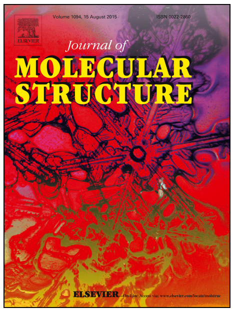

Combined IR-Raman vs vibrational sum-frequency heterospectral correlation spectroscopy

Sandra Roy, Clémentine Beutier, Dennis K. Hore

PII: S0022-2860(18)30111-X

DOI: 10.1016/j.molstruc.2018.01.072

Reference: MOLSTR 24794

To appear in: *Journal of Molecular Structure*

Received Date: 1 January 2018

Accepted Date: 28 January 2018

Please cite this article as: S. Roy, Clé. Beutier, D.K. Hore, Combined IR-Raman vs vibrational sum-frequency heterospectral correlation spectroscopy, *Journal of Molecular Structure* (2018), doi: 10.1016/j.molstruc.2018.01.072.

Combined IR-Raman vs Vibrational Sum-Frequency Heterospectral Correlation Spectroscopy

Sandra Roy, Clémentine Beutier, Dennis K. Hore

Department of Chemistry, University of Victoria, Victoria, Canada, V8W 3V6

Abstract

Vibrational sum-frequency generation spectroscopy is a valuable probe of surface structure, particularly when the same molecules are present in one of the adjacent bulk solid or solution phases. As a result of the non-centrosymmetric requirement of SFG, the signal generated is a marker of the extent to which the molecules are ordered in an arrangement that breaks the up-down symmetry at the surface. In cases where the accompanying changes in the bulk are of interest in understanding and interpreting the surface structure, simultaneous analysis of the bulk IR absorption or bulk Raman scattering is helpful, and may be used in heterospectral surface-bulk two-dimensional correlation. We demonstrate that, in such cases, generating a new type of bulk spectrum that combines the IR and Raman amplitudes is a better candidate than the individual IR and Raman spectra for the purpose of correlation with the SFG signal.

Keywords: bulk composition, surface structure, infrared absorption, Raman scattering, visible-infrared sum-frequency generation

---

1. Introduction

The molecular-level structure of surfaces may be appreciably different from the adjacent bulk phases as a result of adsorption (from solution or vapour) or diffusion from a bulk solid phase. These processes render the surface with unique chemical and physical properties that dictate its subsequent interactions with other molecules and materials. For example, the adhesion of proteins onto artificial surfaces such as synthetic polymers conditions them for subsequent cell adhesion, and important step in the biocompatibility of medical implants [1, 2]. One of the challenges associated with characterizing the molecular details of surfaces is finding a probe that can operate in the native interfacial environment, be non-disruptive, and can provide sufficient selectivity and sensitivity to the surface. The difficulty arises since the same molecules at the surface are often found in the adjacent bulk solid or solution phases, often in far greater numbers. Techniques that make use of grazing angles and evanescent fields to achieve their surface selectivity often probe hundreds of nanometers or microns, but we require discrimination on the order of nanometers. Nonlinear optical methods are ideally suited to such problems, as second-order response functions do not produce any signal except in the absense of inversion symmetry. For achiral materials, this inversion symmetry is broken only at the interface. Among this family of techniques, visible-infrared sum-frequency generation (SFG) is especially valuable as it probes vibrational resonances, thereby providing a label-free sub-molecular structural probe.

In the case of adsorption of molecules onto solid surfaces from dilute solution, there is no interest in monitoring the aqueous phase, as a negligible reduction of concentration accompanies sub-monolayer surface coverage. However, there are many cases in which the changes in bulk phase composition are of interest, and may dictate the adsorption process. One example is that of a binary mixture, where competitive adsorption results in a relative surface population that may be appreciably different from the bulk mole fraction [3–5]. Another example may be found in living systems, where the production of proteins in bacteria is triggered by external stimuli, and therefore modulates what is available for adhesion processes [6–10]. In such cases, the exquisite surface-specificity of SFG is still valuable, but knowledge of the bulk composition profile is a tremendous asset. If vibrational probes are sought, infrared absorption and spontaneous Raman scattering are ideal candidates for combining with SFG experiments [11–14]. As an additional analysis tool, if IR absorption or Raman spectra are collected concomitantly with the SFG spectra (as a function of time, solution pH, ionic strength, or concentration), the surface-bulk relationship may be explored using two-dimensional correlation (2DCOS) techniques [15–18]. In heterospectral correlation analysis, one calculates the complex correlation coefficient

$$C(\omega_1, \omega_2) = \Phi(\omega_1, \omega_2) + i\Psi(\omega_1, \omega_2) \tag{1}$$

where the real and imaginary parts Φ and Ψ are the synchronous and asynchronous correlation coefficients that reveal which spectral changes between ω_1 and ω_2 occur in phase or out of phase, respectively [19–23]. As we will be discussing IR absorption, spontaneous Raman scattering, and vis-infrared sum-frequency generation, ω will be generalized to be the IR wavenumber, or the Stokes shift, as appropriate. We have recently demon-

---

Email address: `dkhore@uvic.ca` (Dennis K. Hore)