## Impact of quantum interference in cascade radiation on the absorption profile

D. Solovyev<sup>(D)</sup>,<sup>1,2,\*</sup> A. Anikin<sup>(D)</sup>,<sup>1,3</sup> T. Zalialiutdinov<sup>(D)</sup>,<sup>1,2</sup> and L. Labzowsky<sup>(D)</sup>,<sup>2</sup>

<sup>1</sup>Department of Physics, St. Petersburg State University, Petrodvorets, Oulianovskaya 1, 198504 St. Petersburg, Russia

<sup>2</sup>Petersburg Nuclear Physics Institute named by B.P. Konstantinov of National Research Center "Kurchatov Institute,"

St. Petersburg, Gatchina 188300, Russia

<sup>3</sup>D.I. Mendeleev Institute for Metrology, St. Petersburg 190005, Russia

(Received 9 November 2023; accepted 13 December 2023; published 9 February 2024)

Spectroscopic measurements of transition frequencies in various atomic systems are a significant part of modern physics. They enable the testing of fundamental interactions, the determination of physical constants, and the study of fundamental symmetries that occur in nature with unprecedented accuracy. Studies based on two-photon spectroscopy of simple atoms represent some of the most accurate experiments to date. The verification of precision experimental results is largely supported by theoretical analysis, which is most rigorous for light, nonrelativistic atoms and ions. In the last decade, much attention in the literature has been paid to the study of the quantum interference effect (QIE) in hydrogen and hydrogenlike atomic systems. This has made it possible to significantly reduce the experimental error in determining the appropriate transition frequency. The theoretical description of the QIE corresponds to the consideration of similar pathways arising for close-lying resonant states into which the transition frequency is measured. In the present work, the influence of the emission process on the absorption profile formation is investigated. The results of the studies carried out in this work show the need to take into account the effect of quantum interference in cascade radiation for the precise determination of the absorption transition frequency to highly excited states in two-photon spectroscopic experiments.

DOI: 10.1103/PhysRevA.109.022806

## I. INTRODUCTION

The continuous improvement in the accuracy of modern spectroscopic experiments, whether it be measuring the transition frequency, spectral linewidth, binding energy, polarizability, etc., in various atomic systems, is aimed not only at consolidating experimental data with a theoretical description, but also at deepening our understanding of the processes under consideration. Simple atomic systems appear to be a clear example of this kind of research with an experimental error of  $10^{-15}$  [1] for the hydrogen atom and  $10^{-12}$  in helium [2]. Within the achieved experimental accuracy, effects at the same level and below should be carefully considered.

The combination of experimental and theoretical efforts made it possible to accurately determine the Rydberg constant and the proton charge radius [3,4]. A more accurate determination of these constants in hydrogen [4] was achieved by taking into account nonresonant (NR) corrections and, in particular, the quantum interference effect (QIE) as the most significant part of them. Such corrections depend on the process used to measure transition frequencies, breaking away from the "standard" QED theory of radiative effects.

In the framework of QED theory, the spectral line profile arises in the resonance approximation for the scattering cross section when all terms except the resonant one are omitted [5]. In most spectroscopic problems, this approximation is sufficient. However, the discarded terms cause asymmetry of the observed line profile, which affects the accuracy of determining the transition frequency extracted from the experimental data (see, e.g., Refs. [6,7]). The NR corrections arising for the differential cross section due to the neighboring level corresponding to the fine structure are more significant [8]. This effect, called quantum interference, has been widely studied in recent years (see, for example, Refs. [8–18]). The peculiarity of the QIE is its angular dependence, which allows compensating the effect by special methods of data processing or using the geometry of the experiment [8].

Well-specified experiments in which the current precision allows accurate line profile measurements can be refined by eliminating the QIE. Recently, the rectification of the asymmetry has been achieved by applying a line profile fitting procedure [4]. The Fano-Voigt contour used in Ref. [4] effectively accounted for the asymmetry parameter determined by the quantum interference at leading order. However, being dependent on the process utilized in the experiment, such effects should be calculated theoretically for each specific case separately. For example, the excitation process is accompanied by radiation, the most significant part of which is cascade emission for excited *ns/nd* states:  $2s + 2\gamma \rightarrow ns/nd \rightarrow$  $\sum_{k=2}^{n-1} kp + \gamma \rightarrow 1s + \gamma$ , where  $\gamma$  denotes the emitted or absorbed photon (the upper link  $ns/nd \rightarrow \sum_{k=2}^{n-1} kp$  is usually detected [19]). The study of the effect of cascade radiation on the measured two-photon absorption line profile is the subject of this work.

For the experiment [4], the effect of line contour asymmetry can be schematically illustrated by the plots shown in Fig. 1. In particular, the top left panel shows the resonant line profile and the line shape considering QIE. The difference is imperceptible to the naked eye. In the logarithmic scale (top right panel), the difference of the two profiles for the red and

2469-9926/2024/109(2)/022806(18)

<sup>\*</sup>d.solovyev@spbu.ru



FIG. 1. Schematic illustration of the line profile asymmetry arising beyond the resonance approximation for the experiment [4]. The graphs are given in arbitrary units on the ordinate axis, and the abscissa axis is given in units of the natural width of the resonance state. The top left panel shows the symmetric (dashed curve) and asymmetric (solid curve) profiles, which are indistinguishable to the naked eye. The same is shown in logarithmic scale in the top right panel. The part of the line profile close to the line maximum region is given in logarithmic scale in the bottom left panel. The difference between symmetric and asymmetric profiles depending on the angle between the polarization of the incident photon and the direction of the emitted photon is shown in the bottom right panel. The scale of profile values is set so that the effect is visible (normalization factor is used), the same with the choice of frequency scale.

blue wings of the profile is observed. The logarithmic scale in the bottom left panel shows the vicinity of the resonance, where the shift of the maximum is clearly visible. Finally, the bottom right panel shows the difference between the line profile within and beyond the resonance approximation on a logarithmic scale. Thus, a similar effect can be expected in the case of quantum interference arising in the cascade emission process.

## II. TWO-PHOTON ABSORPTION WITH THE TWO-PHOTON CASCADE EMISSION

According to the fundamental principles of the QED theory, the photon scattering process should be considered from a stable to a stable state [20]. In the same way, scattering processes for long-lived metastable states can be studied with high accuracy (taking into account the lifetime of a metastable atomic level, the radiative decay of this state can be discarded). For a few reasons, the description of the experiment, in which the measurement of the two-photon absorption transition frequency is accompanied by the registration of the emitted photon, should be given in more detail because of the cascade radiation (see the discussion in Refs. [21,22]). First, the instrumental registration of the emitted photon can be attributed to both the upper and lower links of the cascade emission indistinguishably. Second, the radiative process is



FIG. 2. Schematic illustration of the four-photon scattering process  $2s(1s) + 2\gamma \rightarrow ns/nd \rightarrow kp_{1/2}(kp_{3/2}) + \gamma \rightarrow 1s + \gamma$  with two possible emission branches due to the fine structure of the cascade transition. Solid lines correspond to the initial (2s or 1s), intermediate (resonant ns/nd), and final (1s) states, denoted by *i*, *a*, and *f* in the main text, respectively. The double dashed line corresponds to different angular momenta of the intermediate state kp in cascade radiation. This state is denoted as *b* in the main text. The wavy lines represent absorbed or emitted photons. The natural widths,  $\Gamma_a$  and  $\Gamma_b$ , for the corresponding states are presented in parentheses. In this work, we limit ourselves to considering only cascade quantum interference arising due to the fine structure of the kp state.

efficient even if the absorption occurs in the region of the resonance level width (which is small for higher states) and may depend on the level width into which the excited state decays (which can be large). Since the photon emission for the upper link in the cascade process depends on the sum of the level widths [6,23] and, since the NR corrections are proportional to the linewidth, the enhancement of the effect can be expected. As before, neglecting the cascade radiation process refers to the resonance approximation, going beyond which is the main goal of our work. We also discard the question of the inseparability of cascade and "pure" multiphoton emission, assuming the smallness of such effects [21].

In the framework of the *S*-matrix formalism, when describing a stable-to-stable process with coinciding initial and final states, the conservation law is expressed by a  $\delta$  function containing all frequencies of absorbed and emitted photons:  $\delta(\sum_i \omega_i^{abs} - \sum_i \omega_i^{em})$ . It immediately follows from this that the frequencies of absorbed photons are related to the possible shift of emitted photons. Considering the  $1s + 2\gamma \rightarrow 3s \rightarrow 2p + \gamma \rightarrow 1s + \gamma$  or  $2s + 2\gamma \rightarrow ns/nd \rightarrow \sum_{k=2}^{n-1} kp + \gamma \rightarrow 1s + \gamma$  transitions, the four-photon scattering process should be described as two-photon resonant absorption followed by two-photon cascade emission (see Fig. 2).

In principle, it can be assumed that the process of radiation with more than two photons is less probable because of the lower rate of the corresponding transitions. This can be effectively accounted for by introducing a cascade fraction factor, which we denote here as *x*. We define it as the ratio of the partial decay rate from the resonant state *a* to the cascade state *b* to the total level width of state *a*:  $x = W_{n_a l_a, n_b l_b}^{(1\gamma)} / \Gamma_{n_a l_a}$ . Thus, one can immediately find that x < 1 for close states because the transition frequency included in the transition rate results in  $W_{n_q l_a, n_b l_b}^{(1\gamma)} < \Gamma_{n_a l_a}$ . Since the consideration of multiphoton emission processes with more photons applies to increasingly smaller photon frequencies, the fraction of such cascades becomes progressively smaller. Consequently, in this paper we restrict ourselves to the consideration of four-photon scattering processes only.

In the present study, we also assume the additive nature of the nonresonant corrections. This becomes obvious from the corresponding calculations and the fact that they represent an additional energy shift. To demonstrate the importance of the effect, we omit the consideration of QIE in the absorption process for the resonant excited state (the corresponding angular dependence of the corrections [17,24] is recovered within our description). Furthermore, we give a description of the quantum interference effect arising from the cascade emission process (QIEc), i.e., due to the fine structure of the intermediate levels in the cascade emission.

Starting from the description of four-photon scattering (see Appendix A), the cross section can be reduced to an evaluation of two contributions corresponding to neighboring sublevels of the atomic fine structure  $(kp_{1/2} \text{ and } kp_{3/2})$  in the emission process (see Fig. 2). Then the amplitude can be found in the form where there are two resonant energy denominators. One of them corresponds to the two-photon absorption  $i + 2\gamma \rightarrow a$  profile, and the other describes the photon emission of the upper link,  $a \rightarrow b(b') + \gamma$ . Applying the regularization procedure [5], one can find that the two-photon absorption link contains the width of the resonant state, while the sum of the level widths appears in the second one [6,23]. The amplitude of the four-photon stable-to-stable process [see Eq. (A10)] is

$$U_{fi}^{(a,b,b')} \sim \left[\frac{A_{fb}^{(1\gamma)}A_{ba}^{(1\gamma)}}{E_a - \omega_2 - E_b - \frac{i}{2}(\Gamma_a + \Gamma_b)} + \frac{A_{fb'}^{(1\gamma)}A_{b'a}^{(1\gamma)}}{E_a - \omega_2 - E_{b'} - \frac{i}{2}(\Gamma_a + \Gamma_{b'})}\right] \frac{A_{ai}^{(2\gamma)}}{E_i + 2\omega - E_a - \frac{i}{2}\Gamma_a},\tag{1}$$

where  $A_{ai}^{(2\gamma)}$  represents the two-photon amplitude of the  $i + 2\gamma \rightarrow a$  absorption process, and  $A_{bc}^{(1\gamma)}$  corresponds to the onephoton emission matrix element between the arbitrary b and c states. The states b and b' denote neighboring sublevels for fine splitting of the intermediate resonant state in the cascade.  $\Gamma_n$  represents the natural level width of the corresponding state (here n is equal to one of a, b, or b'; see Fig. 2). The frequencies of the absorbed photons  $\omega_4$  and  $\omega_3$  are set equal according to Refs. [24–26], so that  $\omega_4 + \omega_3 = 2\omega$ ; the frequency  $\omega_2$  in our notations corresponds to the upper cascade link.

Then, using the conservation law  $E_f + \omega_1 + \omega_2 - \omega_3 - \omega_4 - E_i = 0$  and  $\omega_1 = E_b - E_f$ , one can find  $E_b + \omega_2 = E_i + \omega_3 + \omega_4$ . Substituting the latter into Eq. (1), we have

$$U_{fi}^{(a,b,b')} \sim \frac{A_{fb}^{(1\gamma)} A_{ba}^{(1\gamma)} A_{ai}^{(2\gamma)}}{\left[x - \frac{i}{2}(\Gamma_a + \Gamma_b)\right] \left[x - \frac{i}{2}\Gamma_a\right]} + \frac{A_{fb'}^{(1\gamma)} A_{b'a}^{(1\gamma)} A_{ai}^{(2\gamma)}}{\left[x + \Delta E_{bb'} - \frac{i}{2}(\Gamma_a + \Gamma_{b'})\right] \left[x - \frac{i}{2}\Gamma_a\right]}.$$
 (2)

Here the notations  $\Delta E_{bb'} = E_b - E_{b'}$  and  $x = E_i + \omega_3 + \omega_4 - E_a \equiv E_i + 2\omega - E_a$  were introduced.

According to the formalism of Ref. [5], the line profile arises from the squared modulus of the amplitude, i.e., from the cross section. Leaving only the resonance contribution, the transition frequency can be defined as the parameter corresponding to the maximum. Then, considering the second (nonresonant) contribution in Eq. (2), the nonresonant correction (NRc) follows from the extremum condition for the cross section. In the lowest order it can be obtained in the form

$$\delta_{\rm NRc} = \frac{\Gamma_a^2}{4\Delta E_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2} \frac{f_{\rm nr}}{f_{\rm res}},\tag{3}$$

where  $\Gamma_{\Sigma} \equiv \Gamma_a + \Gamma_b \approx \Gamma_a + \Gamma_{b'}, \ f_{\text{res}} = |A_{fb}^{(1\gamma)} A_{ba}^{(1\gamma)} A_{ai}^{(2\gamma)}|^2,$ and  $f_{\text{nr}} = A_{fb'}^{(1\gamma)} A_{b'a}^{(1\gamma)} A_{ai}^{(2\gamma)} (A_{fb}^{(1\gamma)} A_{ba}^{(2\gamma)} A_{ai}^{(2\gamma)})^*.$  Calculation of amplitudes in Eq. (3) can be performed using the methodology summarized in Appendixes B and C. Then, given that the polarization vectors are unit ones, we can find the amplitude ratio as a function of all possible angles between vectors  $\{e_1^*, e_2^*, e_3, e_4\}$ . Here, the asterisk denotes the polarization of the emitted photon, indices 1 and 2 correspond to the lower and upper links of the cascade, respectively, and 3 and 4 are the "second" and "first" absorbed photons.

To obtain the dependence on the angle between the polarization vectors of the absorbed photons and the direction vector of the emitted photons, summation over the polarization vectors  $e_1^*$ ,  $e_2^*$  should be performed (details are given in Appendix D). It is this scheme of the experiment that is discussed below. We also assume that the polarization vectors of the absorbed photons are parallel, and the emitted photons are registered by one detector, i.e., propagate in one direction. The latter circumstance considerably simplifies the calculations.

For the photon scattering process when the initial state 1s or 2s and the excited state ns in hydrogen are given by atomic levels with fixed total momenta  $F_i = 0$  and  $F_a = 0$  (the result is valid for  $F_i = 1$  and  $F_a = 1$ ),  $\Delta E_{bb'} \equiv \Delta E_{kp_{1/2}kp_{3/2}}$  (k < n),  $\Gamma_a \equiv \Gamma_{ns}$ , and  $\Gamma_b \approx \Gamma_{b'} \equiv \Gamma_{kp}$ , we find that the amplitude ratio is constant, i.e., independent of angular correlations (see Appendix E and, in particular, Appendix E 1):

$$\delta_{\rm NRc}(kp_{1/2}) = \frac{\Gamma_{ns}^2}{4\Delta E_{kp_{1/2}kp_{3/2}}} \frac{1}{2} \frac{(\Gamma_{kp} + \Gamma_{ns})^2}{\Gamma_{ns}^2 + (\Gamma_{kp} + \Gamma_{ns})^2}.$$
 (4)

Expression (4) represents the case when  $ns_{1/2}^{F_a=0}$  decays to the cascade state  $kp_{1/2}$  and the interfering path to  $kp_{3/2}$  is taken into account.

Apart from the presence of the correction in the form of Eq. (4), one should take into account the possibility that the state *ns* decays resonantly into the cascade level  $kp_{3/2}$ . Then, we find

$$\delta_{\rm NRc}(kp_{3/2}) = -\frac{\Gamma_{ns}^2}{4\Delta E_{kp_{1/2}kp_{3/2}}} \frac{1}{5} \frac{(\Gamma_{kp} + \Gamma_{ns})^2}{\Gamma_{ns}^2 + (\Gamma_{kp} + \Gamma_{ns})^2}.$$
 (5)

TABLE I. NR corrections to the transition frequency 2s/1s - ns(n = 3, 4, 6, 8, 12) due to cascade emission, Eqs. (4) and (5). The cascade process is shown first; then the values of  $\delta_{\text{NRc}}(kp_{1/2})$  and  $\delta_{\text{NRc}}(kp_{3/2})$  are given in hertz. The last column represents the cascade fraction coefficient. The row "Total" represents the sums of the NR corrections multiplied by x and the overall NR correction (the last value in the row).

Cascade	$\delta_{\rm NRc}(kp_{1/2})$ (Hz)	$\delta_{\rm NRc}(kp_{3/2})$ (Hz)	x
3s-2p-1s	11.5	-4.6	1
4s - 2p - 1s	5.6	-2.2	0.584
4s-3p-1s	19.0	-7.6	0.416
Total	11.2	-4.5	6.7
6s-2 <i>p</i> -1s	1.0	-0.4	0.393
6s-3 <i>p</i> -1s	3.4	-1.4	0.271
6s-4 <i>p</i> -1s	8.1	-3.2	0.192
6s-5 <i>p</i> -1s	15.8	-6.3	0.143
Total	5.1	-2.0	3.1
8s-2p-1s	0.2	$\lesssim -10^{-2}$	0.337
8s-3p-1s	0.8	-0.3	0.228
8s-4p-1s	1.9	-0.8	0.157
8s-5p-1s	3.7	-1.5	0.115
8s-6p-1s	6.4	-2.6	0.090
8s-7p-1s	10.1	-4.0	0.073
Total	2.3	-0.9	1.4
12s-2p-1s	$\lesssim 10^{-2}$	$\lesssim -10^{-2}$	0.298
12s-3p-1s	$\lesssim 10^{-2}$	$\lesssim -10^{-2}$	0.199
12s-4p-1s	0.2	$\lesssim -10^{-2}$	0.134
12s-5p-1s	0.4	-0.2	0.095
12s-6p-1s	0.7	-0.3	0.071
12s-7p-1s	1.1	-0.4	0.056
12s-8p-1s	1.7	-0.7	0.045
12s-9p-1s	2.4	-0.9	0.038
12s-10p-1s	3.2	-1.3	0.033
12s-11p-1s	4.3	-1.7	0.029
Total	0.6	-0.2	0.4

This correction has the opposite sign with respect to Eq. (4) and has a different numerical factor, although still independent of the angles. The latter is determined by the angular algebra combined with the sign in front of  $\Delta E_{kp_{1/2}kp_{3/2}}$  in the energy denominator in the amplitude (2) (see the Appendixes).

Obviously, the corrections  $\delta_{\text{NRc}}(kp_{1/2})$  and  $\delta_{\text{NRc}}(kp_{3/2})$  are the more significant as the width of the excited resonant state *a* is larger and the fine splitting of the cascade state *b* is smaller. Taking into account the cubic decrease of the level widths and fine structure intervals with increasing principal quantum number, it can be found that the NRc should be larger for atomic levels close to the resonance state.

To obtain a quantitative characterization of the corresponding frequency shift, the numerical values of the corrections (4) and (5) are summarized in Table I (the detailed data can be found in Table III in Appendix E 1).

As follows from Table I, the NR corrections are small for the  $4\gamma$  scattering process  $1s(2s) + 2\gamma \rightarrow ns \rightarrow kp + \gamma \rightarrow 1s + \gamma$ . However, direct summation (without the fractional factor) would result in a frequency shift in the region of hundreds of hertz. Combined with the results for the

TABLE II. The NR correction for the state  $nd_{3/2}^{(F=2)}$ . All notations are the same as in Table I.

Cascade	$\delta_{\mathrm{NRc}}(kp_{1/2})$ (Hz)	$\delta_{\rm NRc}(kp_{3/2})$ (Hz)	x
$3d_{3/2}-2p-1s$	-19734.3	-1049.7	1
$4d_{3/2}-2p-1s$	-3638.1	-193.5	0.746
$4d_{3/2}-3p-1s$	-12104.4	-643.8	0.254
Total	-5792.0	-308.1	-6100.1
$6d_{3/2}$ -2p-1s	-335.6	-17.8	0.613
$6d_{3/2}$ -3 <i>p</i> -1 <i>s</i>	-1130.8	-60.1	0.224
$6d_{3/2}$ -4 <i>p</i> -1 <i>s</i>	-2661.9	-141.6	0.103
$6d_{3/2}$ -5 <i>p</i> -1 <i>s</i>	-5103.1	-271.4	0.053
Total	-1005.2	-53.5	-1058.7
$8d_{3/2}-2p-1s$	-61.5	-3.3	0.571
$8d_{3/2}-6p-1s$	-207.6	-11.0	0.210
$8d_{3/2}-4p-1s$	-491.4	-26.1	0.098
$8d_{3/2}$ -5 <i>p</i> -1 <i>s</i>	-955.5	-50.8	0.054
$8d_{3/2}$ -6 <i>p</i> -1 <i>s</i>	-1634.6	-86.9	0.033
$8d_{3/2}$ -7 <i>p</i> -1 <i>s</i>	-2548.2	-135.5	0.021
Total	-285.5	-15.2	-300.6
$12d_{3/2}$ -2p-1s	-5.6	-0.3	0.541
$12d_{3/2}$ -3p-1s	-18.8	-1.0	0.200
$12d_{3/2}-4p-1s$	-44.6	-2.4	0.094
$12d_{3/2}$ -5 <i>p</i> -1 <i>s</i>	-87.0	-4.6	0.052
$12d_{3/2}$ -6 <i>p</i> -1 <i>s</i>	-150.2	-8.0	0.032
$12d_{3/2}$ -7 <i>p</i> -1 <i>s</i>	-238.0	-12.7	0.021
$12d_{3/2}$ -8 <i>p</i> -1 <i>s</i>	-353.6	-18.8	0.015
$12d_{3/2}-9p-1s$	-499.8	-26.6	0.011
$12d_{3/2}$ -10 <i>p</i> -1 <i>s</i>	-677.6	-36.0	0.008
$12d_{3/2}$ -11 <i>p</i> -1 <i>s</i>	-887.6	-47.2	0.006
Total	-47.6	-2.5	-50.2

QIE [17,24,25], the corresponding line profile asymmetry can be significant.

As another demonstration of the cascade effect on the determination of the absorption transition frequency, consider the four-photon scattering process  $n_i s_{1/2}^{F_i=0} + 2\gamma \rightarrow n_a d_{3/2}^{F_a=2} \rightarrow k p_{1/2(3/2)} + \gamma \rightarrow 1 s_{1/2} + \gamma$ . Performing calculations (summarized in Appendix E 2), we arrived at

$$\delta_{\rm NRc} = -13 \sqrt{\frac{2}{5}} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2},\tag{6}$$

$$\delta_{\rm NRc} = -\frac{13}{47} \sqrt{\frac{5}{2} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2}}.$$
 (7)

The numerical results are shown in Table II (the detailed data can be found in Table IV in Appendix E 2).

## **III. CONCLUSIONS**

As follows from Eqs. (6) and (7), the NR corrections have no geometry dependence. Thus, the corresponding asymmetry (as in the previous case) is always present in the measurements. Recently, in Ref. [4], a subtraction procedure was applied to an asymmetric line profile to extract a symmetric contour and determine the "line center." This procedure reduces to the use of the Fano-Voigt profile taking into account the asymmetry parameter. On the basis of the theoretical analysis this would mean the choice of the "magic angle" for the

TABLE III. The NR corrections to the transitions  $n_i s \rightarrow n_a s \rightarrow k p_j \rightarrow 1s$  for the case determined by the angle between the polarization vectors of the absorbed photons and the propagation vectors of the emitted photons. The first column shows the cascade processes, and the second and third columns show the natural level widths  $\Gamma_a$  and  $\Gamma_b$ , respectively. The fourth column contains the fine structure interval  $\Delta_{bb'} = E_{kp_{1/2}} - E_{kp_{3/2}}$  levels. The fifth and sixth columns show NR corrections for the resonant states  $kp_{1/2}$  and  $kp_{3/2}$ , respectively. The fraction, *x*, of the cascade process in the entire radiation is given in the seventh column. The last column summarizes the weighted averages of the partial nonresonant corrections. The row "Total" represents the sums of the NR corrections multiplied by *x* and the overall NR correction (the last value in the row). All values are in hertz.

Cascade	$\Gamma_a$ (Hz)	$\Gamma_b$ (Hz)	$\Delta_{bb'}$ (Hz)	$\delta_{ m NRc}(kp_{1/2})$ (Hz)	$\delta_{\rm NRc}(kp_{3/2})$ (Hz)	x	$\delta^{(\mathrm{av})}_{\mathrm{NRc}}$
3s-2p-1s	$1.0054 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	11.5	-4.6	1	0.8
4s - 2p - 1s	$7.0282 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	5.6	-2.3	0.584	0.4
4s-3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	19.0	-7.6	0.416	1.3
Total				11.2	-4.5	6.7	
6s-2p-1s	$2.9755 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	1.0	-0.4	0.393	0.07
6s-3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	3.4	-1.4	0.271	0.23
6s-4p-1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^9$	8.1	-3.2	0.192	0.54
6s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	15.8	-6.3	0.143	1.05
Total				5.1	-2.0	3.08	
8s-2p-1s	$1.4408 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	0.2	$\lesssim -10^{-2}$	0.337	0.02
8s-3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	0.8	-0.3	0.228	0.05
8s-4p-1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^9$	1.9	-0.8	0.157	0.13
8s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	3.7	-1.5	0.115	0.25
8s-6p-1s		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	6.4	-2.6	0.090	0.43
8s-7p-1s		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	10.1	-4.0	0.073	0.68
Total				2.3	-0.9	1.38	
12s - 2p - 1s	$4.7745 \times 10^{4}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	$\lesssim 10^{-2}$	$\lesssim -10^{-2}$	0.298	$\lesssim 10^{-3}$
12s - 3p - 1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	$\lesssim 10^{-2}$	$\leq -10^{-2}$	0.199	$\lesssim 10^{-3}$
12s-4p-1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	0.2	$\lesssim -10^{-2}$	0.134	0.01
12s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	0.4	-0.2	0.095	0.03
12s-6p-1s		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	0.7	-0.3	0.071	0.05
12s-7p-1s		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	1.1	-0.4	0.056	0.07
12s - 8p - 1s		$1.6603 \times 10^{6}$	$1.70995 \times 10^{8}$	1.7	-0.7	0.045	0.11
12s-9p-1s		$1.1694 \times 10^{6}$	$1.20075 \times 10^{8}$	2.4	-0.9	0.038	0.16
12s-10p-1s		$8.5442 \times 10^{5}$	$8.75542 \times 10^{7}$	3.2	-1.3	0.033	0.22
12s-11p-1s		$6.4308 \times 10^{5}$	$6.57822 \times 10^{7}$	4.3	-1.7	0.029	0.29
Total				0.6	-0.2	0.36	

experimental geometry: at this angle the asymmetry caused by the effect of quantum interference is zero (see also Ref. [8]), which makes the observed line profile symmetric. The numerical results in Tables I and II do not depend on the geometry of the experiment. Therefore, the QIE-based symmetrization procedure utilized for the observed spectral line does not eliminate all asymmetry. The Fano-Voigt profile with necessity should include additional terms corresponding to the cascade emission process. In the case of excitation to  $n_a s$  states, this is of minor importance at the current experimental accuracy. However, for excitation  $n_a d_{3/2}^{F_a=2}$  the resulting asymmetry is very significant, at least for low-lying states, where the NR corrections reach the level of tens of kilohertz (see Table II). The details for the absorption process  $n_i s_{1/2}^{F_a=1} \rightarrow n_a d_{3/2}^{F_a=1,2}$  can be found in Appendix E 3.

The most significant conclusion, however, is that, beyond the resonance approximation, separating the absorption process from radiation is not proper and vice versa. The observed line profile should be approximated not only by the absorption (emission) contour, but also the terms responsible for emission (absorption) in the presence of a cascade should be taken into account. According to the treatment given in Ref. [4], any asymmetric line profile can be symmetrized by choosing an appropriate contour. The choice is determined by the physical process involved in the measurements and, as a rule, can be obtained as a decomposition into symmetric and asymmetric parts [8]. When the asymmetric part is determined, the transition frequency for the symmetrized profile can be extracted [4]. In the case of describing the absorption profile without taking into account the emission process, the Fano-Voigt profile was effectively utilized (see Eq. (2) in Ref. [26], and references therein). However, this approximate contour has to be modified by contributions from cascade radiation. Our results, represented by Eqs. (2) and (3), clearly demonstrate this statement; moreover, they show how it can be fulfilled [by adding amplitudes like Eq. (2) to the Fano-Voigt profile].

The significance of the obtained values of nonresonant corrections can be assessed by directly comparing the frequency shifts with the measurement error of the corresponding transitions. The latter can be found in Ref. [27]. Then we can find that the found corrections due to cascade emission,  $\delta_{\text{NRc}}$ , for measurements of transitions to *ns* states are negligible (see numerical results for the total contribution in Table I).

TABLE IV. NR corrections correspon	ding to correlations	between the pol	arization vectors	of absorbed and	d emitted	vectors. A	ll notations
are as in Table III; values are given in her	z.						

Cascade	$\Gamma_a$ (Hz)	$\Gamma_b$ (Hz)	$\Delta_{bb'}$ (Hz)	$\delta_{ m NRc}(kp_{1/2})$ (Hz)	$\delta_{\rm NRc}(kp_{3/2})$ (Hz)	x	$\delta_{\rm NRc}^{(\rm av)}$ (Hz)
3s-2p-1s	$1.0054 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	46.2	-11.5	1	7.7
4s - 2p - 1s	$7.0282 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	22.6	-5.6	0.584	3.8
4s - 3p - 1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	76.1	-19.0	0.416	12.7
Total				44.8	-11.2	33.6	
6s-2p-1s	$2.9755 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	4.0	-1.0	0.393	0.7
6s-3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	13.6	-3.4	0.271	2.3
6s-4p-1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^9$	32.3	-8.1	0.192	5.4
6s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	63.1	-15.8	0.143	10.5
Total				20.5	-5.1	15.4	
8s-2p-1s	$1.4408 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	0.9	-0.2	0.337	0.2
8s-3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	3.2	-0.8	0.228	0.5
8s-4p-1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^9$	7.6	-1.9	0.157	1.3
8s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	14.8	-3.7	0.115	2.5
8s-6p-1s		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	25.6	-6.4	0.090	4.3
8s-7p-1s		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	40.5	-10.1	0.073	6.8
Total				9.2	-2.3	6.9	
12s - 2p - 1s	$4.7745 \times 10^{4}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	0.1	$\leq -10^{-2}$	0.298	0.02
12s - 3p - 1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^9$	0.3	$\leq -10^{-2}$	0.199	0.06
12s - 4p - 1s		$1.2941 \times 10^{7}$	$1.36795 \times 10^9$	0.8	-0.2	0.134	0.14
12s-5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	1.6	-0.4	0.095	0.27
12s-6p-1s		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	2.8	-0.7	0.071	0.47
12s-7p-1s		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	4.5	-1.1	0.056	0.74
12s-8p-1s		$1.6603 \times 10^{6}$	$1.70995 \times 10^{8}$	6.7	-1.7	0.045	1.11
12s-9p-1s		$1.1694 \times 10^{6}$	$1.20075 \times 10^{8}$	9.5	-2.4	0.038	1.58
12s-10p-1s		$8.5442 \times 10^{5}$	$8.75542 \times 10^{7}$	13.0	-3.2	0.033	2.16
12s-11p-1s		$6.4308 \times 10^{5}$	$6.57822 \times 10^{7}$	17.2	-4.3	0.029	2.87
Total				2.4	-0.6	1.8	

In turn, the determination of transition frequencies for nd states is more sensitive to the effect of quantum interference in cascade emission. The total contribution  $\delta_{NRc}$  (see Table II) reaches the kilohertz level and is a few fractions of the experimental error for the lower states. Since the values of the correction  $\delta_{NRc}$  vary considerably for different states, we do not provide a detailed analysis of their effect on the Rydberg constant and the proton charge radius. We only note that a change of frequency at the kilohertz level changes the third significant digit for the proton radius and the 12th digit for the Rydberg constant [28], i.e., the change leads to relative deviations  $\delta R_{\infty} = 2.39 \times 10^{-12} \, (\Delta R_{\infty} \approx 0.000026 \, \text{m}^{-1})$ and  $\delta r_p \approx 0.00278$  ( $\Delta r_p \approx 0.0024$  fm), which corresponds to the relative standard uncertainty of the values established by the Committee on Data of the International Science Council (CODATA) [27]. In addition, it should be emphasized that the use of the Fano-Voigt profile to process the experimental data resulted in a significant increase in the accuracy of the experiment [4]. Thus, the modification of the line profile by taking into account the cascade asymmetry can be considered as the next step for further improvements.

## ACKNOWLEDGMENTS

A.A. acknowledges the support by the Foundation for the Advancement of Theoretical Physics and Mathematics "BASIS."

## APPENDIX A: DERIVATION OF THE FOUR-PHOTON SCATTERING AMPLITUDE WITH TWO-PHOTON ABSORPTION AND TWO-PHOTON CASCADE EMISSION LINKS

To theoretically describe the line profile of one-photon emission and absorption [4,29] or two-photon absorption [17,28], the resonance approximation is commonly used [6]. In this approach, only that part which corresponds to the resonance process is studied in detail, and the rest is discarded. Extending beyond this approximation implies taking into account other (nonresonant) contributions. Then nonresonant corrections to the transition frequency can be evaluated. The dominant contribution occurs by considering the nearest state with the same symmetry, adjacent to the resonance [8]. The idea of Ref. [8] is widely used in modern studies of the photon scattering processes on atoms (see, for example, Refs. [10,11,13-16]). This effect arising in the differential scattering cross section and called the quantum interference effect (QIE) is most adequate to describe the process used in spectroscopic experiments, when absorption and emission are directed at certain angles (within a small solid angle). Such corrections, however, can be avoided (see Ref. [8]) by choosing the experimental conditions or processing the experimental data (choosing the 'magic" angle between absorbed and emitted photons or using the asymmetry parameter to fit the line profile; see Ref. [4]). On the other hand, as shown



FIG. 3. A Feynman graph depicting a four-photon scattering process with two-photon absorption link. Here *i* and *f* denote the initial and final states, respectively, and  $n_1$ ,  $n_2$ , and  $n_3$  are the intermediate states corresponding to summation in the electron propagators. State *a* is the resonant contribution to the absorbing photons, and *b* reflects the cascade contribution in the radiation process. The frequencies of the emitted photon are denoted by  $\omega_1$  and  $\omega_2$  and the absorbed photons are considered equal with a frequency equal to half the transition energy.

in Ref. [29], this is not generally the case. For example, the QIE may depend on the final state [29] or may not depend on the angles [17,28]. Along with the fact that such corrections depend on the process used in the experiment, these circumstances require a detailed theoretical consideration of nonresonant corrections for each specific case.

In order to improve the accuracy of transition frequency determination in spectroscopic experiments, nonresonant effects should be carefully taken into account. For example, the nonresonant corrections arising from the total cross section can be considered further for this purpose (see Ref. [7] and references therein). They are inevitable when choosing any "experimental geometry," but are much smaller than the QIE and the experimental error [30–33], representing a frequency shift of the order of a few hertz. However, leading to asymmetry of the observed line profile, such effects, especially QIE, have to be taken into account if precision determination of the transition frequency is to be assumed.

The principality of this conclusion consists in going beyond the resonance approximation, for example, in the experimental study of the photon scattering process. Then, as a next stage, the question can be posed about the influence of the emission process on the measured absorption transition frequency. For example, it can be expected that in two-photon cascade radiation the interference effect can be significant (which is confirmed by studies of one-photon scattering [4]). To find the influence of interfering paths in radiation on twophoton absorption, one should consider the total  $i + 2\gamma \rightarrow$  $a \rightarrow b + \gamma \rightarrow f + \gamma$  scattering process. Moreover, the very construction of the QED theory requires a description of photon scattering by atoms, starting from the (meta)stable state and ending with the (meta)stable atomic level. Schematically such a description can be illustrated by the Feynman graph in Fig. 3, where the initial and final states are assumed to be (meta)stable, and the process proceeds through two-photon absorption to a resonant state a culminating in cascading emission with a resonant state b.

If we discard the terms arising from photon permutations (similar expressions can be obtained in the same way), the *S*-matrix element corresponding to the diagram in Fig. 3 is

$$S_{fi}^{(4\gamma)} = (-ie)^4 \int d^4x_1 d^4x_2 d^4x_3 d^4x_4 \overline{\psi}_f(x_1) \times (\gamma^{\mu_1} A^*_{\mu_1}(x_1)) S(x_1, x_2) (\gamma^{\mu_2} A^*_{\mu_2}(x_2)) S(x_2, x_3) \times (\gamma^{\mu_3} A_{\mu_3}(x_3)) S(x_3, x_4) (\gamma^{\mu_4} A_{\mu_4}(x_4)) \psi_i(x_4), \quad (A1)$$

where f and i denote the final and initial states of the atomic electron, respectively.

For an arbitrary atomic state a the electron wave function in Eq. (A1) is represented by

$$\psi_a(x) = \psi_a(\mathbf{r})e^{-iE_a t},\tag{A2}$$

where  $\psi_a(\mathbf{r})$  is the solution of the Dirac equation for the atomic electron,  $E_a$  is the Dirac energy,  $\overline{\psi}_a = \psi_a^+ \gamma_0$  is the Dirac conjugated wave function,  $\gamma_\mu \equiv (\gamma_0, \mathbf{y})$  are the Dirac matrices, and  $x \equiv (t, \mathbf{r})$  is the four-dimensional space-time coordinate. The photon field or the photon wave function  $A_\mu(x)$  is defined by

$$A_{\mu}(x) = \sqrt{\frac{2\pi}{\omega}} e_{\mu} e^{i(\boldsymbol{k}\boldsymbol{r}-\omega t)} = e^{-i\omega t} A_{\mu}(\boldsymbol{r}), \qquad (A3)$$

where  $e_{\mu}$  are the components of the photon polarization fourvector (*e* is a three-dimensional polarization vector for real photons),  $k \equiv (\omega, \mathbf{k})$  is the photon momentum four-vector,  $\mathbf{k}$  is the wave vector, and  $\omega = |\mathbf{k}|$  is the photon frequency. Equation (A3) corresponds to the absorbed photon and  $A_{\mu}^{*}(x)$ corresponds to the emitted photon. Finally, the electron propagator for the bound electron can be presented in the form of the eigenmode decomposition with respect to one-electron Dirac eigenstates  $\psi_n$  with eigenvalues  $\varepsilon_n$ :

$$S(x_1, x_2) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\Omega \, e^{-i\Omega(t_1 - t_2)} \sum_n \frac{\psi_n(\boldsymbol{r}_1)\overline{\psi}_n(\boldsymbol{r}_2)}{\Omega - \varepsilon_n(1 - i0)}.$$
 (A4)

By integrating over time variables, four  $\delta$  functions can be obtained:  $(2\pi)^4 \delta(\varepsilon_f + \omega_1 - \Omega_1) \delta(\Omega_1 + \omega_2 - \Omega_2) \delta(\Omega_2 - \omega_3 - \Omega_3) \delta(\Omega_3 - \omega_4 - \varepsilon_i)$ . Here the frequencies of the absorbed photons are denoted by  $\omega_4$  and  $\omega_3$ , the frequency  $\omega_2$  corresponds to the upper cascade link, and  $\omega_1$  represents the lower cascade link (see Fig. 2 in the main text). Then integration over  $\Omega_i$  reduces them to a  $\delta$  function representing the conservation law of the four-photon scattering process, leading to

$$S_{fi}^{(4\gamma)} = -2\pi e^{4} i \delta \left(\varepsilon_{f} + \omega_{1} + \omega_{2} - \omega_{3} - \omega_{4} - \varepsilon_{i}\right) \int d^{3} r_{1} d^{3} r_{2} d^{3} r_{3} d^{3} r_{4} \overline{\psi}_{f}(\mathbf{r}_{1}) \left(\gamma^{\mu_{1}} A_{\mu_{1}}^{*}(\mathbf{r}_{1})\right) \sum_{n_{1}} \frac{\psi_{n_{1}}(\mathbf{r}_{1}) \overline{\psi}_{n_{1}}(\mathbf{r}_{2})}{\varepsilon_{f} + \omega_{1} - \varepsilon_{n_{1}}(1 - i0)} \times \left(\gamma^{\mu_{2}} A_{\mu_{2}}^{*}(\mathbf{r}_{2})\right) \sum_{n_{2}} \frac{\psi_{n_{2}}(\mathbf{r}_{2}) \overline{\psi}_{n_{2}}(\mathbf{r}_{3})}{\varepsilon_{i} + \omega_{3} + \omega_{4} - \varepsilon_{n_{2}}(1 - i0)} \left(\gamma^{\mu_{3}} A_{\mu_{3}}^{*}(\mathbf{r}_{3})\right) \sum_{n_{3}} \frac{\psi_{n_{3}}(\mathbf{r}_{3}) \overline{\psi}_{n_{3}}(\mathbf{r}_{4})}{\varepsilon_{i} + \omega_{4} - \varepsilon_{n_{3}}(1 - i0)} \times \left(\gamma^{\mu_{4}} A_{\mu_{4}}^{*}(\mathbf{r}_{4})\right) \psi_{i}(\mathbf{r}_{4}).$$
(A5)

Passing to the dipole approximation for transverse photons, using the relations  $S_{fi} = -2\pi i U_{fi} \delta(\sum_{k} E_{fk} - \sum_{k} E_{ik})$  and  $-i m \omega_{nk}(\mathbf{r})_{nk} = (\mathbf{p})_{nk}$  [34], in the nonrelativistic limit one can approximately write

$$U_{fi}^{(4\gamma)} = (2\pi)^2 e^4 \sum_{n_1 n_2 n_3} \frac{\langle f | \mathbf{e}_1^* \mathbf{r}_1 | n_1 \rangle \langle n_1 | \mathbf{e}_2^* \mathbf{r}_2 | n_2 \rangle}{[E_f + \omega_1 - E_{n_1}(1 - i0)]} \frac{\langle n_2 | \mathbf{e}_3 \mathbf{r}_3 | n_3 \rangle \langle n_3 | \mathbf{e}_4 \mathbf{r}_4 | i \rangle \sqrt{\omega_1 \omega_2 \omega_3 \omega_4}}{[E_i + \omega_3 + \omega_4 - E_{n_2}(1 - i0)][E_i + \omega_4 - E_{n_3}(1 - i0)]},$$
(A6)

where the energies correspond to the nonrelativistic solutions of the Schrödinger equation (as well as the wave functions). Furthermore (and in the main text), we introduce the notation for matrix elements  $\langle c|er|d\rangle \equiv A_{cd}^{(1\gamma)}$ . Taking into account the permutation of absorbed photons (( $e_3$ ;  $\omega_3$ )  $\leftrightarrow$  ( $e_4$ ;  $\omega_4$ )), one can organize a two-photon amplitude,  $A_{n_2i}^{(2\gamma)}$ , which includes the third energy denominator and the sum over  $n_3$ . Note additionally that the energy denominator  $E_i + \omega_4 - E_{n_3}(1 - i0)$  does not diverge and one can omit the infinitesimal imaginary part in it. Also, according to the two-photon spectroscopy experiments [35–37], we can set  $\omega_3 = \omega_4 \equiv \omega$  and  $e_3 = e_4$ .

Assuming the immateriality of the common prefactor in Eq. (A6), we arrive at

$$U_{fi}^{(4\gamma)} \sim \sum_{n_1 n_2} \frac{A_{fn_1}^{(1\gamma)} A_{n_1 n_2}^{(1\gamma)}}{E_f + \omega_1 - E_{n_1}(1 - i0)} \frac{A_{n_2 i}^{(2\gamma)}}{E_i + 2\omega - E_{n_2}(1 - i0)},$$
(A7)

where the two-photon amplitude  $A_{n_2i}^{(2\gamma)}$  is

$$A_{n_{2}i}^{(2\gamma)} = \sum_{n_{3}} \frac{\langle n_{2} | \boldsymbol{e}_{3} \boldsymbol{r}_{3} | n_{3} \rangle \langle n_{3} | \boldsymbol{e}_{4} \boldsymbol{r}_{4} | i \rangle}{E_{i} + \omega_{4} - E_{n_{3}}(1 - i0)} + \sum_{n_{3}} \frac{\langle n_{2} | \boldsymbol{e}_{4} \boldsymbol{r}_{4} | n_{3} \rangle \langle n_{3} | \boldsymbol{e}_{3} \boldsymbol{r}_{3} | i \rangle}{E_{i} + \omega_{3} - E_{n_{3}}(1 - i0)}$$
(A8)

and  $\omega_3 + \omega_4 = 2\omega$ . Then, we have resonance conditions for the sums over  $n_1$  and  $n_2$ :  $E_i + 2\omega = E_a$  and  $E_f + \omega_1 = E_b$  ( $n_1 = b$  and  $n_2 = a$ ), where the state *a* represents the resonant excited state into which the absorption process is measured (with the subsequent upper cascade link), and the state *b* corresponds to the resonant intermediate state in the process of cascade radiation (with the subsequent lower cascade link).

According to the conservation law, the lower link of the cascade can be transformed into the upper by the equality  $E_f + \omega_1 + \omega_2 - E_a = 0$ , which leads to  $E_f + \omega_1 = E_a - \omega_2$ . Here and below, we consider the interference effect arising from the fine splitting of the *b* state. This can be taken into account by introducing an additional term in the sum over  $n_1$  (again, we omit the consideration of fine splitting for the state *a*). Then, the amplitude can be written as

$$U_{fi}^{(4\gamma)} \sim \frac{A_{fb}^{(1\gamma)} A_{ba}^{(1\gamma)} A_{ai}^{(2\gamma)}}{[E_a - \omega_2 - E_b(1 - i0)][E_i + 2\omega - E_a(1 - i0)]} + \frac{A_{fb'}^{(1\gamma)} A_{b'a}^{(1\gamma)} A_{ai}^{(2\gamma)}}{[E_a - \omega_2 - E_{b'}(1 - i0)][E_i + 2\omega - E_a(1 - i0)]}.$$
 (A9)

Here we have discarded all remaining contributions in Eq. (A7), which includes sums over  $n_1 \neq b(b')$  and  $n_2 \neq a$ .

Regularization of divergent denominators in Eq. (A9) can be performed by summing an infinite series of successive one-loop self-energy corrections, the imaginary part of which gives the corresponding level width [5]. The radiation represented by the cascade process was accurately considered in Ref. [6], where it was found that for the upper link, the resonant contribution should contain the sum of the level widths (the width of the level *a* from which the emission occurs plus the width of the intermediate resonant state b(b'); see also Refs. [7,23]). Thus, the four-photon amplitude can be rewritten as

$$U_{fi}^{(a,b,b')} \sim \left[\frac{A_{fb}^{(1\gamma)}A_{ba}^{(1\gamma)}}{E_a - \omega_2 - E_b - \frac{i}{2}(\Gamma_a + \Gamma_b)} + \frac{A_{fb'}^{(1\gamma)}A_{b'a}^{(1\gamma)}}{E_a - \omega_2 - E_{b'} - \frac{i}{2}(\Gamma_a + \Gamma_{b'})}\right] \frac{A_{ai}^{(2\gamma)}}{E_i + 2\omega - E_a - \frac{i}{2}\Gamma_a}.$$
 (A10)

#### APPENDIX B: MATRIX ELEMENTS: ANGULAR AND RADIAL PARTS, TENSOR PRODUCT

The one-photon matrix element in Eq. (A6) can be evaluated by separating the dependence on angles as follows. First, we use the definition of scalar product in cyclic coordinates:

$$(\boldsymbol{a} \cdot \boldsymbol{b}) = \sum_{q=0,\pm 1} (-1)^q a_q b_{-q}.$$
(B1)

Then, according to Ref. [38] the matrix element of the cyclic component of the radius vector,  $r_q$ , is given by

$$\langle n'l'j'F'M_{F'}|r_q|nljFM_F\rangle = (-1)^{F'-M_{F'}} \begin{pmatrix} F' & 1 & F\\ -M_{F'} & q & M_F \end{pmatrix} \langle n'l'j'F'||r||nljF\rangle,$$
(B2)

where the set of quantum numbers  $nl jFM_F$  denotes the principal quantum number *n*, the orbital angular momentum *l*, the total angular momentum *F*, and  $M_F$  is the projection of *F*. In this approach, j = l + s (*s* is the electron

spin) and F = j + I (*I* is the nuclear spin momentum). The 3jm Wigner symbol in Eq. (B1) is given by the matrix in parentheses and can be associated with the Clebsch-Gordan coefficient:

$$C_{j_1m_1j_2m_2}^{jm} = \sqrt{2j+1}(-1)^{j_1-j_2+m} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}.$$
 (B3)

The reduced matrix element is

$$\langle n'l'j'F'||r||nljF\rangle = (-1)^{j'+j+l+l'+1/2+F} \prod_{j'jF'F} \begin{cases} j' & F' & l\\ F & j & 1 \end{cases} \begin{cases} l' & j' & 1/2\\ j & l & 1 \end{cases} \langle n'l'||r||nl\rangle.$$
(B4)

Here  $\Pi_{ab\cdots} = \sqrt{(2a+1)(2b+1)\cdots}$  and the expression in braces gives the Racah 6*j* symbol. The remaining reduced matrix element is

$$\langle n'l'||r||nl\rangle = (-1)^{l'} \Pi_{l'l} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \int_0^\infty dr \, r^3 R_{n'l'} R_{nl}, \tag{B5}$$

where  $R_{nl}$  is the nonrelativistic radial part of the hydrogen wave function (the solution of the radial Schrödinger equation).

Combining in pairs the polarization vectors for the amplitude as  $\{e_4, e_3\}$  and  $\{e_2, e_1\}$ , after the summation over projections one can find the angular dependence responsible for the correlations between the absorbed photons and the emitted photon corresponding to the upper link [see Eq. (A6)]. To determine these correlations, we use the definition for the irreducible tensor product of two arbitrary vectors *a* and *b*:

$$\{\boldsymbol{a} \otimes \boldsymbol{b}\}_{x\xi} = \sum_{q_1q_2} C_{1q_11q_2}^{x\xi} a_{q_1} b_{q_2} = (-1)^{\xi} \Pi_x \sum_{q_1q_2} \begin{pmatrix} 1 & 1 & x \\ q_1 & q_2 & -\xi \end{pmatrix} a_{q_1} b_{q_2}.$$
 (B6)

The complex conjugation of the tensor product of two arbitrary vectors  $\boldsymbol{a}$  and  $\boldsymbol{b}$  is given by

$$\{\boldsymbol{a}\otimes\boldsymbol{b}\}_{x\xi}^* = (-1)^{x-\xi}\{\boldsymbol{a}^*\otimes\boldsymbol{b}^*\}_{x-\xi}.$$
(B7)

The scalar product of two irreducible tensors  $A_r$  and  $B_r$  is defined as

$$A_r \cdot B_r = \sum_{\rho} A_{r\rho} B_{r\rho}^*. \tag{B8}$$

## APPENDIX C: ANGULAR ALGEBRA

The amplitude of the process depicted in Fig. 3 contains the following matrix elements:

$$\langle f | \boldsymbol{e}_1^* \boldsymbol{r} | b \rangle \langle b | \boldsymbol{e}_2^* \boldsymbol{r} | a \rangle \langle a | \boldsymbol{e}_3 \boldsymbol{r} | n \rangle \langle n | \boldsymbol{e}_4 \boldsymbol{r} | i \rangle, \tag{C1}$$

and, therefore, in the cross section we have

$$\langle f|\boldsymbol{e}_{1}^{*}\boldsymbol{r}|b\rangle\langle b|\boldsymbol{e}_{2}^{*}\boldsymbol{r}|a\rangle\langle a|\boldsymbol{e}_{3}\boldsymbol{r}|n\rangle\langle n|\boldsymbol{e}_{4}\boldsymbol{r}|i\rangle\langle i|\boldsymbol{e}_{4}^{*}\boldsymbol{r}|n'\rangle\langle n'|\boldsymbol{e}_{3}^{*}\boldsymbol{r}|a'\rangle\langle a'|\boldsymbol{e}_{2}\boldsymbol{r}|b'\rangle\langle b'|\boldsymbol{e}_{1}\boldsymbol{r}|f\rangle.$$
(C2)

Consider the amplitude of the two-photon absorption,

$$A_{ai}^{(2\gamma)} = \sum_{\mathcal{N}} \frac{\langle a|\boldsymbol{e}_{3}\boldsymbol{r}_{3}|\mathcal{N}\rangle\langle\mathcal{N}|\boldsymbol{e}_{4}\boldsymbol{r}_{4}|i\rangle}{E_{i} + \omega_{4} - E_{n}(1 - i0)} \equiv \mathcal{A}_{ai}^{(2\gamma)}\mathcal{G}_{ai},\tag{C3}$$

where  $\mathcal{N}$  denotes the set of quantum numbers n,  $l_n$ ,  $j_n$ ,  $F_n$ , and  $M_{F_n}$ , and  $\mathcal{G}_{ai}$  is defined by

$$\mathcal{G}_{ai} = \sum_{nl_n} \frac{\langle n_a l_a ||r|| nl_n \rangle \langle nl_n ||r|| n_i l_i \rangle}{E_i + \omega_4 - E_n (1 - i0)}.$$
(C4)

The summation over  $M_{F_n}$  of the matrix elements  $\langle b| e_3 r_3 | \mathcal{N} \rangle \langle \mathcal{N} | e_4 r_4 | i \rangle$  results in

$$\mathcal{A}_{ai}^{(2\gamma)} \sim (-1)^{F_i - M_{F_i}} \sum_{x\xi} (-1)^x \Pi_x \{ e_4 \otimes e_3 \}_{x\xi} \begin{pmatrix} F_a & F_i & x \\ M_{F_a} & -M_{F_i} & \xi \end{pmatrix} \begin{cases} 1 & 1 & x \\ F_i & F_a & F \end{cases},$$
(C5)

where the proportionality coefficient is  $\langle n_a l_a j_a F_a || r || n l_n j_n F_n \rangle \times \langle n l_n j_n F_n || r || n_i l_i j_i F_i \rangle \times [\langle n_b l_b || r || n l \rangle \langle n l || r || n_i l_i \rangle]^{-1}$ .

Similarly to Eq. (C5) for the radiation amplitude one can obtain

$$\mathcal{A}_{fb}^{(1\gamma)}\mathcal{A}_{ba}^{(1\gamma)} \sim (-1)^{F_a - M_{F_a}} \sum_{y\eta} (-1)^y \Pi_y \{ \boldsymbol{e}_2^* \otimes \boldsymbol{e}_1^* \}_{y\eta} \begin{pmatrix} F_f & F_a & y \\ M_{F_f} & -M_{F_a} & \eta \end{pmatrix} \begin{cases} 1 & 1 & y \\ F_a & F_f & F_b \end{cases},$$
(C6)

where summation over  $M_{F_b}$  was performed. The states *a* and *b* represent the set responsible for the quantum interference effect for the absorption process (QIE corresponding to the states *a*) and cascade radiation (QIEc corresponding to possible states *b*).

Then, for the four-photon amplitude  $\sum_{M_{Fa}} \mathcal{A}_{fb}^{(1\gamma)} \mathcal{A}_{ba}^{(1\gamma)} \mathcal{A}_{ai}^{(2\gamma)}$ , we find

$$\sum_{M_{F_a}} (-1)^{F_a - M_{F_a}} \begin{pmatrix} F_a & F_i & x \\ M_{F_a} & -M_{F_i} & \xi \end{pmatrix} \begin{pmatrix} F_f & F_a & y \\ M_{F_f} & -M_{F_a} & \eta \end{pmatrix} = \sum_{z\zeta} (-1)^{z-\zeta} \Pi_z^2 \begin{pmatrix} y & x & z \\ \eta & \xi & -\zeta \end{pmatrix} \begin{pmatrix} z & F_i & F_f \\ \zeta & -M_{F_i} & M_{F_f} \end{pmatrix} \begin{cases} F_f & F_i & z \\ x & y & F_a \end{cases}.$$
(C7)

Thus, the tensor product of the four polarization vectors arises using the relation

$$(-1)^{\zeta} \Pi_{z} \begin{pmatrix} y & x & z \\ \eta & \xi & -\zeta \end{pmatrix} \{ \boldsymbol{e}_{4} \otimes \boldsymbol{e}_{3} \}_{x\xi} \{ \boldsymbol{e}_{2}^{*} \otimes \boldsymbol{e}_{1}^{*} \}_{y\eta} = (-1)^{z} \{ \{ \boldsymbol{e}_{4} \otimes \boldsymbol{e}_{3} \}_{x} \otimes \{ \boldsymbol{e}_{2}^{*} \otimes \boldsymbol{e}_{1}^{*} \}_{y} \}_{z\zeta}.$$
(C8)

The four-photon amplitude can be simplified by summing over the momenta  $j_n$  and  $F_n$  of the intermediate states in the absorption part, Eq. (C5):

$$\sum_{j_n F_n} \langle n_a l_a j_a F_a || r || n l_n j_n F_n \rangle \langle n l_n j_n F_n || r || n_i l_i j_i F_i \rangle \begin{cases} 1 & 1 & x \\ F_i & F_a & F_n \end{cases}$$

$$= (-1)^{1+l_i+j_i+j_a+F_a} \prod_{j_i j_a F_i F_a} \begin{cases} j_a & j_i & x \\ F_i & F_a & I \end{cases} \begin{cases} l_a & l_i & x \\ 1 & 1 & l_n \end{cases} \begin{cases} l_a & l_i & x \\ j_i & j_a & 1/2 \end{cases} \langle n_a l_a || r || n_l_n \rangle \langle n l_n || r || n_i l_i \rangle,$$
(C9)

where the last two reduced matrix elements together with the corresponding energy denominator combine to Eq. (C4).

To construct a photon scattering cross section, one should average the square modulus of the amplitude over the initial state momentum projections and sum over the final state momentum projections. The complex-conjugate amplitude can be calculated in the same way as above. Then, summing the remaining 3jm Wigner symbols in Eq. (C7) for the square of the amplitude modulus results in

$$\sum_{M_{F_i}M_{F_f}} (-1)^{F_f - M_{F_i} - M_{F_f}} \begin{pmatrix} z' & F_f & F_i \\ \zeta' & -M_{F_f} & M_{F_i} \end{pmatrix} \begin{pmatrix} z & F_i & F_f \\ \zeta & -M_{F_i} & -M_{F_f} \end{pmatrix} = (-1)^{F_f + z - \zeta + z'} \frac{\{zF_iF_f\}\delta_{zz'}\delta_{\zeta - \zeta'}}{\Pi_z^2},$$
(C10)

where  $\{abc\}$  is the so-called 3j symbol, equal to 1 if the triangle condition for a, b, c is valid, and zero otherwise.

The tensor product of the four polarization vectors arising in the complex-conjugate amplitude has the form

$$\{\{\boldsymbol{e}_1 \otimes \boldsymbol{e}_2\}_{\boldsymbol{\gamma}'} \otimes \{\boldsymbol{e}_3^* \otimes \boldsymbol{e}_4^*\}_{\boldsymbol{\gamma}'}\}_{\boldsymbol{z}'\boldsymbol{\zeta}'}.$$
(C11)

It can be transformed as follows:

$$(-1)^{\zeta} \{ \{ \boldsymbol{e}_1 \otimes \boldsymbol{e}_2 \}_{y'} \otimes \{ \boldsymbol{e}_3^* \otimes \boldsymbol{e}_4^* \}_{x'} \}_{z-\zeta} = \{ \{ \boldsymbol{e}_4 \otimes \boldsymbol{e}_3 \}_{x'} \otimes \{ \boldsymbol{e}_2^* \otimes \boldsymbol{e}_1^* \}_{y'} \}_{z\zeta}^*.$$
(C12)

Then, for the square of the amplitude modulus, one can arrive at the expression

$$U_{fi}^{(4\gamma)}U_{fi}^{(4\gamma)*} = \mathcal{G}_{ai}\mathcal{G}_{a'i}^{*}(-1)^{F_{i}}(-1)^{1+l_{i}+j_{a}+F_{a}}(-1)^{1+l_{a'}+j_{a'}+j_{i}+F_{i}}\Pi_{j_{a}F_{a}j_{a'}F_{a'}}^{2} \\ \times (-1)^{F_{f}}\langle n_{f}l_{f}j_{f}F_{f}||r||n_{b}l_{b}j_{b}F_{b}\rangle\langle n_{b}l_{b}j_{b}F_{b}||r||n_{a}l_{a}j_{a}F_{a}\rangle\langle n_{a'}l_{a'}j_{a'}F_{a'}||r||n_{b'}l_{b'}j_{b'}F_{b'}\rangle\langle n_{b'}l_{b'}j_{b'}F_{b'}||r||n_{f}l_{f}j_{f}F_{f}\rangle \\ \times \sum_{xx'yy'}(-1)^{x+x'+y+y'}\Pi_{xx'yy'}(T_{x,y,z}\cdot T_{x',y',z})\begin{cases} j_{a} & j_{i} & x\\ F_{i} & F_{a} & I \end{cases} \begin{cases} l_{a} & l_{i} & x\\ 1 & 1 & l_{n} \end{cases} \begin{cases} l_{a} & l_{i} & x\\ j_{i} & j_{a} & 1/2 \end{cases} \begin{cases} 1 & 1 & y\\ F_{a} & F_{f} & F_{b} \end{cases} \\ \times \begin{cases} x & y & z\\ F_{f} & F_{i} & F_{a} \end{cases} \begin{cases} j_{a'} & j_{i} & x'\\ F_{i} & F_{a'} & I \end{cases} \begin{cases} l_{a'} & l_{i} & x'\\ 1 & 1 & l_{n} \end{cases} \begin{cases} l_{a'} & l_{i} & x'\\ j_{i} & j_{a'} & 1/2 \end{cases} \begin{cases} 1 & 1 & y'\\ F_{a'} & F_{f} & F_{b'} \end{cases} \begin{cases} x' & y' & z\\ F_{f} & F_{i} & F_{a'} \end{cases} \end{cases},$$
 (C13)

where  $T_{x,y,z} = \{\{e_4 \otimes e_3\}_x \otimes \{e_2^* \otimes e_1^*\}_y\}_z$  and  $\cdot$  denotes the scalar product.

Although the above formula, summed over  $F_f$  according to the conditions of the experiment, when the radiation recorded during measurements is not divided into transitions to specific states (to particular hyperfine sublevels), is sufficient for further numerical calculation, it is more convenient to convert the tensor products to the case when there are only vectors  $e_4$ ,  $e_3$ ,  $e_2$ ,  $e_1$ , but not their complex conjugates. This procedure can be performed by methods using the relations given in Ref. [38]. For brevity, we present only the final result:

$$\sum_{F_{b}F_{b'}F_{f}} U_{fi}^{(4\gamma)} U_{fi}^{(4\gamma)*} = \sum_{F_{f}} (-1)^{l_{f}+l_{b}+j_{b}+l_{b'}+j_{a}+F_{a'}} \Pi_{j_{f}F_{f}}^{2} \Pi_{j_{a}F_{a}j_{a'}F_{a'}}^{2} \Pi_{j_{b}j_{b'}}^{2} \mathcal{G}_{ai} \mathcal{G}_{a'i}^{*} \\ \times \langle n_{f}l_{f}||r||n_{b}l_{b}\rangle \langle n_{b}l_{b}||r||n_{a}l_{a}\rangle \langle n_{a'}l_{a'}||r||n_{b'}l_{b'}\rangle \langle n_{b'}l_{b'}||r||n_{f}l_{f}\rangle \sum_{xx'yy'} (-1)^{x+x'} \Pi_{xx'yy'} (T'_{x,y',z'} \cdot T'_{x',y,z'})$$

$$\times \begin{cases} j_{a} & j_{i} & x \\ F_{i} & F_{a} & I \end{cases} \begin{cases} l_{a} & l_{i} & x \\ 1 & 1 & l_{n} \end{cases} \begin{cases} l_{a} & l_{i} & x \\ j_{i} & j_{a} & 1/2 \end{cases} \begin{cases} j_{f} & j_{a} & y \\ F_{a} & F_{f} & I \end{cases} \begin{cases} j_{f} & j_{a} & y \\ 1 & 1 & j_{b} \end{cases} \begin{cases} j_{a'} & j_{i} & x' \\ F_{i} & F_{a'} & I \end{cases}$$

$$\times \begin{cases} l_{a'} & l_{i} & x' \\ 1 & 1 & l'_{n} \end{cases} \begin{cases} l_{a'} & l_{i} & x' \\ j_{i} & j_{a'} & 1/2 \end{cases} \begin{cases} j_{a'} & j_{f} & y' \\ F_{f} & F_{a'} & I \end{cases} \begin{cases} j_{a'} & j_{f} & y' \\ 1 & 1 & j_{b'} \end{cases} \begin{cases} x' & F_{i} & F_{a'} \\ y & F_{a} & F_{f} \\ z' & x & y' \end{cases} \end{cases} .$$

$$(C14)$$

Here,  $T'_{x,y,z} = \{\{e_4 \otimes e_3\}_x \otimes \{e_2 \otimes e_1\}_y\}_z$ . In the experiment, atoms are prepared in the initial state with fixed  $j_i, F_i$ , so that following the electric dipole two-photon transition selection rules, one defines the excited state's  $j_a, F_a$ . The situation is different for the subsequent cascade process, for which hyperfine structure is not resolved. For this reason one has to perform summation over  $F_b, F_{b'}$ , which was made in Eq. (C14). The result of Eq. (C14) easily generalizes to the arbitrary case: resonant contribution at a' = a and b' = b, nonresonant quadratic contributions at a' = a, b = b', and vice versa, and different variants of interference at  $a' \neq a$  and  $b \neq b'$ . The corresponding contributions are obtained by choosing the intrinsic momenta. For example, the case  $a' \neq a$  and b' = b provides the QIE for the resonant absorption to the *a* state. The instance where a' = a and  $b' \neq b$  represents the effect of quantum interference in the cascade emission process and is the subject of this paper.

### APPENDIX D: SUMMATION OVER PHOTON POLARIZATIONS AND ANGULAR DEPENDENCE

In this section we describe the situation related to experiments in which the polarization of absorbed photons is fixed and emitted photons are registered at a certain angle; i.e., the radiation detector is set in a fixed direction [19,25,26,35–37,39]. Then of interest is the angle between the absorption and the photon from the upper cascade [19,24,26], since the well-known QIE is usually defined exactly through this angle. Moreover, it was shown in Ref. [4] that the symmetrization of the line profile observed in the experiment is carried out by an appropriate choice of this angle.

The dependence on the angle between the polarizations of the absorbed photons (they are set parallel in the experiment) and the "first" emitted photon can be obtained by summing over the polarizations of the emitted photons, designated here as  $e_1$  and  $e_2$ . The vector  $e_2$  corresponds to the upper cascade link, and  $e_2$  to the photon of the lower link. The following expression (in cyclic coordinates) can be used to sum over the polarizations of the emitted photons:

$$\sum_{e} e_{q} e_{q'}^{*} = (-1)^{q} (\delta_{-q \, q'} - \mathbf{v}_{-q} \mathbf{v}_{q'}), \tag{D1}$$

where v is the direction vector of the photon.

For the scalar product  $(T'_{x,y',z'} \cdot T'_{x',y,z'})$  summed over  $e_1$  and  $e_2$  the result is

$$\sum_{e_{1}e_{2}} \left( U'_{x,y',z'} \cdot U'_{x',y,z'} \right) = \frac{\prod_{z'}^{2}}{\prod_{x}} \{ \{e_{4} \otimes e_{3}\}_{x} \otimes \{e_{4}^{*} \otimes e_{3}^{*}\}_{x} \}_{00} \\ + (-1)^{1+x+x'+y+y'} \prod_{z'}^{2} \prod_{yy'} \sum_{a} \left( \left\{ \begin{cases} 1 & a & x' \\ z & y & 1 \end{cases} \right\} \left\{ 1 & a & x \\ z & y' & 1 \end{cases} \{\{e_{4} \otimes e_{3}\}_{x} \otimes \mathbf{v}_{1}\}_{a} \cdot \{\{e_{4} \otimes e_{3}\}_{x'} \otimes \mathbf{v}_{1}\}_{a} \\ + (-1)^{y+y'} \left\{ 1 & a & x' \\ z & y & 1 \end{cases} \left\{ \left\{ 1 & a & x \\ z & y' & 1 \end{cases} \right\} \{\{e_{4} \otimes e_{3}\}_{x} \otimes \mathbf{v}_{2}\}_{a} \cdot \{\{e_{4} \otimes e_{3}\}_{x'} \otimes \mathbf{v}_{2}\}_{a} \right) \\ + \{\{e_{4} \otimes e_{3}\}_{x} \otimes \{\mathbf{v}_{2} \otimes \mathbf{v}_{1}\}_{y'}\}_{z'} \cdot \{\{e_{4} \otimes e_{3}\}_{x'} \otimes \{\mathbf{v}_{2} \otimes \mathbf{v}_{1}\}_{y}\}_{z'}.$$
(D2)

Expressions for particular indices of the tensor product can be found in Ref. [38] and are

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_0 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_0\}_0 = \frac{1}{3}(\boldsymbol{a} \cdot \boldsymbol{b})(\boldsymbol{d} \cdot \boldsymbol{c}), \tag{D3}$$

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_1 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_0\}_1 = -\frac{\mathrm{i}}{\sqrt{6}}[\boldsymbol{a} \times \boldsymbol{b}](\boldsymbol{c} \cdot \boldsymbol{d}), \tag{D4}$$

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_0 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_1\}_1 = -\frac{\mathrm{i}}{\sqrt{6}}(\boldsymbol{a} \cdot \boldsymbol{b})[\boldsymbol{c} \times \boldsymbol{d}],\tag{D5}$$

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_1 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_1\}_0 = \frac{1}{2\sqrt{3}}[(\boldsymbol{a} \cdot \boldsymbol{c})(\boldsymbol{b} \cdot \boldsymbol{d}) - (\boldsymbol{a} \cdot \boldsymbol{d})(\boldsymbol{b} \cdot \boldsymbol{c})], \tag{D6}$$

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_1 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_1\}_1 = -\frac{\mathrm{i}}{2\sqrt{2}}[\boldsymbol{c}(\boldsymbol{d} \cdot [\boldsymbol{a} \times \boldsymbol{b}]) - \boldsymbol{d}(\boldsymbol{c} \cdot [\boldsymbol{a} \times \boldsymbol{b}])], \quad (\mathrm{D7})$$

$$\{\{\boldsymbol{a}_1 \otimes \boldsymbol{b}_1\}_2 \otimes \{\boldsymbol{c}_1 \otimes \boldsymbol{d}_1\}_1\}_1 = \frac{i\sqrt{3}}{\sqrt{2\cdot 5}} \left[\frac{1}{3}(\boldsymbol{a} \cdot \boldsymbol{b})[\boldsymbol{c} \times \boldsymbol{b}] - \frac{1}{2}\boldsymbol{b}(\boldsymbol{d} \cdot [\boldsymbol{a} \times \boldsymbol{c}]) - \frac{1}{2}\boldsymbol{a}(\boldsymbol{d} \cdot [\boldsymbol{b} \times \boldsymbol{c}])\right],\tag{D8}$$

$$\{\{a_1 \otimes b_1\}_1 \otimes \{c_1 \otimes d_1\}_2\}_1 = \frac{i\sqrt{3}}{\sqrt{2 \cdot 5}} \left[\frac{1}{3}(c \cdot d)[a \times b] - \frac{1}{2}c(b \cdot [d \times a]) - \frac{1}{2}d(b \cdot [c \times a])\right],$$
(D9)

$$\{\{a_1 \otimes b_1\}_2 \otimes \{c_1 \otimes d_1\}_2\}_0 = \frac{1}{\sqrt{5}} \left[ \frac{1}{2} (a \cdot c)(b \cdot d) - \frac{1}{3} (a \cdot b)(c \cdot d) + \frac{1}{2} (a \cdot d)(b \cdot c) \right],$$
(D10)

$$\{\{a_1 \otimes b_1\}_2 \otimes \{c_1 \otimes d_1\}_2\}_1 = -\frac{1}{2\sqrt{2 \cdot 5}}[(a \cdot c)[b \times d] + (a \cdot d)[b \times c] + (b \cdot c)[a \times d] + (b \cdot d)[a \times c]], \quad (D11)$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{b}\}_0\otimes\boldsymbol{c}\}_1=-\frac{1}{\sqrt{3}}(\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{c},\tag{D12}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{b}\}_1\otimes\boldsymbol{c}\}_0=-\frac{i}{\sqrt{6}}[\boldsymbol{a}\times\boldsymbol{b}]\cdot\boldsymbol{c},\tag{D13}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{b}\}_1\otimes\boldsymbol{c}\}_1=-\frac{1}{2}[[\boldsymbol{a}\times\boldsymbol{b}]\times\boldsymbol{c}],\tag{D14}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{b}\}_{2}\otimes\boldsymbol{c}\}_{1}=\sqrt{\frac{3}{5}}\left[\frac{1}{3}\boldsymbol{c}(\boldsymbol{a}\cdot\boldsymbol{b})-\frac{1}{2}\boldsymbol{b}(\boldsymbol{a}\cdot\boldsymbol{c})-\frac{1}{2}\boldsymbol{a}(\boldsymbol{b}\cdot\boldsymbol{c})\right].$$
(D15)

Then, given that the polarization vectors of the absorbed photons are parallel,  $e_4 || e_3$ , and the direction vectors of the emitted photons are also parallel (provided they are registered by one detector),  $v_2 || v_1$ , the above expressions are greatly simplified. For  $a \parallel b$  and  $c \parallel d$  the only nonzero relations are given by

$$\{\{\boldsymbol{a}\otimes\boldsymbol{a}\}_0\otimes\{\boldsymbol{c}\otimes\boldsymbol{c}\}_0\}_0=\frac{1}{3},\tag{D16}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{a}\}_{2}\otimes\{\boldsymbol{c}\otimes\boldsymbol{c}\}_{2}\}_{0}=\frac{1}{\sqrt{5}}\bigg(\cos^{2}\theta_{\boldsymbol{a}\boldsymbol{c}}-\frac{1}{3}\bigg),\tag{D17}$$

$$\{\{\boldsymbol{a} \otimes \boldsymbol{a}\}_2 \otimes \{\boldsymbol{c} \otimes \boldsymbol{c}\}_2\}_1 = -\frac{2i}{\sqrt{10}} \cos \theta_{\boldsymbol{a}\boldsymbol{c}}[\boldsymbol{a} \times \boldsymbol{c}], \tag{D18}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{a}\}_0\otimes\boldsymbol{c}\}_1=-\frac{1}{\sqrt{3}}\boldsymbol{c},\tag{D19}$$

$$\{\{\boldsymbol{a}\otimes\boldsymbol{a}\}_{2}\otimes\boldsymbol{c}\}_{1}=\sqrt{\frac{3}{5}}\left(\frac{1}{3}\boldsymbol{c}-\boldsymbol{a}\cos\theta_{\boldsymbol{a}\boldsymbol{c}}\right),\tag{D20}$$

where  $\theta_{ac}$  denotes the angle between vectors a and c.

## APPENDIX E: PARTICULAR EXAMPLES

In this part of the paper, we consider particular examples of allowed electric dipole two-photon absorption transitions followed by two-photon cascade emission. Cascade emission should be considered in two cases: when the resonance corresponds to the state  $b = kp_{1/2}$  or  $b' = kp_{3/2}$ , where k represents the principal quantum number of the intermediate state below the resonance level a. Here we restrict ourselves to the case when the angular dependence of the quantum interference effect arising in cascade radiation is determined by the angle between the polarization vector of the absorbed photons and the direction vector of the emitted upper photon, wherein, for brevity, we assume  $e_4 || e_3$  and  $v_2 || v_1$  (polarization vectors of the absorbed photons coincide with each other and the emitted photons are registered by the same detector).

Using the extremum condition for the scattering cross section determined by the amplitude in Eq. (A10), the non-resonant correction can be found as

$$\delta_{\rm NRc} = \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2} \frac{f_{fi}^{(4\gamma)}(b, b', a, a)}{f_{fi}^{(4\gamma)}(b, b, a, a)},\tag{E1}$$

where functions  $f_{f_i}^{(4\gamma)}(b, b', a, a)$  and  $f_{f_i}^{(4\gamma)}(b, b, a, a)$  are defined by Eq. (C14), and  $\Delta_{bb'}$  is the fine structure interval.  $\Gamma_a$ 

is the natural width of the atomic level a, and  $\Gamma_{\Sigma}$  is the sum of natural level widths of the a and b states (it is assumed that natural widths of states b and b' are equal). This correction arises in a completely analogous way to the well-known QIE effect, i.e., the NR correction for interfering paths to the resonant state a and its neighboring state a'. The latter in the case of the four-photon scattering process is expressed by

$$\delta_{\rm NR} = \frac{\Gamma_a^2}{4\Delta_{aa'}} \frac{f_{fi}^{(4\gamma)}(b, b, a, a')}{f_{fi}^{(4\gamma)}(b, b, a, a)} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2}.$$
 (E2)

Since these corrections, Eqs. (E1) and (E2), represent frequency shifts, they are additive quantities. Therefore, they can be considered separately, and we focus only on the evaluation of the NR corrections.

The energy intervals  $\Delta_{bb'} = E_b - E_{b'}$  used in the present paper are calculated using Eq. (9) (with c = 1) in Ref. [40]:

$$E_{s} = M + [f(n,\kappa) - 1]m_{r} - [f(n,\kappa) - 1]^{2} \frac{m_{r}^{2}}{2M} - \frac{1 - \delta_{l,0}}{\kappa(2l+1)} \frac{(Z\alpha)^{4}m_{r}^{3}}{2n^{3}m_{N}^{2}},$$
(E3)

where  $M = m_e + m_N$  ( $m_e$  is the electron mass and  $m_N$  is the nucleus mass), the reduced mass is given by

 $m_r = m_e m_N / (m_e + m_N)$ , and *l* is the electron orbital momentum. The function  $f(n, \kappa)$  is defined as follows:

$$f(n,\kappa) = \left[1 + \frac{(Z\alpha)^2}{(n-\delta)^2}\right]^{-1/2},$$
 (E4)

with  $\delta = |\kappa| - \sqrt{\kappa^2 - (Z\alpha)^2}$  and  $\kappa = (-1)^{j+l+1/2}(j+1/2)$ , and *j* is the electron total angular momentum. Expression (E3) is sufficient to ensure the accuracy of the NR corrections given in the main text.

The corresponding estimates for  $\delta_{\text{NR}}$  can be addressed to Refs. [17,24]. However, according to the analysis above, an additional factor in Eq. (E2) has emerged. This coefficient is close to unity, but one can find special cases where it should be taken into account. Moreover, the amplitudes in expression (E2) involve matrix elements for four photons in contrast to Refs. [17,24]. We leave a detailed comparison of Eq. (E2) with the results presented in Refs. [17,24] for future works.

# 1. Two-photon absorption to $ns_{1/2}$ states with subsequent two-photon cascade emission

As the first example we consider the  $4\gamma$  scattering process  $n_i s_{1/2} + 2\gamma \rightarrow n_a s_{1/2} \rightarrow k p_j + 1\gamma \rightarrow 1 s_{1/2} + 1\gamma$ , where the principal quantum number of the initial states  $n_i = 1, 2$ , the principal quantum number of the excited resonant state *n* can take arbitrary values corresponding to the resonant state *a*, and the intermediate state  $k p_j$ represents the one of  $b = k p_{1/2}, b' = k p_{3/2}$  atomic levels (see the main text). Considering the hyperfine structure of the levels, it is necessary to describe several partial channels:  $n_i s^{F=0,1} + 2\gamma \rightarrow n_a s^{F=0,1} \rightarrow k p_{1/2(3/2)} + 1\gamma \rightarrow 1 s_{1/2}$ . It was found that the results are the same for transitions:  $n_i s^{F=0} + 2\gamma \rightarrow n_a s^{F=0} \rightarrow k p_{1/2(3/2)} + 1\gamma \rightarrow 1 s_{1/2}$  and  $n_i s^{F=1} + 2\gamma \rightarrow n_a s^{F=1} \rightarrow k p_{1/2(3/2)} + 1\gamma \rightarrow 1 s_{1/2}$ . According to the Landau-Yang theorem, transitions with

According to the Landau-Yang theorem, transitions with different  $F_i$  and  $F_a$  are forbidden in this case [41].

Then, for the cascade link corresponding to  $n_a s_{1/2}^{F=0} \rightarrow k p_{1/2}$ , we obtain

$$\delta_{\rm NRc} = \frac{1}{2} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2} \frac{\Gamma_a^2}{4\Delta_{bb'}},\tag{E5}$$

where  $\Gamma_{\Sigma} = \Gamma_a + \Gamma_b$  and  $\Delta_{bb'}$  is the fine structure interval of  $kp_j$  states. For the case when the upper cascade link corresponds to the resonant transition  $n_a s_{1/2}^{F=0} \rightarrow kp_{3/2}$ , the result is

$$\delta_{\rm NRc} = -\frac{1}{5} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2} \frac{\Gamma_a^2}{4\Delta_{bb'}}.$$
 (E6)

The corrections expressed by Eqs. (E5) and (E6) are angle independent and differ in sign due to the way the fine structure interval is included in the line profile. The prefactors are determined by the corresponding 6i Racah symbols in Eq. (C14).

The numerical results for the frequency shifts [Eqs. (E5) and (E6)] are collected in Table III. Hereinafter, the cascade process is presented in the first column, followed by the calculated values of the widths  $\Gamma_a$  and  $\Gamma_b$  in the second and third columns, respectively; the fine splitting interval of the cascade states,  $\Delta_{bb'}$ , is presented in the fourth column. The fifth

column contains the results of calculations for the resonance state  $b = kp_{1/2}$ , Eq. (E5), and in the sixth column the resonance state is chosen to be  $b' = kp_{3/2}$ , Eq. (E6). The seventh column summarizes the calculated values of the fraction of the cascade process among the entire radiation, *x*. The cascade fraction is calculated as the ratio  $x = W_{n_a l_a \rightarrow n_b l_b}^{(1\gamma)}/\Gamma_a$ , where  $W_{n_a l_a \rightarrow n_b l_b}^{(1\gamma)}$  is the transition probability of a partial one-photon channel. The last column presents the values of the weighted average correction multiplied by the factor *x*. Finally, the total contribution found from all possible cascade transitions is given in each line denoted as "Total."

In Table III we present the results for the weighted average centroid (see, e.g., Ref. [4]) frequency shift, which is defined by

$$\delta_{\rm NRc}^{\rm (av)} = \sum_{j_{a'}} \frac{2j_{a'} + 1}{(2l_{a'} + 1)(2s + 1)} \delta_{\rm NRc}(j_{a'}). \tag{E7}$$

For the cascade decay through the kp states, this expression reduces to  $\delta_{\text{NRc}}(kp_{1/2})/3 + 2\delta_{\text{NRc}}(kp_{3/2})/3$ . The main purpose of this quantity is to demonstrate that the major contribution  $\delta_{\text{NRc}}$  can be avoided. From an experimental point of view, this means that independent measurements of the cascade decays to  $kp_{1/2}$  and  $kp_{3/2}$  should be performed. The determined frequency values can then be averaged as above. Corresponding measurements can be carried out by matching experiments when the detector is tuned to a particular emission frequency. Consequently, the averages should not account for the cascade fraction *x*.

In addition to the data given in Table III (representing the experimental conditions when the radiation direction is taken relative to the polarization vector of the absorbed photon), we consider the nonresonant corrections determined by the angle between the polarization vectors of the absorbed and emitted photons. For brevity, we omit here the cascade fraction, which can be calculated as in the previous table. The results of the calculation give the following expressions:

$$\delta_{\rm NRc}(kp_{1/2}) = \frac{\Gamma_a^2}{2\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2},\tag{E8}$$

$$\delta_{\rm NRc}(kp_{3/2}) = -\frac{\Gamma_a^2}{8\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2}.$$
 (E9)

The numerical results are combined in Table IV.

As in the previous case, the corrections are angle independent and small compared to the present accuracy in measuring the corresponding transition frequencies.

2. Transition 
$$n_i s_{1/2}^{F=0} \rightarrow n_a d_{3/2}^{F=2} \rightarrow k p_{1/2(3/2)} \rightarrow 1 s_{1/2}$$

Here, we present the results for the transition:  $n_i s_{1/2}^{F=0} + 2\gamma \rightarrow n_a d_{3/2}^{F=2} \rightarrow k p_{1/2(3/2)} + 1\gamma \rightarrow 1 s_{1/2}$ . According to Ref. [41], the resonant state is defined by a hyperfine sublevel with  $F_a = 2$ . Then for the decay to the state  $b = k p_{1/2}$  we find

$$\delta_{\rm NRc} = -13\sqrt{\frac{2}{5}} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2}.$$
 (E10)

TABLE V. NR corrections for transitions  $n_i s_{1/2}^{F=0} \rightarrow n_a d_{3/2}^{F=2} \rightarrow k p_{1/2(3/2)} \rightarrow 1s$ . The notations are the same as in Table III. NR corrections are calculated at the "magic angle." All values are given in hertz.

Cascade	$\Gamma_a$ (Hz)	$\Gamma_b$ (Hz)	$\Delta_{bb'}$ (Hz)	$\delta_{\mathrm{NRc}}(kp_{1/2})$ (Hz)	$\delta_{\mathrm{NRc}}(kp_{3/2})$ (Hz)	x	$\delta^{(av)}_{NRc}$ (Hz)
$3d_{3/2}-2p-1s$	$1.0295 \times 10^{7}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	-19734.3	-1049.7	1	-7 277.9
$4d_{3/2}-2p-1s$	$4.4050 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	-3638.1	-193.5	0.746	-1341.7
$4d_{3/2}-3p-1s$		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	-12104.4	-643.8	0.254	-4464.0
Total				-5792.0	-308.1	-6100.1	
$6d_{3/2}$ -2 <i>p</i> -1 <i>s</i>	$1.3368 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	-335.6	-17.8	0.613	-123.8
$6d_{3/2}$ -3 <i>p</i> -1 <i>s</i>		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	-1130.8	-60.1	0.224	-417.0
$6d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	-2661.9	-141.6	0.103	-981.7
$6d_{3/2}$ -5 <i>p</i> -1 <i>s</i>		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	-5103.1	-271.4	0.053	-1882.0
Total				-1005.2	-53.5	-1058.7	
$8d_{3/2}-2p-1s$	$5.7238 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	-61.5	-3.3	0.571	-22.7
$8d_{3/2}$ -6 <i>p</i> -1 <i>s</i>		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	-207.6	-11.0	0.210	-76.6
$8d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	-491.4	-26.1	0.098	-181.2
$8d_{3/2}-5p-1s$		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	-955.5	-50.8	0.054	-352.4
$8d_{3/2}-6p-1s$		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	-1634.6	-86.9	0.033	-602.8
$8d_{3/2}$ -7 <i>p</i> -1 <i>s</i>		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	-2548.2	-135.5	0.021	-939.8
Total				-285.5	-15.2	-300.6	
$12d_{3/2}-2p-1s$	$1.7226 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	-5.6	-0.3	0.541	-2.0
$12d_{3/2}$ -3 <i>p</i> -1 <i>s</i>		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	-18.8	-1.0	0.200	-6.9
$12d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	-44.6	-2.4	0.094	-16.4
$12d_{3/2}$ -5 <i>p</i> -1 <i>s</i>		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	-87.0	-4.6	0.052	-32.1
$12d_{3/2}-6p-1s$		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	-150.2	-8.0	0.032	-55.4
$12d_{3/2}$ -7 <i>p</i> -1 <i>s</i>		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	-238.0	-12.7	0.021	-87.8
$12d_{3/2}-8p-1s$		$1.6603 \times 10^{6}$	$1.70995 \times 10^{8}$	-353.6	-18.8	0.015	-130.4
$12d_{3/2}-9p-1s$		$1.1694 \times 10^{6}$	$1.20075 \times 10^{8}$	-499.8	-26.6	0.011	-184.3
$12d_{3/2}$ -10 <i>p</i> -1 <i>s</i>		$8.5442 \times 10^{5}$	$8.75542 \times 10^{7}$	-677.6	-36.0	0.008	-249.9
$12d_{3/2}$ -11 <i>p</i> -1 <i>s</i>		$6.4308 \times 10^{5}$	$6.57822 \times 10^{7}$	-887.6	-47.2	0.006	-327.3
Total				-47.6	-2.5	-50.2	

The decay to the  $b' = k p_{3/2}$  state yields

$$\delta_{\rm NRc} = -\frac{13}{47} \sqrt{\frac{5}{2}} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2}.$$
 (E11)

The results of the calculations demonstrate evident peculiarities. First, both corrections (E10) and (E11) do not turn to zero at any angle. Second, in contrast to the results of the previous section, the NR corrections arising due to cascade emission for the  $nd_{3/2}^{F=2}$  resonance state reach the level of several kilohertz and hence represent a significant contribution to the line profile asymmetry. Third, the value of  $\delta_{NRc}$ decreases as the principal quantum number of the resonance state *a* increases, since the level width reduces as  $1/n_a^3$ , which is partly compensated by the cubic diminution of  $\Delta_{bb'}$ . Finally, the NR corrections are of the same sign, the latter determined not only by the fine structure interval included in the line profile, but also by the angular dependence.

The numerical results are summarized in Table V with notations as in Appendix E 1.

3. Transition 
$$n_i s_{1/2}^{F=1} \rightarrow n_a d_{3/2}^{F=1,2} \rightarrow k p_{1/2(3/2)} \rightarrow 1 s_{1/2}$$

A different picture emerges for an initial state with fixed total atomic momentum  $F_i = 1$ ; transitions to both  $n_a d_{3/2}^{F=1}$  and  $n_a d_{3/2}^{F=2}$  are allowed. The result for the partial scattering

channel 
$$n_i s_{1/2}^{F=1} \to n_a d_{3/2}^{F=1,2} \to k p_{1/2} \to 1 s_{1/2}$$
 is

$$\delta_{\rm NRc} = \sqrt{\frac{2}{5} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_a^2 + \Gamma_{\Sigma}^2} \frac{7 - 8\cos^2\theta + 3\cos^4\theta}{10 - \cos^2\theta - 3\cos^4\theta}}, \quad (E12)$$

where  $\theta$  is the angle between the polarization vector of the absorbed photons and the direction vector of the emitted photons (it is assumed that both are registered by one detector).

Consideration of the partial scattering channel  $n_i s_{1/2}^{F=1} \rightarrow n_a d_{3/2}^{F=1,2} \rightarrow k p_{3/2} \rightarrow 1 s_{1/2}$  leads to

$$\delta_{\rm NRc} = \sqrt{\frac{5}{2}} \frac{\Gamma_a^2}{4\Delta_{bb'}} \frac{\Gamma_{\Sigma}^2}{\Gamma_b^2 + \Gamma_{\Sigma}^2} \frac{-7 + 8\cos^2\theta - 3\cos^4\theta}{78 - 37\cos^2\theta - 3\cos^4\theta}.$$
 (E13)

The behavior of these corrections repeats that mentioned in Appendix  $E_2$  (see Fig. 5).

The numerical values are collected in Table VI.

## **APPENDIX F: SPECIAL NOTES**

Here we provide some additional explanations not explicitly mentioned in the main text of the paper.

First, we should briefly discuss the approximation used in Refs. [17,24,25] and in our paper. According to the experimental situation, the determination of the transition frequency of two-photon absorption in the hydrogen atom corresponds to the registration of the emitted photon from the Balmer series at any polarization of this fluorescence. Then, the

Cascade	$\Gamma_a$ (Hz)	$\Gamma_b$ (Hz)	$\Delta_{bb'}$ (Hz)	$\delta_{\rm NR}(n_a p_{1/2})$ (Hz)	$\delta_{\rm NR}(n_a p_{3/2})$ (Hz)	x	$\delta_{\rm NRc}^{(\rm av)}$ (Hz)
$3d_{3/2}-2p-1s$	$1.0295 \times 10^{7}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	759.0	-271.1	1	72.3
$4d_{3/2}-2p-1s$	$4.40503 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	139.9	-50.0	0.746	13.3
$4d_{3/2}-3p-1s$		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	465.6	-166.3	0.254	44.3
Total				222.8	-79.6	143.2	
$6d_{3/2}-2p-1s$	$1.3368 \times 10^{6}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	12.9	-4.6	0.613	1.2
$6d_{3/2}$ -3p-1s		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	43.5	-15.5	0.224	4.1
$6d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	102.4	-36.6	0.103	9.7
$6d_{3/2}-5p-1s$		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	196.3	-70.1	0.053	18.7
Total				38.7	-13.8	24.8	
$8d_{3/2}-2p-1s$	$5.7238 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	2.4	-0.8	0.571	0.2
$8d_{3/2}-6p-1s$		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	8.0	-2.8	0.210	0.8
$8d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	18.9	-6.7	0.098	1.8
$8d_{3/2}-5p-1s$		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	36.7	-13.1	0.054	3.5
$8d_{3/2}-6p-1s$		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	62.9	-22.4	0.033	6.0
$8d_{3/2}-7p-1s$		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	98.0	-35.0	0.021	9.3
Total				11.0	-3.9	7.1	
$12d_{3/2}-2p-1s$	$1.7226 \times 10^{5}$	$9.9762 \times 10^{7}$	$1.09437 \times 10^{10}$	0.2	$\leq -10^{-2}$	0.541	$\leq 10^{-2}$
$12d_{3/2}-3p-1s$		$3.0208 \times 10^{7}$	$3.24256 \times 10^{9}$	0.7	-0.3	0.200	$\lesssim 10^{-2}$
$12d_{3/2}-4p-1s$		$1.2941 \times 10^{7}$	$1.36795 \times 10^{9}$	1.7	-0.6	0.094	0.2
$12d_{3/2}$ -5p-1s		$6.6939 \times 10^{6}$	$7.00406 \times 10^{8}$	3.3	-1.2	0.052	0.3
$12d_{3/2}-6p-1s$		$3.9012 \times 10^{6}$	$4.05332 \times 10^{8}$	5.8	-2.1	0.032	0.5
$12d_{3/2}$ -7 <i>p</i> -1 <i>s</i>		$2.4692 \times 10^{6}$	$2.55232 \times 10^{8}$	9.1	-3.3	0.021	0.9
$12d_{3/2}-8p-1s$		$1.6603 \times 10^{6}$	$1.70995 \times 10^{8}$	13.6	-4.9	0.015	1.3
$12d_{3/2}-9p-1s$		$1.1694 \times 10^{6}$	$1.20075 \times 10^{8}$	19.2	-6.9	0.011	1.8
$12d_{3/2}-10p-1s$		$8.5442 \times 10^{5}$	$8.75542 \times 10^{7}$	26.1	-9.3	0.008	2.5
$12d_{3/2}-11p-1s$		$6.4308 \times 10^{5}$	$6.57822 \times 10^{7}$	34.1	-12.2	0.006	3.2
Total				1.8	-0.6	1.2	

TABLE VI. NR corrections for transitions  $n_i s_{1/2}^{F=1} \rightarrow n_a d_{3/2}^{F=1,2}$ . The notations are the same as in Table III. NR corrections are calculated at the "magic angle." All values are given in hertz.

description of the photon scattering process breaks at the state b = 2p (in our notations). This, however, is only allowed within the resonance approximation when the lower cascade link is discarded. Based on this approximation, the frequency shift arising from the nonresonant contribution in the truncated cross section is estimated for the 1s - 3s absorption in



FIG. 4. The total NR correction in hertz for the transitions  $n_i s_{1/2}^{F=1} + 2\gamma \rightarrow n_a d_{3/2}^{F=1,2} \rightarrow k p_{1/2} + 1\gamma \rightarrow 1 s_{1/2} + 1\gamma$  in dependence on the angle between the polarization vector of the absorbed photons  $(e_4 || e_3)$  and propagation vector of the emitted photons  $(v_2 || v_1)$  in radians [see Eq. (E12)]. The solid (red) line refers to the  $3d_{3/2}$  state case, the curve with a small dashed line (blue) refers to the  $4d_{3/2}$  state case, the dotted curve (violet) refers to the  $6d_{3/2}$  state case, the dotted curve (violet) refers to the  $6d_{3/2}$  state case, and the line with a long dashed line (lilac) refers to the  $12d_{3/2}$  state decay case.

Refs. [24,25] and a wider range of transitions in Ref. [17]. (It should be noted that there was an unfortunate typo in Ref. [17]. Leaving the numerical results correct, in the formulas containing the angular dependence for the NR corrections, 2 is missing in the cosine arguments in expressions (28)–(31) and (38)–(41).)

Following the fundamental principles of QED theory, the process under study should be considered from the stableto-stable state, which directly follows from the construction of the evolution operator and the corresponding perturbation theory. Otherwise (description of a "piece" of the process only absorption or emission) the resonance approximation is used, which implies incoherence of the components. The



FIG. 5. The total NR correction in hertz for the transitions  $n_i s_{1/2}^{F=1} \rightarrow n_a d_{3/2}^{F=1,2} \rightarrow k p_{3/2} \rightarrow 1 s_{1/2}$ . Notations are the same as for Fig. 4.

situation is exactly the same with the discarding of the lower link in cascade radiation. Similar to the works [17,24,25], where the coupling of the processes of "truncated" emission and absorption is studied by going beyond the resonance approximation for the resonant state a (in our notations), in our work we study the influence of the total emission process on the determination of the transition frequency in the absorption process.

The study of the total radiation effect on the formation of the absorption line profile is carried out under the assumption of the additive nature of the nonresonant corrections. The latter can be justified as follows. The absorption or emission line profiles can be obtained in the framework of the QED theory considering the photon scattering process (see Refs. [5,6]). In the resonant approximation, the Lorentz line profile emerges as the most significant part due to the discarding of nonresonant contributions in the cross section. In order to go beyond the resonance approximation, the remaining terms in the photon scattering cross section are taken into account, the leading-order terms corresponding to the neighboring states arising due to the fine structure of the levels are considered. At present, such description is sufficient at the current experimental accuracy of the order of a few kilohertz. Then, under the assumption of smallness of the effect (the corresponding asymmetry of the line profile should be insignificant in the resonance approximation), the contribution of these additional terms can be described as a frequency shift.

One evident way to find theoretically this shift corresponds to a search for the "line maximum." For this purpose, the extremum condition is applied to the cross section, which yields

$$\frac{d\sigma}{d\omega}\Big|_{\omega_{\rm res}} = 0, \quad \omega_{\rm res} = \omega_0 + \delta_{\rm NR}. \tag{F1}$$

Here  $d\sigma$  is defined by the square of the photon scattering amplitude in the usual way (see, e.g., Ref. [42]). The appearance of the frequency additive  $\delta_{NR}$  to the transition frequency defined in the resonance approximation,  $\omega_0$ , is precisely the result of the nonresonant terms in the scattering cross section. Then it becomes obvious that adding terms to the scattering amplitude leads to extra shifts; i.e.,  $\delta_{NR}$  is the sum of corrections (frequency as energy has an additive character).

According to the above discussion, one can conclude that excluding a part of the radiation from the scattering amplitude (see Ref. [6] for details) leads to a "truncation" of the cross section. Therefore, by adding the radiation process as well as its subtleties, the accuracy of the transition frequency determination can be investigated, considering the subsequent frequency shifts in  $\delta_{NR}$ .

There is another possibility to take into account all the subtleties of the scattering process on the determination of the transition frequency. It was recently demonstrated in Ref. [4] that a "line center" can be used for this purpose. To find the line center, a modified spectral line profile was employed, represented by the Fano-Voigt contour for the cross section  $d\sigma$  [4]. The latter arises from the series expansion of  $d\sigma$  and the subsequent convolution with the Gaussian contour. This procedure allowed the subtraction of the symmetric part of the observed line shape and, as a consequence, the determination of the transition frequency as the line center. A discussion of frequency shifting using the fitting procedure can also be found in Ref. [25]. As follows from the analysis in Refs. [4,25] (and subsequent works, e.g., Ref. [26]), the subtraction of the symmetric part necessarily requires a theoretical analysis of the nonresonant contributions in the cross section and, in particular, the effect of quantum interference as the dominant contribution. This corresponds precisely to studying the details of the process under consideration beyond the resonance approximation. It also becomes apparent that accounting for the details of the emission process leads to the addition of other nonresonant contributions, which in turn should lead to additional asymmetry parameters in the fitting line profile. Thus, the description of the process beyond the "truncated" cross section is a logical extension, leading to significant results for some measured transitions. In view of the values obtained for the frequency shift, the significance of the QIEc cannot be stated in advance; for each particular transition this effect should be considered separately. The use of any method of extracting the transition frequency (subtracting the nonresonant correction from the "line maximum" or extracting a symmetric part of the observed profile and then determining the "line center") is rather a matter of convenience. We emphasize that a careful theoretical calculation of nonresonant corrections is required to determine the frequency at the line maximum, while in the case of the line center, within the same theoretical framework, a detailed determination of the line profile and the corresponding asymmetry parameters is necessary.

Another important subtlety is that initially the amplitude of the four-photon scattering process, Eq. (A7), depends on two frequencies. Using the energy conservation law, from expression (A7) one can obtain

$$U_{fi}^{(4\gamma)} \sim \frac{1}{E_i + 2\omega - E_a(1 - i0)} \left[ \frac{A_{fb}^{(1\gamma)} A_{ba}^{(1\gamma)} A_{ai}^{(2\gamma)}}{E_i + 2\omega - \omega_2 - E_b(1 - i0)} + \frac{A_{fb'}^{(1\gamma)} A_{b'a}^{(1\gamma)} A_{ai}^{(2\gamma)}}{E_i + 2\omega - \omega_2 - E_{b'}(1 - i0)} \right].$$
 (F2)

Here we have discarded all remaining contributions in Eq. (A7) with  $n_1 \neq b(b')$  and  $n_2 \neq a$ . The amplitude (F2) forms the spectral line contour in the most general case for a four-photon scattering process. To find the transition frequency, one can utilize, for example, the extremum condition. Then it is necessary to study the function of two variables and solve the corresponding set of nonlinear equations. This

procedure is rather complicated, not only for analytical but also for accurate numerical calculations. Thus, reducing the problem to a function of one variable is an approximation still justified by the resonance condition [see the discussion in the main text following Eq. (1)]. Violating this approximation is beyond the scope of this work, as is generalizing the line profile to the case of a larger number of photons.

As a next step in the discussion here, it should be noted that, according to the resonance approximation, the results obtained for the total process ("stable-to-stable") should recover the previous ones, i.e., those obtained for the "truncated" cross section. We do not give here for brevity the corresponding expression with the statement that it is obtained for the ns/nd states: the angular dependence for the QIE is the same as that of Ref. [17]. In addition, given the angular dependence of the amplitudes (resonant and nonresonant), one can find that  $f_{res}$  in Eq. (3) can go to zero, leading to an infinite value of  $\delta_{NRc}$  in some cases. This, however, means that there are no corresponding decay channels in the cross section and leads to the need to redefine the resonance process. We leave a detailed discussion of this circumstance for future works, noting that this is not the case in the present study.

Finally, we briefly discuss the accuracy of the nonresonant correction determination  $\delta_{NRc}$ . Since the quantities included in the definition of the frequency shift  $\delta_{NRc}$  are defined with high precision (see Ref. [43]), the main source of inaccuracy of our calculations is the width of the corresponding level. The latter was calculated within the framework of the nonrelativistic theory. Comparison of the obtained values with completely relativistic calculations and corresponding corrections to them (see Ref. [44] and references therein) shows that the values of nonresonant corrections are confined to five significant digits. However, in some places we have given more significant digits, which is mainly motivated by two circumstances. First, it is the consistency of all given values, and second, it is due to the ongoing reduction of weighted average centroids or significant reduction of values when multiplied by the branching ratios (cascade fraction), x.

- A. Matveev, C. G. Parthey, K. Predehl, J. Alnis, A. Beyer, R. Holzwarth, T. Udem, T. Wilken, N. Kolachevsky, M. Abgrall, D. Rovera, C. Salomon, P. Laurent, G. Grosche, O. Terra, T. Legero, H. Schnatz, S. Weyers, B. Altschul, and T. W. Hänsch, Phys. Rev. Lett. **110**, 230801 (2013).
- [2] R. van Rooij, J. S. Borbely, J. Simonet, M. D. Hoogerland, K. S. E. Eikema, R. A. Rozendaal, and W. Vassen, Science 333, 196 (2011).
- [3] R. Pohl et al., Nature (London) 466, 213 (2010).
- [4] A. Beyer, L. Maisenbacher, A. Matveev, R. Pohl, K. Khabarova, A. Grinin, T. Lamour, D. C. Yost, T. W. Hänsch, N. Kolachevsky, and T. Udem, Science 358, 79 (2017).
- [5] F. Low, Phys. Rev. 88, 53 (1952).
- [6] O. Y. Andreev, L. N. Labzowsky, G. Plunien, and D. A. Solovyev, Phys. Rep. 455, 135 (2008).
- [7] T. A. Zalialiutdinov, D. A. Solovyev, L. N. Labzowsky, and G. Plunien, Phys. Rep. 737, 1 (2018).
- [8] U. D. Jentschura and P. J. Mohr, Can. J. Phys. 80, 633 (2002).
- [9] L. Labzowsky, D. Soloviev, G. Plunien, and G. Soff, Phys. Rev. A 65, 054502 (2002).
- [10] M. Horbatsch and E. A. Hessels, Phys. Rev. A 82, 052519 (2010).
- [11] M. Horbatsch and E. A. Hessels, Phys. Rev. A 84, 032508 (2011).
- [12] C. J. Sansonetti, C. E. Simien, J. D. Gillaspy, J. N. Tan, S. M. Brewer, R. C. Brown, S. Wu, and J. V. Porto, Phys. Rev. Lett. 107, 023001 (2011).
- [13] R. C. Brown, S. Wu, J. V. Porto, C. J. Sansonetti, C. E. Simien, S. M. Brewer, J. N. Tan, and J. D. Gillaspy, Phys. Rev. A 87, 032504 (2013).
- [14] A. Marsman, M. Horbatsch, and E. A. Hessels, J. Phys. Chem. Ref. Data 44, 031207 (2015).
- [15] P. Amaro, F. Fratini, L. Safari, A. Antognini, P. Indelicato, R. Pohl, and J. P. Santos, Phys. Rev. A 92, 062506 (2015).
- [16] P. Amaro, B. Franke, J. J. Krauth, M. Diepold, F. Fratini, L. Safari, J. Machado, A. Antognini, F. Kottmann, P. Indelicato, R. Pohl, and J. P. Santos, Phys. Rev. A **92**, 022514 (2015).
- [17] A. Anikin, T. Zalialiutdinov, and D. Solovyev, Phys. Rev. A 103, 022833 (2021).

- [18] A. Anikin, T. Zalialiutdinov, D. Solovyev, and L. Labzowsky, arXiv:2204.12199.
- [19] A. Grinin, A. Matveev, D. C. Yost, L. Maisenbacher, V. Wirthl, R. Pohl, T. W. Hänsch, and T. Udem, Science 370, 1061 (2020).
- [20] W. Greiner and J. Reinhart, *Quantum Electrodynamics* (Springer-Verlag, Berlin, 2003).
- [21] L. Labzowsky, D. Solovyev, and G. Plunien, Phys. Rev. A 80, 062514 (2009).
- [22] U. D. Jentschura, Phys. Rev. A 81, 012112 (2010).
- [23] T. Zalialiutdinov, Y. Baukina, D. Solovyev, and L. Labzowsky, J. Phys. B: At. Mol. Opt. Phys. 47, 115007 (2014).
- [24] D. C. Yost, A. Matveev, E. Peters, A. Beyer, T. W. Hänsch, and T. Udem, Phys. Rev. A 90, 012512 (2014).
- [25] H. Fleurbaey, S. Galtier, S. Thomas, M. Bonnaud, L. Julien, F. Biraben, F. Nez, M. Abgrall, and J. Guéna, Phys. Rev. Lett. 120, 183001 (2018).
- [26] A. D. Brandt, S. F. Cooper, C. Rasor, Z. Burkley, A. Matveev, and D. C. Yost, Phys. Rev. Lett. **128**, 023001 (2022).
- [27] E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, Rev. Mod. Phys. 93, 025010 (2021).
- [28] A. A. Anikin, T. A. Zalialiutdinov, and D. A. Solovyev, JETP Lett. 114, 180 (2021).
- [29] D. Solovyev, A. Anikin, T. Zalialiutdinov, and L. Labzowsky, J. Phys. B: At. Mol. Opt. Phys. 53, 125002 (2020).
- [30] L. Labzowsky, V. Karasiev, and I. Goidenko, J. Phys. B: At. Mol. Opt. Phys. 27, L439 (1994).
- [31] L. N. Labzowsky, I. A. Goidenko, and D. Liesen, Phys. Scr. 56, 271 (1997).
- [32] L. N. Labzowsky, D. A. Solovyev, G. Plunien, and G. Soff, Phys. Rev. Lett. 87, 143003 (2001).
- [33] L. Labzowsky, G. Schedrin, D. Solovyev, E. Chernovskaya, G. Plunien, and S. Karshenboim, Phys. Rev. A 79, 052506 (2009).
- [34] L. Labzowsky, G. Klimchitskaya, and Y. Dmitriev, *Relativistic Effects in the Spectra of Atomic Systems* (Institute of Physics Publishing, Bristol, UK, 1993).
- [35] B. de Beauvoir, F. Nez, L. Julien, B. Cagnac, F. Biraben, D. Touahri, L. Hilico, O. Acef, A. Clairon, and J. J. Zondy, Phys. Rev. Lett. 78, 440 (1997).

- [36] C. Schwob, L. Jozefowski, B. de Beauvoir, L. Hilico, F. Nez, L. Julien, F. Biraben, O. Acef, J.-J. Zondy, and A. Clairon, Phys. Rev. Lett. 82, 4960 (1999).
- [37] B. de Beauvoir, C. Schwob, O. Acef, L. Jozefowski, L. Hilico, F. Nez, L. Julien, A. Clairon, and F. Biraben, Eur. Phys. J. D 12, 61 (2000).
- [38] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
- [39] O. Arnoult, F. Nez, L. Julien, and F. Biraben, Eur. Phys. J. D 60, 243 (2010).
- [40] E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, J. Phys. Chem. Ref. Data 50, 033105 (2021).
- [41] T. Zalialiutdinov, D. Solovyev, L. Labzowsky, and G. Plunien, Phys. Rev. A 91, 033417 (2015).
- [42] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Wiley-Interscience, New York, 1965).
- [43] M. Horbatsch and E. A. Hessels, Phys. Rev. A 93, 022513 (2016).
- [44] R. Popov and A. Maiorova, Opt. Spectrosc. **122**, 366 (2017).