Broadband near-field mid-infrared spectroscopy and application to phonon resonances in quartz

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Abstract: Infrared (IR) spectroscopy is a versatile analytical method and nano-scale spatial resolution could be achieved by scattering type near-field optical microscopy (s-SNOM). The spectral bandwidth was, however, limited to approximately 300 cm$^{-1}$ with a laser light source. In the present study, the development of a broadband mid-IR near-field spectroscopy with a ceramic light source is demonstrated. A much wider bandwidth (at least 3000 to 1000 cm$^{-1}$) is achieved with a ceramic light source. The experimental data on quartz Si-O phonon resonance bands are well reproduced by theoretical simulations indicating the validity of the present broadband near-field IR spectroscopy.

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References and links

1. M. Ohtsu, Near-Field Nano/Atom Optics and Technology (Springer-Verlag, 1998), Chap. 2.
1. Introduction

The scattering-type scanning near-field optical microscopy (s-SNOM) enabled us to map images overcoming the diffraction limit [1,2] owing to localized and enhanced electromagnetic fields around keen probe tips. The near-field imaging by mid-infrared (mid-IR) lasers has achieved spatial resolutions higher than 30 nm, whereas the bandwidth has been limited to approximately 300 cm$^{-1}$ (about 800 to 1100 cm$^{-1}$) [3].

On the other hand, a standard mid-IR spectroscopy with a thermal light source has several advantages over the IR laser spectroscopy such as less heat production, wide bandwidth, and stability of the light source. Therefore, the conventional IR spectroscopy has been commonly used as the first step of a series of analyses of complex unknown materials such as organic materials in meteorites [4,5].

Broadband light sources such as a thermal source [6–8] and a synchrotron beam [9,10] have been tested by connecting them to conventional IR spectrometers. Although a relatively wide bandwidth (at least 1000–2500 cm$^{-1}$) could be achieved by our s-SNOM system combined with a Fourier transform IR (FT-IR) spectrometer with a ceramic light source [7], a further expansion of the bandwidth was required for more versatile broadband IR spectroscopy. In the present study, due to optimization of the optics, IR signal intensities has been increased by about 5 times, which may enable the broadband IR spectroscopy.

In order to test the validity of the equipment, the near-field s-SNOM IR spectra are compared with near-field scattering theories. Scattering theories such as the point dipole (PD) model [11–18] or the finite dipole (FD) model [3,12,19,20] have often been employed for analyzing phonon resonance IR bands. Since the IR phonon resonance bands have high signal intensities and sharp peak structures [21–23], they are adequate for the quantitative treatments of the probe-sample near-field interactions.

Near-field measurements of phonon resonances have been reported on optically anisotropic materials [22–27]. Using birefringent materials such as quartz [3], BaTiO$_3$ [23], and LiNbO$_3$ [22], polarization of near-field lights on these material surfaces has been studied. Furthermore, anisotropic materials are useful for comparing experimental spectra with calculated spectra because multiple peaks originated from different azimuth directions could
be obtained. Therefore, the quartz was measured in this report for testing the near-field interactions of our equipment with probes [7], which is different from the cantilevers used in previous studies [3].

2. Experimental setup

Our experimental setup of the s-SNOM system is schematically shown in Fig. 1. An Au coated probe, which was previously described as the type B probe without a step structure [7], was situated near the sample surface. The sample on a piezoelectric actuator was vibrated with a frequency of $\Omega$ (2.6 kHz). P-polarized IR beam generated from a ceramic light source through an IR polarizer was focused on the probe tip by a Cassegrainian mirror through an FT-IR optics and a pinhole (radius: 200 µm), then another Cassegrainian mirror placed in the direction of 90 degrees relative to the incident direction collected scattered lights. Detected in-phase signals by MCT detector were demodulated by a lock-in amplifier and returned into the FT-IR.

The probe was vibrated in the XY plain with a frequency of 17.5 kHz, and then attenuation of vibration amplitude due to the sample surface was detected by a laser diode – photo diode feedback control system to keep the probe position near the surface (shear force method).

![Fig. 1. A schematic experimental set-up used for the present broadband near-field IR measurements. A piezoelectric actuator placed beneath the probe tip (radius: 250 nm (See Appendix section)) is oscillated with a frequency of $\Omega$ (2.6 kHz) and an amplitude of 200 nm peak-to-peak. Near-field signals from the MCT detector were demodulated using a lock-in amplifier.](image)

The selected modulation frequency $\Omega$ of 2.6 kHz is smaller than that we used in the previous work [7]. The separation of the modulated signals and the direct current (DC) components (i.e. spectral signals which are not modulated by the stage oscillation) was confirmed by checking the absence of the DC spectra demodulated in around the higher frequency region of the $1\Omega$ spectra. The detected modulated signals became unstable if the modulation frequency was smaller than 2 kHz because the stage feedback of the shear force method followed the modulation. Using the 2.6 kHz modulation frequency, the detected signal became stable. Therefore, it was confirmed that the feedback system did not follow the modulation. By using such a small modulation frequency, the DC and modulated components could be simultaneously extracted by a lock-in amplifier, resulting in merged waveforms with a large center burst. Using the large center burst, multiple interferograms could be accumulated even with our small intensity light source and for low reflectivity samples. The DC components contaminating the waveforms were removed by a Fourier transform. The DC component spectra were able to be checked by connecting the MCT output into FT-IR without using the lock-in amplifier.
An Au mirror and an Au/Si boundary sample fabricated with the electron beam lithography [6] with Au coating thickness of approximately 30 nm were used to test the spectral shape and the signal localization. Polished quartz surface was also tested to measure Si-O phonon resonance bands. Compared with our previous study, the alignment of the optics became better mainly by adjusting the position of a pinhole locating between the FT-IR and the incident Cassegrainian mirror. Finer micrometer-heads also helped us to adjust optics.

3. Bandwidth and signal localization

3.1. Au mirror measurement

While keeping the probe on a surface of an Au mirror, the DC component spectra (taken without using a lock-in amplifier) and 1Ω spectra were detected.

Figure 2(a) shows the DC component spectrum, which indicates the available spectrum band range determined by the light source and the MCT detector. The 1Ω spectra [Fig. 2(b)] (4 cm\(^{-1}\) data interval and 16 cm\(^{-1}\) resolution with zero filling) accumulated 1000 times for approximately 25 minutes showed a bandwidth ranging from 900 to 4000 cm\(^{-1}\), which is wider than any previous s-SNOM IR studies. The absorption bands observed around 1600, 2330, and 3600 cm\(^{-1}\) are due to CO\(_2\) and H\(_2\)O gases in the atmospheric environment.

The 1Ω spectrum showed smaller intensities than those of the DC component spectrum, especially for higher wavenumber regions (Fig. 2) [7]. Similar low-pass cut-off effects have been reported by the terahertz (THz) s-SNOM [27], and this effect can be extended to the mid-IR region.

![Fig. 2. (a) The unmodulated DC component (purple curve) and (b) the 1Ω (green) spectrum taken on the Au mirror surface. The spectra (a) and (b) have been scaled so that their intensities at 1150 cm\(^{-1}\) are equal. The spectrum (b) shows higher signal-to-noise ratio than our previous report [7]. The signal-to-noise ratio is approximately 10 at 2000 cm\(^{-1}\) with 16 cm\(^{-1}\) resolutions and 4 cm\(^{-1}\) data pitch.](image)

3.2. Au/Si boundary measurement

The localization of near-field integral intensities for the \(X\) direction was tested previously [6,7]. Here the near-field spectra taken along the \(X\) direction are displayed in Fig. 3(a). An Au/Si boundary sample formed with the electron beam lithography was tested. Spectra were taken across the boundary with 500 nm intervals from \(X = 0\) to \(8 \mu m\) as shown in Fig. 3(a) (accumulation: 300 times for each spectrum, other measurement conditions are the same as Fig. 2(b)). The Au/Si boundary was at \(X = 5 \mu m\) indicated with arrows and the left side was coated with Au on the Si wafer. Each spectrum was normalized by the spectrum at \(X = 0 \mu m\) in Fig. 3(b). Spectral intensities decayed rapidly around the boundary. Compared with the
spectrum next to the boundary (X = 4.5), the spectral intensity became approximately 50% on the Si area across the boundary. At the wavenumber region higher than 3500 cm$^{-1}$, the intensities fell into the noise levels under this measurement condition due to low signal intensities and H$_2$O vapor fluctuations in experimental atmospheric environments. At this measurement, submicron localization of near-field over a wide spectral range from 1000 to 3000 cm$^{-1}$ was achieved with a ceramic light source for the first time.

Fig. 3. IR spectra were linearly scanned across the Au/Si boundary. An Au was coated on the left side from X = 5 µm on a Si wafer. (a) Spectra were taken at intervals of 500 nm across the Au/Si boundary. (b) Spectra were normalized by the spectrum at X = 0 µm. The cross section curves of 1000 cm$^{-1}$ (i, black), 1500 cm$^{-1}$ (ii, red), 2000 cm$^{-1}$ (iii, blue), 2500 cm$^{-1}$ (iv, purple) and 3000 cm$^{-1}$ (v, green) were depicted respectively. The intensities rapidly decreased across the boundary.

4. Phonon resonances

In order to confirm quantitatively the near field IR spectra obtained by the above s-SNOM IR spectrometer, phonon resonance IR bands of quartz around 1150 cm$^{-1}$ were measured. A natural clear quartz crystal was cut into a thin plate perpendicular to the c-axis. The one surface of this quartz thin plate was polished with alumina and silicon carbide powder and then with a diamond paste of 1 µm. This polished surface of quartz perpendicular to its c-axis was used for s-SNOM spectral measurement as shown in Fig. 4.

Fig. 4. A schematic picture of the quartz measurement is drawn. The surface perpendicular to the c-axis of quartz was polished. The sample was placed so that the c-axis is Z direction. Quartz is a uniaxial crystal and the optical axis of quartz is equal to the c-axis, therefore the blue arrows are the directions of the electric fields coupling to the ordinary ray (o-ray) and the extraordinary ray (e-ray).
In this situation, since the probe direction is parallel to the optical axis (c-axis) of quartz, extraordinary ray (e-ray) components of dielectric functions are expected to couple to the electric fields parallel to the probe direction.

The unmodulated DC component spectra and the $1\Omega$ spectra were measured on an Au mirror and the quartz surface, respectively. Both the $1\Omega$ spectra measured with the Au mirror and the quartz were accumulated 3000 times and other measurement conditions are the same as described for Fig. 2(b). The curve (a) in Fig. 5 shows the DC spectrum of quartz divided by the DC spectrum of the Au mirror. In the DC spectrum, a band around $1200$ cm$^{-1}$ is considered to correspond to reflections of the ordinary ray and another band around $1120$ cm$^{-1}$ to reflections of both ordinary and extraordinary rays [3,28]. The $1\Omega$ spectrum of quartz divided by the $1\Omega$ spectrum of the Au mirror is also shown as the curve (b) in Fig. 5. Note that the $1200$ cm$^{-1}$ band in the DC spectrum has been suppressed in the $1\Omega$ spectrum. If the DC spectra had not been sufficiently removed with the modulating technique, the $1200$ cm$^{-1}$ band would have remained in the $1\Omega$ spectrum. This difference indicates clearly that the background contamination of DC spectra due to ordinary ray was mostly removed in this measurement. Since the noise level of $1\Omega$ spectrum is approximately $\pm 2\%$ for the 2000 - 1500 cm$^{-1}$ region, the observed strong $1120$ cm$^{-1}$ band intensity has the signal-to-noise ratio of approximately 30. Therefore, the spectrum can be quantitatively compared with scattering theories.

Below, the previous theoretical models [3] are used to analyze the $1\Omega$ spectrum. Numerical simulations using the PD model (infinitesimal linear point dipole located at the center of the sphere) and the FD (finite dipole consisting of a point dipole placed at the tip and counter charges induced around opposite direction) model have been performed (Fig. 6). In the PD model, the near-field probe tip is assumed as a sphere with a radius of $a$. On the other hand, in the FD model, the probe tip is a spheroid with length $2L$. The sphere and the spheroid assumed in the PD and FD models are drawn on the SEM (scanning electron microscope) image of the probe tip in Fig. 6. Since the probe has a shaft to support the probe tip, better agreement is expected with the FD model.

In both of the models, the scattering efficiency ($S$) is proportional to the effective polarizability ($\alpha_{\text{eff}}$) with contributions of reflection at the sample surface as follows [3]:

$$ S = \frac{E_s}{E_i} \times (1 + r_p)^2 \alpha_{\text{eff}}, $$

(1)
where $E_s$ is the scattered electric field, $E_i$ is the incident electric field, $r_p$ is the Fresnel coefficient for p-polarized component including the birefringence of quartz.

The dielectric function $\varepsilon(\omega)$ was assumed here to represent harmonic oscillators (characterized by a longitudinal optical phonon frequency $\omega_{LO}$, a transverse optical phonon frequency $\omega_{TO}$, and a damping rate $\gamma$) and a Drude relaxator (characterized by a plasma frequency $\omega_p$ and a damping rate $\gamma$) [3]:

$$\varepsilon(\omega) = \varepsilon_\infty \left( 1 + \sum \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma} + \frac{\omega_p^2}{\omega - i\omega\gamma} \right),$$ (2)

Optical constants such as $\omega_{TO}$ and peak assignments were taken from the literature [3,28]. The geometric mean ($\sqrt{\varepsilon_e \varepsilon_o}$) of the dielectric functions of ordinary ($\varepsilon_o$) and extraordinary ($\varepsilon_e$) rays were used to include the contribution of electric fields which are not parallel to the probe direction. The probe-to-sample distance was modulated at a frequency of $\Omega$ and the 1Ω spectra of the scattered light ($|s|$) were extracted by Fourier transform. Figure 7 shows the

Fig. 7. The 1Ω experimental spectrum for quartz phonon resonance bands (a) blue curve, the same as the blue curve in Fig. 5) is compared with calculated spectra (b) green dashed: FD model with parameters of $L = 1300$ nm, $g = 0.999e^{0.145i}$, (c) red dashed: (b) curve with a smoothing treatment, (d) cyan dashed: PD model with the same parameters). The calculated spectra are scaled to match the peak top of the experimental spectrum.
1Ω spectra calculated for the PD and FD models with the parameters representing the present experiments (probe tip radius: 250 nm, modulation amplitude: 200 nm, incident angle: 45 degrees, L = 1300 nm, g = 0.999e^\text{−i\text{−}45})). The parameter g is a ratio of the totally induced charge found within the range a from the tip end when the probe end is approached to the sample surface [12]. Moreover, the fraction g becomes large for the short sample-to-probe separation [12]. The spectra are scaled to match the top of the calculated peak to that of experimental 1Ω spectrum. Furthermore, a smoothing was applied to the FD model in order to take into account the wavenumber resolution of the instrument.

The FD model gives better agreement with the experimental 1Ω spectrum than the PD model. Since the probe tip’s shape is closer to the spheroid than the sphere, the better fit of the FD model is reasonable. Owing to the presence of a small peak at 1170 cm\(^{-1}\) originated from the ordinary ray in the FD model, a rising peak edge around 1150 to 1100 cm\(^{-1}\) (marked with *) with a shoulder around 1190 to 1170 cm\(^{-1}\) (marked with **) was well reproduced. However, the experimental spectrum deviates from the numerical simulations in the 1000 - 1100 cm\(^{-1}\) range in agreement with previous report [3].

In the early study, the tip radius (a) of 20 nm and the g value of 0.7 were used [3]. Therefore, the parameter g is expected to be nearly 1 in the present study with a large tip radius. The g dependence of the numerical simulation with the FD model was calculated and shown in Fig. 8. By comparing the obtained spectra for varying g values with the experimental one, the value for g is considered to be close to 1 in the present study.

5. Conclusions

In summary, a scattering type broadband and mid-IR near-field spectroscopy with a ceramic light source has been further improved in this study by adjusting the optics and by extracting 1Ω component through a lock-in amplifier with a low modulation frequency of \(\Omega = 2.6 \text{ kHz}\), resulting in the followings: 1) A much wider bandwidth (at least 3000 to 1000 cm\(^{-1}\)) was achieved with about 5 times larger signal intensities with a ceramic light source. 2) In order to test the validity of detected spectra, quartz phonon bands around 1100 cm\(^{-1}\) were measured with the present instrument with a reasonable S/N ratio of 30 (for the peak at 1150 cm\(^{-1}\)). 3) Theoretical simulations of the quartz phonon bands by the PD (point dipole) and FD (finite dipole) models were conducted and the FD model with the parameter g \sim 1 showed the best
match with the experimental spectrum. Therefore, the improved s-SNOM instrument can provide quantitatively reasonable broadband near-field IR spectra with submicron localization.

Appendix: Z scan measurements with probes of 150, 250, and 500 nm radii

In this appendix, we present performances of larger and smaller probe tip radii, in order to explain the reason why the probe radius of 250 nm was used in the present report. Z scan measurements were conducted with other near-field probes having different probe radii (a) of 150, 250, and 500 nm as shown in Fig. 9(a). Modulated integral 1Ω IR signal intensities without dispersion was measured on the Au coated mirror with increasing probe-Au mirror distances with the same method as the previous report [7]. Since changing the near-field probes requires the re-adjustment of the optics, absolute values of detected signals changed and the background component could not be reproduced. However, the measurements with probe radius of 150 nm tended to show smaller intensities than those with 250 nm. This would be due to the decrease of the volume interacted with the near-field. The localization scales (C) extracted with fitted equation $A + B \exp(-Z / C)$ became large with larger probe radii as shown in Fig. 9(b). The localization scale C was nearly equal to the radius a for small probe radius, and tend to be smaller than the probe radius for 500 nm probe. These differences can be originated from the fact that the condition for near field signals (i.e., probe radius is enough smaller than the wavelength: 3-10 µm) was not fulfilled. In order to satisfy both requirements for near field signals (intensity and localization), the radius of 250 nm was selected for the present measurements.

![Fig. 9.](image)

(a) Integral IR intensity [arb. unit] (b) $C \ [nm]

Fig. 9. (a) Z scan measurements with different probe radii (black curve: 150 nm, red: 250 nm, blue: 500 nm). Modulation amplitudes were 200 nm peak-to-peak. The intensities were scaled by the probe radius $a \ [nm]/200$. (b) The localization scale C were determined by fitting the data in Fig. 9(a) with an exponential function $A + B \exp(-Z / C)$ . The localization scale C increases with the probe radius (a).

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