TECHNISCHE UNIVERSITÄT WIEN Vienna | Austria

Institute of Materials Chemistry

A New UHV System Including a High Pressure Cell for In-Situ SFG Spectroscopy

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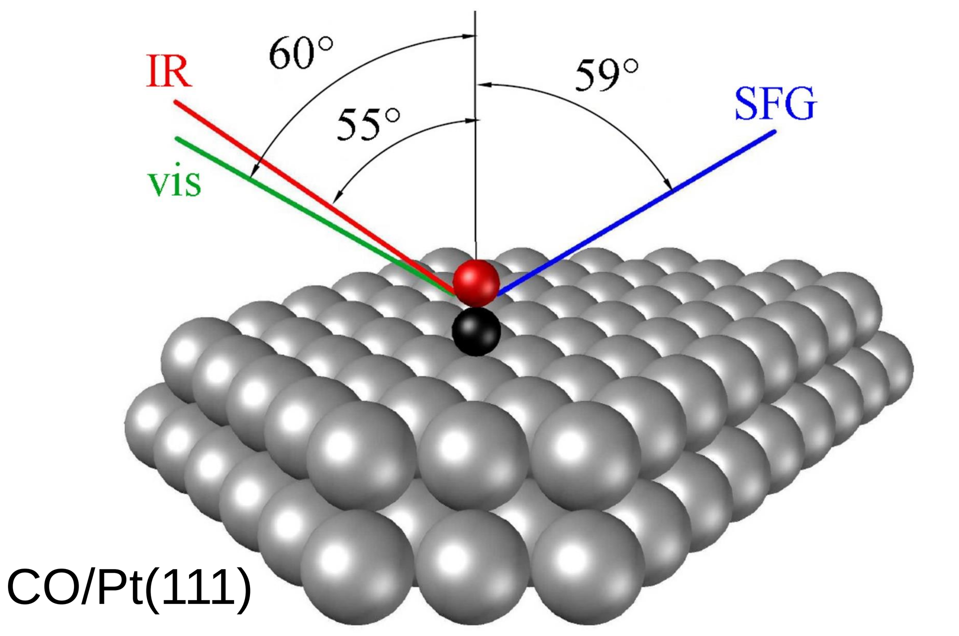
Motivation

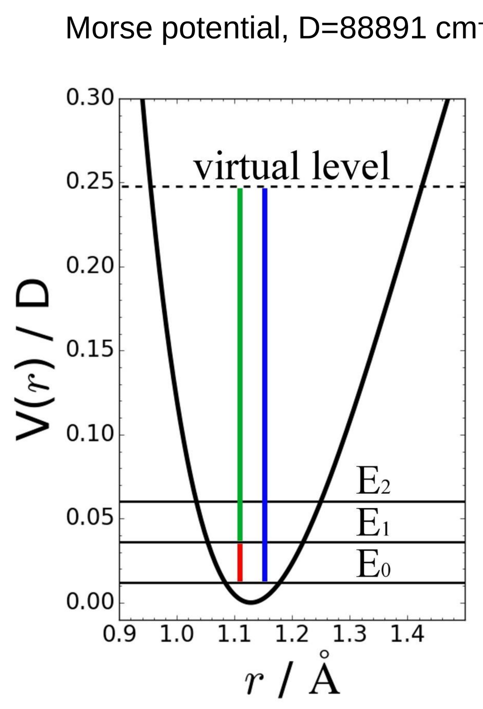
The study of solid surfaces and their interaction with the gas phase is paramount in heterogeneous catalysis. During a catalytic reaction reactants adsorb, intramolecular bonds are cleaved, and new ones formed. Eventually, the desired product desorbs. Knowing which species is present on the surface provides a clue about the reaction mechanism and helps to design better catalysts. Sum frequency generation (SFG) spectroscopy is a surface specific technique which allows to investigate the properties of adsorbates and to bridge the “pressure gap” between the classical ultra-high vacuum (UHV) studies and real catalysis. Here we describe a new setup to prepare and characterize model catalyst samples in controlled UHV conditions and perform SFG and catalytic testing from UHV up to near-ambient pressure and in a wide temperature window.

Methods

- SFG

UHV → atmospheric pressure





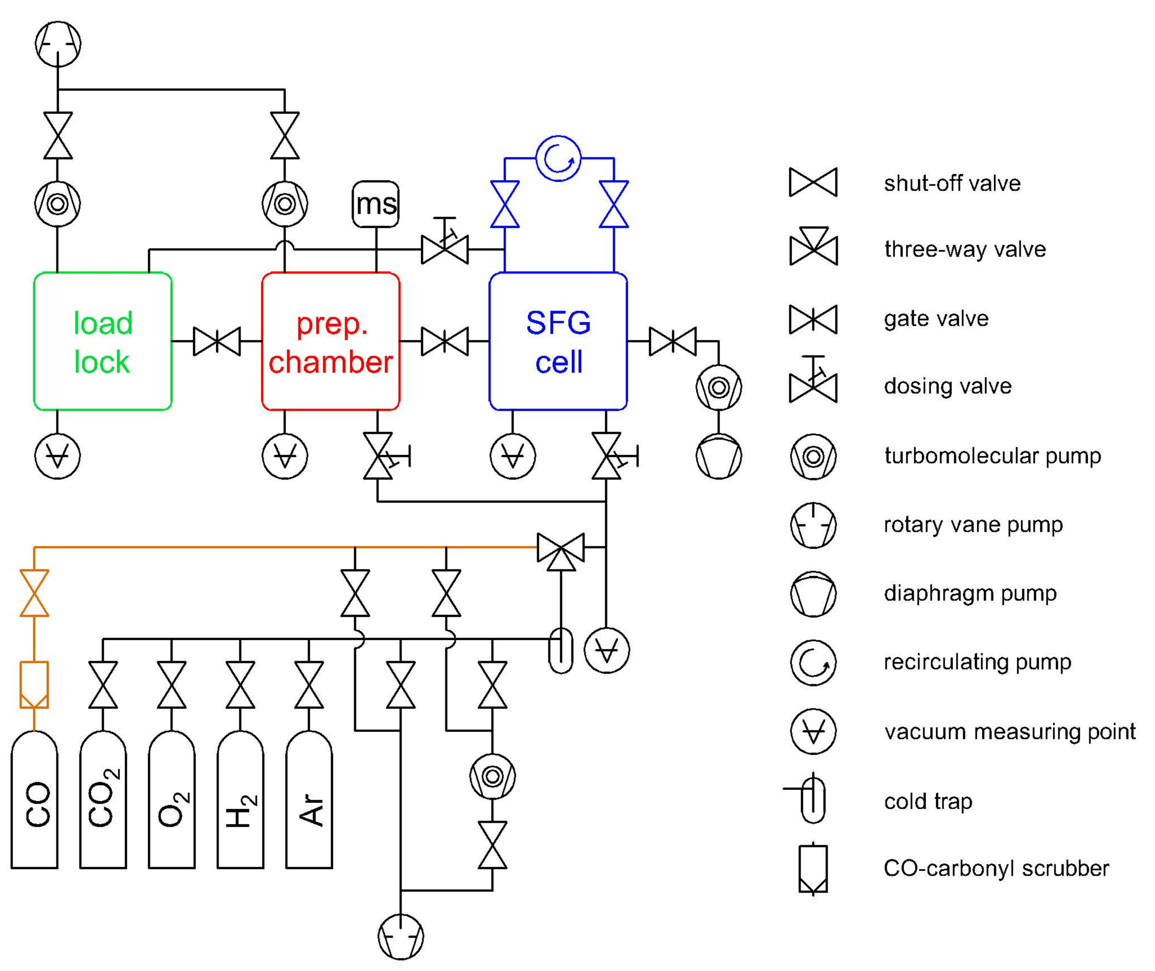
$$I_{SFG} \propto \left|e^{\dagger}_{SFG} \cdot \chi^{(2)} : e_{vis} e_{IR}\right|^2 I_{vis}\, I_{IR}\,; \qquad \chi^{(2)}_{eff} = A_{NR} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q}$$

SFG is a second order non linear optical process in which two laser beams (IR and vis) are overlapped on the sample and generate a signal at the sum of their frequency. The process is allowed only if the inversion symmetry is broken, that is at the surface, while the gas phase is optically inactive. The technique is therefore inherently surface specific.

Standard UHV techniques:

- Ion bombardment and annealing
- Auger electron spectroscopy
- Low-energy electron diffraction
- Temperature programmed desorption
- Evaporation

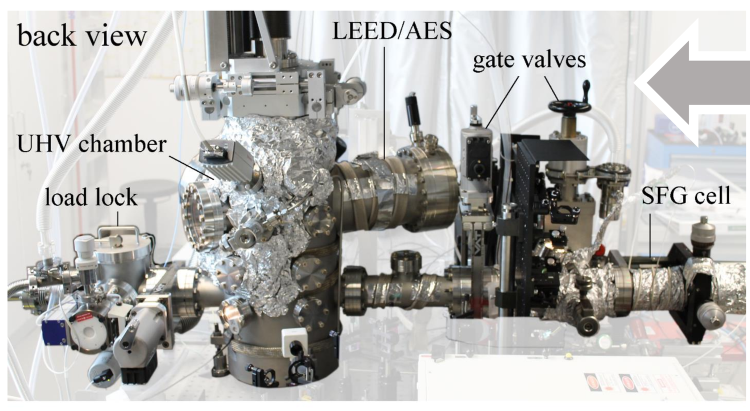
Experimental setup



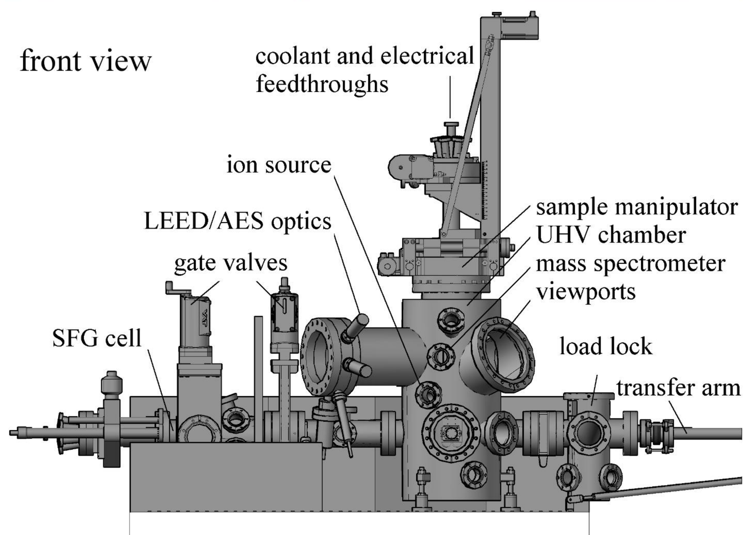
The experimental setup is comprised of three main sections, the load lock, the preparation chamber, and the SFG spectroscopic cell. The load lock allows to fast insert the sample without breaking the vacuum. In the spectroscopic cell SFG and catalytic experiments can be performed from UHV up to 1 atm pressure.

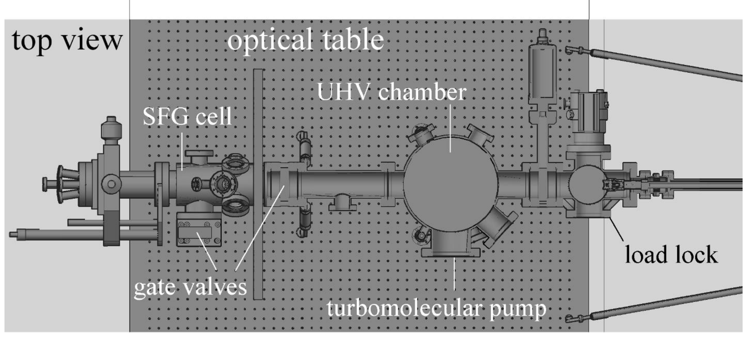
While recording SFG spectra, a mixture of several gases of interest can be admitted to the cell, recirculated by a pump, and directed to the mass spectrometer for analysis.

Experimental setup

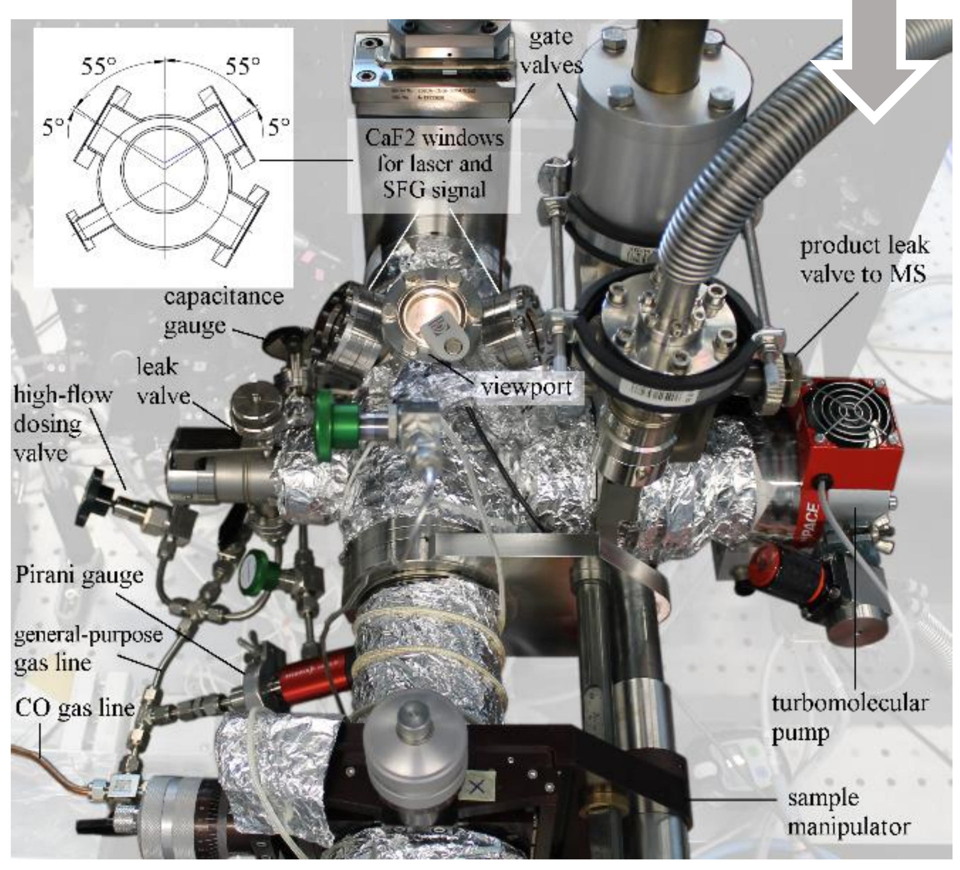


Overview of the experimental setup (CAD project and picture)

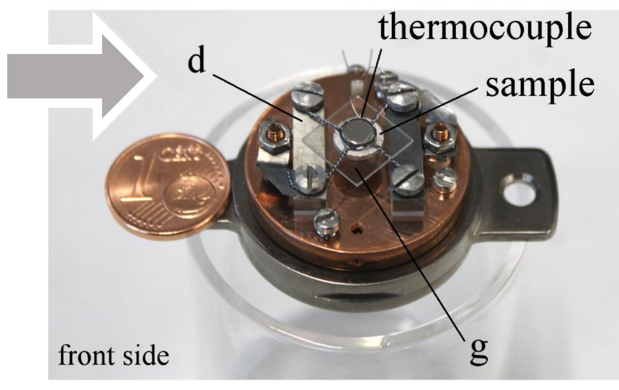


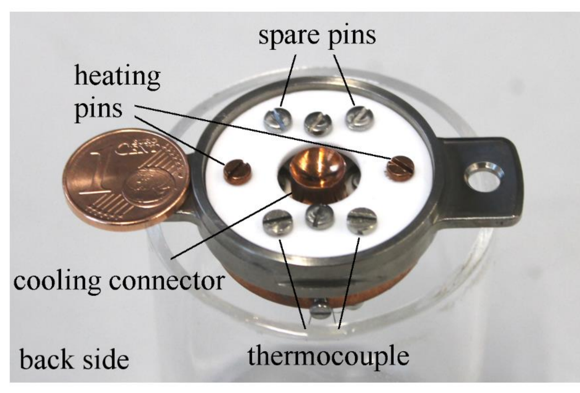


Zoom of the cell for SFG spectroscopy and catalytic testing



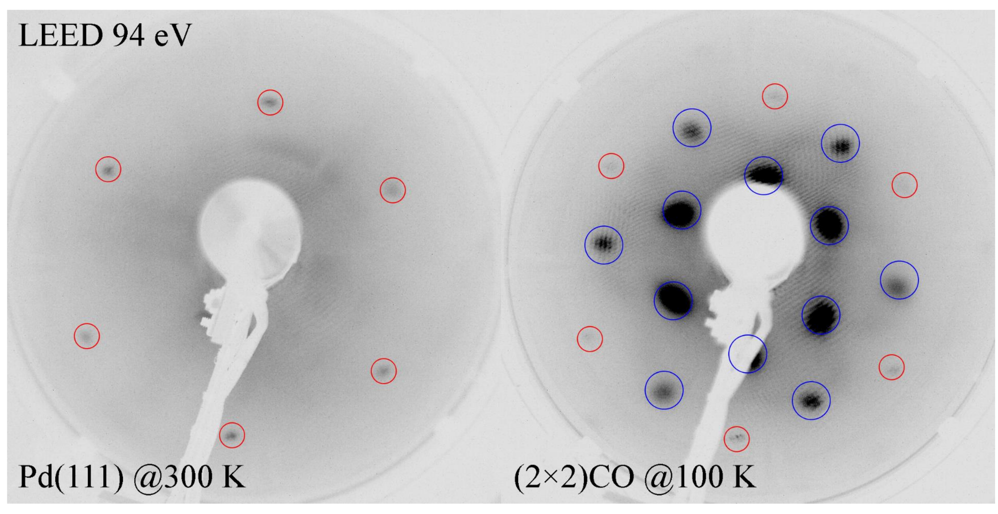
The sample holder, front (**top**) and back (**bottom**) views. Different types of samples, like single crystals, foils, or supported metal nanoparticles, can be heated resistively up to 1300 K. By flowing liquid N_2 through the manipulator a temperature of 77 K can be achieved. The temperature is monitored via type-K thermocouple, and two further spare connections allow to apply an electric potential for electrochemical measurements.

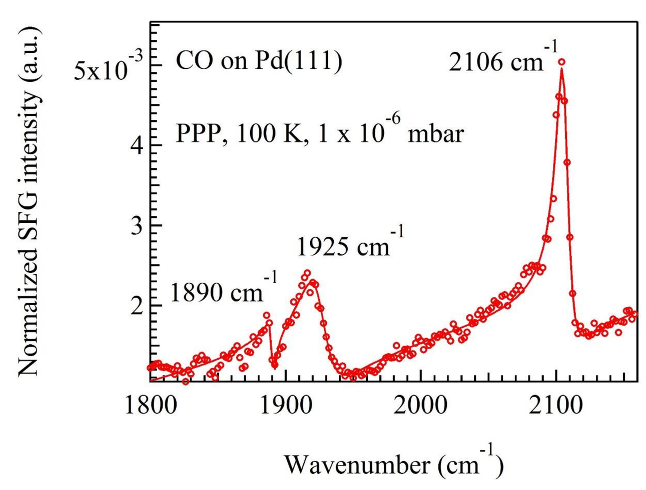




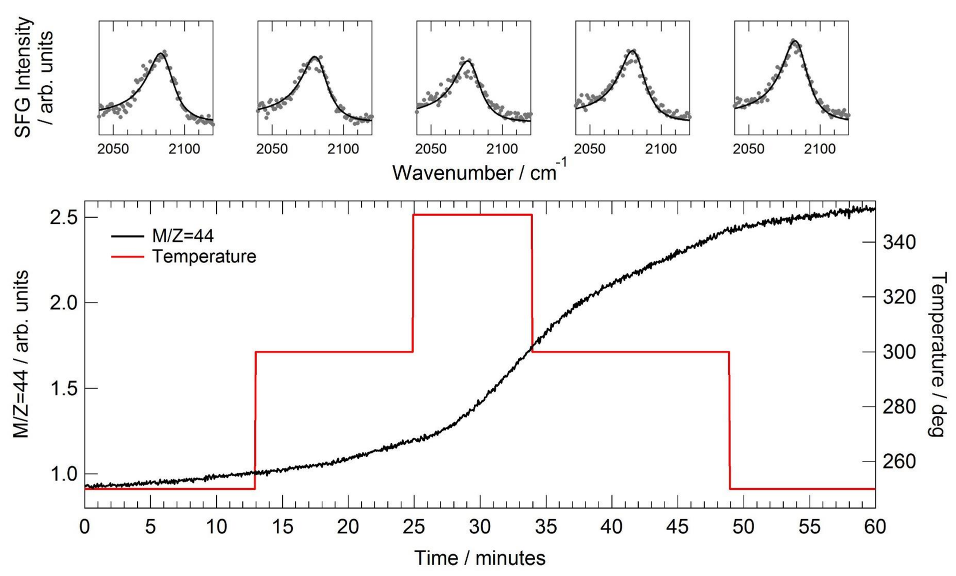
The setup has been produced by OmniVAC, Kaiserslautern, according to our design, while the sample holder, manipulation stage and transfer system are a proprietary design of the company.

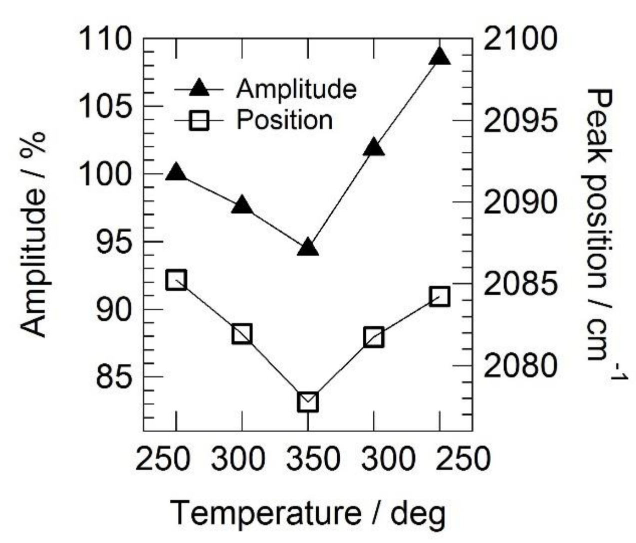
Results and discussion





CO adsorption on Pd(111) at 100 K investigated by LEED and SFG. LEED shows an ordered (2×2) overlayer with 0.75 ML coverage. Hollow, bridge and atop adsorbed CO are identified by SFG, with distinctive vibrational features at 1890, 1925 and 2106 cm-1, respectively.





Simultaneous in-situ SFG spectroscopy and MS analysis of CO oxidation (30 mbar $CO+O_2$ 1:2) by ZrO_2-supported Pt-nanoparticles model catalyst. The CO_2 production rate has a maximum at 350 K, at the same temperature the atop CO/Pt SFG peak is at its minimum of intensity.

Acknowledgements

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FWF Der Wissenschaftsfonds.

Solids4Fun BUILDING SOLIDS FOR FUNCTION

FOXSI Functional Oxide Surfaces and Interfaces