

Single-Photon Laser-Enabled Auger Spectroscopy for Measuring Attosecond Electron-Hole Dynamics

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We propose and simulate a new type of attosecond time-resolved spectroscopy of electron-hole dynamics, applicable particularly to ultrafast hole migration. Attosecond ionization in the inner-valence region is followed by a vacuum ultraviolet probe inducing *single-photon* laser-enabled Auger decay, a one-photon–two-electron transition filling the inner-valence vacancy. The double ionization probability as a function of the attosecond pump–vacuum ultraviolet probe delay captures efficiently the ultrafast inner-valence hole dynamics. Detailed *ab initio* calculations are presented for inner-valence hole migration in glycine.

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Attosecond physics is concerned with the time-resolved study of electron dynamics in atoms, molecules, clusters, and condensed matter on a few-femtosecond or attosecond time scale [1]. The advent of this new field has become possible due to the dramatic technological breakthrough in the development of high-order harmonic generation (HHG) based techniques for the production of attosecond extreme ultraviolet laser pulses [2]. A principal tool of attophysics, attosecond streaking spectroscopy [3] can resolve the ultrafast dynamics in atoms and condensed matter involving the emission of photo- or secondary electrons. This excludes the ultrafast electron transitions of the bound-bound type, for example, the migration of an inner-valence electron hole driven by electron correlation [4–6] (see Ref. [7] for a recent theoretical work on photon emission spectroscopy of hole migration). The alternative techniques of attosecond transient absorption spectroscopy [8] and HHG spectroscopy [9] in their present realizations address the dynamics of outer-valence ionized states. Here, we propose a new type of time-resolved attosecond technique, *single-photon* laser-enabled Auger decay (spLEAD) spectroscopy, that uses a vacuum ultraviolet (VUV) ionizing probe and is particularly suited to characterizing hole migration dynamics in the inner-valence energy region.

Molecular ionization in the inner-valence region below the double ionization potential (DIP) often produces a complex superposition of bound cationic states and thus induces electron-hole dynamics that can occur on subfemtosecond or few-femtosecond time scales [5,6]. Detailed analysis of the cationic eigenstates [5] shows that ultrafast hole migration at fixed molecular geometry is a result of electron configuration mixing. Inner-valence ionized molecular states cannot be characterized as resulting from ionization of a particular molecular orbital (MO). Rather, a specific eigenstate can turn out to be a superposition of two or more such one-hole ($1h$) electronic configurations, as well as higher excited configurations of the two-hole–one-particle ($2h1p$) type. Depending on the nature of this configuration mixing arising from electron correlation

[10], the short-time dynamics induced by inner-valence ionization can be either oscillatory (two $1h$ configuration mixing [5]) or quasiexponential (MO breakdown [11]). On a longer (tens of femtoseconds) time scale, nuclear motion results in electron-hole localization at a particular molecular site that can be different from the site of initial ionization. This has been observed in mass spectrometric measurements and in pump-probe experiments with femtosecond time resolution [12], including the most recent ones [13], which suggest that faster dynamics may well be occurring. However, experimental verification of the critical short-time electron correlation driven dynamics is still lacking. The spLEAD probe technique proposed here addresses this challenge.

Consider an inner-valence ionized state of an atom, for example, $(2s^{-1})\text{Ne}^+$ (see Fig. 1). Such states are Auger inactive; i.e., they lie below the double ionization threshold and decay radiatively on a nanosecond time scale [14]. It is still possible to induce a two-electron Auger-type transition in an isolated inner-valence ionized species by applying a laser field, such that the lacking energy comes from the

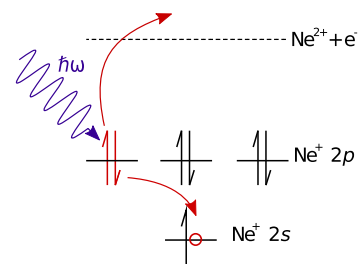


FIG. 1 (color online). A schematic representation of spLEAD in $2s$ -ionized neon. The energy from recombining an outer-valence electron into the vacant inner-valence orbital combined with a single VUV photon ($\hbar\omega > 14$ eV) provides the energy necessary for another outer-valence electron to ionize in a laser-enabled Auger process. In the absence of the VUV photon, the inner-valence vacancy decays radiatively with a lifetime of about 0.2 ns [14].

absorbed photon(s). This process, called laser-enabled Auger decay (LEAD), was recently realized experimentally and described theoretically for $(3s^{-1}) \text{Ar}^+$ in the *multi-photon* regime [15] (see also the early work on laser assisted Auger [16]). Here, we point out that it is the VUV-induced *single-photon* LEAD process that provides a direct, sensitive characterization of the configuration mixing and hole dynamics in the inner-valence ionized states. In the course of the spLEAD, a single VUV photon is used to induce an Auger-type two-electron transition where an inner-valence hole is filled by an outer-valence electron, while another outer-valence electron is ejected into the continuum (see Fig. 1). Clearly, if a molecular inner-valence hole is nonstationary and migrates across the system, the molecular spLEAD transition will be strongly sensitive to these dynamics, as both the recombination and the ionization parts of the process will strongly vary, depending on the instantaneous environment of the electron hole.

The spLEAD of an excited cationic $[(N-1)\text{-electron}]$ state $\Psi_n^{(N-1)}$ at the energy $\text{IP} < E_n < \text{DIP}$ can be described as photoionization accompanied by an electronic rearrangement. In the case of continuous wave ionizing radiation of frequency ω , it can be characterized by the photoionization cross section $\sigma_n(\omega)$. Within the dipole approximation in the length gauge, the spLEAD cross section is given by

$$\sigma_n(\omega) = \frac{4}{3} \pi^2 \alpha \omega \left| \langle \Psi_n^{(N-1)} | \sum_{j=1}^{N-1} \mathbf{r}_j | \Psi_{E_n+\omega}^{(N-1)} \rangle \right|^2, \quad (1)$$

where $\omega \geq \text{DIP} - E_n$ is the photon frequency and $\Psi_{E_n+\omega}$ is the wave function of the final $2h1p$ -like continuum state at the energy $E_n + \omega$, normalized to a δ function in energy (atomic units are used). In the lowest-order approximation, the initial and the final states of spLEAD are described by single electronic configurations (single Slater determinants) of $1h$ and $2h1p$ types, respectively, derived from the Hartree-Fock (HF) solution of the neutral species (frozen orbital approximation). Since the inner-valence hole is filled in the course of the spLEAD transition (see Fig. 1), the two holes of the final $2h1p$ configuration are necessarily distinct from the initial electron hole. According to the Slater-Condon rules, two such electronic configurations cannot be coupled by the single-electron dipole operator [see Eq. (1)] and, as a result, the spLEAD process is forbidden in the first order similarly to the related radiative Auger process [17]. This is in sharp contrast to the multi-photon LEAD [15] which breaks into two or more single-electron transitions, each of them being allowed by the many-body selection rules. spLEAD becomes allowed only once configuration interaction is taken into account, with the $2h1p$ contribution to the initial state of the process playing by far the dominant role. Thus, the single-photon cross section [Eq. (1)] is a direct quantitative measure of the configuration mixing induced by electron correlation and relaxation effects.

The above analysis shows that the theoretical description of spLEAD must include configuration interaction in the many-electron states involved in the process. Here, we describe the initial and final states of spLEAD using the many-body Green's function technique called algebraic diagrammatic construction (ADC) [18]. We use the extended second-order ADC(2) x scheme which represents the $(N-1)$ -electron wave function in the basis of so-called intermediate states [19] of $1h$ (ϕ_i) and $2h1p$ (ϕ_{ij}^a) types derived from the perturbation-theoretically corrected HF ground state of the neutral:

$$\Psi^{(N-1)} = \sum_i c_i \phi_i + \sum_{ija} c_{ij}^a \phi_{ij}^a, \quad (2)$$

where i and j are hole (occupied HF orbital) indices and a is a particle (unoccupied HF orbital) index. ADC(2) x describes the $1h$ -like states up to second order in the many-body perturbation theory, while approximating the $2h1p$ -like states to first order. Our ADC(2) x computations are performed using \mathcal{L}^2 Gaussian bases for the initial (bound) and for the final (continuum) states of the laser-enabled transition. We effectively renormalize the discretized final state wave functions and interpolate the cross sections [Eq. (1)] with respect to the final state energy using the Stieltjes imaging technique [20].

Figure 2(a) shows the total spLEAD cross sections [Eq. (1)] for $(2s^{-1})^2S$ and $(3s^{-1})^2S$ states of Ne^+ and Ar^+ , respectively. The cross sections are shown in the energy region between the spLEAD threshold ($\text{DIP} - E_{1h}$) and the threshold of the first-order (spectator inner-valence hole) ionization process, such as $(2s^{-1}) \text{Ne}^+ + \hbar\omega \rightarrow (2s^{-1}2p^{-1})\text{Ne}^{2+} + e^-$. At higher photon energies, the spectator hole atomic photoionization with typical cross sections of the order of 1 Mb overwhelms the

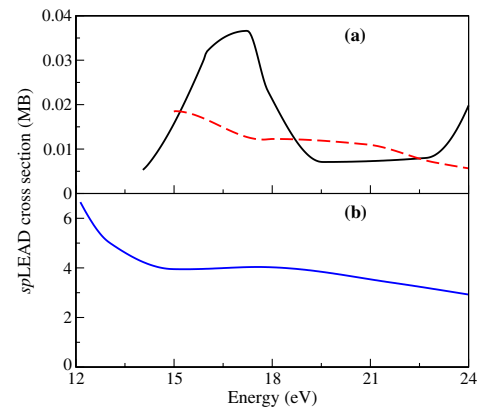


FIG. 2 (color online). spLEAD photoionization cross sections of (a) a $3s$ -ionized argon atom (solid line), a $2s$ -ionized neon atom (dashed line), and (b) $10A'$ -ionized glycine. Calculations were performed using a fully uncontracted cc-pCV6Z basis set [30] augmented with $5s5p5d$ Kaufmann-Baumeister-Jungen (KBJ) diffuse Gaussians [31] for neon and argon, and a cc-pCVDZ basis set augmented with $3s3p$ KBJs, in the GlyI geometry [24] for glycine.

second-order spLEAD process. Production of doubly charged ions through outer-valence ionization (which always accompanies the inner-valence one) requires a slightly higher-energy photon than the spectator hole process (e.g., by about 1.6 eV in the case of Ne). Thus, within the energy window of Fig. 2, spLEAD is the only pathway to doubly charged ion generation.

The configuration interaction between $2h1p$ and $1h$ excitation classes is known to be much stronger in molecules than in atoms, the reason being the lower energies of the $2h1p$ configurations as the two holes can reside on different atomic centers. In the inner-valence region, this interaction leads to a partial loss of $1h$ character of the cationic states and in extreme cases to the complete breakdown of the MO picture of ionization [11]. The increased $2h1p$ content of molecular ionized eigenstates brings about a much higher spLEAD cross section as seen in Fig. 2(b) for a state associated with ionization from the $10A'$ MO in glycine. This general property of molecular inner-valence ionized states is extremely useful for the spLEAD spectroscopy proposed here.

Photoionization does not necessarily result in a cation in a well-defined electronic state. At sufficiently high photon energies, photoionization leads to the production of a series of cationic states, e.g., via a shakeup mechanism [17] that is operational also in the attosecond ionization regime [21] alongside other double-excitation routes [22]. If the time scale of ionization is shorter than that of the relaxation of the system, the resulting cationic state can be described within the sudden approximation [23]

$$\begin{aligned}\Psi_{\text{sudden}} &= \hat{a}_k \Psi_0^{(N)} = \sum_n C_n \Psi_n^{(N-1)}, \\ C_n &= \langle \Psi_n^{(N-1)} | \hat{a}_k | \Psi_0^{(N)} \rangle,\end{aligned}\quad (3)$$

where \hat{a}_k is the annihilation operator corresponding to a given (in our case inner-valence) MO, $\Psi_n^{(N-1)}$ are cationic eigenstates, and $\Psi_0^{(N)}$ is the ground state of the neutral. Inner-valence ionization with the available attosecond pulses, e.g., with 90 eV central photon energy [2], leads to photoelectrons energetic enough to leave the volume of a medium size organic molecule within 100 as, which is fast on the typical time scale of hole migration dynamics. The bandwidth of the available attosecond pulses is sufficient to create a coherent superposition of ionic states several eV apart, as required to initiate inner-valence hole dynamics (e.g., 750 as pulse spans 5 eV). In the remainder of this work, we assume attosecond pulse ionization of inner-valence MOs and describe the resulting cationic wave packet using the sudden approximation.

Once prepared, e.g., by sudden ionization at $t = 0$, a superposition of bound cationic states [Eq. (3)] evolves in time, often leading to migration of the initial hole across the molecule at few-femtosecond or subfemtosecond time scales [5]. This temporal evolution can be fully characterized by the time-dependent hole density [5] or (in the temporal domain only) by the survival probability of the initial state $S(t)$:

$$S(t) = \left| \sum_n |C_n|^2 \exp(-iE_n t) \right|^2. \quad (4)$$

Short VUV pulses can be used to map this survival probability onto the double ionization yield as a function of the VUV pulse delay relative to the initial ionizing pulse. Indeed, if spLEAD is induced by a VUV pulse with broad enough frequency bandwidth, transitions from two populated cationic states of distinct energies E_n and $E_{n'}$ can produce the same continuum state $\Psi_E^{(N-1)}$. Interference between two such transitions creates a modulation at the Bohr frequency $E_n - E_{n'}$ in the doubly charged ion signal as a function of the pulse delay t , analogous to that of the survival probability [Eq. (4)]. With the doubly charged ion signal coming exclusively from the spLEAD of target inner-valence states, this modulation serves as a direct indication of the hole migration dynamics.

Within first-order perturbation theory, the spLEAD probability $P(t)$ as a function of pump-probe delay t for a general superposition of cationic eigenstates is given by

$$\begin{aligned}P(t) &= \frac{\mathcal{E}^2 \tau^2 \pi}{4} \int_{\text{DIP}}^\infty \left| \sum_n C_n \langle \Psi_E^{(N-1)} | \hat{D} | \Psi_n^{(N-1)} \rangle \right. \\ &\quad \left. \times \exp[i(\omega_{E_n} - \omega)t] \exp\left(-\frac{(\omega_{E_n} - \omega)^2 \tau^2}{4}\right) \right|^2 dE,\end{aligned}\quad (5)$$

where we have assumed a Gaussian VUV pulse of duration τ , carrier frequency ω , and field strength \mathcal{E} ; $\omega_{E_n} = E - E_n$ is the frequency of the bound-continuum spLEAD transition; and \hat{D} is the dipole moment operator [cf. Eq. (1)]. The dipole matrix elements are calculated using ADC(2)x wave functions and Stieltjes imaging to renormalize the final continuum states. Here, we sum coherently over all the singly ionized initial states contributing to the spLEAD transition into the given final continuum state and integrate the transition probabilities over the final state energy. Two kinds of initial state-dependent phases contribute to the coherent summation in Eq. (5): the phase of the wave packet expansion coefficients C_n that is determined by the ionization process [e.g., is given by Eq. (3) within the sudden ionization model] and the phase of the transition dipole matrix element $D_{En} = \langle \Psi_E^{(N-1)} | \hat{D} | \Psi_n^{(N-1)} \rangle$. Variation of the latter phase with the initial state cannot be accounted for by the \mathcal{L}^2 theory and is assumed to be small and therefore neglected in the numerical calculations described below.

It is instructive to analyze the delay-dependent spLEAD probability for a model system of two cationic eigenstates (labeled as a and b) representing mixtures of two $1h$ configurations. Assume that the sudden ionization at $t = 0$ resulted in a superposition of these two states with $C_a = C_b = 1/\sqrt{2}$ and that the corresponding dipole matrix elements are energy independent and differ only in the phase $D_{a,b} = D \exp(i\phi_{a,b})$. In this model, the delay-dependent spLEAD probability varies as

$$P(t) = \frac{\mathcal{E}^2 \tau \sqrt{2\pi^3} D^2}{4} \left\{ 1 + \cos[(E_b - E_a)t + \phi_a - \phi_b] \right. \\ \left. \times \exp\left[-\frac{(E_b - E_a)^2 \tau^2}{8}\right] \right\}, \quad (6)$$

whereas the survival probability [Eq. (4)] is given by $\{1 + \cos[(E_b - E_a)t]\}/2$. While both quantities are modulated by the Bohr frequency $\omega_{ab} = E_b - E_a$, the modulation strength of the double ionization signal depends on the magnitude of ω_{ab} relative to the frequency bandwidth of the VUV pulse. The nonzero relative phase of the two transition dipoles $\phi_a - \phi_b$ leads to a shift of the spLEAD probability modulation relative to that of the survival probability. Of course, the delay-dependent modulation [Eq. (6)] is a general property of any transition probability from a superposition of states into a given final state and is characteristic also of the first-order ionization at high enough photon energies. At such energies, however, doubly charged ions will be formed also from the (typically more abundant) outer-valence ionized species, and the inner-valence hole migration dynamics will not map directly onto the doubly charged ion signal. Thus, one has to make sure that the high-energy tail of the probe VUV pulse does not cause appreciable second outer-valence ionization of an outer-valence ionized molecule, as we indeed do for our simulation below.

Let us now simulate an application of the time-resolved spLEAD spectroscopy for a realistic situation of hole migration following sudden inner-valence ionization. Specifically, we consider glycine, which shows two types of hole migration dynamics [24,25]. Figure 3 shows the survival probability [Eq. (4)] and spLEAD probability [Eq. (5)] for sudden ionization of glycine from the $11A'$ MO. Assuming an ionized state of the type of Eq. (3) with $k = 11A'$, the resulting two-state oscillatory dynamics involve beatings between $11A'$ - and $12A'$ -ionized $1h$ configurations. Our *ab initio* calculations demonstrate

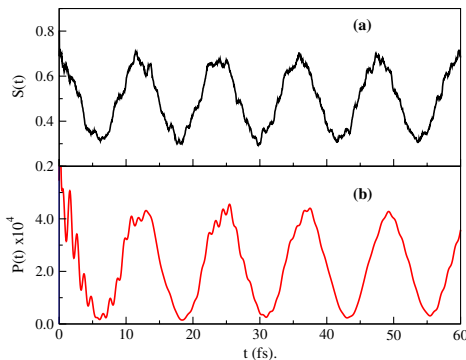


FIG. 3 (color online). (a) Survival probability and (b) spLEAD transition probability of the $11A'$ -ionized state of glycine. VUV pulse parameters: $\tau = 266$ as, $\omega = 15.5$ eV, and $\mathcal{E} = 4.43 \times 10^9$ V m $^{-1}$. cc-pCVDZ basis [30] with $3s3p$ KBJ Gaussian functions on the heavy atoms is used in the ADC(2) x calculations [Eqs. (4) and (5)].

excellent agreement between the periodicity of the delay time modulation of the double ionization probability with the survival probability, showing that this two-state hole migration process is exceptionally well resolved using the proposed spLEAD probe.

While removal of an electron from the $11A'$ MO results predominantly in two- $1h$ -state quantum beats, sudden ionization from the $10A'$ orbital triggers a bit slower oscillatory evolution of the survival probability, involving coupling of a $1h$ configuration to a manifold of the $2h1p$ ones. Figure 4 shows the survival probability of the initial state produced after ionization from the $10A'$ orbital as well as the double ionization probability obtained from the probe pulse. Even in the case of such relatively involved dynamics, the delay-dependent spLEAD transition probability mimics the survival probability of the sudden ionization state well over the first two revivals. One has to keep in mind that the fixed-nuclei approximation adopted here is not expected to be valid on the time scale beyond several tens of femtoseconds [12,13]. However, the demonstrated ability of the spLEAD signal to reproduce the dynamics over longer time scales can be used to track the onset of the nuclear motion effects in time by comparing the experimental and the theoretical (fixed-nuclei) signals.

In conclusion, we have presented and simulated a new attosecond technique, spLEAD spectroscopy, and demonstrated its capability to resolve ultrafast hole migration dynamics. The new attosecond spectroscopy requires the application of an attosecond pulse generating a superposition of bound ionic states and, after a controlled delay, a short (~ 0.5 fs long) VUV pulse inducing a one-photon—two-electron spLEAD transition. The probe VUV pulses with the needed properties can be generated by HHG in krypton and subsequent spectral filtering [26]. As illustrated by our detailed *ab initio* calculations for two qualitatively different hole migration modes in glycine, the VUV spLEAD probe efficiently maps ultrafast hole migration dynamics onto the double ionization yield with no competing processes contributing to the doubly charged ion signal. Thus, we believe that the proposed technique is a feasible and robust method for resolving the dynamics

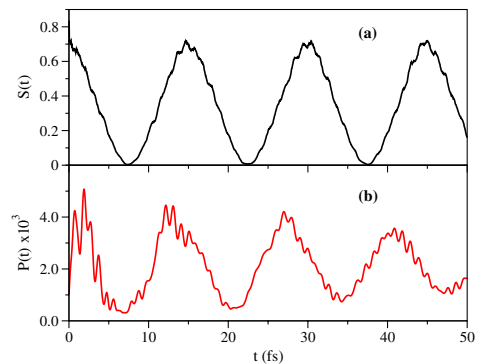


FIG. 4 (color online). As for Fig. 3 for the $10A'$ -ionized state of glycine. VUV pulse parameters: $\tau = 314$ as, $\omega = 13.2$ eV, and $\mathcal{E} = 3.74 \times 10^9$ V m $^{-1}$.

of hole migration on the electronic time scale by straightforward ion count measurement. If the doubly ionized ions generated by the spLEAD probe decompose and cannot be detected directly [27], coincidence [28] or covariance [29] techniques can be used to quantify the singly charged fragments resulting from the dication decomposition. We propose that the spectroscopic method described here is used for solving the long-standing problem of the electronic vs nuclear motion effect on hole migration in molecules [5,6,12,13].

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