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In situ detection and surface coverage measurements of CO during CO oxidation on polycrystalline platinum using sum frequency generation

H. Härle, A. Lehnert, U. Metka, H.-R. Volpp*, L. Willms, J. Wolfrum

Physikalisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany

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Abstract. Optical infrared-visible sum-frequency generation (SFG) surface vibrational spectroscopy was used for in situ detection of CO during heterogeneous CO oxidation on a polycrystalline platinum foil. SFG spectra were recorded in the substrate temperature range 300–700 K at a total pressure of 20 mbar. A least-squares fit procedure was employed to determine the temperature dependence of the vibrationally nonresonant contribution and the frequency, amplitude and halfwidth of the CO vibrationally resonant contribution from the SFG spectra. Thermal desorption measurements were carried out to investigate the relationship between the SFG signal and the instantaneous CO surface coverage. After these calibration measurements, it was possible to derive CO surface coverages from the SFG spectra measured under laminar flow conditions during heterogeneous CO oxidation.

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The use of optical methods which probe interface electronic and vibrational resonances offers significant advantages over conventional surface spectroscopic methods in which, for example, beams of charged particles are used as a probe, or charged particles emitted from the surface/interface after photon absorption are detected [1]. In particular, three-wave mixing techniques such as second-harmonic generation (SHG) have become important tools to study surface reaction processes [2]. SHG is potentially surface-sensitive at non-destructive power densities [3] and its application is not restricted to ultra-high vacuum (UHV) conditions. However, SHG suffers from a serious drawback, namely from its lack of molecular specificity [4]. As a consequence, SHG cannot be used for the identification of unknown surface species. On the other hand, infrared–visible (IR-VIS) sum-frequency generation (SFG) allows surface vibrational spectroscopic measurements with submonolayer sensitivity with the help of a tuneable IR laser [5]. In addition to molecular specificity, SFG also allows a direct probe of the effect of the interface on the bond frequencies of the adsorbed molecules [6]. Recent experiments in which SFG was used to monitor bonding and location of CO surface species during heterogeneous CO oxidation on a Pt(111) single crystal up to atmospheric pressures, showed that SFG can be utilized to bridge the “pressure gap” in the CO/Pt system [7–9]. In recent work [10], SFG was employed to investigate CO adsorption/desorption on a polycrystalline Pt foil in the substrate temperature range $T = 300$–660 K under laminar flow conditions. The present work focused on the extension of these studies to assess the potential of SFG for “bridging the materials gap” by quantitative in situ monitoring of chemisorbed CO during heterogeneous CO oxidation on a polycrystalline Pt foil. However, determination of CO coverages from SFG spectra requires careful calibration measurements employing another independent surface sensitive method, as has been shown in [11] for the CO/Ni(111) system. So far, similar calibration measurements were, to the best of our knowledge, not carried out for the CO/Pt system. Therefore, in the present work experiments were carried out in which SFG measurements were combined with thermal-programmed desorption (TPD) measurements in order to establish a relationship between the resonant contribution of CO SFG spectra and the actual CO surface coverage on a polycrystalline Pt foil. Finally, results from in situ SFG studies of CO oxidation, in which CO coverages were derived from SFG spectra, utilizing the results of the calibration measurements, are reported.

1 Experimental

1.1 Experimental setup

Experiments were carried out in a reaction chamber, which allows studies over a wide pressure range from UHV-conditions (3×10^{-10} mbar) up to atmospheric pressure. In the high pressure regime this experimental arrangement can be used to investigate adsorption/desorption and reactive processes of well-defined stagnation point flows of reactant mixtures on the catalyst surface (a detailed description of the experimental setup can be found in [8, 10]). The reaction cham-

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* Author to whom correspondence should be addressed.
(Fax: +49-6221/54-4255, E-mail: aw2@ix.urz.uni-heidelberg.de)

ber was equipped with a quadrupole mass spectrometer for TPD measurements, a Ar^+ sputter source, a retarding field analyser (RFA) for Auger electron spectroscopy (AES) and low-energy-electron diffraction (LEED) studies and CaF_2 and quartz windows serving as entrance and exit ports for the laser beams and the sum-frequency signal, respectively. A second differentially pumped quadrupole mass spectrometer was connected to the vacuum line behind the reaction chamber which could be used for on-line monitoring of stable reaction products (in the present study, CO_2) in the exhaust gas.

The sample was mounted on a copper block and could be translated, tilted and rotated by means of a manipulator fitted with a differentially pumped rotary feedthrough. The Pt foil (Advent, purity > 99.99%) could be resistively heated. The mounting enabled work in the temperature range 300–1600 K by the use of direct sample heating with a proportional-integral-derivative (PID) control unit. The temperature of the catalyst was measured by a Ni−NiCr thermocouple spot welded to the Pt foil. Clean platinum surfaces could be obtained by applying several cycles of Ar^+ ion sputtering followed by oxidation at 1000 K. After the last sputter cycle, at 300 K with 3 keV Ar^+ ions for 45 min, the sample was heated to 750 K for 5 min. Then the sample was cooled down to 300 K. This procedure ensured reproducibility of the temperature dependent CO-SFG spectra measurements. During the CO oxidation measurements the premixed flows were 30 sccm O_2 (Messer Griesheim, 99.995%), 15 sccm CO (Messer Griesheim, 99.994%), and 105 sccm Ar (Messer Griesheim, 99.998%) at a total pressure of 20 mbar. TPD measurements were carried out with a linear heating rate of 5 K/s, starting at the equilibrium CO surface coverage at 10^{-8} mbar CO pressure and different temperatures. CO surface coverages were derived from the integrated peak areas of the TPD signal.

1.2 Sum-frequency generation (SFG)

For the detection of chemisorbed CO, a 40 ps mode-locked Nd:YAG laser system was used which has been described in detail elsewhere [8, 10]. A part of its output was frequency doubled to 532 nm and used as the visible input frequency for the SFG process. The other part was used to pump an optical parametric system to generate infrared (IR) radiation tuneable in the frequency range (1800–2200 cm^{-1}) with a pulse duration of 25 ps and a bandwidth of 7 ± 1 cm^{-1}. The visible and the IR laser beams were p-polarized and overlapped at the surface. Incident angles were 55° for the visible and 35° for the IR beam with energies of 400 μJ and 30 μJ per pulse, respectively. The spot size of the visible beam was 5 mm diameter and the infrared beam was slightly focused to fall within the visible. Baselines of the SFG spectra were determined by blocking the IR-laser beam. Therefore the baseline represents the background signal due to stray light generated in the reaction cell windows by the visible laser beam. The CO sum-frequency signal reflected from the Pt surface was detected (after filtering of scattered light with a dielectric filter and a monochromator) by a photomultiplier and a gated integrator, and transferred to a laboratory computer. Each point of the recorded CO SFG spectra (see for example Fig. 1) were obtained by averaging over 120 laser shots at a laser repetition rate of 10 Hz.

The fundamental principles of the SFG surface vibrational spectroscopy have been described in detail elsewhere [3]. In the present case the SFG process is a second order non-linear optical process in which a tuneable infrared wave (ω_{IR}) is mixed with a visible (ω_{VIS}) wave to generate a sum frequency output (ω_{SFG}) which, for the CO gas/Pt system, is highly specific to the gas-phase/surface interface region. The SFG signal intensity I_{SFG} is proportional to the product of the nonlinear surface susceptibility $\chi_S^{(2)}$ and its complex conjugate:

$$I_{SFG} \propto \chi_S^{(2)} (\chi_S^{(2)})^* = \left|\chi_S^{(2)}\right|^2 . \tag{1}$$

$\chi_S^{(2)}$ represents a third order tensor quantity which can be described as the sum of a nonresonant $\chi_{NR}^{(2)}$ and resonant term

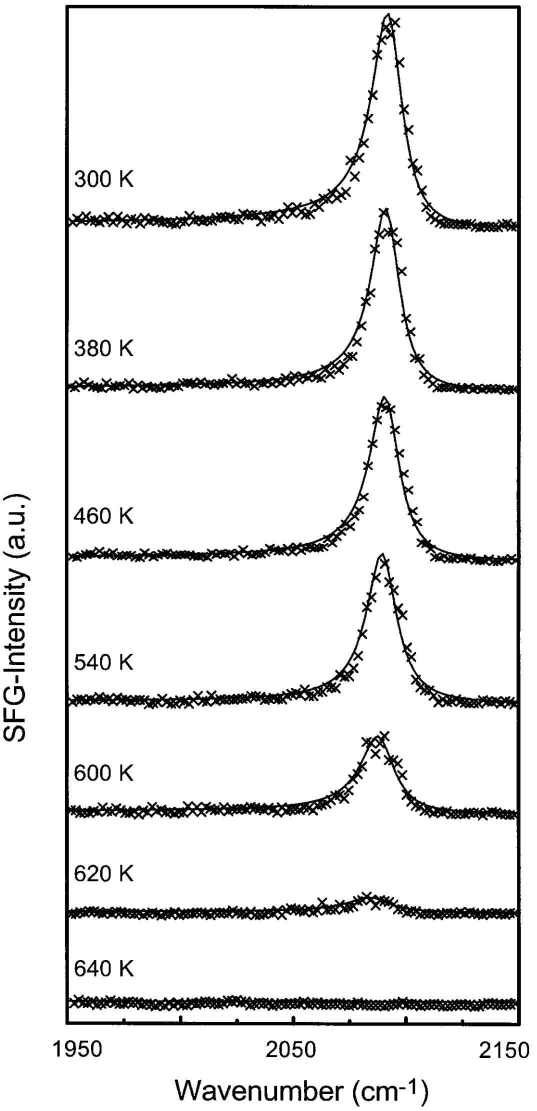

Fig. 1. SFG spectra measured during the heterogeneous CO oxidation on a polycrystalline Pt foil at different substrate temperatures at a pressure of 20 mbar ($p_{CO} = 2$ mbar, $p_{O_2} = 4$ mbar, $p_{Ar} = 14$ mbar). Experimental data points are represented by *crosses*, the *solid lines* represent results of least-squares fits. Details of the fitting procedure are described in the text

$\chi_{\mathrm{R}}^{(2)}$:

$$\chi_{\mathrm{S}}^{(2)} = \chi_{\mathrm{NR}}^{(2)} + \chi_{\mathrm{R}}^{(2)} . \tag{2}$$

The resonant term $\chi_{\mathrm{R}}^{(2)}$, which is associated with a vibrational mode of a surface layer of adsorbates, can be expressed, following the coupled-wave approach, as [4]:

$$\chi_{\mathrm{R}}^{(2)} = \frac{N T_X M_X \Delta\rho}{\hbar(\omega_{\mathrm{IR}} - \omega_X + \mathrm{i}\Gamma)} = \frac{A_{\mathrm{R}}}{(\omega_{\mathrm{IR}} - \omega_X + \mathrm{i}\Gamma)} . \tag{3}$$

Here, N denotes the adsorbate surface density, T_X is the infrared transition moment, M_X is a term proportional to the Raman transition moment of the vibrational mode of the adsorbed molecule X, and ω_X is the corresponding molecular vibrational frequency, Γ is the homogeneous Lorentzian half-width of the mode, and $\Delta\rho$ is the population difference between the ground and vibrational excited states. If the adsorbate vibration is both Raman and infrared active, the resonant contribution becomes significant as the IR laser is tuned through the vibrational transition. As a result, the SFG spectrum provides similar information as can be obtained by conventional vibrational spectroscopy with the difference that the SF signal originates predominately from surface species. In addition, the SF output is coherent and highly directional. A_{R} defined via (3) denotes the amplitude of the resonant contribution. The nonresonant term $\chi_{\mathrm{NR}}^{(2)}$ can, in principle, consist of contributions originating from the adsorbate, the surface, or from cross terms resulting from adsorbate-surface interaction. The nonresonant term $\chi_{\mathrm{NR}}^{(2)}$ can be expressed as

$$\chi_{\mathrm{NR}}^{(2)} = A_{\mathrm{NR}} \mathrm{e}^{\mathrm{i}\Phi} , \tag{4}$$

where A_{NR} is the magnitude of the vibrationally nonresonant contribution due to electronic excitations of the Pt surface and the adsorbate, and Φ is its phase relative to the vibrational resonance [6]. Inserting (3) and (4) into (2) yields the expression ($X = \mathrm{CO}$):

$$\chi_{\mathrm{S}}^{(2)} = \frac{A_{\mathrm{R}}}{(\omega_{\mathrm{IR}} - \omega_{\mathrm{CO}} + \mathrm{i}\Gamma)} + A_{\mathrm{NR}} \mathrm{e}^{\mathrm{i}\Phi} . \tag{5}$$

Equation (5) was used together with (1) for the numerical simulation of the CO SFG spectra measured in the present study.

2 Results and discussion

2.1 *In situ* CO *detection on a polycrystalline Pt foil during* CO *oxidation*

The SFG spectra shown in Fig. 1 were obtained during CO oxidation at different substrate temperatures in the range $T = 300$–700 K at a total pressure of 20 mbar ($p_{\mathrm{CO}} = 2$ mbar, $p_{\mathrm{O_2}} = 4$ mbar, $p_{\mathrm{Ar}} = 14$ mbar). CO and O_2 partial pressures were close to the values present in the exhaust gas of an spark ignition (SI) engine. Spectra were recorded at fixed surface temperatures by tuning the IR laser over the frequency region 1950–2150 $\mathrm{cm^{-1}}$ in which stretching vibrations of terminally adsorbed CO can be excited. Under the present experimental conditions no bridge-bound CO [6] was observed on the Pt foil in the frequency region 1800–1900 $\mathrm{cm^{-1}}$. The solid lines in Fig. 1 are the results of a numerical least squares fit of the experimental data points (crosses) using (5) together with (1). The numerical analysis allowed us to determine the parameters ω_{CO}, Γ, A_{R}, A_{NR} and Φ as a function of the substrate temperature. According to (4), the nonresonant part of the SFG spectra can be described by the amplitude of the vibrationally nonresonant contribution, A_{NR}, and the phase between the non-resonant and the vibrationally resonant contribution, Φ. In agreement with our previous results obtained on disordered Pt(111) [8], the present study also found only a weak dependence of $\chi_{\mathrm{NR}}^{(2)}$ on the substrate temperature. Over the temperature range $T = 300$–620 K where CO could be detected the non-resonant amplitude was considerable smaller than the resonant amplitude (for example: $A_{\mathrm{NR}}/A_{\mathrm{R}} \approx 7 \times 10^{-2}$ at a substrate temperature of 620 K). The values of the vibrational frequency ω_{CO}, the resonant amplitude A_{R}, and the Lorentzian width (FWHM) 2Γ, which determine the resonant contribution of the adsorbed CO, are plotted versus substrate temperature in Fig. 2.

In earlier CO adsorption/desorption studies on a polycrystalline platinum foil [10] a pronounced change of the resonance frequency ω_{CO} was observed. In the latter case, at $T = 300$ K a value of $(2096 \pm 4)\,\mathrm{cm^{-1}}$ was obtained while at $T = 660$ K, the highest temperature where adsorbed CO was observed, a value of $(2057 \pm 5)\,\mathrm{cm^{-1}}$ was found. The latter frequency is lower than the frequencies observed on the (111) [6], (110) [6] and (100) [12] low-index platinum surfaces in the low coverage limit and it was attributed to CO molecules strongly bound to defect sites. Following [13],

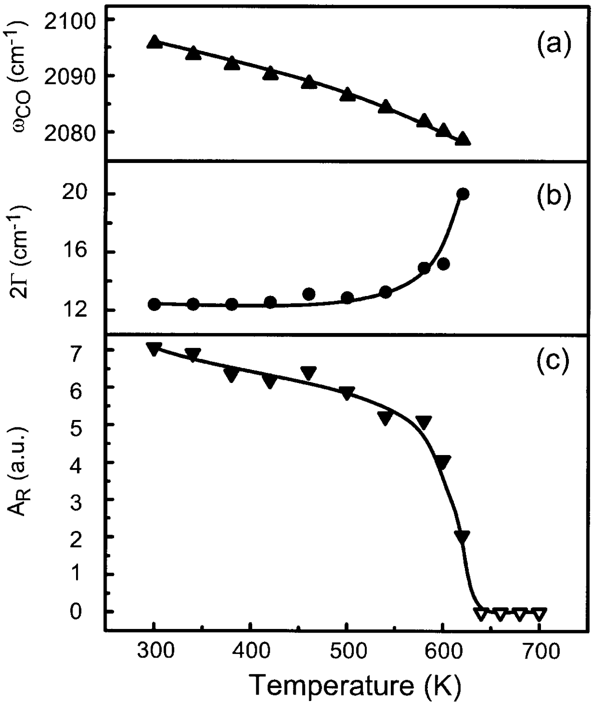

Fig. 2. **a** CO vibrational resonance frequency ω_{CO}; **b** Width (FWHM $= 2\Gamma$) of the resonant contribution of the SFG spectra; **c** Resonant amplitude A_{R} as defined in the text. Values are plotted against the Pt substrate temperature. *Solid lines* are drawn just to guide the eye. The *open triangles* at $T > 620$ K in (**c**) indicate values where within the detection limit no chemisorbed CO could be observed ($A_{\mathrm{R}} \approx 0$)

a low frequency of 2057 cm^{-1} is predicted for CO molecules bound at kinked-site Pt atoms with a coordination number of 6. The ridge atoms of a Pt(110)-(1×2) surface, for example, which have a coordination number of 7 are predicted to show a slightly higher singleton frequency of 2067 cm^{-1}. This value is in good agreement with the results of SFG studies in which a value of 2065 cm^{-1} was measured in the low coverage limit [6]. In [6], the SFG results obtained for the CO/Pt(110) system were found to be in excellent agreement with results obtained using electron energy-loss spectroscopy (EELS).

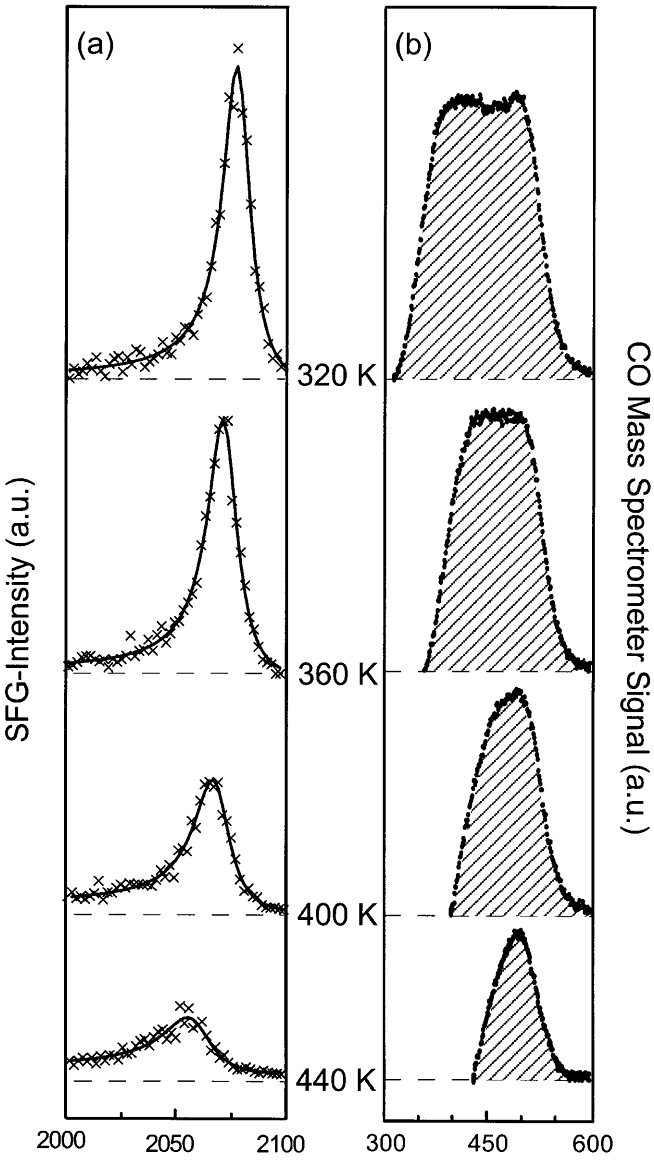

Fig. 3. a SFG spectra of CO adsorbed on the polycrystalline Pt foil recorded at different substrate temperatures at a CO pressure of 10^{-8} mbar. SFG intensity is plotted versus the frequency of the tunable IR laser. Experimental data points are represented by *crosses*, the *solid lines* represent results of least-squares fits. Details of the fitting procedure are described in the text. **b** TPD spectra of CO obtained under molecular flow conditions recorded after the corresponding SFG measurements shown in **a**. Desorption was started at different substrate temperatures at the same CO pressure of 10^{-8} mbar

In the present CO oxidation studies over the whole temperature range ($T = 300$–620 K) where chemisorbed CO could be detected, the resonance frequency ω_{CO} remained at values 2095–2078 cm^{-1} (see Fig. 2a). Hence, the main difference between the CO adsorption/desorption [10] and the present CO oxidation data is the absence of the low-frequency CO contribution from defect sites in the latter case. This observation could be explained by a higher sticking probability of O_2 at the defect sites which blocks CO defect site adsorption when both CO and O_2 are present in the gas-phase. A preferential adsorption of O_2 on step sites has been observed in electron stimulated desorption ion angular distribution (ESDIAD) studies on Pt[3(111)×(100)] [14] and during infrared reflection absorption spectroscopy (IRAS) studies during CO oxidation on Pt[4(111)×(100)] [15].

The temperature dependence of the width (FWHM $= 2\Gamma$) of the resonant contribution of the SFG spectra is depicted in Fig. 2b. A deconvolution of the measured spectra with the laser bandwidth was not performed. Equation (5) was directly used together with (1) for the numerical simulation to obtain the necessary parameters. The same method was used in [6] to analyse SFG spectra of CO terminally adsorbed on a disordered Pt(111) surface where a value of $2\Gamma = 10$ cm^{-1} was reported at $T = 300$ K for saturation coverage. In the same study, a value of $2\Gamma = 12$ cm^{-1} was determined for CO SFG spectra measured on Pt(110) at $T = 300$ K. The corresponding CO frequencies were found to be 2093 cm^{-1} for disordered Pt(111) and 2094 cm^{-1} for Pt(110), respectively. For both Pt(111) and Pt(110), an increase in the width was observed with decreasing coverage. The maximum values observed at low coverages were 17 cm^{-1} and 14 cm^{-1}, respectively, with values of 2076 cm^{-1} and 2079 cm^{-1} for the corresponding frequencies [6]. In the present CO oxidation studies a value of $2\Gamma = (12 \pm 1)$ cm^{-1} was determined at room temperature which increases to a value of $2\Gamma = (20 \pm 2)$ cm^{-1} at $T = 620$ K where the CO coverage is the lowest. Hence the line widths and frequencies measured in the present CO oxidation studies on polycrystalline Pt are comparable with those observed in room-temperature Pt(111) and Pt(110) UHV single crystal CO exposure experiments [6] as well as with those measured in high-pressure CO adsorption/desorption studies on polycrystalline Pt [10], in which a value of $2\Gamma = (17 \pm 1)$ cm^{-1} was obtained at $T = 620$ K.

Although a decrease of the resonant amplitude A_{R} versus substrate temperature as shown in Fig. 2c clearly indicates that the equilibrium concentration of chemisorbed CO decreases with increasing surface temperature, care has to be taken in using A_{R} as a measure of the CO surface coverage. Prior to deducing – for a given adsorbate/surface system – relative CO coverages from SFG measurements, it is indispensable to carry out calibration measurements using another independent surface sensitive method [11].

2.2 Calibration: SFG versus TPD measurements

In the present study we calibrated the SFG signals against TPD measurements. In these calibration measurements SFG spectra of CO adsorbed on the polycrystalline Pt foil were recorded in the temperature range $T = 300$–480 K at a CO pressure of 10^{-8} mbar under adsorption/desorption equilibrium conditions (at $T \geq 480$ K no SFG signal from chemisorbed CO could be observed). SFG spectra (Fig. 3a) were recorded at fixed surface temperatures by tuning the IR laser over the frequency region 1950–2150 cm^{-1} in which stretching vibrations of terminally adsorbed CO can be excited. Under the present experimental conditions no bridge-bound CO [6] was observed on the Pt foil in the frequency region 1800–1900 cm^{-1}. The surface coverage was derived from the integrated area of the TPD spectra (Fig. 3b) measured after each SFG experiment and normalized to the value at the saturation coverage at 300 K. A set of SFG spectra are shown in Fig. 3 together with the corresponding CO TPD spectra which were obtained – in order to avoid isothermal desorption after pumping off the gas – under molecular flow conditions at a CO pressure of 10^{-8} mbar [16]. Desorption was started at the same substrate temperatures at which SFG spectra were previously recorded. A numerical least squares fit procedure was used to determine the parameters A_R, ω_CO, Γ, A_NR and Φ of (5). In this evaluation only a weak dependence of $\chi^{(2)}_\mathrm{NR}$ on the substrate temperature was observed. In Fig. 4, the values of the resonant amplitude A_R and the maximum value of the resonant part of the SFG intensity $I_\mathrm{SFG}(\omega_\mathrm{CO})$, obtained from the corresponding parameters A_R, ω_CO and Γ, are plotted versus the relative CO coverage of the Pt foil. As can be seen from the figure, $I_\mathrm{SFG}(\omega_\mathrm{CO})$ is the spectroscopic quantity which correlates linearly with CO surface coverage.

In order to investigate the dependence of $I_\mathrm{SFG}(\omega_\mathrm{CO})$ on the CO pressure, additional SFG spectra were recorded in the pressure range $p_\mathrm{CO} = 10^{-8}$–10 mbar. All the SFG spectra could be well described by (5) and the corresponding values derived for $I_\mathrm{SFG}(\omega_\mathrm{CO})$ showed no pressure dependence, indicating that $I_\mathrm{SFG}(\omega_\mathrm{CO})$ can be used as a measure of the relative CO coverage in the CO pressure range of $p_\mathrm{CO} = 10^{-8}$–10 mbar. No spectral changes were observed which could serve as an indication for the appearance of new surface species, as has been found in high-pressure CO SFG spectra ($p_\mathrm{CO} \geq 13$ mbar) recorded on Pt(111) (see, for example, Fig. 1 of [17]). Such new surface species and the resulting multiple resonance features in the SFG spectra would require a more complex analytic expression for the simulation of the spectra than that, (5), used in the present work.

2.3 *Application: in situ measurement of* CO *coverages during* CO *oxidation*

The SFG spectra shown in Fig. 1 measured at a total pressure of 20 mbar ($p_\mathrm{CO} = 2$ mbar, $p_{\mathrm{O}_2} = 4$ mbar, $p_\mathrm{Ar} = 14$ mbar) were evaluated in order to determine $I_\mathrm{SFG}(\omega_\mathrm{CO})$ and hence the relative CO coverage as a function of substrate temperature as depicted in Fig. 5. Comparison with the CO coverage measured during CO adsorption/desorption studies (see Fig. 4 of [10]) reveals that if O_2 is present in the stagnation-flow the CO surface coverage at $T = 300$ K is reduced. However, simultaneous mass-spectrometric measurements of the CO_2 formation (see Fig. 5) revealed that the observed decrease of the CO coverage at $T = 300$ K is not due to reaction but is the result of the competitive adsorption between CO and O_2. Also the following slight decrease in the CO surface coverage with temperature in the range $300\,\mathrm{K} < T < 500\,\mathrm{K}$ is due to CO desorption rather than reaction. After the onset of reaction at $T > 500$ K, on the other hand, the CO coverage decreases rapidly with increasing substrate temperature. At $T > 620$ K no chemisorbed CO could be detected, indicating very low equilibrium CO surface concentrations in the temperature range $T = 640$–700 K.

Detailed CO oxidation experiments in which CO was monitored via SFG up to atmospheric pressures were carried out in the group of Somorjai [7]. However, while the present CO oxidation studies were performed at a low CO partial pressure ($p_\mathrm{CO} = 2$ mbar) as typically present in the exhaust gas of a SI engine and on a more realistic Pt catalyst surface, the CO oxidation studies of [7] were carried out at a much higher CO partial pressure ($p_\mathrm{CO} = 53$–133 mbar) over a Pt(111) single crystal. In the latter studies, structural changes of the Pt(111) surface induced by the high pressures of CO were observed which gave rise to a variety of new CO surface species leading to "multi-resonance" SFG spectra. Under the low CO partial pressure conditions of the present work such spectral features were not observed, suggesting that no major reorganization of the polycrystalline Pt

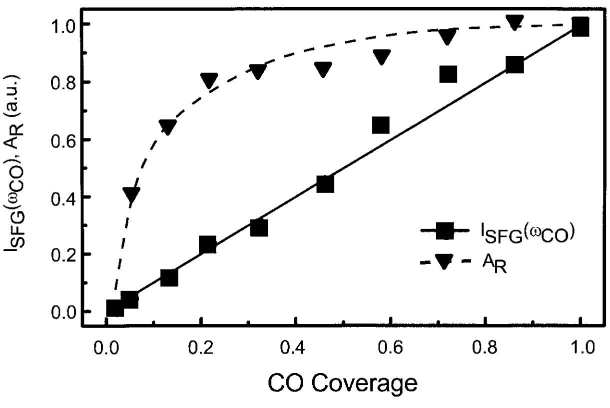

Fig. 4. Plot of the values of the resonant amplitude A_R and the maximum value of the resonant part of the SFG intensity, $I_\mathrm{SFG}(\omega_\mathrm{CO})$, derived from the SFG spectra depicted in Fig. 3a, versus the relative CO surface coverage determined from the corresponding TPD spectra of Fig. 3b. The values of A_R and $I_\mathrm{SFG}(\omega_\mathrm{CO})$ were normalized to unity at saturation coverage

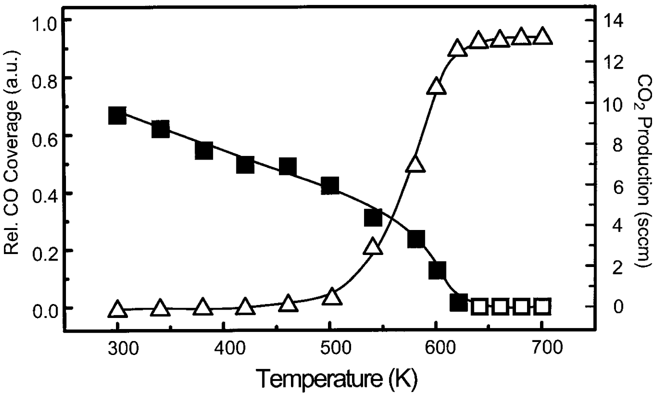

Fig. 5. CO coverage (*filled squares*) as a function of the Pt substrate temperature measured during CO oxidation at a pressure of 20 mbar (*open squares* indicate temperatures where equilibrium CO surface coverages were too low to be detected). CO_2 production (*open triangles*) simultaneously measured by mass-spectrometry in the exhaust gas. The measurements were carried out under laminar flow conditions in a stagnation point flow (CO: 15 sccm; O_2: 30 sccm; Ar: 105 sccm) onto the Pt foil. The *solid lines* are just to guide the eye

surface takes place up to temperatures where CO is almost completely converted into CO_2.

3 Conclusions and outlook

In the present study it has been demonstrated that SFG can be applied for in situ CO coverage measurements during heterogeneous CO oxidation on a polycrystalline Pt foil under laminar stagnation point flow conditions at a total pressure of 20 mbar. The results clearly show that SFG surface vibrational spectroscopy, when combined with appropriate calibration measurements, is a promising experimental method for bridging the “pressure gap” as well as the “materials gap” which separate the UHV single-crystal model studies [18, 19] from technical catalytic investigations [20–22]. Further experimental studies are under way in which the method developed in the present work will be applied to investigate the influence of surface structure, mixture composition and pressure on the ignition behaviour of the $CO/O_2/Pt$-system under technically relevant conditions.

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