Feature Article

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Near-Field Vibrational Spectroscopy

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This article details the research of super resolution in vibrational microspectroscopy through the use of a near-field microscope, which allows for spatial resolution exceeding the diffraction limit of light. We developed an infrared near-field scanning optical microscope that uses a tunable infrared laser and micro-aperture type near-field probes, the latter made by silicon processing. This has been used to observe partially photodissociated regions spectroscopically, using its submicron resolving capability. In addition, by using localized plasmons induced at the apex of a metallic nano-tip, we achieved nano-Raman spectroscopy and nano-imaging on the nanoscale, and found a new Raman effect that is specific to near-field optics.

Introduction

Vibrational microspectroscopy is widely used in the analyses and identifications of materials in the microscopic region. It is employed in a variety of fields ranging from basic science to industrial applications. For example, in infrared microspectroscopy, the absorption spectrum in the microscopic region is obtained by focusing interfered light from a Cassegrain objective mirror[*1] via a Fourier transform infrared spectrometer and by detecting the light transmitted through the sample. The spatial resolution defined by the focus spot is limited by the wavelength of light, and is around several tens of μm. Consequently, the current infrared microspectroscopic technique does not necessarily meet the needs of analyzing nano-materials or cutting-edge functional materials. This article presents a technology, whereby spatial resolution of vibrational microspectroscopy is taken beyond the wavelength. A combination of near-field optical technologies and vibrational spectroscopy realizes a spatial resolution that exceeds the diffraction limit of lightwave. Specifically, we will show principles and measurement examples of an infrared near-field scanning optical microscope[1,2] and near-field nano-Raman microscopy[3-7]. In the former, a tunable high-brightness infrared laser is employed as an IR light source and an atomic force microscope (AFM) cantilever with a small aperture at the apex as a near-field probe. In the latter, a metallic tip, which induces localized plasmon[*2] polaritons[*3] at its apex, is used.

*1: An optical system that gathers light via combination of a large concave mirror and a second, smaller convex mirror. The light gathered by the concave mirror is reflected back and focused by the convex mirror. The light shines through a small opening in the center of the large concave mirror.

*2: A collective oscillation of free electrons occurs when the distribution of electrons in metal lacks equilibrium and the oscillation propagates as waves. A quantum of the quantized waves is called a plasmon (Comprehensive Dictionary of Physics, Maruzen, 2nd Edition [McGraw-Hill Encyclopedia of Physics Second Edition]).

*3: When electromagnetic waves travel through a medium and the oscillation frequency is similar to that of the atomic polarization waves that are specific to the medium, the electromagnetic waves and polarization waves will be coupled and the coupled waves will become the actual waves of that medium. A quantum of the coupled waves is called a polariton (IWANAMI RIKAGAKU JITEN [Comprehensive Dictionary of Physical and Chemical Science, IWANAMI]).

Near-Field Scanning Optical Microscopy
Evanescent Light

When light enters a low-refractive index medium from a high-refractive index medium at an angle greater than the critical angle, total internal reflection occurs on the surface of the high-refractive index medium. At this time, evanescent light, whose field intensity attenuates exponentially with increasing distance from the surface, is generated on the low-refractive index medium. Since the wavelength of the component parallel to the boundary

surface in the low-refractive index medium corresponds with that of the component parallel to the boundary surface in the high-refractive index medium, the wavelength of the evanescent field is shorter than that of the light field that propagates in the low-refractive index medium. On the other hand, since the electric field oscillating in a perpendicular direction to the surface attenuates exponentially, it forms a field localized near the surface. However, since the frequency of light (proportional to light energy) does not change after converting into evanescent light, it is nonradiative and inhomogeneous field, unlike the light field propagating in the space, and is also called near-field light because of its local nature.

Such evanescent light is generated not only by total internal reflection, but also by scattering from structures smaller than the wavelength of the light (light field scattered by the structure includes evanescent light as well as propagating light[8]). The apparent wavelength of the evanescent light is roughly equal to the size of the small structures. Information about the small structure of a sample can be visualized by detecting the evanescent light localized around the structure or by irradiating the sample with evanescent light. If evanescent light can be detected or a sample can be irradiated with it, a resolution much smaller than wavelength of the incident light can be achieved due to the nature of the short wavelength. However, since evanescent light cannot propagate into the space and is localized near the small structures (note that the localization distance is approximately equal to the size of the small structure) because its apparent wavelength is shorter than the wavelength of the light propagating into free space. Near-field optics is used to manage evanescent light or near-field light[9,10]. But conventional optical microscopy cannot manage evanescent light as they only focus the propagating light component with the objective lens, so there is a limit to their resolution (almost equal to the wavelength).

Near-Field Scanning Optical Microscope

A near-field scanning optical microscope is an optical instrumentation that enables us to detect evanescent light localized around small structures or to illuminate such structures with evanescent field. Since evanescent light cannot propagate into free space, a near-field probe must be inserted into the evanescent light field to convert it into propagating light (alternatively, evanescent light must be generated by using a near-field probe and converted into propagating light by coupling with fine structures of the sample). It is possible to observe the sample structure by focusing and detecting the converted propagating light as the probe is scanned near the surface of the sample. This

is the imaging principle of a near-field scanning optical microscopy. Since evanescent light is localized within the distance roughly equivalent to the size of the small structure or probe structure, the probe has to be scanned close to the sample structure.

Near-Field Probe

There are two types of near-field probes. One is a Small-apertured probe that has an opaque film with an aperture smaller than wavelength of the light[11]. The other is a needle-type scattering probe that has an apex with a smaller diameter than the wavelength of the incident light[12].

A typical apertured probe is an optical fiber probe (Figure 1 (a)) made from optical fibers sharpened either by heating while adding tension or by chemical etching. It is then coated with a metal film with a small aperture at its apex[13]. However, the optical throughput of the fiber probe is low, because the light reaching the aperture is attenuated due to scattering or absorption by the metal coating as it approaches the sub-wavelength region in the fiber. To overcome this, a cantilever (Figure 1 (b)) with a wide cone angle tip configured by anisotropic etching, has been developed[14]. Not only has the wide cone angle shape improved the optical throughput, but also since the tip can be hollowed, the probe can be used over the entire mid-infrared region.

For a scattering-type near-field probe, an electric field can be considered generated by the direct excitation of the electric dipole at the tip. Especially, a scattering-type near-field probe made from metal (Figure 1(c)) can induce an extremely strong electric field by exciting surface plasmon polaritons via the resonant coupling of light and collective oscillation of free electrons[9] at the tip.
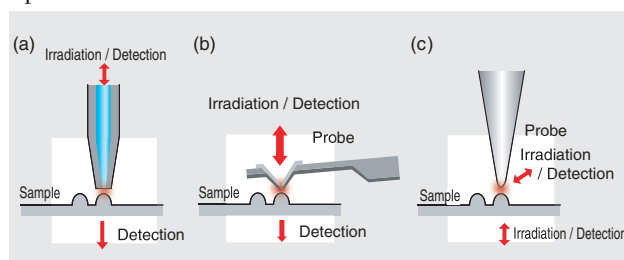

Figure 1 Near-Field Probe
(a) Small-apertured optical fiber probe
(b) Small-apertured cantilever probe
(c) Scattering-type probe

As the light induced becomes evanescent, it is confined at the tip of the probe and a nano-light-spot about the same size as the diameter of the probe is produced (Figure 2). In addition, bright signal lights can be obtained via the enhancement of the electric field. Recently, near-field measurements using such metallic probes have been applied to Raman spectroscopy[3,4,15], two-photon-excitation fluorescence[16], etc.
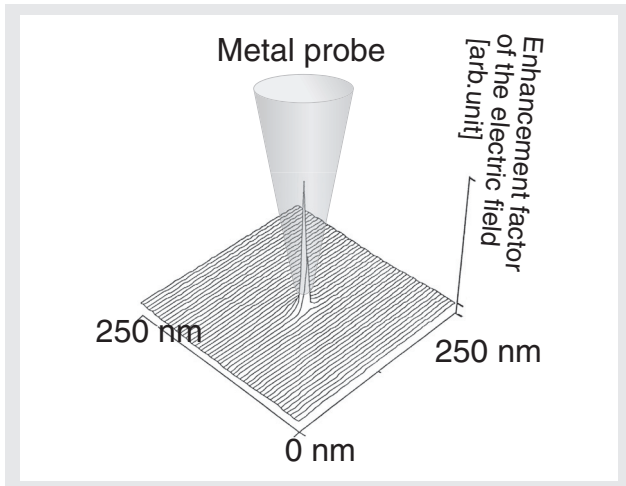

Figure 2   Nano-light-spot Generated by a Metallic Nano-tip

Infrared Near-Field Scanning Optical Microscopy

To realize near-field spectroscopy in the infrared region, it is important to consider the infrared light source and the near-field probe. Infrared spectroscopic analyses including conventional infrared microspectroscopy using heat sources such as globar light source[*4] are mainly used as infrared light source. Even though a spectral bandwidth can be successively covered from 2.5 µm to 10 µm or more, the brightness is low, and it is difficult to concentrate energy of the infrared light spatially because the light emission area is wide for such light sources. Moreover, the light sources are extremely dark for infrared near-field spectroscopy. With the recent progress in laser technologies, several types of tunable infrared lasers have been developed and are being used for infrared near-field scanning optical microscopes. An example is the Differential Frequency Generated (DFG) infrared light pumped by ultrashort pulse laser (Ti:Sa laser, etc.) and free electron laser (FEL).

As for probes, while infrared fibers made from fluoride glass[17,18] or chalcogenide glass[*5[19, 20]] are often used, as mentioned above, the optical throughput is quite low, and the spectral range of mid-infrared spectroscopy with transmission range of infrared fibers are not covered

entirely. To overcome these problems, we employed an apertured cantilever in our research[1,2]. Several cantilevers can be created simultaneously, while high reproducibility of the small-aperture diameter is realized as well, by using a micro-electromechanical system (MEMS) based on silicon processing and by drilling the aperture with focused ion beams. Figure 3 shows the cantilevers created using this method (aperture diameter: 500 nm). Compared to a chalcogenide fiber probe, the optical throughput has been improved by two digits.
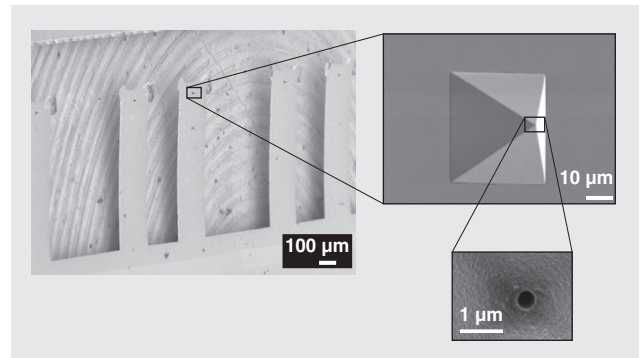

Figure 3   The Apertured Cantilever

Figure 4 shows a schematic illustration of the infrared near-field scanning optical microscope, which we designed and developed. The microscope is mainly composed of an infrared microscope, an atomic force microscope, and an infrared laser. Infrared light from the laser was irradiated on a sample through a small aperture and detected with mercury cadmium telluride photodiode (MCT) while the sample was scanned. We used an infrared free electron laser (5 - 16 µm: IR FEL Research Center, Tokyo University of Science) and differential frequency generated infrared light (mainly 3 - 6 µm)
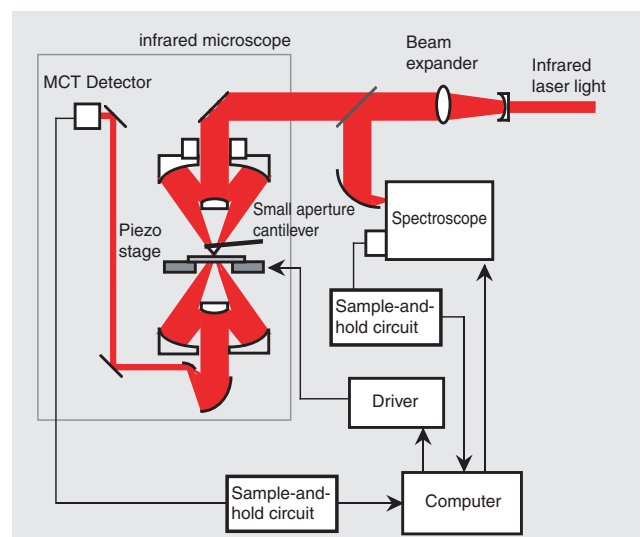

Figure 4   Infrared Near-Field Microscope

pumped by an ultrashort pulse laser; this allows us to detect most of the mid-infrared region.

Using this device, we performed a near-field imaging of molecular change in cholesteryl oleate (the primary cause of arteriosclerosis) ablated by the infrared FEL[1]. A cholesteryl oleate thin film (2 µm- thick) was decomposed into cholesterol and oleic acids by being irradiated with the pulsed IR light (irradiation wavelength: 5.75 µm, 5 µJ on the sample surface) from the infrared FEL via an infrared microscope. The irradiated area was observed with the infrared near-field scanning optical microscope that employed differential-frequency generated IR pulsed-light (observation wavelength: 5.75 µm, 0.1 nJ on the sample surface) and a cantilever probe with an aperture (diameter: 2 µm). Figure 5(a) shows the near-field IR absorption images of cholesteryl oleate thin film we obtained. IR FEL light was irradiated on the outside of the area depicted in the dashed lines of Figure 5. While the absorption of infrared light by the ester bond was observed in the non-irradiated area, the absorption of IR

light was lower at the irradiated region. Judging from the result, we observed, with a higher spatial resolution than diffraction limit, that the ester bond is broken and cholesteryl oleate is decomposed into cholesterol and oleic acid within the area irradiated by the IR FEL. Figure 5 (b) shows near-field IR image of the same area as Figure 5 (a) obtained with 5.30 µm wavelength IR light which was not absorbed by the sample. The image does not have any specific contrast relevant to absorption. In addition, by comparing the amounts of absorbed IR light in the non-irradiated area, it was verified that below the surface of the region irradiated with the IR FEL light, the molecular structure had changed up to 1 µm.

*4: An infrared light source obtained by applying a current through a SiC rod and heating it to about 1000 °C (IWANAMI RIKAGAKU JITEN [Comprehensive Dictionary of Physical and Chemical Science, IWANAMI]).
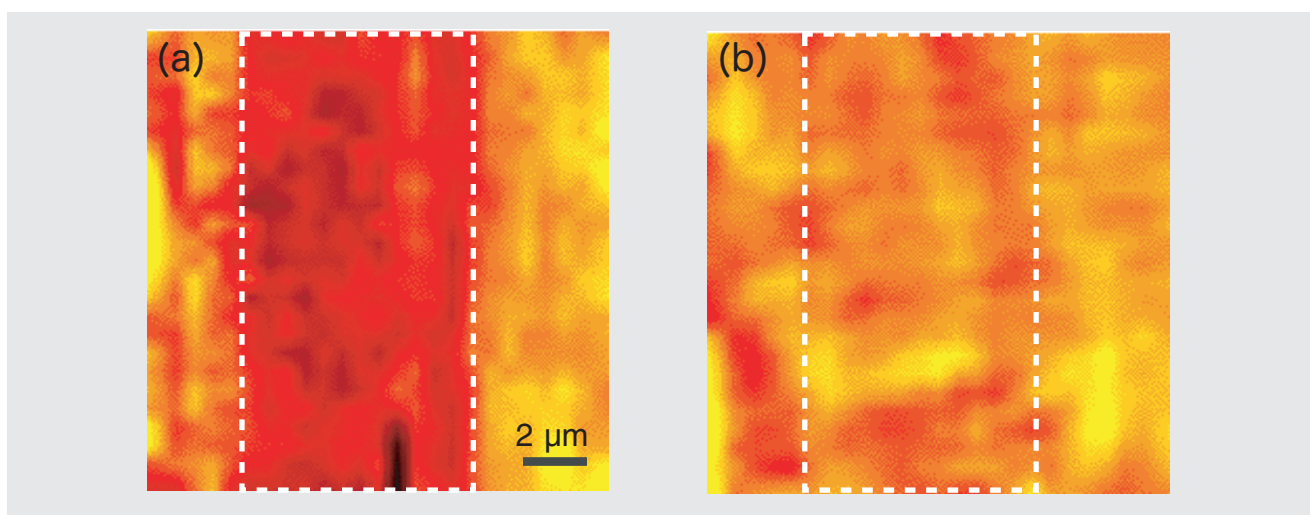
*5: A generic term for sulfide, selenide and telluride.

Figure 5   Infrared Near-field Absorption Image of Cholesteryl Oleate thin Film
(a) Ester bond absorption wavelength (5.75 µm)   (b) Wavelength without absorption (5.30 µm)

Near-Field Nano-Raman Microscopy

Vibrational spectrum of molecules can also be obtained by detecting Raman scattering, induced by the inelastic scattering of light with molecules. Since incident photons and scattered photons are relevant to the optical process of Raman scattering, the occurrence probability of the Raman scattering process is much lower than that of absorption/fluorescence process and then the intensity of Raman scattered light is extremely weak. To achieve a near-field Raman spectroscopy, we devised a metallic nano-tip which enhances electric field locally and amplifies Raman scattered light[3,4]. In other words, we achieved high-sensitivity and high spatial resolution by

inducing surface enhanced Raman scattering (SERS) only at the metallic nano-tip and by using an electromagnetic and chemical enhancement effect[5,6].

Here we present the results, using the instrument we developed, of the near-field nano-Raman spectroscopy of a nanocrystal of adenine molecules, which is one of the DNA-based molecules. Figure 6(a) shows a near-field Raman spectrum obtained by bringing the metallic nano-tip in close proximity to the nanocrystal. Nine Raman bands (indicated by arrows) were observed. Figure 6(b) shows the Raman spectrum of the same sample as Figure 6 (a) obtained by retracting the nano-tip from the sample surface. The electric field was no longer enhanced locally and no Raman scattering from the adenine molecule was observed except the peak of 924 cm^{-1},

which is due to Raman scattering from the cover glass because the metal nano-tip was too far away. Comparing the intensities of the Raman band (@739 cm^{-1}) with or without a metallic nano-tip, the enhancement factor of Raman scattered light per unit area can be estimated at ca. 2700 times.
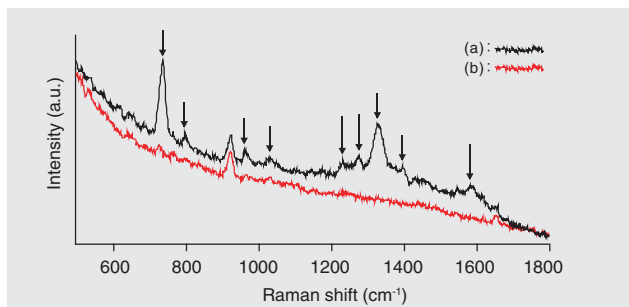

Figure 6   Raman Spectrum of Adenine Nanocrystal:
(a) Raman spectrum obtained with the metallic nano-tip
(b) Raman spectrum measured obtained without the metallic nano-tip

Figure 7(a) presents a near-field nonlinear Raman image of network structures composed of double stranded DNA of poly(dA-dT) by inducing coherent anti-Stokes Raman Scattering (CARS), which is a nonlinear optical phenomenon, with the metallic nano-tip[6]. Wavenumber for observation is coincided with vibration frequency of ring breathing mode (1337 cm^{-1}) of five-membered ring in adenine molecules. Figure 7(b) shows a near-field image of the same area, obtained with a non-resonant condition (1278 cm^{-1}) for all vibration modes of adenine, thymine or sugar chains. Due to the non-resonance for all molecular vibrations, no CARS light were induced. 15 nm spatial resolution was achieved, so the resolution was improved by a factor of two better than the result accomplished with a spontaneous near-field Raman observation (showing a linear response).
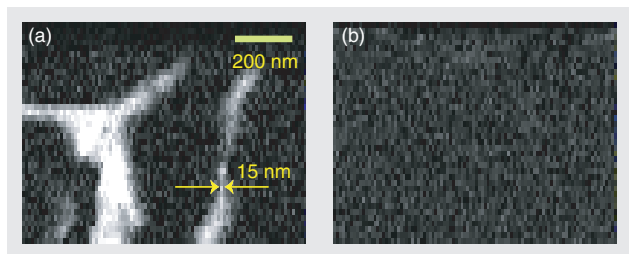

Figure 7   Near-field CARS Imaging of Poly (dA-dT) DNA Network Structures
(a) Observed wavenumber: 1337 cm^{-1}
(b) Observed wavenumber: 1278 cm^{-1}

As mentioned above, SERS detects Raman scattered light from molecules adsorbed on metallic nanostructures. Since the metallic nano-tip plays a role in an isolated metallic nanostructure, the same scattering phenomenon as SERS occurs at a metallic nano-tip. Figure 8(a) shows

the near-field Raman spectrum of an adenine nanocrystal again. Compared with the Raman spectrum obtained without the metallic nano-tip, which is just a conventional micro-Raman spectrum, the Raman band on breathing modes of six- and five-membered ring that appears usually at 724 cm^{-1}, shifts toward a higher wavenumber (739 cm^{-1}) in the near-field Raman spectrum. Furthermore, the near-field Raman spectrum (Figure 8(a)) is partly different from the SERS spectrum of adenine molecules adsorbed on silver island film (Figure 8(b)). We observed that the Raman band in near-field Raman spectrum is higher than that in the SERS spectrum by more than 5 cm^{-1}. Since the SERS spectrum originates from adenine molecules adsorbed on silver nanostructures, Raman frequency obtained in the experiment coincides with calculated Raman frequency (Figure 8(c)) for an adsorbed model of a complex composed of adenine and silver atoms. Then, we performed vibration calculations of Ag-adenine complex for which the bonding distance between a silver atom and an adenine molecule has been changed. From the experimental and calculated results, we have found that the specific Raman band shifts toward higher wavenumbers[7] in the near-field Raman spectrum by giving a force to molecules and deforming the complex via the metallic nano-tip. As the position of the metallic nano-tip can be controlled by AFM, it can be expected that this method will be able to define the orientations of molecules, as well as identify molecule species[21].
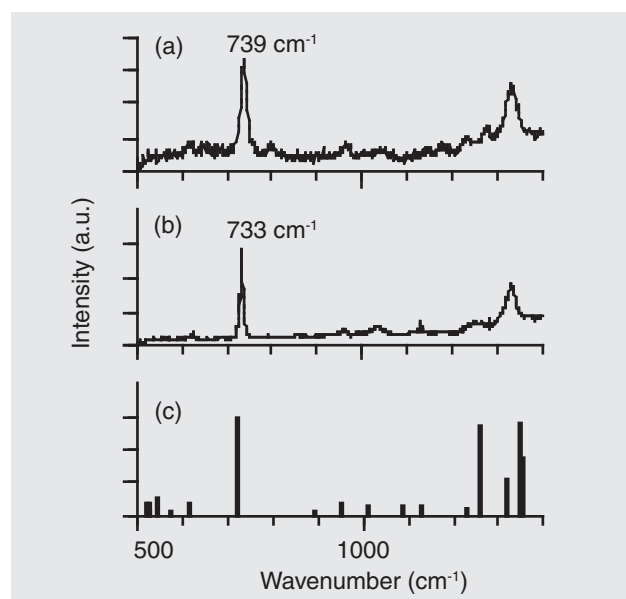

Figure 8   Raman Spectrum of Adenine Molecule
(a) Near-field Raman spectrum
(b) Surface enhanced Raman spectrum
(c) Raman spectrum of Ag-adenine complex obtained with vibration calculation

Conclusion

In this article, we have described that we measured vibration spectrum of molecules and obtained molecular imaging with spatial resolution that exceeds diffraction limit of lightwave, by applying near-field optical technique to vibrational spectroscopy. In particular, we have shown, through our experiments, the importance of choosing the right near-field probes for infrared spectroscopy and Raman spectroscopy. Quantitative analysis is possible in near-field infrared spectroscopy while extremely high spatial resolutions can be achieved in near-field Raman spectroscopy by using a metallic nano-tip and nonlinear optical phenomena and by applying mechanical perturbation. Through further development of near-field vibrational spectroscopy, single molecule analyses with molecular-level spatial resolutions will become reality.

(Publication members have responsibility for the translation)

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