Bending vibration-driven activation of CO_2 on Cu surfaces

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Heterogeneous catalysis of small molecules such as hydrogen, methane and carbon dioxide, especially if activated by "state-to-state chemistry", represents a potentially economic strategy for utilization of fossil feedstock and reducing the emission of greenhouse gases. A central event in gas-surface reaction dynamics is bond rupture/formation of vibrationally and/or translationally excited molecules (Fig. 1). We report a hitherto unknown bond formation reaction driven by the bending vibration via an Eley-Rideal (E-R) type mechanism. Hot CO_2 in a molecular beam is found to react directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces to form formate adspecies at 120–220 K. The reaction probability is promoted up to ~10^{-3}, compared to that of ~10^{-12} in the previous high pressure cell experiments [1]. The vibrational energy of CO_2 is effective for the reaction via lowing the energy level of LUMO, but not the translational energy [2]; and the reaction rate is independent of the surface temperature. The experimental results are consistent with a recent density functional theory study, which predicts that exciting the bending mode of CO_2 enhances the formate formation via the E-R type mechanism [3,4]. Such bending mode activation in thermal non-equilibrium can open up novel industrial pathways of efficiently converting CO_2 to value-added chemicals such as formic acid and methanol.

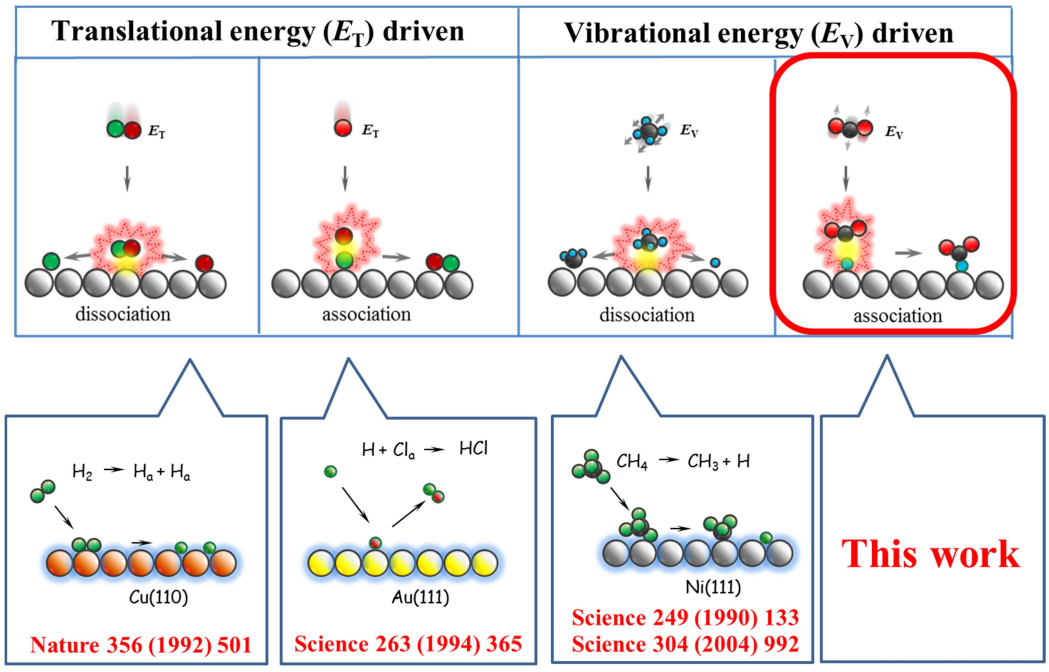

Figure 1. Translational energy driven reactions and vibrational energy driven reactions

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