Structural characteristics of surfaces, including the orientation of molecules, are of pivotal importance for various physicochemical properties and processes. One of the state–of–the–art experimental techniques for the precise characterization of molecules on any type of interface (e.g., gas-liquid) is Vibrational Sum–Frequency Generation (VSFG). VSFG is a nonlinear optical spectroscopic technique that probes single molecular vibrations near the interface. In the VSFG experiment, a measured new output beam is obtained from the combination of two input laser beams: one from the IR range, resonant with the energy differences corresponding to excitations of molecular vibrations, and one from the visible (VIS) range, off–resonant with any excited state but enhancing the signal through the nonlinear response. VSFG may be viewed as a complementary method to the popular infrared (IR) and Raman spectroscopies, but in contrast to those, VSFG is based on second-order nonlinear optical phenomenon, requires using several high–intensity lasers, has high spatial resolution, and measures the signal coming only from the surface (and not the inner parts of the bulk). VSFG has been used to study a wide range of functionalized interfaces, including polymers, surfactants, ionic liquids, nanoparticles, lipid membranes, and electrodes. However, among all, ice and aqueous surfaces have gained special interest due to their universal presence and importance in most of the chemical and physical processes — most notably, VSFG provided experimental proofs on the different ordering of water molecules on various surfaces.

The simulations of VSFG spectra can be based on quantum mechanics and, in fact, they can be performed in a fully non–empirical way providing a deeper insight into the nature of measured VSFG spectra — one can directly link simulated bands to particular structural motifs at molecular level. For that reason, for many years there has been a strong synergy between experimental and computational VSFG studies. Despite their many successes, **VSFG computer simulations share one common flaw: anharmonic effects are accounted for in unsystematic manner (force fields in molecular dynamics) or they rely on the harmonic oscillator (HO) approximation of the VSFG microscopic response.** The HO model is a first–level approximation of vibrational motion (nuclei constrained to move on an n-dimensional parabola) and is valid only for the smallest nuclear displacements. For larger atomic displacements, for example, when molecular bonds are stretched significantly (far from equilibrium) or when intermolecular bonds are present, one must account for the inherent anharmonic nature of nuclear movement.

The current project falls into the field of computational spectroscopy. **The project aims at the development and implementation of new theoretical model of VSFG that surpasses the HO formalism by introduction of vibrational anharmonic effects. The implementation of the project will greatly improve the reliability of first–principles quantum–chemical simulations of the VSFG spectra, leading to more accurate predictions.** For example, in computer simulations of IR and Raman spectra, the anharmonicity of molecular vibrations has been shown to have a crucial impact — it affects the position and intensity of the simulated absorption bands and leads to the emergence of new combinatorial bands. Moreover, the new protocol will allow for a first systematic analysis of the role of anharmonic effects, which can further create a stimuli for improvements in other commonly used approaches for simulations of the VSFG spectra. The exemplary simulations based on the new approach will be performed for molecular systems in limelight, like water clusters or amino acids.