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ABSTRACT

A peculiar electron correlation effect, leading to orbital rotation upon ionization, theoretically predicted long ago, was never experimentally characterized. The effect is expected to appear prominently in the photoionization of chiral molecules, due to the lack of symmetry constraints on wave-function mixing. This is observed to have a profound effect on the photoelectron dynamics, as here demonstrated by investigating the β asymmetry parameter and partial cross-section observables in the Cl 3p Cooper minimum region of epichlorohydrin, a chiral prototype system. Angle-resolved photoelectron spectroscopy with tunable synchrotron radiation allowed measuring Cooper minimum β oscillations, which were observed for solely two valence photoionization channels. The nature and number of channels exhibiting such dynamical behavior, along with the extent of the observed oscillation amplitudes, could not be accounted for by predictions based on Hartree-Fock and density functional theory. These features could only be explained by incorporating correlation effects, which mix single-hole configurations of identical symmetry, in the characterization of the four lowest-lying molecular cation states via equation-of-motion coupled-cluster-singles-and-doubles Dyson orbitals.

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I. INTRODUCTION

Removal of a single electron (for instance, by photoionization) is the most elementary excitation of a many-body system. In the Independent Particle Approximation (IPA), it is directly connected with the negative orbital energies, and photoionization has provided an enormous understanding of the orbital structure of molecules. However, the IPA is only a first-order model and thus offers only a simplified representation of electron interactions. Correlation effects alter this picture in several ways, so photoionization offers a unique laboratory to study correlation effects. Indeed, a strong interplay between photoionization experiments and electronic structure theory has existed since the inception of the technique.^{1–3}

Among the several effects displayed and analyzed, one of the most elusive is *orbital mixing*, i.e., the fact that the “electron–hole” orbital relative to a particular final ionic state, instead of resembling one of the occupied Hartree–Fock (HF) orbitals of the ground state, is a linear combination, with significantly large coefficients, of two or more of them, but still of norm close to one. In more precise terms, the Dyson orbital,^{4–7} which characterizes ionization to a specific final state, becomes a mixture of ground-state orbitals and can be considered as a kind of orbital rotation upon ionization.

Although discovered theoretically many years ago,^{8,9} orbital mixing has remained a theoretical curiosity, since it cannot be assessed on pure energy grounds—that is, by means of photoelectron spectroscopy. Specifically, it is well established that electron–correlation effects in inner-valence molecular ionization lead to a breakdown of the independent-electron approximation, giving rise to shake-up and shake-down processes. Experimentally, these are readily observed as satellite transitions at energies displaced from the main line. However, with the advent of more advanced computational methods, it has become clear that weaker correlation effects can also mix canonical orbitals in the outer-valence region, where the independent-electron picture has traditionally been assumed to hold. A challenge for experimental verification is that such mixing only minimally perturbs the eigenvalues, causing any shifts in ionization energies to remain essentially undetectable. Only transition properties, typically dynamical photoionization observables, such as cross sections or angular distributions, can probe the nature of the Dyson orbital and reveal differences in its composition. This effect is characteristic of the outer valence shell, where electron correlation is generally weaker, hence not to the point of complete breakdown of the single-particle picture, as is commonly observed in the inner valence region.^{10,11} It may be associated with differential relaxation properties of the HF orbitals, e.g., due to different localization/delocalization structure, or differential correlation of their main atomic orbital (AO) composition. This is often the case between s, p, and d AOs in transition metal complexes¹² and even between s and p orbitals relative to different shells, such as in elements of the second and third period. Obviously, the mixing is more efficient when initial orbital energies are quite close so that a relatively small perturbation can induce significant mixing. Thus, mixing is expected to be common in molecules with a dense manifold of outer valence orbitals of the same symmetry, which are the only ones allowed to mix. This is commonly the case in low-symmetry systems, and indeed, orbital mixing may prove rather frequent in chiral molecules with no symmetry. A recent surge of interest in

the phenomenon has been stimulated by the possibility of inducing the formation of a non-stationary electron wavepacket by photoionization and studying attosecond phenomena,⁹ for instance, charge migration in pump–probe experiments, e.g., in propiolic acid¹³ and the PENNA molecule.¹⁴ More recent studies are reported in Refs. 15 and 16. An example has also been detected in studying photoelectron circular dichroism (PECD) in the ionization of a chiral molecule.¹⁷ Photoelectron dynamics involves the study of the properties of photoelectrons emitted from matter. In the case of randomly oriented species and in the electric dipole approximation, it entails the knowledge of the partial, angle-integrated, photoionization cross sections (σ) and of the angular distribution (the β asymmetry or anisotropy parameter) as a function of photon energy. Moreover, specific to chiral systems with circularly polarized light, a further angular (dichroic) parameter, β_1 or D , can be obtained, the so-called PECD effect. The experimental determination of these observables is ideally performed with synchrotron radiation (SR), an easily tunable photon source with controlled polarization, and Angle-Resolved PhotoElectron Spectroscopy (ARPES). One of the most striking and informative dynamical effects exhibited by $\sigma(h\nu)$ and $\beta(h\nu)$ is the Cooper minimum (CM).^{18,19} This phenomenon manifests itself in the form of a minimum of $\sigma(h\nu)$ when the photoionization process involves electron ejection from an atomic orbital with a radial node, since the minimum occurs because of the change in sign of radial matrix elements governing the transition moment, as the photon energy is increased from the ionization threshold. Concomitant with this σ behavior, the β parameter is strongly affected and displays, in the same CM energy region, a rapid oscillation characterized by a maximum and a minimum. This latter, $\beta_{\min}$, occurs at a photon energy which approaches closely that of $\sigma_{\min}$. The CM phenomenon was thoroughly investigated theoretically^{18,19} and experimentally^{20–23} as a purely atomic effect. Interestingly, this effect was discovered to persist also in molecular photoionization by Carlson and co-workers.^{24–29} Minima in both σ and β were experimentally observed, and theoretically confirmed, for all cases in which the photoionization process, in the one-electron picture, involves the electron ejection from a non-bonding MO (lone-pair) with strong atomic character due to an AO with radial nodes, namely, the S 3p or Cl 3p lone-pairs in the investigated systems. The good agreement between the measured and the calculated profiles of both σ and β allowed us to associate the atomic CM phenomenon with a molecular CM. This concept was further enriched by observing CM dynamical effects, although to a lesser extent, in photoionization processes involving σ -bonding MOs with partial contribution from AOs with radial nodes.^{24–31} Generally, the CM dynamical features of β are found to be much more pronounced than those of σ , making β the most sensitive probe with regard to CM dynamics. Such values are easier to measure experimentally than the corresponding σ value changes. It was found that the lower the $\beta_{\min}$ value, the closer the nature of the MO to the AO from which it derives, as revealed, for instance, by the Cl 3p AO contributions to different MOs involved in a large number of chlorinated molecules.^{24,26–32} Analogous studies were also accomplished on the bromine atom CM in bromobenzene.^{33–35}

The characterization of orbital nature via detection of the CM offers a remarkable experimental possibility of detecting the orbital rotation effect. Because of the complexity and lack of symmetry of

chiral molecules, with an associated manifold of closely lying ionic states, such effects can be expected to be quite common in such systems.

Monosubstituted oxiranes (ethylene oxides) have been studied experimentally and theoretically as important model chiral molecules. Particularly, methyloxirane ($\text{C}_3\text{H}_6\text{O}$, also known as propylene oxide) has been studied with SR by several authors.^{36–39} The interaction of chiral molecules with circularly polarized radiation is considered to be a plausible mechanism connected to the abiotic origin of life. In this context, it is worth mentioning that propylene oxide has recently been detected in space as the first organic chiral molecule.⁴⁰ (Chloromethyl)oxirane (epichlorohydrin), derived from methyloxirane by hydrogen substitution with chlorine, has also been investigated with SR.^{41,42}

In the present work, we report very clear evidence of the phenomenon of orbital mixing in the asymmetry parameter β (and in the cross section σ) in the photoionization of epichlorohydrin, where the participation of Cl 3p AOs can be experimentally highlighted by the very strong Cooper minimum effect in the asymmetry parameters. A high-level theoretical treatment is provided, showing excellent agreement with the experimental results, indicating the interplay of correlation in the bound states, described by accurate Dyson orbitals obtained by the highly correlated equation-of-motion (EOM) coupled cluster singles and double (CCSD) approach,^{6,43–45} coupled with a time-dependent density functional theory (TDDFT) description of the molecular continuum, which includes interchannel coupling.^{45–47}

II. METHOD

A. Experimental

The experimental Photoelectron (PE) spectra were measured on the Circularly Polarized Beamline⁴⁸ of ELETTRA (Trieste) by photoionization of epichlorohydrin racemic samples (Aldrich, $\geq 99\%$ purity) with linearly polarized radiation. The PE spectra were recorded in the 13–54 eV photon energy range using the ARPES-TPES end station^{49–52} by operating the electron spectrometer in the ARPES mode. Both electron detection angles of 0° and 54.7° (the magic angle) with respect to the polarization plane of the linearly polarized radiation were set. The asymmetry parameters $\beta_i(h\nu)$, characterizing the photoelectron angular distribution, were measured as a function of photon energy as derived from the equation $\beta = (R - 1)$,^{53,54} with $R = A(0^\circ)/A(54.7^\circ)$ being the ratio between the peak areas of the considered PE band obtained at $\theta = 0^\circ$ and $\theta = 54.7^\circ$, respectively. The vapor, generated from the epichlorohydrin liquid sample, was admitted to the interaction region by an effusive source through a nonmagnetic hypodermic needle. The liquid sample was kept at room temperature (23°C) during the measurements, and the gas rating was adjusted to set a constant pressure of 1.0×10^{-6} mbar in the ionization chamber. This pressure was monitored during the experiment. For signal normalization purposes, the incident photon flux was recorded, along with the photoelectron signal, with two different methods, namely, as the current of a silicon photodiode (IRD-AXUV-100) set as a beam stopper after the interaction region and as the current of the gold-coated refocusing mirror mounted at the entrance of the ionization chamber. The measurements, performed in a large photon energy range, required using both the Normal Incidence Monochromator (NIM) and the

Spherical Grazing monochromator (SGM) of the beamline. The PE spectra were corrected by the spectrometer transmission function, as appropriate, considering the change in electron detection efficiency due to the different values of the electron kinetic energy and the selected constant-pass energy value. For this purpose, PE spectra of two reference gases, He and Ar, were recorded at the magic angle and at different kinetic energies and pass energies (5 and 10 eV). Furthermore, the PE spectrum of the first four PE bands of epichlorohydrin was systematically acquired at the photon energies of 22.5 eV (NIM range) and 34.5 eV (SGM range) and at 0° detection angle, as reference spectra, to monitor possible small changes in the density of the vapor sample in the ionization region during the measurements.

The $\sigma_i(h\nu)$ and $\beta_i(h\nu)$ values were extracted from the spectra by determining the relative intensities of single PE components via a global multipeak fitting (see Section S1 for details). Spectra were first normalized to the photon flux and molecular target density and corrected for the spectrometer transmission. Backgrounds, modeled as an arctan plus linear term, were obtained from spectra without epichlorohydrin using χ^2 fitting and subtracted, including the onset region. This correction was particularly important at low PE kinetic energies. All bands, being asymmetric with longer high-ionization-energy tails, were fit using asymmetric bi-Gaussian functions^{55,56} (two half-Gaussians sharing a peak maximum) described by four parameters: peak position (E_0), left and right widths (σ_l , σ_r), and scale factor δ , this latter being related to the peak area ($\delta(\sigma_l + \sigma_r)/2$) and the peak height ($\delta/\sqrt{2\pi}$). The position of the first band (labeled 24a, HOMO) was treated as a free parameter per spectrum and aligned to the ionization energy (IE) value reported in Ref. 42, while the position of the other bands was expressed relative to the HOMO and shared across spectra. For the first four bands, each peak retained its own shape, whereas the six higher-energy bands shared a common shape (single σ_l and σ_r) across spectra recorded at different photon energies and angles. Scale factors δ_i were free for each spectrum. All spectra, measured at different photon energies for both $\theta = 0^\circ$ and $\theta = 54.7^\circ$ detection angles, were simultaneously fit in the global multipeak analysis.

This procedure provided a consistent measurement of the PE band relative intensities and enabled the extraction of $\beta_i(h\nu)$ and $\sigma_i(h\nu)$ for the valence photoionization channels of epichlorohydrin as a function of photon energy. Errors on the epichlorohydrin β values were estimated by measuring, with the same experimental procedure, the well-known asymmetry parameters of reference gases, namely, Ar, He, and O_2 , in a wide photon energy range and exhibiting a large variety of β values.^{57–59}

B. Theoretical

The differential cross section for photoionization relative to a final ionic state Ψ_i^{N-1} (for randomly oriented molecules and linearly polarized light, in the dipole approximation) is given by the well-known formula,

$$\frac{d\sigma_i}{d\theta} = \frac{\sigma_i}{4\pi} [1 + \beta_i P_2(\cos \theta)], \quad (1)$$

where σ_i is the cross section, β_i is the asymmetry parameter, and θ is the angle between the electron's linear momentum and the direction of the light.

Calculating the photoionization parameters σ_i and β_i requires evaluation of the dipole matrix elements between the initial bound state Ψ_0^N and the final continuum state Ψ_{Ei}^N that describes the bound state Ψ_i^{N-1} and the photoelectron with energy E (all other quantum numbers are omitted for simplicity). At the single determinant level (IPA), employing a common set of orbitals $\{\phi_p\}$, describing both bound and continuum states,

$$\Psi_0^N = |\phi_1 \dots \phi_i \dots \phi_N\rangle \quad \text{and} \quad \Psi_{Ei}^N = |\phi_1 \dots \phi_E \dots \phi_N\rangle, \quad (2)$$

we have

$$D_{E\alpha}^{0i} = \langle \Psi_{Ei}^N | D_\alpha | \Psi_0^N \rangle = \langle \phi_E | d_\alpha | \phi_i \rangle, \quad (3)$$

where the subscript α indicates the electric dipole Cartesian component. In the static DFT approach, all orbitals are eigenstates of the ground state Kohn–Sham Hamiltonian, h_{KS} ,⁶⁰

$$h_{KS}\phi_p = E_p\phi_p. \quad (4)$$

The one-particle Schrödinger equation can be solved accurately both for the bound and continuum states employing a B-spline basis and a Galerkin approach for the continuum eigenstates.^{61,62}

In general, occupied bound DFT orbitals are quite close to the Hartree–Fock ones. However, in critical cases, it is interesting to compare the results obtained using the DFT orbitals with those obtained employing the Hartree–Fock orbitals as initial orbitals in the Koopmans’ description.

In fact, correlation effects in the bound states can be taken accurately into account by employing as the initial orbital in Eq. (3) the Dyson orbital^{4,5,7} relative to the initial Ψ_0^N and final ionic state Ψ_i^{N-1} computed from highly correlated wavefunctions,^{6,32,63,64}

$$\phi_i^d = \langle \Psi_i^{N-1} | \hat{\psi}(x) | \Psi_0^N \rangle = \sum_p \gamma_{ip} \phi_p; \quad \gamma_{ip} = \langle \Psi_i^{N-1} | a_p | \Psi_0^N \rangle, \quad (5)$$

where $\hat{\psi}(x) = \sum_q \phi_q(x) a_q$ and a_p are field and orbital annihilator operators, respectively.⁴⁵ Thus,

$$D_{E\alpha}^{0i} = \langle \phi_E | d_\alpha | \phi_i^d \rangle. \quad (6)$$

Moreover, the squared norm of the Dyson orbital, defined as

$$R_i = \|\phi_i^d\|^2 = \sum_p \gamma_{ip}^2, \quad (7)$$

can be used as the intensities of the bands to simulate the photoelectron spectrum. R_i is known as the pole strength, spectral strength, or spectroscopic factor of the final ionic state Ψ_i^{N-1} .

In this study, we use Dyson orbitals obtained at the equation of motion coupled cluster singles and doubles (EOM-CCSD) level of theory.^{6,43,44} Within EOM-CCSD theory, one has distinct left ($\phi_i^{d,L}$) and right ($\phi_i^{d,R}$) Dyson orbitals,^{6,43,44}

$$\phi_i^{d,L} = \sum_p \gamma_{ip}^L \phi_p \quad \gamma_{ip}^L \equiv \langle \Psi_{0L}^N | a_p^\dagger | \Psi_{iR}^{N-1} \rangle, \quad (8)$$

$$\phi_i^{d,R} = \sum_p \gamma_{ip}^R \phi_p \quad \gamma_{ip}^R \equiv \langle \Psi_{iL}^{N-1} | a_p | \Psi_{0R}^N \rangle. \quad (9)$$

In the case of ionization from the electronic ground state,

$$\gamma_{ip}^L = \langle \text{HF} | L^{\text{IP}} e^{(-T_2-T_1)} a_p e^{(T_1+T_2)} | \text{HF} \rangle, \quad (10)$$

$$\gamma_{ip}^R = \langle \text{HF} | (1 + \hat{\Lambda}) e^{(-T_2-T_1)} a_p^\dagger R^{\text{IP}} e^{(T_1+T_2)} | \text{HF} \rangle, \quad (11)$$

where we adopted standard EOM-CCSD notation,⁶⁵

$$\hat{\Lambda} = \sum_{\lambda_1=\lambda_2} \bar{t}_{\lambda_1} \tau_{\lambda_1}^\dagger, \quad (12)$$

$$R^{\text{IP}} = \sum_i r_i a_i + \frac{1}{2} \sum_{aij} r_{ij}^a a_i^\dagger a_j a_i. \quad (13)$$

Since right and left Dyson orbitals are different in EOM-CC, we here use as EOM-CC spectroscopic factors the dot product of the left and right Dyson orbital pairs,⁴⁵

$$R_i = \sum_p (\gamma_{ip}^L \gamma_{ip}^R). \quad (14)$$

The individual products $\gamma_{ip}^L \gamma_{ip}^R$ will be used as weights for specific p orbital contributions to a given ionization i .

Because of the non-variational nature of CC, the calculation of the photoelectron transition dipole matrix element, Eq. (6), also requires generalization. As discussed in the SI of Ref. 44, the transition strength (matrix element) between initial state 0 and final state i is written as (we omit the subscript E for ease of notation),

$$S_{\alpha\beta}^{0i} = \frac{1}{2} \{ D_{\alpha}^{0i} D_{\beta}^{i0} + (D_{\beta}^{0i} D_{\alpha}^{i0})^* \}, \quad (15)$$

where the left and right moments are

$$D_{\alpha}^{0i} = \langle \Psi_0 | d_\alpha | \Psi_i \rangle^L; \quad D_{\alpha}^{i0} = \langle \Psi_i | d_\alpha | \Psi_0 \rangle^R. \quad (16)$$

The labels L or R highlight once again that in EOM-CC, the above are not true scalar products, since they are not Hermitian, $D_{\alpha}^{i0} \neq (D_{\alpha}^{0i})^*$. We then write

$$D_{L,\alpha}^{0i} = \langle \phi_i^{d,L} | d_\alpha | \phi_E \rangle; \quad D_{R,\alpha}^{i0} = \langle \phi_E | d_\alpha | \phi_i^{d,R} \rangle. \quad (17)$$

The transition moments in Eq. (17) are now true scalar products (as computed in our program Tiresia⁶⁶) between the continuum and the left and right Dyson orbitals. Using the above expressions, we then consider the photoelectron transition strength matrix,

$$\begin{aligned} S_{\alpha\beta}^{i0} &\equiv \langle \Psi_i | d_\alpha | \Psi_0 \rangle \langle \Psi_0 | d_\beta | \Psi_i \rangle \\ &= \frac{1}{2} \left[\langle \phi_E | d_\alpha | \phi_i^{d,R} \rangle \langle \phi_i^{d,L} | d_\beta | \phi_E \rangle + \left(\langle \phi_E | d_\beta | \phi_i^{d,R} \rangle \langle \phi_i^{d,L} | d_\alpha | \phi_E \rangle \right)^* \right] \\ &= \frac{1}{2} \left[\langle \phi_E | d_\alpha | \phi_i^{d,R} \rangle \langle \phi_E | d_\beta | \phi_i^{d,L} \rangle^* + \langle \phi_E | d_\alpha | \phi_i^{d,L} \rangle \langle \phi_E | d_\beta | \phi_i^{d,R} \rangle^* \right]. \end{aligned} \quad (18)$$

Thus, in practice, any expression in our code for the cross section (originally written for variational wavefunctions⁶⁶) that contains Hermitian products of two dipole matrix elements is transformed, in the non-variational CC case, as

$$D_{\alpha}^{i0} (D_{\beta}^{0i})^* \rightarrow \frac{1}{2} \{ D_{R,\alpha}^{i0} D_{L,\beta}^{0i*} + D_{L,\alpha}^{0i} D_{R,\beta}^{i0*} \}, \quad (19)$$

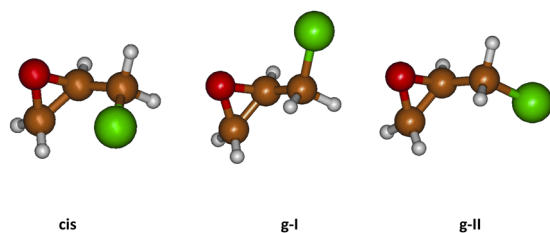


FIG. 1. The three rotamers of epichlorohydrin.

where α and β refer to different Cartesian components x , y , or z . We refer to our previous studies^{44,45,63} for further details.

A step further is to include multielectron effects in the continuum states. A full treatment requires, in principle, the use of a close-coupling approach (equivalent to CI in the continuum), which is expensive and typically restricted to relatively small systems. A practical approximation is to include the response effects induced by the electromagnetic field on the electron cloud. This effect is well described by TDDFT (or RPA in *ab initio*) and, in practice, amounts to substituting the bare dipole operator d_α with the self-consistent potential (or dressed dipole) operator V_α^{SCF} in the evaluation of dipole matrix elements,^{45,46,67}

$$\langle \phi_E | V_\alpha^{\text{SCF}} | \phi_i \rangle. \quad (20)$$

Despite being computationally much more demanding, continuum TDDFT is still practical for rather large and complex molecules.⁴⁵

Summarizing, we have three choices for the initial orbital ϕ_i in Eq. (3), i.e., DFT and HF molecular orbital (MO) or EOM-CCSD Dyson, and two for the continuum states, either static DFT or TDDFT. The combination of the EOM-CCSD Dyson with the TDDFT continuum provides the most accurate description. For further computation details, see the [supplementary material](#) (Sec. S2).

The epichlorohydrin molecule has conformational flexibility, with three stable conformers, denominated g-I, g-II, and cis,^{42,68} of which g-II is the dominant one.

The three conformers are shown in Fig. 1.

All results reported are averages over those obtained for the separate conformers, with appropriate statistical weights (see Sec. S2 in the [supplementary material](#) for more details).

III. RESULTS AND DISCUSSION

Epichlorohydrin is a closed shell molecule with 48 electrons; hence, the highest occupied molecular orbital (HOMO) is number 24, HOMO-1 is number 23, and so on. In the following, we will label the final ionic states by the orbital from which we ionize according to the single determinant description, which is exact for the DFT or HF treatment. In the Dyson case, however, the same label will be associated with the actual wavefunction, starting from the lowest-energy ionic state. Thus, the ionization energies will be labeled as 1A, 2A, 3A, ..., and the corresponding Dyson orbitals (and channels) will be labeled as 24a, 23a, 22a, ..., with "A"/"a" indicating the symmetry irreducible representation of the ionic state/ionized orbital.

A. Electronic structure

Ionization energies and pole strengths computed at the EOM-IP-CCSD/aug-cc-pVDZ level for the three conformers are reported in Table I, together with experimental values for the IEs from Ref. 42. We note that the pole strength values are large and close to 0.9 for

TABLE I. $\text{C}_3\text{H}_5\text{OCl}$. Ionization energies (IE, eV) and intensities (pole strengths R_i) computed using EOM-IP-CCSD/aug-cc-pVDZ. Experimental values from Ref. 42. We also indicate, in parentheses, the "orbital label" assigned to the Dyson orbital corresponding to each ionization.

	cis		g-I		g-II		Expt.
Ionic state $i(\text{Dyson})$	IE	R_i	IE	R_i	IE	R_i	IE ⁴²
1A (24a)	10.29	0.8917	10.48	0.8917	10.51	0.8906	10.56
2A (23a)	11.00	0.9082	11.03	0.9062	11.16	0.9096	11.28
3A (22a)	11.32	0.9052	11.13	0.9056	11.41	0.9051	11.55
4A (21a)	11.68	0.9005	11.72	0.9013	11.65	0.9005	11.81
5A (20a)	13.49	0.9046	13.79	0.8983	13.61	0.8970	13.54
6A (19a)	13.80	0.8922	14.03	0.8980	13.99	0.9045	14.16
7A (18a)	14.62	0.8999	14.55	0.8977	15.13	0.8946	15.01
8A (17a)	16.06	0.8935	15.79	0.8952	15.49	0.8941	15.64
9A (16a)	16.43	0.8876	16.67	0.8861	16.59	0.8861	16.49
10A (15a)	17.68	0.8791	17.68	0.8805	17.70	0.8821	17.47

TABLE II. Epichlorohydrin. Highest coefficients $\gamma_p^I \gamma_p^R$ for each ionization channel. Numbers in parentheses labeled 'HF' denote the Hartree-Fock molecular orbitals contributing to the given ionization/Dyson orbital. Only contributions >0.1 are reported.

Ionic state (Dyson)	cis	g-I	g-II
1A (24a)	0.198(HF 21a) +0.108(HF 22a) +0.267(HF 23a) +0.307(HF 24a)	0.304(HF 21a) +0.250(HF 22a) +0.244(HF 24a)	0.376(HF 21a) +0.455(HF 23a)
2A (23a)	0.373(HF 23a) +0.513(HF 24a)	0.312(HF 23a) +0.526(HF 24a)	0.884(HF 24a)
3A (22a)	0.133(HF 21a) +0.461(HF 22a) +0.238(HF 23a) +0.132(HF 24a)	0.110(HF 21a) +0.151(HF 22a) 0.510(HF 23a)	0.425(HF 21a) +0.424(HF 23a)
4A (21a)	0.544(HF 21a) +0.313(HF 22a)	0.438(HF 21a) +0.455(HF 22a)	0.822(HF 22a)
5A (20a)	0.883(HF 20a)	0.834(HF 20a)	0.874(HF 20a)
6A (19a)	0.885(HF 19a)	0.114(HF 18a) +0.718(HF 19a)	0.887(HF 19a)
7A (18a)	0.871(HF 18a)	0.773(HF 18a) +0.108(HF 19a)	0.838(HF 18a)
8A (17a)	0.861(HF 17a)	0.885(HF 17a)	0.850(HF 17a)
9A (16a)	0.844(HF 16a)	0.874(HF 16a)	0.872(HF 16a)

all ionizations. These should not be confused with the height of the peaks in the experimental PE spectra, which depends on the photon energy at which the PE spectra are recorded.

As can be seen, the IE change from one conformer to the other is not negligible, being up to a few tenths of an eV. The ionization energies computed for the dominant g-II conformer compare pretty well with the experimental ones. HF and DFT eigenvalues are reported in Table S1 (supplementary material). The Dyson orbital composition in terms of HF MOs is displayed in Table II. Table S2 reports the atomic 2p (and Cl 3p) populations of the HF MO (other populations, with the exception of H 1s, are very small and therefore omitted).

The Dyson orbitals of the first four ionized states show a heavy mixing of the four outermost (e.g., 24a, 23a, 22a, and 21a) Hartree-Fock MOs, while those of the inner ones have mostly pure, unmixed character, except minor mixing for 6A (19a) and 7A (18a) in g-I. In addition, HF MO populations change significantly from one conformer to the other, although Cl 3p always dominates orbitals 24a and 23a, which are essentially Cl lone pairs. They seem to indicate a corresponding softness of the orbital composition such that even modest conformational changes induce significant variations in individual orbitals. The final Dyson orbitals, on the other hand, appear more robust, as evidenced by the relatively modest changes in the β profiles evaluated for the three conformers in Fig. S3.

B. Photoelectron angular distribution measurements

The anisotropy parameters $\beta_i(h\nu)$ associated with epichlorohydrin's outer valence Photoelectron (PE) bands observed

in the 10–19 eV IE range have been studied experimentally and theoretically as a function of photon energy. Pairs of PE spectra recorded at two different angles, $\theta = 0^\circ$ and $\theta = 54.7^\circ$, from which the β values have been derived (see Sec. II and Sec. S1 of the supplementary material for details), are reported in Fig. 2 for a representative set of photon energies.

C. Anisotropy β

The experimental $\beta_i(h\nu)$ values of the outermost valence ionizations 24a–21a are reported in Figs. 3 and 4 (black dots in panels a–d), together with the simulated results. The latter differ in the continuum description, with DFT in Fig. 3 and TDDFT in Fig. 4.

The dynamical behaviors of the experimental β parameters, shown in Fig. 3, display clear similarities in the low energy region. All the β values are slightly negative or nearly zero at threshold and rapidly increase with photon energy to reach, at 30 eV, largely positive values of approximately +1.0. A steeper increase is observed for the 23a and 22a channels with a change in slope at around 32 eV. Here, a maximum is located, which corresponds to β values of +1.1 (23a) and +1.35 (22a). These two curves are the only ones exhibiting an oscillatory behavior. This is characterized by a high-energy minimum, which is measured for both channels at ~ 43 eV (see panels b and c in Figs. 3 and 4). Worth noting is the difference between the two channels in the β oscillation amplitude, namely, the maximum-to-minimum β change, with these amplitudes being 0.3 and 0.5 for 23a and 22a, respectively. A change in slope in the β curve at 32 eV is also observed for the other two photoionization processes, 24a and 21a. While the slope change is modest for the 24a

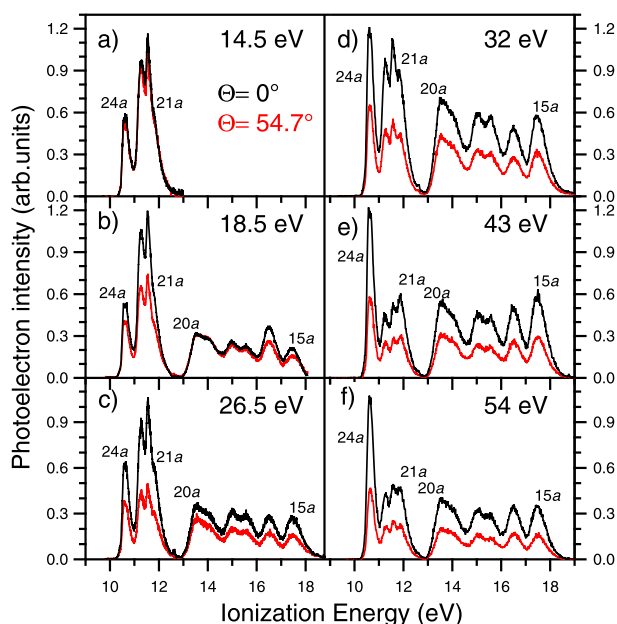


FIG. 2. Experimental outer valence PE spectra of epichlorohydrin recorded at the magic angle $\theta = 54.7^\circ$ (red) and $\theta = 0^\circ$ (black) and at different photon energies (panels a–f).

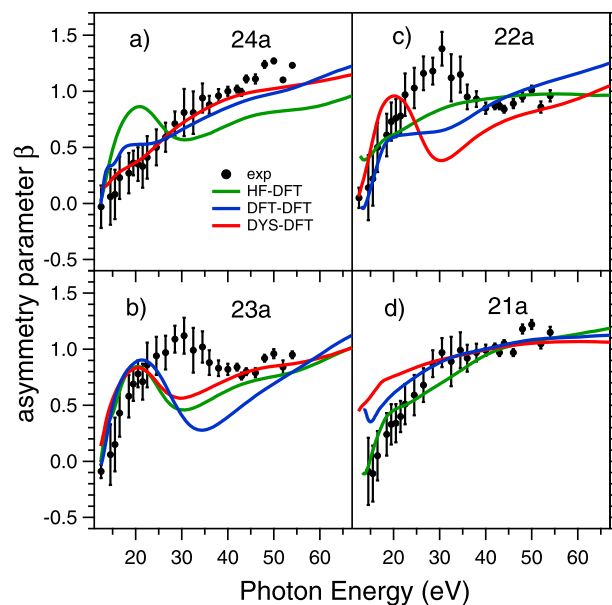


FIG. 3. Asymmetry parameters β_i as a function of the photon energy for orbitals (channels) 24a, 23a, 22a, and 21a. Experiment vs computational results obtained using a DFT representation of the continuum together with Hartree-Fock (label HF-DFT), Density Function Theory (label DFT-DFT), and EOM-CCSD Dyson (label DYS-DFT) orbitals.

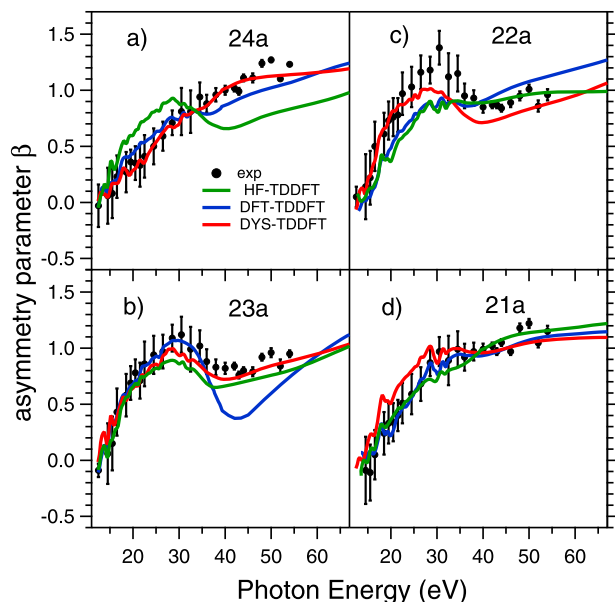


FIG. 4. Asymmetry parameters β_i as a function of the photon energy for orbitals (channels) 24a, 23a, 22a, and 21a. Experiment vs computational results obtained using a TDDFT representation of the continuum together with Hartree-Fock (HF-TDDFT), Density Function Theory (DFT-TDDFT), and EOM-CCSD Dyson (DYS-TDDFT) orbitals.

channel, the change observed is instead large in the 21a curve, where a clear plateau appears in the 30–43 eV photon energy region with $\beta = +1.0$. The β increase at low energies for the first four PE bands is also evident in Fig. 2. Here, isotropic β values, $\beta = 0$, are measured at 14.5 eV (panel a), as the spectra recorded at 0° and 54.7° almost perfectly coincide. In going from 14.5 to 32 eV, from panel a to panel d, the relative intensities of these bands in the 0° spectra clearly display a gradual increase, which corresponds to the β monotonic increase quoted in the panels of Fig. 3 at low energies. The $\beta_i(h\nu)$ parameters have also been measured for the other outer valence ionizations 20a–15a (see the [supplementary material](#)). They do not exhibit an oscillatory behavior and show an increase similar to those of 24a and 21a channels, reaching values in the range of 0.9–1.2 at 54 eV photon energy.

In Fig. 3 are also shown the computational results relative to the same DFT continuum but with different initial orbitals, DFT, HF, and EOM-CCSD Dyson (labeled DYS). The marked differences show the sensitivity of the calculated asymmetry parameter to the bound-state description, particularly between HF and DFT orbitals, which are generally believed to be quite close to each other. The most notable difference is the position of the maximum and of the oscillation expected from the CM effect. With HF orbitals, the CM feature appears strong in the HOMO (24a) and in the 23a channel, with comparable amplitude. DFT shows instead a small hint of it in 24a, another inflection in 22a, and a very strong oscillation in 23a. The use of Dyson orbitals correctly displays the CM feature in the 22a and 23a channels and follows the experimental trend with a larger amplitude in 22a compared with 23a. In all cases, the energy positions of the maximum and the minimum are strongly shifted toward

the threshold by almost 10 eV. For 21a, all approaches are qualitatively correct, with no sign of the CM feature. Here, HF gives the best agreement at low energy, while both DFT and Dyson results are overestimated; then, at higher energy, the shape favors the latter. A good agreement with experiment is obtained from the Dyson results for the HOMO (24a) and for the steep rise at low energy in channels 22a and 23a. Due to the energy shift of the CM feature, it is difficult to argue for the intermediate energy region.

TDDFT continuum strongly improves the position of the CM feature, as is displayed in Fig. 4 for the same three descriptions of the bound states. The improvements brought about by the TDDFT continuum are, in fact, dramatic. This has been observed long ago in the case of rare gas atoms^{67,69} and in small molecules containing second row elements, such as PH_3 or Cl_2 .^{46,70} In the present case, the agreement of the EOM-CCSD Dyson/TDDFT approach is almost quantitative. The energy positions of the CM maximum and minimum are now correct, as is the range of the oscillation, perhaps only slightly underestimated for the 22a ionization. In addition, the overall shapes, including the shape of the low energy rising leg and the high energy behavior, are very well reproduced. Even the behavior of the other curves (DFT and HF) is improved due to the correct energy position of the CM feature, although the shortcomings are already noted, i.e., the misplacement of the CM feature in 24a by the HF orbitals, the overestimate of it in 23a by DFT, and the underestimate by both HF and DFT in 22a, are of course unchanged. The high energy slope is also not well reproduced in some cases.

Both the wide-range oscillation in β and its energy position are a strong indication of Cl 3p AO participation. They are essentially atomic properties of Chlorine, and TDDFT is mainly responsible for the correct energy position. The amplitude (or more precisely, the full shape of the oscillation) is instead connected with the weight of the Cl 3p participation in the Dyson orbital (which reduces to the HF or DFT one in a single determinant description), but it is also impacted by interference with the remaining contributions. Hence, the amplitude is not a simple measure of Cl 3p participation, although the absence of an amplitude is a clear sign of negligible contribution from Cl 3p.

To summarize, the use of the TDDFT continuum is paramount to obtain the correct location of the CM feature, and it generally improves the overall description of the β profiles. The location and full shape of the oscillation are entirely due to the nature of the initial orbitals, and specifically their AO composition, and give a very clear experimental signature of the orbital rotation effect upon ionization theoretically predicted.⁸

D. Partial cross sections

The behavior of the cross sections tells a similar story, although less vivid. As before, experimental results and theoretical curves relative to the DFT continuum are reported in Fig. 5.

Again, two different behaviors are observed experimentally for channels 22a and 23a, where a sudden drop in σ is seen in the region of the CM, around 40 eV, and for 21a, 24a, where the decrease is smoother. Note also the slight (log scale) but well visible recovery of the cross section after the CM. As before, HF results show the step-like decline in the HOMO 24a, while it misses it in 22a. DFT also misses it in 22a, while it exaggerates it in 23a, basically shifting most Cl 3p contribution to this ionization. The cross-section decrease in

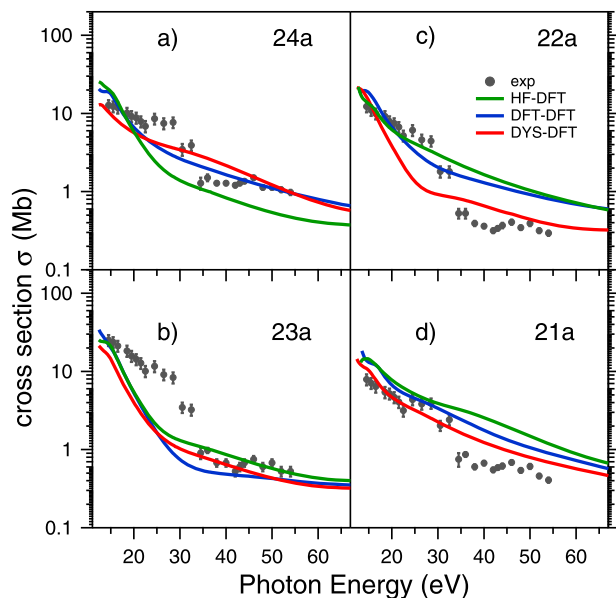


FIG. 5. Cross section σ (Mb, logarithmic scale) as a function of the photon energy for orbitals (channels) 24a, 23a, 22a, and 21a. Experiment vs computational results obtained using a DFT representation of the continuum together with Hartree-Fock (HF-DFT), Density Function Theory (DFT-DFT), and EOM-CCSD Dyson (DYS-DFT) orbitals.

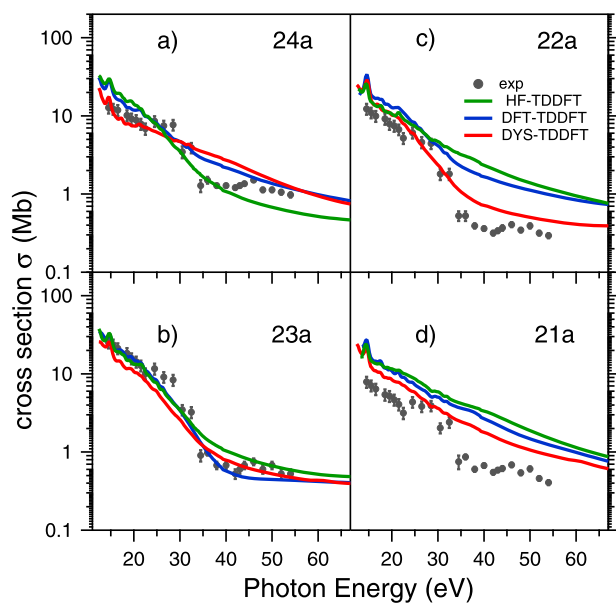


FIG. 6. Cross section σ (Mb) as a function of the photon energy for orbitals (channels) 24a, 23a, 22a, and 21a. Experiment vs computational results obtained using a TDDFT representation of the continuum together with Hartree-Fock (HF-TDDFT), Density Function Theory (DFT-TDDFT), and EOM-CCSD Dyson (DYS-TDDFT) orbitals.

21a is smoother in all approaches, and the same occurs for DFT and Dyson also for 24a. One could expect that the CM features were propagated from 23a and 22a, where it is native due to the Cl 3p participation, to the neighboring channels due to interchannel coupling, absent in DFT but included in the TDDFT continuum. However, this is not borne out, as seen in Fig. 6, where TDDFT vastly improves the description of 22a and 23a, while the effect is less marked for 24a and 21a, as TDDFT mostly affects the CM feature.

There is no sign of the cross section intensity recovery after the minimum. Since this feature is more or less similar in all experimental channels, it may not be significant, and no clear signs of interchannel coupling effects appear in the experiment. Clearly, the overall final agreement is less good than for the β values. Moreover, the experiment seems to indicate more structure than is theoretically predicted. It should be mentioned that the experimental measurement of cross sections is intrinsically more difficult than that of the β parameters and that the CM effect in cross sections manifests itself as a much weaker relative intensity change. As a consequence, it is more difficult to describe theoretically. Since only relative cross sections have been experimentally measured, a conversion to the absolute scale was required to make a direct comparison between experiment and theory possible (see Figs. 5 and 6). The conversion factor was determined by comparing the sum of the experimental cross sections of the 24a ionization channel measured at all the selected photon energies to the sum of the corresponding theoretical values calculated by the Dyson-TDDFT method.

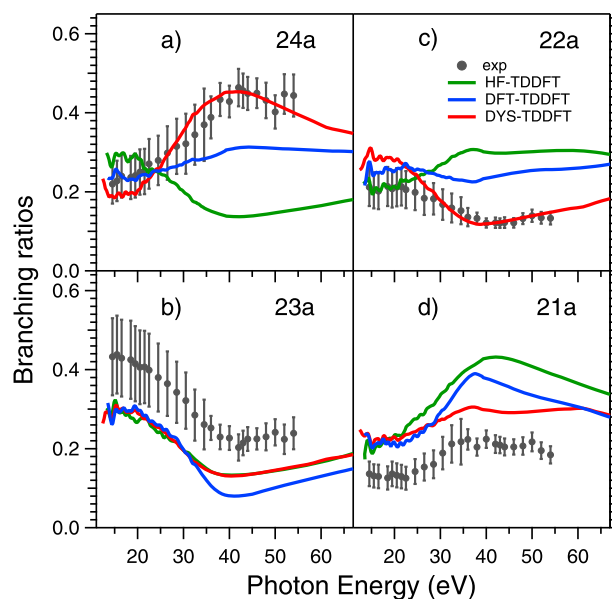


FIG. 7. Branching ratios for orbitals (channels) 24a, 23a, 22a, and 21a as a function of the photon energy. Experiment vs computational results obtained using a TDDFT representation of the continuum together with Hartree-Fock (HF-TDDFT), Density Function Theory (DFT-TDDFT), and EOM-CCSD Dyson (DYS-TDDFT) orbitals.

An alternative presentation of the comparison between experimental and theoretical cross sections, which eliminates the ambiguity in the absolute values, is the use of branching ratios (BR), i.e., in the present case, the ratio of individual channel cross sections to their sum relative to the four channels considered. Experimental and theoretical values relative to the TDDFT continuum are reported in Fig. 7, and those corresponding to the DFT continuum are available in the [supplementary material](#) (see S7).

The drawback of the BR is that a strong resonant feature present in one channel influences all the others so that even a channel with a smooth cross section will display induced features. The upside is that spurious fluctuations in the cross sections cancel out, and the profiles are cleaner and independent of normalization. In Fig. 7, the difference between the alternative descriptions is very clear, and the same features already discussed for each channel appear prominently. An excellent description is provided by the DYS-TDDFT approach for the 24a and 22a channels. For the 23a and 21a ones, the shape is very well reproduced, but the ratio is underestimated for 23a and correspondingly overestimated for 21a. While an obvious suggestion is a difficulty in the deconvolution of partially overlapping bands, of different widths and shapes, we do not have an unequivocal attribution of this disagreement presently either to a deficiency of the processing of experimental data or the inadequacy of the theoretical approach.

A brief analysis of the remaining ionizations, 15a–20a, is presented in the [supplementary material](#) (see Sec. S3).

IV. CONCLUSIONS

Photoionization cross sections σ and angular distributions β have been accurately measured for the entire outer valence region of the chiral molecule epichlorohydrin over an extended energy range, which is important to fully characterize specific signatures. Prominent features in the β parameters appear in two of the four outermost ionizations, attributed to Cooper minimum effects linked to a Cl 3p participation in the relevant orbitals. Detailed theoretical calculations employing DFT, HF, and Dyson orbitals computed at the EOM-CCSD level provide different energy positions of the Cooper minimum features in the β parameters, a clear signature of important correlation effects upon ionization, only observable in transition properties such as photoionization dynamical parameters. Such effects, predicted long ago but never observed, do not show up in ionization energies or pole strengths, which remain close to 1, so they are not due to a *breakdown of the one-particle picture* (according to Cederbaum's definition^{10,11}) but represent an *orbital mixing* or *orbital rotation upon ionization* caused by differential relaxation and correlation upon ionization. The use of the TDDFT continuum is essential for the proper energy prediction (i.e., its position on the energy axis) of the Cooper minimum, and in general, coupling the TDDFT continuum to the Dyson orbital description of the bound initial and final states provides a very accurate description of the experimental results. Although less prominent, such orbital mixing effects also manifest themselves in the cross section and in the branching ratios. While their shapes are very well described by theoretical results, a discrepancy in some absolute values is apparent, whose origin is not clear at present. Additional discrepancies between DFT and HF initial orbitals are also of interest and clearly highlighted by the present results, which are shown to be highly informative on the electronic structure of the molecule. Although

less dramatic, such effects are also seen in the remaining part of the valence shell.

To conclude, we note that because of the lack of symmetry and the dense manifold of valence orbitals in chiral molecules, such orbital mixing effects are expected to be relatively common in their photoionization properties, and in particular in their PECD spectra, as already observed in Ref. 17, for which the present methodology is expected to provide an accurate description. Although the dichroic parameter β_1 decreases fast with increasing electron kinetic energy and is therefore a less sensitive probe of the CM, it will probably be strongly affected by the orbital rotation.¹⁷ Since theoretical simulations of PECD, such as in conventional CD, are almost mandatory to interpret the observed signal, the present study has strong implications for future PECD studies. Further investigations in this regard are in progress.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the spectral extraction of the experimental β parameters (S1), computational details (S2), higher energy ionizations (deeper ionizations) (S3), Cartesian coordinates of the three rotamers (Bohr units) (S4), additional tables and figures (S5), comparison between experimental and theoretical observables (S6), and derivation of β_{av} over conformers (S7).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

L. Schio: Data curation (lead); Formal analysis (equal); Investigation (lead); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **M. Alagia:** Data curation (lead); Formal analysis (equal); Investigation (lead); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **T. Moitra:** Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal);

Software (equal); Visualization (equal); Writing – original draft (supporting); Writing – review & editing (supporting). **D. Toffoli**: Formal analysis (equal); Investigation (equal); Software (equal); Visualization (equal); Writing – review & editing (equal). **A. Ponzi**: Formal analysis (equal); Investigation (equal); Software (equal); Visualization (supporting); Writing – review & editing (equal). **M. Stener**: Formal analysis (equal); Investigation (equal); Software (equal); Visualization (supporting); Writing – review & editing (equal). **S. Coriani**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Software (equal); Supervision (equal); Visualization (supporting); Writing – original draft (lead); Writing – review & editing (equal). **P. Decleva**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Supervision (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **O. Rebrov**: Investigation (equal); Writing – review & editing (equal). **V. Zhaunerchyk**: Investigation (equal); Supervision (equal); Writing – review & editing (equal). **M. Larsson**: Investigation (equal); Visualization (equal); Writing – review & editing (equal). **S. Falcinelli**: Investigation (equal); Writing – review & editing (equal). **A. A. Dias**: Investigation (equal); Writing – review & editing (equal). **D. Catone**: Investigation (equal); Writing – review & editing (equal). **S. Turchini**: Investigation (equal); Writing – review & editing (equal). **N. Zema**: Investigation (equal); Writing – review & editing (equal). **F. Salvador**: Resources (equal); Writing – review & editing (equal). **D. Benedetti**: Resources (equal); Writing – review & editing (equal). **D. Vivoda**: Resources (equal); Writing – review & editing (equal). **B. Botta**: Funding acquisition (equal); Writing – review & editing (equal). **S. Stranges**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Supervision (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#), and the data that support the findings of this study are available from the corresponding author upon reasonable request.

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