VIBRATIONAL SPECTROSCOPY, DRIFTS AND RAMAN, ON CATALYSTS IN AFTERTREATMENT

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DRIFTS (diffuse reflectance FTIR) and MicroRaman Spectroscopy in Catalysts of Aftertreatment

- **Study of surface species is critical in developing a fundamental understanding of storage and aging mechanism in NOx/SOx absorbers**

  -In-situ probe

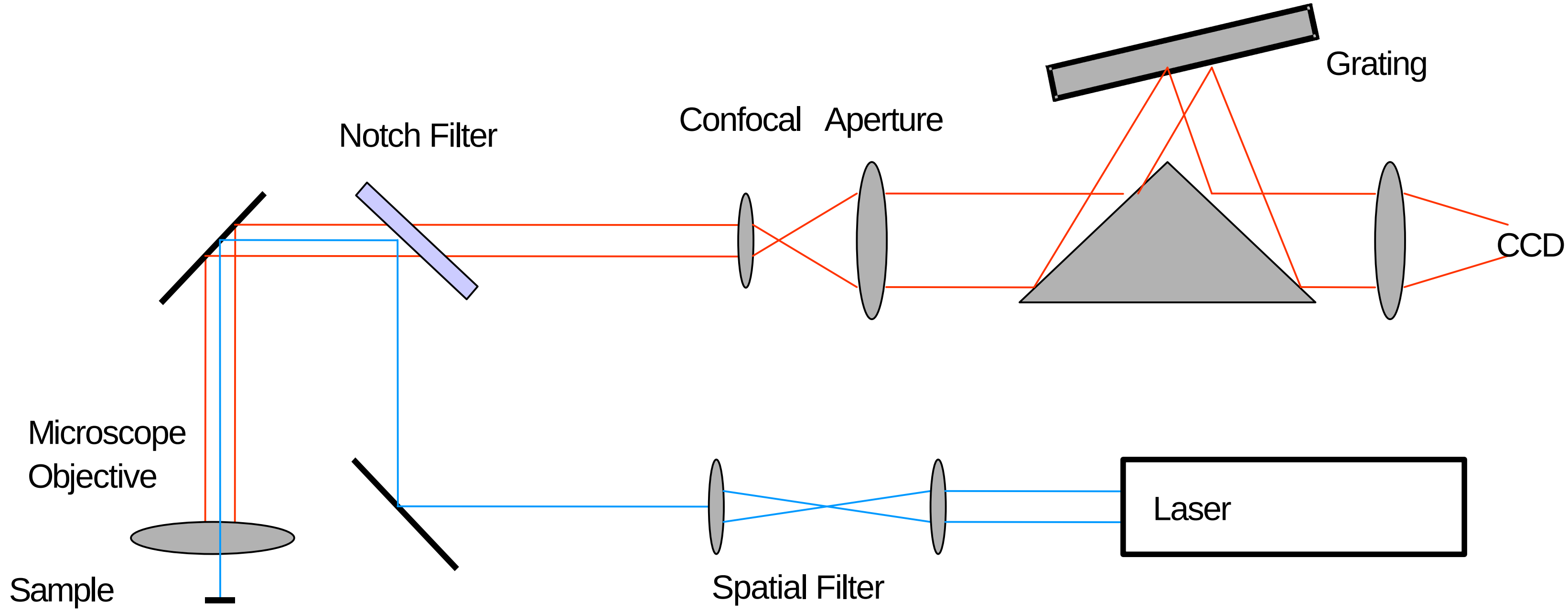
- **Able to derive thermodynamic and kinetics parameters from absorption vs. temperature and time**

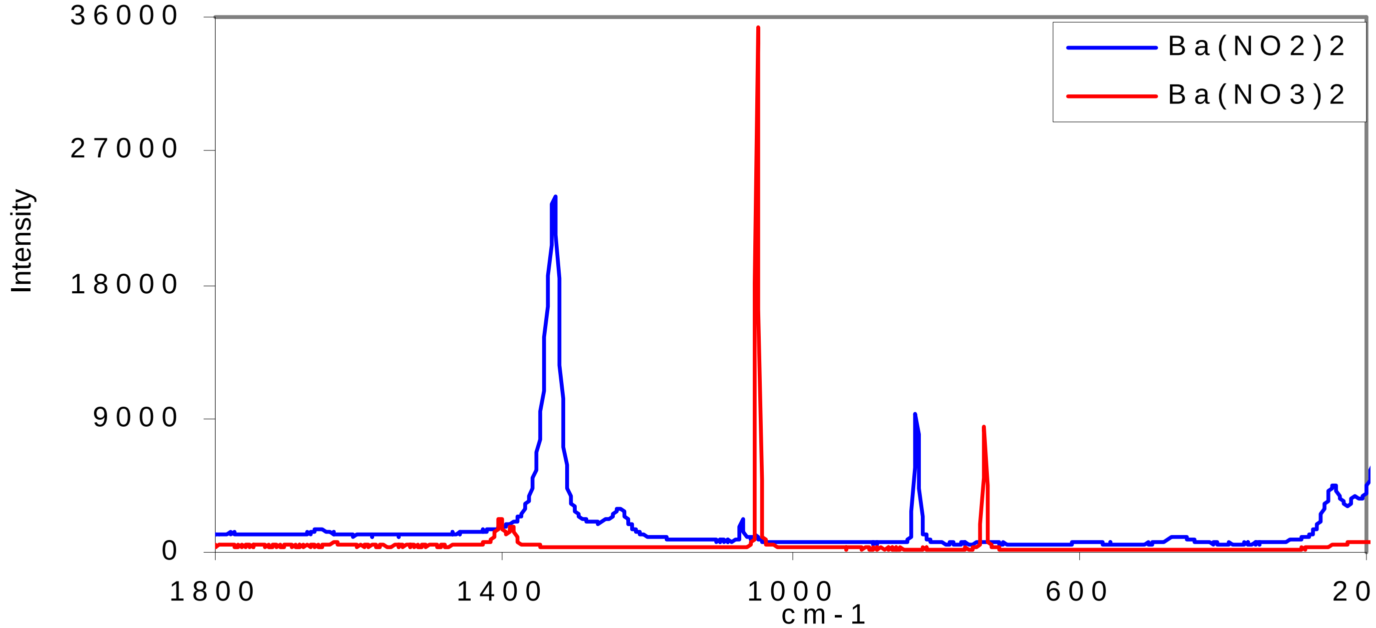
  -Required for model development and catalyst design

- **Delineate S-poisoning mechanism in NOx absorbers by monitoring adsorbed species**

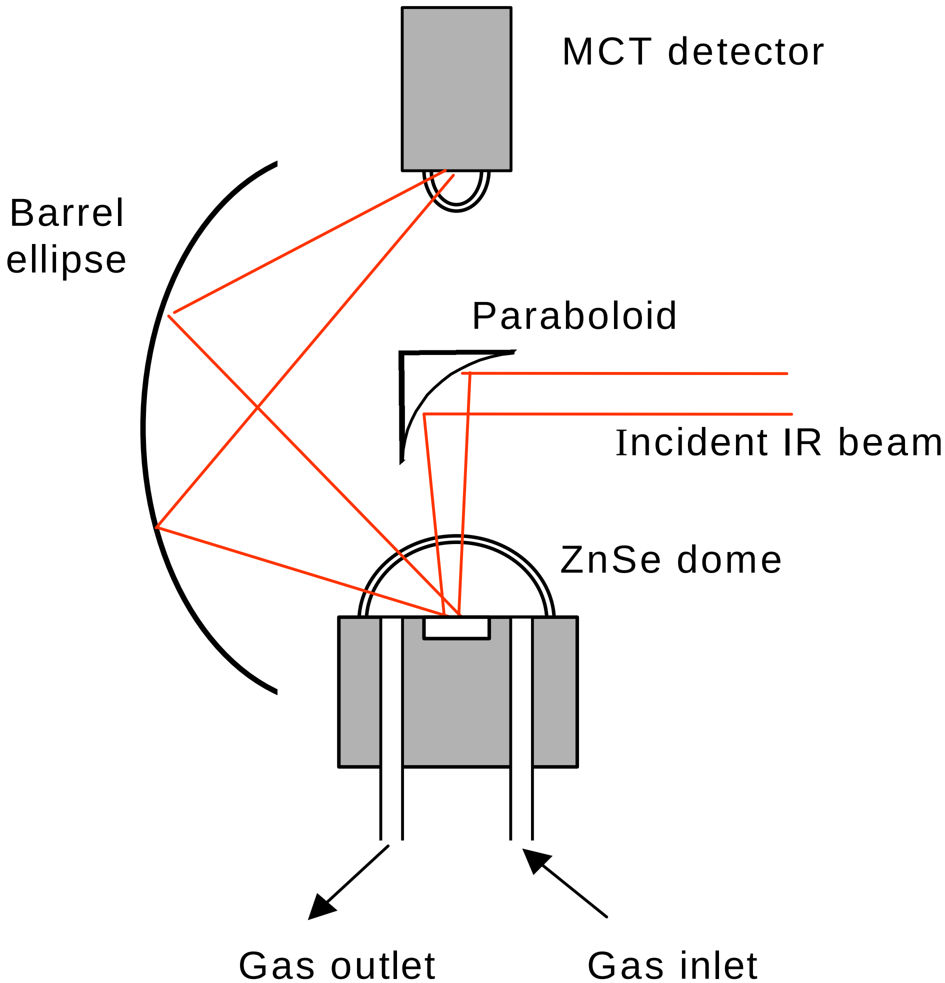
  -Raman bandwidth of certain active components can be correlated to particle size and sintering effects

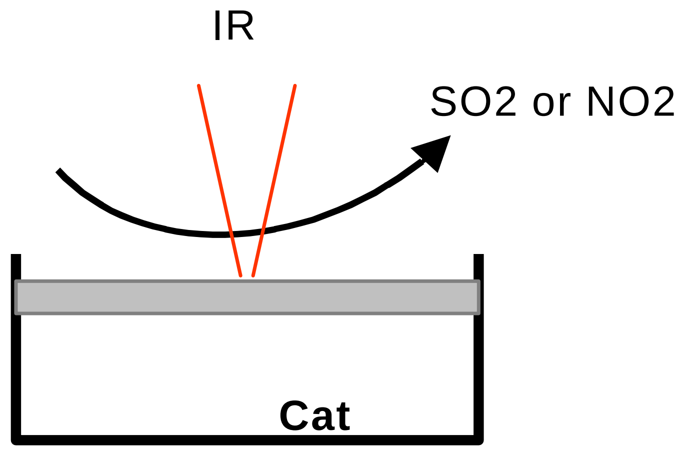
Confocal Configuration of MicroRaman





DRIFTS monitors the product buildups on 2-dimensional overlayer





$dP/dt = k[SO_2 \text{ or } NO_2][Cat]_{site}$

$= k'[Cat]_{site}$

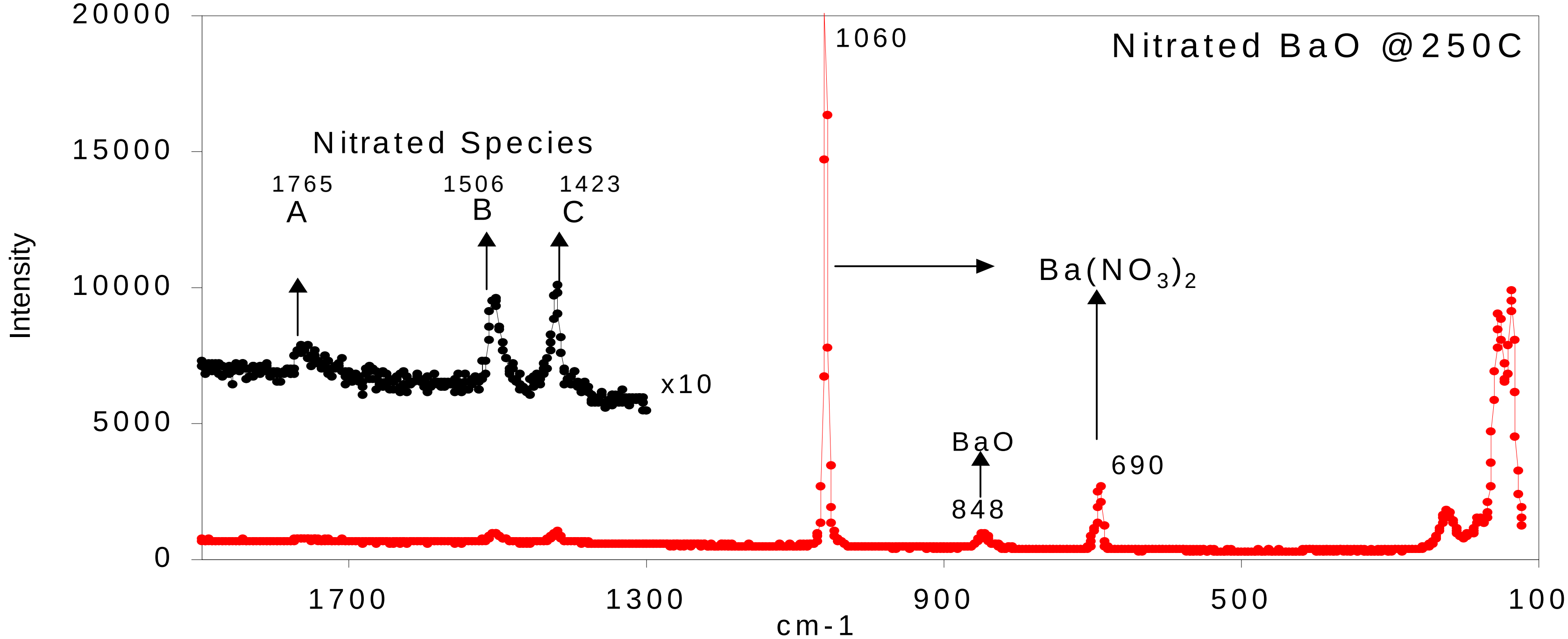
$P = At + B(1 - e^{-\alpha t})$

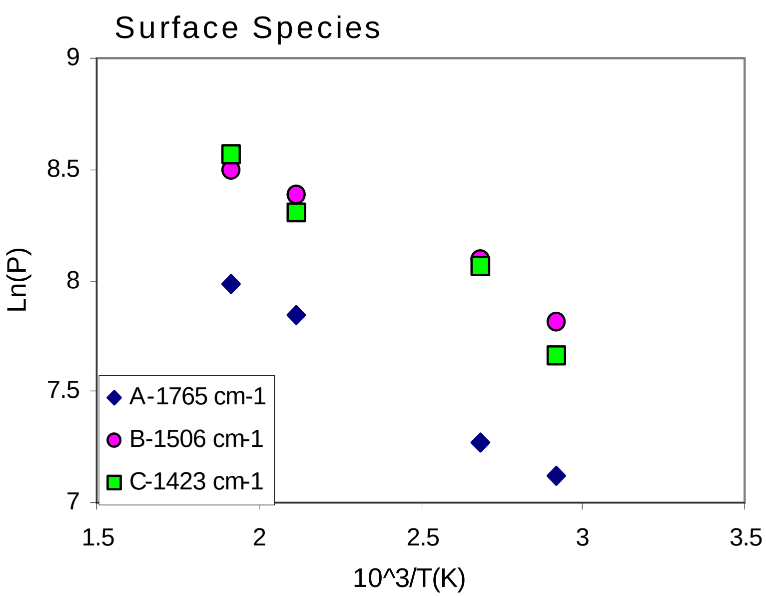
Empirical parameters A, B and

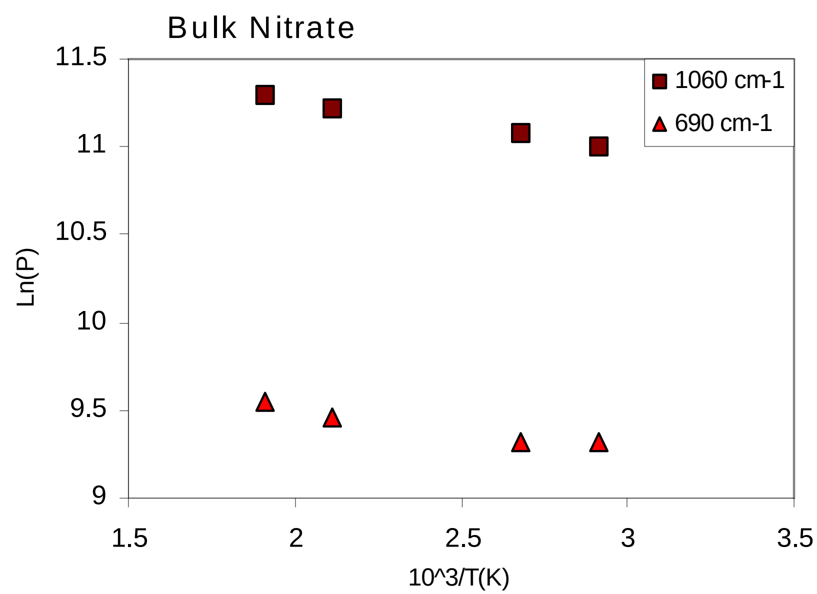
α

can be derived from curve fitting

Nitration Kinetics of BaO by Raman

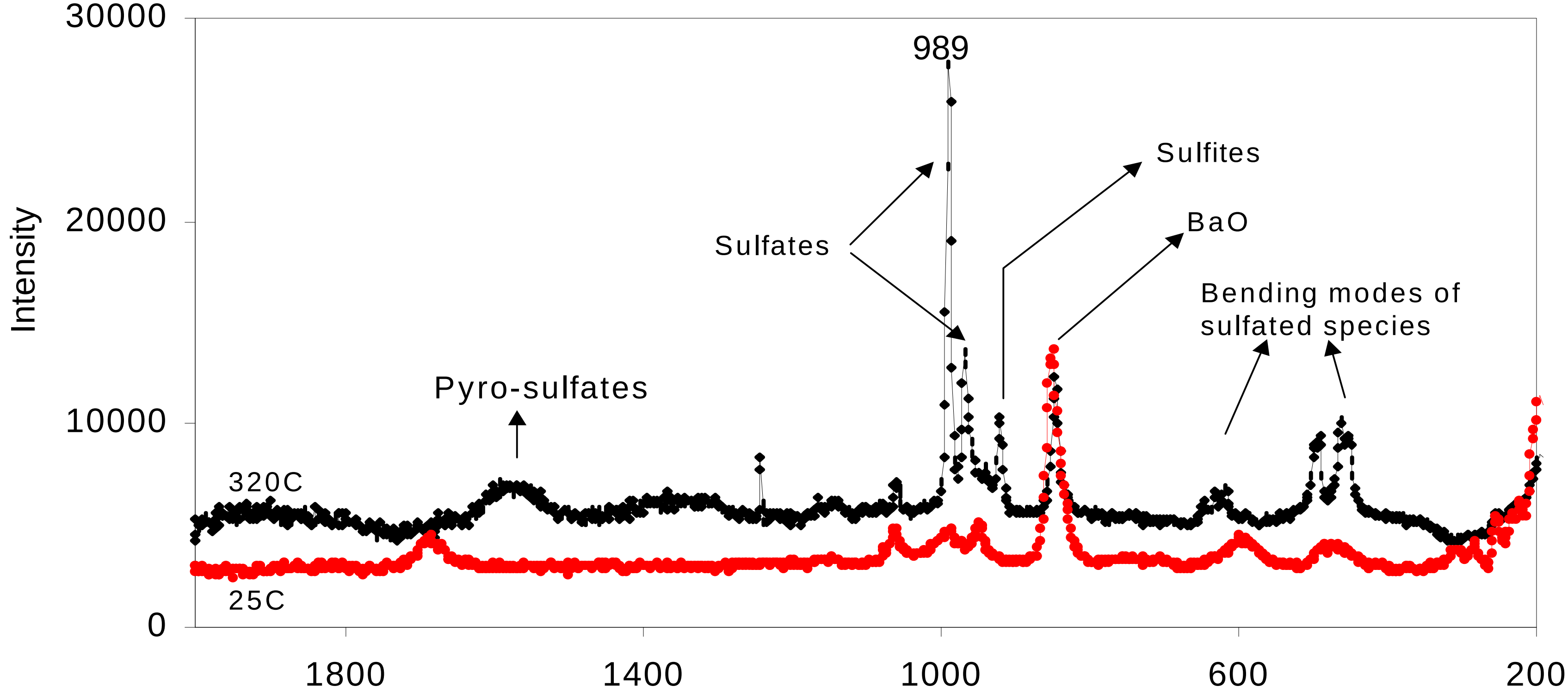




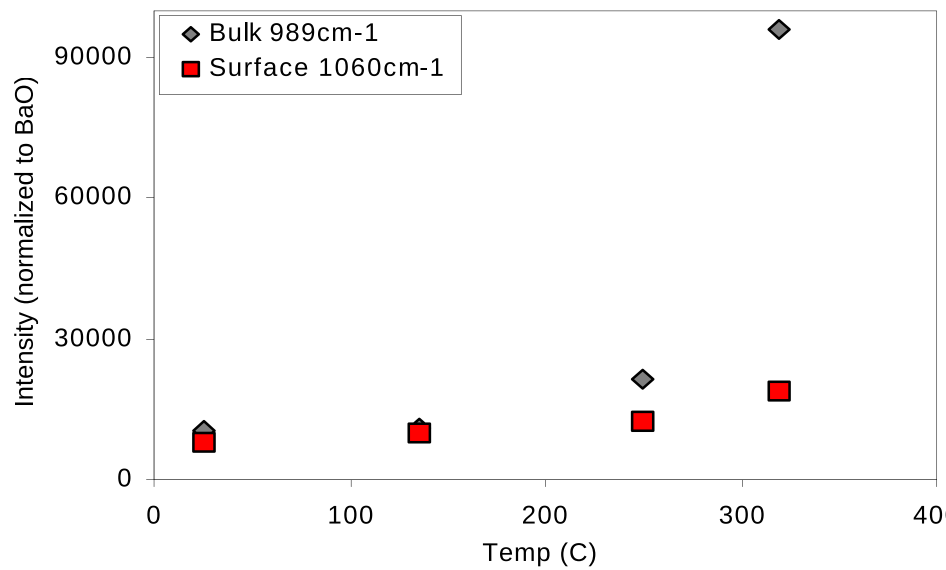


Surface adsorbed species show higher activation energies (larger slope) than the bulk nitrates

Raman Probe of Sulfation on BaO

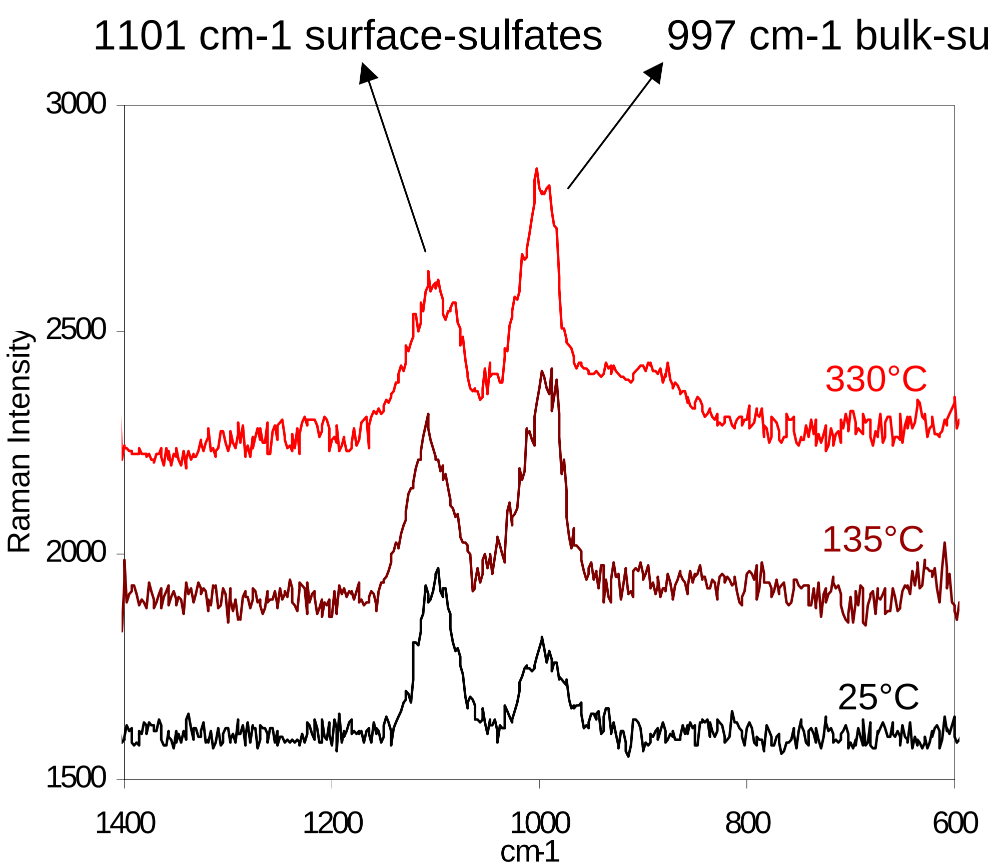


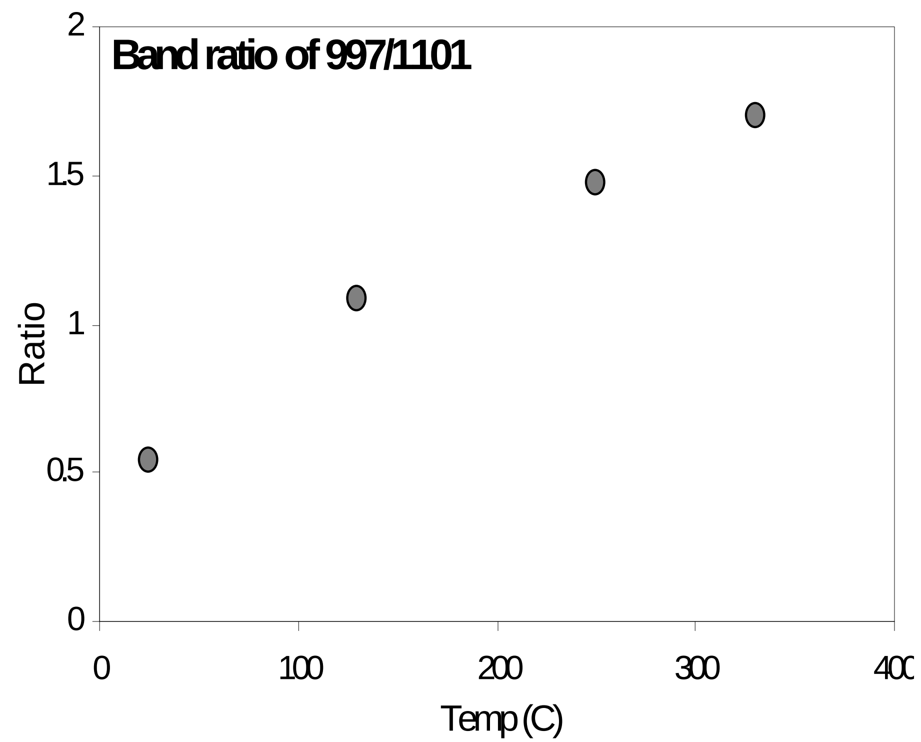
- Sulfation of BaO powder (purged by 1000 ppm SO_2) at various temperatures
- Bulk-sulfate formation (989 cm^{-1}) occurs at high temperatures
- Pyro-sulfates are observed



RAMAN ANALYSIS OF SULFATION ON MgO

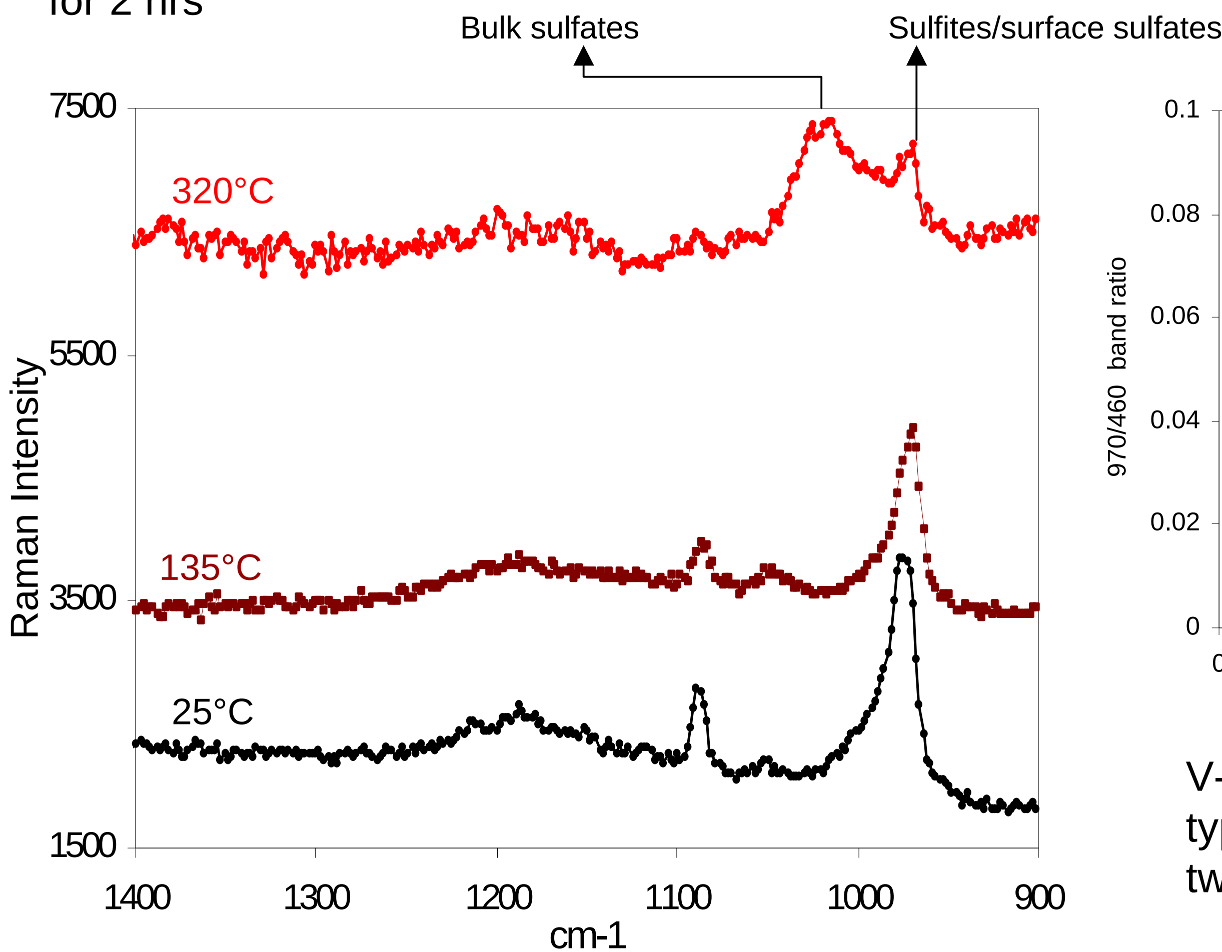
- MgO powder (25 m^2/g) shows no Raman response in 600-1400 cm^{-1} region except a weak feature at 1074 cm^{-1}
- After an exposure to SO_2/air for 2 hrs under a flow reactor, MgO shows two Raman features at 997 cm^{-1} (bulk sulfate) and 1101 cm^{-1} (surface-sulfate/bisulfate)
- As temperature increases from 25 to 330°C, surface-sulfate species are gradually converted into bulk-sulfates

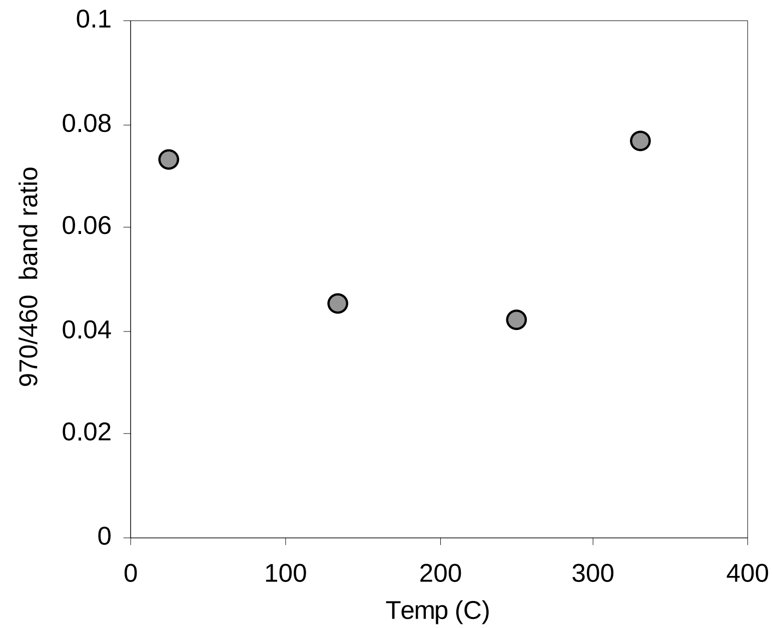




RAMAN ANALYSIS OF SULFATION ON COMMERCIAL SOX TRAP

Catalyst powder was exposed to SO_2/air under various temperatures with a flow reactor for 2 hrs

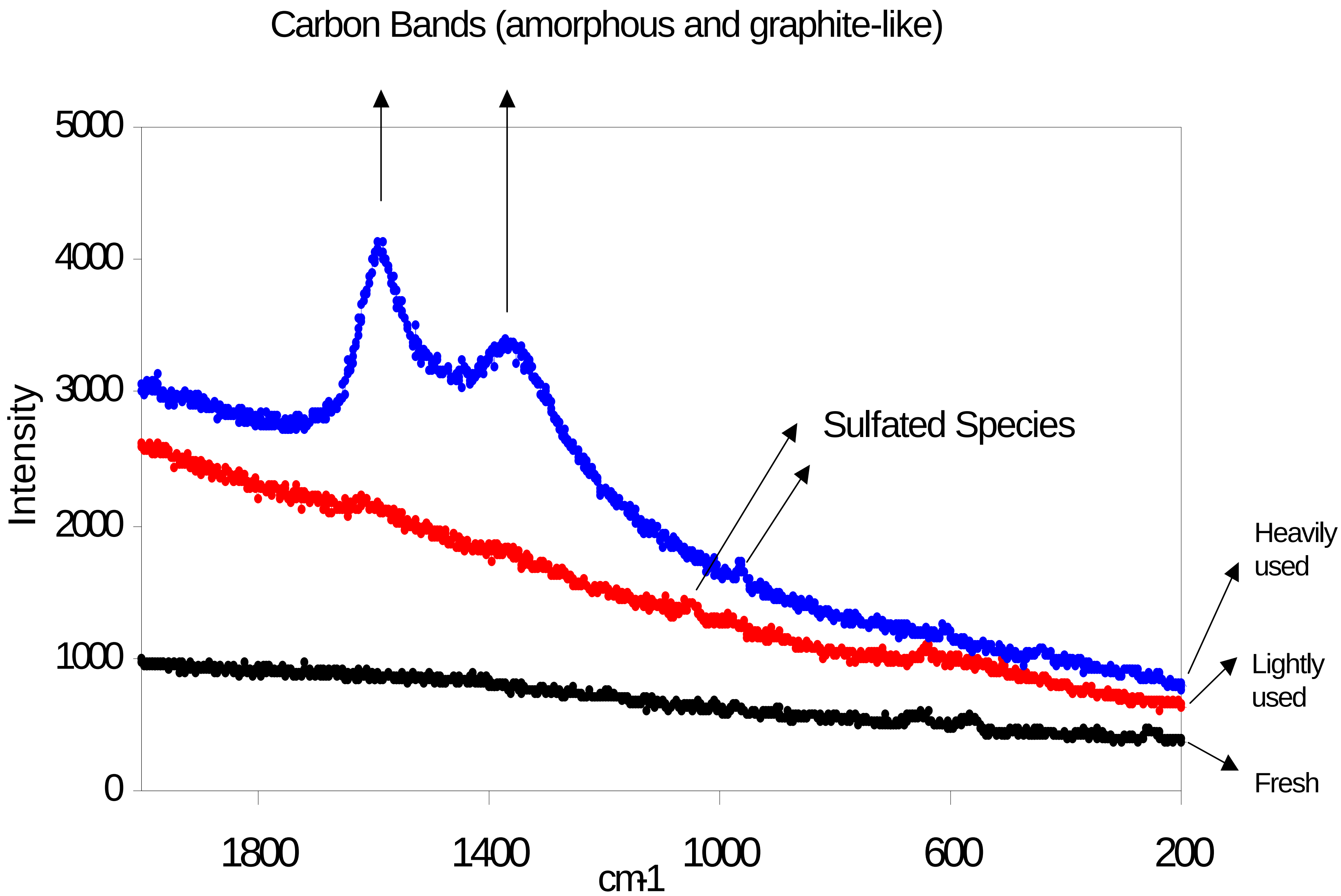




V-shape response reflects two types of kinetics associated with two different temperature regions

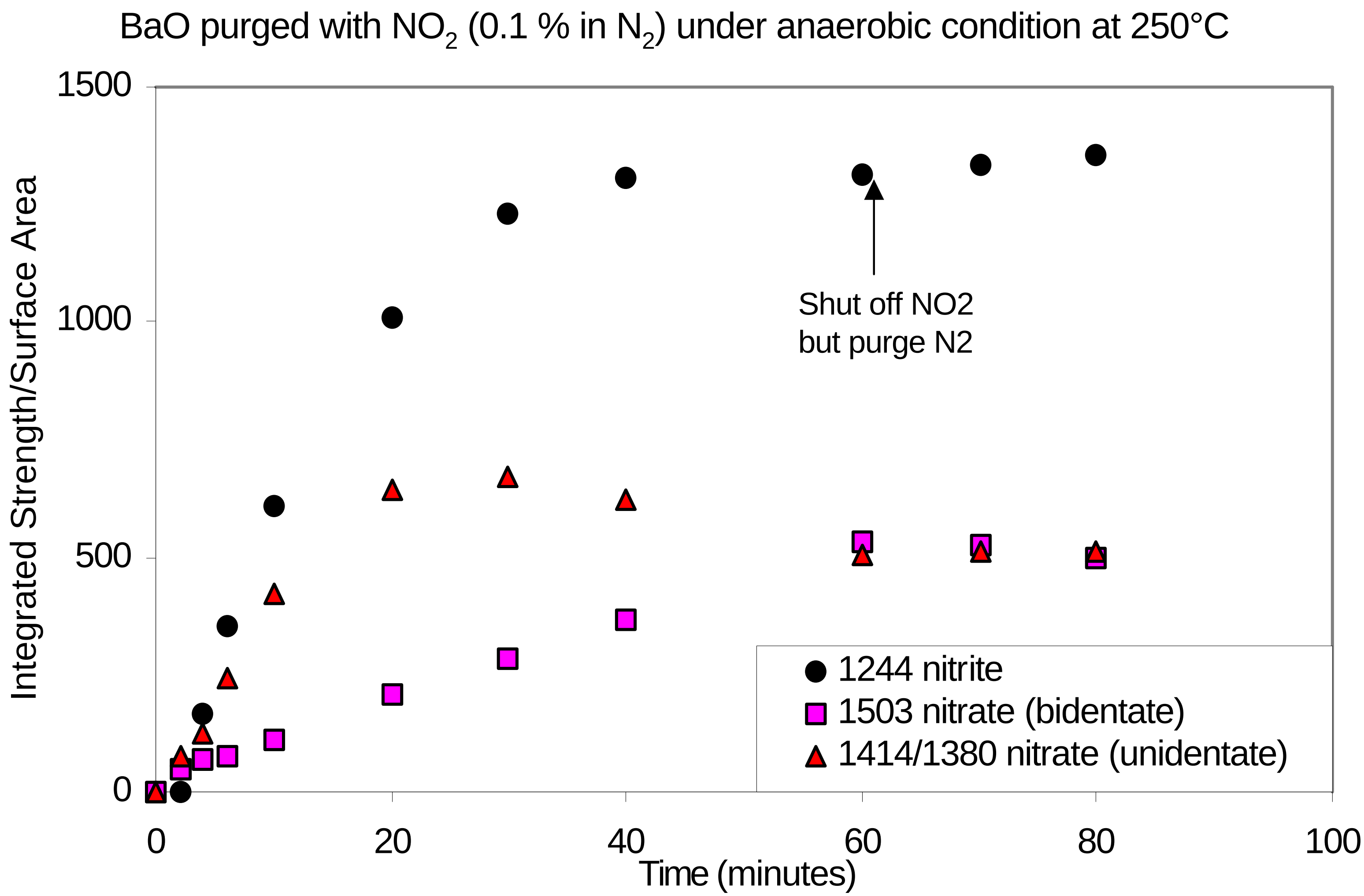
- All data are normalized against the CeO_2 band at 460 cm^{-1}
- Sulfites or surface sulfates are converted into bulk sulfates at higher temperature; consistent with DRIFTS data
- The more sulfation, the higher the fluorescence background

Raman Analysis in Aging of Commercial NOx Absorbers

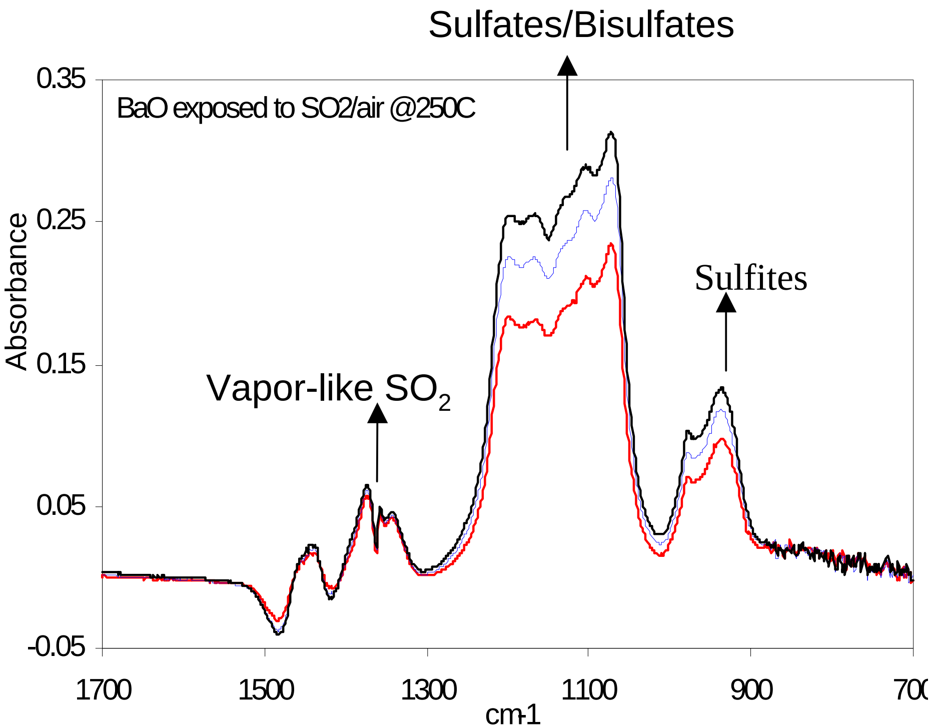


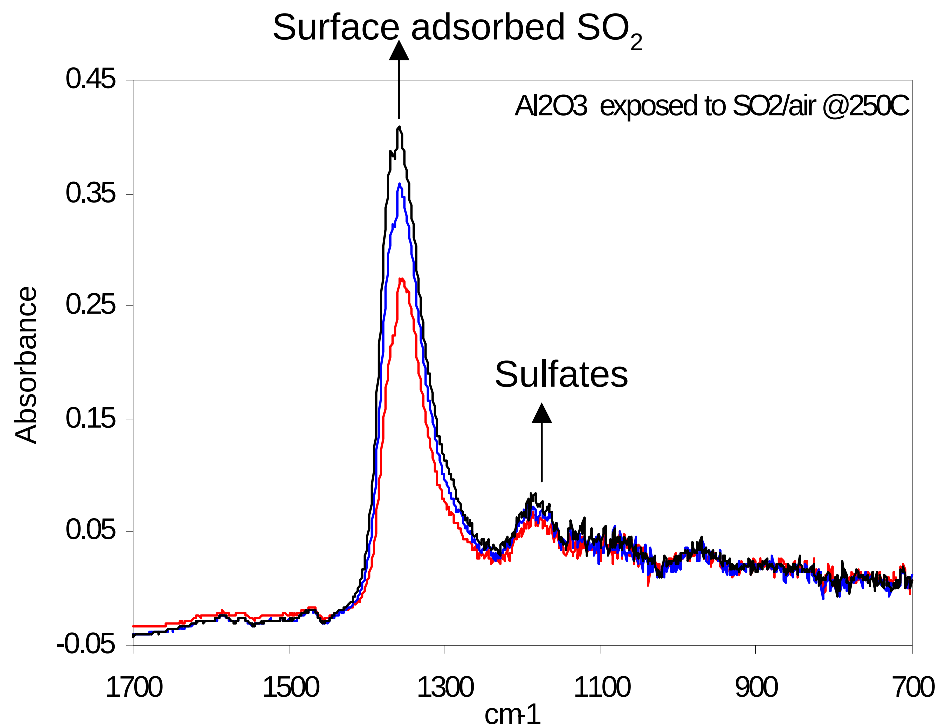
The presence of soot exhibits interference on Raman analysis

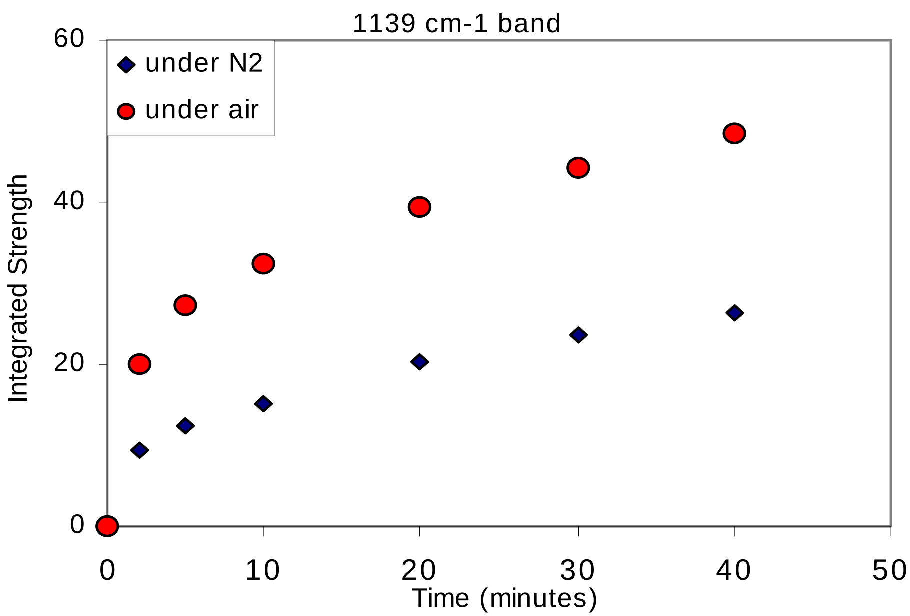
Nitration Kinetics by DRIFTS

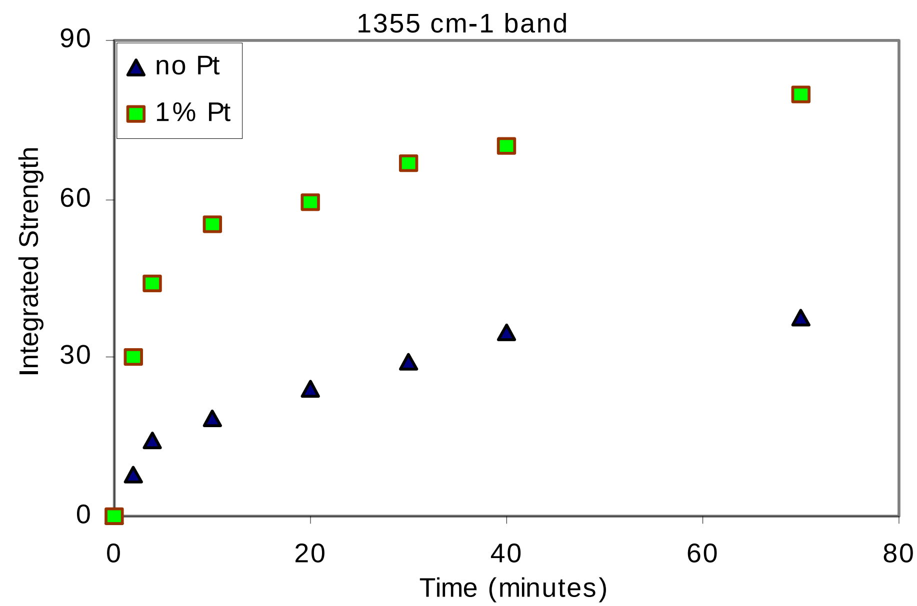


Sulfation of model metal oxides









CONCLUSIONS

- **Both DRIFTS and Raman are sensitive tools for identifying surface species responsible for NOx/SOx absorption**

  -With appropriate calibration to internal reference, quantitative measurement using Raman can be obtained

  -Raman analysis can be easily interfered by soot

  -Raman is more characteristic to probe S-species due to their sharper bands than IR

- **Distribution of various nitration species is surface basicity dependent**

  -Trapping capacity follows BaO > CaO > Al_2O_3 > TiO_2

  -Major nitration species are surface adsorbed NO_2, nitrites and nitrates and their relative abundance is a function of temperature and catalyst

- **Major sulfation species are surface adsorbed SO_2, sulfites, sulfates and bi-sulfates**

  -Ratios of sulfite/sulfate and SO_2/sulfate are catalyst dependent and may play major roles in determining trapping capacity

  -Surface sulfated species can be converted into pyro- or poly-sulfates which are precursors responsible for S-poisoning in NOx absorbers