# Detection of the $^1P^e$ Series of Doubly Excited Helium States below $N = 2$ via the Stark Effect

K. C. Prince,[1,2,*] M. Coreno,[3,4] R. Richter,[1] M. de Simone,[2,4] V. Feyer,[3,†] A. Kivimäki,[2] A. Mihelič,[5] and M. Žitnik[5]

[1]*Sincrotrone Trieste, in Area Science Park, I-34012 Basovizza (Trieste), Italy*

[2]*Gasphase Beamline@ ELETTRA, INFM-TASC, in Area Science Park, I-34012 Basovizza (Trieste), Italy*

[3]*CNR-IMIP, Montelibretti (Rome), I-00016 Italy*

[4]*INSTM, Trieste, Italy*

[5]*J. Stefan Institute, 1000 Ljubljana, Slovenia*

(Received 24 August 2005; published 6 March 2006)

The Stark effect on the doubly excited states of helium below the $N = 2$ threshold has been studied by vacuum ultraviolet fluorescence yield spectroscopy. Two new series of states are observed at moderate fields ($< 10$ kV/cm), and assigned to the previously unobserved even $^1P^e$ series, and a group of $^1D^e$ series. The $^1S^e$ states are observed indirectly via their mixing with nearby $^1P^o$ states. The observations at moderate field contradict theoretical predictions that field strengths about an order of magnitude greater are necessary to observe the Stark effect on He doubly excited states at low quantum numbers.

DOI: 10.1103/PhysRevLett.96.093001 PACS numbers: 32.80.Fb, 31.25.Jf, 32.60.+i

The helium atom is the simplest three body system that is both calculable and experimentally manageable, so that it is a benchmark system for both experiment and theory, and there exists a vast body of literature related to its interaction with electromagnetic fields. The effects of static electric fields on singly excited helium were studied long ago [1], and more recently [2] using synchrotron radiation. Studies of the doubly excited states of helium, which lie in the Extreme Ultraviolet spectral range, have deepened our understanding of correlation in the excited helium atom, from the early observation by Madden and Codling of two of the dipole allowed $^1P^o$ series [3], to the characterization of all three series [4]. More recently investigation of the photon induced fluorescence spectra (PIFS) and metastable decay channels [5–10] has shown the importance of radiative decay, and relativistic effects which invalidate the LS coupling scheme close to threshold.

Many predicted doubly excited states of helium are not accessible by simple photoabsorption, but it is of great fundamental interest to verify experimentally their existence and theoretical energies. The energies of singlet and triplet $S$, $P$, $D$, and $F$ doubly excited states of He below the $N = 2$ threshold have been calculated by Lipsky *et al.* [11], Liu *et al.* [12] and Chen [13] (and references therein). There are ten singlet $S$, $P$, and $D$ series below $N = 2$: two $^1S^e$, three $^1P^o$, one $^1P^e$, one $^1D^o$, and three $^1D^e$ series. To date the three optically allowed $^1P^o$ series [3–7,9,10] have been studied, as well as some members of the $^3P^o$ and $^3D^o$ series [8]. The first term of the $^1D^e_2$ series has been detected in angle resolved photoelectron spectra [14], and some of the low lying terms with $n \leq 5$ of $^1S^e$, $^{1,3}P^o$, and $^1D^e_2$ series have been studied by electron scattering [15,16]. However none of the six even series can be observed in simple photoabsorption due to the selection rule requiring a parity change.

Forbidden states of even parity can be made Stark allowed in an electric field, but detailed examination of the Stark effects on these doubly excited states is just beginning [17–20]. Chung *et al.* [17] estimated that field strengths of about 50 kV/cm were necessary to observe effects on doubly excited resonances below $N = 2$ and for $n = 6$, and this estimate appears reasonable: fields up to 500 kV/cm were employed to induce Stark effects in the related three body system, the hydrogen negative ion [21]. Harries *et al.* [19] observed strong Stark mixing of the doubly excited states of He at fields up to 84 kV/cm, supporting this estimate. They measured the ion yield of the autoionizing states over a narrow energy range (near $n = 6$) and found complex spectra with many more states Stark mixed than predicted by theory. In this and the work cited above, individual members of series of even states were observed but no complete characterization of a series was reported.

In this Letter, we report the PIFS spectra of doubly excited He states over a wide energy range up to $N = 2$, and we identify a new, theoretically predicted series of doubly excited states. The spectra are considerably simpler than the ion yield spectra reported by Harries *et al.* near $n = 6$, and cover a wider range (from $n = 5$ up to threshold). Moreover, the field strengths used are an order of magnitude smaller than expected, or used in the recent study.

The experiments were performed at the Gas Phase Photoemission beamline, Elettra, Trieste [22], with the photon resolution set to between 2 and 3.5 meV, and the fluorescence yield spectra were measured with an yttrium aluminum perovskite scintillator and photomultiplier detector [23]. The advantages of the PIFS method are: the Lorentzian rather than Fano profile allows better resolution of closely spaced lines; emitted photons are not influenced by electric fields; and the sensitivity to some series is enhanced with respect to electron or ion detection. Zero field ion yield spectra for calibration were taken simultaneously with all fluorescence yield spectra. Photon energies were calibrated to the values of Domke *et al.* [24], in

 

particular, the $(5,-1)^0\ {}^1P^o$ state is at 64.907 eV [the notation $(n,K)^A$ follows Ref. [25] ]. The pressure for vacuum-ultraviolet (VUV) yield spectra was typically $3\times10^{-2}$ mbar, and electric fields **F** were applied by two parallel, graphite coated stainless steel plates separated by 5 mm ($\pm$ 2%). The synchrotron light was linearly polarized and emission was detected perpendicular to **F**.

VUV fluorescence yield spectra taken with **F** parallel to the polarization vector of the light **P** are shown in Fig. 1. The VUV yields of the $(n,1)^-\ {}^1P^o$ and $(n,-1)^0\ {}^1P^o$ states are reduced by the electric field, even for values of **F** as low as 0.5 kV/cm, and $n=5,6$ [Fig. 1(b)]; the decrease is greater for the $(n,-1)^0$ series. At higher values of $n$, new intensity appears above the $(n,0)^+\ {}^1P^o$ states; two examples are indicated in Fig. 1(a) by arrows. Figure 2 shows fluorescence spectra with **F** perpendicular to **P**. The zero field spectrum resembles that of Rubensson *et al.* [6], and when a low field **F** is applied, the spectrum changes dramatically at higher quantum numbers; for example, for 3 kV/cm and $n>11$, most peak intensities increase substantially. Two new series of states appear, and the first (labeled "1") is present for $\mathbf{F}>3$ kV/cm and $n>6$, and appears between each $(n-1,-1)^0/(n,1)^-{}^1P^o$ pair and the following $(n,0)^+\ {}^1P^o$ state. The second, labeled "2," appears just above the $(n,0)^+\ {}^1P^o$ series, and rapidly merges with it; this series is most pronounced for $n>9$. It does not appear to be a single series because the peak is asymmetric and about 9–10 meV wide, much broader than the 1 states or the field-free spectral features. The energies of both series do not change measurably (<1 meV) with field, so that the field-free energies of the states are equal to those with field applied. In Fig. 3 the intensities of three states have been normalized to the integrated intensity of the $(5,-1)^0/(6,1)^{-1}\ {}^1P^o$ doublet at lower energy, as this is not expected to change substantially with field as shown below.

To determine the quantum defects of these states we first fitted the energy positions of the $(n,0)^+\ {}^1P^o$ series without field, and obtained a quantum defect of $-0.19\pm0.005$, slightly different from the value of $-0.18$ obtained by Penent *et al.* [8]. The quantum defect of the states labeled 1 is $-0.435\pm0.005$, which agrees very well with the value $-0.439\,76$ of Lipsky *et al.* [11] for the $n=7$ member of the ${}^1P^e$ *a* series [in the present notation, the $(7,0)^-\ {}^1P^e$ state]. For lower members of the series the calculated absolute value of the quantum defect is slightly smaller. No other singlet states have similar quantum defects so we assign the states labeled 1 to the ${}^1P^e$ series, and discuss this further below.

For the second series, labeled 2, more calculations are available. For instance, Chung *et al.* [17] have calculated that in an interval of 40 meV above the $(6,0)^+\ {}^1P^o$ state there are many high angular momentum even states (up to $l=6$). Chen [13] calculated the *S*, *P*, and *D* but not the higher angular momentum series and placed the $(6,0)^0\ {}^1D^e$ and $(6,-1)^0\ {}^1D^e$ state at 21 meV and 38 meV, respectively, above the $(6,0)^+\ {}^1P^o$ state. Extrapolating these calculations, at $n=10$ the energy interval shrinks to less than 10 meV suggesting the assignment of this broad feature to these two ${}^1D^e$ series and possibly higher angular momentum, Stark allowed (even) states.

We have repeated the calculations [11] with a larger basis set to obtain reliable energies of the ${}^1S^e$, ${}^1P^e$, ${}^1D^e$ doubly excited states up to $n=10$. The relatively weak

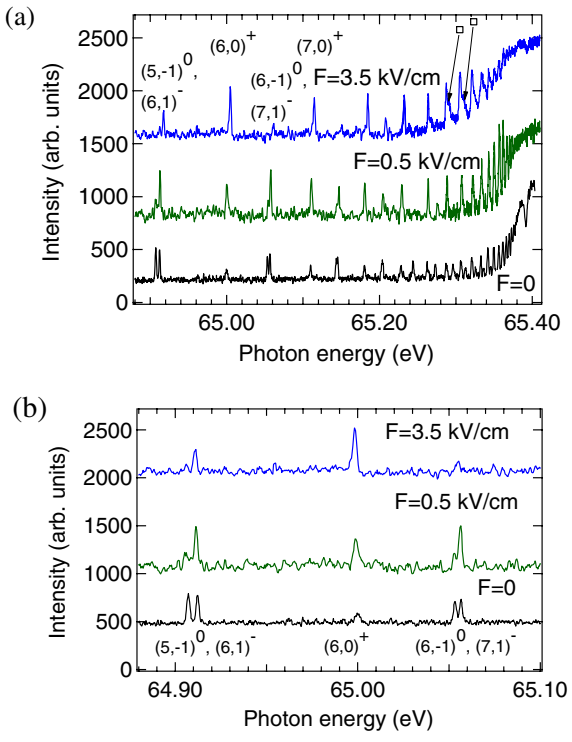


FIG. 1 (color online). (a) Partial fluorescence yield spectra of helium below $N=2$ with **F** parallel to **P**. Spectra are normalized to the increase in fluorescence at the $N=2$ threshold. (b) Enlarged view of first 5 states.

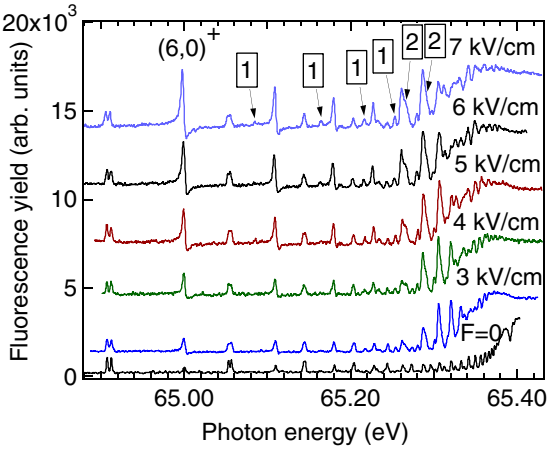


FIG. 2 (color online). Partial fluorescence yield spectra of helium below $N=2$ with **F** perpendicular to **P**. New features are labeled 1 and 2.

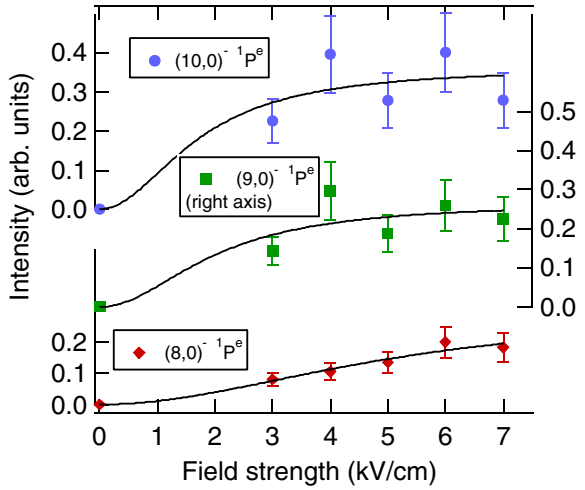


FIG. 3 (color online). Integrated intensities of the Stark induced states labeled 1 in Fig. 2, assigned to the $(n, 0)^-\ ^1P^e$ series. Solid line: calculated intensity using parameters $a_n$ $(\mathrm{kV/cm})^2$: 0.012, 0.029, 0.063 and $c_n$ $(\mathrm{kV/cm})^2$: 1, 2.4, 5.4, for the $n = 8, 9, 10\ ^1P^e$ states, respectively. ($c_n$ has been normalized to 1 for $n = 8$).

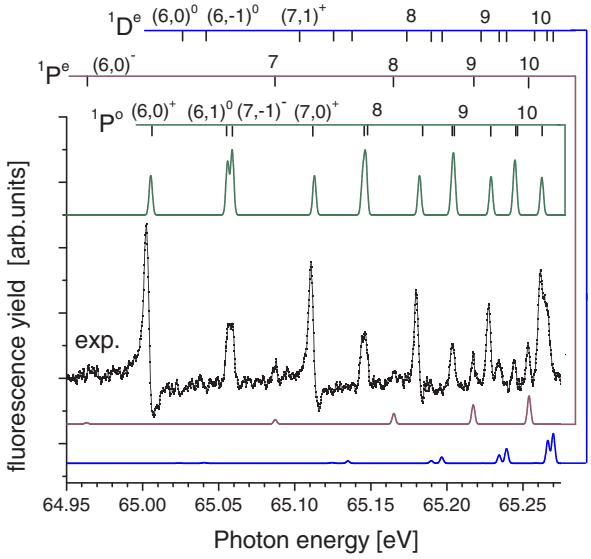


FIG. 4 (color online). Comparison of experimental (dotted line) and calculated (solid lines) primary fluorescence spectra of unperturbed $^1P^o$, $^1P^e$, and $^1D^e$ states of He. $\mathbf{F} = 5$ kV/cm, $\mathbf{F}$ perpendicular to $\mathbf{P}$.

field $\mathbf{F}$ and limited set of low $n$ states justify a first order approach to modelling the results, except for the high lying $^1S^e$ states which are nearly degenerate with the $^1P^o$ states. The perturbation term in the Hamiltonian is $\mathbf{F} \cdot (\mathbf{r}_1 + \mathbf{r}_2)$, so that only the three above-mentioned even parity multiplets gain an admixture of the dipole allowed $^1P^o$ symmetry states. The matrix elements of perturbation between the zero order states are governed by the same dipole selection rules as photoabsorption. Moreover, selection rules allow $\Delta M = \pm 1$ transitions for absorption of linearly polarized light if $\mathbf{P}$ is perpendicular to $\mathbf{F}$ [2], and $\Delta M = 0$ transitions if it is parallel. Since the mixing coefficient of the allowed $^1P^o$ component is nonzero only for the $M = \pm 1$ components of the perturbed $^1P^e$ state, these considerations explain the absence of this series in the measurements with the parallel setup, as well as the insensitivity of the $(5, -1)^0/(6, 1)^{-1}\ ^1P^o$ doublet intensity to the electric field strength in the perpendicular setup. On the other hand, $^1S^e$ states ($M = 0$) are excited only if $\mathbf{P}$ is parallel to $\mathbf{F}$. The $^1D^e$ series is expected to be excited in both geometries with similar probability as also seen in the experimental spectra.

The calculated oscillator strengths of the perturbed even states were multiplied by the corresponding fluorescence decay branching rates of the unperturbed states [26] to estimate their primary VUV yield for the perpendicular geometry, Fig. 4. The result for the $^1P^e$ series is compared to the primary fluorescence yields of the three unperturbed $^1P^o$ series [27] and shows that the expected intensity of the VUV photon yield from the $^1P^e$ series is comparable to the intensity of the newly observed series. The fluorescence yield method is particularly adapted for the observation of the $^1P^e$ series for the following reason. Because of parity conservation, these unperturbed states below $N = 2$ cannot decay by autoionization and do so only by fluorescence to singly excited $^1P^o$ states which decay by further fluorescence [27]. Thus, for weak fields the $^1P^e$ fluorescence cross section is approximately equal to the $^1P^e$ photoabsorption cross section. The situation is different for states of $^1S^e$ and $^1D^e$ symmetry because some of them are strongly autoionizing (quantum label $A = +$) [28], so that the calculated photoabsorption cross section gives only an upper estimate of the fluorescence cross section.

The Stark effect at low field does not reduce oscillator strength, but only transfers some of it from allowed zero field transitions to energetically close forbidden transitions [2,17]. This redistribution of the oscillator strength induces the fluorescence signal from $^1P^e$ states in the perpendicular geometry. In addition, the branching ratios for decay channels (fluorescence and autoionization) may change as a function of the applied field. We observe that the measured VUV yield of the $^1P^e$ state increases with the field strength $\mathbf{F}$; according to first order theory the oscillator strength of these states increases as $c_n\ \mathbf{F}^2$, where $c_n$ is a state specific parameter independent of $\mathbf{F}$. The observed nonlinear trend can be explained if we take into account that the Stark effect not only mixes dipole character with the $^1P^e$ states, but also changes the decay character by influencing their autoionization or fluorescence branching ratio [20]. Since the autoionization decay rate $\Gamma_n^a$ of the $n$th $^1P^e$ state is also proportional to $\mathbf{F}^2$ the fluorescence yield of this state, $Y_n$ is related to the field strength by

$$Y_n \propto c_n \mathbf{F}^2/(1 + a_n \mathbf{F}^2). \qquad (1)$$

The parameter a $a_n = \Gamma_n^a/(\Gamma_n^f \mathbf{F}^2)$ does not depend on $\mathbf{F}$ because the fluorescence decay rate $\Gamma_n^f$ of the $n$th state can

be approximated well by the zero field value of 10 $ns^{-1}$ at low field [28]. After the initial quadratic dependence, the VUV yield enters a linear regime and finally levels off at higher field strengths. As shown in Fig. 3 the dependence of the VUV yield on field strength, and the variation of the constants $c_n$ and $a_n$ calculated for the perturbed states is in reasonable agreement with the observed trends for the three $n = 8$–$10$ $^1P^e$ states and the field induced $^1P^e$ fluorescence is observed in the intermediate region. At high field strengths where saturation occurs, the first order perturbation scheme may no longer apply, while the detection of the initial quadratic dependence of the $^1P^e$ yield is hindered by the signal to noise ratio.

We believe that a similar mixing effect causes the spectral changes observed in the parallel geometry (Fig. 1). A decrease of the VUV yield from slowly autoionizing $(n, 1)^-$ $^1P^o$ and especially $(n-1, -1)^0$ $^1P^o$ states can be explained by a small but increasing admixture of a strongly autoionizing $(n-1, -1)^+/(n, 1)^+$ $^1S^e$ doublet in the vicinity, which is photoexcited only when **P** is parallel to **F**. An increase in the branching ratio for the fluorescence decay channel may be the reason for the enhancement of the intensity in the states just below the IP.

With regard to the $^1D^e$ states, the calculations of oscillator strengths show that all three series, $(n, 1)^+$, $(n, 0)^0$, and $(n, -1)^0$ are excited, but the first is most strongly excited, in agreement with propensity rules for doubly excited states in an electric field [20]. However, the VUV yield mainly originates from the two $A = 0$ states [26] due to their much larger fluorescence to autoionization branching ratio. The presence of both peaks explains the width of the spectral features in Figs. 1 and 2. As noted above within a first order perturbation scheme, the assignment to $^1D^e$ states is correct, but for higher order perturbation (larger **F** or higher $n$), higher angular momentum components may also be present.

We have not discussed here the intensity of $(n, 0)^+$ $^1P^o$ series, because this signal is subject to spurious effects. At these resonances there is substantial decay by autoionization so that the ion yield changes significantly with respect to the continuum yield. Part of the intensity increase with increasing field is due to fluorescence generated by collisions of charged particles. At high fields and especially in the perpendicular configuration, it can dominate the yield and generates a signal that follows the autoionization signal (a Fano profile). However, this effect is negligible for the other resonances, for which the autoionization decay is expected to be at least 100 times less probable than fluorescence.

In conclusion we have observed the $^1P^e$ Rydberg series of doubly excited helium below the second ionization threshold, as well as features assigned to more than one $^1D^e$ series. A decrease of the VUV yield from $(n, -1)^0$ and $(n, 1)^-$ $^1P^o$ states in the parallel geometry is interpreted as an indication of the presence of energetically close and strongly autoionizing $^1S^e$ states. $^1S^e$, $^1P^e$, $^1D^e$ states become Stark allowed in moderate fields (several kV/cm), but the Stark shift was below 1 meV. Partial VUV fluorescence detection is a sensitive method for detecting these states, which can be observed at much weaker fields than expected.

We thank our colleagues at Elettra for support, particularly H. Farrokhpour, M. Afsar, and M. Danailov; and J.-E. Rubensson and coauthors for communicating results prior to publication.

*Note added in proof.*—A very recent study of the Stark effect has also been carried out by Såthe *et al.* [29] in the parallel geometry and for higher quantum numbers. Where comparison is possible, the data were generally in agreement with the present results.

*Electronic address: Prince@Elettra.Trieste.It
†Permanent address: Institute of Electron Physics, 88017 Uzhgorod, Ukraine.

[1] J. S. Foster, Phys. Rev. **23**, 667 (1924).
[2] J. W. Cooper and E. B. Saloman, Phys. Rev. A **26**, 1452 (1982).
[3] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963); Astrophys. J. **141**, 364 (1965).
[4] M. Domke *et al.*, Phys. Rev. Lett. **77**, 3086 (1996).
[5] M. K. Odling-Smee, E. Sokell, P. Hammond, and M. A. MacDonald, Phys. Rev. Lett. **84**, 2598 (2000).
[6] J.-E. Rubensson *et al.*, Phys. Rev. Lett. **83**, 947 (1999).
[7] T. W. Gorczyca *et al.*, Phys. Rev. Lett. **85**, 1202 (2000).
[8] F. Penent *et al.*, Phys. Rev. Lett. **86**, 2758 (2001).
[9] S. Mickat *et al.*, J. Phys. B **38**, 2613 (2005).
[10] M. Coreno *et al.*, Phys. Rev. A **72**, 052512 (2005).
[11] L. Lipsky, R. Anania, and M. J. Conneely, At. Data Nucl. Data Tables **20**, 127 (1977).
[12] Chien-Nan Liu, Ming-Keh Chen, and C. D. Lin, Phys. Rev. A **64**, 010501 (2001).
[13] Ming-Keh Chen, Phys. Rev. A **56**, 4537 (1997).
[14] B. Krässig *et al.*, Phys. Rev. Lett. **88**, 203002 (2002).
[15] M. J. Brunger *et al.*, J. Phys. B **30**, 3267 (1997).
[16] P. J. Hicks and J. Comer, J. Phys. B **8**, 1866 (1975).
[17] Kwong T. Chung, T. K. Fang, and Y. K. Ho, J. Phys. B **34**, 165 (2001).
[18] T. K. Fang and Y. K. Ho, Phys. Rev. A **60**, 2145 (1999).
[19] J. R. Harries *et al.*, Phys. Rev. Lett. **90**, 133002 (2003).
[20] X. M. Tong and C. D. Lin, Phys. Rev. Lett. **92**, 223003 (2004).
[21] P. A. M. Gram *et al.*, Phys. Rev. Lett. **40**, 107 (1978).
[22] K. C. Prince *et al.*, J. Synchrotron Radiat. **5**, 565 (1998).
[23] M. Coreno *et al.*, J. Electron Spectrosc. Relat. Phenom. **144–147**, 39 (2005).
[24] M. Domke *et al.*, Phys. Rev. A **53**, 1424 (1996).
[25] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).
[26] M. Žitnik and A. Mihelič (to be published).
[27] M. Žitnik *et al.*, Phys. Rev. A **65**, 032520 (2002).
[28] C. D. Lin, Phys. Rev. A **25**, 76 (1982); **26**, 2305 (1982).
[29] C. Såthe *et al.*, Phys. Rev. Lett. **96**, 043002 (2006).