CFEL SCIENCE

SEMINAR

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Experiments on vibrational energy pooling and transport in condensed phases using a mid-IR superconducting nanowire single photon detector

Superconducting nanowire single-photon detectors (SNSPDs) provide sufficient sensitivity to enable laser induced fluorescence (LIF) experiments in the mid-infrared, an exciting technical development for physical chemistry given the importance of vibrational spectroscopy to molecular science. In this talk, I will describe how an SNSPD works and how to use it. I will also present results of experiments on the vibrational dynamics of monolayers and multilayers of solid CO adsorbed at the surface of a NaCl crystal, to show the capabilities of time-resolved infrared LIF spectroscopy and provide observations of astonishing phenomena arising from dipole-dipole coupling between molecules.

(see more details on the next page)

Host: Jochen Küpper/ CFEL Molecular and Ultrafast Science Seminar

EXPERIMENTS ON VIBRATIONAL ENERGY POOLING AND TRANSPORT IN CONDENSED PHASES USING A MID-IR SUPERCONDUCTING NANOWIRE SINGLE PHOTON DETECTOR

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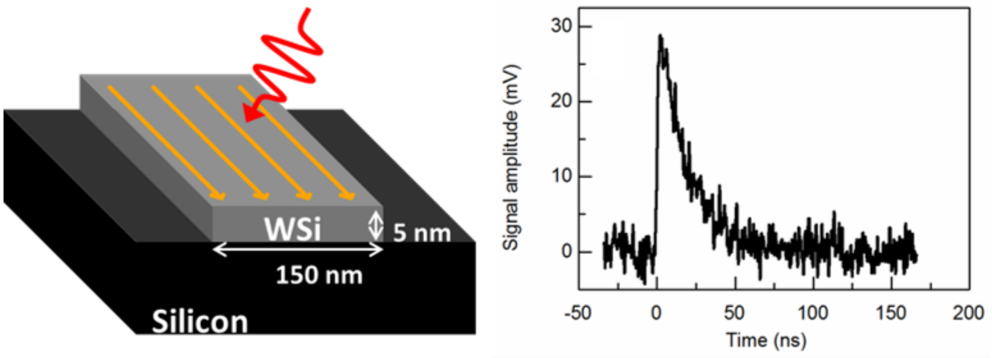
In these experiments, a laser light pulse excites about half of the CO to its $v = 1$ state within a few nanoseconds. Sitting behind a monochromator, the SNSPD detects wavelength and time-resolved mid-infrared emission from CO. We detect vibrational states up to $v = 27$ that are produced by vibration-vibration (V-V) energy transfer—$CO(v = m) + CO(v = n) \rightarrow CO(m - 1) + CO(n + 1)$. We find that kinetic Monte Carlo (kMC) simulations can reproduce how the population distribution evolves with time. This shows that vibrational energy collects in a few CO molecules at the expense of those up to eight lattice sites away and that NaCl's transverse surface phonons take up the excess energy associated with each V-V transfer step. This gives rise to peculiar bottlenecks in the march up the vibrational ladder.

The relaxation of these hot molecules is also fascinating. Most of us would expect that the anharmonicity of the interaction potential allows CO vibrational energy transfer to NaCl phonon excitation—a picture analogous to intramolecular vibrational relaxation in polyatomic molecules—and that the larger the anharmonicity, the faster the relaxation. However, we find that the vibrating CO molecules behave like classical antennae, losing their energy to NaCl lattice-vibrations via the electromagnetic near-field. In fact, the theory that explains this phenomenon is an extension to the atomic-scale, of Sommerfeld's theory of ground waves that he developed to understand radio wave propagation. This is a weak coupling limit where the anharmonic interatomic forces normally so important to energy flow can be completely neglected.

We are also able to observe orientational isomerization—new lines appear in the infrared emission spectra when vibrational energy converts "the right-side up" CO to an "up-side down" metastable structure. In its ground vibrational state, $C^{\delta-}O^{\delta+}$ binds with its C atom adjacent to a Na^+ ion. In vibrationally excited states the electrostatics change and $C^{\delta+}O^{\delta-}$ binds with its O atom next to the Na^+ ion. The lifetime of the metastable state increases dramatically, when buried beneath other adsorbed molecules. Finally, I will show a novel concept of mid-infrared light harvesting, where a thick overlayer absorbs many infrared photons and, due to the properties of V-V energy transfer, it is possible to transport a large fraction of this vibrational energy to the interface, where it drives the CO flipping reaction. The vibrational energy transport seen here is physically similar to Förster energy transfer.



The energy absorbed by a single infrared photon is sufficient to destroy a nanowire's superconductivity and produce a transient resistance that can be seen as a voltage pulse in a constant current circuit. The right panel shows an oscilloscope trace from a single 5-micron photon.

References

1 Lau, J. A., Choudhury, A., Li, C., Schwarzer, D., Verma, V. B. & Wodtke, A. M. Observation of an isomerizing double-well quantum system in the condensed phase. *Science* **367**, 175 (2020).

2 Chen, L., Lau, J. A., Schwarzer, D., Meyer, J., Verma, V. B. & Wodtke, A. M. The Sommerfeld ground-wave limit for a molecule adsorbed at a surface. *Science* **363**, 158-161 (2019).

3 Chen, L., Schwarzer, D., Lau, J. A., Verma, V. B., Stevens, M. J., Marsili, F., Mirin, R. P., Nam, S. W. & Wodtke, A. M. Ultra-sensitive mid-infrared emission spectrometer with sub-ns temporal resolution. *Optics Express* **26**, 14859-14868 (2018).

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