Detection and Speciation Analysis of Uranium and Technetium by Surface Enhanced Raman Spectroscopy

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Raman Spectroscopy

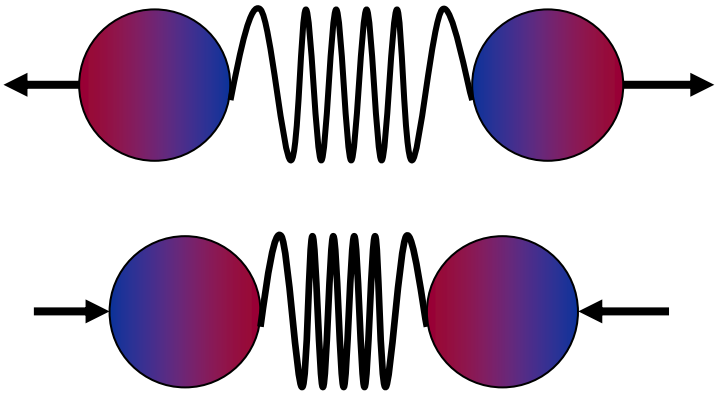
- A new technique and a tool - Micro-Raman and surface enhanced Raman spectroscopy (SERS) can be used for U and Tc detection and speciation analysis at low concentrations
- Complementary tool to APS, KPA, others, and quicker results
- Potential for *in situ* measurements via fiber optics

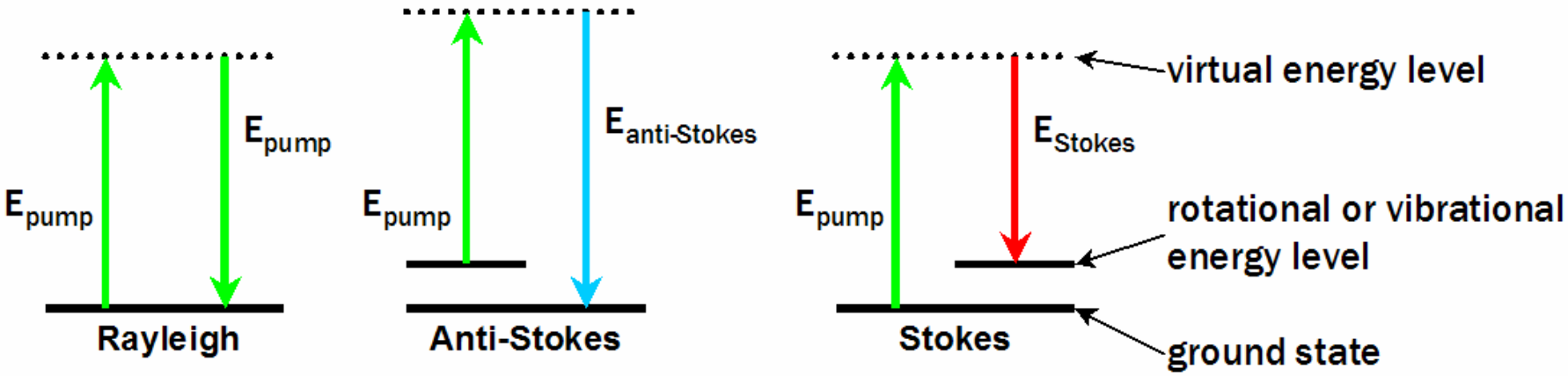
Raman Scattering

Inelastic scattering

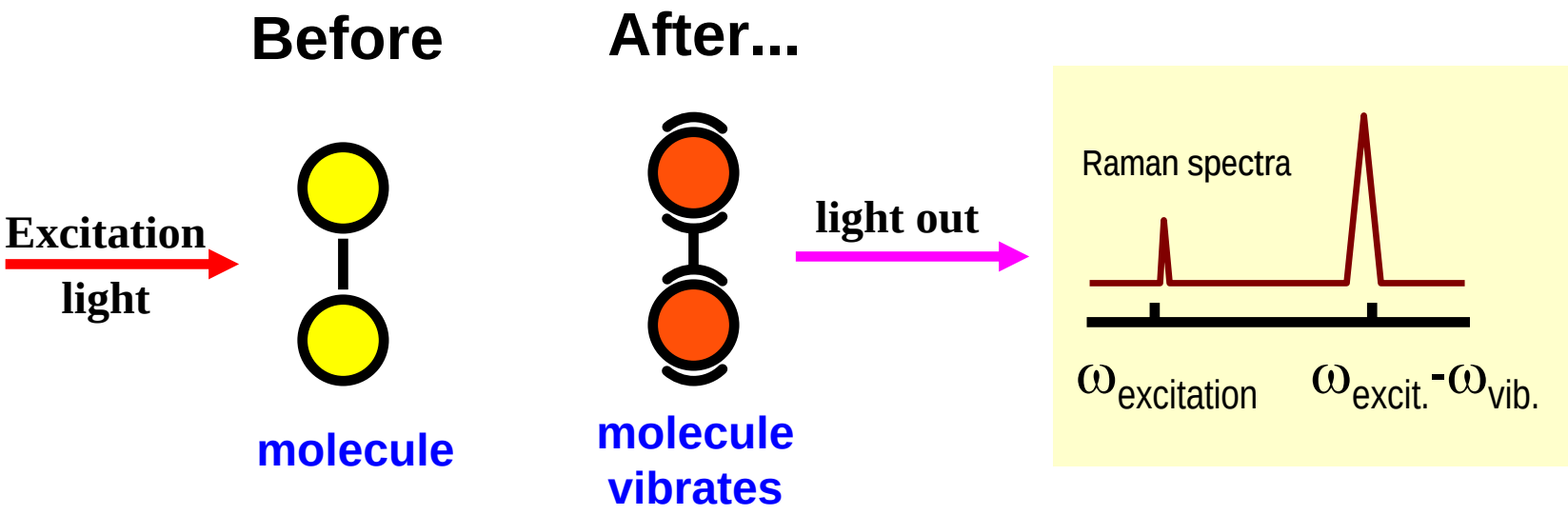
Discovered: 1928

Nobel Prize: 1930





Raman Spectroscopy

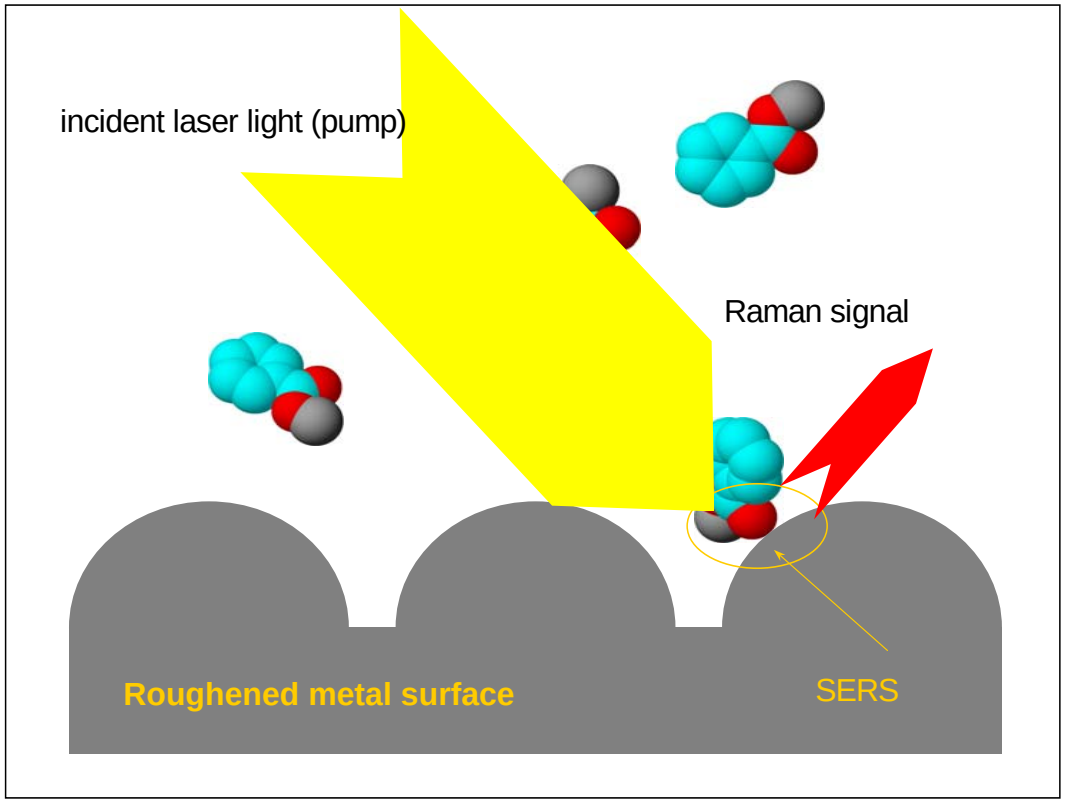


- **Light loses energy to the molecule vibration**
- **Spectra reveal molecular vibration frequencies, thus the nature of chemical bonds or signatures of chemical species**

Raman Spectroscopy

But, normal Raman - an insensitive technique,

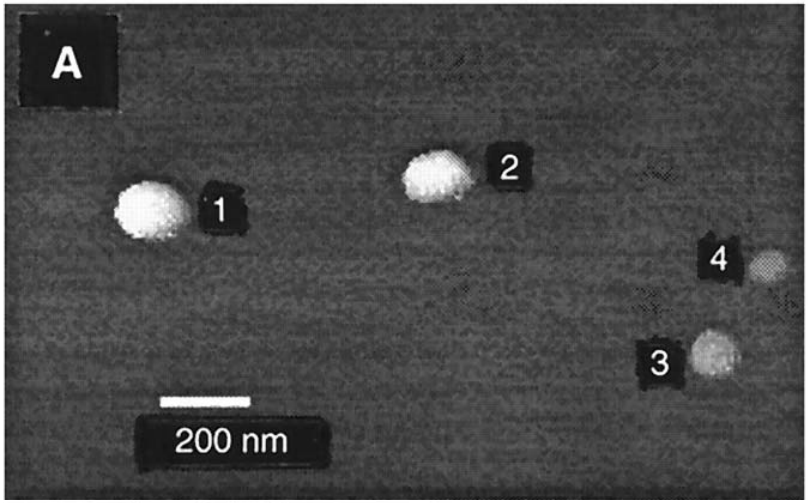
until recently ...

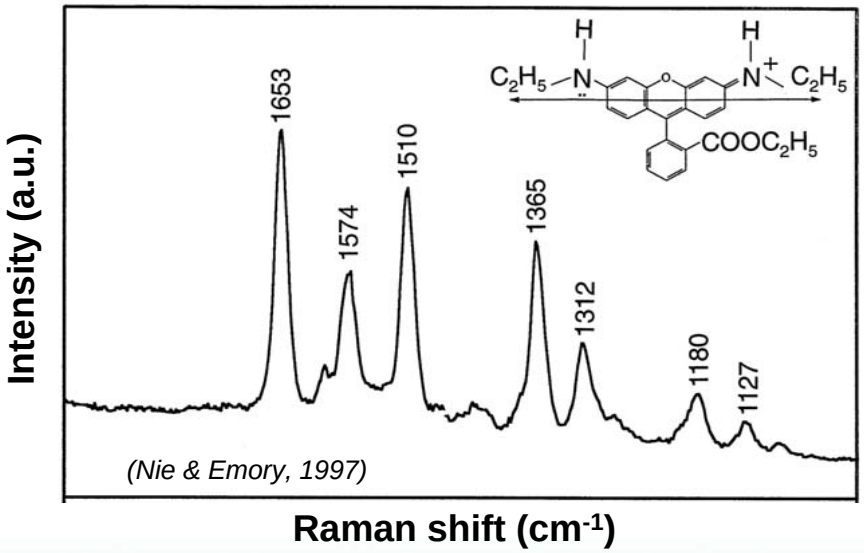


- **Raman signal significantly enhanced on roughened metal surfaces (e.g., Ag, Au)**
- **Enhancement factor:**

  ~10^{14} – 10^{15}

Surface Enhanced Raman Spectroscopy (SERS)



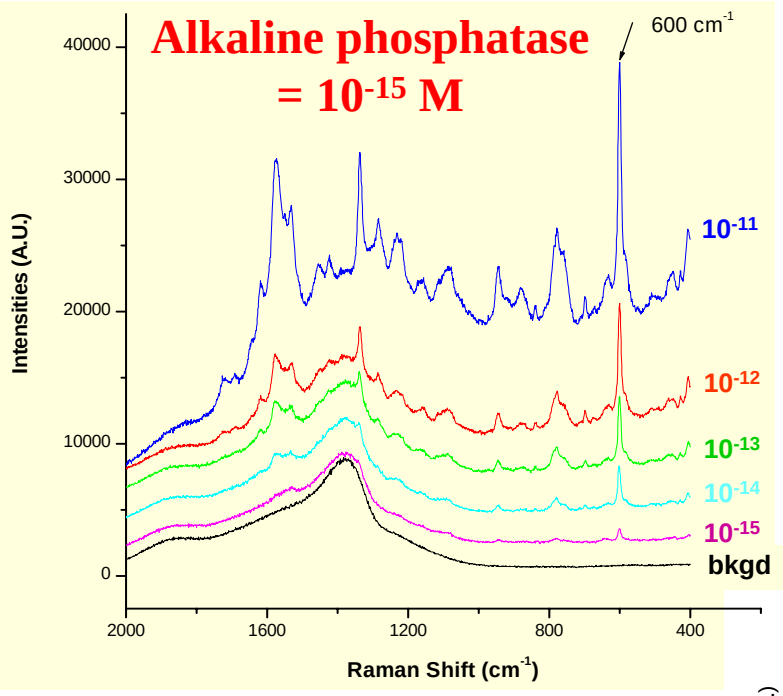


- **Single molecule detection of Rhodamine 6G on Ag nanoparticles**

Nie & Emory (1997) Sci. 275, 1102.

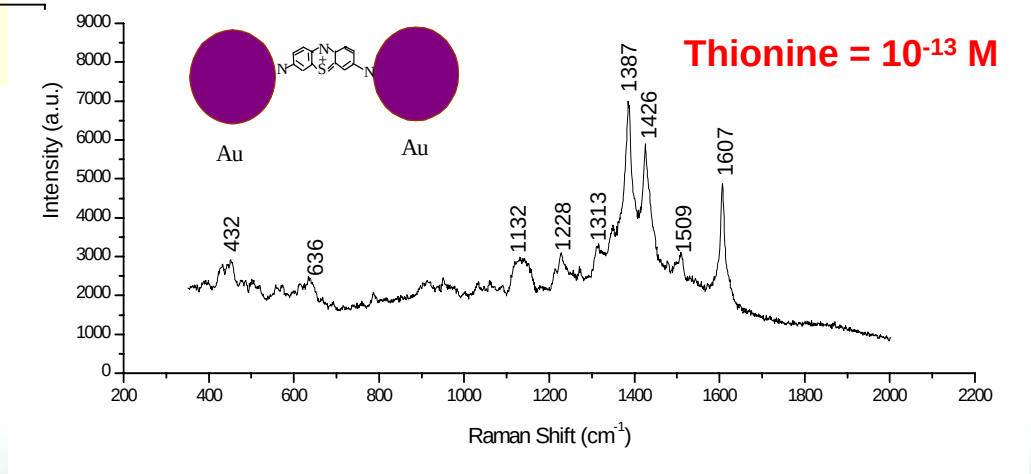
Kneipp et al. (1997) PRL 78, 1667.

SERS and Single Molecule Detection



(Ruan, Wang, Gu. 2006, Anal. Chem. 78:3379)

Detection of Thionine on Au Nanoparticles

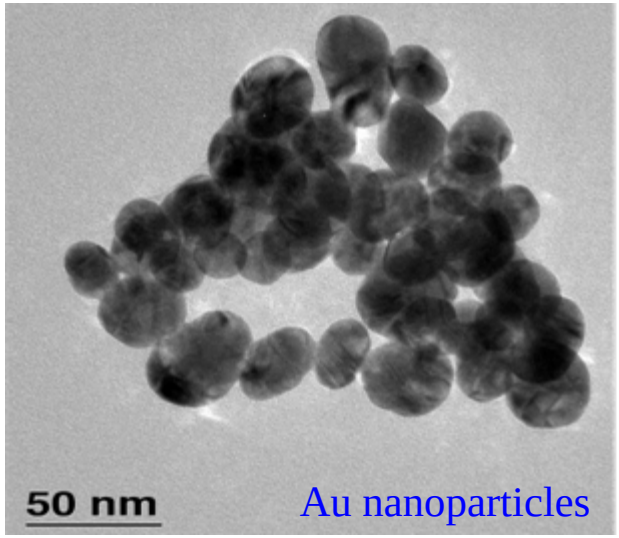


SERS for Uranium and Technetium Detection

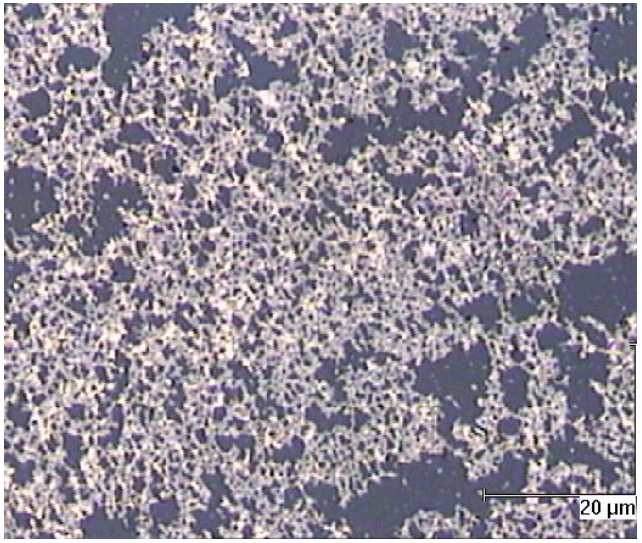
- Can SERS be used for U and Tc detection (at ppm or ppb levels)?
- Can SERS be used for U and Tc speciation analysis?

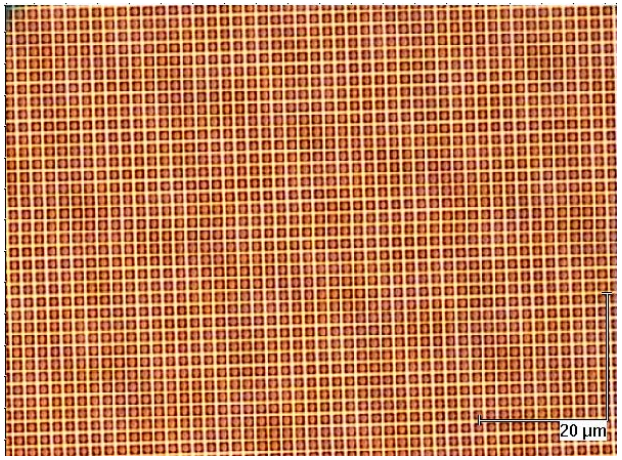
- The key is develop and fabricate sensitive SERS substrates

SERS Substrates

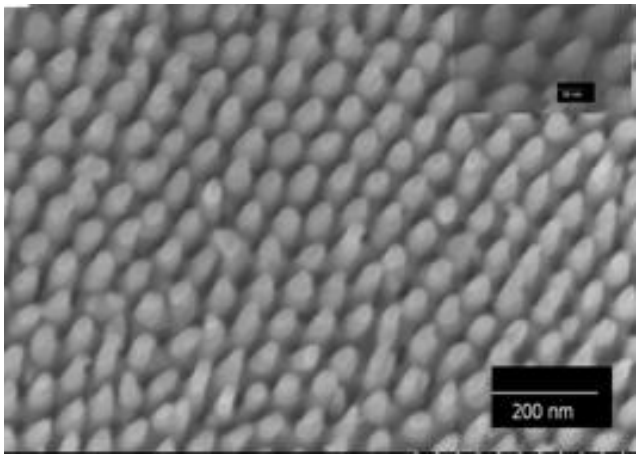


Au nanoparticles





Patterned Au substrate by lithography



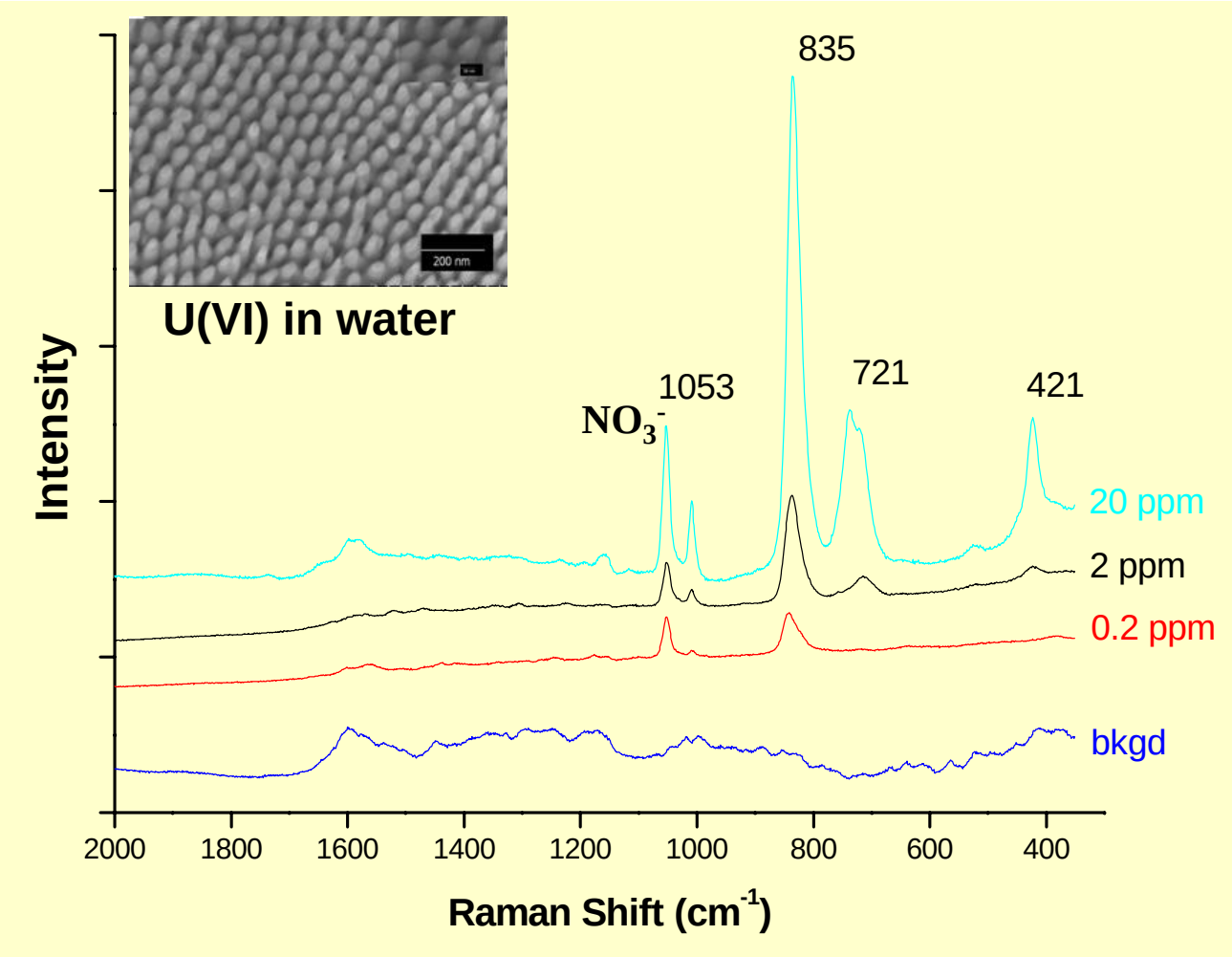
Ordered Au nanopillar arrays

Raman Instrument

- Small sample quantity (< 1 μL)
- Water an ideal solvent
- Non-contact, non-destructive analysis

- Direct imaging (small sample area, e.g. 1-10 μm)

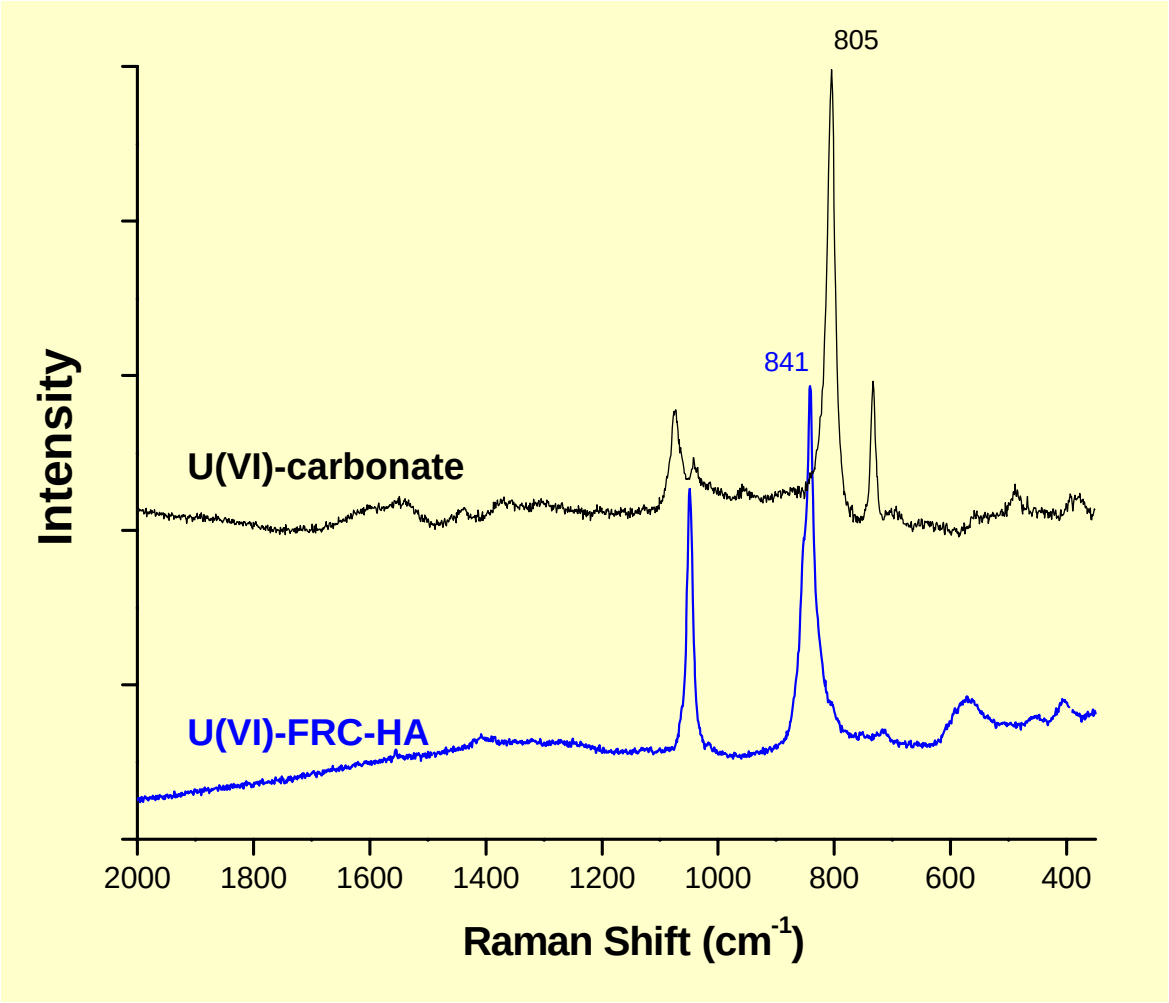
SERS for Uranium(VI) Detection



Uranyl, UO_2^{2+}, characteristic vibration frequency at ~835 cm^{-1}

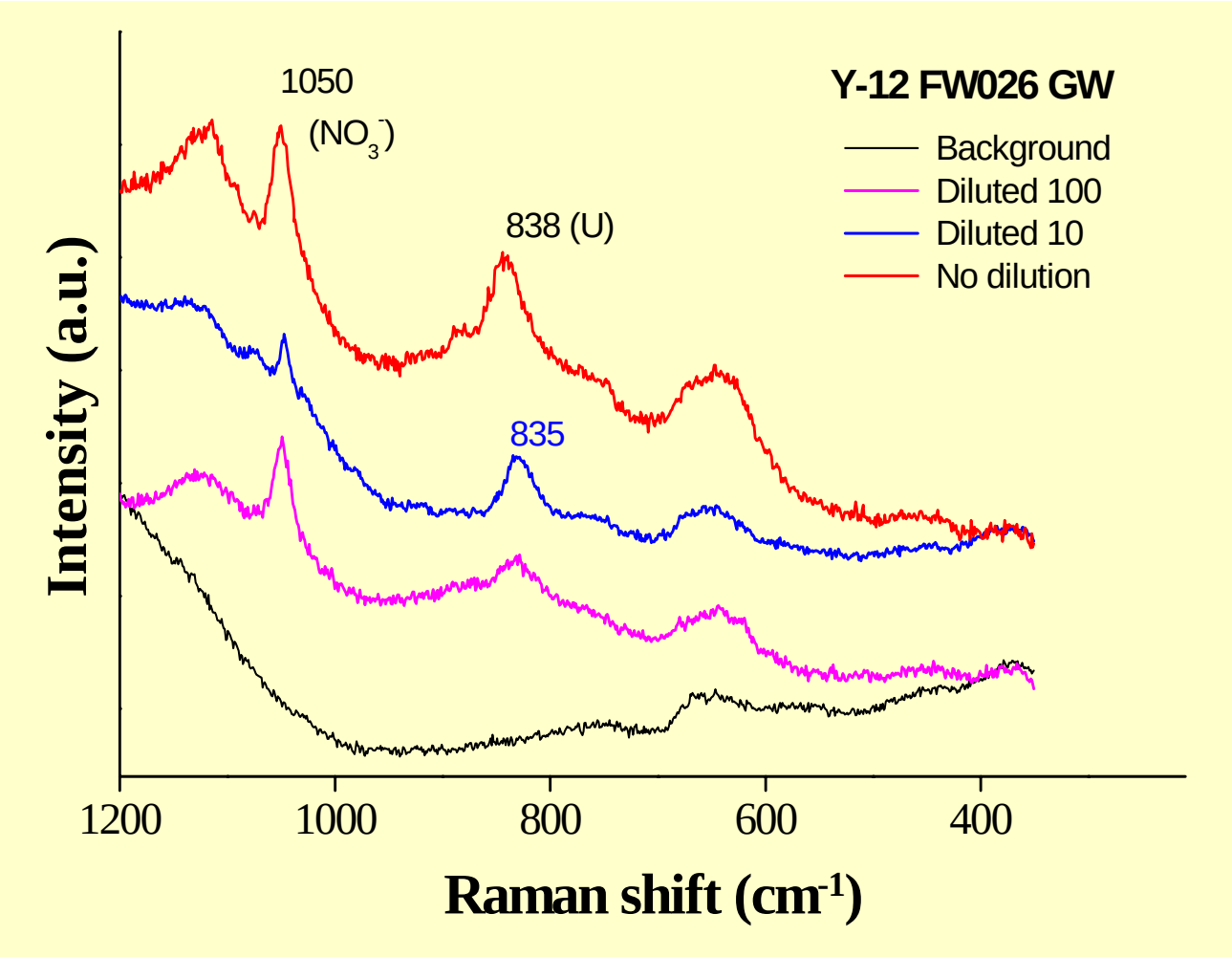
Intensity increases with concentration

SERS for Uranium(VI) Species



U(VI) vibration frequency shift due to complexation with carbonate (805 cm^{-1}) or with FRC humic acid (841 cm^{-1})

Detection of U in Y-12 Groundwater



No sample pretreatment

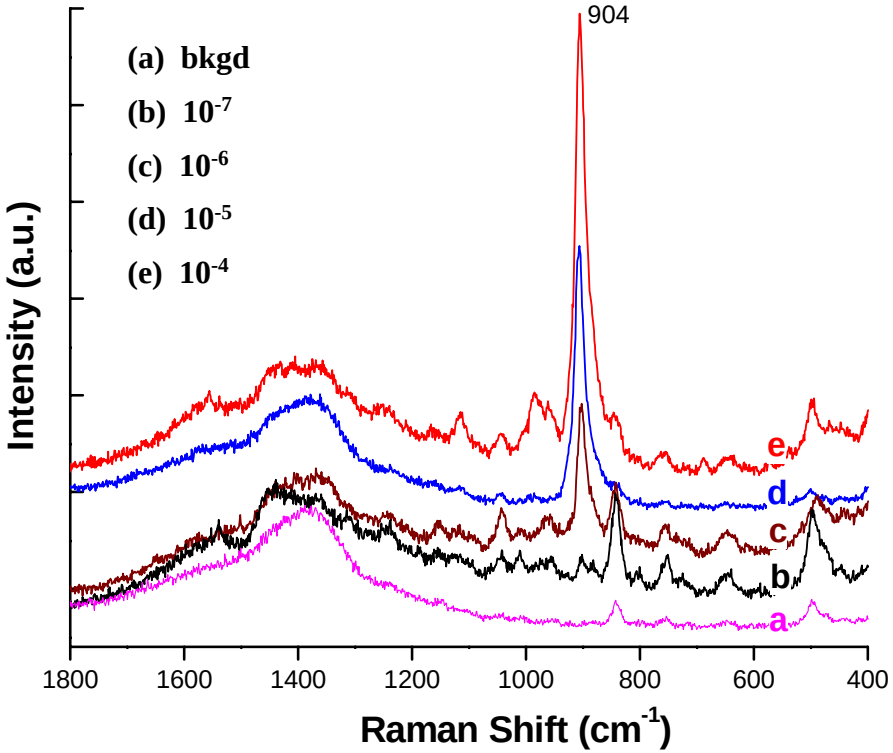
Uranyl, UO_2^{2+}, vibration band clearly identified, even at 100× dilutions

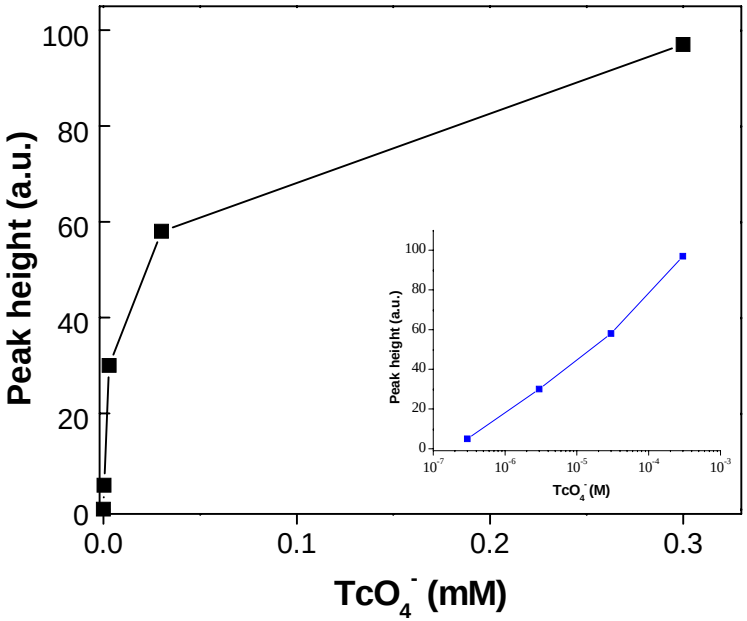
Sample with high nitrate concentration (~8000 mg/L)

SERS for Tc Detection and Speciation Analysis

- Tc-99 usually analyzed by liquid scintillation counting (for total activity only)
- Difficult for speciation analysis at micromolar concentrations
- Reduced Tc(IV) may not form precipitates in the presence of organic ligands

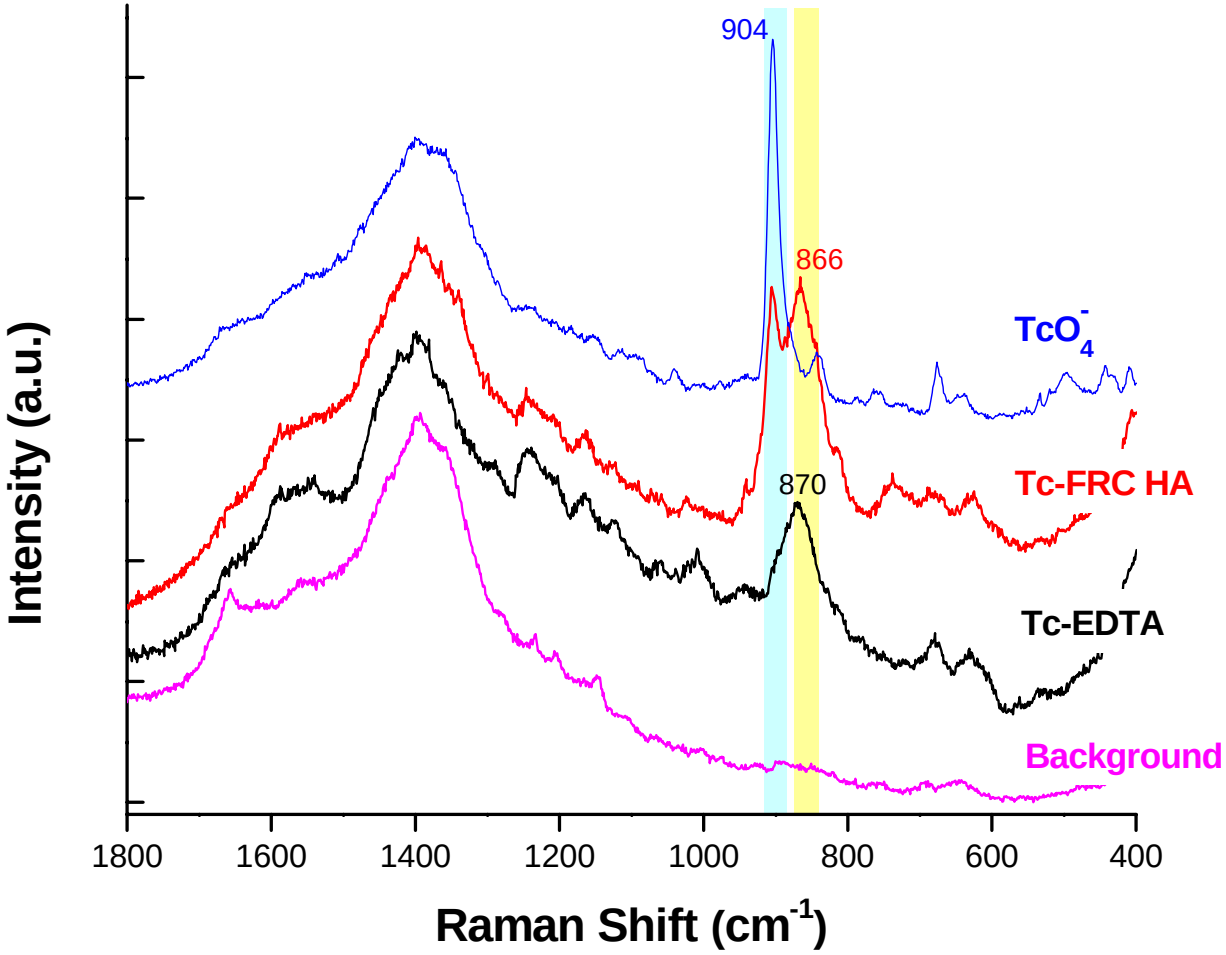
SERS Detection of Technetium in water





Pertechnetate, TcO_4^-, characteristic vibration frequency at ~904 cm^{-1}

SERS for Tc Speciation Analysis



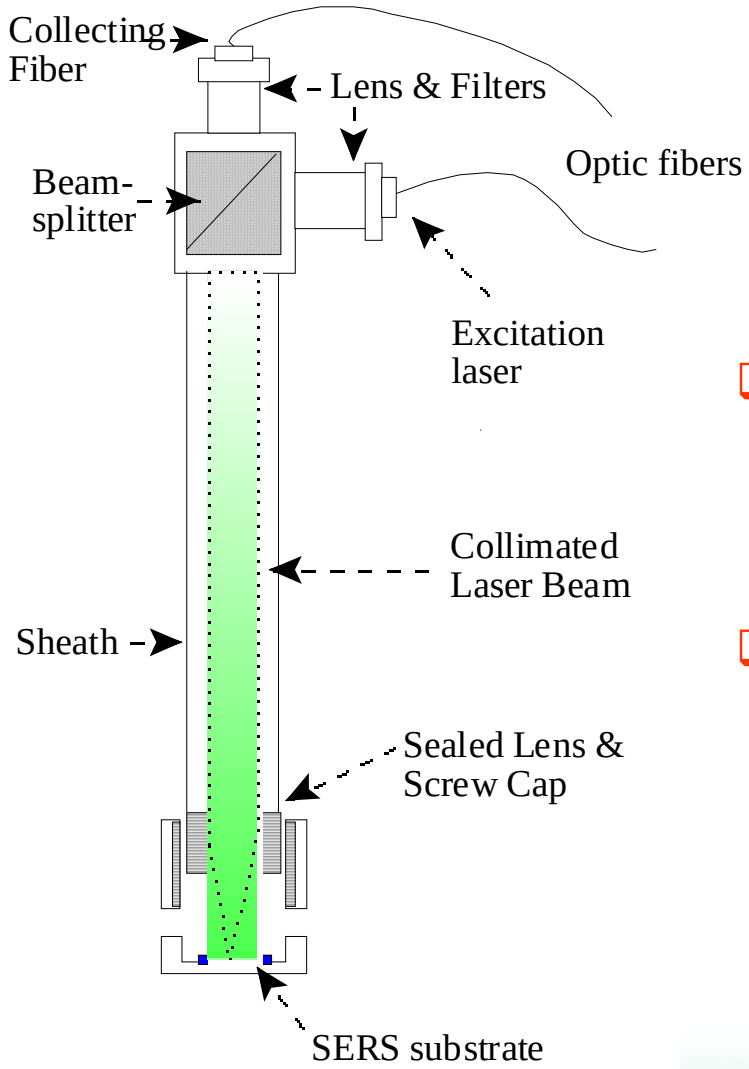
Reduced $Tc(IV)O_2$ identified at vibration frequency ~870 cm^{-1}

Tc(IV) form soluble complexes with FRC-HA or EDTA, causing frequency shift to ~866 and 870 cm^{-1}

Summary and Conclusions

- SERS – a new tool, capable of directly analyzing U and Tc in groundwater samples at low concentrations
- Micro-Raman can also be used for solid sample analysis
- Small sample volume, and water an ideal sovent
- Technique complementary to APS
- Maybe configured for *in situ* analysis via fiberoptics – get information quicker

Field Applications via a Fiberoptic Probe



- **Potential field applications for *in situ* measurements**
- **Confocal SERS fiberoptic probe**

Acknowledgement

- **Chuanmin Ruan, Sheng Dai at ORNL**

- **DOE ERSP support and ORNL Seed program**