

# Strongly resonant reconstruction of attosecond beating by interference of two-photon transitions on lithium

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The process of reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) can become resonant with a discrete atomic level either in the intermediate or the final continuous states. Experimental observations of the former [Phys. Rev. Lett. **104**, 103003 (2010)] and latter [Nature Commun. **7**, 10566 (2016)] resonant processes revealed modification of only those parts of the photoelectron spectrum that overlapped directly with the resonance. In the lithium atom and other members of the alkali-metal family, the valence shell  $ns \rightarrow np$  transition to the intermediate RABBITT state affects the whole photoelectron spectrum in the final state. The strong additional resonant channel modifies entirely the ionization dynamics and opens direct access to the resonant phase of the two-photon transitions, which is common for various single and multiple electron ionization processes. Elucidation of this phase has wider implications for strongly resonant laser-matter interaction.

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Valence shell dipole transitions are commonly used for optical manipulation of alkali-metal atoms. This includes optical pumping [1], trapping [2], and cooling [3]. These processes are of importance for many quantum technologies such as metrology [4], information processing [5], computations [6], and simulations [7]. Lithium, the lightest member of the alkali atom family, can be magneto-optically trapped [8], cooled [9], and pumped selectively to various  $2p_m$  magnetic substates [10]. These manipulations make lithium an ideal target for collision [9] and strong laser physics [8,10] experiments.

The process of reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [11,12] has become a widely used tool for attosecond chronoscopy of atoms [13], molecules [14,15], liquids [16], and solids [17,18]. In RABBITT, XUV driven primary ionization is augmented by secondary IR photon absorption or emission. These two latter processes lead to the same final continuous state whose population depends on the relative phase of the absorption or emission amplitudes. Experimental access to this phase makes it possible to obtain the timing information and to resolve photoemission on the attosecond time scale. RABBITT can become resonant with a discrete atomic level either in the intermediate or the final continuous states. In the former process, a discrete atomic state substitutes a missing continuous intermediate state that falls below the ionization threshold. Such an under-threshold RABBITT (or uRABBITT) has been observed in He [19] and Ne [20,21]. Alternatively, the final continuous state can be tuned to a Fano resonance. Such experiments were conducted on He [22] and Ar [23,24]. In both cases, the resonance has a mild effect on the observed photoelectron spectrum in the final state modifying only those parts that overlap directly with the resonance.

In this Letter, we demonstrate a very strong modification of the whole photoelectron spectrum in lithium when

the  $2s \rightarrow 2p$  transition becomes resonant with the intermediate RABBITT state. The strong additional resonant channel modifies entirely the ionization dynamics beyond its simple interpretation in terms of the relative absorption/emission phase converted to the atomic time delay.

The conventional RABBITT on either of the Li  $2s/2p$  initial states is illustrated graphically in Fig. 1(a). The atom absorbs an odd number of the linearly polarized photons of the fundamental frequency  $(2q \pm 1)\omega$  to get ionized to one of the intermediate states, which are marked in the photoelectron spectrum by the harmonic order  $H_{2q \pm 1}$ . Subsequent emission or absorption of one IR photon leads to the same final state, which appears in the photoelectron spectrum as a sideband  $SB_{2q}$ . The SB population oscillates when a time delay  $\tau$  is introduced between the ionizing XUV and the dressing IR pulses

$$S_{2q}(\tau) = A + B \cos(2\omega\tau - C) \quad (1)$$

The simplest interpretation of the parameters entering Eq. (1) is provided by the lowest-order perturbation theory (LOPT):

$$A = |\mathcal{M}_a|^2 + |\mathcal{M}_e|^2, \quad B = 2\text{Re}[\mathcal{M}_a \mathcal{M}_e^*] \\ C = \arg[\mathcal{M}_a \mathcal{M}_e^*] = 2\omega\tau_a. \quad (2)$$

Here we introduce the complex amplitudes of the XUV absorption, augmented by absorption  $\mathcal{M}_a$  or emission  $\mathcal{M}_e$  of an IR photon. The phase of the RABBITT oscillation

$$C = \Delta\phi_{2q \pm 1} + \Delta\phi_w + \Delta\phi_{cc} \quad (3)$$

is the sum of the phase difference of the neighboring odd harmonics ( $\Delta\phi_{2q \pm 1} = \phi_{2q+1} - \phi_{2q-1}$ ), the analogous difference of the phases of the XUV absorption (the so-called Wigner phase difference)  $\Delta\phi_w$ , and the phase difference of the IR driven transitions (the so-called continuum-continuum or CC

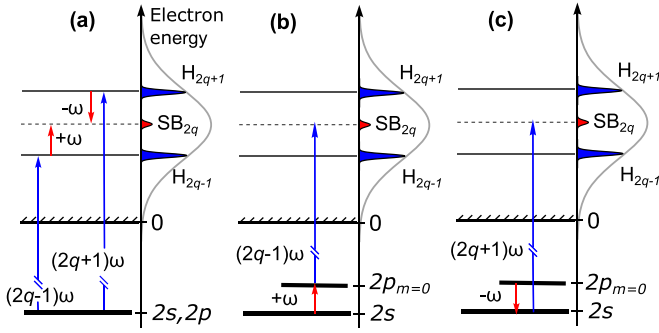


FIG. 1. (a) Schematic representation of the conventional RABBITT process on either of the Li  $2s/2p$  initial state. (b) Same for the resonant Li  $2s$  RABBITT process when the photon energy is in resonance with the level spacing  $\omega \simeq E_{2p} - E_{2s}$ . (c) Same for the resonant Li  $2p_{m=0}$  process.

phase difference)  $\Delta\phi_{cc}$ . The latter phase differences are converted to the corresponding time delays by a finite difference formula [25]

$$\tau_W = \Delta\phi_W/(2\omega), \quad \tau_{cc} = \Delta\phi_{cc}/(2\omega). \quad (4)$$

The two time delays in Eq. (4) add up to the atomic time delay  $\tau_a = \tau_W + \tau_{cc}$ , which is the group delay of the photoelectron wave packet propagating in the combined field of the ion remainder and the dressing IR field relative to its free space propagation.

The resonant  $2s \rightarrow 2p$  RABBITT process on the ground  $2s$  state of Li is illustrated in Fig. 1(b). In this process, the IR photon absorption promotes the electron to the  $2p_{m=0}$  intermediate bound state. Then the XUV  $(2q-1)\omega$  absorption elevates it to the same final state  $SB_{2q}$ . A similar resonant channel on the  $2p_{m=0}$  initial state is exhibited in Fig. 1(c). Here the IR photon is first emitted and then the XUV  $(2q+1)\omega$  absorption populates  $SB_{2q}$ . In both Figs. 1(b) and 1(c) the resonant RABBITT process does not involve a CC transition and lacks the  $\phi_{cc}$  phase. Instead, it contains the resonant phase, which can be approximated by a simplified expression [20]

$$\phi_r \approx \arg[\omega + E_{2s} - E_{2p} - i\Gamma]^{-1} = \arctan(\Gamma/\Delta). \quad (5)$$

Here  $\Gamma$  is the spectral width of the IR pulse and  $\Delta \equiv \omega + E_{2s} - E_{2p}$  is the detuning. More elaborate expressions for the resonant two-photon absorption phase are derived in Refs. [26,27].

The relative contribution of the resonant and nonresonant RABBITT processes and their phases depends on the strength of the corresponding ionization channels. This strength can be gauged from the partial photoionization cross sections exhibited in Fig. 2. In the limits of the small and large photoelectron energy  $E$ , these cross sections satisfy the following relations:

$$\begin{aligned} \sigma_{2p} &= 14 \text{ Mb} \gg \sigma_{2s} = 1.3 \text{ Mb} \quad \text{for } E \simeq 0 \\ \sigma_{2p} &\propto E^{-9/2} \ll \sigma_{2s} \propto E^{-7/2} \quad \text{for } E \gg I_p \end{aligned} \quad (6)$$

The above relations show that the  $2p$  primary ionization is much stronger than the  $2s$  one when the photoelectron energy is low. When this energy is high, it is the  $2s$  primary ionization that is dominant over the  $2p$  one. The  $2s$  and  $2p$  resonant channels exhibited in Figs. 1(b) and 1(c) are driven by the

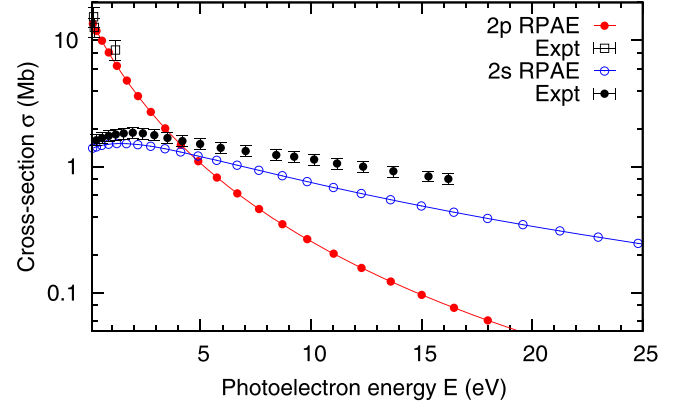


FIG. 2. Partial photoionization cross sections of the Li atom. Present calculations within the random phase approximation with exchange (RPAE) [28] are compared with the experimental data for the Li atom in the  $2s$  [29] and  $2p$  [30,31] initial states.

$(2q-1)\omega$  and  $(2q+1)\omega$  XUV photon absorption, respectively. The former process approaches the threshold closely for the lower SB orders whereas the latter process always stays away from the threshold. Accordingly, the resonant channel of Fig. 1(b) weakens away from the threshold relative to the nonresonant  $2s$  channel exhibited in Fig. 1(a). Conversely, the resonant process exhibited in Fig. 1(c) is uniformly strong for all the SB's in comparison with its nonresonant  $2p$  counterpart. Therefore the resonant phase in this channel is dominant over the nonresonant one. Notably, the  $2p_{m=1}$  initial state does not mix with the intermediate  $2s_{m=0}$  state and the corresponding RABBITT process lacks the resonant phase in this case.

Accurate nonperturbative treatment of the RABBITT process requires numerical solution of the time-dependent Schrödinger equation (TDSE). We seek this solution in the single-active electron (SAE) approximation [32] with an effective one-electron potential [33]. This approximation is valid in the photon energy considered here, which is well below the  $1s$  threshold at  $\simeq 60$  eV. The TDSE SAE approach to RABBITT has been tested successfully on He [34], Ne [35], and heavier noble gas atoms [36]. The TDSE is driven by a superposition of an XUV attosecond pulse train (APT) and the IR pulse in several fixed increments of the IR-XUV. delay  $\tau$ .

The APT is modeled with the vector potential

$$\begin{aligned} A_x(t) &= \sum_{n=-5}^5 (-1)^n A_n \exp\left(-2 \ln 2 \frac{(t - nT/2)^2}{\tau_x^2}\right) \\ &\times \cos[\omega_x(t - nT/2)], \end{aligned} \quad (7)$$

where

$$A_n = A_0 \exp\left(-2 \ln 2 \frac{(nT/2)^2}{\tau_T^2}\right).$$

Here  $A_0$  is the vector potential peak value and  $T = 2\pi/\omega$  is the period of the IR field. The XUV central frequency is  $\omega_x$  and the time constants  $\tau_x, \tau_T$  are chosen to span a sufficient number of harmonics in the range of photon frequencies of interest for a given atom.

The vector potential of the IR pulse is represented by the cosine squared envelope

$$A(t) = A_0 \cos^2 \left( \frac{\pi(t - \tau)}{2\tau_{\text{IR}}} \right) \cos[\omega(t - \tau)]. \quad (8)$$

In the present work, the APT is centered at  $\omega_x = 15\omega$  and its spectral width  $\Gamma = 0.4$  eV. Typical XUV and IR field intensities are  $5 \times 10^9$  and  $3 \times 10^{10}$  W/cm<sup>2</sup>, respectively. In this low intensities regime, our numerical results depend weakly on variation of these parameters.

The photoelectron spectrum is obtained by projecting the time-dependent wave function at the end of the time evolution on the basis of Volkov states. Numerical details are given in the preceding publications [35,36].

Results of our simulations are shown in Fig. 3 for the Li atom initially in the  $2p_m$  state summed over  $m = 0, \pm 1$  [Fig. 3(a)] and the  $2s$  state [Figs. 3(b), 3(c)]. The photon energy  $\omega = 1.55$  eV in Figs. 3(a), 3(b) and 1.65 eV in Fig. 3(c). In Fig. 3 we display the RABBITT traces, which are comprised of the stack of angular integrated photoelectron spectra taken while varying the XUV-IR delay  $\tau$ . As the two-photon RABBITT transitions are weaker than the one-photon primary photoionization, the harmonic peaks are normally much stronger than the sidebands (see Fig. 1 for graphical illustration). To highlight the SB's, we conduct yet another computation with the XUV ionization only and subtract the resulting photoelectron spectrum from the XUV-IR RABBITT spectra at each time delay. Thus the primary harmonic peaks are all but removed and the RABBITT traces of Fig. 3 display the sidebands very clearly.

The sidebands are integrated over the energy window  $2q\omega \pm \Gamma/2$  and their time dependence is fitted with Eq. (1). The resulting phases  $C_{2q}$  for each SB are marked on the RABBITT traces and joined by the solid blue lines. These lines guide the eye through the SB centers on each panel of Fig. 3. The striking difference between the Figs. 3(a) and 3(b), 3(c) is that the SB's are perfectly aligned in the case of the  $2p$  initial state whereas they are visibly tilted for the  $2s$  initial state. The direction of this tilt is opposite for the photon energies of 1.55 eV and 1.65 eV.

The lack of a SB dispersion for the  $2p$  initial state can be understood from Eq. (3). In our simulations, the APT is composed of the pulselets of altering polarity and  $\Delta\phi_{2q\pm 1} = \pi \forall q$ . In comparison, both the Wigner  $\Delta\phi_W$  and the CC  $\Delta\phi_{cc}$  phase differences are small away from the threshold. Also the resonant phase  $\phi_r$  (5) does not depend on the photoelectron energy  $E$ . Thus the resulting RABBITT phase is nearly constant for all the SB's.

The phase variation with the photoelectron energy and the fundamental photon frequency  $\omega$  is analyzed in more detail in Fig. 4. In the three panels of this figure, from top to bottom, we display the net RABBITT phase corresponding to the  $2p_{m=0}$ ,  $2p_{m=1}$  and  $2s$  initial states, respectively. The harmonic phase difference  $\Delta\phi_{2q\pm 1} = \pi$  is subtracted for clarity. The fundamental photon frequency  $\omega$  varies across the resonant  $2s - 2p$  transition. For the  $2p_{m=0}$  initial state, the net RABBITT phase depends strongly on  $\omega$  but remains flat with  $E$ . Conversely, the  $2p_{m=1}$  phase does not depend either on  $\omega$  or on  $E$ . And, finally, the  $2s$  phase depends strongly both on  $\omega$  and  $E$ . The sign of the  $E$  dispersion depends on  $\omega$ . It turns from positive to negative

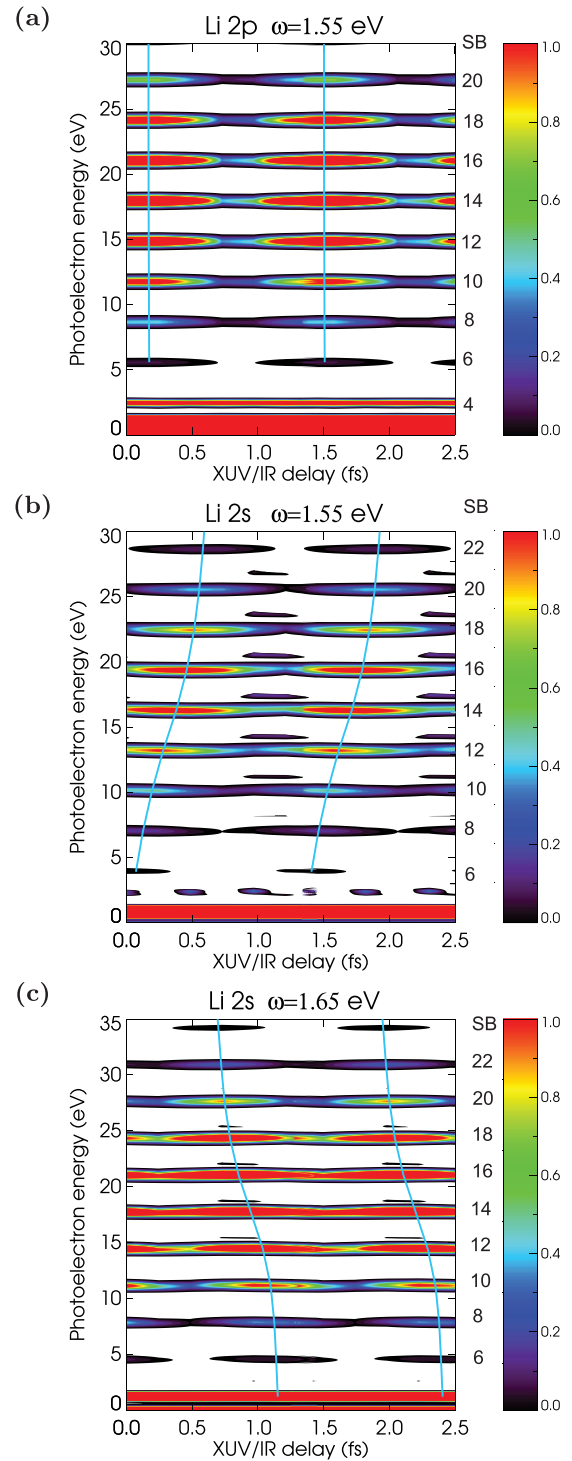


FIG. 3. RABBITT traces of the Li atom initially in the (a)  $2p$  and (b), (c)  $2s$  states at the fundamental frequency  $\omega = 1.55$  eV,  $\lambda = 800$  nm (a), (b) and  $\omega = 1.65$  eV,  $\lambda = 729$  nm (c). The corresponding SB orders are marked on the right vertical axis of each panel. The blue solid lines guide the eye through the centers of the sidebands.

when  $\omega \geq 1.65$  eV. This transition corresponds to the photon energy approaching the level spacing  $E_{2p} - E_{2s}$  (1.68 eV in our model potential and 1.86 eV in the experiment [37]).

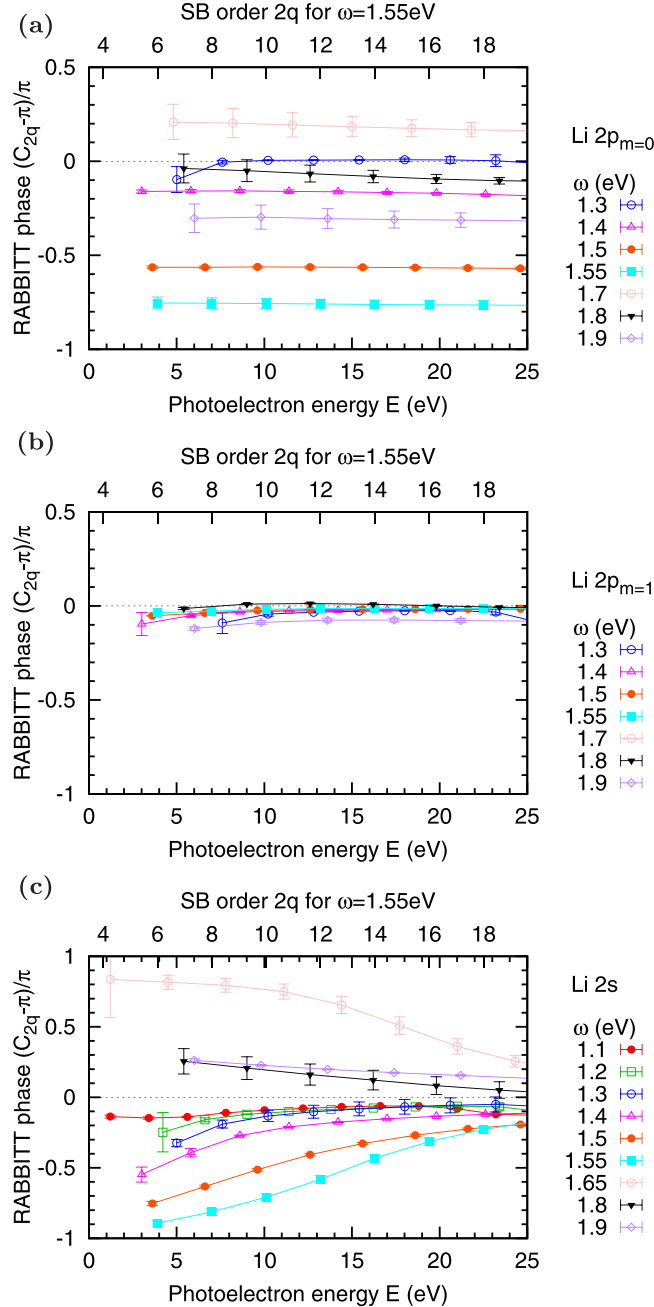


FIG. 4. (a) The  $2p_{m=0}$  RABBITT phases  $C_{2q}$  for various sidebands are plotted for several fixed photon energies. The top scale indicates the SB order for  $\omega = 1.55$  eV. (b) and (c) is the same for the  $2p_{m=1}$  and  $2s$  RABBITT phases, respectively.

The resonant transition of the  $2p_{m=0}$  and  $2s$  RABBITT phases is shown more distinctively in Fig. 5 where we select just a single SB<sub>8</sub> and trace its phase as a function of the photon energy. This low SB<sub>8</sub> is dominated by the resonant channel for both the initial states. For the  $2p_{m=0}$  initial state, this resonant character is retained by the higher-order SB's and their phases remain nearly flat over an extended range of the photoelectron energy  $E$  as displayed in Fig. 4(a). Conversely, for the  $2s$  initial state, the resonant character of the higher-order SB's weakens and their phases approach  $\Delta\phi_{2q\pm 1} = \pi$

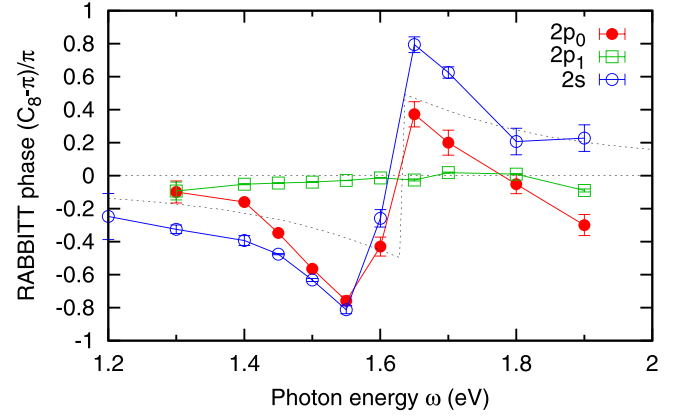


FIG. 5. The  $C_8$  phase variation with the photon energy  $\omega$  is plotted for  $2p_{m=0,1}$  and  $2s$  initial states. The dotted line visualizes Eq. (5).

as exhibited in Fig. 4(c). Thus the corresponding RABBITT phases demonstrate a significant energy dispersion with  $E$ .

Up to now, we examined the angular integrated RABBITT spectra. The angular dependence of these spectra can also be explored by tracing the SB position and deducing its phase as a function of the photoelectron emission angle  $\theta$ . This tracing is exhibited in Fig. 6 for the  $2p_{m=0}$  [Fig. 6(a)],  $2p_{m=1}$  [Fig. 6(b)], and  $2s$  [Fig. 6(c)] initial states. Here the RABBITT phase  $C(\theta) - C(\theta = 0)$  is plotted relative to the polarization direction corresponding to  $\theta = 0$ . In the case of the  $2p_{m=1}$  initial state, which is not resonant with its  $2s$  counterpart, there is no angular variation of the RABBITT phase except its sharp rise above  $\theta \simeq 60^\circ$ . The smooth and rather uniform angular dependence appears in the RABBITT phase for the  $2p_{m=0}$  initial state, which is consistently resonant with the  $2s$  state for all the SB's. In both cases, the angular dependence originates from the competition of the two continuous final states,

$$2p \xrightarrow{(2q\pm 1)\omega} \epsilon d \xrightarrow{\mp\omega} Ep, Ef,$$

each supported by their own spherical harmonics. The population of the  $\epsilon s$  intermediate state is ten times smaller and can be neglected. The  $Ef$  channel should normally dominate over the  $Ep$  one because of the Fano propensity rule [38], which was confirmed in other RABBITT studies [20,39]. A single dominant spherical harmonic does not provide any angular dependence below its kinematic node. This is indeed the case for the nonresonant  $2p_{m=1}$  initial state where the angular dependence is missing for all the SB's below the node of  $Y_{31}$  ( $63.4^\circ$ ). For the resonant  $2p_{m=0}$  initial state, the angular dependence is also uniform but it is noticeable for all the emission angles. This is the evidence of several competing spherical harmonics. Finally, for the  $2s$  initial state, the angular dependence is strong for lower-order SB's but it gradually weakens for higher-order SB's. For a nonresonant  $ns$  initial state, it is the competition of the  $\epsilon p \xrightarrow{\pm\omega} Es, Ed$  transitions that introduces the angular dependence of the RABBITT phase [34]. Such a dependence, however, reveals itself only beyond the kinematic node  $Y_{20}$  ( $54.7^\circ$ ). In the present case of the resonant  $2s$  initial state, the angular dependence onsets at significantly smaller

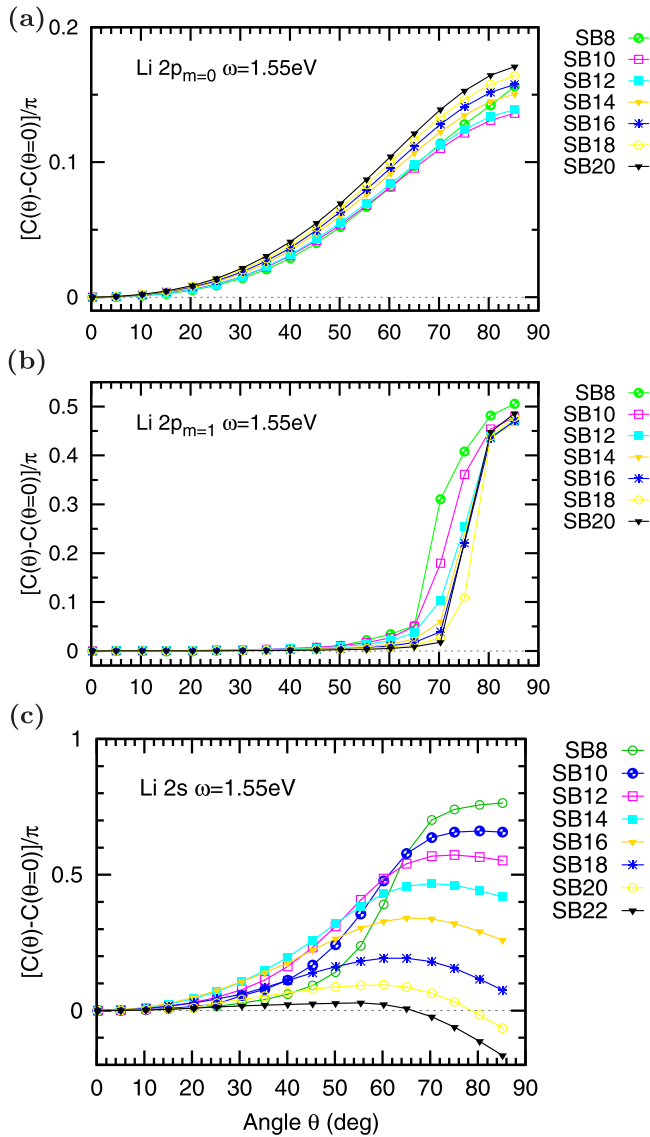


FIG. 6. Variation of the RABBITT phase relative to the polarization direction  $C(\theta) - C(\theta = 0)$  on the (a) Li  $2p_{m=0}$ , (b)  $2p_{m=1}$ , and (c)  $2s$  initial states. The photon energy  $\omega = 1.55$  eV.

angles. The angular dispersion is strong and positive for small SB's. It becomes weak and negative for higher SB orders, which is typical for a nonresonant He  $1s$  initial state [34].

In conclusion, we studied systematically the RABBITT processes in the Li atom prepared initially in the  $2s$ ,  $2p_{m=0}$ , and  $2p_{m=1}$  states. The properties of the RABBITT process in lithium are very diverse. Experimentally, the population of the Li atom in various  $2p_m$  substates is achieved by resonant pumping by the linearly [8] or circularly [10] polarized laser pulses. The three initial states demonstrate different interplay between the resonant and nonresonant RABBITT processes. The contribution of the resonant channel is selective for the  $2s$  initial state. It is very strong for the lower-order SB's near the threshold but it weakens as the SB order and the

corresponding photoelectron energy grow. Such a variable competition between the resonant and nonresonant channels leads to a strong SB energy and angular dispersion. The sign of the energy dispersion changes abruptly when the photon energy passes through the resonance corresponding to the energy spacing between the  $2s$  and  $2p$  initial states. In the case of the  $2p_{m=0}$  initial state, the resonant channel makes a uniformly dominant contribution for all the SB orders. In this case, the energy dispersion of the SB's is very weak while the angular dependence is uniform and moderate. Finally, the resonant channel does not contribute for the  $2p_{m=1}$  initial state. In this case, both the energy and angular dispersion of the SB's are absent. It needs to be stressed that a strong resonant channel invalidates the conventional definition of the atomic time delay via the RABBITT phase by way of Eq. (2). Indeed, the resonant phase is contained only in one of the  $(2q \pm 1)\omega$  XUV absorption arms and the finite difference expression (4) for the phase derivative cannot be used.

Our study broadens significantly the catalog of the resonant RABBITT processes reported so far in the literature. In the previous studies, only one selected sideband was affected by the resonance either in the intermediate state (the so-called uRABBITT process [19,20]) or by tuning it to a Fano resonance in the final state [22–24].

The strongly resonant RABBITT should be found in other members of the alkali atoms family. Their valence shell dipole  $ns \rightarrow np$  transitions overlap with NIR laser frequencies and make these atoms convenient targets for optical manipulation. Importantly, because of the identical principle quantum numbers, the oscillator strength of the  $ns \rightarrow np$  transition is several times greater than that of the higher-order transitions. This makes the resonant behavior of the  $ns$  RABBITT very robust and clear. In the meantime, a nonresonant  $np_{m=1}$  RABBITT can serve as a stable reference, which displays no sideband dispersion except the high-order harmonics group delay (the attochirp). The latter instrumental effect is identical for both initial states and thus can be easily eliminated.

The significance of the present findings goes beyond the specificity of the RABBITT process. It opens direct access to the resonant phase of the two-photon transitions. The resonant phase can be extracted straightforwardly by taking the difference between the  $np_{m=0}$  and  $np_{m=1}$  RABBITT measurements. This phase is common for various single and multiple electron ionization processes. Several theoretical models describing this phase [20,26,27] can thus be validated. This will have wider implications for strongly resonant laser-matter interaction. The combination of the RABBITT and magneto-optical trapping is technically challenging at present [40]. Nevertheless, we hope that we provided sufficient motivation for such an experiment to be conducted. The alkali-metal atoms are the natural candidates for future attosecond studies once the traditional noble gas targets are exhausted.

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