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Transient CO Desorption From Thin Pt Films Induced by Mid-IR Pumping

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Resonant and off-resonant mid-infrared pump-probe spectroscopy is used to measure the vibrational dynamics of CO adsorbed to thin (0.2 nm, 2 nm and 10 nm) heterogeneous Pt layers in an aqueous solution. The transient signals observed with resonant pumping are dominated by vibrational relaxation of the CO internal stretch vibration with a lifetime of $T_1 \sim 3$ ps in all cases. Off-resonant pumping suppresses that contribution to the signal, and singles out a signal, which is attributed to heating of the metal layer, as well as transient desorption of the CO molecules. Due to the small photon energy (0.2 eV) used as pump pulses, the mechanism of desorption must be thermal, in which case the desorption yield depends exclusively on the fluence of absorbed light, and not its wavelength. The thin Pt layers facilitate CO desorption, despite a relatively low pump pulse fluence, as they concentrated the absorbed energy in a small volume.

I. INTRODUCTION

Time-resolved infrared (IR) spectroscopy using ultra-short pulses has proven to be an essential tool in investigating small molecules' dynamics adsorbed on metal surfaces. Upon laser excitation, the coupling between photo-excited charge carriers in the metal and the vibrational degrees of freedom of the adsorbates can lead to vibrational excitation, relaxation, energy transfer, diffusion, desorption, and oxidation of adsorbates.¹⁻⁴ In this regard, CO adsorbed on Pt (Pt-CO) stands out as a benchmark system to investigate these fundamental processes both for its relevance in catalysis and for its high oscillator strength in the mid-IR. A significant part of the time-resolved studies done on Pt-CO so far has been performed under ultrahigh vacuum (UHV) using single crystals.⁵⁻¹² These highly idealized conditions have allowed the investigation of the adsorbed layers' vibrational properties in exceptional detail.

Recently in our group, we have performed time-resolved IR measurements of CO, CN, and H adsorbed on Pt layers to investigate vibrational relaxation and adsorbate-substrate energy transfer.¹³⁻¹⁵ Our working conditions are in high contrast to the idealized systems referred above, as we work under ambient pressure and temperature, using heterogeneous (sputtered) metal layers in the solution phase. Working in such conditions provides the potential to study photo/electrocatalysts under real-world conditions.

Most of our time-resolved studies on heterogeneous metal layers have been measured for Pt layers that are <1 nm in order to eliminate strong IR absorption of the metal layer and, even more crucially, the line-shape distortions (Fano line shapes) that appear as a result of adsorbate's discrete state coupling to the metal's continuum of states. For this reason, adsorbates on thicker heterogeneous metal layers remain mostly unexplored in time-resolved IR spectroscopy. Recently, we have proposed a scheme to correct distorted line shapes for two-dimensional IR (2D IR) and IR pump-probe

spectroscopy.¹⁶ Briefly, we tune the phase (ϕ_{corr}) of the the Fano line shape to obtain a symmetric line shape. Correction of the distorted spectra enabled the straightforward interpretation of the spectra of thicker metal layers.

In the present paper, we would like to test the effect of thicker Pt layers on the vibrational dynamics of adsorbed CO. Application of such heterogeneous metal layers within a wide range of thickness are common in photo/electrocatalysis, and it is essential to understand the interaction of the metal layer with the adsorbate for transient IR experiments in electrochemical environments. Furthermore, owing to their plasmonic nature, thicker (rougher) metal layers provide higher signal enhancements by enhancing the near-field.¹⁶⁻¹⁸ To that end, we employ both resonant and off-resonant IR pump-probe spectroscopy in reference to the excitation of the internal stretch mode of CO adsorbed on Pt in CO saturated aqueous solutions for a range of Pt thicknesses (0.2, 2, and 10 nm). By probing its dynamics and spectral shifts, we can resolve processes of vibrational relaxation, metal-induced heating, adsorbate-metal coupling, and desorption.

Femtochemistry on metal surfaces³, including processes such as diffusion, desorption, and oxidation of adsorbates, has been performed mostly using excitation pulses in the ultraviolet (UV) to near-IR. Earlier studies on IR induced desorption on metal and insulator surfaces are performed by resonantly exciting specific modes.^{19,20} However, excitation by mid-IR on metal surfaces is mostly limited to investigations of vibrational energy relaxation, with no bond-breaking involved. It is one of the goals of this paper to extend the scope of femtochemistry on metal surfaces to the mid-IR range.

II. METHODS

CaF₂ windows were sputter-coated with thin layers of Pt (Baltic Präparation) using an Ar⁺-ion sputter coater (Safematic CCU-010 HV) under the following condi-

tions: working distance 7 cm, current 20 mA, pressure $8 \cdot 10^{-5}$ mbar and Ar pressure of $5 \cdot 10^{-2}$ mbar, resulting in the sputtering rate of 0.02 nm/s. The average thickness (mass thickness) of the Pt layers were monitored with a quartz microbalance. CO-saturated aqueous solutions were prepared by bubbling CO (4.8 grade, Pangas) for 15 min to D₂O. D₂O was used instead of H₂O to avoid solvent heating due to excitation of O-H bending mode of H₂O, which is located in the spectral window of the off-resonant pump (1650 cm⁻¹) (see Fig. S1 in SI). The CO-saturated aqueous solutions was sandwiched between the Pt coated and uncoated 2 mm thick CaF₂ windows separated by a 6 μ m spacer.

IR absorption spectra were acquired with a commercial FTIR spectrometer (Bruker VERTEX 80V) with 4 cm⁻¹ spectral resolution. Background measurements were taken with the Pt coated CaF₂ window with the solvent. The solvent was then exchanged with a CO-saturated solution to acquire the spectra.

Ultrafast pump-probe measurements were done by using short mid-IR pulses of 180 cm⁻¹ bandwidth, centered at 2050 cm⁻¹ that were generated in an OPA²¹ pumped with a 1 kHz amplified Ti-Sapphire laser system (Spectra Physics Tsunami and Spitfire). The OPA's output was split into pump, probe, and reference beams with a BaF₂ wedge. All beams were then collected with an off-axis parabolic mirror and focused on the sample with all beams polarized in parallel. The probe beam ($\sim 80 \mu$ m) was overlapped with the pump beam ($\sim 100 \mu$ m, 14 J/m² fluence if not noted otherwise). We note that low pump energies were intentionally used here to avoid pump-induced damage of the plasmonic metal layers.^{16,18} Probe and reference beams were spectrally dispersed and imaged with a spectrograph (Jobin-Yvon Triax, 150 lines mm⁻¹ grating) onto a 2x32 pixel MCT array detector (Infrared Associates) for detection with a resolution of ~ 7 cm⁻¹. The mid-IR pulses of a second OPA centered at 1650 and 3100 cm⁻¹ were used as a pump for the off-resonant experiments.

III. RESONANT PUMPING: VIBRATIONAL RELAXATION OF THE CO MODE

We start by comparing the pump-probe spectra of the three samples that are resonantly excited, covering the spectral window corresponding to the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions of the internal stretch vibration of a linearly bound (atop) CO to Pt (**Pt-CO**). All the pump-probe spectra measured in this study, except for the 0.2 nm **Pt-CO**, sit on a broad negative offset resulting from the heating of the metal layer after excitation (see Fig. S2 in SI), which was subtracted to focus only on the adsorbate response. The offset is not present for the 0.2 nm **Pt-CO**, because the thickness is below the metal layer's percolation threshold, resulting in disconnected metal islands making the layer electrically non-conductive.^{14,22-24} Sim-

ilar transient offsets were observed in other IR-pump-IR-probe experiments performed in reflection geometry, where the metal-induced signal was explained by the decrease in reflectance (ΔR) due to an increase of temperature in the metal after excitation.⁶⁻⁸ In this regard, a decrease in ΔR corresponds to a negative difference absorbance (ΔA) in our transmission geometry, in line with the negative offsets we observe.

As we have pointed out earlier,¹⁶ the IR spectra of metal-adsorbates on thicker heterogeneous metal surfaces can show distorted lineshapes. These Fano-lineshapes originate from the coherent coupling of the vibrator with the plasmon resonance of the metal layer. The sputtered surfaces used here can be considered (potentially connected) nanoparticles with rather undefined sizes and shapes, and consequently one obtains a very broad distribution of plasmon resonances, which extend into the IR, see Fig. S1a of Ref. 16. The extent to which this is happening depends on the thickness of the metal layer, and consequently also the phase needed to correct the Fano-lineshapes.

Fig. 1a exemplifies this effect by showing the measured (uncorrected) IR pump-probe spectrum of 2 nm **Pt-CO**. A IR pump-probe spectrum of a single vibrational mode is expected to have a negative ground state bleach/stimulated emission band ($\nu_{0 \rightarrow 1}$), together with an anharmonically red-shifted excited state absorption band ($\nu_{1 \rightarrow 2}$), which is not what Fig. 1a shows. We thus apply the correction scheme of Ref. 16 to all samples to obtain the corrected spectra. Figure 1b-d shows the corrected IR pump-probe spectra obtained by applying $\phi_{corr}=0.43$, 1.3 and 0.75 rad for 0.2, 2 and 10 nm **Pt-CO**, respectively, which were obtained from the IR absorption spectra (see Fig. S3 in SI).

Fig. 1b shows the pump-probe spectrum of the 0.2 nm **Pt-CO**. The $\nu_{0 \rightarrow 1}$ and $\nu_{1 \rightarrow 2}$ bands are observed at 2040 cm⁻¹ and 2010 cm⁻¹, respectively. Spectral width and anharmonic shift agree with previous works on heterogeneous Pt surfaces.^{13,25} Both bands have decayed completely within 20 ps and a single-exponential fit to $\nu_{0 \rightarrow 1}$ yields a time constant of 2.5 ps for the vibrational population relaxation (T_1) (Fig. 2a, black line). The time constant is within the same ballpark of our previous measurements^{13,14} and also with previous electrochemical^{26,27} and gas-phase measurements on single-crystals⁷. The significantly shorter T_1 observed for CO on metals, as compared to insulators, semiconductors or small metal nanoparticles,²⁸ are explained by the excitation of electron-hole pairs in the metal caused by the oscillations of charge (electronic friction) between the CO $2\pi^*$ orbitals and the metal as the C-O bond vibrates, resulting in a strong substrate-adsorbate coupling.²⁹

Fig. 1c and d shows the pump-probe spectra for 2 and 10 nm **Pt-CO**. The central frequencies of the $\nu_{0 \rightarrow 1}$ band is blue-shifted ~ 30 cm⁻¹ relative to 0.2 nm **Pt-CO** band, which we attribute to different metal particles sizes.³⁰ While both $\nu_{0 \rightarrow 1}$ and $\nu_{1 \rightarrow 2}$ bands decay to zero for the 0.2 nm **Pt-CO**, $\nu_{0 \rightarrow 1}$ bands of 2 and 10 nm **Pt-**

FIG. 1. (a) Uncorrected IR pump-probe spectrum of 2 nm **Pt-CO** after resonant excitation, as well as corrected IR pump-probe spectra of (b) 0.2 nm, (c) 2 nm and (d) 10 nm **Pt-CO**. Metal offsets of all spectra (except 0.2 nm **Pt-CO**) were subtracted before applying the correction scheme. Arrows indicate the spectral positions considered for the kinetic traces shown in Figure 2.

CO are still present after 20 ps. There are also longer-lived positive bands on the lower energy sides of $\nu_{0 \rightarrow 1}$, which are not present for 0.2 nm **Pt-CO**. These positive bands are not a continuation of the $\nu_{1 \rightarrow 2}$ decay, as their spectral positions and line shapes are significantly different from the broad $\nu_{1 \rightarrow 2}$ bands present at earlier times.

The remaining $\nu_{0 \rightarrow 1}$ contribution at longer times can be better seen in Fig. 2a, which shows the temporal evolution of the normalized $\nu_{0 \rightarrow 1}$ signals for all three samples. The decay profiles for the 2 and 10 nm **Pt-CO** follow the single-exponential fit of the 0.2 nm **Pt-CO** (black line) up to ~ 4 ps, but deviate afterwards, which leads us to divide the decay profiles of the 2 and 10 nm **Pt-CO** into two phases: (i) a fast component related to T_1 relaxation, where all samples decay similarly and (ii) a

slow component, which is related to a thermal effect, as discussed below, and has a dependence on metal thickness. The T_1 contribution can be singled out by looking at the low-frequency wing of the $\nu_{1 \rightarrow 2}$ band, indicated by the downward facing arrows in Fig. 1c,d. The kinetics of 2 and 10 nm **Pt-CO** then follow the 0.2 nm **Pt-CO** data reasonably well (Fig. 2b). Single-exponential fitting reveals time constants of 2.1, 2.3 and 1.80 ps for 0.2, 2 and 10 nm **Pt-CO**, respectively. Hence, the effect of electronic friction is about the same for all metal layer thicknesses.

FIG. 2. The temporal evolution of (a) $\nu_{0 \rightarrow 1}$ and (b) $\nu_{1 \rightarrow 2}$ bands marked by the arrows in Fig. 1 for 0.2 (black), 2 (red) and 10 nm **Pt-CO** (blue). Solid black lines represent single exponential fits to the pump-probe data of 0.2 nm **Pt-CO**.

FIG. 3. Corrected 2D IR spectra of 2 nm **Pt-CO** at population times of (a) 1, (b) 10 and (c) 100 ps. Metal offsets of all spectra were subtracted from a signal free region. Panels (a) and (b) are normalized to maximum signal, panel (c) is on the same scale as panel (b).

IV. OFF-RESONANT PUMPING: THE CO MODE AS MOLECULAR THERMOMETER

Fig. 3 provides further insight to the origin of the long-lived signals by showing 2D IR spectra at population times of 1, 10 and 100 ps for 2 nm **Pt-CO**. A 2D IR spectrum maps the vibrational signals along two axes, ω_{pump} and ω_{probe} , providing resolution on the excitation energy.³¹ In the context of this paper, 2D IR spectroscopy is used to reveal the off-resonant character of the long-lived signals. At 1 ps, we observe the normal 2D IR spectrum of an isolated vibrational transition with a $\nu_{0 \rightarrow 1}$ and a $\nu_{1 \rightarrow 2}$ band located at a ω_{pump} position where $\nu_{0 \rightarrow 1}$ is resonant. However, a clear elongation of positive and negative bands along the whole ω_{pump} axis is present for 10 and 100 ps, which correspond to the bands observed in the pump-probe spectra of 2 and 10 nm **Pt-CO** (Fig. 1c and d) at longer times. Their presence for all excitation energies shows that the long-lived signals are due to an

off-resonant effect.

To investigate the off-resonant component in more detail, the dominant T_1 relaxation contribution must be excluded. We achieve this by performing off-resonant IR pump-probe experiments with a pump frequency (1650 cm^{-1}) significantly below the **Pt-CO** resonance. Fig. 4 shows the transient spectra of 2 and 10 nm **Pt-CO** obtained in this way. The pump-probe spectra display negative bands around the initial $\nu_{0 \rightarrow 1}$ frequency and positive bands on the lower frequency side, resembling the resonant spectra's features of Fig. 1c,d at longer delay times. Off-resonant excitation of 0.2 nm **Pt-CO** did not show any transient signal in its pump-probe spectrum (see Fig. S4 in SI), in accordance with the observation that no longer-lived signals are present after resonant pumping in this case (Fig. 1b).

The IR absorption measurement of a 0.2 nm Pt layer without CO shows no IR absorption, due to the fact that the layer is macroscopically non-conductive, while there is very broad metallic absorption for 2 and 10 nm Pt

FIG. 4. Corrected IR pump-probe spectra of (a) 2 nm and (b) 10 nm **Pt-CO** excited off-resonantly at 1650 cm^{-1} . Metal offsets were subtracted before applying the correction scheme. + and × symbols show the pixels that are considered for the integration of the positive and negative bands, respectively.

layers (see Fig. S5 in SI). The latter will, of course, absorb light at 1650 cm^{-1} . All these observations hint towards metal heating being the origin of the transient response of 2 and 10 nm **Pt-CO** after non-resonant pumping.

In this regard, we consider the positive band as the appearance of a red-shifted $\nu_{0\rightarrow 1}$ band, without direct excitation of the CO internal stretch vibration. Earlier works have explained this red-shift by anharmonic coupling to thermally excited lower-frequency modes;^{32–34} presumably the frustrated rotation at $\nu_{rot} = 411\text{ cm}^{-1}$ and/or the frustrated translation $\nu_{tr} = 60\text{ cm}^{-1}$.^{8,33,35} The transient spectra we present here are difference spectra and can be considered as the combination of a time-independent bleach signal before excitation and a time-dependent positive signal that emerges after excitation. As the frequency shift is small compared to the line-width of the absorption band, the amplitude of transient signal is proportional to the frequency shift, and is a measure of the temperature of the adsorbed CO molecule. It is important to keep in mind that the signal sizes cannot be used as absolute measures of temperature when comparing 2 nm **Pt-CO** and 10 nm **Pt-CO**, since the surface coverage might be different, and signal enhancement has been shown to depend on layer thickness as well.¹⁸

V. TRANSIENT CO DESORPTION

A closer analysis of Fig. 4 reveal that there is more to it. To that end, Fig. 5 shows the time dependence of the negative and positive bands, by examining the integrated areas (in order to suppress effects of changing lineshapes). The intensities of the negative and positive bands are expected to be the same, if the effect were

FIG. 5. Normalized temporal evolutions of the negative (blue) and positive (red) bands of 2 nm (left panels, a,b) and 10 nm (right panels, c,d) **Pt-CO** after off-resonantly pumping at 1650 cm^{-1} (top panels, a,c) and 3100 cm^{-1} (bottom panels, b,d). The full data behind the bottom panels are shown in Fig. S6 in SI.

only a frequency shift of the $\nu_{0\rightarrow 1}$ band. The intensities initially rise in parallel, peak at about 1 ps, and subsequently decrease again. At about 10 ps, however, the negative signal (shown in blue) stops decaying and remains almost constant for $\sim 40\text{ ps}$, while the positive band (red) continues to decay. This suggests that the band's recovery is retarded by another bleaching process. Qualitatively the same response is obtained regardless whether the pump frequency is 1650 cm^{-1} (Fig. 5, top panels) or 3100 cm^{-1} (Fig. 5, bottom panels), and for

FIG. 6. The two-temperature model the temperatures of the electronic (T_{el}) and phonon (T_{ph}) heat baths, both of which couple to the adsorbate, whose temperature is T_{ad} . $g_{el,ph}$ is the electron-phonon coupling constant, and $\eta_{el,ad}$ and $\eta_{ph,ad}$ are the coupling constants from the electron and phonon systems, respectively, to the adsorbate molecules.

both 2 nm **Pt-CO** (Fig. 5, left panels) as well 10 nm **Pt-CO** (Fig. 5, right panels), with the retardation time being somewhat longer in the second case. In addition, negative and positive bands don't evolve completely identically even at early times for 10 nm **Pt-CO**, which we attribute to the stronger broadening of the positive band in this case (see Fig. 4b), an effect that is not completely suppressed by integrating the areas.

The only plausible explanation for the bleaching of the internal stretch band is CO desorption and re-adsorption. That is, the absorption frequency of free CO in water is outside the spectral window of Fig. 4, and in addition, its absorption cross section is minuscule, hence the signal of desorbed CO disappears. Comparing the size of the transient signal with that of the steady-state absorbance of 2 nm **Pt-CO**, we estimated that about 0.3% of molecules desorb transiently.

Desorption of CO molecules from metal surfaces has been observed before, considering single-crystal surfaces in the gas-phase and with high pump fluences.^{9,12,33,36-42} These experiments are typically discussed in the context of the well-known two-temperature model of metal surfaces after laser excitation (Fig. 6):^{3,43} (i) Upon laser excitation, a nascent electron distribution is generated, (ii) which rapidly thermalizes by electron-electron scattering on a 100 fs timescale. The initial electronic temperature T_{el} can be very high, since the electronic heat capacity C_{el} is small.³ The excited electrons then couple to the phonons on a somewhat slower timescale of a few picoseconds, increasing the phonon temperature T_{ph} .^{8,44} In addition to the two-temperature model, Fig. 6 considers the temperature T_{ad} of the adsorbate molecules, which are coupled to both the electron and the phonon system. The system is described by the following set of

equations:^{3,8,9,41,43,44}

$$\begin{aligned} C_{el} \frac{\partial T_{el}}{\partial t} &= \frac{\partial}{\partial z} \left[k_{el} \frac{\partial T_{el}}{\partial z} \right] - g_{el,ph}(T_{el} - T_{ph}) + S(z, t) \\ C_{ph} \frac{\partial T_{ph}}{\partial t} &= g_{el,ph}(T_{el} - T_{ph}) \\ \frac{\partial T_{ad}}{\partial t} &= \eta_{el,ad}(T_{el} - T_{ad}) + \eta_{ph,ad}(T_{ph} - T_{ad}), \end{aligned} \quad (1)$$

where C_{el} and C_{ph} are the heat capacities of electrons and phonons, respectively, k_{el} a heat diffusion constant, $g_{el,ph}$ the electron-phonon coupling constant, and $\eta_{el,ad}$ and $\eta_{ph,ad}$ coupling constants from the electron and phonon systems, respectively, to the adsorbate molecules (we don't expect that $\eta_{el,ad}$ is one-to-one related to the coupling giving rise to the Fano-lineshapes).

$S(z, t)$ is a source term:

$$S(z, t) = F(1 - R) \frac{\exp \left[-\frac{z}{\alpha} - \left(\frac{t}{\tau_p} \right)^2 \right]}{\sqrt{\pi} \tau_p \alpha}, \quad (2)$$

where F is the pump laser fluence, R the reflectivity of the Pt-layer, α the penetration depth, and τ_p the pulse duration. Since the electronic heat capacity:⁴⁵

$$C_{el} = \gamma T_{el}. \quad (3)$$

as well as the heat diffusion constant:^{3,43}

$$k_{el} = k_0 \frac{T_{el}}{T_{ph}} \quad (4)$$

depend on electron and/or phonon temperatures, the set of equations Eq. 1 is nonlinear and has to be solved numerically (see Fig. 7).

The initial electronic temperature and final phonon temperature are cornerstones of the subsequent arguments, and can be calculated analytically and independently from Eq. 1. From Eq. 3 and $C_{el} = \partial U_{el} / \partial T_{el}$ (with U_{el} the internal energy of the electron system), we obtain by integration:

$$T_{el} \approx \sqrt{\frac{2F_{abs}}{d \cdot \gamma}}. \quad (5)$$

where F_{abs} is the fluence of absorbed light (the absorbance and reflectivity have been deduced from Fig. S5), and d the thickness of the Pt layer. The energy contribution from room temperature (T_0) can be neglected due to the small heat capacity at T_0 . With an electronic heat capacity constant $\gamma = 750 \text{ J m}^{-3} \text{ K}^{-2}$,⁴⁵ we estimated initial electronic temperatures of 1910 K and 1540 K for the 2 nm and 10 nm Pt layers, respectively.

For the phonon temperature T_{ph} after equilibration with the electron system, we assume that the phonon heat capacity C_{ph} is essentially temperature independent (since the Debye temperature of Pt is below room temperature), in which case we obtain:

$$T_{ph} \approx \frac{F_{abs}}{d \cdot C_{ph}} + T_0 \quad (6)$$

We can now neglect the contribution of the electron bath, as its heat capacity C_{el} is small at the lower temperature reached after electron-phonon thermalisation. With $C_{ph} = 2.8 \cdot 10^6 \text{ J m}^{-3} \text{ K}^{-2}$,⁴⁶ we estimated temperatures of 790 K and 620 K for the 2 nm and 10 nm Pt layers, respectively. In either case, these temperatures are well above the gas phase desorption temperature (400 K) of Pt-CO.^{47,48}

With these numbers in mind, we return to the experimental results. In essence, we perform a temperature-jump experiment,⁵⁰ and think of the response of the positive band shown in red in Fig. 5 as a molecular thermometer. The signal peaks at about 1 ps, which determines the response time of that thermometer. That timescale is faster than what is typically known for electron-phonon coupling,⁴⁶ hence it seems that the thermometer measures both electronic and phononic temperature. In fact, the peak of the adsorbate temperature at 1 ps can be reproduced from model Eq. 1 when setting $\eta_{el,ad} = \eta_{ph,ad} = 2 \cdot 10^{12} \text{ s}^{-1}$, see magenta line in Fig. 7a. The electronic temperature then drops within the first few picoseconds due to the coupling to the phonon system (see Fig. 7a), and on a longer 100 ps timescale, since the thin Pt film is in thermal contact with the solvent and the substrate (which is not included in the model Eq. 1).

CO adsorbed to Pt vs CO in solution are in chemical equilibrium, and heating the surface shifts that equilibrium towards the desorbed state. A certain fraction of molecules will consequently desorb on a somewhat retarded timescale, which reflects the kinetics of that equilibrium. The time window, in which the temperature jump is large enough to desorb CO molecules, is about 40 ps (in the case of the 2 nm film, see left panels in Fig. 5). The temperature of the Pt film then drops below a certain threshold, and CO molecules start to re-adsorb. About 30% of the desorbed CO molecules re-adsorb within 100 ps, the time window of our experiment. This is too fast to be explained by re-adsorption from the bulk solvent. Unlike in UHV conditions³³ where the desorbed CO molecules can escape from the surface ballistically, most will be trapped in solution by a solvent cage, and thus re-adsorb to the surface by geminate recombination,⁵¹ explaining the fast timescale of re-adsorption. In the case of the 10 nm film (see Fig. 5, right panels), the temperature jump lasts a little longer, since the surface-volume ratio is smaller and hence cooling into the solvent is slower.

One can think of three scenarios for CO desorption, all of which have been discussed in literature. The first scenario involves the population of the $2\pi_a^*$ antibonding orbitals of the CO molecule from nascent electrons of the metal before electronic thermalisation of the latter. It is a non-thermal scenario, and the excitation wavelength determines the distribution of nascent electrons.⁵² The $2\pi_a^*$ antibonding orbitals of the CO molecule lie 4.2-4.5 eV above the Fermi level of Pt.^{53,54} However, the time-scale of electronic thermalisation is very fast (100 fs), and there

seems to be an increasing consensus in the literature that this mechanism probably plays no role.³ In our case, with a photon energy of only 0.2 eV (1650 cm^{-1}), this scenario is completely out of question.

The second scenario is thermal-electronic after electronic thermalisation of the electrons of the metal. Depending on the electronic temperatures reached, there will be a certain fraction of hot electrons described by a Fermi-Dirac distribution, whose energy might be higher than the photon energy, and may thus reach the $2\pi_a^*$ antibonding orbitals, even if the photon energy is below (e.g. 400 nm or 800 nm). The third scenario is a phonon-mediated process and is related to the conventional picture of thermal desorption by heating, where vibrational energy is transferred to a desorption coordinate.³⁸ The vibrational temperature of the adsorbate T_{ad} is coupled to electron as well as the phonon temperature (see Fig. 6), and both might contribute.

With the electron temperatures we estimated from Eq. 5 ($1910 \text{ K} \triangleq 0.16 \text{ eV}$), the Boltzmann factor for the second scenario $\exp(-E_{2\pi_a^*}/k_B T) = 4 \cdot 10^{-12}$ seems to be too small for the this mechanism to be of any relevance in our case. The phonon temperature is smaller, but the temperature jump lasts longer, and more importantly, the activation energy in this case is on the electronic ground state of the CO molecule and thus will be significantly lower. We conclude that the third scenario is probably the one we have to consider here.

Nonetheless it is important to stress that the excitation wavelength plays only a minor role in the second and third scenario, both of which are thermal, i.e., via the absorption coefficient of the electron system, which is slightly wavelength dependent. The dominating factor is the fluence of absorbed light, irrespective of its wavelength, as it determines electron and phonon temperatures (see Eqs. 5 and 6). Pt absorbs light all the way from the IR spectral range up to its plasma frequency in the UV with very high absorption coefficients. We therefore think that there is no conceptual difference between our experiment, pumping at 1650 cm^{-1} or 3100 cm^{-1} , and those that used 800 nm or 400 nm pulses to pump the metal surface^{9,12,33,41}.

There are however differences in detail, which we attribute to the very thin Pt layers considered here, as well as the fact that we performed the experiments in water instead of vacuum. First, we deduced from Fig. S5 a penetration depth of $\alpha_{film} = 8 \text{ nm}$ at 1650 cm^{-1} , in contrast to $\alpha_{bulk} = 20 \text{ nm}$ for bulk Pt.⁵⁵ We assume that the smaller penetration depth is related to the partially plasmonic character of our rough metal layers.

Second, there is no loss of energy into the bulk in the case of thin metal films. The common two-temperature model includes a term for diffusion of electronic temperature (see Eq. 1), with a heat diffusion constant that depends on both electron and phonon temperature (Eq. 4).^{3,43} Initially, at a high electronic and low phonon temperature, heat diffusion is very efficient. By numerical integration of Eq. 1, we find that the elec-

FIG. 7. Temperatures of the electrons (T_{el}), phonons (T_{ph} , green) and adsorbate (T_{ad} , magenta) calculated from Eq. 1 for (a) 10 nm and (b) 100 nm Pt layer. Electronic temperatures are calculated for the surface ($z=0$ nm, red) and the back ($z=10$ or 100 nm, blue) of the layer. The parameters used in these simulations are: $T_0=300$ K, $\gamma=750 \text{ Jm}^{-3}\text{K}^{-2}$,⁴⁵ $C_{ph} = 2.8 \cdot 10^6 \text{ Jm}^{-3}\text{K}^{-2}$,⁴⁶ $k_0 = 68 \text{ Wm}^{-1}\text{K}^{-1}$,⁴⁹ $g_{el,ph}=2.5 \cdot 10^{17} \text{ Wm}^{-3}\text{K}^{-1}$,⁴⁶ $\eta_{el,ad} = \eta_{ph,ad} = 2 \cdot 10^{12} \text{ s}^{-1}$, $\tau_p=80$ fs, $F=14 \text{ Jm}^{-2}$, $R=0.11$, and $\alpha = 8$ nm (the latter two values have been determined from Fig. S5, see SI for details).

tronic temperature homogenizes on a 100 fs timescale within a 10 nm Pt film, see Fig. 7a, and even faster for the 2 nm film. For these thin films, one could in fact ignore z -diffusion in Eq. 1, and Eqs. 5 and 6 are sufficient to estimate the relevant temperatures. This is no longer the case for thicker layers, and owing to the very nonlinear character of heat diffusion (Eqs. 3 and 4), the situation changes very quickly as the layer becomes thicker. Already a layer of 100 nm can be considered bulk with essentially no heating at the back side of the film (blue line in Fig. 7b). Nonetheless, the surface temperature $T_{ph,bulk}=400$ K is significantly lower after electron-phonon thermalisation (Fig. 7b), as compared to $T_{ph,film}=620$ K for the 10 nm film (Fig. 7a). Both factors, the shorter penetration depth and the lack of energy loss into the bulk, compensate for significantly lower pump fluence we used here (14 J/m^2) as compared to typical gas phase experiments.

Finally, Fig. 8 shows the pump fluence dependence of the effect. Both the peak signal and the amplitude of the retarded signal, i.e., the fraction of desorbed molecules, scale in essence linearly with pump fluence. To see that, we compare the red and black data in Fig. 8, where the latter is lower-fluence data scaled up by the ratio of pump fluences. The linear dependence is in sharp discrepancy to gas phase experiments, where a very nonlinear pump fluence dependence is typically observed, indicating that desorption is a thermally activated process.⁴¹ We attribute the linear pump fluence dependence to the fact that CO desorption and re-adsorption are chemical equilibrium processes in solution phase, in contrast to the gas phase. In that case, the surface coverage is described by a “Temkin adsorption isotherm” with a linear dependence on temperature in equilibrium, owing to the repulsive interaction of adsorbed CO molecules among each other.⁵⁶ The desorption yield is small (0.3%), despite the sizeable temperature jumps we induce (Fig. 7a), indicating that the system does not really equilibrate during the short

FIG. 8. Temporal evolutions of the negative band of 10 nm **Pt-CO** after off-resonantly pumping at 3100 cm^{-1} in dependence of pump fluence: red for 21 J/m^2 and blue for 10 J/m^2 . The black symbols show the 10 J/m^2 data up-scaled by a factor 2.1 to facilitate a better comparison.

time window given by the cooling of the metal layer into the solvent and the substrate. Nevertheless, this consideration shows that there can be a qualitative difference in mechanism when comparing solution with gas phase experiments. It will be interesting to investigate the pump fluence dependence of CO desorption in more depth.

VI. CONCLUSION

In conclusion, we have investigated the vibrational dynamics of CO adsorbed on 2, and 10 nm heterogeneous Pt surfaces by IR pump-probe spectroscopy. The inherent line shape distortions for such plasmonic layers have been corrected, which enabled the comparison of

these thicker layers with the previously studied ultrathin ones. First, we have observed the expected vibrational relaxation to electron-hole-pairs for all samples by using resonant IR excitation, giving similar time constants to the ultrathin layers. On the other hand, off-resonant IR pump-probe experiments allowed us to observe transient frequency shifts due to anharmonic coupling of the C-O internal stretch mode with the low-frequency modes induced by the heating of the metal layer. Besides the heat dissipation to the low-frequency modes, we have observed desorption of CO. The thin Pt layers we used in the present experiments facilitate CO desorption, despite the low pump pulse fluence, as they concentrated the absorbed energy in a small volume. Apart from such subtle differences, however, there is no fundamental difference between pumping in the mid-IR vs pumping at 800 nm or 400 nm, since the only quantity that determines electronic and/or phononic temperature is the fluence of absorbed light, irrespective of the wavelength of the excitation light.

Supporting Information: Spectra of pump pulses,

raw pump-probe spectra, line-shape distorted and corrected IR absorption spectra, off-resonant pump-probe response of the 0.2 nm **Pt-CO**, IR absorption spectra of the bare films, as well as the off-resonant pump-probe results after 3100 cm⁻¹ pumping are shown as Figs S1-S6), respectively.

Data availability statement The data used in this article have been deposited on Zenodo (the link will be added at the proof stage)

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