Vibrational energy transfer upon the collision of NO with VO_2 thin films across the insulator-to-metal transition

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Vibrational energy transfer between molecule and metal surface is perhaps one of the most illustrative and chemically relevant examples, where Born Oppenheimer Approximation (BOA) - the cornerstone of molecular level understanding of chemical reactions - is routinely violated. During recent decade tremendous improvements in the state-of-the-art of molecule's preparation and detection yielding overwhelming amount of detailed experimental data that triggered a wave of theoretical advances [1].

However, to the date, the vast majority of our understanding has been gained from scattering experiments conducted on single crystal metal surfaces, while there have not been any fundamental experiments extending our fundamental knowledge on this topic to complex functional surfaces, able to change their electronic properties, bearing on vibrational energy transfer, under external stimuli. In this respect, vanadium dioxide, VO_2, appears to be particularly fascinating as it can morph itself between insulator and metal in only a few degrees temperature range, known as the insulator-to-metal or Mott transition. While this remarkable property of VO_2 triggered numerous technological applications e.g. smart windows, switches, resonators, sensors, field effect transistors, to mention a few, little is known how metal-to-insulator transition impacts vibrational energy transfer. This situation is unfortunate, since vibrational energy transfer in molecule – surface encounters is particularly relevant to understanding the elementary process of bond cleavage, since the vibration of two atoms against one another is precisely the motion needed to induce a reaction.

Here we report clear observations of direct scattering of translationally hyperthermal, vibrationally excited NO from thin VO_2 films across the insulator-to-metal transition [2]. We observed a measurable enhancement of vibrational relaxation probability of NO (v_I=3,11) molecules when the VO_2 transforms from its insulating to metallic phase at 68^{o}C, accompanied by four-order decrease in resistivity. Surprisingly, the enhancement in vibrational relaxation of NO(v_I=3,11) upon insulator-to-metal transition in VO_2 is rather small (order of few percent), in contrast to the stark differences observed between vibrational relaxation probabilities on "typical" metal and insulating surfaces, such as Au or Ag and LiF, respectively. Moreover, the magnitude of vibrational relaxation of the metallic phase of VO_2 is significantly lower than expected, considering the knowledge accumulated for single crystal metal surfaces. We are able to explain the low propensity of NO vibrational relaxation on VO_2 based on electron-transfer mediated vibrational relaxation mechanism, assuming inefficient image charge stabilization of affinity level, as opposed to scattering from coinage metals, which, to the date, shaped our understanding in the field. We believe that our findings will trigger developments in first-principles electronic structure calculations and nonadiabatic dynamics simulations that will promote our understanding of vibrational energy transfer on complex substrates to the level achieved for single crystal metal surfaces

References

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