Environment assisted electron capture

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Synopsis Electrons scattering off isolated atoms or positive atomic ions may be captured in the non-resonant photorecombination or resonant dielectronic recombination processes with the excess energy carried off by a photon. We demonstrate that in a medium a new interatomic process becomes important, where in the electron capture by an atom or atomic ion the energy is transferred to a neighbouring species ionising it. We discuss different manifestations of this interatomic Coulombic electron capture and estimate its efficiency for a number of realistic systems.

Slow electrons may be captured by isolated atoms or positive atomic ions in the photorecombination process. In the non-resonant photorecombination an electron is captured into an unoccupied orbital of species A leading to the formation of $A^-$, while the excess energy is carried off by a photon. In the resonant dielectronic recombination the impinging electron is first captured in an autoionising state of $A^-$ which subsequently stabilises by photon emission.

In an environment different electron capture mechanisms appear alongside the photorecombination. Thus, the energy shed by the electron in the capturing process can be transferred not to a photon but to the electrons localised on the neighbouring species. This energy transfer is possible due to the correlated motion of the electrons localised on different centres which operates over significant distances due to the long-range nature of the Coulomb interaction. We identified the following capture mechanisms (see Figure 1): interatomic Coulombic electron capture (ICEC), and dielectronic ICEC (dICEC) [1]. In ICEC an electron is captured by A to form the ground or an excited state of $A^-$, while another electron is simultaneously emitted from the neighbour B. In dICEC the incoming electron is captured into a resonance of $A^-$ which subsequently stabilises by ionising B. This decay of an intermediate resonance state relates dICEC to the experimentally and theoretically studied resonant interatomic Coulombic decay process [2], where an inner-valence excited state produced in photon absorption decays by ionising a neighbour.

The estimates of the ICEC and dICEC cross sections in a number of atom-atom and atom-molecule systems let us conclude that for slow incoming electrons the interatomic capture dominates photorecombination for interatomic distances of the order of 1 nm. We also showed that the corresponding cross sections are significantly enhanced if several neighbours are present or when the neighbours are molecules. This makes ICEC a potentially interesting process in systems where free electrons exist in atomic or molecular environment of sufficient density, i.e. solutions or biological systems. It can also be important for signal transfer in larger systems.

Figure 1. [a,b] ICEC - the electron of energy $\varepsilon$ is captured into an unoccupied orbital of A (empty oval), the excess energy is used to ionise a neighbour B (shaded oval). [c] dielectronic ICEC - in the first step an electron is captured into an autoionising state of ($A^-$) which stabalisates by ionising B.

References

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