Radiative Decay of Doubly Excited States in Helium below the He^+ ($N = 2$) Ionization Threshold

M. K. Odling-Smee,[1] E. Sokell,[2] P. Hammond,[1] and M. A. MacDonald[3]

[1]*Department of Physics and Astronomy, University of Manchester, Manchester M13 9PL, United Kingdom*
[2]*Experimental Physics Department, University College Dublin, Belfield, Dublin 4, Eire*
[3]*Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

(Received 5 January 1999)

The radiative decay of $^1P^o$ doubly excited states in helium has been investigated using a novel apparatus in which metastable atoms and vacuum ultraviolet photons are detected. The intensity ratio of the energetically narrow $(sp, 2n-)^1P^o$ and $(2p, nd)^1P^o$ series to the broader $(sp, 2n+)^1P^o$ series is strikingly enhanced in comparison with conventional photoabsorption, photoion, or photoelectron measurements using synchrotron radiation. The experimental approach is a new way forward for the study of energetically narrow doubly excited states.

PACS numbers: 32.80.Dz, 32.50.+d, 32.80.Fb

Doubly excited states in helium have been the subject of much theoretical and experimental work since the first observations of the $(sp, 2n+)^1P^o$ series by Madden and Codling [1]. Many of the states in this series are short lived and readily autoionize. Following photoabsorption, interference between the autoionizing decay route of the excited state and direct ionization to the continuum results in a Fano line shape [2] in photoion and photoelectron spectra. Photoexcitation from the He $1\,^1S$ ground state can access three series converging on the He^+ ($N = 2$) ionization threshold: namely, the $(sp, 2n+)^1P^o$, $(sp, 2n-)^1P^o$, and the $(2p, nd)^1P^o$ series. The first members of each of these series have widths of approximately 37 meV, 0.5 meV, and 1 μeV, respectively [3]. In each series it is expected that the linewidth decreases as n increases, having an n^{-3} dependence [4]. It is only with recent improvements in synchrotron radiation sources, to produce energy resolution less than 5 meV in the 60–80 eV photon energy range, that the $(2p, nd)^1P^o$ series has been observed [5,6].

Our novel apparatus is shown in Fig. 1. Monochromatic vacuum ultraviolet (VUV) photons with a resolution of 0.018 nm (60 meV at 65 eV) produced on beam line 3.3 at the SRS, Daresbury UK, were crossed at right angles with a helium gas beam effusing from a hypodermic needle. The principal polarization vector ($P \approx 0.8$) of the incident VUV photon beam was aligned with the axis of the hypodermic needle. Two detectors placed around the interaction region were sensitive to neutral particles only. Potentials applied to the repeller electrode sets prevented all charged particles originating in the interaction region from reaching the channel electron multipliers, which were sensitive to incident neutral particles with an internal energy $\geq$10 eV. The maximum electric field strength between the repeller electrodes was 2.5×10^4 V m^{-1}. This field strength is capable of field ionizing Rydberg atoms of $n \approx 34$ [7]. A third detector was capable of electron energy selection and detection. An electric field could be formed in the interaction region by applying voltages to two molybdenum plates.

This experimental arrangement was adopted to coarsely discriminate between excited atoms and VUV photons [8,9]. The neutral detector in line with the gas beam was primarily sensitive to long-lived excited atoms. The time of flight, at thermal atom velocities, from the interaction region to the detector was $\approx$40 μs, so that only metastable, singly or doubly excited Rydberg atoms could be detected. Discrimination against the detection of VUV photons is expected because of the alignment of the principal polarization vector with the gas beam. The second neutral detector, perpendicular to the gas beam, was primarily sensitive to emitted VUV photons, as few excited atoms are expected to travel in this direction. These two detectors will be referred to as the metastable atom and VUV photon detectors, respectively. The electron energy selector measured

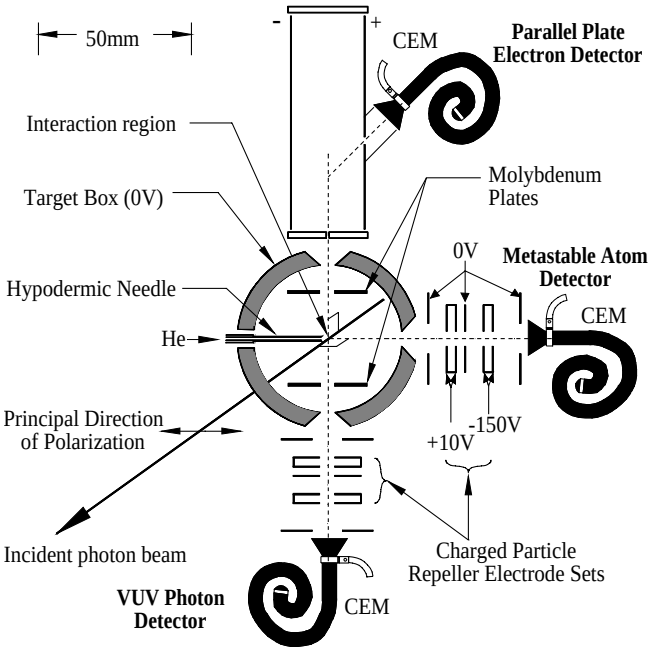

FIG. 1. Apparatus assembly for the measurement of metastable atom, VUV photon, and photoelectron spectra (to scale).

 0031-9007/00/84(12)/2598(4)$15.00

the photoelectron spectrum associated with the production of He^+ ($N = 1$).

Data were simultaneously recorded in all three detectors. The photon energy scale was calibrated to an accuracy of ± 5 meV using the $(sp, 2n+)^1P^o$ series in the photoelectron spectrum [3,5,10].

Figure 2 shows the metastable atom and VUV photon spectra obtained in the energy region spanning the doubly excited states converging on the He^+ ($N = 2$) ionization threshold. In Fig. 2(a) the step increase in the signal level above the He^+ ($N = 2$) ionization threshold, apparent in both the metastable atom and VUV photon spectra, is due to near isotropic VUV photon emission from the He^+ ($2p \rightarrow 1s$) transition [11,12].

A striking feature in the metastable atom spectrum in Fig. 2(a) is the broad, asymmetric peak at 65.378(6) eV lying below the He^+ ($N = 2$) ionization threshold at 65.401 eV [6]. This feature was observed in a previous study [11] using an apparatus in which neutral particles incident on a surface were detected by secondary ion or electron production. This method was of low detection efficiency and was replaced with the present more direct method of detection. In the new metastable atom spectra, additional weaker, symmetric peaks at the energies of the $(sp, 22+)^1P^o$ and $(sp, 23-)^1P^o$ states are observed. Peaks were not observed at these energies in the VUV photon spectrum of Fig. 2(a) because of the statistical accuracy. Yield in our spectra arises from the excitation and radiative decay probabilities for each state. The excitation yield is a product of the excitation cross section of the state and a convolution of the natural energy width of the state with the energy width of the incident photon beam.

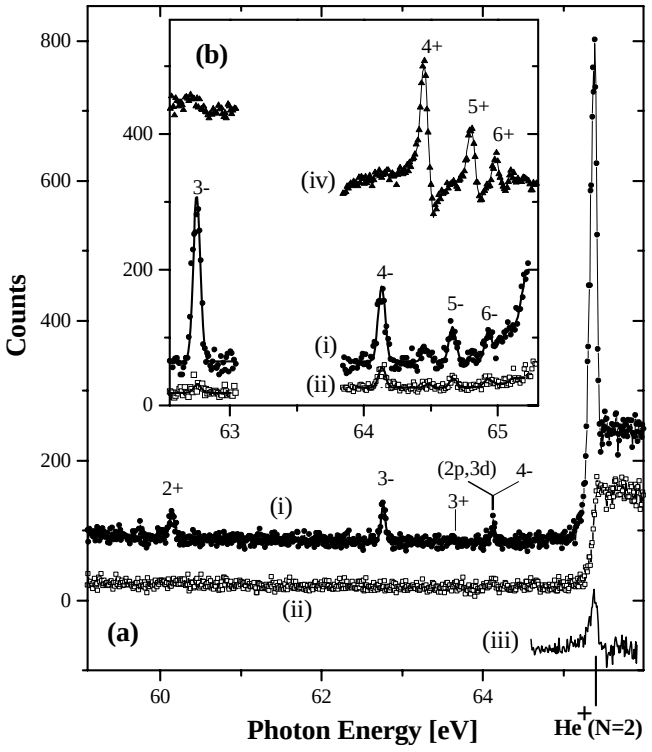

FIG. 2. Metastable atom (i), VUV photon (ii) and (iii), and photoelectron (iv) spectra in the energy region of doubly excited states converging on the He^+ ($N = 2$) ionization threshold. Short form notation is used where, e.g., $2+ \equiv (sp, 22+)^1P^o$. The photon spectrum (iii) is shown following subtraction of the signal arising from the VUV He^+ ($2p \rightarrow 1s$) transition. Spectra shown in (b) are of significantly improved statistical accuracy over those shown in (a). The metastable atom spectrum in (a) has been offset by 50 counts. The photoelectron yield in (b) has been divided by a factor of 15.

The metastable atom and VUV photon spectra are radically different from the photoelectron spectrum as shown in Fig. 2(b). In these spectra symmetric peaks are observed at the energies of states belonging to both the $(sp, 2n+)^1P^o$ and $(sp, 2n-)^1P^o$ series up to $n = 6$. For $n > 6$ it is difficult to resolve the overlapping peaks. The peaks at the energies of states in the $(sp, 2n+)^1P^o$ series and the $(sp, 23-)^1P^o$ state can be unambiguously assigned as there are no other $^1P^o$ states at these energies. For $n \geq 4$, the $(sp, 2n-)^1P^o$ states lie very close in energy to the $(2p, [n-1]d)^1P^o$ states, with the maximum separation of the two series being 16 meV for $n = 4$. With the photon resolution used in our measurements it was not possible to energetically isolate each of these series. In the photoelectron spectrum the states in the $(sp, 2n+)^1P^o$ series dominate and have the characteristic Fano line shapes with only the $n = 3$ member of the energetically narrower $(sp, 2n-)^1P^o$ series being distinguished.

Metastable atoms and VUV photons produced by a number of processes may contribute to the spectra recorded. Atoms in doubly excited states may be expected to be metastable for high values of n. For the lifetime to be ≈ 10 μs (i.e., of the order of the flight time to the detector) the value of n would need to be greater than 1460, 320, and 50 for the $(sp, 2n+)^1P^o$, $(sp, 2n-)^1P^o$, and $(sp, 2d)^1P^o$ series, respectively, assuming an n^3 lifetime dependence [4]. It is therefore unlikely that doubly excited states were directly detected.

Doubly excited atoms of $^1P^o$ symmetry can radiatively decay to singly excited atoms of ^1S and ^1D symmetry. These $n\,^1S$ and $n\,^1D$ Rydberg atoms have lifetimes ≈ 10 μs for $n > 22$ and 26, respectively, and preferentially decay to low-$n\,^1P$ states [13]. The branching ratio for the decay of $n\,^1P$ states is approximately 97% to the ground state and 3% to the metastable $2\,^1S$ state, which has a lifetime of 20 ms [14]. The doubly excited states can also radiatively decay directly to the metastable $2\,^1S$ state or the ground state [15,16].

We observe metastable atoms and VUV photons at incident photon energies corresponding to low-n doubly excited states. The presence of a signal at these energies in both spectra suggests that radiative decay to singly excited states is responsible for a significant fraction of the yield in our spectrum. Alternative decay routes would not produce a signal that could be observed in both channels. Radiative decay to long-lived doubly excited states would result in photons that are not sufficiently energetic to be detected,

whereas radiative decay to the ground state does not result in the production of metastable atoms.

It is intriguing to note the differences between the peak intensity trends in the metastable atom and VUV photon spectra in Fig. 2(b). In Table I are given the intensities of the peaks in each type of spectrum, relative to the peak at the energy of the $(sp, 24-)^1P^o$ state. In the metastable atom spectrum the intensities of the $(sp, 2n-)^1P^o$ states decrease smoothly as n increases. In the VUV photon spectrum, for the same states, the peak intensity doubles between $n = 3$ and $n = 4$, and then decreases at $n = 5$, but by a smaller factor than observed in the metastable atom spectrum. We propose that this intensity behavior is accounted for by the presence of the energetically narrow $(2p, [n-1]d)^1P^o$ states for $n \geq 4$ which may decay preferentially via spectator type transitions to $(1s, md)^1D$ atoms, where $m \approx n$, and that the radiative decay of $(sp, 24-)^1P^o$ states primarily populates the metastable $2\,^1S$ state. These radiative decay routes are summarized in Fig. 3.

Such an interpretation is supported by Baltzer and Karlsson [17] who identified various radiative transitions from doubly excited states below the He^+ $(N = 2)$ ionization threshold populated in a microwave discharge. Specifically they clearly observed transitions from the $n = 3$, 4, and 5 members of the $(sp, 2n-)^1P^o$ series to the $2\,^1S$ metastable state, while only a weak unidentified line at 28.499 nm may be associated with the $(2p, 3d)^1P^o \rightarrow 2\,^1S$ transition. A strong line in their spectrum corresponded to the $(2p, 3d)^1P^o$ to $(1s, 3d)^1D$ transition providing evidence that the $(2p, nd)^1P^o$ series radiates preferentially to states of ^1D symmetry. They did not identify any radiative transitions from the $(sp, 2n+)^1P^o$ series which is consistent with the weak intensity of these states in the VUV photon spectrum presented here.

There is very limited theoretical work relating to the radiative decay of doubly excited states to the metastable $2\,^1S$ state [18]. Some theoretical work has considered photoexcitation from metastable helium to doubly excited states below [19–21] and above [22–24] the He^+ $(N = 2)$ ionization threshold. For photoexcitation from metastable helium it is predicted [19–21] that there will be a strong enhancement of the narrow doubly excited states. The $(sp, 2n+)^1P^o$ series is expected to be more weakly excited than either the $(sp, 2n-)^1P^o$ or the $(2p, nd)^1P^o$ series, with only the $(sp, 22+)^1P^o$ state of comparable intensity. Although we have observed the decay to the metastable $2\,^1S$ state, our results are in qualitative agreement with these theoretical predictions. We see a dramatic enhancement of the signal from the narrower, longer lived doubly excited states. To our knowledge there is no experimental work covering direct photoexcitation from metastable $2\,^1S$ to doubly excited states.

A broad, asymmetric peak is observed below the He^+ $(N = 2)$ ionization threshold in the metastable atom spectrum of Fig. 2(a). A similar feature can also be distinguished in the VUV photon spectrum of Fig. 2(a) when the contribution of the signal from the He^+ $(2p \rightarrow 1s)$ transition is removed by a least squares fitting procedure. The procedure, applied to a number of VUV spectra, produced similar results.

The asymmetric peak maximum occurs at 65.378(6) and 65.382(7) eV in the metastable atom and VUV spectra, respectively, and energetically corresponds to doubly-excited states of principal quantum number $n \approx 25$, in agreement with previous findings [11]. This peak is likely to be comprised of overlapping peaks centered at the energies of individual doubly excited states. The photon energy resolution in the present experiment did not allow the identification

TABLE I. Relative intensities of the observed peaks in the metastable atom and VUV photon spectra. The numbers in parentheses are the estimated uncertainty of the last digit(s). The relative intensities have been derived from a number of metastable atom and VUV photon spectra including those shown in Fig. 2.

$^1P^o$ State Electron configuration	Relative intensity Metastable atom spectra	VUV photon spectra
$(sp, 22+)$	147(24)	...
$(sp, 23+)$	15(4)	17(14)
$(sp, 24+)$	17(3)	24(4)
$(sp, 25+)$	15(3)	26(6)
$(sp, 23-)$	208(8)	45(6)
$(sp, 24-)$ and/or $(2p, 3d)$	100	100
$(sp, 25-)$ and/or $(2p, 4d)$	49(3)	73(6)
$(sp, 26-)$ and/or $(2p, 5d)$	37(3)	58(7)

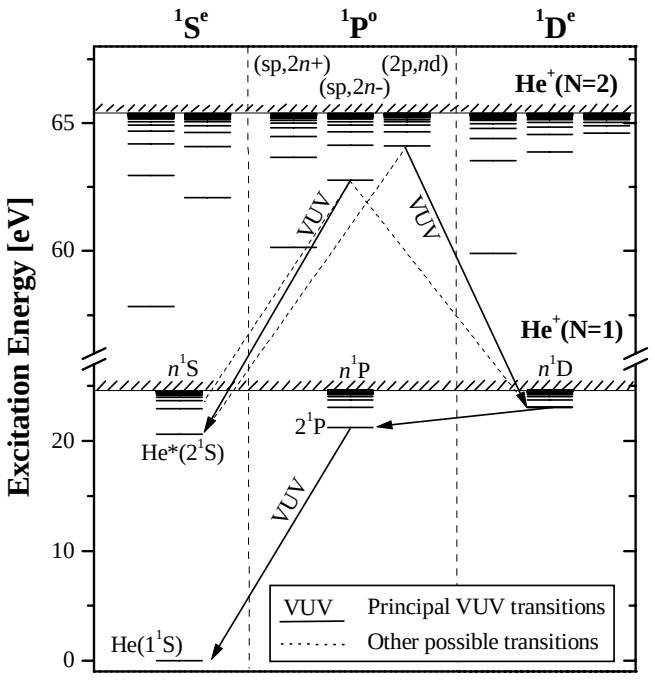

FIG. 3. Schematic diagram of the radiative decay scheme: illustrated for the decay of the $(sp, 23-)^1P^o$ and $(2p, 3d)^1P^o$ doubly excited states. Transitions labeled "VUV" produce photons that could have been detected. Singly excited states are metastable for high n.

of the principal $^1P^o$ series which contributed to the underlying structures. The detection systems used did not allow the admixture of $2\,^1S$ to high-n Rydberg atoms or the emitted VUV photon energies to be determined.

In the absence of detailed information about the identity of the states and decay processes involved, we suggest that the branching ratio between radiative decay and autoionization increases as n increases. This suggestion is necessary to account for the observed increase in the yield of VUV photons near the He^+ ($N = 2$) ionization threshold. If there were no change in the branching ratio the yield would be proportional to the excitation cross section, and the spectra would appear much like any other Rydberg series spectra, without the broad peak. Even a small change in the branching ratio to favor the radiative decay pathway would give rise to a peak due to the large density of states near the ionization threshold. It seems plausible that as the radiative decay route becomes more favorable the population of metastable states, including the $2\,^1S$ state, will show a corresponding increase. These metastable states may also include singly excited states where n is sufficiently high for such atoms to reach the metastable detector. Consequently this radiative decay mechanism could also go some way to explaining the broad asymmetric peak in the metastable atom channel.

These measurements do not discount various other mechanisms [11] which may give rise to the below threshold peak in the metastable atom spectrum. It is possible that $(2p,[n-1]d)^1P^o$ atoms may be directly detected for sufficiently high values of n. As the doubly excited state lifetimes increase collisional deexcitation to singly excited states may become important. The pressure dependence of the peak intensity was experimentally explored as a function of target gas pressure and did not indicate that collisional processes play a significant role in the formation of the states.

Residual electric fields may also enhance the lifetime of the initial doubly excited states due to Stark mixing. Investigations of the intensity of the broad asymmetric peak in the metastable atom spectrum as a function of the strength of the applied electric field in the interaction region were performed. It was found that the yield of metastable atoms increased by approximately 30% in a linear manner as the field was increased from 0 to 6 $kV\,m^{-1}$. The yield was largely unaffected by further increasing the field to the maximum value of 10 $kV\,m^{-1}$. Such behavior is broadly consistent with field stabilization of singly excited high-n Rydberg states [7]. However, during the recording of the spectra presented here, the applied field was zero and hence field stabilization is not thought to be responsible for the broad asymmetric peak. As radiative decay to singly excited states plays a significant role in the decay of the low-n doubly excited states, it seems likely that they are also responsible for a significant part of the broad asymmetric peak associated with high-n states.

In summary, we have made the first observations of symmetric features associated with members of the $(sp,2n+)^1P^o$, $(sp,2n-)^1P^o$, and $(2p,[n-1]d)^1P^o$ series up to $n = 6$ using detectors sensitive to excited atoms and VUV photons. Features in the metastable atom spectrum appear to be associated primarily with the $(sp,2n+)^1P^o$ and $(sp,2n-)^1P^o$ series via radiative decay to singly excited metastable $2\,^1S$ and high-n Rydberg states. Features in the VUV photon spectrum appear to be particularly strong at the energies of the $(2p,[n-1]d)^1P^o$ series and are probably associated with radiative decay to $m\,^1D$ atoms with $m \approx n$. A broad asymmetric peak at 65.38 eV, just below the He^+ ($N = 2$) ionization threshold is probably due to the detection of singly excited metastable $2\,^1S$ and high-n Rydberg atoms arising from the radiative decay of high-n members of the $(sp,2n-)^1P^o$ and $(2p,[n-1]d)^1P^o$ series. These decays may be accentuated by a change in the branching ratio in favor of radiative decay as n increases.

The proposed interpretation suggests that an excellent method for studying the highly correlated $(2p,[n-1]d)^1P^o$ states is via radiative decay rather than autoionization. Calculations of the radiative decay of doubly excited states to singly excited states are urgently required.

[1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963).
[2] U. Fano, Phys. Rev. **124**, 1866 (1961).
[3] M. Domke *et al.*, Phys. Rev. A **53**, 1424 (1996).
[4] M. Domke *et al.*, Phys. Rev. Lett. **66**, 1306 (1991).
[5] M. Domke *et al.*, Phys. Rev. Lett. **69**, 1171 (1992).
[6] K. Shultz *et al.*, Phys. Rev. Lett. **77**, 3086 (1996).
[7] T. F. Gallagher, *Rydberg Atoms* (Cambridge University, Cambridge, England, 1994).
[8] M. K. Odling-Smee *et al.*, in Proceedings of the 20th ICPEAC, 1997, Program and Abstracts book.
[9] M. K. Odling-Smee *et al.*, in Proceedings of the VUV-12, 1998, Program and Abstracts book.
[10] J. M. Rost *et al.*, J. Phys. B **30**, 4663 (1997).
[11] E. Sokell *et al.*, J. Phys. B **29**, L863 (1996).
[12] J. Jimenez-Mier *et al.*, Phys. Rev. A **44**, 5615 (1991).
[13] C. E. Theodosiou *et al.*, At. Data Nucl. Data Tables **36**, 97 (1987).
[14] R. S. van Dyck *et al.*, Phys. Rev. A **4**, 1327 (1971).
[15] A. V. Snegursky *et al.*, J. Phys. B **27**, 1589 (1994).
[16] D. R. DeWitt *et al.*, J. Phys. B **28**, L147 (1995).
[17] P. Baltzer and L. Karlsson, Phys. Rev. A **38**, 2322 (1988).
[18] H. O. Dickeson and M. R. Rudge, J. Phys. B **3**, 1284 (1970).
[19] B. Zhou *et al.*, J. Phys. B **26**, L337 (1993).
[20] T. N. Chang and M. Zhen, Phys. Rev. A **47**, 4849 (1993).
[21] T. K. Fang and T. N. Chang, Phys. Rev. A **56**, 1650 (1997).
[22] B. Zhou and C. D. Lin, Phys. Rev. A **49**, 1057 (1994).
[23] I. Sanchéz and F. Martín, Phys. Rev. A **47**, 1520 (1993).
[24] J. Z. Tang and I. Shimamura, Phys. Rev. A **50**, 1321 (1994).