Molecular Auger Interferometry

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(Dated: June 16, 2019)

We introduce and present a theory of interferometric measurement of a normal Auger decay lifetime in molecules. Molecular Auger interferometry is based on the coherent phase control of Auger dynamics in a two-colour ($\omega/2\omega$) laser field. We show that, in contrast to atoms, in oriented molecules of certain point groups the relative $\omega/2\omega$ phase modulates the total ionisation yield. A simple analytical formula is derived for the extraction of the lifetimes of Auger-active states from a molecular Auger interferogram, circumventing the need in either high-resolution or attosecond spectroscopy. We demonstrate the principle of the interferometric Auger lifetime measurement using inner valence decay in CH_3F.

Auger decay [1, 2] is a fundamental process, where in the presence of an inner-shell vacancy, a valence electron recombining with this vacancy supplies another (Auger) electron with sufficient energy to leave an atom or a molecule. Auger decay is intensely studied due to its importance for such diverse areas as surface science, atmospheric chemistry, radiation biology, X-ray spectroscopy and attosecond physics.

Advances in laser and X-ray technology have initiated a new chapter in the study of Auger processes, enabling time-resolved measurements of the Auger decay lifetimes [3], matching the spectral resolution of the best available energy-resolved experiments [4]. Furthermore, several new Auger-based radiative processes have been explored, such as laser-assisted Auger decay (LAAD) [5–7] or laser-enabled Auger decay (LEAD) [8] with multiple photons. In both of them, the Auger decay is initiated by the X-ray and laser pulses. For LAAD the Auger decay is energetically allowed, whereas in the case of LEAD, the Auger process is initially energetically forbidden, but becomes allowed if the system can absorb additional energy from a laser field. Another example is single-photon laser-enabled Auger decay (spLEAD), first predicted theoretically in [9]. In this process, the ionisation of an Auger-inactive ionic state occurs due to a two-electron transition filling the inner-valence vacancy with simultaneous photon absorption. Recently, atomic spLEAD was confirmed experimentally [10] using an $\omega/2\omega$ coherent control scheme [11] and light from a free-electron laser (FEL). Variation of the relative phase of the two frequencies resulted in modulation of the angular distribution of the electrons emitted by ionised Ne atoms.

We show analytically that for oriented molecules belonging to the molecular point groups C_s, C_n, C_{nv}, $C_{\infty v}$, C_{3h}, D_3, D_{3h}, and T_d, one can control not merely the angular distribution but also the total yield of the Auger or spLEAD electrons or, equivalently, the yield of doubly ionised molecules. Molecular orientation in the gas phase has been repeatedly demonstrated [12]. It is well-recognised that the total yield can be controlled even in the atomic case via schemes employing same-parity transitions, e.g. $\omega/3\omega$, however within the photon energy regime relevant for the Auger dynamics practical realisation of such control schemes appears problematic [13].

Here we present Auger interferometry, i.e. a theory of coherent control of Auger decay and spLEAD in ionised molecules. The theory is applied to the CH_3F ion which has an Auger-active state (AAS) with energy only slightly above the double ionisation potential (DIP) and, as a result, a decay width that is challenging to predict theoretically. We show that attosecond resolution can be gained without using attosecond pulses, by simply controlling the relative $\omega/2\omega$ phase. The accuracy of the retrieved time-resolved dynamics is determined by the accuracy with which the $\omega/2\omega$ phase difference is controlled, and by the accuracy with which intensities of the ω- and 2ω-field and transition dipole moments are determined.

We study the ionisation dynamics of a molecule under the influence of two long XUV (FEL) pulses. In general, the system can have several AASs within the energy region around the resonant energy. We consider the ground state φ_0^{N-1}, $|0\rangle$, M AASs φ_m^{N-1}, $|m\rangle$, $(m = 1,..,M)$ with $N-1$ electrons, and a doubly ionised state $|E\rangle$, described by the electron in the continuum χ_E^n and the associated dicationic state φ_n^{N-2}, where n is the index of the ionic channel. The AASs $|m\rangle$ are above the DIP. In the case of spLEAD the states $|m\rangle$ are below the DIP.

The laser field transfers the molecule from the ground

state $|0\rangle$ to the doubly ionised state $|E\rangle$ by two interfering ionisation paths, directly by 2ω-photon absorption, and by absorption of two ω-photons via the intermediate decaying states $|m\rangle$. The faster the intermediate states decay, the weaker the second path becomes, so that the maximum yield of emitted electrons is limited by the lifetimes of the $|m\rangle$ states. Destructive interference or complete suppression of the yield requires a balance of the paths that can be reached by tuning the intensity of the ω-field relatively to the intensity of the 2ω-field.

In molecules, this interference between single- and two-photon (a Resonant Multiphoton Ionisation process (REMPI) [14]) transitions is possible if the expansion of the direct product of the representation of a dipole operator or components thereof, D_{dipole}, itself contains the dipole representation:

$$D_{dipole} \otimes D_{dipole} \supset D_{dipole}\,. \tag{1}$$

This is for the present case of linear, parallel polarisation of the two frequencies which implies that the dipole operator components belong to the same irreducible representation (IRREP). The case of orthogonal polarisations is considered in the Supplemental Material (SM) and the allowed point groups for linear polarisation with perpendicular polarisation of ω and 2ω are listed. The condition (1) is trivially fulfilled for all symmetry groups where one of the dipole components belongs to the fully symmetric IRREP, namely for C_s, C_n, C_{nv} and $C_{\infty v}$. Apart from those symmetry groups, the condition (1) is satisfied for molecules of the point group symmetries D_3, D_{3h} and T_d.

To describe theoretically the molecular Auger interferometry, we solve the time-dependent Schrödinger equation (TDSE), atomic units are used throughout,

$$i\frac{\partial \Psi^{N-1}(t)}{\partial t} = \hat{H}(t)\Psi^{N-1}(t) \tag{2}$$

for the Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$, where $\hat{H}_0$ is the unperturbed Hamiltonian of the $(N-1)$-electron system

$$\begin{aligned} \hat{H}_0\varphi_m^{N-1} &= \tilde{E}_m^{N-1}\varphi_m^{N-1} \\ \hat{H}_0\left[\chi_E^n\varphi_n^{N-2}\right] &= E_n^{N-1}\left[\chi_E^n\varphi_n^{N-2}\right]. \end{aligned} \tag{3}$$

The energies $\tilde{E}_m^{N-1} = E_m^{N-1} - i\Gamma_m$ of the AASs $|m\rangle$ $(m = 1, ..., M)$ take into account the natural energy (or decay) half-width at half maximum (HWHM) Γ_m, denoted below "the energy width". For the ground state $|0\rangle$ the energy is real $\tilde{E}_0^{N-1} = E_0^{N-1}$, and $E_n^{N-1} = E_n^{N-2} + E$ is the energy of the doubly ionised state, with E the energy of the continuum electron. The term $\hat{V}(t) = -d\mathcal{E}$ describes the interaction with a linearly polarised two-colour laser field

$$\mathcal{E} = \mathcal{E}_1\cos(\omega t) + \mathcal{E}_2\cos(2\omega t + \phi), \tag{4}$$

where $\mathcal{E}_1$ and $\mathcal{E}_2$ are the electric field amplitudes of the field with frequencies ω and 2ω, respectively, and ϕ is their relative phase.

The total wave function $\Psi^{N-1}(t)$ is given by

$$\begin{aligned} \Psi^{N-1}(t) =& c_0(t)\varphi_0^{N-1}e^{-iE_0^{N-1}t} + \sum_{m=1}^{M} c_m(t)\varphi_m^{N-1}e^{-i\tilde{E}_m^{N-1}t} \\ &+ \sum_n \int dE c_E^n(t)\chi_E^n\varphi_n^{N-2}e^{-iE_n^{N-1}t}. \end{aligned} \tag{5}$$

The last term in Eq. (5) includes a sum over different ionic channels n.

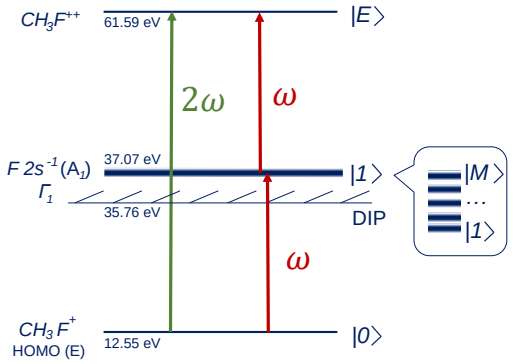


Figure 1. Auger interferometry scheme for the case of the coherent control of Auger decay of a F $(2s^{-1})$ hole in CH_3F with ω and 2ω laser fields. The frequency of the transition between the ground state $|0\rangle = \varphi_0^{N-1}$ of the molecular cation and the AAS $|1\rangle = \varphi_m^{N-1}$ (or a series of them) with energy HWHM Γ_1 equals the fundamental frequency ω. The doubly ionised final state $|E\rangle = \chi_E^n\varphi_n^{N-2}$ can be reached by two paths: either from the ground state directly by absorbing a 2ω-photon or from the ground state via the intermediate AAS by absorbing two ω-photons. Interference between these two transitions can be controlled by the relative phase ϕ between the two laser fields.

We substitute the total wave function (5) into the TDSE (2), and by using the standard rotating-wave approximation obtain the usual system of differential equations for the complex amplitudes (see (S2) in the SM). This system of equations for the induced transitions between the ground state of the ionised molecular system, single AAS $(M = 1)$ and the doubly-ionised state of the molecule with an electron in the continuum (see Fig. 1), can be solved fully analytically (neglecting field-induced transitions between doubly ionised states described by the transition dipole moments $d^{nn'}$ (S3) which are much weaker than the other transitions in our case) by applying the procedure of the adiabatic elimination of the continuum [15–17]. The case of two AASs is discussed separately in the SM. The complex amplitudes of the continuum states become stationary when the XUV pulse is much longer than the lifetimes

of the considered states, which formally corresponds to taking the $t \to \infty$ limit. In this case the full time-dependent expression for c_E^n can be simplified:

$$c_E^n = -\frac{\alpha^n}{(\tilde{E} - i\tilde{\Gamma} - E)^2 - \delta^2}, \tag{6}$$

where α^n depends on the molecular parameters including Γ_1, and δ can be associated with the doubled complex Rabi frequency [18] (see the SM for more detail). Here $\tilde{E} = \frac{1}{2}(E_0 + E_1 + 3\omega)$ is a manifestation of the energy conservation law and $\tilde{\Gamma} = \frac{1}{2}(\Gamma_0^i + \Gamma_1^i + \Gamma_1)$ is a total energy HWHM, where $\Gamma_0^i = 2\pi \sum_n |V_{0E}^n|^2$ and $\Gamma_1^i = 2\pi \sum_n |V_{1E}^n|^2$ are the ionisation widths of the ground $|0\rangle$ and the intermediate $|1\rangle$ states, respectively.

Generally, the equation (6) looks similar to a Lorentzian profile but has a much more complicated character due to the complex form of δ, and is less amenable to straightforward analysis. However, for the resonant case ($\Delta_{01} = E_1 - E_0 - \omega = 0$) Eq. (6) can be rewritten in the form allowing analysis. In this case the resonant yield can be presented in the form

$$|c_E^r|^2 = \frac{V_{01}^2|V_{1E}|^2 + |V_{0E}|^2\Gamma_1^2 + 2V_{01}|V_{0E}||V_{E1}|\Gamma_1 \sin(\phi + \phi_{01})}{(V_{01}^2 + \Gamma_1\Gamma_0^i)^2 + (4\pi V_{01}|V_{1E}||V_{0E}|\cos(\phi + \phi_{01}))^2}, \tag{7}$$

where the matrix elements $V_{01} = -d_{01}\mathcal{E}_1/2$, $V_{0E} = -d_{0E}\mathcal{E}_2/2$ and $V_{1E} = -d_{1E}\mathcal{E}_1/2$ contain transition dipoles d_{01}, $d_{0E} = \sum_n |d_{0E}^n| e^{i\phi_0^n}$ and $d_{1E} = \sum_n |d_{1E}^n| e^{i\phi_1^n}$ (see (S3) in the SM). Eq. (7) is derived within the assumption that the phase difference $\phi_{01}^n = \phi_0^n - \phi_1^n$ is constant for different channels ($\phi_{01}^n \approx \phi_{01}$) of a particular molecular system (see SM for details). The dependence of the resonant yield (7) on the relative phase ϕ is contained in the numerator and disappears when $\Gamma_1 = 0$. In the denominator the dependence on ϕ is weak and can be neglected if at least one of the following conditions

$$\mathcal{E}_1^2/\mathcal{E}_2 \ll \Gamma_1|d_{0E}|/(2d_{01}|d_{1E}|)\,,\ \mathcal{E}_2 \ll d_{01}/(2\pi|d_{0E}||d_{1E}|) \tag{8}$$

is satisfied. The conditions (8) correspond to the regime of moderate intensities, when only processes described by the first order of perturbation theory contribute sufficiently. In this case the resonant yield (7) is modulated and the modulation depth $\mathcal{M}$ can be derived as

$$\mathcal{M} = 2/\left(\frac{V_{01}|V_{1E}|}{|V_{0E}|\Gamma_1} + \frac{|V_{0E}|\Gamma_1}{V_{01}|V_{1E}|}\right) \tag{9}$$

for given Γ_1. The modulation depth (9) maximum value is 1 and can be achieved when $|V_{0E}|\Gamma_1 = V_{01}|V_{1E}|$. This means that for any value of Γ_1 a high contrast $\mathcal{M}$ can be obtained by tuning the field intensities. The modulation depth $\mathcal{M}$ can be measured experimentally within the relative phase scan of the resonant yield and used for extraction of the AAS energy width Γ_1 value within a simple analytical expression

$$\Gamma_1 = \frac{1 - \sqrt{1 - \mathcal{M}^2}}{\mathcal{M}} \frac{V_{01}|V_{1E}|}{|V_{0E}|}. \tag{10}$$

Here one can notice that Γ_1 is proportional to the ω-field intensity I_1 and inversely proportional to the square root of the intensity I_2 of the 2ω-field ($I_{1,2} = \mathcal{E}_{1,2}^2$). Transition dipole moments can be calculated using, for instance the algebraic diagrammatic construction (ADC) technique [19]. The other way to find the factor $d_{01}|d_{1E}|/|d_{0E}|$ is to carry out two additional measurements: (i) with only 2ω-field giving the absolute value of the transition dipole moment d_{0E} which can be extracted from the yield $|c_E^r|^2 = 1/(4\pi^2|d_{0E}|^2 I_2)$, and (ii) with only ω-field giving the yield $|c_E^r|^2 = |d_{1E}/d_{01}|^2$ from which the transition dipole moment d_{1E} absolute value can be found by using the transition dipole moment d_{01}, the value of which is relatively easy to calculate with the accuracy of $5-10\%$ or better [20–22].

To demonstrate the principal of the molecular Auger interferometry, we choose a molecular system, fluoromethane (CH_3F), that has a $2s$-ionised AAS [23–26] with an energy only slightly above the DIP. We study the dynamics of the oriented singly ionised molecule CH_3F calculating the behaviour of the total yield $\int dE|c_E|^2$, see Eq. (6) either of doubly ionised molecules or electrons. We calculate the transition dipole moments using the *ab initio* many-body Green's function - based technique called ADC [19], of extended second order, ADC(2)x. Computational details are discussed in the SM.

We consider the parameters of the field (4) such as the intensity of each field component and the frequency ω which changes with the detuning from the resonance Δ_{01}. First, we investigate the behaviour of the line shape of the emitted electrons $|c_E|^2$. The line shape as a function of the relative phase ϕ for selected intensities shown in Fig. 2 demonstrate that for all values of the relative phase ϕ we observe an asymmetry of the spectrum relative to the central energy $E = E_0 + 2\omega$ of the emitted electrons. The emission is on average stronger for the relative phase ϕ in the interval $0 - \pi$, while for the $\pi - 2\pi$ region it is weaker or has disappeared ("switched off"). Detailed results are given in the SM. This can be a basis for phase control of the emitted electron spectrum by setting the relative phase ϕ for appropriate intensities. Since the value of Γ_1 is unknown, it was chosen to lie in within the range of $10^{-3} - 10^{-2}$ atomic units.

We show that the AAS energy width value can be retrieved from the total yield of the emitted electrons ($\int dE|c_E|^2$), and this yield is controlled by the relative phase ϕ and intensities $I_{1,2}$. Fig. 3(a-c) presents

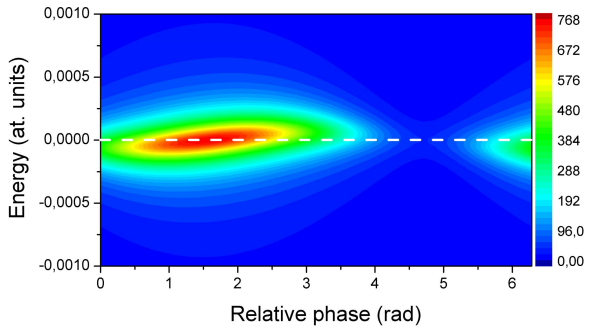


Figure 2. The spectrum of emitted electrons ionised by a laser field (4) for the case of CH_3F^+ with the energy width Γ_1 as a function of the relative phase ϕ. The zero of the electron energy E (y-axis) corresponds to the resonant energy $E_0 + 2\omega$. The intensities of the ω- and 2ω-field are $6.7 \cdot 10^{12}$ W/cm^2 and $\Gamma_1 = 5 \cdot 10^{-3}$ atomic units.

Auger interferograms showing the dependence of the population of the doubly ionised state of CH_3F (or the electron yield) as a function of the relative phase ϕ and the energy width Γ_1 of the singly ionised AAS of CH_3F, for the different intensity ratios. One can see that for the different decay widths, the depth of the population modulations varies. In Fig. 3(d) we show the dependence of the modulation depth on the energy width Γ_1 summarising the results presented in Auger interferograms in Fig. 3(a-c) as well as the detuned case discussed in the SM. Here one can see that the detuning from the resonance Δ_{01} affects the modulation depth of the total yield. Also one can notice that the intensity ratio equal to 1 corresponds to a higher modulation depth on average over the whole range of Γ_1 values. Fig. 3(d) shows the comparison between the total and resonant yield (9) for zero detuning (see the SM for more details) which shows an excellent agreement when the conditions (8) are satisfied. This provides a way to extract the AAS energy width using the simple expression (10). For the case when two different values of Γ_1 correspond to one value of modulation depth $\mathcal{M}$ (see Fig. 3(d)) the uncertainty can be eliminated by carrying out one additional measurement with changed intensity ratio. For instance, if the ω-field is kept constant and the intensity ratio is reduced by decreasing the 2ω-field intensity, then if the modulation depth becomes higher it corresponds to the higher value of the energy width and vice versa. This illustrates that information about an AAS such as energy width (or lifetime) can be obtained using this interferometric method.

In summary, we introduced molecular Auger interferometry as a measurement of the total yield of a normal Auger decay (or spLEAD) in molecules of particular point groups as a function of the relative $\omega/2\omega$ phase. Our analytical theory predicts that the Auger decay lifetime can be reconstructed from the relative phase scan of the Auger yield modulation. The interference contrast onto which the decay width is mapped [Eqs. (9,10)] can be maximised at any decay width by controlling the ratio of the ω- and 2ω-field intensities. As a result, the interferometric measurement proposed here is free of the limitations of both high-resolution Auger electron spectroscopy (struggling to characterise decay widths smaller than the instrumental energy resolution) and attosecond time-resolved spectroscopy (struggling to characterise decay rates faster than the available pulse durations). We suggest a method of extracting this information from the Auger interferograms by applying a simple analytical formula. An illustrative example dealing with inner valence hole decay in CH_3F shows that molecular Auger interferometry is well within the present-day experimental capabilities of the modern FEL facilities, such as FERMI@Elettra. More generally, the same coherent control scheme can be used to study any type of ultrafast hole dynamics, e.g. hole migration [27, 28].

Acknowledgements. MK acknowledges support by The Royal Society (NF161013). BC acknowledges financial support STFC ST/R005133ST/1. KU acknowledges support by "Five-star Alliance" in "NJRC Mater. & Dev." and IMRAM project. PK acknowledges financial support by the Czech Science Foundation (Project GAČR No. 17-10866S). VA and MI acknowledge support by EPSRC/DSTL MURI-MIR grant EP/II08680/1.

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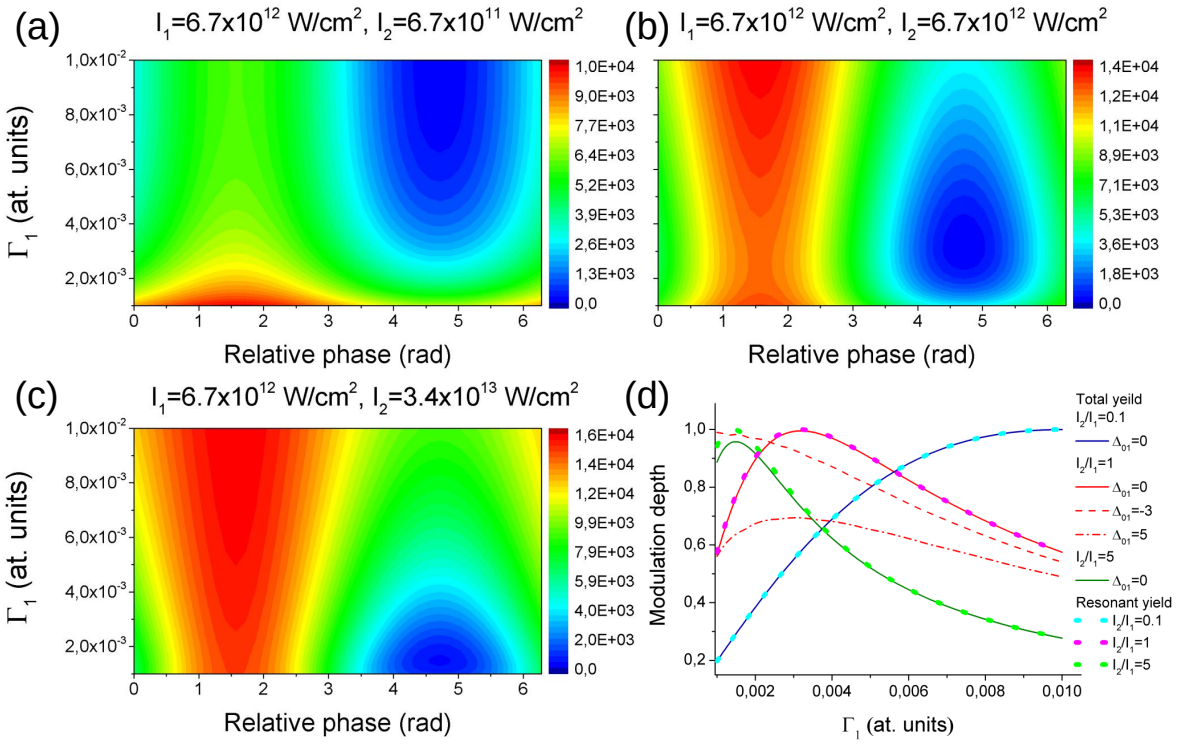


Figure 3. (a-c) Auger interferograms. The total yield of electrons emitted by a bichromatic laser field for the case of CH_3F^+ as a function of the relative phase ϕ and the Γ_1 (y-axis). (d) Modulation depth of the total yield for zero (thin solid lines) and non-zero detuning (thin dashed lines), and the resonant yield (thick dotted lines) as a function of the AAS energy width Γ_1. The intensities are the same as for (a-c) used, and detunings Δ_{01} are shown in 10^{-3} of atomic units.

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