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Intermolecular Energy Flows between Surface Molecules on Metal Nanoparticles

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Abstract

Three model systems are designed to investigate energy transport between molecules on metal nanoparticle surfaces. Energy is rapidly transferred from one carbon monoxide (CO) molecule to another CO molecule or an organic molecule on adjacent surface sites of 2 nm Pt particle within a few picoseconds. However, energy flow from a surface organic molecule to an adjacent CO molecule is significantly slower, and in fact within experimental sensitivity and uncertainty the transfer is not observed. The energy transport on particle surface (about 2 km/s) is almost ten times faster than inside a molecule (200 m/s). The seemingly perplexing observations can be well explained by the combination of electron/vibration and vibration/vibration coupling mechanisms that mediate molecular energy dynamics on metal nanoparticle surface: the strong electron/vibration coupling rapidly converts CO vibrational energy into heat that can be immediately sensed by nearby molecules; but the vibration/vibration coupling dissipates the vibrational excitation in the organic molecule into low frequency intramolecular vibrations that may or may not couple to surface electronic motions.

1. Introduction

Chemical adsorption and kinetic energy dissipation are basic steps of reactions on metal surfaces¹. The kinetic energy of a reactant can internally convert into heat or dissipate through surface electronic motions if molecules are close enough to the metal surface²⁻⁶. The intertwining nuclear and electronic motions have been suggested to be responsible for the amazing complexity and delicacy of chemical dynamics on metal surfaces⁵⁻¹³.

Ultrafast vibrational spectroscopy has provided very useful molecular information and dynamics on metal nanoparticles, the major component of many heterogeneous catalysts. For examples, Beckerle *et al* applied ultrafast vibrational spectroscopy to record diatomic molecule-carbon monoxide (CO) energy relaxation on Pt nanoparticle surface.¹⁴ They observed a strong coupling between CO vibration and surface electronic motion. In very recent studies, however, Kraack *et al* demonstrated that the diatomic nitrile group dissipates vibrational energy to surrounding solvents rather than surface electronic motion.¹⁵ Another very interesting work showed that heat generated from electronic excitation on Au nanoparticles can rapidly transport to surface molecules¹⁶. These previous results focus on particle/molecule interactions, illustrating the relative importance of electron/vibration and vibration/vibration coupling in mediating molecular energy dissipation on metal particle surfaces. Nevertheless, very few studies were to investigate energy transfers among molecules on surface of metal nanoparticles.

In this work, using three model systems with vibrational modes as “thermometer” to probe molecular heat, we are able to measure energy transfers between molecules on the surface of metal nanoparticle. We deposit energy in one molecule by vibrationally exciting one of its high frequency modes, and detect the response of another molecule nearby. We examine intermolecular energy flows between surface CO and organic molecules: the energy transfer from CO to the

organic molecule is fast but the reverse process is very slow. We also find that the electron/vibration coupling-mediated energy migration is about 2 km/s between molecules on Pt surface, and the rate is slowed down for almost one order of magnitude to 200 m/s inside a molecule.

2. Experimental details

The optical setup has been reported elsewhere¹⁷. Briefly, one picosecond (ps) amplifier and one femtosecond (fs) amplifier are synchronized by the same seed pulse from an oscillator. The ps amplifier pumps an optical parametric amplifier (OPA) to produce 0.7~0.9 ps mid-IR pulses with a bandwidth of 10-35 cm^{-1} in a tunable frequency range of 1000 cm^{-1} to 4000 cm^{-1} with energy ranging from 10-40 $\mu\text{J}/\text{pulse}$ at 1 kHz as pump beam. The probe beam is generated by the light from the fs amplifier inducing a high-intensity mid-IR and terahertz super-continuum broadband (400-4000 cm^{-1}) pulse with duration of ~ 100 fs at a repetition rate of 1 kHz. The spectral resolution of the ultrafast measurement is ± 8 cm^{-1} and ± 1 cm^{-1} for the steady-state FTIR measurements.

Synthetic method of 2 nm Pt NP has been reported before¹⁸. Briefly, K_2PtCl_4 (3 mM ethylene glycol solution) and 10 mM sodium acetate were mixed in hot 1, 2-ethanediol at 80 °C, stirring for 30 min. The black solution was then cooled down. In case 1 (the MTS sample), 0.0047 g Methyl thiosalicylate (MTS) in 3 ml ethylene glycol (EG) was added into the mixture solution. In case 2, there was no more chemical adding into mixture solution. For both cases, CO gases were bubbled into the solutions at a rate of 200 mL/min for 30 min inside a fume hood. The solutions were mixed with 1/3 water (v/v) and centrifuged for 20 hours at 40,000 rpm. This centrifugation process was repeated three times. The sediments were suspended into several drops of 1,2-ethanediol and transferred onto the CaF_2 windows. The samples were placed into the vacuum oven overnight to remove excess solvent and covered with another CaF_2 window. Therefore, the measured samples

are solid film samples without spin coating. The entire samples were then transferred into a vacuum chamber to measure spectrums. During ultrafast experiments, the excitation power was ~ 5 mW at 2000 cm^{-1} . Synthetic method and characterization data of 5 nm Pt nanoparticle with CO and PVP coating on surface had also been reported in our previous publication¹⁹. Briefly, 5 ml ethylene glycol was used to dissolve Pt(II) acetylacetonate (80 mg) and polyvinylpyrrolidone (PVP, 55 mg, MW=55,000) in room temperature. The mixture was transferred to a microwave reactor (Anton Paar Monowave 300) with following reacting parameters. The heating temperature was set to $200\text{ }^{\circ}\text{C}$, stirring rate was modulated at 1200 rpm and reacting time was 5 min. Then the reaction mixture was cooled to room temperature. Acetone (45 ml) was added to the solution to precipitate the Pt nanoparticles. And 10 ml ethylene glycol was used to add into the sediments to remove excess PVP. The CO gases coating method and sample preparation method for optical measurement followed the same procedure above.

3. Results and Discussion

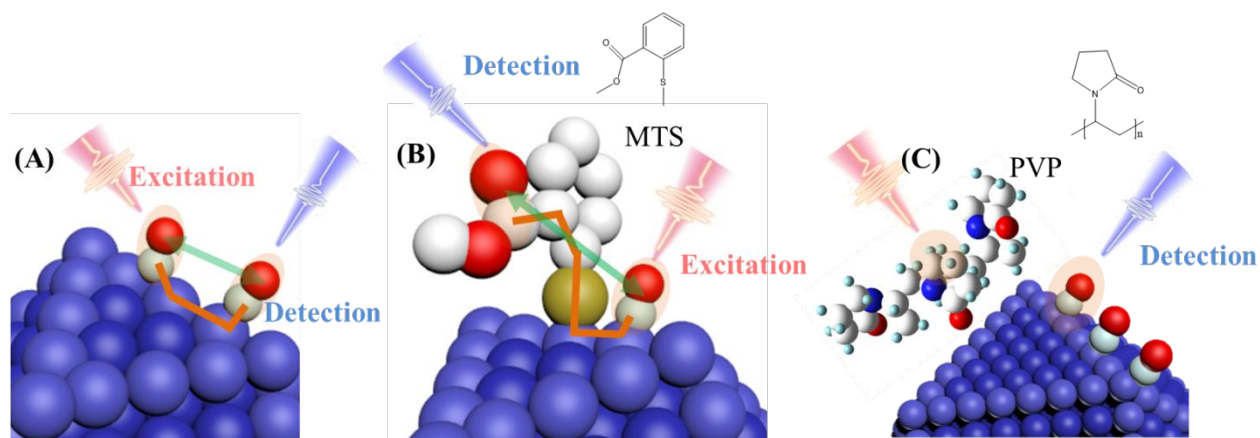


Figure 1. Three energy distribution model systems: (A) from bridge CO to step CO on Pt particle, (B) from step CO to the carbonyl stretch of methyl thiosalicylate (MTS) on Pt particle, and (C) from C-H of PVP to step CO on Pt particle surface.

Fig.1 displays three model systems used in experiments. There are at least three major types of CO binding sites on the particle surface: (I) the CO molecule sits on the top of one Pt atom of the terrace (Terrace site); (II) the CO molecule sits on one Pt atom of the edge step (Step site); (III) the CO molecule sits between two Pt atoms of the terrace (Bridge site). In fig. 1A, the photon energy is deposit into CO molecules on the bridge sites of 2 nm Pt particle, using an ultrafast infrared (IR) pulse to resonantly excite its CO stretch mode (1840 cm^{-1}). Another IR pulse as probe is then applied to detect how the bridge CO vibrational energy flows to CO molecules on the step sites (2030 cm^{-1}). In fig. 1B, energy is deposit into CO molecules on the step sites, and the energy sensor is the carbonyl (C=O) group (1713 cm^{-1}) of methyl thiosalicylate (MTS) also attaching to Pt nanoparticle surface. In fig. 1C, energy is deposit into the CH stretches (2940 cm^{-1}) of surface polyvinylpyrrolidone (PVP) molecules, and the energy sensor is the step CO molecules.

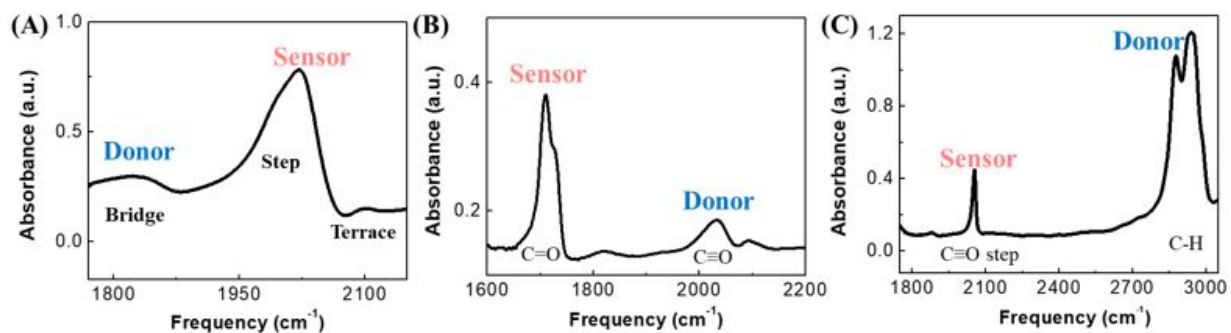


Figure 2. FTIR spectra of (A) CO molecules on different surface sites of 2nm Pt particle; (B) MTS CO stretch and step CO stretch on 2nm Pt particle; (C) PVP CH stretches and step CO on 5nm Pt surface. Donor refers to the vibrational mode that gains energy directly from laser excitation. Sensor refers to the mode that senses energy dissipated from the donor.

The vibrational frequencies of the energy donors and sensors are displayed in fig.2. The donors gain energy directly from the mid infrared laser resonance excitation, lifted to their vibrational 1st excited state. The excited donors dissipate energy into electronic motions or low

frequency vibrations and ultimately propagate away in the form of heat. Once energy reaches the vibration sensors, the sensors' vibrational frequencies shift and peak absorption intensities change (typically to the red side) due to temperature increase or vibrational coupling²⁰⁻²³. During the process, direct vibrational energy transfer with vibration dipole-dipole coupling from donors to sensors is negligible (*supporting information*) because the electron/vibration coupling and intramolecular vibrational coupling are significantly stronger than the intermolecular coupling between donors and sensors.

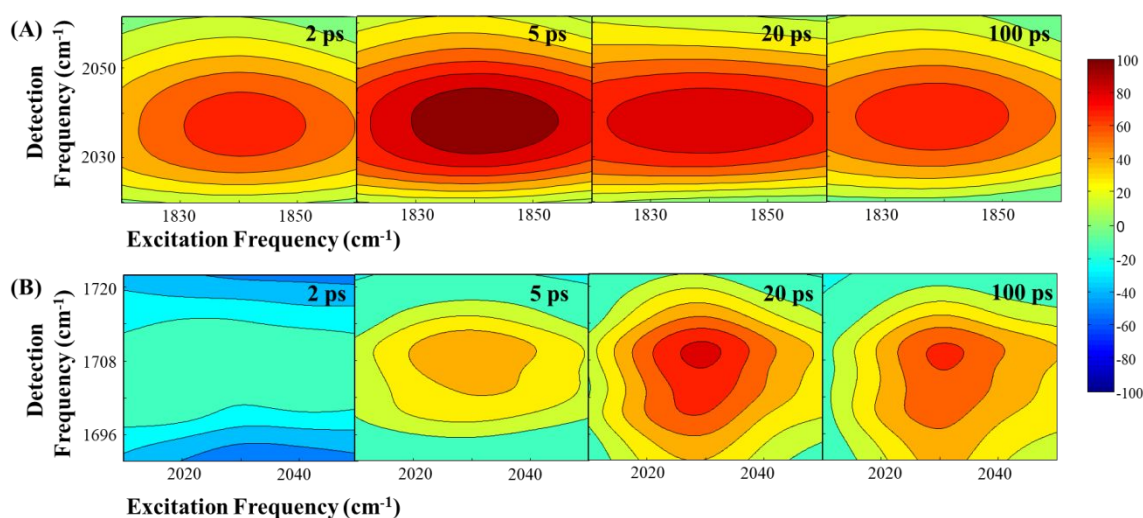


Figure 3. Waiting time dependent 2D IR spectra of (A) the step CO stretch after the bridge CO is excited; and (B) the carbonyl stretch of MTS after the step CO is excited.

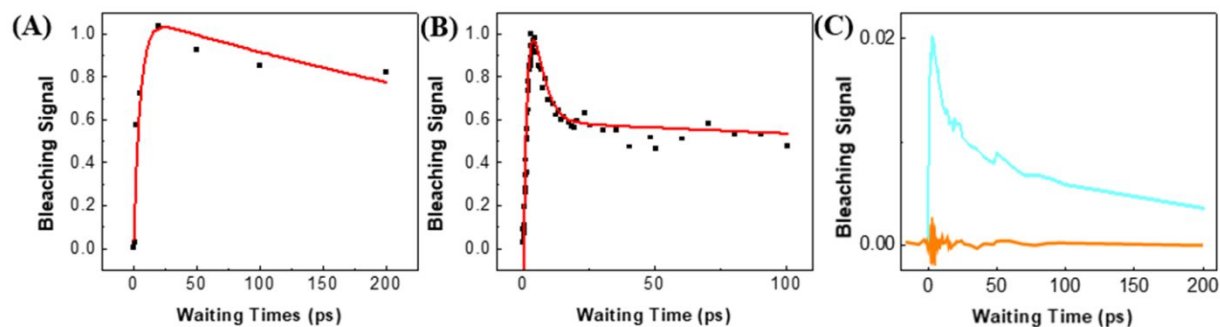


Figure 4. Waiting time dependent intensities of (A) step CO stretch after bridge CO is excited on 2nm Pt particle; (B) carbonyl stretch of MTS after step CO is excited on 2nm Pt particle; and (C)

step CO stretch after bridge CO is excited (cyan) on 5 nm Pt particle and step CO stretch after CH stretches of PVP are excited (orange) on 5 nm Pt particle.

The waiting time dependent 2D IR spectra (red peak) of step CO after the bridge CO is vibrational excited are displayed in fig.3A. The excitation frequency 1840 cm^{-1} is the bridge CO stretch 0-1 transition frequency, indicating the signal originates from bridge CO. The detection frequency is the step CO 0-1 transition frequency, reflecting the response of step CO caused by the bridge CO vibrational excitation. The 2D IR signal is plotted in red, representing bleaching signal. As briefly described above, the vibrational energy of bridge CO dissipates as surface electronic excitation which quickly thermalizes within a couple of ps and raises local temperature. The temperature increase cause a frequency redshift of step CO vibration and the reduction of its transition dipole moment. Both origins contribute to the bleaching signals at its 0-1 transition frequency. Therefore, the signal intensity can be viewed as a molecular “thermometer”, monitoring the local temperature. As displayed in fig.4A, the signal quickly reaches maximum at 5 ps, and decays sharply within 20 ps and then slowly falls off. Quantitative analyses with a tri-exponential (line is analysis and dots are data in fig.4A. Fitting parameters are listed in supporting information) reveal three dynamic processes the step CO experiences. The first process indicates a temperature increase with a time constant 2.2 ± 0.3 ps. It is followed by a fast temperature decrease of 4.2 ± 0.7 ps and a slow energy dissipation of 1000 ± 200 ps. The three time constants have clear physical origins. Previous studies have suggested that CO molecules dissipate vibrational energy to surface electronic motions which then quickly convert into metal lattice vibrations within a couple of ps on metal surfaces.^{15,24,25} In our previous experiments¹⁹, the vibrational relaxation of bridge CO is 1.8 ps. The distance between step CO and bridge CO is about 6.57 \AA (see p.5 in SI). If the lattice motions transport from one CO to the other at the speed of sound in Pt metal (about 2000 m/s), it

will take about 330 fs. The vibrational relaxation time 1.8 ps plus this transport time 0.33 ps is 2.13 ps, which is very close to the temperature rising time 2.2 ps. Thus 2.2 ps is very likely the time that it takes for the thermal energy to reach the probe molecule, starting from the bridge CO vibrational excitation. Within 2.2 ps, the energy is yet to be balanced throughout the entire particle. From the results, we could estimate the energy transport rate through bond from bridge CO to step CO is around 2 nm/ps. Fast decay component 4.2 ps is proposed to be the time constant for heat to reach global equilibrium on the particle surface. After this intraparticle thermal equilibrium, heat slowly dissipates into environment with a time constant of 1 ns.

The dynamics (fig.3B&4B, lines are calculations and dots are data) of MTS carbonyl stretch is quantitatively different. Its rising seems slower and the decay is smooth without any abrupt event. A bi-exponential fitting is sufficient to describe the dynamics. The signal has a rising time of 5 ± 1 ps and a decay of 600 ± 100 ps. The rising time constant 5 ps is slower than 2.2 ps observed for the CO probe discussed above. This difference stems from the fact that the carbonyl group is not directly linked to Pt. Through bond it is about 6 Å away from particle surface (See p.5 in SI). The vibrational lifetime of the energy donor for this system is 2.2 ps within which its energy is converted into Pt lattice motions. Estimated from the speed of sound, it takes a couple of hundred fs for the lattice motions to transfer to Pt-S bond, and about 2-3 ps to reach the carbonyl group. Based on this physical picture, the heat transport rate inside MTS is about 2 Å/ps. This value is slightly faster than previously reported intramolecular vibrational energy redistribution rate 1.25 Å/ps.²⁶ Such a faster dynamics is not surprising because vibrational modes involved in heat transport are more delocalized and on quasi-resonance. The time for heat to reach the probe carbonyl group is approximately the same as the time for it to reach equilibrium across the entire particle. Therefore, the global thermal distribution on the particle doesn't reduce the temperature

that the carbonyl group senses. After the thermal energy reaches equilibrium on the particle surface, it dissipates to the environment. Compared to the CO probe, MTS provides more channels for energy to redistribute or dissipate and therefore we see a slightly faster energy dissipation rate for the carbonyl probe. In summary, no matter the probe (the CO probe) is directly attached to the particle surface, or far away from the surface (the carbonyl group), they can easily detect the thermal energy dissipated from the donor that is directly connected to the particle surface.

In the third model system (fig.1C), the energy donors CH stretches are not directly attached to the particle surface. Regardless of their higher IR absorptions (fig.2C), compared to the CO donors for the other two systems, no heat transport to the probe CO is observed (orange line in fig.4C). This is in stark contrast to the system with donor attached to the surface (cyan line in fig.4C). The seemingly surprising difference can be rationalized in terms of coupling mechanism. On the PVP-coated 5 nm Pt particle, the CH stretches are far away from the particle surfaces. Their coupling with surface electrons is too small compared to intramolecular vibrational coupling²⁷, and therefore their energy relaxation pathways are dominated by redistributing to intramolecular low frequency modes. Most of these acceptor modes presumably do not directly interact with particle surface electrons or lattice motions, because the group on PVP attached to the particle surface is its carbonyl group which only has a relatively weak intermolecular binding to Pt. Therefore, most of the donor energy cannot transport to the particle and the temperature change that the CO probe detects is negligibly small. It is interesting to note that 200 ps in fig.4C is sufficiently long to detect heat (if any) from PVP molecules. The molecular weight of PVP is 55000 with about 400-500 repeat units, and its through-bond length is about 60 nm. Taking half of the length to estimate the heat distribution time within the polymer chain with the speed of 200 m/s, the time is about 150 ps. In reality, most polymer chains coil on the particle surface, and the

through-space distance from the particle surface is much shorter. No heat detected is a little surprising. We therefore estimate the possible amplitude of temperature increase if all energy absorbed by PVP is assumed to be converted into heat without considering further dissipation into environments. It turns out to be only ~ 0.9 °C (see SI for more details). Considering possible dissipation to environments, the actual value is probably smaller. This estimation is consistent with the experimental results that no heat induced signal is observed.

The situations for the two CO energy donors are very different. Because the surface electrons enter the antibonding orbitals of CO molecules²⁸, the coupling between electrons and the molecules are strong and the dominant energy dissipation pathway for the CO molecules is the electronic motions²⁹. Most of the donor energy can be efficiently converted into electronic motions and subsequently into lattice vibrations that can effectively transport to surface molecules through resonant or quasi-resonant vibrational energy transfers²⁰. In other words, the amount of energy transferred to the probe is large enough that it produces sensible temperature changes detected by the probes.

It is interesting to note that the dynamics of step CO on 2 nm (fig.4A) and 5 nm (fig.4C) Pt particles look different. In fact, both samples have three dynamic processes: one rising step and two dissipating steps. We already know that CO on difference sizes NPs (>2 nm) have similar vibrational energy relaxation rates¹⁹. Therefore, the first two steps: the rising (about initial 5 ps) and the first dissipation through Pt lattice (within 20 ps) are expected to be similar, and actually they are (fig.S7). However, the second dissipation step (to environment) is related to surface molecules, and it is dependent on detailed surfaces. The 5 nm Pt surface is covered with PVP which offers a good heat dissipation pathway, leading to a faster second dissipation step.

4. Conclusions

Three model systems are designed to investigate the energy dissipation dynamics on metallic Pt nanoparticles. The dynamics are monitored with vibrational probes located at different distances from the particle surfaces which are sensitive to molecular thermal energy changes. Energy donors directly attached to particle surfaces can effectively dissipate their energy to the particle surfaces and produce enough thermal energy to heat up the particle surface and the surface molecules. The heating process and energy flow can be easily detected by probes either directly on or several angstroms away from the surface. However, for energy donor that is not directly attached to the particle surface, the particle surface cannot be heated up by its energy relaxation or another molecule on the surface cannot receive energy from it. The seemingly surprising energy flows between surface molecules and Pt particles are the natural consequence of intertwining vibration/vibration and vibration/electron couplings that mediate molecular energy dynamics on metal surfaces. For donors that are attached to particle surfaces, most of their energy can be converted into molecular heat via vibration/electron coupling and subsequently transfer to surface molecules through resonant or quasi-resonant vibrational coupling. For donor that is away from the surface, most of its energy is firstly converted into low frequency intramolecular vibrations that may not be able to couple to the particle surface. The dynamics also confirms that the heat diffusion rate between two molecules on metal nanoparticles is highly chemical bond dependent. The results also reveal that the heat transport through lattice vibrations between two molecules on Pt nanoparticle is about 2 nm/ps, which is one order of magnitude faster than that (2 Å/ps) inside an organic molecule MTS.

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Additional information

Supplementary Information

Competing financial interests: The authors declare no competing financial interests.

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