Influence of the Radiative Decay on the Cross Section for Double Excitations in Helium

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The fluorescence yield spectrum of the double excitations in helium has been measured. All three Rydberg series converging to the $N = 2$ threshold are resolved, and the intensity of the individual lines is determined. The intensity variation through each series indicates that the radiative decay channel cannot be neglected when discussing the double excitations in helium. This calls for a revision of the interpretation of the absorption spectrum, and sets the limit for using the ion yield method to monitor the absorption probability.

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The doubly excited states of helium are fundamental for our understanding of electron correlation. Consequently, they have been extensively studied ever since their discovery [1]. The pioneering synchrotron radiation work by Madden and Codling [2] revealed a photoabsorption spectrum, particularly rich in narrow structures. The complexity of the spectrum is limited only by the experimental resolution, and today the double excitation spectrum remains a challenge for the most powerful beam lines at the third generation synchrotron radiation sources [3].

The analysis of the absorption features as resonances in the cross section for photoemission [4,5] laid the foundation for the understanding of vacuum ultraviolet absorption spectra in general. The theory was based on the assumption that the doubly excited states decay by autoionization and therefore interfere with the direct photoionization channel, resulting in the characteristic Fano profiles. The radiative decay channel was tacitly neglected. This may have been justified when discussing the data from the early experiments. However, in spite of all theoretical efforts to understand later accurate measurements, the influence of the radiative channel has so far not been considered. In this paper we will show that it is essential to take fluorescence into account. It may be immediately realized that the overlap between the two electrons decreases as we go to higher Rydberg states. Therefore, the autoionization decay rate must decrease, and eventually it becomes smaller than the radiative decay rate, which is much less dependent on the electron overlap. Towards the ionization thresholds the radiative decay probability approaches unity.

Radiative decay of the doubly excited states was observed for the first time in a microwave discharge [6]. The observation of metastable neutral atoms excited below the $N = 2$ threshold by Sokell *et al.* [7] suggested an appreciable radiative decay probability for doubly excited states populated in the photoabsorption process. This was recently confirmed by the same authors [8].

Here we present the fluorescence yield (FY) spectrum of helium below the $N = 2$ threshold. We observe all three Rydberg series which are seen in the ion yield (IY) spectrum. For the lowest excitations, the FY intensity is largest for the series which are the least intense in the IY spectrum, but higher up in the Rydberg series this intensity order is reversed. Our results imply that the radiative decay channel indeed dominates at the higher excitations close to threshold, but also for the lower excitations of series with smaller excitation cross section. This has a profound impact on the interpretation of the absorption spectrum as well as on the practice of using IY spectra as a measure for the absorption cross section.

The experiment was performed at the gas phase beam line 6.2L at ELETTRA [9]. Helium gas was let in through a hypodermic needle into a differentially pumped chamber to a background pressure of 5×10^{-5} torr. The fluorescence yield was measured perpendicular to the photon beam in the plane of the polarization, using a 40 mm multisphere plate detector placed close to the interaction region to cover 10% of the solid angle. A 1000 Å polyimide filter in front of the detector surface ensured that the signal was unaffected by charged particles and metastable atoms. To facilitate the energy calibration the conventional IY spectrum was measured simultaneously in a gas cell. The resolution of the beam line was set to be 3 meV for the most intense lines, and reduced to 7 meV, to achieve a reasonable count rate during the long range scans.

The classification of the doubly excited states of He can be based on a description of the electron correlation in hyperspherical coordinates, leading to a set of correlation quantum numbers K and T [10], associated with angular correlation, and A, associated with the radial correlation.

For the three series converging to the threshold for ionizing the atom with the remaining electron in the $N = 2$ level the latter quantum number takes the values $A = +1, -1$, and 0. The $A = +1$ wave function has an antinode at $r_1 \approx r_2$ (r_1 and r_2 being the distances of the electrons to the nucleus), where the $A = -1$ wave function has a node. This gives an intuitive understanding of the higher intensity and larger autoionization rate of the $A = +1$ relative to the $A = -1$ resonances. The wave functions of the $A = 0$ states, finally, are similar to the wave functions of singly excited states.

In the following we designate the states as (n, A), where n is the principal quantum number for the highest excited electron, the lowest excited electron being in $N = 2$.

The most intense peaks in the FY spectrum are the $(3, 0)$ and $(4, -1)$ resonances (Fig. 1a), which are relatively weak in the IY spectrum. First, we note that the peaks can be fitted with symmetric Gaussian functions, representing the resolution of the monochromator.

The Fano theory for photoabsorption is based on the assumption that autoionization is the dominating decay mechanism for the intermediate doubly excited states. The final state is the ionic ground state and one electron in the continuum. Since this state can be reached also by direct photoemission, the channels interfere to give asymmetric line profiles. The alternative radiative decay channel leaves the atom in a neutral singly excited state. The fluorescence intensity can be assigned to $1s^2 \rightarrow (n, A) \rightarrow 1sn'l$ transitions, where $l = 0$ or 2 due to the dipole selection rules. In either case the final state is long lived and will only contribute to the total fluorescence intensity over cascade decay. The nonresonant inelastic scattering to the $1sn'l$ final states has a too small amplitude to be of importance. We can therefore, to a good approximation, separate the excitation and emission processes into two separate steps. This leads to the observed symmetric line shapes, and a simplification of the intensity determination. The measured intensity is proportional to the product of the probabilities for excitation and fluorescence decay.

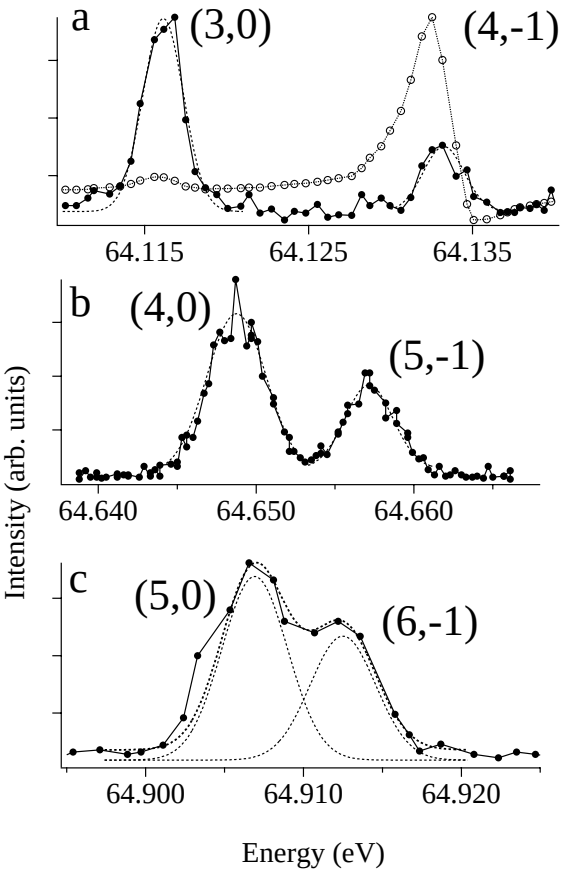

FIG. 1. (a) FY (filled circles) and IY (open circles) of the $(3, 0)$-$(4, -1)$ resonances, (b) the FY of $(4, 0)$-$(5, -1)$, and (c) the FY of $(5, 0)$-$(6, -1)$ resonances. The fits (dashed lines) are pure Gaussians with a width corresponding to the instrumental resolution.

Second, we note that the FY intensity order is reversed compared to the IY intensities. Only during the past decade has one come to an agreement regarding the energy ordering of these states, and there is still a large variation in the predictions of their relative intensities. The discrepancy between recent predictions of these intensity ratios and IY data was taken as evidence for poorly converged calculations by the theorists [11]. An alternative explanation for the lack of agreement is that the intensity ratios measured in IY do not correspond to the absorption cross section due to the competing radiative decay channel. If the fluorescence rate were of the same order of magnitude as the autoionization rate, the results in Fig. 1 would imply that the IY measurements underestimate the $\frac{(n,0)}{[(n+1),-1]}$ intensity ratio. Correction for fluorescence would bring theory and experiment into closer agreement. We will show below that indeed the fluorescence and the autoionization probabilities are of the same order of magnitude for these states.

In the $(4, 0)$-$(5, -1)$ and $(5, 0)$-$(6, -1)$ doublets (Figs. 1b and 1c), the $\frac{(n,0)}{[(n+1),-1]}$ intensity ratio decreases, and the $(6, 0)$-$(7, -1)$ doublet can no longer be resolved. The FY intensity for the consecutive double peaks decreases, and as seen in Fig. 2, the intensity of the merged series also falls with increasing n. The resonance corresponding to $(12, 0)$-$(13, -1)$ can still be discerned in the spectrum. These are the highest excited states of these series observed so far. At higher quantum numbers they cannot be separated from the $A = +1$ series. The intensity of this series increases slightly with n. For very low n there is little intensity, and we were not able to measure the intensity of the $(2, +1)$ peak. Closer to threshold, this series becomes more intense than the $A = -1$ and $A = 0$ series. When the energy spacing between the lines is so small that they can no longer be separated, a continuum of increasing intensity is observed. This intensity distribution has two maxima at 20 and 35 meV below the $N = 2$ threshold (65.40 eV). The intensity drops to a constant value at the ionization limit, where the $2p \rightarrow 1s$ transition in He^+ is observed.

We use a simple two-step model to interpret the intensity variations. The FY intensity S_n for the state n in a series

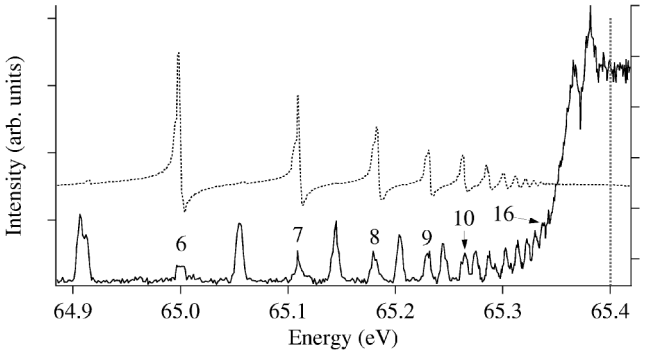

FIG. 2. FY (solid line) and IY (dashed line) spectra of the Rydberg series converging to the $N = 2$ threshold. The numbers refer to the principal quantum number of the $A = +1$ series, which is the most pronounced series in the IY spectrum. The $(n, 0)$-$(n + 1, -1)$ doublets are found on the high-energy side of the $(n, +1)$ peaks. The vertical line at 65.40 eV indicates the $N = 2$ ionization limit.

is given by

$$S_n \propto \sigma_n \times \frac{\Gamma_{f,n}}{(\Gamma_{f,n} + \Gamma_{a,n})}, \qquad (1)$$

where σ_n is the excitation cross section, and $\Gamma_{f,n}$ and $\Gamma_{a,n}$ are the rates for fluorescence and autoionization, respectively.

For high n, both σ_n and $\Gamma_{a,n}$ are proportional to $(n - \delta)^{-3}$, where δ is the quantum defect [5]. Hence, reduced quantities, $\tilde{\sigma}$ and $\tilde{\Gamma}_a$, characteristic of the whole Rydberg series, can be defined as $\sigma_n = \frac{\tilde{\sigma}}{(n-\delta)^3}$ and $\Gamma_{a,n} = \frac{\tilde{\Gamma}_a}{(n-\delta)^3}$.

We assume that $\Gamma_{f,n} = \tilde{\Gamma}_f$ is independent of n. This approximation is reasonable, since the fluorescence is dominated by the transfer of the inner electron to the $N = 1$ level. This transition is little influenced by the electron correlation. Equation (1) can then be rewritten as

$$S_n \propto \frac{\tilde{\sigma}}{(n - \delta)^3} \times \frac{\tilde{\Gamma}_f}{(\tilde{\Gamma}_f + \frac{\tilde{\Gamma}_a}{(n-\delta)^3})}. \qquad (2)$$

If $\tilde{\Gamma}_f \ll \frac{\tilde{\Gamma}_a}{(n-\delta)^3}$, Eq. (2) reduces to $S_n \propto \tilde{\sigma} \times \frac{\tilde{\Gamma}_f}{\tilde{\Gamma}_a}$; i.e., the FY intensity is predicted to be independent of n. On approaching the ionization threshold the opposite limit will eventually be reached and we have $S_n \propto \frac{\tilde{\sigma}}{(n-\delta)^3}$. Thus, a fast decrease of the FY signal with n will be observed if the radiative channel dominates the decay.

In Fig. 3 we plot the predictions of Eq. (2), together with the measured intensities. We have chosen the parameters $\tilde{\Gamma}_a = 200$, 0.35, and 0.01 meV, and $\delta = 0.18$, 0.71, and -0.25 for the $A = +1$, $A = -1$, and $A = 0$ series, respectively. These are theoretical values derived by Domke *et al.* [12]. We have set the radiative rate to $\tilde{\Gamma}_f = 6.6\ \mu$eV, corresponding to the radiative lifetime of the $2p$ state of He^+ (0.0997 ns [13]). To generate the theoretical curves in Fig. 3, $\tilde{\sigma}$ has been treated as a parameter, leading to a $\tilde{\sigma}$ ratio for the $A = +1/A = -1/A = 0$ series of 100/2.2/1.1.

This simple model accounts for most of the observed trends. Especially, it reproduces the intensity decrease

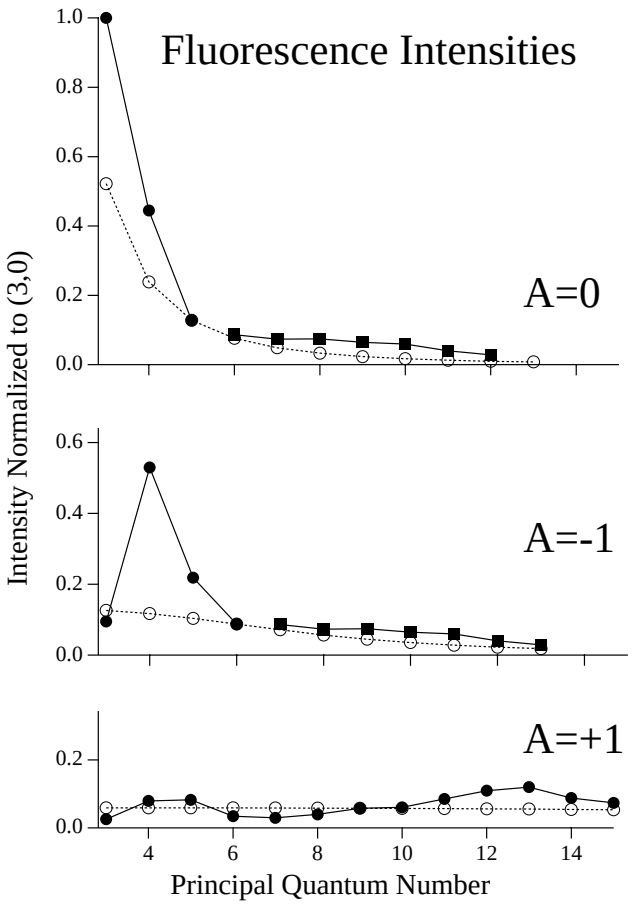

FIG. 3. FY (filled circles) intensities for the three series normalized to $(3, 0)$, and the predictions of the simple model (open circles) as described in the text. The unresolved intensities of the $A = 0$ and $A = -1$ series are plotted in both of the upper panels as filled squares.

with n in the $A = 0$ and $A = -1$ series. For the $A = 0$ series, $\Gamma_{f,n}$ is, in fact, larger than $\Gamma_{a,n}$ already at the first resonance; for the $A = -1$ and $A = +1$ series, $\Gamma_{f,n} \approx \Gamma_{a,n}$ at $n = 7$ and $n = 31$, respectively.

The fitted $\tilde{\sigma}$ ratios between the series differ significantly from what has earlier been determined (100/1.7/0.35) [12]. This suggests that the cross sections for the less probable excitations have been underestimated due to the neglect of the radiative decay channel. In IY spectra the measured peak heights decrease with increasing n. This is normally understood as an effect of the decreasing lifetime widths in combination with the limited experimental resolution [12]. According to the present result, the lifetime widths of the states approach a constant $\tilde{\Gamma}_f$ as n increases. The reason for the decreasing peak heights, with increasing n, in the IY spectra must therefore instead be directly related to the rapid decrease of σ_n.

Note that, if $\Gamma_{f,n}$ is independent of n and $\Gamma_{f,n} \ll \Gamma_{a,n}$, Eq. (1) implies that $S_n \propto q_n^2$, where q_n is the Fano parameter. The slight intensity variation in the $A = +1$ series probably shows the limit of the simple model, rather than suggesting an n dependence of q_n. When $\Gamma_{f,n} \geq \Gamma_{a,n}$, however, $\Gamma_{f,n}$ significantly influences the q

parameter. This explains why the q_n values of the first states of the $A = 0$ series measured in IY are an order of magnitude higher than the predicted values [11].

Close to threshold the resonances cannot be resolved in the FY spectrum, and we measure a continuous intensity increase. Note that this increase occurs quite far from threshold, and is not simply due to a broadened onset of emission from the $2p$ states of He^+.

For a Rydberg series at high n, the density of states is $\frac{\partial n}{\partial E} = \frac{(n-\delta)^3}{2I_H}$ which together with Eq. (2) implies that the FY intensity is proportional to $(n - \delta)^3$ as long as $\Gamma_{f,n} \ll \Gamma_{a,n}$. In the opposite limit S_n becomes independent of n. This explains the observed increase in intensity as well as the leveling off close to threshold. From the above analysis it is obvious that the $A = +1$ series is responsible for the high FY intensity close to threshold, while the intensity from the other series is negligible.

The simple theory does not, however, describe the two maxima at about 20 and 35 meV below threshold. The models used so far to describe the double excitations of helium did not aim to describe states of such high quantum numbers. Note that there are three $N = 2$ thresholds, due to the splitting between $j = 1/2$ and $j = 3/2$ which is about 700 μeV, and the smaller splitting between the $2s_{1/2}$ and the $2p_{1/2}$ states, due to the Lamb shift. Disregarding correlation, there are therefore (at least) three Rydberg series converging to these three thresholds. Here, the LS coupling scheme breaks down and the ^1P states are split over an intermediate coupling regime into jj-coupled states just below the three thresholds.

At $n \approx 30$, at about 15 meV below threshold, the splitting between the states due to correlation (as determined by the quantum defect of the three series) becomes less than the splitting due to the coupling of the angular momenta of the inner electron ($j = 1/2 - j = 3/2$). We speculate that the dip in the FY structure at about 20 meV is due to the mixing of the three series due to spin-orbit (including Darwin term and mass correction) interaction. Mixing in the $A = 0$ and $A = -1$ series would lead to a decrease in FY. The maximum just below threshold can then not be discussed in terms of the conventional correlated models, while electron correlation is less important for the character of these states.

Since the radiative decay rate limits the lifetime, the spacing between the levels approaches the lifetime broadening in the vicinity of threshold ($n \approx 120-130$, about 1 meV from threshold). Here, the states interfere to form wave packets and the fast time scale electron dynamics will be reflected in the decay spectra [14,15]. At these quantum numbers the Kepler period corresponds to the lifetime of the core hole, and a quasiclassical approach can be an appropriate starting point [16]. Presently, the resolution is too low to address these issues experimentally, but with the development of vacuum ultraviolet (VUV) interferometric techniques they may be investigated in the future.

One would expect a dip in the IY spectrum before threshold corresponding to the excitation of states which predominantly decay radiatively. At closer inspection such a structure is indeed visible in the most carefully measured IY spectra [12,17]. The intensity seems to drop at about 5% relative to the intensity just above the ionization limit. The intensity drop in the IY spectrum gives an estimate of the ratio between the cross section for exciting highly excited Rydberg states and direct photoionization. This ratio approaches the ratio between the cross sections for ionization to $N = 2$ and $N = 1$, just above the $N = 2$ threshold, which is about 10% [18].

In conclusion, the fluorescence yield spectrum of the double excitations in helium below the $N = 2$ threshold reveals several new aspects of this prototype system. The radiative decay channel competes significantly with the autoionization channel. This has a profound impact on the theoretical description and the interpretation of earlier experimental results.

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