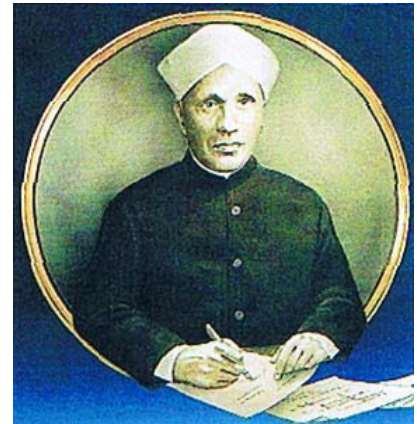


Raman spectroscopy: Basic principles and applications

Christian Hess

- **Basic principles**
 - Resonance Raman scattering
 - Surface Enhanced Raman Scattering (SERS)
- **Instrumentation**
 - Spectrometer
 - Excitation sources
- **Raman in catalysis**
 - In situ cells
 - In situ Raman (of working catalysts)

C.V. Raman (1928)



- **Basic principles**
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Introduction

Why Raman spectroscopy?

- Information on rotational and **vibrational** levels
- Raman effect small but accessible by use of **lasers**
- **Complementary** information **to IR** spectroscopy
 - homonuclear diatomic molecules, low frequency range
- **In situ analysis** of organic and inorganic compounds
- Analysis of **aqueous solutions and solids** (powders)
- Using resonance and surface enhancement effects $\sim 10^{10}$
 - **Trace gas/single molecule analysis** - molecular structure

Classical description

- Spatial charge separation under influence of electric field \mathbf{E}

→ induced dipole moment $\boldsymbol{\mu}$:

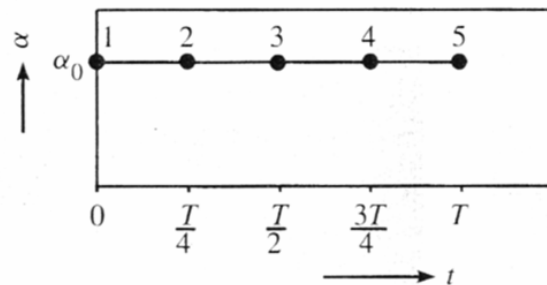
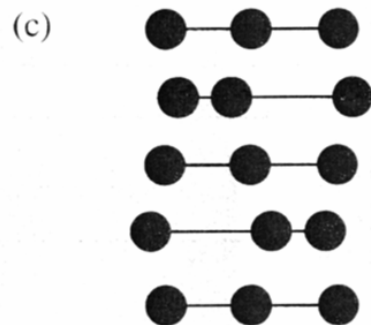
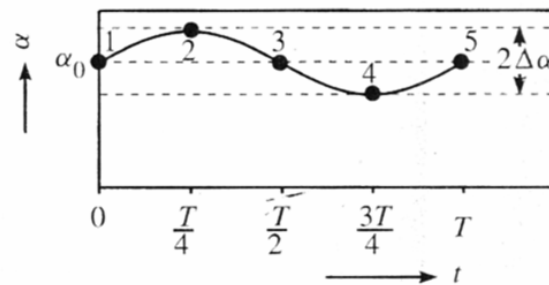
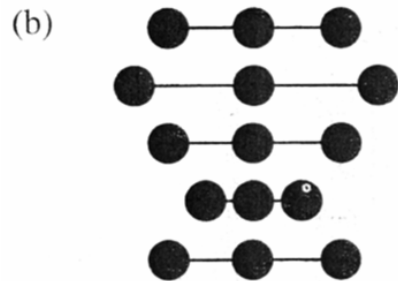
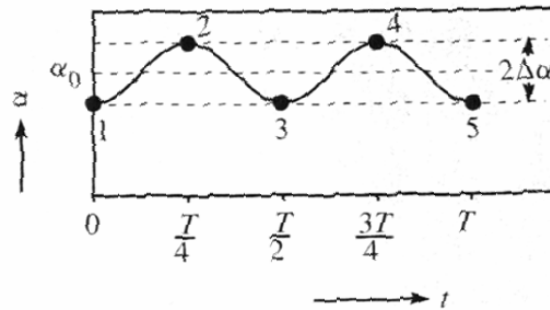
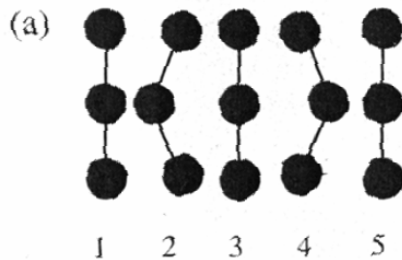
$$\boldsymbol{\mu} = \alpha \mathbf{E} \quad (1)$$

α : polarizability

→ *Example: polarizability changes during CO₂ vibrations*

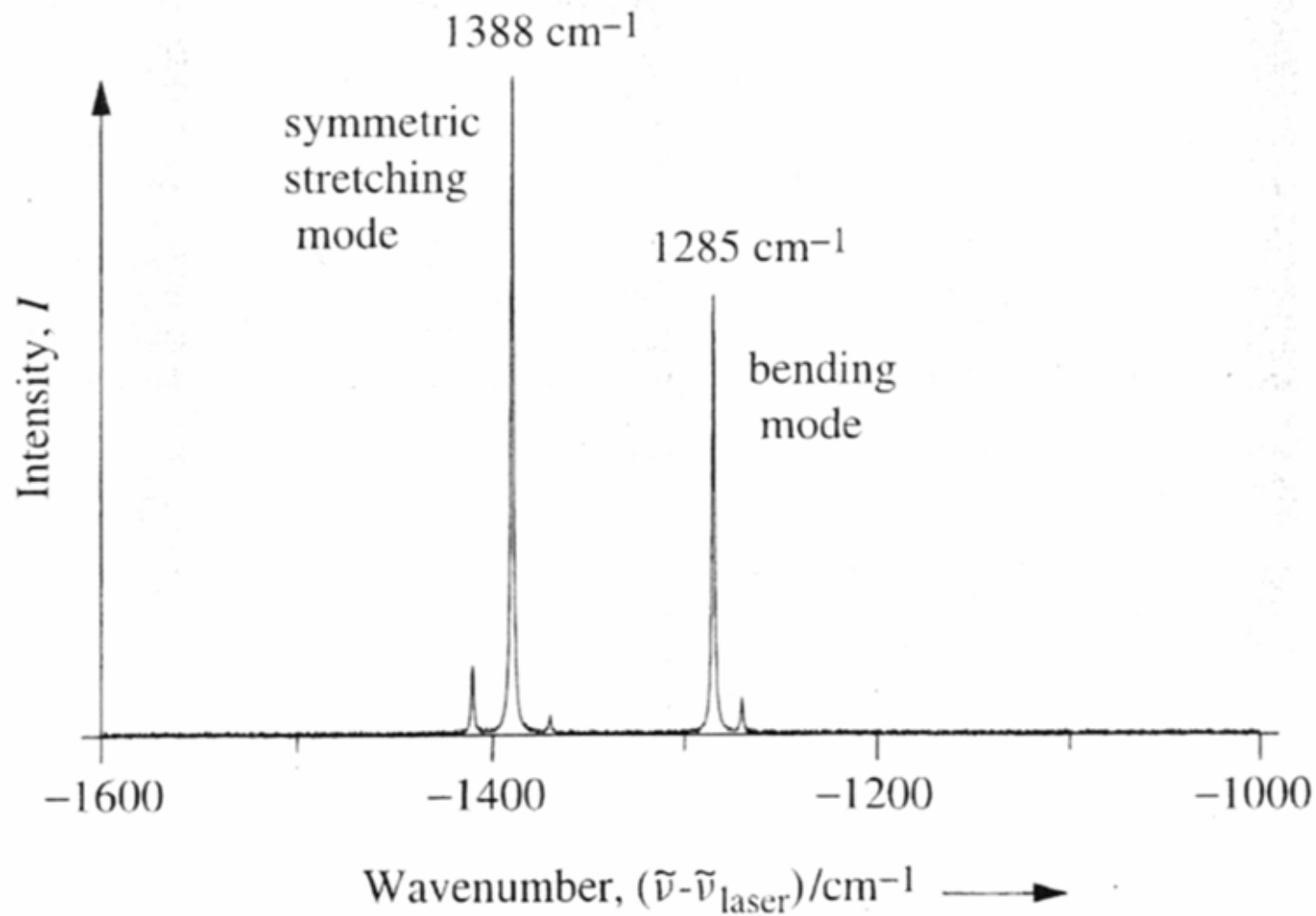
Example: Polarizability changes CO₂

Vibrational modes of CO₂



Example: Polarizability changes CO₂

Vibrational modes of CO₂



Classical description

- Spatial charge separation under influence of electric field \mathbf{E}

→ induced dipole moment $\boldsymbol{\mu}$:

$$\boldsymbol{\mu} = \alpha \mathbf{E} \quad (1)$$

α : polarizability

- Electric field \mathbf{E} due to electromagn. wave with frequency ν_0

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi \nu_0 t \quad (2)$$

$$\rightarrow \boldsymbol{\mu} = \alpha \mathbf{E}_0 \cos 2\pi \nu_0 t \quad (3)$$

→ emission of light at same frequency ν_0

$$\begin{aligned} \rightarrow I &= (2/3c^3) \mu^* \\ &= (16\pi^4 \alpha^2 E_0^2 / 3c^3) \nu_0^4 \end{aligned} \quad \mu^* = \overline{\left(\frac{d^2 \mu}{dt^2} \right)^2} \quad (4)$$

Classical description

- Internal vibrational motion with Eigenfrequency ν_M

$$q = q_0 \cos 2\pi \nu_M t \quad (5)$$

- Polarizability $\alpha \rightarrow$ develop in series

$$\alpha = \alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q + \text{higher order terms} \quad (6)$$

$$\rightarrow \boldsymbol{\mu} = \alpha \mathbf{E} \quad (7)$$

$$= (\alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q_0 \cos 2\pi \nu_M t) \mathbf{E}_0 \cos 2\pi \nu_0 t$$

$$= \underbrace{\alpha_{q=0} \mathbf{E}_0 \cos 2\pi \nu_0 t}_{\text{Rayleigh}} + \frac{1}{2} (\partial\alpha/\partial q)_{q=0} q_0 \mathbf{E}_0 [\cos 2\pi (\nu_0 - \nu_M) t + \cos 2\pi (\nu_0 + \nu_M) t]$$

Rayleigh

Stokes/Anti-Stokes

Q.M. description

→ harmonic oscillator: $\Delta v = \pm 1$

inelastic impact	elastic impact	inelastic impact
$\Delta E_M > 0$	$\Delta E_M = 0$	$\Delta E_M < 0$
$v = v_0 - v_{\text{vib}} < v_0$	$v = v_0$	$v' = v_0 + v_{\text{vib}} > v_0$
<p>Diagram illustrating Stokes scattering: An incident photon with energy $h\nu_0$ excites a molecule from the ground state ($v=0$) to the first excited state ($v=1$). The molecule then relaxes to a lower vibrational level ($v=1$) and emits a photon with energy $h(\nu_0 - \nu_{\text{vib}})$.</p>	<p>Diagram illustrating Rayleigh scattering: An incident photon with energy $h\nu_0$ excites a molecule from the ground state ($v=0$) to the first excited state ($v=1$). The molecule then relaxes to the ground state ($v=0$) and emits a photon with energy $h\nu_0$.</p>	<p>Diagram illustrating Anti-Stokes scattering: An incident photon with energy $h\nu_0$ excites a molecule from the ground state ($v=0$) to the first excited state ($v=1$). The molecule then relaxes to the ground state ($v=0$) and emits a photon with energy $h(\nu_0 + \nu_{\text{vib}})$.</p>
Stokes	Rayleigh	Anti-Stokes

Q.M. description

Raman intensity?

$$\rightarrow I_s = N_i \sigma_R(i \rightarrow f) I_L \quad (8)$$

N_i : initial state population

$\sigma_R(i \rightarrow f)$: Raman cross section for transition $E_i \rightarrow E_f$

I_L : Laser intensity

→ thermal equilibrium: Boltzmann distribution for state N_i at T

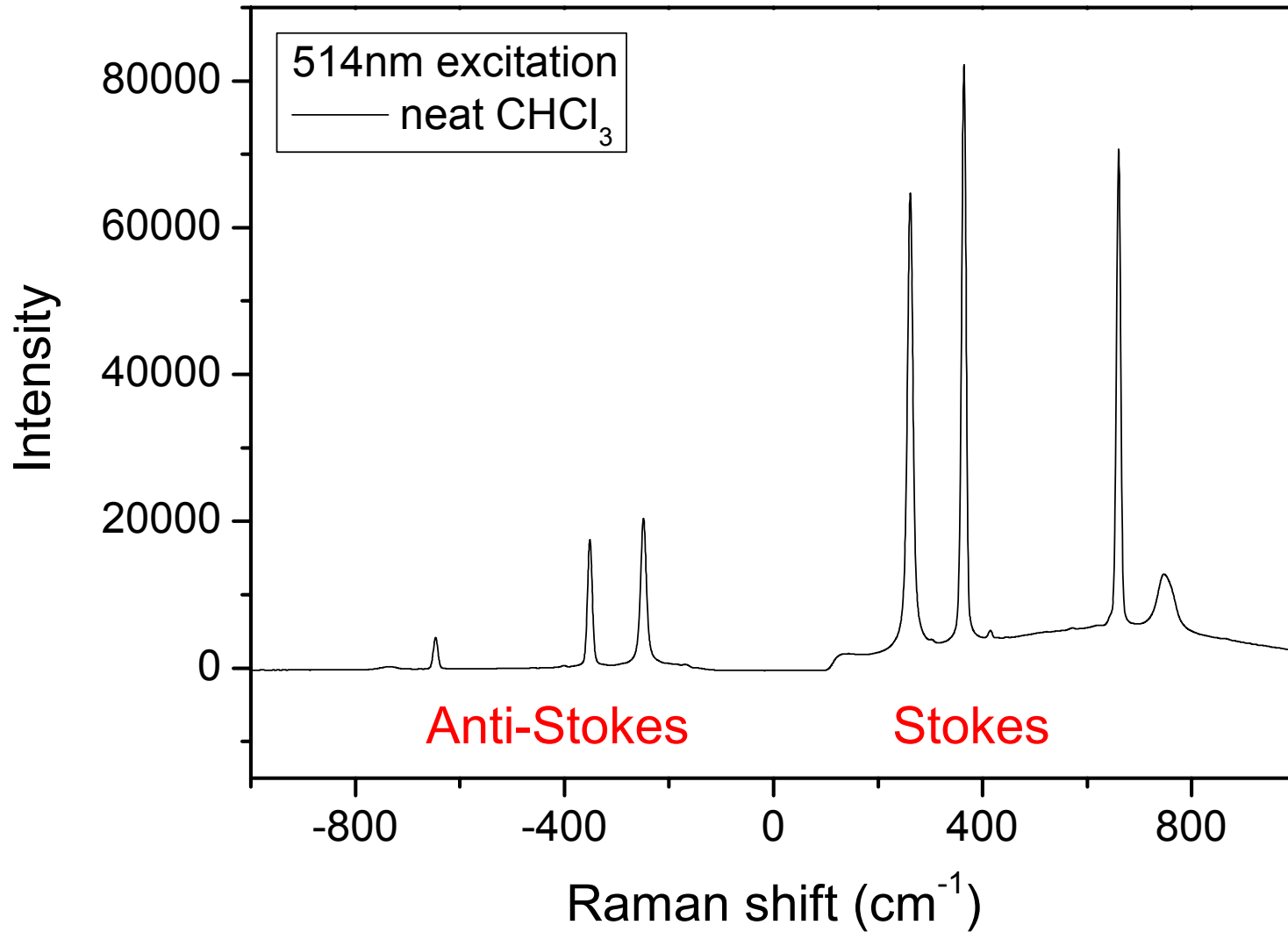
$$N_i = N_0 \exp(-ih\nu_{\text{vib}}/kT) \quad (9)$$

→ lower energy state: higher initial state population

$I(\text{Stokes}) > I(\text{Anti-Stokes})$

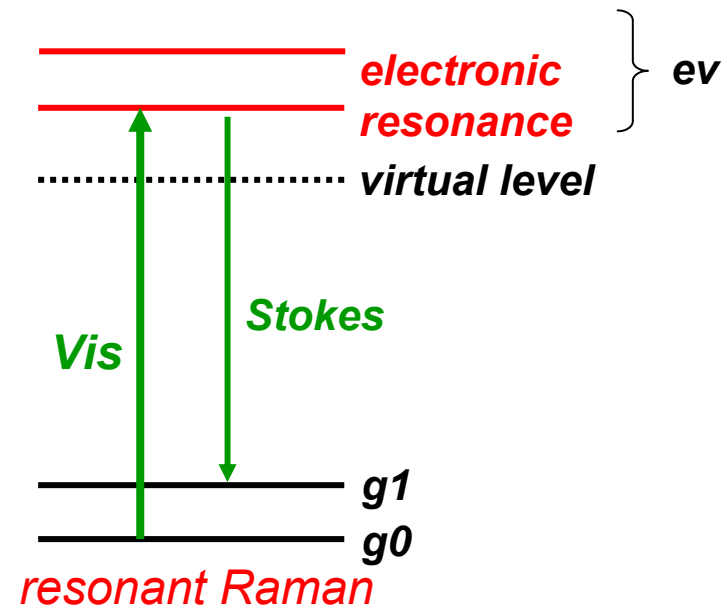
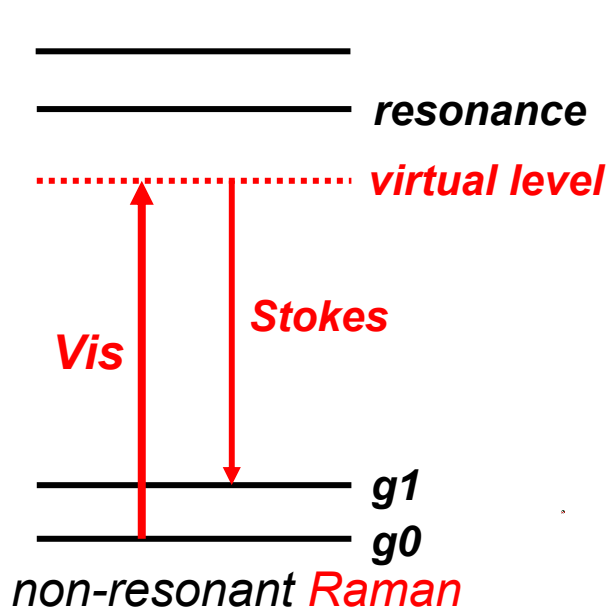
→ *Example: Stokes/Anti-Stokes intensities of CHCl_3*

Q.M. description



- **Basic principles**
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- **Instrumentation**
 - **Spectrometer**
 - **Excitation sources**
- **Raman in catalysis**
 - **In situ cells**
 - **In situ Raman (of working catalysts)**

Introduction to Resonance Raman scattering

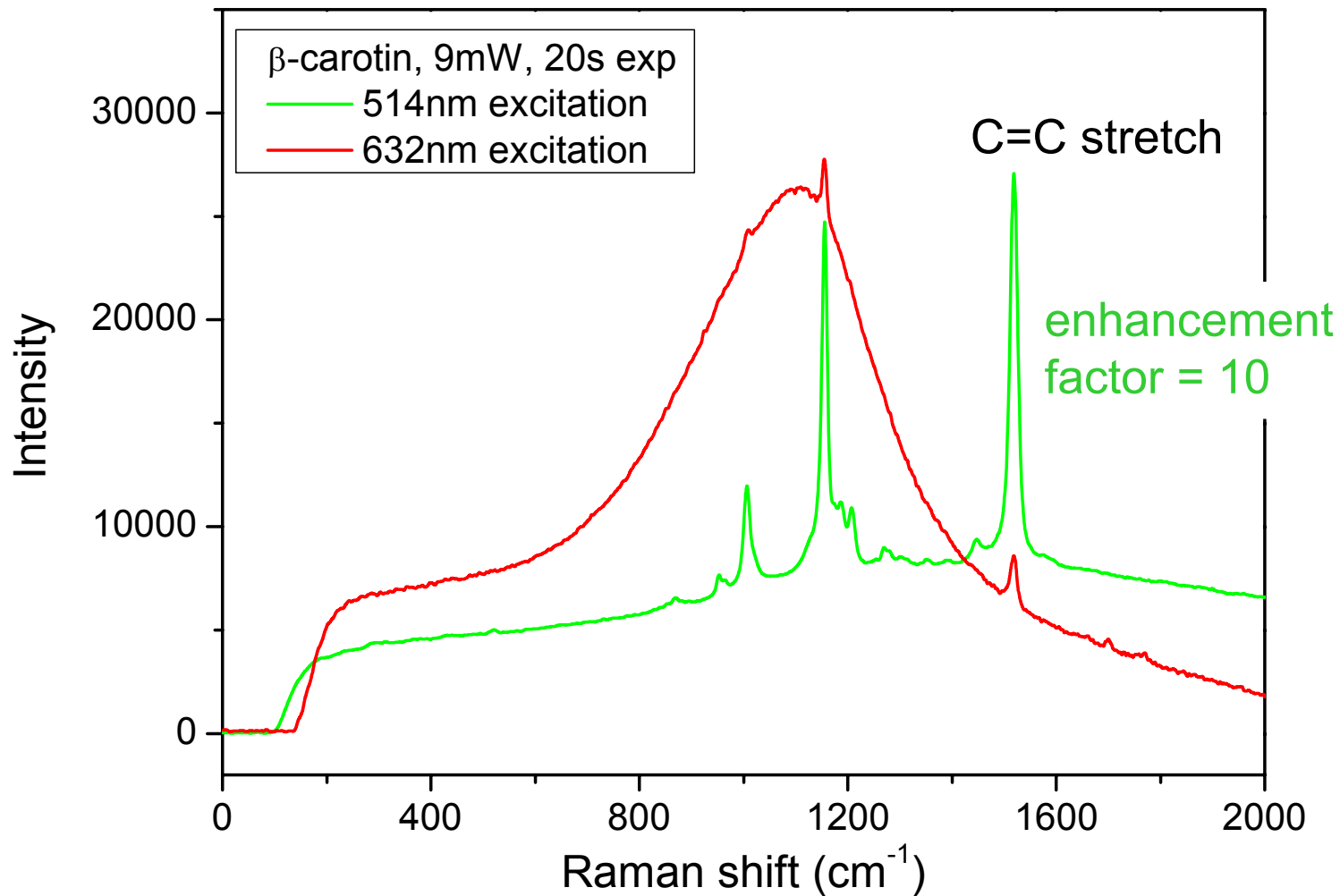


→ Polarizability tensor α (single e state):

$$\alpha_{\alpha\beta} = \frac{1}{\hbar} \sum_v \left(\frac{\langle g1 | \hat{\mu}_\alpha | ev \rangle \langle ev | \hat{\mu}_\beta | g0 \rangle}{w_{ev,g0} - w_0 + i\Gamma_{ev}} \right)$$

$\hat{\mu}_\alpha, \hat{\mu}_\beta$: Electric dipole moment operator
i.a. with incident/scattered light

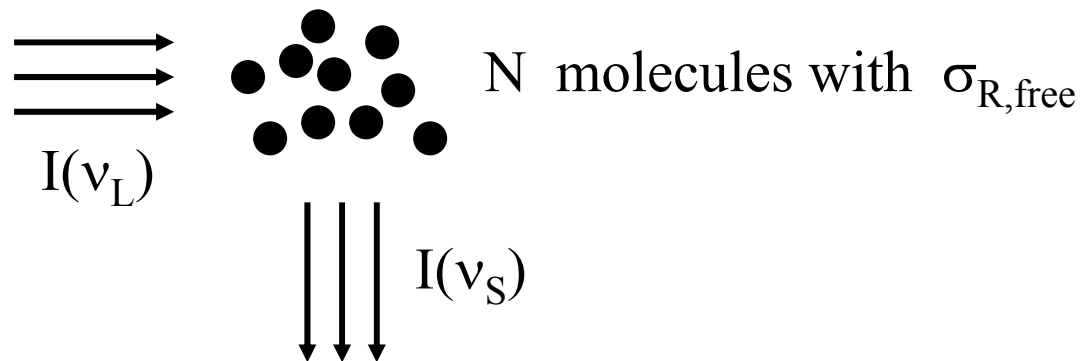
Example: β -Carotin



- **Basic principles**
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Introduction to SERS

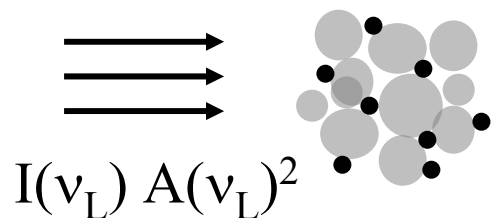
'Normal' Raman scattering



$$I_{NRS}(\nu_S) = N I(\nu_L) \sigma_{R,free}$$

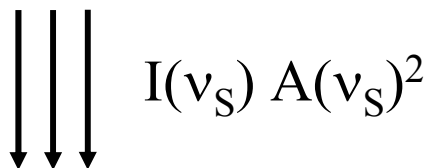
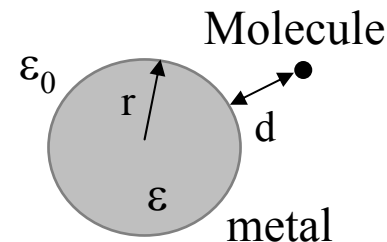
SERS mechanism - enhancement factors

Surface-enhanced Raman scattering



N' with $\sigma_{R,ads}$, $N' \leq N$

● “*Rough*” surface
e.g. metal nanostructure



$$I_{SERS}(\nu_S) = N' I(\nu_L) A(\nu_L)^2 A(\nu_S)^2 \sigma_{R,ads}$$

$$A(\nu) = \frac{E_M(\nu)}{E_0(\nu)}$$

(1) E.m. field enhancement

max. $\sim 10^6$ (isolated Ag,Au)

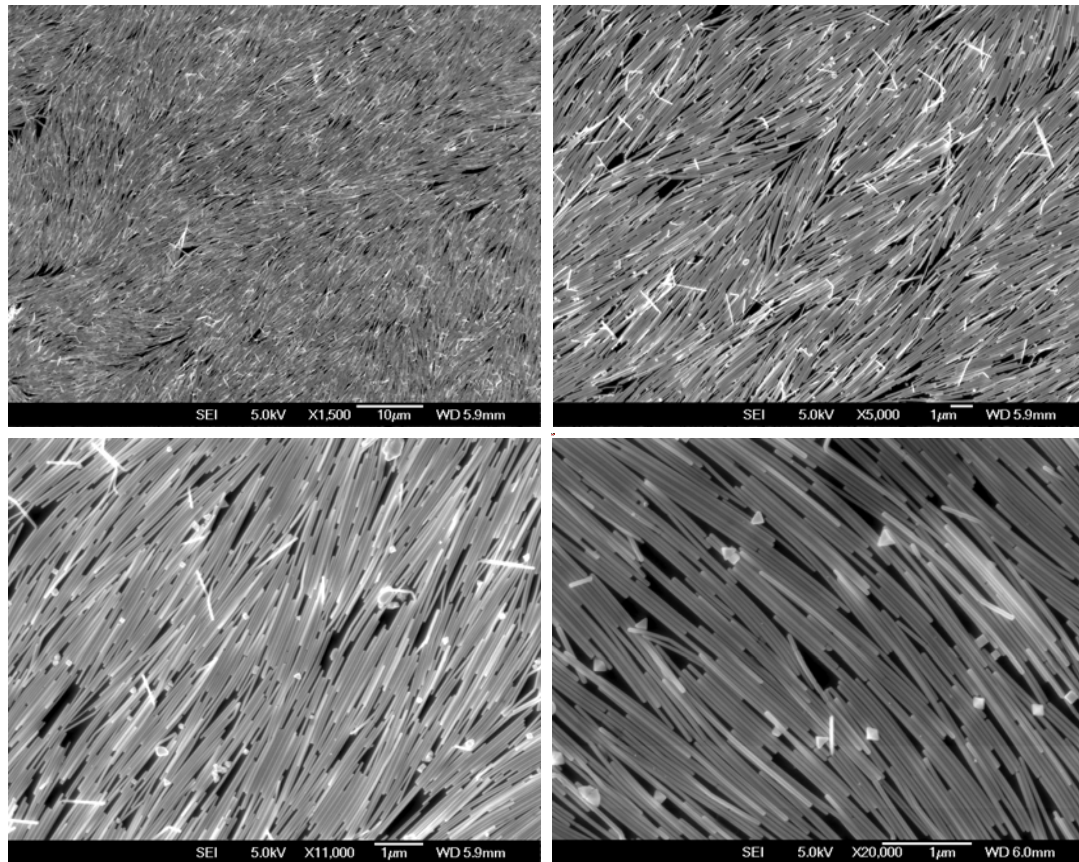
max. $\sim 10^8$ (coupled)

(2) Chemical enhancement

max. 10-100

SERS substrate

SEM images of the silver nanowire ML on Si wafer

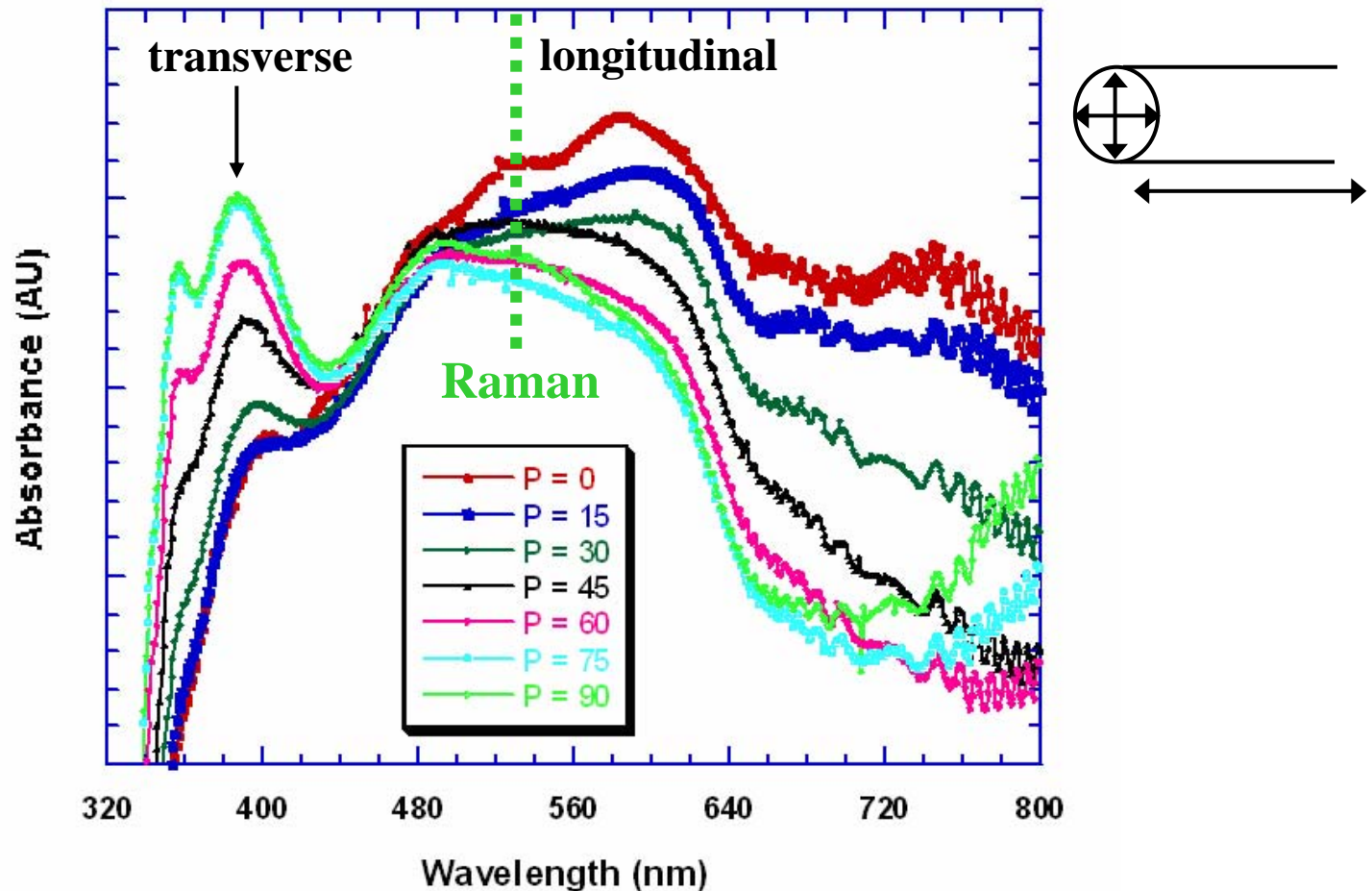


⇒ Deposited ML shows domains of aligned silver nanowires

A. Tao, F. Kim, C. Hess, J. Goldberger, R. He, Y. Sun, Y. Xia, P. Yang, Nano Lett. 3 (2003) 1229

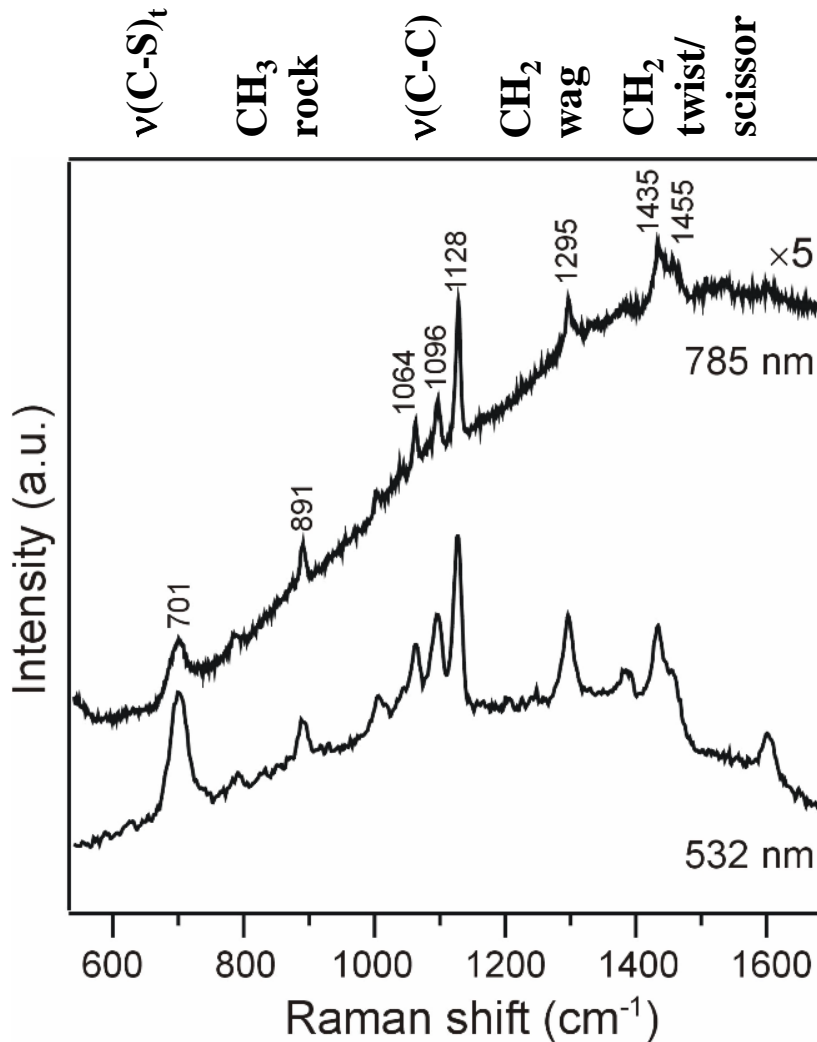
SERS substrate

UV-VIS absorption spectra of silver nanowire ML



⇒ Broadened extinction 500-600 nm due to wire-wire coupling

SERS example: 1-hexadecanthiol/Ag-LB film



- Enhancement factor EF:

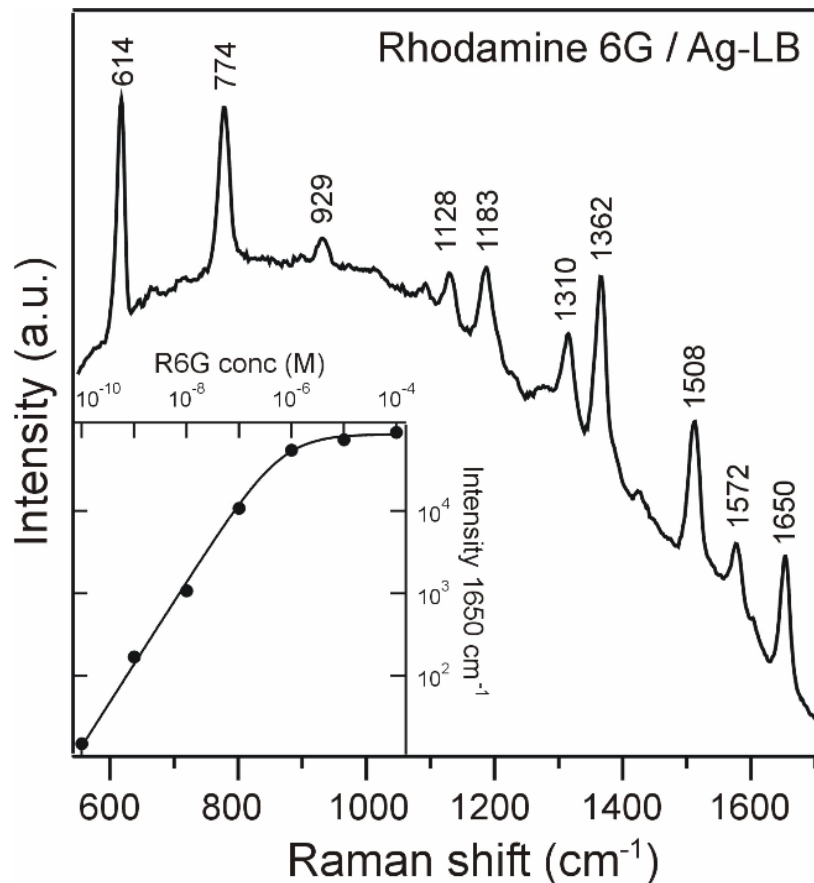
$$EF = [I_{\text{SERS}}]/[I_{\text{Raman}}] \times [M_b]/[M_{\text{ads}}]$$

- thiol head group $(2.3 \text{ \AA})^2$, closed-packed layer
 - ⇒ molecule conc. on surface: $2.5 \times 10^{14}/\text{cm}^2$
 - ⇒ 532nm, band at 1295 cm^{-1}

$$\Rightarrow EF = 2 \times 10^5$$

SERRS example: Rhodamine 6G/Ag-LB film

SERRS = Surface Enhanced Resonance Raman Scattering



- Linear relationship between intensity and concentration
⇒ surface not saturated

- Langmuir description using

$$M_{\text{ads}} = M_{\text{ads,max}} \frac{K a_0}{(1 + K a_0)}$$

yields $\Delta G_{\text{ads}} = 46 \text{ KJ/mol}$

- Large EF = 10⁹ as result of SERS and Resonant Raman

- **Basic principles**
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Raman spectrometer

Challenges to record (good) spectra

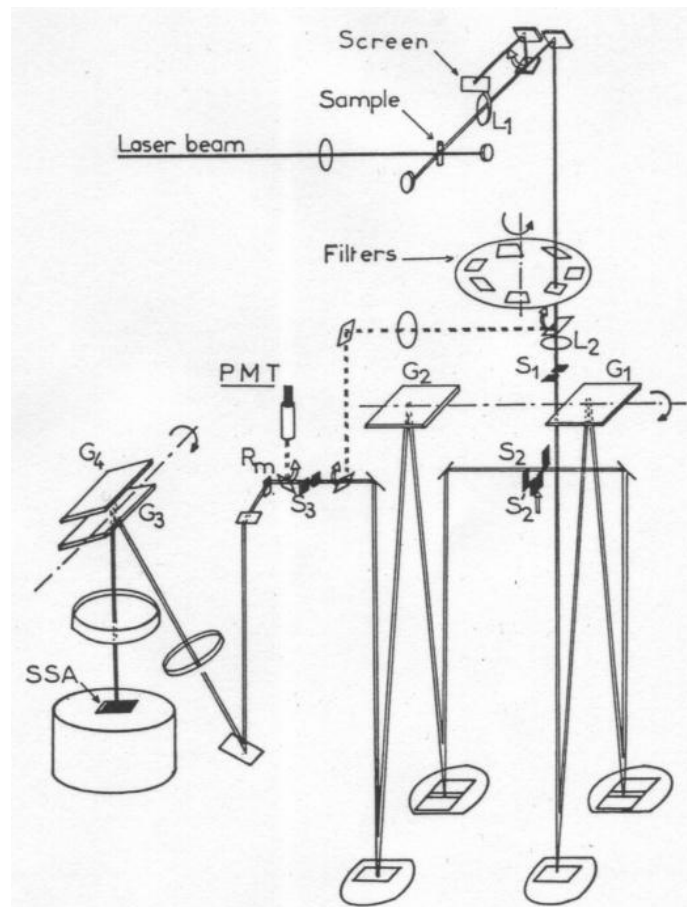
- Separate inelastically scattered from Rayleigh (99.99999%) light
- Collect the maximum number of inelastically scattered photons

Triple spectrograph

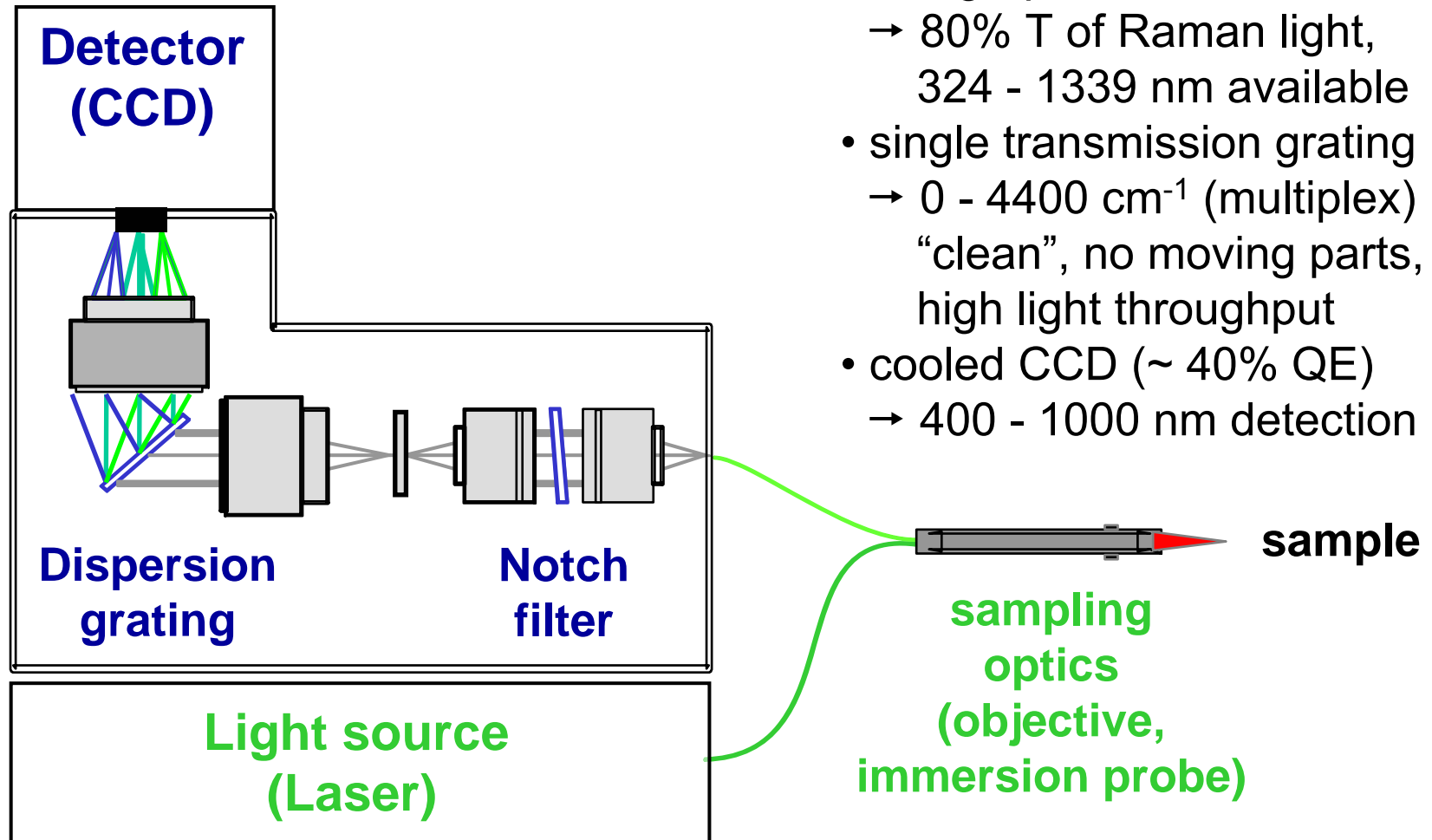
- first 2 gratings subtractive
 - removal Rayleigh (40% E)
- grating 3/4 creates dispersion
- detection: diode array

Fourier Transform (FT) - Raman

- Michelson interferometer (Jacquinot, multiplex)
- NIR (1.064 μm) excitation,
 - less fluorescence
 - self absorption



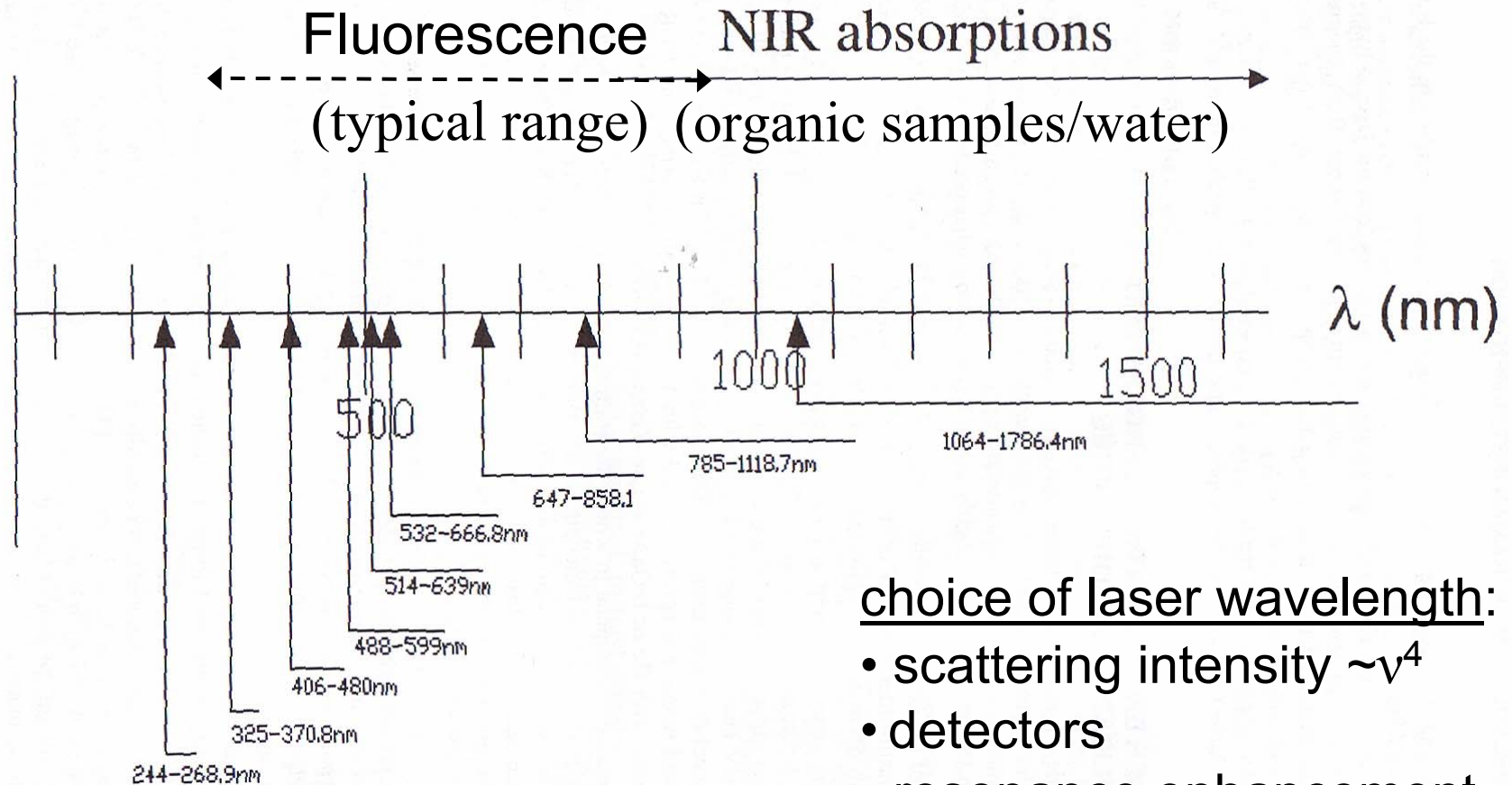
Modern Raman spectrometer



- holographic notch filters
→ 80% T of Raman light,
324 - 1339 nm available
- single transmission grating
→ 0 - 4400 cm^{-1} (multiplex)
“clean”, no moving parts,
high light throughput
- cooled CCD ($\sim 40\%$ QE)
→ 400 - 1000 nm detection

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Laser excitation wavelengths

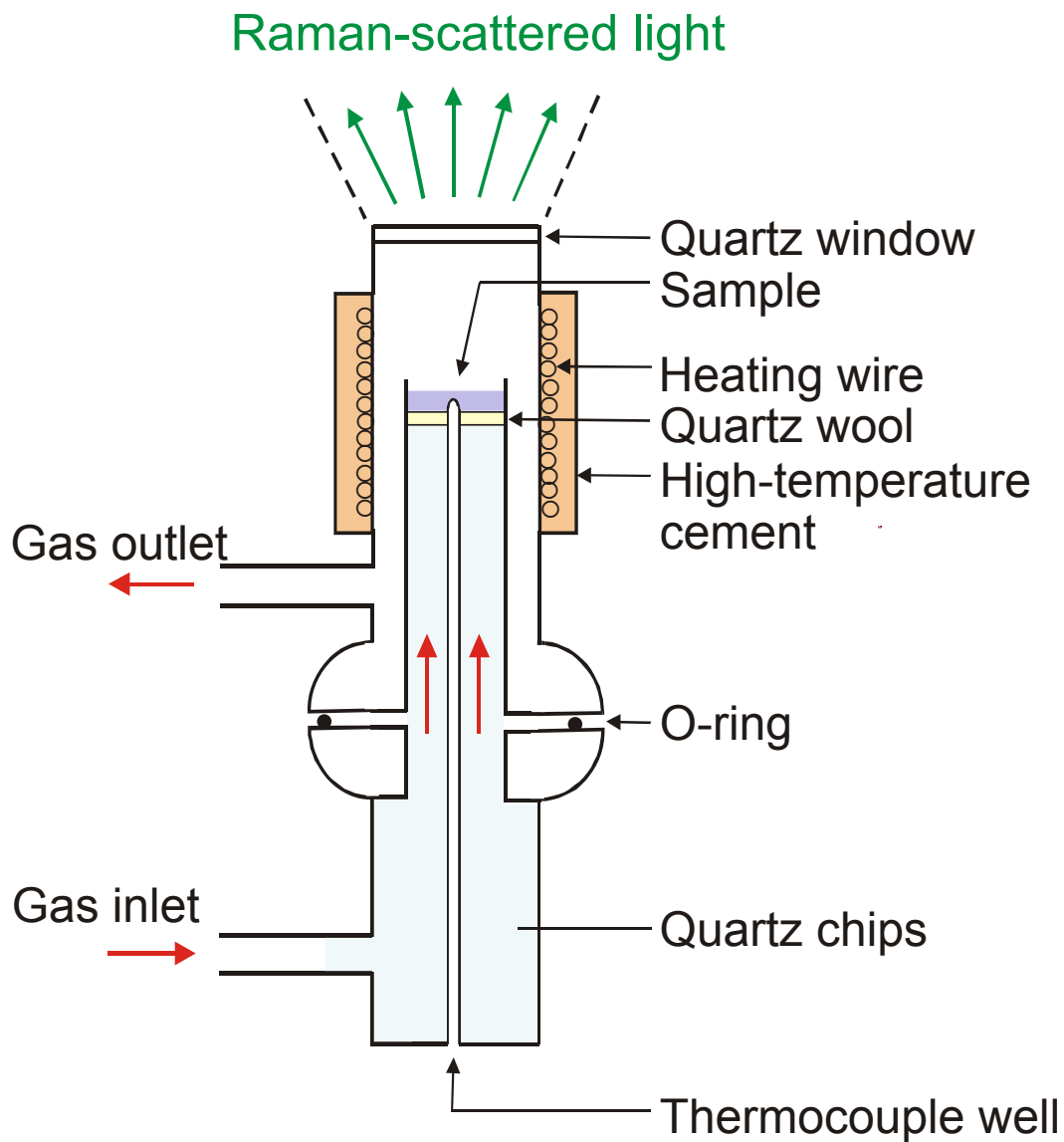


choice of laser wavelength:

- scattering intensity $\sim \nu^4$
- detectors
- resonance enhancement
- self-absorption of sample
- fluorescence (\rightarrow NIR, UV)

- **Basic principles**
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In situ Raman cells

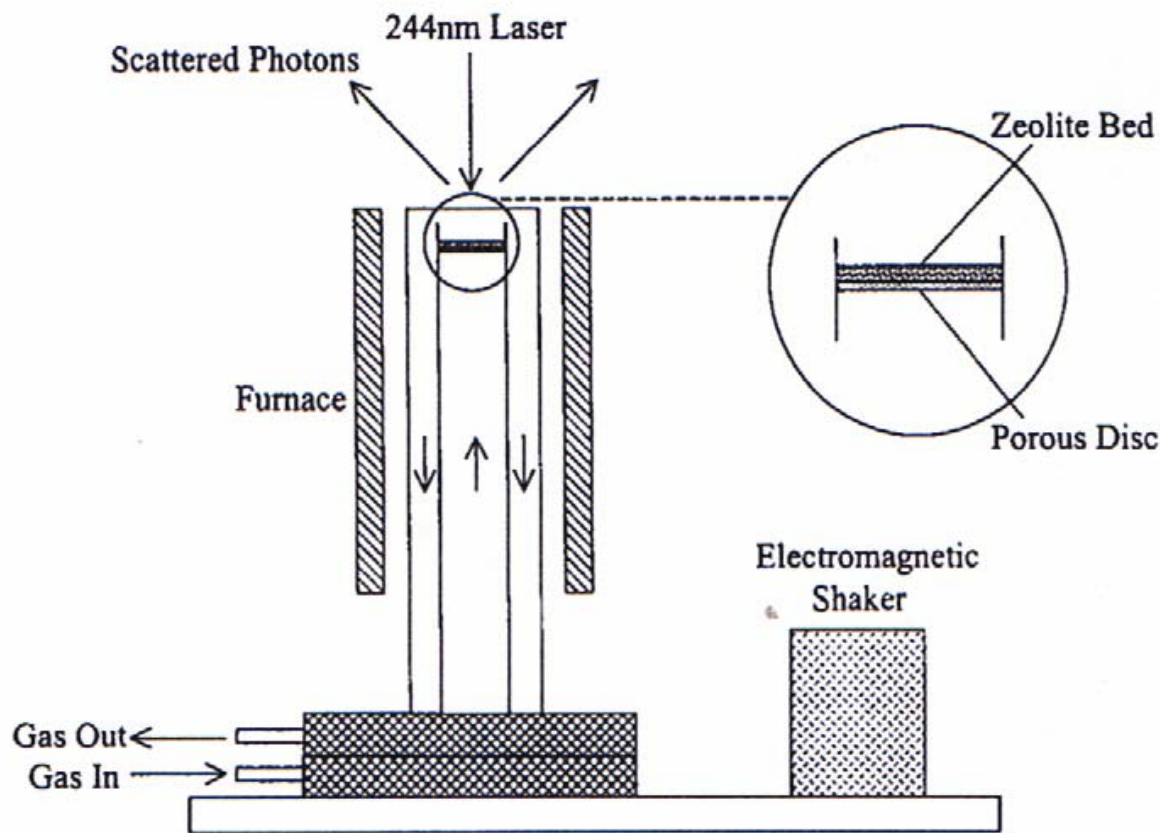


- Laser excitation at low laser power to minimize heating
- Raman cell design mimics **plug-flow reactor**: gases flow through catalyst bed
- 50 – 100 mg sample

Plug-flow reactor

In situ Raman cells

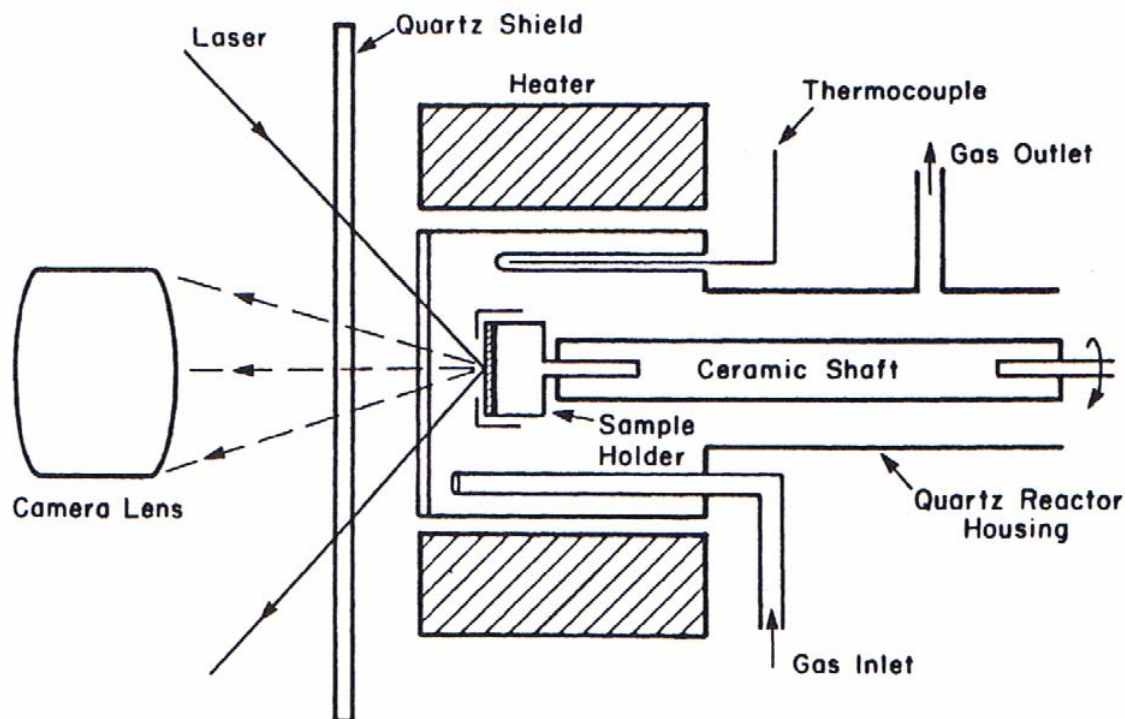
Fluidized bed reactor



- Particle motion
→ reduces laser beam exposure
- Raman cell mimics **fluidized bed reactor**:
gases flow through catalyst bed
- ~200 mg sample
- UV laser excitation

In situ Raman cells

Rotating Raman cell

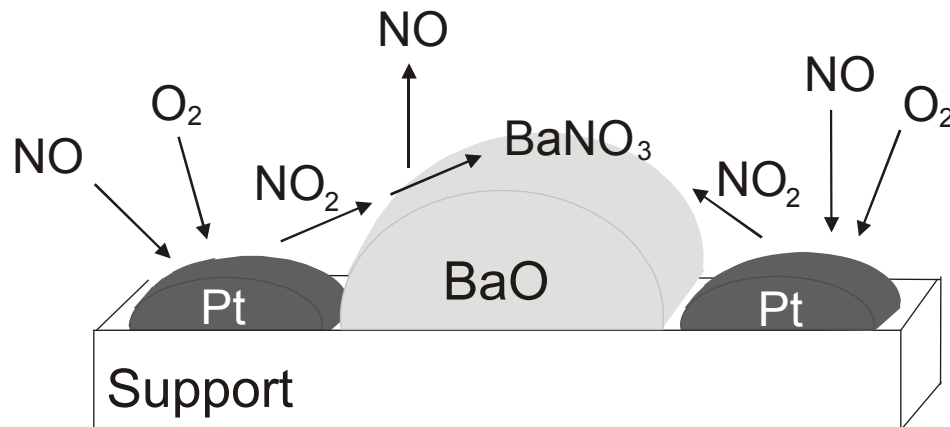


- Sample rotation
→ reduces laser beam exposure
- Gas flow over catalyst bed
- Requires pellets
- ~200 mg sample

- **Basic principles**
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 - In situ cells
 - In situ Raman (of working catalysts)

The NO_x storage-reduction concept

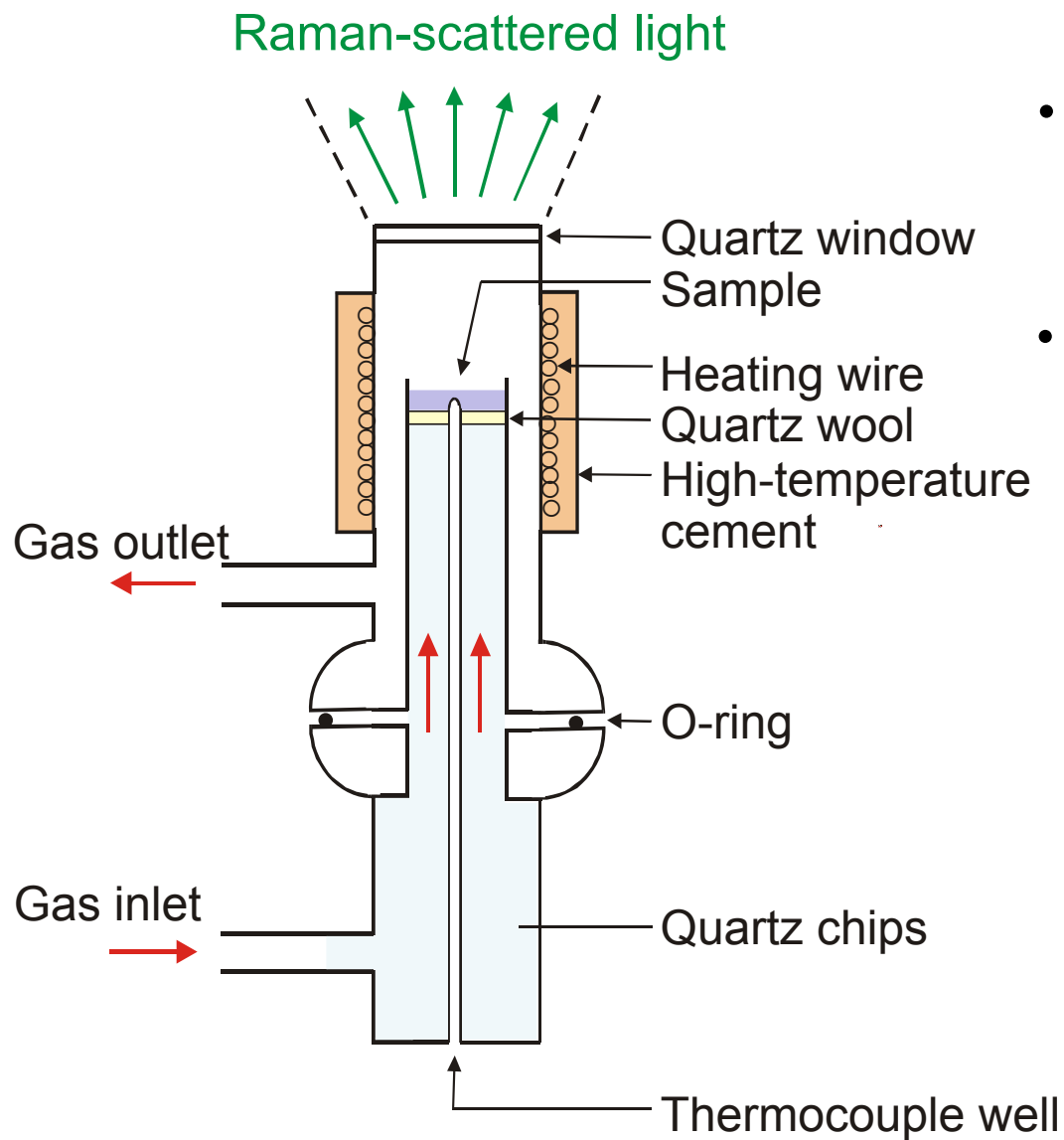
- **Lower fuel consumption** by use of engines operating with **excess oxygen**
 - **Problem: Reduction of NO_x**
 - **Solution: Storage of NO_x** followed by short rich periods for reduction
- Typical storage catalysts consist of **storage material** (BaO) and **metal** (Pt)



- **BaO/Al₂O₃ deactivates** at higher temperatures (due to **Ba-Al alloying**)*
 - Focus on **BaO/MgO** which is **stable up to at least 900°C**

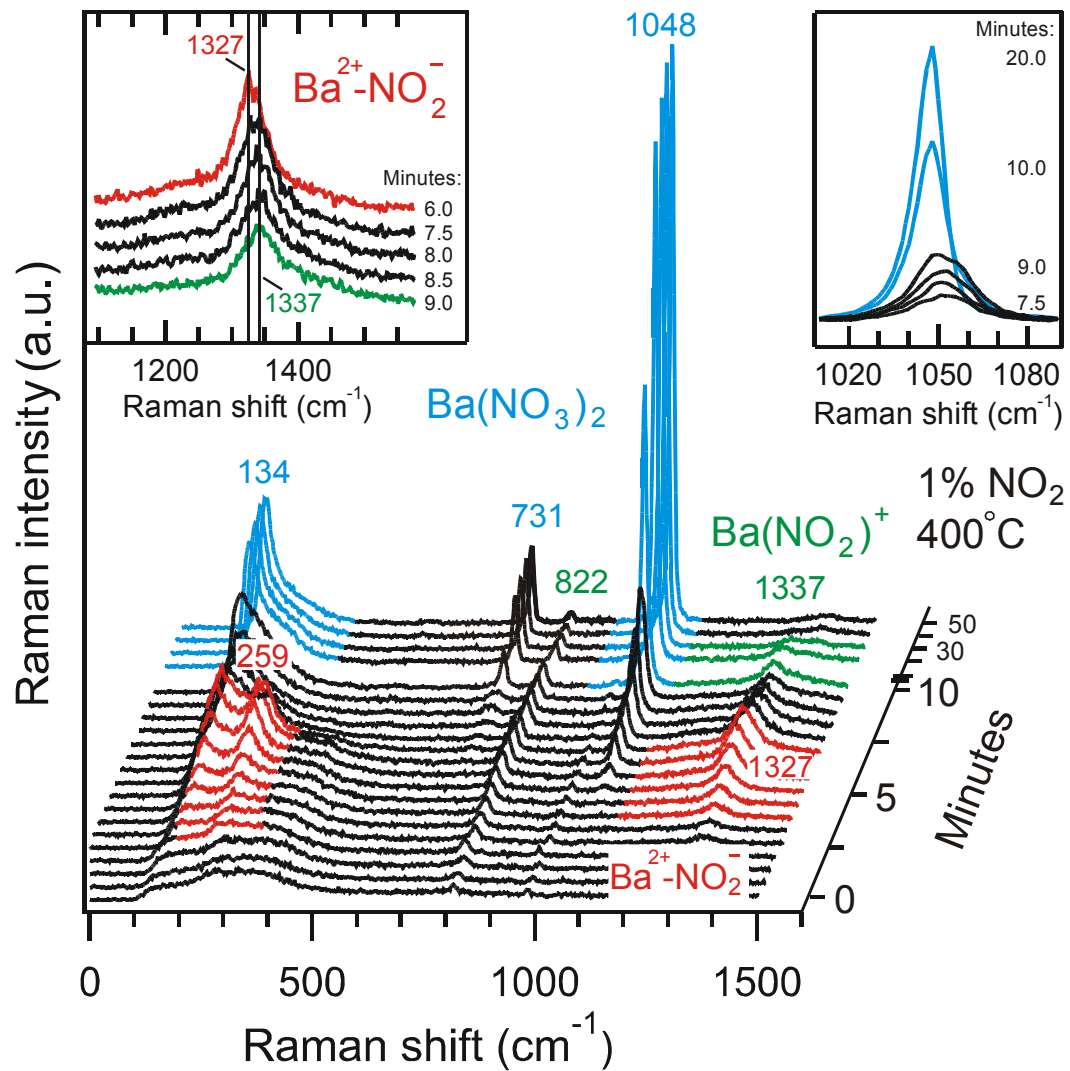
* Jang et al., Catal. Lett. 77 (2001) 1

Experimental setup: *In situ* Raman spectroscopy



- Laser excitation at **532 nm**, low laser power of **~6 mW** minimizes heating of sample
- Raman cell design mimics typical **plug-flow reactor**: Gases flow through catalyst bed (50 mg) at **~40 ml/min**

In situ Raman spectra during NO₂ exposure

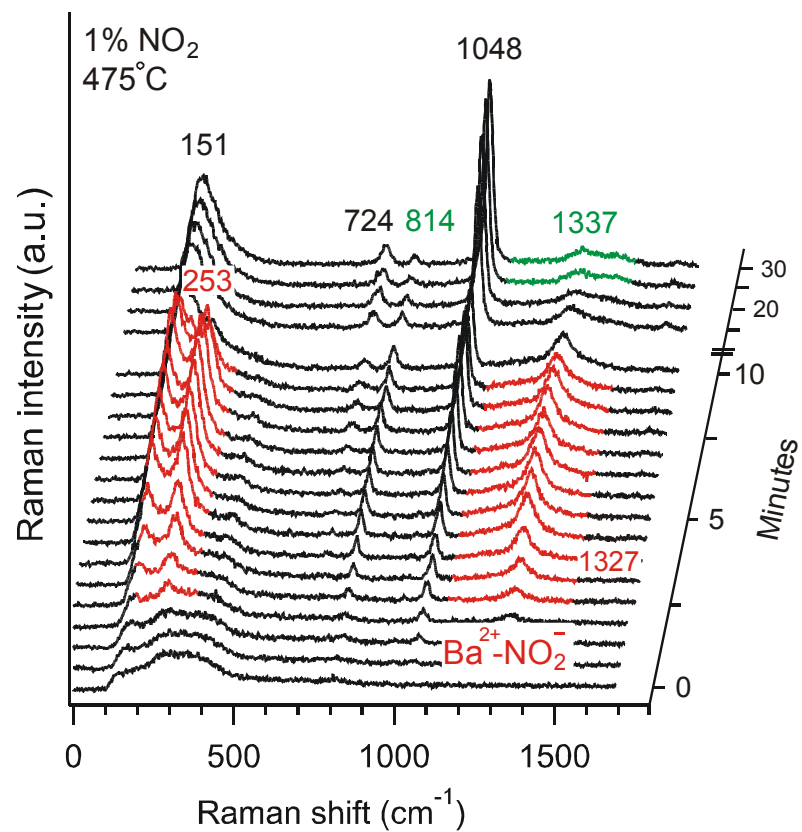
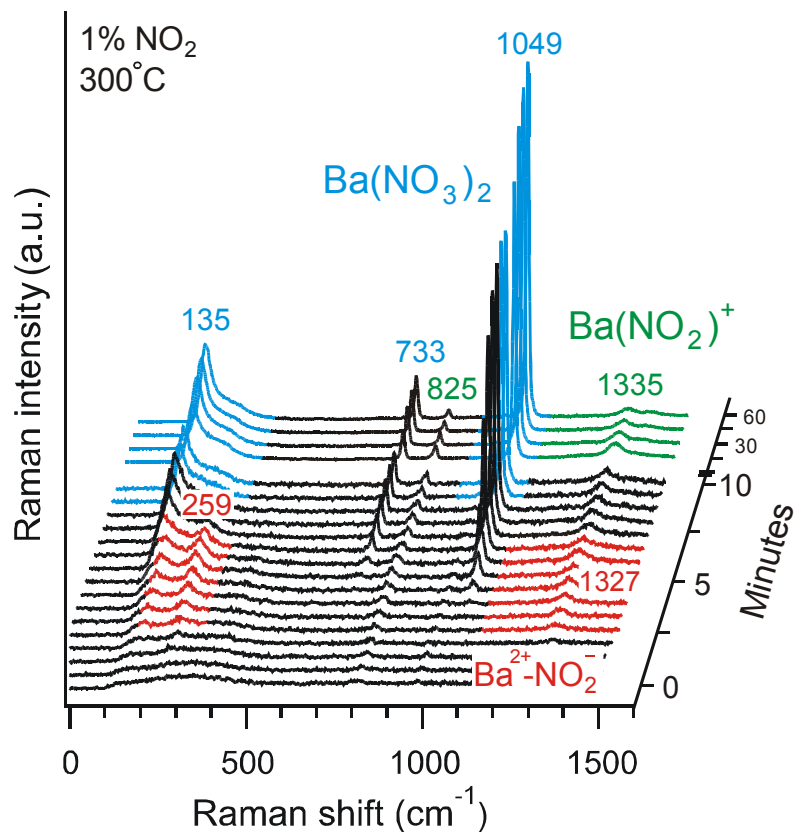


→ Formation of **nitro species precedes** that of **nitrates**

C. Hess, 2006

In situ Raman spectra during NO₂ exposure

Temperature dependence

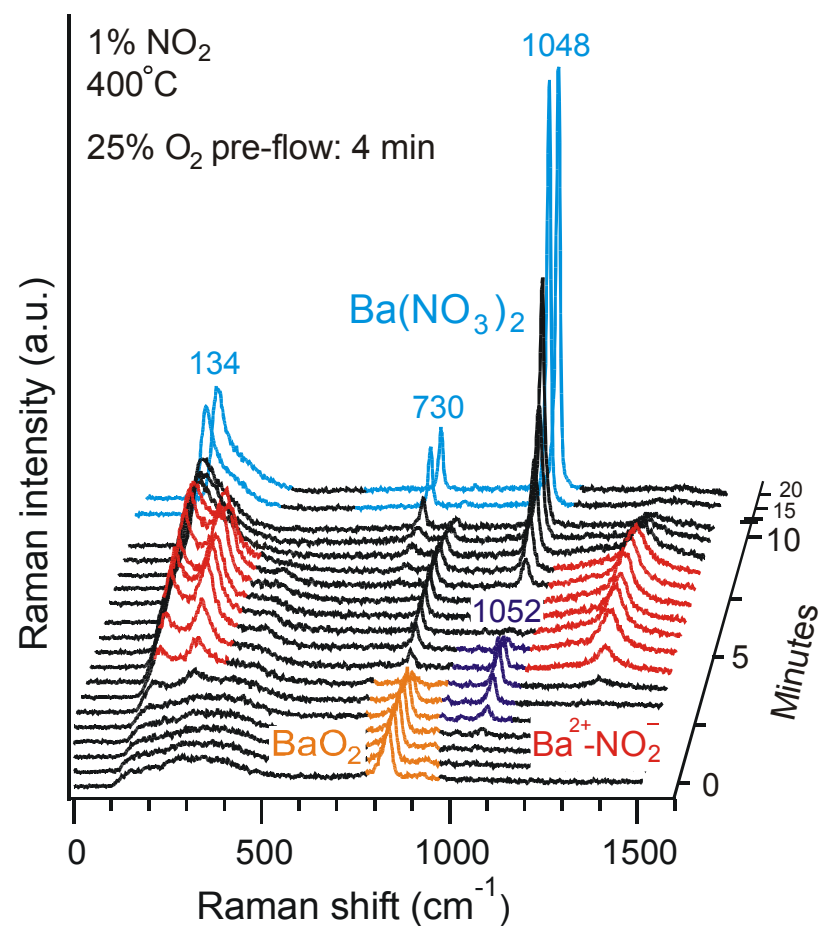
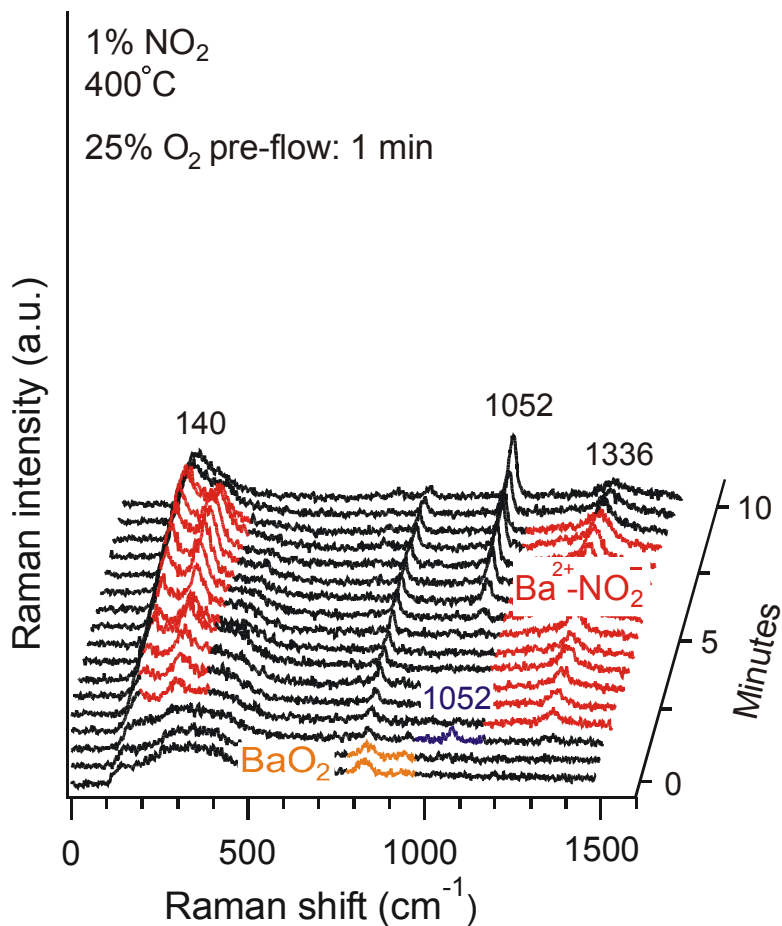


- **300°C:** Formation of **nitro species precedes nitrates** (as at 400°C)
- **475°C:** Higher rate of NO₃⁻ formation but smaller storage capacity

In situ Raman spectra after catalyst pre-oxidation

Dependence on pre-oxidation time

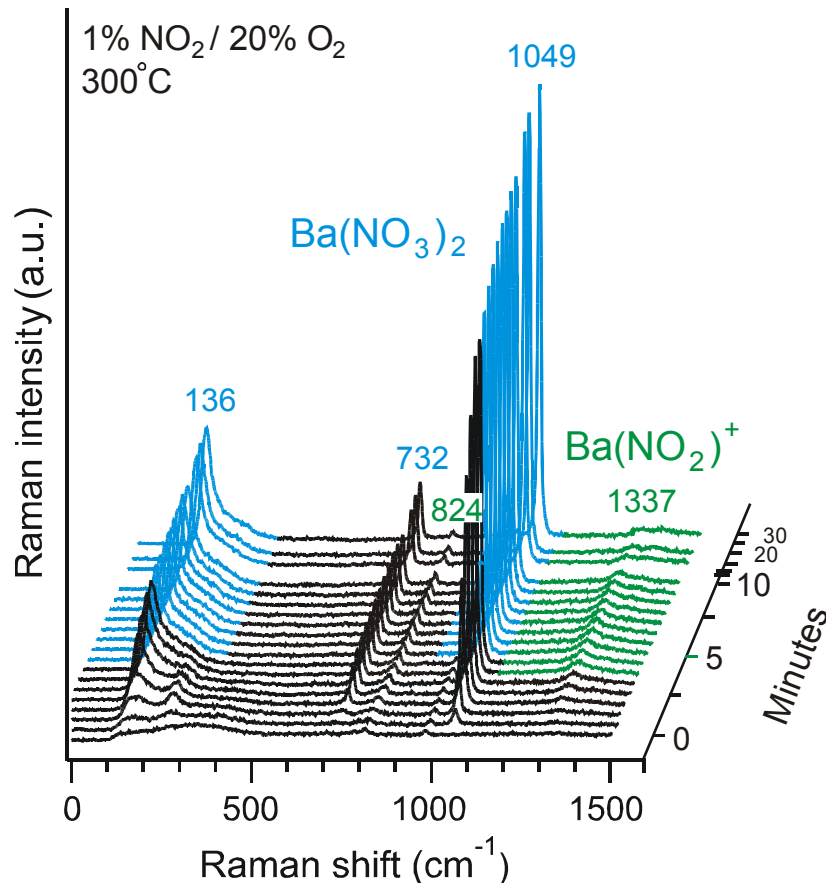
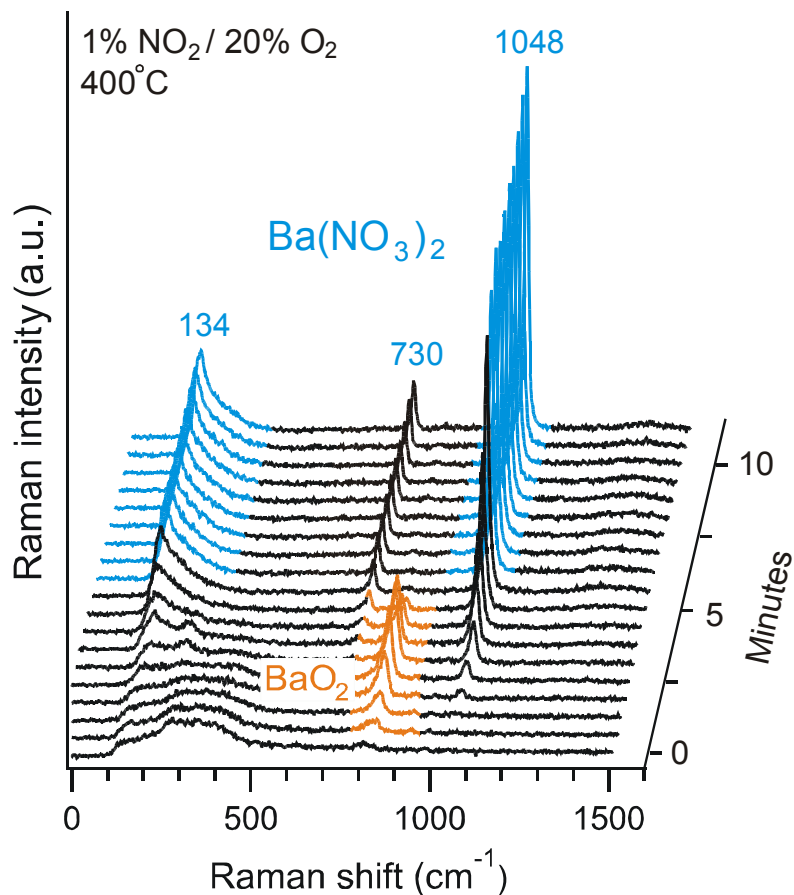
C. Hess, 2006



→ **Pre-oxidation of BaO enables direct nitrate formation at 400°C**

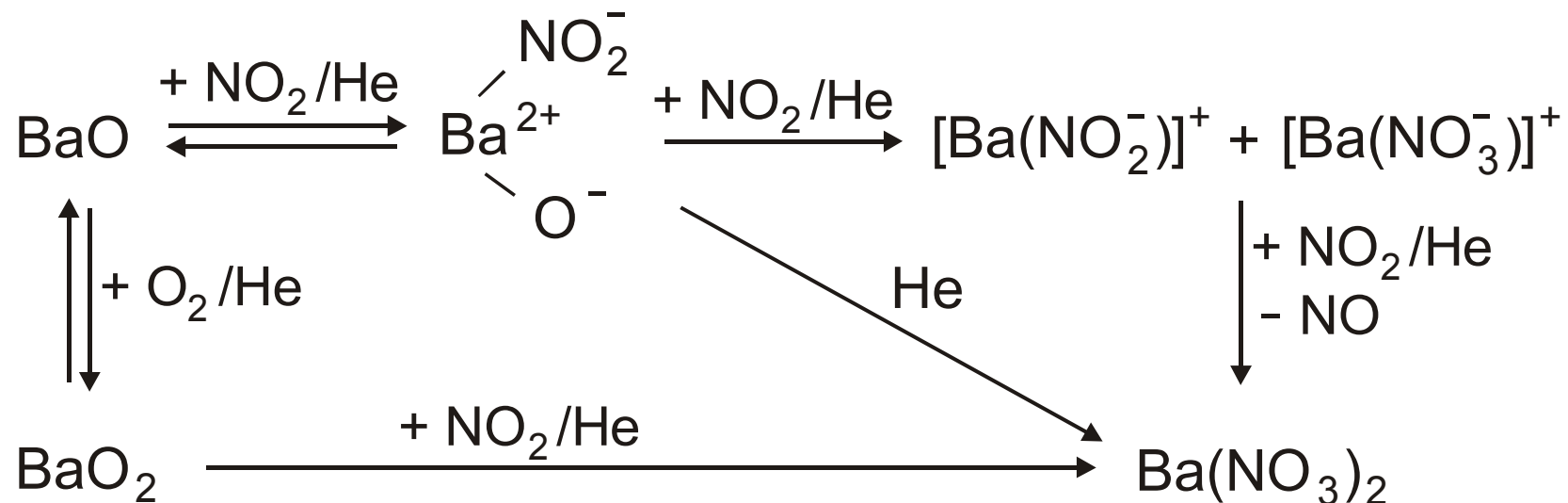
In situ Raman spectra during NO₂ /O₂ exposure

Temperature dependence



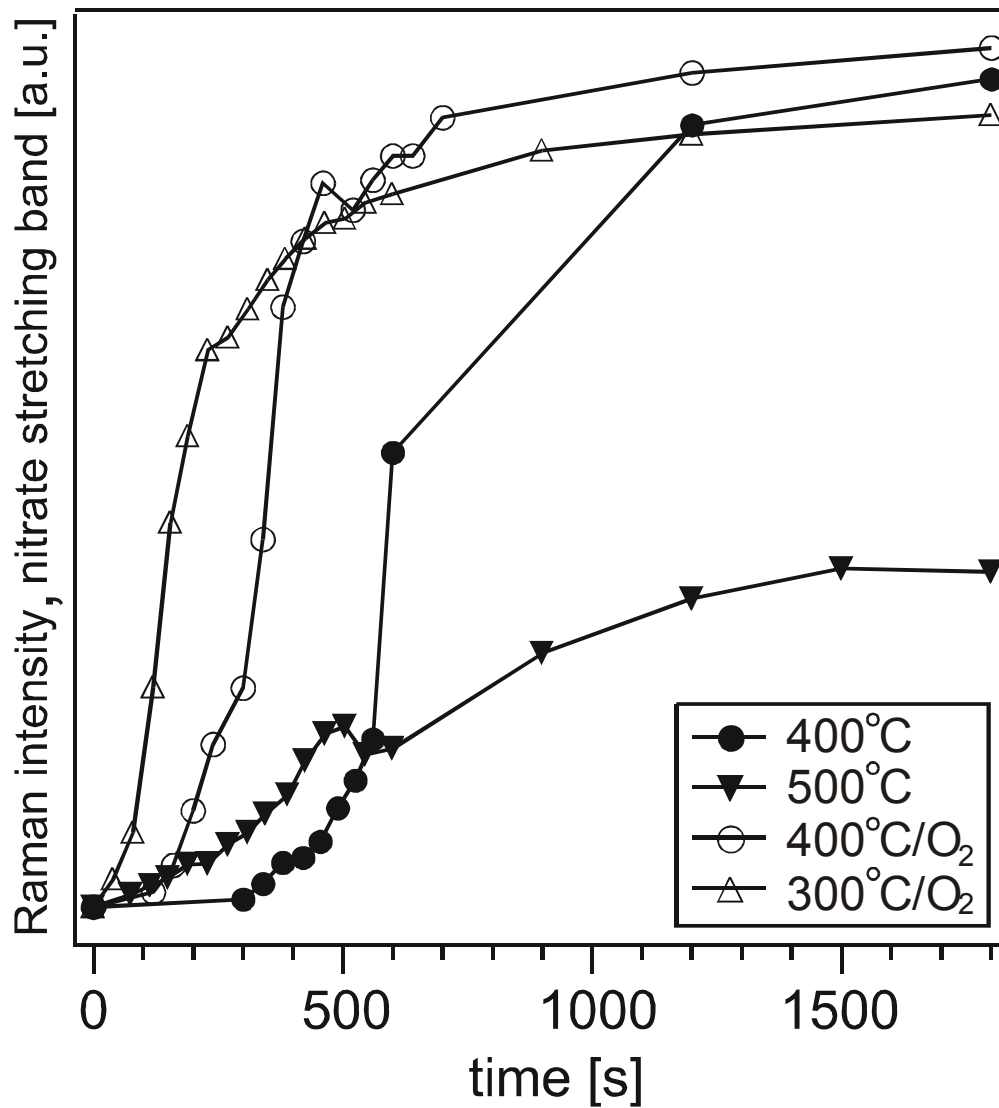
→ Presence of **oxygen suppresses formation of nitro species**
increases the rate of nitrate formation

Summary - Mechanism for NO₂ storage



C. Hess and J.H. Lunsford, JPCB 106 (2002) 6358
 C. Hess and J.H. Lunsford, JPCB 107 (2003) 1982

Summary - NO₂ storage capacity

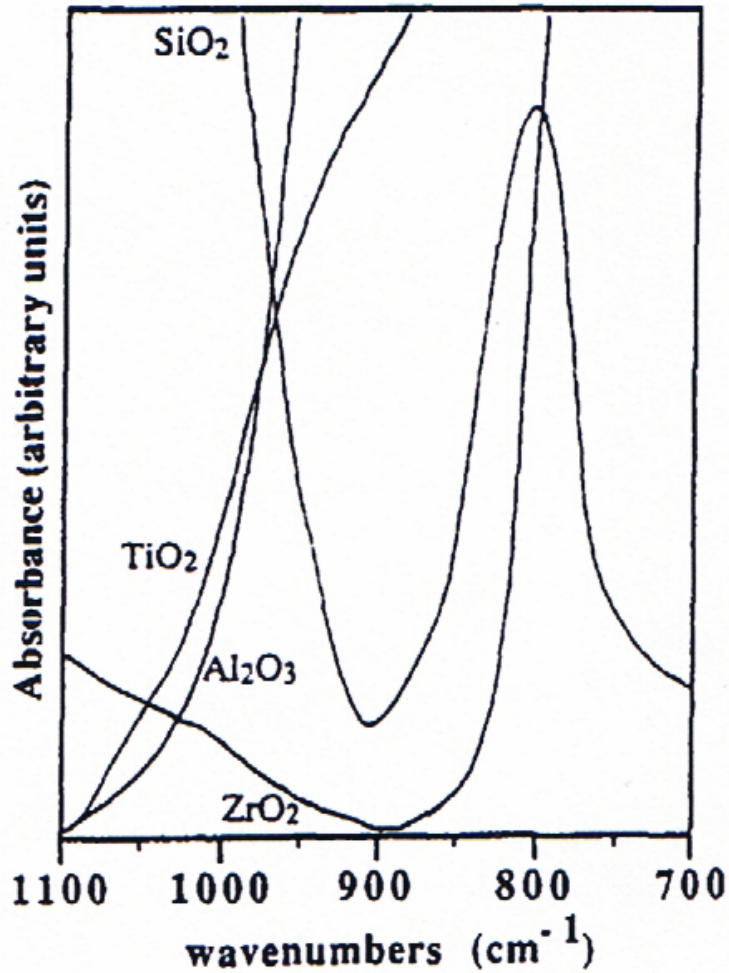


Summary: Study reveals Raman key features

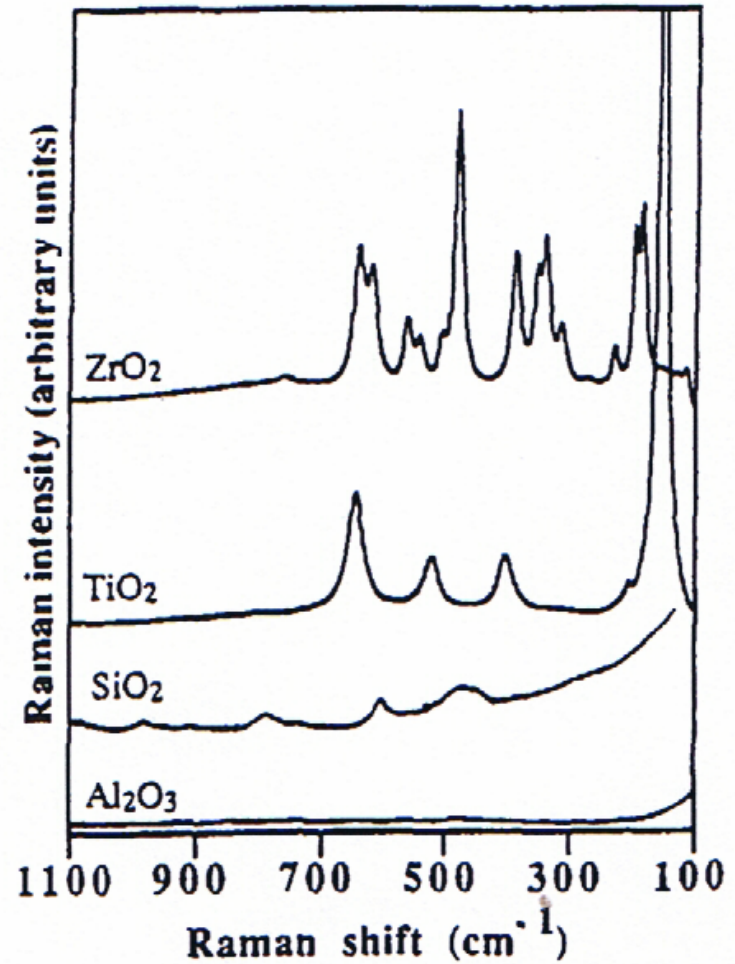
- Raman spectra without interference of gas phase
- simple glass/quartz cell
- *in situ* spectra can be recorded at high temperatures (500°C)
- time-dependent *in situ* experiments
- Raman spectra down to $\sim 100 \text{ cm}^{-1}$
- detection of IR inactive peroxide vibrations
- detection of adsorbed species and catalyst bulk phase
- quantification using internal reference
- self scattering of MgO support low
 - Raman spectra of supported phase
 - other supports?

IR vs Raman of typical oxide supports

IR

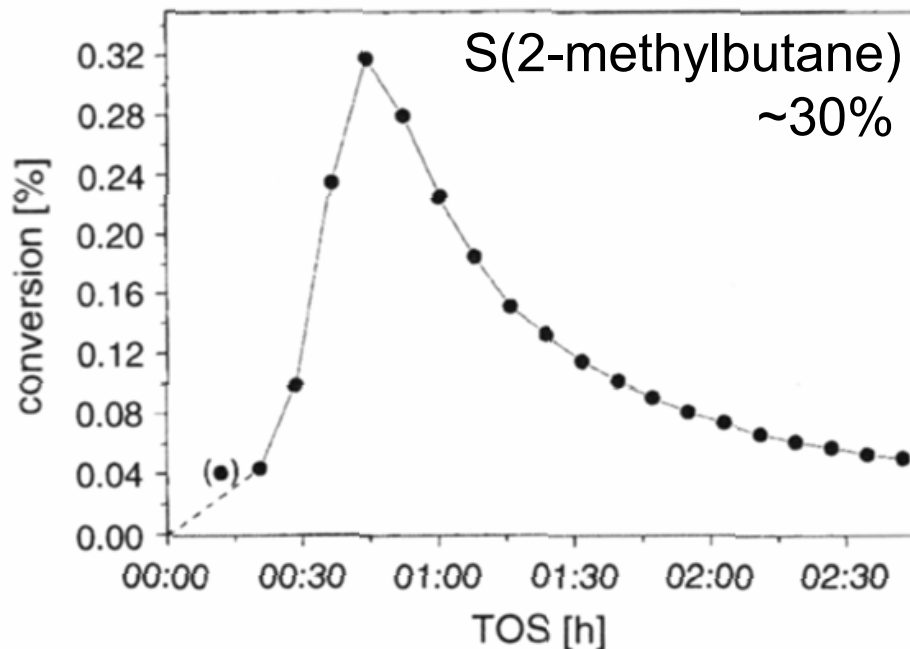
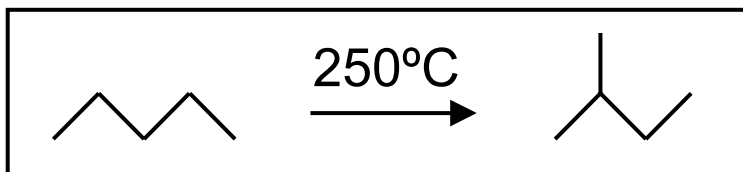


Raman

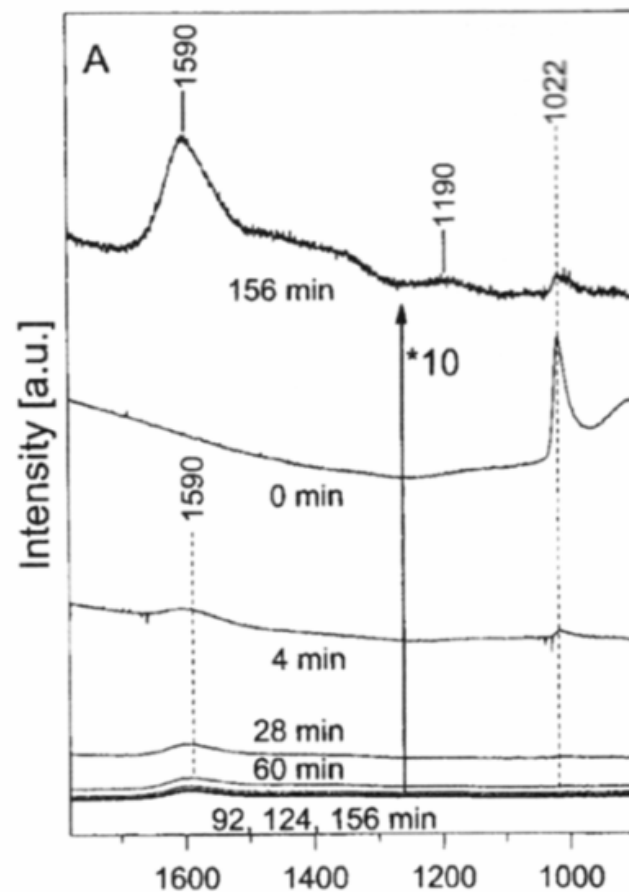


n-pentane isomerization over 17 wt% WO₃/ZrO₂

1% *n*-pentane in He, 10 ml/min



C=C (coke) W=O



Relation of Raman intensity to sample reflectance

Raman intensity based on Kubelka-Munk formalism:

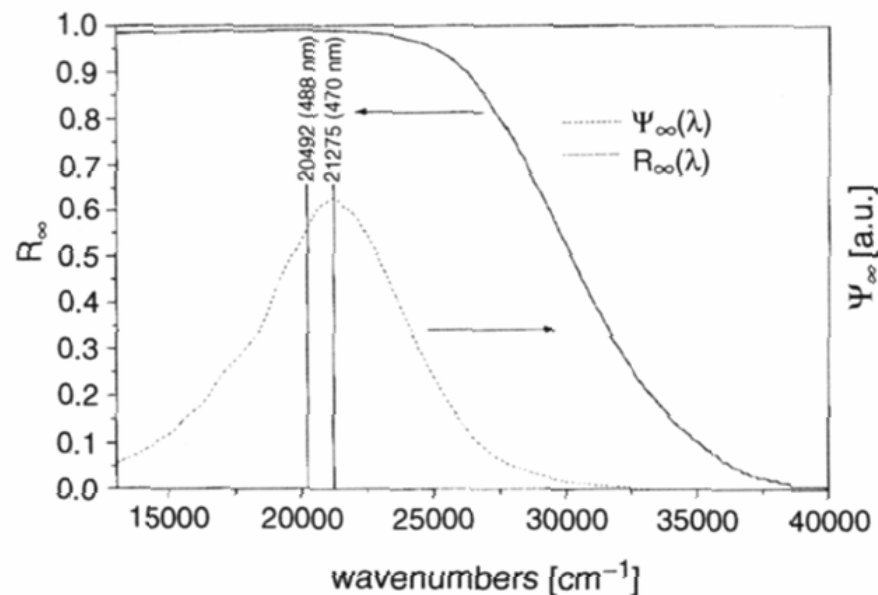
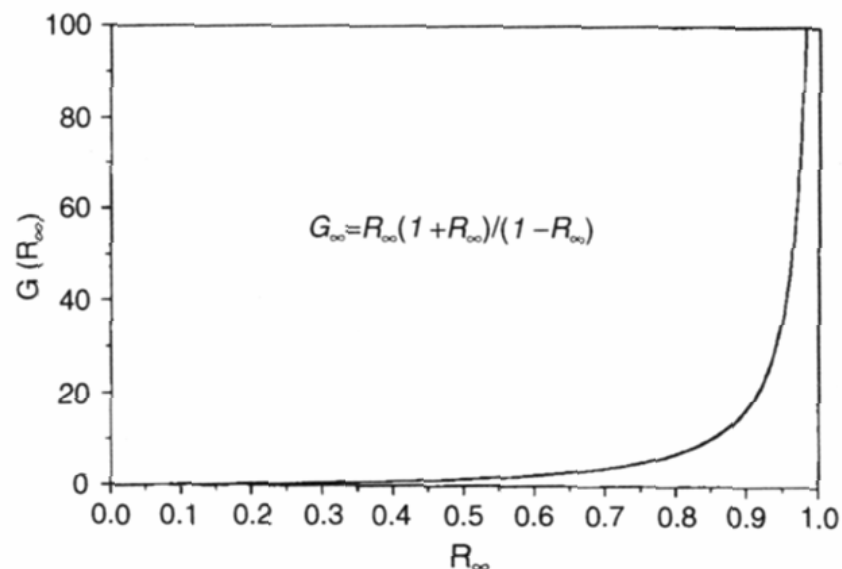
$$\psi_{\infty} = \frac{\rho I_o}{s} \frac{R_{\infty}(1+R_{\infty})}{(1-R_{\infty})} = \frac{\rho I_o}{s} G(R_{\infty})$$

ρ : Raman coefficient ($\sim \nu^4$)

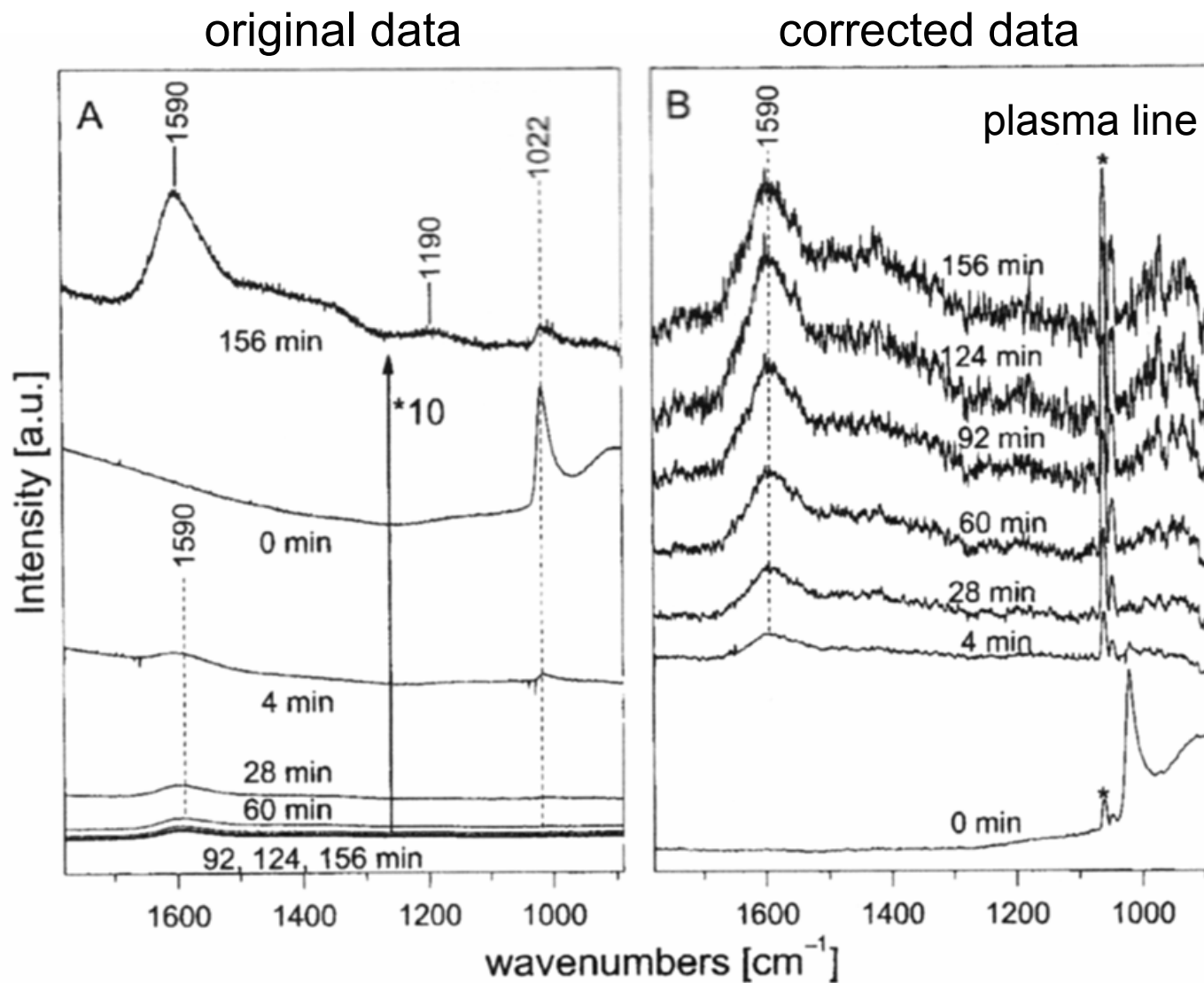
s : scattering coefficient

$$\begin{aligned} \psi_{\infty}(\nu) &= \frac{c\nu^4 I_o}{s} \frac{R_{\infty}(\nu)[1+R_{\infty}(\nu)]}{[1-R_{\infty}(\nu)]} \\ &= \frac{cI_o}{s} G[R_{\infty}(\nu)]\nu^4 \end{aligned}$$

$R_{\infty}(\nu)$: can be measured by diffuse reflectance UV-Vis

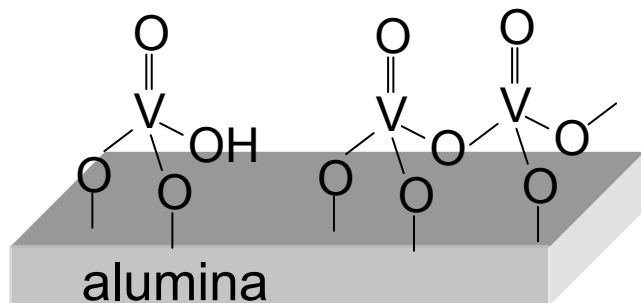


Raman intensity correction



Structure of vanadia in V_xO_y/Al_2O_3

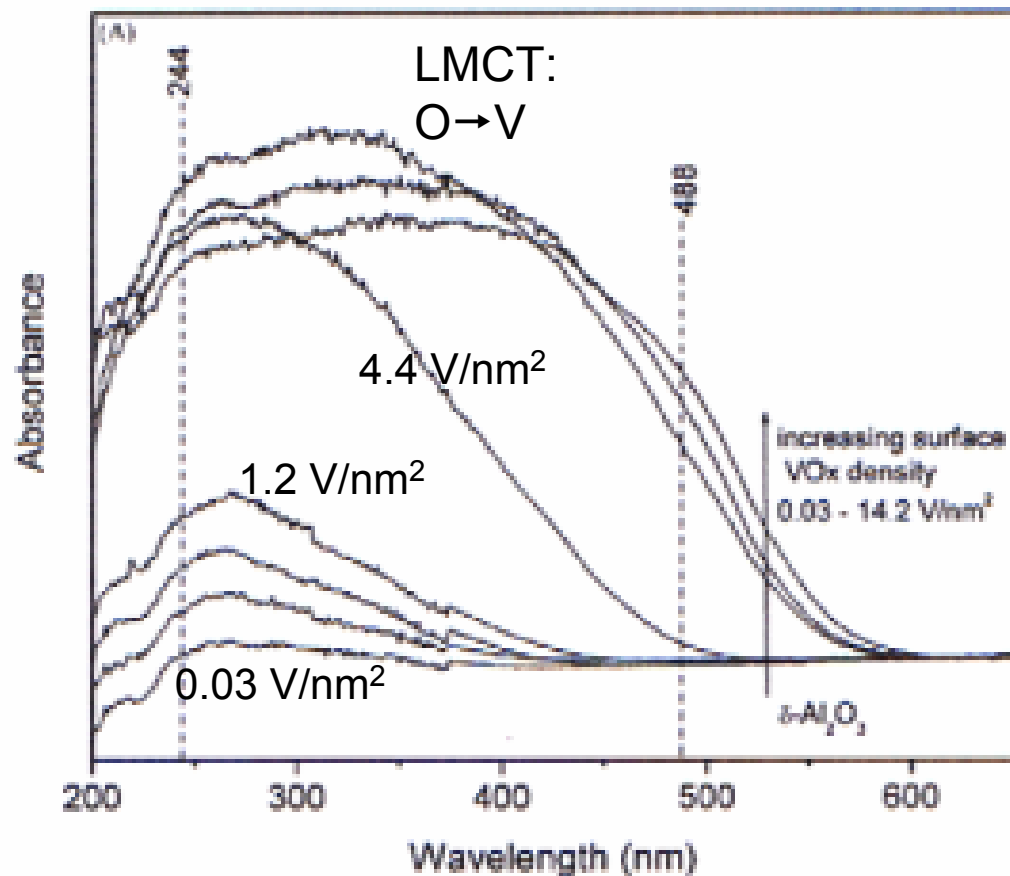
dehydrated vanadia:
isolated vs polymeric



*Preferential excitation
of structurally different
 V_xO_y species possible?*

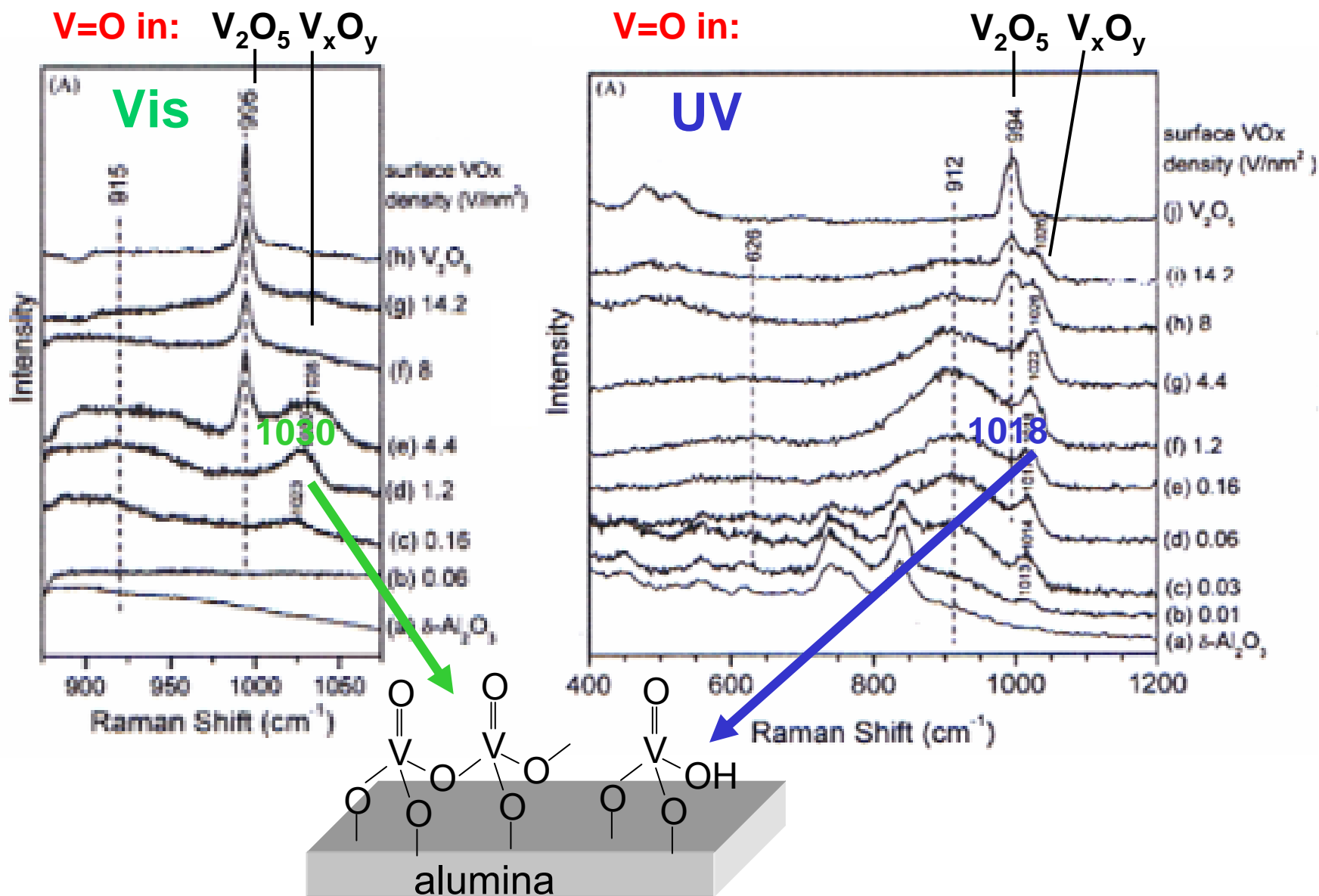
UV laser

Visible laser



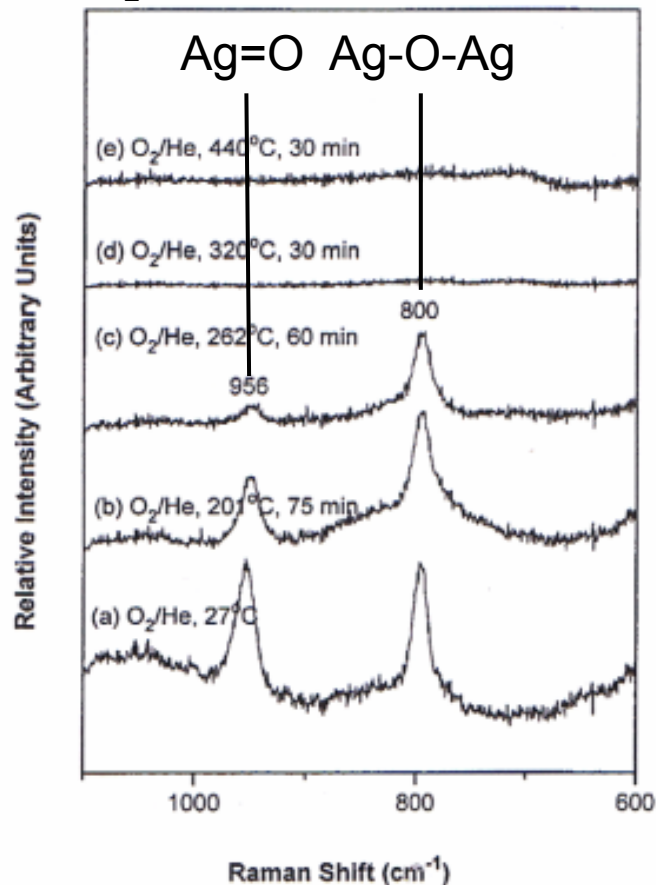
Z. Wu, H.-S. Kim, P.C. Stair,
S. Rugmini, S.D. Jackson, JPCB (2005)

UV Raman – selective resonance enhancement



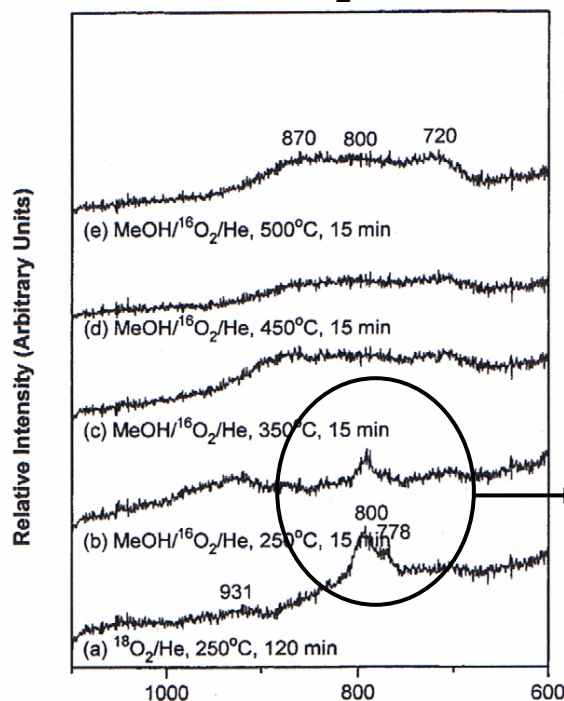
MeOH partial oxidation on polycryst. Ag (SERS)

O_2 flow after pretreatment



- thermal cycles
- 2 diff. atomic O species (isotope shifts $\sim 20\text{ cm}^{-1}$)

$MeOH/O_2 = 3$



- decreasing Ag-O-Ag int in $MeOH/O_2$
- active site?
- assignment?
- subsurface?

TABLE 2: Methanol Conversion and Product Selectivities Formed over 50 mg of a Polycrystalline Ag Catalyst with a Methanol Concentration of 6.16 mol% and a Total Flow Rate of 100 mL/min (helium used as balance gas) at a Molar Ratio of $MeOH/O_2 = 3.08$

T ($^{\circ}C$)	conv. (%)		selectivity		
	MeOH	HCHO	MF	DMM	CO_2
250	15.9	29.9	47.0	0.0	23.1
300	39.8	42.1	28.2	0.3	29.4
350	55.8	69.9	13.4	0.2	33.5
400	69.0	83.8	5.7	0.2	9.5
450	79.8	90.0	2.1	0.1	7.8
500	81.4	92.5	0.8	0.0	6.7

Summary: Raman for catalytic applications

- Raman spectra accessible without interference of gas phase
- simple glass/quartz cell
- *in situ* spectra can be recorded at high temperatures (500°C)
- time-dependent *in situ* experiments
- Raman spectra of adsorbates and catalyst down to $\sim 100 \text{ cm}^{-1}$
- quantification using internal reference
 - correction for changes in sample reflectance (→ DR UV-Vis)
- self scattering of common support materials low
 - Raman spectra of supported phase
- Signal enhancement as result of resonance Raman and SERS

Questions?