Major role of multielectronic $K$-$L$ inter-shell resonant recombination processes in Li- to O-like ions of Ar, Fe, and Kr

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Dielectronic and higher-order resonant electron recombination processes including a $K$-shell excitation were systematically measured at high resolution in electron beam ion traps. Storing highly charged Ar, Fe, and Kr ions, the dependence on atomic number $Z$ of the contribution of these processes to the total recombination cross section was studied and compared with theoretical calculations. Large higher-order resonant recombination contributions are found, especially for systems with $10 < Z < 36$. In some cases, they even surpass the strength of the dielectronic channel, which was hitherto presumed to be always the dominant one. These findings have consequences for the modeling of high-temperature plasmas. Features attributed to inter-shell quadrupole recombination were also observed. The experimental data obtained for the He-like to O-like isoelectronic sequences compare well with the results of advanced relativistic distorted-wave calculations employing multiconfiguration Dirac-Fock bound state wave functions that include threefold and fourfold excitations.

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I. INTRODUCTION

Electron-electron interaction is a fundamental aspect of both atomic and molecular structure and reactions. It governs the level structure and the time dependence of atomic collision processes, and thus also the behavior of laboratory and astrophysical plasmas. Understanding electronic correlations and their consequences is therefore of great importance for the development of theory, and a good knowledge of these is crucial for all aspects of plasma diagnostics.

Among the different processes involving electron-electron interaction, dielectronic recombination (DR) and its time reversal, the Auger decay following photoexcitation of inner-shell electrons [1,2] are preeminent. In the first-order DR process (see left side diagram in the top panel of Fig. 1), a free electron is captured in a collision with an ion, thereby transferring the sum of its energy to another bound electron and exciting it resonantly. The ion is then left in a (usually) doubly-excited state which can decay radiatively, completing the DR process. Extended experimental and theoretical investigations on DR with highly charged ions (HCI) have been carried out in recent years by various groups (e.g. [3–8]).

Usually, DR is described in an independent-particle model, only taking into account the interaction between the two electrons involved – the initially free one and an active bound one. Higher-order electron correlations are not accounted for in this approach. This is illustrated in the bottom diagram of Fig. 1 – left side, where the interaction process is represented by the Feynman diagram of one virtual photon exchange. Hence, the DR process is usually denoted by the states of the electrons of concern; for instance, a $K$-$LL$ DR process (Auger notation, cf. [9]) denotes the excitation of an inner-shell $K$ electron to the $L$-shell with a resonant capture of the free electron also to the $L$-shell. However, our recent investigations have shown that higher-order correlations with the active excitation of more than one electron may contribute considerably to recombination and affect plasma parameters noticeably [10] [11]. We focus on these higher-order effects in this paper.

Trielectronic recombination (TR) as an intra-shell process, where two bound $L$-shell electrons are excited within the same shell through the capture of one free electron, was reported as results of low-energy storage ring DR measurements (cf. [12] [14]). In our previous experiments at electron beam ion traps (EBIT), we found that the higher-order recombination process can also lead to far more energetic inter-shell excitations [10] [11] with a rather large contribution. The corresponding process with $\Delta n = 1$ excitation is exemplified in the middle diagram in Fig. 1 showing an inter-shell $KL$-$LLL$ TR process, where a $K$- and an $L$-shell electron are excited simultaneously to vacant higher-lying $L$ levels under resonant capture of the free electron, here also to the $L$-shell.

As more than two electrons are actively involved in TR, independent–particle models such as the (Dirac-)Hartree-Fock method cannot adequately describe it. Electron correlations must be included using, e. g., multiconfiguration or many-body perturbation theory methods. Within the perturbative picture (at least) two virtual photons must be exchanged for TR. Three out of six possible interactions are shown in the central part of Fig. 1 (b).

Inter-shell TR in highly ionized Kr ions was observed and compared [10] with extended calculations based on the multiconfiguration Dirac-Fock (MCDF) procedure [5] [10] [15]. In that work, the first indications of third-order inter-shell quadrupole recombination (QR) were also found. On the right side of Fig. 1, inter-shell $KLL$-$LLL$ QR is visualized. Here, electron capture to the $L$-shell occurs simultaneously with the ex-
In this paper we report in detail on our systematic investigations, because in the low-Z regime, electron correlations are expected to become stronger due to the relative decrease of the central Coulomb force compared to the Z-independent electron-electron interaction.

Our studies cover a range of elements relevant to different fields of plasma physics: the study of Fe ions is central in astrophysics, and Ar as well as Kr ions have diagnostic uses e.g. in fusion plasma devices [18, 19].

In our more recent work [11], higher-order inter-shell recombination effects have also been reported for highly charged Ar and Fe ions. We found that TR could overwhelm the first-order DR process for some ionic species in light elements, being the dominant recombination channel for these ions. We have extended the range of observed isoelectronic sequences, ranging now from He-like to O-like ions.

For the observation of the weak and blended higher-order structures, high-resolution experimental techniques are required. Therefore, we give also insight into the forced evaporative ion cooling technique, essential for high-resolution experiments. With this method, lower-Z elements, which require higher absolute resolution because of their lower fine-structure splittings, become more readily accessible. This is mandatory for the aim of our investigations, because in the low-Z regime, electron correlations are expected to become stronger due to the relative decrease of the central Coulomb force compared to the Z-independent electron-electron interaction.

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II. THEORETICAL APPROACH

In a resonant recombination process, resonant electron capture is followed by the radiative decay and stabilization of the ion’s intermediate autoionizing state. It proceeds from an initial state \( i \), consisting of the ground-state ion and a continuum electron with an asymptotic momentum \( \vec{p}_i \), through the intermediate autoionizing state \( d \) to the bound final state \( f \). The cross section for a specific resonant recombination channel is given (in atomic units) as a function of the electron’s kinetic energy \( E \) in terms of the resonance strengths \( S_{i \rightarrow d \rightarrow f} \) as (see, e.g. [20] [22])

\[
\sigma_{i \rightarrow d \rightarrow f}(E) = S_{i \rightarrow d \rightarrow f} L_d(E),
\]

\[
S_{i \rightarrow d \rightarrow f} = \frac{2\pi^2}{p^2} \frac{2J_d + 1}{2(2J_i + 1)} \frac{\Gamma_d}{\Gamma_d - \Gamma_{d \rightarrow i}}.
\]

Here, the Lorentzian line shape function

\[
L_d(E) = \frac{\Gamma_d/(2\pi)}{(E - E_{\text{res}})^2 + \Gamma_d^2/4}
\]

is normalized to unity on the energy scale, \( \int L(E)dE = 1 \), and is centered around the resonance energy \( E_{\text{res}} \), calculated as the difference of the intermediate and initial ionic level energies: \( E_{\text{res}} = E_d - E_i \). \( J_d \) and \( J_i \) are the total angular momenta of the intermediate and the initial states of the recombination process, respectively. The free electron momentum associated with the kinetic energy of the initially free electron at resonance is given by

\[
p = |\vec{p}| = \sqrt{(E_{\text{res}}/c)^2 - c^2}.
\]

The total radiative width of the autoionizing intermediate state is \( \Gamma_d = \sum_f \Gamma_{d \rightarrow f} \), and \( \Gamma_d = \sum_i \Gamma_{d \rightarrow i} \) is the total autoionization width of the initial state.
In this equation, the transition amplitude, i.e., the matrix element of the sum of the Coulomb and Breit interactions $V = V^C + V^B$, is calculated with the initial bound-free antisymmetrized product state $|\Psi_i; E; J_i, \Pi_i, \bar{\mu} m_\mu\rangle$ and the resonant intermediate state. After averaging over the initial magnetic quantum numbers $M_\mu$, $m_\mu$ and the direction $(\theta, \phi)$ of the incoming continuum electron, and after performing a summation over the magnetic quantum numbers $M_d$ of the autoionizing state, one obtains the partial wave expansion of the reduced matrix elements, as given in the last line of the equation (3). $\kappa$ is the relativistic angular momentum quantum number appearing in the decomposition of the continuum scattering state [23]. The last line of Eq. (3) also shows that, owing to the usual Coulomb interaction (or, generally, electron-electron interaction) selection rules, the total angular momentum of the initial state (consisting of the bound ionic electrons and the continuum electron partial wave) and that of the autoionizing state must be equal. The same holds for the parities $\Pi$ (given as the product of the single-electron parities) of the initial and autoionizing states.

In the case of dielectronic recombination, the autoionizing state may be approximately described by a single configuration state function. For example, for C-like ions initially in their ground state, $|\Psi_i\rangle = |1s^22s^22p_{1/2}^1\rangle$, the $K$-$LL$ DR autoionizing states may be $|1s2s2p_{3/2}^1/22p_{3/2}^2, J_d\Pi_d\rangle$, with $J_d = \{1/2, 3/2, 5/2\}$ and $\Pi_d = +1$. This notation expresses that a configuration state function is constructed from antisymmetrized single-particle wave functions coupled to a given $J_d$ and the corresponding energy levels may be calculated by the multiconfiguration Dirac-Hartree-Fock (MCDF) approach with additional quantum electromagnetic and mass shift corrections [6, 24, 25]. The bound state wave functions obtained numerically may be used to construct continuum orbitals and the matrix elements entering Eq. (3) [6, 21, 22, 26].

The transition amplitude of the three-body interaction accounting for tri-electronic recombination into a state $|1s2s^22p_{3/2}^22p_{3/2}^1, J_d\Pi_d\rangle$ may be described in a perturbative approximation as

$$\frac{\langle 1s2s^22p_{1/2}^12p_{3/2}^3, J_d\Pi_d|V|1s2s^22p_{1/2}^12p_{3/2}^2, J_d\Pi_d\rangle}{E_{TR} - E_{DR}}$$

$$\times\langle 1s2s^22p_{1/2}^12p_{3/2}^3, J_d\Pi_d|V|1s2s^22p_{1/2}^2 J_i; J_i, J_d\Pi_d\rangle$$

Here, $E_{TR}$ and $E_{DR}$ stand for the energy eigenvalues associated with the states $|1s2s^22p_{1/2}^12p_{3/2}^3, J_d\Pi_d\rangle$ and $|1s2s^22p_{1/2}^12p_{3/2}^3, J_d\Pi_d\rangle$, respectively. Note that since the operator $V$ is a two-body operator, i.e., it only changes the occupation numbers of two single-electron states, the tri-electronic process cannot be described by first-order perturbation theory,

$$\langle 1s2s^22p_{1/2}^12p_{3/2}^3, J_d\Pi_d|V|1s2s^22p_{1/2}^2 J_i; J_i, J_d\Pi_d\rangle = 0.$$
interaction, giving rise to significant TR peaks [27]. This demonstrates that for an adequate description of resonant recombination processes, mixing effects in both the initial and intermediate states has to be taken into account.

The ratio of TR to DR amplitudes is given by the fraction in the first line of Eq. (4). At low Z, this fraction may approach unity since the electron interaction operator V acts on the strongly overlapping TR and DR state functions, and the interaction energy in the numerator lies close to the \( (E_{\text{TR}'} - E_{\text{DR}'} \) splitting. The TR capture rates may thus become comparable to the DR capture rates. Because of this, it is necessary to treat the trielectric process non-perturbatively: the autoionizing state formed by the trielectric process is described as the linear combination

\[
|\text{TR}| = c_1|1s2s^22p_{1/2}2p_3^1, J_d\Pi_d) + c_2|1s2s^22p_{1/2}2p_3^2, J_d\Pi_d), \tag{6}
\]

and the autoionizing state populated by dielectronic capture is represented as

\[
|\text{DR}| = \tilde{c}_1|1s2s^22p_{1/2}2p_3^1, J_d\Pi_d) + \tilde{c}_2|1s2s^22p_{1/2}2p_3^2, J_d\Pi_d). \tag{7}
\]

The expansion coefficients may be obtained by diagonalizing the total Hamiltonian of the system in a configuration interaction approach or by the MCDF method.

Note that in equations (6) and (7), the first configuration is not necessarily the dominant one; this holds only true in the high-Z limit where the \( jj \)-coupling scheme is applicable. The question may arise whether it is meaningful to define the number of electrons excited in a correlated many-electron shell, which may be described by strongly mixing configurations in the low-Z limit. We find that, since a state such as (6) contains two electronic holes, one in the \( K \) shell and one in the \( L \) shell, which may both decay separately by photon emission, the process leading to its population can indeed be termed as trielectric recombination.

Equations (6) and (7) may be easily extended to the case when 3 or more levels sharing the same \( J_d\Pi_d \) quantum numbers are energetically close. Correlation effects may be accounted for more accuracy by including further configurations of the same symmetry \( J_d\Pi_d \) in a multiconfiguration approach.

### III. EXPERIMENTAL PROCEDURE

Resonant recombination was experimentally investigated by using electrons as projectiles and HCl as targets. The target ions are produced and confined in an EBIT by electron impact ionization of neutral target atoms. Electron beams with currents of 50 to 200 mA compressed to typical diameters of around 50 \( \mu \text{m} \) by a magnetic field of 6 to 8 T ensured a high current density in the reaction volume and thus a high ionization rate. This current density leads to a negative space charge potential that confines the positively charged ions in the radial direction around the electron beam axis. An arrangement of drift tubes allows for generating a potential well to trap the ions in the axial direction. This basic principle of an EBIT is displayed in Fig. 2.

Projectile electrons are provided by the monoenergetic electron beam of the EBIT. Its energy is controlled by the voltage difference between the cathode of the electron gun (\( V_{\text{cath}} \)) and the central drift tube surrounding the reaction volume (\( V_{\text{DT}2} \)). The variable bias acceleration voltage \( V_{\text{DT pot}} \) is applied to all drift tubes, while keeping the ions trapped within a potential well of constant depth determined by the potential difference between the central drift tube and its immediate neighboring electrodes. We have used the FLASH-EBIT [17] for the Ar and Fe experiments and the Heidelberg EBIT [14] for the Kr measurements. The experimental procedure was the same in both devices.

For the experiments, we follow the widely applied scheme described in Ref. [25]. Here, we slowly vary the electron beam energy across a range of interest in a saw-tooth ramp with a slow slew rate of 2 V/s in order to ensure steady-state conditions. Recombination involving \( K-L \)-excitation was monitored by measuring the characteristic \( K \) x-ray photons that are emitted by radiative stabilization of the \( K \)-hole excited state formed by resonant electron capture. At specific electron energies, an enhancement of \( K \)-photon emission indicates a photocombination resonance. A high-purity germanium x-ray detector is pointed at the reaction volume side-on with respect to the electron beam through a 250-\( \mu \text{m} \) thick beryllium window. For the photon energy range of interest
(from 2 to 14 keV) this window is nearly transparent.

A two-dimensional intensity plot in dependence of the electron beam energy and the emitted x-ray photon energy is displayed in Fig. 3a (top panel). The electron recombination resonances appear as bright spots. In this figure, an overview of resonant recombination processes with $K$-shell excitation in He- to O-like Ar is presented, showing both the $K$-$LL$ region this paper is focused on, and resonances for $K$-$LM$, $K$-$LN$, ..., etc. recombination processes. These resonances involving the $K$-shell and a higher-shell can also be seen as bright spots in the $K\beta$ photon energy region. In addition, $K$-$MM$ resonances can be identified at electron beam energies around 3.25 keV. The projections shown below in Fig. 3b (bottom panel) represent the $K\alpha$ emission ($K\alpha$ cut) and $K\beta$ and higher emission as a function of the electron energy.

For the investigation of weak resonances, a good resolution on the electron energy is a prerequisite for separating them from stronger lines. In an EBIT, the resolution in recombination measurements is limited by the energetically broadened electron beam 29 30. Earlier experiments used low electron beam currents for minimizing the absolute space charge potential, its width, as well as the ion heating caused by electron impact 30. However, a low beam current leads to a strong reduction of the ion production rate and also to a diminished recombination rate.

In our experiments we improved the resolution by forced evaporative cooling in combination with electron beam currents sufficient for an efficient ionization and abundant recombination yield. This was realized by lowering the axial potential applied to the drift tubes. To compensate a remaining trap generated by the space charge potential of the drift tubes having different diameters 30 31, a positive offset voltage has to be applied to the central drift tube referring to the surrounding ones. Under these settings, only a cold ion ensemble remains in the trap and the measurements can be performed with relatively high electron beam currents.

With this method, the resolution, defined as the ratio of the FWHM width to the space charge, was improved by roughly a factor of 5 in comparison with the common measurement scheme 31. Fig. 4a demonstrates this advantage for two strong adjacent DR resonances in C-like...
Kr ions, namely, the \((|1s2s^22p_1^2\rangle|(2p_3^2)\rangle|\frac{5}{2}/2,3/2_{+1/2}\rangle|\) lines. The resolution (full width at half maximum, FWHM) of the resonance with \(J = \frac{5}{2}\) is plotted versus the voltage of the central drift tube with respect to the outer ones at an electron beam current of 200 mA. The former unresolved lines become clearly separated at the optimized point of cooling. In Fig. 5b, a very well resolved recombination spectrum allows for both a clear separation of charge state-specific resonances and the observation of otherwise blended weak features.

IV. RESULTS AND DISCUSSION

We investigate the \(K-LL\) energy region of resonant recombination into the He- to O-like charge states of Ar, Fe and Kr ions in order to gain insight in the \(Z\)-behavior of resonance energies and strengths and systematic studies of higher-order processes. In an EBIT, different charge states of an element are stored simultaneously. By using a constant strong injection of neutrals, the charge state distribution can be made sufficiently flat in order to make recombination resonances from He- to O-like ions appear together in the spectra. The high resolution allows for a good separation of the resonance groups for different ionic species, as indicated in Fig. 5 by bars above each spectrum.

In this figure, we show the recombination spectra of the investigated ions in the specified energy region. We calibrate the electron energy scale by taking the predicted values of two well-separated resonance lines of He-like ions which have small theoretical uncertainties. In the case of Ar it was possible to use two strong resonances from the \(K-LL\) and \(K- LM\) regions. In order to account for the \(Z\)-dependence of the resonance energies, the energy scales of the spectra are normalized by multiplying with a factor \(1/Z^2\) (Rydberg scaling).

The curves shown in Fig. 5 display resonance energies, and relative resonance strengths, as well as the respective \(Z\) dependences. In the normalized representation given, the \(Z\)-dependences of the resonance energies (beyond the dominant \(Z^2\)-dependence) can be seen.

In Fig. 6 we compare our recombination spectra for the astrophysically relevant Fe ions with our theoretical predictions, where the abundances of the different charge state fractions have been adjusted to match the measured ones.

In general, a very good agreement both in the position of the resonances relative to those of the calibration resonances of He-like ions, and in (relative) resonance strengths can be stated. This strengthens our confidence on the reliability of the calculations also for the higher-order resonances, which we identify based on their predicted energy values.

Contributions from TR resonances can clearly be seen in Fig. 6 as well as in Fig. 5 for initially B-like, C-like, and N-like ions around 4.88, 4.95, and 5.04 keV, respectively. The DR spectrum for Li-like ions is especially rich and broad for \(K-L\) excitation since not only the 2\(p\) levels are accessible but also the 2\(s\) level has a vacancy. According to the calculations, TR resonances from Li-like ions are hidden under the strong DR lines of the Be-like sequence.

Beyond the lowest-order \(Z^2\)-scaling of the binding energy, we have to consider the electron-electron interaction decreasing with \(Z^{-1}\) in importance relative to the central Coulomb force, and relativistic effects increasing rapidly with \(Z^4\) for heavy ions. For the heavier species, the influence of the latter is dominant. The range of ions studied here is characterized by a transition from the electron correlation-dominated range to one dominated by relativistic effects, leading already here to a large fine-structure splitting. Hence, for the heavier system of Kr, and, to some extent also for Fe, we find more lines resolved in the spectra. For the measurement with Ar ions, the resonances within one charge state overlap more strongly, and despite the high experimental abso-
FIG. 6: (Color online) Comparison of the Fe photorecombination spectrum with our theoretical predictions. To show weak details, a 20-fold magnified spectrum is also displayed. On the top, the resonances belonging to different recombination orders are indicated separately, and are color-coded according to their He-like to O-like charge states.

Absolute resolution of only about 5 eV they can be barely resolved. In comparison to the transition energies, the relative resolution is roughly equivalent to the absolute one of 13 eV seen in the case of Kr as the heaviest considered element.

In Fig. 7 we show the $Z$ dependence of the relative resonance energies for the strongest recombination lines of initially He-like to O-like ions. The curves normalized by $Z^2$ are based on our theoretical values including electron-electron correlations. These spectra show clearly the transition region, from the strong electron-electron interaction at low $Z$ to the increased relativistic influence at higher $Z$. These trends are confirmed experimentally, as spectra for Ar, Fe and Kr overlaid to the graph in Fig. 7 demonstrate.

We now discuss the resonance strengths of C-like ions, which among all isoelectronic sequences with an open $L$ shell are expected to have the strongest TR contributions. The occupation rules – partially also in combination with parity rules (cf. Section II) – allow for several resonances. With initially four vacancies in the open $L$-shell and with two $2s$ as well as $2p$ electrons, many possible excitation as well as relaxation channels for TR processes appear. In contrast, the B-like sequence has a smaller number of excitable electrons, and N-like ions contain less vacancies into which excitation can occur. For the Li-like sequence there is only one $2s$ electron left for the additional intra-shell excitation in TR. These differences in the recombination strengths of TR in different ionic sequences are also illustrated below in Fig. 11.

The region of interest of the recombination spectra for the C-like isoelectronic sequence is enlarged in Fig. 8.

The resonance areas for DR and TR are indicated in full blue and red, respectively. For Kr the spectrum is equivalent to our data from [10], with the two prominent DR double lines for C-like ions (at 7.27 and 7.28 eV/$Z^2$) followed by the double DR line for N-like Kr ions (at 7.36 and 7.37 eV/$Z^2$). In between (at around 7.32 eV/$Z^2$) we find the faint structure for C-like TR process contributing in total only 6% to all the resonant recombination processes in this C-like case.

Proceeding down in $Z$ to the Fe ions, the importance of electron-electron interaction increases and, correspondingly, TR can be expected to be more important there. For C-like Fe ions we find the $K$-$LL$ DR double line at 7.28 and 7.30 eV/$Z^2$ and the $KL$-$LLL$ TR double line at 7.32 and 7.34 eV/$Z^2$; however, the relative TR contribution increases already dramatically to about 50% of the DR contribution [11]. Continuing further down in $Z$ to Ar, the doublets for C-like ions are not any more resolved experimentally due to the reduced fine structure splitting of the contributing different $j$ components – see the broad $K$-$LL$ DR line at 7.37 eV/$Z^2$. The stronger line around 7.42 eV/$Z^2$ corresponds to the higher-order $KL$-$LLL$ TR process of C-like Ar ions. Here, the TR process overwhelms already the corresponding first-order $K$-$LL$ DR by a factor of about 1.5. This strong effect shows how higher-order electron-electron correlation can surpass the (intuitively stronger) first-order process [11].

The resonance energies for ions as a function of the atomic number $Z$; the resonance energies are normalized by $Z^2$. The calculations are described in Section II. Experimental values from the measured spectra for $Z=18, 26, 36$ (Ar, Fe, Kr, respectively) appear as dots overlaid in gray. Trielectronic recombination resonances are marked by dashed lines.
FIG. 8: (Color online) Partial magnified spectrum showing photorecombination resonances of Be-like to N-like ions of Ar, Fe, and Kr. DR, TR and QR processes are marked for C-like ions.

In order to understand this unexpected increase in the relative importance of the higher-order process of TR at low \( Z \) compared to DR, one has to consider the absolute resonance strength. Following the general formula [1], it can be described as the product of the Auger rate responsible for the population of the excited intermediate state and the fluorescence yield determining its decay to the final state. The fluorescence yield is determined by the ratio of the radiative decay rate to the total decay rate, which is the sum over all possible radiative and Auger channels.

The calculated \( Z \)-scalings for the contributing parameters for selected DR and TR resonances in initially C-like ions are sketched in Figs. 9 and 10. Resonances with total angular momenta \( J = 5/2 \) and \( J = 3/2 \) have been selected for demonstration; note that DR and TR states may mix with each other within a set of levels possessing the same \( J \). The radiative rates (b) increase generally with \( \Gamma^r \alpha Z^4 \) (see, e.g. [2] or the overview in [32]), whereas the normal (two-electron) Auger rates (c), relevant for DR, are almost \( Z \)-independent, \( \Gamma^a_{2e} \propto Z^0 \). Relativistic wave function and Breit interaction corrections introduce terms scaling with even powers of \( Z \) at higher charge numbers [33]; however, these are not of relevance for the light and medium-heavy elements where higher-order recombination processes are observable.

For high \( Z \) values, in the case of DR, the fluorescence yield is dominated by the radiative decay and thus it approaches unity, whereas for small \( Z \) it is governed by the Auger rate, see Fig. 9a. Following Eq. [1] and including the phase-space factor \( 1/p^2 \approx 1/(2E) \), this yields the following scaling law for the strength [34, 35]:

\[
S_{\text{DR}} \propto \frac{Z^2 Z^0}{a_1 Z^4 + a_2 Z^2} = \frac{1}{a_1 Z^2 + a_2 Z^{-2}}. \tag{8}
\]

Thus, in a simple nonrelativistic approximation, the DR strength is roughly proportional to \( Z^2 \) at low atomic numbers, decreases for high \( Z \) with \( 1/Z^2 \), and it is almost constant in the mid-\( Z \) region.

In a similar way, scaling laws may be derived for the higher-order resonances. The \( Z \)-dependence of the contributing parameters for the TR processes are shown as dashed lines in Figs. 9 and 10. The Auger rates caus-
The perturbative factor in the first line of Eq. (4) introduces an additional scaling factor of $1/Z$ to the transition amplitude of TR, therefore, the three-electron Auger rates (and the TR capture rates) decrease approximately as $\Gamma_{\mathrm{a,4e}} \propto Z^{-2}$ at high $Z$ values. This three-electron Auger rate has also to be taken into consideration in the calculation of the total decay rate, and thus the $Z$-scaling of the TR resonance strength follows the parameterization:

$$S_{\mathrm{TR}} \propto \frac{1}{Z^2} \frac{Z^4 Z^{-2}}{b_1 Z^4 + b_2 Z^0 + b_3 Z^{-2}} = \frac{1}{b_1 Z^4 + b_2 + b_3 Z^{-2}}. \quad (9)$$

At higher atomic numbers, the TR resonance strength decreases as $\propto Z^{-4}$, i.e., significantly faster than the DR strength, therefore, the TR process can hardly be observed in heavier ions.

Independently on that feature, at low $Z$ values, the second-order Auger rate responsible for TR is comparable to or larger than the first-order Auger rate corresponding to DR (see the case with $J = 3/2$ in Fig. 10(c)). The rate for radiative decay following trielectronic capture may also be larger than the corresponding radiative decay rate for DR (Fig. 10(b)), resulting in a TR resonance stronger than DR. In some cases, e.g., in $J = 5/2$ resonances in initially C-like ions, the three-electron Auger rate may even be weaker than the two-electron Auger rate (see Fig. 10(b)), yet the larger radiative rate overcompensates this and yields a higher strength for TR than for DR.

In the present experiments the total absolute resonance strengths are not accessible directly. However, the calculated ratio of the strength of TR and the corresponding DR process within a single ionic sequence can be compared with the measurements, see the top panel of Fig. 11. As discussed above, for low $Z$, the importance of TR increases and for C-like ions TR dominates over the DR process for $Z < 20$. The sequence for B- and N-like ions shows a similar behavior, but for these charge states TR does not have a dominant influence on the total recombination yield. For Li-like ions, TR contributes only little to the recombination because of the limited number of excitation channels: only one electron is available in the $L$ shell to be excited simultaneously with a $K$-shell electron.

One can state for the TR/DR strength ratio an excellent agreement between our experimental findings and our calculations. This is not only true for the $Z$-dependence of the strength ratio, but holds also for the dependence on the ionic sequence. In the bottom panel of Fig. 11 we display for Li- to N-like Fe ions the corresponding strength ratio TR/DR including also the ratio QR/DR.

For Fe ions, the nuclear charge $Z$ is low enough to show sizable contributions of higher-order resonances and high enough to ensure a good resolution of the resonance spectrum. The QR/DR strength ratio seems also be confirmed within the experimental uncertainty by the calculations. Although the statistics for QR are insufficient for a precise determination of resonance energies, the spectrum shown in Figs. 6 and 8 shows an obvious indication of QR resonances. Our calculations and the experimental findings agree convincingly well (see the correspondingly marked resonance in Fig. 6). The faint structures seen around an electron energy of 4.980 keV correspond thus to QR in both C- and Be-like Fe ions.

An approximate scaling law for QR may be derived in an analogous manner to that found for TR, using similar considerations for the four-electron Auger rate ($\Gamma_{\mathrm{a,4e}} \propto Z^{-4}$):

$$S_{\mathrm{QR}} \propto \frac{1}{Z^2} \frac{Z^4 Z^{-4}}{c_1 Z^4 + c_2 Z^0 + c_3 Z^{-2} + c_4 Z^{-4}} = \frac{1}{c_1 Z^4 + c_2 Z^2 + c_3 + c_4 Z^{-2}}. \quad (10)$$

FIG. 10: (Color online) Same as Fig. 9 but for $J = 3/2$ resonances in initially C-like ions. These quantities are given for the case of the $1s2s^22p_{1/2}^1(2p_{3/2}^1)$, $J = 3/2$ DR resonance (straight blue line) and the $1s2s^22p_{1/2}^12p_{3/2}^1$ (TR$_1$, dashed red line) and $1s2s^22p_{1/2}2p_{3/2}^3$ (TR$_2$, dotted red line) $J = 3/2$ TR resonances.
FIG. 11: (Color online) Higher-order TR contributions relative to the corresponding DR resonance strengths as functions of the atomic number $Z$ for Li-like to N-like ionic species. The calculations are compared with the experimental results. (Full gray points are calculated ab initio, dashed curves show interpolations; experimental data points show error bars.) For Fe ions, the strength ratios TR/DR and QR/DR for different charge states are given in the bottom graph.

Here, we have taken into account that autoionizing states formed by quadruelectronic capture may decay by two-, three- or four-electron Auger processes. The QR resonance strength diminishes for high $Z$ even faster than the strength of TR, namely, as $\propto Z^{-6}$. However, its experimental signatures have become measurable, and a systematic study of the interesting isoelectronic sequences as a function of $Z$ could provide better insight into the complex mutual interactions of same-shell electrons, beyond what is possible by studying the single neutrals giving name to those sequences.

V. CONCLUSIONS

Unexpected large contributions of higher-order electronic recombination processes have been found for inter-shell $K$-$L$ excitation. For these processes, high momenta are exchanged during recombination and hence, large contributions from higher orders are generally not expected. As shown, the second-order resonant electron recombination process, TR, may even overwhelm the strength of the first-order DR process, as observed in the case of C-like Ar, cf. Fig. 11. In most cases, the second-order TR process contributes about 10% to the total electronic recombination cross section, and its relative contribution decreases with increasing $Z$. Even the third-order process, QR, was clearly identified, contributing typically a few % of DR.

These novel findings on the importance of higher-order processes in resonant inter-shell electronic recombination were made possible by enhanced energy resolution and good experimental statistics, both points being achieved by evaporative axial cooling of the trapped ions.

Beyond the obvious $Z$ trends seen in the resonance energies and caused by the balance between electron correlation and relativistic effects, strikingly apparent higher-order electron-electron correlation effects are found at lower atomic numbers. Here, the strength of higher-order recombination processes can surpass that of the corresponding first-order DR process [11].

Since the inter-shell $K$-$LL$ photorecombination process is a far more efficient cooling mechanism in high-temperature plasmas than intra-shell processes, due to the much higher energy of the emitted photons, a good knowledge of its energy-dependent cross section is essential. Therefore, hitherto neglected contributions from higher-order effects to electron recombination, and especially of the second-order, the trielectronic channel, have to be taken into account. Plasma simulations used for modeling fusion devices or astrophysical matter have to include them for improved accuracy. The presence of sizable TR resonances has implications for the opacity and energy transfer inside the radiative zone of stars, and for the temperature and ionization equilibrium of those and other astrophysical plasmas. Models not considering these higher-order effects in plasmas containing light-$Z$ species can therefore not describe correctly the status in a plasma. Moreover, for the time-reversed processes of resonant photoionization [30], i.e., the resonant excitation to an autoionizing intermediate state, also those higher-order processes may be of equal importance. Even beyond TR, quadruelectronic recombination has been observed for different ionic species.

Studying photorecombination in all orders of complexity, from DR to TR and QR, can become a fruitful approach for understanding more complex multi-electron processes such as shake-up and shake-off in outer shells, especially for heavier species [37, 38]. Arguably, even higher recombination orders involving more than four simultaneous electronic excitations, which are more likely
to be expected in recombination of open $M$-shell ions having many equivalent electrons and vacancies energetically closely spaced, should be investigated to learn about the stepwise buildup of a many-electron wave function. The role of relativistic corrections to the Coulomb electron interaction, i.e., the Breit interaction \cite{33,39}, in such higher-order processes is also an unexplored field. With the ion charge as a variable parameter and a constant number of electrons, isoelectronic sequences in highly charged ions are perfectly suited for this type of investigations. Furthermore, such a multi-electron behavior may also be manifested in resonant processes occurring due to the presence of neighboring atoms or ions in dense plasmas or molecules \cite{40,41}.

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