

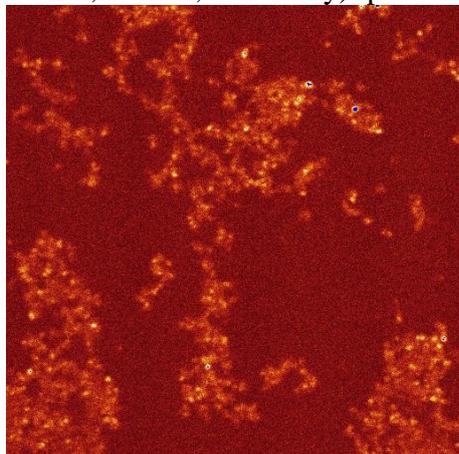
SECARS IMAGING OF THIOPHENOL ADSORBED ON SILVER COLLOIDS

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The very large enhancement of the Raman signal observed in SERS (Surface-enhanced Raman Spectroscopy)[1] enabling single molecule sensitivity in some cases, makes it very appealing to apply this same experimental approach to non-linear techniques like CARS spectroscopy as higher enhancement factors are expected due to the quadratic dependence of the signal with the pump laser intensity. In spite of this and though several groups have tried the SECARS (Surface-enhanced Coherent Anti-Stokes Raman Spectroscopy) with different success [2], there is not yet a definitive proof-of-principle of this experimental approach. To this latter goal has been devoted this work. We have recorded the forward CARS images of thiophenol adsorbed on silver nanoaggregates through the 8a ring stretching mode resonance at 1574 cm^{-1} . This is a very strong and characteristic band in the SERS of thiophenol and therefore is also expected to yield a strong signal in SECARS. For this purpose, 1mW of the fundamental output of a Nd:Van laser (Picotrain, HighQ lasers GmbH, Hohenems, Austria) at 1064 nm was directly coupled into a commercial scanning microscope, serving as the Stokes beam, while $500\mu\text{W}$ of the output of an optical parametric oscillator (Emerald OPO, APE GmbH, Berlin, Germany) provided the pump and probe beam tuned around 911.9 nm.



In Figure 1 the forward CARS resonant image of the silver nanoaggregates with thiophenol at 1567.9 cm^{-1} is shown. To our knowledge this is the first SECARS image of silver colloids. It can be seen the signal intensity is not homogenous and some brighter spots can be observed as it is already known from SERS imaging. It should also be noted that the CARS resonant condition shows a red peak shift when compared to the SERS spectrum what it is typical of a CARS spectrum.

Figure 1: Forward SECARS image of thiophenol at the 1567.9 cm^{-1} resonant condition

[1] E.C. Le Ru; P.G. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects*. Elsevier, Amsterdam, 2009

[2] See for instance, a)“Experimental observation of surface-enhanced coherent anti-stokes Raman spectroscopy”, E. J. Liang, A. Weippert, J.-M. Funk, A. Materny, W. Kiefer, *Chemical Physics Letters* **227**,115-120 (1994) b)“Single-molecule detection of biomolecules by surface-enhanced coherent anti-stokes Raman scattering, T-W Koo, S. Chan, and A. A. Berlin, *Optics Letters* **30**, 1024-1026 (2005).