Spectroscopy in the isolated gas phase:

If we can see an object with our naked eyes, we can easily tell its shape and structure in details very accurately. It would be of course fun if we would see the molecules. But unfortunately they are too small and we use spectroscopy as a tool to see them. Now the question is how accurately we can see the structure and shape of the molecules using spectroscopy. If we put the molecules in bulk water and record an electronic spectrum using a commercial UV-Vis absorption spectrophotometer, we obtain a broad spectrum (Fig. 1a). Here most of the valuable information about the structure of the molecules is lost underneath the broad envelope due to intermolecular interactions as well as perturbations from bulk water. On the other hand, if we remove the bulk water surrounding the molecules of our interest i.e. bring them in the gas phase and expand the gas molecules seeded with a carrier gas into a high vacuum through a small orifice (Supersonic expansion) and electronically excite them using an Ultraviolet (UV) laser, we get a simplified and more informative electronic spectrum (Fig. 1b). We have built a REMPI-TOF (Resonantly Enhanced Multiphoton Ionization – Time Of Flight) mass spectrometer coupled with supersonic molecular beam source where we can ionize the molecules by excitation through an intermediate excited electronic state ($S_1$) using a tunable UV laser. When we scan the laser through the $S_1$ vibronic state (different vibrational levels of the excited electronic state) and detect the 2-photon ionization signal, we obtain vibrationally resolved electronic spectrum (Fig. 1b). As we detect the ions using the Time Of Flight set up, we can obtain the mass spectrum (Fig. 2) as well. Thus our Instrument can record the mass spectrum as well as the vibrationally resolved electronic spectrum for every mass channel without interference from each other. Once we know the electronic spectrum of an isolated molecule in supersonic jet, we can introduce another Infrared (IR) laser to probe the group vibration (-OH, -NH, -C=O, -C-H etc.) of a molecule. This experiment is done using two or three lasers simultaneously which needs spatial overlap as well as temporal synchronization of the laser beams.
What we can study using our Instrument?

Physiological activities of biomolecules are very much dependent on their specific shape. Thus it is quite interesting and challenging to explore their shape accurately. We can study multiple low energy conformations of small to medium sized biomolecules in isolated gas phase as well as microhydrated environment using our Instrument.

This study will mimic the shape of various biomolecules which are in hydrophobic medium as well as the role of water on the conformations of the molecules. It is quite obvious that gas phase data are much more relevant for hydrophobic medium like protein interior or lipidic membranes. As for example, we can study the folding motifs of medium sized peptides in absence of water molecules as well as the intrinsic role of water molecules in peptide folding. Conformations of other microsolvated biomolecules like DNA base pairs etc. could be also studied in great details. In principle, we can synthesize and study microsolvated water clusters of small biomolecules in the gas phase under ultracold condition of supersonic expansion which will mimic the structure of the biomolecules in presence of tightly bound water molecules in the first solvation shell. The biomolecules will be brought into gas phase using laser-desorption technique.
Fig. 3. Time of Flight Mass spectrum of aniline using home built REMPI-TOF mass spectrometer. Here we can select a particular mass channel and record the electronic spectrum [Fig. 1(b)] by tuning the laser wavelength through the $S_1$ vibronic state.

Fig. 4. Resonantly Enhanced Multiphoton Ionization (REMPI) scheme.