Double Excitations of Helium in Weak Static Electric Fields

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A dramatic electric field dependence has been observed in the fluorescence yield spectrum of the doubly excited states in helium, where a rich phenomenology is encountered below the $N = 2$ threshold. Fluorescence yields of certain states can be tuned to zero, while other dipole-forbidden states are significantly enhanced, for fields much weaker than 1 kV/cm. Using an R-matrix multichannel quantum defect theory, spherical-to-parabolic frame transformation method, we are able to reproduce the main features of the observed spectrum, and we discuss the qualitative behavior in terms of weak electric field mixing.

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The helium atom is the prototypical two-electron system, and consequently it has been extensively studied over the years. The analysis of the photoabsorption spectrum [1] associated with doubly excited states by Fano and coworkers [2] in the 1960s was a touchstone for the understanding of vacuum ultraviolet photoabsorption. By the end of the century, it was realized that detection of uncharged secondary particles, such as photons [3–7] and metastable atoms [4,8], could give important new information about the absorption process.

The prediction of external-field effects on these excitations is a theoretical challenge because it involves the influence of electron correlation as well as the various decay pathways. Apart from the fundamental interest, such investigations are also relevant for dielectronic recombination experiments, where external electric fields ($\mathcal{E}$ fields) are of crucial importance [9,10]. Recently, the first observation of an influence of static external electric fields on the photoexcitation spectrum of helium doubly excited states below the $N = 2$ threshold was reported [11]. Attention was given to relatively high fields (up to 100 kV/cm), where Stark shifts and splittings can be readily measured. Theoretical work has so far also dealt with fields on this order of magnitude [12–15].

Here we report dramatic effects in the fluorescence yield (FY) spectrum already at moderate fields of a few V/cm. At such small fields, the Stark shifts are not directly measurable, but instead the $\mathcal{E}$ field has a strong influence on the balance between the two decay mechanisms, autoionization and fluorescence. As a consequence, we find a rich phenomenology, and here we describe the most striking features of the $\mathcal{E}$ field dependence.

The experiment was carried out at the angle-resolved photoemission spectroscopy (ARPES) end station of the gas-phase beam line [16] at ELETTRA. The energy resolution for the measurements was set to be around 1.5 meV. The sample was contained in a differentially pumped gas cell with an estimated pressure of around 10^{-3} torr. Ultrathin (1000 Å) filters separated the sample gas from two 40 mm diameter microchannel plate detectors, measuring in the direction perpendicular to the directions of the incident beam and its polarization. The filters ensured that charged particles and metastable atoms could not reach the detectors, and the filter material (aluminum/carbon) was chosen to give high transmission around 40 eV (around 20%), corresponding to the radiative decay of the doubly excited states, while blocking secondary emission at energies below 25 eV (transmission less than 1%). Electrodes were positioned in the cell, 3 mm apart, with flat surfaces 16 mm along the beam and 1 mm perpendicular, to apply a uniform $\mathcal{E}$ field parallel to the polarization of the incoming beam. For reasons described below, the $\mathcal{E}$ field is calibrated using the observed FY oscillations at high E fields.

Our theoretical method for treating this problem begins with an R matrix, multichannel quantum defect theory approach, similar to what was used in a recent study of spin-orbit effects in the helium FY spectrum [5] (hereafter referred to as I). In I, a further LS-to-JK frame transformation method was applied to incorporate spin-orbit effects. The result of including the spin-orbit operator was that states with large oscillator strengths but small fluorescence branching ratios (FBR) were able to mix with states having smaller oscillator strengths but larger FBR, thereby increasing the overall fluorescence observed.

The present calculations were performed in the same spirit as those in I, but rather than applying a LS-to-JK frame transformation, we apply a spherical-to-parabolic [17] frame transformation [18–21] including the radi-

ation field [22]. Specifically, we first recouple the two-electron wave function from a $|Nl's', nls, LSJ\rangle$ to a $|Nl's', s, J_Q, nl, J\rangle$ scheme, then decouple to a $|NJ_QM_Q\rangle|nlm\rangle$ product wave function, and finally recouple just the outer-electron wave function from a spherical $|nlm\rangle$ to a parabolic $|nn_1m\rangle$ representation. The latter yields a separable wave equation in parabolic coordinates, even in the presence of external electric fields, for the long-range Rydberg-electron solution [17], which we solve for using the WKB method [23].

Further technical details of our calculations are as follows. First, unlike in I where only the total final angular momentum $J = 1$ and parity $\pi = -1$ (odd) was allowed, giving the $2l'nl\ LS$ terms $^1P_1^0$, $^3P_1^0$, and $^3D_1^0$ (the spin-orbit operator mixes only terms with the same total J and π), now we need to consider *all* possible $2l'nl\ LS$ terms since the electric field operator $H_\mathcal{E} = \mathcal{E}r\cos\theta$ mixes outer-electron states with angular momentum and parity differences $\Delta l, \Delta\pi = \pm 1$. In practice, we included all states with $l \leq 4$.

The main physical effects not included in our method are twofold. First, since uncoupled WKB wave functions are used for each long-range channel solution, the infinite-range degenerate channel coupling (see [24], for example) is neglected. Thus, the oscillator strengths and quantum defects are not fully converged in our R-matrix part of the calculation. Second, our WKB approach assumes that the Rydberg-electron wave function is purely bound; this approximation breaks down for energies near the downhill potential $[V(r) = -\frac{1}{r} - \mathcal{E}r]$ barrier, which has a maximum of $-2\sqrt{\mathcal{E}}$ at $r = 1/\sqrt{\mathcal{E}}$. Thus, we expect our results to break down at incident photon energies somewhat below $E = E_{\text{thresh}} - 2\sqrt{\mathcal{E}}$, where E_{thresh} is the $N = 2$ threshold energy.

In Fig. 1, we compare the measured and predicted FY spectra at various $\mathcal{E}$ fields below the $N = 2$ threshold. The $\mathcal{E} = 0$ spectrum was already described in I as being the somewhat stronger n^+ series interspersed with the (unresolved experimentally) $(n+1)^-/n^0$ series, where the n^+, n^-, n^0 states are represented qualitatively [2] by the mixed $(2snp + 2pns)\,^1P_1^0$, $(2snp - 2pns)\,^1P_1^0$, and $2pnd\,^1P_1^0$ states, respectively. The n^+ series has a large ground-state oscillator strength and autoionization rate (a small FBR), whereas the n^- and n^0 series have much smaller ground-state oscillator strengths and autoionization rates (large FBR).

As $\mathcal{E}$ is increased above zero, we start to see significant changes to the spectrum. First, the intensity dip at 65.39 eV begins to disappear, and by 44 V/cm it has vanished. Near threshold, as described in I, the mixing with spin-forbidden states oscillates; strong mixing increases the fluorescence, and zero mixing decreases it again to the LS-predicted value. Evidently, the additional influence of even a weak $\mathcal{E}$ field destroys the interference between spin-orbit and Rydberg nodal structures, which was responsible for the intensity dips below threshold [5]. The field strength here

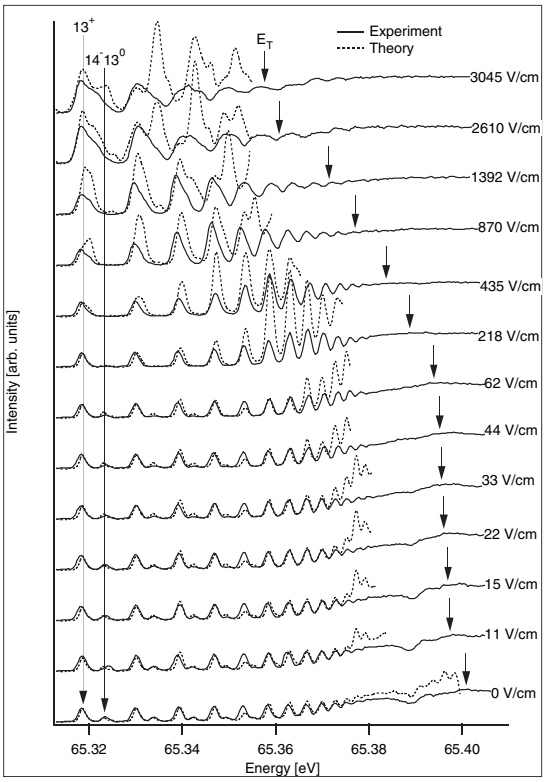

FIG. 1. Experimental and theoretical fluorescence yield spectra close to the $N = 2$ field-modified ionization thresholds (indicated by the arrows), excited at various $\mathcal{E}$ fields. Just below 65.32 eV the 13^+ state appears, the peaks in this series having almost constant intensity. Less intense and with decreasing intensity we find the unresolved $(n+1)^-$ and n^0 peaks in between the n^+ and $(n+1)^+$ states, with the unresolved $14^-/13^0$ just above 65.32 eV.

($\mathcal{E} \approx 10^{-8}$ a.u.) may seem extremely small. However, in the vicinity of these $n \approx 35$ electrons, with mean radii $r \approx n^2 \approx 10^3$ a.u., the influencing potential $V(r) = \mathcal{E}r \approx 10^{-5}$. This is comparable to the energy spacing between Rydberg manifolds $\Delta E = n^{-3} \approx 2 \times 10^{-5}$ a.u., so strong $\mathcal{E}$ field mixing here is not surprising.

The influencing potential is proportional to n^{-5}. Given a substantial state mixing at $n \approx 40$ for $E \approx 40$ V/cm, this implies that at $n/3 \approx 13$ near photon energies of 65.32 eV it would take an electric field of $E \approx 3^5 \times 40 \approx 10^4$ V/cm for similar mixing to occur.

But even at field strengths less than 10^3 V/cm, strong changes in the FY spectrum are apparent at these lower n. First, the FY due to the $(n+1)^-/n^0$ states quickly disappears as $\mathcal{E}$ is increased above zero, and by $\mathcal{E} =$ 435 V/cm the $14^-/13^0$ feature is unobservable. On the other hand, the features attributed to the n^+ states become more prominent with increasing $\mathcal{E}$. This observed behavior is reproduced qualitatively in the calculations. One reason for the quantitative discrepancies may be pressure effects, which are known to influence the field-free spectrum at these relatively high target pressures. At the used pressures spectral variations are somewhat suppressed in the field-

free FY spectrum. Another reason may be the theoretical atomic description is not fully converged. This may influence the mixing and thereby the predicted intensities. Nevertheless, the theoretical results can be studied in finer detail to reveal the underlying weak-field-mixing effects.

In Fig. 2, the theoretical FY spectra are shown for three field strengths. At $\mathcal{E} = 0$, the strong (and broad) 13^+ state is located at about 65.319 eV with the spin-forbidden $2pnd\,^3D_1^0$ state (masked when convoluted) in its right wing just above 65.32 eV. At $\mathcal{E} = 0$, the other strong features are the 14^- and 13^0 states at about 65.323 and 65.325 eV, respectively. Also observable in the unconvoluted results are the three other spin-forbidden yet dipole-allowed $(2snp \pm 2pns)\,^3P_1^0$ and $2pnd\,^3P_1^0$ states. At $\mathcal{E} = 435$ V/cm, the unconvoluted 14^- and 13^0 features become reduced to the point that they are essentially unobservable in the convoluted spectrum (the unconvoluted 13^0 peak height at $\mathcal{E} = 0$ is off the scale at 0.85 Mb), and this can be attributed to their noticeably increased autoionization width, which therefore decreases their FBR. Since the autoionization rates of these two states are relatively small, even small $\mathcal{E}$ field mixing with dipole-forbidden states possessing large autoionization rates decreases the FY. Then at $\mathcal{E} = 1329$ V/cm, the more broadened unconvoluted 13^0 feature nevertheless retains the same height, leading to an increase in the convoluted spectrum near 65.325 eV. Since the FBR has decreased in going from $\mathcal{E} = 435$ V/cm to $\mathcal{E} = 1329$ V/cm, the ground-state oscillator strength must have increased, and we attribute this increase to the high-field mixing with the 13^+ state. The 13^+ feature, on the other hand, remains essentially unaffected, except for a noticeable Stark shift in energy, even for $\mathcal{E} = 1392$ V/cm. However, just to the right of this feature a manifold of dipole-forbidden states becomes populated, giving a much broader and taller convoluted feature. While it seems that these new states would derive from mixing with the spin-forbidden $2pnd\,^3D_1^0$ state, a separate calculation omitting spin-orbit effects yielded the same qualitative pattern, so these states are attributed to $\mathcal{E}$ field mixing with spin-allowed states. Specifically, the 13^+ state mixes weakly with a large number of dipole-forbidden (but singlet) states, sharing only a small fraction of its oscillator strength. However, these mixed states have small autoionization rates and therefore large FBR. The net result is that the FY of the broad 13^+ state is essentially unaffected, but the FY of the narrower mixed states becomes comparable in magnitude.

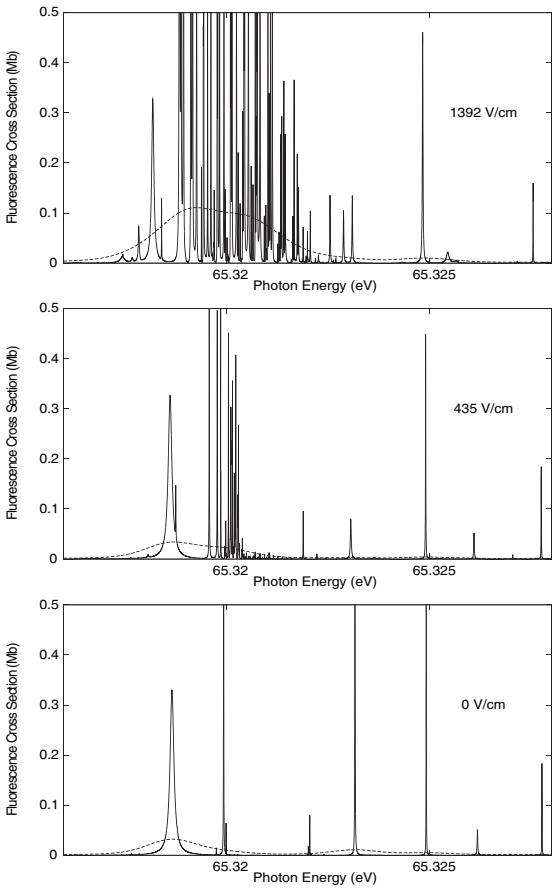

FIG. 2. Unconvoluted (solid line) and convoluted (dashed line) theoretical fluorescence yield results in the vicinity of the 13^+, 14^-, and 13^0 states as $\mathcal{E}$ is increased above zero.

The discussed trends continue to develop at higher fields in qualitative agreement with the theoretical predictions (Fig. 3).

Note that the period of the oscillations when approaching threshold is reproduced by the theory up to the (classical) ionization limit, where the theory is no longer expected to hold. The observed oscillations continue above the ionization thresholds with monotonically decreasing energy spacing between consecutive intensity dips. These oscillations can be understood using a different approach, as such oscillations are generally expected for excitation spectra of Rydberg atoms in an external electric field [25].

The same periodicity is found when simply considering the WKB bound-state solutions [23] to a spherically symmetric model system with an uphill potential $V(r) = -\frac{1}{r} + \mathcal{E}r$, using the Bohr-Sommerfeld quantization condition $\int_0^{r_c} \sqrt{2[E - V(r)]}\,dr = n\pi$, where $r_c = (E/2\mathcal{E}) + \sqrt{(E/2\mathcal{E})^2 + (1/\mathcal{E})}$ is the classical turning radius; the energies E are then quantized by n and differ from the usual $-1/2n^2$ values due to the additional $\mathcal{E}$ field potential.

As the periodicity can be predicted with high precision by two separate theoretical methods, we use these results to achieve an absolute calibration of the $\mathcal{E}$ field. The more straightforward way to determine the $\mathcal{E}$ field from the power supply settings and field simulations in the experimental geometry turned out to consistently give a lower $\mathcal{E}$ field by a factor 1.5. The former calibration method is chosen as we judge it to be the most accurate. Presently we cannot fully account for the discrepancy between the two methods.

In conclusion, we have shown that a weak external $\mathcal{E}$ field has a dramatic influence on the FY spectrum of helium in the region of the doubly excited states below

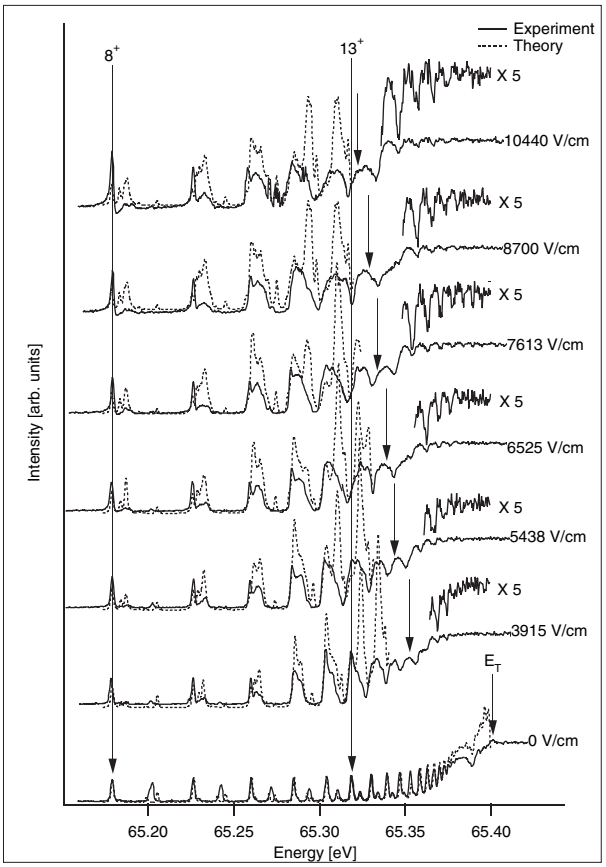

FIG. 3. Fluorescence yield spectra at higher $\mathcal{E}$ fields. Here the peaks at the lowest energy correspond to 8^+.

the $N = 2$ threshold. The main effect of the field is to mix the n^+ series, which has a small FBR, with other states having larger FBR, thereby increasing the overall FY for these states. The n^- and n^0 series, on the other hand, mix with states having smaller FBR, reducing their FY. The observed behavior was reproduced in our R-matrix calculations, similar to what was found in I. Unlike the work in I, however, here we have an *adjustable* electric field to alter radically the observed FY.

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