Anomalous transient blue-shift in the internal stretch mode of CO on Pd(111)

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The internal stretch mode (IS) of polar molecules adsorbed on metal surfaces, being decoupled in energy from the rest of vibrational modes of the system, can be monitored during a reaction using state-of-the-art time-resolved vibrational spectroscopy. This gives access to the subpicosecond dynamics occurring at the surface. On the other hand, from the theoretical point of view, these systems appear as an exceptional test-bed in which to benchmark the validity many-body theories with experimental data. Here we study non-adiabatic effects on the internal stretch mode of CO adsorbed on the Pd(111) surface by means of first principles calculations [1].

The theoretical treatment that we employ, including electron-hole pair excitations and electron-mediated coupling between the vibrational modes [3], [4], allows us to study the IS mode under pump-probe experimental conditions. This is achieved by evaluating the phonon self-energy as a sum of first- and second-order terms in the e-ph coupling

$$\pi_\lambda(\omega) = \pi_\lambda^{[1]}(\omega) + \pi_\lambda^{[2]}(\omega), \qquad (1)$$

where $\pi_\lambda^{[1]}$ and $\pi_\lambda^{[2]}$ correspond to dominant inter-band and intra-band contributions, respectively. The first order accounts for nonadiabatic coupling (NC) to electron-hole pairs, while the second order corresponds to the so-called electron mediated phonon-phonon coupling (EMPPC). Within these two mechanisms it has been possible to simulate the conditions that a femtosecond infrared pump pulse generates on the CO/Cu(100) system, obtaining a remarkable agreement between theory and experiment [2], [3], [4].

To simulate the laser–induced nonthermal conditions in the CO/Pd(111) system, electron and phonon distributions are described, respectively, by Fermi-Dirac and Bose-Einstein distributions. These distributions are completely defined by time-dependent electronic $T_e(t)$ and lattice $T_l(t)$ temperatures that are calculated with a two temperature model (TTM) [see Fig. 1(a)]. As it is shown in Fig. 1(b), our calcualtions for the CO/Pd(111) system predict an anomalous transient blue-shift in the internal stretch frequency that is followed in the picosecond regime by a red-shift. From Fig. 1 it becomes evident that the NC (EMPPC) contribution is driven by the changes in the electronic (lattice) temperature. We show that the initial blue-shift arises purely form temperature-dependent electronic structure effects, while the subsequent red-shift occurs due to the coupling to other phonon modes [1].

References

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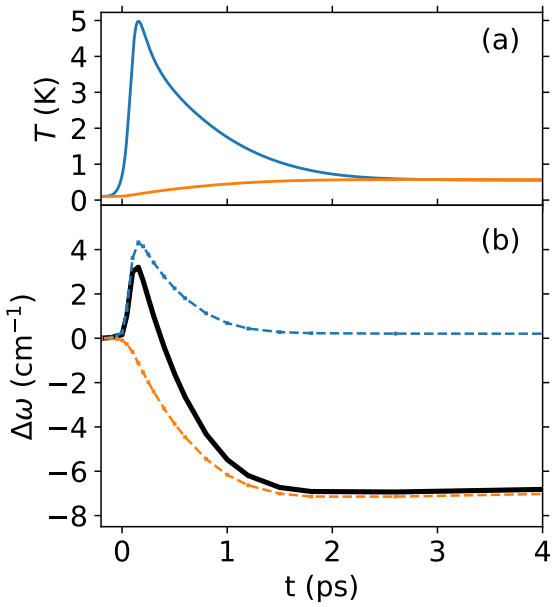

Fig. 1. Transient changes induced in CO/Pd(111) by a 450 nm pump pulse (100-fs duration and absorbed fluence of 40 J/m^2) that hits the surface at $t = 0.1$ ps. The initial temperature is 100 K. (a) Electron $T_e(t)$ (blue) and lattice $T_l(t)$ (orange) temperatures calculated with TTM. (b) Transient frequency shift of the CO IS mode: black line is $\Delta\omega(t)$ and dashed blue and orange lines are the contributions of the NC and EMPPC, respectively.