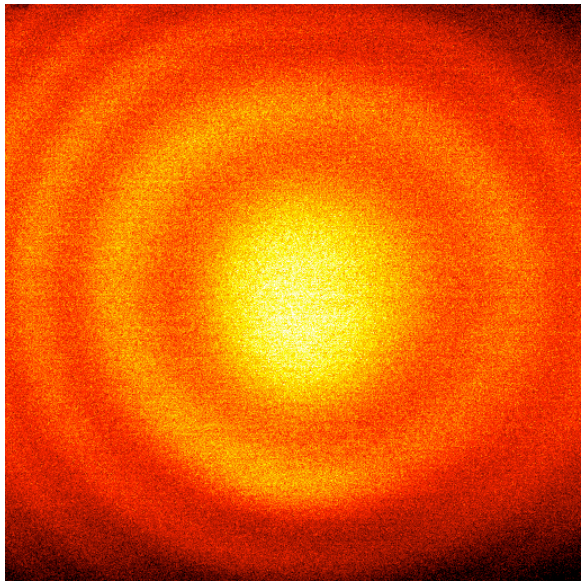
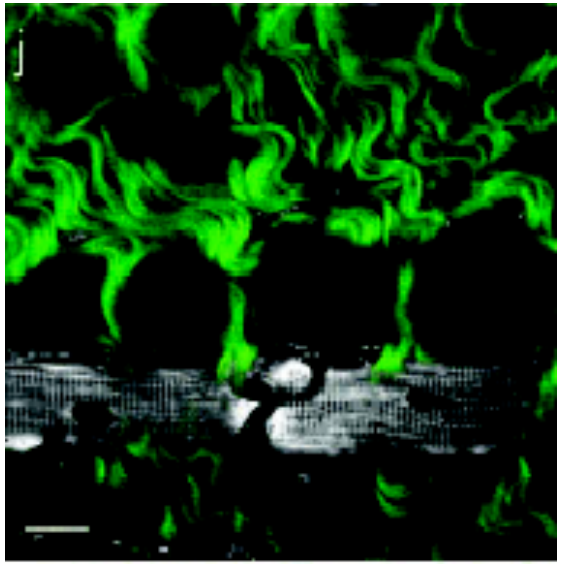
Fourth order Raman

CARS



- $\chi^{(3)}$
- vibrationally sensitive
- not surface sensitive

SHG



- $\chi^{(2)}$
- not vibrationally sensitive
- surface sensitive

Raman and surface sensitivity

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Interface-Specific $\chi^{(4)}$ Coherent Raman Spectroscopy in the Frequency Domain

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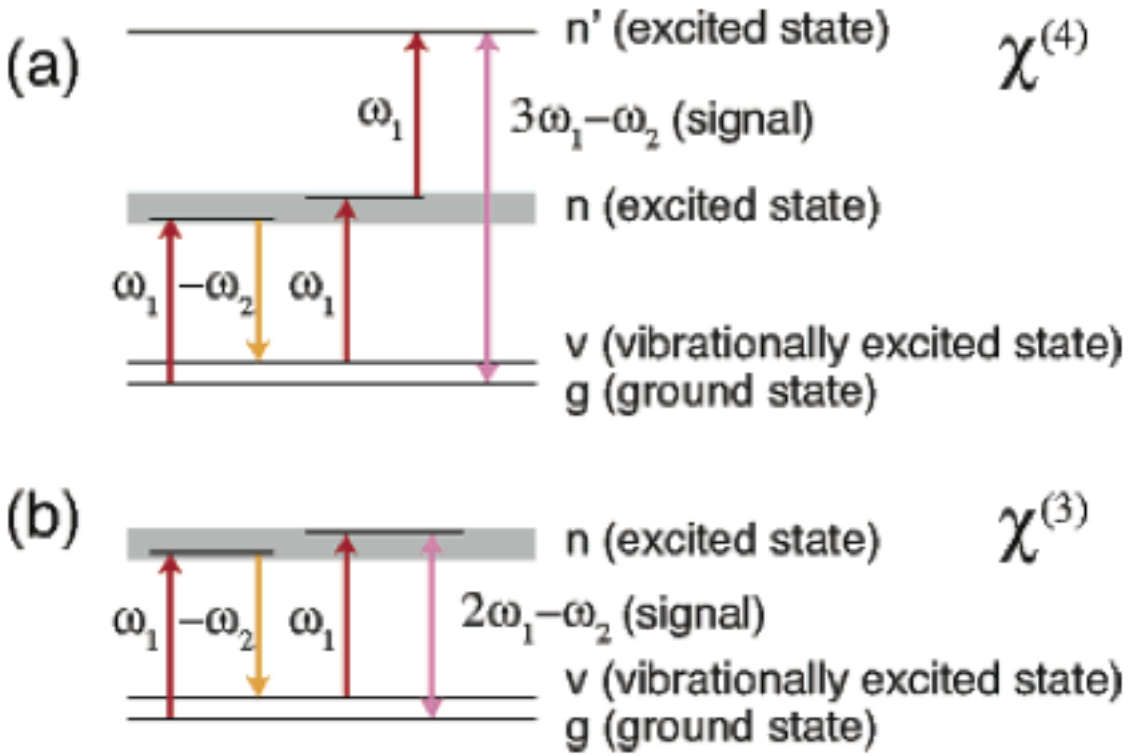
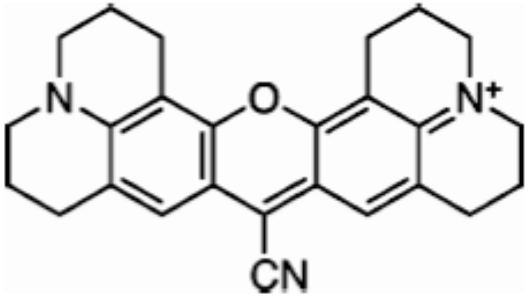
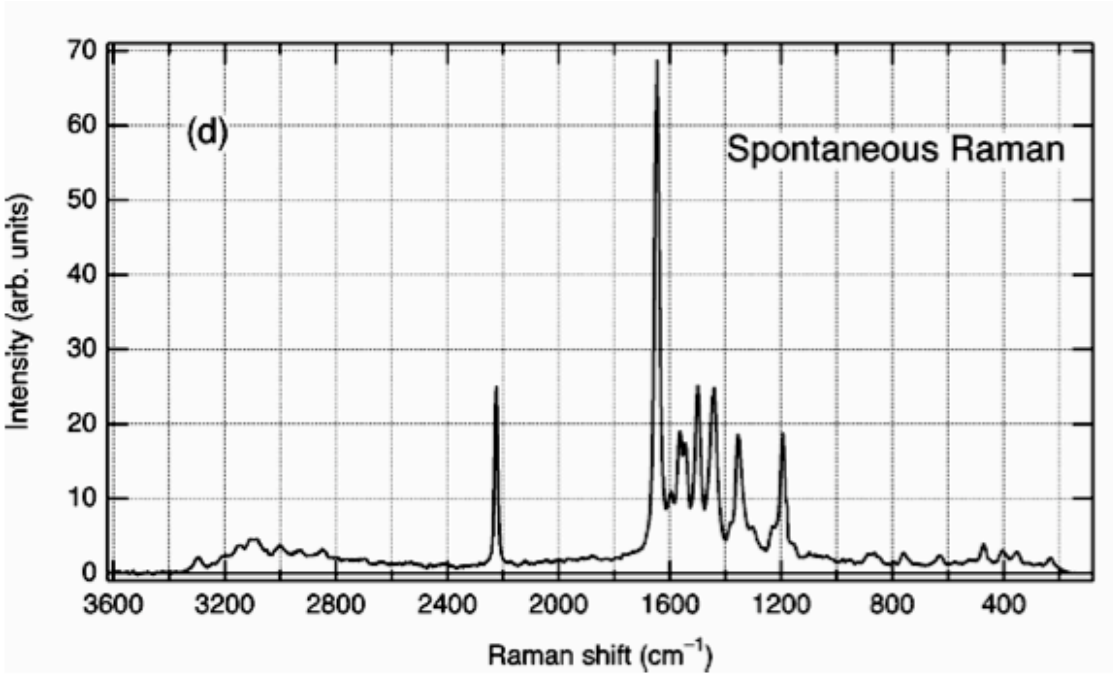
We demonstrate interface-specific fourth-order ($\chi^{(4)}$) coherent Raman spectroscopy in the frequency domain for the first time. Because the $\chi^{(4)}$ Raman spectroscopy uses only visible (vis) or near-IR light, it is expected to be a potential alternative to the widely utilized IR−vis sum frequency generation spectroscopy that cannot be applied to interfaces buried in thick IR absorbers such as water. We present the vibrational $|\chi^{(4)}|^2$ spectrum of rhodamine 800 at the air/water interface in a wide spectral range 100−3600 cm^{-1}. Comparison of the $|\chi^{(4)}|^2$ spectrum with the $|\chi^{(3)}|^2$ spectrum leads us to conclude that the present $\chi^{(4)}$ spectroscopy successfully probes the interface distinguished clearly from the bulk.

$\chi^{(3)}$ and $\chi^{(4)}$

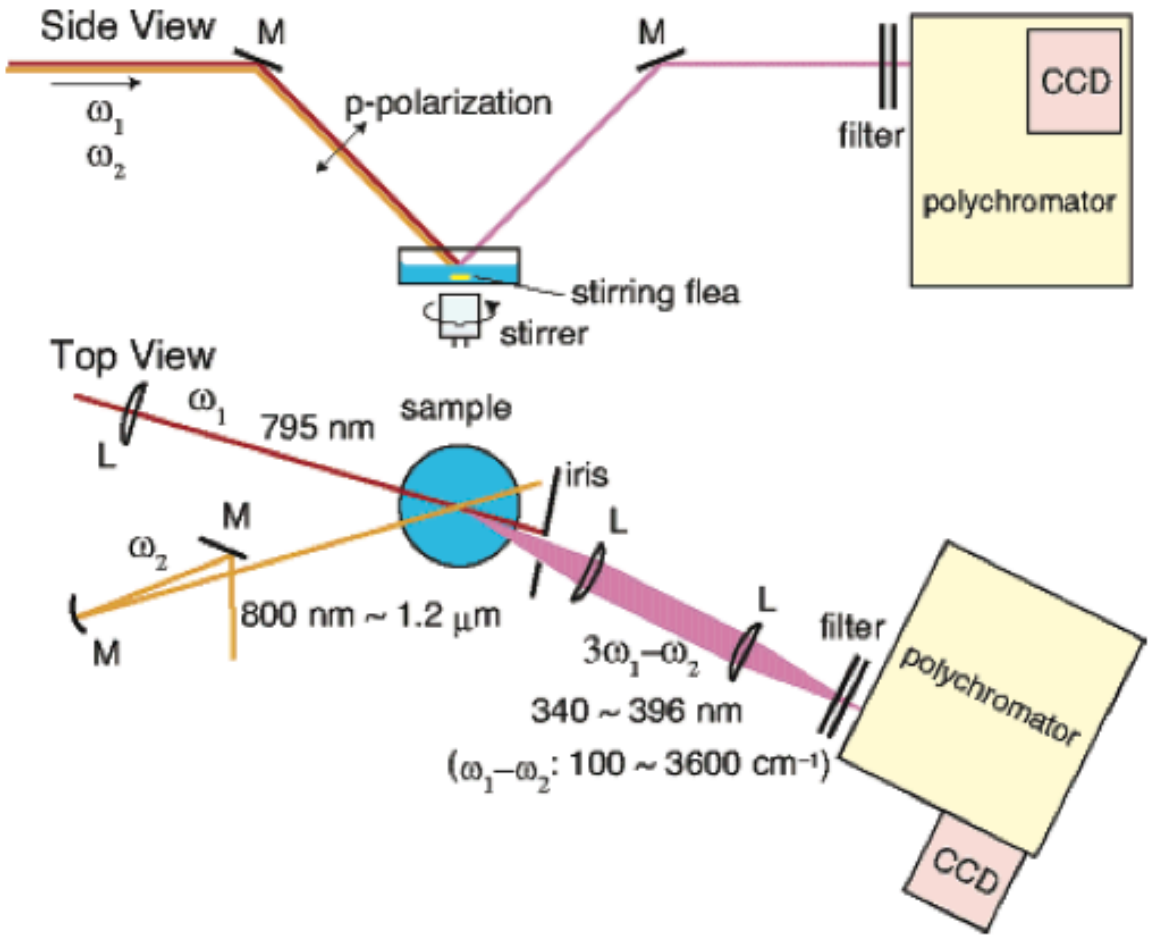


Resonant Raman of Rhodamine

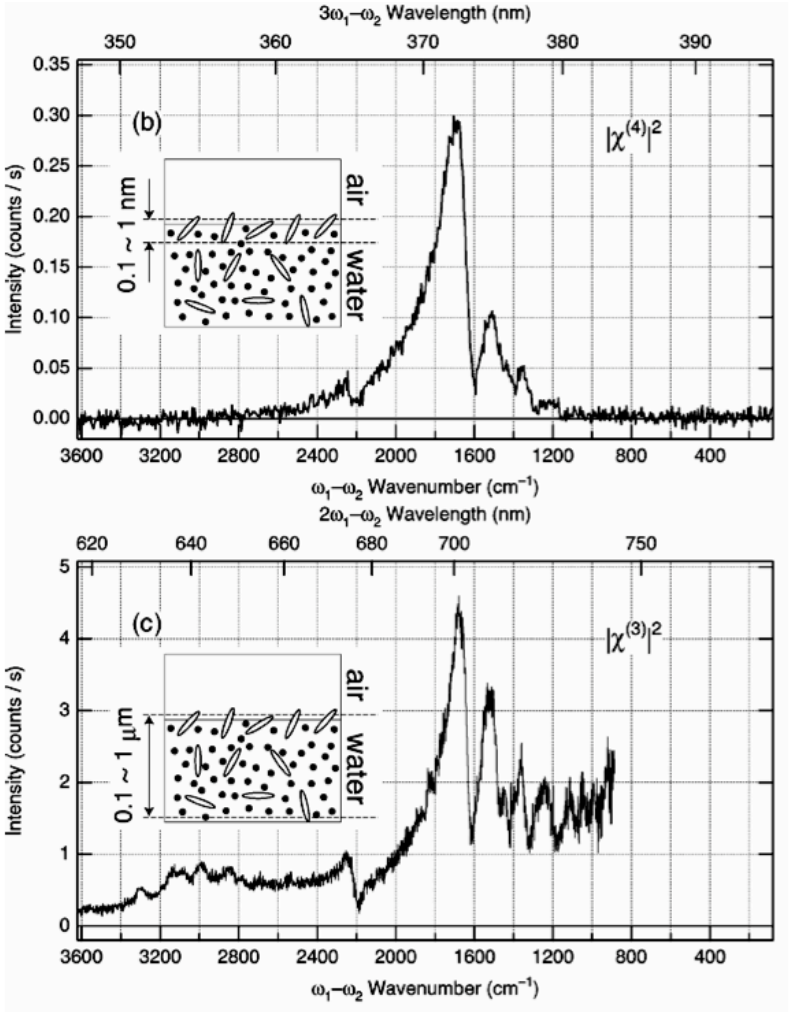




Setup


Side View
M
M
ω_1
ω_2
p-polarization
filter
CCD
polychromator
stirring flea
stirrer
Top View
ω_1
795 nm
sample
L
iris
M
L
ω_2
L
filter
polychromator
800 nm ~ 1.2 μm
$3\omega_1-\omega_2$
M
340 ~ 396 nm
($\omega_1-\omega_2$: 100 ~ 3600 cm^{-1})
CCD

Spectra


3ω1−ω2 Wavelength (nm)
350
360
370
380
390
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
(b)
|χ(4)|2
air
water
0.1 ~ 1 nm
Intensity (counts / s)
3600
3200
2800
2400
2000
1600
1200
800
400
ω1−ω2 Wavenumber (cm−1)
2ω1−ω2 Wavelength (nm)
620
640
660
680
700
750
5
4
3
2
1
0
(c)
|χ(3)|2
air
water
0.1 ~ 1 μm
Intensity (counts / s)
3600
3200
2800
2400
2000
1600
1200
800
400
ω1−ω2 Wavenumber (cm−1)