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Relativistic effects in molecular photoemission delays

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Attosecond ionization delays in molecules are novel probes of electron correlations in the molecular environment. Relativistic effects in molecules due to spin-orbit coupling are known to figure in structural chemistry and can affect chemical reactions, but the anisotropic potential and congested spectra make it difficult to disentangle contributions from neighboring spin-orbit states. Here, we measure the energy-dependent relative delays between the photoelectron wave packets from two valence spin-orbit states of methyl iodide. We observe substantial modulations in the time-delay photoelectron spectrum from 5-20 eV, a region that includes both spin-orbit and two-electron states. Our calculations show this complex delay spectrum is connected to the interplay between relativistic spin-orbit activated interchannel coupling (SOAIC) and spin-flip transitions, as well as the high density of two-electron transitions. This work establishes spin-orbit resolved time delay measurements as a viable tool to probe electronic correlations in molecules and highlights the significant role of relativistic effects on molecular time delay measurements.

Attosecond pulses have enabled the time-resolved investigation of electron dynamics in atomic and molecular photoionization [1–11]. The development of attosecond photoionization metrology was a key achievement recognized with the 2023 Nobel Prize [12]. Over the past decade, the majority of studies have focused on atomic time delays, although molecular measurements have become more common in recent years. Photoionization delays in molecules are far more complex, due to the lack of spherical symmetry, nuclear-electronic couplings, and other key issues [13–15]. These represent challenges to both theorists and experimentalists, as the field turns toward more complex polyatomic molecules and the nature of chemical reactions.

Spin-orbit coupling plays a significant role in many photochemical reactions, with internal conversion and intersystem crossings [16, 17] being one of the key explanations for the long phosphorescence lifetimes of certain molecules such as the ones found in OLED’s, or in the case of absorption, for explaining the increased efficiency of dye-based solar cells [18]. Spin-orbit coupling has also been shown to impact the behavior of certain chemical reactions [19], and molecular dynamics around conical intersections where the Born-Oppenheimer approximation breaks down [14]. Thus it is of great interest to be able to directly probe these effects within the context of attosecond time delays, as it allows for the detailed observation of fine-structure effects within molecules and allows one to test the limits of different molecular photoionization theories.

So far, molecular time-delay studies have been interpreted using non-relativistic calculations [5, 11, 20, 21],

justified by the fact that the time-delay measurements were unable to resolve relativistic effects, due to spin-orbit coupling, in molecular photoionization. Molecules have a much higher density of states and anisotropic molecular potentials, leading to more congested ionization spectra compared to atomic targets. Although prior studies have observed relativistic effects in xenon, which are known to occur only when the influence of spin-orbit coupling is significant [22–26], relativistic signatures in molecular time delays have not been previously observed.

In this letter, we measure the relative time delay between photoionization channels leading to the $\tilde{X}^2E_{3/2}$ and $\tilde{X}^2E_{1/2}$ cationic states of methyl iodide (CH_3I^+), corresponding to the removal of an electron from the non-bonding $5p$ orbital of the iodine atom. Methyl iodide exhibits a spin-orbit splitting (0.62 eV) amongst its valance states, and was therefore chosen to investigate relativistic effects arising from the high- Z ($Z=53$) iodine atom.

We observe a maximum spin-orbit delay of 98 ± 46 as near threshold, followed by a pronounced dip. We find that this dip cannot be explained by the non-relativistic molecular theory. Rather, it is due to the interplay between spin-orbit activated interchannel coupling (SOAIC) [22–24, 27] and spin-flip transitions. SOAIC effects result from the many-body correlations between two spin-orbit split photoionization channels, while spin-flip transitions describe the case where the spin of the photoelectron is altered by the effective magnetic field caused by its orbital motion. Both effects are purely relativistic since they depend on the strength of the spin-orbit interaction and can be modelled by the relativistic calculation of atomic iodine.

The methods and results outlined in this letter should be applicable to other iodoalkane molecules [11], since the participating $5p$ orbitals of iodine are typically non-

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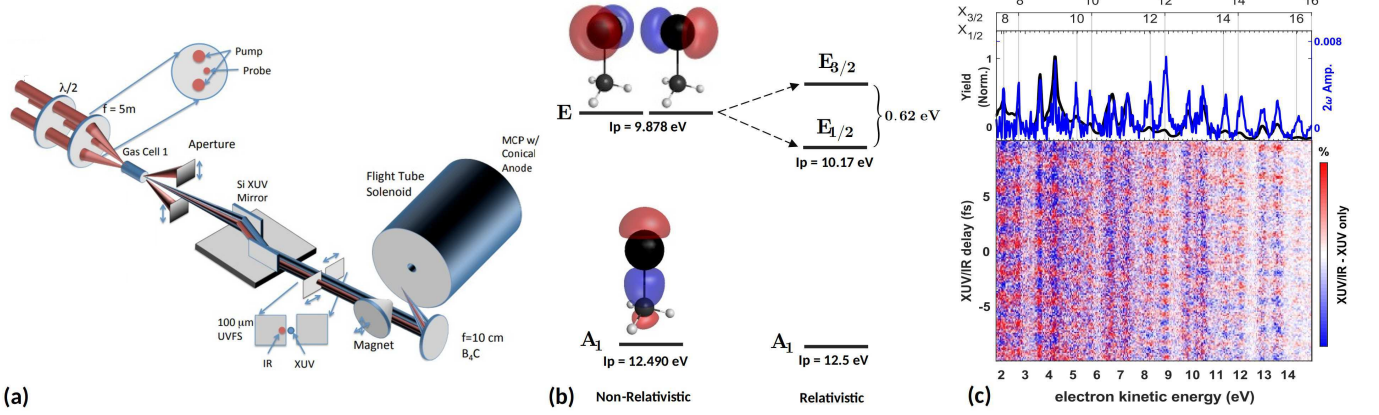


FIG. 1. (a) Schematic of the attosecond beamline. Two IR beams (“Pump”) overlap temporally and drive HHG in argon. A third IR beam (“Probe”) precedes the HHG-driving beams at the gas cell and gets delayed with a glass plate downstream to ensure proper temporal overlap. Both the XUV and IR fields are then focused into the interaction region of the magnetic bottle spectrometer. (b) Comparison between the non-relativistic and relativistic molecular orbitals of methyl iodide. (c) RABBITT spectra for CH₃I. Bottom panel shows the raw RABBITT spectrum as a function of XUV-IR delay. Top panel shows the delay-average (black) and the amplitude of the 2ω Fourier component (blue) of the delay-dependent spectrum.

bonding and would therefore not be substantially altered by molecular substitution. The degree of the spin-orbit splitting however can be altered by the molecular environment. We employ the method of reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [1, 28, 29], where the target is ionized by an extreme ultraviolet (XUV) attosecond pulse train (APT) in the presence of an infrared (IR) dressing field. The ionized electron can then absorb or emit IR photons, thereby changing its energy. By scanning the XUV-IR delay τ and analyzing the modulation of the photoionization yields, it is possible to extract the time delay for a particular photoionization transition.

The experimental setup uses a Ti:Saph laser system (810 nm, 30 fs, 34 mJ pulses at 100 Hz repetition rate) to drive high harmonic generation (HHG) in argon gas. As shown in Fig. 1a the experimental geometry is such that an APT is produced by $\sim 90\%$ of the infrared (IR) power using a crossed-beam configuration. The remaining 10% have an adjustable time-delay and is used as the probe beam. The HHG-driving IR beams separate from the XUV APT and can be physically blocked in the far field, removing most of the unwanted IR background. Other details of this setup have been described in Ref. [30]. The CH₃I target is photoionized by the combined XUV/IR fields and the photoelectron kinetic energy spectrum is measured as a function of the delay, τ , using a magnetic bottle electron time-of-flight spectrometer. As shown in Fig. 1c, the delay-averaged electron kinetic energy spectrum (black trace) consists of harmonic and sideband photoelectron features, and the delay-dependent spectrum (color map) modulates with τ , where the delay-average has been subtracted. The primary photoionization channel produces the two lowest lying spin-orbit states of the CH₃I⁺ cation, with a weaker contribution from the A-cation band [31]. The

measured spin-orbit splitting between CH₃I⁺ X -states is 0.62 eV.

The intensity of each $2q^{\text{th}}$ order sideband can be related to the XUV-IR delay τ according to,

$$I_{\text{SB}}^{(2q)} = C + S \cos(2\omega\tau + \Delta\phi^{(2q)} + \Delta\phi_{\text{XUV}}^{(2q)}), \quad (1)$$

where C and S are constants over τ , ω is the angular frequency of the IR laser field, and $\Delta\phi^{(2q)} + \Delta\phi_{\text{XUV}}^{(2q)}$ represent the phase shift contributions due to the two-photon matrix element and the XUV group delay. Details on the analysis of the RABBITT spectrum and phase retrieval are given in the Supplementary [32].

We subtract the $\tilde{X}^2E_{1/2}$ phase-shift from the $\tilde{X}^2E_{3/2}$ phase-shift, sideband-by-sideband, to obtain the spin-orbit delay τ_{SO}

$$\tau_{\text{SO}}(2q) = (\Delta\phi_{3/2}^{(2q)} - \Delta\phi_{1/2}^{(2q)}) / (2\omega), \quad (2)$$

where the contribution from the XUV group delay cancels out in the subtraction. This spin-orbit delay is a direct measurement of the two-photon ionization delay between the continuum electrons.

The spin-orbit delay extracted from the experimental spectrogram is shown in Fig. 3b. The delay shows a general trend of increasing delay with decreasing photoelectron kinetic energy, which is expected for photoemission measurements in a Coulomb field [33]. There is a pronounced departure from the monotonic behavior expected for a Coulomb potential just below 10 eV, which we can understand with theoretical modeling.

The relativistic random phase approximation [34] was used to describe the relativistic effects intrinsic to the iodine atom within CH₃I (i.e. spin-orbit coupling and spin-flip transitions), while a non-relativistic molecular quantum scattering theory [35, 36] was used to account for the effects of the molecular environment.

For the atomic theory, we calculate the transition matrix elements of every $5p_j \rightarrow \epsilon \bar{\ell}_j$ transition. All of the allowed dipole transition matrix elements $D_{5p_j \rightarrow \epsilon \bar{\ell}_j}$ for a given sub-shell of I^- can then be averaged over different orientations for each photoionization channel. The angle-dependent transition amplitudes for the $5p_{1/2}$ state are listed below (see Ref. [37] for the $5p_{3/2}$ angle-dependent transition amplitude formulas)

$$[T_{10}^{(1+)}]_{5p_{1/2}} = \frac{1}{\sqrt{6}} D_{5p_{1/2} \rightarrow \epsilon s_{1/2}} Y_{00} + \frac{1}{\sqrt{15}} D_{5p_{1/2} \rightarrow \epsilon d_{3/2}} Y_{20} \quad (3)$$

$$[T_{10}^{(1-)}]_{5p_{1/2}} = -\frac{1}{\sqrt{10}} D_{5p_{1/2} \rightarrow \epsilon d_{3/2}} Y_{21}, \quad (4)$$

where the spherical harmonics are given by $Y_{\ell m} = Y_{\ell m}(\theta, \phi = 0)$ and describe the angle-dependence of the photoelectron wavepacket in the laboratory frame. The angle θ describes the angle between the outgoing electron momentum and the polarization of the ionizing laser field. From the transition amplitudes, the Wigner time delay [38–40] can be calculated by taking the energy derivative of the argument of the transition amplitude.

$$\tau_W^{(\pm)} = \frac{\partial}{\partial E} \arctan \left[\frac{\text{Im} \left\{ T_{10}^{(1\pm)} \right\}}{\text{Re} \left\{ T_{10}^{(1\pm)} \right\}} \right] \quad (5)$$

From this it is possible to calculate the spin-averaged Wigner time delay for the $5p_{1/2}$ shell, by simply weighting the contribution of each time delay τ_W by the respective transition probabilities for the spin-up and spin-down cases.

$$\tau_{5p_{1/2}} = \frac{\tau_W^+ |T_{10}^{(1+)}|^2 + \tau_W^- |T_{10}^{(1-)}|^2}{|T_{10}^{(1+)}|^2 + |T_{10}^{(1-)}|^2} \quad (6)$$

The spin-averaged Wigner time delay for the $5p_{3/2}$ shell was calculated with the same procedure, and therefore the total spin-orbit Wigner delay is simply the difference between the individual $5p_{3/2}$ and $5p_{1/2}$ delays. The result of Eq. 6 can be seen in Fig. 2a which also shows the spin-averaged $5p_{3/2}$ channel and the $5p$ spin-orbit time delay.

Our choice of using a relativistic theory of atomic I^- to describe the photoionization behavior of CH_3I relied on the following arguments. First, the highest-occupied molecular orbitals are non-bonding and therefore behave as though they are simply the $5p_x$ and $5p_y$ atomic orbitals of iodine (see Fig. 1b). Second, the σ bond between the $5p_z$ orbital of iodine and the $2p$ orbital of carbon, leads to a larger electron density on the iodine atom due to its higher electronegativity compared to carbon. Therefore, it is reasonable to assume that the initial photoionization of the $E_{3/2}$ and $E_{1/2}$ states of CH_3I can both be approximated as I^- . Finally, a relativistic quantum chemistry calculation of methyl iodide supports this, as the molecular orbitals look similar to the non-bonding $5p$ orbitals of iodine (see Fig. 2a of Ref. [41]).

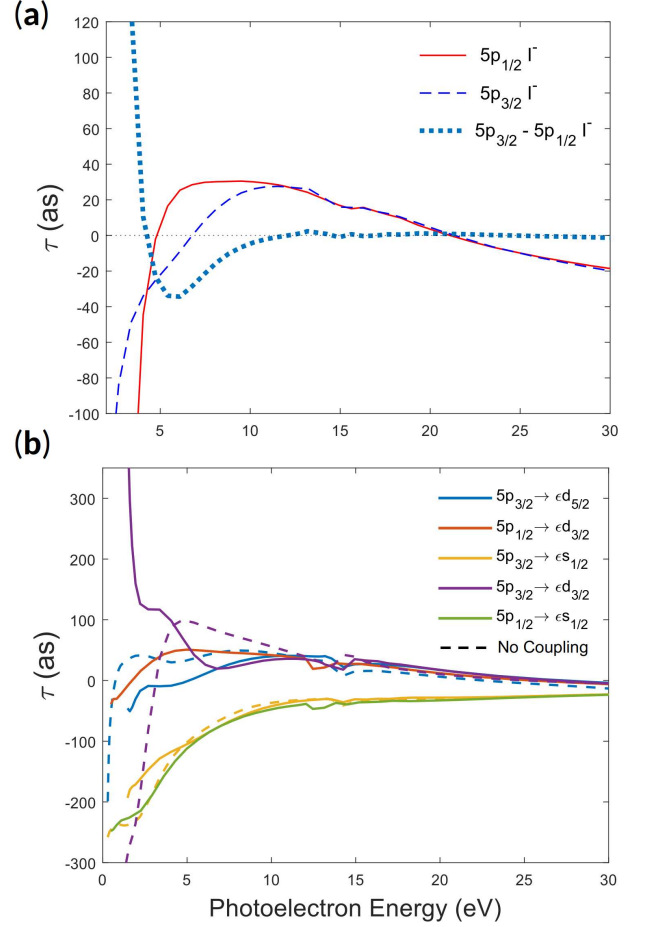


FIG. 2. (a) Relativistic atomic calculations for I^- . (b) Time delay calculations for individual channels of I^- . The colored dashed lines indicate the case of uncoupled channels ($5p_{3/2}/5p_{1/2}$). The photoionization channels associated with spin-flip transitions are the $5p_{3/2} \rightarrow \epsilon d_{3/2}$ and $5p_{1/2} \rightarrow \epsilon s_{1/2}$.

The delays of individual ionization channels can be calculated using Eq. 5, where the spin-resolved transition matrix (T) is replaced with the dipole transition matrix element (D). It is also possible to calculate the Wigner delays where the coupling between the valence $5p_{3/2}$ channels and the $5p_{1/2}$ channels is artificially removed (dashed lines in Fig. 2b). From these calculations it is apparent that the $5p_{3/2} \rightarrow \epsilon d_{3/2}$ spin-flip ionization channel is the most impacted by SOIAC effects, as the lack of interchannel coupling with the $5p_{1/2}$ channels significantly alters the time delay below 10 eV. The alteration of the $5p_{3/2}$ spin-flip channel minimizes the cross-over between the average $5p_{3/2}$ and $5p_{1/2}$ delays, which results in a smaller dip in the overall spin-orbit delay (see Fig. 3a).

To account for the effects of the anisotropic molecular potential in the photoionization amplitudes, we used a molecular quantum scattering program [35, 36]. The quantum chemistry package GAMESS [42] was used to compute the initial bound state wave functions of CH_3I

at the SPK-TZP basis set level. The geometry of methyl iodide was fixed in the C_{3v} point group, with equilibrium bond lengths of 2.18 Å and 1.075 Å for the C-I and C-H bonds respectively.

From the initial bound state wavefunctions of the neutral state, the molecular quantum scattering theory treats the process of photoionization under the single-active electron approximation and therefore the final wavefunction is simply the product of the molecular ion and the photoelectron with a given momentum $\mathbf{k}$ (e.g. $\Psi_{f,\mathbf{k}} = \psi_{ion} \otimes \psi_{e^-}$). A variational procedure [43] is employed to compute the continuum wavefunction ψ_{e^-} under the influence of the potential of the remaining $N - 1$ electron molecular cation. It should be noted within the static-Hartree framework, multi-electron correlations (e.g. polarization effects, two-electron ionization, and orbital relaxation) are not accounted for, although we do not expect orbital relaxation to play a significant role for photoionization processes of valence states. The grey regions in Fig. 3b indicate the energies where two-electron transitions are known to occur [44].

From the dipole matrix element, one can compute angle-dependent molecular frame time delays [4, 45, 46], from which the average time delay of a particular transition can be determined by averaging over all possible molecular orientations and photoelectron emission angles. By computing the average delay for the degenerate HOMO case (see Fig. 1b), the molecular spin-orbit delay between the $\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ states can be approximated as the difference between the calculated photoionization delay and the same curve shifted by the spin-orbit splitting ($\Delta E_{SO} = 0.63$ eV for CH_3I).

$$\tau_{SO}(E) = \tau_{X_{3/2}} - \tau_{X_{1/2}} \approx \tau(E + \Delta E_{SO}) - \tau(E) \quad (7)$$

For both the relativistic atomic and the non-relativistic molecular theories, the calculated average spin-orbit delays need to be corrected by an additional term, which accounts for the delay caused by the IR laser field interacting with the photoelectron in the continuum. The continuum-continuum delay τ_{cc} is well-studied and does not depend on the precise nature of the target species. Instead, it can be described by a universal analytical formula [7], which only depends on the energy of the incoming IR photon, the momentum of the outgoing photoelectron before (k) and after (κ) interacting with the IR field, and finally, the charge of the remaining ion Z . For the purposes of this work, we use the phase and amplitude corrected version $\phi_{cc}^{(P+A')} = \phi_{cc}$ which can be related to τ_{cc} via Eq. 104 in Ref.[7].

$$\phi_{cc} = \arg \left\{ \frac{(2\kappa)^{iZ/\kappa} \Gamma[2 + iZ(1/\kappa - 1/k)] + \gamma(k, \kappa)}{(2k)^{iZ/k} (\kappa - k)^{iZ(1/\kappa - 1/k)}} \right\} \quad (8)$$

$$\gamma(k, \kappa) = iZ \frac{(\kappa - k)(\kappa^2 + k^2)}{2\kappa^2 k^2} \Gamma[1 + iZ(1/\kappa - 1/k)], \quad (9)$$

where Γ is the incomplete upper gamma function to avoid nonphysical behaviors near the atomic core where the Coulomb potential dominates [7]. This allows for a more

accurate description of the interaction of the photoelectron with the IR laser field, especially as one approaches the near threshold region.

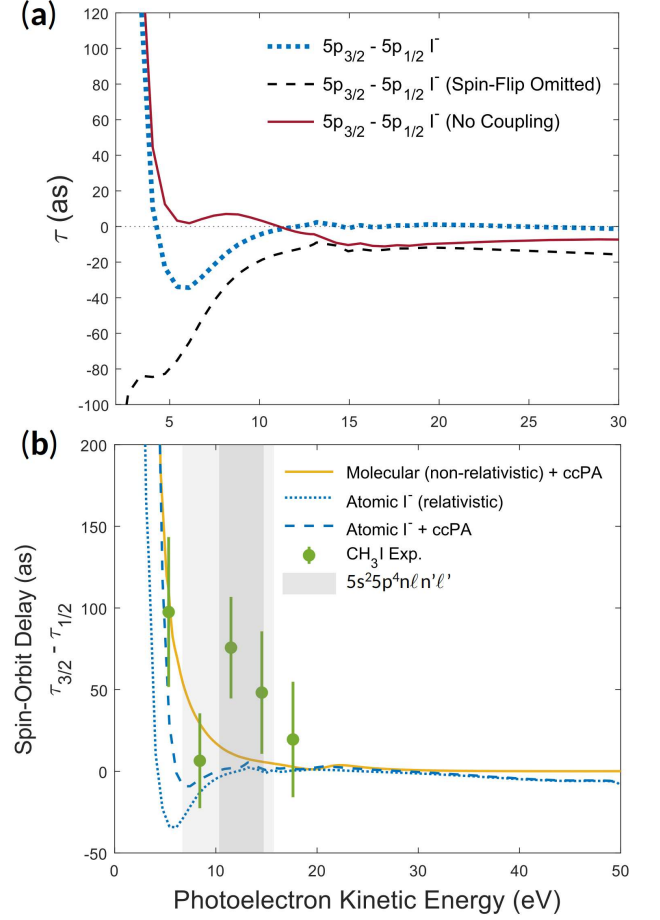


FIG. 3. (a) Relativistic atomic calculations for I^- . (b) Measured and calculated spin-orbit delays. The relativistic curve (blue dotted) conveys the spin-orbit delay of I^- if no continuum-continuum delays are present, whereas Atomic I^- + ccPA (blue dashed) takes into account the additional delays caused by absorption and emission of IR photons via Eq. 8. The light and dark grey refer to the respective energy regions with a lower and higher number density of two-electron transitions.

Fig. 3a illustrates the difference in the average Wigner spin-orbit delays between the $5p_{3/2}$ and $5p_{1/2}$ states of I^- , calculated from the relativistic atomic calculation. At approximately 5 eV above threshold, the calculated spin-orbit delays deviate from one another, but closely agree at higher photoelectron energies. The origin of the ‘dip’ seen in the I^- spin-orbit delay is due to a crossover between the individual delays of the $5p_{3/2}$ and $5p_{1/2}$ states.

When spin-flip transitions are excluded, the character of the spin-orbit delay drastically changes and does not include a dip at 9 eV. Likewise, if one still includes spin-flip transitions, but removes the coupling between the $5p_{3/2}$ and $5p_{1/2}$ states, the ‘dip’ in the spin-orbit de-

lay becomes much less pronounced. This indicates that SOIAC effects and spin-flip transitions both play a crucial role in explaining the crossover between the average $5p_{3/2}$ and $5p_{1/2}$ delays, as Figures 2b and 3a highlight. It is this crossover which results in the experimentally measured dip around 9 eV.

Figure 3b juxtaposes the experimental spin-orbit delays with the two theoretical photoionization models discussed previously (relativistic atomic versus non-relativistic molecular). The relativistic atomic $5p$ spin-orbit delays follow the overall trend of the experimental data quite well, as it accurately predicts the large increase in spin-orbit delays near threshold followed by a significant ‘dip’ on the order of 50-100 as. However, it is not until the continuum-continuum contribution is incorporated that one sees a significant quantitative agreement with experiment. By including the additional delays accrued by the photoelectron in the continuum in the IR field, both the location and minimum of the ‘dip’ are then corrected towards the experimental values. This further validates treating the relativistic effects arising from the spin-orbit states of methyl iodide in terms of the negatively charged iodide atom, whilst understanding that the positive potential of the molecular cation must still be accounted for. We expect this near threshold behavior of the atomic contribution from iodine to be universal across all iodoalkanes when the non-bonding $5p$ orbitals of iodine are ionized, as the short-range potential of the iodine atom should be the most significant factor.

The molecular quantum scattering calculation does not incorporate *ab initio* relativistic effects, but by manually setting the experimental spin-orbit splitting of 0.63 eV, one sees a moderate agreement with experiment. Importantly, the non-relativistic molecular theory, which excludes the coupling between the two spin-orbit states and the spin-flip transitions, cannot reproduce the experimentally observed dip near 9 eV.

From Fig. 3b it is clear that the observed spin-orbit delays possess an additional feature between the photoelectron energies of 11-16 eV, which is not captured in theoretical curves. This region contains high density of autoionizing states corresponding to two-electron transitions [44], which are not accounted for in either theory. Note that similar discrepancy between theory and experiment was observed in the prior measurements of xenon [25]. Xenon also has a dense region of autoionizing states and two-electron transitions in the 13-20 eV range [47], corresponding to photon energies in the 25-32 eV range [32].

In conclusion, we have measured a ‘dip’ in the relative delay between the photoelectron wave packets of the

$\tilde{X}^2E_{1/2}$ and $\tilde{X}^2E_{3/2}$ spin-orbit states of methyl iodide, and show this is due to an interplay between spin-orbit activated interchannel coupling (SOIAC) and spin-flip transitions. This dip is not present in the non-relativistic description of the molecule but is well described by relativistic atomic theory. We also observed surprisingly large relative spin-orbit delays at energies of 11-16 eV, corresponding to a high density of correlated two-electron transitions. This indicates significant relativistic effects in shake-up transitions, pointing to the importance of developing correlated fully relativistic treatments of photoionization. Also, by aligning the molecule along its dipole moment, future spin-orbit time delay measurements could obtain angle-resolved spin-orbit delays in the molecular frame and therefore probe subtle relativistic differences in the molecular environment (e.g. molecular shape resonances). To estimate what the results would look like for such an experiment, we performed angle-resolved spin-orbit delay calculations for methyl iodide using the same molecular scattering theory discussed previously. Our theoretical results (see Sec. B of the Supplemental), confirm that the angle-resolved spin-orbit delay is a sensitive probe of the molecular environment and the strength of the spin-orbit energy splitting [32].

Finally, relativistic effects normally act as only a small correction on electron dynamics in molecules. However, they can be pivotal in dynamics around conical intersections, where small perturbations will have a large impact on the pathway of a chemical reaction or molecular dissociation. Moreover, as the molecule traverses the conical intersection, the energy splitting between neighboring spin-orbit states changes [14]. This splitting will be specific to the particular iodoalkane molecule, highlighting the importance of the molecular environment. Hence, our work underscores the versatility of molecular RABBITT measurements, as it allows for the simultaneous extraction of the spin-orbit splitting and time delay, thereby opening the door to time-resolved studies of relativistic effects in molecular bonding and dissociation.

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