High Resolution Inner-Shell Excitation as a Probe of Dynamics in Core-Excited Van der Waals Clusters

E. Rühl[1], R. Flesch[1], W. Tappe[1], A.A. Pavlychev[2]

[1]Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49069 Osnabrück, GERMANY
[2]Department of Physics, St. Petersburg State University, 198904, St. Petersburg, RUSSIAN FEDERATION

Recent progress in the field of inner-shell excitation of free Van der Waals clusters is reported. High-resolution, state-of-the-art beamlines at high brilliance storage rings allow to investigate size- and site-dependent properties of variable size Van der Waals clusters. We report on recent work on rare gas clusters as well as clusters of simple diatomic molecules.

Site-specific excitation in Kr clusters is investigated by high resolution spectroscopy in the Kr 3d-excitation regime (90-96 eV). Size- and site-dependent spectral changes are observed which correspond to the evolution of atomic Rydberg states into cluster Rydberg states as well as surface and bulk excitons.

Molecular clusters containing nitrogen ($(N_2)_n$) or carbon monoxide ($(CO)_n$) are studied in the 1s-excitation regime, i. e. near the core-to-valence transitions as well as in the corresponding inner-shell continua. Experimental results recorded with a spectral resolution $E/\Delta E>10^4$ reveal small, but distinct spectral red-shifts from the isolated molecule to the corresponding clusters. These spectral shifts also occur along with changes in spectral line shapes. In the case of nitrogen clusters one observes a red-shift of ≈ 6 meV upon excitation of the vibrationally resolved N 1s $1\sigma_u \rightarrow 1\pi_g\ \pi^*$ progression.

A smaller red-shift of ≈ 2 meV is observed for the C 1s $\rightarrow \pi^*$ transition in $(CO)_n$ clusters. Moreover, a significant blue-shift of the σ^*-shape resonances is found in nitrogen clusters as well as in solid nitrogen, whereas no spectral shift is found for the σ^*-shape resonances in carbon monoxide clusters. The origin of these spectral shifts and spectral line shapes is discussed in detail, including recent progress that is obtained from the quasiatomic approach, which addresses the issues of dynamic localization and stabilization in core-excited molecules and clusters.