PAPER

Intermolecular energy flows between surface molecules on metal nanoparticles†

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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 particles within a few picoseconds. On the contrary, 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 surfaces (about 2 km s^{-1}) is almost ten times faster than inside a molecule (200 m s^{-1}). The seemingly perplexing observations can be well explained by the combination of electron/vibration and vibration/vibration coupling mechanisms, which mediate molecular energy dynamics on metal nanoparticle surfaces: 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 as low-frequency intramolecular vibrations that may or may not couple to surface electronic motions.

1. Introduction

Chemical adsorption and kinetic energy dissipation are the basic steps of reactions on metal surfaces.[1] The kinetic energy of a reactant can internally convert into heat or dissipate through surface electronic motions if the molecules are close enough to the metal surface.[2–6] The intertwining nuclear and electronic motions have been suggested to be responsible for the amazing complexity and delicacy of chemical dynamics on metal surfaces.[5–13]

Ultrafast vibrational spectroscopy has provided very useful molecular information and the dynamics occurring on metal nanoparticles, the major components of many heterogeneous catalysts. For example, Berkerle *et al.* applied ultrafast vibrational spectroscopy to record diatomic molecule-carbon monoxide (CO) energy relaxation on a 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 as surface electronic motion.[15] Another very interesting work showed that heat generated from electronic excitation on Au nanoparticles can

rapidly transfer to surface molecules.[16] 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 have investigated energy transfers among molecules on the surface of metal nanoparticles.

In this work, by using three model systems with vibrational modes as "thermometers" to probe molecular heat, we are able to measure energy transfers between molecules on the surface of metal nanoparticles. We deposit energy in one molecule by vibrationally exciting one of its high-frequency modes and detect the response from 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^{-1} between molecules on the Pt surface, and the rate is slowed down by almost one order of magnitude to 200 m s^{-1} inside a molecule.

2. Experimental details

The optical setup has been reported elsewhere.[17] Briefly, a one-picosecond (ps) amplifier and a 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

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10–35 cm^{-1} in a tunable frequency range of 1000 cm^{-1} to 4000 cm^{-1} with energy ranging from 10–40 μJ per pulse at 1 kHz as the 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 a 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.

The synthetic method of 2 nm Pt NPs has been reported previously.[18] Briefly, K$_2$PtCl$_4$ (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 added into the mixture solution. For both cases, CO gases were bubbled into the solutions at a rate of 200 ml min^{-1} 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 in several drops of 1,2-ethanediol and transferred onto the CaF$_2$ windows. The samples were placed into a 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 the spectra. During ultrafast experiments, the excitation power was ∼5 mW at 2000 cm^{-1}. The synthetic method and characterization data of the 5 nm Pt nanoparticles with CO and PVP coating on the surface have also been reported in our previous publication.[19] Briefly, 5 ml ethylene glycol was used to dissolve Pt(II) acetylacetonate (80 mg) and polyvinylpyrrolidone (PVP, 55 mg, M_W = 55 000) at room temperature. The mixture was transferred to a microwave reactor (Anton Paar Monowave 300) with the following reacting parameters. The heating temperature was set to 200 °C, the stirring rate was modulated at 1200 rpm and the reacting time was 5 min. Then, the reaction mixture was cooled down to room temperature. Acetone (45 ml) was added to the solution to precipitate the Pt nanoparticles. 10 ml ethylene glycol was added into the sediments to remove excess PVP. The CO gases coating method and the sample preparation method for optical measurement followed the same procedure as given above.

3. Results and discussion

Fig. 1 displays the three model systems used in the experiments. There are at least three major types of CO-binding sites on the particle surface: (I) the CO molecule sits on 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 deposited into the CO molecules on the bridge sites of the 2 nm Pt particle by using an ultrafast infrared (IR) pulse to resonantly excite its CO stretch mode (1840 cm^{-1}). Another IR pulse as a probe is then applied to detect how the bridge CO vibrational energy flows to the CO molecules on the step sites (2030 cm^{-1}). In Fig. 1B, energy is deposited into the CO molecules on the step sites and the energy sensor is the carbonyl (C=O) group (1713 cm^{-1}) of methyl thiosalicylate (MTS) also attached to the Pt nanoparticle surface. In Fig. 1C, energy is deposited into the CH stretches (2940 cm^{-1}) of the surface polyvinylpyrrolidone (PVP) molecules, and the energy sensor is the step CO molecules.

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 and are lifted to their vibrational first excited state. The excited donors dissipate energy as electronic motions or low-frequency vibrations and ultimately propagate away in the form of heat. Once the 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 coupling.[20–23] During the process, direct vibrational energy transfer with vibration dipole–dipole coupling between the donors and the sensors is negligible (ESI†) because the electron/vibration coupling and intramolecular vibrational coupling are significantly stronger than the intermolecular coupling between the donors and sensors.

The waiting time-dependent 2D IR spectra (red peak) of the step CO after the bridge CO is vibrationally excited are displayed in Fig. 3A. The excitation frequency 1840 cm^{-1} is the bridge CO stretch 0–1 transition frequency, indicating that the signal originates from the bridge CO. The detection frequency is the step CO 0–1 transition frequency, reflecting the response of the step CO caused by the bridge CO vibrational excitation.
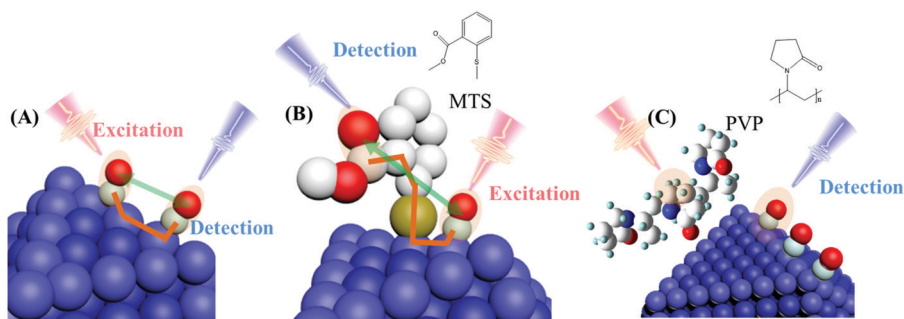

Fig. 1 Three energy distribution model systems: (A) from bridge CO to step CO on the Pt particle, (B) from step CO to the carbonyl stretch of methyl thiosalicylate (MTS) on the Pt particle, and (C) from C–H of PVP to step CO on the Pt particle surface.
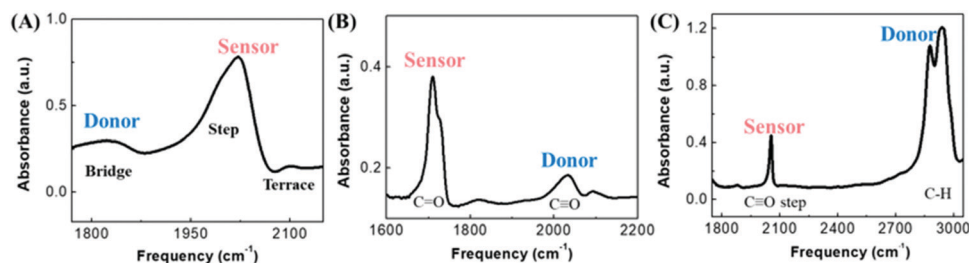
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Phys. Chem. Chem. Phys., 2019, **21**, 4240–4245 | **4241**

Fig. 2 The FTIR spectra of (A) CO molecules on different surface sites of the 2 nm Pt particle; (B) the MTS CO stretch and step CO stretch on the 2 nm Pt particle; (C) the PVP CH stretches and step CO on the 5 nm 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.
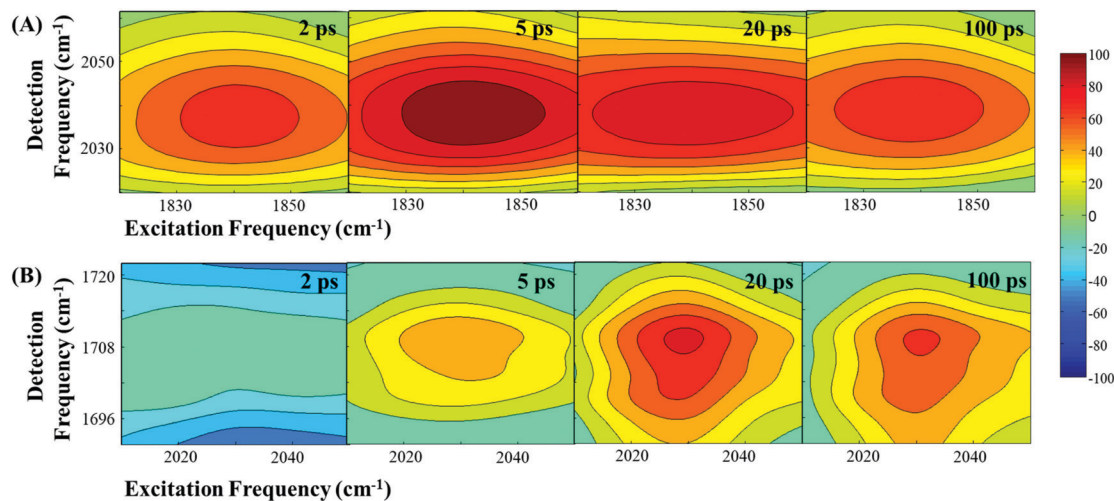

Fig. 3 Waiting time-dependent 2D IR spectra of (A) the step CO stretch after the bridge CO is excited and (B) the carbonyl stretch of MTS after the step CO is excited.

The 2D IR signal is plotted in red, representing a bleaching signal. As briefly described above, the vibrational energy of the bridge CO dissipates as surface electronic excitation, which quickly thermalizes within a couple of ps and raises the local temperature. The temperature increase causes a frequency redshift of the step CO vibration and 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 the maximum at 5 ps and declines 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 ESI†) reveal the three dynamic processes that the step CO experiences. The first process indicates a temperature increase with the time constant at 2.2 ± 0.3 ps. This is followed by a fast temperature decrease at 4.2 ± 0.7 ps and a slow energy dissipation at 1000 ± 200 ps. The three time constants have clear physical origins. Previous studies have suggested that CO molecules dissipate vibrational
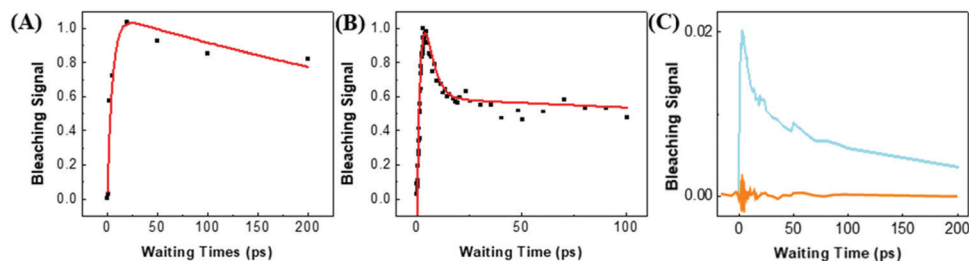
Fig. 4 Waiting time-dependent intensities of (A) step CO stretch after bridge CO is excited on the 2 nm Pt particle; (B) carbonyl stretch of MTS after step CO is excited on the 2 nm Pt particle; and (C) step CO stretch after bridge CO is excited (cyan) on the 5 nm Pt particle and step CO stretch after CH stretches of PVP are excited (orange) on the 5 nm Pt particle.

is covered with PVP, which offers a good heat dissipation pathway, leading to a faster second dissipation step.

4. Conclusions

Three model systems were 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 the 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 the surface molecules and the Pt particles are natural consequences 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 transferred to surface molecules through resonant or quasi-resonant vibrational coupling. For a 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 the Pt nanoparticle is about 2 nm ps^{-1}, which is one order of magnitude faster than that (2 Å ps^{-1}) inside an organic molecule MTS.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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4244 | *Phys. Chem. Chem. Phys.*, 2019, **21**, 4240–4245

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