

Femtosecond Time-Resolved Infrared-Resonant Third-Order Sum-Frequency Spectroscopy Towards Label-Free Imaging

Jizhou Wang^{1,3}, Kai Wang¹, Yujie Shen¹, Zehua Han¹, Fu Li¹, Zhe He², Da-wei Wang^{3,4}, Alexei V. Sokolov^{1,5}, Marlan O. Scully^{1,5}

¹Institute for Quantum Science and Engineering, Texas A&M University, College Station, TX 77840, USA

²Department of Electrical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

³Interdisciplinary Center for Quantum Information and State Key Laboratory of Modern Optical Instrumentation, Zhejiang Province Key Laboratory of Quantum Technology and Device, and Department of Physics, Zhejiang University, Hangzhou 310027, China

⁴Zhejiang Laboratory, Hangzhou 311121, China

⁵Baylor Research Innovative Center, Baylor University, Waco, TX 76798, USA

Abstract: We experimentally demonstrate a time-resolved infrared-resonant third-order sum-frequency spectroscopy. This technique provides a new way to measure the dynamics of the infrared active vibrational states. It can be combined with microscopes for label-free imaging. © 2021 The Author(s)

The mid-infrared (MIR) radiation whose wavelength stretches from 3 μm to 20 μm can interact with a molecule's vibrational modes, which represent the “fingerprints” to identify different materials. Traditional MIR spectroscopy measures infrared (IR) absorption directly, e.g. Fourier-transform infrared (FTIR) spectroscopy. FTIR has several drawbacks: first, it is hard to apply it to samples containing water due to its strong absorption in the MIR region. Second, FTIR requires long acquisition time and lacks the capability of detecting fast dynamics. Third, it uses IR detectors which are more expensive and less efficient than silicon based detectors. Also, FTIR can be transferred to IR microscopes for label-free imaging, but its spatial resolution is limited by the long wavelength.

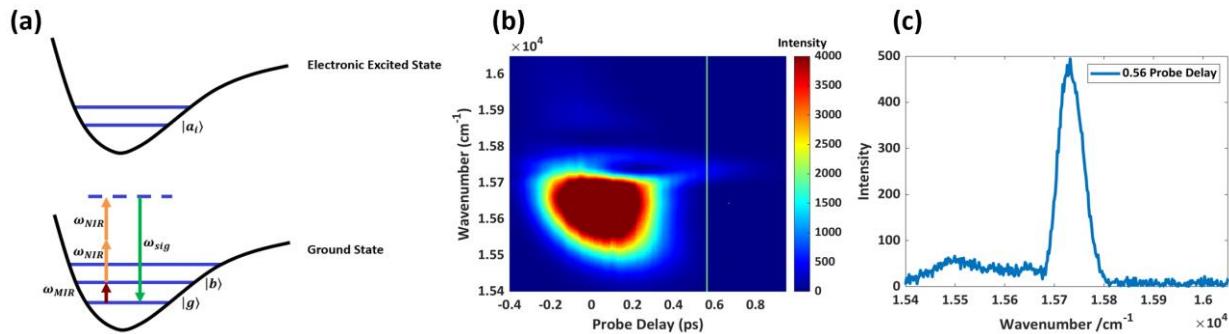


Fig. 1. (a) Energy scheme of the ITS spectroscopy. (b) 2D spectrum of the LDPE film. X-axis is the delay between the MIR and NIR probe pulses. Y axis is the ITS signal converted to wavenumber. (c) The spectrum at 0.56 ps delay.

To overcome these issues that FTIR spectroscopy has, we proposed a new type of MIR spectroscopy called infrared-resonant third-order sum-frequency (ITS) spectroscopy. The energy level diagram is shown in Fig. 1 (a). A MIR beam is used to resonantly excite molecules and creates coherence between the ground state $|g\rangle$ and the excited state $|b\rangle$. Then one excited molecule can absorb two photons from a NIR probe beam and emit a signal photon in the visible range, which contains the information about the excited state $|b\rangle$.

We have experimentally demonstrated the ITS spectroscopy with two femtosecond IR beams which are generated from two optical parametric amplifiers (OPAs) (OPerA Solo kHz OPA, Coherent Co.) and used a Low-Density Polyethylene (LDPE) film as the sample. We tuned the MIR beam around 3535 nm to excite the 2853 cm^{-1} CH_2 vibrational mode and used a 1550 nm probe beam. The two pulses were focused on the sample by a concave mirror ($f=100\text{ cm}$). We scanned the delay between the two IR pulses with 6.7 fs step size and plotted the 2D spectrum in Fig. 1(b). At zero probe delay, the output signal contains both the ITS signal and strong non-resonant four-wave-mixing (FWM) background. Because the molecular vibrational mode has relatively long decoherence time, the FWM background can be suppressed by adding a proper time delay between the two IR pulses. Fig. 1(c) shows the spectrum at 0.56 picosecond (ps) probe delay; it only contains the ITS signal generated from the 2853 cm^{-1} CH_2 vibrational mode.

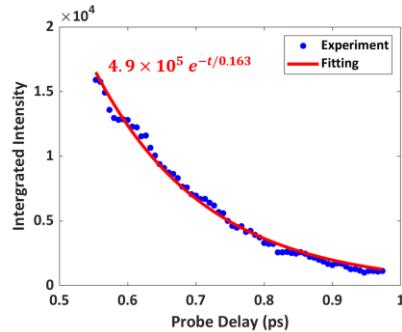


Fig. 2. The integrated intensity at different probe delay times. The blue dots are the experimental data, the red line is the exponential decay fitting.

The femtosecond ITS spectroscopy can also measure the dynamics of the IR-active modes. In this experiment, the decayed ITS signal contained the decoherence information of the vibrational mode. We summed all the ITS signals and plotted the total ITS signals starting from 0.55 ps delay. The data and fitting result are shown in Fig. 2. The fitted result shows the decoherence time of the 2853 cm^{-1} CH_2 vibrational mode in the LDPE film is about 163 fs. This technique has potential applications in studying phonon dynamics, phonon-exciton coupling in low-dimensional materials, environmental dynamics and chemical reactions.

We propose to combine the femtosecond time-resolved ITS spectroscopy with microscopes for label-free imaging. The ITS microscopy has many advantages compared with traditional IR microscopy, such as achieving supper resolution, because its spatial resolution is determined by the visible ITS signal instead of the two IR input beams. Also, it can be applied to bio-samples in their natural water-rich states because the visible ITS signal can travel through in water for a long distance.

This work is supported by the the Welch Foundation (awards A-1261 and A-1547).