Anomalous transient blueshift in the internal stretch mode of CO/Pd(111)

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In time-resolved pump-probe vibrational spectroscopy the internal stretch mode of polar molecules is utilized as a key observable to characterize the ultrafast dynamics of adsorbates on surfaces. The adsorbates non-adiabatic intermode couplings are the commonly accepted mechanisms behind the observed transient frequency shifts. Here, we study the CO/Pd(111) system with a robust theoretical framework that includes electron-hole pair excitations and electron-mediated coupling between the vibrational modes. A mechanism is revealed that screens the electron-phonon interaction and originates a blueshift under ultrafast non-equilibrium conditions. The results are explained in terms of the abrupt change in the density of states around the Fermi level, and are instrumental for understanding dynamics at multi-component surfaces involving localized and standard s or p states.

The use of intense femtosecond laser pulses opened a new and efficient pathway to initiate reactions at surfaces. The interplay between laser induced hot electrons and the nuclear degrees of freedom offers the possibility of activating the adsorbates dynamics within the subpicosecond timescale. As such, femtosecond laser pulses have extensively been used to trigger diverse electronic processes like adsorbates desorption [1, 2], diffusion [3], and different chemical reactions [4, 5]. The main challenge is to understand how the highly excited electrons couple to the adsorbates dynamics and how this energy flows into the different vibrational modes.

Femtosecond pump-probe vibrational spectroscopy permits tracking in time domain the adsorbates dynamics initiated by the pump laser pulse with unprecedented time-resolution [6]. The internal stretch (IS) vibrational mode of dipolar adsorbates, having a very distinct frequency, appears as the good observable to be followed over the reaction coordinate [7, 8]. Several experiments have been made on Ru, Ir, Pt and Cu surfaces including different coverages of CO and NO molecules [8–15]. In all those cases, the IS mode frequency exhibits a fast redshift, followed by a slower recovery in the time scale of picoseconds. The frequency shifts are explained within the widely established models in terms of couplings to the low energy CO modes and possible changes in the adsorption site. In both cases, it is the increasing and decreasing population of the CO antibonding $2\pi^*$ that is thought to cause the weakening and strengthening of the IS mode, respectively. An important assumption in these models is that the IS mode only brings information on the adsorbates dynamics. However, there are examples showing that there might be other factors contributing to the transient frequency changes. This is the case of the blueshift observed in the rather more complex system formed by CO molecules coordinated to ruthenium tetraphenylporphyrin on a Cu(110) surface [16], which neither the intermode couplings nor the adsorption site changes are able to explain.

In this Letter we study the ultrafast transient dynamics of 0.5 ML of CO on the Pd(111) surface, using the theoretical framework of Ref. [17] that correctly reproduced the experimental ultrafast time-resolved vibrational spectra of CO on Cu(100) [15]. Our calculations predict an unusual blueshift occurring within the subpicosecond time scale that is not related to the commonly accepted intermode coupling, but to the peculiar properties of the surface electronic structure. In solids, the electron-phonon scattering strength is expected to increase with the electronic temperature causing a softening in the frequency because more electrons participate in the interaction [18, 19]. This is what explained the subpicosecond redshift in the CO/Cu(100) system [17]. Here we show that the strong reduction of the Pd(111) density of states around the Fermi level can revert this normal behavior at the extreme laser-induced high temperatures. Hence the predicted blueshift of the IS mode brings information on the surface electronic structure rather than the intermode couplings. The present results show that dipolar molecules can serve alternatively as a direct probe of ultrafast electron dynamics of metal surfaces, providing time-dependent chemical potential shifts, structure of density of states, electron temperatures, and coupling strengths.

The transient vibrational spectra of the CO adlayer is calculated, following Ref. [17], in terms of the phonon self-energy expressed up to second-order in the electron-phonon (e-ph) interaction, i.e.,

$$\pi_\lambda(\omega, \mathbf{q}) \approx \pi_\lambda^{[1]}(\omega, \mathbf{q}) + \pi_\lambda^{[2]}(\omega, \mathbf{q}),$$

where $\lambda$, $\omega$, and $\mathbf{q}$ denote the index, energy,
and momentum of the phonon mode, respectively. In the femtosecond pump-probe experiments of interest, the CO molecules are initially prepared with their IS mode vibrating in phase by illuminating them with an IR pulse. Thus, only the \( q = 0 \) excitations are considered.

The expression for the first-order term that exclusively accounts for the electron-hole pair (de)excitations (i.e., the usual nonadiabatic coupling, NC) reads [20],

\[
\pi_1^{[1]}[\omega; T_e(t)] = \sum_{\mu\mu'k,\sigma} \left| g_{\mu'k}(k,0) \right|^2 \frac{f(\epsilon_{\mu'k}) - f(\epsilon_{\mu,k})}{\omega + \epsilon_{\mu'k} - \epsilon_{\mu,k} + i\eta},
\]

where \( \mu, k, \) and \( \epsilon_{\mu,k} \) are the electron band index, momentum, and energy, respectively; \( g_{\mu'k}(k,q) \) are the e-ph matrix elements; and the summation over \( \sigma \) accounts for the spin degree of freedom. The function \( f(\epsilon_{\mu,k}) = 1/(e^{\beta(\epsilon_{\mu,k} - \mu(T_e))} + 1) \) is the Fermi-Dirac distribution function, where \( \beta = 1/(k_BT_e) \), \( k_B \) is the Boltzmann constant, \( T_e \) is the electronic temperature, and \( \mu(T_e) \) is the chemical potential at \( T_e \). Following previous works [20, 21], we fix the broadening parameter to a finite, physically motivated value of 30 meV [22, 23]. As it will soon become apparent, in the above expression not only the e-ph matrix elements, but also the Pd(111) electronic structure are crucial to understand the ultrafast transient dynamics of the CO adlayer. The results obtained in both structural spectroscopy experiments [9–15]. The predicted blueshift occurs within the first hundreds of femtoseconds, reaches a maximum value of \( \approx 3 \text{ cm}^{-1} \), and progressively vanishes giving rise to a late steady redshift of about \( -7 \text{ cm}^{-1} \). The comparison between the time evolution of the transient frequency shift \( \Delta\omega(t) \) and that of the electronic and phononic temperatures, \( T_e(t) \) and \( T_l(t) \) [Fig. 1(a)], suggests that the initial blueshift and subsequent redshift follow \( T_e(t) \) and \( T_l(t) \), respectively.

By analyzing the contribution to \( \Delta\omega(t) \) coming from the first order interband NC term \( \Delta\omega^{[1]}(t) \) and the second-order intraband EMPPC term \( \Delta\omega^{[2]}(t) \) [blue- and orange-dashed lines in Fig. 1(b), respectively], it is evi-
FIG. 1. Transient changes induced in CO/Pd(111) by a 450 nm pump pulse (100-fs duration and absorbed fluence of 40 J/m\(^2\)) that hits the surface at \(t = 0\). The initial temperature is 100 K. (a) Electron \(T_e(t)\) (blue) and lattice \(T_l(t)\) (orange) temperatures calculated with TTM. Inset: top view of the \(c(4 \times 2)-2\text{CO}\) unit cell. (b) Transient frequency shift of the CO IS mode: \(\Delta \omega(t)\) (black solid), \(\Delta \omega^{[1]}(t)\) (blue dashed), and \(\Delta \omega^{[2]}(t)\) (orange dashed). Contributions of the CO and surface phonons to \(\Delta \omega^{[2]}(t)\) are shown by red- and green-dotted lines, respectively.

The above analysis reveals a different mechanism behind the subpicosecond transient blueshift that is correlated to the \(T_e\)-dependence of the nonadiabatic coupling between the IS mode and the laser-induced hot electrons. One naively should expect an enhancement in the e-ph scattering strength as temperature rises. This is what would cause the transient subpicosecond redshift in the CO/Cu(100) system found by both experiments [15] and theory [17]. Thus, the obtained NC blueshift suggesting an effective screening of the e-ph interaction by the hot electrons is somehow anomalous. It must be related to the peculiarities of the CO/Pd(111) electronic structure. Compared to the mentioned CO/Cu(100) system, the presence of the \(d\)-band edge near \(\epsilon_F\) causes a sharp decrease of the CO/Pd(111) density of states (DOS) around the Fermi level [see Fig. 2(a)]. As \(T_e\) increases, the population and depopulation of states above and below \(\mu(T_e)\) compensate each other, assuring conservation of the number of electrons \(N_e\). Thus, the CO/Pd(111) chemical potential shifts to higher energies to counterbalance the strong asymmetry of the DOS around \(\epsilon_F\).

FIG. 2. (a) Electronic DOS of the CO/Pd(111) system. Vertical red dashed line marks the Fermi level. Insets: constant energy cuts of the band structure over the Brillouin zone at \(\epsilon = \mu(T_e)\) for \(T_e = 100\) K (top) and \(T_e = 3000\) K (bottom). (b) Dependence of the chemical potential with the electronic temperature. (c) Change in the real part of \(\chi\) (blue) and in \(\Delta \omega^{[1]}\) (orange) as a function of \(T_e\).
zone in the insets of Fig. 2(a) for \( T_e = 100 \) K (top) and \( T_e = 3000 \) K (bottom). There is an evident reduction of the electronic states that would support the above interpretation of the blueshift as a weakening of the e-ph interaction. The results calculated with \( \mu(T_e) = \varepsilon_F \) further confirm this idea \([33]\).

The dependence of the NC term \( \Delta \omega^{[1]} \) on \( T_e \) is not monotonic. As shown in Fig. 2, \( \Delta \omega^{[1]}(T_e) \) (orange curve, right axis) initially increases with \( T_e \) up to reaching its maximum value at around 4000 K and it starts to decrease, becoming negative at temperatures larger than 7000 K. There are two factors ruling the first-order phonon self-energy \( \pi^{[1]} \) that can affect the temperature dependence of \( \Delta \omega^{[1]} \), the e-ph matrix elements and the electronic structure. To disentangle each contribution, it is useful to evaluate the response function \( \chi(\omega) \) under the constant matrix elements approximation \([36]\), that reads,

\[
\chi(\omega) = \sum_{\mu\sigma} \frac{f(\epsilon_{\mu\sigma}) - f(\epsilon_{\mu\sigma} - i\eta)}{\omega + \epsilon_{\mu\sigma} - \epsilon_{\mu\sigma}^F + i\eta}.
\]

Mathematically, the above expression coincides with setting the e-ph matrix elements to one in the first-order phonon self-energy expression \([cf. \ Eq. (1)]\), allowing us to single out the effect of the electronic structure in the temperature dependence of \( \pi^{[1]}(\omega, T_e) \). Figure 2(c) shows that the change in the real part of the response function (blue, left axis) grows monotonically with \( T_e \) in contrast to the non-monotonous behavior of \( \Delta \omega^{[1]} \). Altogether, these results suggest that the initial blueshift that is observed in the initial stage dynamics of Fig. 1(b) is a direct consequence of the electronic structure. This mechanism competes with the strength of the e-ph coupling that tends to redshift the frequency as \( T_e \) increases. It is only for extreme large electronic temperatures that the latter will dominate the frequency change. Therefore, the next step is to elucidate how the amount of energy that is deposited on the system affects the IS mode dynamics.

We compare in Fig. 3 the results obtained for three different pump laser absorbed fluences: \( F = 6 \) (purple lines), 19 (blue lines), and 40 J/m\(^2\) (green lines). The pulse maximum is at \( t = 0.1 \) ps and the system initial temperature is 100 K. (a) Electron temperature \( T_e(t) \), (b) lattice temperature \( T_l(t) \), and (c) transient frequency shift of the CO IS mode \( \Delta \omega(t) \).

In summary, our calculations reveal that the e-ph interaction can be screened upon femtosecond laser pulse irradiation provided the electronic density of states of the system changes abruptly around the Fermi level. In particular, we study the ultrafast transient dynamics of the internal stretch mode of CO adsorbed on Pd(111). To do so, we combine density functional theory with many-body perturbation theory and evaluate the phonon self-energy up to second order in the e-ph interaction \([17]\). This allows us to characterize the two main mechanisms that participate in the vibrational relaxation of the internal stretch mode: the first order interband non-adiabatic coupling and the intraband electron mediated phonon-phonon coupling. Under current state-of-the-art femtosecond pump-probe experimental conditions, the large transient electronic temperatures that are induced in the femtosecond regime (with \( T_e > T_l \)) give rise to an unconventional blueshift in its frequency. The latter is followed in the picosecond regime by a redshift, larger in magnitude. We show that the initial fast blueshift arises purely from temperature-dependent electronic structure effects,
while the subsequent redshift occurs due to the coupling of the internal stretch mode with other phononic modes. The similarity of the results presented here and those of Ref. [16] suggests that an analogous mechanism might be behind the blueshift that was observed for CO molecules coordinated to Ruthenium tetraphenylporphyrin on a Cu(110), where large planar molecules might introduce localized high-density states close to Fermi level in equivalence to the $d$ states in the present case. Our results are accessible to current experimental setups and we hope they will stimulate further research on the ultrafast dynamics of polar molecules on complex metallic surfaces with localized states.

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