4. RAMAN SPECTROSCOPY

4.1. ADVANTAGES OF (IR AND) RAMAN SPECTROSCOPY

Raman spectroscopy is one of the most powerful tools for the study of heterogeneous catalysis systems because of its ability to analyze both the molecular reagents and the solid catalytic material in a single measurement under reaction conditions.

Unfortunately, for many realistic catalyst systems, e.g. supported metal catalysts, metal oxides, and zeolites etc. interference from fluorescence emission made Raman measurements impossible. Almost 20 years ago it was demonstrated by exciting the Raman scattering at ultraviolet wavelengths below about 260 nm, the *fluorescence* interference could be avoided. (Practically all heterogeneous catalytic systems or oxide based supports exhibit strong fluorescence due to their high adsorption capabilities as highly surface active materials). The so-called *UV Raman spectroscopy* has several challenges.

Firstly in a short wavelength excitation due to the ν_0^4 rule (ν_0 is the excitation wavenumber) the Raman effect strongly enhanced (for example the effect with 244 nm is 360 times stronger as compared to the 1064 nm near IR excitation) consequently low laser power is sufficient to produce spectra also with weak heating effect.

Secondly, dark colored or black samples can be measured more successfully than with visible lasers (less blackbody effect).

Thirdly, most molecules have electronic absorption bands in the UV region the ability to excite resonance Raman scattering with UV laser excitation which can give resonantly enhanced Raman scattering (enhancement is about 10^3-10^5) and in comparatively small molecular systems. This has opened up the possibility of identifying and quantifying the variety of surface species at very low concentration present in the typical inhomogeneous mixture that exists on a catalyst.

NIR infrared (750-1100 nm) laser excitation also helps to overcome fluorescence problems since not really electronic excitations are common in this region.

- **Not very expensive**
- ***In situ***
- **Catalytic condition**
- **Information on molecular level**
- **Aqueous systems (R)**
- **Microprobe, microscopy**
- **Fibres**
- **FT, optical multichannel detection**

PROBLEMS	SOLUTION
♦ **Sensitivity (R)**	**RR, SERS, 10^5-10^6)**
♦ **Flourescence (R)**	**NIR or UV excitation** **Burn-out**
♦ **Heating effect (R)**	**Rotating sample; red laser**
♦ **Not transparent below ~ 1000 cm^{-1} (IR)**	**Use not transmittance technique**

PROBLEMS:

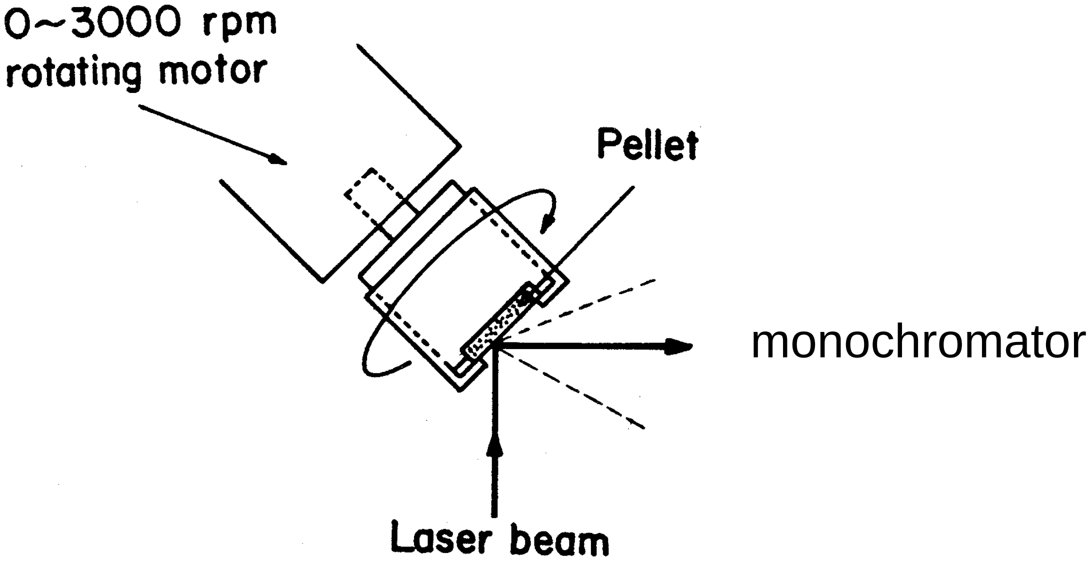
- **Catalysts are surface active materials, adsorption of fluorogene molecules, fluorescence**
- **Black/dark colored powders, adsorption, heating effects**
- **S/N small, noisy spectra**

SOLUTIONS:

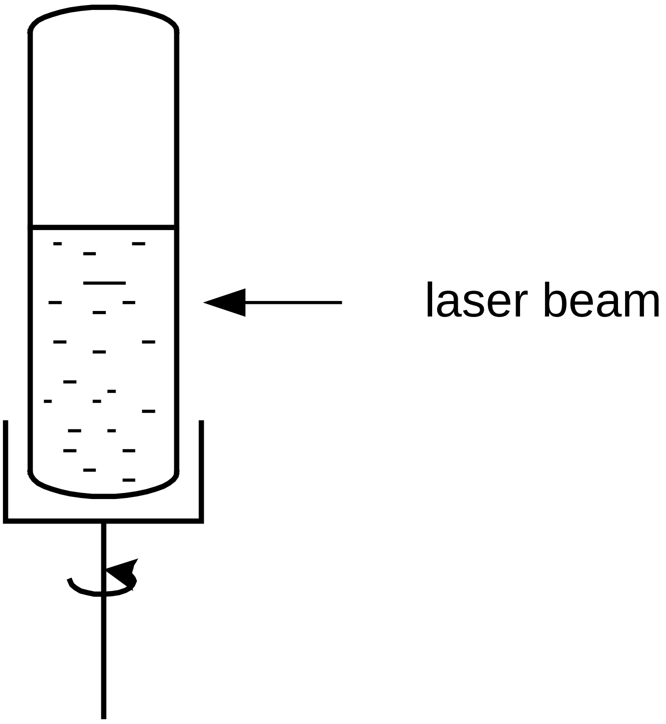
- **Resonance Raman (RR)**
- **Surface enhanced Raman**
- **UV excitation**
- **FT-Raman**

4.2. EXPERIMENTAL TECHNIQUES

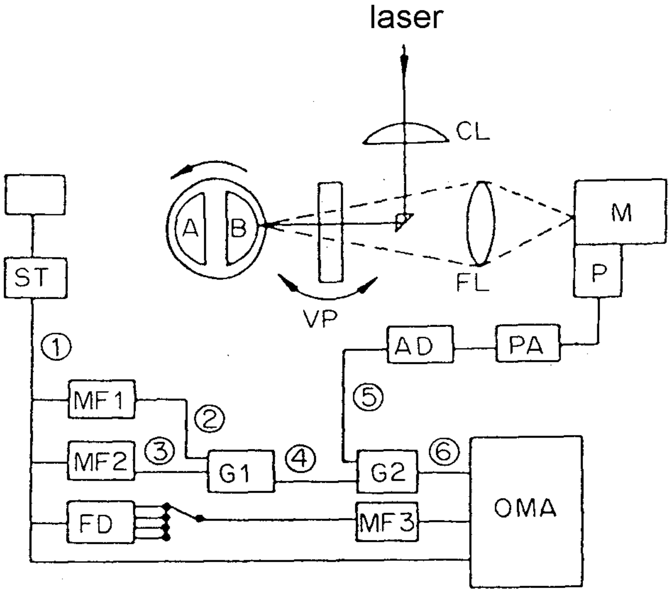
a) Rotating cell (open)



b) Rotating cell (closed)

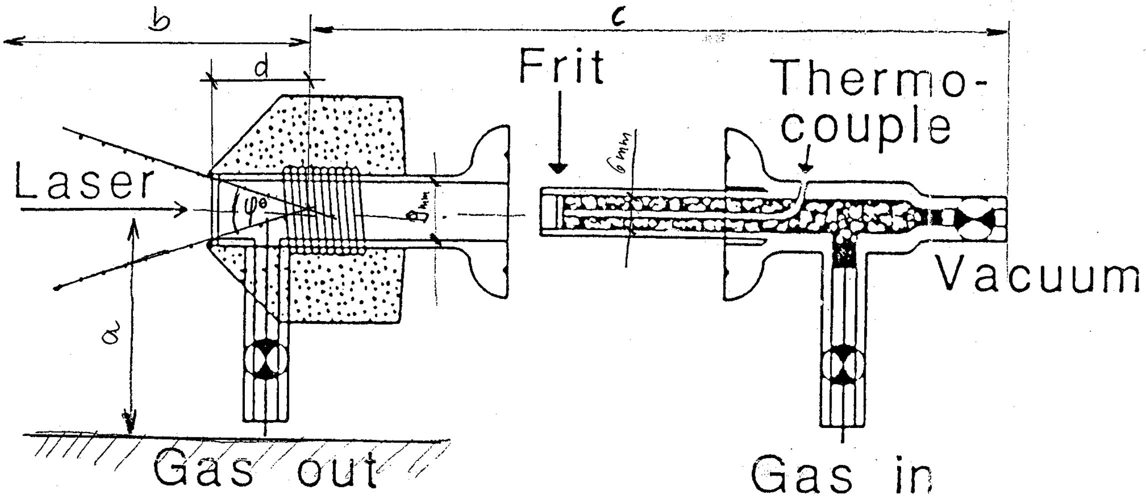


c) Rotating double cell



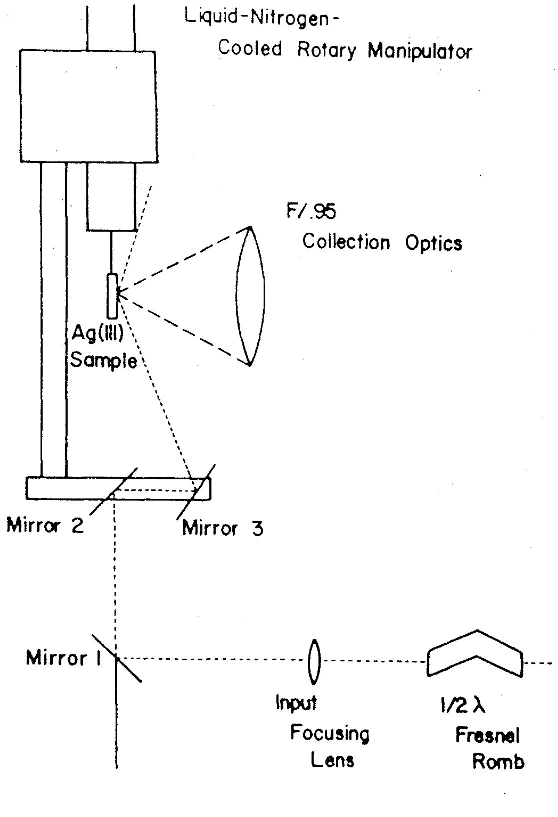
A-Sample: SiO_2/Pt/CO
B - Support: SiO_2/Pt

d) *In situ* Raman cell



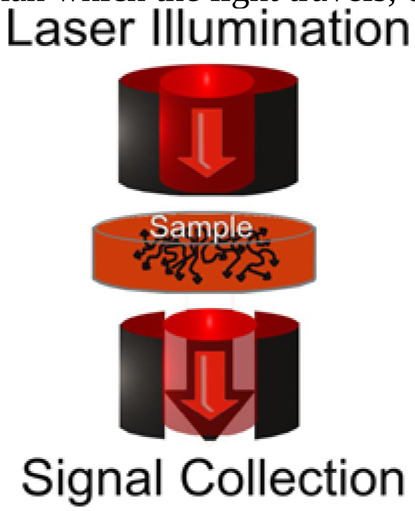
Heatable *in situ* Raman cell

e) Study single crystal surfaces



Raman transmission accessory (NEW)

The transmission Raman spectroscopy to be undertaken can be realized in a simple and efficient format. It provides a cost effective access to technique, ideally suited to bulk materials of opaque samples powders like heterogeneous catalysts. Transmission Raman is based on the collection of Raman light propagating through the sample in the direction of the excitation laser – in essence, the sample is illuminated with the excitation laser from one side, and the Raman signal is collected from the other. Unlike its more traditional back-scattering counterpart which is vastly predominant in most dispersive Raman systems, the transmission configuration allows analysis of the full volume through Transmission Raman which the light travels, even for opaque samples.



Principe of transmission Raman spectroscopy

The set of optics to change the beam diameter for transmission Raman spectroscopy.

The Transmission Raman Accessory provides fast, reliable information about:

- Surface species , catalysts and supports
- Polymorphs analysis
- Crystallinity of samples
- Powder composition and purity
- Content uniformity
- Determination of ingredients in tablets, etc.
-

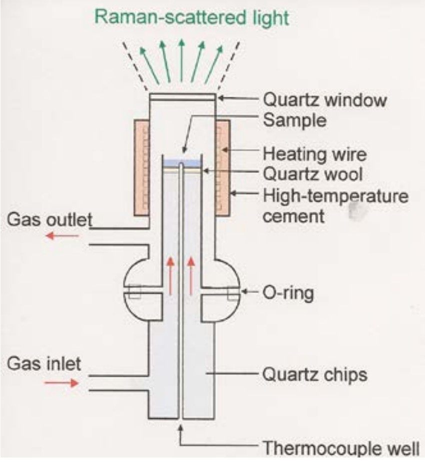
Temperature controlled *in situ* cells

In situ study of catalysts is important for several reasons. The catalytic active sites are not stable; their structure changes with conditions and structure should be different for before, during and after the reaction. Beside these the structure of surface species are also variable during the process of reaction.

For rather large catalytic cells it is necessary to have large space below thee microscope. This unique construction made possible to use large samples, large low and high temperature (catalytic) cells, large and heavy stages, etc.

Most commonly used LINCAM catalytic cell

As a very brief description can be mentioned: maximum temperature of use is 600 ^{o}C, minimum temperature is -196 ^{o}C with additional LNP 95 unit. Maximum heating rate is 150 ^{o}C/min and XY manipulate travel is 16 mm. The cell can be used both for FTIR and Raman microscopes as well.



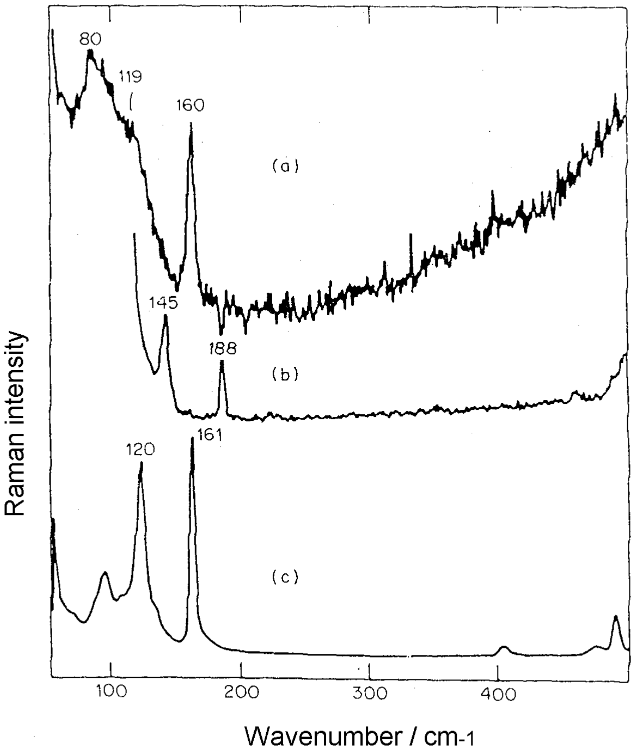
Simple “home made” quartz catalytic cell.

This apparatus makes is possible to study catalyst systems under a wide range of temperatures from liquid nitrogen to 1000 ºC under reaction gases.

4.3. EXAMPLES

$C_6H_6/Ni/SiO_2$	**304**
	995
	1056
	3016
	3040
	3060
$C_2H_4/Ni/SiO_2$	**3000**
	2924
	2860
	1128
	990

$Os_3(CO)_{12}/Al_2O_3$



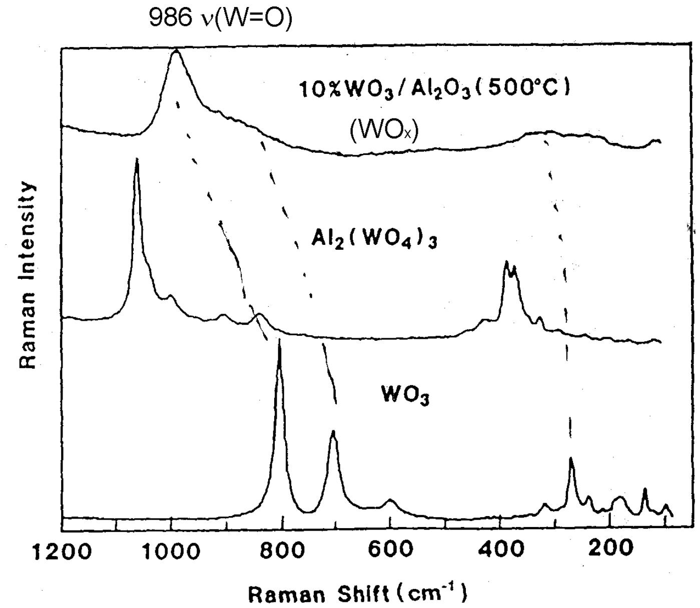
$Os_3(CO)_{12}$ on Al_2O_3 support

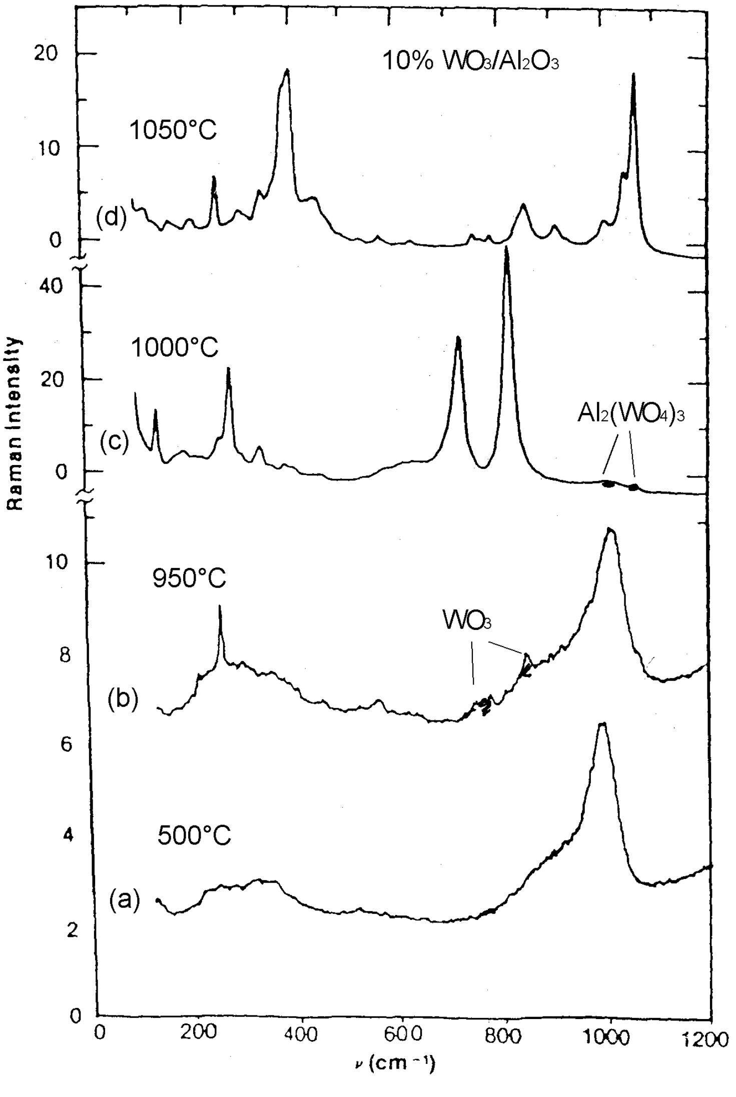
$H_2Os_3(CO)_{10}$ reference

$Os_3(CO)_{12}$ reference

The Os_3 stretching band at 160 cm^{-1} is preserved, the metal skeleton is existing

Metal oxide catalysts (HDS-catalysts)





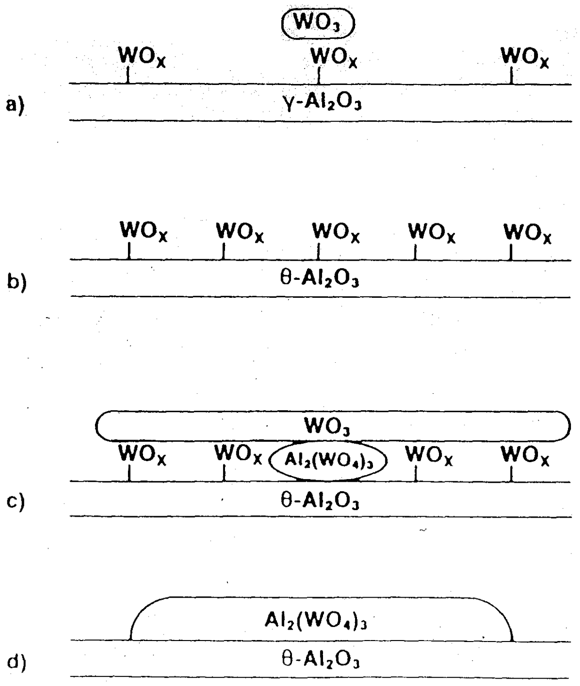
$Al_2(WO_4)_3$ / θAl_2O_3

WO_3 / θAl_2O_3

WO_x / θAl_2O_3

WO_x / γAl_2O_3

Explanation of the above spectral changes.

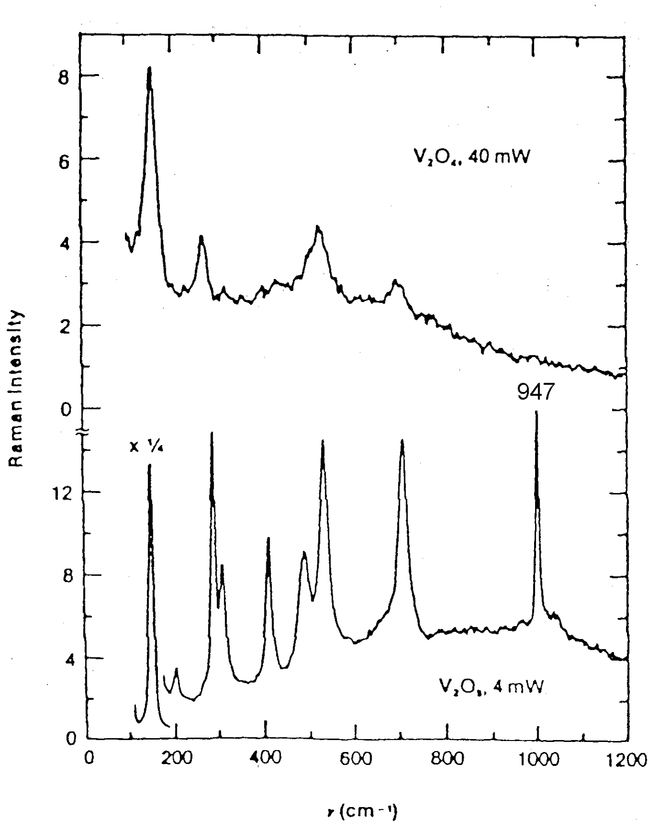


500°C

950°C

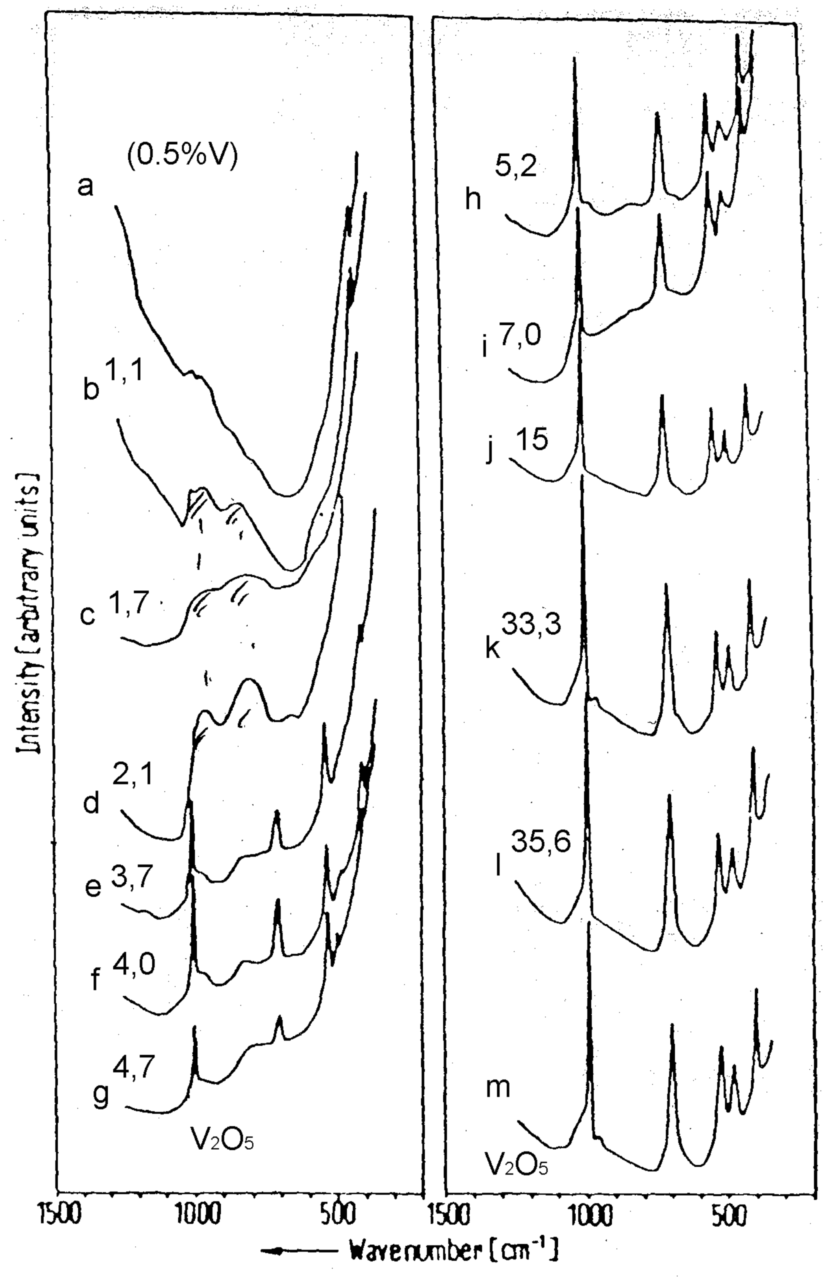
1000°C

1050°C



SO$_2$
CO
HC

Oxidation



Other supports for V_2O_5: CeO_2, Cu_2O_3, SiO_2, TiO_2

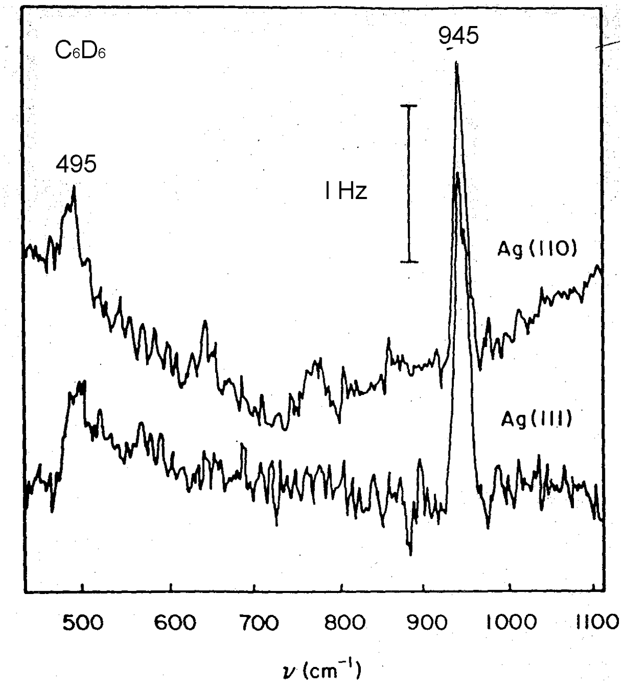
ZrO_2, MgO (1-40 %)

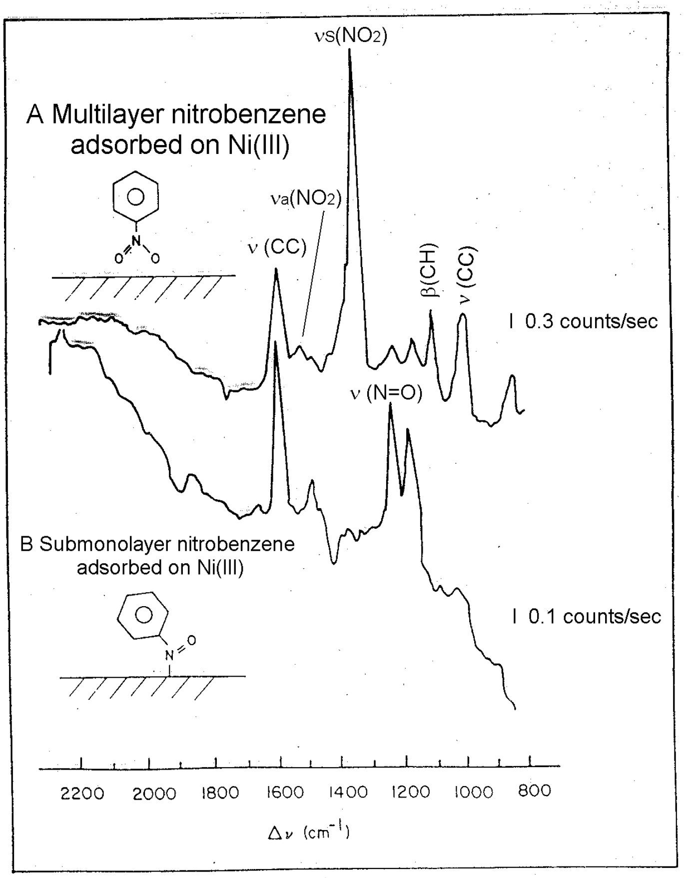
↓

ZrV_2O_7

Temperature treatment: 370-1070 K
TiO_2: oxidation of o-xylene to phtallic anhydride

Single crystals





100 L

3 L

4.4. SURFACE ENHANCED RAMAN (SERS)

Fleischmann
Hendra } 1974 Ag/Py (electrode surface)
McQuilar

METALS: Ag, Au, Cu, Ni, Strong
Pt, Cd, Al, Hg, Pd, weak

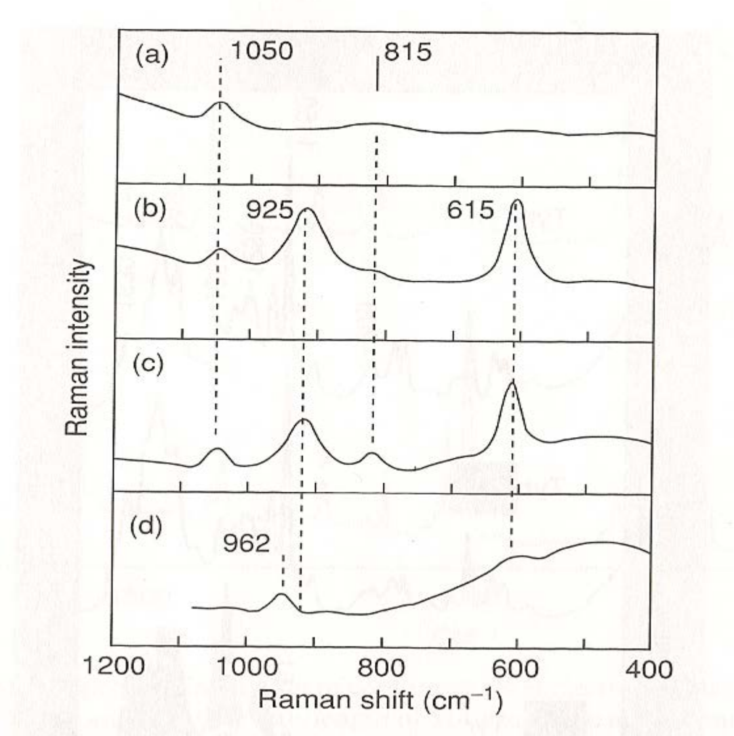
LASER WAVELENGTHS:
647.1 nm Cu, Au }
514.5 nm Ag } surfaces, strong effect

THEORY: 1. electromagnetic interactions
2. Theory of surface plasmons

APPLICATIONS:
Electrochemistry: Ag/organic molecules
Colloids: Ag, Au, particle size
UV-absorption dependent
Analytical chemistry:
Water analysis: - pollutants
-algaes

TLC
GC, LC-columns

Catalysis



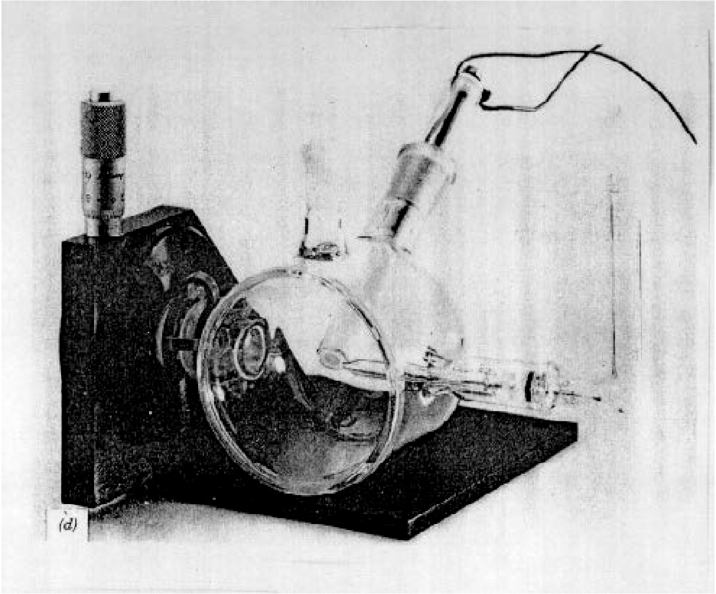
Ag/He

+ SO_2 (gas)
Formation SO_3^{2-} (925, 615 cm^{-1})

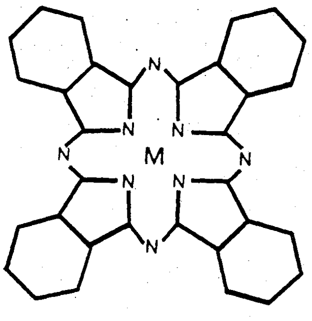
$SO_2 + O_2$

Heating to 380K
Formation SO_4^{2-} (962 cm^{-1})
Thermal desorp. of SO_3^{2-}

SERS from finely divided Ag powder
Catalytic oxidation of SO_2 to SO_3^{2-} and SO_4^{2-}

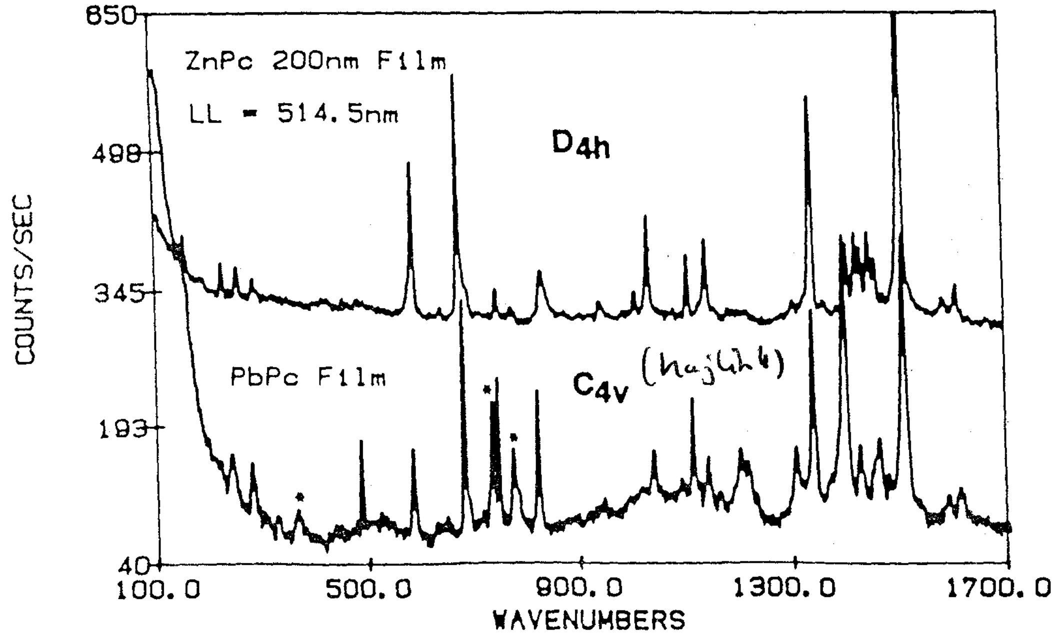


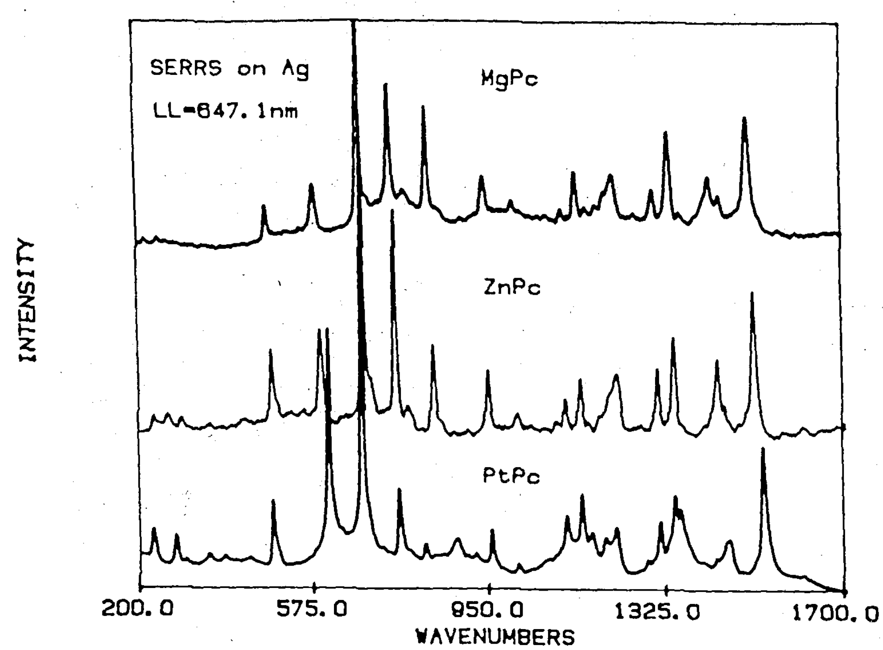
Electrochemical cell for SERS measurements



M = Mg, Cu, Zn, Pt and Pb

Pthalocyanides (Pc)

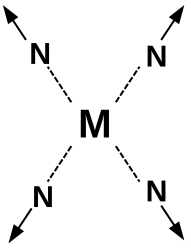




1 nm films on Ag surfaces

Vibrational assignment of the observed a_{1g} modes of CuPc molecule, derived from the PED of the normal coordinate analysis

	Wavenumber	Interpretation
a_{1g}	1590	C=C benzene + C=C pyrrole
	1528	C=N aza + C=C pyrrole + C=C benzene
	1452	Pyrrole st. + benzene st. + benzene def.
	1431	Pyrrole st. + benzene def.
	1140	Pyrrole st. + aza st. + Cu-N
	1106	C-H bend + benzene st.
	1037	Benzene def. + benzene st.
	831	C-H bending + benzene st.
	678	In-phase pyrrole + benzene st. mode
	588	Benzene radial + aza bending
	236	Cu-N in-phase motion of pyrrole and aza groups



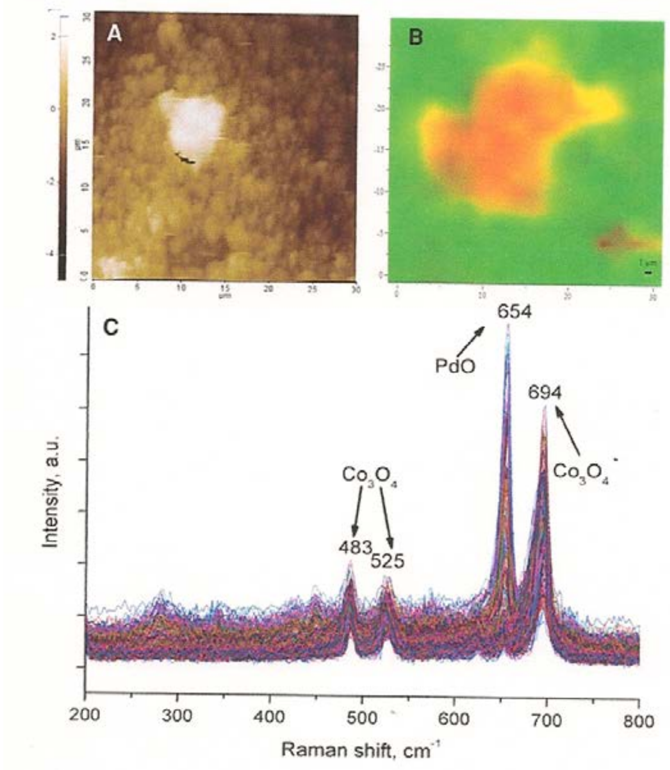
$$\underbrace{\begin{matrix}\text{Mg,} & \text{Cu,} & \text{Zn,} & \text{Pt}\\ 243 & 236 & 232 & 223\end{matrix}}_{a_{1g}}\quad\underbrace{\begin{matrix}\text{Pb}\\ 234\end{matrix}}_{a_1}$$

Raman imaging capabilities

4.5. Raman imaging capabilities

Confocal imaging is obtained by moving the illuminated sample, step by step (downm to 5 nm /step).

Raman imaging can be used for study the surface heterogeneity of catalytic materials at various stages of their preparation and obtain molecular properties of surface species. Raman pectroscopy and microscopy has been particularly invaluable in three aspects: determination of catalyst oxidation state, evaluation of the role of support, and identification of adsorbed intermediates. One example is shown in Fig. below.



AFM and Raman imaging of cobalt oxide catalyst doped with palladium deposited on Kanthal steel. A, AFM topology map 30x30 µm; B, Raman image map 30x30 µm of the same area obtained using two marker bands ofCr$_3$O$_4$ (694 cm^{-1}) and PdO (654 cm^{-1}); C, a stack of Raman spectra collected at each points of map B. (J. Lojewska at al, *Top Catal.* 2013, 56, 1088).

4.6. Homogeneous catalytic systems

Not much publication is available in the literature with application of Raman spectroscopy in homogeneous catalysis. It is also true for FTIR applications as compared to those of Raman and infrared studies of heterogeneous catalysts.

When both the reaction mixture and the catalyst are in liquid phase than the monitoring can be easily done with frequent recording the Raman, infrared or UV-vis spectra of the system to monitor concentration changes and to detect intermediate species.

More complicated the situation when heterogenized catalysts are used in homogeneous catalysis. Up till now there are no really publications giving hints for spectroscopic investigation of the heterogeneous phase under liquid reaction mixture.

Combined study of liquid phase reactions.

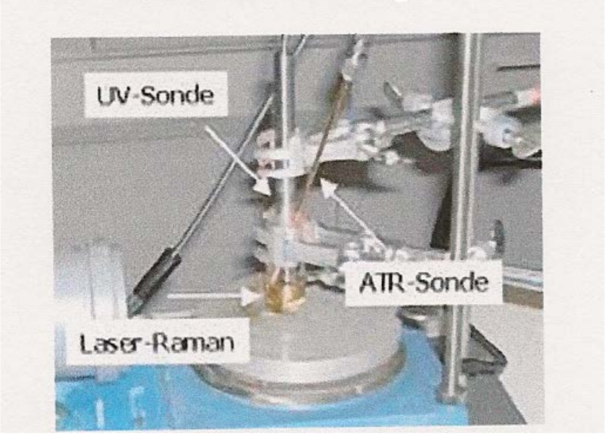
For the most effective characterization homogeneous catalysts and the study of their behavior under reaction condition, different *in situ* and *operando* spectroscopic methods (Raman, FTIR and UV-vis) can be applied simultaneously. Such a combined *in situ* cell design is shown in Figure 10.

Combining operando Raman, FTIR and is particularly useful for studying homogeneous catalysis in solution. Transition-metal complexes can perform catalytic oxidation reactions on organic molecules; however, much of the corresponding reaction pathways are still unclear. Understanding organometallic catalytic activity on organic molecules is incredibly valuable for the further development of material science and pharmaceuticals.

For measuring the Raman spectra, the laser beam of the fiber optical Raman spectrometer () is focused through the quartz reactor onto the catalyst bed or the reaction solution. Additionally, a Raman immersion probe is available for measurements in liquid phase. Furthermore, *operando* spectroscopic studies of gas-solid reactions can be carried out as well on a Raman microscope equipped with a special reaction cell (LINKAM).

For measurements of infrared spectra in liquid phase, a fiber optical diamond ATR probe (infrared fiber sensors) can be used, coupled to the FTIR spectrometer (); here the probe is directly immersed into the reaction solution. A special homemade ATR-FTIR flow-through cell enables homogeneous catalytic reactions to be monitored.

The measurements of UV-vis spectra can be carried out in reflectance/transition mode using various quartz optical fiber sensors (AVASPEC, Avantes) which are directly positioned in the catalyst bed or in the solution. Operando UV/vis spectroscopy is particularly useful for many homogeneous catalytic reactions because organometallic species are often colored. Fiber-optical sensors allow monitoring of the consumption of reactants and production of product within the solution through absorption spectra.



Simultaneous Raman, ATR-FTIR and UV-vis investigation of liquid phase reactions.

Raman spectroscopic study of heterogenized catalyst systems.

In today practice it is a very common to use heterogenized catalysts in homogeneous reactions. This leads to the situation where the catalyst is in solid phase and the reaction mixture in liquid phase. The spectroscopic monitoring of liquid phase can be performed analogously as it was described above in 1.2.1. Chapter.

Our new idea for recording Raman spectra of both the sediment (from the solid catalyst) and the liquid phase simultaneously is illustrated in Figure 11.

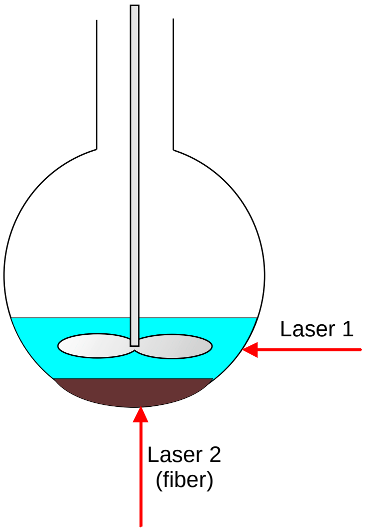


Illustration of the experimental set-up for simultaneous Raman spectroscopic monitoring of the liquid (Laser 1) and the solid phase (Laser 2) in a reaction vessel.

There is a possibility to use such a Raman spectrometer which can provide beside the “normal” horizontal excitation geometry shoved by Laser 1 a fiber optic set up illustrated by Laser 2 from the same laser source with alternating measurement sequences. This construction provides simultaneous *in situ* monitoring of the solid and liquid phases.