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Ultrafast, Multidimensional Attenuated Total Reflectance Spectroscopy of Adsorbates at Metal Surfaces

Jan Philip Kraack, Davide Lotti, and Peter Hamm*

Department of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

ABSTRACT: Ultrafast dynamics of molecules at solid–liquid interfaces are of outstanding importance in chemistry and physics due to their involvement in processes of heterogeneous catalysis. We present a new spectroscopic approach to resolve coherent, time-resolved, 2D vibrational spectra as well as ultrafast vibrational relaxation dynamics of molecules adsorbed on metallic thin films in contact with liquids. The setup is based on the technique of attenuated total reflectance (ATR) spectroscopy, which is used at interfaces between materials that exhibit different refractive indices. As a sample molecule, we consider carbon monoxide adsorbed in different binding configurations on different metals and resolve its femtosecond vibrational dynamics. It is presented that mid-infrared, multidimensional ATR spectroscopy allows for obtaining a surface-sensitive characterization of adsorbates' vibrational relaxation, spectral diffusion dynamics, and sample inhomogeneity on the femtosecond time scale.

**SECTION:** Spectroscopy, Photochemistry, and Excited States
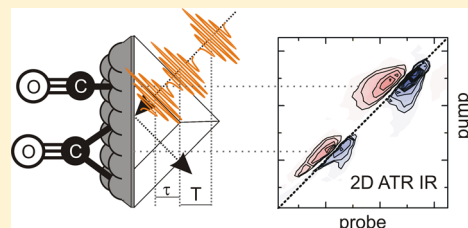
Vibrational dynamics at interfaces are at the forefront of current interest in time-resolved spectroscopy.[1−5] In particular, vibrational spectra and dynamics on time scales of femto- to picoseconds for molecules adsorbed on solid substrates bear important information on processes such as photoinduced chemical reactions, interaction of samples with local environment, and molecular structure. In this context, solid–liquid and solid–gas interfaces are important samples because they are involved in heterogeneous catalysis of chemical reactions.[6−8]

A versatile method for gaining vibrational and structural information about molecules at interfaces is attenuated total reflectance (ATR) infrared (IR) spectroscopy.[9−11] Stationary ATR IR spectroscopy is widely applied to obtain linear vibrational spectra of a broad range of samples including self-assembled monolayers,[12] heterogeneous catalyzed reactions,[9] or biochemical systems.[13] It is thus astonishing that no attempts have been made as of yet to combine the ATR IR technique with established methods from ultrafast, multidimensional spectroscopy. Exactly this path is taken here by merging two extremely powerful methods of vibrational spectroscopy, that is, ATR IR and femtosecond, pump probe, and 2D IR spectroscopy.[14−16] Using an ATR sample cell in a 2D IR spectrometer, it becomes possible to fully characterize vibrational dynamics and acquire multidimensional spectra of molecules at surfaces. With carbon monoxide (CO) adsorbed at different metal surfaces as a reference system, we report on pump probe and 2D ATR IR signals of molecules adsorbed from the liquid phase at different thin-film metal–water interfaces.

Our method uses a single-reflection ATR cell with a CaF_2 prism as a substrate (Scheme 1). Using CaF_2 as an ATR material avoids multiphoton IR absorption of pump pulses, which occurs in alternative substrates such as ZnSe, Ge, or Si.

Scheme 1. Schematic Ultrafast ATR Experiment in Pump-Probe Configuration for Multi-Dimensional Dynamics of Carbon Monoxide (CO) Adsorbed at a Metal–Liquid (e.g., platinum (Pt)–water, grey) Interface[a]
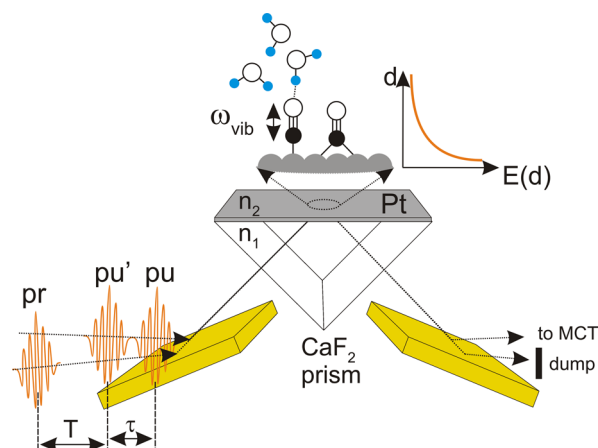
[a]Pulses pu and pu′, separated by τ, are spatially overlapped on the reflecting plane of an ATR element with a pr pulse, delayed by population time T. Evanescent fields, $E(d)$, penetrate into material of refractive index ($n_2 < n_1$).

The ATR cell is combined with a 2D IR setup in pump probe configuration.[17,18] (For details, see the Experimental Section.) Pump and probe beams enter the ATR prism with a mutual angle of ∼7° and both with an angle of ∼85° with respect to

the normal of the ATR plane of the prism. This angle is chosen to maximize reflectance signals that occur far away from the critical angle of the CaF_2/water system (~70°) used here. At the ATR interface, evanescent fields $E(d)$ of pump and probe beams penetrate into the medium of lower refractive index ($n_2 < n_1$).[9] CO molecules adsorbed on, for example, platinum (Pt) or gold/palladium (Au/Pd) alloys within the penetration depth (d) can thus be addressed. Here we use very thin (<1 nm) layers of metals sputtered on the ATR prism for two reasons. First, IR excitation pulses can induce carrier dynamics in the only partially IR-transparent metal (vide infra). Reduction of the layer thickness reduces this effect and singles out the response of the adsorbate. Second, thick metal layers (≫ 1 nm) can influence band shapes of adsorbates in ATR experiments.[19] This effect plays a negligible role if subnanometer layers are used.

At metal surfaces, CO can be either bound in linear or in bridged/multibound configurations (Scheme 1).[20] If CO-saturated water is flown above the Pt-coated ATR prism, in situ measured stationary ATR spectra show predominately one asymmetric band at ~2050 cm^{-1} in the investigated spectral region (1900−2100 cm^{-1}, blue, Figure 1). In contrast, if a
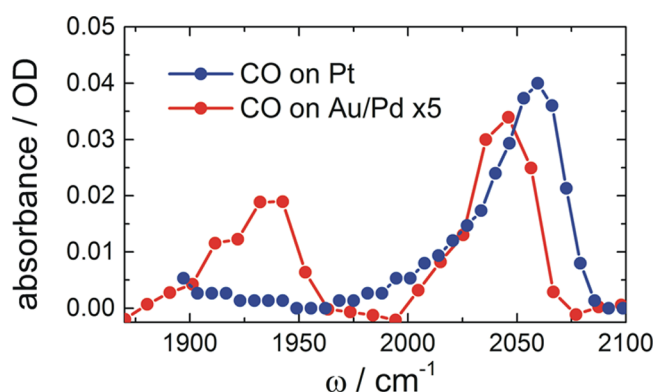
Figure 1. Stationary ATR infrared spectra of CO adsorbed on thin metal films. The blue spectrum represents CO adsorbed on platinum (Pt). The red spectrum represents CO adsorbed on gold/palladium (Au/Pd, (80/20)). ω represents the vibrational frequency.

similar layer of Au/Pd is used, adsorbed CO shows two asymmetric bands at ~2045 and 1930 cm^{-1} (red), which correspond to linear- and bridged/multibound CO, respectively.[20] The bands exhibit a width of about 30−40 cm^{-1}, typical for CO on thin metal-layers.[20]

Excitation of adsorbed CO with ~100 fs IR pulses results in vibrational relaxation on femto- to picosecond time scales (Figure 2). For CO on Pt, a combined ground-state bleach/stimulated emission (GSB/SE) band is observed at ~2050 cm^{-1} (~30−40 cm^{-1} fwhm) together with a broad (>50 cm^{-1} fwhm) excited-state absorption (ESA) band. The ESA signal is initially (≤300 fs) centered around 1975 cm^{-1} and blue shift to ~2010 cm^{-1} within picoseconds, while the GSB/SE signals blue shift on the same time scale but with moderate spectral changes (~10 cm^{-1}). ESA and GSB/SE signals of CO decay within ~20 ps, leaving behind a broad enhanced reflectance signal that slowly decays on a time scale of hundreds of picoseconds. This slowly decaying signal originates from a photoexcitation process of the metal electrons near the Fermi edge: Starting from a nonequilibrium electron distribution directly after mid-IR excitation, energy redistribution predominantly to lattice
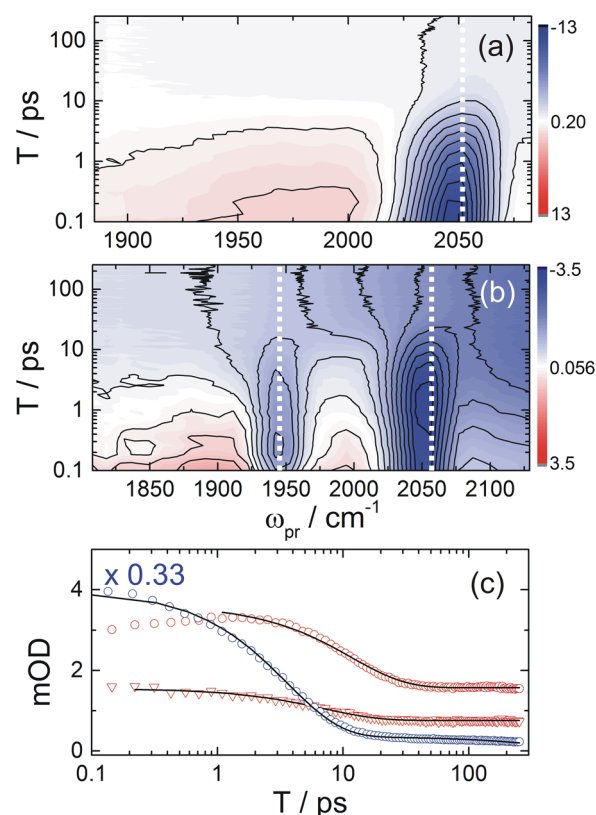

Figure 2. ATR pump probe signals of CO on (a) Pt and (b) Au/Pd. Blue and red signals represent GSB/SE and ESA, respectively. The colored axis is in mOD and ω_{pr} represents the detection frequency. (c) Representative cuts at positions indicated with dashed lines in panels a and b for Pt (blue) and Au/Pd data (red, circles: ~2050 cm^{-1}; triangles: ~1950 cm^{-1}). Solid lines represent biexponential fits.

phonons of the metal, or surrounding molecules (e.g., solvent) quickly (≪ 1 ps) establishes a hot electron distribution near the Fermi-edge as well as a vibrationally excited lattice.[3,21] Both of these contributions subsequently cool down again on time scales of multiple tens to hundreds of picoseconds, depending on the employed experimental conditions. Details of the observed dynamics will be presented elsewhere. Fitting of the pump probe data (Figure 2c, blue symbols) with a double-exponential function (black line) reveal time constants for the CO- and metal-related signals as 3.6 ps and >400 ps, respectively.

Analogous signals from CO adsorbed on Au/Pd (80/20) reveal the CO dynamics for different binding configuration (Figure 2b). GSB/SE and ESA signals are observed for bridged and linear CO at 1940/2050 cm^{-1} and 1900/1980 cm^{-1}, respectively. These again decay within ~20 ps. The bridged CO bands, however, decay slightly faster compared with the linear CO (vide infra). Only mild evolution of band positions (<10 cm^{-1}) is observed compared with Pt data. Notably, the ESA signal of linear CO strongly overlaps with the GSB signals of the bridged CO, thus resulting in a pronounced difference in GSB signal intensities for the different binding configurations. Also in the case of CO adsorbed on Au/Pd, a very slowly decaying enhanced reflectance spectrum is observed for hundreds of picoseconds after excitation. Again, this signal stems from excitation of the metal layer. The kinetic traces at GSB positions for CO on Au/Pd (red symbols, Figure 2c) are reasonably fit by a biexponential function with a very slow

(>500 ps) and a ~9 ps component (~2050 cm^{-1})/~7 ps component (~1950 cm^{-1}). From these, the former accounts for the decay of the metal-related signal, while the latter describes the CO-related dynamics.

While the presented ATR pump probe experiments clearly allows for a characterization of vibrational relaxation, the obtained signals fail to reveal information such as disentanglement of strongly overlapping ESA and GSB/SE bands, quantification of inhomogeneous broadening, or characterization of spectral diffusion. This information can be obtained from absorptive ATR 2D IR signals at different population times. For instance, Figure 3 shows characteristic 2D IR spectra
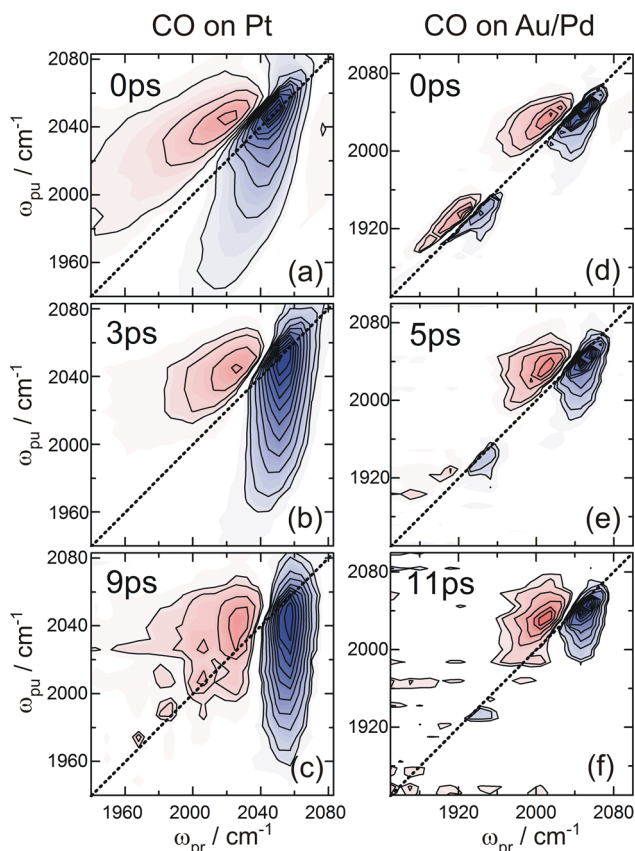
Figure 3. ATR 2D IR signals of CO on Pt (a−c) and Au/Pd (d−f) in dependence of population time T. Blue signals represent GSB/SE; red signals represent ESA. Contour lines are drawn equally spaced at 10% increments. $\omega_{pu/pr}$ represents the excitation and detection frequencies, respectively.

for CO on Pt (a−c) and Au/Pd (d−f). The spectra have been obtained after subtraction of consecutively obtained data sets acquired for aqueous solutions with and without CO. Early 2D spectra (0 ps) for both samples exhibit ESA (red) and GSB/SE (blue) signals, strongly elongated along the diagonal (dashed line) for linear (Pt and Au/Pd) as well as bridged CO signals (only Au/Pd). This diagonal elongation indicates a very inhomogeneous distribution of transition frequencies. The antidiagonal width of ESA and GSB/SE bands is only low (~17 cm^{-1} for Pt, ~15 cm^{-1} for Au/Pd) compared with the diagonal width (35−40 cm^{-1}). From these values, we can estimate a homogeneous dephasing time of ~0.3 to 0.35 ps.

The obtained 2D IR spectra moreover give an explanation of shapes and spectral evolution of the congested pump probe spectra (Figure 2). Consider, for instance, CO on Pt, which

shows initially strongly separated ESA and GSB/SE signals (Figure 2a). At 0 ps, the 2D spectrum (Figure 3a) shows elongated GSB/SE and a similarly influenced ESA signal (~2020 cm^{-1}). Projection of the 2D spectrum onto the probe axis results in partial cancellation at the blue-detuned wing of this ESA signal, which shifts of the ESA maximum to lower frequencies. As relaxation proceeds, this cancellation of ESA and GSB/SE signals is diminished due to the rotation of ESA and GSB/SE bands.

Additionally, the 2D spectra also reveal more detailed information about vibrational anharmonicities. Still, exact values can only be obtained from fitting 2D spectra to a model including a realistic line-shape function.[14] Differences of maxima and minima obtained from 2D spectra of CO on Pt consistently give values of ~25 cm^{-1}. This value is thus larger than generally observed for, e.g., transition metal−carbonyl complexes,[22,23] but similar to gas-phase CO.[24] 2D spectra of Au/Pd data furthermore allow one to compare anharmonicities for linear and bridged CO. Here linear CO obtains an even larger shift of ~30 cm^{-1}, while bridged CO shows values of only 15−20 cm^{-1}. From these values, it can be estimated that the potential curve of bridged CO is more harmonic compared with linear CO.

Finally, 2D IR spectra at various population times report on spectral diffusion as local sample environments interconvert.[14] A measure for spectral diffusion is represented by the temporal changes of the nodal slope between ESA and GSB/SE signals in 2D IR spectra (Figure 4).[14] Applying single-exponential fits
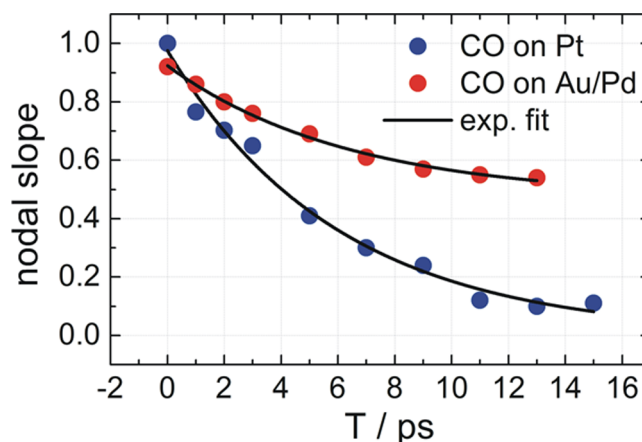
Figure 4. Spectral diffusion dynamics of linearly adsorbed CO. Symbols represent experimental data for CO on Pt (blue) and CO on Au/Pd (red). Solid lines represent exponential fits.

together with static offsets to the data, we find time constants for spectral diffusion for CO on Pt and Au/Pd as 6.0 and 6.4 ps, respectively. A likely origin of inhomogeneity is represented by local dynamic solvation of CO molecules after excitation. The similar time constants observed for Pt and Au/Pd data suggest that solvent interaction, possibly via hydrogen-bonding with water, is the dominant source of this term.

A second feature in the spectral diffusion data is the appearance of different static offsets that are required to fit the data to a single exponential decay. In the case of Au/Pd, a significant offset of 0.47 is observed, while for Pt data the offset is only very low ~0.01. An additional source of inhomogeneity is represented by static structural heterogeneity of the metal layer, which could explain the significant offset in case of Au/Pd

data. In this regard, different static inhomogeneity can be expected because sputtered alloys of Au/Pd should obtain more spatially varying environments compared with layers consisting of pure Pt. The significantly lower static offset observed for Pt data is, however, astonishing in the sense that sample inhomogeneity for the sputtered Pt layer would originate predominantly from local solvation, whereas local static structures play only a minor role. In fact, very thin (<1 nm) layers of Pt are expected to exhibit nonuniform sample properties such as thickness and morphology,[25] possibly including the formation of metal islands on the substrate from which a larger static contribution would be expected. A consistent reasoning of the missing significant static offset in the spectral diffusion data for Pt thus requires further investigation by use of CO adsorption on, for example, single-crystal surfaces of different metals as well as sputtered surfaces from a broad range of preparation conditions. The results of such experiments will be reported elsewhere.

The previously presented results highlight the capabilities of ultrafast, multidimensional ATR spectroscopy for studying vibrational dynamics of molecules at metal−liquid interfaces. Surface-adsorbed CO has been investigated previously with numerous techniques, including FT-IR ATR spectroscopy.[19,26,27] Our data correspond well to these previous reports in terms of asymmetric band shapes, positions, or intensities. With regard to ultrafast measurements, vibrational relaxation of adsorbed CO has also been investigated by use of different methods and yielded time constants that lie in a rather broad range of 2−8 ps.[1,24,28−30] Taking into account different preparation conditions, influence of employed metals, and experimental temporal resolution, literature values correspond reasonably with the dynamics encountered here (3−10 ps). A reasoning for the different lifetimes derived here for CO on sputtered metal layers and previous values is most likely that reported short lifetime values have been observed mainly for samples at single crystal surface.[2,24,28,30]

To the best of our knowledge, only a single work investigated multidimensional signals of adsorbed CO by use of heterodyne-detected sum-frequency-generation (SFG) spectroscopy.[31] Although different preparation conditions for metal surfaces and sample solutions were used in these experiments, values for, e.g., anharmonicities from 2D spectra are similar (22 cm^{-1}),[31] as derived here, and sample inhomogeneity was pointed out as well. However, no characterization of vibrational dynamics was reported. Here we unraveled such dynamics using 2D IR ATR signals that report on spectral diffusion and quantification of static inhomogeneity as well as vibrational relaxation dynamics for linear and bridged CO.

One certainly powerful advantage of 2D IR spectroscopy is the possible resolution of vibrational coupling or energy transfer by identification of cross-peaks between bands in the 2D IR spectra.[14] Regarding results on surface absorbed CO, cross-peaks may be thought to appear between linear and bridged bound CO molecules or between subsets of oscillators within the asymmetrically broadened band for linear CO. From the current data (Figure 3), such features can, however, not be identified unambiguously, allowing for the conclusion that, for example, interaction between different CO binding configurations is very low or even negligible.

In the context of spectral, temporal, and structural information on molecules at interfaces, femtosecond SFG spectroscopy is the most commonly used approach for obtaining such information.[1,2,4,31] In contrast with ATR spectroscopy, SFG exploits combinations of IR and visible laser pulses to derive vibrational spectra of molecules in exclusively non-centro-symmetric environments. SFG has even earlier been demonstrated to yield phase-sensitive 2D IR spectra and dynamics.[2,31] However, especially when high temporal resolution and phase-sensitive, multidimensional information is sought, SFG spectroscopy is experimentally more demanding compared with ATR. This is due to the fact that SFG involves the creation of multiple beams with different frequencies and phase-stability in the visible.[31] Opposed to ATR, SFG has the great benefit not to be restricted to interfaces involving solids, which allows a broader range of samples to be studied.

In conclusion, we have presented a versatile approach for resolving multidimensional, ultrafast, vibrational dynamics of molecules adsorbed at interfaces by ATR spectroscopy. Specifically, we have measured pump probe and 2D IR spectra of linear- and bridged-bound CO on platinum and gold/palladium thin layers adsorbed from aqueous solutions. A broad range of aspects of vibrational dynamics have been characterized in detail including vibrational relaxation, spectral diffusion, as well as information concerning congested transient spectra, anharmonicity, and static sample inhomogeneity. The results demonstrate that a 2D IR experiment can be straightforwardly upgraded for studying ultrafast dynamics with surface sensitivity. 2D ATR IR spectroscopy thus has the potential to result in a broad range of applications for ultrafast, interface-related research.

■ EXPERIMENTAL SECTION

IR beams are generated from a single optical parametric amplifier (OPA)[32] giving ∼1.5 μJ pulse energy at 5 kHz. A fraction (∼100 nJ) of the OPA output is taken with a BaF$_2$ wedge as probe and reference beams (pr/ref) for balanced detection. For 2D IR experiments, a Mach−Zehnder interferometer is introduced to the pump beam, delivering replica of pump pulses (pu/pu′) as described elsewhere.[18] ATR prisms (10 × 10 mm, CaF$_2$) are sputter-coated with metal films (<1 nm) whose thickness is determined with a quartz-microbalance. Pu/pu′ and pr/ref beams are focused on the back side of the reflecting plane of the prism using off-axis concave (r = 30 cm) and plane gold mirrors. After recollimation, pr/ref pulses are detected by a 2 × 32 pixel MCT array.

Doubly deionized water is saturated with argon (4.8 Pangas), followed by CO (4.8 Pangas). The solution is slowly flown at the metal-coated surface of the CaF$_2$ prism. CO adsorption is monitored by recording in situ, stationary ATR spectra. Adsorption is complete within a few minutes and is constant during experiments, indicating good stability of the metal layer for at least 3 to 4 h.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.hamm@chem.uzh.ch. Phone: +41 44 63 544 31. Fax: +41 44 63 568 38.

Notes

The authors declare no competing financial interest.

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