Analysis of Lignin by Surface Enhanced Raman Spectroscopy

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Micro-Raman

SERS

Lignin

Conventional Raman

Micro-Raman

FT-Raman

UVRR

Rayleigh Scattering

Laser

Raman Scattering
Outline

- What is SERS
- Mechanisms – surface plasmon and CT
- Near-IR lignin SERS
- Spectral characteristics
- Carbohydrate contribution
- CT mechanism - XPS analysis
- Lignin models
- Applications
- Conclusions
What is surface enhanced Raman scattering or SERS

Raman effect is greatly enhanced when a molecule is close to a rough metal surface.

(Nano- and micro-particles)
What is the origin of the enhancement?

1. Electromagnetic mechanism – $10^6$ to $10^{13}$ enhancement
2. Charge transfer (CT) mechanism – up to 100 times enhancement
Electromagnetic mechanism

surface plasmons

E-field

Metal sphere

e⁻ cloud
Second mechanism is charge transfer
CT mechanism

SERS

SERS contribution due to polarizability modification of the adsorbed molecule
Ag, Au, Cu, Li, K, and Na have shown SERS effect.

Dielectric properties of the noble metals most suited to plasmon resonance.

Light scattering efficiency

\[ E_{\text{local}} = E_0 / [\varepsilon(\omega) + 2] \]
Shape dependence of the surface plasma excitations
Au nanorods with increasing aspect ratios.
Aggregation vs. unaggregation.
Another example and enhancement factor calculation
Muconic acid
Enhancement factor

Compared to the intensity of an equivalent # of molecules in solution
SERS of lignin
Spruce MWL - Normal vs. SERS
reproducibility

same spot
Intensity reproducibility and standard deviation

10 SERS spectra

Significant SD
as little as 10 μ gram of lignin by SERS
Chemical modification due to adsorption on Ag?
1D $^{13}$C NMR

post adsorption
2D NMR
Lignin SERS - dilution effects
Modes of lignin aggregation

Packing density

A. Isolated Particles

B. Submonolayer

C. Monolayer

D. Bulk
Spectral characteristics

- Shifted band frequencies
- Altered band intensities
- Appearance of new bands
- Most bands belong to the aromatic unit
- Bands enhanced only in the region 250-1750 cm\(^{-1}\) region
- Relaxation of selection rules
Lignin in Wiley-milled wood
Aggregates of silver (a) and wood (b) particles (SEM)
No carbohydrate contribution
Lignin in unbleached KP
SERS Unbleached kraft pulp
Control pulp
100 nm Ag
Mechanisms operating in lignin SERS
Diffuse reflectance excitation spectra (near-IR)

1. EM mechanism

2. 3.5 μ Ag particles

9398 cm⁻¹ or 1064 nm
2. Charge Transfer

Evidence of CT complex
CT mechanism
3d 3/2 and 3d 5/2 electron emission from silver

Only Ag particles

XPS
3d $3/2$ and 3d $5/2$ electron emission from silver

MWL + Ag

XPS
SERS of lignin models

40 lignin models studied
Electron withdrawing groups on or conjugated groups
Multiple electron-withdrawing groups
Differences between G and S

SERS strengthening
Applications
Sensor – lignin detection in cotton linters
**G- vs. S-MWL SERS**

![Graph showing Raman spectra of B Spruce and Aspen with peaks at 586, 1272, 1270, 1308, and 1319 wavenumbers.](image)

- **Intensity/Arbitr. Units**
- **Wavenumber/cm⁻¹**

- **B Spruce**
- **Aspen**
Differences in lignin SERS of wood, MWL and Unbl. KP
Conclusions

• SERS of MWL, WMW and Unbl. KP were obtained
• Lignin can be selectively detected without separation
• As little as 10 μ gram of lignin can be detected
• Lignin is chemisorbed on Ag
• G- and S-lignins were easily distinguished
• Models work - insights on structural attributes important in SERS