Nano- & Atomic-Scale Optical Spectroscopy at Surfaces

○Takashi Kumagai (Institute for Molecular Science)

kuma@ims.ac.jp

Optical spectroscopy is a powerful tool for chemical analysis, offering a wealth of information on structures, properties, and dynamics of materials. However, the challenge posed by the diffraction limit prevents resolving nanoscale structures directly in optical spectroscopy. This physical limitation can be overcome by near-field optics, capable of controlling electromagnetic fields well below the diffraction limit. In particular, localized surface plasmon resonance of metal nanostructures can lead to strong confinement and enhancement of electromagnetic fields, enabling ultrasensitive optical spectroscopy. Surface- and tip-enhanced spectroscopy, utilizing gap-mode plasmon, has been widely recognized to perform nanoscale and even single-molecule spectroscopy [1-3]. A notable advancement in this area is the integration of tip-enhanced spectroscopy with a low-temperature scanning tunneling microscope, which has achieved sub-molecular resolution in optical spectroscopy [4-7]. This cutting-edge technique not only provides unprecedented insight into light–matter interactions at atomic scales [8] but also will pave the way for Ångström-scale photonics.

Our group aims at developing advanced tip-enhanced spectroscopy to investigate nano- and atomic-scale structures, properties, and light–matter interactions [9-16]. In the talk, I will present our recent results on single atomic-/molecular-level Raman spectroscopy [17, 18], nanoscale coherent spectroscopy [19], and ultrabroadband nanospectroscopy. First, I will discuss Raman scattering of a single atom adsorbed on a metal surface, revealing how atomic-level structures within the plasmonic 'picocavity' influence the scattering process. Second, I will discuss anti-Stokes Raman spectroscopy within a single-molecule junction, which demonstrates 'Joule heating' of single C_{60} molecule. Third, I will show nanoscale coherent spectroscopy using 10-fs pulsed laser. This method has enabled us to observe and analyze the ultrafast non-equilibrium dynamics of electron and phonon within the STM junction. Lastly, I will introduce our latest development of ultrafast and ultrabroadband scanning near-field optical microscopy and its application to nanomaterials.

References

[1] *Chem. Rev.* **117**, 7583 (2017). [2] *Chem. Rev.* **117**, 6447 (2017). [3] *Chem. Soc. Rev.* **46**, 4020 (2017). [4] *Nature* **568**, 78 (2019). [5] *Natl. Sci. Rev.* **6**, 1169 (2019). [6] *Nat. Photon.* **14**, 693 (2020). [7] *Science* **373**, 95 (2021). [8] *Nat. Rev. Phys.* **3**, 441 (2021). [9] *Phys. Rev. Lett.* **121**, 226802 (2018) [10] *Nano Lett.* **19**, 3597 (2019). [11] *Nano Lett.* **19**, 5725 (2019). [12] *Nano Lett.* **20**, 5879 (2020). [13] *Nano Lett.* **21**, 4057 (2021). [14] *ACS Photonics* **8**, 2610 (2021). [15] *Nano Lett.* **22**, 2170 (2022). [16] *Phys. Rev. Lett.* **128**, 206803 (2022). [17] *ACS Nano* **16**, 16443 (2022). [18] *ACS Nano* **17**, 10172 (2023). [19] *Sci. Adv.* **8**, eabq5682 (2022).

Website of Kumagai Group: http://kumagai.ims.ac.jp/