Surface resonant Raman scattering: Analysis of vibrations at clean surfaces and monolayer films

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Raman spectroscopy is a standard analytical method to study organic and inorganic material structures. For analysing ultrathin films, plasmonic surface enhancement (SERS) or tip enhancement (TERS) is common nowadays. However, even without such plasmonic field enhancement, Raman spectroscopy can be sensitive enough to record surface phonons, surface resonances or adsorbate vibrations. This is strongly favoured by surface resonant Raman scattering, i.e. resonance enhancement involving surface electronic transitions. By choosing an appropriate energy of the exciting laser line, a surface specific resonance enhancement may be achieved.

On clean surfaces, confined phonons and phonon resonances have been detected using surface resonant excitation on Si, Ge, III-Vs and Cu. The termination of surfaces by adsorbates has been analysed with sub-monolayer precision, e.g. for Sb on III-V(110) substrates, Pb and Au on Si(111), H on Si(111) and O on Cu(110).

In collaboration with theory groups, DFT-based calculations of the structure and electronic bands have revealed the mechanism of surface resonant Raman Scattering. Moreover, comparison of theory and experiment allows one to conclude on particular surface/adsorbate structures. In particular, I will discuss the interplay between atomic and electronic structure, metal-semiconductor transition and the effect of strong electron-phonon-coupling in quasi 1D-nanowires (In and Au on Si(111) and Si(553)).

On conductive samples, Raman scattering by the charge transfer mechanism may play an important role, in addition to deformation potential scattering. Please note that charge transfer is an important part of SERS and TERS, called chemical enhancement effect. The free carrier concentration in the scattering volume may lead to a notable difference for Raman spectroscopy on surfaces as well, e.g. for conductive nanowire structures and for metals.

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