Surface-Sensitive Spectro-electrochemistry Using Ultrafast 2D ATR IR Spectroscopy

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ABSTRACT: A new method is presented for the combination of spectro-electrochemistry and femtosecond 2D IR spectroscopy. The key concept is based on ultrathin (∼nm) conductive layers of noble metals and indium–tin oxide (ITO) as working electrodes on a single-reflection attenuated total reflectance (ATR) element in conjunction with ultrafast, multidimensional ATR spectroscopy. The ATR geometry offers prominent benefits in ultrafast spectro-electrochemistry, that is, surface sensitivity for studying electrochemical processes directly at the solvent–electrode interface as well as the application of strongly IR-absorbing solvents such as water due to a very short effective path length of the evanescent wave at the interface. We present a balanced comparison between usable electrode materials regarding their performance in the ultrafast ATR setup. The electrochemical performance is demonstrated by vibrational Stark-shift spectroscopy of carbon monoxide (CO) adsorbed to platinum-coated, ultrathin ITO electrodes. We furthermore measure vibrational relaxation and spectral diffusion of the stretching mode from surface-bound CO dependent on the applied potential to the working electrode and find a negligible impact of the electrode potential on ultrafast CO dynamics.

INTRODUCTION

The dynamics of molecules at solid–liquid interfaces, which can be electriﬁed on demand, are of signiﬁcant importance in different ﬁelds of chemistry and physics, but are difﬁcult to access experimentally.1−7 Particularly, ultrafast vibrational spectroscopy offers a high potential regarding identiﬁcation and characterization of transient species at electrode–electrolyte interfaces. These signals bear information on the structural dynamics of, and interaction between, molecules and their environment. The availability of ultrafast IR signals of samples at electrode interfaces is valuable in many ways, and time-resolved spectroscopy for such samples gained considerable attention in recent years.5,7−12 Spectro-electrochemistry in conjunction with time-resolved spectroscopy is an intense ﬁeld of research, for instance, concerning redox-related biochemical processes,13 electrocatalytic reactions14 or solar cells.4 In these disciplines, very often questions emerge that relate to vibrational, orientational, and energy-transfer dynamics of molecules in direct contact with or in the vicinity of electrode–solvent interfaces.

Ultrafast IR spectroscopy allows one to resolve vibrational dynamics with sub-picosecond temporal resolution.15−18 It is well-known that two-dimensional infrared (2D IR) spectroscopy15−18 allows obtaining such detailed information in advantageous ways. In analogy to 2D NMR spectroscopy, a correlation between two frequency axes in time-resolved signals allows for the resolution of, for example, vibrational coupling, chemical exchange, energy transfer, vibrational relaxation, or spectral diffusion of chemical bonds in 2D IR spectroscopy.15−18 Such dynamics are largely unexplored to date for interfacial systems and, in particular, near electrodes. It is therefore highly desirable to make this information available also from electrode–electrolyte interfaces.

In this paper, we report on a new spectroscopic method for the resolution of ultrafast, multidimensional signals from immobilized molecules at electrodes in solution. Our method is based on attenuated total reﬂectance (ATR) spectro-electrochemistry13,19,20 in combination with the recently developed ultrafast 2D ATR IR spectroscopy,21−23 which yields interface-sensitive, multidimensional signals with sub-picosecond temporal resolution. Recent studies have shown that 2D ATR IR spectroscopy allows the investigation of even organic monolayers equipped with low-absorbing (ε < 200 M−1 cm−1) local vibrational probes at submonolayer coverages.21,22 Here, we compare different electrode materials regarding their applicability in time-resolved ATR IR spectroscopy and resolve ultrafast dynamics from carbon monoxide (CO) adsorbed on the electrode surfaces. We evaluate strengths and weaknesses of electrode materials and show that a variation of the electrochemical potential applied to the electrode shifts the vibrational frequency of the immobilized CO with a rate of ∼24 cm−1 V−1 on the basis of the vibrational Stark-shift effect.24,25 We monitor ultrafast vibrational relaxation as well as spectral diffusion of the CO molecules dependent of the electro-
chemical potential and resolve that both quantities are only very mildly sensitive to the applied potential.

■ MATERIALS AND METHODS

Spectro-Electrochemical Cell. Figure 1 shows a schematic drawing of the home-built electrochemical ATR cell for ultrafast experiments. The assembly consists of a right-angle, single-reflection CaF$_2$ prism (top surface 10 × 14 mm, Thorlabs), the reflecting plane of which is sputter-coated with an ultrathin layer of either platinum (Pt) or indium–tin oxide (ITO). These layers are used as the working electrode (vide infra). The sputtered layer is incorporated in an electrochemical circuit containing a potentiostat (IviumStat Inc.) via a thin adhesive aluminum foil (Electron Microscopy Science Inc.) sandwiched between the cell and the sputter-coated prism surface. Additionally, the potentiostat is connected to counter and reference electrodes, which are assembled inside a home-built polyetherketone (PEEK) sample flow cell. The counter electrode consists of a Pt-coated Ti wire (E-DAQ Inc.) and is centered in the chamber of the flow cell. The reference electrode (Ag/AgCl, Biosense Inc.) is located at the front side of the PEEK cell.

The sample cell assembly is mounted on top of the reflecting plane of the sputter-coated ATR prism using an O-ring (Teflon) to allow solvent flow above the working electrode. The O-ring has an inner diameter of 7 mm, which determines the area of the electrochemically active surface. The sample chamber of the flow cell is centered above the reflecting plane of the ATR prism and has an inner diameter of about 5 mm and a volume of about 0.5 cm$^3$. Inlets and outlets of the sample cell (I/O) are located on opposite sides of the flow cell and are connected to Teflon tubes (outlet not shown in Figure 1).

Conductive layers as working electrodes on the ATR prism are obtained by use of either Pt or ITO as an electrode material. The ultrathin layers are sputter-coated on the reflecting plane of the CaF$_2$ ATR prism using Ar$^+$ ion sputtering. In the case of ITO a working distance of 50 mm, a base pressure of 8 × 10$^{-5}$ mbar, and a working pressure of 9 × 10$^{-2}$ mbar are used in a Safematic CCU 100 sputter coater (ZMB, Zürich, Switzerland). Deposition is performed with a sputtering current of 60 mA, which results in a deposition rate of about 0.1 nm s$^{-1}$. The average thickness was measured using a quartz microbalance. The sputtering process yields a structured surface of ITO nanoparticles (NPs, Figure 2a), as determined by scanning electron microscopy analysis (SEM Auriga 40, Carl Zeiss, Oberkochen, Germany). For an average thickness of 5 nm ITO of CaF$_2$, the NPs (light gray) form a heterogeneous layer of NPs, the diameters of which are all below 10 nm. These NPs are largely interconnected, and only few gaps are formed (dark gray), the size of which is estimated from the SEM images to be <5 nm. In this form, the sputtered ITO layers have a typical resistance of about 0.5–10 kΩ measured with two tips of a
manual multimeter separated by about 1 cm, which is sufficiently low for a quick equilibration of the electrochemical potential on the surface.

Pt layers are sputter-coated either on top of the ITO electrode layers (in this case with an average thickness of 0.1 nm) or on bare CaF₂ prisms (average thickness of 2.5 nm) using a sputtering current of 6 mA, which resulted in a deposition rate of about 0.02 nm s⁻¹. Otherwise, the deposition parameters were the same for ITO (vide supra). In the case of co-sputtered Pt/ITO layers, the 0.1 nm thin Pt layer serves only as the adsorption site for the carbon monoxide (CO), whereas in the case of the pure Pt layers (2.5 nm), the entire layer functions as an electrode as well as adsorption site of the CO. We note that the additional deposition of 0.1 nm Pt on top of the ITO layers does not influence the general conductivity of the substrate. The 0.1 nm co-sputtered Pt layers do not qualitatively change the overall structure of the ITO electrode layer (Figure 2b). The electrode surface consists again of interconnected NPs (2−10 nm) with only a very few gaps (<5 nm). We state that for the very thin Pt ad-layers (0.1 nm) on ITO it is not possible to discriminate between the ITO and Pt NPs in the SEM image.

The deposition of Pt with an average thickness of 2.5 nm results in an approximately continuous layer of Pt NPs, which form large and interconnected island-type structures with sizes exceeding 100 nm (Figure 2c). Here, narrow corrugations (<5 nm) are formed between the Pt islands. The large Pt islands consist of aggregates formed by much smaller Pt NPs (<5 nm). The sputtered Pt electrode layers exhibit a similar resistance (0.5−10 kΩ) as compared to the ITO layers.

With regard to liquid sample preparation, CO-saturated aqueous solutions were prepared by bubbling CO (4.8 grade, Pangas) for 15 min through a double-distilled water solution containing 0.1 M NaClO₄ (puriss. p.a., Sigma-Aldrich) as electrolyte. The prepared CO solutions were allowed to equilibrate across the electrode for a few minutes until adsorption was complete.23

**RESULTS**

We start with comparing two different materials for application as ultrathin (~nm) conductive layers in ultrafast ATR IR spectroscopy, that is, sputter-coated metal layers (Pt, average thickness = 2.5 nm) and ITO layers (average thickness = 5 nm). To choose a suitable electrode material for ultrafast spectroscopy, a few key points need to be considered. Sputter-coated metal layers of at least 2 nm thicknesses generally approach the percolation threshold (vide supra), and the resulting conductivity allows them to be usable as electrodes. This is guaranteed for both materials employed here, as demonstrated in the Supporting Information (Figure SI 1) by recording cyclic voltammograms (CVs) of the sputter-coated samples in the presence of 0.1 M NaClO₄ electrolyte solution. As such, both materials are usable as electrodes.

With regard to mechanical stability of the conductive layers, however, we find empirically during the processes of sample preparation, handling, sample-cell assembling, and cleaning that ultrathin Pt layers are significantly more susceptible to mechanical stress compared to the ITO layers. This is of particular importance in, for example, establishing the contact between the conductive tape and the metal layer (Figure 1). As such, ITO can be considered as an “easier to handle” material regarding spectro-electrochemistry.

Another aspect is that the materials need to transmit the IR evanescent wave in ATR spectroscopy. Specifically regarding ultrafast spectroscopy, it is desirable to minimize the intrinsic absorbance of the electrode layer to have available the maximum light intensity for excitation and probing of the adsorbate signals. For the two materials employed here, we find that ITO exhibits the lower values of IR absorbance compared to Pt samples (Figure SI 2). This hence makes ITO the more suitable material because more photons are available for the excitation of the adsorbate by the evanescent wave.

To demonstrate the applicability of the ultrathin layers in ATR IR spectroscopy of adsorbates, Figure 3 shows in situ measured ATR spectra of CO adsorbed to a sputter-coated Pt layer (average thickness = 2.5 nm, black) on a bare CaF₂ prism along with CO on a sputter-coated Pt layer (average thickness = 0.1 nm, orange) on a 5 nm ITO layer on a CaF₂ prism. Both materials result in a single band in the range of

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**Figure 3.** In-situ measured ATR IR absorption spectrum of CO on Pt/ITO (0.1 nm/5 nm) electrodes (orange) versus ATR IR absorption spectrum of CO on 2.5 nm Pt (black). The 2.5 nm Pt spectrum appears inverted as an antiabsorptive signal (negative ATR absorbance) due to line shape effects stemming from the metal layer.
2000–2100 cm$^{-1}$, which corresponds to linear bound CO on Pt.$^{23}$ We note that the different CO band positions are most likely the result of a dependence of the CO band position on metal particle sizes as observed previously.$^{30}$ An absorptive band is observed for Pt/ITO layers, whereas anti-absorption$^{31–33}$ is determined for the 2.5 nm Pt layer. The anti-absorption signals are the result of line shape distortion effects generally observed for adsorbates on metal surfaces near the percolation threshold.$^{31,33–37}$ We note that the thickness of the Pt layer as used here has been purposely tuned to result in this anti-absorption signal to avoid band shapes with dispersive contributions.$^{31,33–37}$

Next, we evaluate the applicability of the two different electrode materials regarding the implementation in ultrafast IR spectroscopy. Because the conductive layers intrinsically absorb IR light (Figure S1 2), a background signal is observed in time-resolved spectroscopy from the electrode materials alone (in the absence of adsorbed CO) as shown below. To minimize this effect, it is thus advantageous to keep the conductive layers as thin as possible. Figure 4 shows ATR pump–probe signals for different measurements of a 2.5 nm Pt film on CaF$_2$ (left column) and of 0.1 nm Pt on 5 nm ITO (right column). Signals are shown for bare conductive layers incubated with the electrolyte solution (a, b) and after CO adsorption (c, d), along with the difference signals between CO adsorption and the electrolyte-incubated electrode layers (e, f). For 2.5 nm Pt layers (a), a spectrally broad and positive (red) signal is observed, which evolves slowly on the experimental time scale of 40 ps. This signal stems from direct Pt excitation of conduction electrons at the Fermi edge and subsequent thermal energy redistribution (heating) of the substrate. This signal is changed in the presence of adsorbed CO (c) to higher/lower signal magnitudes in spectral regions of GSB/SE ($\sim$2070 cm$^{-1}$)/ESA ($\sim$2025 cm$^{-1}$), which correspond to the CO signal contributions. Note that the CO signals are inverted with respect to the conventional representation of differential absorbance (GSB/SE $\equiv$ decrease absorbance, ESA $\equiv$ increase in absorbance) in pump–probe spectroscopy due to the anti-absorptive line shape of the CO band (Figure 3, black line). The difference between the signals in (a) and (c) reveals the signal contributions of only the adsorbed CO (e), which clearly shows GSB/SE signals (red) as well as ESA signals (blue), decaying on a 10 ps time scale.

In the case of ITO/Pt layers the bare electrode signal (b) is negative (reduced absorption, blue), and the dominant signal intensity ceases during the initial 500 fs after excitation. The pure CO signals (GSB/SE $\sim$ 2060 cm$^{-1}$ and ESA $\sim$ 2020 cm$^{-1}$ (f)) are again obtained after subtraction of the bare Pt/ITO background signals from the CO on ITO/Pt data (d). Note that here the GSB/SE and ESA signals are negative/positive differential absorption as expected from the positive absorption signals of the CO ATR band (Figure 3). The CO signals decay on a time scale of about 10 ps, as seen also for CO on Pt (e). The temporal evolution of the CO-related signals is discussed below.

Overall, both conductive layers are applicable in ultrafast spectroscopy to reveal the sought adsorbate signals. However, due to the much shorter-lived background signal of the ITO as well as the better mechanical stability of ITO, we will focus on the application of ITO/Pt layers in ultrafast measurements throughout the rest of the paper.

**Vibrational Stark-Shift Spectroscopy.** We now turn to the application of the ultrathin conductive layers in spectroelectrochemistry. The linearly bound CO on Pt NPs sensitively responds to electrochemical potentials of the electrode.$^{38,39}$ Incorporation of the conductive layers as working electrodes in an electrochemical circuit therefore allows for vibrational Stark-shift spectroscopy,$^{5,24,38,40–45}$ as demonstrated below. The CO stretch frequency can be varied in a potential range from $-1$ V to about +0.5 V. In this potential range CO is stable on small Pt NPs, whereas complete CO oxidative desorption is observed for potentials larger than +0.5 V.$^{38,39}$ Cyclo-voltammetry (CV) is used here to demonstrate the electrochemical characteristics of the sputter-coated Pt and ITO layers, covered with Pt NPs.
and adsorbed CO. Starting at 0 V toward positive potentials with a scan rate of 50 mV s\(^{-1}\), the CV of the 2.5 nm Pt sample (Figure 5, black) shows an intense oxidation peak at about 0.45 V versus Ag/AgCl, which corresponds to the characteristic oxidative desorption of CO on Pt.\(^{44,45}\) In contrast to that, a CV (Figure 5, orange) shows a much broader oxidative desorption wave with lower intensity, which peaks at about 0.4 V. This reduced wave simply corresponds to a lower number of adsorption sites for the CO due to a much lower average Pt thickness.

To demonstrate the vibrational Stark-shift spectroscopy, Figure 6 shows 2D ATR IR spectra of CO on ITO/Pt for a population delay of 1 ps and for three potentials, those being −1.0 V (a), 0.0 V (b), and +0.4 V (c), all versus Ag/AgCl. These signals have been obtained by subtraction of two separately measured spectra of the electrolyte solution on the ITO electrodes with and without CO.\(^{23}\) GSB/SE (blue) are observed together with ESA signals (red). As the potential is varied from negative (−1.0 V (a)) to positive (+0.4 V (c)) values, the central frequency of the CO band changes between 2037 and 2070 cm\(^{-1}\). Recording the CO band maxima projected on the probe axis at a series of different potentials (Figure 6d) reveals that the central frequency (open circles) is shifted upon potential variation in a linear manner. A linear fit to the data yields a slope of ∼24 cm\(^{-1}\) V\(^{-1}\), which is in good agreement with previous results (25−30 cm\(^{-1}\) V\(^{-1}\)).\(^{8,38,39}\)

The origin of this spectral shift in known as a vibrational Stark-effect,\(^{5,24,38,40−43}\) which is based on alterations of the vibrational properties and chemical binding properties of adsorbates in electric fields near electrodes. We note that due to the heterogeneous structure of the sputter-coated electrode layers in our experiment, there will be a spatial variation of the local electric field around the NPs, which is difficult to quantify. Due to the applied s-polarization of excitation and probing beams in our experiments, however, the dominant signal stems from molecules adsorbed at the sides of the NPs. In this respect, the close agreement between the observed Stark-tuning rate in this work and previous\(^{8,38,39}\) results indicates that the spatial variation of the local electric field is not significantly different.

For all potentials the GSB/SE signals in the 2D ATR IR spectra are strongly elongated along the diagonal, indicating a large degree of inhomogeneity in the vibrational line shape of the immobilized CO, as discussed previously.\(^{23}\) The center-line slope (CLS) method\(^{46,47}\) is used here to quantify inhomogeneity of the GSB/SE signals. We state that linear fits to the CLS for the different 2D spectra at 1 ps delay show very similar values (−0.75 to −0.8), irrespective of the potential. This indicates that the distribution of oscillators contributing to the broad absorption band does not significantly depend on the applied potential. A detailed analysis of the temporal evolution of the CLS values from 2D ATR IR signals will be discussed further below.

**Ultrafast CO−Dynamics in Dependence of Potential.**

We additionally studied ultrafast vibrational relaxation of the adsorbed CO molecules on the Pt/ITO dependent on the applied potential. Figure 7 shows cuts along the temporal axis of background-subtracted ATR IR pump−probe data at the position of the maximum GSB/SE signal for CO at the two potentials of +0.4 V (open circles, ∼2070 cm\(^{-1}\)) and −1.0 V (solid triangles, ∼2037 cm\(^{-1}\)), which are the two potentials of highest charge employed in this study. Experimental data are
represented by symbols, whereas single-exponential fits are represented by solid lines. We find vibrational relaxation time constants of $2.5 \pm 0.1 \text{ ps} (-1.0 \text{ V})$ and $3.1 \pm 0.1 \text{ ps} (+0.4 \text{ V})$. Both values are slightly faster, but in overall good agreement with previously reported ($3-4 \text{ ps}$) vibrational relaxation of CO on ultrathin metal layers. This demonstrates that the CO vibrational lifetime is only very mildly dependent on the applied electric field at the surface.

Furthermore, ultrafast spectral diffusion of CO on ITO/Pt electrodes was investigated by recording 2D ATR IR spectra for a series of population delays during the vibrational relaxation dependent on the applied potential. Being able to record spectral diffusion dynamics at electrode–electrolyte interfaces allows, for instance, obtaining information on how and on which time scales the adsorbate interacts with the electrolyte molecules. Figure 8 shows 2D ATR IR spectra for population times of 0.5 and 7 ps for CO adsorbed on ITO/Pt, again for the two most separated potentials of +0.4 V (a, b) and −1.0 V (c, d). For both potentials, the GSB/SE signals are initially (a, c) strongly elongated along the diagonal line with similar CLS values of about 0.8–0.85. Temporal evolution of the GSB/SE signals reduces the CLS values to about 0.6, again very similar for both potentials (b, d).

Plotting CLS values dependent on a series of population times $T$ allows gaining insight into the temporal dynamics underlying spectral diffusion (Figure 9). For both potentials the CLS curves start at values about 0.8–0.85 and evolve to values around 0.4 during 10 ps of relaxation. Note that the temporal window for investigations is limited by the vibrational lifetime of about 3 ps (Figure 7), which prevents observation of the complete decay of the CLS curves. The temporal evolution of both curves suggests an exponential decay including an offset $(\text{CLS}(T) = \Delta_1 \exp(-T/\Delta_2) + \Delta_2)$, which we use to fit the data. On the basis of the limited temporal window for the investigation we cannot decide whether the offset is a truly static contribution or if it represents dynamics on a time scale that is much longer than our observation window. The fits return $\tau_\text{SD}/\Delta_2$ values of $8.6 \pm 0.9 \text{ ps}/0.26 \pm 0.4 \text{ V}$ (open circles) and $9.7 \pm 0.6 \text{ ps}/0.21 \pm (-1 \text{ V}, \text{ solid triangles})$. The similarity between these time constants and offsets indicates that the dynamics of spectral diffusion are very similar for the two potentials.

### DISCUSSION

Our results demonstrate the potential of 2D ATR IR spectroscopy regarding the resolution of vibrational dynamics dependent on an electrochemical potential of adsorbates on electrode surfaces. The main information of this study is represented by the vibrational relaxation along with spectral diffusion of CO adsorbed to an electrode surface (Figures 4, 7, and 9) under the influence of the vibrational Stark-effect. Traditionally, the effect of variations in vibrational frequency of adsorbates with an applied external electric field is explained by either changes in the electron density in (anti)bonding orbitals, that is, strengthening and weakening of a chemical bond, or alterations of the relative energetic positions of vibrational levels within an anharmonic potential. The latter effect stems from a larger average bond-length (and thus a higher dipole moment) for excited vibrational levels, which is shown to experience different energetic (de)stabilization in an external electric field relative to the vibrational ground state. A combination of vibrational Stark-shift and ultrafast spectroscopy, as developed here, therefore allows experimentalists to gain valuable insight into intra- and intermolecular dynamics under the impact of purposely applied electric fields.

Vibrational relaxation typically occurs on the picosecond time scale and provides insight into the interaction between an adsorbate and its environment. In the case studied here, the environment of adsorbed CO consists of the electrode surface as well as the electrolyte solution. Aside from variations in bond strengths and (de)stabilization of vibrational levels (vide supra), the interfacial electric field can also affect the alignment of the adsorbate molecules with respect to the surface or alter the structure and dynamics of the solvent (electrolyte) environment. All of these points can influence the redistribution of the adsorbates’ excess vibrational energy after excitation. The results presented here for vibrational relaxation of CO on sputter-coated, polycrystalline Pt layers are in a good agreement with the nearly potential-invariant...
vibrational lifetime of CO on single-crystal Pt electrodes observed with sum-frequency generation (SFG) spectroscopy.\textsuperscript{51,52} It can therefore be concluded that the vibrational lifetime is in a general manner only very mildly affected by changes in the sigma-donating, \(\pi^*\)-accepting electronic bonding mechanism of CO to the Pt NPs\textsuperscript{41} as well as charge-induced structural changes of the complex hydrogen-bond network of water molecules near the charged surface.\textsuperscript{51,49,50}

It is furthermore well-known, that the vibrational lifetime of adsorbed CO depends strongly on the electronic structure of the surface. For instance, the vibrational lifetime is different by multiple orders of magnitude for metals (e.g., Pt, Cu) and insulators (NaCl) as surfaces for immobilization.\textsuperscript{53} This result has been interpreted in that there exists strong coupling between the vibrational states and the continuum electronic states of the metal to which the excess vibrational energy is transferred after excitation.\textsuperscript{53,54} The results presented here thus moreover indicate that this electron–nuclear coupling is not strongly affected by (i) changes in the electron density of the metal NPs upon change of the potential at the interface and (ii) the Stark-shifted ground and excited vibrational levels of the adsorbate and (iii) possible image dipole contributions as invoked previously\textsuperscript{44} for adsorbates at metal surfaces.

Next we turn to the spectral diffusion dynamics, which originate from the temporal fluctuations of individual oscillator frequencies under the envelope of the CO absorption band. In general, spectral diffusion also occurs on time scales of a few hundreds of femtoseconds up to tens or hundreds of picoseconds with usual broadening mechanisms stemming from, for example, solvent–sample interaction, intramolecular fluctuations of the samples’ structure, or static inhomogeneity.\textsuperscript{15,47,55} Because the diatomic molecules employed here lack the possibility of intramolecular structural fluctuations, the main contributions to spectral diffusion are likely to stem from solvent–adsorbate interaction and molecular alignment on the surface as well as static inhomogeneity. In general, we observe that the GSB/SE signal elongation represented by the CLS values are fairly high at early delays (>0.8 at <1 ps, Figure 9). This is thus similar to that observed previously\textsuperscript{23} in 2D ATR IR spectroscopy, but our CLS values are higher than observed, for instance, by 2D SFG spectroscopy.\textsuperscript{7} We note, however, that these differences are most likely due to different sample preparation techniques for 2D ATR and 2D SFG spectroscopy.

The static contributions (\(\Delta_s\)) in the CLS dynamics (Figure 9) probably originate from the specific structure of the NPs on the electrode surface (Figure 2). In this respect we note that similar static offsets in spectral diffusion of CO on noble metal alloys have been observed previously\textsuperscript{25} as well and have been interpreted in terms of the spatially varying NP structure in the alloy. It is therefore likely that the \(\Delta_s\) values observed here are of the same origin. By the observation of similar elongation of the GSB/SE peaks along the diagonal line at a series of potentials (Figure 6) along with very similar static offsets in spectral diffusion dynamics (Figure 9), we can therefore conclude that no significant potential-dependent alignment or ordering of adsorbed molecules with respect to the surface occurs which would change the static offsets in the CLS curves or interaction between the water molecules and the adsorbate at the interface.

The largest part of spectral diffusion stems from the dynamic contribution (\(\Delta_d\), 8–10 ps, Figure 9), which originates from, for example, the hydrogen-bonding interaction with the adsorbed CO and reorientation of the water molecules\textsuperscript{25} in the electrolyte solution. The determined spectral diffusion time constants are rather slow as compared to, for example, hydrogen-bonded carbonyl functional groups in amides.\textsuperscript{56,57} This sluggish spectral diffusion is likely to stem from the confined nature of the water at the solid–liquid interface.\textsuperscript{58–60} In this context, investigations of the structure of interfacial water in direct contact with charged oxide surfaces have revealed significant structural variations of water molecules dependent on surface charge.\textsuperscript{1,49,50} For instance, water is known to form spatially extended hydrogen-bond networks, specifically at negative surface charge when the first layer of water molecules is strongly hydrogen-bonded to, for example, the surface oxide. Here, our results obtain only indirect information about the water dynamics\textsuperscript{11,50} via spectral diffusion of the surface-bound CO molecules. The observed near invariance of spectral diffusion with the electrode potential may indicate that a simple electrostatic influence of the applied electric field on reorientation and hydrogen bonding of water molecules in close proximity to the surface is too weak to influence the intermolecular dynamics. It is thus more likely that the near-surface water molecules need to establish a certain chemical interaction, such as hydrogen bonding between the negatively charged surface oxides and the water,\textsuperscript{1,50} to significantly influence spectral diffusion dynamics. Such chemical interactions are not very likely for the charged Pt NPs employed here.

**General Context of 2D ATR IR Spectro-electrochemistry.** Most studies concerning ultrafast vibrational spectroscopy at electrified or charged interfaces employ ultrafast SFG spectroscopy, which is based on a combination of mid-IR and visible beams.\textsuperscript{57–59,12,49,50,54,61} Recent studies also successfully demonstrated 2D IR spectroscopy combined with electrochemistry in external reflection conditions\textsuperscript{62} using a metal mirror as an electrode, however, without signals directly from the interface.\textsuperscript{63,64} When working in such a configuration, the excitation light travels through the (generally) aqueous electrolyte solution twice, which demands liquid layers of only a few micrometers in thickness, due to the spectrally broad and strong IR absorbance of water.\textsuperscript{63,64} This is a little less of an issue in external reflection SFG spectroscopy, because the signal light is frequency-converted to the visible spectral range at the interface before the second path through the liquid phase. In ATR spectroscopy, in contrast, challenges concerning sample thicknesses are circumvented due to the very low penetration depth of the evanescent wave at the interface. The highest intensity of the evanescent field is present directly at the solid–liquid interface, giving rise to the well-known surface sensitivity of ATR spectroscopy. In addition to molecules immobilized at the surface, ATR spectroscopy is also expected to be able to resolve dynamics from molecules within the Helmholtz double layer.\textsuperscript{59} As a rule of thumb, the evanescent fields produced at the interface exhibit penetration depths of about one wavelength of the applied light (here ca. 5 \(\mu m\)), thin enough so that water absorption is not yet a severe problem.\textsuperscript{56} Moreover, the penetration depth can easily be tuned to both smaller and larger values by varying the angle of incidence\textsuperscript{56} and the polarization\textsuperscript{67} of the IR light. A penetration depth of a few micrometers is sufficiently large to also investigate electrochemically active samples in bulk solution. We note that a polarization dependence of 2D ATR IR signals of adsorbates has been presented recently\textsuperscript{68} and reveals that both p- and s-polarizations are exploitable to reveal information about signals from the interface.
CONCLUSION

We have presented a new method for measuring time-resolved, multidimensional IR spectra from immobilized molecules at electrode–electrolyte interfaces. Experimental benefits and pitfalls of different electrode materials have been compared and emphasize the advantages of ultrathin (∼nm) conductive layers. Using a combination of electrochemical ATR spectroscopy with ultrathin ITO electrodes and the recently developed 2D ATR IR spectroscopy, multidimensional vibrational Stark-shift spectra of CO adsorbed to platinum nanoparticles have been acquired. In a potential window from −1.0 to +0.5 V the CO band was Stark-shifted at a rate of ∼24 cm⁻¹ V⁻¹. Vibrational relaxation as well as spectral diffusion of immobilized CO has been investigated in detail and shows negligible dependence on the applied electrode potential. From the presented results we expect that ultrafast 2D ATR IR spectro-electrochemistry will find broad application in various research fields which involve purposely charged interfaces as well as redox- and electron-transfer dynamics across solid–liquid interfaces.

It is well-known that upon binding to metal NPs, the oscillator strength of the CO molecule increases due to a chemical enhancement effect.36,69 This chemical enhancement effect thus contributes here as well, together with recently characterized electromagnetic enhancement effects in 2D ATR IR spectroscopy for sputter-coated metal layers.68 Such enhancement effects significantly help the investigation of ultrafast vibrational dynamics at interfaces, where the number of contributing sample molecules is only low.

A first future extension of the current work will involve the transfer of redox-active samples from bulk solution to organic electrocatalysts to allow investigations of electrocatalytic transfer of redox-active samples from bulk solution to organic electrocatalysts. From chemical enhancement as well as redox- and electron-transfer dynamics across solid–liquid interfaces.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00395.

Stability of working electrodes and infrared spectra of electrode materials (PDF)

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