Rapid Chiro-sensitive Detection by Coherent Raman Optical Activity (CARS-ROA) Spectroscopy

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Molecular chirality governs the most of biological events, therefore, the study of chiral molecules and reactions involving these molecules is of great importance in biology, pharmaceutical industry, biochemical and material sciences. Among several methods for investigating chiral molecules, chiro-optical spectroscopy offers advantages of being non-invasive and chiro-selective relying on the inherent optical activities of the chiral molecules. The two popular vibrational chiro-optical spectroscopy techniques are spontaneous Raman optical activity (ROA) and vibrational circular dichroism (VCD). VCD works well for organic molecules but faces difficulties when applied in biological environment due to strong IR absorption by water molecules. Spontaneous ROA is well suited for aqueous environment. However, ROA signals are very small, typically only ~10^{-4}-10^{-5} of the spontaneous Raman signals. This makes acquisition of a ROA spectrum very time consuming. Typically, it requires several hours to record a decent ROA spectrum of a diluted solution of chiral molecules. Therefore, spontaneous ROA is not suitable for investigating small concentrations and monitoring reactions involving chiral molecules. Interestingly, in the coherent version of spontaneous ROA called Coherent Anti-Stokes Raman Scattering-Raman Optical Activity (CARS-ROA) spectroscopy, the chiral signal is enhanced by many orders of magnitude. The first experimental demonstration of CARS-ROA was the heterodyne-detected CARS-ROA spectra of enantiomers of a chiral liquid and those required just one minute of acquisition times for each [1]. In a step further, we have shown first CARS-ROA spectra of solutions of chiral molecules MOM-BINOL, a precursor to a family of widely used organocatalysts in asymmetric synthesis, dissolved in an achiral organic solvent, acquired in one minute [2]. I will present our recent results on CARS-ROA setup and experiments where we further reduce the acquisition time below one second for CARS-ROA spectra of diluted samples.

[1] Hiramatsu K, Okuno M, Kano H, Leproux P, Couderc V, Hamaguchi H-o. Phys. Rev. Lett. (2012); 109, 083901

[2] Kumar V, Reichenauer T, Supovec L, Jansen D, Brodt N, Zając G, Domagała A, Barańska M, Niemeyer J, Schlücker S, J Raman Spectrosc. (2023); 54, 1011