1 Atomic and Molecular Science

1-1 Large Resonances due to Doubly Excited States of Methane and Ammonia

The dynamics and spectroscopy of doubly excited molecules are one of the most interesting research targets today since the breakdown of both the independent electron model and the Born-Oppenheimer approximation are observed in them. We have measured the correct and absolute cross sections for the emission of dispersed fluorescences from the excited hydrogen atoms in the photoexcitation of CH_4 [1] and NH_3 [2] as a function of incident photon energy in the vacuum ultraviolet range at BL-20A for the first time. It is expected that the structures attributed to the doubly excited states resulting in the formation of the neutral hydrogen atoms, H(n), are shown up in the cross section curves for the fluorescences from H(n) since the contribution from ionization is suppressed to a large extent. Fig. 1 shows the measured cross sections for the H(n=4→n'=2) fluorescence, Balmer-β, in the photoexcitation of CH_4 as a function of incident photon energy.

We have found that the green peak is attributed to the well-known singly-excited states, the $(2a_1)^{-1}(n"pt_2)$ states, and the red peak is attributed to the newly found doubly-excited state, labeled D2, built on the $(1t_2)^{-2}(3a_1)$ ion core. The excitation of two electrons by single-photon absorption should be much weaker than that of a single electron within the independent electron model since the interaction with photons is expressed by the electric dipole moment, a sum of electron coordinates that are single-electron operators. Since the appearance of the large peak originating from the doubly excited state is remarkable and interesting, we have studied this point quantitatively in terms of the oscillator strengths. The integration of the green and red curves gives the oscillator strengths for the H(n=4→n'=2) fluorescence originating from the precursor singly and doubly excited states, respectively. The results are shown in Fig. 2 together with those for the other Balmer fluorescences. It is remarkable that the oscillator strengths for the H(n=4-7→n'=2) fluorescences originating from the doubly excited D2 states amount to twice those from the singly excited $(2a_1)^{-1}(n"pt_2)$ states contrary to the independent electron model. The 'satellite' peak (red peak) is stronger than the 'main' peak (green peak). Such large resonance peaks due to the doubly excited D2 states are indicative of the breakdown of the independent electron model in the inner valence range, which arises from the electron correlation.

The similar experiments have been carried out for NH_3, which has also ten electrons as CH_4, and the results that are not amenable to the independent electron model have been obtained again. The use of polyatomic molecules as well as diatomic molecules gives us deeper knowledge about the dynamics and spectroscopy of doubly excited molecules.

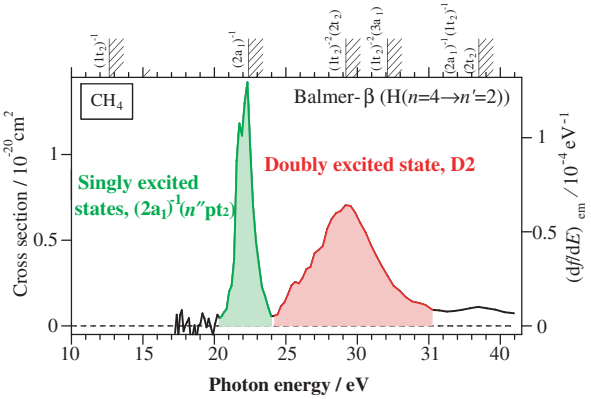

Figure 1
Cross sections (left axis) and oscillator strength distributions (right axis) for the H(n=4→n'=2) fluorescence in the photoexcitation of CH_4 as a function of incident photon energy. The ionization potentials are also shown in the upper part.

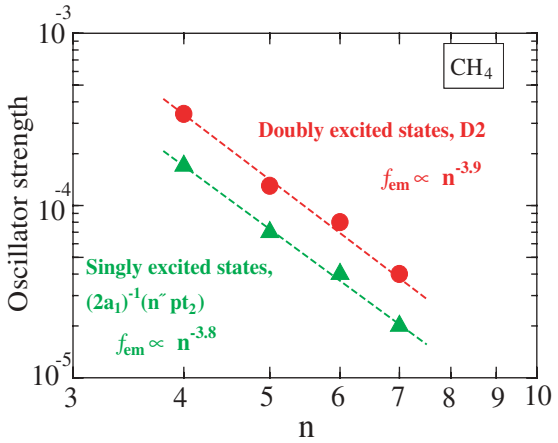

Figure 2
Oscillator strengths for the H(n→n'=2) fluorescences from CH_4 originating from the doubly excited D2 states and singly excited $(2a_1)^{-1}(n"pt_2)$ states against the principal quantum number of the upper level of the hydrogen atom, n.

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1-2 Energy Exchange between Photoelectron and Auger Electron during Inner Shell Hole Decay

In crude models of matter, electrons are usually treated as independent particles. Such an approximation fails however to reproduce many important properties such as autoionisation, double photoionisation, superconductivity, and so on. It is one of the task of atomic physics to describe and try to understand electron-electron interactions, or the so-called 'electronic correlations'. Several phenomena are particularly well suited for this quest, such as the double photoionisation process in Helium atoms, where details of electron correlations are revealed by the 2 escaping electrons [1]; or the mutual interactions of the 2 bound electrons in doubly excited He** atomic states [2].

Another process is of great interest: sequential double photoionisation in an atom A brought by Auger effect. A simplified 2-step description is often used to describe it: an energetic photon ejects an inner shell electron, forming an intermediate highly excited singly charged ion of short lifetime (of the order of a few fs), that de-excites by releasing an Auger electron of fixed energy. Electronic interactions between the photoelectron and the Auger electron in the presence of the ionic core are called 'post collision interactions' or PCI. They are important at threshold when the photoelectron escapes slowly and is overtaken by the Auger electron: the suddenly increased charge of the ionic core (from A+ to A++), seen by the photoelectron results in exchange of energy, and possibly of angular momentum, with deceleration of the slow photoelectron mirrored by acceleration of the fast Auger. Strongest effects are expected right at threshold when the photoelectron emerges with zero energy as a 'threshold electron'. Whereas many studies have focussed separately on one or the other electrons [3], we chose here to detect both in coincidence. Such an approach offers the advantage of isolating clearly the final state.

Experiment was performed on BL-16B, and used

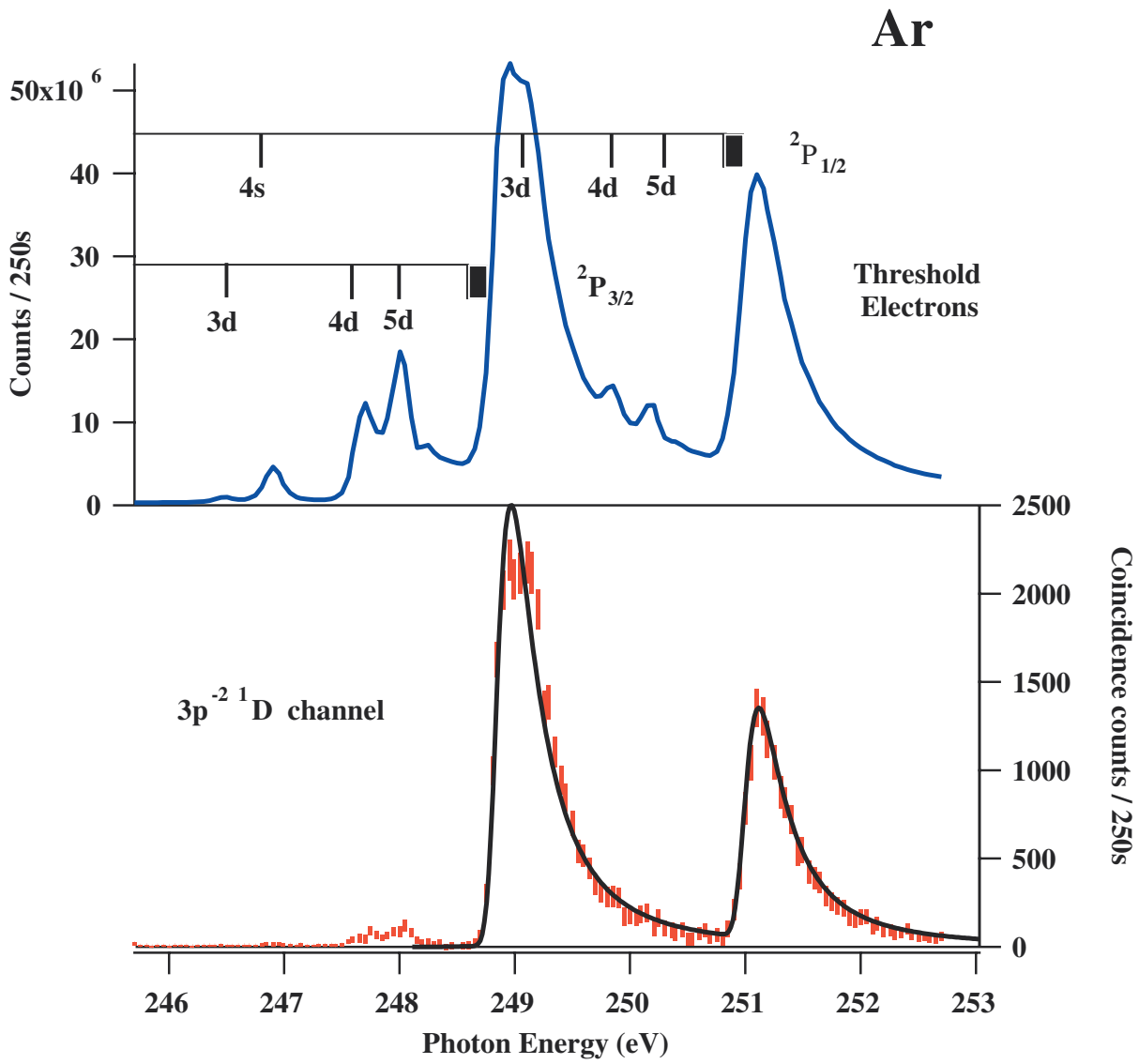

Figure 3
PCI process associated with ionisation of Argon in the 2p shell. Top : yield of threshold electrons. Bottom : yield of threshold electrons in coincidence with an Auger electron selecting the Ar^{2+} $3p^{-2}$ (^1D) final state (red bars) compared to theoretical predictions (black curve)

a threshold electron detector coupled to a hemispherical analyzer equipped with position sensitive detection, as described previously [4]. Fig. 3 (top) shows yield of threshold electrons in the vicinity of 2p ionization thresholds in Argon. Due to PCI, release of the zero energy 2p electron is delayed above threshold. Secondary emission of threshold electrons is also observed on 2pnd resonances. Many PCI theories [3] tried to reproduce the shape of this curve, but a detailed comparison with experiment demonstrated that none was completely satisfactory [4]. We suggest here that discrepancy may arise from an insufficient selection of the final state. Fig. 3 (bottom) represents coincidences of this threshold electron with an electron of variable energy to ensure formation of the Ar^{2+} $3p^{-2}$ (^1D) state. The coincidence spectrum can thus be considered as a filtering of the threshold electrons yield associated with the formation of Ar^{2+} $3p^{-2}$ (^1D) state. It is seen that this channel is almost free of the contribution of secondary processes on resonances, and that the agreement with theory (black curve) is now excellent. Analysis of the Ar^{2+} $3p^{-2}$ (^3P) channel revealed a stronger contribution of secondary processes on resonance, and also above threshold, due to the process of recapture of the photoelectron [6].

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References

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[3] See for instance Schmidt V 1997 Electron Spectrometry of Atoms using Synchrotron Radiation (Cambridge: Cambridge University Press).

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