

# Ultrafast Vibrational Spectroscopy and Vibrationally Mediated Reaction Control Using Infrared Plasmonics

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The light in the mid-infrared (mid-IR) range, where a large number of molecules exhibit characteristic vibrational transitions, has a great potential for molecular structure analysis and reaction control. In the last two decades, mid-IR ultrafast laser technologies have enabled nonlinear vibrational spectroscopy, providing direct insight into the molecular structures and dynamics[1]. Mid-IR pulses have also enabled multi-quantum vibrational excitation and have opened a way to bond-selective control of molecular reactions[2]. Despite their fascinating potential, however, their applications are somewhat limited by poor sensitivity/efficiency due to the relatively weak absorption cross-sections of molecular vibrations.

We may resolve these issues to open a new avenue toward nonlinear vibrational spectroscopy and bond-selective chemistry by combining ultrafast laser technology with plasmonics in the mid-IR range. Surface plasmon excitation provides electric-field enhancements on a nanometer scale, which offers extensive potential for amplifying light-matter interactions. Such enhancements have been utilized in surface-enhanced infrared absorption spectroscopy[3]. It is noteworthy that higher-order nonlinear processes are more significantly enhanced because of their higher-order dependence on field strengths.

Here we demonstrate surface-enhanced ultrafast vibrational spectroscopy by employing periodically-arranged IR-resonant nanoantennas[4,5]. We successfully obtain amplified nonlinear vibrational signals in reflected light of the nanoantennas using IR pump energy of 10 nJ, with local signal enhancement of more than 7 orders of magnitude. Our scheme is useful for unravelling structures and dynamics of minute-volume of molecules such as monolayer materials, as well as paves the way to nonlinear vibrational spectroscopy with compact light sources of oscillator-level.

Furthermore, we employ the combination of temporally-shaped mid-IR pulses and strong field enhancement by plasmon excitation, to boost the multi-quantum vibrational excitation, and thereby successfully realize bond-cleavage of condensed-phase molecules for the first time[6]. This successful demonstration proves that the combination of ultrafast optics and nano-plasmonics in the mid-IR range is useful for multi-quantum vibrational excitation, paving the way toward bond-selective chemistry.

## References

- [1] P. Hamm and M. Zanni, “ Concepts and Methods of 2D Infrared Spectroscopy, ” Cambridge University Press (2011).
- [2] K. Heyne, O. Kuhn, “ Infrared laser excitation controlled reaction acceleration in the electronic ground state, ” J. Am. Chem. Soc. 141, 11730 (2019).
- [3] F. Neubrech, C. Huck, K. Weber, A. Pucci, and H. Giessen, “ Surface-enhanced infrared spectroscopy using resonant nanoantennas, ” Chem. Rev. 117, 5110 (2017).
- [4] F. Kusa, I. Morichika, A. Takegami, and S. Ashihara, “ Enhanced ultrafast infrared spectroscopy using coupled nanoantenna arrays, ” Opt. Express 25, 12896 (2017).
- [5] I. Morichika, F. Kusa, A. Takegami, A. Sakurai, and S. Ashihara, “ Antenna-enhanced nonlinear infrared spectroscopy in reflection geometry, ” J. Phys. Chem. C 121, 11643 (2017).
- [6] I. Morichika, K. Murata, A. Sakurai, K. Ishii, and S. Ashihara, “ Molecular ground-state dissociation in the condensed phase employing plasmonic field enhancement of chirped mid-infrared pulses, ” Nat. Commun. 10, 2893 (2019).