FY23 Lew Allen Award

Low-level Organic Detection on Icy Worlds using Surface-Enhanced Raman Spectroscopy

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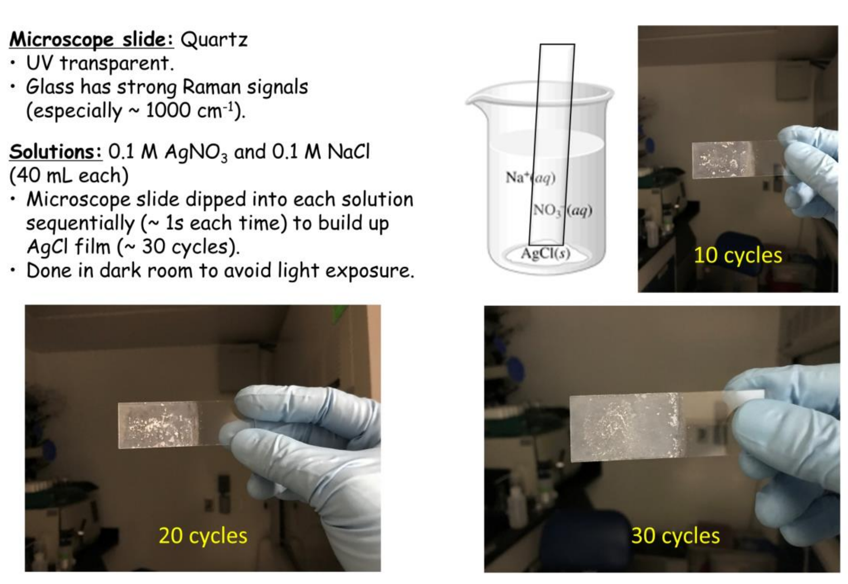
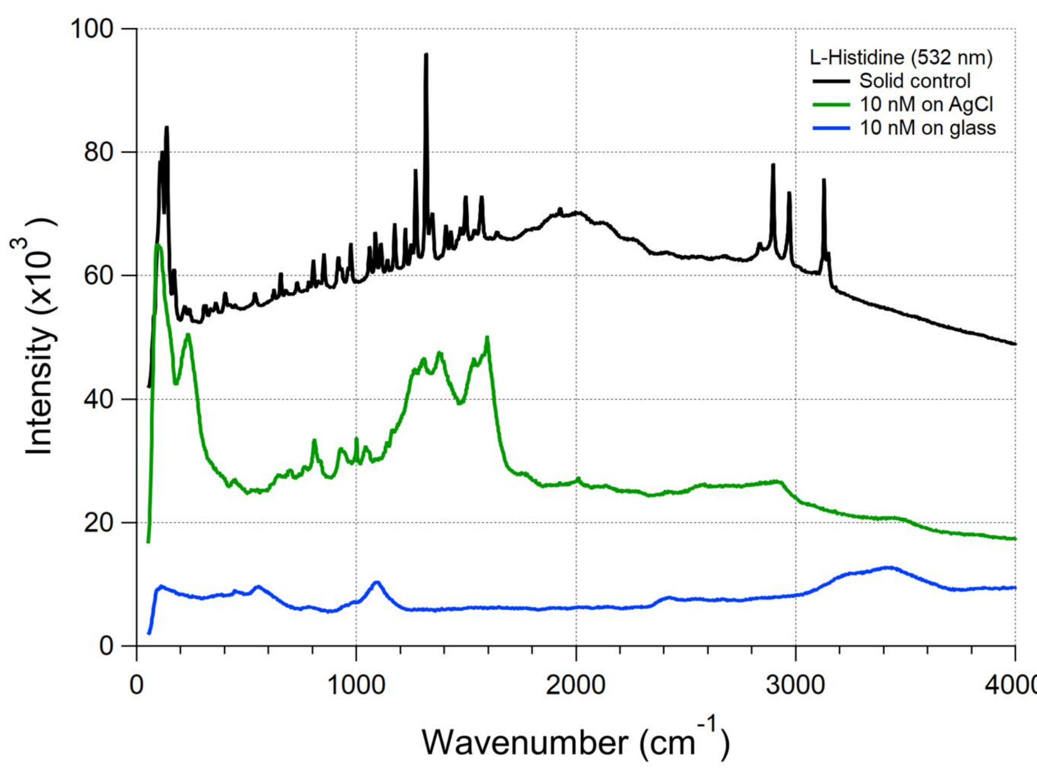
OBJECTIVES: The goals of this project are to (i) develop a reliable method for the synthesis of an AgCl-based substrate for surface-enhanced Raman spectroscopy (SERS) and (ii) to characterize the detection limit for organic molecules that can be achieved with this approach. AgCl crystals can offer improved stability over conventional SERS substrates, as well as being generally inert. As such, they could remain inactive until the time of deployment and thus be suitable for long-duration space flight.

BACKGROUND: SERS, first discovered in the 1970's, is an established technique for enhancement of inherently weak Raman scattering signals of trace analytes. It has been shown to be capable of single-molecule sensitivity [1], and could be a powerful analytical tool for the detection and identification of low-concentration materials. However, noble metal-based SERS substrates can readily lose their ability to enhance Raman signature over time (~ days or weeks after fabrication even when stored under vacuum) [2,3]. This lack of longevity has hindered the application of SERS in space exploration. The alternative approach of fabricating SERS substrate from an AgCl coating could help overcome this limitation by keeping the layer inert until they are activated via photo-reduction to Ag particles by the Raman laser.

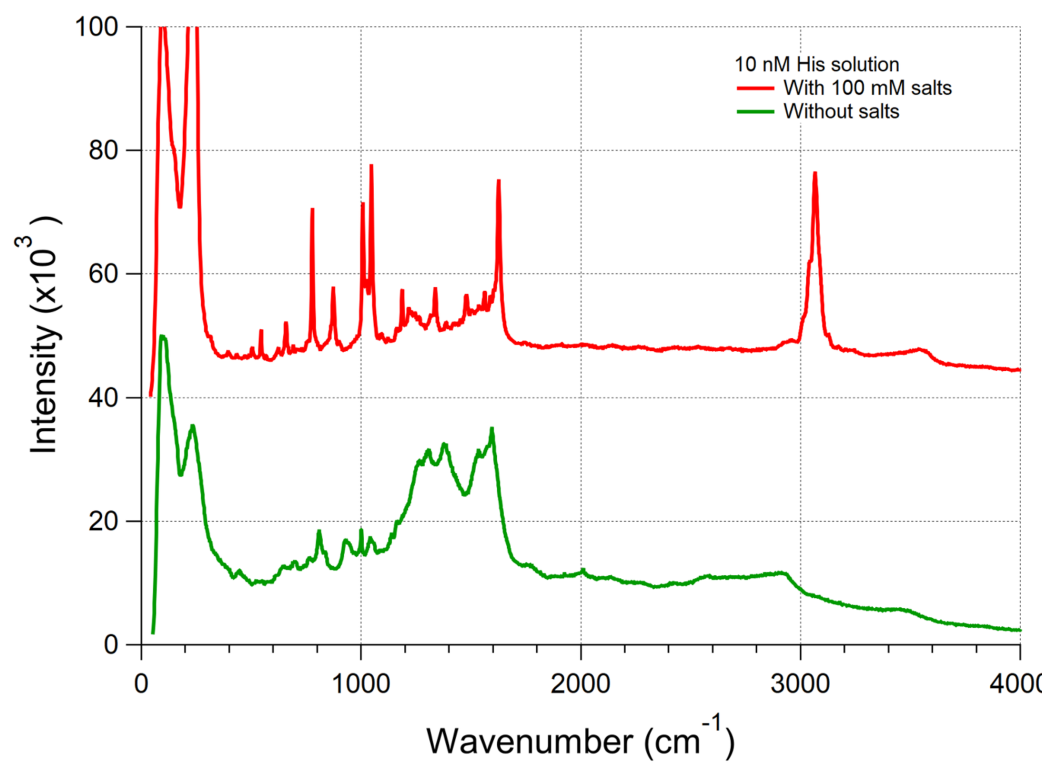
APPROACH AND RESULTS:



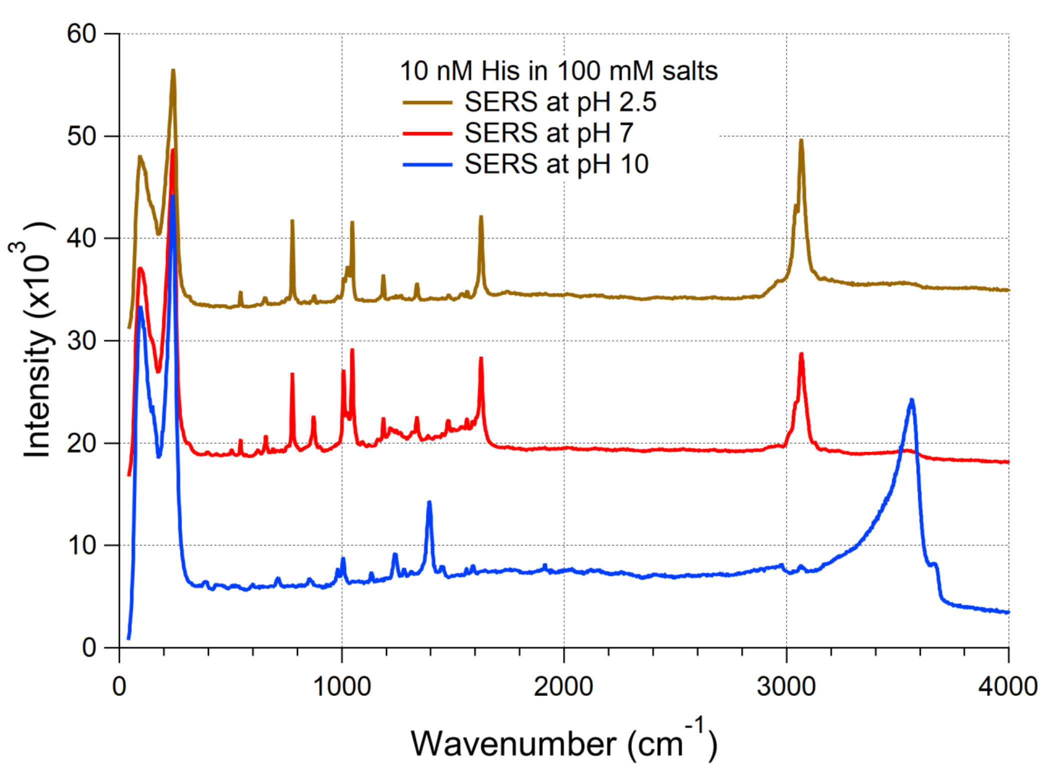
Crystals of AgCl are grown on quartz microscope slides via a liquid-phase deposition method, whereby the slides are first submerged in a solution of 0.1 M $AgNO_3$ followed by dipping into another beaker containing 0.1 M NaCl. These chemicals react to form insoluble AgCl precipitates which accumulate on the surface of the slides. The process is repeated for dozens of cycles to gradually develop a sufficiently thick layer of AgCl. Quartz is preferred over the standard glass slides as the latter tends to exhibit strong interfering Raman signals, especially in the 1000 cm^{-1} fingerprint region. As AgCl is very light-sensitive, the entire synthesis is done in the dark to avoid photo-degradation.



Demonstration of SERS activity on the detection of amino acid, where droplets of 10 nM L-histidine solution are deposited on the AgCl substrate. SERS effect is evident compared to the spectrum on the uncoated slide.



Addition of a putative Europa brine (Na, Mg, Cl, SO_4) does not suppress SERS activity. On the contrary, the presence of salts can be beneficial to SERS by significantly enhancing the SNR of the spectrum (top trace).



The AgCl substrate is exposed to different pH's (acidic to basic) to test for robustness. Both the substrate and the SERS effect do not appear to be adversely affected by pH environments.

SIGNIFICANCE/BENEFITS TO JPL AND NASA: The AgCl-based SERS technique is a powerful capability that can be supplemented to in situ Raman instruments to vastly improve their sensitivity for organic detection by many orders of magnitude, including amino acids at the nanomolar levels (such as called for in the Europa Lander SDT report).

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References:
[1] Nie, S.; Emory, S.R. (1997) "Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering". *Science* 275 (5303), 1102-1106
[2] Natan, M.J. (2006) "Concluding Remarks Surface Enhanced Raman Scattering". *Faraday Discuss.* 132, 321-328.
[3] Scherzer, R.D. (2017) *UNF Graduate Theses and Dissertations*, 760

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