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Highly excited states: New experimental windows in photoexcitation

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Abstract

In a recent series of experiments, it has been demonstrated that highly excited states, formed through photoexcitation using vacuum-ultra-violet (VUV) synchrotron radiation, have a significant probability of decaying via the fluorescence decay route. This decay route has products of VUV fluorescence photons and, in some cases, long lived metastable atoms. In helium, studies using high resolving powers at third generation synchrotron light sources utilising this decay route to the metastable atoms have enabled the identification of three series of triplet doubly-excited states below the $N = 2$ ionisation threshold which are excited by single photon impact from the singlet ground state. The pulsed nature of synchrotron light and the detection of fluorescence photons has been utilised to enable fluorescence lifetime measurements and the determination of the $(2p3d)^1P$ lifetime. Fluorescence timing measurements have also allowed the nearly-energy-degenerate ion states 3^2S, 3^2P and 3^2D to be separated through their different lifetimes to allow ion state specific cross sections as a function of energy to be extracted. These groups of measurements have stimulated new theoretical work which explicitly includes both the fluorescence and autoionisation decay routes to reveal for some states a branching ratio in favour of fluorescence.

Keywords: Photoexcitation; Synchrotron radiation; Helium; Radiative decay; Metastable atoms; Autoionisation; Fluorescence; Lifetime; Doubly-excited states

1. Introduction

Atomic and molecular structure is most commonly thought about in terms of the combination of many single electron orbitals. These orbitals result in radial probability densities which describe the charge distribution in the system to roughly concentrate in certain regions in radius from the nuclear core and relate to the shell structure of systems. For many processes, and particularly in the ultra-violet (UV) and vacuum-ultra-violet (VUV), it is only the outermost electrons that are considered optically active, and in many situations involving excitation, only one electron is excited. States in which two electrons are simultaneously promoted to other orbitals are called "doubly-excited" or "highly-excited". It is these types of state that are the subject of the present studies.

Historically, the earliest mention in the literature for the existence of doubly-excited states seems to be by Kruger [1] in 1930 in an analysis of the spectral lines produced in arc discharges in helium. Many years passed, before the doubly-excited states of helium were studied in photoabsorption from the ground state by Madden and Codling [2] in 1963 using synchrotron radiation. These photoexcited doubly-excited states were observed as resonances interpreted by Cooper et al. [3] and identified as being of $^1P^o$ character belonging to the series $(sp,2n+)$ converging on the $N = 2$ ionisation limit at 65.4 eV. The existence of two further series of energetically narrower states $(sp,2n-)$ and $(2pnd)$, both of $^1P^o$ character was predicted. The line shapes of the resonances observed by Madden and Codling were as predicted by Fano [4] resulting from interference between continuum ionisation and the resonant photoexcitation with subsequent autoionisation of the doubly-excited states. Following these studies, experimental efforts were concentrated into photoabsorption, photoion and photoelectron spectroscopy. Photoion spectroscopy came to dominate the study of doubly-excited states partially because of the extremely good measurement sensitivity that could be achieved, and in helium marvellously detailed experiments were performed (e.g. [5,6]). Photoelectron spectroscopy was used less extensively but did provide the capability to study the decay by autoionisation of doubly-excited states into

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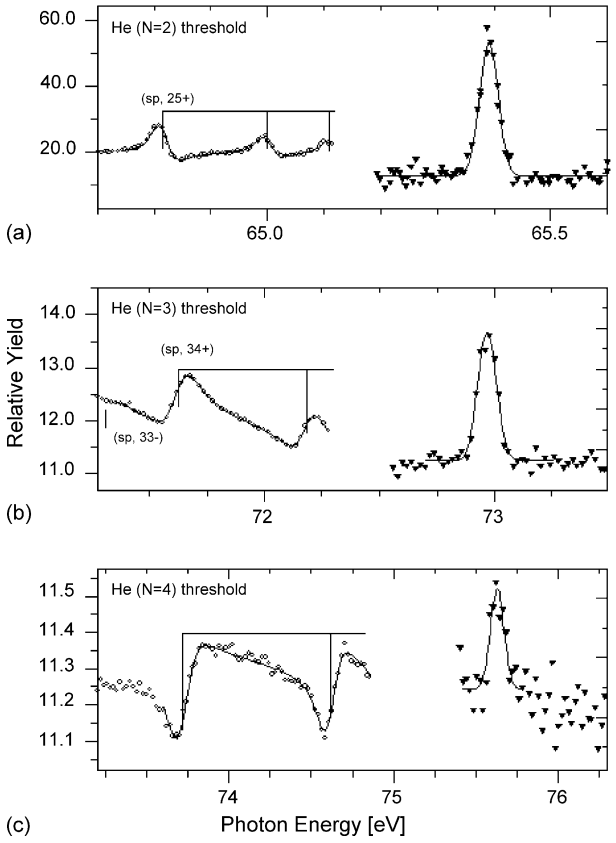

Fig. 1. Secondary ion signal (RHS) and conventional photoion signal (LHS) i the energy regions of (a) $N = 2$, (b) $N = 3$ and (c) $N = 4$ ionisation thresholds in helium (from [15]).

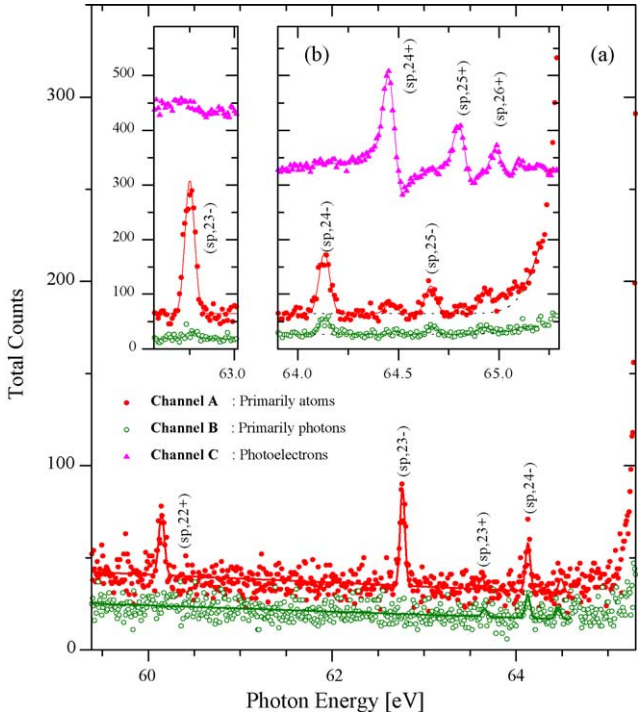

Fig. 2. (a) Neutral particle spectra over the energy region of series of doubly-excited states converging on the $He^+(N = 2)$ threshold. (b) Neutral particle spectra recorded with improved statistical accuracy and compared with the photoelectron spectrum (arising from autoionisation) (adapted from [15]).

selected final states of the helium ion and termed "constant ion state" (CIS) spectra (e.g. [7]). Theoretical modelling was in very good agreement with photoabsorption, photoion and photoelectron data (e.g. [8,9]). Fluorescence from doubly excited states has been observed in beam foil spectroscopy [10] and following electron excitation [11].

The new sequence of experiments began in late in 1994, when Hammond's group in Manchester, during the course of making photoelectron spectroscopy measurements of helium [7] at the Daresbury synchrotron radiation source with a resolving power of ~1000, noticed a peak like structure at the $N = 1$ ionisation threshold observed in what was thought to be an ion detection system. It was established that this peak was arising from neutral particles leaving the interaction region of gas and photon beams since photoions were prevented from leaving the interaction region by the presence of a weak electric field. Photoelectrons were also excluded by an appropriately biased mesh. Thus, only neutral particles and photons could enter the detector region where a channel electron multiplier, out of line of sight of the interaction region, could be biased to detect either electrons or ions produced by secondary processes within the detector. The right hand side of Fig. 1 shows the structures recorded near the $N = 2$–4 ionisation thresholds in helium when secondary ions were detected. The relative yield scale applies to these spectra. The yield of secondary ions arose from the field ionisation of highly excited Rydberg atoms produced in the fluorescence decay of high n doubly-excited states. The left hand side of Fig. 1 shows photoion signal, recorded with no electric field in the interaction region. Overall, the core advantage of this in-direct detection system was the insensitivity to VUV photons. This allowed experiments to be conducted above the $He^+(N = 2)$ ionisation threshold where the fluorescence of excited ions masks the neutral particle signal in line-of-sight detection experiments. A major concern in these early studies was whether the signal recorded was the result of direct excitation or the effects of secondary processes (discussed in detail in [12,13]). The detailed VUV transition measurements from doubly to singly excited states of helium in a microwave discharge by Baltzer and Karlsson [14] significantly contributed to the interpretation of our new spectra as arising from a direct process.

More detailed studies were performed, including pressure dependencies, electric field dependencies and time-of-flight spectra which were reported at a sequence of conferences and finally in *Physical Review Letters* [15] and detailed in the Ph.D. thesis of Odling-Smee [13]. Fig. 2 shows a key spectrum recorded during these studies in which, though the energy resolution was ~60 meV, peaks in both the metastable atom spectrum and the fluorescence photon spectrum can be assigned to the energetically narrow series $(sp,2n-)^1P$ and which have intensities similar to the peaks arising from the $(sp,2n+)^1P$ series. Very significantly the