Advances in Analytical Resonance Raman Spectroscopy

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The goal of this work is to improve the analytical chemistry aspects of several modes of Raman spectroscopy (RS) : resonance Raman (RRS), surface-enhanced resonance Raman (SERRS) and time-resolved resonance Raman (TRRRS).

Following a brief introduction, an extensive overview is given of the current state-of-the-art in RRS and its most important analytical achievements. Subsequently, the following research projects are described:

- At-line coupling of capillary electrophoresis with SERRS. Here, we make use of the surface enhanced Raman effect combined with resonance excitation. This approach improves *sensitivity* and reduces *fluorescence interference*.

- Exploring of the discrimination power of deep-UV RRS (excitation below 260 nm). This offers higher *sensitivity* and reduces *fluorescence interference*, but results in a reduced spectral information content Nevertheless, we could discriminate pyrene derivatives based on their RRS spectra.. With state-of-the-art computational methods we could simulate RRS spectra using linear-response time-dependent density functional theory (TDDFT) and thus add *identification power* to the method.

- Unexpectedly, strong overtones and combination bands were observed with deep-UV excitation. This can provide additional spectral information and ultimately improve the *identification power* of RRS.

- We constructed a TRRRS setup for the visible and UV region using a fast-gated intensified CCD camera. This allows time discrimination between the instantaneous Raman scatter and fluorescence that will spread over a few nanoseconds. This relatively simple, easy-to-use system has great potential in the bio-analytical field, making use of the *enhanced selectivity* and *improved sensitivity* of RRS and at the same time reduce the *fluorescence interference.*