



COLLOQUIUM
**Inelastic tunneling processes
for single molecule on metal surfaces**

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Special and state selective chemistry on individual molecules is nowadays being driven by inelastically tunneled electrons from an STM tip. Molecules adsorbed on substrates such as metals or semiconductors are good examples. Such molecular manipulation is often coupled with the excitation of vibrational modes. Vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule [1] but also for investigating how molecular vibration can couple with the relevant dynamical processes [2]. The response of vibrationally mediated molecular motion to applied bias voltage, namely an “action spectrum”, can reveal vibrational modes that excited through STM inelastic tunneling processes, because the molecular motion is induced only *via* the inelastic tunneling processes [3]. Thus, the action spectrum would be a candidate for detecting which vibrational mode is actually excited and associated with molecular motions. The mechanism to excite vibrational modes of molecules is revealed to be a resonant mechanism. Examples are given for dissociation of dimethyl disulfide to methylthiolates on Cu(111) and also hopping of the reaction product, methylthiolate, on the same surface [4-6]. Action spectra observed for both cases are well explained by accepting a resonant-excitation model *i.e.* the electronic state accepting electron via the transfer between the tip and the molecule acts as a resonant state to perturb the vibrational states to be excited. The coupling between vibrational states plays an important role on whether reaction coordinated can be perturbed when a certain vibrational state is excited. The key is the rate of anharmonic coupling between the vibrational modes of interest. At the symposium, we will discuss also on the dynamics of the coupling.

References : [1] Y. Kim, T. Komeda, and M. Kawai, Phys. Rev. Lett. **89**, 126104 (2002). S. Katano, M. Trenary, Y. Kim and M. Kawai, Science **316** (2007) 1883. [2] T. Komeda, Y. Kim, M. Kawai, et al., Science **295**, 2055 (2002). [3] Y. Sainoo, Y. Kim, T. Okawa, et al., Phys. Rev. Lett. **95**, 246102 (2005). [4] M. Ohara, Y. Kim and M. Kawai, Langmuir **21**, 4779 (2005). [5] M. Ohara, Y. Kim and M. Kawai, Chem. Phys. Lett. **426**, (2006) 357. [6] M. Ohara, Y. Kim and M. Kawai, Phys. Rev. Lett. (2008) to appear April 18 on line..

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