

## Vibrational Spectroscopy and Dynamics

### Ab Initio Molecular Dynamics Study of CO on NaCl(100): Spectroscopy and Energy Pooling

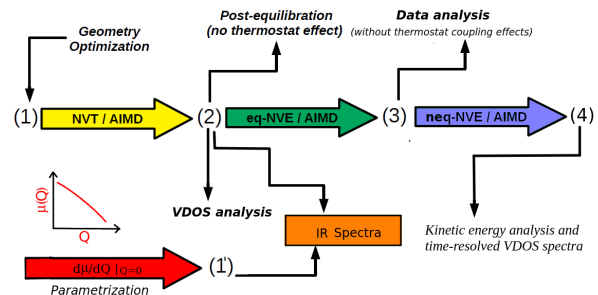
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#### In Short

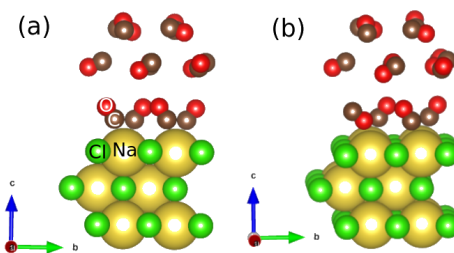
- We combined AIMD with Time-Dependent Correlation Function approach to simulate vibrational density of states, infrared spectra and sum vibrational sum frequency response of different phases of CO/NaCl(100), at different temperatures and coverages including mode coupling, anharmonicities, and finite temperature.
- We studied vibrational energy transfer via non-equilibrium dynamics of pre-excited CO molecules on NaCl(100).
- We want to extend our study to a buried monolayer of CO/NaCl(100) with  $\alpha$ -CO overlayers and look into changes induced by the overlayer in vibrational progressions and processes like vibrational energy transfer and CO flipping on the NaCl surface.
- Producing training and validation data for constructing a machine learned potential for our CO/NaCl(100) system is also one of the objectives of our extended study.

CO on NaCl(100) is an ideal system to study adsorbate-adsorbate interactions, because the C-O stretch vibration on this insulating surface is quite long-lived (in the order of milliseconds) and the dipole-dipole interactions are much stronger compared to the adsorbate-surface interactions. This results in a plethora of interesting phenomena like vibrational energy pooling on laser excitation of the CO adsorbates, Sommerfeld radiowave like interaction between the adsorbates and the NaCl substrate [1], orientational flipping of highly vibrationally excited "C-down" CO and trapping of the "O-down" isomer with overlayers of CO at temperatures as low as 7 K [2]. Moreover, several phases of this system with different relative orientations of the CO molecules on the NaCl (100) surface has been identified experimentally and theoretically [4]. Recently [5], we investigated the adsorption, energetics and isomerisation pathways (C-down to O-down) of CO on NaCl(100) surfaces using different periodic models with the help of DFT (Density Functional Theory) based methods for different phases such as the most stable tilted/antiparallel (T/A) phase, where two CO molecules in one unit cell are tilted with an Na-C-O angle of  $162^\circ$  and are antiparallel to each other as

well as the parallel/upright (P/U) phase. The latter phase is known to be more stable above 35 K and more likely at lower CO coverages.

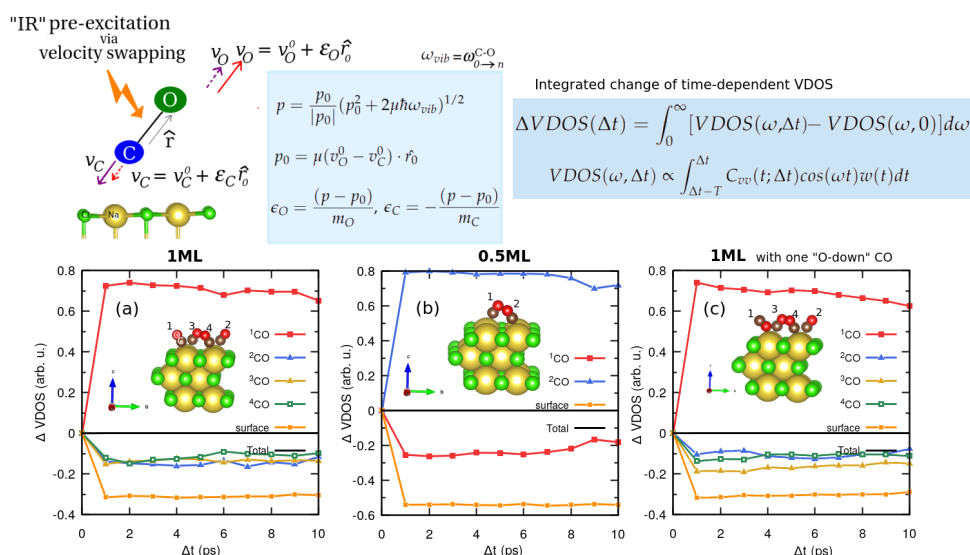


**Figure 1:** Schematic representation of the AIMD protocol used here. eq. and neq. stand for equilibrium and non-equilibrium, respectively.  $\mu(Q)$  is the dipole moment function w.r.t bond coordinate,  $Q$ .



**Figure 2:** Configurations of monolayer tilted/antiparallel (T/A) phase CO on NaCl(100) with (a) all "C-bound" CO (b) one "O-bound" CO, buried with 2 overlayers of  $\alpha$ -CO on top. All configurations in this figure serve as buried monolayer models. Note:  $\alpha$ -CO is the crystal structure of solid-phase bulk CO which is known to have a  $p(2 \times 2)$  structure belonging to the space group  $P2_13$ .

In this study, we employed Ab Initio Molecular Dynamics (AIMD) simulations within the canonical (NVT) and microcanonical (NVE) ensembles in conjunction with Time Dependent Correlation Functions (TDCF) [6], to extract vibrational spectra, which aid in correlating specific spectral signatures to such distinct orientations/structures of the adsorbed CO molecules on the NaCl(100) surface and go beyond the normal mode picture to capture effects like anharmonicities, mode couplings, and finite temperature. A schematic representation of the AIMD approach can be found in Figure 1. In fact, we observed that temperatures as high as 300 K already lead to desorption dynamics in CO adsorbates, giving also a grass of spectral features in the high frequency CO stretch region, compared to low temperature spectra ( $\sim 30$  K).



**Figure 3:** Top: The velocity swapping approach to study non-equilibrium dynamics.  $\hat{r}_0$  is the unit vector parallel to  $r_O - r_C$  and  $\mu$  is the reduced mass of the CO bond.  $v_C^0$  and  $v_O^0$  are the unperturbed velocities. Bottom: (a) Time evolution of the integrated change of VDOS curves from the non-equilibrium NVE AIMD trajectories with one pre-excited CO molecule ( $^1$  CO in all three cases), averaged over three trajectories for (a) 1ML T/A (b) 0.5 ML T/A (c) 1ML T/A with one "O-down" CO of CO/NaCl(100).  $\Delta t=0$  indicates the time at which the pre-excitation occurs. Insets show the starting configurations.

We also modelled the pre-excitation of some CO adsorbates via the velocity-swapping method [7] and propagated them in the NVE ensemble to observe transient changes in the kinetic energies of the different adsorbate molecules and the energy flow between them and to the surface. The integrated change of time dependent VDOS, for example, helps to identify efficient channels for vibrational energy transfer between different subsystems of our system (here, CO adsorbates, NaCl surface). A decrease/increase in  $\Delta VDOS$  corresponds to vibrational energy flow from/into the corresponding subsystem (cf. Figure 3).

We now plan to extend our study to calculate vibrational spectra and non-equilibrium dynamics for the buried monolayer CO/NaCl(100) (cf. Figure 2), relative to the free monolayer system, for different temperatures and CO orientations, since the addition of CO overlayers would change the spectral signatures to some extent and may also influence isomerization dynamics. For instance, the recent observation of an uni-directional targeted vibrational energy flow from the  $^{12}C^{16}O$  overlayers to the isotopically different  $^{13}C^{18}O$  monolayer on the NaCl(100) surface, leading to 30 % higher vibrational density at the interface by Lau *et al.* [3], makes it an attractive topic for the surface science community. Also, as part of our future efforts, we will construct machine learned potentials for such systems, due to the limited time-scales and computational effort of AIMD, especially to investigate longer timescale processes such as "energy pooling".

#### WWW

<https://www.uni-potsdam.de/en/theochem/index>

#### More Information

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