Interaction of short wavelength photons with atomic and molecular ions: 50 years some examples

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Abstract
Steve Manson has been involved with the study of the photoionisation of atomic ions since the early 70’s. Over the half century since, much has happened in terms of theory and experiment. This short paper provides some examples of the inner-shell photoionisation of atomic ions, which demonstrate different experimental approaches and the important ongoing symbiotic nature of combined theoretical and experimental studies. Recent initiatives in the study of the photoionisation of small molecular ions are also briefly described.

1. Introduction

The interaction of ionising photons with positively charged ions is a fundamental process in nature, with implications for the understanding of a wide range of laboratory, atmospheric and astrophysical plasmas. Extensive theoretical investigations are needed to understand and quantify the complex interactions arising from the many-body nature of the phenomena. Experimental investigations are required to provide fundamental data such as cross sections and to help benchmark the various theoretical approaches.

Steve Manson’s long and distinguished series of theoretical investigations of atomic ions began with a number of papers published during the 1970’s. In the introduction to their highly cited paper [1] published in 1979, Reilman and Manson state ‘A knowledge of photoabsorption cross sections for low-Z positive atomic ions is of importance in solar physics and astrophysics for photon energies from threshold to about 5 keV. In this energy range, photoionisation and photoabsorption are essentially synonymous, so we shall use the terms interchangeably. Experimentally very little is known. Photoionisation cross sections as a function of energy have been measured only for Li$^+$ and Na$^+$ (Lucatorto and McIlrath 1976, McIlrath and Lucatorto 1977). In addition, a point at a single hv has been measured for Xe$^+$ (Cairns and Weissler 1962). Thus the need for theoretical calculations.’

This quotation makes it very clear that it was fully recognised at the time that considerable efforts would need to be made both experimentally and theoretically. One recurring theme of Steve Manson’s extensive research portfolio, spanning over 50 years, has been his stimulation and support for experimental studies. In this short paper, examples of combined theoretical and experimental investigations of the photoionisation of atomic ions are presented to provide some insight into different experimental approaches and to emphasise the crucial interplay between theory and experiment for advancing the field. Recent advances in the study of small molecular ions are also presented.

1.1. Resonant laser driven ionisation (RLDI): examples

On the experimental side the investigations of Lucatorto and McIlrath, referred to by Reilman and Manson in their 1979 paper, exploited the Resonant Laser Driven Ionisation approach (RLDI) [2–4]. In RLDI an ionised column is produced when a sufficiently intense laser beam is tuned to match an absorption transition in the parent neutral species. Through super-elastic collision assisted ionisation [5], a column of ions is produced along the path of the laser beam through the parent atomic vapour. A BRV source was used to provide the short wavelength backlighting continuum. The RLDI technique was later extended to produce a doubly ionised...
column and enabled an examination of the isonuclear series Ba, Ba$^+$ and Ba$^{2+}$ [6]. The experiments require however a starting vapour column and lasers tunable to suitable atomic transitions.

1.2. Dual laser plasma (DLP) experiments: examples

Coincidentally, during the same decade an alternative Dual Laser Plasma (DLP) approach was being developed in Dublin and Padua. In DLP experiments separate synchronised laser beams are used to produce the absorbing ionised column and the required short wavelength back-lighting continuum source. Early experiments indicated that with suitable targets a laser produced plasma can emit very useful broadband continua throughout the extreme ultraviolet/soft-xray regions of importance for the inner-shell photoionisation of positive atomic ions [7–9]. The potential of the DLP technique was illustrated by the early study of Li$^+$ [10] where, in addition to outer-shell ionisation, for the first time the doubly-excited resonances were observed in a He-like ion. The use of a laser produced plasma continuum source contrasted with the BRV light source used by Lucatorto and McIlrath in their RLDI studies.

Further developments in the DLP technique and the many experiments over the years at Dublin and Padua have been well described in [11–16] and references therein. The DLP technique proved to be a very flexible and useful approach for the investigation of the interaction of short wavelength radiation with a wide range of positive atomic ions. It has proved particularly useful for the study of isonuclear or isoelectronic sequences but is usually limited to providing (at best) relative cross sections only.

The flexibility and power of the DLP technique is nicely illustrated in the study of the neon isoelectronic sequence ions, Na$^+$, Mg$^{2+}$, Al$^{3+}$ and Si$^{4+}$ [17]. By using different solid targets along with carefully optimised laser irradiation conditions and inter-laser-pulse time delays the column densities of neon-like ions could be maximised and their inner-shell photoabsorption studied systematically as the stage of ionisation increases. The experimental observations indicated an unusual behaviour of the 2p excitation cross section for the Si$^{4+}$ ion near the threshold limit, which lies at a photon energy of about 170 eV.

This near threshold anomaly for Si$^{4+}$ proved interesting to Steve Manson and his collaborators from Madras who carried out a detailed calculation of the photoabsorption cross section for the neon like ion species extending from neutral neon up to $Z = 100$. Figure 1, taken directly from reference [17], shows the calculated photoionisation cross section at the $^{2}P_{1/2}$ threshold versus the initial state charge, for the early members of the sequence without (5 channel) and with (7 channel) coupling between the 2p and 2s channels. The dramatic difference for the case of Si$^{4+}$ is seen in the 7 channel coupled calculation.

Essentially the 7 channel calculation takes into account the 2s $\rightarrow$ 3p innershell transition which moves from well above the 2p ionisation threshold to below the threshold as you move up the isoelectronic sequence through Si$^{4+}$. The overlap of the innershell resonance energy with the 2p ionisation threshold for Si$^{4+}$ causes the dramatic anomalous behaviour observed both experimentally and theoretically. The paper concluded that ‘interpolation or extrapolation of photoionisation and recombination cross sections along sequences should be viewed with extreme caution unless the role of innershell transitions is accurately included’ [17]. The Si$^{4+}$ case is a nice example of an experimental observation stimulating theoretical investigations which led to deeper insight into the generic nature of the phenomenon.

Figure 1. Calculated photoionisation cross section at the $^{2}P_{1/2}$ threshold, with and without coupling between the 2s and 2p channels, versus the initial state charge for the neon isoelectronic sequence. Reprinted figure with permission from [17]. Copyright 1999 by the American Physical Society.
1.3. Synchrotron radiation and atomic ions: examples

The use of synchrotron radiation to explore photoionisation of ions was pioneered by Lyon, Peart, West and Dolder at the Daresbury Laboratory synchrotron facility in the 1980's [20–22]. They used a merged ion and synchrotron photon beam approach to study the photoionisation of some ground state singly charged atomic ions. A key advantage of this technique is the linear dependence of the detected photoions on the photoionisation cross section. This contrasts strongly with the DLP approach in which the transmitted light changes logarithmically with the cross section, according to the Beer–Lambert absorption law. A further key advantage is that the synchrotron based merged beam technique allows absolute cross sections to be determined [20–22].

The measurement of the absolute photoionisation cross section for Si$^2+$ in the region of the 2p threshold [18] illustrates the above mentioned advantages of the synchrotron based merged beam approach. In this experiment, carried out at the SuperACO synchrotron facility in Orsay France, the photoionisation of the doubly charged ion was investigated over the 90–160 eV photon energy range.

In Figure 2, taken directly from reference [18], both the single (solid line) and the double ionisation channel (dashed line) cross sections are shown. Strong resonances are seen above 110 eV leading to limits in the 135 eV region, following which continuum absorption is seen to higher photon energies particularly in the double ionisation channel.

Figure 2 also shows weak resonances at about 97 eV, which are due to the existence in the merged ion beam of metastable ions. This often presents as a problem in the merged beam technique as excited states produced in the ion source can be sufficiently long lived to reach the photon ion interaction zone. In the Si$^2+$ experiment the population of the metastables was estimated to be less than 3% of the ground state population.

The data were compared with the results of advanced theoretical calculations including the Relativistic Random Phase Approximation (RRPA) and the Relativistic Multichannel Quantum Defect Theory (RMQDT), to which Manson and collaborators contributed [18]. The experiments were both stimulated by and facilitated by prior DLP experiments which provided energies of the various resonances for both ground [23] and metastable states [24]. The photon energy scanning nature of synchrotron based techniques and the often limited beam time available at large scale facilities means that prior information on the photon energy regions of interest obtained by the complementary laboratory based DLP technique can be very valuable.
Over the last two decades or so the experimental capabilities of storage ring based synchrotron radiation-emitting facilities for the study of photoionisation of ions have greatly improved. Dedicated merged photon ion setups such as those at Aarhus (Denmark), Photon Factory (Japan), SOLEIL (France), ALS at Berkeley (USA) and PETRA III (Germany) have all contributed to extensive high quality results on a fairly wide range of atomic ions. The data are important as they help to benchmark advanced theoretical treatments that may then be used for ions for which there are no experimental results available. Synchrotron based experiments have been extensively reviewed in the literature [25–28]. The most recent development has been the Photon-Ion Spectrometer at PETRA III (PIPE) which is capable of very high resolution investigations over the 250 eV to 3000 eV photon range [29].

1.4. Photoionisation of small molecular ions: examples

While there have been extensive investigations of positive atomic ions the situation is very different for positively charged small molecular ions. Despite their fundamental, astrophysical and technological importance, photoionisation studies of small molecular ions are still rather scarce. When the merged photon ion technique is applied to atomic ions, the synchrotron photon interacts with the ion of interest to produce a more highly charged ion. Because of the small mass of the ejected electronic(s) the path of the ‘parent’ ion is hardly disturbed and the photoionised ion can still be detected in the usual way. Consider on the other hand the case of a small positively charged molecular ion. In this case, following the absorption of a high energy photon, fast Auger decay followed by molecular dissociation occurs and a relatively heavy nucleus can leave in any direction. The resulting momentum transfer to the ion left behind can be very substantial and means that the photoionised ion no longer travels in the same direction and may not be detected.

A few experiments with molecular ions have either avoided or solved this issue. For example, for very large fullerene type molecular ions successful merged photoion experiments have been carried out [30–32]. For the special case of the small CO$^+$ molecule in the valence excitation region, the photoionised cation (CO$^{2+}$) is left in a long lived metastable state which survives to the detection zone [33–35].

A different approach has been adopted in a small number of crossed beam fragmentation experiments using FEL radiation. Specialised detectors are used which are capable of recording the fragmentation particles after the photoionisation event. The small molecular ions HeH$^+$, H$_3$O$^+$, H$^+$ (H$_2$O)$_2$ have all been explored in this way [36–38]. The x-ray absorption spectrum of N$_2$ was recorded in the K-shell excitation regime by irradiating ions stored in a cryogenic radio frequency trap at the BESY storage ring [39].

An alternative strategy, recently successfully initiated with the standard merged photon ion beam setup, is to study the photoionisation of hydride molecular ions. In this case the nuclei which leave are the lightest possible and the disturbance to the flight path, of the resulting relatively heavy ion by dissociation is minimised. An example of this approach is the investigation of the SiH$_n^+$ molecular series with $n=1\rightarrow3$ [19]. The experiments were carried out using the high resolution merged photon ion Multi-Analysis Ion Apparatus (MAIA) system on the Pleiades beamline at the SOLEIL synchrotron. Figure 3 (taken directly from 19) shows the measured cross section in the 105–120 eV photon energy range for the series ranging from the bare atomic ion Si$^+$ through to the SiH$_3^+$ molecular ion.

The data were recorded in the dominant Si$^{2+}$ decay channel. The cross sections for the hydride molecules were put on a Mb scale by assuming the cross section at 120 eV photon energy, where direct photoionisation in the 2p subshell dominates, is the same as that previously measured in absolute terms for the parent atomic ion Si$^+$ [40]. As the number of hydrogens increases there is a clear systematic trend of the cross section towards lower energies, consistent with the concomitant increasing shielding of the core. The cross section behaviour for each molecular ion is broadly similar showing (1) a broad and shallow peak on the low energy side (below about 107 eV) associated with 2p excitation to strongly dissociating anti-bonding orbitals, (2) a strong ‘valence excitation’ region analogous to 2p→3d type transitions in the corresponding united atoms and (3) extended Rydberg series leading to ionization limits which move to lower photon energies as the number of hydrogens increases.

In addition to being more intricate experimentally, the study of photoionisation of molecular ions requires also considerably more complex theoretical calculations. Reference 19 shows comparison of the experimental data with the results of detailed ab initio calculations. The comparisons show that photoexcitation from both ground and excited-state configurations needed to be taken into account. Qualitative agreement exists between theory and experiment [19] but detailed agreement will require further efforts.

While the first experimental data stimulated the theoretical calculations of reference [19], predictions provided by the calculations stimulated later experiments at lower photon energies which showed uniquely vibrationally resolved structures for the SiH$_4^+$ ions in the 98–102 eV range [41]. This nice example of juxtapositioning in the order of theory and experiment underlines their critical synergistic interaction.

Inner-shell excitations of the CH$^+$ and OH$^+$ ions [42] and NH$^+$ [43] have also been investigated in the K-shell excitation regime using the same SOLEIL merged photon ion MAIA facility. At the PIPE facility located
at the PETRA III synchrotron, a number of small molecular ions including IH\textsuperscript{+} \([44]\), NH\textsubscript{y}\textsuperscript{+} (\(y = 0–3\)) \([45]\) and CH\textsubscript{x}I\textsuperscript{+} (\(x = 0–3\)) \([46]\) have been studied.

A final example, which further shows the critical interface of experiment and theory in understanding the physics of the interaction of short wavelength photons with small molecular ions, is seen in the case of carbon hydride molecular ions. In studying the series CH\textsubscript{n}\textsuperscript{+} (\(n = 0–3\)) in the K-shell excitation regime, in an analogous way to the SiH\textsubscript{n}\textsuperscript{+} (\(n = 0–3\)) series in the L-shell regime described earlier, it was found that on moving from the bare atomic ion C\textsuperscript{+} to CH\textsuperscript{+} there was a similar move of the cross section towards lower energies associated with the analogous core shielding \([42]\). However on moving to the cases of CH\textsubscript{2}\textsuperscript{+} and CH\textsubscript{3}\textsuperscript{+} the situation changed dramatically with the dominant resonance cross sections apparently absent. This led to an intensive follow up theoretical investigation which provided key insight into the x-ray photochemistry of carbon molecular ions \([47]\), important for interstellar chemistry. The results showed that after absorption of a short wavelength photon the molecular ion (CH\textsubscript{2}\textsuperscript{+} or CH\textsubscript{3}\textsuperscript{+}) undergoes very fast Auger decay and subsequent fragmentation into channels other than the experimentally measured C\textsuperscript{2+} channel. In addition to explaining the experimentally observed low yield in the C\textsuperscript{2+} channel, the theoretical investigations showed that in the case of CH\textsubscript{2}\textsuperscript{+} the dominant final products are C\textsuperscript{+}/H\textsuperscript{+}/H or CH\textsuperscript{+}/H\textsuperscript{2} and for CH\textsubscript{3}\textsuperscript{+} the system breaks into CH\textsubscript{2} and H\textsuperscript{+}. The latter case shows a new route to form CH\textsubscript{2}\textsuperscript{+} near an x-ray source. The calculations also provide valuable information on the kinetic and internal energies of the product fragments.

1.5. Conclusions
Over the last 50 years or so the experimental and theoretical insights into the interaction of short wavelength photons with atomic and molecular ions have made substantial progress. In particular, the study of the photoionisation of atomic ions can now be considered a reasonably mature field. The study of the interaction of ionising radiation with small molecular ions however is still in its relative infancy. The few examples discussed in this paper illustrate some of the experimental approaches and especially underline the importance of the close interaction of experimentalists with their theorist counterparts. Following recent world-wide source developments such as x-ray FELs it is anticipated that studies of the interaction of short wavelength photons with ions, both atomic and molecular, will gather further welcome momentum.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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