Optical spectroscopy and biosensors for investigation of biomolecules and their interactions

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Surface-Enhanced Infrared Absorption Spectroscopy

Content

- Implementation for fingerprinting of molecular species, complementarity of Raman and infrared absorption spectroscopy.
- Optical configurations used for the IR absorption.
- Quantum cascade lasers.
- Amplification of weak IR absorption signal - SEIRA.
- Plasmonic confinement of IR absorption

Raman @ IR Absoprtion Spectroscopy

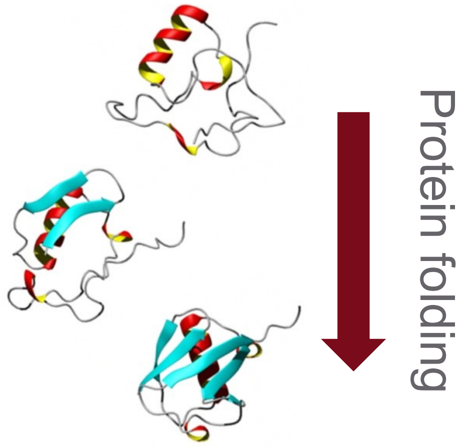
Vibrational spectroscopies - IR and Raman are the most common vibrational spectroscopies for assessing molecular motion and fingerprinting species.

IR and Raman obeys complementary selection rules

- Selection rules dictate, which molecular vibrations are probed.
- Some vibrational modes are both IR and Raman active.

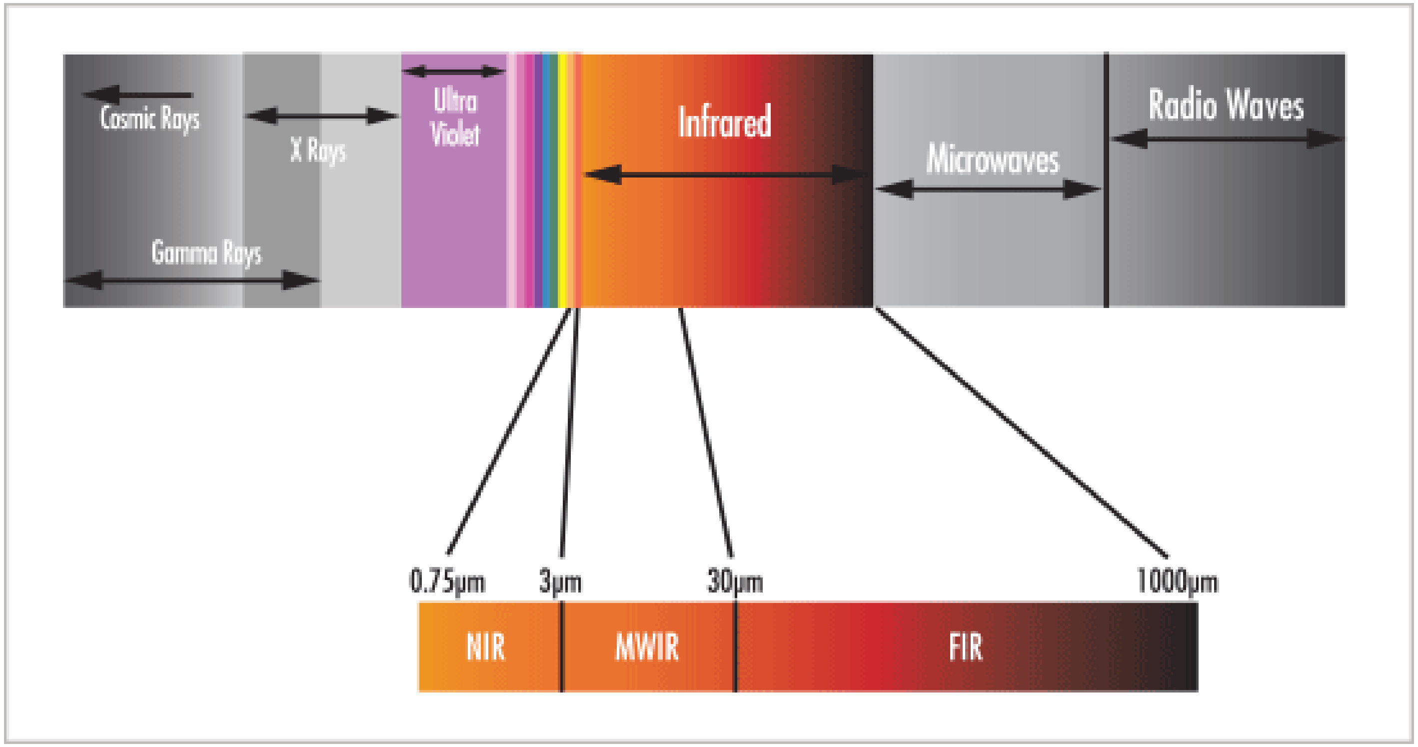
Applications

- Commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified.
- For larger molecules – information on conformation changes can be obtained rather than identification of a protein itself.



http://web.mit.edu/~tokmakofflab/ResearchProtein.htm

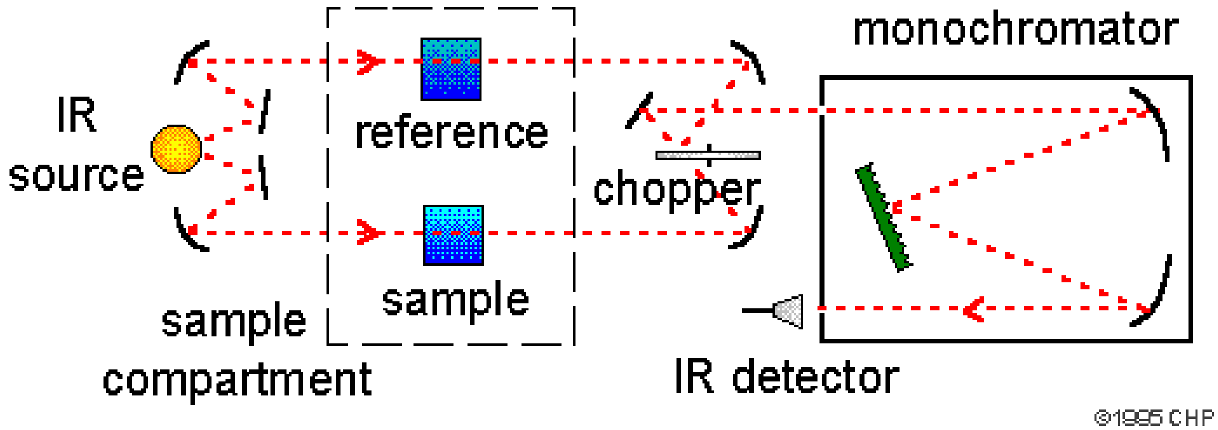
IR Spectral Range



www.edmundoptics.com

- Measuring in the spectral range of several – tens of µm

IR Absorption Spectroscopy

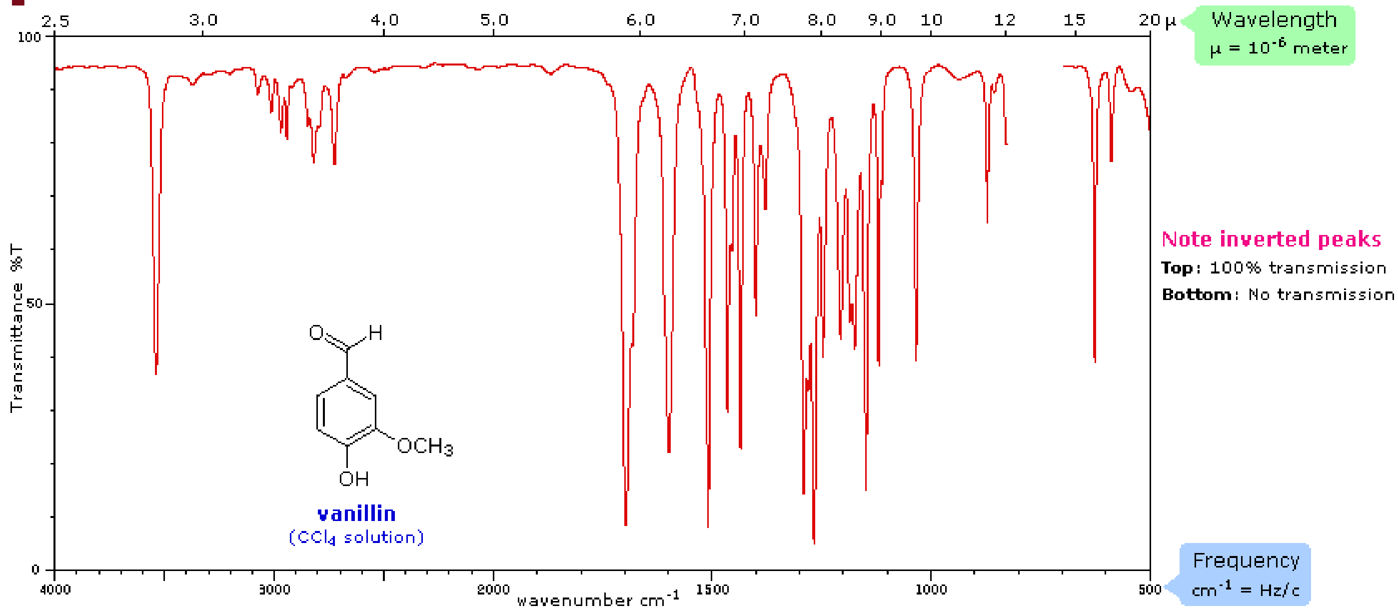


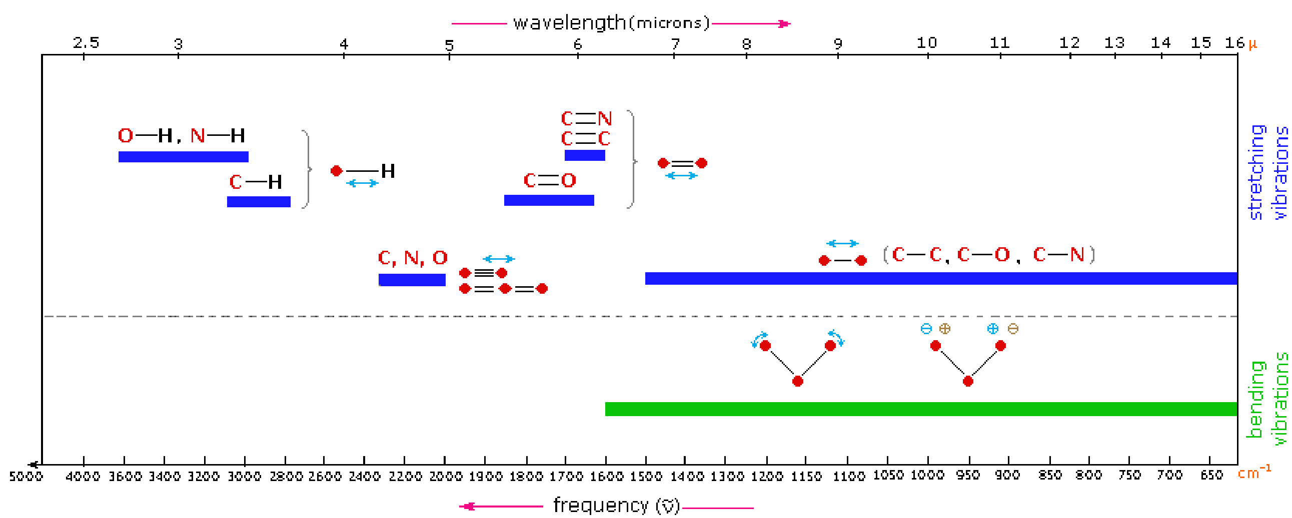
http://www.pci.tu-bs.de/aggericke/PC4/Kap_I/ir-instr.htm

- As a light-source, a polychromatic beam can be used on conjunction with a spectrometer (typically FTIR) or a monochromatic beam at a wavelength tuned for selected bands (quantum cascade lasers, monochromator)
- Detectors based on semiconductors with low bandgap (PbS, InGaAs,) or bolometers.

https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm

IR Spectra





https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm

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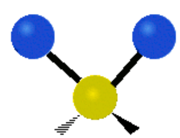
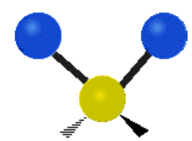
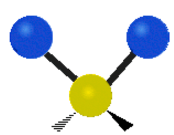
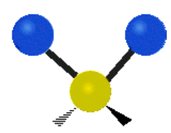
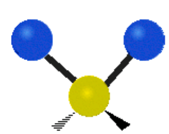
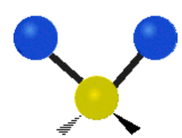
Examples of Vibration Modes

Symmetry / Direction	Symmetric	Antisymmetric
Radial	 Symmetric stretching (ν_s)	 Antisymmetric stretching (ν_{as})
Latitudinal	 Scissoring (δ)	 Rocking (ρ)
Longitudinal	 Wagging (ω)	 Twisting (τ)

- IR bands arise with the transition from a ground state to higher vibrational state of specific modes.
- Symmetry matters and some transitions are not allowed (symmetrical molecules seen in Raman, not in IR). Selection rules.
- The bigger molecule, the more complex is the spectrum.

https://en.wikipedia.org/wiki/Infrared_spectroscopy

Optical Components Used in IR Absorption Spectroscopy

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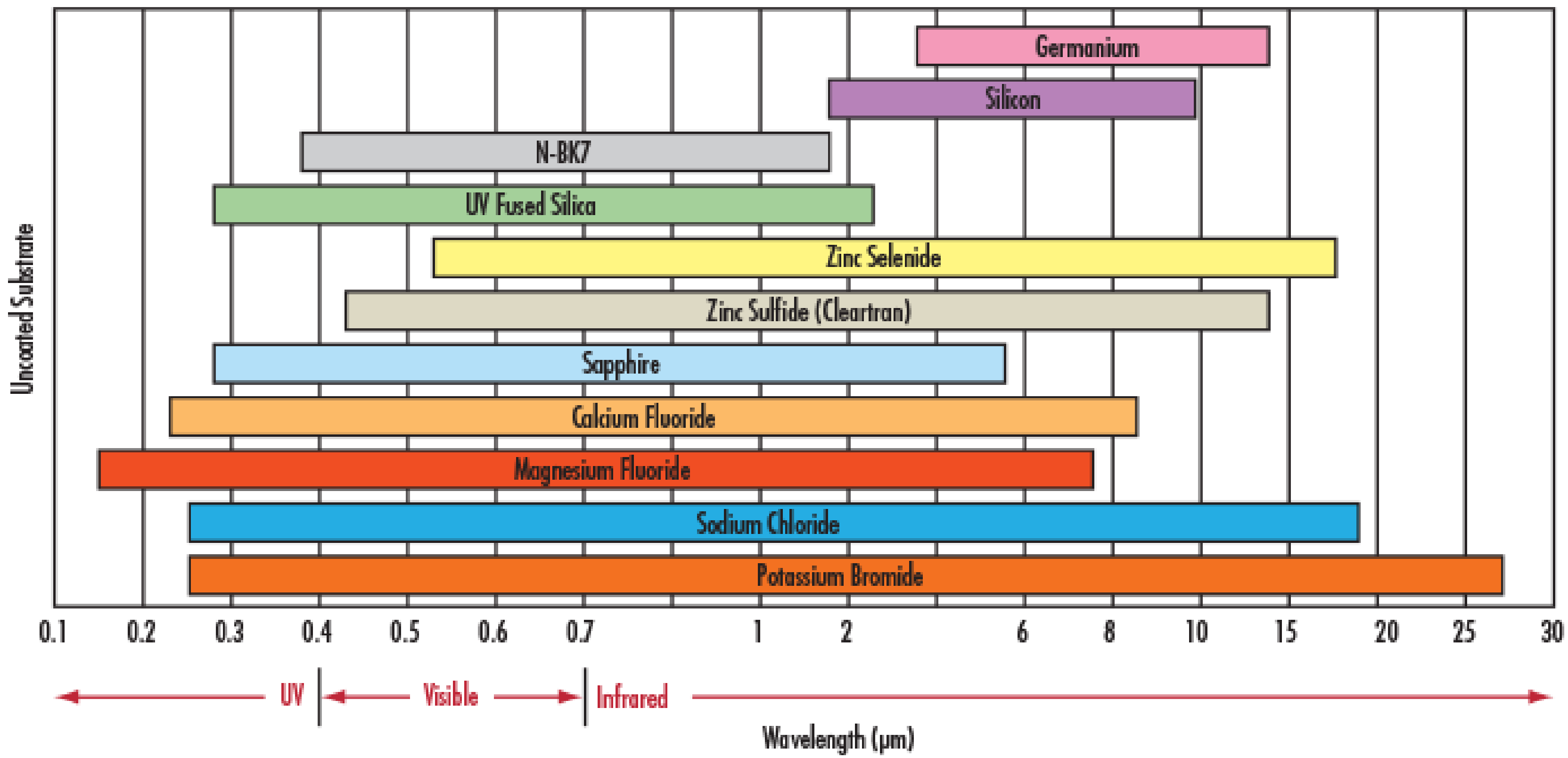
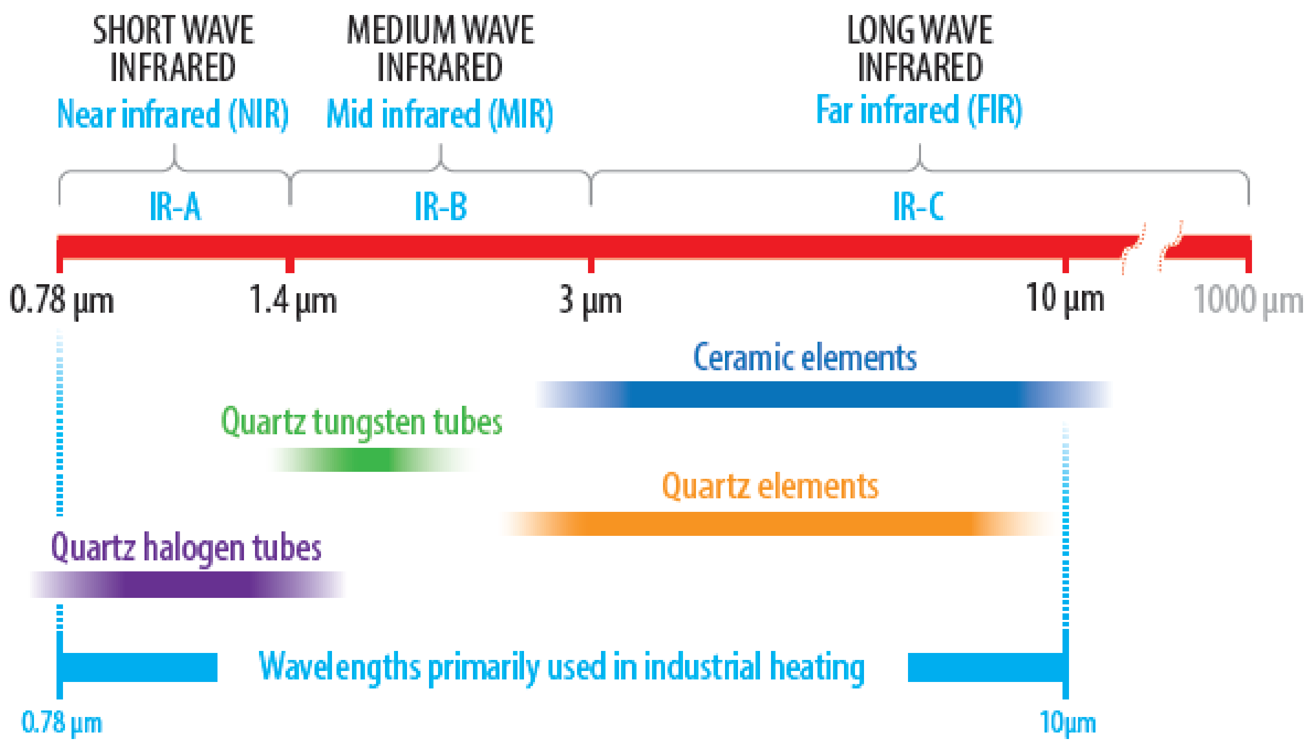
IR Transmission



- The components need to be built from materials that offer decent transmission in selected spectral range.

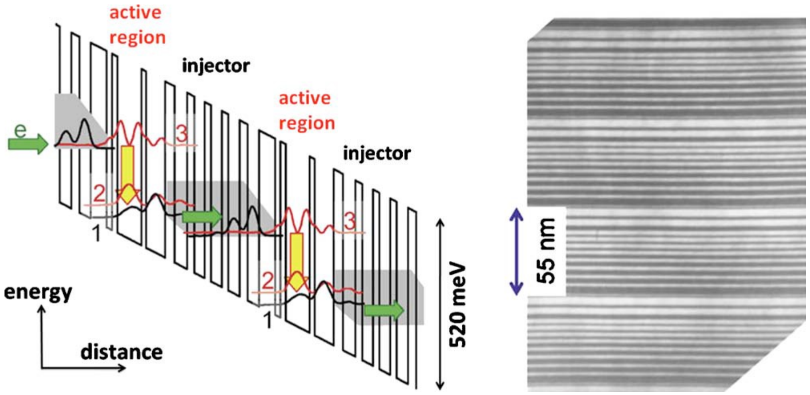
IR Lightsources



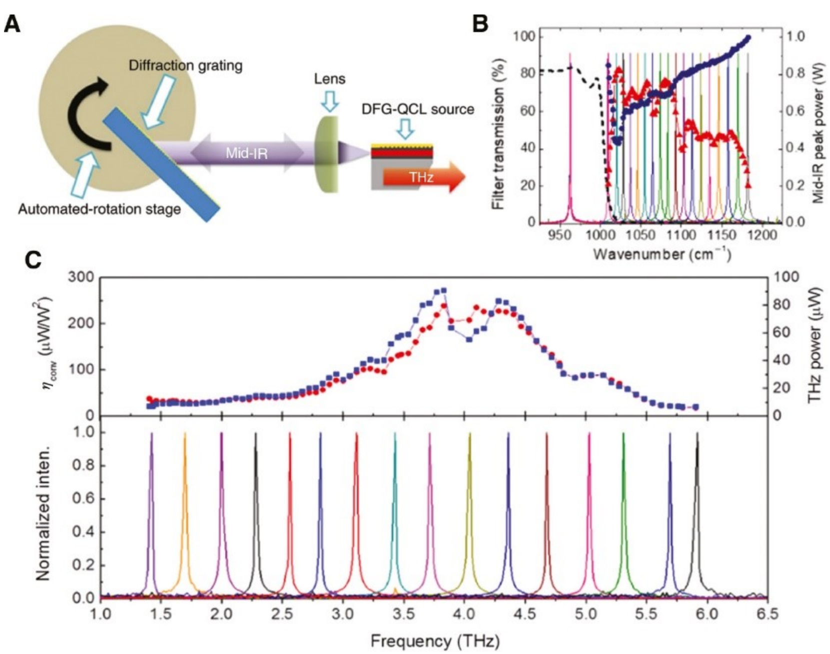
/wecointernational.com

- Simple heat sources can be employed for broad band spectral applications.

IR Quantum Cascade Lasers



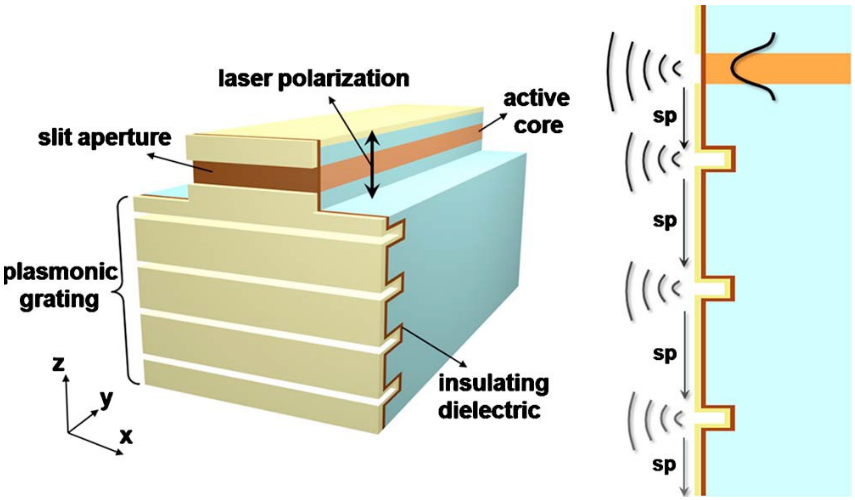
•https://doi.org/10.1364/JOSAB.27.000B18

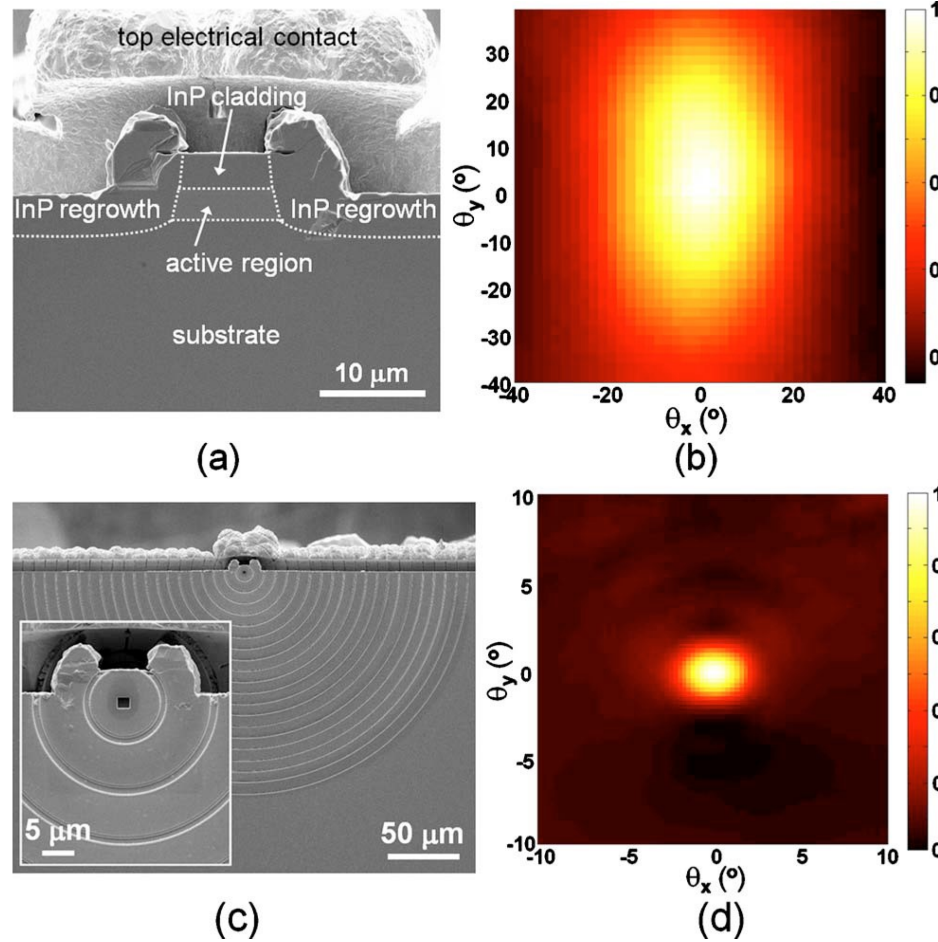


- Composed of stacks of quantum wells prepared from semiconductor layers.
- Narrow wavelength bands emitted in NIR range. Various configurations including those with tuneable emitting wavelength.

https://doi.org/10.1515/nanoph-2018-0093

IR Quantum Cascade Lasers





- Capasso lab: example of manipulating with NIR QCL beam via diffraction coupling of surface plasmons

•https://doi.org/10.1364/JOSAB.27.000B18

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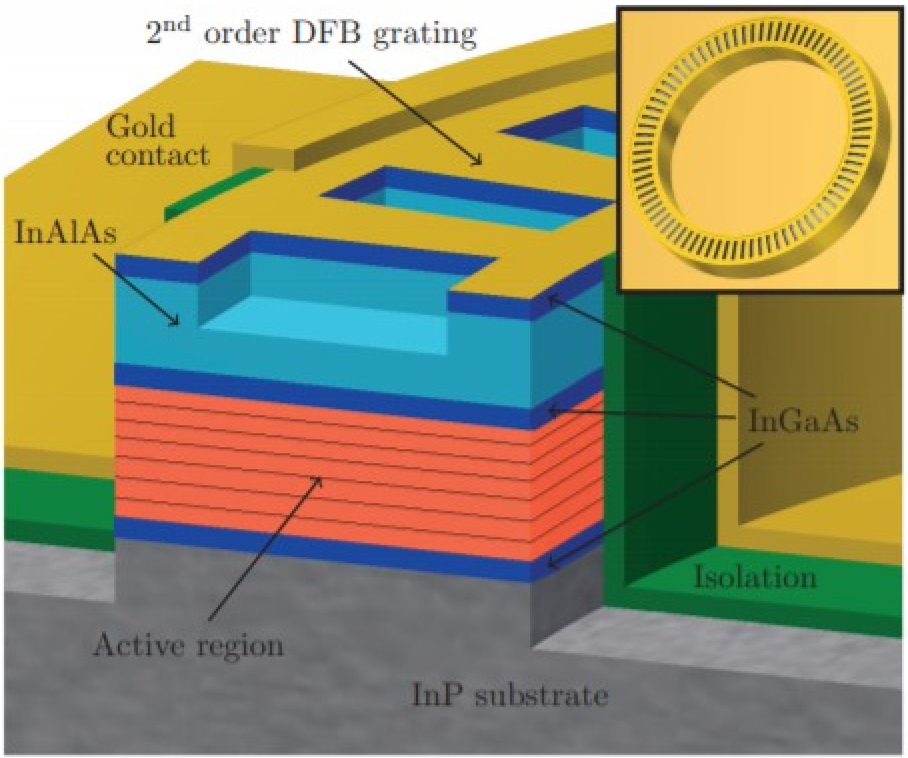
IR Quantum Cascade Lasers



- Strasser lab: example of manipulating with NIR QCL beam via coupling of surface plasmons travelling in a ring architecture.
- Controlled far field properties of the beam, towards on chip IR spectroscopy.

• https://doi.org/10.1364/OE.22.015829

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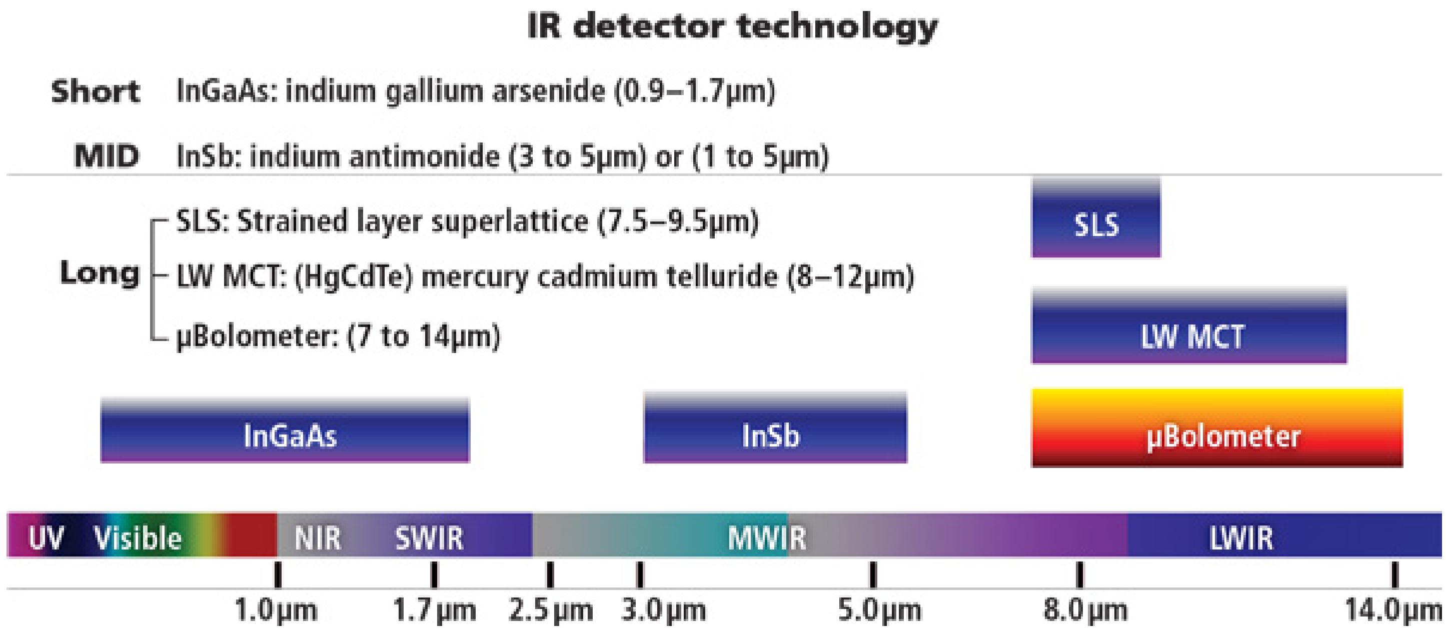
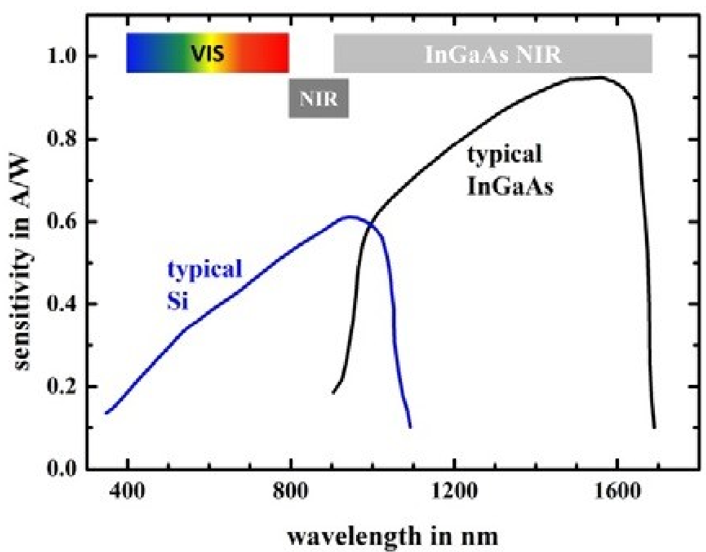
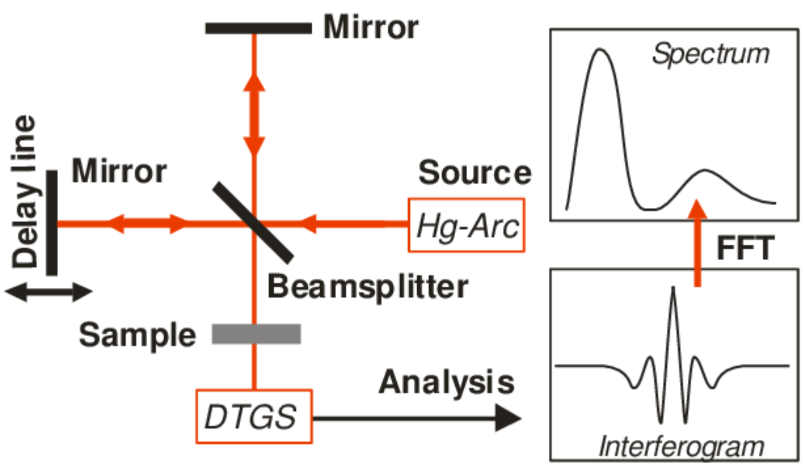
IR Detectors

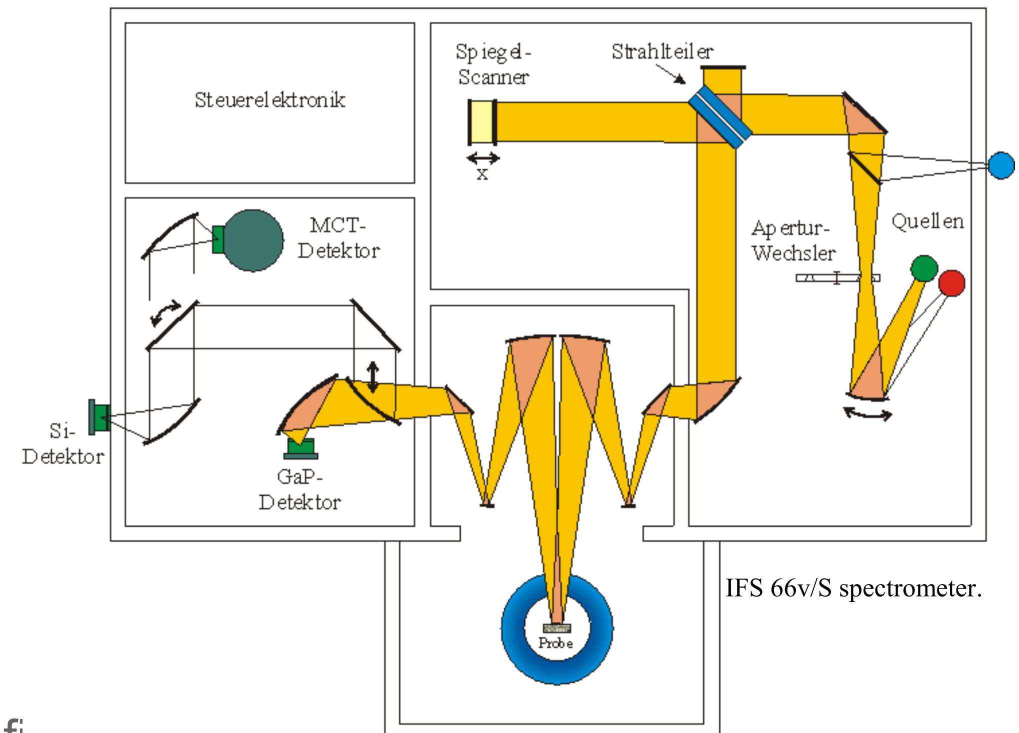




- Semiconductor or bolometer type. Often need to be cooled.
- Classical Si-based detectors not useable due to its large bandgap

Fourier Transform Spectrometer

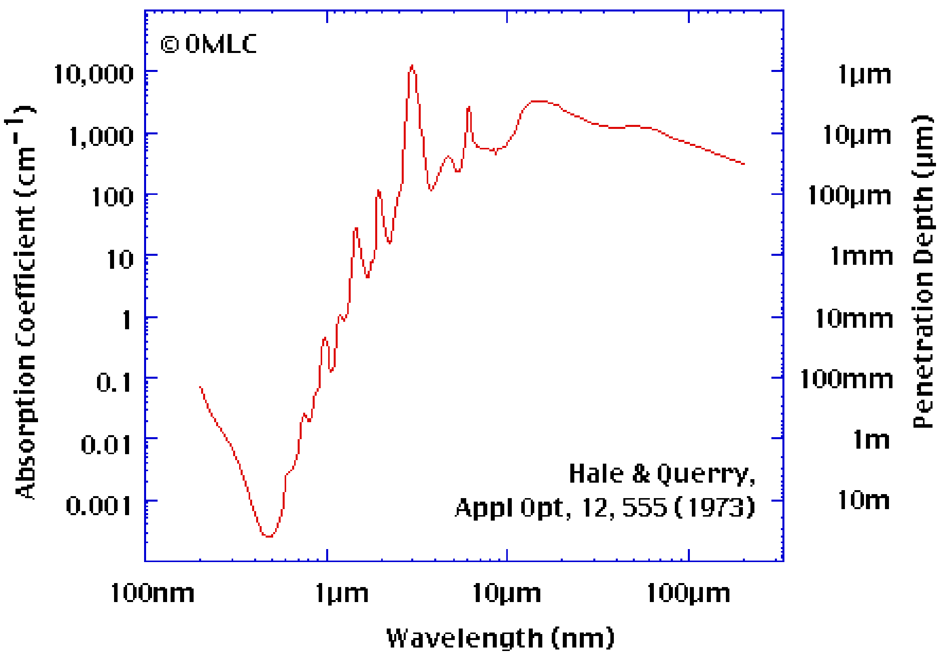


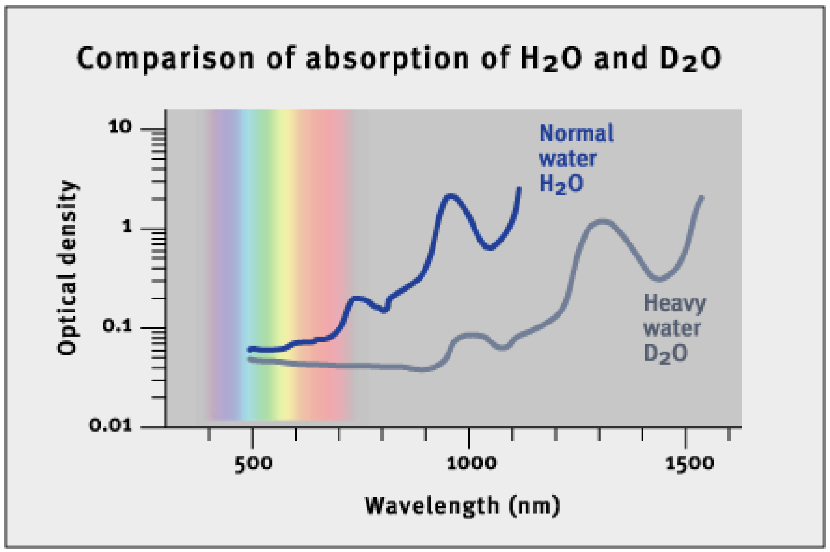


IFS 66v/S spectrometer.

- Michelson interferometer configuration used with varied distance for measuring of an interferogram that is converted to transmission spectrum by using Fourier transform.

IR Absorption of Water





- Water (or humidity is often a problem in IR spectroscopy measurements due to its strong absorption that masks the bands of investigated specimen.
- The optical systems are thus purged with N_2, H_2O replaced with D_2O, or very strong beam intensity can be used.

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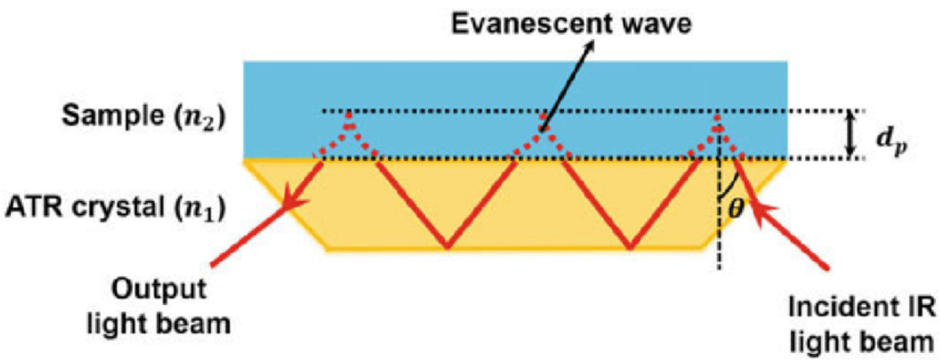
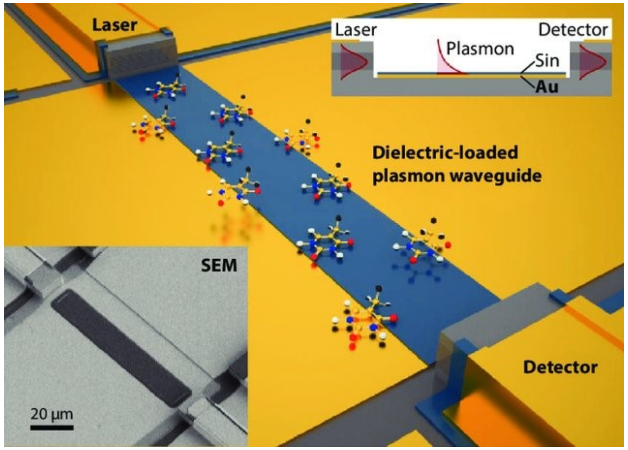
Surface-Enhanced IR Absorption Spectroscopy - SEIRA

Multiple Reflection IR Absorption Spectroscopy

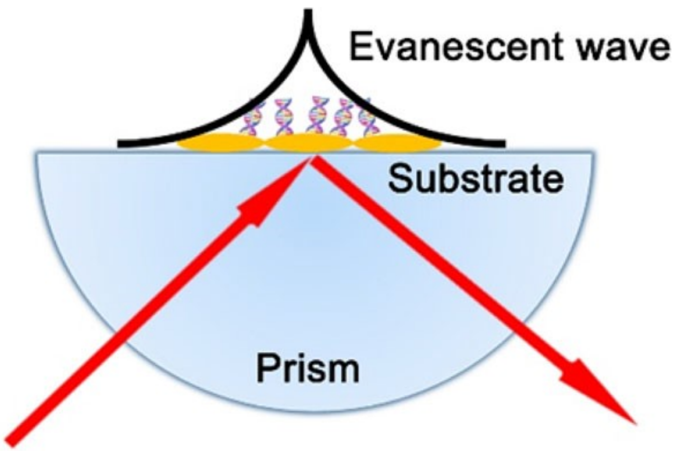




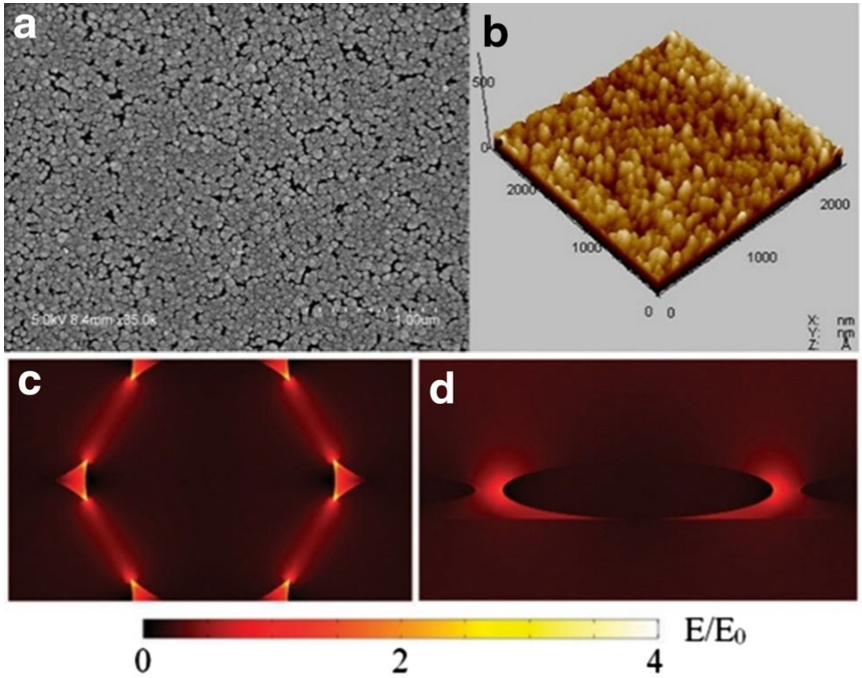
Strasser Lab.

- IR absorption from monolayers is possible to measure by using evanescent field.
- Multiple reflections allow to increase the sensitivity, alternatively a monolithic integration is possible by using surface plasmons

Surface-Enhanced IR Absorption Spectroscopy



10.1007/s41664-017-0009-5



- IR absorption amplification by rough metallic surfaces was investigated for biointerface studies (up to 10^5 enhancement claimed).
- Confinement of the optical probing allows also for suppressing of the effect of water absorption.

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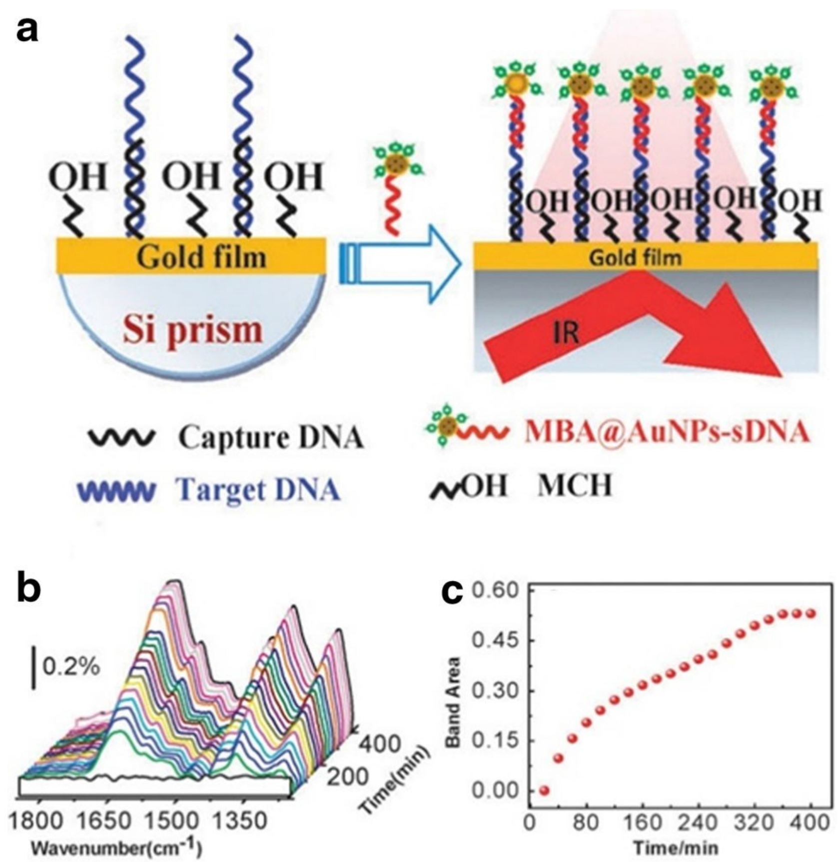
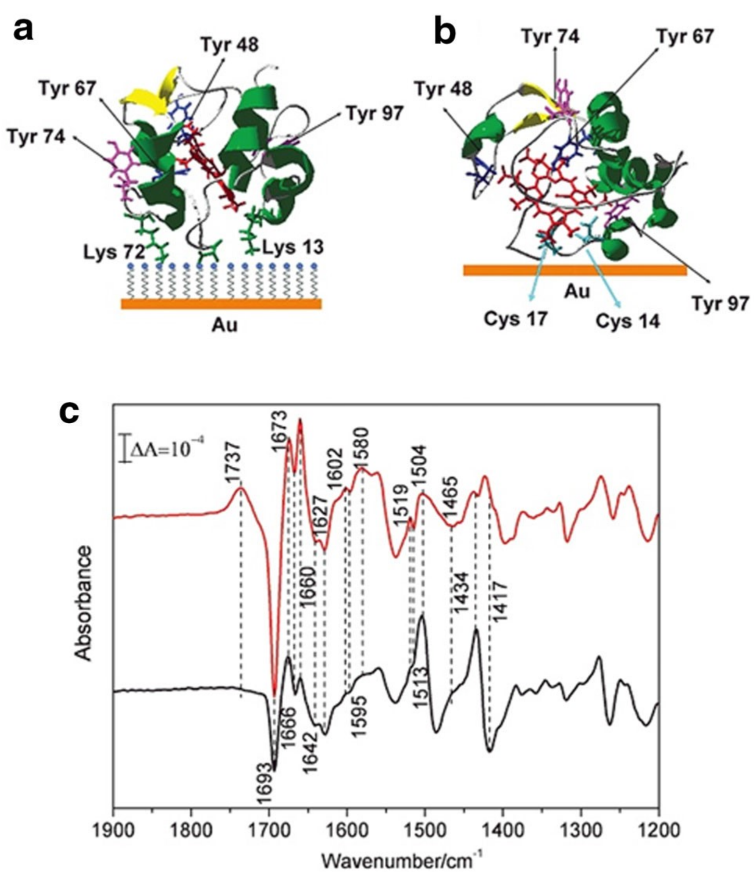


- *In situ* DNA hybridization observation on Au nanoislands on a Si prism.

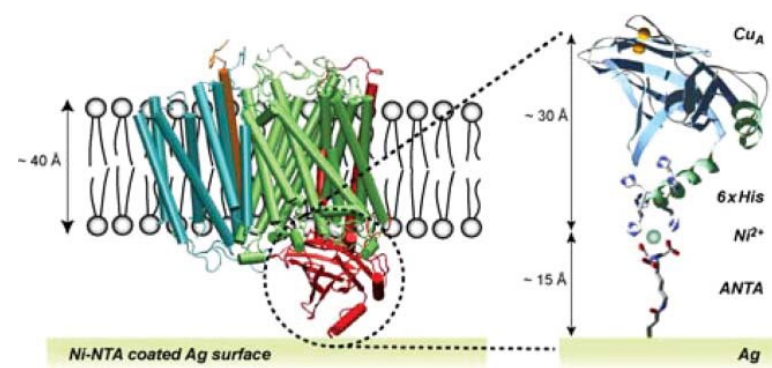
Tanaka K, Hirano-Iwata A, Miyamoto K, Kimura Y, Niwano M. In situ surface infrared study of DNA hybridization on Au island films evaporated on silicon surfaces. Jpn J Appl Phys. 2009;48:04C186

Surface-Enhanced IR Absorption Spectroscopy



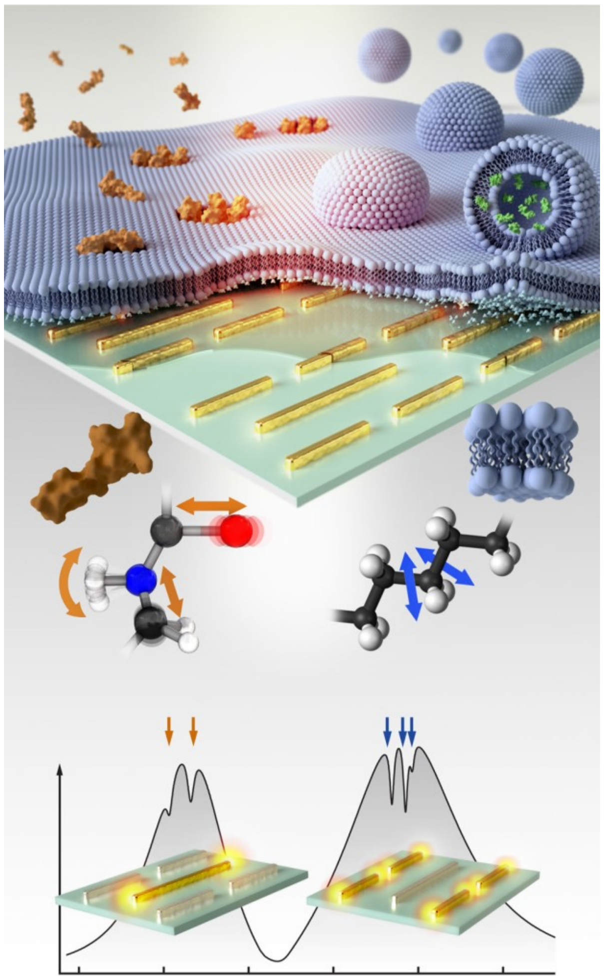
Lin SR, Jiang XE, Wang LX, Li GH, Guo LP. Adsorption orientation of horse heart cytochrome c on a bare gold electrode hampers its electron transfer. J Phys Chem C. 2012;116:637–42.

- Studies of cytochrome C on gold electrode, possible embedding on lipid membranes. See former studies of Knoll and Naumann.



https://doi.org/10.1039/B410998H

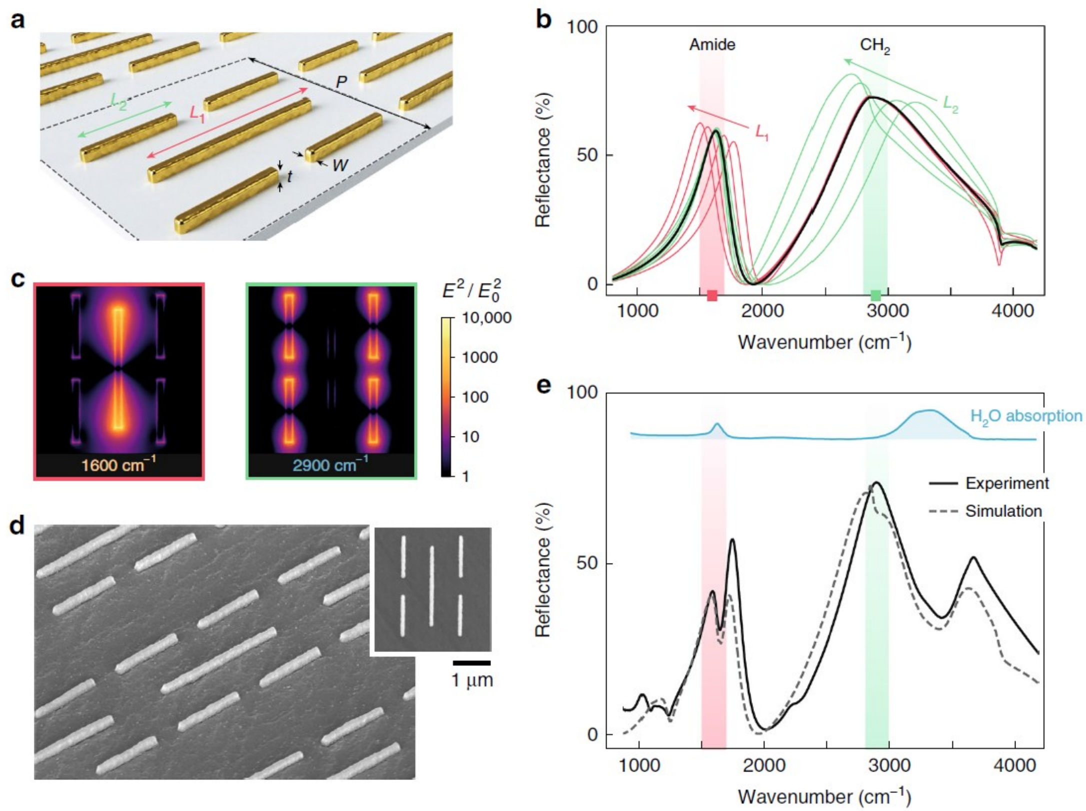
SEIRA on Engineered Antennas



- Arrays of plasmonic antennas tuned to excite localized surface plasmons at specific spectral bands.
- Antenna resonance positions are engineered to simultaneously overlap with the vibrational signatures of both the amide I, II, and the CH2, CH3 absorption bands, allowing for the simultaneous enhancement and detection of lipid- and protein-induced absorption changes.

https://www.nature.com/articles/s41467-018-04594-x

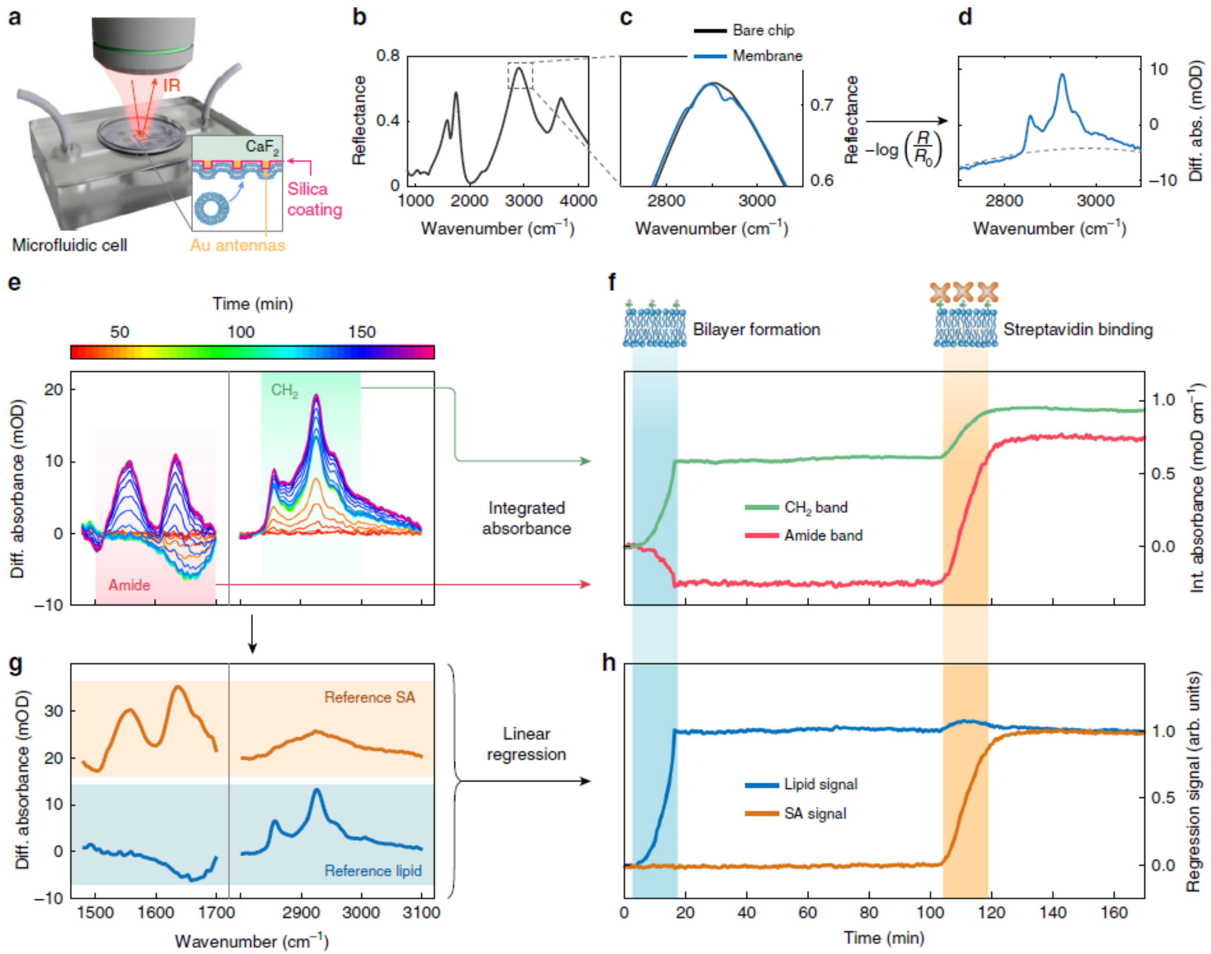
SEIRA on Engineered Antennas



- Multi-resonant gold nanorods proposed for covering of multiple spectral bands at the same time.

https://www.nature.com/articles/s41467-018-04594-x

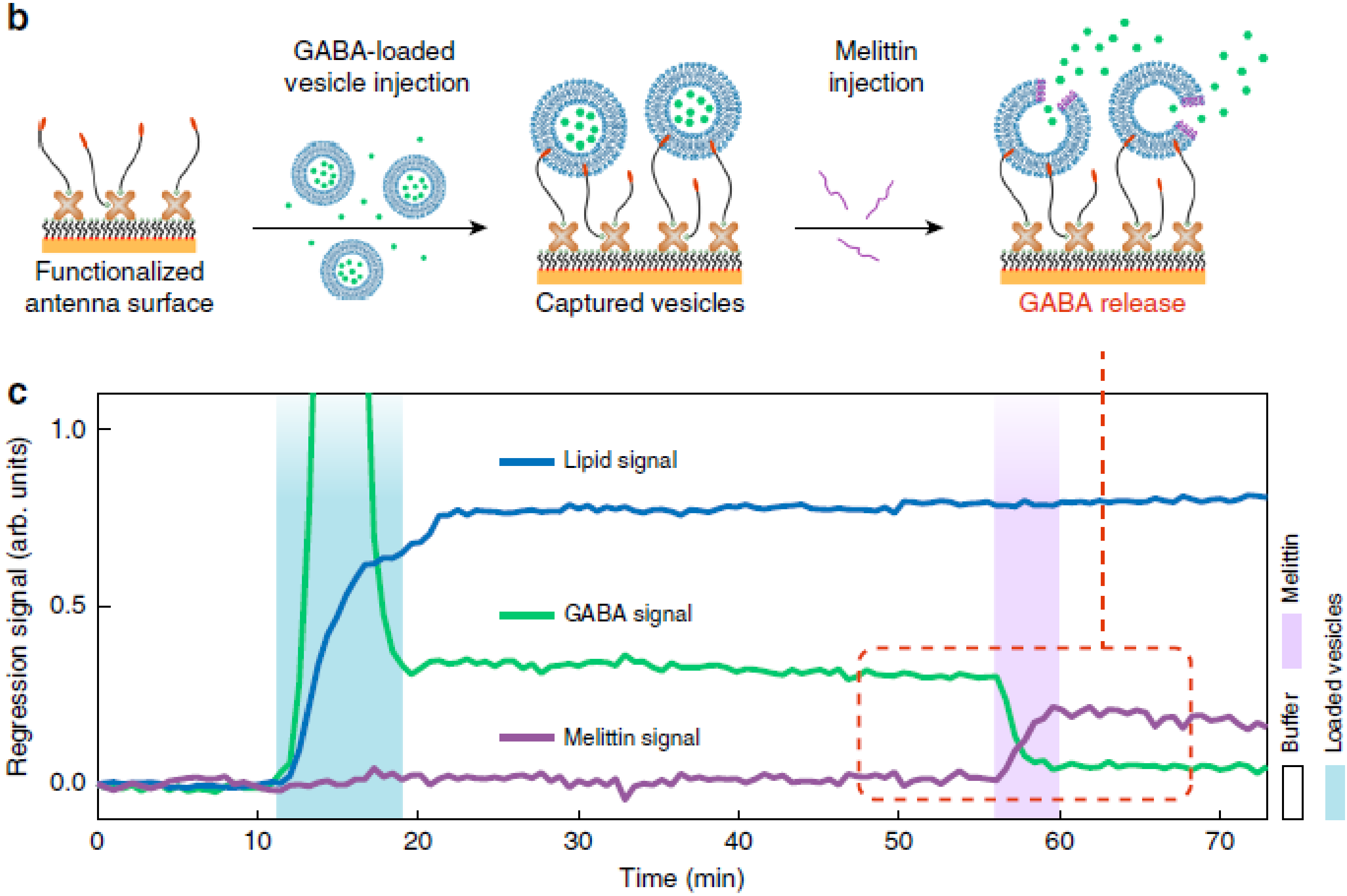
SEIRA on Engineered Antennas



- Probing at specific bands allows distinguishing different biointerface constituents

https://www.nature.com/articles/s41467-018-04594-x

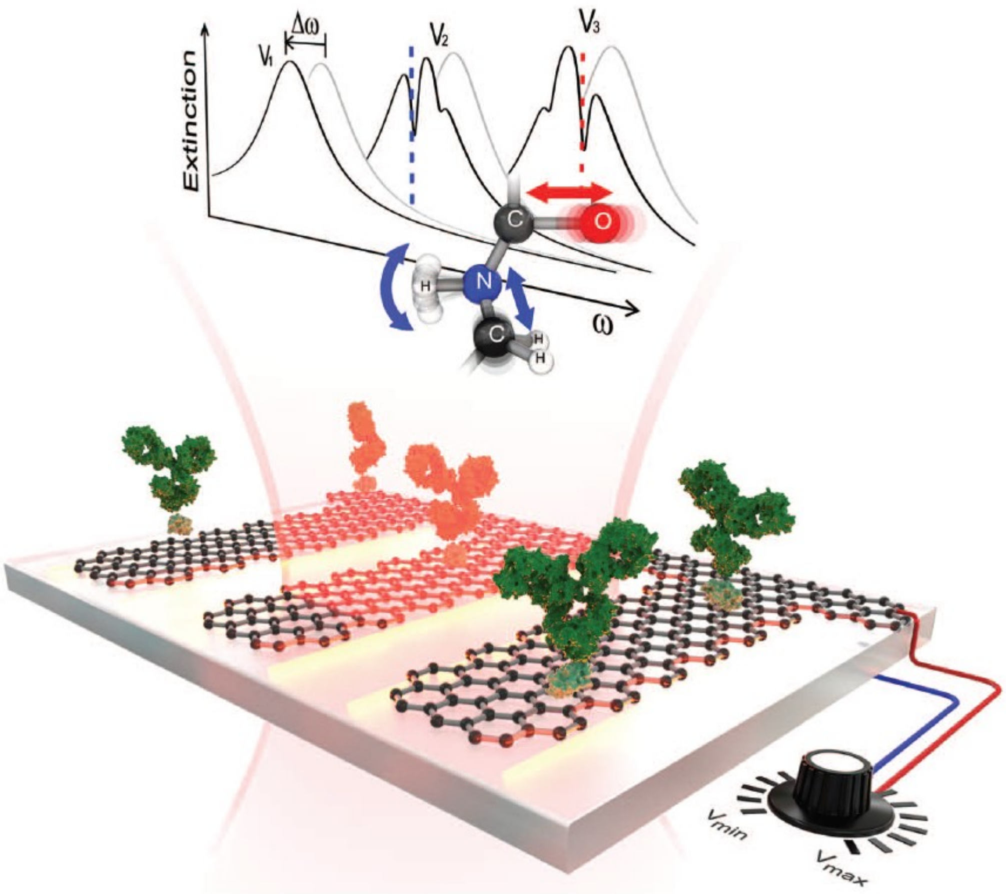
SEIRA on Engineered Antennas



➧ Monitoring of cargo release from tethered lipid vesicles.

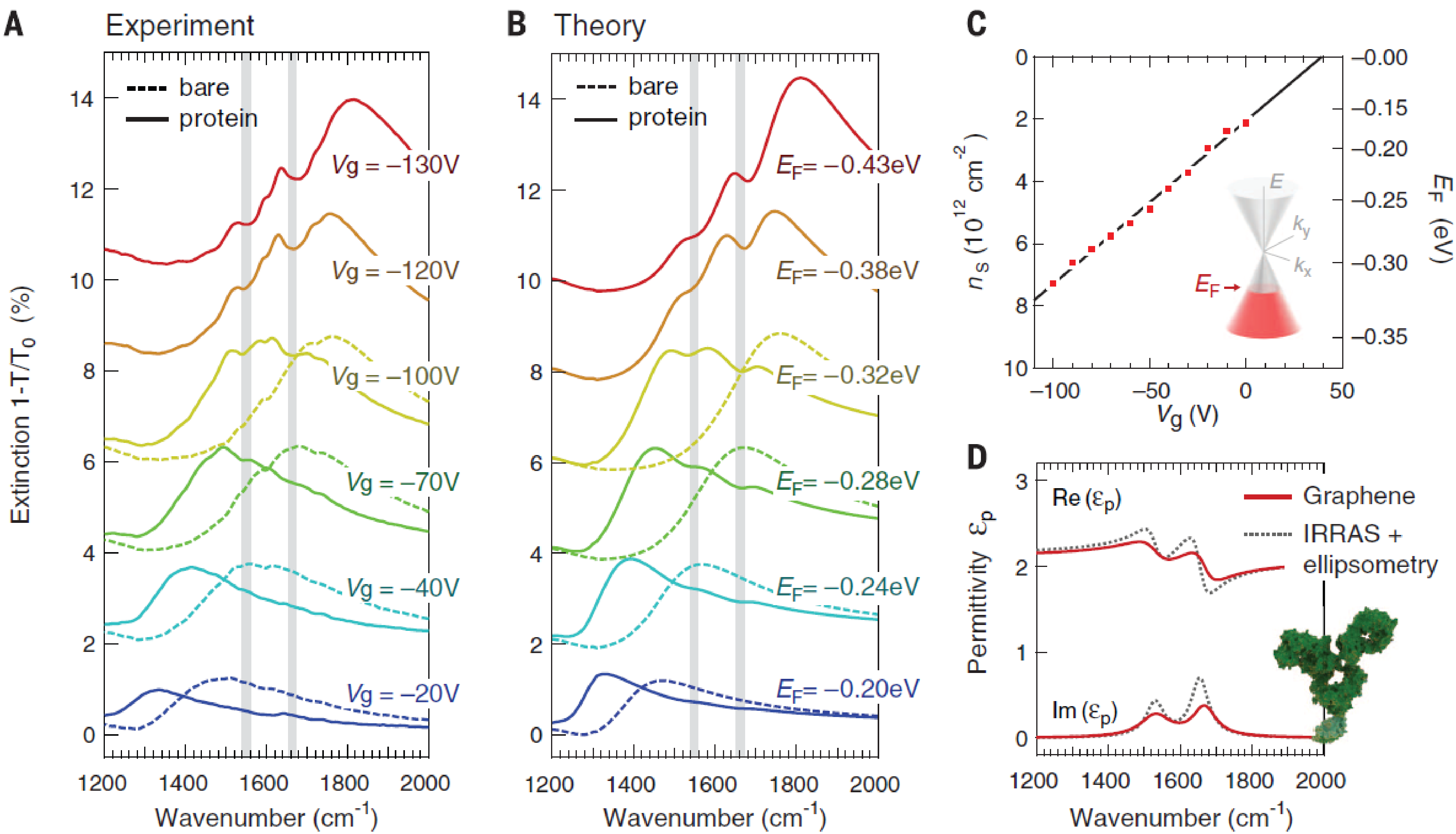
https://www.nature.com/articles/s41467-018-04594-x

SEIRA on Tunable Graphene Antennas



- Graphene is semiconductive material and exhibits surface plasmons in the NIR spectral range (lower plasma frequency)
- Its properties can be electronically tuned and thus enable for active tuning of its plasmonic properties.

10.1126/science.aab2051



Tuning of plasmonic band by modulating charge carried concentration (n_s).

10.1126/science.aab2051