Theoretical description of circular dichroism in photoelectron angular distributions of randomly oriented chiral molecules after multi-photon photoionization

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Photoelectron circular dichroism refers to the forward/backward asymmetry in the photoelectron angular distribution with respect to the propagation axis of circularly polarized light. It has recently been demonstrated in femtosecond multi-photon photoionization experiments with randomly oriented camphor and fenchone molecules [C. Lux et al., Angew. Chem. Int. Ed. 51, 5001 (2012); C. S. Lehmann et al., J. Chem. Phys. 139, 234307 (2013)]. A theoretical framework describing this process as (2+1) resonantly enhanced multi-photon ionization is constructed, which consists of two-photon photoionization from randomly oriented molecules and successive one-photon ionization of the photoselected molecules. It combines perturbation theory for the light-matter interaction with \textit{ab initio} calculations for the two-photon absorption and a single-center expansion of the photoelectron wavefunction in terms of hydrogenic continuum functions. It is verified that the model correctly reproduces the basic symmetry behavior expected under exchange of handedness and light helicity. When applied to it fenchone and camphor, semi-quantitative agreement with the experimental data is found, for which a sufficient \(d\) wave character of the electronically excited intermediate state is crucial.

I. INTRODUCTION

Photoelectron spectroscopy is a powerful tool for studying photoionization dynamics. Intense short laser pulses for the ionization, which easily drive multi-photon transitions, allow to observe effects in tabletop experiments that otherwise would require synchrotron radiation. A recent example is the photoelectron circular dichroism (PDCD) of chiral molecules [1–5]. It refers to the forward/backward asymmetry with respect to the light propagation axis in the photoelectron angular distribution (PAD) obtained after excitation with circularly polarized light [6–8]. When the PAD is expanded in Legendre polynomials, a PDCD is characterized by the expansion coefficients of the odd-order polynomials with the highest order polynomial being determined by the order of the process, i.e., the number of absorbed photons [6, 9].

A theoretical description of such experiments with intense femtosecond laser pulses requires proper account of the multi-photon excitation pathways. In the pioneering work of McClain and co-workers [10–13], a model for the simultaneous absorption of two photons including the corresponding modified molecular selection rules was formulated. Two-photon circular dichroism was developed in Ref. [14], attributing the effect to a difference in the absorption coefficient for the two left and two right polarized photons. These approaches are based on a perturbation expansion of the light-matter interaction. The strong-field approximation provides an alternative description which is particularly suited for very intense fields [15, 16].

Multi-photon transitions driven by strong femtosecond laser pulses may or may not involve intermediate states. In recent experiments with bicyclic ketones [1–5], a 2+1-REMPI process was employed. The nature of the intermediate state remains yet to be clarified. A first theoretical study used the strong-field approximation [17]. While the standard strong-field approximation using a plane wave basis for the photoelectron was found to fail in describing PCD, accounting for the Coulomb interaction between photoelectron and photoion in the Born approximation allowed for observation of PCD. However, the PAD did not agree with the experimental ones. This may be explained by the role of the intermediate state in the REMPI process which necessarily is ignored in the strong-field approximation [17].

Here, we take the opposite approach, starting with a perturbation theory treatment of the multi-photon process. Thus, ionization is viewed as a (weak) one-photon transition into the continuum, the 'initial' state of which is prepared by non-resonant two-photon absorption. Such an approach is motivated by the moderate intensities, of the order of 10^{12} W/cm^2, used in the experiments [1–5]. Although clearly in the multi-photon regime, such intensities can be described comparatively well by low order perturbation theory [18–20].

The non-resonant two-photon preparation step yields an important difference compared to pure one-photon excitation [21]. In the latter case, the first order Legendre polynomial alone accounts for the PCD [22–24]. This results from the random orientation of the molecules, or, in more technical terms, from integrating the differential cross section over the Euler angles. In contrast, non-resonant two-photon excitation may lead to an orientation-dependent probability distribution of the molecules in the resonant intermediate state [2]. In this case, the maximum order of Legendre polynomials contributing to the PAD is not limited to 2, but for a 2+1 process. Whether the two-photon absorption is
orientation-dependent is determined by the two-photon transition matrix elements. Here, we calculate the two-photon transition matrix elements using state of the art \textit{ab initio} methods. However, for molecules as complex as camphor and fenchone, it is extremely challenging to model the complete photoionization process from first principles, even when using the most advanced \textit{ab initio} methods. We therefore split the theoretical description into two parts.

As long as all electrons remain bound, state of the art quantum chemical approaches, for example the coupled cluster methods, can be used to accurately determine the electronic wave functions. However, once an electron starts to leave the ionic core, the standard basis sets of electronic structure theory are not well adapted. An alternative is offered by a single-center expansion into eigenfunctions of a hydrogen-like atom for which both bound and continuum functions are known analytically. The hydrogenic continuum functions properly account for the long-range Coulomb interaction between ionic core and ejected electron but neglect the effect of short-range correlations in the ionization step. The basis functions for the single center expansion are chosen such as to yield the simplest possible model that is able to reproduce the laboratory-frame photoelectron angular distributions (LF-PADs) resulting from a 2+1-REMPI process in randomly oriented chiral molecules. The two descriptions are matched at the resonant, electronically excited intermediate state by projecting the numerically calculated wavefunction onto the basis functions of the single center expansion.

Our approach of calculating the PAD as a one-photon absorption cross section for an effective “initial” state in a single center expansion, while neglecting dynamical effects, allows us to generalize our findings to chiral molecules other than fenchone or camphore. In particular, we analyze the role of the laser polarization for each step in the 2+1 ionization process and determine the conditions on the two-photon absorption matrix elements for yielding PECD.

The remainder of the paper is organized as follows: Our theoretical framework is introduced in Sec. II. In detail, Sec. II A defines the PAD as one-photon photoionization cross section and summarizes the single center expansion. To make connection with experiment, the cross sections need to be transformed from the molecule-fixed frame into the laboratory frame and averaged over the random orientations of the molecules. The corresponding expressions for a 2+1 REMPI process are presented in Sec. II B with the details of the derivation given in the appendix. The symmetry properties required for observing PECD are analyzed in Sec. II C. Section III is dedicated to \textit{ab initio} calculations for the intermediate, electronically excited states and the two-photon absorption matrix elements. Section III A presents the computational details and Sec. III B the results. The one-center reexpansion required for matching the numerical results to the single-center description derived in Sec. II is described in Sec. III C. Our numerical results for the PAD of camphor and fenchone and the corresponding PECD are presented in Sec. IV with Sec. IV A dedicated to fenchone and Sec. IV B to camphore. Our findings are summarized and discussed in Sec. IV C. Section V concludes.

II. MODEL

We model the resonantly enhanced multi-photon photoionization as a 2+1 process, assuming the last photon to constitute a weak probe of the molecular state that is prepared by non-resonant two-photon absorption. For simplicity, we employ the strict electric dipole approximation. That is, contributions from magnetic dipole terms, which are important for circular polarization dependent differences in absorption cross sections, and higher order electric and magnetic multipole terms are neglected.

Defining two coordinate systems, the molecular frame of reference \( \mathcal{R} \) and the laboratory frame \( \mathcal{R}' \), \( \epsilon_{\mathcal{R}}' \) denotes the polarization of the laser field with respect to the laboratory frame (where we distinguish the polarization of the ionizing photon, \( \epsilon_{\mathcal{R}} \), from that of the first two photons, \( \epsilon_{\mathcal{R}}' \)). For convenience, we work in the spherical basis. Thus, \( \epsilon_{\mathcal{R}}' \) and \( \epsilon_{\mathcal{R}} \) correspond to the spherical unit vectors in the laboratory frame, with \( \varrho_{1,2} = \pm 1 \), 0 denoting left/right circular and linear polarization of the laser beam which propagates in the positive \( z' \) direction (the relation between the spherical and Cartesian unit vectors is found in Eq. (A7)). Primed (unprimed) coordinates refer to the laboratory (molecular) frame of reference throughout. Both frames, \( \mathcal{R}' \) and \( \mathcal{R} \), are related by an arbitrary coordinate rotation \( D(\alpha|\beta|\gamma) \), where \( \omega = (\alpha, \beta, \gamma) \) denote the Euler angles defining the orientation of \( \mathcal{R} \) with respect to \( \mathcal{R}' \).

Consider a one-photon (1P) transition in a molecule whose orientation with respect to \( \mathcal{R}' \) is given by the Euler angles \( \omega \). The corresponding differential photoionization cross section, when measured in the molecular frame \( \mathcal{R} \), reads, within perturbation theory and the electric dipole approximation and in SI units [25],

\[
\frac{d^2 \sigma_{1P}}{d\omega d\Omega_k} = c_0 \left| \langle \Psi_k | \epsilon_{\mathcal{R}}' \cdot \mathbf{r} | \Psi_o \rangle \right|^2,
\]

where \( c_0 = 4 \pi^2 \alpha h \omega_{\mathcal{R} \mathcal{P}h} \) with \( \alpha \) being the fine-structure constant, \( h \omega_{\mathcal{R} \mathcal{P}h} \) the energy of the ionizing photon, \( h \) the reduced Planck constant and \( \mathbf{r} \) the position operator of the electron (or a sum of the various position operators in the multi-electron case). The polarization of the electric field in the laboratory frame of reference is specified by \( \epsilon_{\mathcal{R}}' \), where \( \varrho_{2} \) takes the value 0 for linear and \( +1(-1) \) for left (right) circular polarization, respectively. \( |\Psi_k\rangle \) denotes an energy normalized molecular state with one electron transferred to the ionisation continuum with asymptotic electron linear momentum \( \mathbf{k} \). \( |\Psi_o\rangle \) is the (bound, unity normalized) molecular state prepared by the non-resonant two-photon absorption, which is defined in the
molecular frame of reference. In Eq. (1), we employ the standard notation for doubly differential cross sections in the molecular frame of reference [24, 26, 27] that depend not only on the solid angle $\Omega_k$ but also on the orientation of the molecule via the Euler angles $\omega$. We utilize a single-center approximation [28] which allows us to calculate the matrix elements in Eq. (1) explicitly. That is, we project the multi-electron wave function obtained from ab initio calculations, $|\Psi_o\rangle$, on one-electron basis functions and neglect electron correlations in the continuum description. We first discuss in Sec. II A our choice of $|\Psi_o\rangle$ and then explain below in Sec. II B how to connect the differential ionization cross section to the experimentally measured photoelectron angular distributions.

### A. Single center expansion

The “initial” state for the one-photon ionization is a multi-electron wavefunction which is usually expanded in specially adapted basis functions developed in quantum chemistry. In contrast, the single center expansion is based on the fact that any molecular wavefunction can be written as a linear combination of functions about a single arbitrary point [28]. Of course, such an ansatz will converge very slowly, if the multi-center character of the wavefunction is important. Writing the wavefunction of the electronically excited state of the neutral molecule, that is prepared by the two-photon absorption process, as $|\Psi_o\rangle = |\Psi_o(r)\rangle$, we expand it into eigenfunctions of a hydrogen-like atom,

$$
|\Psi_o\rangle = \sum_{n_o=0}^{n_{\text{max}}-1} \sum_{\ell_o=0}^{\ell_{\text{max}}} \sum_{m_o=-\ell_o}^{\ell_o} a_{m_o}^{\ell_o}(n_o) R_{\ell_o}^{m_o}(r) Y_{\ell_o}^{m_o}(\Omega_r) .
$$

Here, $a_{m_o}^{\ell_o}(n_o)$ stands for the unknown expansion coefficients, $R_{\ell_o}^{m_o}(r)$ denotes the radial eigenfunctions of the hydrogen-like atom, and $Y_{\ell_o}^{m_o}(\Omega_r)$ are the spherical harmonics. $\Omega_r = (\theta_r, \phi_r)$ refers to the polar and azimuthal angles of the position vector $r$ in the molecular frame of reference. Note that all information about the geometry and the symmetry properties of the “initial” electronically excited state is contained in the expansion coefficients $a_{m_o}^{\ell_o}(n_o)$. The number of basis functions must be truncated in any actual calculation, i.e.,

$$
|\Psi_o\rangle \approx \sum_{n_o=m_{\text{min}}}^{n_{\text{max}}} \sum_{\ell_o=0}^{\ell_{\text{max}}} \sum_{m_o=-\ell_o}^{\ell_o} a_{m_o}^{\ell_o}(n_o) R_{\ell_o}^{m_o}(r) Y_{\ell_o}^{m_o}(\Omega_r) .
$$

Strictly speaking, all molecular orbitals that are involved in Slater determinants describing the excited state should be subject to the single center expansion. In the present model, we employ an effective one-electron picture by expanding only one representative virtual orbital around the single center, namely the one that is additionally occupied in the supposedly leading configuration for the respective excited state.

We will also ask what the simplest possible model is that gives rise to PECD. In this case, we assume a single quantum number $n, n = n_o$, to contribute to Eq. (2), i.e.,

$$
|\Psi_o\rangle \approx \sum_{\ell_o=0}^{\ell_{\text{max}}} \sum_{m_o=-\ell_o}^{\ell_o} a_{m_o}^{\ell_o}(n_o) R_{\ell_o}^{m_o}(r) Y_{\ell_o}^{m_o}(\Omega_r) ,
$$

where $L_{o,\text{max}}$ refers to the highest angular momentum state appearing in the “initial” wavefunction. It follows from basic symmetry arguments that the minimal value of $L_{o,\text{max}}$ for which a PECD can be expected is $L_{o,\text{max}} = 2$, that is, at least $d$-orbitals are required.

We model the photoionization as a one-electron process arising from a hydrogenic-like system exclusively, which allows for neglecting the bound molecular part (the remaining molecular parent ion) in $|\Psi_k\rangle$. Thus, the resulting continuum wave functions, $\Psi_k(r)$, are expanded into partial waves in a way that allows for an explicit expression of the photoionization cross section in terms of the scattering solid angle $\Omega_k$ [23, 27, 29, 30],

$$
\Psi_k(r) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{k,\ell,m}(r) R_{\ell}^{m}(r) Y_{\ell}^{m}(\Omega_r) .
$$

Here, $Y_{\ell}^{m}(\Omega_r)$ and $R_{\ell}^{m}(r)$ correspond to the spherical harmonics describing the orientation of the photoelectron position and momentum, respectively, and $\phi_{k,\ell,m}(r)$ is the radial part of the photoelectron wavefunction. For simplicity, we use here and in the following $Y_{\ell}^{m}(\Omega_r)$ as an abbreviation for $(Y_{\ell}^{m}(\Omega_r))^\dagger$. Modeling photoionization as a one-electron process, we can approximate

$$
\phi_{k,\ell,m}(r) \approx e^{-i\delta_{\ell}} G_{k,\ell}(r) ,
$$

where $G_{k,\ell}(r)$ are the well-known radial continuum wavefunctions of the hydrogen atom, recalled in Appendix A 1, and $\delta_{\ell}$ stands for the Coulomb phase shift of the $\ell$-th scattered partial wave, with $\delta_{\ell} = \Gamma(\ell + 1 - 1/k)$ [24, 27, 30]. Note that we expect the phase shift for molecules to depend on $\ell_o$ and $m_o$ since the molecular potential of chiral molecules is not spherically symmetric. Neglecting the $m_o$-dependence of the phase shift involves no approximation when using Eq. (2) since the hydrogen eigenfunctions form a complete orthonormal basis. However, this is not true anymore when truncating the basis, cf. Eq. (3). Our ansatz thus involves an additional approximation, namely Eq. (6).

By construction, Eq. (6) yields orthogonality between bound and unbound wavefunctions which is required to avoid spurious singularities [29] and reproduce the correct threshold behavior of the photoionization cross sections [31]. With the approximation of Eq. (6), we account for the long-range Coulomb interaction between photoelectron and a point charge representing the ionic core but neglect the short-range static exchange. Also, dynamic changes in the electron distribution, such as adjustments of the electronic cloud due to nuclear motion, as well as the interaction of the outgoing photoelectron
with the driving electric field upon photoionization are neglected.

Inserting Eq. (6) into Eq. (5) yields

$$\Psi_k(r) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^{l} e^{-i\beta} G_{k,l}(r) Y^{*\ell}_{m}(\Omega_k) Y^{\ell}_{m}(\Omega_r),$$

and we can evaluate the matrix element in Eq. (1). Because the wavefunctions are given in the molecular frame, we need to rotate the spherical unit vector $\epsilon_\ell'$ in Eq. (1) into that frame [24]. Expanding the rotation operator $D(\alpha \beta \gamma)$ connecting $r$ and $r'$ into irreducible rank 1 tensor representations, cf. Appendix A 3, Eq. (1) becomes

$$d^2\sigma_{1P} d\omega \, d\Omega_k = c_0 \sum_{q=-1}^{1} \sum_{q'=-1}^{1} D^{(1)}_{q,2}^{(1)}(\omega) D^{(1)}_{q',2}(-\phi_2, \phi_2, \phi_2) \times (-1)^{q-q'} \langle \Psi_k | \Psi_q | \Psi_q | \Psi_q \rangle^*.$$

Inserting Eqs. (4) and (7) to evaluate the overlap integrals yields

$$d^2\sigma_{1P} d\omega \, d\Omega_k = c_0 \sum_{n_{\ell,\ell_0}} \sum_{m_{\ell,\ell_0}} \sum_{n'_{\ell',\ell_0}} \sum_{m'_{\ell',\ell_0}} \sum_{q=-1}^{1} \sum_{q'=-1}^{1} (-1)^{\ell'-\ell} e^{i(\ell q - \ell' q')} \times a_{\ell_0 m_0}^{n_0} a_{\ell' m'_0}^{e n_0} I^{(1)}_{\ell_0} (\ell_0, \ell_0) I^{(1)}_{\ell'_0} (\ell'_0, \ell'_0) \times Y^{(1)}_{m_0}(\Omega_k) Y^{(1)}_{m'_0}(\Omega_k) D^{(1)}_{q,2}^{(1)}(\omega) D^{(1)}_{q',2}(-\phi_2, \phi_2, \phi_2) \times S^{(1)}_{\ell_0, m_0}(q) S^{(1)}_{\ell'_0, m'_0}(q').$$

In Eq. (9), we have introduced radial and angular integrals $I^{(1)}_{\ell_0}(\ell_0, \ell_0)$ and $S^{(1)}_{\ell_0, m_0}(q)$, given by

$$I^{(1)}_{\ell_0}(\ell_0, \ell_0) = I_0 \left[ 0^{+\infty} r^3 G_{k,\ell}(r) R^{n_0}_{\ell_0}(r) \, dr \right]$$

for a fixed $n_0$ in Eq. (2) with $I_0 = 4\pi/3$, and

$$S^{(1)}_{\ell_0, m_0}(q) = \int Y^{(1)}_{\ell_0}(\Omega_0) Y^{(1)}_{q}(\Omega_0) Y^{(1)}_{m_0}(\Omega_0) \, d\Omega_0$$

$$= (-1)^{-m} b_{\ell,\ell_0} \begin{pmatrix} \ell & 1 & \ell_0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & 1 & \ell_0 \\ -m & q & m_0 \end{pmatrix}$$

with

$$b_{\ell,\ell_0} = \sqrt{3(2\ell + 1)(2\ell_0 + 1)/4\pi}$$

and using Wigner 3j symbols [32–35]. The angular integrals $S^{(1)}_{\ell_0, m_0}(q)$ determine, for each spherical unit vector $q = 0, \pm 1$, the selection rules between the angular components of the bound exited electronic state with quantum numbers $\ell_0, m_0$ and the partial wave components of the continuum wavefunction with quantum numbers $\ell, m$. Equation (10b) implies that transitions are allowed if and only if $\ell + 1 - \ell_0$ is even and $m_0 + q - m_0 = 0$ for all $|\ell_0 - 1| \leq \ell \leq \ell_0 + 1$. This is a special case of the more general rule for multipole transitions derived in Ref. [9]. The angular integrals can be evaluated analytically using the standard angular momentum algebra, whereas the radial integrals in Eq. (10a) are computed numerically.

The choice of basis to describe the radial part of the continuum wavefunction determines the weight with which each excited state expansion coefficient $a_{\ell_0 m_0}^{e n_0}(n_0)$ contributes to the PAD, cf. Eqs. (9) and (10a). Thus, choosing for example plane waves, i.e., the eigenfunctions of the “free” photoelectron, which is described in terms of the Bessel functions [32, 33, 35], and does not take into account the Coulomb interaction between the outgoing photoelectron and the remaining ion, would translate into a PAD different from the one obtained with the hydrogenic continuum wavefunctions of Eq. (7). Whether or not the model is able to reproduce the measured Legendre coefficients will to some extent depend on the choice of basis for the radial part in Eq. (5).

The missing ingredient to determine the differential photoionization cross section, Eq. (1), are the expansion coefficients, $a_{\ell_0 m_0}^{e n_0}(n_0)$, of the intermediate excited state wavefunction. They can either be used as fitting parameters or determined from ab initio calculations, see Sec. III.

Two more steps are then required to connect the differential ionization cross section to the experimentally measured PAD. First, the PAD is measured in the laboratory frame and the differential ionization cross section thus needs to be rotated from the molecular into the laboratory frame. Second, the orientation of the molecule with respect to the laboratory frame, defined by the polarization axis of the laser electric field, is arbitrary. We therefore need to average over all possible orientations, i.e., integrate over the Euler angles $\omega = (\alpha, \beta, \gamma)$, as we consider a randomly oriented initial ensemble of molecules.

### B. Photoelectron Angular Distributions

Rotating the differential cross section from the molecular into the laboratory frame requires rotation of the continuum state $|\Psi_k\rangle$ into $|\Psi_k\rangle$ using the inverse of Eq. (A4). This leads to
\[
\frac{d^2\sigma_{1P}}{d\omega \, d\Omega_k'} = c_0 \sum_{\ell,m} \sum_{\ell',m'} \sum_{q,q'} (-i)^{\ell'-\ell} e^{i(\delta_{\ell'}-\delta_{\ell})} \mathcal{A}_{m,m'}^{\ell\ell'}(n_o \rightarrow n_a \rightarrow n_a') I_{k}^{(\ell,\ell')}(l,\ell') I_{k'}^{(\ell',\ell')} \mathcal{S}_{m,m'}^{\ell\ell'}(q \rightarrow q') \times \sum_{\mathcal{L}=l-l'} \left( \begin{array}{ccc} \ell & \ell' & \mathcal{L} \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} \ell & \ell' & \mathcal{L} \\ m & m' & -m \end{array} \right) \right)_{\mu=\mathcal{L}} \mathcal{D}_{q,\nu}^{(1)}(\omega) \mathcal{D}_{-q',\nu'}^{(1)}(\omega) \mathcal{D}_{m,m'}^{(\mathcal{L})}(\omega) \rho_{2P}(\omega) \frac{\omega}{\hbar} e^{i\omega \phi_k'} \times (2\mathcal{L} + 1) \delta_1^{2P}(\ell,\ell') (-1)^{m'+q'-g_2},
\]

where \(\delta_1^{2P}(\ell,\ell')\) is defined in Eq. (B5) in Appendix B1. \(P_{\mathcal{L}}^{(1)}(\cos \theta_{1P}'\ell)\) denotes the associate Legendre polynomials. A detailed derivation of Eq. (11) is found in Appendix B1.

When averaging over all orientations in the second step, we need to account for the fact that the probability for non-resonant two-photon absorption from the ground state to the intermediate electronically excited state is, depending on the properties of the two-photon absorption tensor, not isotropic. The differential ionization cross section in the laboratory frame therefore needs to be weighted by the probability of the electronically excited state to be occupied after absorption of the first two (identical) photons. Thus, the cross section for photoemission into a solid angle \(d\Omega_{k'}\) around the axis \(k'\) in the laboratory frame, after one-photon transition from the electronically excited intermediate state, is given by

\[
\frac{d^2\sigma_{2+1}}{d\omega \, d\Omega_k'} = \rho_{2P}(\omega) \frac{d^2\sigma_{1P}}{d\omega \, d\Omega_k'},
\]

where \(\rho_{2P}(\omega)\) denotes the orientation-dependent probability to reach the intermediate excited state by absorption of two identical photons from the ground state. Equation (12) assumes a molecule to have, in its electronic ground state, an initial orientation of \(\omega = (\alpha, \beta, \gamma)\) with respect to the laboratory frame of reference. Note that Eq. (12) makes an additional assumption, namely the relative phase between the two-photon and one-photon steps to be irrelevant for the photoelectron spectrum and angular distribution. For a discussion of similar approximations in related multiphoton transitions between bound states, see for instance Refs. [11, 12].

The theoretically measured PAD contains contributions from all molecules in the sample, each with a specific orientation \(\omega\). The total photoelectron signal is therefore obtained by an incoherent summation over the contributions from all molecules. This is equivalent to integrating Eq. (12) over the Euler angles weighted by the probability of two-photon absorption. The “averaged” photoionization cross section in the laboratory frame therefore reads,

\[
\frac{d\sigma_{2+1}}{d\Omega_k'} = \int \rho_{2P}(\omega) \frac{d^2\sigma_{1P}}{d\omega \, d\Omega_k'} d\omega,
\]

where the integration is carried over the Euler angles \(\alpha, \beta, \gamma\).

The orientation-dependent probability to reach the intermediate excited state, \(\rho_{2P}(\omega)\), is obtained from the transition probability for two-photon absorption from the ground state \(|\Psi_o\rangle\) to the intermediate electronically excited state \(|\Psi_{o}\rangle\). The latter in general is defined as [36]

\[
A_{o,g}^{(2)} = \tilde{N}_0(\omega_{ph}) |\mathcal{M}|^2,
\]

where \(\mathcal{M}\), in the strict electric dipole approximation, \(\omega_{ph} \approx 1\), reads

\[
\mathcal{M} = \sum_n \left\{ \frac{(e_1 \cdot (\Psi_o | r | \Psi_o)) (\langle \Psi_o | r | \Psi_o \rangle \cdot e_2)}{\hbar \omega_{ph} - \hbar \omega_{n} + i \hbar \omega_{ph,2}} + \frac{(e_1 \cdot (\Psi_o | r | \Psi_o)) (\langle \Psi_o | r | \Psi_o \rangle \cdot e_2)}{\hbar \omega_{ph} - \hbar \omega_{n} + i \hbar \omega_{ph,1}} \right\}
\]

In Eq. (14b), \(e_j\) denotes the polarization direction (without specifying a certain frame of reference) of photon \(j (j=1,2)\) with energy \(\hbar \omega_{ph,j}\). To shorten notation, the polarization independent quantity \(\tilde{N}_0(\omega_{ph})\) in Eq. (14a) contains all prefactors,

\[
\tilde{N}_0(\omega_{ph}) = \frac{2\pi e^4}{\hbar^2} (F_1 \hbar \omega_{ph,1}) I(\omega_{ph,2}),
\]

with \(c_0\) being the elementary charge, and where \(F_1\) and \(I(\omega_{ph,2})\) refer to the incident laser-photon-flux (of type 1) and the energy flux per unity frequency (of type 2), respectively [36]. Evaluation of Eq. (14b) requires a frame transformation, since the wavefunctions involved in the two-photon transition matrices are known in the molecular frame whereas the polarization directions of the photons are given in the laboratory frame of reference. As before, transformation of the polarization directions from the laboratory frame to the molecular frame is carried out by means of the Wigner rotation matrices around the Euler angles \(\omega = (\alpha, \beta, \gamma)\). Consequently, the orientation dependent two-photon absorption probability is obtained as

\[
\rho_{2P}(\omega) = \left( \frac{8\pi^2 \hbar}{3} \right)^2 \tilde{N}_0(\omega_{ph}) \left| \sum_{q_1,q_2} \mathcal{D}_{q_1,\nu_1}^{(1)}(\omega) \mathcal{D}_{q_2,\nu_1}^{(1)}(\omega) T_{q_1,q_2} \right|^2,
\]

where we have applied the properties of the rotation matrices between both frames, detailed in Appendix A3, to Eq. (14b). In Eq. (15a), \(T_{q_1,q_2}\) denotes the two-photon
absorption tensor in the molecular frame of reference, whose tensor elements reads,
\[
T_{q_1,q_2} = \sum_n \frac{(\Psi_a|r_1|n\rangle\langle n|r_2\Psi_g)}{\hbar \omega_g - \hbar \omega_n + \hbar \omega_{ph,2}} + \frac{(\Psi_a|r_2|n\rangle\langle n|r_1\Psi_g)}{\hbar \omega_g - \hbar \omega_n + \hbar \omega_{ph,1}}.
\]
(15b)

In Eq. (15a), \(g_1\) denotes the polarization direction in the laboratory frame of reference, i.e. \(g_1 = \pm 1,0\), driving the two-photon absorption process, both photons having the same polarization direction. Additionally, the indexes \(q_1\) and \(q_2\) take the values \(\pm 1,0\). Finally, \(r_{q_2}\) denotes the spherical component of the position operator \(\mathbf{r}\), with \(q_k = \pm 1,0\). The correspondence between the spherical and Cartesian components of \(r_k\) are detailed in Eq. (A8), in Appendix A 3.

Hence, it is straightforward to write \(T_{q_1,q_2}\) in terms of the tensor elements written in the Cartesian basis, \(T^{\alpha\beta}(\omega_{ph})\), for \(\alpha, \beta = x, y, z\), cf. Eq. (C4). The correspondences are detailed in Eq. (A8), in Appendix A 3.

A further step consists of normalizing the probability density, such that the normalization condition,
\[
\int \rho_{2P}(\omega) \, d\omega = 1
\]
(16)
is fulfilled. Using the properties of addition of angular momenta, it is straightforward to find that the normalization factor reads, upon integration of Eq. (15a) over the Euler angles,
\[
\mathcal{N}_0(g_1) = \overline{g}(\omega_{ph}) B(g_1)
\]
(17a)
where we have defined,
\[
B(g_1) = \sum_{q_1, q_2} T_{q_1,q_2} T^*_{q_1,q_2} \sum_{Q=0}^2 (2Q + 1) \begin{pmatrix} 1 & 1 & Q \\ q_1' & q_2' & -q_1' - q_2' \end{pmatrix} \begin{pmatrix} 1 & 1 & Q \\ g_1 & g_1 - 2g_2 & -g_1 - 2g_2 \end{pmatrix} \begin{pmatrix} 1 & 1 & Q \\ q_1 & q_2 & -q_1 - q_2 \end{pmatrix},
\]
(17b)

with \(\overline{g}(\omega_{ph}) \equiv (8\pi^2\hbar/3)^2 \mathcal{N}_0(\omega_{ph})\). To retrieve Eqs. (17b), we have made use of the properties involving the product of two Wigner rotations matrices, as well as the integration involving a product of three Wigner rotations matrices, and apply them to Eq. (15a). These properties are outlined in Eq. (A9) and Eq. (B16), in Appendix A 3 and Appendix B 3, respectively.

Finally, the orientation dependent probability density reads,
\[
\rho_{2P}(\omega) = \mathcal{N}_0(g_1) \left| \sum_{q_1, q_2} \mathcal{D}^{(1)}_{q_1,g_1}(\omega) \mathcal{D}^{(1)}_{q_2,g_1}(\omega) T_{q_1,q_2} \right|^2,
\]
\[\text{with } \mathcal{N}_0(g_1) = \mathcal{B}^{-1}(g_1). \]
(18)

where \(\mathcal{N}_0(g_1) = \mathcal{B}^{-1}(g_1)\). In order to alleviate notations, and unless otherwise stated, we write \(\mathcal{N}_0 = \mathcal{N}_0(g_1)\). It is important to note, however, that in practice, computation of \(\mathcal{N}_0\) is not required, since this factor is common to all Legendre coefficients, and all of them are given, as in the experiment \([1, 4]\), normalized with respect to \(\mathcal{C}_0\).

Each component of the second-rank tensor \(T_{q_1,q_2}\) determines a property of the system, namely, the average transition rate. As a result of that the tensor \(T_{q_1,q_2}\) has two types of symmetry properties. The first one is due to an intrinsic symmetry originated from the property itself. For instance, \(T_{q_1,q_2}\) defines the probability of an absorption of two identical photons. Since two photons of the same energy and polarization are not the same,
with \( s = q_1 + q_2 - q_3 - q_4 \), and where we have defined

\[
g^{(K)}_{q_1, q_2, q_3, q_4}(\vartheta_1) = \sum_{Q=0}^{2} \sum_{Q'=0}^{\infty} \sum_{K=|Q-Q'|}^{\min(Q, Q')} \gamma^{(K)}_{Q, Q'} \left( \begin{array}{ccc} 1 & 1 & Q \\ q_1 & q_2 & -q_1 - q_2 \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & Q \\ \vartheta_1 & \vartheta_1 & -2\vartheta_1 \end{array} \right) \times \left( \begin{array}{ccc} 1 & 1 & Q' \\ q_3 & q_4 & -q_3 - q_4 \end{array} \right) \left( \begin{array}{ccc} Q & Q' & K \\ q_1 + q_2 & -q_3 - q_4 & -s \end{array} \right) \left( \begin{array}{ccc} 2\vartheta_1 & -2\vartheta_1 & 0 \end{array} \right) \right) \right)
\tag{19b}
\]

with \( \gamma^{(K)}_{Q, Q'} = (2Q + 1)(2Q' + 1)(2K + 1) \). In Eq. (19a), the orientation dependence is contained in \( D \), the polarisation dependence in \( g \) and the dependence on molecular parameters in \( T \). The derivation of Eqs. (19), employing the standard angular momentum algebra, is presented in Appendix B 2. We make once more use of the products \( K \) in Appendix B 3. Thus, a product of three rotation matrices is obtained when inserting Eqs. (19) and (B12), into Eq. (12). Evaluating the products of the Wigner 3j symbols, the differential cross section, Eq. (12), for a specific orientation \( \omega \) of the molecule becomes

\[
d^2\sigma_{\alpha+1} = \sum_{\substack{L \geq 0 \mu = -L \mu}} \sum_{\xi} b^\mu_L(\xi) P^\mu_L(\cos \vartheta_k) \sin \vartheta_k \, d\omega \, d^3 k',
\tag{20a}
\]

where the only orientation-dependent quantity, \( b^\mu_L(\xi) \), is given by

\[
b^\mu_L(\xi) = \sum_{\lambda} \kappa(\lambda) D_{s,0}^{\mu}(\xi) D_{q-q',0}^{\nu}(\omega) D_{m',-m,-\mu}(\omega).
\tag{20b}
\]

Note that the summation in Eq. (20b) runs over all indices, except \( L \) and \( \mu \), i.e., \( \lambda = \{ K, \nu, Q, Q', q, q', s, q_k, o, o', \ell, \ell, \ell, \ell' \} \), with \( K = 1, 2, 3, 4 \) and \( \nu = 0, 1, 2 \) appearing from the coupling of the first and second Wigner rotation matrices in Eq. (11), c.f. Eq. (B11). The specific form of \( \kappa(\lambda) \) is detailed in Eq. (B15), in Appendix B 3.

We can now use the integral properties of a product of three Wigner rotation matrices [32, 33, 35], c.f. Eq. (B16) in Appendix B 3. Integration of \( b^\mu_L(\xi) \) over the Euler angles then yields

\[
e^\mu_{\ell, \lambda} = \int b^\mu_L(\xi) d^3\omega \sin \vartheta_k \, d^3 k'.
\tag{21}
\]

\[
e^\mu_{\ell, \lambda} = \sum_{\nu} \kappa(\lambda) \left( \begin{array}{ccc} K & \nu & \nu' \\ q & q' & m' \end{array} \right) \left( \begin{array}{ccc} K & \nu & \ell \\ 0 & 0 & 0 \end{array} \right) \delta_{\mu, 0}.
\]

Note that the second Wigner symbol in the right-hand side of Eq. (21) is non-zero only if \( \mu = 0 \) and \( K + \nu + \ell \) is even with \( |K - \nu| \leq \ell \leq K + \nu \). Because \( \mu = 0 \), the terms depending on the azimuthal angle in Eq. (11) do not contribute and we retrieve cylindrical symmetry for the PAD of Eq. (13) which can thus be expressed in terms of Legendre polynomials. Furthermore, according to the fifth and sixth Wigner symbols in Eq. (19b), \( K = 0, \ldots, 4 \), because \( |Q - Q'| \leq K \leq Q + Q' \), and \( 0 \leq |K| \leq 2 \) according to the first and second Wigner symbols in Eq. (19b). The same applies to \( Q' \), reflecting the addition of angular momentum in a two-photon absorption process.

Making use, in Eq. (21), of the fact that the non-zero contributions for \( \nu \) are given by \( \nu = 0, 1, 2 \), c.f. Eq. (B11), one obtains that \( L \) runs from 0 to 6, and higher orders give only vanishing contributions. Therefore, the highest order Legendre polynomial that contributes to the PAD is \( L_{\text{max}} = 6 \), as expected for a 2+1 process from the \( 2(n + n) - 1 \) rule [22].

Finally, evaluating Eq. (13) with the help of Eq. (21) yields the experimentally measured PAD that is obtained for an initial ensemble of randomly oriented molecules,

\[
d^2\sigma_{\alpha+1} = \sum_{\ell = 0}^{6} c^{\ell}_L P^\ell_L(\cos \vartheta_k) \sin \vartheta_k \, d^3 k'.
\tag{22a}
\]

with coefficients

\[
c^{\ell}_L(\vartheta_1, \vartheta_2) = \sum_{\ell, \ell'} \sum_{m, m'} \sum_{q, q'} \sum_{q_k, o_k} \sum_{\ell, \ell'} 2^4 (-1)^{\ell + \ell'} (2\nu + 1)(2\ell + 1) a^{\ell, \ell}_m(n_0) a^{\ell', \ell'}_m(n_0) T^{q_k, \ell, \ell'}_{q, q_k, q} (\vartheta_1) \times (-1)^{\ell - \ell'} (-1)^{m' - q - q_2} e^{i(\delta_q - \delta_q)} g^{(K)}_{q_k, q, \ell, \ell'} (\vartheta_1, \vartheta_2) I^{n_{\ell, n_{\ell'}}}_{m} = 0 \right) \left( \begin{array}{ccc} \ell & \ell & L \\ m & -m' & m' - m \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & 1 \\ q & -q' & -q \end{array} \right) \left( \begin{array}{ccc} 2\vartheta_1 & -2\vartheta_1 & 0 \end{array} \right) \right) \right)
\tag{22b}
\]
with $\omega = 4\pi c_0$, and $\zeta(\ell, \ell') = \sqrt{(2\ell + 1)(2\ell' + 1)}$. Derivation of Eq. (22) is explicitly detailed in Appendix B3. Note that the coefficients $c_\ell(\gamma_1, \gamma_2)$ depend on the expansion coefficients $a^o_{m_o}(n_o)$ describing the intermediate electronically excited state, the two-photon absorption tensor elements, $T_{\gamma_1, \gamma_2}$, and the laser polarization directions of the two-photon absorption step, $\gamma_1$, and of the one-photon ionization, $\gamma_2$.

We would like to emphasize that the contribution of Legendre polynomials with order higher than 2 in Eq. (22) is due to the orientation dependence of populating the intermediate electronically excited state by two-photon absorption from the electronic ground state. That is, the density $\rho(\omega)$ expresses the fact that molecules with a certain orientation $\omega = \omega_1$ have a larger probability to undergo non-resonant two-photon absorption than molecules with some other orientation $\omega = \omega_2$. So although the molecules are assumed to be completely randomly oriented with respect to the laser beam axis when they are in their electronic ground state, an effective alignment results for those molecules that absorb two photons. This effective alignment results from selection of certain orientations rather than rotational dynamics which would occur on a much slower timescale. The contribution of higher order Legendre polynomials to the PAD is then entirely determined by the properties of the two-photon absorption tensor and the electronically excited state. In order to interpret the experimentally observed PADS for fenchone and camphor in terms of their expansion in Legendre polynomials, at least qualitatively, we estimate $a^o_{m_o}(n_o)$ and $T_{\gamma_1, \gamma_2}$ using $ab\ initio$ calculations or via fitting. Before presenting the corresponding details in Sec. III, we discuss below the basic symmetry properties of these parameters of our model as well as the dependence on the laser polarization directions $\gamma_1$, $\gamma_2$.

**C. PECD and symmetry**

By definition, PECD is obtained if the sign of the odd Legendre coefficients change when the helicity of the electric field changes. Analogously, for fixed electric field helicity, the odd Legendre coefficients change sign when enantiomers are interchanged. We therefore first inspect sign changes in the Legendre coefficients for molecules of opposite handedness within our one-center expansion framework. The relation between a given enantiomer and its mirror image is given by the parity operator, which changes the coordinates $\mathbf{r}$ to $-\mathbf{r}$. We therefore check, in the following, that our model transforms properly under parity.

Moreover, we determine the role that the excited state coefficients $a^o_{m_o}(n_o)$ and two-photon absorption tensor elements play for each Legendre coefficient that contributes to the PAD. To this end, we rewrite Eq. (22b), expressing each $c_\ell(\gamma_1, \gamma_2)$ explicitly in terms of the $a^o_{m_o}(n_o)$ and

$$T_{\gamma, \gamma'},$$

$$c_\ell(\gamma_1, \gamma_2) = \sum_{n_m} \sum_{n_{m_o}} n_{m_o} a^o_{m_o}(n_o) T_{\gamma_1, \gamma_2} T_{\gamma_3, \gamma_4} \times T_{\gamma_2, \gamma_4}.$$  

(23)

Equation (23) allows for determining each Legendre coefficient as a function of the intermediate electronically excited state via $a^o_{m_o}(n_o)$ and $T_{\gamma, \gamma'}$, i.e., it connects the measured Legendre coefficients to the electronic structure properties. We can thus compare the contribution of different $a^o_{m_o}(n_o)$ to different Legendre coefficients $c_\ell$ and explain differences, observed e.g. for different molecules, in terms of the electronic structure. This is important because investigation of camphor and fenchone revealed, for example, the same order of magnitude for the first and third Legendre coefficient in camphor, in contrast to fenchone where $c_3$ is about one order of magnitude smaller than $c_1$ [1, 4]. This observation suggests a significantly different electronic structure despite the fact that the two bicyclic monoketones are constitutional isomers which differ only in the position of the geminal methyl groups [40].

In the following, we discuss the behavior under parity and the contribution of the $a^o_{m_o}(n_o)$ and $T_{\gamma, \gamma'}$ to the $c_\ell(\gamma_1, \gamma_2)$ separately for the excited state coefficients, the two-photon absorption tensor and the laser polarization.

1. Role of the excited state expansion coefficients

In this section, we explicitly show that our single-center expansion for the $(2 + 1)$ REMPI process properly transforms under parity. Note that the two-photon absorption process conserves parity, which implies that exchanging enantiomers results in a parity change of the expansion coefficients of the intermediate electronically excited state, from $a^o_{m_o}(n_o)$ to $(-1)^{\ell_0} a^o_{m_o}(n_o)$. For practical convenience, we define the following quantity present in Eq. (22b) depending on $\ell_0$ and $m_o$:

$$P_L = a^o_{m_o}(n_o) a^c_{m_o}(n_o') S_{\ell_0, m_o}^{\ell_0, m_o}(q) S_{\ell_0, m_o}^{\ell_0, m_o}(q') \ell \ell' \mathbf{L} = 0 0 0.$$  

(24)

Upon application of the parity operator, Eq. (24) becomes

$$\tilde{P}_L = (-1)^{\ell_0 + \ell_0'} a^o_{m_o}(n_o) a^c_{m_o}(n_o') \times S_{\ell_0, m_o}(q) S_{\ell_0, m_o}(q') \ell \ell' \mathbf{L} = 0 0 0.$$  

(25)
Furthermore, we make use of the following property of the Wigner 3j symbols [25, 32, 33, 35],
\[
\begin{pmatrix}
  j & j' & J \\
  m & m' & M \\
\end{pmatrix}
= (-1)^{j'+j+J} \begin{pmatrix}
  j & j' & J \\
  -m & -m' & -M \\
\end{pmatrix},
\]
and apply it to the first Wigner 3j symbol in the expressions for \( S^\ell_{\ell_0,m_0}(q) \) and \( S_{\ell_0,m_0}'(q') \), i.e. Eq. (10b), containing triple zeros in the second row. The parity-transformed \( P_L \) thus becomes
\[
\tilde{P}_L = (-1)^{\ell_o+\ell_o'}(-1)^{\ell+\ell+\ell+\ell} \times S^\ell_{\ell_0,m_0}(q) S^{\ell',m_0'}_{\ell_0,m_0}(q') \times (-1)^{\ell+\ell+L} \begin{pmatrix}
  \ell & \ell' & L \\
  0 & 0 & 0 \\
\end{pmatrix}.
\]
Applying Eq. (26) once more to the Wigner 3j symbol in Eq. (27) allows for eliminating the explicit dependence of \( P_L \) on the partial waves \( \ell \) and \( \ell' \),
\[
\tilde{P}_L = (-1)^{\ell+\ell+\ell+\ell} \times \begin{pmatrix}
  \ell & \ell' & L \\
  0 & 0 & 0 \\
\end{pmatrix}.
\]
Because \( P_L \) and \( \tilde{P}_L \) refer, by construction, to enantiomers of opposite handedness, Eq. (28) implies a change of sign for \( L \) odd, cf. Eq. (22), when interchanging enantiomers, and no sign change for \( L \) even. Our model properly reproduces this basic symmetry behavior. The corresponding behavior under change of the light helicity, keeping the same enantiomer, is checked below in Sec. IIIC2.

Next we check the dependence of the non-zero Legendre coefficients contributing to the PAD on the maximum order \( L_{o,max} \) of the excited state coefficients, \( a^\ell_{\ell_0,m_0}(n_o) \), cf. Eq. (4). According to Equation (22b), a non-zero projection of the electronically excited state onto \( d \)-orbitals \((\ell_o = 2)\) is required to ensure that higher orders \( c_L \) are non-zero. In fact, an additional requirement to reach \( L_{max} = 6 \) is that \( L_{o,max} \geq 2 \). This is straightforward to see by inspecting the term
\[
\begin{pmatrix}
  \ell & \ell' & L \\
  0 & 0 & 0 \\
\end{pmatrix}
\]
in Eq. (22b), defining the PAD for a \((2 + 1)\) REMPI process. This term vanishes unless \( \ell + \ell' + L \) is even and \(|\ell - \ell'| \leq L \leq \ell + \ell' \). In order to reach \( L_{max} = 6 \), the minimal requirement in terms of the angular momentum for the continuum wavepacket is \( \ell_{max} = 3 \). Together with the selection rule \( \ell_{max} = L_{o,max} + 1 \), cf. Eq. (10b), this implies \( L_{o,max} = 2 \), i.e., presence of \( d \)-waves in the resonantly excited state. Note that a contribution from higher partial waves only modifies the algebraic value of the Legendre coefficients, but does not lead to higher orders because, as we have already pointed out, the maximal order of the Legendre coefficients is also limited by the term
\[
\begin{pmatrix}
  K & \nu & L \\
  0 & 0 & 0 \\
\end{pmatrix}
\]
in Eq. (22b).

Perhaps even more interestingly, for circular polarization direction \((q_1 = q_2 = \pm 1)\), \( c_5 \) vanishes if the projection of the electronically excited state onto \( \ell_o = 3 \) is zero. In other words, expansion of the electronically excited state in terms of \( s \), \( p \) and \( d \) orbitals results in non-zero Legendre coefficients \( c_L \) for \( L \) up to 6, except for \( c_5 \). In fact, we found \( c_5 \) to appear only in presence of a non-vanishing contribution of \( f \) orbitals. This does not result from selection rules as discussed before, but rather from an accidental compensation of terms in the summations in Eq. (22b) which arises from the central symmetry of our single center basis functions.

Given the experimental observation of Ref. [1, 4], we expect the electronically excited state for fenchone and camphor to have non-vanishing projections onto \( s \)-, \( p \)-, and \( d \)-orbitals, respectively. Also, the eventual expansion coefficients of the electronically excited state will most likely be different for fenchone and camphor to account for the different ratios of \( c_3 \) and \( c_1 \) observed for the two molecules [1, 4].

2. Role of Polarizations \( q_1 \) and \( q_2 \)

Having shown sign inversion for the odd Legendre coefficients for enantiomers of opposite handedness and a fixed circular polarization direction, we outline, in the following, an analogous symmetry property that is relevant when considering the same enantiomer but inverting the polarization direction. By definition, PECD requires all odd Legendre expansion coefficients for a given enantiomer to change sign when changing circular polarization from left to right, and vice versa. In order to show that our approach also properly reproduces this behavior, we employ again the symmetry properties of the Wigner 3j symbols in Eq. (22b), similarly to Sec. IIIC1. For the sake of completeness, we consider the general case of independent polarizations for the two-photon absorption and the one-photon ionization processes.

First, we consider all terms in Eq. (22b) depending on \( \epsilon^{\ell_o}_{L_{o}} \). We apply Eq. (26) to the fourth and sixth Wigner 3j symbol in Eq. (22b) for \( c_L(-q_1, -q_2) \). This yields
\[
\begin{pmatrix}
  1 & 1 & \nu \\
  \bar{q}_2 + q_2 & 0 \\
\end{pmatrix} = (-1)^{2+\nu} \begin{pmatrix}
  1 & 1 & \nu \\
  q_2 - \bar{q}_2 & 0 \\
\end{pmatrix}
\]
(29a)
for the fourth Wigner $3j$ symbol, and
\[
\begin{pmatrix}
K & \nu & L \\
0 & 0 & 0
\end{pmatrix} = (-1)^{K+\nu+L}
\begin{pmatrix}
K & \nu & L \\
0 & 0 & 0
\end{pmatrix}
\] (29b)
for the sixth Wigner $3j$ symbol in Eq. (22b) when the polarization direction driving the ionization process is $-q_2$. Next, we evaluate the expression containing the information about the photoionization process.

This implies, according to Eq. (22b),
\[
\epsilon_L(-q_1, -q_2) = (-1)^{\epsilon} c_L(\epsilon q_1 + q_2, q_2)
\] (31)
i.e., indeed, only odd Legendre coefficients change sign when changing simultaneously the polarization directions $q_1$ and $q_2$, whereas all even coefficients remain unchanged.

Next, we evaluate all non-vanishing Legendre coefficients as a function of the polarization directions $q_1$ and $q_2$ without making any assumptions on the two-photon absorption tensor $T$. To this end, we first consider the case where the two-photon absorption process is driven by linearly polarized light, $q_1 = 0$. The second Wigner $3j$ symbol in Eq. (19b) then becomes
\[
\begin{pmatrix}
1 & 1 & Q \\
-\varphi_1 & \varphi_1 & -2\varphi_1
\end{pmatrix} = \begin{pmatrix}
1 & 1 & Q \\
0 & 0 & 0
\end{pmatrix}.
\]
It does not vanish if and only if $Q = 0, 2$; and analogously for the fourth Wigner symbol in Eq. (19b) involving $Q'$. Furthermore, the sixth Wigner $3j$ symbol in Eq. (19b) becomes
\[
\begin{pmatrix}
Q & Q' & K \\
0 & 0 & 0
\end{pmatrix},
\]
which is non-zero only if $K$ is even, because $Q$ and $Q'$ are even, and $|Q - Q'| \leq K \leq Q + Q'$. As a consequence, because both $Q$ and $Q'$ are restricted to 0 and 2, $K$ must be equal to 0, 2 or 4. Now, we consider the fourth Wigner $3j$ symbol in Eq. (22b), namely
\[
\begin{pmatrix}
1 & 1 & \nu \\
\varphi_2 - \varphi_2 & 0
\end{pmatrix},
\] (32)
which contains the information about the photoionization transition. If the photoionization process is driven by linearly polarized light ($\varphi_2 = 0$), the allowed values for $\nu$ in Eq. (32) are $\nu = 0, 2$. Therefore, the last Wigner symbol in Eq. (22b),
\[
\begin{pmatrix}
K & \nu & L \\
0 & 0 & 0
\end{pmatrix},
\] (33)
has non-vanishing values only for $|K - \nu| \leq L \leq K + \nu$ and $K + \nu + \nu$ must be even due to the triple zeros in the second row. Because $K = [0, 2, 4]$ for $q_1 = 0$ and $\nu = 0, 2$ for $q_2 = 0$, the maximal order of Legendre coefficients is $L_{\text{max}} = 6$ and the non-vanishing Legendre coefficients are those for $L = 0, 2, 4, 6$, i.e., there are no odd Legendre polynomials in the PAD for $q_1 = q_2 = 0$.

On the other hand, if we keep $q_1 = 0$ but the photoionization transition is driven by circularly polarized light ($q_2 = \pm 1$), the non-vanishing values in Eq. (32) are not anymore restricted to even $\nu$, but instead to $\nu = 0, 1, 2$. Using these values for $\nu$ together with the requirement $|K - \nu| \leq L \leq K + \nu$ in Eq. (33), we obtain, for $K = 0, 2, 4$ (due to $q_1 = 0$), even as well odd Legendre polynomials in the PAD, i.e., $L = 0, 1, \ldots, 6$. Next we check whether PECD can arise, i.e., whether the non-zero odd coefficients change sign under changing the light helicity, for $q_1 = 0$ and $q_2 = \pm 1$. To this end, we explicitly write out the dependence of Eq. (22b) on the polarization direction $\varphi_2$ driving the ionization step and define
\[
\zeta_L^{K, \nu}(\varphi_2) = \begin{pmatrix}
1 & 1 & \nu \\
\varphi_2 - \varphi_2 & 0
\end{pmatrix},
\] (34a)
corresponding to the fourth and sixth Wigner $3j$ symbol in Eq. (22b). For the opposite polarization direction $-\varphi_2$, this quantity becomes
\[
\zeta_L^{K, \nu}(-\varphi_2) = \begin{pmatrix}
1 & 1 & \nu \\
-\varphi_2 & 0
\end{pmatrix},
\]
\[
= (-1)^{2\nu + K + L} \begin{pmatrix}
1 & 1 & \nu \\
\varphi_2 - \varphi_2 & 0
\end{pmatrix},
\] (34b)
where we have applied Eq. (26) to both Wigner 3j symbols in Eq. (34b), together with the fact that $K$ is even for $q_1 = 0$, as previously discussed. Finally, inserting Eq. (34b) into Eq. (22b) yields
\[ c_L(q_1 = 0, -q_2) = (-1)^L c_L(q_1 = 0, +q_2). \tag{35} \]
As a consequence, also for linearly polarized light driving the two-photon absorption process, odd Legendre coefficients change sign when the polarization direction of the ionizing field is changed from right to left, and vice versa. Whereas $K$ must be even for $q_1 = 0$, $\nu$ is $0, 1, 2$ for $q_2 = \pm 1$, allowing $L$ to take odd and even values in Eq. (34b). This implies that there is no need for circular polarization to drive the two-photon absorption process: Two-photon absorption driven by linearly polarized light followed by photoionization with circularly polarized light is sufficient for observing PECD in chiral molecules. In Section II C 3 we investigate the specific role of the two-photon absorption tensor for all the cases discussed above. Conversely, the two-photon transition may be driven by circularly polarized light followed by photoionization with linearly polarized light, i.e., $q_1 = \pm 1$ and $q_2 = 0$. As shown in Eq. (B26) in Appendix B 4, such a configuration leads to a PAD consisting exclusively of even Legendre contributions.

In Eq. (31) we have shown that only odd Legendre coefficients change sign when changing simultaneously the polarization direction driving the two-photon absorption and the one-photon ionization. In Appendix B 5, we show that
\[ c_L(q_1, q_2) = (-1)^L c_L(q_1, -q_2), \tag{36} \]
i.e., odd Legendre coefficients change sign when the polarization direction of the photoionization transition is changed, whereas the polarization of the field driving the two-photon absorption is kept fixed. This suggests the polarization direction of the ionizing field alone to impose the sign for all odd Legendre coefficients; the polarization direction in the two-photon absorption process plays no role. To verify this statement, we calculate $c_L(-q_1, q_2)$ in Appendix B 6 and find indeed
\[ c_L(-q_1, q_2) = c_L(+q_1, q_2). \tag{37} \]
That is, the two-photon process determines only the degree of anisotropy prior to ionization.

To summarize, using linearly polarized light for both two-photon absorption and one-photon ionization results in a PAD consisting only of even Legendre polynomials, i.e., vanishing PECD. In contrast, when the $(2+1)$ REMI process is driven by circularly polarized light, higher order odd Legendre polynomials may contribute, depending on the geometric properties of the resonantly excited state. The occurrence of non-zero Legendre coefficients for all polarization combinations is summarized in Table 1 below.

3. Role of two-photon absorption tensor

The number of Legendre coefficients that contribute to PECD in our model of the $(2+1)$ REMPI process is determined by how anisotropic the ensemble of electronically excited molecules is. This, in turn, follows from the properties of the two-photon absorption tensor. Here, we check the conditions that $T_{q_1,q_2}$, to determine in order to give rise to this anisotropy. To this end, we introduce the two-photon absorption amplitude $A_{2P}(\omega)$, where for convenience the multiplying factor in Eq. (18) has been dropped,
\[ A_{2P}(\omega) = \sum_{q_1} \sum_{q_2} D^{(1)}_{q_1,q_2}(\omega) D^{(1)}_{q_2,q_1}(\omega) T_{q_1,q_2}, \tag{38} \]
i.e., $\rho_{2P}(\omega) \propto |A_{2P}(\omega)|^2$, cf. Eq. (18). For simplicity, we define $\hat{A}_{2P}(\omega)$ such that $A_{2P}(\omega) = \frac{1}{2} \hat{A}_{2P}(\omega)$. We first check the ‘trivial’ case of an isotropic two-photon absorption tensor, i.e., a two-photon tensor that is diagonal in the Cartesian basis with equal elements. In this case, $\hat{A}_{2P}(\omega)$ becomes
\[ \hat{A}_{2P}(\omega) = +D^{(1)}_{0,0}(\omega) D^{(0)}_{0,0}(\omega) T_{zz} - \frac{1}{2} D^{(1)}_{0,-1,1}(\omega) D^{(1)}_{1,-1,1}(\omega) (T_{xx} + T_{yy}) - \frac{1}{2} D^{(1)}_{1,1,1}(\omega) D^{(1)}_{-1,-1,1}(\omega) (T_{xx} + T_{yy}), \]
where we have employed the transformation between spherical and Cartesian basis, cf. Eq. (A7). Taking the elements to be equal, $T_{xx} = T_{yy} = T_{zz} = 1$ without loss of generality, $\hat{A}_{2P}(\omega)$ can be written as
\[ \hat{A}_{2P}(\omega) = D^{(1)}_{0,0}(\omega) D^{(1)}_{0,0}(\omega) - 2D^{(1)}_{-1,1,1}(\omega) D^{(1)}_{1,-1,1}(\omega) \]
\[ = \sum_{\mu = 0, \pm 1} (-1)^\mu D^{(1)}_{\mu,0,0}(\omega) D^{(1)}_{-\mu,0,0}(\omega) \]
\[ = \sum_{\mu = 0, \pm 1} (-1)^\mu D^{(1)}_{\mu,0,0}(\omega) D^{(1)}_{-\mu,-0,0}(\omega) \]
\[ = (-1)^{q_1} \delta_{q_1,-q_2}, \tag{39} \]
where we have used Eq. (B10). That is, for an isotropic two-photon tensor, it is not possible to reach an anisotropic distribution by absorption of two identical photons. The PAD for the $(2+1)$ REMPI process then reduces to the well-known one for one-photon ionization of randomly oriented molecules, i.e., only $P_0$ and $P_2$ contribute if $q_2 = 0$, and $P_0$, $P_1$ and $P_2$ are non-zero for $q_2 = \pm 1$.

In what follows, we discuss a general two-photon absorption tensor, decomposing it as
\[ T = \alpha_o I_{3 \times 3} + \begin{pmatrix} \beta_{xx} & 0 & 0 \\ 0 & \beta_{yy} & 0 \\ 0 & 0 & \beta_{zz} \end{pmatrix} + \begin{pmatrix} 0 & T_{xy} & T_{xz} \\ T_{yx} & 0 & T_{yz} \\ T_{zx} & T_{zy} & 0 \end{pmatrix} \]
\[ \equiv T_{\text{Id}} + T_d + T_{\text{nd}}, \tag{40} \]
where we have split the diagonal elements into $T_{\text{Id}}$ and $T_d$ in order to differentiate between isotropic and
anisotropic two-photon tensors. The contributions of odd and even Legendre polynomials to the PAD as a function of $L_{o,\text{max}}$, the number of partial waves in the electronically excited state, the polarizations $\epsilon_{q_1}$ and $\epsilon_{q_2}$, and the two-photon absorption tensor are summarized in Table I. If the complete $(2+1)$ REMPI process is driven by linearly polarized light and only $\alpha_0 \neq 0$, then $P_2$ and $P_0$ contribute to the PAD as just discussed. If the two-photon absorption tensor is anisotropic, even Legendre polynomials of higher order can appear. For a molecule characterized by such a two-photon absorption tensor, odd Legendre polynomials can contribute to the PAD as just discussed. If the two-photon absorption tensor might have isotropic or anisotropic parts. This determines whether the $(2+1)$ process is allowed or not. We refer the reader to Refs. [37, 38] for more detailed discussion of this issue.

III. AB INITIO CALCULATIONS

The theoretical framework to model PECD presented above involves a number of molecular parameters. These can either be obtained by fitting the theoretical PAD to the experimental results or from ab initio calculations. Below we provide ab initio results for the two-photon absorption tensor for non-resonant transitions from the electronic ground state to the lowest-lying electronically excited states of fenchone and camphor. To assess the quality of these calculations, we employ different basis sets and different levels of treating electronic correlation.

A. Computational details

The linear response coupled cluster method with single and double (CC-SD) cluster amplitudes is used to calculate the intermediate electronically excited state and the two-photon absorption tensor in the electric dipole approximation. Moreover, time-dependent density functional theory (TD-DFT) calculations with the B3LYP

| isotropic | $\epsilon_{q_1}/\epsilon_{q_2}$ | $\epsilon_{q_1}/\epsilon_{q_0}$ | $\epsilon_{q_0}/\epsilon_{q_0}$ | $\epsilon_{q_1}/\epsilon_{q_1}$ | $\epsilon_{q_1}/\epsilon_{q_1}$ |
|-----------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| $c_0$     | s p d f                        | s p d f                        | s p d f                        | s p d f                        | s p d f                        |
| $c_1$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_2$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_3$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_4$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_5$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_6$     | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |

| anisotropic | $\epsilon_{q_1}/\epsilon_{q_1}$ | $\epsilon_{q_1}/\epsilon_{q_0}$ | $\epsilon_{q_0}/\epsilon_{q_0}$ | $\epsilon_{q_0}/\epsilon_{q_1}$ | $\epsilon_{q_1}/\epsilon_{q_1}$ |
|-------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| $c_0$       | s p d f                        | s p d f                        | s p d f                        | s p d f                        | s p d f                        |
| $c_1$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_2$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_3$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_4$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_5$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |
| $c_6$       | - - • •                        | - - • •                        | - - • •                        | - - • •                        | - - • •                        |

- contributing to the PAD
- not contributing to the PAD
exchange-correlation functional are performed. The molecular structure was energy minimized in all cases by performing DFT calculations with the B3LYP exchange-correlation functional and the def2-TZVP basis set on all atoms, using the TURBOMOLE program package [41]. In Fig. 1, the energy-minimized molecular structures of fenchone and camphor are shown, where the black vectors represent the Cartesian coordinate system located at the center of mass of the molecular systems. These structures and orientations correspond to the ones used subsequently for the calculation of the two-photon absorption tensors. Cartesian coordinates of the oriented structures are reported in the Supplemental Material [42].

Calculations for the two-photon transition strength tensor were performed using the DALTON program package [43]. Details of the implementation of the two-photon absorption tensors within the linear response coupled cluster (CC) scheme are found in Refs. [44, 45]. The orbital unrelaxed methodology was employed in the linear response calculations of the two-photon absorption tensors on the coupled cluster level. Electrons occupying the 11 energetically lowest-lying molecular orbitals that are dominated by 1s orbitals of the various carbon atoms or the oxygen were excluded from the correlation treatment on the coupled cluster levels (so-called frozen core approximation). The evaluation of the two-photon absorption tensor was performed at the CC-SD/Rydberg-TZ level of theory. It is worth noting that two-photon transition strength tensor $T_{i,j}$, $(i,j=x, y, z)$ is calculated in the coupled cluster framework as a symmetric product of two-photon transition moments from initial to final state and from final to initial state (the left and right two-photon transition moments). As explained in more detail in Appendix C, in coupled cluster theory, the symmetrized biorthogonal structure inhibits identification of the left and right two-photon absorption tensors. Thus, using the results of coupled cluster theory directly in the calculation of PAD might be problematic, because the model constructed in Sec. II depends on only one two-photon absorption tensor. We present a solution to this problem in Appendix C. In Fig. 1, the eigenvectors of the left and right two-photon absorption tensors for the third excited state of fenchone and camphor are shown (blue and red vectors).

To benchmark the quality of the electronic structure calculations, electronic excitation energies for transitions to the energetically lowest lying singlet states are performed on the CCSD and approximate second order coupled cluster (CC2) level for the n-aug-cc-pVNZ hierarchy of basis sets (see below). The TURBOMOLE program package [41] was used for calculations on the CC2 level within the resolution of the identity (RI) approximation. Select results were compared to conventional CC2 calculations with the MOLPRO program package [46], confirming that the RI approximation has little impact on the computed excitation energies (typically less than 10 meV). CCSD calculations for excitation energies were performed with MOLPRO. Again, electrons occupying the 11 energetically lowest-lying molecular orbitals were kept frozen in all coupled cluster calculations.

The following basis sets were employed:

- **TurboMole-TZVP** with H: [3s,1p], C: [5s,3p,1d], O: [5s,3p,1d].
- **Rydberg-TZ** with H: [2s], C: [5s,3p,1d], O: [5s,4p,3d,2f], ‘q’: [1s,1p,1d], where ‘q’ is a “dummy” center, positioned at the center of mass of the molecule. Primitive diffuse s, p, d Gaussian basis functions with the exponent coefficients equal to 0.015 $a_0$ were placed on this center. With this basis we can expect quite a reliable description of the higher excited states (which, according to Ref. [47], are diffuse Rydberg states) but most likely not for the lowest lying excited state.
- **The (n-aug-)cc-pVNZ hierarchy of basis sets** which are correlation consistent polarized valence N-tuple zeta basis sets, with $N = D, T, Q$, referring to double-$\zeta$, triple-$\zeta$ and quadruple-$\zeta$, respectively. On the oxygen nucleus, these basis sets have been also augmented by further diffuse functions with $n = s, d, t, q$ implying single, double, triple and quadruple augmentation, respectively. We used the procedure described in Ref. [48] for producing these aforementioned augmented basis sets.

The single center reexpansion is performed in two steps. First, the orbitals of the hydrogen atom are calculated with a large uncontracted basis set [13s11p9d8f]. For manually adjusting the phases of the atomic orbitals, we have computed numerically the radial part of the hydrogenic wavefunction using the following procedure. The atomic wavefunction

$$|\psi_i\rangle = \sum_j |\chi_j\rangle C_{ji} \quad (41)$$

\[FIG. 1. The oriented structures of fenchone (left) and camphor (right). The black vectors represent the Cartesian coordinate system located at the center of mass of the molecular systems. The blue and red vectors refer to the eigenvectors of the right and left two-photon tensors corresponding to the third excited state (for more information see Appendix C).\]
TABLE II. Experimental and calculated excitation energies (in eV) for fenchone (top) and camphor (bottom) obtained by TD-DFT and CC-SD/Rydberg-TZ used for subsequent calculation of the two-photon transition tensor.

| state | experiment [47] | DFT-β3LYP | CC-SD |
|-------|-----------------|------------|-------|
| A / n → π⁺ | 4.25 | 4.24 | 4.44 |
| B / n → 3s | 6.10 | 5.41 | 6.19 |
| C₁/n → 3p | 6.58 | 5.75 | 6.53 |
| C₂ | 5.82 | 6.60 |
| C₃ | 5.86 | 6.62 |
| D₁/n → 3d | 7.14 | 7.04 |
| D₂ | 7.09 |
| D₃ | 7.10 |
| D₄ | 7.12 |
| D₅ | 7.14 |
| A / n → π⁺ | 4.21 | 4.15 | 4.37 |
| B / n → 3s | 6.26 | 5.53 | 6.33 |
| C₁/n → 3p | 6.72 | 5.87 | 6.73 |
| C₂ | 5.90 | 6.75 |
| C₃ | 5.98 | 6.78 |
| D₁/n → 3d | 7.28 | 7.21 |
| D₂ | 7.27 |
| D₃ | 7.29 |
| D₄ | 7.31 |
| D₅ | 7.33 |

is considered, where $|\chi_j\rangle$ is a gaussian basis function and reads

$$|\chi_j\rangle = \frac{1}{\sqrt{2^{-3/2}l_j \alpha_j^{-1/2}l_j}} e^{-\alpha_j r^2} r^{l_j},$$

(42)

where $\alpha$ refers to the gamma function. The $C_{ji}$, the atomic orbital coefficients, are calculated by using the quantum chemical software Turbomole. The angular part can be chosen as the so-called real valued spherical harmonic and the integral over angular part is

$$\langle Y_{l_jm_j}(\theta, \phi)|Y_{l_km_k}(\theta, \phi)\rangle = \delta_{l_jl_k}\delta_{m_jm_k}. $$

(43)

In this way, one can calculate the radial part of Eq. (41) and compare it with Eq. (A3b)(which was used originally for reexpansion of the the electronically excited state of the neutral molecules under investigating (see Eq. (2))) and thus adjust the phases of atomic orbitals.

In the second step, the relevant molecular orbitals were calculated by projecting them onto hydrogen-like atom orbitals placed at the center-of-mass of camphor and fenchone, respectively, which is called the blowup procedure in the Turbomole context [41]. This calculation was carried out at the Hartree Fock(HF)/TZVP level of theory.

B. Results and discussion

The excitation energies of the lowest lying excited states for fenchone and camphor are presented in Tables II-VII. The labeling of the states follows the one for the absorption spectra of Ref. [47]. The states B, C and D are comparatively close in energy. In principle, the order in which the states are obtained in the calculations is unknown and the states may be interchanged due to an insufficient level of the correlation treatment or the smallness of the basis set. Nevertheless, we suppose that if the difference between the theoretical excitation energies and the experimental ones is smaller than the energy difference between the two states, then the order of the states is correctly reproduced. Table II shows that the quite accurate excitation energies for the states B, C and D are obtained in the CC-SD calculations with the Rydberg-TZ basis set for both camphor and fenchone. The A state is less accurately described with this basis set, while TDDFT result for state A is very close to the corresponding experimental value. For Rydberg states, it is well documented that the TDDFT method has severe limitations [49], and we observe, indeed, relatively large deviations between the computed excitation energies into Rydberg states and the corresponding experimental excitation energies as shown in Table II. We this did not perform the calculation of excitation energies into even higher Rydberg states for the present molecular systems.

Tables III and IV report more detailed information on the electronic structure of fenchone, obtained by employing both the CC2 and CCSD methods with systematically improved basis sets. Enlarging the set of augmenting diffuse functions on the O atom improves the excitation energies of the molecule under investigation. The energy of state A changes only mildly with increasing number of diffuse functions and increasing the multiple zeta quality. Excitation energies for the state A evaluated at the CC2/d-aug-cepVQZ and CC-SD/t-aug-pVDZ level of theory are in good agreement with the experimental one reported in Ref. [47]. For state B, a similar dependence on changing the augmented basis sets on the O atom and increasing the multiple zeta quality can be observed. Furthermore, we report a quite clear description for all members of the $n \rightarrow 3p$ Rydberg transitions, corresponding to the C band of the experimental spectrum reported in Ref. [47], whose individual components are experimentally not resolved. The theoretical spacing among all components of the band C approaches to the experimental one when increasing the augmented basis sets on the O atom and the multiple zeta quantity can be observed. For state A, the CC2 and CCSD produce the results close to each other, whereas for Rydberg states, deviation between the results obtained by employing the CC2 and CC-SD methods is getting...
larger as was seen previously for different molecular systems [50]. Based on results of excitation energies evaluated at CC2/t-aug-cc-pVDZ, d-aug-cc-pVTZ, t-aug-cc-pVTZ and d-aug-cc-pVQZ as well as CC-SD/t-aug-cc-pVDZ, we estimate the excitation energies for fenchone at CC-SD/t-aug-cc-pVQZ as described in the following. We add $\Delta E_1$ (which is the energy difference calculated using the CC2 method for basis sets d-aug-cc-pVQZ and d-aug-cc-pVTZ) as well as $\Delta E_2$ (which is the energy difference evaluated using CC2 for basis sets t-aug-cc-pVTZ and t-aug-cc-pVDZ) to the excitation energies calculated at the CC-SD/t-aug-cc-pVQZ level of theory. This procedure allows to estimate only few excitation energies of the fenchone molecule at the CCSD/t-aug-cc-pVQZ level of theory. This way of estimation does not work for all Rydberg states because the CC2 method is not accurate enough for calculating excitation energies of these states. We should mention that the direct calculation at the CCSD/t-aug-cc-pVQZ level of theory was beyond our computational facilities. The corresponding results are shown in Table V. In order to justify this way of estimation, we employed it for acetone, for which it is possible to calculate the excitation energies at the CC-SD/t-aug-cc-pVQZ level of theory. This allows us to compare the excitation energies at the CC-SD/t-aug-cc-pVQZ level of theory with the estimated ones. The corresponding results were presented in Tables S7 and 8 of the supporting information. It can be seen that the estimate values are very close to the corresponding ones calculated at the CC-SD/t-aug-cc-pVQZ level of theory. As an important remark, the excitation energies produced in Table II using the CC-SD/Rydberg-TZ level of theory are closer to the experimental values than those generated using the CC-SD/t-aug-cc-pVQZ level of theory or the estimated values at the CC-SD/t-aug-cc-pVQZ level of theory (see Tables III and V).

For camphor, the calculated excitation energies for state A, the lowest excited state, are in reasonable agreement with experiment for all methods and basis sets, cf. Tables II, VII and VI. Here, we again observe that enlarging the set of augment diffuse function on the O atom and the multiple zeta quality improves the results for the excitation energies. Furthermore, increasing the augmented basis sets on the O atom and the multiple zeta quality leads to a decrease (of less than 0.1 eV) in the theoretical spacing among all components of the C and D states, which again is in line with the experimental finding [47]. The estimated excitation energies at CC-SD/t-aug-cc-pVQZ level of theory are calculated in the same way as done for fenchone. These results are shown in Table V. We should mention that the excitation energies produced in Table II using the CC-SD/Rydberg-TZ level of theory are better than those generated using the CC-SD/t-aug-cc-pVDZ level of theory or the estimated values at the CC-SD/t-aug-cc-pVQZ level of theory (see Tables VI and V).

In the following, we report the two-photon absorption tensor elements for fenchone and camphor calculated with the TD-DFT and CC-SD methods. The computational details for the coupled cluster calculations are presented in Appendix C. The elements of the two-photon absorption tensor for fenchone and camphor in the Cartesian basis are generally independent because the molecules have the C1 point group symmetry [37]. However, as we consider absorption of two photons with same the frequency, the two-photon tensor must be symmetric [37]. Table VIII presents the results for fenchone. The A state in terms of the excitation energy is of no real concern for our present purposes because the wavelength and spectral width of the laser pulses employed in the 2 + 1 REMPI process [1, 4] practically rule out that A is the relevant intermediate state. As inferred from Table VIII, changing the method accounting for the electron correlations i.e TD-DFT and CC-SD, alters considerably the skeleton of the two-photon transition matrix and in particular there are changes in the signs of matrix elements when employing different electron correlation methods. As the excitation energies for the B and C states, calculated with the CC-SD/Rydberg-TZ level of theory, are in good agreement with experimental ones, cf. Table II, we expect the corresponding two-photon absorption tensor elements to be more reliable for the evaluation of PECID than those obtained with TD-DFT. We therefore use the two-photon absorption tensor elements calculated at the CC-SD/Rydberg-TZ level of theory for calculating PAD in Sec. IV.

Table IX presents the two-photon absorption tensor elements for camphor. Changing the method accounting of electron correlations, TD-DFT or CC-SD, alters considerably the skeleton of the two-photon transition matrix. For camphor, similar observation as mentioned for fenchone can be mentioned here; the A state is very unlikely to be the intermediate state probed in the 2 + 1 REMPI process [1, 4] practically rule out that A is the relevant intermediate state. As inferred from Table IX, changing the method accounting for the electron correlations i.e TD-DFT and CC-SD, alters considerably the skeleton of the two-photon transition matrix and in particular there are changes in the signs of matrix elements when employing different electron correlation methods.

C. Single center reexpansion of molecular wavefunctions

In order to match the \textit{ab initio} results with our model for the 2+1 REMPI process, we perform a single center reexpansion of the relevant molecular orbitals (see Figs. 2 and 3) obtained from a HF calculation with the TZVP basis set, projecting them onto hydrogenic atomic orbitals placed at the center-of-mass of the molecule. The hydrogenic orbitals are chosen in the form $\varphi(a_\nu, \ell_a, m_a) \equiv \{\ell_a,m_a\}$ where $a_\nu$ denotes a complete set of quantum numbers, $i \equiv (n_a, \ell_a, m_a)$, $R_i(r)$ are the radial functions the hydrogen and $T_i(\theta, \phi)$ the real spherical harmonics. The transformation between the expansion coefficients $\tilde{a}_i$ and $a_i$, defined in Eq. (2) with the standard
TABLE III. Lowest vertical electronic singlet excitation energies (in eV) for fenchone as computed with the CC2 and CCSD method. The column heading indicates the basis set, but augmented basis functions were only used on O and deleted from H and C. Thus, for H and C the cc-pVDZ basis set was used throughout.

| State | Exp. [47] | transition | cc-pVDZ | aug-cc-pVDZ | d-aug-cc-pVDZ | t-aug-cc-pVDZ |
|-------|-----------|------------|---------|-------------|---------------|---------------|
|       |           |            | CC2     | CCSD        | CC2           | CCSD          |
| A     | 4.25      | n → π     | 4.38    | 4.35        | 4.36          | 4.35          |
| B     | 6.10      | n → 3s    | 7.32    | 7.94        | 7.23          | 7.77          |
| C1    | 6.58      | n → 3p    | 7.92    | 8.27        | 7.72          | 8.07          |
| C2    |           |            | 8.07    | 8.52        | 7.93          | 8.31          |
| C3    |           |            | 8.07    | 8.52        | 7.93          | 8.31          |
| D     | 7.14      | n → 3d    | 8.22    | 8.83        | 8.20          | 8.78          |
|       | 8.27      |            | 9.02    | 9.35        | 8.85          | 9.20          |

TABLE IV. Lowest vertical electronic singlet excitation energies (in eV) for fenchone as computed with the CC2 method. The column heading indicates the basis set, but augmented basis functions were only used on O and deleted from H and C.

| State | Exp. [47] | cc-pVTZ | aug-cc-pVTZ | d-aug-cc-pVTZ | t-aug-cc-pVTZ | d-aug-cc-pVQZ |
|-------|-----------|---------|-------------|---------------|---------------|---------------|
| A     | 4.25      | 4.32    | 4.29        | 4.29          | 4.27          | 4.28          |
| B     | 6.10      | 6.83    | 6.15        | 6.01          | 5.68          | 5.96          |
| C1    | 6.58      | 7.51    | 7.40        | 6.32          | 6.13          | 6.36          |
| C2    |           | 7.53    | 7.50        | 6.39          | 6.14          | 6.41          |
| C3    |           | 7.69    | 7.62        | 6.46          | 6.17          | 6.45          |
| D     | 7.14      | 7.90    | 7.70        | 7.58          | 6.83          | 7.36          |
|       | 8.27      | 8.63    | 8.47        | 8.20          | 7.28          | 8.04          |

a In this calculation, the basis set cc-pVQZ on C and O atoms is used.

TABLE V. The estimated lowest vertical electronic singlet excitation energies (in eV) for fenchone and camphor at CC-SD/t-aug-cc-pVQZ level of theory.

| State | fenchone | camphor |
|-------|----------|---------|
| A     | 4.45     | 4.17    |
| B     | 6.22     | 6.52    |
| C1    | 6.89     | 7.00    |
| C2    | 6.90     | 7.02    |
| C3    | 6.92     | 7.06    |
| D     | 7.79     | 7.73    |

The projection quality of the orbitals 42 (highest occupied molecular orbital (HOMO) for the electronic ground state) and 43 (one of the two singly occupied molecular orbitals (SOMOs) for state A) for both camphor and fenchone is rather low. It amounts to 28% and 45% for fenchone and to 24% and 51% for camphor. This is expected for the HOMO and SOMO which are localized orbitals. In contrast, for the orbitals representative of the Rydberg states B and C in all cases the projection quality is higher than 90% for the corresponding SOMO. For these states, the results of the reexpansion are presented in the Supplemental Material [42]. We find the B state to be of s-type, that is, the s-wave contributes more than all other waves together; whereas the C states are of p-type. This is in agreement with the results of Refs. [47, 51], where these states were also found to be of s- and p-type, respectively. The d wave contributions for SOMOs orbitals corresponding to the B and C1, C2 and C3 states in fenchone and camphor are 2%, 3%, 5% and 6%, respectively.

complex spherical harmonics, is given in Appendix A4.

The projection quality of the orbitals 42 (highest occupied molecular orbital (HOMO) for the electronic ground state) and 43 (one of the two singly occupied molecular orbitals (SOMOs) for state A) for both camphor and fenchone is rather low. It amounts to 28% and 45% for
and C. Thus, for H and C the cc-pVDZ basis set was used throughout.

| State | Exp. [47] | transition | cc-pVDZ | aug-cc-pVDZ | d-aug-cc-pVDZ | t-aug-cc-pVDZ |
|-------|-----------|------------|---------|-------------|---------------|---------------|
| A     | 4.21      | n → π⁺    | 4.27    | 4.25        | 4.25          | 4.22          |
| B     | 6.72      | n → 3s     | 7.40    | 8.05        | 7.32          | 6.44          |
| C₁    | 0.84      | n → 3p     | 7.69    | 8.10        | 7.90          | 6.93          |
| C₂    | 8.23      |            | 8.84    | 8.11        | 8.63          | 7.32          |
| C₃    | 8.38      |            | 9.03    | 8.78        | 9.11          | 8.60          |
| D     | 7.28      | n → 3d     | 8.62    | 9.22        | 8.90          | 8.62          |
|       |           |            |         |             |               |               |
|       | 7.94      |            | 9.04    | 9.51        | 8.83          | 9.45          |

| TABLE VI. Lowest vertical electronic singlet excitation energies (in eV) for camphor as computed with the CC2 and CCSD method. The column heading indicates the basis set, but augmented basis functions were only used on O and deleted from H and C. Thus, for H and C the cc-pVDZ basis set was used throughout. |

| TABLE VII. Lowest vertical electronic singlet excitation energies (in eV) for camphor as computed with the CC2 method. The column heading indicates the basis set, but augmented basis functions were only used on O and deleted from H and C. |

| TABLE VIII. Two-photon transition matrix elements (in Bohr-Ångströms²) for fenchone. The specific orientation used is shown in Fig. 1. |

| TABLE IX. The same as Table VIII but for camphor. |

| IV. PHOTOELECTRON ANGULAR DISTRIBUTIONS |

The experimental measurements indicate a PECD effect of 10% for fenchone and 6.6% for camphor [4]. We
first check the range of PECD that our model allows for. To this end, we optimize, as a preliminary test, PECD, allowing all molecular parameters, i.e., two-photon absorption tensor elements and excited state expansion coefficients, to vary freely. We expand up to \( d \) and \( f \) waves for a single quantum number \( n_0 \), taken to be \( n_0 = 3 \) and \( 4 \), respectively. The optimization target is to maximize (or minimize, depending on the sign) PECD in order to determine the upper bounds. Following the definitions in Refs. [4, 17], we define an optimization functional,

\[
J = \frac{1}{c_0} \left( 2c_1 - \frac{1}{2}c_3 + \frac{1}{4}c_5 \right),
\]

where the Legendre coefficients are calculated according to Eq. (22b). All optimizations are carried out using the genetic algorithm for constrained multivariate problems as implemented in Ref. [52], using 500 iterations. We find numerical bounds of about 35% for both expansion cut-offs. The experimentally observed PECD effects are well within these bounds.

We now present calculations of the PAD for fenchone and camphor, using two different strategies to evaluate Eq. (22). First, we aim at identifying the minimal requirement in terms of structure and symmetry properties of the intermediate electronically excited state for reproducing, at least qualitatively, the experimental data. To this end, we minimize the difference between theoretically and experimentally obtained Legendre coefficients, \( \delta_j = |(c_j - c_{j,exp})|/c_{j,exp} \), taking the excited state expansion coefficients, \( a_{n_0}^L \), cf. Eq. (4), as optimization parameters, with \( n_0 = 3 \) fixed. This allows for \( L_{o,\text{max}} = 2 \), i.e., \( s \), \( p \) and \( d \) waves. Second, we test the agreement between theoretically and experimentally obtained Legendre coefficients when utilizing the expansion coefficients and two-photon tensor elements obtained by \textit{ab initio} calculations, cf. Section III. Here, our aim is to explain the differences observed experimentally in the PADS for fenchone and camphor in terms of the intermediate electronically excited state.

In the first approach, treating the excited state coefficients as optimization parameters, the optimization can be performed for the odd Legendre moments only, focusing on reproducing PECD, or for both odd and even Legendre moments, in order to reproduce the complete PAD. The different experimental uncertainties for odd and even Legendre coefficients [4] motivate such a two-step approach. Moreover, optimizing for the odd Legendre coefficients alone allows to quantify the minimal requirements on the intermediate electronically excited state for reproducing PECD.

In the second approach, when using the \textit{ab initio} two-photon absorption tensors and expansion coefficients, we need to account for the unavoidable error bars of the \textit{ab initio} results. To this end, we also utilize optimization, allowing the two-photon tensor matrix elements to vary, whereas the excited state coefficients are taken as is from the reexpansion of the \textit{ab initio} wavefunctions.

### A. Fenchone

We start by addressing the question of how many partial waves are required in the intermediate electronically excited state to yield odd Legendre coefficients with \( L > 1 \), as observed experimentally. To this end, we consider the expansion of the intermediate electronically excited state, cf. Eq. (3), with \( L_{o,\text{max}} = 2 \) and \( L_{o,\text{max}} = 3 \), i.e., up to \( d \) and \( f \) waves, for the states B and C, and employ the two-photon tensor elements from
the CCSD/Rydberg-TZ calculations, cf. Table VIII. The results are presented in Table X. Presence of \( f \)-waves is required to obtain a non-zero coefficient \( c_5 \), as expected from Table I. Allowing for \( f \)-waves (with \( n_0 = 4 \)) results in a perfect match for the odd coefficients for states C1, C2 and C3, cf. the upper part of Table X. In contrast, for state B, \( c_3 \) and \( c_5 \), while having the correct sign, are off by an order of magnitude. Modifying the optimization weights improves \( c_5 \) for state B, but only at the expense of the agreement for \( c_1 \) and \( c_3 \). State B can therefore be ruled out as intermediate electronically excited state. This is further confirmed by the lower part of Table X, showing the results for both odd and even Legendre coefficients in the optimization target. For state B, the sign of \( c_6 \) does not match the experimental one. Fitting both odd and even Legendre coefficients also allows to differentiate between the C states—only state C3 reproduces the correct sign of \( c_6 \). For all other Legendre moments, signs and order of magnitude of the coefficients match the experimental ones for all three C states. Fitting to all and not just the odd Legendre coefficients decreases the agreement between theoretical and experimental results for all C states. This may indicate that the model, with a single \( n_0 \), is not capable of reproducing the full complexity of the process, or it may be due to different experimental error bars for even and odd Legendre coefficients. In our fitting procedure, we have neglected the experimental error bars to keep the calculations manageable. The experimental error bars for the even Legendre coefficients are much larger than for the odd ones [4], and ignoring them may introduce a bias into the optimization procedure that could also explain the decreased agreement.

While already Table X suggests that C3 is likely the intermediate electronically excited state state probed in the \( 2+1 \) photoexcitation process, the ultimate test consists in using \( \text{ab initio} \) results for all parameters in Eq. \( (\text{22}) \), i.e., the excited state expansion coefficients and the two-photon tensor elements, and compare the resulting Legendre coefficients to the experimental data. The results are shown in Table XI (“fixed tensor elements”). Choosing a slightly larger photoelectron energy, specifically 0.58 eV instead of 0.56 eV, with the shift of 0.02 eV well within the error bars of the calculated excitation energies, considerably improves the agreement between theoretical and experimental values, in particular for the \( c_1 \) coefficient. Additionally, we allow the tensor elements to vary within a range of \( \pm 20\% \) to account for unavoidable errors in the electronic structure calculations. The best tensor elements within the error range are obtained by minimization. The corresponding functional is defined as

\[
\Gamma = \frac{1}{\Gamma^{(0)}} \sum_{j=1}^{6} \omega_j \left( \frac{c_j - c_{j,\text{exp}}}{c_{j,\text{exp}}} \right)^2 , \tag{45}
\]

where \( \omega_j \) are optimization weights and \( \Gamma^{(0)} \) is the value of the functional using the fixed tensor elements. Table XI confirms state B to be ruled out, since it does not reproduce correctly even a single sign of the odd coefficients. For all states C, the correct signs are obtained for the lower order Legendre coefficients, up to \( c_4 \). State C1 yields the correct sign of \( c_5 \) only if the tensor elements are allowed to vary within \( \pm 20\% \); the same holds for C2 and the sign of \( c_7 \). C3 does not reproduce the correct sign of \( c_5 \), but the value of \( c_5 \) is very small and close to zero when accounting for the error bars. In terms of PECD, the most important coefficient for fenchone is \( c_1 \), since its experimental value is an order of magnitude larger than that of the other odd coefficients. For \( c_1 \), the best agreement is obtained for state C3, differing from the experimental value by a factor of five. In contrast, the difference is by a factor of about twenty for state C1, and even larger for state C2. While \( c_1 \) is too small by more than an order of magnitude for states C1 and C2, \( c_3 \) is overestimated by a factor of five for \( c_1 \) and a factor of three for \( c_2 \). For states C1 and C2, the largest odd Legendre coefficient is thus \( c_3 \), unlike the experimental result where it is \( c_1 \). In contrast, the theoretical result for \( c_3 \) is in quantitative agreement for state C3 which therefore yields the correct ordering of the odd Legendre coefficients in terms of their magnitude. We thus conjecture that for fenchone, state C3 is most likely the intermediate electronically state probed in the experiment, despite the fact that \( c_5 \) is very close to zero. The reason for the discrepancy exclusively for \( c_5 \), while all other coefficients match the experimental ones at least qualitatively, is not entirely clear. A necessary condition for non-vanishing \( c_5 \) is, according to Table I, that the \( d \)-wave contribution of the intermediate state to be non-vanishing. The results shown in Table XI thus suggest that our calculations underestimate the \( d \)-wave character of C3. This may be caused by an improper description of long-range interaction between the photoelectron and the remaining ion, i.e., by the fact that the true potential felt by the photoelectron is neither central nor point-like, or by the interaction between the laser field and the photoelectron whose time dependence is neglected in our model. Finally, the error bars of the two-photon tensor elements may be larger than \( 20\% \). Indeed, allowing error bars of \( \pm 50\% \) in the two-photon absorption tensor elements removes the disagreement for \( c_5 \) and state C3. At the same time, these error bars do not significantly improve the agreement for the other two states. For example, the coefficient \( c_1 \) is \(-0.0061 \) for state C1 and \(-0.0045 \) for state C2, leaving the conclusion that state C3 is the intermediate resonance unchanged.

A systematic increase of the two-photon tensor error bars for state C3 is presented in Table XII. We compare minimization of the functional \( (45) \) with equal weights for all Legendre coefficients (upper part of Table XII) to that with a ten times larger weight of \( c_5 \) (lower part of Table XII). The motivation behind the second choice is to see whether the correct sign can be obtained for \( c_5 \) without the need to increase the error bars to a very high value. When increasing the error bars of the two-photon tensor elements, while using the same optimiza-
TABLE X. Legendre coefficients for the PAD of fenchone (calculated at a photoelectron energy of 0.56 eV and normalized with respect to \( c_0 \)), obtained by fitting to the experimental values with the excited state coefficients \( a_{m\ell}^* \) as free parameters. Only odd (top) and both odd and even (bottom) contributions were accounted for in the fitting procedure. The Rydberg states B, C1, C2 and C3 of fenchone are characterized by their two-photon absorption tensor, cf. Tab. VIII.

| Coeffs. | Exp. [4] | State B | State C1 | State C2 | State C3 |
|---------|---------|---------|---------|---------|---------|
| \( c_1 \) | -0.067 | -0.067 | -0.067 | -0.067 | -0.067 |
| \( c_2 \) | +0.008 | +0.080 | +0.080 | +0.008 | +0.008 |
| \( c_3 \) | +0.004 | - | +0.0005 | - | +0.004 |
| \( c_1 \) | -0.067 | -0.028 | -0.041 | -0.045 | -0.036 |
| \( c_2 \) | -0.580 | -0.076 | -0.102 | -0.274 | -0.176 |
| \( c_3 \) | +0.008 | +0.006 | +0.005 | +0.006 | +0.008 |
| \( c_4 \) | -0.061 | -0.004 | -0.004 | -0.021 | -0.012 |
| \( c_5 \) | +0.004 | - | +0.0001 | - | +0.001 |
| \( c_6 \) | -0.008 | +0.0002 | +0.0003 | +0.0007 | +0.0001 |

TABLE XI. Legendre coefficients for the PAD of fenchone (calculated at a photoelectron energy of 0.58 eV and normalized with respect to \( c_0 \)), obtained by employing the excited state coefficients and two-photon tensors from the \textit{ab initio} calculations. When including error bars, the tensor elements are allowed to vary within ±20%.

| Coeffs. | Exp. [4] | Fixed | Error bars | Fixed | Error bars | Fixed | Error bars | Fixed | Error bars |
|---------|---------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|
| \( c_1 \) | -0.067 | +0.003 | +0.003 | -0.004 | -0.003 | -0.002 | -0.001 | -0.013 | -0.015 |
| \( c_2 \) | -0.580 | -0.238 | -0.193 | -0.272 | -0.217 | -0.409 | -0.358 | -0.250 | -0.213 |
| \( c_3 \) | +0.008 | -0.030 | -0.029 | +0.050 | +0.038 | +0.033 | +0.025 | +0.008 | +0.010 |
| \( c_4 \) | -0.061 | -0.095 | -0.113 | -0.084 | -0.105 | +0.010 | -0.015 | -0.023 | -0.048 |
| \( c_5 \) | +0.004 | -0.001 | -0.001 | +0.003 | +0.002 | -0.004 | +0.003 | -0.0004 | -0.0004 |
| \( c_6 \) | -0.008 | -0.003 | -0.005 | +0.003 | -0.001 | -0.004 | -0.017 | -0.013 | -0.007 |

Overall, already the two-photon tensor elements taken directly from the \textit{ab initio} calculations yield a satisfactory agreement for the PAD between theory and experiment for state C3. The agreement is further improved by allowing the two-photon tensor elements to vary within a range of ±20% to account for the error bars of the \textit{ab initio} calculations. All Legendre coefficients except \( c_3 \) are sensitive to a variation within this range. Except for \( c_5 \), i.e., underestimation of the excite state \( f \)-wave character, a surprisingly good agreement between theoretical and experimental values is obtained, with the numerical values differing from the experimental ones up to a factor of five. The semi-quantitative agreement between theory and experiment is further illustrated in Fig. 4 where we compare calculation results for two specific photoelectron...
energies, 0.56 eV and 0.58 eV, to the experimentally obtained Legendre coefficients. The differences for the Legendre coefficients for 0.56 eV and 0.58 eV indicates the dependence of our results on the error bar of the calculated excitation energy of the intermediate electronically excited state. Additionally, Fig. 4 also shows the result of integrating over a normal distribution of photoelectron energies centered at 0.56 eV with a full width at half maximum (FWHM) of 200 meV. This accounts for the experimental averaging over photoelectron energies [4].

The disagreement between theoretical and experimental results amounts to a factor of about two which translates into a “mean” PECD of 3% and 4% for the fixed and ±20% adjustable tensor elements, respectively, compared to the experimental value of 10.1% [4]. The dependence of the calculated Legendre coefficients on the photoelectron energy is investigated in more detail in Fig. 5. A non-monotonic behavior is observed for all orders. Such a non-monotonic behavior of the Legendre coefficients as a function of the photoelectron energy has already been reported for c_1 in the one-photon ionization of randomly oriented molecules [53]. It reflects the dependence of the Legendre coefficients on the radial part of the photoelectron wavefunction. This dependence is studied further in Table XIII, where we compare the Legendre coefficients obtained with the Kummer confluent functions, i.e., the hydrogenic continuum wavefunctions defined Appendix A1, to those obtained with plane waves. The latter completely neglect the Coulomb interaction between photoelectron and photon. The plane waves clearly fail to reproduce the experimentally observed PECO, see in particular the values for 0.58 eV. Moreover, their values vary drastically with photoelectron energy. This difference is most likely explained by the highly oscillatory nature of plane waves even at short distances, in contrast to the hydrogenic scattering functions. Our finding is in line with the observation of Ref. [17] for the strong field approximation where plane waves fail completely to produce any PECO. In our model, non-zero odd Legendre coefficients are obtained, but a description of the photoelectron continuum that accounts for the Coulomb interaction between photoelectron and photon provides clearly better results.

### B. Camphor

We now turn to camphor, for which the experimentally recorded photoelectron spectrum peaks at 0.52 eV [4]. Analogously to our discussion for fenchone, we first investigate possible candidates for the intermediate resonance by considering the respective two-photon tensor alone and treating the excited state expansion coefficients as free optimization parameters. The results are displayed in Table XIV, comparing the optimization that targets only the odd Legendre coefficients to that considering both odd and even c_j. For all states, a non-zero c_5 coefficient is only obtained by including f-waves in the electronically excited state (corresponding to n_f = 4), as expected. When expanding up to f-waves, all four candidates allow for odd Legendre coefficients close to the experimental ones, unlike the case of fenchone, where state B could already be ruled out at this stage. However, states C2 and C3 do not allow for the correct sign of c_3, when the optimization targets both odd and even Legendre coefficients.

Once again, the ultimate test to rule out a given state consists in using both two-photon tensor elements and...
TABLE XIII. Legendre coefficients in the PAD of fenchone for state C3 and different photoelectron energies, obtained with hydrogenic continuum functions which include the Coulomb interaction between photoelectron and photon and plane waves where this interaction is neglected. \( \rho(E) \) stands for integration over a Gaussian distribution of photoelectron energies centered at 0.56 eV with a FWHM of 200 meV.  

| coeff. | exp. [4] | hydrogenic continuum functions | plane waves | photoelectron energy (eV) | | photoelectron energy (eV) |
|--------|---------|-------------------------------|------------|-------------------------|---|-------------------------|
| \( c_1 \) | -0.061 | -0.002 | -0.012 | -0.058 | -0.037 | 0.36 | 0.58 | 0.75 | \( \rho(E) \) | +0.002 | +0.006 | +0.002 | -0.017 |
| \( c_2 \) | -0.580 | -0.341 | -0.250 | -0.385 | -0.411 | +0.034 | +0.012 | -0.029 | -0.126 |
| \( c_3 \) | +0.008 | -0.008 | +0.008 | +0.170 | +0.005 | -0.006 | -0.006 | -0.012 | +0.009 |
| \( c_4 \) | -0.061 | +0.002 | -0.023 | -0.008 | -0.030 | +0.114 | -0.178 | -0.001 | -0.051 |
| \( c_5 \) | +0.004 | -0.001 | -0.0004 | +0.192 | -0.00003 | +0.0001 | -0.004 | -0.001 | +0.00001 |
| \( c_6 \) | -0.008 | -0.004 | -0.007 | +0.001 | -0.004 | +0.001 | -0.013 | +0.006 | -0.004 |

TABLE XIV. Legendre coefficients for the PAD of camphor (calculated at a photoelectron energy of 0.52 eV and normalized with respect to \( c_0 \)), obtained by fitting to the experimental values [4] with the excited state coefficients \( a_{m_n}^e \) as free parameters. Only odd (top) and both odd and even (bottom) contributions were accounted for in the fitting procedure. The Rydberg states B, C1, C2 and C3 of camphor are characterized by their two-photon absorption tensor, cf. Tab. VIII.  

| coeff. | exp. [4] | \( d \) waves | \( f \) waves | \( d \) waves | \( f \) waves | \( d \) waves | \( f \) waves | \( d \) waves | \( f \) waves |
|--------|---------|------------|------------|------------|------------|------------|------------|------------|------------|
| \( c_1 \) | +0.026 | +0.026 | +0.024 | +0.028 | +0.026 | +0.020 | +0.027 | +0.025 | +0.026 |
| \( c_3 \) | -0.053 | +0.038 | -0.025 | -0.038 | -0.040 | -0.032 | -0.042 | -0.042 | -0.047 |
| \( c_5 \) | +0.008 | - | +0.004 | - | +0.006 | - | +0.006 | - | +0.005 |
| \( c_1 \) | +0.026 | +0.099 | +0.096 | +0.051 | +0.054 | +0.054 | +0.041 | +0.040 | +0.048 |
| \( c_2 \) | -0.670 | -0.198 | -0.248 | -0.130 | -0.209 | -0.135 | -0.170 | -0.193 | -0.230 |
| \( c_3 \) | -0.053 | -0.034 | -0.022 | -0.023 | -0.020 | +0.037 | +0.043 | +0.028 | +0.013 |
| \( c_4 \) | +0.012 | +0.013 | +0.013 | +0.014 | +0.013 | +0.017 | +0.018 | +0.011 | +0.019 |
| \( c_5 \) | +0.008 | - | +0.001 | - | +0.001 | - | +0.002 | - | +0.002 |
| \( c_6 \) | -0.001 | -0.001 | -0.001 | -0.001 | -0.001 | -0.003 | -0.002 | -0.001 | -0.003 |

excited state expansion coefficients obtained from the \textit{ab initio} calculations. The corresponding results are shown in Table XV. First of all, Table XV confirms that states C2 and C3 are not the intermediate resonance probed in the experiment, since both states yield the wrong sign for both \( c_1 \) and \( c_3 \). Comparing the remaining two candidates, states B and C1, a much better agreement is observed for C1 which yields the correct signs for all Legendre coefficients. In contrast, state B only yields correct signs for the lower orders, \( c_1 \), \( c_2 \), and \( c_3 \). When accounting for the error bars in the two-photon tensor, a correct sign is additionally obtained for \( c_4 \), but the signs for \( c_5 \) and \( c_6 \) still cannot properly be reproduced with state B as intermediate resonance. As to the state C1, not only all signs but also the correct order of magnitude for \( c_2 \), \( c_3 \) and \( c_4 \) is observed, whereas the values are too small by one order of magnitude for \( c_1 \) and by two orders for \( c_5 \) and too large by one order of magnitude for \( c_6 \). Allowing the two-photon absorption tensor for state C1 to vary within an error range of \( \pm 20\% \) does not yield any significant improvement. It therefore does not seem to be the unavoidable error in the two-photon tensor elements that is important.

A second source of error in the \textit{ab initio} calculations is found in the excitation energy of the intermediate electronically excited state. This is reflected in the photoelectron energy. We thus present results for a second photoelectron energy, 0.58 eV in Table XVI. For state C1, all signs still match, and the correct order of magnitude is now obtained for \( c_1 \) to \( c_4 \). In particular, \( c_1 \) is now in quantitative agreement with the experimental value, and \( c_2 \) and \( c_3 \) differ by less than factor of 1.5, respectively 2.5. Despite the disagreement in the numerical values for \( c_5 \) and \( c_6 \), C1 is clearly the state the best matches the experimental data—the results obtained for states B, C2 and C3 show the same deficiencies as in Table XV.

The agreement with the experimental data obtained for state C1 can be further improved by allowing for larger error bars in the two-photon tensor elements. This is demonstrated in Table XVII. In fact, the agreement can be made fully quantitative, except for \( c_5 \), when increasing the error bars up to \( \pm 50\% \), as indicated by the small value of the optimization functional. In comparison to fenchoe, cf. Table XII, minimization results in significantly smaller values for \( \Gamma \), as the error range is increased. Also, the higher order Legendre coefficients are found to be more sensitive to modifications of the two-photon tensor elements than the lower ones. This is not surprising since the higher order coefficients depend more strongly on the anisotropy induced by the two-photon absorption. Analogously to fenchoe, \( c_5 \) has the correct sign but remains too small by one order of magnitude. This
calculations. When including error bars, the tensor elements are allowed to vary within $\pm c$ with respect to

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
coeff. & exp. [4] & state B & & state C1 & & state C2 & & state C3 \\
\hline
$c_1$ & +0.026 & +0.003 & +0.002 & +0.002 & +0.001 & -0.002 & -0.002 & -0.001 & -0.001 \\
$c_2$ & -0.678 & -0.384 & -0.383 & -0.389 & -0.401 & -0.395 & -0.395 & -0.421 & -0.425 \\
$c_3$ & -0.053 & -0.025 & -0.022 & -0.020 & -0.017 & +0.005 & +0.008 & +0.004 & +0.003 \\
$c_4$ & +0.012 & -0.066 & -0.050 & +0.020 & +0.023 & +0.004 & -0.002 & -0.008 & +0.0001 \\
$c_5$ & +0.008 & -0.002 & -0.001 & +0.0001 & +0.0001 & +0.001 & +0.001 & +0.0003 & +0.001 \\
$c_6$ & -0.001 & +0.043 & +0.035 & -0.026 & -0.023 & -0.008 & -0.001 & +0.005 & -0.0004 \\
\hline
\end{tabular}
\caption{Legendre coefficients for the PAD of camphor (calculated at a photoelectron energy of 0.52 eV and normalized with respect to $c_0$), obtained by employing the excited state coefficients and two-photon tensor elements from the \textit{ab initio} calculations. When including error bars, the tensor elements are allowed to vary within $\pm 20\%$.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
coeff. & exp. [4] & state B & & state C1 & & state C2 & & state C3 \\
\hline
$c_1$ & +0.026 & +0.033 & +0.030 & +0.026 & +0.027 & -0.005 & -0.009 & -0.004 & -0.002 \\
$c_2$ & -0.678 & -0.450 & -0.498 & -0.477 & -0.502 & -0.431 & -0.427 & -0.432 & -0.437 \\
$c_3$ & -0.053 & -0.029 & -0.031 & -0.024 & -0.022 & -0.003 & -0.0002 & +0.001 & -0.003 \\
$c_4$ & +0.012 & -0.074 & -0.034 & +0.003 & +0.009 & -0.022 & -0.036 & -0.026 & -0.018 \\
$c_5$ & +0.008 & -0.001 & -0.001 & +0.0001 & +0.0001 & +0.0002 & +0.001 & +0.0002 & +0.0001 \\
$c_6$ & -0.001 & +0.030 & +0.024 & -0.015 & -0.011 & -0.020 & -0.010 & +0.0001 & +0.0003 \\
\hline
\end{tabular}
\caption{The same as Table XV but for a photoelectron energy of 0.58 eV.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
coeff. & exp. [4] & fixed & $\pm 20\%$ & $\pm 30\%$ & $\pm 50\%$ \\
\hline
$c_1$ & +0.026 & +0.026 & +0.027 & +0.026 & +0.022 \\
$c_2$ & -0.678 & -0.477 & -0.502 & -0.515 & -0.529 \\
$c_3$ & -0.053 & -0.024 & -0.022 & -0.020 & -0.014 \\
$c_4$ & +0.012 & +0.003 & +0.009 & +0.012 & +0.012 \\
$c_5$ & +0.008 & +0.0001 & +0.0001 & +0.0001 & +0.0003 \\
$c_6$ & -0.001 & -0.015 & -0.011 & -0.008 & -0.001 \\
\hline
$\Gamma$ & 1.0 & 0.50 & 0.26 & 0.01 \\
\hline
\end{tabular}
\caption{Legendre coefficients for the PAD of camphor (calculated at a photoelectron energy of 0.58 eV and normalized with respect to $c_0$), obtained by employing the excited state coefficients and two-photon tensor elements from the \textit{ab initio} calculations for state C3 and increasing error bars of the two-photon tensor elements. Minimization of the functional $\Gamma$ in Eq. (45) is carried out with equal optimization weights.}
\end{table}

indicates once more that we underestimate significantly the $d$-wave contribution to the intermediate electronically excited state. It amounts to just 6% for both fenchone and camphor in our calculations.

The discussion above is summarized and illustrated in Fig. 6 which shows, besides the Legendre coefficients for photoelectron energies of 0.52 eV and 0.58 eV, those obtained when integrating over a normal distribution of photoelectron energies, centered at 0.52 eV, with a FWHM of 200 meV. The latter mimics the spectral bandwidth in the experiment. Introducing a distribution of photoelectron energies slightly worsens the agreement between theory and experiment. This can be attributed to the striking sensitivity of the Legendre coefficients on photoelectron energy, as shown in Fig. 7. A further improvement of the theoretical model would thus require experimental data for more than one photoelectron energy and with better energy resolution.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Comparison of experimentally obtained and theoretically calculated Legendre coefficients in the PAD for R- (+)-camphor, using state C1 and right circular polarization. The calculations considered fixed photoelectron energies of 0.52 eV and 0.58 eV as well as an integration over a Gaussian distribution of energies centered at 0.58 eV with a FWHM of 200 meV.}
\end{figure}

C. Discussion and Summary

Before concluding our paper, we briefly summarize our main findings. Our model describing the one-photon
quantitative agreement between theoretical and experi-
C3. For the lower order Legendre coefficients, a semi-
our model underestimates the
f observed in the Legendre coefficient
cnent than all other states. The largest disagreement is
dexcitation, state C3 has a much larger
cited states that could be accessed by the two-photon
photon tensor. Compared to the other electronically ex-
lar if the calculations account for error bars in the two-
state wavefunctions confirm this conjecture, in particu-
lar when including error bars of the two-photon
absorption tensor. The agreement is found to depend
very strongly on the photoelectron energy, with semi-
quantitative agreement found for a slightly larger value
than the experimental one. Such an energy shift could be
explained by the error bars of the calculated excitation
energy or by the dynamic Stark shift, which is neglected
in our model.

Our model accounts for the electronic structure of the
experimentally investigated examples of fenchone and
camphor in terms of their two-photon absorption ten-
sor and intermediate electronically excited state based
on a perturbative treatment of the light-matter interac-
tion within the electric dipole approximation and com-
bines an ab initio description of the non-resonant two-
photon absorption with a single-center expansion of the
photoelectron wavefunction into hydrogenic continuum
functions. This allows to account for the Coulomb in-
teraction between photoelectron and photion as well as
electronic correlations in the transition to the interme-
diate electronically excited state. It neglects static ex-
change and dynamic correlations in the interaction of the
photoelectron with the parent ion as well as the time-
dependence of the laser pulse and the possible multi-
center character of the continuum wavefunction. The
model correctly reproduces the basic symmetry behavior
expected under exchange of handedness and exchange of
light helicity.

Making use of the fundamental selection rules for two-
photon absorption and one-photon ionization, we have
shown which Legendre coefficients may be expected in
the photoelectron angular distributions, depending on
the basic geometric properties in the electronic structure
of the molecules as well as the possible combinations of
polarization for two-photon absorption and one-photon
ionization. We have identified the role of the two-photon
absorption tensor and intermediate state wavefunction—
it is the partial wave decomposition of the latter which
determines PECD whereas the two-photon absorption
tensor (in the electronic dipole approximation) merely

V. CONCLUSIONS & OUTLOOK

We have derived a theoretical model to study PECD af-
fter (2+1) resonantly enhanced multi-photon ionization in
randomly oriented chiral molecules. The model is based
on the strong-field approximation [17], where plane
waves completely fail to produce any PECD.

In contrast to fenchone, knowledge of the two-photon
tensors for camphor is not sufficient to point to a single
state as the intermediate resonance. However, calcula-
tions accounting for the ab initio two-photon absorption
matrix elements and excited state wavefunctions strongly
suggest state C1 to be the intermediate resonance, in
particular when including error bars of the two-photon
absorption tensor. The agreement is found to depend
very strongly on the photoelectron energy, with semi-
quantitative agreement found for a slightly larger value
than the experimental one. Such an energy shift could be
explained by the error bars of the calculated excitation
energy or by the dynamic Stark shift, which is neglected
in our model.

We find proper account of the Coulomb interaction be-
tween photoelectron and photion to be crucial. When
replacing, in our expansion of the photoelectron contin-
umum wavefunction, hydrogenic basis functions by plane
waves, no agreement with the experimental values is ob-
tained. This is in line with an earlier study of PECD
using the strong-field approximation [17], where plane
waves completely fail to produce any PECD.

FIG. 7. Dependence of the calculated Legendre coefficients in
the PAD of camphor, state C1, on the photoelectron energy
within the range of 0.50 eV to 0.58 eV using right circularly
polarized light.

mental values is obtained.

Our model correctly reproduces the basic symmetry behavior
expected under exchange of handedness and exchange of
light helicity.

We have derived a theoretical model to study PECD af-
fter (2+1) resonantly enhanced multi-photon ionization in
randomly oriented chiral molecules. The model is based
on the strong-field approximation [17], where plane
waves completely fail to produce any PECD.
introduces an anisotropic distribution of photoexcited molecules. Notably, the anisotropy is achieved by selection and not by rotational dynamics which would occur on a much slower timescale than that of femtosecond laser excitation.

We have applied our theoretical framework to fenchone and camphor, which have been studied extensively in recent experiments [1–5]. The \textit{ab initio} calculations employed the coupled cluster method as well as density functional theory. Due to the Rydberg-like character of the intermediate electronically excited state, diffuse basis functions needed to be added to the standard basis sets. This has allowed to reach a reasonable agreement with experimental values for the excited state energies.

We have used the electronic structure data to calculate the photoionization cross section. Accounting for the basic structure of the two-photon absorption tensor alone has already allowed us to qualitatively reproduce the experimental results for fenchone and camphor. The minimal requirement was identified to be a contribution of \(d\)-waves in the intermediate electronically excited state. Such a contribution can be expected if the two-photon absorption tensor is anisotropic. Employing the \textit{ab initio} data in the calculation of the photoelectron angular distribution, we have obtained a semi-quantitative agreement between theoretical and experimental Legendre coefficients characterizing the photoelectron angular distribution.

The satisfactory agreement of our model with the experimental data encourages a number of follow-up studies. First of all, a fully time-dependent description should be employed, following the lines of Ref. [54], because the photoelectron angular distributions depend on the polarization as well as the dynamics [53]. Based on the model developed here, an extension to time-dependent studies is straightforward, but will require substantial numerical effort. Such an extension will allow to investigate the dependence of the photoelectron angular distribution on the laser parameters, including intensity, central frequency, spectral bandwidth and varying polarization. The latter would be a first step towards the coherent control of PECD.

In parallel to accounting for time-dependent effects, the electronic structure treatment may be improved. In particular, the multi-center character of the continuum wavefunctions can be accounted for by employing Dyson orbitals in the calculation of the photoelectron angular section [31, 55, 56]. Moreover, a perturbative treatment of the static exchange for the photoelectron and extension to beyond the electric dipole approximation should be straightforward. The former would allow for a detailed study of the dependence of the angular distribution on the photoelectron energy, including low photoelectron kinetic energies. It would thus open the way toward investigating the role of the chiral ionic core in the dynamics leading to the photoelectron angular distributions. An extension to beyond the electric dipole approximation would allow for a unified theoretical treatment of further observables beyond PECD, such as circular dichroism in laser mass spectrometry of photoions [57–59], as well as comparison with different levels of electronic structure theory [60].

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**Appendix A: Wavefunctions and rotation matrices**

In the following, we summarize for completeness the properties of the continuum wavefunctions, rotation matrices and complex spherical harmonics in Secs. A 1, A 3 and A 4 that were used in the calculations in the main body of the paper.

1. **Radial continuum wavefunctions of the hydrogen atom**

An explicit expression of the radial continuum wavefunctions is given in terms of the Kummer confluent hypergeometric functions [25],

\[
G_{k,\ell}(r) = C_{E,\ell} (2kr)^\ell e^{-ikr} F_1(\ell + 1 + i/k, 2\ell + 2, 2ikr). \tag{A1}
\]

The factor

\[
C_{E,\ell} \equiv \sqrt{\frac{2\mu k}{\pi \hbar^2}} \frac{\Gamma(\ell + 1 - i/k)}{(2\ell + 1)!} e^{\pi/2k},
\]

where \(\Gamma(\cdot)\) refers to the Euler Gamma function, ensures proper normalization such that

\[
\int_0^{\infty} G_{E,\ell}(r)G_{E',\ell}(r) r^2 dr = \delta(E - E').
\]

In order to avoid numerical instabilities when generating the radial continuum wavefunctions, Eq. (A1) may be written in integral form [61],

\[
G_{k,\ell}(r) = \sqrt{\frac{2\mu k}{\pi \hbar^2}} \frac{\Gamma(\ell + 1 - i/k)}{(2\ell + 1)!} e^{\pi/2k} (2kr)^\ell e^{-ikr} \\
\times \int_0^1 s^{\ell + i/k} (1 - s)^{\ell - i/k} e^{2iks} ds. \tag{A2}
\]
2. Bound state wavefunctions of the hydrogen atom

As for the radial part of bound states for hydrogenic wavefunctions, \( R_{\ell n}^j(r) \), cf. Eq. (2), they can also be expressed in terms of the Kummer confluent hypergeometric functions [61],

\[
R_{\ell n}^j(r) = \left( 4k^3n_0 \frac{(n_0 + \ell_o - 1)!}{[(n_0 + \ell_o)]!} \right)^{1/2} (2k_{n_o}r)^j \times F_1(\ell_o + 1 - n_o, 2\ell_o + 1, 2k_{n_o}r) e^{-k_{n_o}r},
\]

with

\[
k_{n_o} = \frac{1}{1 + \frac{1}{M_o} a_o} \approx \frac{1}{n_o a_o} \tag{A3b}
\]

where \( m_e, M_o \) and \( a_o \) refer to the masses of the electron and that of the nucleus and the Bohr’s radius, respectively.

3. Rotation matrices

We summarize here some useful properties that are utilized in the derivation of the photoionization cross section, following the standard angular momentum algebra as found in Refs. [25, 32–35]. Any irreducible tensor field \( f^k \) of rank \( k \) is transformed from the molecular frame to the laboratory frame as follows [32, 33]:

\[
f^k_{m_k}(r') = D(\alpha|\beta)(r) f^k_{m_k}(r)
= \sum_{m'_k=-k}^{+k} f^k_{m'_k}(r) D^{(k)}_{m'_k,m_k}(\alpha|\beta), \tag{A4}
\]

where \( D^{(j)}_{m'_j,m_j}(\alpha|\beta) = \langle j, m'| D(\alpha|\beta) | j, m \rangle \) refers to the Wigner rotation matrix of rank \( j \), and the subscripts \( m_k \) and \( m'_k \) stand for the projection of the total angular momentum \( k \) onto the \( z \) axis in the molecular, respectively laboratory, frame. Conversely, the inverse of the transformation (A4) is given by

\[
f^k_{m_k}(r) = D^{-1}(\alpha|\beta)(r) f^k_{m_k}(r')
= \sum_{m'_k=-k}^{+k} f^k_{m'_k}(r') D^{(k)}_{m'_k,m_k}(\alpha|\beta). \tag{A5}
\]

We express all vector quantities in spherical coordinates,

\[
r' = \sqrt{\frac{4\pi}{3}} r \sum_{\mu=0,\pm 1} (-1)^\mu Y^\mu_\ell(\Omega') \epsilon'_-\mu,
\]

where \( \epsilon'_-\mu \) refers to the spherical unit vector in the laboratory frame, and \( \mu = 0, \pm 1 \) denotes linear, left and right unit components, respectively. The correspondence between the components of a arbitrary vector operator \( \mathbf{V} \) in spherical and cartesian basis is given by [32, 33, 62],

\[
\mathbf{V}_{-1} = \frac{1}{\sqrt{2}} (V_x - iV_y) \quad \mathbf{V}_0 = V_z \quad \mathbf{V}_{+1} = -\frac{1}{\sqrt{2}} (V_x + iV_y), \tag{A7}
\]

Transforming the spherical components \( r_q \), with \( q = \pm 1, 0 \) into the Cartesian basis using Eq. (A7) and Eq. (C4), we find the two-photon absorption tensor in the spherical basis,

\[
T_{-1,-1} = \frac{1}{2} (T_{xx} - 2iT_{xy} - T_{yy}) \\
T_{-1,0} = \frac{1}{\sqrt{2}} (T_{xx} - iT_{yz}) \\
T_{-1,1} = -\frac{1}{2} (T_{xx} + iT_{yy}) \\
T_{0,0} = T_{zz} \\
T_{0,1} = -\frac{1}{\sqrt{2}} (T_{xx} + iT_{yz}) \\
T_{1,1} = \frac{1}{2} (T_{xx} + 2iT_{xy} - T_{yy})
\]

Because \( T_{\alpha,\beta} = T_{\beta,\alpha} \) with \( \alpha, \beta = x, y, z \), cf. Eq. (C4), it can be straightforwardly shown, using Eq. (A7), that \( T_{q_1,q_2} = T_{q_2,q_1} \).

In the derivations we make heavily use of the product rule for two Wigner rotations matrices of ranks \( k \) and \( k' \),

\[
D_{\mu',\nu'}^{(k')}(\omega) D_{\mu,\nu}^{(k)}(\omega) = \sum_{J=|k-k'|}^{k+k'} (2J+1) D^{*(J)}_{-\mu,-\nu,-\mu'-\nu'}(\omega) \\
\times \langle k k' | \mu' - \mu | J \rangle \langle \mu' - \mu' | -\nu - \nu' \rangle,
\]

together with the following symmetry property,

\[
D_{\mu,\nu}^{(k)} = (-1)^{\mu-\nu} D_{-\mu,-\nu}^{(k)}(\omega), \tag{A9b}
\]

where \( (\ast) \) denotes the complex conjugate.

4. Conversion to complex spherical harmonics

The standard complex spherical harmonics \( Y^\mu_{\ell m}(\Omega) \) are related to the real spherical harmonics \( Y_{\ell |m|}(\Omega) \) by

\[
Y^\ell_{m}(\Omega) = \begin{cases} 
\frac{1}{\sqrt{2}} \left( Y_{\ell,|m|}(\Omega) - i Y_{\ell,-|m|}(\Omega) \right) & \text{if } m \leq 0, \\
\frac{1}{\sqrt{2}} \left( Y_{\ell,|m|}(\Omega) + i Y_{\ell,-|m|}(\Omega) \right) & \text{if } m = 0, \\
\left( (-1)^m \right) \frac{1}{\sqrt{2}} \left( Y_{\ell,|m|}(\Omega) + i Y_{\ell,-|m|}(\Omega) \right) & \text{if } m \geq 0.
\end{cases}
\]

Therefore the excited state expansion coefficients \( a_{\ell m}^{(n)} \), defined in Eq. (2), are connected to the coefficients in the
TABLE XVIII. Definition of the non-normalized real spherical harmonics in Cartesian coordinates.

| designation | real spherical harmonic |
|-------------|------------------------|
| S0          | 1                      |
| P0          | x                      |
| P1          | y                      |
| P2          | z                      |
| D0          | $-x^2 - y^2 + 2z^2/\sqrt{12}$ |
| D1a         | $x^2$                  |
| D1b         | $y^2$                  |
| D2a         | $xy$                   |
| D2b         | $(x^2 - y^2)/2$        |
| F0          | $-3x^2 - 3y^2 + 2z^2/\sqrt{60}$ |
| F1a         | $-x^2 - xy + 4xz^2/\sqrt{40}$ |
| F1b         | $-y^2 - xy - 4yz^2/\sqrt{40}$ |
| F2a         | $xy$                   |
| F2b         | $(x^2 - y^2)/2$        |
| F3a         | $(x^3 - 3xy^2)/\sqrt{24}$ |
| F3b         | $(y^3 - 3xz^2)/\sqrt{24}$ |

basis of real spherical harmonics by

$$a^\ell_{m_o}(n) = \begin{cases} \frac{1}{\sqrt{2}}(a^\ell_{m_o}(n) + i\tilde{a}^\ell_{m_o}(n)) & \text{if } m \leq 0, \\ \frac{(-1)^o}{\sqrt{2}}(a^\ell_{m_o}(n) - i\tilde{a}^\ell_{m_o}(n)) & \text{if } m = 0, \\ \frac{1}{\sqrt{2}}(a^\ell_{m_o}(n) - i\tilde{a}^\ell_{m_o}(n)) & \text{if } m \geq 0. \end{cases}$$

The naming of the real spherical harmonics used in the reexpansion of the molecular wavefunctions is explained in Table XVIII.

Appendix B: Derivations

Here, we provide details of the derivation of the one-photon transition rate, two-photon absorption tensor and the photoionization cross section in Secs. B1 to B3 as well as the behavior of the Legendre coefficients under change of helicity in the one-photon photoionization and two-photon absorption processes in Secs. B4 to B6.

1. One-photon transition rate

This section is devoted to deriving the rate for the photoionization transition from the intermediate electronically excited state to the continuum, driven by an electric field with polarization $\epsilon'_{q'\gamma}$. The starting point is the doubly differential cross section in the molecular frame given in Eq. (7). It contains the laboratory-frame product $\epsilon'_{q_2} \cdot r'$, which, using Eq. (A6), becomes

$$\epsilon'_{q_2} \cdot r' = \sqrt{\frac{4\pi}{3}} r Y^1_{q_2} (\Omega_{q'}) \equiv r'_{q_2}.$$  

This is rotated into the molecular frame, employing Eq. (A4), resulting in

$$\epsilon'_{q_2} \cdot r' = \sqrt{\frac{4\pi}{3}} r \sum_{q=0, \pm 1} D^{(1)}_{q_2q} (\omega) Y^1_q (\Omega_r).$$  

Inserting Eq. (B2) into Eq. (7) yields the photoionization cross section in the molecular frame as a function of the Euler angles $\omega \equiv (\alpha, \beta, \gamma)$, cf. Eq. (8).

Evaluating Eq. (8) requires evaluation of the product $\langle \Psi_k | r_q | \Psi_o \rangle | \Psi_k | r_{q'} | \Psi_o \rangle$. Inserting Eqs. (4) and (7) yields, for a fixed polarization direction $q$, 

$$\langle \Psi_k | r_q | \Psi_o \rangle = \sum_{\ell, m, n, \ell_o, m_o} (-i)^o e^{i\delta_{k,q}} I^{\alpha,\beta,\gamma}_k (\ell, \ell_o) S^{L,\mu}_{\ell_o, m_o, \ell, \mu}(q) \times \gamma^L_{\ell_o, m_o} (n_o) Y^L_{m_o} (\Omega_k)$$

with $I^{\alpha,\beta,\gamma}_k (\ell, \ell_o)$ and $S^{L,\mu}_{\ell_o, m_o, \ell, \mu}(q)$ defined in Eqs. (10a) and (10b) such that Eq. (8) comprises the product $Y^\ell_k (\Omega_k) Y^{*\gamma'}_{m'} (\Omega_k)$. Using the symmetry properties of the spherical harmonics, we can write

$$Y^{\ell'}_{m'} (\Omega_k) Y^{*\gamma'}_{m'} (\Omega_k) = (-1)^{m'} Y^{\ell'}_{m'} (\Omega_k) Y^{*\gamma'}_{m'} (\Omega_k) = (-1)^{-m} \sum_{L=|\ell-\ell'|}^{\ell+\ell'} \tilde{\gamma}(\ell, \ell', L) \left( \begin{array}{ccc} \ell & \ell' & L \\ m & -m' & -m \end{array} \right) Y^L_{m-m'} (\Omega_k)$$

with

$$\tilde{\gamma}(\ell, \ell', L) = \sqrt{(2\ell + 1)(2\ell' + 1)(2L + 1)/4\pi}$$

and $\Omega_k = (\vartheta_k, \phi_k)$ referring to polar and azimuthal angles of the momentum vector in the molecular frame of reference. In order to express the photoionization direction in the laboratory frame, we need to apply the inverse transformation (A5) to $Y^\ell_{m-m'} (\Omega_k)$, i.e.,

$$Y^\ell_{m-m'} (\Omega_k) = D^{-1}(\omega) Y^\ell_{m-m'} (\Omega_k) = \sum_{\mu=-\ell}^{\ell} D^{(L)}_{\mu, m-m'} (\omega) Y^L_{\mu} (\Omega_k) = \sum_{\mu=-\ell}^{\ell} (-1)^{m'-m-\mu} D^{(L)}_{\mu, m-m'-\mu} (\omega) Y^L_{\mu} (\Omega_k)$$

$$= \sum_{\mu=-\ell}^{\ell} \frac{(2\ell + 1)(L - \mu)!}{(L + \mu)!} (-1)^{m'-m} D^{(L)}_{\mu, m-m'-\mu} (\omega) P^L_{\mu} (\cos \vartheta'_k) e^{i\varphi'_k}$$

(B4a)
Using Eq. (B4a), Eq. (B3a) then becomes,

\[ Y_{m'}^{\ell'}(\Omega_k)Y_{m''}^{\ell''}(\Omega_k) = (-1)^{m''} \sum_{\ell = |\ell - \ell'|}^{\ell + \ell'} (2\mathcal{L} + 1) \varsigma_\mathcal{L}(\ell, \ell') \begin{pmatrix} \ell & \ell' & \mathcal{L} \\ m & m' & m'' \end{pmatrix} \begin{pmatrix} \ell & \ell' & \mathcal{L} \\ 0 & 0 & 0 \end{pmatrix} \times \sum_{\mu = -\mathcal{L}}^{\mathcal{L}} D_{m'' - m, -\mu}^{(\mathcal{L})}(\omega) P_{\mathcal{L}}^{\mu} (\cos \vartheta_k') e^{i\mu \varphi_k'} \]  

(B4b)

with

\[ \varsigma_\mathcal{L}(\ell, \ell') = \sqrt{\frac{(2\ell + 1)(2\ell' + 1) (\mathcal{L} - \mu)!}{16\pi^2 (\mathcal{L} + \mu)!}} \]  

(B5)

In Eq. (B4), we have used the equality between spherical harmonics and associate Legendre polynomials, including the Condon-Shortley phase convention [25, 32, 62],

\[ Y^{(1)}_\mu (S', \vartheta', \varphi') = (-1)^{\mu} \sqrt{\frac{(2L + 1)(L - \mu)!}{4\pi (L + \mu)!}} L^{\mu} (\cos \vartheta_k') e^{i\mu \varphi_k'} . \]  

(B6)

Inserting Eq. (B4) into Eq. (9), we obtain the differential one-photon cross section in the laboratory frame of reference for a fixed molecular orientation defined in Eq. (11).

2. Two-photon absorption tensor

The probability of two-photon absorption, Eq. (15a), of a molecule that is oriented with angles \( \omega = (\alpha, \beta, \gamma) \) with respect to the laboratory frame of reference contains the product \( D^{(1)}_{q_1, q_1}(\omega)D^{(1)}_{q_2, q_2}(\omega)D^{(1)}_{q_3, q_3}(\omega)D^{+ (1)}_{q_4, q_4}(\omega) \). Using Eqs. (A9), we obtain

\[ D^{(1)}_{q_1, q_1}(\omega)D^{(1)}_{q_2, q_2}(\omega) = \sum_{Q_1 = 0}^2 (2Q + 1) D^{(Q)}_{q_1 + q_2, 2}_1(\omega) \begin{pmatrix} Q & Q' & K \\ q_1 + q_2 - q_3 - q_4 & -s \end{pmatrix} \begin{pmatrix} Q & Q' & K \\ q_1 & q_2 \end{pmatrix} \]  

(B7a)

and analogously for \( D^{(1)}_{q_3, q_3}(\omega)D^{(1)}_{q_4, q_4}(\omega) = \sum_{Q_2 = 0}^2 (2Q + 1) D^{(Q')}_{q_3 - q_4, -2}_1(\omega) \begin{pmatrix} 1 & 1 & Q \\ q_3 - q_4 - q_4 \end{pmatrix} \begin{pmatrix} 1 & 1 & Q \\ q_1 & q_2 \end{pmatrix} \).  

(B7b)

Inserting Eqs. (B7) into (15a) and using

\[ D^{(Q)}_{q_1 + q_2, 2}_1(\omega)D^{(Q')}_{-q_3 - q_4, -2}_1(\omega) = \sum_{K = 0}^4 (2K + 1) D^{(K)}_{s, 0}(\omega) \begin{pmatrix} Q & Q' & K \\ q_1 + q_2 - q_3 - q_4 - s \end{pmatrix} \begin{pmatrix} Q & Q' & K \\ q_1 & q_2 \end{pmatrix} \]  

with \( s = q_1 + q_2 - q_3 - q_4 \), the orientation-dependent probability of two-photon absorption becomes,

\[ \rho_{2\mathcal{L}}(\omega) = \sum_{q_1, q_2} T_{q_1, q_2} \sum_{q_3, q_4} T_{q_3, q_4} (-1)^{q_3 + q_4} \sum_{Q = 0}^2 (2Q + 1) \begin{pmatrix} 1 & 1 & Q \\ q_1 & q_2 \end{pmatrix} \begin{pmatrix} 1 & 1 & Q \\ q_1 & q_2 \end{pmatrix} \times \sum_{Q = 0}^2 (2Q + 1) \begin{pmatrix} 1 & 1 & Q' \\ q_3 & q_4 \end{pmatrix} \begin{pmatrix} 1 & 1 & Q' \\ q_1 & q_2 \end{pmatrix} \times \sum_{K = 0}^4 (2K + 1) \begin{pmatrix} Q & Q' & K \\ q_1 & q_2 \end{pmatrix} \begin{pmatrix} Q & Q' & K \\ q_1 & q_2 \end{pmatrix} D^{(K)}_{s, 0}(\omega) \]

(B8)

cf. Eq. (19). Two useful properties of the Wigner 3j symbols utilized throughout this work, involve odd permutation of two columns [35],

\[ \begin{pmatrix} j & j' & J \\ m & m' & M \end{pmatrix} = (-1)^{j + j' + J} \begin{pmatrix} j' & j & J \\ m' & m & M \end{pmatrix} , \]  

(B9)
as well as the unitary condition for the Wigner rotation matrices \[35\],
\[
\sum_{M=-J}^{J} \mathcal{D}_{M,M'}^{(j)}(\omega) \mathcal{D}_{M,M'}^{*(j)}(\omega) = \delta_{M,M'}.
\] (B10)

3. Cross section for (2+1) photoionization

In order to simplify the expression of the cross section for the (2+1) REMPI process, we utilize the properties defined in Eq. (A9), to the product involving the first and second Wigner 3j symbols in Eq. (11),

\[
\mathcal{D}_{\nu,0}^{(1)}(\omega) \mathcal{D}_{\nu',0}^{(1)}(\omega) = (-1)^{\nu'-\nu} \sum_{\nu=0}^{2}(2\nu+1) \mathcal{D}_{\nu,0}^{(\nu)}(\omega) \left( \begin{array}{ccc} 1 & 1 & \nu \\ q & q' & -q' \\ \nu & \nu & 0 \end{array} \right).
\] (B11)

This allows for exploiting, in the integration over the Euler angles, the well-known properties for integrating over a product of three Wigner 3j symbols. With Eq. (B11), Eq. (11) takes the following form,

\[
\frac{d^2 \sigma_{1P}}{d\omega d\Omega'} = c_o \sum_{\ell,m} \sum_{\ell',m'} \sum_{q,q'} (-1)^{\ell-\ell'} e^{i(\delta_{\ell}-\delta_{\ell'})} a_{m_0} a_{m_0}^* I_k(\ell,\ell_0) I_k(\ell',\ell_0') \mathcal{S}_{\nu}^{\ell,m}(q) \mathcal{S}_{\nu'}^{\ell',m'}(q')
\times (2\mathcal{L} + 1) \left( \begin{array}{ccc} 0 & 0 & \mathcal{L} \\ m & -m' & -(m-m') \end{array} \right) \sum_{\mu=-\mathcal{L}}^{\mathcal{L}} \mathcal{S}_{\nu}^{\mu}(\ell,\ell') (-1)^{m'-q'-q} P_{\mathcal{L}}^{\mu}(\cos \theta_1^k) e^{i\varphi_1}
\times \sum_{\nu=0}^{2}(2\nu+1) \left( \begin{array}{ccc} 1 & 1 & \nu \\ q & q' & -q' \\ \nu & \nu & 0 \end{array} \right) \mathcal{D}_{\nu,0}^{(\nu)}(\omega) \mathcal{D}_{\mathcal{L}}^{(\mathcal{L})}(m',-m,-\mu)(\omega).
\] (B12)

Inserting Eq. (B8) and Eq. (B12) into Eq. (12), the PAD measured in the laboratory frame, resulting from a fixed molecular orientation \( \omega \) reads,

\[
\frac{d^2 \sigma_{2+1}}{d\omega d\Omega'} = N_0 c_o \sum_{m,m'} \sum_{q,q'} (-1)^{\ell-\ell'} e^{i(\delta_{\ell}-\delta_{\ell'})} a_{m_0} a_{m_0}^* I_k(\ell,\ell_0) I_k(\ell',\ell_0') \mathcal{S}_{\nu}^{\ell,m}(q) \mathcal{S}_{\nu'}^{\ell',m'}(q')
\times (2\mathcal{L} + 1) \left( \begin{array}{ccc} 0 & 0 & \mathcal{L} \\ m & -m' & -(m-m') \end{array} \right) \sum_{\nu=0}^{2}(2\nu+1) \left( \begin{array}{ccc} 1 & 1 & \nu \\ q & q' & -q' \\ \nu & \nu & 0 \end{array} \right)
\times \sum_{q_1,q_2} T_{q_1,q_2}^{(K)} \sum_{q_3,q_4} T_{q_3,q_4}^{(K)} \sum_{K=0}^{4} \sum_{s=-\mathcal{L}}^{\mathcal{L}} \mathcal{S}_{\nu}^{\mu}(\ell,\ell') (-1)^{m'-q'-q} P_{\mathcal{L}}^{\mu}(\cos \theta_1^k) e^{i\varphi_1}
\times \mathcal{D}_{s}^{(K)}(\omega) \mathcal{D}_{q-q',0}^{(1)}(\omega) \mathcal{D}_{m'-m,-\mu}^{(\mathcal{L})}(\omega),
\] (B13)

with \( s = q_1 + q_2 - q_3 - q_4 \). Equation (B13) may be written in the more compact form of Eqs. (20), namely,

\[
\frac{d^2 \sigma_{2+1}}{d\omega d\Omega'} = N_0 c_o \sum_{\mathcal{L}=0}^{\infty} \sum_{\mu=-\mathcal{L}}^{\mathcal{L}} b_{\mu}^{K}(\omega) P_{\mathcal{L}}^{\mu}(\cos \theta_1^k) e^{i\varphi_1},
\] (B14a)

In Eq. (B14a), the only orientation-dependent quantity, \( b_{\mu}^{K}(\omega) \), is given by

\[
b_{\mu}^{K}(\omega) = \sum_{\lambda} \kappa(\lambda) \mathcal{D}_{s,0}^{(K)}(\omega) \mathcal{D}_{q-q',0}^{(1)}(\omega) \mathcal{D}_{m'-m,-\mu}^{(\mathcal{L})}(\omega).
\] (B14b)
with $\kappa'_{\ell}^{\mu}(\lambda)$ defined as

$$
\kappa'_{\ell}^{\mu}(\lambda) = (-i)^{\ell - \ell'} e^{i(\delta_{\ell} - \delta_{\ell'})} a_{m}^{\mu}(q) a_{m'}^{\mu}(q') S_{\ell,\ell'}^{m,m'}(q,q') S_{\ell',\ell}^{m',m}(q,q') (\ell, \ell') \times
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
-1 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
1 & 1 & 1 \\
q' & q & -q - q_2
\end{pmatrix}
\begin{pmatrix}
1 & 1 & 0 \\
-1 & -1 & -m'
\end{pmatrix}
T_{q_1,q_2}(-1)^{q_1+q_2} T_{q_3,q_4}^* g_{q_1,q_2,q_3,q_4}(2\nu + 1)(2\ell + 1)(-1)^{m' - q - q_2} (B15)
$$

where $\lambda$ comprises all summation indices, except for $\mathcal{L}$ and $\mu$, as described in Sec. B3. Next, according to Eq. (13), we need to average over all initial orientations, i.e., integrate the doubly differential cross section over the Euler angles. To this end, we utilize the following integration property involving the product of three Wigner 3j symbols [32, 33, 35],

$$
\int D_{s,0}^{(K)}(\omega) D_{q-q',0}^{(\nu)}(\omega) D_{m,-m,-\mu}^{(\mathcal{L})}(\omega) d^3\omega = \begin{pmatrix} K & \nu & \mathcal{L} \\ s & q - q' & m' - m \end{pmatrix} (B16)
$$

with $d^3\omega \equiv d^3(\alpha, \beta, \gamma) = da d\alpha(\cos(\beta)) d\gamma / 8\pi^2$. Finally, following Eq. (13), integration of Eq. (B13) over the Euler angles $\omega \equiv (\alpha, \beta, \gamma)$, denoting Eq. (B16), gives the expression of the laboratory frame PAD resulting from a randomly ensemble of molecules in the context of a $(2+1)$ REMPI process, defined in Eq. (22). In particular, due to the second Wigner 3j symbol in Eq. (B16), it is clear that the integral vanishes if $\mu \neq 0$. As a consequence, this requirement translates into cylindrical symmetry of the PAD measured in the laboratory frame, as $\mu$ also appears in the azimuthal angle dependent term $e^{i\nu\varphi}$ in Eq. (B13). Thus, we retrieve the expression defined in Eq. (22).

4. Non-zero Legendre coefficients for two-photon absorption with circularly polarized light and ionization with linear polarization

In this section, we show that a $(2+1)$ REMPI process for which the two-photon absorption process is driven by circular polarized light, followed by linearly polarized light for the radiative process, lead within the electric dipole approximation exclusively to even Legendre coefficients. To this end, we exploit the symmetry as well as invariance properties of Eq. (22b), by making a change of variables for $q_1, q_2, q_3$ and $q_4$ in Eq. (22b) that preserves $c_{\ell}(q_1, q_2)$ and also keeps $s = q_1 + q_2 - q_3 - q_4$ invariant (in order to keep the fifth Wigner 3j symbol in Eq. (22b) unchanged). A change of variables fulfilling this property reads,

$$
\begin{pmatrix}
q_1' \\
q_2' \\
q_3' \\
q_4'
\end{pmatrix} = \begin{pmatrix}
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -1 \\
-1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
q_1 \\
q_2 \\
q_3 \\
q_4
\end{pmatrix}, \quad (B17)
$$

i.e. it interchanges $q_1 \leftarrow -q_3$ and $q_2 \leftarrow -q_4$. For simplicity, we define the quantity,

$$
c_{\ell}(q_1,0) = c'_{\ell}(q_1,0), \quad (B19)
$$

Using Eq. (B17), the tensor elements appearing in Eq. (22b) then transform according to

$$
T_{q_1,q_2}^{q_3,q_4} = T_{-q_1,-q_2}^{q_3,q_4} = (-1)^{q_1+q_2} T_{q_3,q_4}^* \quad (B20a)
$$

and

$$
T_{q_1,q_2}^* = T_{-q_1,-q_2}^* = (-1)^{q_1+q_2} T_{q_1,q_2} \quad (B20b)
$$

Using Eq. (B20), Eq. (B18) reads, upon transformation,

$$
\Lambda_{\theta}(q_1) = \sum_{q_1,q_2,q_3,q_4} \sum_{l,m} (-1)^{q_1+q_2} g_{q_1,q_2,q_3,q_4}(q_1) T_{q_1,q_2}^* T_{q_3,q_4}^* \times W_{\theta}(s), \quad (B21)
$$

with $\Lambda_{\theta}(q_1) = \Lambda'_{\theta}(q_1)$. Next, we evaluate the quantity $g_{q_1,q_2,q_3,q_4}(q_1)$ present in Eq. (B21) using Eq. (19b), we find


where we have interchanged the dummy indices $Q$ and $Q'$. Application of Eq. (26) to the first and third Wigner 3$j$ symbol in Eq. (B22) gives,

\[
\left( \begin{array}{ccc}
1 & 1 & Q' \\
-q_3 - q_4 & q_4 & -q_3 - q_4 \\
\end{array} \right) = (-1)^Q \left( \begin{array}{ccc}
1 & 1 & Q' \\
q_3 & q_4 & q_3 + q_4 \\
\end{array} \right) \tag{B23a}
\]

and

\[
\left( \begin{array}{ccc}
1 & 1 & Q \\
-q_1 - q_2 & q_1 + q_2 & q_1 - q_2 \\
\end{array} \right) = (-1)^Q \left( \begin{array}{ccc}
1 & 1 & Q \\
q_1 & q_2 & q_2 - q_1 \\
\end{array} \right) \tag{B23b}
\]

respectively. Next, we permute the first and second column in the fifth Wigner 3$j$ symbol in Eq. (B22), following Eq. (B9), which yields

\[
\left( \begin{array}{ccc}
Q' & Q & K \\
-q_3 - q_4 & q_1 + q_2 & s \\
\end{array} \right) = \left( \begin{array}{ccc}
Q & Q' & K \\
q_1 + q_2 & -q_3 - q_4 & s \\
\end{array} \right) \times (-1)^{Q+Q'+K} \tag{B23c}
\]

Finally, inserting Eqs. (B23) into Eq. (B22) together with the property $\Lambda(\varrho_1) = \Lambda(\varrho_2)$, we find

\[
\sum_{K} \sum_{q_1 q_2 q_3 q_4} (-1)^{q_3+q_4} g_{q_1 q_2 q_3 q_4}^{K} (\varrho_1) T_{q_1 q_2} T_{q_3 q_4}^{*} W_{\vartheta}(s) = \sum_{K} \sum_{q_1 q_2 q_3 q_4} (-1)^{q_3+q_4} g_{q_1 q_2 q_3 q_4}^{K} (\varrho_1) (-1)^{K} T_{q_1 q_2} T_{q_3 q_4}^{*} W_{\vartheta}(s) \tag{B24}
\]

with $W_{\vartheta}(s)$ invariant as $s$ invariant, and where $g_{q_1 q_2 q_3 q_4}^{K} (\varrho_1)$ is defined in Eq. (19b). Eq. (B24) means that the summations over $K$ and $q_4$ is invariant under the transformation $g^K \to (-1)^K g^K$. Using Eq. (B24), we find for $\varrho_1 = \pm 1$ and $\varrho_2 = 0$,

\[
c'_{\vartheta}(\varrho_1, 0) = N_{0} c_0 \sum_{n, l, m, n', l', m'} \sum_{q, q', \varrho = 0, K = 0} (-1)^{q_3+q_4} (2\nu + 1)(2\ell + 1) a_{m_\varrho}(n_\varrho) a_{m'_\varrho}(n'_\varrho) T_{q_1 q_2} T_{q_3 q_4}^{*} \times (-1)^{\ell - \ell'} (-1)^{m'-m} e^{i(\delta_{\ell}-\delta_{\ell'})} g_{q_1 q_2 q_3 q_4}^{(K)} (\varrho_1) T_{\ell}(\ell, \ell') I_{\varrho}(\ell', \ell, \ell') S_{l_{\varrho} m_{\varrho}}(q) S_{l'_{\varrho} m'_{\varrho}}(q') \left( \begin{array}{ccc}
\ell & \ell' & \nu \\
0 & 0 & 0 \\
q & -q' & q' - q \\
0 & 0 & 0 \\
\end{array} \right) \times (-1)^{K} (-1)^{K + \nu + \ell} \tag{B25}
\]

In Eq. (B25), the factors $(-1)^{K}$ and $(-1)^{\nu + K + \ell}$ arise from Eqs. (B24) and from application of the property defined in Eq. (26) to the sixth Wigner 3$j$ symbol in Eq. (B25), respectively. Furthermore, we used the property that $\nu$ is even, i.e. only even $\nu$ contribute to the summation, due to the triple zeros in the second row of the fourth Wigner 3$j$ symbol. Finally, using Eq. (B19), it follows that for $\varrho_2 = 0$,

\[
c_{\vartheta}(\varrho_1, 0) = (-1)^{\ell} c_{\vartheta}(\varrho_1, 0) \tag{B26}
\]

Because no assumptions have been made on the polarization direction $\varrho_1$, Eq. (B26) shows that only even Legendre coefficients are present in the PAD if the radiative photoabsorption is driven by linearly polarized light, i.e. $\varrho_2 = 0$, independently of the polarization direction, $\varrho_1$. 


driving the non-resonant two-photon absorption process. As a consequence, only even Legendre orders contribute to the PAD if \( g_1 = \pm 1, 0 \) and \( g_2 = 0 \), translating into a vanishing PECD.

5. Behavior of Legendre coefficients when changing the helicity of the one-photon photoionization

The easiest way to prove Eq. (36) consists of making the change of variables defined in Eq. (B17), and evaluate \( c_L'(g_1, g_2) \), using the property

\[
c_L(g_1, -g_2) = c_L'(g_1, -g_2),
\]

where the unprimed (primed) quantities in Eq. (B27) refer to the Legendre coefficients before (after) the change of variables, respectively.

Keeping \( \epsilon_{g_1} \) is fixed while changing the polarization direction \( g_2 \) transforms the fourth Wigner 3\( j \) symbol in Eq. (22b) according to,

\[
\begin{pmatrix}
1 & 1 & \nu \\
-g_2 & g_2 & 0
\end{pmatrix} = (-1)^\nu \begin{pmatrix}
1 & 1 & \nu \\
g_2 & g_2 & 0
\end{pmatrix},
\]

where we used Eq. (26). Inserting Eqs. (B24) and (B28) to Eq. (22b), for \( c_L'(g_1, -g_2) \) gives,

\[
c_L'(g_1, -g_2) = \mathcal{N}_0 \mathcal{C}_0 \sum_{\ell, m, m'} \sum_{q_1, q_2, q_3} \sum_{q_4} (1)^{q_3+q_4} (2\nu+1)(2\ell+1) a_{q_1, q_2, q_3, q_4} \sum_{o, m} \sum_{o'} \sum_{m'} (\rho - \sigma) \times \left( \begin{array}{c}
m - m' \\
m - m'
\end{array} \right) \left( \begin{array}{c}
\ell & \ell' & \ell
\end{array} \right) \left( \begin{array}{c}
1 & 1 & \nu
\end{array} \right) \times \left( \begin{array}{c}
q - q' & q' - q
\end{array} \right) \left( \begin{array}{c}
g_2 - g_2 & 0
\end{array} \right) \times \left( \begin{array}{c}
s & q - q' & m' - m
\end{array} \right) \left( \begin{array}{c}
0 & 0 & 0
\end{array} \right) \right).
\]

\[
= (-1)^{2\mu} c_L(g_1, +g_2).
\]

In Eq. (B29), the factors \((-1)^K\) and \((-1)^\nu\) arise from the invariance property defined in Eq. (B24) for the transformation defined in Eq. (B17), and (B28), respectively. Application of the property defined in Eq. (26) to the sixth Wigner 3\( j \) symbol in Eq. (B29) gives rise to the factor \((-1)^{K+\nu+L}\). The terms in \( K\) and \( \nu\) compensates, giving rise to the factor in \((-1)^{2\mu}\) alone. Finally, using (B27) and comparing Eq. (22b) for \( g_1 \) and \( g_2 \) Eq. (B29) for \( g_1 \) and \(-g_2\), determines the proof for Eq. (36), i.e.,

\[
c_L(g_1, -g_2) = (-1)^2 c_L(g_1, +g_2).
\]

6. Behavior of Legendre coefficients when changing the helicity of the two-photon absorption process

In this section, we present the proof of Eq. (37). To verify that it is the polarization direction of the ionizing field alone which imposes the sign for all odd Legendre coefficients, whereas the polarization direction of the two-photon absorption plays no role, we define the following transformation

\[
\begin{pmatrix}
q_1' \\
q_2' \\
q_3' \\
q_4'
\end{pmatrix} = \begin{pmatrix}
0 & 0 & 0 & -1 \\
0 & 0 & -1 & 0 \\
0 & -1 & 0 & 0 \\
-1 & 0 & 0 & 0
\end{pmatrix} \begin{pmatrix}
q_1 \\
q_2 \\
q_3 \\
q_4
\end{pmatrix},
\]

which interchanges the indices \( q_1 = -q_4 \) and \( q_2 = -q_3 \) while keeping Eq. (22b) unchanged and \( s \) invariant. In particular, the tensor elements appearing in Eq. (22b) then transform according to,

\[
T_{q_1', q_2'} = T_{-q_1, -q_3} = (-1)^{q_3+q_4} T_{q_1, q_3} = (-1)^{q_3+q_4} T_{q_1, q_3},
\]

(\text{B32a})

and

\[
T_{q_3', q_4'} = T_{-q_2, q_1} = (-1)^{q_1+q_2} T_{q_2, q_1} = (-1)^{q_1+q_2} T_{q_2, q_1},
\]

(\text{B32b})

where we have made use of the correspondence between the components of a vector operator in spherical and cartesian basis, defined in Eq. (A7) in Appendix A.3, in \( T_{q_1, q_3} \), for \( q_1, q_3 = \pm 1, 0 \), together with the fact that the two-photon absorption tensor is symmetric in cartesian coordinates, i.e., \( T_{i,j} = T_{j,i} \) for \( i, j = (x, y, z) \).

We define \( \Lambda_\theta(g_1) \), according Eq. (B18) and we study the symmetry properties of \( \Lambda_\theta(g_1) \) upon transformation defined in Eq. (B31). In particular, because the quantity given by,

\[
(-1)^{q_1'+q_3'} T_{q_1', q_2'} T_{q_3', q_4'} W_\theta(s'),
\]

(\text{B33})

is (as for the earlier transformation defined in Eq. (B17)) invariant under transformation defined in Eq. (B31), we may neglect it in the following, avoiding cumbersome notations. We outline, however, that a full notation was used in Section B.4. Therefore, given such invariance
properties, we may consider the behavior of $g^K$ under exchange $g_1 \rightarrow -g_1$ alone, and neglect the extra terms depending on $K, q_1, \ldots, q_4$ in the expression for $\Lambda'_g(s)$.

Equation (B34), leads to a compensation of the terms

![Equation (B34)](image)

Inserting the symmetry transformations (B35) into Eq. (B34) gives,

![Equation (B34)](image)

where we have interchanged the indexes $Q$ and $Q'$. Next we apply the symmetry property given in Eq. (26), followed by an odd permutation of the first and second columns, according to Eq. (B39), to the first Wigner 3j symbol in Eq. (B34). We find,

![Equation (B35a)](image)

The same procedure is applied to the third symbol in Eq. (B34), i.e.,

![Equation (B35b)](image)

Next, odd permutation of the first and second columns in the fifth Wigner 3j symbol gives,

![Equation (B35c)](image)

Application of Eq. (26), followed by permutation of the first two rows leaves the sign of the second Wigner 3j symbol unchanged for all $Q'$, namely

![Equation (B35d)](image)

and analogously for the fourth Wigner symbol involving $Q$. It is to note that, the left side of Eq. (B35d) is related to $g^K(-g_1)$ while the right side is related to $g^K(+g_1)$.

Permuting the first two rows of the fifth Wigner symbol in Eq. (B34) gives,

![Equation (B35e)](image)

Inserting the symmetry transformations (B35) into Eq. (B34), leads to a compensation of the terms

Because $g_1$ is changed to $-g_1$ while $g_2$ is kept fixed, we consider $g^K(-g_1)$ which becomes, upon transformation defined in Eq. (B31),

![Equation (B34)](image)

where $\gamma_{Q,Q'}^{(K)}$ is given in Eqs. (B35c) and (B35e). Finally, comparing Eq. (B34) and Eq. (19b) gives the following property,

![Equation (B36)](image)

which implies $c_L(-g_1, g_2) = c_L(g_1, g_2)$ according to Eq. (22b), cf. Eq. (37).

Appendix C: Evaluation of the two-photon transition moments in the framework of coupled cluster theory

The rotationally averaged two-photon transition strength strength $\delta^{TP}$ (in a.u.) and the two-photon transition probability rate constant $K_{go}$ are defined in units of cm$^3$s as follows [63–66]

![Equation (C1a)](image)

![Equation (C1b)](image)

where $a_0$ is the Bohr radius, $t_0 = h/E_b$ is the atomic unit of time, $\alpha$ the fine structure constant and $\omega_{ph,1}$ and $\omega_{ph,2}$ the photon energies. $F, G$ and $H$ are parameters depending on the arrangement and polarization of the laser used in the experiment [63–66]. In Eq. (C1a), the parameters $\delta_F, \delta_H$ and $\delta_G$ read [63, 65]

![Equation (C2)](image)

where $\alpha, \beta = x, y$ and $z$. Here $g$ and $a$ refer to the ground and excited states. In the above relations, $S_{\alpha\beta,\gamma\delta}$, the so-
called transition strength, is defined as follows [63, 65]
\[
S_{\alpha\beta,\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) = \frac{1}{2} \left[ T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}) T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}) \right. \\
\left. + T_{\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) T_{\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) \right]
\]
where the \( T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}) \) and \( T_{\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) \) are called the two-photon transition matrix elements. These tensors where the transition strength, is defined as follows [63, 65]
\[
T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}, 2) = \sum \left[ \frac{\langle \psi_0 | \beta | n \rangle \langle n | \alpha | \psi_0 \rangle}{E_g - E_n + \hbar \omega_{\text{ph}, 1}} + \frac{\langle \psi_0 | \alpha | n \rangle \langle n | \beta | \psi_0 \rangle}{E_g - E_n + \hbar \omega_{\text{ph}, 2}} \right]
\]
\[
= T_{\alpha\beta}^{\text{go}}(-\omega_{\text{ph}}, 2)^*,
\]
(C3)
where \( \alpha \) and \( \beta \) are Cartesian components of the position operator \((\alpha, \beta = x, y, z)\). \( \hbar \omega_{\text{ph}, 1} \) and \( \hbar \omega_{\text{ph}, 2} \) are the photon energies which satisfy the matching condition \( \hbar \omega_{\text{ph}, 1} + \hbar \omega_{\text{ph}, 2} = \hbar \omega_{\text{go}} = E_o - E_g \). For variational \textit{ab initio} methods, the two-photon absorption tensor is symmetric with respect not only to the permutation of the operators \( \alpha \) and \( \beta \) (assuming that \( \omega_{\text{ph}, 2} \) is replaced by \( \omega_{\text{go}} = -\omega_{\text{ph}, 2} \)) but also to complex conjugation combined with a simultaneous inversion of the frequencies and exchange of the initial and final states [63, 65]. In coupled cluster response theory, the two-photon absorption tensors \( T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}, 2}) \) and \( T_{\gamma\delta}^{\text{go}}(-\omega_{\text{ph}, 2}) \) are in general not each other complex conjugate \textit{i.e.} \( T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}, 2}) \neq T_{\gamma\delta}^{\text{go}}(-\omega_{\text{ph}, 2})^* \), whereas for the transition strengths, which are calculated as a symmetrized product of right \( T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}) \) and left \( T_{\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) \) two-photon absorption tensors as shown in Eq. (C3), we have [63, 65]
\[
S_{\alpha\beta,\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) = S_{\alpha\beta,\gamma\delta}^{\text{go}}(-\omega_{\text{ph}})^*,
\]
\[
= S_{\gamma\delta,\alpha\beta}^{\text{go}}(\omega_{\text{ph}})^* = S_{\beta\delta,\alpha\beta}^{\text{go}}(\omega_{\text{go}} - \omega_{\text{ph}})^*.
\]
(C5)
These two-photon absorption tensors \( T_{\alpha\beta}^{\text{go}}(\omega_{\text{ph}}) \) and \( T_{\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) \) are called right and left two-photon absorption tensor from the ground state \( g \) to the excited state \( \alpha \), respectively [63, 65]. As a side remark, the imaginary part of two-photon absorption tensors calculated using the CC method vanishes in the limit of complete cluster expansion and thus it does not influence the results of the two-photon absorption tensor [67].

We should mention that Eq. (C4) is presented in a general form and in the Cartesian basis. However, we interest in the special case two photons with same polarization and energy values (\textit{i.e.} \( \omega_{\text{ph}, 1} = \omega_{\text{ph}, 2} = \omega_{\text{ph}} \)). If one uses the inverse relations of Eq. (A8) and inserts them into Eq. (C4), it will give Eq. (15h), which is two-absorption tensor in the spherical basis.

The left and right two-photon absorption tensors change under a rotation \( R \), whereas the transition strength \( S_{\alpha\beta,\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) \) remain unchanged \( (S_{\alpha\beta,\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) = RS_{\alpha\beta,\gamma\delta}^{\text{go}}(\omega_{\text{ph}}) R^\dagger) \). The left and right two-photon absorption tensors for fenchone and camphor (calculated at the rotated arrangement (see Fig. 1) such that the origin is at the center of mass and principal axes of inertia are along coordinate axes) are shown in Tables XX and XXI. In Fig. 1, the eigenvectors of the left (red vectors) and right (blue vectors) two-photon absorption tensor corresponding to the third electronically excited states of fenchone and camphor are shown. The corresponding eigenvalues of the left and right two-photon absorption tensor are \((-10.96, 0.20, 13.38)\) and \((-5.58, 0.10, 6.83)\), respectively for fenchone and \((-11.06, -0.92, 10.51)\) and \((-5.73, -0.47, 5.40)\), respectively for camphor. From this information, the rhombicity \( (T_r) \), axiality \( (T_a) \) and the ratio \( (R = T_r/T_a) \) of these symmetric tensors can be calculated using the following relations:
\[
T_r = a_3^2 E_h^{-1} \frac{2}{3} (b - e) \\
T_a = a_3^2 E_h^{-1} (b - e) \\
R = \frac{T_r}{T_a},
\]
(C6)
where \( b \) and \( e \) are
\[
b = T_{xx}^h - T_{yy}^h \\
e = T_{yy}^h - T_{zz}^h \\
T_0^h = \frac{1}{3} (T_{xx}^h + T_{yy}^h + T_{zz}^h)
\]
Here \( h \) refers to the left and right two-photon absorption tensors and \( T_{xx}^h \) and \( T_{yy}^h \) refers to the diagonal elements of the the left and right two-photon absorption tensors. Based on Eq. (C6), the corresponding numerical values for the rhombicity \( (T_r) \), axiality \( (T_a) \) and an their ratio \( (R) \) are shown in Table. XIX. As inferred from Table. XIX, these values for fenchone and camphor are close to each other. Furthermore, we report the parameters \( \delta_F \), \( \delta_G \), \( \delta_H \), \( \delta_{TP} \) and \( K_{go} \) for different types of polarisations in Tables XXII, XXIII, XXIV and XX.

As indicated, there are two two-photon transition matrices obtained when we employ the coupled cluster method. This is problematic in the calculation of photoelectron angular distributions of the molecules under investigations, because the model constructed for this purpose (see Sec. II) depends on only a single two-photon transition tensor. Thus, the computational procedure based on the CC calculation would not work for the evaluation of photoelectron angular distributions, unless the left and right two-photon transition tensors are combined.

| TABLE XIX. Axiality and rhombicity for fenchone and camphor. | T_r | T_a | R |
|----------------------------------------------------------|-----|-----|---|
| tefenone | -7.44 | -3.78 | 6.76 | -3.50 |
| camphor  | 12.50 | 6.38  | 11.00 | 5.68  |
| R        | -0.59 | -0.59 | -0.61 | -0.61 |
TABLE XX. Left ($T^{αβ}_{gg}$) and right ($T^{αβ}_{go}$) two-photon absorption tensors in units of $a_0^2 E_h^{-2}$ for fenchone as obtained with the CCSD method.

| States | $T^{αβ}_{gg}$ | $T^{αβ}_{ag}$ | $T^{αβ}_{bg}$ | $T^{αβ}_{pg}$ | $T^{αβ}_{po}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| A      | −0.15          | −0.09          | −0.05          | −0.02          | 0.130          | 0.05           | −0.37          | −0.20          | 0.27           | 0.14           |
| B      | 2.21           | 1.14           | 23.70          | 12.34          | 10.39          | 5.40           | −2.31          | −1.20          | −0.34          | −0.17           |
| C1     | −0.30          | −0.15          | −10.60         | −5.40          | −5.74          | −2.93          | 1.57           | 0.82           | 1.43           | 0.73           |
| C2     | −29.42         | −15.34         | 7.58           | 3.90           | −1.87          | −0.93          | −8.39          | −4.29          | −2.62          | −1.33          |
| C3     | −39.74         | −20.68         | −2.18          | −1.10          | 5.69           | 2.95           | −11.02         | −5.63          | 0.03           | 0.08           |

TABLE XXI. Left ($T^{αβ}_{gg}$) and right ($T^{αβ}_{go}$) two-photon absorption tensors in units of $a_0^2 E_h^{-2}$ for camphor as obtained with the CCSD method.

| States | $T^{αβ}_{gg}$ | $T^{αβ}_{ag}$ | $T^{αβ}_{bg}$ | $T^{αβ}_{pg}$ | $T^{αβ}_{po}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ | $T^{αβ}_{go}$ |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| A      | −0.46          | −0.27          | −0.35          | −0.20          | −0.67          | −0.34          | 0.58           | 0.29           | −0.04          | −0.02          |
| B      | 1.66           | 1.00           | 12.91          | 6.80           | 17.38          | 9.18           | 9.15           | 4.73           | 6.50           | 3.36           |
| C1     | 10.42          | 5.37           | 0.61           | 0.27           | 1.22           | 0.55           | −4.83          | −2.48          | −4.90          | −2.54          |
| C2     | 4.39           | 2.14           | 0.35           | 0.22           | −5.72          | −2.94          | 5.76           | 2.92           | 2.65           | 1.39           |
| C3     | −29.68         | −15.55         | 1.46           | 0.65           | 4.10           | 1.96           | −2.69          | −1.41          | −1.59          | −0.82          |

such that the two-photon transition strength and the total cross section remain unchanged when compared to the conventionally chosen recipe for coupled cluster calculations.

The effective two-photon transition matrix element can be written as follows,

$$T^{αβ}_{go}(ω_{ph}) = \sqrt{2} \text{sign}(j) \sqrt{\frac{T^{αβ}_{gg}(-ω_{ph})T^{αβ}_{go}(ω_{ph})}{2}} \quad (C8)$$

and the sign($j$) of $T^{αβ}_{go}(ω_{ph})$ being the same as the signs of the left $T^{αβ}_{gg}$ and right $T^{αβ}_{go}$ two-photon absorption tensors for each electronic state as shown in Tables XX and XXI.

Employing Eq. (C8) leaves the transition strength of $S^{αβ}_{gg}$, and the two-photon transition probability rate constant unchanged. Thus all parameters $δ_F$, $δ_C$, $δ_H$, $δ_{TP}$ as well as $K_{gg}$ in Eqs. (C1) and (C2) are the same as before combining the right and left transition moments. Thus, employing Eq. (C8) provides exactly the same reported values in Tables XXII, XXIII, XXIV and XX. The lower part of Tables VIII and IX presents the (symmetric) effective two-photon transition matrix elements (transition moments) based on Eq. (C8) for fenchone and camphor.

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TABLE XXII. $\delta^{TP}$ and $K_{go}$ referring to the rotationally averaged two-photon transition strength and the two-photon-transition probability rate constant, respectively for fenchone. $\delta_F$, $\delta_G$, $\delta_H$ are calculated by using Eq. (C2). $\delta^{TP}$ is given in units of $a_0^4 \ E_h^{-2}$ and $K_{go}$ in units of cm$^{-1}$ s.$^{-1}$.

| states | $\delta_F$ | $\delta_G$ | $\delta_H$ | $\delta^{TP}$ | $K_{go}$ |
|--------|------------|------------|------------|---------------|----------|
| A      | 0.01       | 0.00       | 0.00       | 0.02          | 3.61 x 10^{-36} |
| B      | 0.22       | 23.62      | 23.62      | 141.31        | 4.59 x 10^{-52} |
| C1     | 0.12       | 5.08       | 5.08       | 30.27         | 1.09 x 10^{-52} |
| C2     | 28.54      | 18.70      | 18.70      | 55.12         | 2.03 x 10^{-52} |
| C3     | 62.31      | 32.24      | 32.24      | 68.81         | 2.55 x 10^{-52} |

$^a$ both photon circularly polarized i.e., $F = -\frac{1}{2}$, $G = \frac{1}{2}$, and $H = -\frac{1}{2}$

$^b$ both photon circularly polarized i.e., $F = \frac{1}{2}$, $G = -\frac{1}{2}$, and $H = \frac{1}{2}$

TABLE XXIII. $\delta^{TP}$ and $K_{go}$ referring to the rotationally averaged two-photon transition strength and the two-photon-transition probability rate constant, respectively for fenchone. $\delta^{TP}$ is given in units of $a_0^4 \ E_h^{-2}$ and $K_{go}$ in units of cm$^{-1}$ s.$^{-1}$.

| states | $\delta^{TP}$ | $K_{go}$ | $\delta^{TP}$ | $K_{go}$ |
|--------|---------------|----------|---------------|----------|
| A      | 0.00          | 1.04 x 10^{-54} | 0.02         | 4.62 x 10^{-37} |
| B      | 94.92         | 3.80 x 10^{-52} | 117.90       | 3.82 x 10^{-52} |
| C1     | 20.57         | 7.43 x 10^{-53} | 25.30        | 9.14 x 10^{-53} |
| C2     | 131.87        | 4.86 x 10^{-52} | 64.96        | 2.39 x 10^{-52} |
| C3     | 253.58        | 9.39 x 10^{-52} | 98.88        | 3.66 x 10^{-52} |

$^a$ both photons polarized linearly with parallel polarization i.e., $F = G = H = 2$

$^b$ both photons circularly polarized linearly with parallel polarization i.e., $F = G = H = 2$

$^c$ both photons polarized linearly with perpendicular polarization i.e., $F = -1$, $G = 4$ and $H = 4$

$^d$ both photons polarized linearly with perpendicular polarization i.e., $F = -1$, $G = 4$ and $H = 1$
TABLE XXIV. Same as Table. XXII but for camphor.

| states | $\delta_P$ | $\delta_G$ | $\delta_H$ | $\delta_{TPa}$ | $K_{go}^b$ |
|--------|------------|------------|------------|----------------|------------|
| A      | 0.04       | 0.08       | 0.08       | 0.37           | $6.02 \times 10^{-55}$ |
| B      | 7.92       | 21.34      | 21.34      | 112.22         | $3.80 \times 10^{-52}$ |
| C_1    | 0.04       | 4.02       | 4.02       | 24.05          | $9.21 \times 10^{-53}$ |
| C_2    | 0.05       | 3.40       | 3.40       | 20.31          | $7.84 \times 10^{-53}$ |
| C_3    | 19.58      | 16.21      | 16.21      | 58.13          | $2.26 \times 10^{-52}$ |

$^a$ both photon circularly polarized i.e., $F = -\frac{1}{2}, G = \frac{7}{2}$ and $H = -\frac{1}{2}$

$^b$ both photon circularly polarized i.e., $F = -\frac{1}{2}, G = \frac{7}{2}$ and $H = -\frac{1}{2}$

TABLE XXV. The same as Table. XXIII but for camphor.

| states | $\delta_{TPa}$ | $K_{go}^b$ | $\delta_{TPc}$ | $K_{go}^c$ |
|--------|----------------|------------|----------------|------------|
| A      | 0.39           | $6.29 \times 10^{-55}$ | 0.33           | $5.47 \times 10^{-55}$ |
| B      | 10.21          | $3.42 \times 10^{-52}$ | 98.80          | $3.34 \times 10^{-52}$ |
| C_1    | 16.16          | $6.18 \times 10^{-52}$ | 20.06          | $7.68 \times 10^{-53}$ |
| C_2    | 13.72          | $5.29 \times 10^{-53}$ | 16.96          | $6.54 \times 10^{-53}$ |
| C_3    | 104.02         | $4.04 \times 10^{-52}$ | 61.49          | $2.39 \times 10^{-52}$ |

$^a$ both photons polarized linearly with parallel polarization i.e., $F = G = H = 2$

$^b$ both photons polarized linearly with parallel polarization i.e., $F = G = H = 2$

$^c$ both photons polarized linearly with perpendicular polarization i.e., $F = -1, G = 4$ and $H = -1$

$^d$ both photons polarized linearly with perpendicular polarization i.e., $F = -1, G = 4$ and $H = -1$

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