Ultrafast vibrational spectroscopy at surfaces deciphered

D. Novko, J. C. Tremblay, M. Alducin, J.I. Juaristi

1Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Bijenička 46, 10000 Zagreb, Croatia
2Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain
3Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
4Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain
5Departamento de Física de Materiales, Facultad de Químicas UPV/EHU, Apartado 1072, 20080 Donostia-San Sebastián, Spain

*To whom correspondence should be addressed; E-mail: dino.novko@gmail.com

Time-resolved vibrational spectroscopy constitutes an invaluable experimental tool for monitoring hot-carrier induced surface reactions. However, the absence of a full understanding on the precise microscopic mechanisms causing the transient spectral changes has been limiting its applicability. Here we introduce the first robust theoretical framework that successfully explains both the nonthermal frequency and linewidth changes of the CO internal stretch mode on Cu(100) induced by femtosecond laser pulses. Two distinct processes engender the changes: the nonadiabatic coupling underlies the nonthermal frequency shifts, while electron-mediated vibrational mode coupling gives rise
to linewidth changes. Furthermore, the origin and precise sequence of coupling events are finally identified. Its *ab initio* nature confers to the new theory a unique predictive character, heralding a new era in ultrafast vibrational spectroscopy at metallic substrates.

**One Sentence Summary:** An atomistic *ab initio* theory of time-resolved vibrational spectroscopy unveils the subpicosecond nonadiabatic coupling mechanisms of adsorbates on metals

One of the ultimate goals in surface science is to comprehend the fundamental processes that bring about the specific time scales of surface reactions (1–3). To acquire such a time-resolved insight, numerous experiments have studied the ultrafast elementary motions of adsorbates on metal surfaces by means of time-dependent techniques, including vibrational motion (4–6), molecular desorption (7–11), diffusion (12, 13), and dissociation (14). In these experiments, the transient condition achieved by the use of intense femtosecond laser pulses genders the energy exchange mechanisms between the laser-excited surface electrons and the vibrational modes of the adsorbates and surface lattice.

In time-resolved infrared (IR) spectroscopy experiments, the initial adsorbate dynamics commenced by the pump pulse is directly probed by tracking the frequency shift and linewidth changes of the IR-active internal stretch (IS) mode. In all adsorbate-surface systems investigated thus far [e.g., CO/Ru(001) (10), NO/Ir(111) (14), CO/Pt(111) (6, 15), CO/Cu(100) (11)], the IS frequency mode exhibits an initial redshift followed by a rapid blueshift. However, the origin of such a characteristic behavior is still a matter of controversy. It is either ascribed to anharmonic coupling with other low-energy (LE) modes (10, 16, 17), or additionally to energy transfer from the laser-excited hot electrons to the adsorbate motion via nonadiabatic coupling (NC) (6, 11, 14, 18). This lack of consensus effectively prevents us from harnessing the full
potential of time-resolved vibrational spectroscopy, as well as from extracting the information about subpicosecond dynamics of surface reactions buried within.

As demonstrated here, this limitation is solved using a recently developed approach based on many-body perturbation theory. Our first-principles formalism accounts for electron-phonon coupling processes up to second order, including the aforementioned NC as well as vibrational intermode coupling due to the indirect interaction with hot electrons. This so-called “electron-mediated phonon-phonon coupling” (EMPPC) allows the interaction of phonons with incommensurate frequencies, even in the absence of direct anharmonic coupling (19). Our theoretical framework is here applied to investigate the early stage dynamics of nonthermal CO adsorbates on Cu(100). This system, which is considered as the benchmark system for electron-induced dynamics at surfaces, has recently been monitored with time-resolved sum-frequency generation spectroscopy with unprecedented subpicosecond resolution (11). The results show that our quantitative and predictive theoretical method is finally able to unveil the microscopic processes behind the reported nonthermal frequency shifts and the accompanying linewidth changes, while also establishes the specific sequence and strength of the nonadiabatic and intermode coupling mechanisms involved. More specifically, we show that the coupling mechanisms behind the transient frequency and linewidth changes are in fact different. The first-order NC contribution describing nonthermal charge transfer dominates the frequency shifts and acts rapidly. In contrast, linewidth changes are mostly due to EMPPC, which operates on longer timescales, up to tens of picoseconds. Furthermore, the explicit sequence of events affecting the transient adsorbate motion are unambiguously identified and quantified from our calculations, as illustrated in Fig. 1. On the subpicosecond timescale, the coherent IS phonon mode (probed by the IR light) is strongly coupled to the thermally-activated incoherent IS phonon modes. Here, coherent and incoherent refer to the in-phase ($q = 0$) IS phonon mode and to the incoherent averaging of all IS adsorbate phonon modes with $q > 0$, respectively. After around
1 ps, this coupling weakens and the coherent IS mode couples predominantly to the adsorbate LE modes. Interestingly, energy exchange between the IS mode and surface atom motions is important at all times, due to the sheer number of these modes. These microscopic details provide an unprecedented and quantitative time-resolved insight into the vibrational motion on metal surfaces. Even more, our observations challenge the current belief that only intermode coupling to the LE adsorbate modes are involved in the subpicosecond dynamics upon femtosecond laser excitation (2, 10, 11, 14, 16, 17), while the importance of the surface and incoherent IS motions is generally understated.

Within many-body perturbation theory the phonon frequency renormalization and linewidth due to NC are given in terms of the real and imaginary parts of the phonon self-energy $\pi_\nu(\omega; t)$, i.e., $\omega^2 - \omega^2_\nu = 2\omega_\nu \text{Re} \pi_\nu(\omega; t)$ and $\gamma_\nu = -2\text{Im} \pi_\nu(\omega; t)$, respectively ($\nu$ denotes the IS mode) (20–23). The real part encodes how the C–O interaction and concomitant IS frequency adapt to the environment brought out of equilibrium by the external light source. The imaginary part reveals how the IS mode decays because of inelastic collisions with the system electrons and phonons. In the present work, we consider that the phonon self-energy consists of first- and second-order terms in the electron-phonon coupling, i.e., $\pi_\nu(\omega; t) = \pi_\nu^{[1]}(\omega; t) + \pi_\nu^{[2]}(\omega; t)$ (19, 20). These are simultaneously the dominant interband and intraband contributions, respectively. The former term accounts for electron-hole pair excitation processes (20) including nonthermal charge transfer to unoccupied states (e.g., antibonding CO states). The latter term is responsible for the EMPPC (19). These two features are known to be instrumental for explaining the long wavelength part of the phonon spectrum in metallic bulk systems (21, 23–25). The processes behind $\pi_\nu^{[1]}$ depend on the electron distribution, while $\pi_\nu^{[2]}$ depends on both electron and phonon distributions (19). In our theory, the first and second-order contributions depend indirectly on time via the electron $T_e(t)$ and lattice $T_l(t)$ temperatures describing the excited electron and phonon distributions. These are brought out of equilibrium by coupling with the pump-laser
pulse, and their time evolution is obtained from the two temperature model (TTM) (26, 27). Thus far, the TTM was mostly used to complement molecular dynamics simulation of isolated adsorbates on surfaces and, therefore, only surface motion was included in $T_l(t)$ (28, 29). In our formulation, however, the EMPPC term $\pi^{[2]}_0$ contains information on intermode couplings between the IR-excited IS mode and all other modes in the system. These include the incoherent IS motion, the external stretch (ES) mode, frustrated rotations and translations (FR and FT), as well as surface motion (19). Consequently, $T_l(t)$ represents the total lattice temperature coming from all excited modes in CO/Cu(100) [see (30) for further details]. As an example, Figs. 2(a) and 2(b) show the time evolution of $T_e(t)$ and $T_l(t)$ when the experimental 400 nm pump laser, with 170 J/m$^2$ absorbed fluence and 150 fs duration, heats the surface electrons at 0.3 ps. Altogether, this combination of first principles many-body perturbation theory up to second-order with the TTM that accounts for the time-dependent excited electron and phonon distributions, constitutes a substantial improvement upon state-of-the-art theories, including $ab$ $initio$ first-order vibrational damping rate theories (31–33) and parametric models of pure dephasing mediated by anharmonic coupling (16,17) or electron-hole pair creation (18,34,35).

Figures 2(c) and 2(d) show, respectively, the frequency and linewidth changes of the IS mode, i.e., $\delta\omega_{IS}$ and $\delta\gamma_{IS}$ [see (30)], calculated at various absorbed laser fluences $F$ of the experimental pump laser pulse. The frequencies are characterized by a red shift over the course of the first 0.3 ps, followed by a blue shift. The phonon linewidths increase at short times, reaching their highest values when the frequency redshifts are at the maximum, and decrease at longer times. Also, both $\delta\omega_{IS}$ and $\delta\gamma_{IS}$ are more pronounced as the absorbed fluence becomes more intense. A good example of the remarkable agreement between the calculated $\delta\omega_{IS}$ and the experimental shifts is shown in Fig. 2(e) for the specific absorbed fluence of 170 J/m$^2$ (11). Importantly, the time dependence of both $\delta\omega_{IS}$ and $\delta\gamma_{IS}$ obtained here shows a very close resemblance to results of ultrafast vibrational spectroscopy experiments of other adsorbate-surface systems,
e.g., CO/Ru(001) (10), NO/Ir(111) (14), or CO/Pt(111) (6, 15). Since these nonthermal effects are universal and represent the fingerprint of ultrafast surface vibrational dynamics (2), the applicability of our theory can be extended to a variety of adsorbate-surface systems, and thus, help to elucidate other intriguing surface reactions as well.

In Figs. 2(e) and 2(f) the contributions to $\delta\omega_{IS}$ and $\delta\gamma_{IS}$ arising from the first order NC processes (i.e., $\pi^{[1]}$) and from the EMPPC (i.e., $\pi^{[2]}$) are depicted as blue and orange bars, respectively. Surprisingly, the mechanisms ruling the frequency shift and the lifetime are different. Thus, $\delta\omega_{IS}$ is dominated during the first picosecond by the electron-hole pair excitations, while the EMPPC brings only a small contribution. Conversely, $\delta\gamma_{IS}$ is dominated by the EMPPC mechanism from the onset. At later times, i.e., when $t = 50$ ps and $100$ ps, the EMPPC is the only contributor to both $\delta\omega_{IS}$ and $\delta\gamma_{IS}$ (see also Table[1]). These findings are in contradiction with the usual assumption that both transient frequency and linewidth changes of the IS mode can be explained by means of a single dominating nonthermal mechanism. In particular, the experimental observations are often attributed either to pure dephasing induced by anharmonic coupling between the IS and a single LE mode (10, 16, 17), or to thermally-induced charge transfer from metal occupied states to an antibonding state of the CO adsorbate (14).

Furthermore, since $\pi^{[1]}$ depends on the electron distribution excited by the laser trough $T_e$ and $\pi^{[2]}$ on both the distributions of excited electrons and phonons via $T_e$ and $T_l$, our theory remarks the existence of a direct correlation between nonthermal changes and the time-dependent temperatures. In particular, the NC mechanism contributes to a softening of the IS bond as $T_e$ increases, which causes the observed initial red shift in the IS frequency that decreases in magnitude as $T_e$ starts to decrease. Additionally, the increase in the linewidth due to the NC also follows the changes in $T_e$. In contrast, changes due to the EMPPC are influenced by both temperature effects. The latter manifests in the time dependence of $\delta\gamma_{IS}$ as an increase up to around 0.4 ps, which correlates with $T_e(t)$, followed by a decrease to a finite offset with re-
spect to the original value, which reflects the increase experienced by the lattice temperature in this interval. Stated differently, both the excited electrons and phonons, which are described through $T_e$ and $T_l$ in the many-body response term $\pi^{[2]}$, trigger a similar, positive trend in $\delta \gamma_{\text{IS}}$. Interestingly, these two temperature effects compete in the EMPPC contribution to $\delta \omega_{\text{IS}}$: an increase of $T_e$ induces a blue shift, while an increase of $T_l$ induces a red shift [see (30) for more details]. Transient changes of the IS phonon under nonequilibrium conditions were correlated with the corresponding $T_e$ in CO/Pt(111) (6). However, a complete and quantitative correlation along with a microscopic insight can only be given by matching such experimental data with a first-principles theory including nonthermal NC [i.e., $\pi^{[1]}(T_e)$] and intermode [i.e., $\pi^{[2]}(T_e, T_l)$] couplings, as presented in this work for the first time.

Our theory further allows to resolve the different mode contributions in $\delta \omega_{\text{IS}}$ and $\delta \gamma_{\text{IS}}$ (Table I) at different instants during the thermal equilibration process. Since $\delta \omega_{\text{IS}}$ is mostly dominated by the first order NC term during the time of interest spanned by the experiment, we focus our discussion on the relevant time-resolved intermode couplings responsible for $\delta \gamma_{\text{IS}}$. We select three instants representative of the different thermal conditions reached during the equilibration stage: $t = 0.4 \text{ ps} (T_e \gg T_l \approx 100 \text{ K}), t = 1 \text{ ps} (T_e > T_l > 100 \text{ K}),$ and $t = 50 \text{ ps} (T_e \approx T_l)$. At the onset of nonthermal vibrational dynamics, the EMPPC mechanism is mostly prompted by the nonequilibrium electron distribution, since $T_e \gg T_l$. During that period, the prevailing mode coupling is between the probed (coherent) IS mode and the incoherent IS modes. We dub this mechanism “intramode coupling”. This unexpected result is due to a much rapid increase of the electron-mediated IS-IS coupling strength with the rise of $T_e$, when compared to other molecular intermode coupling strengths [cf. (30)]. In other words, when $T_e \gg T_l$ the small energy gap of around 10 meV that exists between coherent and incoherent IS modes (19) is efficiently compensated by the broad distribution of hyperthermal electrons, leading to a strong electron-mediated IS-IS scattering. When $T_e > T_l > 100 \text{ K} (t \approx 1 \text{ ps})$, but also when the sys-
tem is almost thermalized \((t \gg 1 \text{ ps})\), the time-dependent EMPPC processes arise prevalently from the thermal excitation of the LE modes. In particular, the FR and FT modes are found to be the major contributors to the nonthermal changes. Aside from the molecular modes, the remaining Cu surface motions are also crucial for describing \(\delta \gamma_{\text{IS}}\). Once the electron-mediated IS-Cu mode coupling mechanism has been activated, it remains active until the final equilibration. This originates from the abundance of surface Cu modes at low energy that are easily excited by heat.

This work explains thus far unresolved intricacies of nonadiabatic and intermode couplings at surfaces under nonequilibrium conditions. Contrary to the common understanding, the CO internal stretch mode undergoes different mode coupling mechanisms on the subpicosecond and the picosecond timescales. Equally intriguing, transient frequency shifts turned out to be underlain by electron-hole pair excitations, while linewidth changes are mostly governed by the electron-mediated phonon-phonon coupling. This implies that the C–O interaction, which is in the end responsible for the IS frequency, is more sensitive to the transient excitations created in the electronic system, while it is the coupling to the excited phonon modes that contributes more to the IS linewidth. All in all, the presented theory is destined to be the theoretical counterpart in future vibrational spectroscopy investigations. The time-resolved nanoscopic insights that this theory can provide not only are fundamental to the development of vibrational spectroscopy at surfaces, but additionally to advance in our goal of controlling surface reactions at the molecular level.

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Supplementary materials

Materials and Methods
Figs. S1 to S5
Table S1
References (36-50)

Fig. 1. Time-resolved microscopic details behind the hot-carrier induced vibrational motion of CO on Cu(100). In the simulated time-resolved sum frequency generation (TR-SFR) spectroscopy experiment, the coherent IS phonon mode is indirectly probed in time domain, while starting at $t = 0.3\text{ ps}$ the UV pump laser efficiently excites the electronic system up to temperatures as elevated as 6000 K. The so-created hot electrons/carriers subsequently couple and excite the CO/Cu(100) phonon system from the initial 100 K to about 400 K. An example of the time evolution followed by the electron and phonon temperatures is plotted in the middle panel. Left panels show the electron and phonon density of states (DOS) at $t = 0.4\text{ ps}$ (bot-
tom) and \( t = 10 \) ps (top). Orange curves delimit the electron and phonon distributions for the corresponding temperatures reached at each \( t \). The time evolution of the hot-carrier induced CO dynamics is depicted in the right panels. The corresponding nonequilibrium state \((T_e \gg T_i)\) promotes several intriguing surface processes. First order NC process, which includes nonthermal charge transfer to CO states, is active between around 0.3 and 0.6 ps (blue frame). The electron-mediated vibrational mode coupling EMPP starts at around 0.3 ps and operates until equilibration (green frame). Specifically, the probed (coherent) IS phonon mode couples via electron-hole pairs to incoherent IS modes between approximately 0.3 and 1.0 ps. Afterwards, electron-mediated intermode coupling among the coherent IS mode and low-energy modes prevails. The IS mode is strongly coupled to surface modes at all times.

**Fig. 2. Transient changes in the CO/Cu(100) system induced by 400 nm pump laser pulses with 150 fs duration.** (a) Electron \( T_e(t) \) and (b) lattice \( T_l(t) \) temperatures as a function of time for an absorbed fluence \( F = 170 \text{J/m}^2 \). Initial temperature is 100 K. Time-dependent (c) frequency and (d) linewidth changes of the IS mode under nonthermal condition induced by the UV pump at \( t = 0.3 \) ps. Blue, orange, and green represent the results for different \( F \). Panels (e) and (f) depict the contribution-resolved analysis of frequency and linewidth changes when \( F = 170 \text{J/m}^2 \). Blue represents the contribution coming from the first order NC term, orange shows the EMPPPC contribution, while gray circles are the sums of the two. Light blue and magenta points show the corresponding results for \( t = 50 \) ps and 100 ps, respectively. Green squares are experimental frequency shifts obtained from Refs. (11).

**Table 1. Quantitative analysis of transient changes.** Contribution- and mode-resolved analyses of the IS mode nonthermal frequency \( \delta \omega_{IS} \) and linewidth \( \delta \gamma_{IS} \) changes are shown for several snapshots when \( F = 170 \text{J/m}^2 \). The upper part of the table resolves the contributions associated with the first order NC term \( \pi^{[1]} \) (electron-hole pair excitations) and the EMPPPC term \( \pi^{[2]} \). In the bottom part of the table, the EMPPPC term is further separated in its mode-resolved
contributions, including intermode coupling between the coherent (in-phase) IS mode and the incoherent IS, ES, FR, FT and Cu modes of the system. All reported frequency shifts and linewidth changes are in cm$^{-1}$.

**Table 1:**

|       | $t = 0.4\text{ ps}$ | $t = 1\text{ ps}$ | $t = 50\text{ ps}$ |
|-------|---------------------|-------------------|-------------------|
|       | $\delta\omega_{\text{IS}}$ | $\delta\gamma_{\text{IS}}$ | $\delta\omega_{\text{IS}}$ | $\delta\gamma_{\text{IS}}$ | $\delta\omega_{\text{IS}}$ | $\delta\gamma_{\text{IS}}$ |
| $\pi^{[1]}$ | -12.27 | 2.40 | -2.75 | 0.18 | -0.16 | -0.01 |
| $\pi^{[2]}$ | 0.88 | 10.76 | -0.69 | 3.48 | -0.62 | 2.30 |
| IS     | 0.19 | 3.03 | 0.02 | 0.20 | 0.00 | 0.03 |
| ES     | 0.06 | 0.22 | 0.01 | 0.04 | 0.00 | 0.02 |
| FR     | 0.03 | 0.91 | -0.13 | 0.68 | -0.15 | 0.39 |
| FT     | 0.00 | 0.75 | -0.14 | 0.72 | -0.15 | 0.44 |
| Cu     | 0.60 | 5.85 | -0.45 | 1.84 | -0.32 | 1.42 |

Figure 1:
Figure 2: