# Interference Effects in SFVS of Thin Polymer Films: an Experimental and Modeling Investigation

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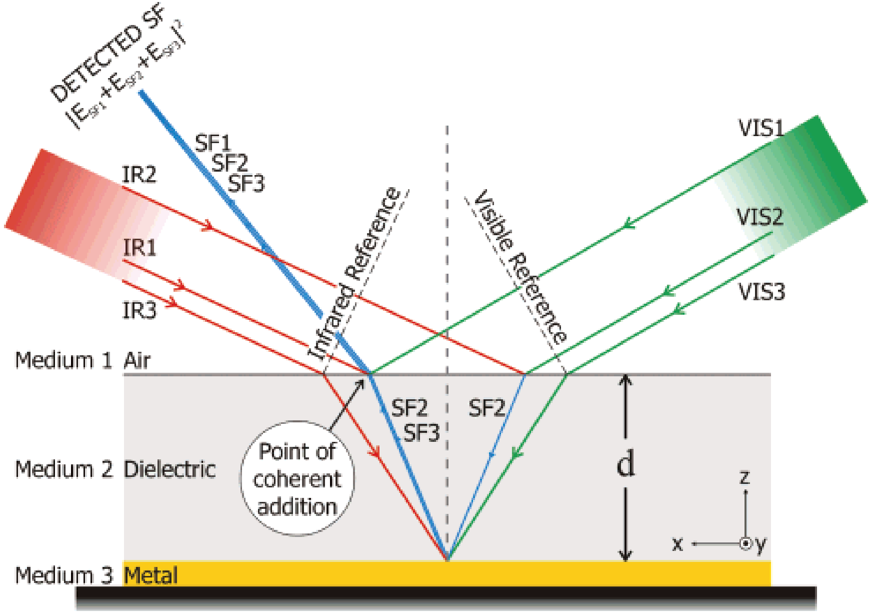
# Outline

- The Composite Substrate Model
- CDC and PDMS films on gold substrates
- Model Including Multiple Reflections
- Multiple Reflections and a Resonant Contribution from the Polymer/Gold Interface
- SFVS of spin-coated CDC and PDMS of different film thicknesses on a gold substrate
- SF spectra of PDMS and CDC solvent cast onto gold

# The Composite Substrate Model

**SF spectra of a composite substrate consisting of a silane monolayer on mica backed with gold**




Schematic diagram of the composite dielectric/metal substrate. The three sum frequency beams generated in the point of coherent addition.

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# Model Including Multiple Reflections

$$\begin{aligned}\mathbf{E}_z &= (E_z^{\mathrm{I}} + E_z^{\mathrm{R}} + E_z^{\mathrm{M}})\hat{\mathbf{z}} \\ &= (E_z^{\mathrm{I}} + r_{\mathrm{p}}E_z^{\mathrm{I}} + mE_z^{\mathrm{I}})\hat{\mathbf{z}} \\ &= E_{\mathrm{p}}^{\mathrm{I}} \sin\theta_{\mathrm{I}}\,(1 + r_{\mathrm{p}} + m)\hat{\mathbf{z}}\end{aligned}$$

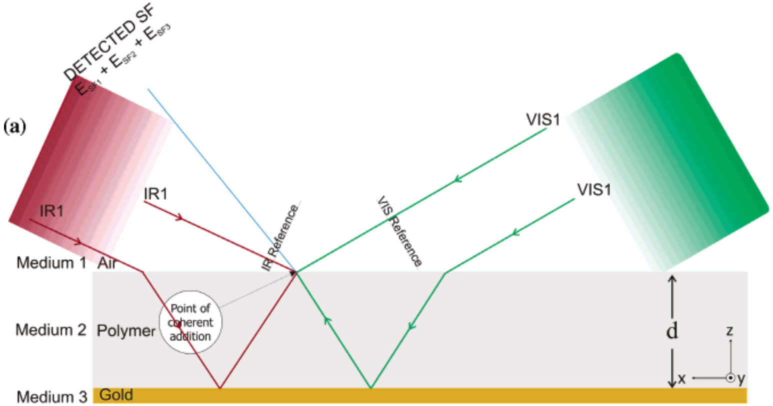
$$\begin{aligned}\mathbf{E}_x &= (E_x^{\mathrm{I}} + E_x^{\mathrm{R}} + E_x^{\mathrm{M}})\hat{\mathbf{x}} \\ &= (E_x^{\mathrm{I}} + r_{\mathrm{p}}E_x^{\mathrm{I}} + mE_x^{\mathrm{I}})\hat{\mathbf{x}} \\ &= E_{\mathrm{p}}^{\mathrm{I}} \cos\theta_{\mathrm{I}}(1 - r_{\mathrm{p}} - m)\hat{\mathbf{x}}\end{aligned}$$

$$\begin{aligned}m &= t_{12}t_{21}r_{23}\mathrm{e}^{i\alpha_1} + t_{12}t_{21}r_{23}^2 r_{21}\mathrm{e}^{i2\alpha_1} + t_{12}t_{21}r_{23}^3\, r_{21}^2\mathrm{e}^{i3\alpha_1} + \ldots. \\ &= \frac{t_{12}t_{21}r_{23}\mathrm{e}^{i\alpha_1}}{1 - r_{21}r_{23}\mathrm{e}^{i\alpha_1}}\end{aligned}$$

where $\alpha_1$ is given by

$$\alpha_1 = \frac{4\pi d}{\lambda}\left(\frac{n_2}{\cos\theta_{23}} - n_1 \tan\theta_{23} \sin\theta_{12}\right)$$

# Ray diagram: the generation of the SF1 beam




$$K_{x,\mathrm{vis}}^{\mathrm{mod}} = \cos\theta_{\mathrm{I,vis}}(1 - r_{\mathrm{p}} - m)$$

$$K_{z,\mathrm{vis}}^{\mathrm{mod}} = \sin\theta_{\mathrm{I,vis}}(1 + r_{\mathrm{p}} + m)$$

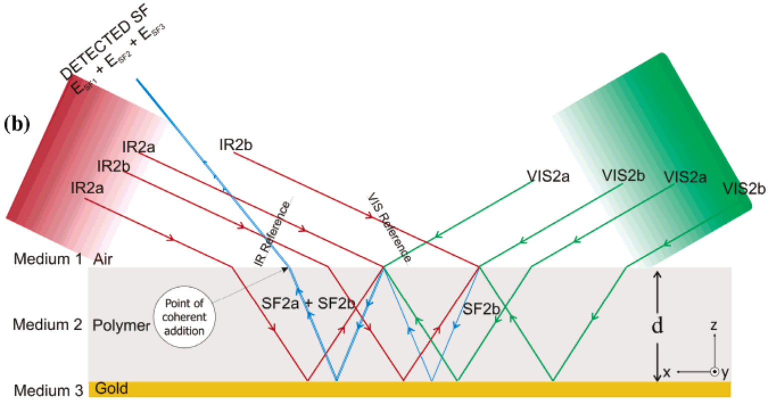
$$K_{x,\mathrm{IR}}^{\mathrm{mod}} = -\cos\theta_{\mathrm{I,IR}}(1 - r_{\mathrm{p}} + m)$$

$$K_{z,\mathrm{IR}}^{\mathrm{mod}} = \sin\theta_{\mathrm{I,IR}}(1 + r_{\mathrm{p}} + m)$$

## SF spectra of spin-coated CDC and PDMS films on gold substrates

$$\begin{aligned}
\mathbf{E}_{\mathrm{p,SF1}} &\propto |\mathbf{E}_{x,\mathrm{SF1}}| + |\mathbf{E}_{z,\mathrm{SF1}}| \\
&\propto |L_x \mathbf{P}^{(2)}_{x,\mathrm{SF1}}| + |L_z \mathbf{P}^{(2)}_{z,\mathrm{SF1}}| \\
&\propto |(L_{r,x}\chi^{(2)}_{xxz} K^{\mathrm{mod}}_{x,\mathrm{vis}} K^{\mathrm{mod}}_{z,\mathrm{IR}} + \\
&\qquad L_{r,x}\chi^{(2)}_{xzx} K^{\mathrm{mod}}_{z,\mathrm{vis}} K^{\mathrm{mod}}_{x,\mathrm{IR}}) e^{i(\Delta_{\mathrm{vis1}} + \Delta_{\mathrm{IR1}})}| + \\
&\qquad |(L_{r,z}\chi^{(2)}_{zzz} K^{\mathrm{mod}}_{z,\mathrm{vis}} K^{\mathrm{mod}}_{z,\mathrm{IR}} + \\
&\qquad L_{r,z}\chi^{(2)}_{zxx} K^{\mathrm{mod}}_{x,\mathrm{vis}} K^{\mathrm{mod}}_{x,\mathrm{IR}}) e^{i(\Delta_{\mathrm{vis1}} + \Delta_{\mathrm{IR1}})}|
\end{aligned}$$

# Ray diagram: the generation of the SF2 beam

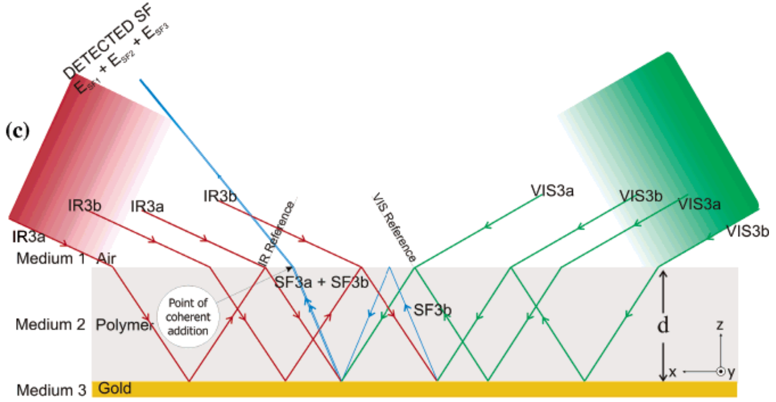



$$
\begin{aligned}
\mathbf{E}_{\mathrm{p,SF2}} &\propto |\mathbf{E}_{x,\mathrm{SF2}}| + |\mathbf{E}_{z,\mathrm{SF2}}| \\
&\propto |L_{t,x}\mathbf{P}^{(2)}_{x,\mathrm{SF2}}| + |L_{t,z}\mathbf{P}^{(2)}_{z,\mathrm{SF2}}| \\
&\propto |(m_{\mathrm{SF2}}L_{t,x}\chi^{(2)}_{xxz}\,K^{\mathrm{mod}}_{x,\mathrm{vis}}\,K^{\mathrm{mod}}_{z,\mathrm{IR}} + \\
&\qquad m_{\mathrm{SF2}}L_{t,x}\chi^{(2)}_{xzx}\,K^{\mathrm{mod}}_{z,\mathrm{vis}}\,K^{\mathrm{mod}}_{x,\mathrm{IR}})e^{i(\Delta_{\mathrm{vis1}}+\Delta_{\mathrm{IR1}})}| + \\
&\qquad |(m_{\mathrm{SF2}}L_{\mathrm{t},z}\chi^{(2)}_{zzz}\,K^{\mathrm{mod}}_{z,\mathrm{vis}}\,K^{\mathrm{mod}}_{z,\mathrm{IR}} + \\
&\qquad m_{\mathrm{SF2}}L_{t,z}\chi^{(2)}_{zxx}\,K^{\mathrm{mod}}_{x,\mathrm{vis}}\,K^{\mathrm{mod}}_{x,\mathrm{IR}})e^{i(\Delta_{\mathrm{vis1}}+\Delta_{\mathrm{IR1}})}|
\end{aligned}
$$

$$
\begin{aligned}
m_{\mathrm{SF2}} &= r_{23}t_{21}e^{i\alpha_2} + r_{23}^{2}r_{21}t_{21}e^{i2\alpha_2} + r_{23}^{3}\,r_{21}^{2}t_{21}e^{i3\alpha_2} + \ldots \\
&= \frac{r_{23}t_{21}e^{i\alpha_2}}{1 - r_{23}r_{21}e^{i\alpha_2}}
\end{aligned}
$$

$$
\alpha_2 = \frac{4\pi n_2 d}{\cos\theta_{23}\lambda}
$$

# Ray diagram: the generation of the SF3 beam




$$\mathbf{E}_{\mathrm{p,SF3}} \propto |L_{r,z}\mathbf{P}^{(2)}_{z,\mathrm{SF3}}|$$

$$\propto |m_{\mathrm{SF3}} L_{r,z} E_{\mathrm{NR}} \mathrm{e}^{i(\epsilon+\Delta_{\mathrm{vis3}}+\Delta_{\mathrm{IR3}})} K^{\mathrm{gold}}_{z,\mathrm{vis}} K^{\mathrm{gold}}_{z,\mathrm{IR}}|$$

$$K^{\mathrm{gold}}_{z,\mathrm{vis}} = \sin\theta_{\mathrm{I,vis}} m_{\mathrm{gold}} (1 + r_{\mathrm{p}})$$

$$K^{\mathrm{gold}}_{z,\mathrm{IR}} = \sin\theta_{\mathrm{I,IR}} m_{\mathrm{gold}} (1 + r_{\mathrm{p}})$$

$$m_{\mathrm{gold}} = \frac{t_{21}}{1 - r_{23} r_{21} \mathrm{e}^{i\alpha_1}}$$

$$m_{\mathrm{SF3}} = \frac{t_{21} \mathrm{e}^{i\Delta\mathrm{SF3}}}{1 - r_{23} r_{21} \mathrm{e}^{i\alpha_2}}$$

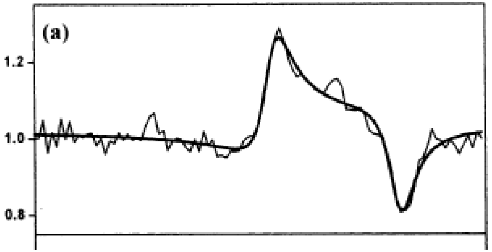
# Multiple Reflections and a Resonant Contribution from the Polymer/Gold Interface

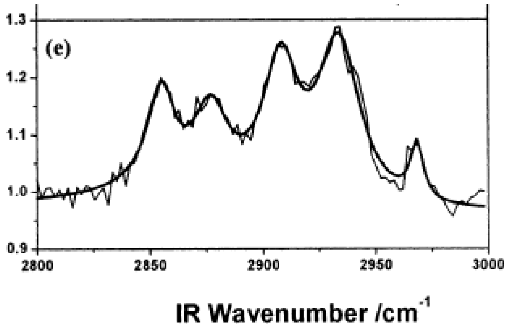
$$\begin{aligned}\mathbf{E}_{\mathrm{p,SF4}} &\propto |\mathbf{E}_{x,\mathrm{SF4}}| + |\mathbf{E}_{z,\mathrm{SF4}}| \\ &\propto |L_{r,x}\mathbf{P}^{(2)}_{x,\mathrm{SF4}}| + |L_{r,z}\mathbf{P}^{(2)}_{z,\mathrm{SF4}}| \\ &\propto |(m_{\mathrm{SF3}}L_{r,x}\chi^{(2)}_{xxz}K^{\mathrm{gold}}_{x,\mathrm{vis}}K^{\mathrm{gold}}_{z,\mathrm{IR}} + \\ &\qquad m_{\mathrm{SF3}}L_{r,z}\chi^{(2)}_{zzz}K^{\mathrm{gold}}_{z,\mathrm{vis}}K^{\mathrm{gold}}_{z,\mathrm{IR}})\mathrm{e}^{i(\Delta_{\mathrm{vis3}}+\Delta_{\mathrm{IR3}})}|\end{aligned}$$

**The total intensity of the generated SF light may consequently be expressed as**

$$\begin{aligned}I_{\mathrm{p,SF}} = {} & |\mathbf{E}_{x,\mathrm{SF1}} + \mathbf{E}_{x,\mathrm{SF2}} + \mathbf{E}_{x,\mathrm{SF3}} + \mathbf{E}_{x,\mathrm{SF4}}|^2 + \\ & |\mathbf{E}_{z,\mathrm{SF1}} + \mathbf{E}_{z,\mathrm{SF2}} + \mathbf{E}_{z,\mathrm{SF3}} + \mathbf{E}_{z,\mathrm{SF4}}|^2\end{aligned}$$

# SF spectra of PDMS and CDC solvent cast onto gold




The SF spectrum of PDMS:

the r+ symmetric (2908 $cm^{-1}$)

the r- anti-symmetric (2963 $cm^{-1}$)

The SF spectrum of CDC :

the r+ mode of the PDMS backbone (2908 $cm^{-1}$)
the resonance at 2968 $cm^{-1}$(a combination of the r- modes of the backbone and the cetyl side chains of the polymer)

The difference in r- phase for the original solvent cast CDC and PDMS spectra is due solely to different film thicknesses in the solvent cast samples.

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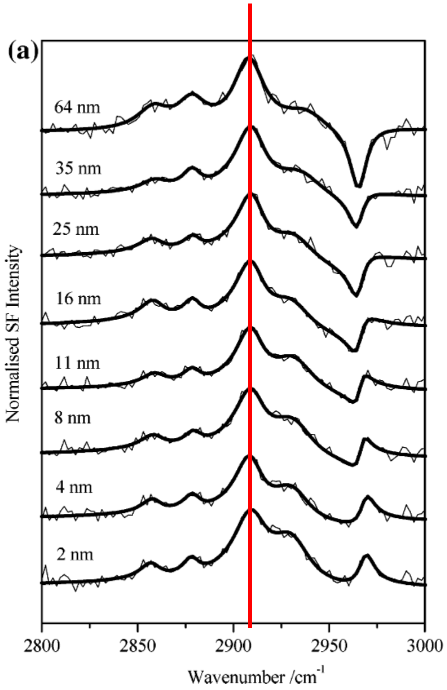
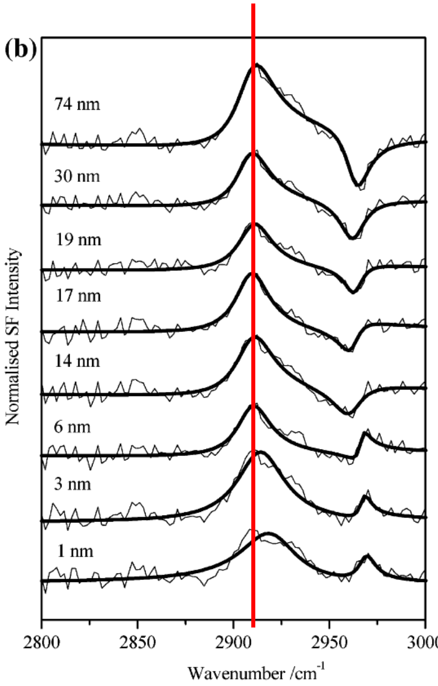
# SFVS of spin-coated CDC and PDMS of different film thicknesses on a gold substrate.

For both PDMS and CDC:

- the 2908 $cm^{-1}$ r+ resonance of the methyl groups is a spectral peak (positive phase) over the thickness range investigated.
- the r- resonance is a spectral peak (positive phase) at small polymer film thicknesses, changes to a differential shape as the film thickness increases, and finally becomes a spectral dip (negative phase) for the thickest samples investigated.




CDC




PDMS