Development of infrared spectroscopy based on frequency modulation AFM

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Infrared spectroscopy (IR), such as optical vibrational spectroscopy and Raman spectroscopy, is remarkably powerful in analyzing the chemical compositions and molecular structures of samples, utilizing the vast IR database. However, its spatial resolution is limited to 3–10 μm due to its optical wavelength. Meanwhile, the AFM has significantly better resolution, although its chemical analysis capabilities are limited. Recently, the combination method of IR and contact- or tapping-mode AFM, known as AFM-IR [1], has been developed and is attracting considerable attention. In this method, pulsed-infrared light impinges on samples, causing the impact response to the deflection or oscillation of an AFM cantilever due to light absorption at the sample's specific wavelengths, which results in instantaneous thermal expansion. However, its achievable resolution is limited to a few nanometers, and non-destructive analysis is not guaranteed due to tip contact. Thus, we develop an infrared spectroscopy method based on frequency modulation (FM)-AFM to achieve higher spatial resolution in non-contact mode, which we refer to as tip-oscillation synchronized detection of infrared spectroscopy (TS-IR).

Figure 1 schematically shows the principle of the TS-IR. The sample surface under the oscillating tip in FM-AFM mode is irradiated with a linearly-polarized infrared pulsed laser beam; the irradiation timing is synchronized with the tip oscillation (Fig. 1(b)) during the tip retraction from the sample surface. The irradiation alters the electric dipoles at the sample's specific wavelengths, leading to a change in the interaction force between the tip and the sample. The change is represented as a hysteresis in the force-distance curve (Fig. 1(c)), and the area enclosed by the curve can be evaluated by detecting the change in dissipation energy using a function of the FM-AFM in non-contact mode, which is operated independently of the surface topographic imaging using the detection of resonance frequency shift of the AFM cantilever. We obtained the IR spectra by sweeping the wavelength of the infrared beam, while observing the FM-AFM images using a home-built FM-AFM operated in ultrahigh vacuum.

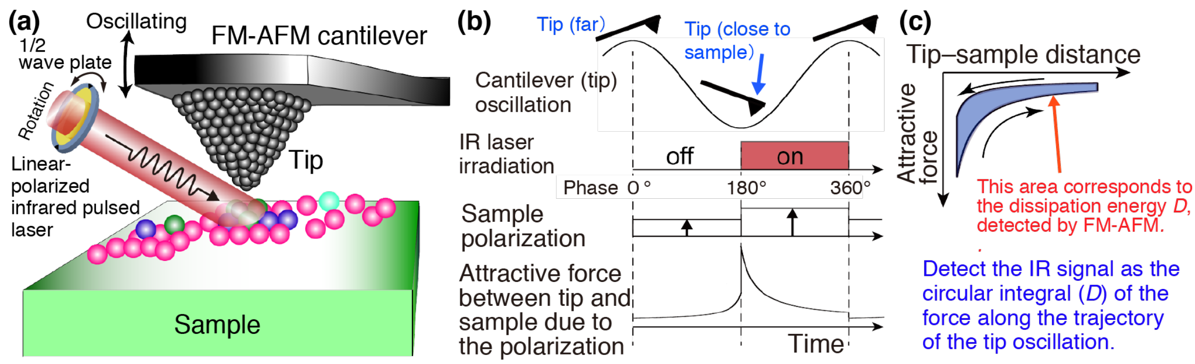

Figure 1. Schematic principle of the tip-oscillation synchronized detection of infrared spectroscopy (TS-IR) developed based on the FM-AFM.

Reference

[1] J. Mathurin, et al. J. Appl. Phys. **131,** 010901 (2022).