Substrate Matters: Surface-Polaritton Enhanced Infrared Nanospectroscopy of Molecular Vibrations

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Scattering-type scanning near-field optical microscopy (S-SNOM & nano-FTIR)

IR spectra of PEO

substrate
CaF$_2$
Si
Au
c-SiO$_2$
c-SiO$_2$ + Au

Nano Lett. 2019, 19, 11, 8066-8073
Introduction to infrared nanospectroscopy (nano-FTIR)

Substrate-enhanced nano-FTIR of molecular vibrations (non-resonant)

Phonon-polariton resonant substrates for nano-FTIR
Infrared spectroscopy is a powerful tool for material analysis.

Infrared light is highly sensitive to:
- molecular vibrations $\rightarrow$ chemical composition
- crystal lattice vibrations $\rightarrow$ structural properties
- plasmons in doped semiconductors, graphene $\rightarrow$ electron properties
- ...

Chemical mapping is possible, but spatial resolution is diffraction limited $> \lambda/2 \approx 10 - 100 \ \mu m$
Resolution in (far-field) IR spectroscopy is limited

The lateral resolution in (far-field) IR spectroscopy is limited to about $\lambda/2$

Near-field IR microscopy (s-SNOM or nano-FTIR) overcomes diffraction limit by orders of magnitude

Focused laser beam illuminates AFM tip

Tip creates nano-focus

nature Mat. 3, 606-609 (2004)
Nanoidentification by infrared s-SNOM and nano-FTIR

s-SNOM is based on atomic force microscopy and interferometric detection of the tip-scattered light.

nano-FTIR spectroscopy allows for chemical nanoidentification

Quasi-electrostatic dipole model of s-SNOM (bulk samples)

Keilmann, Hillenbrand, in Nano-Optics and Near-Field Optical Microscopy (Artech House, 2008)

Sample properties are measured via near- and far-field reflection coefficients ($\beta$ and $r$)
Table of contents

Introduction to infrared nanospectroscopy (nano-FTIR)

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Phonon-polariton resonant substrates for nano-FTIR
Reflective substrates strongly enhance nano-FTIR signals

14x signal enhancement
by using a highly reflective Au substrate compared to CaF₂

Sketch of experiment

Nano-FTIR amplitude essentially probes near-field reflection of PEO

11.3.2020
Nanolight 2020, Benasque
Reflective substrates strongly enhance nano-FTIR signals

Sketch of experiment

- PEO molecule
- Au or CaF₂

Substrate reflectivities

- $r_{Au} = 1$
- $r_{CaF₂} = -0.06$
- $\beta_{Au} \approx 1$
- $\beta_{CaF₂} \approx 0.3$

Increased tip-substrate coupling

Incident and scattered light reflected via substrate

Nano-FTIR amplitude essentially probes near-field reflection of PEO

14x signal enhancement by using a highly reflective Au substrate compared to CaF₂

Experiment and simulation graphs showing the enhanced signal for PEO on Au compared to CaF₂.

Reflective substrates strongly enhance nano-FTIR signals.
Resonant enhancement of near-fields at the tip apex

Strong field-enhancement can be provided e.g. by:

**Resonant S-SNOM tips**
- e.g. tailored probe tip length

![Resonant S-SNOM tips diagram](image)

Huth, *Nano Lett.* 2013, 13, 1065-1072

- Sophisticated fabrication

**Resonant tip-antenna coupling**
- e.g. in plasmon-resonant gold nanowire

![Resonant tip-antenna coupling diagram](image)

O’Callahan, *J. Phys. Chem. C* 2019, 123, 17505-17509

- Sophisticated fabrication
- Localized hotspots on sample

**Resonant tip-substrate coupling**
- e.g. phonon- or plasmon-polariton resonance

![Resonant tip-substrate coupling diagram](image)

Calculations J. Aizpurua (DIPC, Spain)

- + flat surface
- + simple (no fabrication required)
- + hotspot independent of position

Electron energy loss spectroscopy maps

Near-field intensity

$E_{sca} = \beta p$

$\beta > 1$ \hspace{1cm} $\beta < 1$

+ flat surface
+ simple (no fabrication required)
+ hotspot independent of position
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Resonant tip-substrate coupling (here SiC substrate)

Far-field reflectivity

Dielectric function of SiC-sample
\[ \varepsilon = \varepsilon' + i\varepsilon'' \]

Near-field spectrum dipole model
\[ S = E_{\text{sca}}^2 \]

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Tip-substrate resonance of quartz matches PEO's vibrational resonance

Resonant tip-substrate coupling provides large (additional) field enhancement

Phonon-polariton resonant substrate, such as c-SiO2

Resonance condition \( \varepsilon \approx -1 \)

→ We aim to exploit polariton-resonance to further increase nano-FTIR signals of PEO

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\[ \text{Resonance condition } \varepsilon \approx -1 \]

\[ p' = p \cdot \frac{\varepsilon - 1}{\varepsilon + 1} \]

→ We aim to exploit polariton-resonance to further increase nano-FTIR signals of PEO

Resonant tip-substrate coupling boosts nano-FTIR signal beyond Au

\[ \Delta s_4 = \text{Difference of curves (c-SiO}_2^*\text{)} - \text{(PEO on c-SiO}_2\text{)} \]

Dip in resonance indicates large coupling between molecule and tip-induced phonon-polariton

(Analog to SEIRA effect, but in near-field microscopy)
Comparison of substrate-enhancements

Metal substrate yields 14x higher spectral contrast than CaF2

Polariton-resonant substrate yields further 3x enhancement
Comparison of substrate-enhancements

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Polariton-resonant substrate + illumination of tip via gold surface (+ illumination via propagating SPhP) yields two orders of magnitude enhancement (compared to CaF2)
Outlook

Strong spectral contrast $\Delta s_4$ predicted even for nm-thin molecular layers

Wide range of materials host polariton resonances that can enhance sensing ($\varepsilon \approx -1$)

Polar crystals
strong lattice vibrations (phonons)
e.g. SiO$_2$, SiC, Al$_2$O$_3$, …

Metals / doped semiconductors
collective free electron oscillations (plasmons)

Tip-substrate coupling increases for thin molecular layers

plasma frequency
(longitudinal oscillation)

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Non-resonant tip-substrate coupling (e.g. Au substrate) $\rightarrow$ 14x enhancement compared to CaF$_2$

Phonon-resonant tip-substrate coupling (e.g. Quartz substrate) $\rightarrow$ further 3x enhancement

Resonant tip-substrate coupling (Quartz) + efficient tip illumination (via Au) $\rightarrow$ 7.5x enhancement compared to Au $\rightarrow$ 14x enhancement compared to Silicon

Autore, *Nano Lett.* 2019,19,11, 8066-8073
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