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Femtosecond sum frequency generation at the metal–liquid interface

Sylvie Roke [a,*], Aart W. Kleyn [a,b], Mischa Bonn [a,c]

[a] *Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[b] *FOM-Institute Rijnhuizen, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*
[c] *FOM-Institute AMOLF, Kruislaan 407, 1089 SJ Amsterdam, The Netherlands*

Abstract

We present a study of the C–H and C–N vibrational modes of acetonitrile molecules at the interface between the bulk liquid and a gold film using both time and frequency domain femtosecond sum frequency generation. Acetonitrile is adsorbed on the gold surface with the N atom towards the interface. Due to the surface roughness there are different adsorption sites, leading to an inhomogeneous distribution of vibrational frequencies of the C–N stretch vibration of different molecules. This is observed most clearly in the time domain SFG measurements, while the frequency domain measurements are much less sensitive to the inhomogeneity. In contrast to the C–N stretch mode, the C–H stretching modes are unaffected by the surface and display homogeneous line broadening.

Keywords: Non-linear optical method; Sum frequency generation; Vibrations of adsorbed molecules; Gold; Solid–liquid interfaces

1. Introduction

Interfaces and surfaces play an important role in many chemical and physical processes occurring, for example, in heterogeneous catalysis and electrochemistry [1–3]. In many of these processes, the vibrational degrees of freedom of the molecules involved play a key role. The study of vibrational dynamics of molecules at surfaces requires a technique that specifically probes vibrations of molecules at the interface, with sufficient time resolution to resolve the dynamics (occurring typically on a sub-picosecond time scale). As a second-order non-linear optical tool, femtosecond vibrational sum frequency generation (SFG) is ideally suited for this purpose [4].

In a vibrational SFG experiment an interface is probed by simultaneous (non-linear) interaction of an infrared (IR) and a visible (VIS) photon with the surface region. This results in the generation

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[*] Corresponding author. Fax: +31 715274451.
E-mail addresses: roke@mf.mpg.de (S. Roke), bonn@amolf.nl (M. Bonn).

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of a third photon, with the sum of the two frequencies. When the infrared field is resonant with a vibrational mode of a molecule at the surface, a resonant infrared polarization (**P**$_{IR}$) is created, with a magnitude determined by the transition dipole moment (μ) and the infrared field. The infrared polarization decays in time, a process called the Free Induction Decay (FID), and is upconverted by the visible field in an SFG experiment. Due to the resonant excitation of molecular vibrations, the resulting sum frequency field is resonantly enhanced and contains information about the surface molecular vibrations.

In the experiments described here, we have used two different ways of performing SFG using femtosecond pulses, one to obtain time resolution and one to obtain frequency resolution. The first is performed using temporally short infrared and visible pulses (~100 fs). By delaying the pulses with respect to each other (see Fig. 1), the temporal decay of the resonant vibrational polarization can be followed in real-time [5–7]. The decay occurs typically on a ~1 ps time scale. Although very high time resolution can be obtained in this approach, no frequency resolution can be achieved because both pulses have a large frequency content.

The second way—with very good frequency resolution—relies on combining a short infrared pulse with a long visible pulse (with a narrow frequency spectrum). As a consequence, the frequency distribution of the vibrationally enhanced SFG light is determined by the vibrational distribution, so that high frequency resolution is achieved. These two complementary approaches allow us to obtain information about the binding site (through the resonance frequency) and follow the vibrational dynamics of the polarization in real time.

In this article, we use time and frequency domain sum frequency generation to study acetonitrile (CH_3CN) molecules from the liquid phase adsorbed on a very thin gold film. We show that although both time and frequency domain mea-

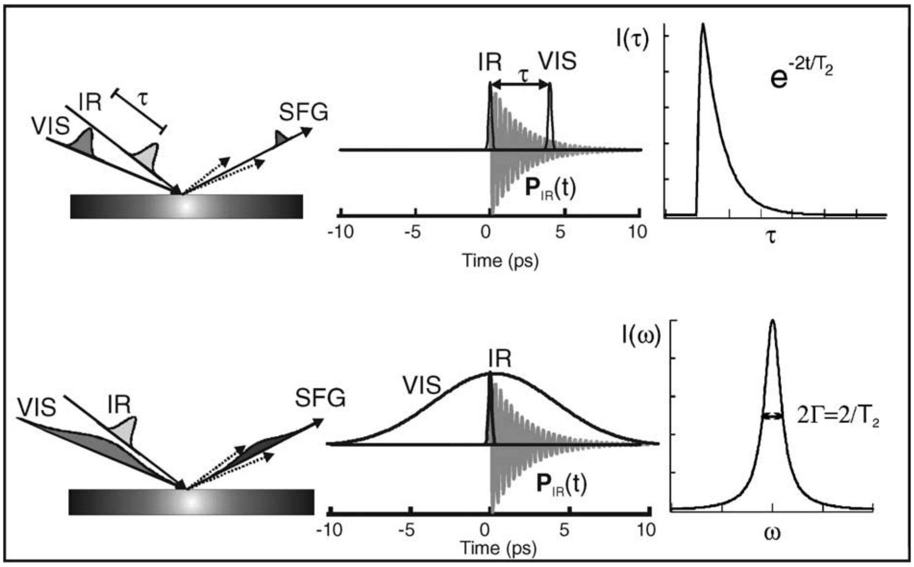

Fig. 1. Schematic illustration of a time domain (top) and a frequency domain (bottom) SFG experiment. In the time domain experiment, short pulses are employed, delayed by τ and the frequency-integrated SFG signal is recorded as a function of delay time between the infrared and visible pulses. In a frequency domain experiment, temporally long (spectrally narrow) visible pulses are used to upconvert the infrared-induced polarization at the surface and the time integrated signal is recorded as a function of frequency. The pictures in the middle panel illustrate the sequence of events in the time domain, showing the induced infrared polarization ($P_{IR}(t)$ that decays with a time constant T_2 and is upconverted by the visible pulse. The right panel displays the measured intensity in both scenarios.