Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intermolecular Energy Flows between Surface Molecules on Metal Nanoparticles

Jiebo Li[b], Yufan Zhang[a], Junrong Zheng[a,*]

[a] College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, Beijing 100871, China

[b] Beijing Advanced Innovation Center for Biomedical Engineering, School of Biological Science and Medical Engineering, Beihang University, Beijing, 100083

* To whom correspondence should be addressed: junrong@pku.edu.cn, and zhengjunrong@gmail.com

This file includes:

Figure S1 to S7

Supporting Information text

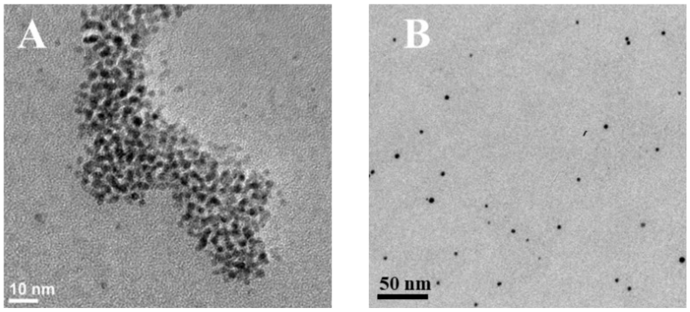

Fig. S1TEM Characterization of 2nm (A) and 5 nm (B) Pt samples

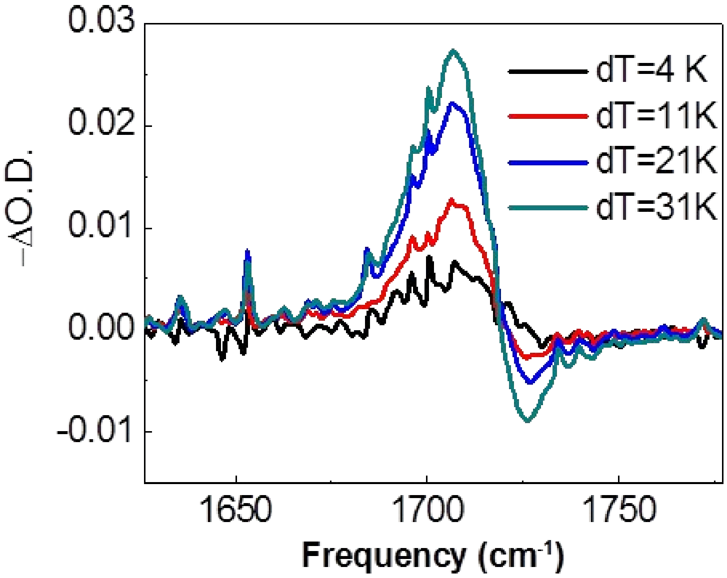

Fig. S2 Temperature dependent FTIR of carbonyl group of MTS.

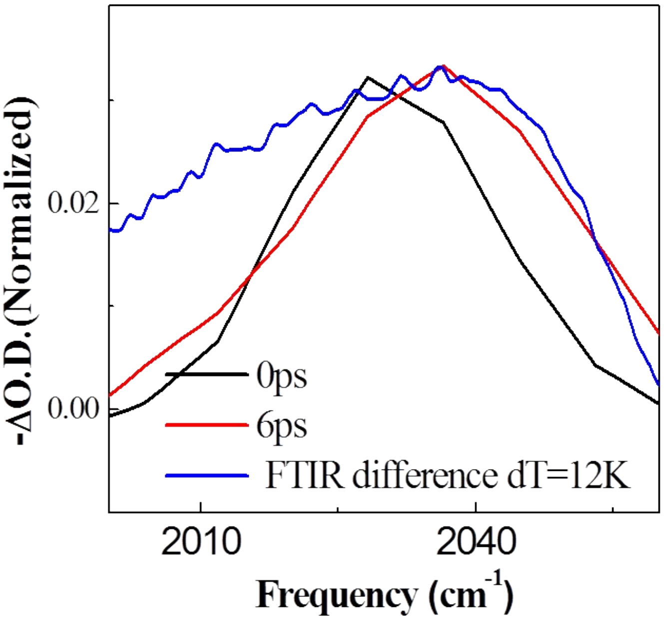

Fig. S3 Temperature dependent FTIR and pump probe spectrum of carbon monoxide on 2 nm PtNP.

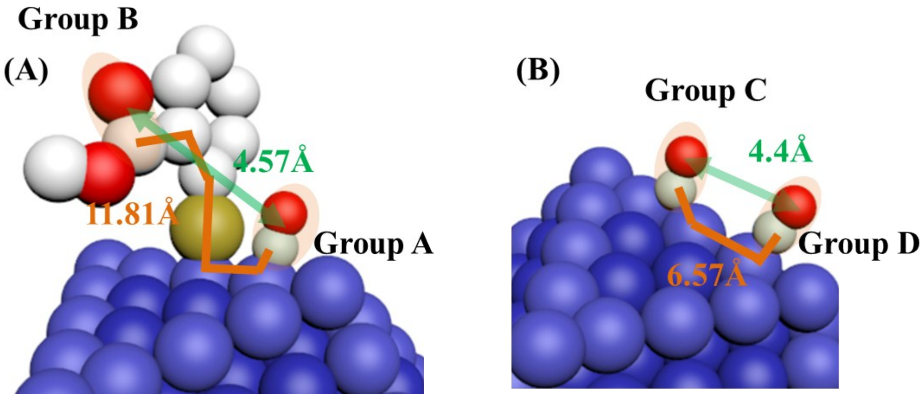

Fig. S4 Cartoon illustration of distances between two groups through bonds (orange) and space (green) (A) CO (group A) and carbonyl (group B) (B) CO (bridge CO) and CO (step CO).

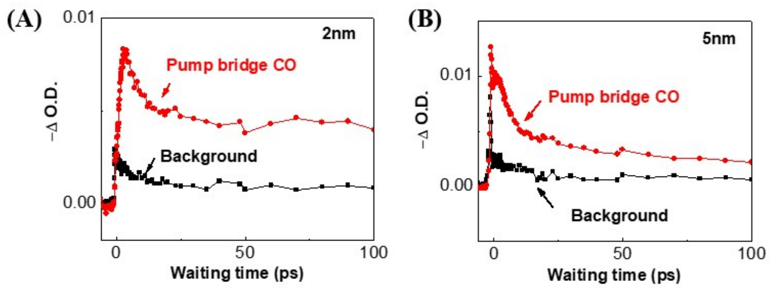

Fig. S5 Waiting time dependent intensities of step CO stretch after bridge CO is excited on 2nm (A) and 5nm (B) Pt particle (red); step CO stretch after heating particle with IR light (2220 cm^{-1}) (black).

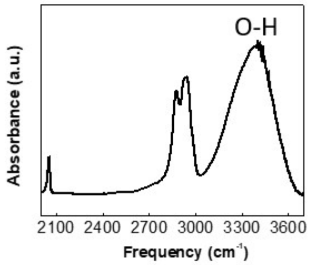

Fig. S6 FTIR of water absorption peak (3400 cm^{-1}) on 5 nm Pt nanoparticle coating with PVP.

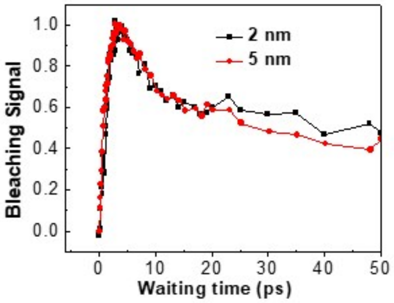

Fig. S7 Waiting time dependent normalized intensities of step CO stretch after bridge CO is excited on 2nm and 5nm particles.

Fitting parameters for energy transport of two cases

Energy transport from CO on surface to carbonyl on the MTS:

$y=A_1\exp(-x/t_1)+A_2\exp(-x/t_2)+y_0$

$A_1=-1.04$, $t_1=5$ ps, $A_2=1.08$, $t_2=600$ ps, $y_0=0$; (parameter t_1 could be varied from 4 ps to 6 ps. Thus, in the manuscript, we gave the average rate with err bar is 5±1 ps. Parameter t_2 is varied from 500 ps to 700 ps. Thus, the average rate with err bar is 600±100 ps.)

Energy transport from CO on surface bridge site to CO on surface step site:

$y=A_1\exp(-x/t_1)+ A_2\exp(-x/t_2)+ A_3\exp(-x/t_3)$

$A_1=-2.8$, $t_1=2.2$ ps, $A_2=2.4$, $t_2=4.2$ ps, $A_3=0.59$, $t_3=1000$ ps. (parameter t_2 could be varied from 3.5 ps to 4.8 ps. Thus, in the manuscript, we gave the average rate with err bar is 4.2±0.7 ps. Parameter t_3 is varied from 800 ps to 1200 ps. Thus, the average rate with err bar is 1000±200 ps.)

Surface energy donor and sensor distances The 2 nm Pt nanoparticle contains ~ 300 Pt atoms in total. There are 162 pt atoms on the surface of 2 nm Pt nanoparticle. In total, 53% Pt atoms are on the surface. 0.0047g MTS is designed to occupy half of surface Pt atoms. The rest half Pt surface atoms are saturated with CO in EG solution as the following procedure. Based on the absorption peaks' ratio (FTIR), we obtain that C=O (MTS): C≡O (step) ratio is around 6:1. MTS occupies half of the surface. CO takes the other half. If the center Pt atom is occupied at Pt (111) surface, the six Pt atoms must be attached by CO on steps. In other words, MTS binding Pt and CO binding Pt are next to each other. Therefore, as shown in Fig. S4, the nearest distance between donor C≡O to reporter C=O is around 11.8 Å ($2.0_{Pt\text{-}C}+2.77_{Pt\text{-}Pt}+2.33_{Pt\text{-}S}+1.78_{S\text{-}C}+1.39_{C=C}+1.54_{C\text{-}C}$).[1-3] The C=O distance to the surface is around 5.9 Å ($1/2*2.33_{Pt\text{-}S}+1.78_{S\text{-}C}+1.39_{C=C}+1.54_{C\text{-}C}$). The space distance 4.57 Å for case 1 determination uses the condition of parallel situation between C≡O and phenol ring. For the second case (Pt NP with step and bridged CO)Because C≡Os are saturated. The nearest distance between CO_{step} and CO_{bridge} is 6.57 Å ($2.0_{Pt\text{-}C}+2.77_{Pt\text{-}Pt}+1.8_{Pt\text{-}C}$) through bond. The space distance 4.4 Å determination is with the assumption that two C≡O molecules are parallel to each other on surfaces.

Dipole-dipole coupling transfer rate upper limit Let's estimate if no electronic mediating two molecules on surface energy transport, how fast two molecule exchange energy based on dipole-dipole coupling. The distance between COs are ~4.4 Å. Assuming transition dipole of CO is 0.4 D, the calculated coupling between two COs is around 4.6 cm^{-1}. The calculated coupling was then used to calculate the energy transfer rate from CO_{step} to CO_{Bridge} with dephasing time (0.37 ps)[4] and energy mismatch (190 cm^{-1}).

$$k_{DA} = \frac{2}{1+e^{\frac{-\Delta\omega}{kT}}}\beta^2 \frac{\frac{1}{\tau}}{\left(\Delta\omega\right)^2+4\beta^2+\tau^{-2}} = \frac{2}{1+\exp(-190/200)}4.6^2\frac{\frac{1}{\tau}}{190^2+4.6^2+14.4^2} = 1/441(\mathrm{ps}^{-1})$$

Eq. S1

The donor acceptor rate ratio is based on the detailed balance k_{DA}/k_{AD}=exp(ΔE/KT)=exp((2030-1840)/206)=2.5. Thus, the energy transfer rate from CO on bridge to CO on step is 1/1102 ps^{-1}, which comes from (1/2.5)*(1/441). Thus, for case 1, the C=O at 1713 cm^{-1} is even larger than bridge CO (1840 cm^{-1}), it is definitely much slower rate. Therefore, the signals from fig 3 and fig 4 are reporting heat dynamics not 1st vibrational energy exchanging.

Estimated of temperature increase for the PVP coated sample: the laser spot is 200-300 microns, the sample thickness is 100 microns, the laser pulse energy is about 10uJ (assumed to be completely absorbed), the density of PVP is about 0.8 g/cm-3, and the heat capacity is assumed to be 0.8 cal/degree.g. The estimated temperature increase is about 0.9 ^{0}C without considering any dissipation. Water molecules absorbed by PVP (fig. s6) may also facilitate the energy dissipation to environments.

References:

(1) Orita, H.; Inada, Y. DFT investigation of CO adsorption on Pt (211) and Pt (311) surfaces from low to high coverage. *J Phys Chem B* **2005**, *109*, 22469-22475.

(2) Wei, G.-F.; Liu, Z.-P. Restructuring and hydrogen evolution on Pt nanoparticle. *Chemical science* **2015**, *6*, 1485-1490.

(3) Lin, X.; Ramer, N. J.; Rappe, A. M.; Hass, K. C.; Schneider, W. F.; Trout, B. L. Effect of particle size on the adsorption of O and S atoms on Pt: A density-functional theory study. *J Phys Chem B* **2001**, *105*, 7739-7747.

(4) Li, J.; Yuan, K.; Chen, H.; Miranda, A.; Chen, Y.; Shen, Y.; Jiang, B.; Zhang, Y.; Guo, X.; Zheng, J. Non-Resonant Vibrational Energy Transfer on Metal Nanoparticle/Liquid Interface. *J Phys Chem C* **2016**, *120*, 25173-25179.