Condition Assessment of Kevlar Composite Materials Using Raman Spectroscopy

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Overview

- Goals & Objectives
- Hypothesis
- Kevlar Composite Material
- Raman Spectroscopy
- Review of Literature
- Experimental
- Results & Discussion
- Conclusions

Goals and Objectives

- Goal: To evaluate Raman spectroscopy as a potential NDE tool for the detection of stress rupture in Kevlar.

- Objective: Test a series of strand samples that have been aged under various conditions and evaluate differences and trends in the Raman response

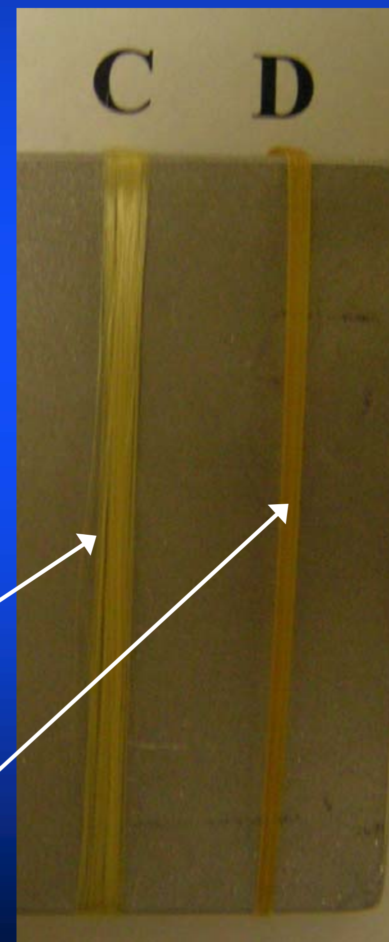
Hypothesis

- Reduction in strength associated with stress rupture may manifest from changes in the polymer at a molecular level. If so, than these changes may effect the vibrational characteristics of the material, and consequently the Raman spectra produced from the material

Problem Statement

- Kevlar composite over-wrapped pressure vessels (COPVs) on the space shuttles are greater than 25 years old
- Stress rupture phenomena is not well understood for COPVs
- Other COPVs are planned for hydrogen-fueled vehicles using Carbon composite material

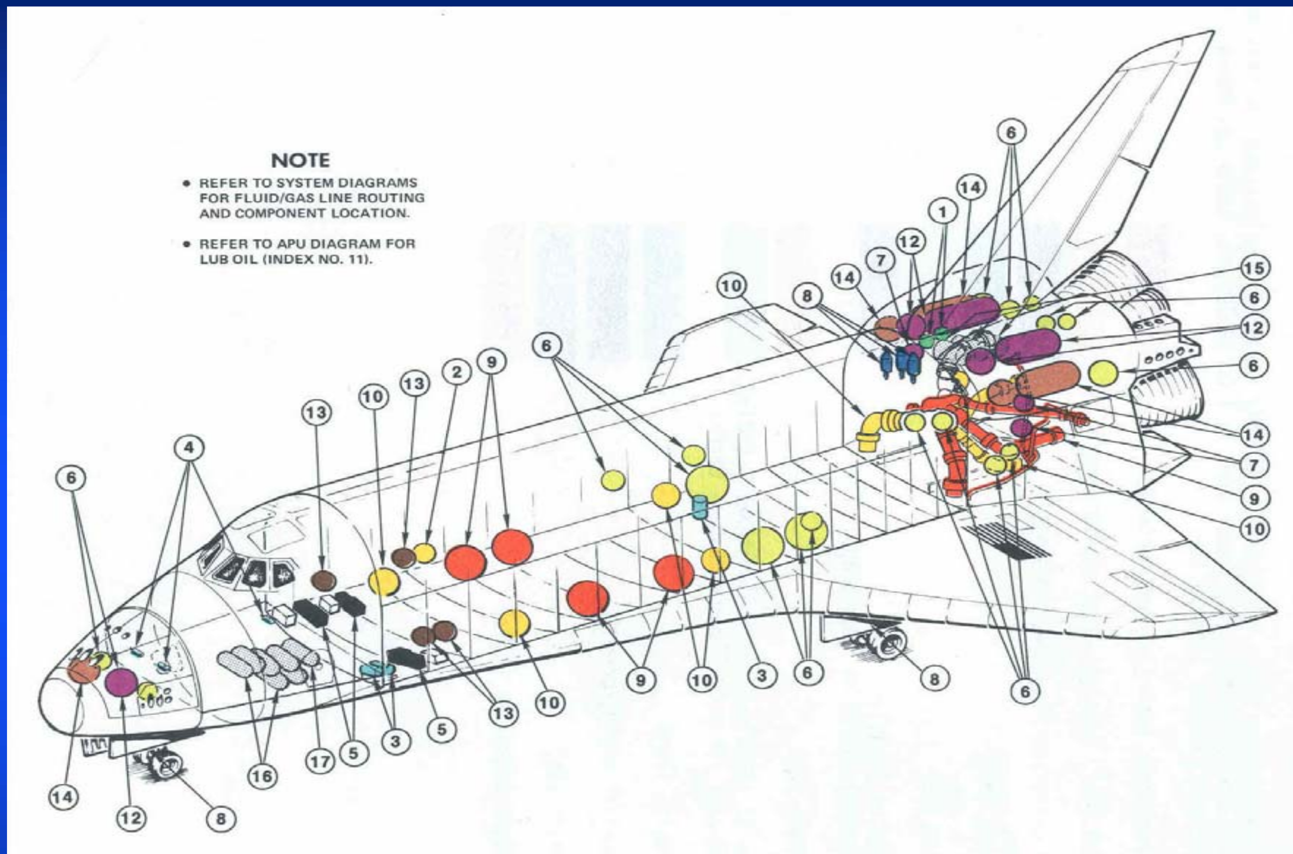
COPVs on Shuttle Orbiter



Kevlar yarn

Kevlar/epoxy composite strand

COPVs on Shuttle Orbiter



- Composites used primarily for the high strength-to-weight ratio

Stress Rupture Phenomena

- Material under constant load over long periods of time fails without an increase in the load
- Fibers are strained at a molecular level until rupture with associated creep (exact mechanism of material weakening is not known)
- Currently there is no known method to detect stress rupture by nondestructive means
- Raman spectroscopy may be a solution to this problem

Fiber Failure

- In fiber composite material, once a fiber fails the stress is transferred to the adjacent fibers
  - This can start a chain reaction that ends in a catastrophic failure of the entire composite
    - Local variations in the state of stress/strain
- Strain associated with creep may modify the Raman spectra of a fiber

Fiber Failure

- Fibers may also degrade by chain scission
  - Breaking of interatomic bonds
  - Resulting in changes in vibrational characteristics
- General loss of order in the Kevlar polymer
  - chain cross-linking
  - Resulting in changes in vibrational characteristics

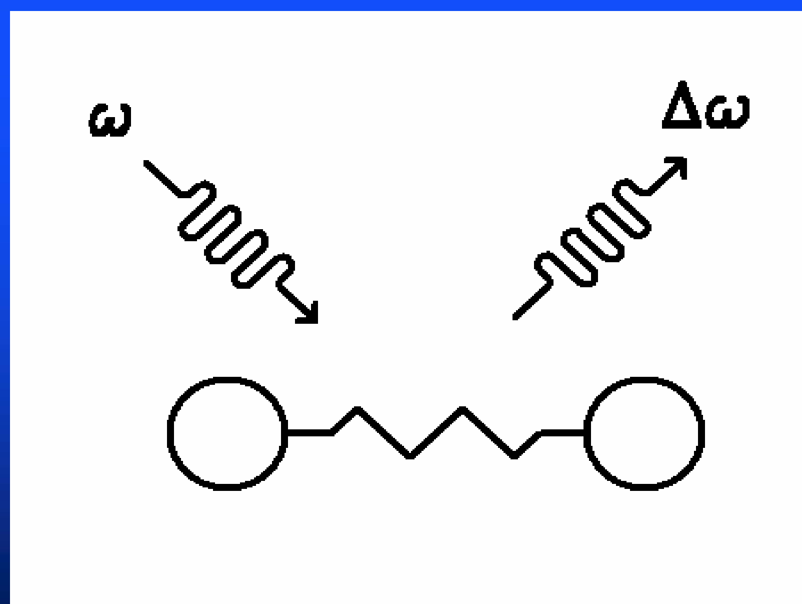
Raman Spectroscopy

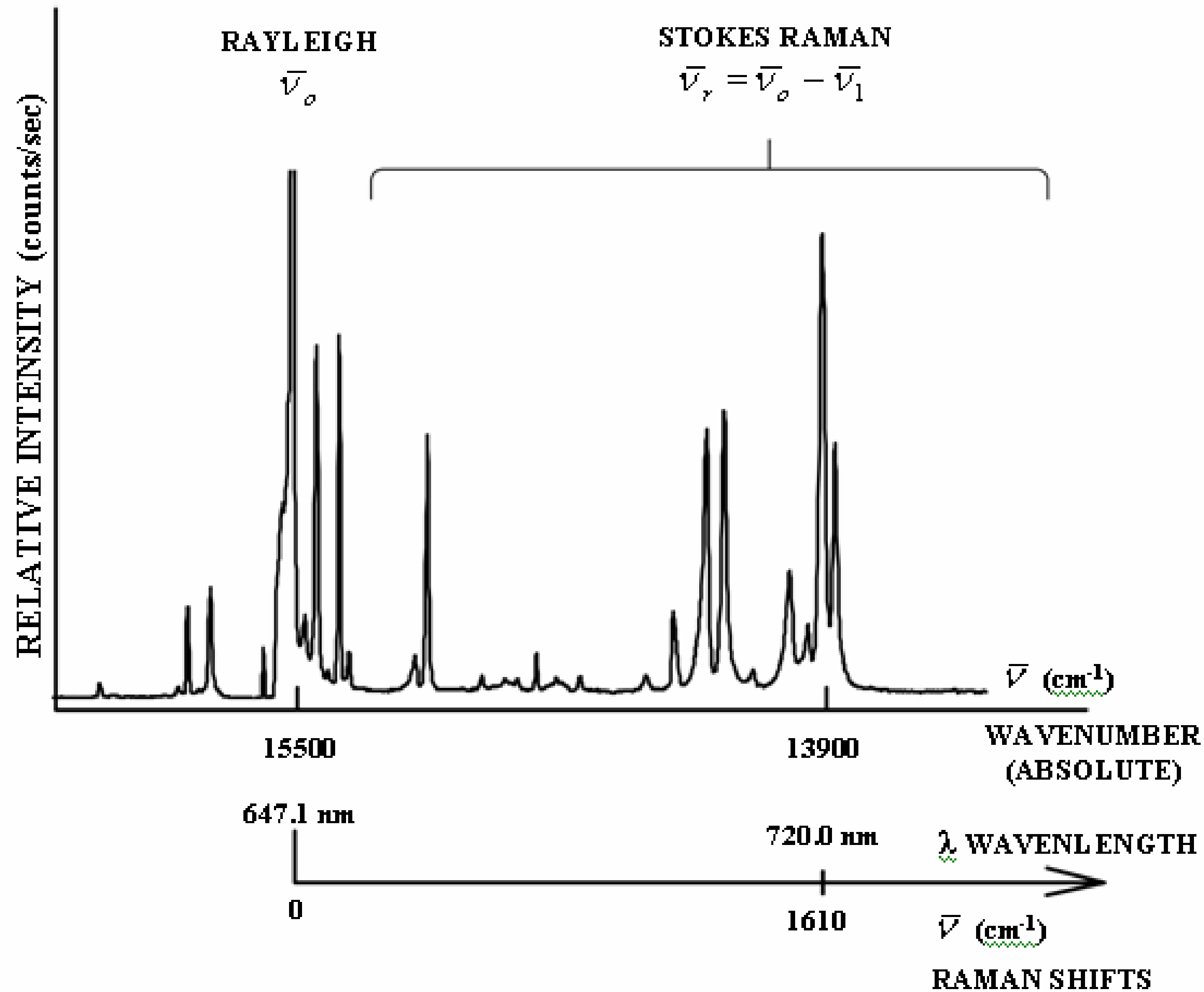
- Laser technique that is sensitive to molecular interactions in materials such as Kevlar, graphite and carbon
- Measures changes in frequency (wavelength) resulting from inelastic scattering processes

Scattered Light

- Rayleigh scattered light (elastic)
- Raman scattered light (inelastic)

Raman Molecular Interaction





RAYLEIGH
$\bar{\nu}_o$
STOKES RAMAN
$\bar{\nu}_r = \bar{\nu}_o - \bar{\nu}_1$
RELATIVE INTENSITY (counts/sec)
$\bar{\nu}$ (cm^{-1})
15500
13900
WAVENUMBER
(ABSOLUTE)
647.1 nm
720.0 nm
λ WAVENLENGTH
0
1610
$\bar{\nu}$ (cm^{-1})
RAMAN SHIFTS

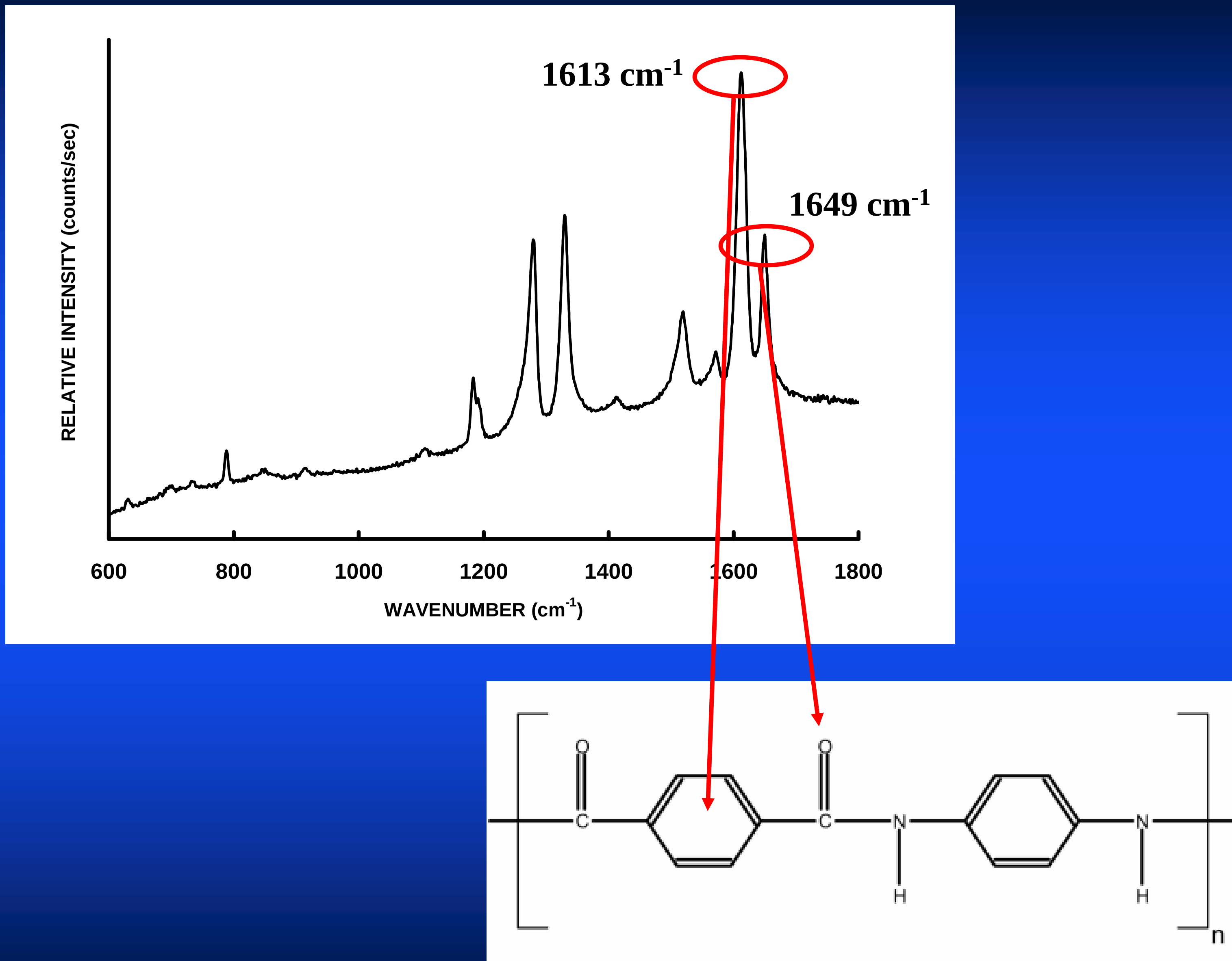
Raman Spectroscopy

- The shifts in frequency of the incident light relates to the vibrational properties of the molecule
  - Vibrational modes of a molecule can be modeled and Raman scattering predicted
    - Polarizability of the molecule
    - Interatomic forces between atoms
  - Peak shifts depend on
    - Strain
    - Crystallinity
    - Molecular structure
    - Temperature

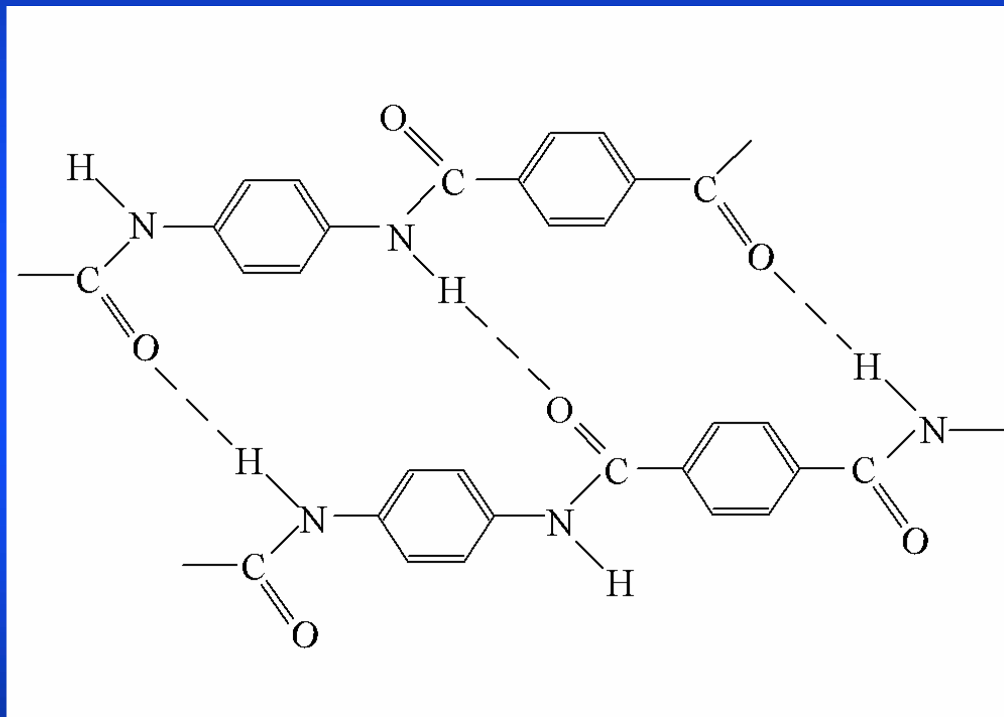
Vibrational modes associated with peaks found in the Raman spectra

Frequency / cm^{-1}	Assignment
630, 732, 786	ring vibrations
845	C-H out-of-plane bending
863	ring vibrations
1103	C-H in-plane bending
1181, 1277, 1327, 1514	C-C ring stretching
1318	C-H in-plane bending
1569	amide II (60% N-H bending; 40% C-N stretching
1610	C-C ring stretching
1648	amide I (80% C=O stretching; 10% C-N stretching 10% N-H bending)

B. H. Stuart, Polymer Bulletin **35,** 727-733 (1995)


1613 cm-1
1649 cm-1
RELATIVE INTENSITY (counts/sec)
600
800
1000
1200
1400
1600
1800
WAVENUMBER (cm-1)
O
C
O
C
N
H
N
H
n

Kevlar Aramid Fiber



Chemical Structure of Kevlar

Review of Literature

Peak shift (~1613 cm^{-1}) With Stress

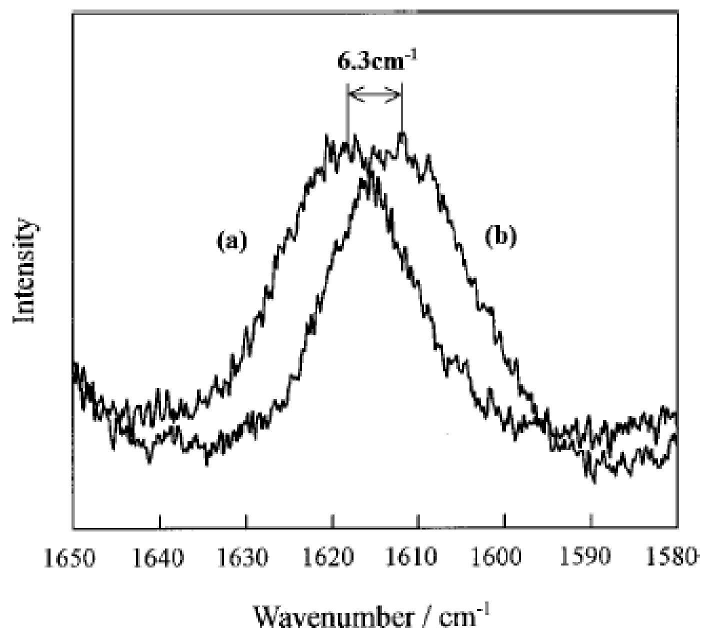
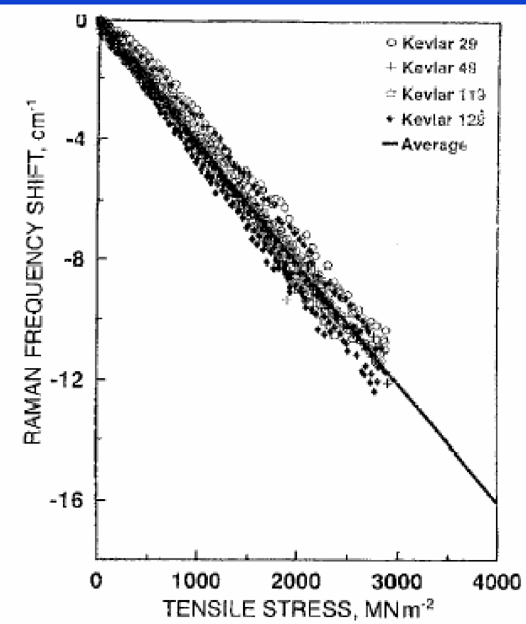


Figure 2. Raman spectra for a free-standing single fibre of Kevlar 49 subjected to tensile stress of (a) 1.76 GPa and (b) to no stress.



11 Raman frequency shift *v.* applied tensile stress for several aramid fibres: solid line represents least squares fitted line to raw data

Kawagoe et al. (1999) **Schadler et al. (1995)**

Schadler et al. (1995)

- As a material is strained, the interatomic distance changes resulting in a change in the interatomic force, and thus a change in the vibrational frequency
- The ~1613 cm^{-1} peak exhibits the highest sensitivity with stress/strain

Prasad et al. (1990)

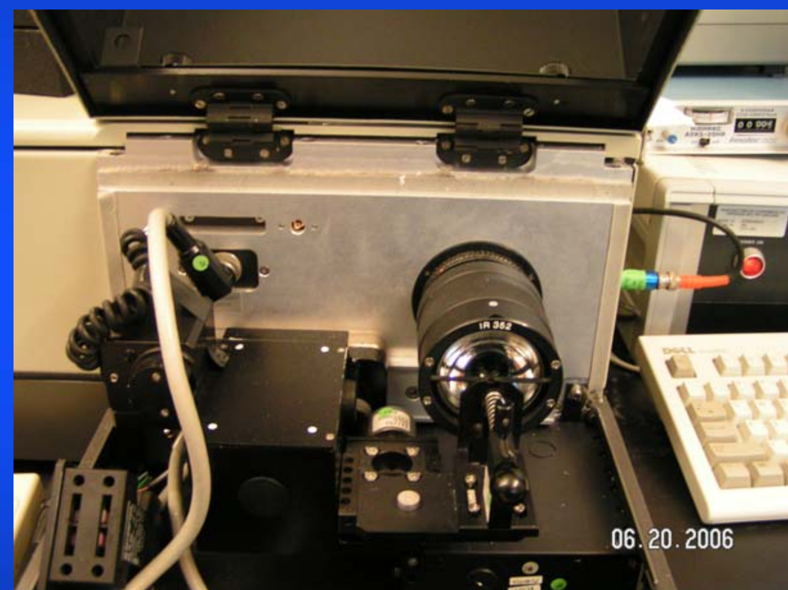
- Raman band broadening due to defects in the molecular chain
- Defects possibly from stress or harsh environmental conditions

Stuart (1995)

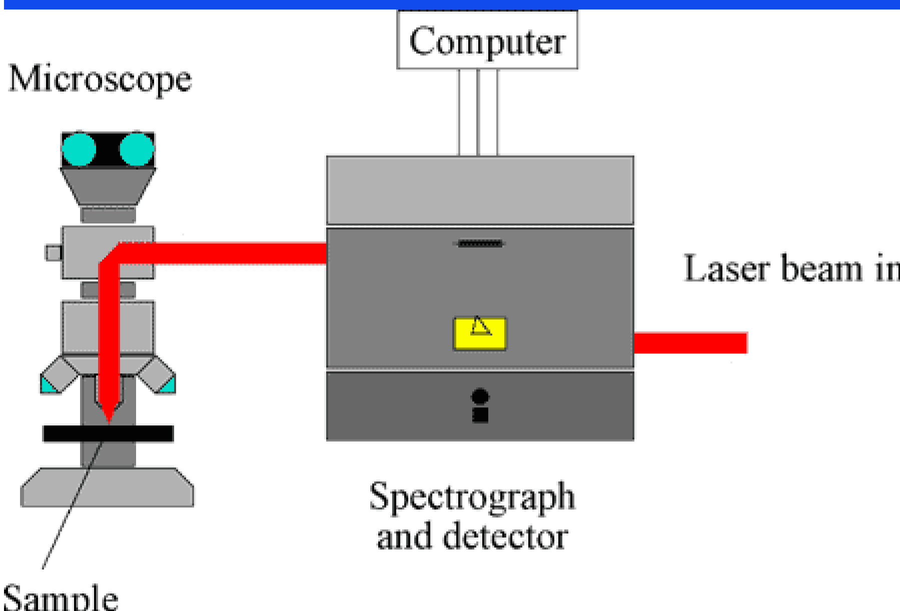
- Used a 1064 nm incident laser to investigate water absorption in Kevlar
- Found a decrease in intensity for the 1613 cm^{-1} Raman band

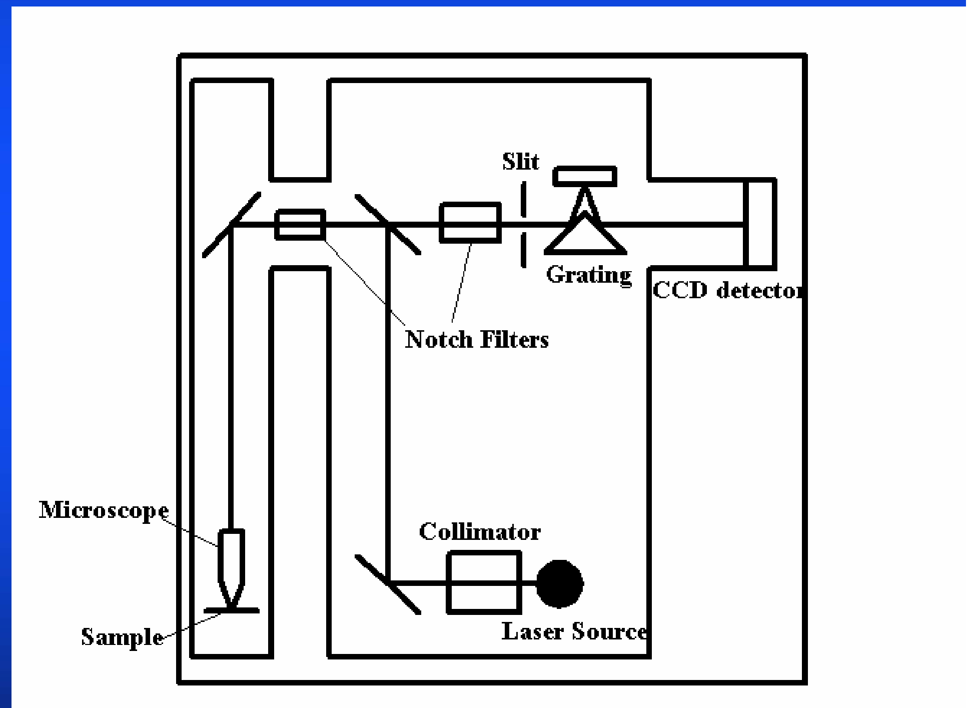
Experimental

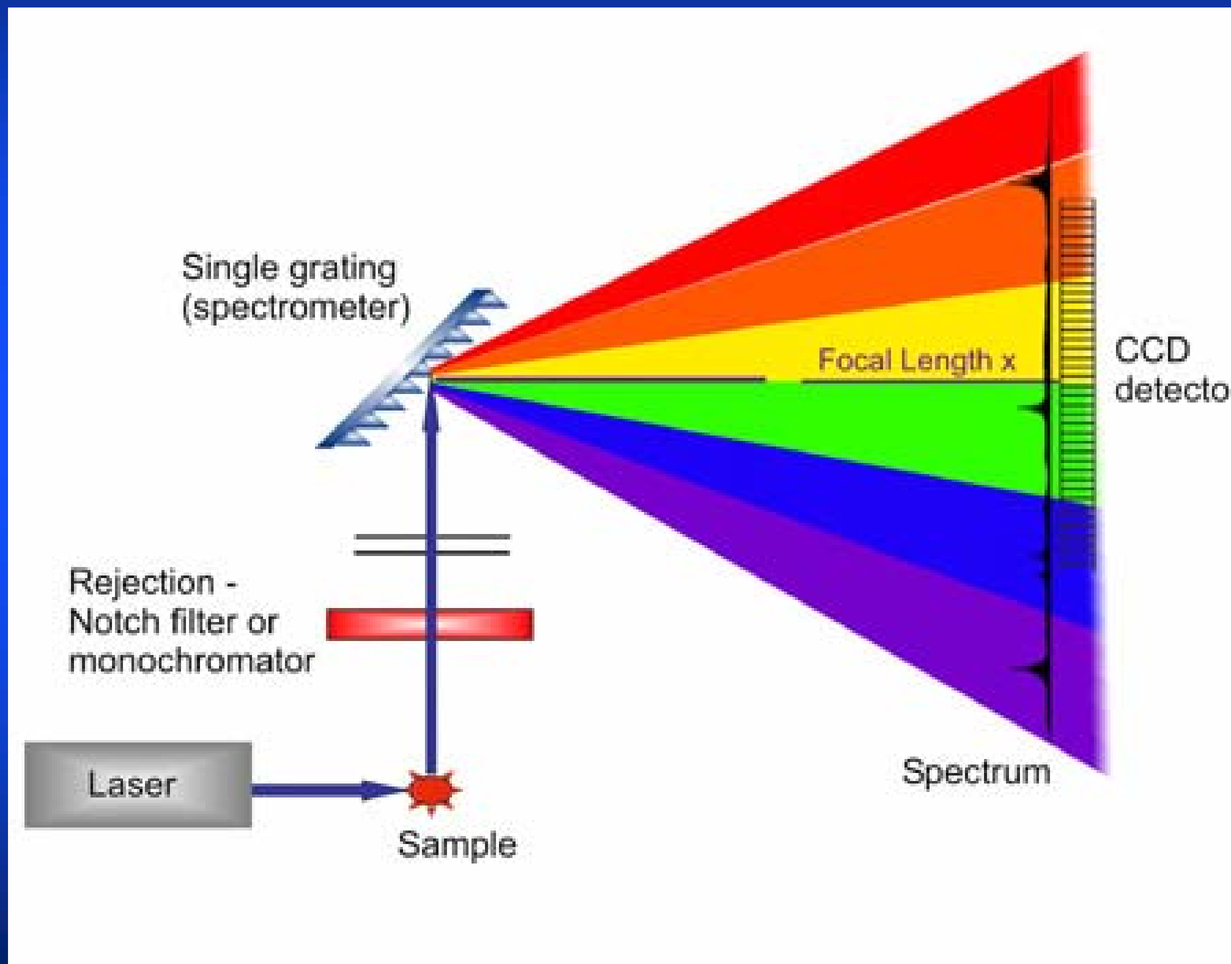
- Renishaw Raman inVia spectrometer
- FT Raman system



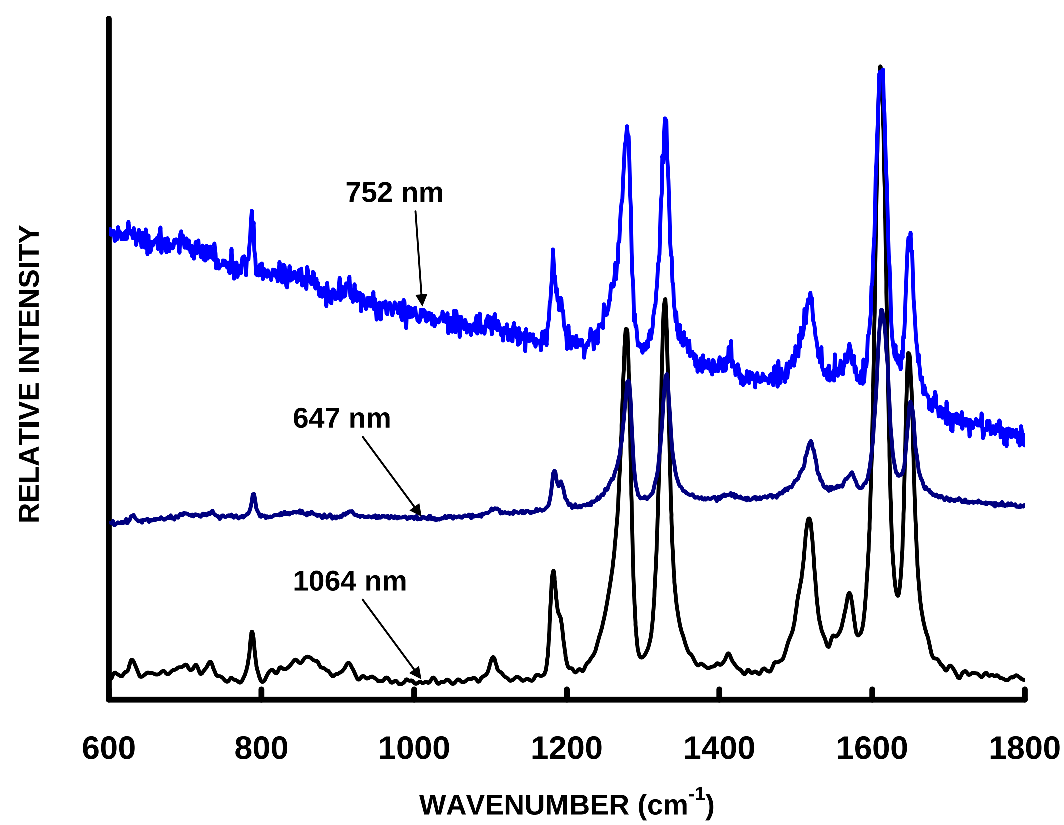
- Typical Micro-Raman Spectrometer



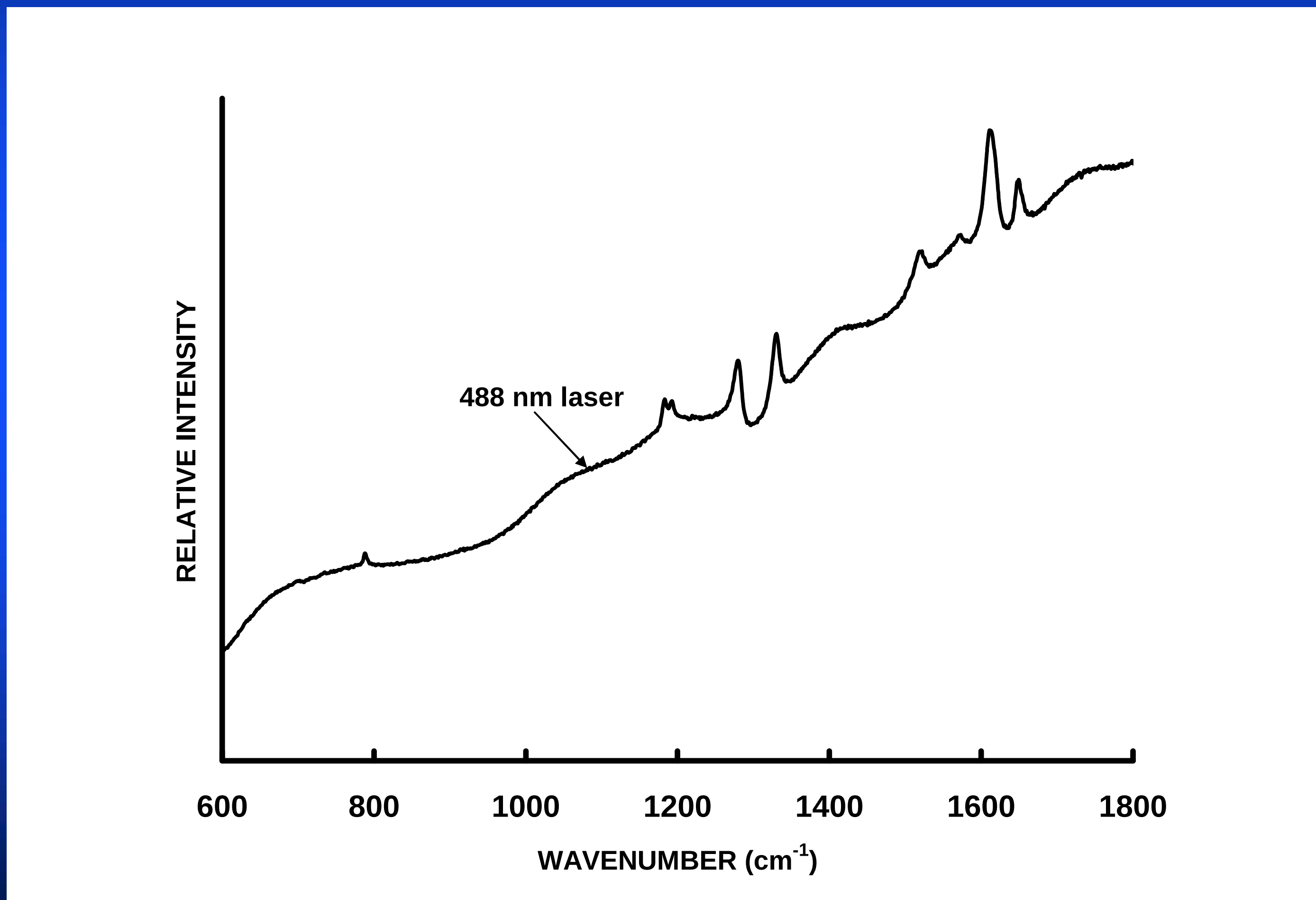



Single grating
(spectrometer)
Focal Length x
CCD
detector
Rejection -
Notch filter or
monochromator
Laser
Sample
Spectrum

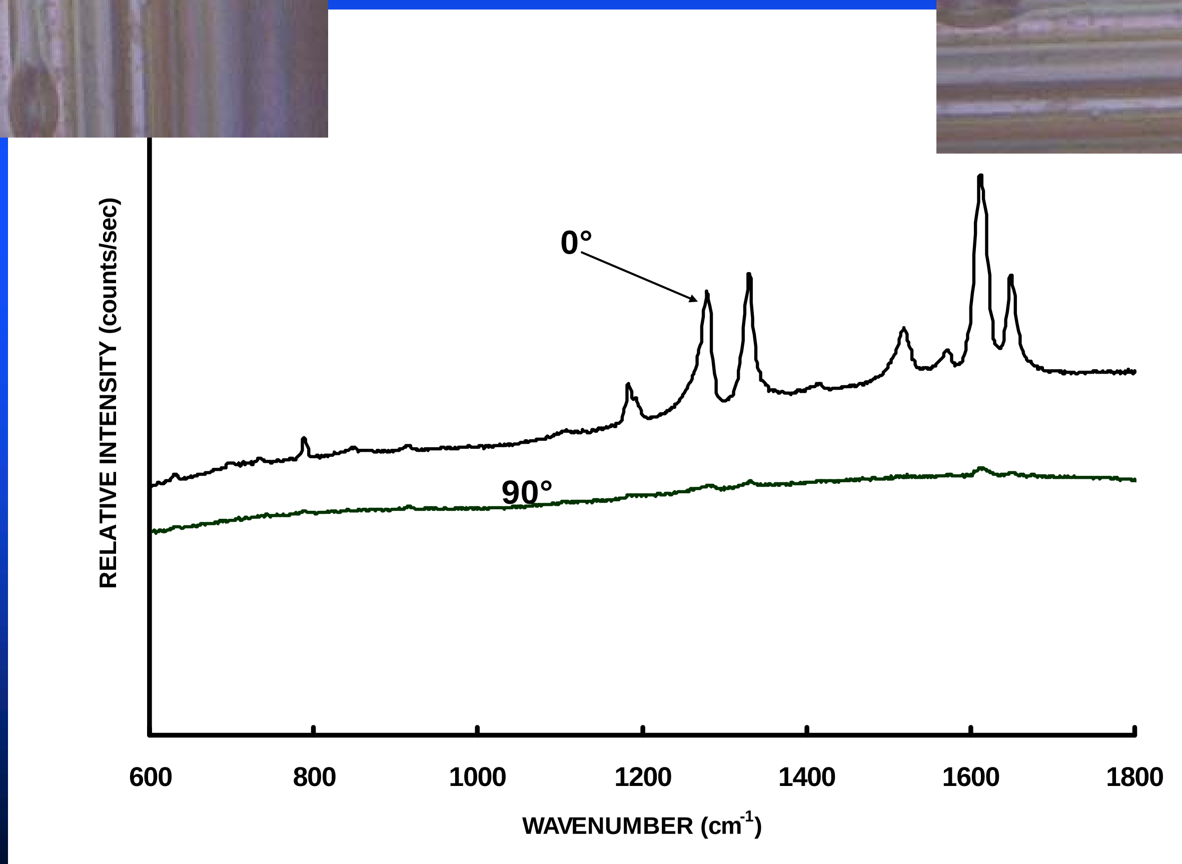
Spectra from Kevlar with incident laser wavelengths of 647, 752 and 1064 nm



Spectra from Kevlar with Incident laser wavelengths of 488 nm



Fiber Alignment



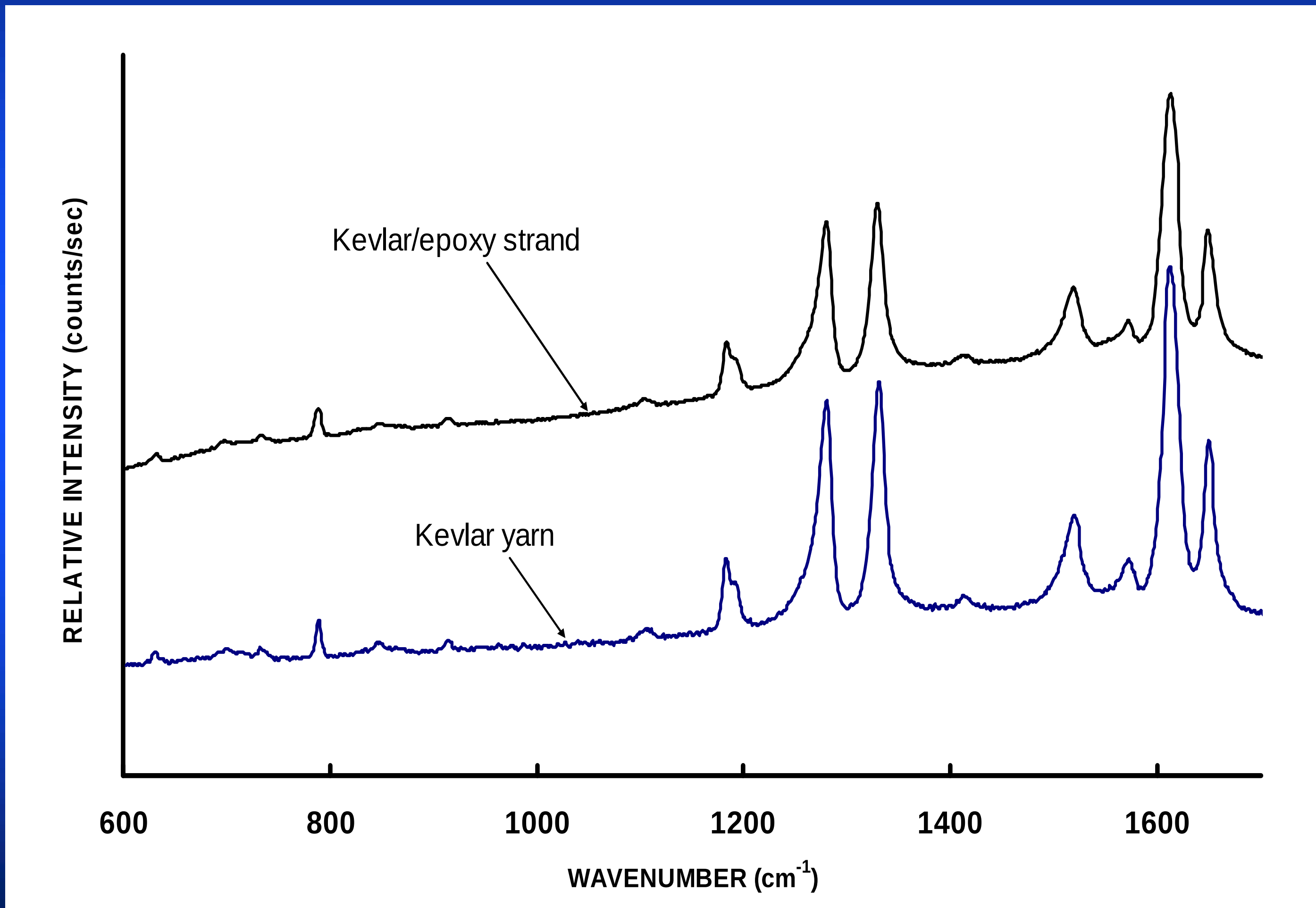
Comparison of Raman Peaks for Kevlar

RAMAN PEAKS (cm^{-1})						
TEST TYPE						
Theoretical		Kevlar yarn	Kevlar strand			
Penn and Milanovich Peaks	Kim et al. Peaks	(647 nm)	(488 nm)	(647 nm)	(752 nm)	(1064 nm)
632	637	631		631	630	630
698	694	700		700	697	695
734	725	731		731	732	732
789	773	790	784	789	787	787
-	853				847	845
-	-	914		915	913	918
1104	1106	1105		1105	1105	1108
1187	1187	1184	1186	1184	1185	1186
1192	1188					1194
1279	1283	1280	1278	1280	1278	1283
1331	1332	1331	1331	1330	1329	1332
1409	1400	1413		1411	1415	1417
1518	1516	1519	1520	1518	1517	1521
1570	1567	1572	1577	1571	1570	1574
1615	1615	1613	1612	1613	1612	1615
1649	1654	1649	1649	1649	1649	1651

Penn, L., Milanovich, F., *Raman Spectroscopy of Kevlar 49 Fiber*. Polymer, 1979. **20**(1): p. 31-36.

Kim, P.K., Chang, C., Hsu, S.L., *Normal Vibrational Analysis of a Rigid Rod Polymer: poly(p-phenylene terephthalamide)*. Polymer, 1986. **27**(1): p. 34-46.

Kevlar yarn vs composite strand



Strand Samples

Sample Type	Notes	488 nm	647 nm	752 nm	1064 nm
TRI Virgin Kevlar 49 Strands	original virgin strands, 1140 denier		X	X	X
TRI Virgin Kevlar 49 Yarn	original virgin yarn, 1420 denier		X		X
TRI Creep Test Samples	65% ult strength (65 lbs) at different times and temperatures		X	X	X
Fleet Leader Tank SN007	*S/N 007, 50% pressure ~4200 psi*		X		X
Fleet Leader Tank SN032	*SN032, pressure 50% ~4200 psi*	X	X		X
ATK Kevlar prepreg	4560 denier, cured and uncured		X		X
SIM Kevlar Strands	Stepped isothermal strands; 14o5, 21o5, 23d5, 23o5		X		X

Strand Specimens

SIM Strands

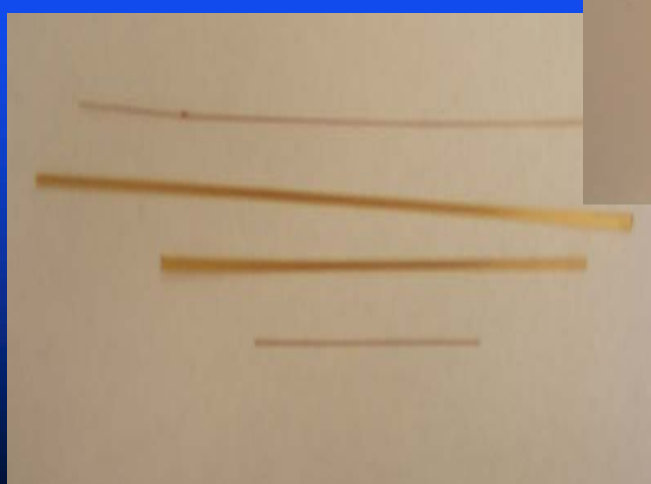
Sample	Tensile Strength	Temp (°C)	Time at Failure Temp (sec)	Total Time (sec)
14o5	65%	90	8770	58770
21o5	65%	90	480	50480*
23d5	65%	103	8130	68130
23o5	65%	104	210	60210

TRI Creep Strands

Specimen	Aged (hrs)	Temp (°C)	Failed?
2F1	9	92	yes
Virgin	0	room	
2F9	1	90	yes
2F10	4	90	yes
2F11	9	92	yes
2F12	1	76	yes


03.01.2006


12.11.2006




07.31.2006

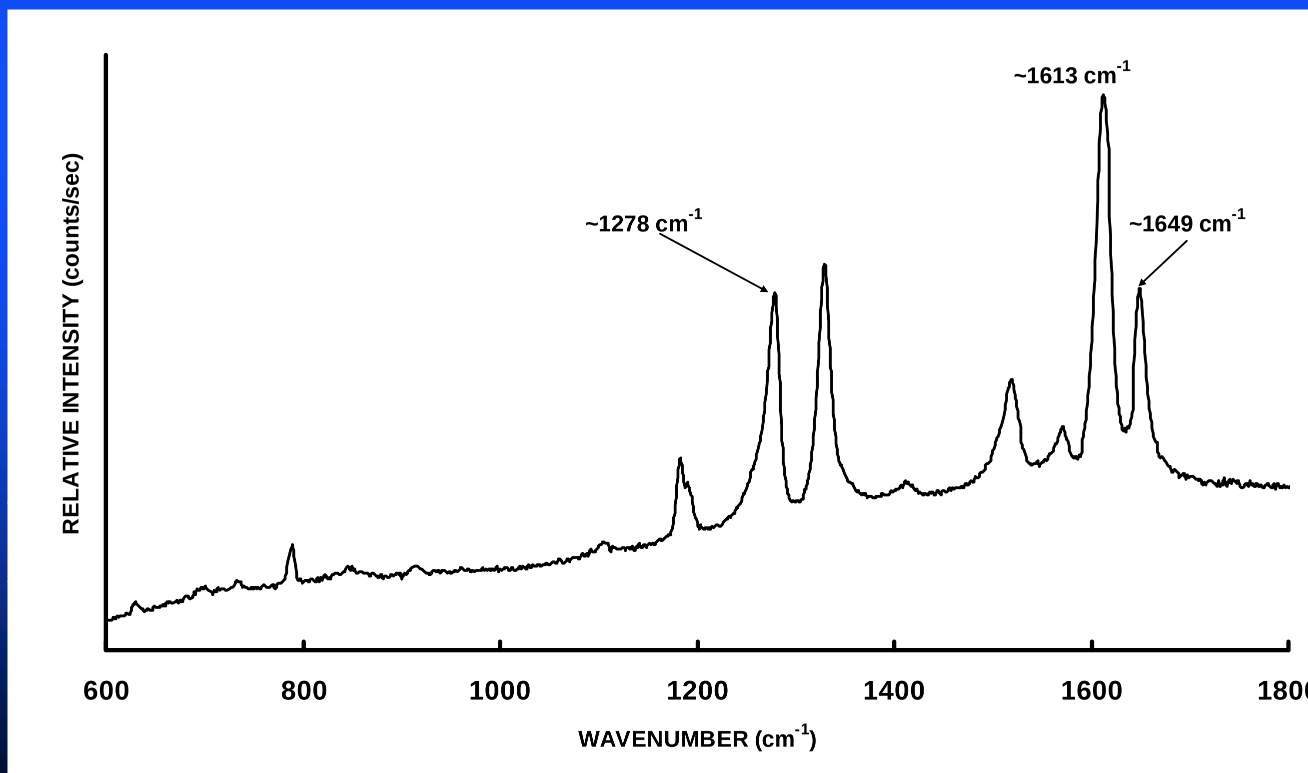

07.31.2006

Full width at half maximum (FWHM) ratio

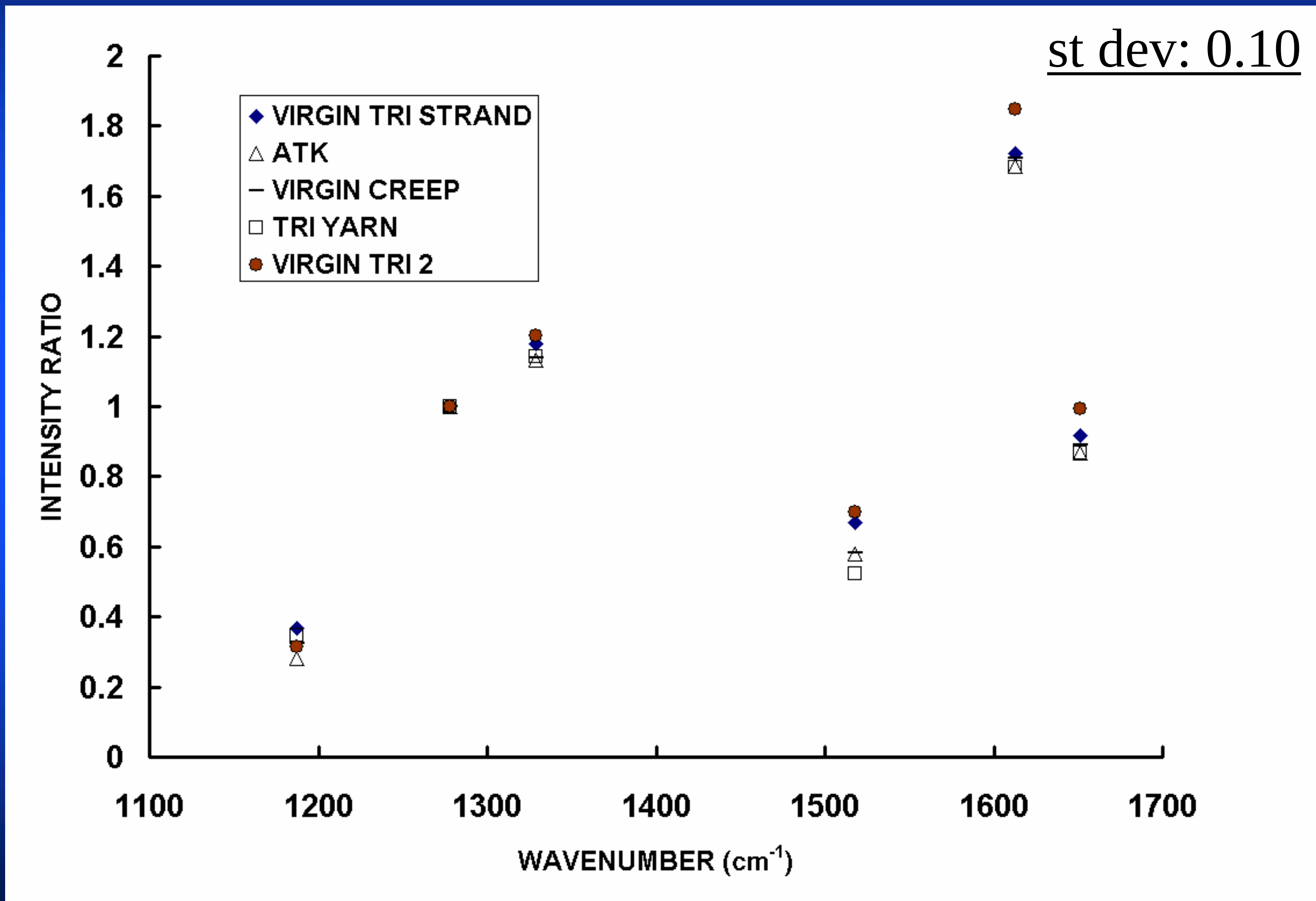
$$\eta_i = \frac{FWHM_i}{FWHM_{1278}}$$

Intensity ratio

$$\chi_i = \frac{I_i}{I_{1278}}$$

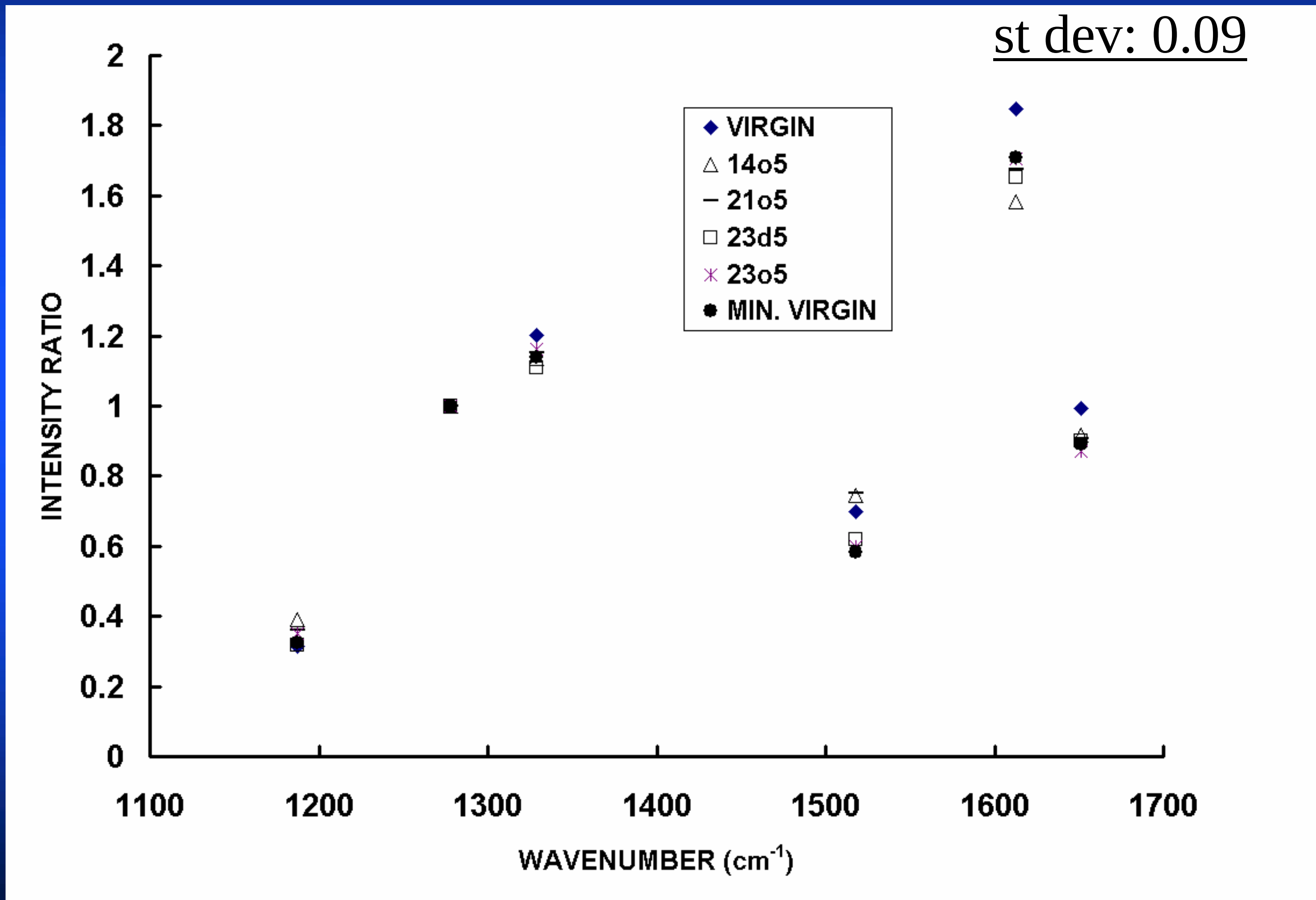


Intensity Variations (relative to 1278 cm^{-1}) for Virgin Strands, 647 nm incident wavelength

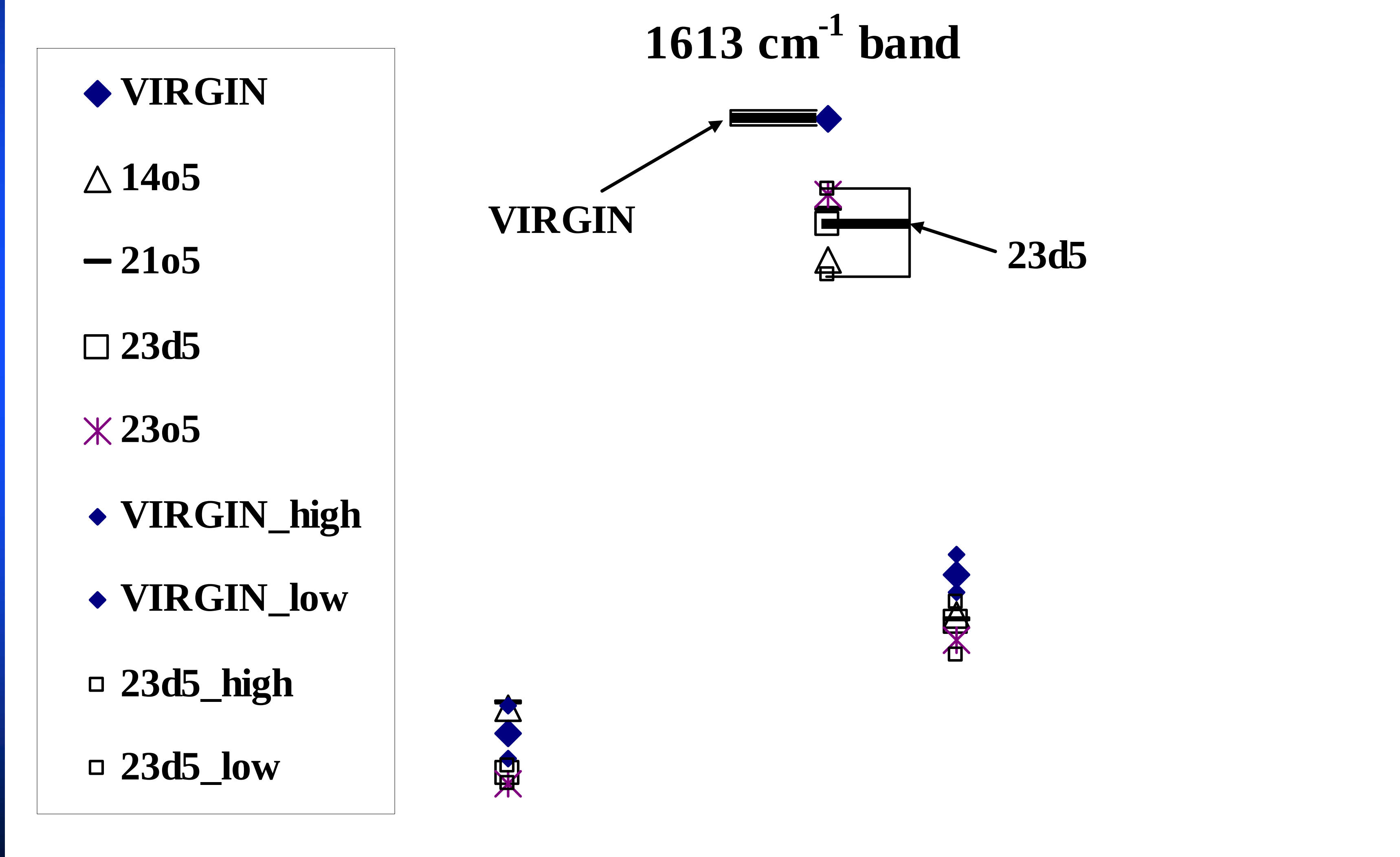


Variations in the intensity of different virgin materials

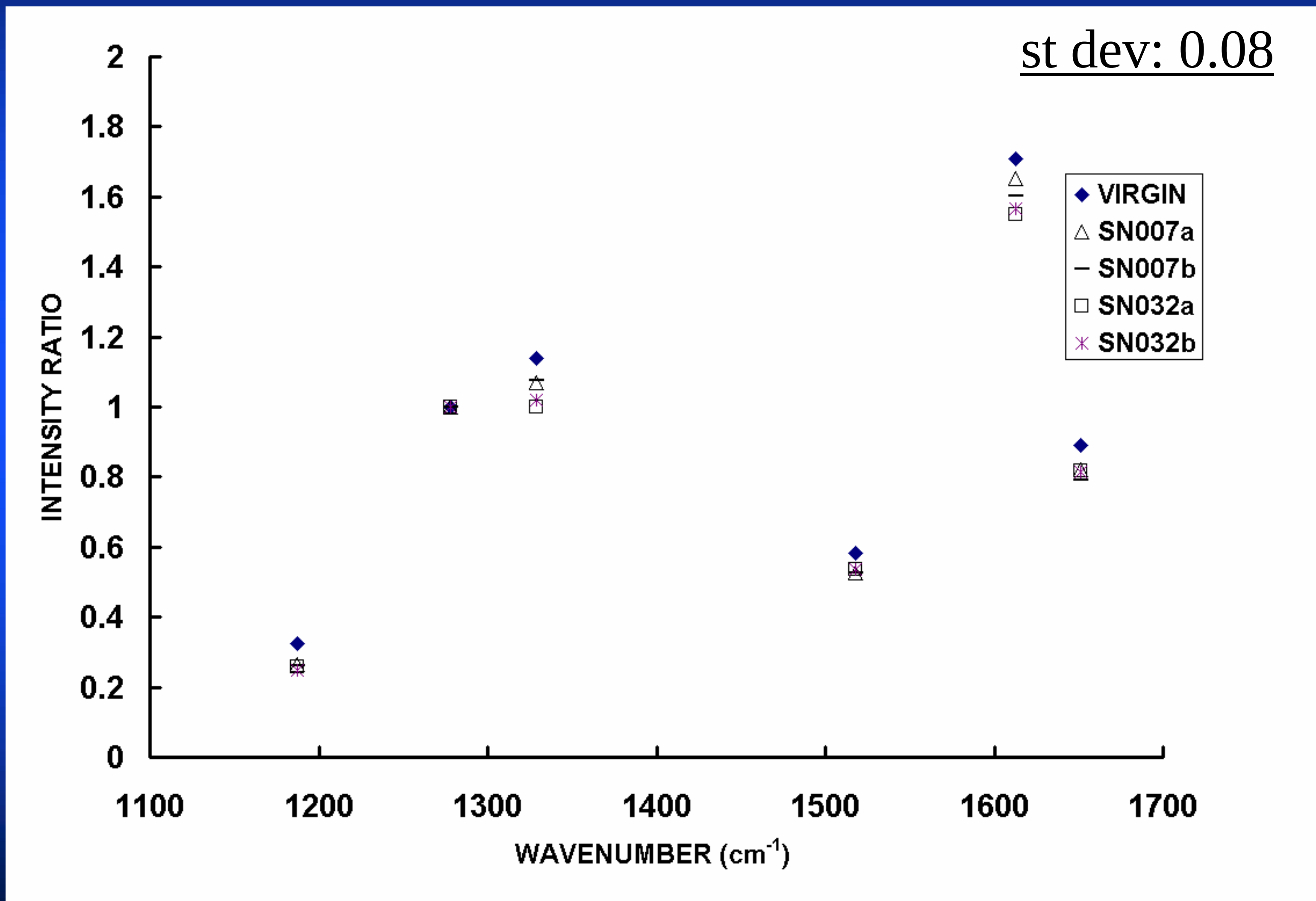
Intensity Variations (relative to 1278 cm^{-1}) for Virgin Strands vs SIM specimens, 647 nm



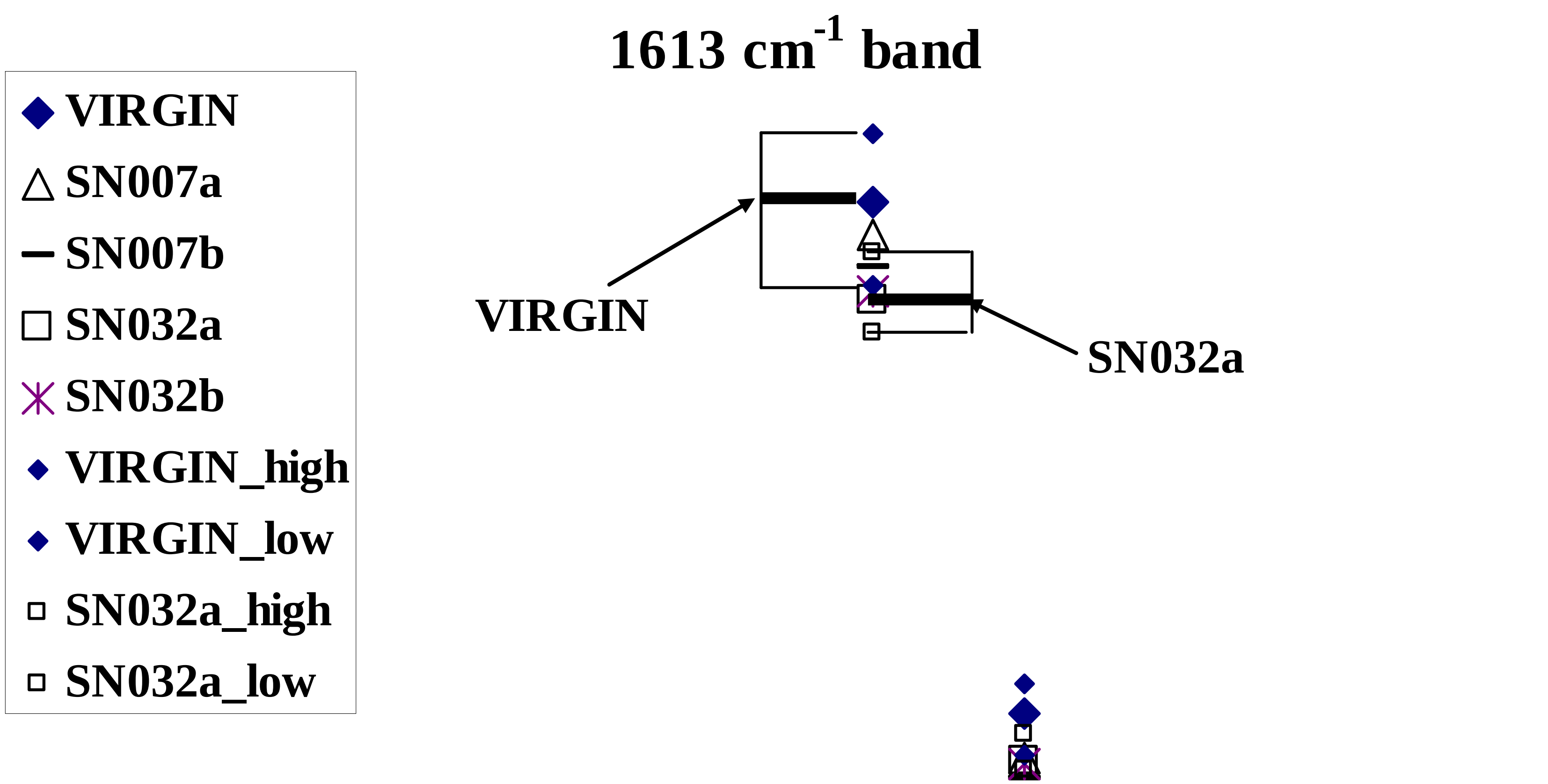
Intensity Variations (relative to 1278 cm^{-1}) for Virgin Strands vs SIM specimens, 647 nm



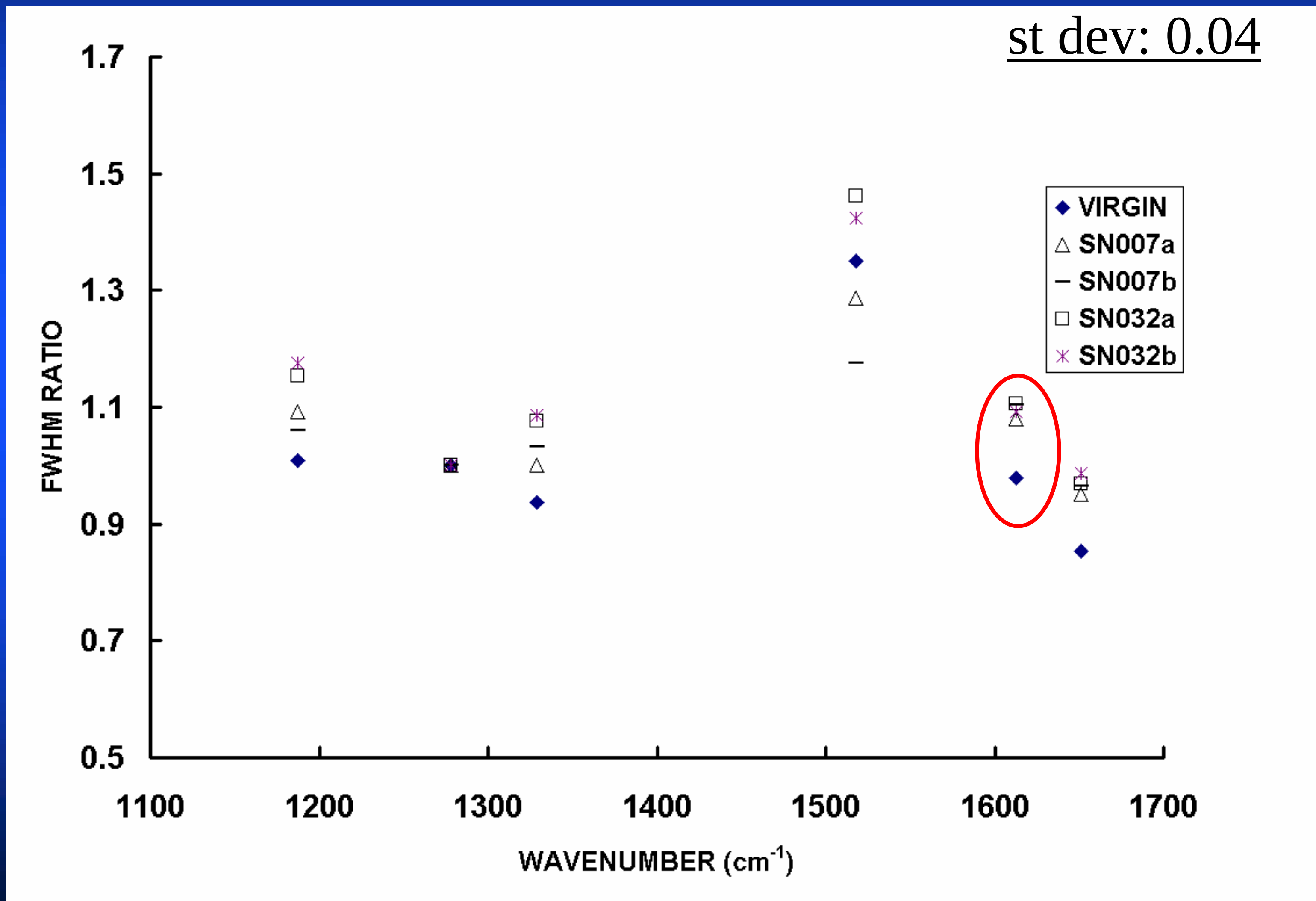
Intensity Variations (relative to 1278 cm^{-1}) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength



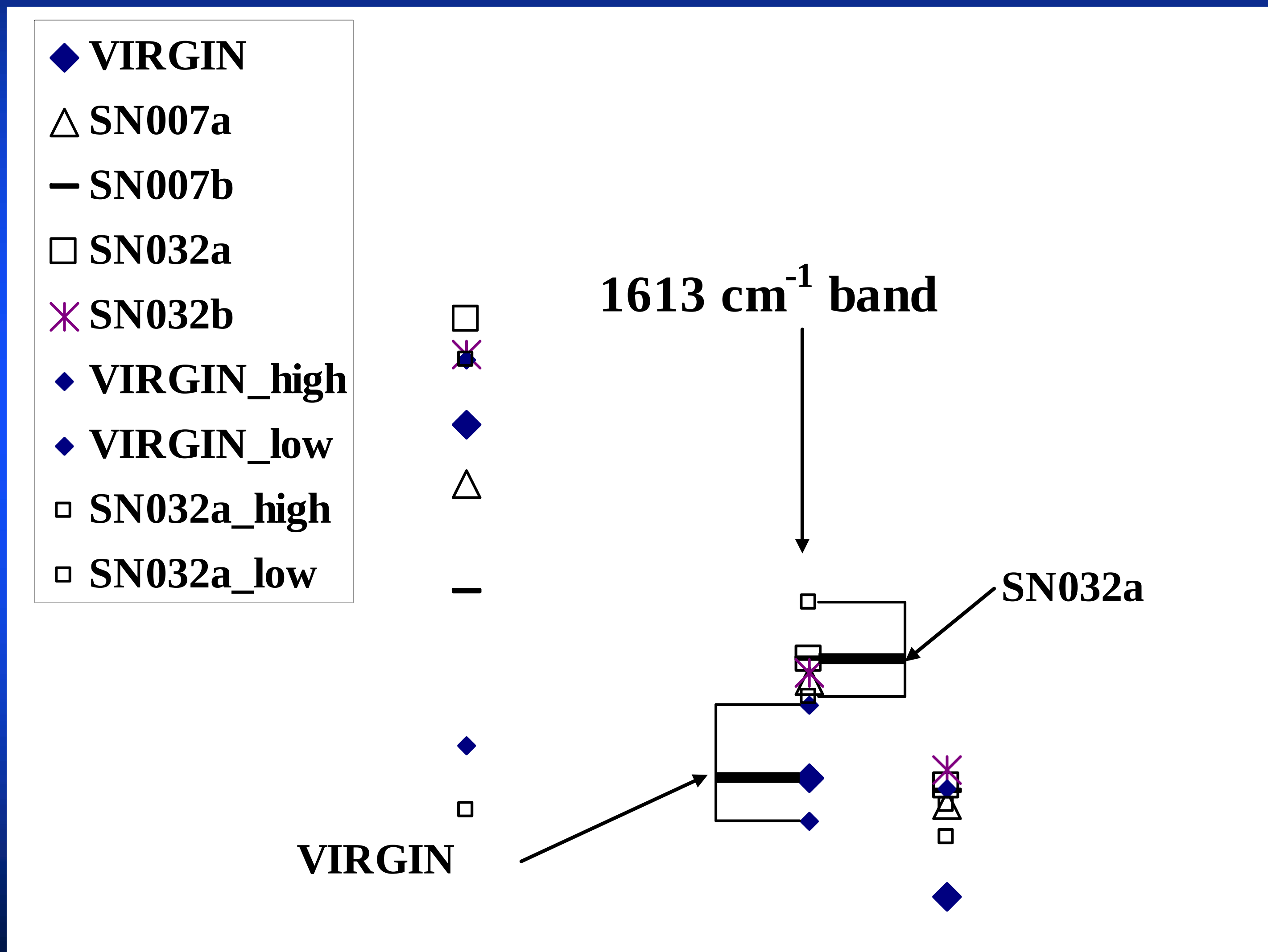
Intensity Variations (relative to 1278 cm^{-1}) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength



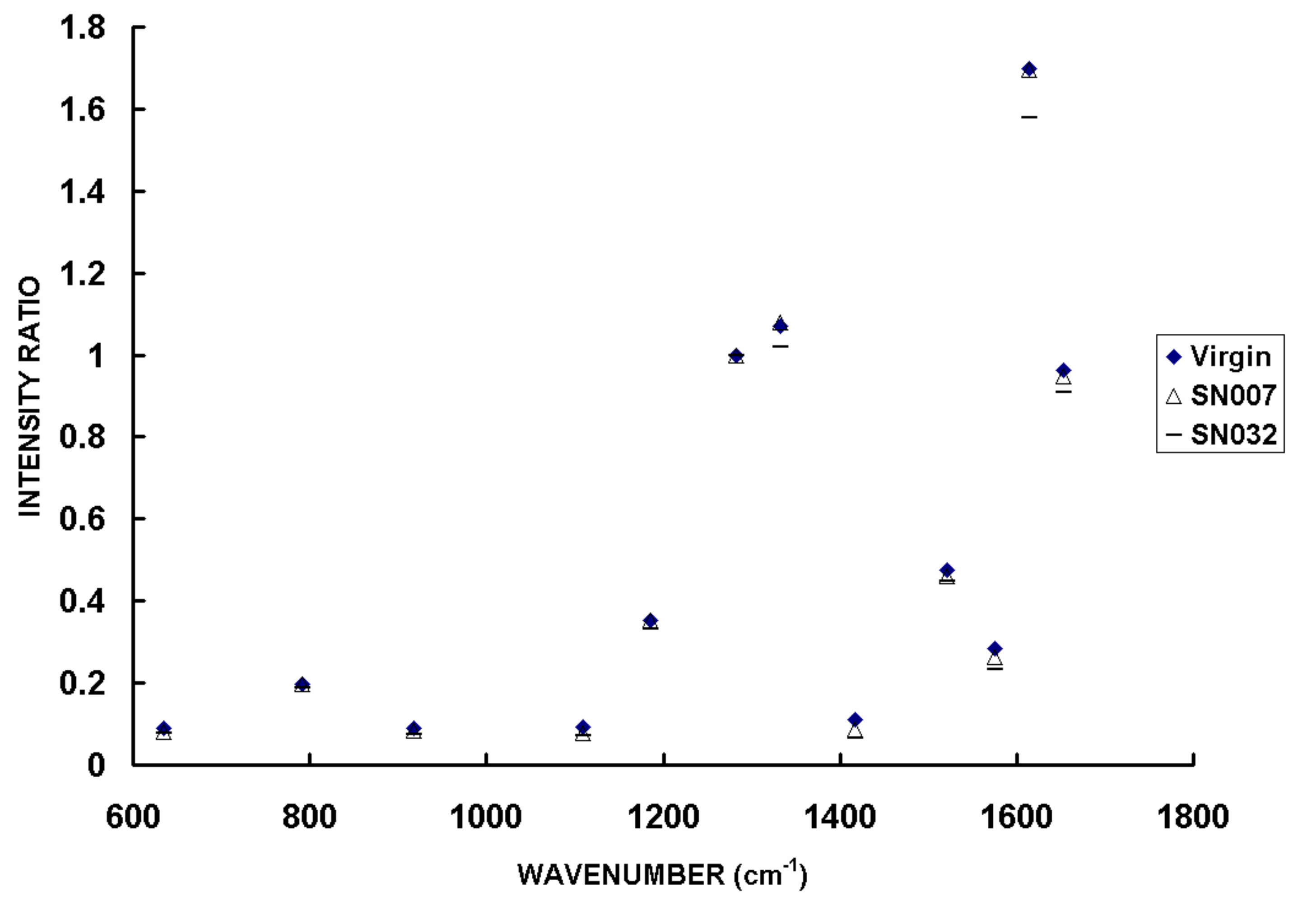
FWHM (relative to 1278 cm^{-1}) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength



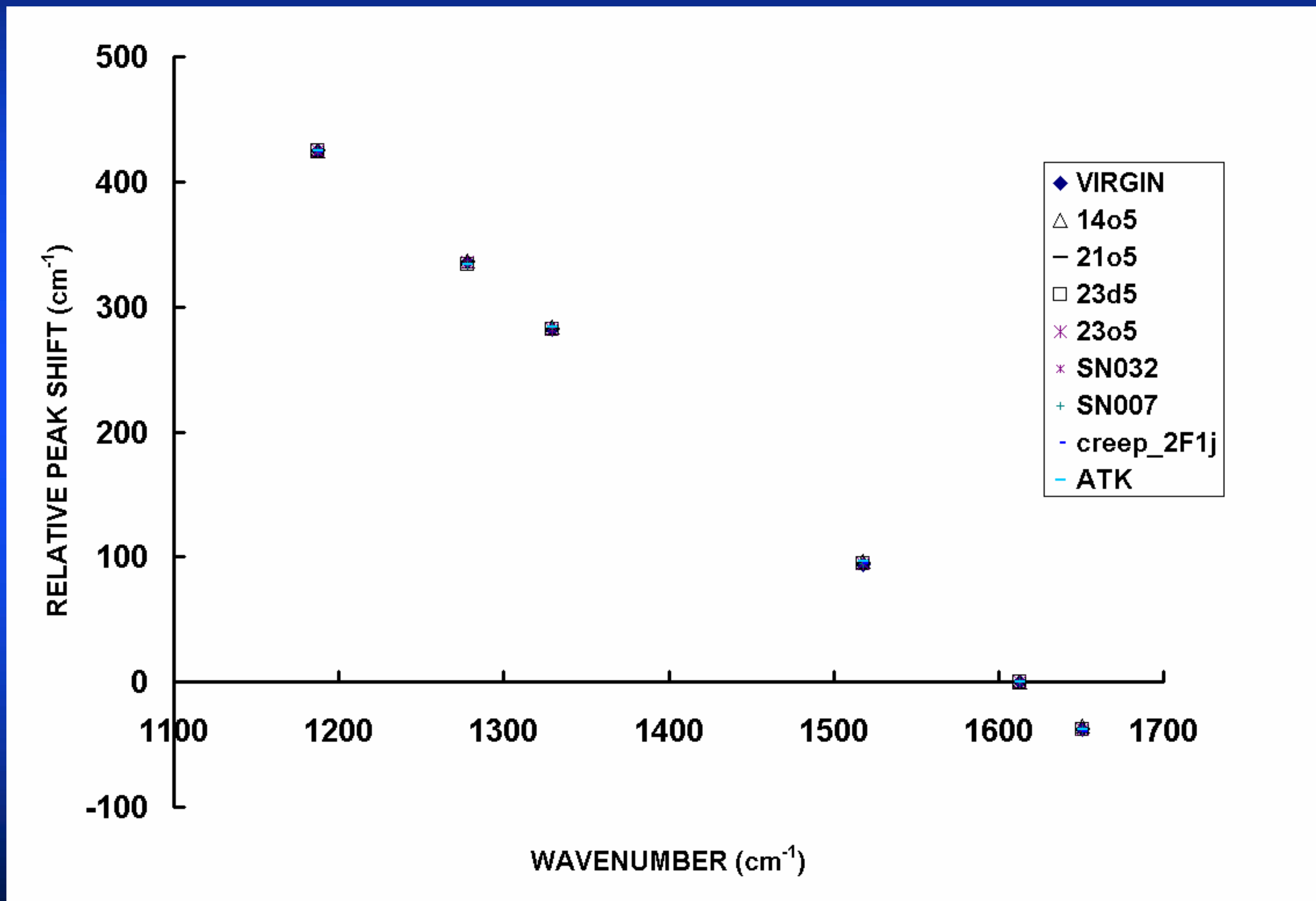
FWHM (relative to 1278 cm^{-1}) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength



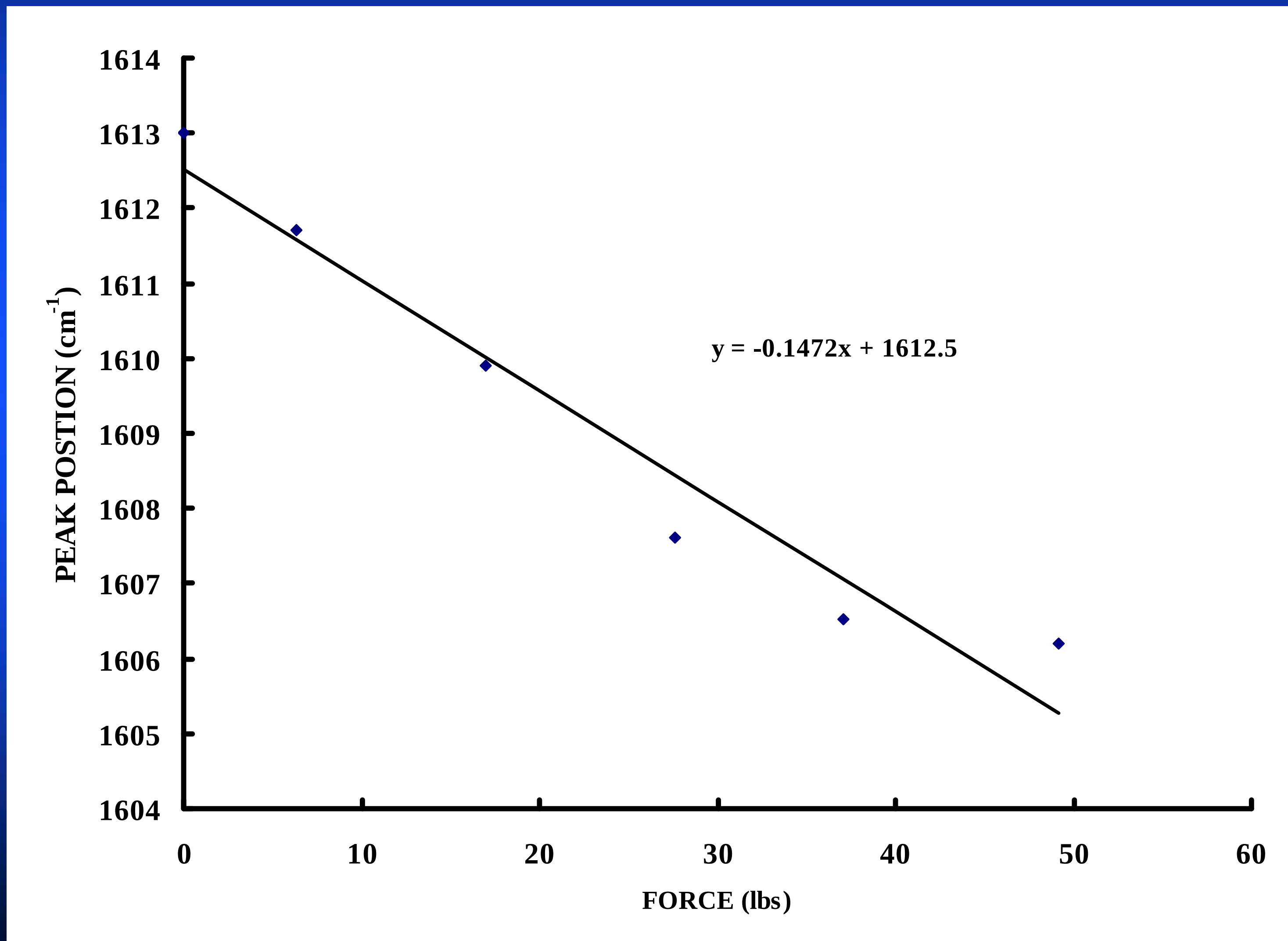
FT Results – Fleet Leader



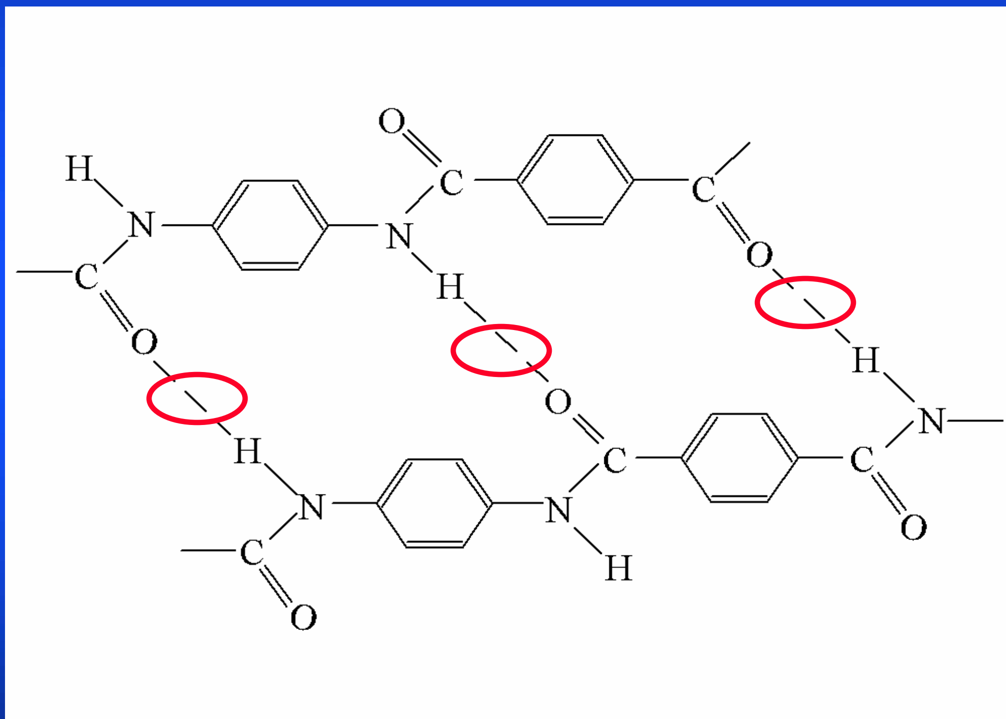
Peak shifts for all strand specimens



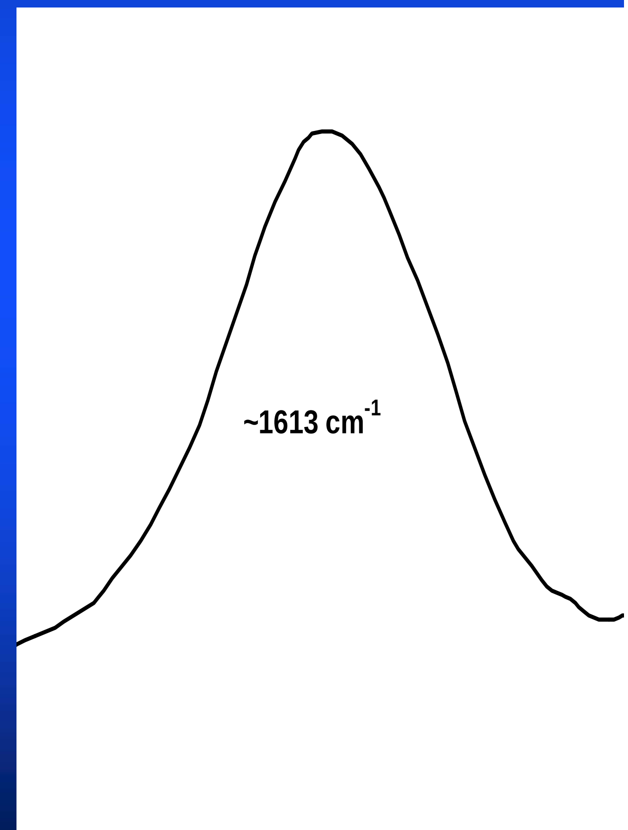
1613 cm^{-1} Peak Shift with Applied Force, 647 nm



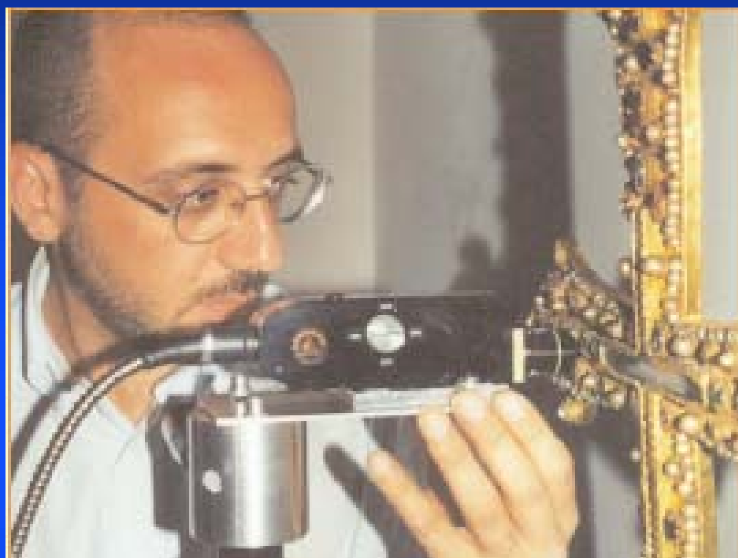
Defects in molecular structure -perhaps for hydrogen bonds



Chemical Structure of Kevlar



Fiber Optic Raman Systems



Renishaw

Avalon Inst.

The laser beam is directed through a fiber optic probe which can be taken out in the field for measurements

Summary

- Raman spectroscopy is being explored as an NDE technique to predict the onset of stress rupture in Kevlar composite materials
- Test aged Kevlar strands to discover trends in the Raman response
- Strength reduction in Kevlar polymer will manifest itself on the Raman spectra

Conclusions

Raman spectroscopy has shown

- Relative changes in the intensity and FWHM of the ~1613 cm^{-1} peak
  - Reduction in relative intensity for creep, fleet leader, and SIM specimens compared to the virgin strands
  - Increase in FWHM has been observed for the creep and fleet leader specimens compared to the virgin strands
  - Changes in the Raman spectra may result from redistributing loads within the material due to the disruption of hydrogen bonding between crystallites or defects in the crystallites from aging the Kevlar strands
- Peak shifting has not been observed to date. Analysis is ongoing……
- Stress measurements may provide a tool in the short term

Questions?

MISSOURI

Thank You