

A Study Effect of Complementary Vibrational Spectroscopy

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ABSTRACT

Vibrational spectroscopy, comprised of infrared absorption and Raman scattering spectroscopy, is widely used for label-free optical sensing and imaging in various scientific and industrial fields. The two molecular spectroscopy methods are sensitive to different types of vibrations and provide complementary vibrational spectra, but obtaining complete vibrational information with a single spectroscopy device is challenging due to the large wavelength discrepancy between the two methods. Here, we demonstrate simultaneous infrared absorption and Raman scattering spectroscopy that allows us to measure the complete broadband vibrational spectra in the molecular fingerprint region with a single instrument based on an ultra short pulsed laser. The system is based on dual-modal Fourier-transform spectroscopy enabled by efficient use of nonlinear optical effects. Our proof of concept experiment demonstrates rapid, broadband and high spectral resolution measurements of complementary spectra of organic liquids for precise and accurate molecular analysis.

Key words: Complementary vibrational, spectroscopy

INTRODUCTION

Vibrational spectroscopy is a fundamental method for chemical analysis used in a variety of scientific fields such as organic/inorganic chemistry, geology, biomedical, material, food, environmental, and forensic science. The label-free noninvasive molecular spectroscopy enables us to acquire bond-specific chemical information of specimen, and it is known that infrared (IR) absorption and Raman scattering spectroscopy provide complementary information of molecular vibrations: the former is active for anti-symmetric vibrations that alter the dipole moment, while the latter for symmetric vibrations that alter the polarizability. IR absorption spectroscopy, which is active for polar bonds such as O-H or N-H, is often used for identification of functional groups of molecules, while Raman scattering spectroscopy, active for bonds such as C=C, S-S, or C-S4, is used for identification of skeletal structures. The group theory states that fundamental vibrational modes of molecules with the center of symmetry cannot be both IR and Raman active which is known as the rule of mutual exclusion, while there are some exceptions. Therefore, to acquire the complete information of molecular vibrations for more accurate and precise chemical analysis, both the IR and Raman spectra must be measured. Measuring the complete information of molecular vibrations enables us to analyze complex molecular phenomena such as catalytic chemical reactions.

Simultaneous measurement of IR and Raman spectra is a grand challenge in spectroscopy because wavelength regions of these two spectroscopy methods are largely separated, that is, mid-infrared ($2.5\text{-}25\ \mu\text{m}$, corresponding to $400\text{-}4000\ \text{cm}^{-1}$) for IR spectroscopy and visible to near-infrared ($0.4\text{-}1\ \mu\text{m}$, corresponding to $10,000\text{-}25,000\ \text{cm}^{-1}$) for Raman spectroscopy, respectively. Since this large wavelength discrepancy causes the difficulty of sharing light sources and optics, a primitive combination of conventional Fourier-transform infrared spectroscopy (FT-IR) and Raman spectrometers has never been a convincing approach. Such a system requires a complex instrument comprises different spectroscopy methods based on a Michelson interferometer and a dispersive spectrometer with two independent light sources such as an incoherent lamp source and a visible continuous wave laser. Additionally, these conventional methods do not provide state of the-art sensitivity and data acquisition speed because of the low brightness of the lamp source for FT-IR (especially when spatial mode filtering is required to have a small focusing spot) and the inherent weakness of spontaneous Raman scattering. Meanwhile, the technical advancement of nonlinear optics based on ultra short pulsed lasers has enabled us to have higher brightness of coherent IR sources and stronger Raman signals through the coherent Raman scattering and some approaches have been made towards IR/Raman dual-modal spectral acquisition with a single pulsed laser. However, these techniques neither have capability of simultaneous acquisition of complementary IR/Raman spectra nor broadband and high resolution spectral acquisition covering the molecular fingerprint region ($800\text{-}1800\ \text{cm}^{-1}$), where the richest vibrational modes exist. Here, we propose and demonstrate a simple yet powerful technique, called complementary vibrational spectroscopy (CVS), that allows us to simultaneously measure broadband IR and Raman spectra covering the fingerprint region at the same

