Experimental confirmation of photon-induced spin-flip transitions in helium via triplet metastable yield spectra

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Doubly excited states below the $N = 2$ ionization threshold are populated by exciting helium atoms in a supersonic beam with monochromatized synchrotron radiation. The fluorescence decay of these states triggers a radiative cascade back to the ground state with large probability to populate long lived singlet and triplet helium metastable states. The yield of metastables is measured using a multichannel plate detector after the beam has passed a singlet-quenching discharge lamp. The variation of the yield observed with the lamp switched on or off is related to the triplet-singlet mixing of the doubly excited states.

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I. INTRODUCTION

The realization that the radiative decay channel is important for a detailed understanding of the photoabsorption spectrum of helium [1–4] generated a lot of attention during the latest decade [5–12]. It was demonstrated that it is essential to go beyond the LS coupling scheme to understand the fluorescence yield (FY) spectra close to the $N = 2$ thresholds, and new Rydberg series [13,14] of doubly excited states were observed. Whereas earlier only the three LS allowed Rydberg series below the $N = 2$ thresholds had been observed, now three of the four predicted triplet-dominated series could be clearly resolved in metastable atom yield (MY) spectra [13].

The formation of metastable atoms is linked to the radiative decay of the doubly excited states to singly excited final states below the ionization limit. These states will cascade radiatively, and the atom may end up in metastable $2\,^1S$ and $2\,^3S$ states, which are easily detected. As crucial properties of singly excited states in the cascades, e.g., fluorescence decay rates and triplet-singlet mixing, are very well known, the population of triplet metastable states can be related to the LS coupling in the doubly excited states. Thus, the yield of metastable triplets strongly depends on the triplet-singlet mixing in the doubly excited states.

In the experiment we use a supersonic beam of helium atoms, which are excited to $2lnl'$ states by monochromatized synchrotron radiation. After radiative cascades to metastable states, the atom beam passes a singlet-quenching helium discharge lamp [15]. Thereby the singlet states are depopulated and the remaining $2\,^3S$ excited atoms are detected downstream in a multichannel plate detector. By comparing the total MY spectrum and the quenched MY spectrum consisting mainly of triplet metastables (TMY), the singlet or triplet character of doubly excited states is demonstrated, and the contrast between the two signals reveals the magnitude of triplet-singlet mixing in the doubly excited states.

II. EXPERIMENT

The measurements were done at the Gas Phase Photoemission beamline at ELETTRA [16]. We used a supersonic beam and a metastable atom detector placed 0.37 m from the interaction region (Fig. 1). The large distance reduces the background due to photons and ions emanating from the interaction region. The detector consists of a stack of three multichannel plates with the front surface at a negative potential of −2750 V. After the interaction region the atom beam passes through a singlet-quenching helium discharge lamp. Infrared radiation from this lamp induces efficiently the $2\,^1S \rightarrow 2\,^1P$ transition, which is followed by $2\,^1P \rightarrow 1\,^1S$, thereby removing singlet metastables from the beam [15]. The discharge lamp is made of 1-cm inner-diameter Pyrex glass and stainless steel electrodes. The cathode is a water-cooled hollow cylinder. The length of the lamp along the atom beam is 60 mm, and it is run at a current of 36 mA and a voltage of −800 V. The helium gas pressure in the lamp is adjusted for maximum performance and we estimate it to be around 1 mbar. To maximize the efficiency, the radiation source is surrounded by an aluminum foil reflector. The concentration of singlet metastable atoms in the beam is expected to decrease exponentially, $I = I_0 \exp[-\phi\sigma d/v]$, where ϕ is the photon flux, σ is the absorption cross section, d is the path length through the radiation field, and v is the speed of the atoms. The attenuation is estimated by measuring the effect of the lamp on the $3^0/4^-\,^1P$ doublet intensity, which is derived almost entirely from singlet metastables (Fig. 2). Under the conditions of stable photon flux we have found that $I/I_0 \approx 0.10$.

The measured relative intensity in metastable spectrum is very well reproduced by propagating the cascade decay of initial population of the singly excited state as given by complex rotation with Sturmian basis (CRSB) theory [9] toward the singlet metastable state for each of the two resonances. In this case the multiconfiguration Hartree-Fock (MCHF) result [7] differs considerably from the experimental data, mainly due to underestimation of $3^0/4^-$ relative fluorescence decay probability directly into the final singlet metastable state.

III. RESULTS

In Fig. 3(b) we present both the quenched and the normal MY spectra measured in the $65.1 < h\nu_1 < 65.3$ eV energy range. We use a simplified notation, which originates in the first-order description of doubly excited states: $(2snp + 2pns)$, $(2snp - 2pns)$, and $2pnd$ are denoted $n^+\,^1P$, $n^-\,^1P$, and $n^0\,^1P$, respectively. These three odd-parity LS series are

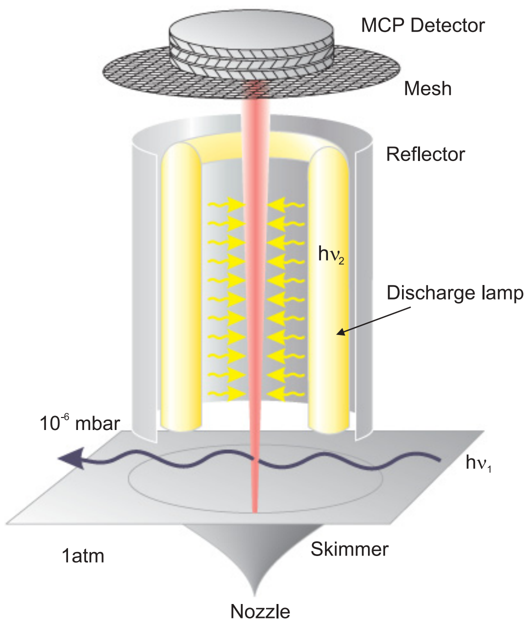

FIG. 1. (Color online) Schematics of the experimental setup. A nozzle and a skimmer make a well-defined supersonic beam with essentially collision-free conditions. $2lnl'$ states which are excited by the synchrotron radiation $h\nu_1$ rapidly decay to $1snl'$ states which further decay to metastable $2\ ^1S$ and $2\ ^3S$ states. When passing close to the discharge lamp the $2\ ^1S$ states are quenched by the lamp radiation field $h\nu_2$, and the remaining MY is monitored by the MCP detector.

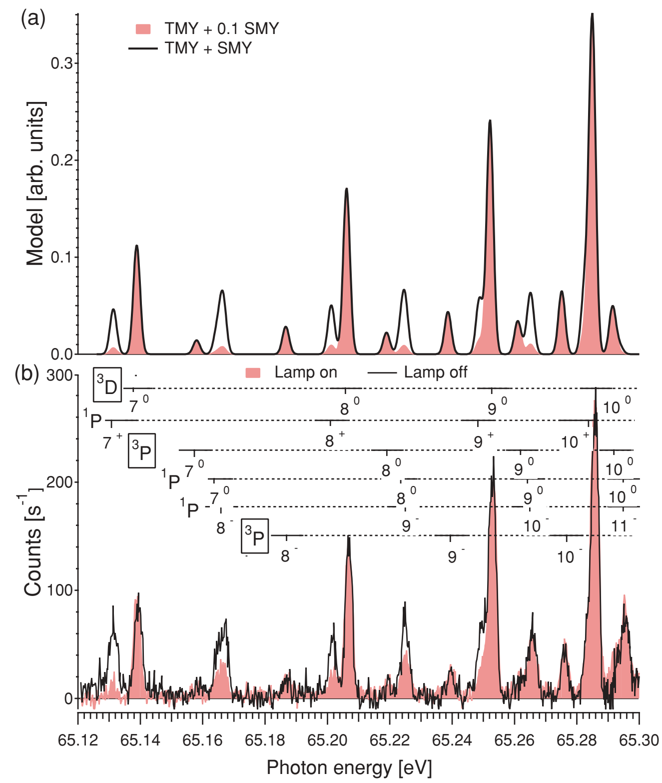

FIG. 3. (Color online) (a) Calculated and (b) measured spectra of He metastables with lamp on (fill to zero) and lamp off (line). TMY and SMY denotes triplet and singlet metastable yield, respectively.

the only ones allowed in the nonrelativistic dipole approximation, and they were observed in the absorption spectrum [17] before the radiative decay channel was considered. The spin-orbit (SO) mixing provides dipole component for four additional $J = 1$ odd parity series. They are denoted with the dominating LS term and the correlation superscript in an analogous way: $n^{+}\ ^3P$, $n^{-}\ ^3P$, $n^0\ ^3P$, and $n^0\ ^3D$. The

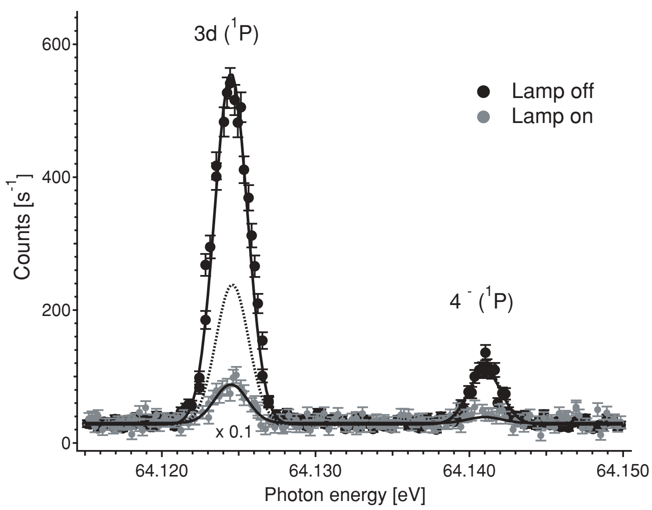

FIG. 2. A metastable spectrum in the region of $3^0/4^-\ ^1P^o$ resonances. Two model results are given: MCHF [7] (dotted line) and CRSB [9] (full lines). The theoretical spectra are normalized to the 4^- peak in the spectrum recorded with the lamp off. To coincide with the spectrum recorded with the lamp on the CRSB theory is multiplied by 0.1, as indicated.

latter three series were observed in MY spectra [13,14], in general agreement with theoretical predictions [7]. All six series which have earlier been observed are clearly visible in Fig. 3(b). In general we note that the states with singlet character are mostly attenuated by the discharge lamp in accordance with our expectations.

The $n^0\ ^3D$ series gets the most MY intensity in this energy region, and the peak intensity increases monotonically with n in the $7 \leqslant n \leqslant 10$ range. The states in this series mostly cascade to triplet states, and for $8^0\ ^3D$ the singlet-triplet branching ratio is around 10^{-5} [7]. Therefore we assume that the quench lamp does not affect this series and normalize the experimental spectra to each other accordingly. The validity of the assumption that the states in the $n^0\ ^3D$ series are unaffected by the quench lamp is supported by the fact that a normalization is found for which the spectra coincide at all the resonances in the series.

Immediately at the low-energy side of the $n^0\ ^3D$ resonances we find the $n^{+}\ ^1P$ states, which are the dominant resonances in the absorption spectrum. The peak intensity is fairly constant in this small n range. For this series, the dependence on the quench lamp is dramatic; the resonances in this series are strongly attenuated. The attenuation efficiency decreases with n so that the $7^{+}\ ^1P$ is consistent with decays to singlets only, considering the quenching efficiency (90%) in the present experiment, whereas there is only a small observable attenuation for the $10^{+}\ ^1P$ resonance as it has merged with $10^0\ ^3D$ state. This observation is in accordance with the prediction that 10 times more singlets than triplets are populated via $8^{+}\ ^1P$ excitations and that this ratio is rapidly decreasing with n.

The remaining LS allowed series, $n^{-}\,{}^1P$ and $n^0\,{}^1P$, are close in energy and cannot be resolved in the present experiment. We note that the attenuation by the quench lamp is strongly n dependent; while the $7^0/8^{-}\,{}^1P$ doublet is attenuated by roughly 50%, the $9^0/10^{-}\,{}^1P$ doublet does not seem to be affected by the quench lamp at all. This indicates a steep increase in triplet or singlet mixing through these series, and, intriguingly, the $9^0/10^{-}\,{}^1P$ resonances seem to decay dominantly to triplet metastables. Although such a steep variation is indeed predicted, the theoretical singlet-triplet population ratio is much too large to account for the observed lack of attenuation [7]. The two rather weak $n^{-}\,{}^3P$ and $n^0\,{}^3P$ series do not seem to be affected by the quench lamp, in accordance with the prediction that the triplet branching ratio should be 5–6 orders of magnitude larger than the singlet branching ratio.

In Fig. 3(a) we take the previously reported singlet and triplet metastable cross sections [7] to reproduce the measured MY spectrum with and without the singlet quenching. Since the cross sections are calculated only up to $n=8$, we have extrapolated the results to $n=10$ to cover the experimental data range. The resonance energies are assigned to precise values, calculated by CRSB in the nonrelativistic approximation [18]. The power law extrapolation n^a with $a\,\approx\,3$ was employed to estimate TMY under the odd parity $n^0\,{}^1P$, $n^{-}\,{}^3P$, $n^0\,{}^3P$, and $n^0\,{}^3D$ resonances for $n>8$ while $a\approx 6$ was found suitable for extrapolation of TMY for $n^{\pm}\,{}^1P$ resonances. The difference stems from the fact that autoionization decay rate for the latter states is much larger than their fluorescence decay rate. As argued by Penent *et al.* [14], the admixture of $n^0\,{}^3D$ state in an unperturbed LS state $n^{+}\,{}^1P$ due to the SO interaction is proportional to n^6, and the same dependence is displayed by TMY since the n^{-3} dependence of the photoionization cross section cancels out with n^{-3} dependence of the $n^{+}\,{}^1P$ autoionization rate. The $n^{+}\,{}^3P$ series was not detected at present since its large autoionization probability redirects its decay strengths from the metastable channel. Apart from using the precise energies of doubly excited states, the metastable signal of the $n^0\,{}^3D$ states in Fig. 3(a) is scaled down by a factor of $(\Delta\epsilon_n/\Delta E_n)^2 \approx 0.66$. Namely, we note that $n^{+}\,{}^1P - n^0\,{}^3D$ energy separation ΔE_n is overestimated by MCHF with respect to the CRSB value $\Delta\epsilon_n$ which, according to the first-order perturbation theory, leads to an overestimation of the spin-orbit mixing of the pair. No similar correction could be applied to other triplet resonances since they are mixed by several more distant neighboring singlet states with comparable strengths, although it is likely that in this case too, the spin-orbit mixing is overestimated in the MCHF model.

The agreement between the model and experimental data in Fig. 3 is relatively good, apart from the fact that much less quenching is observed for higher-lying $n^0/(n+1)^{-}\,{}^1P$ resonance pairs; the metastable signal for $n=10$ pair of singlets is practically not affected by the lamp-on or lamp-off condition similar to the dominantly triplet resonances, while the $n^{+}\,{}^1P$ resonances are quenched strongly as expected. Such behavior may be explained by the effect of SO mixing in singly excited states which causes "leaking" of singlet intensity into the final triplet metastables (Fig. 4). As the $n^{+}\,{}^1P$ resonances most probably populate $n\,{}^1S$ states while the $n^0/(n+1)^{-}\,{}^1P$ pair mostly populates $n\,{}^1D$ singly excited states in the first step of the radiative cascade [7], one expects a larger effect in the latter case, because the SO mixing of $n\,{}^1L$–$n\,{}^3L$ is stronger for higher angular-momentum states. The precisely calculated singlet-triplet mixing coefficients α_L are reported by Drake [19]. They are of the order of 0.00025, 0.01, and 0.5 for the P, D, and F states, respectively, and for $L>3$ the mixing is essentially complete ($|\alpha_L| \approx 1/\sqrt{2}$). We have propagated the radiative cascade decay of specific initial population of singly excited states for several high-lying resonances with and without taking into consideration the SO mixing in singly excited states. The difference is clearly seen in Fig. 5, where the measured lamp-on or lamp-off metastable signals are

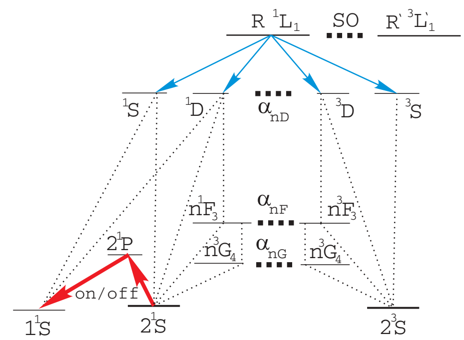

FIG. 4. (Color online) Radiative cascade scheme of a doubly excited state R started by primary fluorescence [thin (blue) arrows] and ending in the ground or metastable states of helium. Dots denote the SO interaction in doubly and singly excited states (α_{nL}). The weak dotted lines indicate possible start and end points for cascades. The switchable singlet metastable quenching transition is denoted by thick (red) arrow.

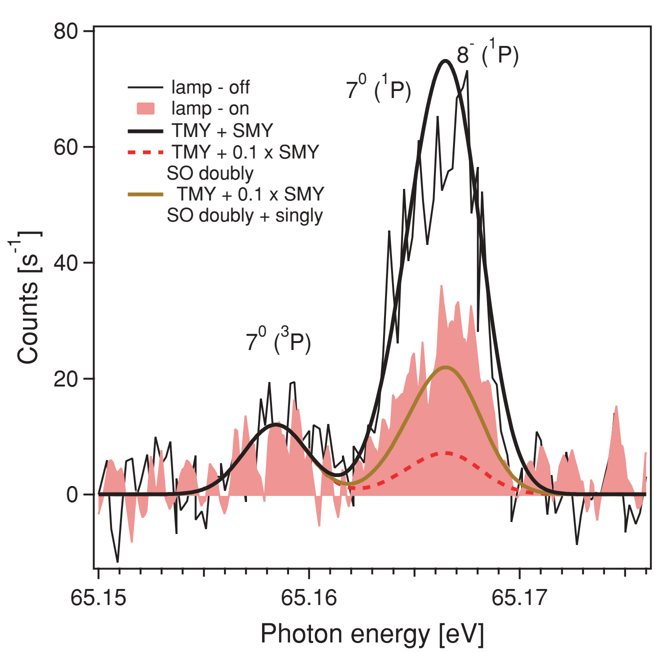

FIG. 5. (Color online) A region of experimental metastable spectra in comparison with the model result for lamp-on or lamp-off conditions considering SO mixing in doubly excited states only (dashed line) and considering SO mixing in doubly and singly excited states [grey (brown) line]. In both cases the model lamp-off signal (black line) is normalized to the $7^0\,{}^1P/8^{-}\,{}^1P$ peak.

compared to the two model results. It seems that in the case of $7^0/8^-\ ^1P$ doublet the SO mixing in singly excited states provides a dominant contribution to the metastable intensity when the lamp is on, apart from the signal due to the incomplete singlet quenching. According to our estimates which involve the cascade propagation along singly excited states with $L \leqslant 4$ and tabulated transition rates [20], the SO mixing in singly excited states results in about 10 times larger signal of triplet metastables than the signal originating from the primary fluorescence decay of predominantly singlet doubly excited states into the pure triplet branch of the cascade. Although we did not attempt to obtain cascade corrections for doubly excited states at higher n, it is clear that the observed quenching should be further reduced for singlet resonances on account of increased SO mixing in doubly excited states themselves. On the other hand, the modeling of the neighboring $7^0\ ^3P$ resonance does not indicate any significant change in intensity either due to the cascade correction or due to changing the lamp-on or lamp-off condition. It is much more difficult to observe an admixture of singlet component in predominantly triplet doubly excited state than vice versa because the singlet strength is strongly "diluted" (≈98.5%) by the decay into the helium ground state.

Further experiments can be done to address the issue of SO mixing, for example, by measuring for each resonance the signal of strong $n\ ^3D$, $n\ ^3S \rightarrow 2\ ^3P$ and $n\ ^1D$, $n\ ^1S \rightarrow 2\ ^1P$ fluorescence transitions. These transitions bypass the cascade and the corresponding (groups of) lines do not overlap in energy as soon as $n > 6$ (singlets: 344–370 nm, triplets: 371–401 nm). Since SO mixing in high n D states is negligible, the relative fluorescence intensity may be directly linked to the singlet-triplet mixing in doubly excited states. That way one could overcome the dilution problem but probably still have to deal with lower experimental efficiency.

IV. CONCLUSIONS

We have demonstrated the feasibility to measure triplet yield spectra of helium using a supersonic beam and a singlet quenching discharge lamp. The infrared-induced attenuation of the metastable yield monitors the singlet-triplet mixing in the doubly excited states of helium. Whereas the intensity of the triplet-dominated series are unaffected by the quench lamp, no triplet contribution can be demonstrated for the $n^+\ ^1P$ states and the triplet mixing in the $n^-\ ^1P$ and $n^0\ ^1P$ series seems to be much larger than has earlier been expected. On the basis of available calculations, we suggest this is partially due to the effect of singlet-triplet mixing in singly excited states populated by the cascade decay toward the final metastable states. To reach firm conclusions, new experiments are needed as well as precise and extended calculations of SO mixing for high lying doubly excited states.

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