Excitation of ^1S and ^3S Metastable Helium Atoms to Doubly Excited States

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We present spectra of triplet and singlet metastable helium atoms resonantly photoexcited to doubly excited states. The first members of three dipole-allowed $^{1,3}P^o$ series have been observed and their relative photoionization cross sections determined, both in the triplet (from $1s2s\ ^3S^e$) and singlet (from $1s2s\ ^1S^e$) manifolds. The intensity ratios are drastically different with respect to transitions from the ground state. When radiation damping is included the results for the singlets are in agreement with theory, while for triplets spin-orbit interaction must also be taken into account.

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Doubly excited states of helium are a prototype system to study electron correlation in atoms. The first evidence of their existence dates to the early 20th century [1,2], but only since their spectroscopic characterization by Madden and Codling [3] and interpretation by Cooper *et al.* [4] have they been subject to systematic experimental [5,6] and theoretical studies [7,8]. In the early 1990s, the development of synchrotron radiation facilities and soft x-ray monochromators permitted high resolution studies of Rydberg series converging to higher thresholds below the double-ionization limit [9–12]. The first studies concentrated on the ionization channel, but it became clear that the inclusion of the fluorescence decay channel is crucial for a correct description [13–15]. Especially below the second ionization limit, the detection of fluorescence has permitted the (background free) observation of resonances which were too weak to be studied in the autoionization decay channel [16,17]. Thus it has been shown that even for an atom as light as helium, the LS coupling scheme breaks down and transitions between singlet and triplet manifolds of states can be observed [18]. An increase in sensitivity was obtained by monitoring the metastable neutral states produced following fluorescence decay [16]. In various experiments the dipole-allowed odd parity states below $N = 2$ were observed, and a comprehensive picture of the decay channels and their relative importance has been constructed theoretically and to a large extent verified experimentally [19,20].

In all of the synchrotron radiation work to date the doubly excited states were investigated using one-photon excitation from the helium ground state, but theoretical studies have also investigated the ionization and excitation of metastable atoms [21–25] revealing different relative absorption cross sections and nearly Lorentzian line shapes. Experimental studies of metastable helium atoms are expanding in some laboratories [26,27], but synchrotron radiation studies have not yet been performed because the sample is extremely dilute. Here we present a study of the excitation of triplet and singlet metastable helium atoms to doubly excited states, and their detection via autoionization. In the triplet manifold we observe the lowest energy members of the dipole-allowed $^3P^o$ series and compare their relative ionization cross sections with theoretical predictions. In the singlet manifold we observe transitions from the $1s2s\ ^1S^e$ state to the $^1P^o$ states, also accessible in absorption from the ground state.

The experiment was carried out at the Gas Phase beam line at the storage ring Elettra (Trieste, Italy) [28]. Metastable helium atoms were prepared in a skimmed, continuous molecular beam using an electrical discharge [29]. The yield of metastable helium atoms in our experiments was not determined, but for similar sources yields of 10^{-4}–10^{-6} have been reported. This extreme dilution of the target makes the experiment very challenging and required a careful optimization of the experimental setup. A commercial hemispherical photoelectron analyzer (VG220i) was used to record most of the spectra, although some were taken with other detectors with higher transmission. A major problem was background signal due to metastable atoms striking the electron multiplier in some detectors. The photoelectron analyzer has the advantage (compared to higher transmission detectors) of a well

characterized transmission, better signal/noise ratios, and low background. The analyzer with a specified angular acceptance of 8° was mounted perpendicular to both the photon and atomic beams, in the direction of the light polarization vector ($\theta = 0$). The kinetic energy resolution required to distinguish between ground state and metastable atom ionization is very low, so it was set to 1 eV. For each resonance, the kinetic energy detected by the analyzer was set to the expected kinetic energy of the emitted electrons and kept constant, while the beam line monochromator was scanned. The width of the resonances is much smaller than the analyzer resolution so the transmission is nearly constant in the range of the scan. The experimental resolution is thus determined by the photon bandwidth (≈5 meV in most spectra). The variation of the analyzer transmission was checked using ground state helium ionization spectra over the whole kinetic energy range used. All results are corrected for this small (<5%) change in transmission.

The doubly excited P states below the $N = 2$ ionization threshold can be approximated by a linear combination of $2snp$, $2pns$, and $2pnd$ configurations, so states can be populated from the metastable $1s2s$ states by "$1s$ to np" one-electron transitions. This leads to a large absorption cross section in these transitions, when compared to the equivalent ground state two-electron excitations.

First we examine "fully" allowed transitions from the metastable $1s2s\ ^3S^e$ state to doubly excited triplet states $^3P^o\ n^+$, n^-, and nd (the notation of [4,15] is followed). The first, strongest transition in Fig. 1 is to the $2^+\ ^3P^o$ state and has an experimental linewidth of 7 ± 1 meV. At higher energies two series of very different intensities are identified, assigned to the n^+ and n^- progressions [22,25].

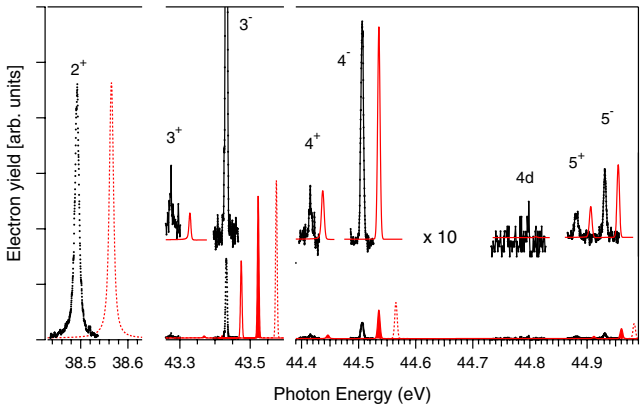

FIG. 1 (color online). Resonant photoionization spectra of $^3S^e$ metastable helium in the region of low-lying $^3P^o$ resonances. Points: Experimental data. Dashed lines (red): Calculated PI without radiation damping. Filled peaks (red): PI with radiation damping correction. Full lines (red): PI with radiation damping and angular correction (4). Theory is offset in energy for clarity and scaled to experiment at the 2^+ peak where both corrections are negligible.

Their widths are essentially given by the beam line resolution. While the transitions were never studied in absorption before, the energies of the excited states are known from emission and theoretical studies. The strongest transition has been observed in fluorescence emission [30], and its lifetime width has been determined in beam-foil experiments [6] and our results agree well. Using the energy of that transition to calibrate the experimental spectrum we find all observed transitions in the triplet manifold of states to be within 3 meV of the energies calculated by Argenti and Moccia [25]. This value corresponds approximately to the precision of our experimental photon energy scale.

We measured the photoionization (PI) cross section at a single electron emission angle, and not the photoabsorption cross section, so that angular distribution and the alternative fluorescence decay channel need to be taken into account when comparing the data with theory. We calculated the PI cross section along the lines described in Ref. [31] starting from $1s2s\ ^{1,3}S^e$ metastable states with the radiation damping included. The eigenenergies and autoionization widths of $^{1,3}P^o$ resonances were obtained by separate diagonalization of the complex-scaled nonrelativistic Hamiltonian in the Sturmian basis, and match very well the published data [22,25]. The calculated radiative widths of triplet and singlet resonances also agree well with previous results [15]. PI of the n^- and especially of the nd series is strongly suppressed on account of the fluorescence decay. This explains why the observed $^3P^o$ nd signal is very weak. The calculated PI spectrum is convoluted with the experimental linewidth and compared to experimental data in Fig. 1. While relative intensities of different members of the same series are well reproduced within the LS approximation, there remains a significant discrepancy in the relative intensity of $^3P^o\ n^+$ versus n^- series: when the theory is scaled to the 2^+ peak, the n^- signal appears to be too low by a factor of about 2. As shown below, this is attributed to the difference in the effective asymmetry parameter β and interpreted as an angular effect due to the spin-orbit interaction within an autoionizing triplet state.

The dipole photoinduced autoionization of the helium singlet metastable state ($S_i = 0$) into the singlet $\mathrm{He}^+ 1s\epsilon p$ continuum ($S_f = 0$) proceeds only through resonance states with total angular momentum $J = 1$ and is characterized by a zero angular momentum transfer $\mathbf{j}_t = \mathbf{S}_f - \mathbf{S}_i$ [32]. For triplets ($S_i, S_f = 1$) the process occurs through the resonance states with $J = 0, 1, 2$. Three values of j_t are possible and each of them corresponds to a specific value of the asymmetry parameter: $\beta_0 = 2$, $\beta_1 = -1$, and $\beta_2 = 1/5$ for $j_t = 0$, 1, and 2, respectively [33]. For our process, β is given by an incoherent sum of all three contributions,

$$\beta(E) = \frac{\beta_0|\bar{S}(0)|^2 + 3\beta_1|\bar{S}(1)|^2 + 5\beta_2|\bar{S}(2)|^2}{|\bar{S}(0)|^2 + 3|\bar{S}(1)|^2 + 5|\bar{S}(2)|^2}. \quad (1)$$

$\bar{S}(j_t)$ denotes the rotationally invariant, energy dependent

scattering matrix element for a given momentum transfer. According to [32] it is related to the scattering matrix elements $S(J)$ for a given total angular momentum,

$$\bar{S}(j_t) = \sum_{J=0,1,2} (-1)^J (2J+1) \begin{Bmatrix} 1 & 1 & J \\ 1 & 1 & j_t \end{Bmatrix} S(J). \quad (2)$$

If the LS coupling approximation applies, the resonance term splitting is zero and $S(0) = S(1) = S(2)$. The matrix elements $\bar{S}(1)$ and $\bar{S}(2)$ cancel out exactly throughout the resonance region, so that $\beta = 2$. When the degeneracy is removed due to the spin-orbit interaction, the autoionization occurs at all three values of j_t, and β can become considerably smaller than 2 in the resonance region. The difference in angular distribution therefore stems from the fact that the natural width of the low-lying $^3P^o\ n^+$ resonances is much larger than the spin-orbit splitting of a multiplet (giving $\beta \approx 2$) while for the $^3P^o\ n^-$ and nd the resonance widths are smaller than the term separation, so that $\beta < 2$.

To quantify the effect we have calculated the spin-orbit splittings for the low-lying $^3P^o$ resonances by diagonalizing the Breit-Pauli Hamiltonian in a basis of configurations composed of hydrogenlike ($Z = 2$) orbitals. The ATSP package was used as in [15], but the basis set was truncated at $n = 9$, and $^1D^o$, $^3F^o$ multiplets were considered in addition to $^1P^o$, $^3P^o$, $^3D^o$ to obtain the mixing for $J = 2$. As shown by [34], the spin-orbit interaction has a strong effect on electron angular distribution close to the $N = 2$ threshold. For $n \leq 5$ the singlet-triplet mixing is too weak to change considerably the emission pattern because the mixing coefficients are very small ($|c_2| < 0.01$). A typical term splitting of triplets is at most a few hundred μeV and it does not change much at low n. Specifically, for 3^+ (3^-) states the $^3P_1 - {}^3P_0$ and $^3P_2 - {}^3P_0$ splitting was calculated to be 108(95) μeV and 353(285) μeV, respectively, while the resonance width $\Gamma = \Gamma^a + \Gamma^r$ (autoionization + fluorescence) is 2.2 meV (56 μeV). To estimate the effect of multiplet splitting on the angular distribution, the Fano amplitudes

$$S(J) = \exp(i\delta)\left[R\frac{q+\epsilon_J}{i+\epsilon_J} + r\right] \quad (3)$$

were inserted into (2) and the energy dependence of the asymmetry parameter (1) was calculated. Each term has a different energy position $\epsilon_J = 2(E - E_J)/\Gamma^a + i\Gamma^r/\Gamma^a$, and in the first approximation they are assigned the same LS value of Γ^a, Γ^f, q, and δ (the phase). Indeed, as a simple Dirac-Fock calculation shows, the phase difference of $\epsilon p_{1/2}$ and $\epsilon p_{3/2}$ electron waves in the potential of the $He^+ 1s$ ion is less than 0.1 at $\epsilon \approx 40$ eV and spin-orbit interaction in the continuum can be neglected. R/r was set to 1:2 for all the terms, but $\beta(E)$ is not very sensitive to the partitioning of interacting or noninteracting continua, because the Fano parameters are relatively large ($q = -16.2$ and -1056 for the 3^+ and 3^- resonance, respectively). We note that the same results are obtained when $\beta(E)$ is directly expressed by the reduced dipole matrix elements M_{ljJ} of Kabachnik and Sazhina [Eq. (27) in [35]] and substituted with the corresponding Fano amplitudes (3) to handle the interaction between discrete levels and the continuum.

If $B(E - E')$ is the photon bandwidth of the beam line at energy E, according to the well-known angular form [33] the electron signal is proportional to

$$I(E,\theta) \propto \int dE' B(E - E') \times \sum_{J=0,1,2} \sigma_J(E', E_J)[1 + \beta(E')P_2(\cos\theta)]. \quad (4)$$

The term-dependent PI cross sections σ_J are generated from $\sigma(E)$, the nonrelativistic PI cross section scaled down by $(2J+1)/9$ and shifted in energy according to the calculated spin-orbit splitting. When β depends only weakly on photon energy (the case of $^3P^o\ n^+$) or the multiplet width is much smaller than the experimental resolution (the case of $^3P^o\ n^-$ and nd), an effective asymmetry parameter of the multiplet can be defined: $\bar{\beta} = \int \sum_J \sigma_J(E)\beta(E)dE / \int \sigma(E)dE$. The intensity ratio of multiplets 1 and 2 is then $I_1/I_2 = A_{1,2}(\theta)(\sigma_1/\sigma_2)$, where the angular factor $A_{1,2}(0) = (1 + \bar{\beta}_1)/(1 + \bar{\beta}_2)$ applies to the signal recorded along the incoming polarization direction (a small correction due to the finite acceptance angle of the spectrometer is neglected) and σ_i is the total PI cross section of the ith multiplet in the LS coupling approximation. Considering again the 3^+ and 3^- resonances, $\bar{\beta}_{3^+} = 1.99$ and $\bar{\beta}_{3^-} = 0.63$, so that $A_{3^-,3^+}(0) \approx 0.55$. Similar values are obtained for $n = 4, 5$. The spin-orbit interaction therefore essentially modifies the angular distribution of electrons emitted by weakly autoionizing doubly excited triplet states. Only when the radiative damping and spin-orbit effect are included does theory come into agreement with the measured intensities in the triplet manifold (Fig. 1). The strength of the angular momentum transfer formalism is shown by the fact that exactly the same formula (1) was used in the case of Cl $3s$ to predict strong variation of β due to the interference of ^2S, ^2P, ^2D continuum photoionization channels caused by anisotropic electron-core interaction [36].

In the singlet manifold we observed transitions from the $1s2s\ ^1S^e$ state to the lowest members of all three dipole-allowed series of states: $^1P^o\ n^+$, n^-, and nd (Fig. 2). These states are well studied in absorption from ground state helium [10], but transitions from metastable states have not been observed before. As predicted [21,22], there are dramatic differences in the relative intensities of the transitions, and symmetric line shapes indicate a relatively weak bound state-continuum interaction. In the n^- series we observe transitions to the two lowest members (3^- and 4^-), while the other two features in the spectrum are due to transitions to the 2^+ and $3d$ states. The transition to the 3^+

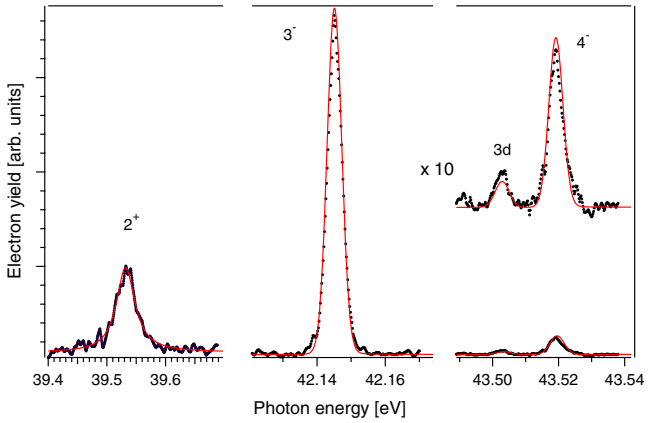

FIG. 2 (color online). Resonant photoionization spectra of $^1S^e$ metastable helium in the region of low-lying $^1P^o$ resonances. Points: Experimental data. Full line (red): Calculated PI with radiation damping correction. Theory is scaled to the measurement at the 2^+ peak.

state, also lying in this energy range, is too weak to be observed here. The observed linewidth for the 2^+ state is 37 meV, in good agreement with the width determined by Domke *et al.* [10]. For singlet excitations there seems to be no strong angular effect: the convoluted nonrelativistic PI with radiation damping fits very well the measured spectra, and $\beta = 2$ is expected to apply for the spectrum in Fig. 2.

In summary, we have observed transitions from metastable helium atoms to the low-lying doubly excited states below $N = 2$. The observations are in good agreement with calculated spectra which account for the fluorescence decay (singlets and triplets) and the modification of the photoelectron angular distribution due to the spin-orbit splitting of the resonant triplet states. The many previous theoretical PI studies of metastable helium [7,15,21–25,37] agree well for the energy of the doubly excited states, but much less so for the relative cross sections (where they are given). Zhou *et al.* [22] and Argenti and Moccia [25] provided detailed predictions, but did not include the fluorescence decay channel. Taking it into account and including the spin-orbit induced angular effects in the triplet manifold, their predictions are in good agreement with our results. Further high resolution measurements on metastable states, as well as accurate relativistic calculations, are needed to trace out the complex behavior of the β parameter at higher n.

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