Surface-Enhanced 2D Attenuated Total Reflectance IR Spectroscopy for Studying Surface-Sensitive Ultrafast Vibrational Dynamics

Jan Philip Kraack[†], and Peter Hamm[‡]

Department of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057
[†]*philip.kraack@chem.uzh.ch,* [‡]*peter.hamm@chem.uzh.ch*

We present our latest developments towards establishing 2D attenuated total reflectance (ATR) IR spectroscopy as a versatile, surface-sensitive method for obtaining ultrafast vibrational signals from solid-liquid interfaces. Surface-enhancement mechanisms are characterized in detail and we report the development of 2D ATR IR for spectro-electrochemistry at electrode surfaces.

Dynamics and structures of molecules at solid-liquid interfaces are of significant importance in chemistry and physics. To study ultrafast vibrational properties of samples near solid-liquid interfaces, we recently developed two-dimensional attenuated total reflectance infrared spectroscopy (2D ATR IR)[1-4]. 2D ATR IR spectroscopy is a third-order nonlinear method which employs short-range (sub-µm) evanescent fields at reflecting planes of an ATR crystal, guaranteeing maximum light intensity at the interface and the well-known surface-sensitivity of the ATR technique. We focus on the two most recent major developments of 2D ATR IR.

Firstly, we use ultrathin (~nm) noble metal layers to immobilize molecules at the ATR interface and to enhance the weak nonlinear signals[3] from sub-monolayer surface coverages[2]. Using polarization-dependent 2D ATR IR signals, we clarify the mechanisms of signal enhancement and evaluate contributions from electromagnetic and chemical contributions[3]. We demonstrate that s-polarization (solid lines, Fig. 1 (a)) optimally enhances 2D ATR IR signals from voids between metal nanoparticles (NPs, Fig. 1 (b) – (c)), while p-polarization (dashed lines, Fig. 1 (a)) enhances signals from outside the voids with different degrees of enhancement.

Secondly, we report on a combination of 2D ATR IR spectroscopy with spectro-electrochemistry (SEC), using the ultrathin conductive layers at the ATR interface as electrodes [4]. We outline experimental key-points in the development of 2D ATR IR SEC and use vibrational Stark-shift spectroscopy of carbon monoxide (CO) adsorbed to platinum (Pt) NPs to demonstrate the electrochemical performance of the electrode surfaces (Fig. 1 (d) – (g)). Furthermore, we characterize potential-dependent ultrafast vibrational relaxation as well as spectral diffusion of surface-bound CO (Fig. 1 (h)).
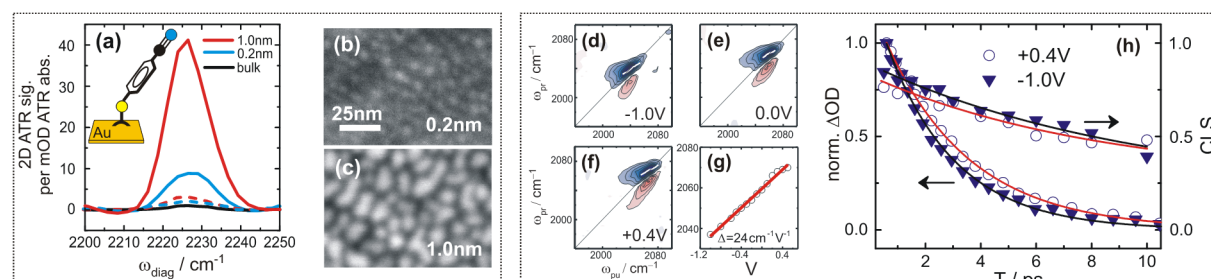

Figure 1. (a) – (c) Characterization of surface-enhancement mechanisms with diagonal 2D ATR IR signals (a) and electron-microscopy analysis (b) – (c) of different surfaces from Gold NPs. (d) – (f) 2D ATR IR SEC signals of CO adsorbed ot Pt NPs at different electrode potentials. (g) Ground-state bleach vibrational Stark-shoft signals of CO. (h) Potential-dependent vibrational relaxation (left scale) and spectral diffusion (CLS, right scale) of surface-bound CO. In (g) and (h), open symbols are experimental data, solid lines represent linear- or exponential fits.

[1] J.P. Kraack, D. Lotti, P. Hamm, J. Phys. Chem. Lett., 2014 **5**, 2325-2329.
[2] J.P. Kraack, D. Lotti, P. Hamm, J. Chem. Phys., 2015 **142**, 212413.
[3] J.P. Kraack, A. Kaech, P. Hamm, J. Phys. Chem. C, 2016,**120**, 3350-3359.
[4] D. Lotti, P. Hamm, J.P. Kraack, J. Phys. Chem. C, 2016, **120**, 2883-2892