

Vibrational Spectroscopy and Dynamics

An Ab-Initio Molecular Dynamics Study of CO on NaCl(100)

S. Sinha, P. Saalfrank, *Institut für Chemie, Universität Potsdam*

In Short

- We characterised and studied "O-down" oriented CO on NaCl(100) at different coverages and phases: 2D potential energy surfaces and minimum energy pathways for isomerisation.
- We combined AIMD with Time-Dependent Correlation Function approach to simulate vibrational density of states and infrared spectra of different phases of CO:NaCl(100), 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 will study CO inversion (C-down to O-down and vice-versa), observed experimentally, after high vibrational pre-excitation of "C-down" and "O-down" CO, by AIMD.

The adsorption of small molecules like CO on ionic surfaces is important not only from a benchmarking point of view for electronic structure methods but for practical reasons, one example being the use of vibrational signatures of CO on ionic surfaces as sensitive probes for unravelling processes in heterogeneous catalysis [1]. Besides this, CO:NaCl(100) monolayer system has been identified to display vibrational energy pooling, in which the CO molecules efficiently transfer vibrational energy within groups of adsorbed molecules, from one excited vibrational energy level to another [2]. Also, the rotation of CO, from the usual C-down to an O-down configuration,

after vibrational excitation, has been observed experimentally [3].

We have investigated the adsorption, energetics, 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° 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. We found that inversion of CO from the pragmatic "C-down" configuration to the "O-down" configuration (where the O-end of CO is closer to the surface) costs approximately 80 meV (ca. 8 kJ/mol) per molecule, largely independent of coverage. Harmonic frequencies obtained *via* normal mode analysis showed that most of the normal modes for the "O-down" isomer were red-shifted as compared to those of the "C-down" isomer, with the C-O stretch red-shifted by nearly 15 cm^{-1} [4]. These phases are likely to be distinguishable in vibrational spectroscopy such as Vibrational Density of States (VDOS), IR (Infrared) and VSF (Vibrational Sum Frequency), the latter being surface-sensitive, which, therefore, serve as useful tools to correlate specific spectral signatures to 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.

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), to provide detailed description and statistical information pertaining to the above mentioned effects for the CO:NaCl(100) system, which appear in the experimental spectra. AIMD computes "on the fly" trajectories, without the need to precompute potential energy surfaces and since velocities are a natural output of such simulations, the velocity-velocity autocorrelation functions (VVAFs) can be used to compute Vibrational Density of States (VDOS) and IR spectra following the methodology of Ohto *et al.* [5]. Here, the IR response could be calculated with a parameterized dipole moment derivative along the C-O bond and a subset of VVAFs, which solely depend upon the nuclear motion and therefore could be converged within shorter MD trajectories than the otherwise required dipole-dipole autocorrelation

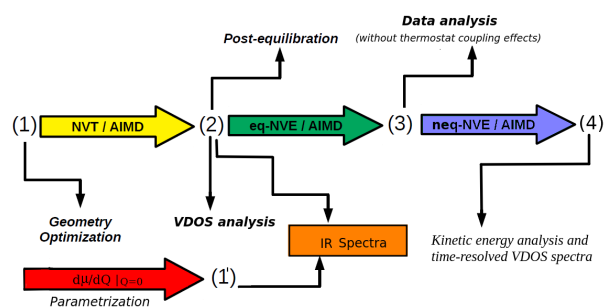


Figure 1: Schematic representation of the AIMD protocol used here. *eq.* and *neq.* stand for equilibrium and non-equilibrium, respectively.

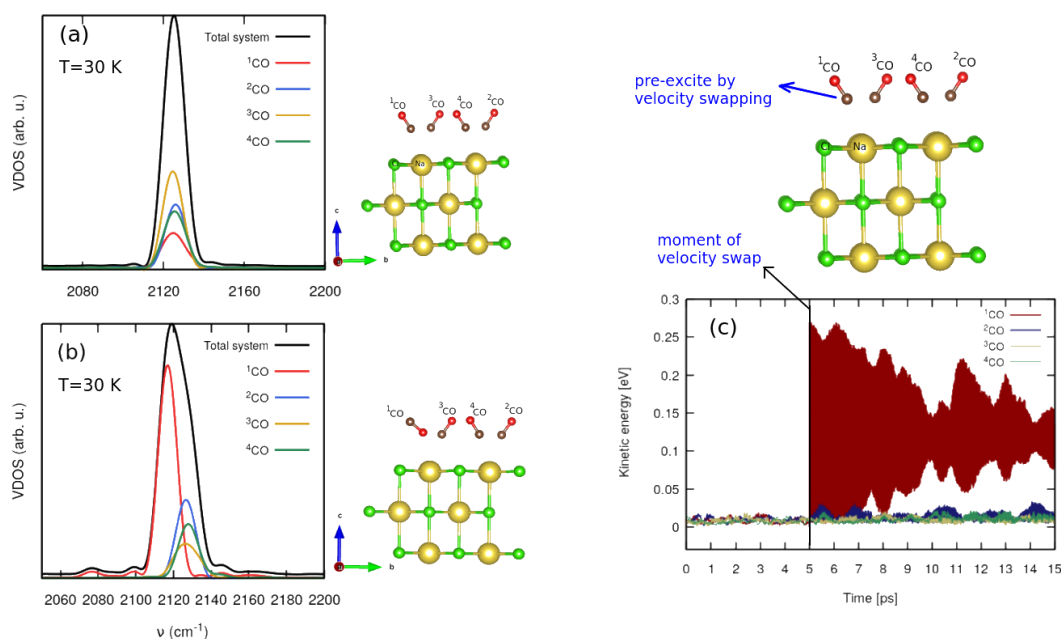


Figure 2: VDOS curves obtained by NVT AIMD at 30 K, starting from initial configurations (a) 1 ML T/A phase and (b) 1 ML T/A phase with one "O-down" CO) shown beside each plot. The plots show the VDOS for the full system and different subsystems in the C-O stretch [2060:2200] cm⁻¹ region. (c) Kinetic energy analysis of the neq NVE-AIMD simulations, averaged over three trajectories. Averaged kinetic energies of individual CO molecules with one CO pre-excited by one vibrational quanta ~ 0.26 eV. The CO molecule was perturbed after initial 5 ps of the eq. NVE phase.

functions. A schematic representation of the approach utilised has been highlighted in Figure 1.

VDOS curves for two configurations in the T/A phase at 30 K have been reported in Figure 2, together with the contribution of individual CO molecules to the total VDOS. We also performed AIMD calculations with vibrationally pre-excited CO molecules, to study vibrational energy transport to neighbouring adsorbates and the NaCl surface by following kinetic energy flow with time (*cf.* Figure 2(c)). For the pre-excited CO molecules, we observe a rapid and periodic transfer of this excess energy into potential energy in the beginning of the non-equilibrium phase and then a further periodic redistribution into other modes and to neighbouring molecules, on a ~ 10 ps timescale. There is negligible energy transfer to the surface.

In the next funding period, we will extend our AIMD/TDCF approach to study the isomerization dynamics (in both directions) by pre-exciting both the "C-down" and "O-down" CO molecule(s) to higher vibrational states, and following their non-equilibrium dynamics. We also wish to study whether CO coverage has any role to play in modifying the isomerization threshold of our system.

In summary, the extension of this project will give a better microscopical insight into the vibrational spectroscopy, the vibrational energy transfer and the reactions of a prototypical system of surface science, which continues to attract attention in the surface

science community.

WWW

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

More Information

- [1] A. D. Boese and P. Saalfrank, *J. Phys. Chem. C*, **120**, 12637-12653 (2016). doi: 10.1021/acs.jpcc.6b03726
- [2] L. Chen, J. A. Lau, D. Schwarzer, J. Meyer, V. B. Verma, and A. M. Wodtke, *Science*, **363**, 158-161 (2019). doi:10.1126/science.aav4278
- [3] J. A. Lau, A. Choudhury, L. Chen, D. Schwarzer, J. Meyer, V. B. Verma, and A. M. Wodtke, *Science*, **367**, 175-178 (2020). doi: 10.1126/science.aaz3407
- [4] S. Sinha, P. Saalfrank, *Phys. Chem. Chem. Phys.*, **23**, 7860-7874 (2021). doi: 10.1039/D0CP05198E
- [5] T. Ohto, K. Usui, T. Hasegawa, M. Bonn, and Y. Nagata, *J. Chem. Phys.*, **143**, 124702 (2015). doi:10.1063/1.4931106

Funding

DFG