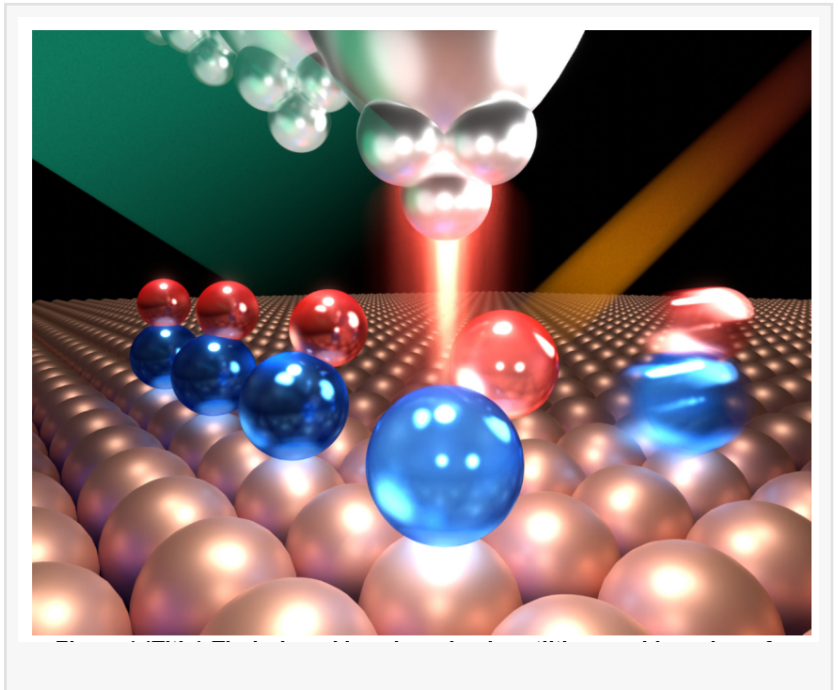


CO molecular tilting detected by red-shifted TERS

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[/EINPresswire.com/](https://www.einpresswire.com/) -- The interaction between a probing tip and an adsorbed molecule can significantly impact the molecular chemical structure. The tip-induced bond weakening, tilting, and hopping processes of a single molecule were investigated by sub-nanometre resolved tip-enhanced Raman spectroscopy (TERS). The C–O stretching mode is always redshifted as the tip approaches, revealing the weakening of the C–O bond. Further analyses of the vibrational Stark effect and TERS imaging suggest a delicate tilting of the adsorbed CO molecule.



The invention of scanning probe microscopy (SPM) techniques, including scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), has led to a paradigm shift in the visualization and understanding of surface structures and related properties at the atomic scale. In most imaging cases, the SPM tip only acts as a perfect probe to characterize the intrinsic properties of the surfaces and adsorbed molecules, and the influence of the tip is usually ignored. On the other hand, the SPM tip is also capable of manipulating single molecules on surfaces. In this case, the tip–molecule interaction is in action, and in some cases, the approaching tip can push a molecule away. However, the detailed physico-chemical mechanism of how this happens remains elusive due to the challenge of tracking the structural variations at the single-chemical-bond level during the tip-approaching process.

In a new paper published in *Light: Advanced Manufacturing*, a team of scientists led by Professors Zhenchao Dong and Yao Zhang from the University of Science and Technology of China have developed a new approach for in-situ tracking tip-induced molecular configurational changes by Ångstrom-resolved TERS, providing new opportunities for the visualization and understanding of surface structures at the atomic level.

By adopting carbon monoxide ([CO](#)) molecules adsorbed on Cu(100) as a model system, they used tip-enhanced Raman spectroscopy (TERS) to explore the tip-induced bond weakening, tilting, and hopping of a single CO molecule on the surface. Vibrational frequencies can provide structural and strength information about chemical bonds, which has been demonstrated by STM-based inelastic electron tunnelling spectroscopy (IETS) at the single-molecule level. Nevertheless, IETS is usually sensitive to vibrational modes close to the Fermi level, and the C–O stretching vibration energy approaches the detection limit. Indeed, most gap-distance-dependent IETS studies on CO molecules have focused on the frustrated rotation (FR) and frustrated translational (FT) modes in the low-frequency region. However, these low-frequency modes are associated with in-plane vibrations parallel to the surface. They cannot directly reveal the changes in the bond length and tilting angle of the adsorbed CO molecule.

In contrast, TERS is a technique with both sensitive chemical specificity and high spatial resolution and can provide rich vibrational information over a wide range of vibrational frequencies. Recent advances in TERS not only demonstrated its powerful chemical mapping capabilities at the single-molecule level, but also pushed the spatial resolution further down to the Ångström scale, allowing probing of the bond breaking and making processes, as well as highly localized surface chemistry at the single bond level. This ability makes it possible to directly monitor the strength variations of single chemical bonds under different tip–molecule interaction conditions. In fact, previous TERS studies have indicated that the C–O stretching vibration of a CO molecule attached at the tip apex is highly sensitive to the variations of local electrostatic fields.

By using sub-nanometre resolved TERS, the research team not only determine the adsorption configuration of a CO molecule adsorbed on Cu(100), but also unravel the microscopic mechanisms of tip-induced bond weakening, tilting, and hopping of a CO molecule on the surface. Specifically, the vibrational frequency of the C–O stretching mode is always redshifted as the tip moves closer to the top O atom of the upright CO molecule, which signifies the weakening of the C–O bond owing to tip–molecule interactions. Further investigations on the vibrational Stark effect at different gap distances, together with theoretical simulations of the optimized CO adsorption configurations, indicate that such tip–molecule interactions can be classified into two regions, van-der-Waals attractive interaction and Pauli repulsive force, depending on whether the tip–molecule distance is smaller or larger than the van der Waals separation of ~ 3.65 Å between the Ag atom at the tip apex and the O atom of the CO molecule.

Their results demonstrate that TERS can provide an insightful understanding of the chemical structure, tip–molecule interactions, and tip-induced molecular motions at the single-bond level, which opens up a promising route to explore the microscopic mechanisms of surface reactions and catalysis.

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References

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Wendy Chen

TranSpread

+1 865-405-5638

[email us here](#)

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