To investigate changes in the resonance Raman signal into intermolecular interactions, we used an experimental and theoretical study of two series of peptides containing tyrosine and cysteine, and tryptophan and propargylglycine (PG), in solution and on the surface of titania nanorods. Four technical barriers were shown in the course of this study. The first barrier was the resonance Raman signal expected that the electronic states could not be neglected. Our results show that for tyrosine, high-energy electronic states out of resonance with the excitation can influence the Raman response and that intermolecular interactions can act in the molecular electronic states. The second barrier was the preparation of amino acid or peptide samples in close contact with the nanoparticle surfaces where primary interactions arise from molecules on the surface. This correct calculation of peptides in contact with a transition metal code including the excited electronic states, the correct selection of test molecules that demonstrate change in response to the presence of a surface.

**Theory**

For the calculation of RRS and RR-SERS profiles, the sum-over-states approach is used. Excitation profiles are the RRS cross section at a given vibrational mode as a function of excitation energy. Within the simplified sum-over-states approach, the resonance Raman cross section is represented as a sum over excited electronic states and is obtained by straightforward differentiation of the sum-over-states expression of the frequency-dependent polarizability with respect to a vibrational quantum number.

The differential Raman scattering cross section for a given normal mode is written as

\[
\sigma_{\text{RRS}}(\omega) = \frac{2}{\hbar} \int \frac{d\omega'}{\omega'} \langle \tilde{P}(\omega', \omega) \rangle \delta(\omega - \omega')
\]

where \(\omega_i\) is the electronic state transition frequency of the \(i\)th electronic state, \(\omega\) is the Raman shift, and \(\omega'\) is the Raman shift of the \(i\)th excited electronic state. This expression cannot be computed from first principles. Thus, we approximated \(\sigma_{\text{RRS}}\) in resonance Raman spectra by the breadth function derived from the experimental absorption spectrum.

**Experimental values of theoretical electronic structures**

- Resonant Raman theoretical predicting and relative peak intensities validated with experimental measurements.
- Resonant Raman theoretical predicting and relative peak intensities validated with experimental measurements.
- Theoretical electronic structure validated with UV-Vis absorption measurements.

**Methods**

Raman spectroscopy is a very sensitive tool that has a high degree of chemical specificity. However, its sensitivity is limited by the scattering efficiency of the target molecules.

Non-resonance Raman, RRS, and SERS measurements were performed both for solution and solid phase samples. The solution phase samples for the cross section measurements were prepared by dissolving the material of interest in ultrapure water. To mitigate the photodegradation of the tyrosine samples, the samples were stored in small glass caps during the measurements, so that the laser beam was continuously exposed to fresh sample. The wave length of the Vio light-transparent quartz cover slips to prevent evaporation of the acetone internal standard.

**Results**

For excitation on plasmon resonance (532), 8a and 8b peaks remain the same with increasing chain length.

**Conclusions**

A study has been performed to determine the role of the intermolecular interaction on the resonance Raman cross section. Theoretical electronic structure validated with UV-Vis absorption measurements. For the calculation of RRS and RRS excitation profiles, the sum-over-states approach is used. The sum-over-states expression of the frequency-dependent polarizability with respect to a vibrational quantum number.

- Resonant Raman theoretical predicting and relative peak intensities validated with experimental measurements.

- Theoretical electronic structure validated with UV-Vis absorption measurements.