

# POLARIZATION-DEPENDENT SFG SPECTROSCOPY OF NEAR AMBIENT PRESSURE CO ADSORPTION ON Pt(111) AND Pd(111)

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## INTRODUCTION

For many years, the surface science approach to heterogeneous catalysis was restricted to gas pressures of  $10^{-6}$  mbar and below, giving rise to the well-known “pressure gap” problem [1,2]. This limitation was overcome when surface-sensitive methods were developed that could be operated at least in the mbar pressure range. Sum frequency generation (SFG) vibrational spectroscopy has high surface sensitivity and selectivity, most importantly, it is non-destructive and without vacuum-limitation, which make it popular in the study of surface/interface sciences including the catalysis reactions. Polarization-dependent (PD-) SFG has been proven an excellent tool in providing the microscopic information of adsorbed molecules at interfaces, such as molecular structure, orientation, symmetry, chirality, and dynamics [3-5]. However, the detail analysis of CO on model catalysts (Pt(111) and Pd(111)) is still lack. This is because usually only one polarization-combinations (i.e. PPP) spectra could be measured before [6,7], resulting in the missing of the orientation information.

## EXPERIMENTS

The experiments on Pt(111) and Pd(111) single crystals were performed in a new UHV surface analysis system equipped with an SFG-compatible UHV-high pressure cell [8]. Both Pt and Pd surfaces were cleaned by circles of  $\text{Ar}^+$  ion bombardment (beam energy 1.3 keV at  $5 \times 10^{-6}$  mbar of Ar) at room temperature and subsequent annealing at 1200 K for 2 min. If necessary, oxidation in  $1 \times 10^{-6}$  mbar  $\text{O}_2$  was used to remove carbon contamination. The surface structure of single crystal was examined by low energy electron diffraction (LEED). SFG was performed using a Nd:YAG (neodymium-doped yttrium aluminum garnet, Nd:  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) fundamental radiation of a PL 2241 laser (EKSPLA, 1064 nm, 30 mJ/pulse), with a 20 ps pulse width and 50 Hz repetition rate. The visible beams (532 nm) and tunable IR beam ( $1000\text{-}4300 \text{ cm}^{-1}$ ) are spatially and temporally overlapped on the single crystal surface in a co-propagating geometry at an incidence angle of  $58.5^\circ$  ( $\alpha_{\text{vis}}$ ) and  $55^\circ$  ( $\alpha_{\text{IR}}$ ) with respect to the surface normal, respectively. The polarization of visible beam and SFG signal can be switched between P and S using Glan-Taylor prism and a half-wave plate, while the IR polarization was kept as P because S-polarized field would be canceled on a metal surface [9].

## RESULTS AND DISCUSSION

SSP and PPP spectra of near ambient pressure CO on Pt(111) at room temperature have been obtained, as shown in Fig. 1. However, no SSP signal of CO on Pd(111) was observed. Moreover, PPP signal of CO on Pd(111) was much smaller than on Pt(111) (Fig. 2a) [10]. Similar increase of SSP and PPP spectra with increasing CO pressure showed that the orientation of CO molecules on Pt(111) surface was independent of the gas pressure.

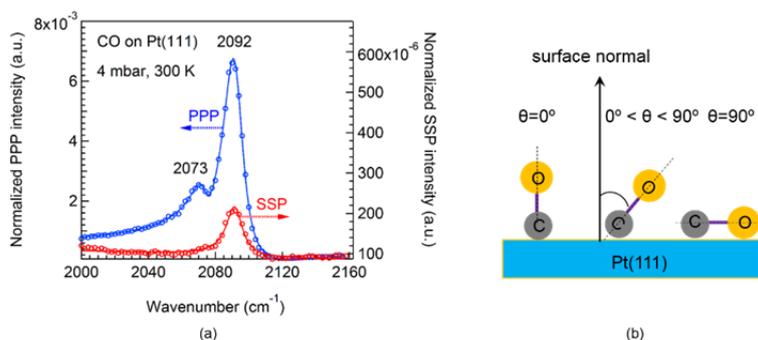


Fig. 1 Polarization-dependent SFG spectra of CO adsorption on Pt(111) at 4 mbar and 300 K. Symbols refer to experimental data. Blue circles: PPP polarization; Red circles: SSP polarization; Solid lines represent the global fitting curves with Lorentzian lineshapes. b Schematic diagram of tilt angles of CO on a Pt surface.

A modelling analysis of influences of incidence angles ( $\alpha_{\text{IR}}$  and  $\alpha_{\text{vis}}$ ) and refractive indices of substrates on the SFG intensity and orientation, as well as the relationship of SFG intensity, orientation and molecular hyperpolarizability ratio ( $R$ ), has been discussed in detail (e.g. Fig. 2). Results showed that SFG spectral intensity is much more sensitive to  $\alpha_{\text{vis}}$  than  $\alpha_{\text{IR}}$ . Based on a larger simulated  $I_{\text{PPP}}/I_{\text{SSP}} = 48$ , and a smaller experimental PPP signal of CO on Pd(111), the effective surface number density of CO molecules should be smaller than that of CO on Pt(111) [10].

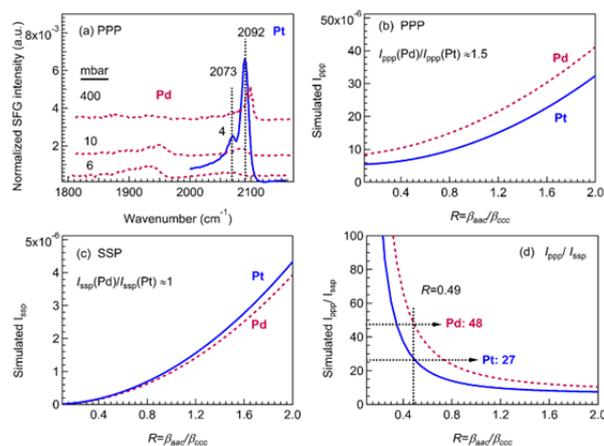


Fig. 2 Comparison of spectral intensity of on-top CO on Pd(111) and Pt(111). a. Experimental PPP spectra at 300 K,  $I_{\text{PPP}}(\text{Pd}) < I_{\text{PPP}}(\text{Pt})$ . Dark red: CO on Pd(111). Blue: CO on Pt(111): 4 mbar. b. Simulated  $I_{\text{PPP}}$  versus  $R$ . c. Simulated  $I_{\text{SSP}}$  versus  $R$ . d.  $I_{\text{PPP}}/I_{\text{SSP}}$  versus  $R$ . The following parameters were used in the simulation:  $\omega_{\text{IR}} = 2090 \text{ cm}^{-1}$ ,  $\alpha_{\text{IR}} = 55^\circ$ ;  $\omega_{\text{vis}} = 532 \text{ nm}$ ,  $\alpha_{\text{vis}} = 58.5^\circ$ ;  $N_s = 1$ ,  $\beta_{\text{ccc}} = 1$ , and  $\theta = 0^\circ$ .

## CONCLUSION

An exact value of molecular hyperpolarizability ratio of CO molecules,  $R=0.49$  (assumed tilting angle of  $0^\circ$ ), has been determined according to the polarization-dependent SFG spectra of CO on Pt(111) surface. Pressure-dependent SFG spectra on Pt(111) ( $10^{-4}$  to 36 mbar) did not indicate any orientation change of adsorbed CO. A proper experimental configuration (especially  $\alpha_{\text{vis}}$ ) plays important role in measuring SSP and PPP spectra with good signal-to-noise ratio. Weaker PPP and non-SSP signals of CO on Pd(111) implied a smaller surface number density of ordered CO molecules.

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