

Topic 1

On the properties of atomic and molecular Rydberg states and how to measure them by high-resolution spectroscopy

This first part serves as a general introduction to the main theme of the lectures: Rydberg states. Rydberg states are electronically excited states the spectral positions of which can be described by Rydberg's formula. Most physical properties of Rydberg states vary very rapidly with the principal quantum number n , typically as an integer power of n , i.e., as n^α with $\alpha = \pm 1, \pm 2, \pm 3 \dots$: The lifetime is proportional to n^3 , the polarisability to n^7 , the binding energy to n^{-2} , the van-der-Waals interaction between two Rydberg atoms to n^{11} , the induced dipole moments and transition moments between neighboring states to n^2 , etc.). The origin of these n -scaling laws can be derived from the properties of the eigenfunctions of the hydrogen atom. The rapid variation of the physical properties of Rydberg states implied by the scaling laws leads to very unusual properties of these states at high n values and forms the basis for a growing number of applications of Rydberg states in physics and chemistry. The physical and chemical properties of atomic and molecular Rydberg states also strongly depend on the quantum numbers ℓ and m_ℓ , and this dependence is of great importance if one is to understand and optimally exploit the properties of high Rydberg states. In many atomic and molecular systems, the dynamical and structural properties of high Rydberg states can be rationalized using multichannel quantum defect theory (MQDT), a theoretical approach that extends the description of electron-ion collisions to the range of negative collision energies.

A brief survey of the high-resolution spectroscopic methods used to study high atomic and molecular Rydberg states will also be presented. The methods used in my research group, high-resolution vacuum ultraviolet spectroscopy, millimeter wave spectroscopy and selective field ionization, will be presented, and their use in (a) the preparation of atomic and molecular samples in well defined quantum states and (b) the quantum-state-selective detection of Rydberg states will be discussed.

An introduction to this topic is:

[1] "Molecules in high Rydberg states", F. Merkt, *Ann. Rev. Phys. Chem.* **48**, 675 (1997).

I also recommend the monographs "Quantum mechanics of one- and two-electron atoms" by H. A. Bethe and E. E. Salpeter (Springer, Berlin, 1957) and "Rydberg atoms" by T. F. Gallagher (Cambridge University Press, Cambridge, 1994).