecond laser pulse do not significantly hamper the efficiency of the state preparation.

In conclusion, we calculated and demonstrated experimentally a multi-photon ionization scheme where strong circular dichroism occurs in the photoelectron energy distribution. Specifically, polarized atomic lithium in the excited Li (2p, $m = +1$) state is ionized by intense circularly polarized radiation of both helicities with a frequency near the 2p excitation energy. If the laser electric field and the target electron current density counter-rotate in the same plane, the photoelectron energy spectrum exhibits a single peak at about $2\hbar \omega - I_P + U_P$ following simple energy conservation, with $\omega$, $I_P$, and $U_P$ being the field frequency, the ponderomotive energy shift, and the ionization potential of the excited initial state, respectively. For the co-rotating case, in contrast, this energy relation is violated, because the 2p initial state and the 2s ground state are coupled by the laser field resulting in the Außer-Townes splitting of both states. This effect enables to control photoelectron energies by the field’s intensity and polarization and induce shifts which, in the current experiment, amount up to 40% of the average continuum energy.

The multi-photon ionization scheme discussed in this Letter is ideally suited and directly applicable to create spin-polarized electron beams. It has been shown earlier that photoelectrons have a nonvanishing spin polarization depending on their continuum energy in multiphoton [30] or strong-field [29] ionization of noble gas atoms by circularly polarized light. Due to the state preparation of the target by optical pumping in the present scheme, not only the orbital angular momentum but also the spin of the single valence electron are aligned in the initial state [29]. Therefore, a nearly complete spin polarization of the photoelectrons can be expected, irrespective of their final energy. The polarization-dependent energy shift discussed above provides an extremely fast, femtosecond switchable dial to control the electron energy on a level of a few meV. This way, femtosecond spin-polarized electron pulses can be created with applications in electron diffraction experiments probing, e.g., ultrafast spin dynamics of magnetic domains.

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[1] T. Jahnke et al., Phys. Rev. Lett. 88, 073002 (2002).
[2] J. Berakdar and H. Klar, Phys. Rev. Lett. 69, 1175 (1992).
[3] V. Mergel et al., Phys. Rev. Lett. 80, 5301 (1998).
[4] J. M. Feagin, Phys. Rev. Lett. 88, 043001 (2002).
[5] J. Hofbrucker, A. V. Volotka, and S. Fritzsche, Phys. Rev. Lett. 121, 053401 (2018).
[6] C. E. Loving and P. G. H. Sandars, J. Phys. B 8, L336 (1975).
[7] P. Bucksbaum, E. Commins, and L. Hunter, Phys. Rev. Lett. 46, 640 (1981).
[8] N. Böwering, T. Lischke, B. Schmidtke, N. Müller, T. Khalil, and U. Heinzmann, Phys. Rev. Lett. 86, 1187 (2001).
[9] G. A. Garcia, L. Nahon, S. Daly, and I. Powis, Nature Communications 4, 2132 (2013).
[10] L. Nahon, G. A. Garcia, and I. Powis, Journal of Electron Spectroscopy and Related Phenomena 204, 322 (2015) gas phase spectroscopic and dynamical studies at Free-Electron Lasers and other short wavelength sources.
[11] R. E. Goetz, C. P. Koch, and L. Greenman, Phys. Rev. Lett. 122, 013004 (2019).
[12] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, and T. Baumert, Angewandte Chemie International Edition 51, 5001 (2012).
[13] C. Lux, A. Senfftleben, C. Sarpe, M. Wollenhaupt, and T. Baumert, J. Phys. B 49, 02LT01 (2015).
[14] S. Beaulieu et al., Nature Physics 14, 484 (2018).
[15] A. Jorissen and C. Cerf, Origins of life and evolution of the biosphere 32, 129 (2002).
[16] L. Nahon, G. Garcia, I. Powis, U. Meierhenrich, and A. Brack, in Instruments, Methods, and Missions for Astrobiology X, Vol. 6694, edited by R. B. Hoover, G. V. Levin, A. Y. Rozanov, and P. C. W. Davies, International Society for Optics and Photonics (SPIE, 2007) pp. 19 - 34.
[17] T. Mazza et al., Nature Communications 5, 3648 (2014).
[18] Massive particles carrying oriented angular momentum do generally not have an intrinsic chirality, i.e. these systems are still superimposable with their mirror images. However, there is an anisotropy in photoionization given by the propagation direction of the incoming photon beam. The particle’s helicity combined with the anisotropy results in a handedness which sometimes is referred to as “external chirality” [17].
[19] J. M. Choi, J. M. Kim, Q.-H. Park, and D. Cho, Phys. Rev. A 75, 031381 (2007).
[20] T. Herath, L. Yan, S. K. Lee, and W. Li, Phys. Rev. Lett. 109, 043004 (2012).
[21] S. Eckart et al., Nature Physics 14, 701 (2018).