Femtosecond laser-nanostructured substrates for surface enhanced Raman scattering (SERS)

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Motivation

Raman spectroscopy has applications in:

• Pharmaceuticals
• Homeland Security
• Forensics
• Medical diagnostics
• Analytical chemistry
Motivation

However, Raman scattering cross sections are very small (~$10^{-30}$ cm$^2$)

Trace detection using Raman spectroscopy is insensitive, and not widely used
Motivation

SERS promises to enable the use of Raman spectroscopy in a wide variety of new applications
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SERS promises to enable the use of Raman spectroscopy in a wide variety of new applications

However, a current dearth of inexpensive, reliable, high performance substrates is limiting the application of SERS
Outline

• Raman scattering
• Surface enhancement
• Femtosecond laser-structured substrates
• Experimental results
• Conclusions
Outline

• *Raman scattering*
  • Surface enhancement
  • Femtosecond laser-structured substrates
  • Experimental results
  • Conclusions
Raman scattering

\[ \text{Energy} \]

- \{ Virtual state \}
- \{ Electronic states \}
- \{ Vibrational states \}
- Ground state
Raman scattering

\[ \Delta \nu = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} \]
Raman scattering: a classical approach
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Outline

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Surface enhancement

$\varepsilon_2$

$\varepsilon_1$

$a < 0.05 \lambda$
Surface enhancement

\[ a < 0.05 \lambda \]

\[ E_0 \]
1. Near-field scattered electric field enhances polarization of molecules located near surface.

\[
\frac{|E_s|}{|E_0|} \propto \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}
\]

Surface enhancement
1. Near-field scattered electric field enhances polarization of molecules located near surface

2. Field from molecular polarization generates polarization of surface at Raman frequency

\[ \omega_0 \pm \omega_k \]
1. Near-field scattered electric field enhances polarization of molecules located near surface

2. Field from molecular polarization generates polarization of surface at Raman frequency

3. Surface polarization radiates Raman field into far field
Surface enhancement

\[ SERS \text{ Enhancement Factor} = \frac{I_{SERS}}{I_{\text{Normal Raman}}} \propto \left( \left| \frac{E_s (\omega_0)}{E_0 (\omega_0)} \right| \right)^2 \times \left( \left| \frac{E_s (\omega_0 - \omega_k)}{E_0 (\omega_0 - \omega_k)} \right| \right)^2 \]

\[ \approx \left( \left| \frac{E_s (\omega_0)}{E_0 (\omega_0)} \right| \right)^4 \]
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• **Femtosecond laser-structured substrates**
• Experimental results
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Femtosecond laser-structured substrates
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Experimental procedure

Benzenethiol self-assembled monlayer (SAM)
Enhancement factor calculation

20x, 0.25NA Objective

500µm spacer

Coverslip

Neat benzenethiol

Glass slide
Neat Benzenethiol, baseline corrected

0.8mW 633nm excitation
1 sec. integration time
Enhancement factor calculation

20x, 0.25NA Objective
Benzenethiol SAM on fs laser–nanostructured Si

80nm Ag film
3.8mW 633nm excitation
1 sec. integration
Benzenethiol SAM on fs laser-nanostructured Si

Neat Benzenethiol
Benzenethiol SAM on fs laser–nanostructured Si

Neat Benzenethiol
Enhancement factor calculation

\[ SERS \text{ Enhancement Factor} = \left( \frac{I_{SERS}}{I_{Raman}} \right) \times \left( \frac{N_{Raman}}{N_{SERS}} \right) \]

<table>
<thead>
<tr>
<th>Band</th>
<th>Enhancement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 cm(^{-1})</td>
<td>(1.9 \times 10^{10})</td>
</tr>
<tr>
<td>1572 cm(^{-1})</td>
<td>(1.5 \times 10^{11})</td>
</tr>
</tbody>
</table>
SERS substrates: important characteristics

1. Large cross-section enhancement factor

2. Signal is reproducible, uniform across substrates
Signal uniformity

-200
-150
-100
-50
0
50
100
150
200
Y (µm)
-200 0 200
X (µm)
x10^-3
50
55
60
65
70
75
80
85
90
20 µm
0 dB
-3.5 dB
Signal uniformity

Intensity Histogram of Raman Map

$\mu = 7023$

$\sigma = 910$
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Conclusions

Laser nanostructured substrates are easy, cheap to produce
Conclusions

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We have demonstrated SERS from laser nanostructured substrates;
- enhancement factor, signal uniformity of substrates are very competitive in the field
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We have demonstrated SERS from laser nanostructured substrates;
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Enhancement mechanism needs to be better understood;
future work will focus on understanding operation of substrates
- near field optical profiling, etc.
Thank you!

Mazur Group, NDSEG Fellowship, Horiba Jobin Yvon
http://mazur-www.harvard.edu
Femtosecond laser-structured substrates
Signal uniformity (linear scale)
Motivation

1. Raman scattering/spectroscopy reveals the unique vibrational spectrum of a molecule

2. Molecular Raman scattering cross sections are very small: 
   \(~10^{-30} \text{ cm}^2\): Raman scattering is difficult to detect for spectroscopy applications (\(~1\) in \(10^7\) incident photons are Raman scattered from a molecule)

3. Efficient, inexpensive enhancement mechanisms and substrates will enable the use of Raman scattering in a host of new applications
Raman scattering: a classical approach

\[ p^{(1)} = \alpha \cdot E \]

\[ Q_k(t) = Q_{k0} \cos(\omega_k t + \delta_k) \]

\[ E(t) = E_0 \cos(\omega_0 t) \]

\[ \alpha \approx \alpha_0 + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k + \ldots \]
Raman scattering: a classical approach

\[ p^{(1)}(t) = \alpha_0 E_0 \cos(\omega_0 t) + \frac{1}{2} \sum_k \alpha'_k E_0 Q_k \left[ \cos((\omega_0 - \omega_k)t - \delta_k) + \cos((\omega_0 + \omega_k)t + \delta_k) \right] \]

Polarization at the Raman frequencies is LINEAR in \( E_0 \).
Raman scattering: possibility of enhancement?

\[ p^{(1)} = \alpha \cdot E \]

Enhance \( \alpha, \alpha'_k \)?

Enhance \( E \)?
Surface enhancement

\[ E_0 \]
Surface Enhancement

Surface enhancement

Quasi-static approximation (Rayleigh particle limit)

\[ a < 0.05 \lambda \]
Surface enhancement

Quasi-static approximation (Rayleigh particle limit)
\[ a < 0.05 \lambda \]

Near-field enhancement factor
\[
\left| \frac{E_s}{E_0} \right| \propto \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}
\]
Surface enhancement

Quasi-static approximation
(Rayleigh particle limit)

\[ a < 0.05 \lambda \]

Near-field enhancement factor

\[
\frac{|E_s|}{|E_0|} \propto \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}
\]

For Ag particle on resonance,

\[ EF \sim 10 \]