Polarization-Dependent SFG Spectroscopy of Near Ambient Pressure CO Adsorption on Pt(111) and Pd(111) Revisited

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Abstract
Polarization-dependent sum frequency generation (SFG) vibrational spectroscopy was employed to examine CO overlayers on Pt(111) and Pd(111) single crystal surfaces at room temperature. Utilizing different polarization combinations (SSP and PPP) of the visible and SFG light allows to determine the molecular orientation (tilt angle) of interface molecules but the analysis of the measured \( \frac{I_{ppp}}{I_{ssp}} \) is involved and requires a proper optical interface model. For CO/Pt(111), the hyperpolarizability ratio \( R = \frac{\beta_{acc}}{\beta_{ccc}} = \frac{\beta_{bce}}{\beta_{ccc}} \) is not exactly known and varying \( R \) in the range 0.1–0.5 yields tilt angles of 40°–0°, respectively. Based on the known perpendicular adsorption of CO on Pt, an exact \( R \)-value of 0.49 was determined. Polarization-dependent SFG spectra in the pressure range 10\(^{-4}\) to 36 mbar did not indicate any change of the tilt angle of adsorbed CO. Modeling also indicated a strong dependence of \( \frac{I_{ppp}}{I_{ssp}} \) on the incidence angles of visible and IR laser beams. Complementing previous low temperature/low pressure data, room temperature CO adsorption on Pd(111) was examined from 10\(^{-6}\) to 250 mbar. The absolute PPP and SSP spectral intensities on Pt and Pd were simulated, as well as the expected \( \frac{I_{ppp}}{I_{ssp}} \) ratios. Although CO on Pt and Pd should exhibit similar intensities (at high CO coverage), the higher \( \frac{I_{ppp}}{I_{ssp}} \) ratio for Pd (48 vs. 27 on Pt) renders the detection of adsorbed CO in SSP spectra difficult. The presence or absence of CO species in SSP spectra can thus not simply be correlated to tilted or perpendicular CO molecules, respectively. Careful modeling, including not only molecular and interface properties, but also the experimental configuration (incidence angles), is certainly required even for seemingly simple adsorbate–substrate systems.

Keywords Sum frequency generation · Carbon monoxide · Single crystals · Orientation · Model catalysis

1 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 [1–3]. This limitation was overcome when surface-sensitive methods (or modes thereof) were developed that could be operated at least in the mbar pressure range. Among the first were sum frequency generation (SFG) vibrational spectroscopy and high pressure scanning tunneling microscopy (HP-STM), both methods and their application to catalytic problems being pioneered by Somorjai and coworkers [4–6]. A specific asset of SFG was the ability to monitor adsorbed molecules in situ during the ongoing catalytic reaction at mbar gas pressure and elevated temperature, i.e. under technologically relevant conditions [7]. To date, Somorjai’s group has examined a vast range of reaction systems, mostly on Pt surfaces, spanning from ethylene, propylene and cyclohexene hydrogenation/dehydrogenation via CO oxidation/dissociation and CO/hydrocarbon coadsorption to selective aldehyde hydrogenation [8–13], to name just a few. As Pt model catalysts, various low-Miller-index as well as stepped and kinked single crystal surfaces were utilized (linking the SFG in situ work to Somorjai’s early high pressure cell studies without spectroscopy), complemented by thin films as supports for shape-controlled colloidal nanoparticles [14, 15]. This enabled to examine metal-support interactions for nanoparticles that often occur in reducing (hydrogen) atmosphere [16–18].

SFG vibrational spectroscopy can also be used to probe the orientation (tilt angle) of molecules adsorbed on metallic, semiconductor and insulator surfaces, making use of the dependence of intensities of different polarization
2 Basic Theory of SFG

SFG is a second-order nonlinear optical process during which two photons of certain frequencies interact simultaneously with a surface molecule to instantaneously emit a new photon at the sum of the two frequencies. The unique advantage of SFG, distinct from other surface-sensitive techniques, is attributed to its interface selectivity. This originates from the fact that coherent second-order optical processes are forbidden in media with inversion symmetry, while they are allowed for an interface layer, where this centro-symmetry is naturally broken. The SFG intensity (\(I_{SFG}\)) is proportional to the two incident laser intensities (\(I_{VIS}\) and \(I_{IR}\)) and the absolute square of second-order nonlinear susceptibility (\(\chi_{eff}^{(2)}\)), as shown in Eq. 1.

\[
I_{SFG} \propto \left| \chi_{eff}^{(2)} \right|^2 I_{VIS} I_{IR}
\]

The surface susceptibility \(\chi_{eff}^{(2)}\) is composed of a non-resonant (\(\chi_{NR}^{(2)}\)) and resonant part (\(\chi_R^{(2)}\))

\[
\chi_{eff}^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)} = \chi_0 e^{i\phi} + \sum a_{ijR} e^{-i\Gamma_q} \tag{2}
\]

Here \(\chi_0\) is the magnitude of the non-resonant susceptibility \(\chi_{NR}^{(2)}\) due to electronic excitations of the substrate and the adsorbate, and \(\phi\) is its phase relative to the resonant term. \(a_{ijR}\), \(\Gamma_q\) represent the resonance amplitude, frequency and damping constant of the \(q\)th vibrational mode, respectively. \(a_{ijR}\) is the frequency of the IR laser beam. In general, \(\chi_{NR}^{(2)}\) should be small and real when the substrate is not resonant with either \(a_{ij}\) of incident visible, IR and output SFG beams. For dielectric interfaces, it is negligible. However, for metal or semiconductor substrate interfaces, \(\chi_{NR}^{(2)}\) generally becomes complex and can no longer be ignored. \(\chi_{eff}^{(2)}\) depends on the experimental polarization and geometry, and there are an infinite number of combinations of experimental configurations that can give different \(\chi_{eff}^{(2)}\). In this paper, we mainly study \(\chi_{eff}^{(2)}\) with a linear combination of independent experimental polarization combinations, namely, SSP (S-polarized sum frequency, S-polarized visible and P-polarized infrared) and PPP as shown in the following:

\[
\begin{align*}
\chi_{eff,SSP}^{(2)} & = L_{\gamma\gamma}(\omega_{SFG}) L_{\gamma\gamma}(\omega_{VIS}) L_{\gamma\gamma}(\omega_{IR}) \sin \alpha_{IR} \chi_{xyz} \\
\chi_{eff,PPP}^{(2)} & = - L_{\chi\lambda}(\omega_{SFG}) L_{\chi\lambda}(\omega_{VIS}) L_{\chi\lambda}(\omega_{IR}) \cos \alpha_{SFG} \cos \alpha_{VIS} \sin \alpha_{IR} \chi_{xxz} \\
& - L_{\lambda\chi}(\omega_{SFG}) L_{\chi\lambda}(\omega_{VIS}) L_{\lambda\chi}(\omega_{IR}) \cos \alpha_{SFG} \sin \alpha_{VIS} \cos \alpha_{IR} \chi_{xxy} \\
& + L_{\chi\chi}(\omega_{SFG}) L_{\chi\chi}(\omega_{VIS}) L_{\chi\chi}(\omega_{IR}) \sin \alpha_{SFG} \sin \alpha_{VIS} \cos \alpha_{IR} \chi_{xxxx} \\
& + L_{\chi\chi}(\omega_{SFG}) L_{\chi\chi}(\omega_{VIS}) L_{\chi\chi}(\omega_{IR}) \sin \alpha_{SFG} \sin \alpha_{VIS} \sin \alpha_{IR} \chi_{xzz} \\
\end{align*}
\]

Here \(\omega_{SFG}, \omega_{VIS}\) and \(\omega_{IR}\) are the frequencies; \(a_{SFG}, \alpha_{VIS}\) and \(\alpha_{IR}\) are the angles (with respect to the surface normal), of the SFG signal, visible and IR laser beams, respectively. \(L_{ij}(\omega)\) denotes the Fresnel factor at frequency \(\omega\), for the local field corrections, which can be calculated with the knowledge of \(\eta\) and refractive indices \(n_1\) (medium 1, the air in which incident and SFG photons propagate), \(n_2\) (medium 2, the single crystal phase) and \(n'\) (interfacial layer). In this paper, the \(n'\) values were estimated by the modified Lorentz model, and the expression is 

\[n' = n_1 n_2 \sqrt{\frac{\sin^2 n_2^2 - \sin^2 n_1^2}{4 n_2^2 + 2 n_2^2}} \tag{[26]}\]

when \(n_1 = 1\), then 

\[n' = n_2 \sqrt{\frac{n_2^2 + n_1^2}{4 n_2^2 + 2 n_2^2}} \tag{[27]}\]

\(\chi_{eff}^{(2)}\) is the macroscopic sum frequency susceptibility, which is related to the microscopic hyperpolarizability tensor elements \(\beta_{ij'jk}\) in the molecular coordinates system. \(\chi_{ij}^{(2)}\) can be deduced from SFG measurement with three different input/output polarization combinations, for example, SSP, SPS, PSS and PPP.

For \(\chi_{SSP}\), symmetry group, such as CO, OH, –CH, there are only two independent nonvanishing components in \(\beta_{ij'jk'}\) and \(\beta_{0ij'} = \beta_{0j'i}\). Then, the non-zero macroscopic elements of \(\chi_{ij}^{(2)}\) for a rotationally isotropic interface which are obtained through integration over the Euler angles (\(\phi\), azimuth angle; \(\psi\), twist angle) can be expressed as follows [27, 28].

\[
\begin{align*}
\chi_{xxy}^{(2)} & = \chi_{xxx}^{(2)} = \frac{1}{2} N \beta_{ecx} \left[ (1 + R)(\cos \theta) - (1 - R)(\cos \theta)^3 \right] \\
\chi_{xzy}^{(2)} & = \chi_{xyz}^{(2)} = \chi_{yzy}^{(2)} = \frac{1}{2} N \beta_{exx} \left[ (1 - R)(\cos \theta) - (1 + R)(\cos \theta)^3 \right] \\
\chi_{xzz}^{(2)} & = \frac{1}{2} N \beta_{ccc} \left[ R(\cos \theta) + (1 - R)(\cos \theta)^3 \right] \\
\end{align*}
\]

Here \(\beta_{ij'jk'}^{(2)}\) is the molecular hyperpolarizability tensor. The hyperpolarizability ratio is \(R = \beta_{acx}/\beta_{exc} = \beta_{bxc}/\beta_{ecx}\). For a single bond with \(C_{1v}\) symmetry, the R-value equals to the bond polarization derivative ratio \(r\). Different R-values will

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lead to different results in the SFG orientational analysis [21, 27, 28]. θ is the orientation angle of the moiety of the symmetry axis with respect to the surface normal. \( N_s \) is the effective surface number density of molecules contributing to the SF signal. Then, based on Eqs. 1–4, we can determine the orientation (θ) and/or molecular hyperpolarizability ratio (R) of the moiety by the measurements of the ratio of independent nonvanishing \( \chi_{ijk}^{(2)} \) components assuming a δ-function distribution for θ. The latter assumption is frequently applied because only a small angular distribution is expected.

3 Experimental Section

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 [25] (setup similar to that described in Refs. [2, 29]). Both Pt and Pd surfaces were cleaned by cycles of Ar ion bombardment (beam energy 1.3 keV at 5 × 10⁻⁶ mbar of Ar, 10 min) and subsequent annealing at 1200 K for 2 min. If necessary, oxidation in 1 × 10⁻⁶ mbar \( \text{O}_2 \) was used to remove carbon contamination. The surface structure was examined by LEED. Before transferring to the SFG cell, the clean single-crystal surface was exposed to 5 × 10⁻⁷ mbar of \( \text{CO} \) gas at room temperature via a leak valve, in order to passivate the surface and to avoid unwanted adsorption of impurities on the surface during sample transfer.

SFG was performed using a Nd:YAG (neodymium-doped yttrium aluminum garnet; Nd:Y\(_3\)Al\(_5\)O\(_{12}\)) fundamental radiation of a PL2241 laser (EKSLPA, 1064 nm, 30 mJ/pulse), with a 20 ps pulse width and 50 Hz repetition rate. Part of the fundamental laser is frequency converted to second harmonics (532 nm) realized in K\(^+\)DP nonlinear crystals.

One part of laser pulses at 532 nm is used as visible input for the surface SFG experiment. Another part of the 532 nm beam is used to pump an optical parametric (BBO crystal)/difference frequency generation (AgGaS\(_2\) crystal) system and generate tunable infrared light from 1000–4300 cm⁻¹ (2.3–10 \( \mu \)m) with a spectral width < 6 cm⁻¹. The visible and infrared beams are spatially and temporally overlapped on the single-crystal surface in a co-propagating geometry at an incidence angle of 58.5° and 55° with respect to the surface normal, respectively. The energy is ~40 \( \mu \)J/pulse for the visible beam and energies between 90 and 130 \( \mu \)J/pulse were used for the tunable infrared pulse with frequencies between 1800 and 2160 cm⁻¹. CaF\(_2\) and quartz windows served as entrance and exit ports for the incident laser beams and output SFG radiation, respectively. The SFG signal is filtered with a monochromator and detected with a photo-multiplier tube (PMT). The polarization of the visible light and SFG signal were switched between P and S using a Glan–Taylor prism and a half-wave plate, while the infrared polarization was always kept as P (an S-polarized field would be canceled on a metal surface) [30].

4 Results and Discussion

4.1 SFG Spectra of CO on Pt(111)

Polarization-dependent SFG spectra of CO/Pt(111) in the C–O stretch region were acquired at mbar pressure and 300 K. SSP and PPP spectra are presented in Fig. 1a. Because of the SFG selection rules [28], the SSP spectral intensity is much weaker than PPP. However, the spectra still had a good signal-to-noise ratio. The PPP spectrum of CO exhibits two peaks both attributed to linearly bonded CO molecules (with the carbon atom bound to a single Pt atom), but adsorbed at different sites of the single crystal. The sharp peak around 2092 cm⁻¹ characterizes the on-top CO species adsorbed on terrace sites [31, 32], whereas the smaller shoulder around 2073 cm⁻¹ is assigned to species adsorbed on step-sites on the surface [24, 33]. Unlike the PPP spectrum, in the SSP spectrum only on-top CO molecules adsorbed on terrace sites were detected, while the step-sites CO was not clearly observed (likely due to lower surface number density). The asymmetric lineshape of the SFG spectra, which is particularly pronounced for the lower frequency band in the PPP spectrum, is due to the interference of resonant and non-resonant terms (Eq. 2); particularly when \( \chi_{NR} \) is real and has the same sign as \( \chi_q \) [34].

The correspondence between C–O stretch frequencies and defect sites (steps or kinks) has been well documented for CO on Pt(111) using infrared spectroscopy [33, 34–38]. Frequencies for CO on defect sites are in general between 2058 and 2078 cm⁻¹, lower than the frequencies of the terrace site vibrations. In a room-temperature SFG study of CO adsorbed on a disordered Pt(111) surface at a low coverage, a single vibrational frequency of 2072 cm⁻¹ was reported by Daum and co-workers [24], but this frequency blue-shifted to 2093 cm⁻¹ at higher coverage. For CO on a flat and well-ordered Pt(111) surface, the frequency of the C–O stretching vibration increases with exposure from 2083 to 2093 cm⁻¹ at 300 K [24]. In addition, CO molecules prefer to adsorb on the step sites first, and then on the terrace-site of a defect-rich Pt(111) surface [33]. Similarly, studies of other surfaces with a high step density, such as Pt(533), also indicated that the adsorption of CO initially occurs in a linearly bonded configuration at step sites [37]. Thus, the appearance of a peak at 2073 cm⁻¹ in Fig. 1a is attributed to the existence of steps on Pt(111).

Adsorbates on metal surfaces are usually considered not to produce (S or P) SFG signals for the SP (S-vis, P-IR)
combination if the adsorbates have vibrational modes oscillating only along the surface normal [39]. The perpendicularly adsorbed CO on Pt(111) should thus not yield an SSP signal. However, in agreement with previous studies [22, 23] (in which some of us have demonstrated that this simplification is not valid), our experiment showed that both SSP and PPP spectra of on-top CO at terrace sites of the Pt(111) single crystal had a good signal-to-noise ratio. Fitting the peaks with Lorentzian lineshapes using Eq. 2 provided an accurate \( \frac{I_{ppp}}{I_{ssp}} \) value of 27 for the on-top CO stretch mode.

Next, we used the ratio of \( \frac{I_{ppp}}{I_{ssp}} \) to analyze the orientation (tilt) angle (definition is illustrated in Fig. 1b) or molecular hyperpolarizability ratio (\( R \)-value) of on-top CO at the gas/Pt(111) interface.

4.1.1 Simulated \( \frac{I_{ppp}}{I_{ssp}} \) Versus Tilt Angle (\( \theta \)) and Hyperpolarizability Ratio (\( R \)-Value)

According to Eq. 4, the value alone is not sufficient to calculate the orientation angle of a certain surface molecule or functional group, because the hyperpolarizability ratio (\( R \)-value) must be known as well. Because SSP spectra of CO on single-crystal surfaces were rarely obtained, and the orientation angle of on-top CO was generally assumed to be 0° [22, 23], the orientation analysis has never been discussed in depth before. Almost two decades ago, only Badelli et al. [23] deduced an \( R \)-value of 0.6 and 1.5 for on-top CO and bridge-CO species on Pt(111) electrodes, respectively, based on the ratio of \( I_{ssp}/I_{ppp} \) for CO molecules oriented parallel to the surface normal.

Since both the tilt angle \( \theta \) and \( R \)-value are unknown parameters, we theoretically simulated the ratio of \( I_{ppp}/I_{ssp} \) as a function of tilt angle with different \( R \)-values (Fig. 2a) and, vice versa, as a function of \( R \)-value assuming a 0° tilt angle (Fig. 2b). Refractive indices used in the simulations are summarized in Table 1. Incidence angles of visible (532 nm) and infrared (2092 cm\(^{-1} \)) beams in the simulation were 58.5° and 55°, respectively.

For a CO molecule with a \( C_{\infty v} \) symmetry, the \( R \)-value equals to its bond polarizability derivative ratio \( r \). Generally, \( 0 \leq r < 1 \) applies for a single chemical bond [28]. The \( I_{ppp}/I_{ssp} \) value of 27, obtained from our SFG results, corresponds to \( R \approx 0.5 \) (see Fig. 2a), assuming a 0° tilt angle, which is close to the 0.6 \( R \)-value reported earlier for on-top CO [23]. The difference of the calculated \( R \)-value may be due to different values of refractive indices of bulk and/or interfacial Pt (Ref. [23] did not specify them). However, the on-top CO molecules may not stand exactly upright on the Pt atoms. If we keep \( I_{ppp}/I_{ssp} = 27 \), the tilt angle of on-top CO is 40°, 30°, 22° and 0° in the case of adopting \( R \)-values of 0.1, 0.3, 0.4 and 0.5, respectively. When \( R = 0.6 \), there is no intersection at any tilt angle, according to our experimental result. Based on the discussion above, due to the uncertainty of \( R \)-values, it is difficult to determine the precise orientation of CO molecules on Pt surfaces without complementary information from other methods. For example, the Raman depolarization ratio (\( \rho \)) and bond polarizability derivative model have already been used to obtain a quantitative (but not fully accurate) description of the hyperpolarizability tensor ratios (\( R \)) in SFG analysis for stretching vibrational modes of the CH\(_3\), CH\(_2\) and CH groups [21, 41, 42]. The \( \rho \)-value can be accurately measured with polarized Raman techniques [28, 43, 44] and the \( R \)-value can be deduced from the \( \rho \)-value, for
C<sub>∞v</sub> symmetry, the relationship between \( R \) or \( r \)-value and \( \rho \)-value is:

\[
\rho = \frac{3}{(4 + 5(1 + 2r)/(1 - r))^2} \quad [28]
\]

Thus, if one can get the Raman depolarization ratio of CO molecules directly via experiments or theoretical calculations, the molecular hyperpolarizability or bond polarizability tensor ratio can be obtained, and the orientation analysis of adsorbed CO molecules becomes feasible. However, the \( \rho \)-value of CO molecules has not yet been reported.

Similarly, if the orientation angle is known, the precise \( R \)-value can also be determined. As the ratio of \( I_{\text{ppp}}/I_{\text{ssp}} \) decreases, the \( R \)-value increases (Fig. 2b). More specifically, when \( I_{\text{ppp}}/I_{\text{ssp}} > 40 \), the \( R \)-value is hardly sensitive to changes of \( I_{\text{ppp}}/I_{\text{ssp}} \); whereas a small drop of the intensity ratio between 0 and 40 corresponds to a significant increase of the \( R \)-value. However, when the value of \( I_{\text{ppp}}/I_{\text{ssp}} \) is smaller than 10, no reasonable \( R \)-value can be obtained anymore. Taking tilt angles of 0° and 30° as example, the exact \( R \)-value is 0.49 and 0.31 (Fig. 2b), respectively. Obviously, only 0.18 difference of \( R \)-value may lead to 30° tilt angle deviations, indicating that the determination of the orientation of surface CO molecules is rather difficult.

### 4.1.2 Pressure-Dependent SFG Spectra of CO Bond Stretching

Taking advantage of the high pressure capability of SFG, pressure-dependent spectra of CO adsorption on Pt(111) were also measured (Fig. 3). The SSP and PPP spectral intensities simultaneously changed with the CO pressure, yielding almost the same \( I_{\text{ppp}}/I_{\text{ssp}} \) ratio (20 ± 2) at different pressures. Apparently, the orientation of CO did not change at 300 K in the studied pressure range. Similarly, it was previously reported that there was no significant variation of the tilt angle upon increasing coverage of CO molecules adsorbed on (100) surfaces of body-centered cubic transition metals (Fe, Mo, Cr, and W) [45]. The peak position of CO at high pressure is shifted about 16 cm<sup>-1</sup>, as compared to those of Fig. 1. This can be explained by the CO-induced roughening of the surface, an effect that has also been reported by the Somorjai group [46]. CO-induced roughening was also observed for supported Pt nanoparticles [47].

There were only small changes in intensity and frequency upon increasing the pressure, since at 300 K saturation is almost reached at 10<sup>−4</sup> mbar. This agrees with previous results of CO on smooth Pt(111) [31]. The observed increase of spectral intensity in PPP and SSP spectra can be attributed to the increasing surface coverage at constant orientation angle.

The absence of a vibrational band of bridge-bound CO on Pt(111) at 300 K can be explained by the strong broadening of the linewidth 2\( \Gamma \) at high temperature [24]. Schweizer et al. [48], for example, had reported that CO on bridge sites had a linewidth of 37 cm<sup>-1</sup> at 300 K. The linewidth broadening has been attributed to an order–disorder transition [49] with a partial loss of local order of the CO adlayer around 300 K [48].

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**Table 1** Bulk and interface refractive indices of air, Pt, and Pd at different wavelengths

|          | \( \lambda \) (µm) | \( n_1 \) (air) | \( n_2 \) (Pt) [40] | \( n' \) (Pt) | \( n_2 \) (Pd) [40] | \( n' \) (Pd) |
|----------|-------------------|----------------|---------------------|---------------|-------------------|---------------|
| SFG      | 0.479             | 1              | 1.91 + 3.3i         | 1.14 + 1.4i   | 1.47 + 3.4i       | 0.89 + 1.4i   |
| Vis      | 0.532             | 1              | 2.04 + 3.6i         | 1.18 + 1.6i   | 1.60 + 3.7i       | 0.94 + 1.6i   |
| IR       | 4.785             | 1              | 3.89 + 18.9i        | 1.96 + 9.4i   | 3.3 + 20.2i       | 1.66 + 10.0i  |
simulated examine the effect of incidence angles on SFG spectra, we
ence on the incidence angles of the laser beams. In order to
magnitude of the spectral intensity has a strong depend-
and IR laser beams, respectively. Obviously, the relative
the experimental configuration of 55° and 58.5° for visible
R-configurations with 

As mentioned above, our results showed
Ippp/Issp (Fig. 4a, green line) and Ippp/Issp could reach more than
800, which is consistent with a previous report [50]. How-
ver, for 

In more detail, as evident from Fig. 4c, d, the value of
Ippp/Issp has a very strong dependence on 

4.1.3 The Effect of Incidence Angles of Visible and IR Laser
Beams

SSP spectra of CO on Pt(111) have been rarely reported in
previous SFG studies. However, as reported by Baldelli
et al. [23] and herein, both SSP and PPP spectra with
good signal-to-noise ratio can be acquired. In Ref. [23],
a Ippp/Issp value of 1.25 (comparable spectral intensity
of SSP and PPP) was obtained using incidence angles of
33° and 45° for visible and IR laser beams, respectively.
As mentioned above, our results showed Ippp/Issp was 27
(spectral intensity of SSP is much smaller than PPP) for
the experimental configuration of 55° and 58.5° for visible
and IR laser beams, respectively. Obviously, the relative
magnitude of the spectral intensity has a strong depend-
ence on the incidence angles of the laser beams. In order to
examine the effect of incidence angles on SFG spectra, we
simulated Ippp/Issp (Fig. 4a) and Ippp/Issp of CO molecules
on Pt (assuming 0 = 0° and R = 0.49) for different inci-
dence angles (αVis and αIR). For better display, the curves
of Ippp/Issp versus αIR (Fig. 4b) and αVis are shown in sepa-
rate diagrams, and Ippp/Issp versus αVis is even divided into
two regions: one in the range of αVis = 0°–75° (Fig. 4c),
and another in the range of αVis = 75°–90° (Fig. 4d). The
parameters of refractive indices, used for the simulations,
are shown in Table 1.

We first consider the spectral intensity changes. In
Fig. 4a, for αVis = 55°, Ippp and Issp showed a strong but
similar dependence on αIR, and reach the maximum for
αIR = 72°. The ratio of Ippp/Issp is less sensitive to αIR
(Fig. 4b), as a result of the similar intensity response to
αIR, which is consistent with a previous report [50]. How-
ever, for αIR = 55°, Ippp and Issp depended on αVis differently,
Ippp changed non-monotonically (increased first and then
decreased), whereas Issp decreased monotonically, result-
ing in a gradually increasing Ippp/Issp ratio (Fig. 4c, d).

In more detail, as evident from Fig. 4c, d, the value of
Ippp/Issp shows a strong dependence on αVis at fixed αIR.
A continuous increase of Ippp/Issp with increasing αVis
indicates that the SSP signal will be rather difficult to obtain
(as compared to PPP polarization), when a larger αVis is
used. For example, when αVis is in the range of 0°–60°,
Ippp/Issp is smaller than 30 (Fig. 4c), and Ippp reaches the
maximum value at αVis = 60°; however, when αVis is larger
than 70°, there are more than two orders of magnitude dif-
ference between Ippp and Issp (Fig. 4d), e.g. when αVis = 80°,
Ippp is (unexpectedly) 309 times larger than Issp. Increasing
αVis further, the ratio of Ippp/Issp could reach more than
800 (Fig. 4d), and Issp decreases gradually (Fig. 4a, green
solid line). This shows that especially αVis plays a crucial
role in polarization-dependent SFG studies. A previous
study of the effects of refractive index and αVis on the sum
frequency generation intensity at air/liquid and solid/liquid
interfaces also demonstrated the significance of αVis [51].

In analogy to using the ratio of Ippp/Issp at a specific
experimental configuration, the R-value at a selected tilt
angle can also be deduced by measuring the ratio of Ippp
collected from different experimental configurations.
The two methods could then be used to mutually verify
each other. Accordingly, for R = 0.49 (deduced from
Ippp/Issp = 27), the simulated ratio of Ippp of Configuration
1 (αIR = 55°, αVis = 58.5°) and Ippp of Configuration 2
(αIR = 45°, αVis = 37°) would be 2.11, as shown in Fig. 5.
Unfortunately, due to limitations of our UHV-compatible
SFG setup, the incidence angles of IR and visible beams
can be only adjusted within a few degrees. We are thus
currently unable to experimentally determine the ratio of
Ippp at different experimental configurations and to con-
firm the R-value that was deduced from Ippp/Issp. How-
ever, the suggested method may be applied in the future
using SFG setups that can widely vary the experimental
configuration.

Fig. 3 Pressure-dependent a PPP and b SSP spectra of CO on Pt(111)
at 300 K
4.2 SFG Spectra of CO on Pd(111)

Pd is used in many catalytic processes such as hydrogenation, oxidation/combustion, etc. [52, 53], and CO adsorption has also been used to characterize mono- and bimetallic surfaces [54, 55]. The pressure- and temperature-dependent CO adsorption on Pd(111) has thus been extensively studied, mostly using PPP polarization [56–59]. However, PPP and SSP spectra of CO/Pd(111) with good signal-to-noise ratio (I_{ppp}/I_{ssp} = 10) were also obtained at 90 K, for an experimental configuration of $\alpha_{\text{Vis}} = 55^\circ$ and $\alpha_{\text{IR}} = 55^\circ$. At the low temperature (90 K), the 0.75 ML 2 × 2 saturation structure of CO was (predominantly) present and the signal of on-top CO (2108 cm$^{-1}$) was much stronger than the signal of hollow (1890 cm$^{-1}$) and bridge (1925 cm$^{-1}$) bonded CO. At higher temperature (200 K), i.e. lower coverage, the signal of bridge (1951 cm$^{-1}$) and on-top (2081 cm$^{-1}$) CO species became comparable in PPP, whereas no adsorbate species could be detected in the SSP spectra.

Herein, we have acquired PPP and SSP spectra for CO adsorption on Pd(111) at 300 K, complementing the measurements in Ref. [22], and have also used higher CO gas pressure (Fig. 6). Apparently, the hollow peak at ~1899 cm$^{-1}$ (present as shoulder) and the bridge peak (1923 cm$^{-1}$) rather than the on-top peak (2071 cm$^{-1}$) dominated the PPP spectra [56–59] (due to coverage lower than that of the low-temperature PPP spectra in Ref. [22]). From 1 × 10$^{-6}$ mbar to 250 mbar an approximate 12 cm$^{-1}$ blue shift was observed for bridge-bonded CO due to increased coverage. For on-top CO a second peak appeared at 2053 cm$^{-1}$ in 6 mbar. Apparently, at room temperature the CO overlayer is not perfectly ordered but rather a superposition of several CO structures in
the coverage range 0.5–0.6 ML. For more detailed descriptions see Refs. [59, 60].

At 250 mbar, on-top CO not only existed in two species but there was also another higher frequency “feature” at 2144 cm\(^{-1}\) in PPP. Previous infrared reflection-adsorption spectra (IRAS) of 50 mbar CO on Pd(111) at 300 K also displayed a C–O vibrational feature, which is due to gas phase CO absorption (2143 cm\(^{-1}\)) [61].

As shown in Fig. 6, the SFG spectral intensity gradually increased from low pressure to 6 mbar due to increasing surface CO coverage, but the spectral intensity strongly decreased at 250 mbar. As illustrated by Eq. 1, the SFG intensity depends on the effective surface IR and visible intensities. Although no SFG signal is generated by gas phase CO, the SFG process is indirectly influenced by the loss of IR-light via absorption by high-pressure CO gas. Thus, the (on-top) SFG signal may drop because the IR energy arriving at the sample is reduced in higher pressure CO. All SFG spectra were normalized by the IR and Vis energies but the energy-detector was located outside the input window, thus this normalization does not account for the CO gas phase absorption, which explains the unusual peak at 2144 cm\(^{-1}\) in PPP. It can be attributed to the 5.4 cm distance between the input window and the sample surface. In Refs. [56, 57, 59], using recessed IR windows, the distance was only 1.5 cm, so no IR absorption was observed even in 1000 mbar CO gas. For the current setup, normalization could be achieved by using GaAs references, by measuring the reflected IR light after the exit window, or by putting a 5.4 cm gas cell in front of the IR detector [2].

Unfortunately, in SSP polarization the peak intensities were too small for CO on Pd to be detected. In the following, we will explain the specific reason by comparing experimental and simulation results for CO on Pt and Pd.

### 4.3 Comparison of CO on Pt(111) and Pd(111)

In order to better illustrate the observed intensity differences, we have plotted the PPP spectra of CO on Pt(111) and Pd(111) together with some spectra from Refs [56, 59]. (Fig. 7a). Since on-top CO species were observed on both surfaces, we focus on discussing SFG intensity changes of on-top CO. The PPP spectral intensity of CO on Pt(111) is obviously much larger than that on Pd(111). However, the on-top CO intensity on Pd(111) is strongly coverage dependent and we have thus included spectra at 10 and 400 mbar, when the higher CO coverage leads to intense CO peaks.

To better understand the distinctive intensity differences of the SFG experiments, we simulated \(I_{ppp}(\text{Pt})\) (Fig. 7b), \(I_{ssp}(\text{Pt})\) (Fig. 7c) and \(I_{ppp} / I_{ssp}\) (Fig. 7d) versus \(R\) for on-top CO on Pt and Pd surfaces. For simulations, we assumed the same values of tilt angle \(\theta=0^\circ\), effective surface number density \(N_s=1\) and molecular hyperpolarizability \(\beta_{ccc}=1\) for Pt and Pd single crystals. Refractive indices used in the simulation can be found in Table 1. Interestingly, according to the theoretical simulation results, \(I_{ppp}(\text{Pd})\) is about three times larger than \(I_{ppp}(\text{Pt})\), and \(I_{ssp}(\text{Pd})\) is about two times larger than \(I_{ssp}(\text{Pt})\) in the whole range of \(R=0.1–2\). The simulated results are thus different from the experimental ones, for which Pt typically exhibits stronger SFG signal. Nevertheless, both experiment and theory deviate not too far in the order of magnitude of the SFG signal.

According to SFG theory, the factors influencing the SFG intensity of molecules adsorbing on different surfaces under the same experimental conditions (mainly referring to incidence angles of IR and visible beams), include the
effective surface number density \((N_s)\), molecular orientation angles \((\theta)\), polarizations (e.g. SSP, PPP, etc.), Fresnel factors \([L_\text{ii}]\), related to laser incidence angles and refractive indices of bulk phases \((n)\) and interfacial layer \((n')\), molecular hyperpolarizability tensor \((\beta_{ccc})\) and tensor ratio \((R = \beta_{aac}/\beta_{ccc} = \beta_{bbc}/\beta_{ccc})\). All possible changes of the influence factors were considered for CO adsorption on Pt and Pd surfaces, except assuming identical \(N_s\). Thus, the conflicting results of experiments \([I_{\text{PPP}}(Pd) < I_{\text{PPP}}(Pt)]\) and simulations \([I_{\text{PPP}}(Pd) > I_{\text{PPP}}(Pt)]\), plus the fact that the intensity of an SFG peak is proportional to the square of \(N_s\), implies that the \(N_s\) of CO on the Pd surface should be much smaller than that on the Pt surface.

Assuming that the molecular hyperpolarizability ratio \((R\text{-value})\) of CO molecules is identical on different single crystal surfaces (based on the result of \(R = 0.49\) and assumed \(\theta = 0^\circ\)) for CO on Pt, the theoretical value of \(I_{\text{PPP}}/I_{\text{SSP}}\) would be 48 for the Pd surface. This is much larger than the value of 27 for CO on Pt. Taking into account the small PPP signal on Pd (Fig. 7a) and the simulated large value of \(I_{\text{PPP}}/I_{\text{SSP}}\), this indicates that SSP spectra of on-top CO on Pd(111) are difficult to measure at room temperature. Consequently, no reasonable SSP spectra could be acquired.

**5 Conclusions**

Polarization-dependent sum frequency generation (SFG) vibrational spectroscopy is a useful method, providing interface-specific spectra of adsorbed molecules, even at elevated gas pressure. For CO overlayers on Pt(111) and Pd(111) single crystal surfaces at room temperature, different polarization combinations (SSP and PPP) of the visible and SFG light were utilized to determine the molecular orientation (tilt angle) of CO. However, since the hyperpolarizability ratio \((R = \beta_{aac}/\beta_{ccc} = \beta_{bbc}/\beta_{ccc})\) is not exactly known, we have rather determined this value \((R = 0.49)\) by assuming perpendicular adsorption of CO (tilt angle of \(0^\circ\)). Pressure-dependent SFG spectra on Pt(111) (10^{-4} to 36 mbar) did not indicate any orientation change of adsorbed CO. Modeling the expected SFG ratio indicated a strong dependence on...
the experimental configuration, especially on the incidence angle of the visible beam.

Room temperature CO adsorption on Pd(111) was examined in the pressure range of $10^{-6}$ to 250 mbar but only PPP and no SSP could be acquired. Modeling the absolute PPP and SSP spectral intensities on Pt and Pd, as well as the expected ratios, explained the absence of SSP signals on Pd. Care must apparently be taken even for the orientation analysis of seemingly simple adsorbate–substrate systems, with the interface model not only including refractive indices, but also the experimental configuration (incidence angles) and surface coverages.

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