EXPLORING THE ROLE OF DYNAMICS IN THE BAROCALORIC NATURE OF SPIN CROSSOVER COMPOUNDS

14/02/24 PULKIT PRAKASH

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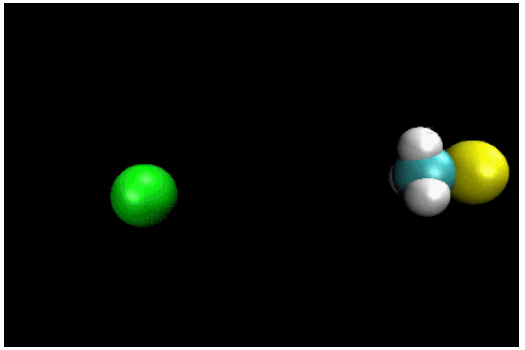
PHD AND POSTDOC DAYS

OUTLINE:

1. Introduction
2. Temperature dependence of Raman and Infrared spectra
3. Pressure dependence of Raman and Infrared spectra
4. Comparison between Raman and Infrared spectra
5. Future Work

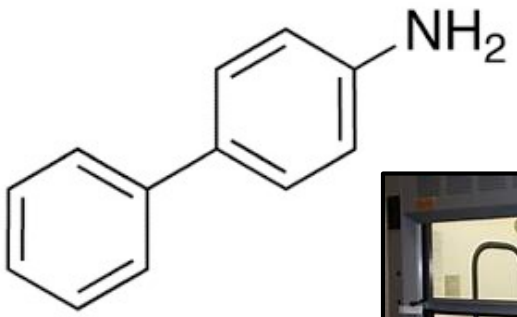
INTRODUCTION

Chemical synthesis route !

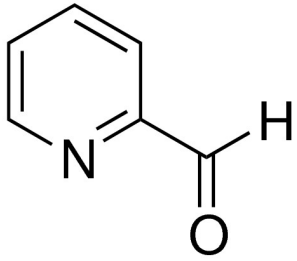


Compound: $[Fe(Pm\text{-}BiA)_2(NCS)_2]$

4-aminobiphenyl

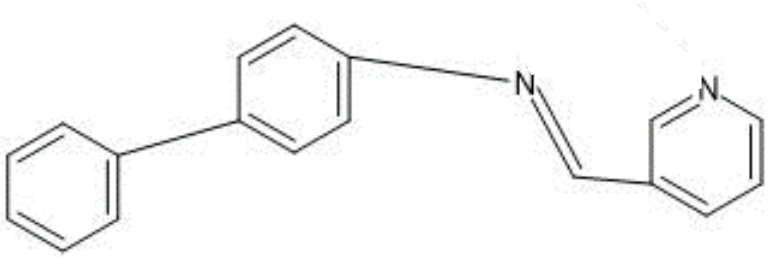


+

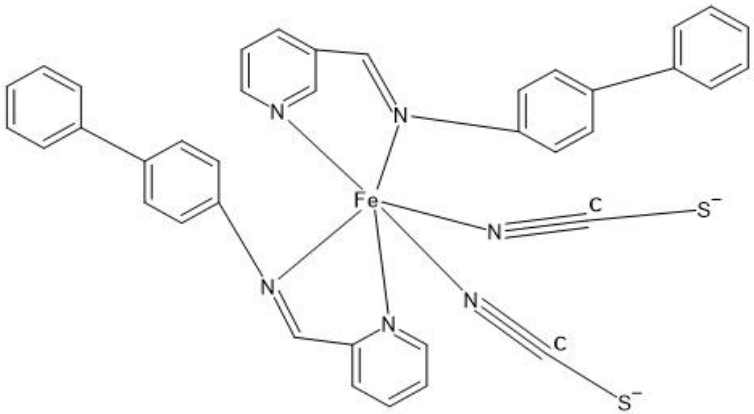


Pyridin-2-aldehyde

Schlenk line



N-(2-pyridylmethylene)-4-aminobiphenyl



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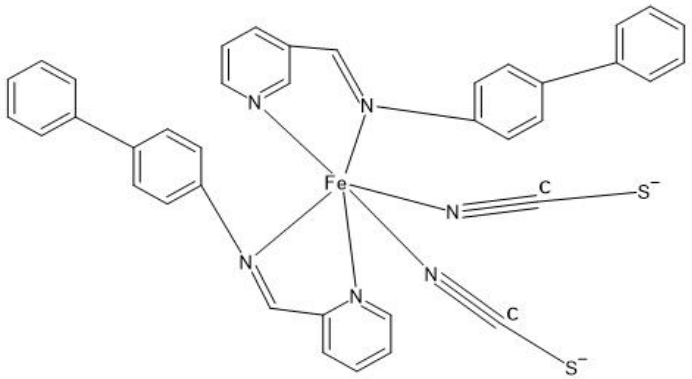
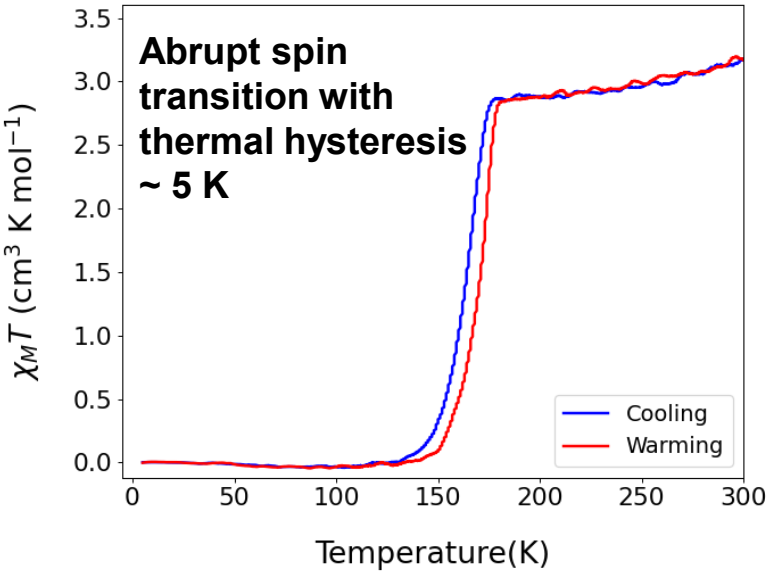
ABRUPT AND GRADUAL SCO BEHAVIOR

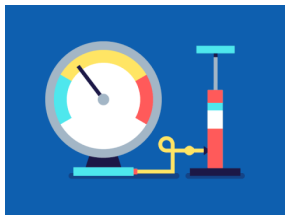


Orthorhombic
Pccn

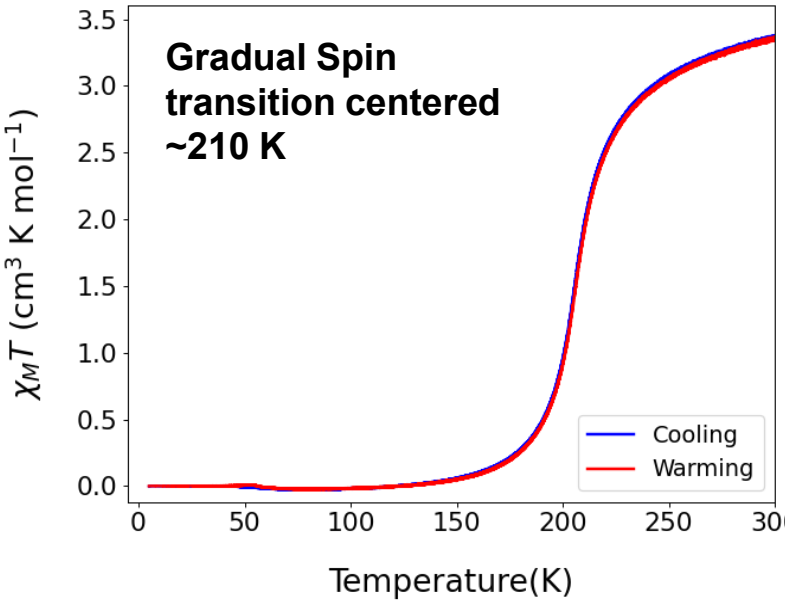
Monoclinic
P2$_1$/c



Pressure

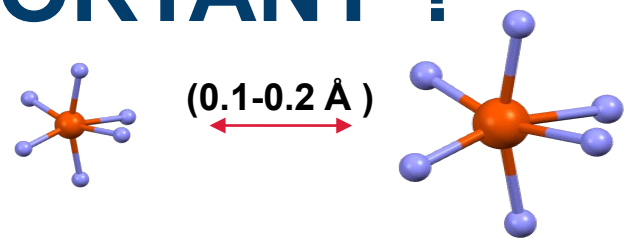


Temperature **Light**

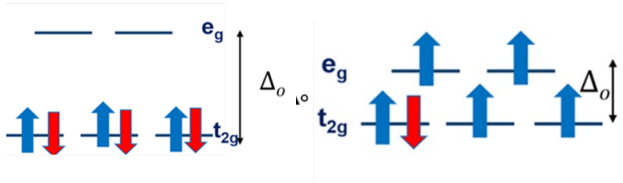


H. Shahed et al. *Acta Crystallogr. Sec. B* 2023.

WHY STUDYING PHONONS IS IMPORTANT ?



SCO an Entropy driven process



LS
S = 0
Diamagnetic

HS
S = 2
Paramagnetic

ΔS_{ele}
$K_B \ln(\mathcal{S})$= 13.5 J mol^{-1} K^{-1}

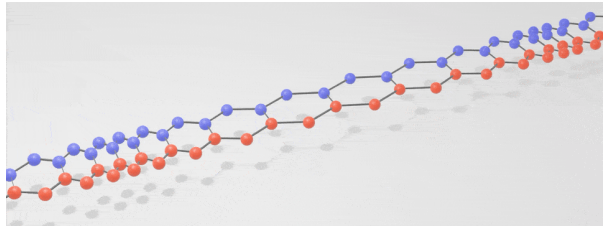
ΔS_{TOT}

ΔS_{vib}

)30-80 J mol^{-1} K^{-1}
(70% of ΔS_{TOT})

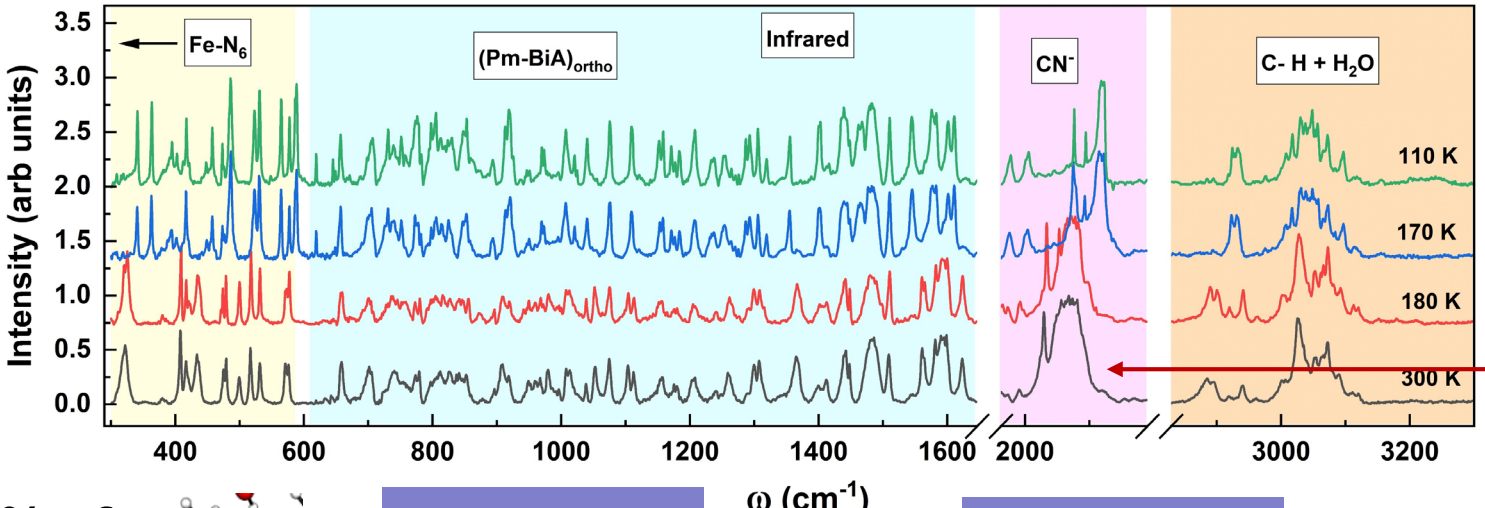
ΔS_{conf}
Negligible contribution ?

ΔS_{rot}
Negligible contribution ?

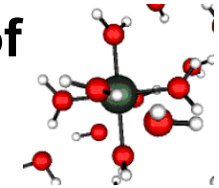


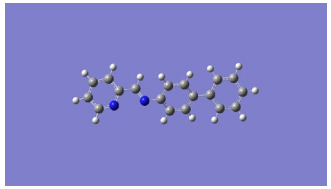
HOW WOULD A SPECTRA LOOK LIKE ?

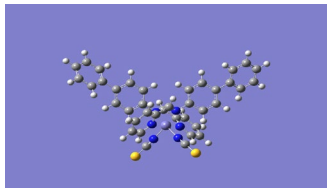
Orthorhombic:
(*Pccn* #56)
(D_{2h})
335
450



70% of ΔS_{vib}

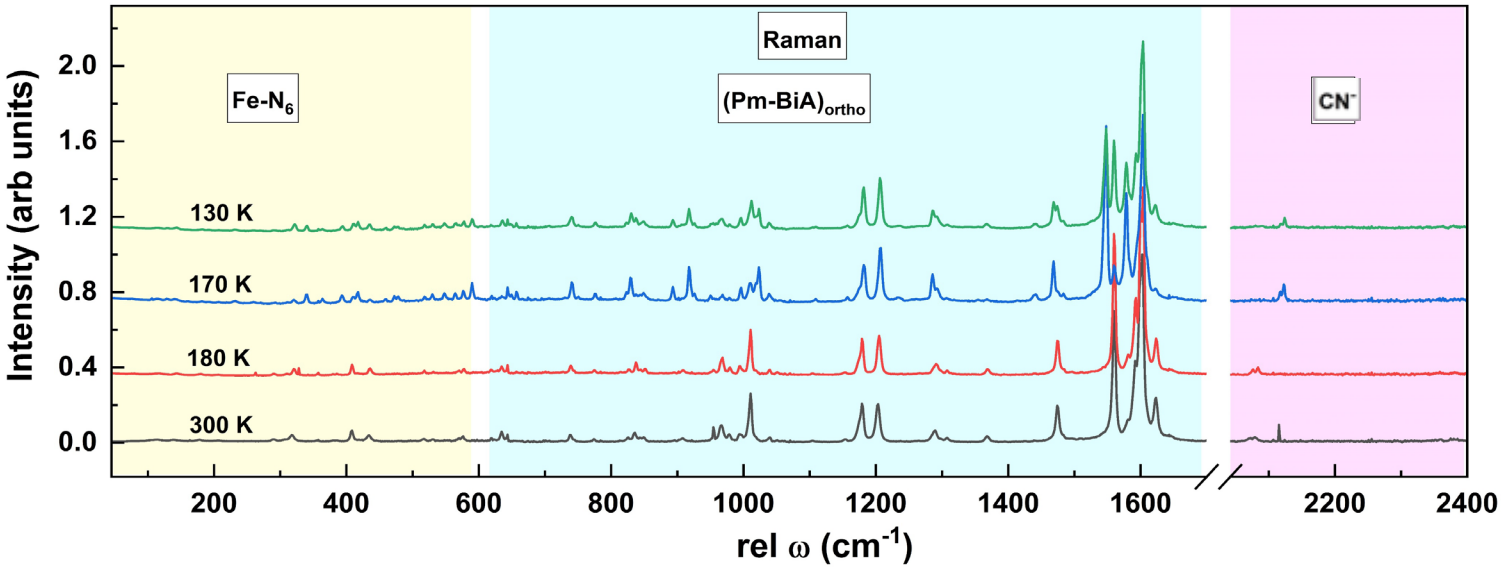






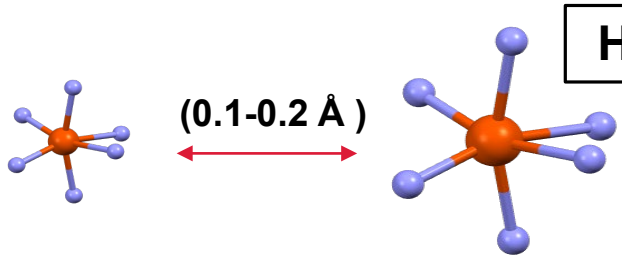
Marker Bands

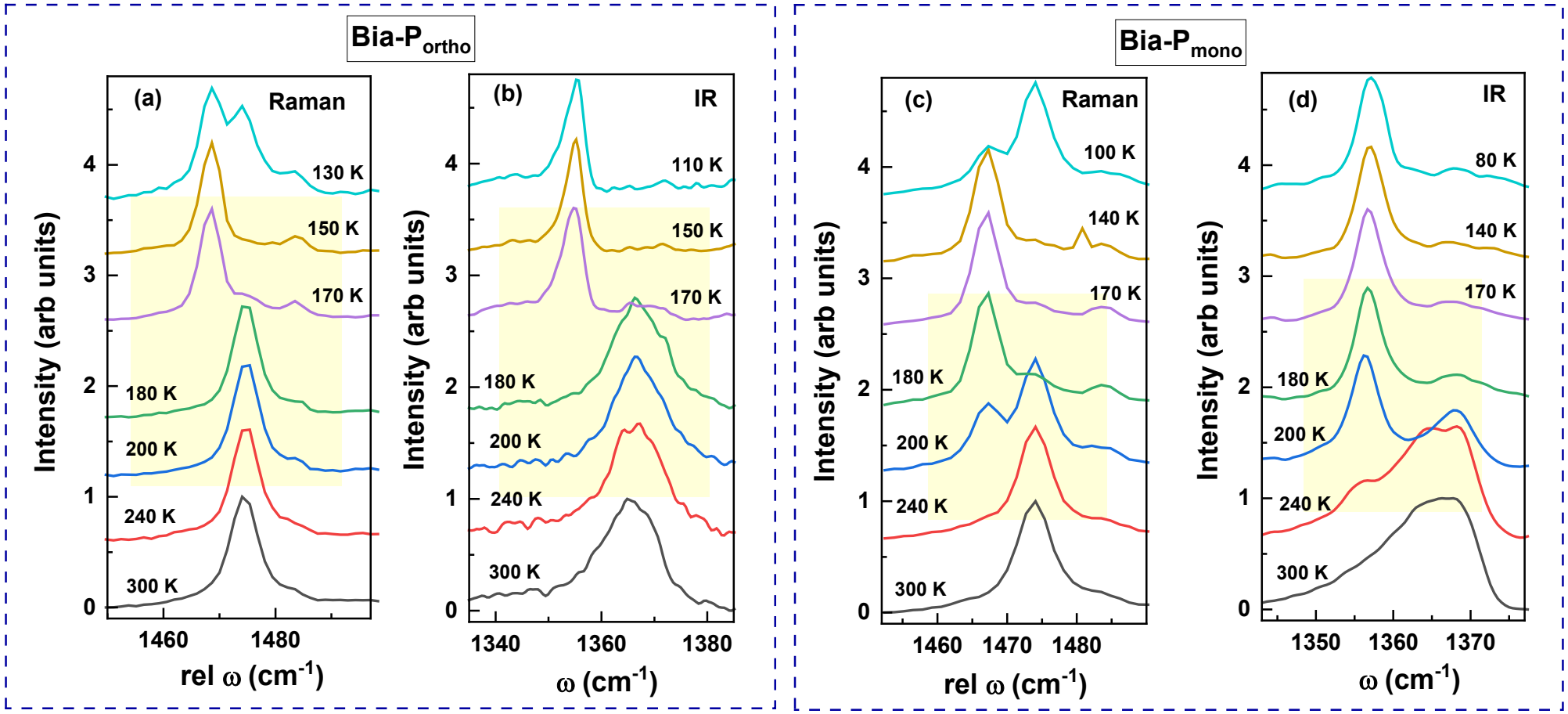
Monoclinic:
(*P*2_1/*c* #14)
(C_{2h})
513
516



TEMPERATURE DEPENDENCE

Comparison between Raman and Infrared





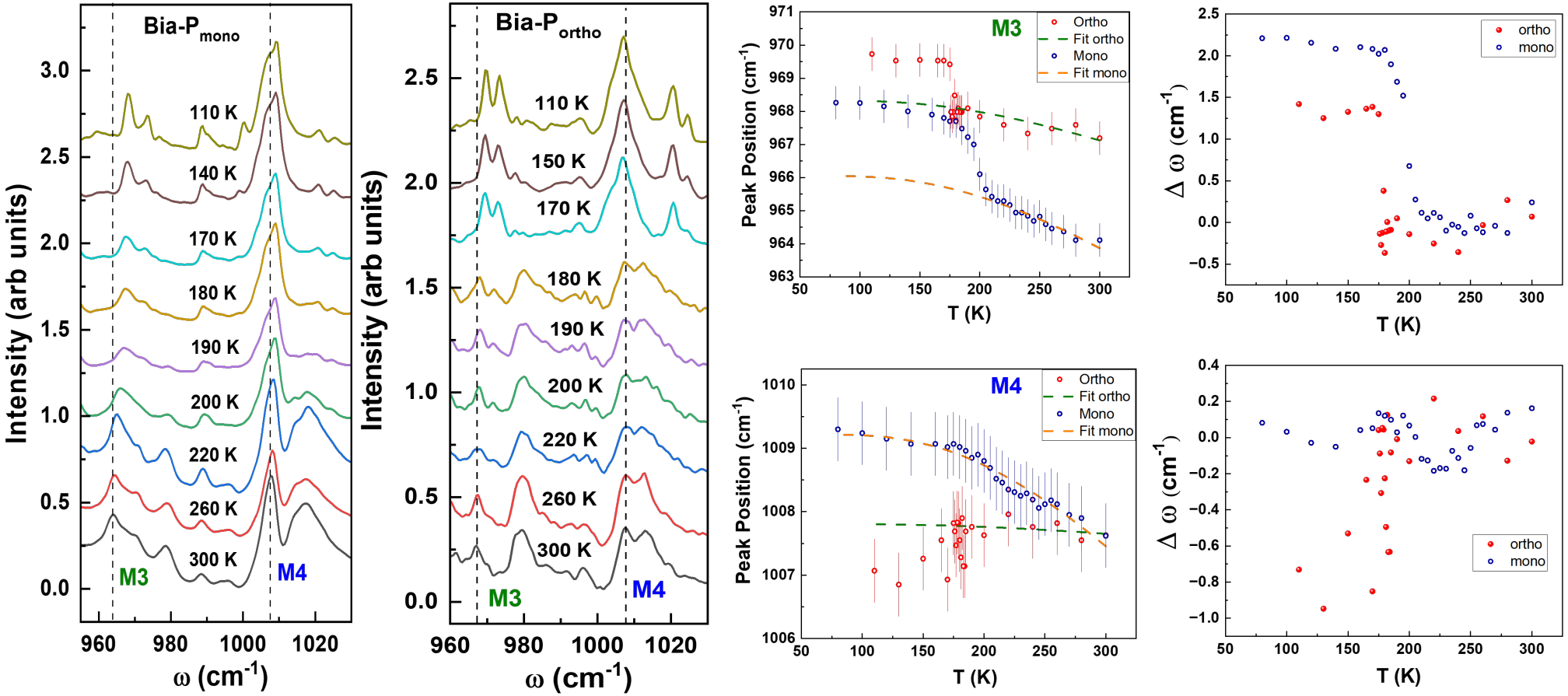
Abrupt Change in Phonon Modes

Gradual Change in Phonon Modes

Softening in Phonon Modes

TEMPERATURE DEPENDENCE

Infrared



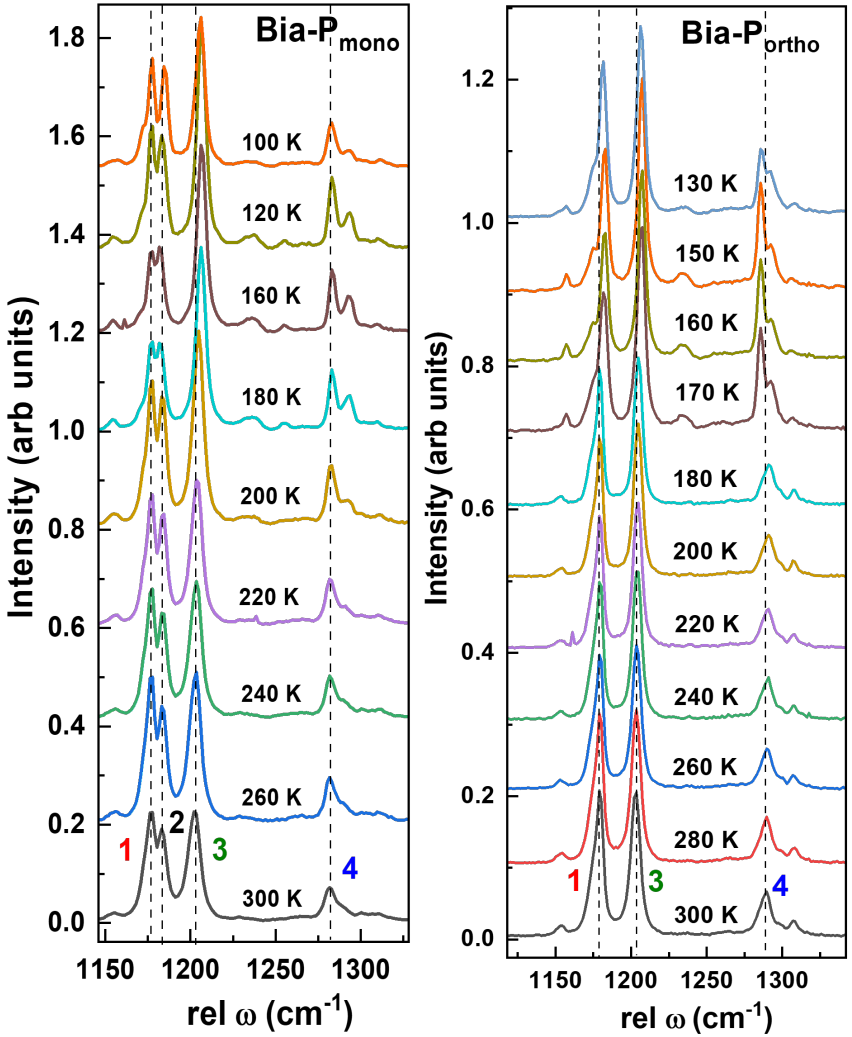
Stark contrast in the behavior of phonon modes associated with ligands

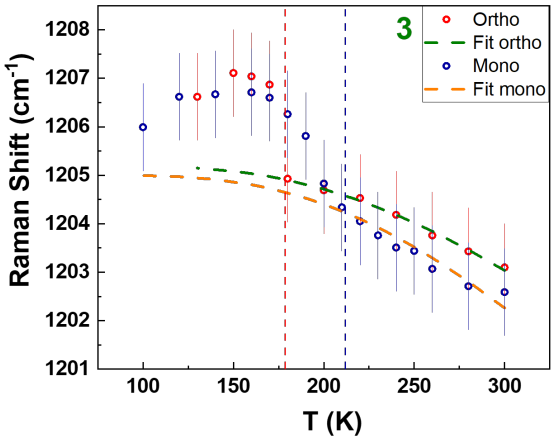
Anharmonic phonon-phonon scattering:

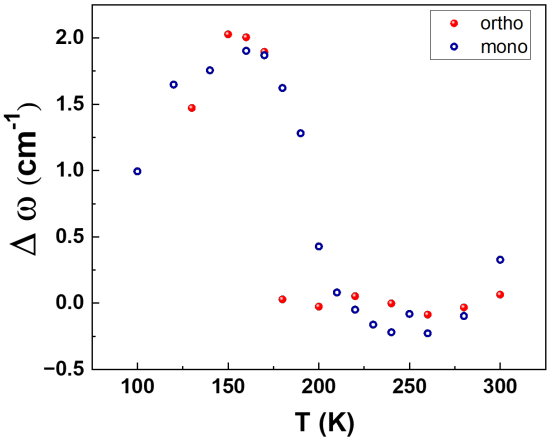
$$\omega(T) = \omega_0 - C\left(1 + \left(\frac{2}{e^{\frac{\hbar\omega_0}{2k_BT}} - 1}\right)\right)$$

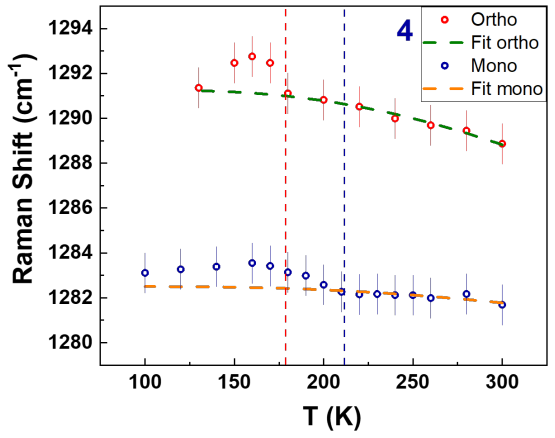
TEMPERATURE DEPENDENCE

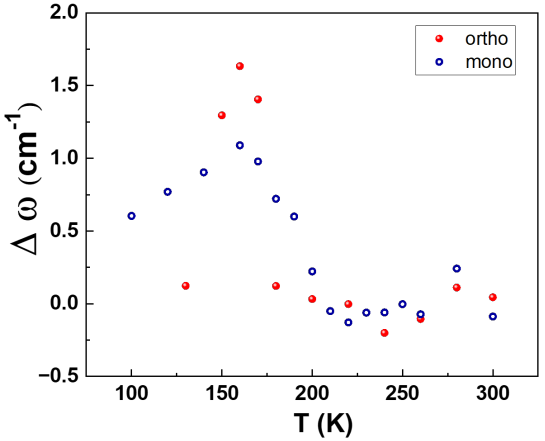
Raman









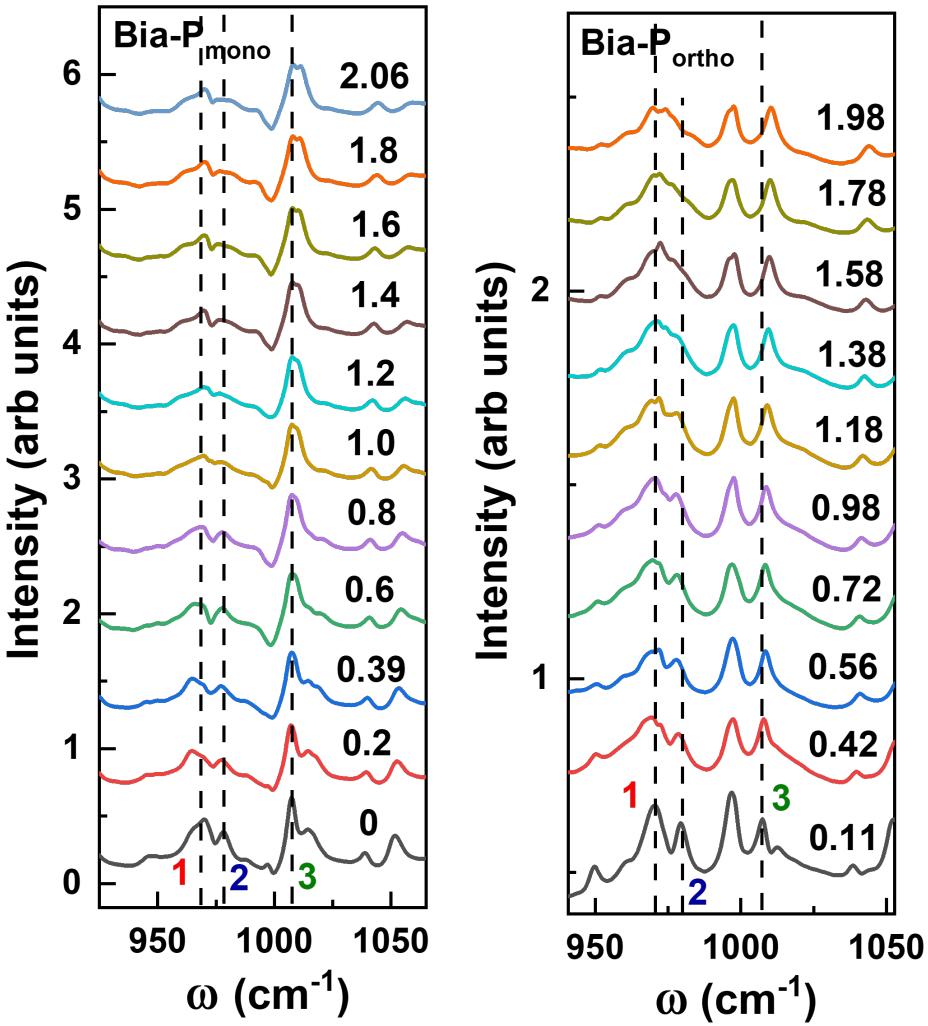


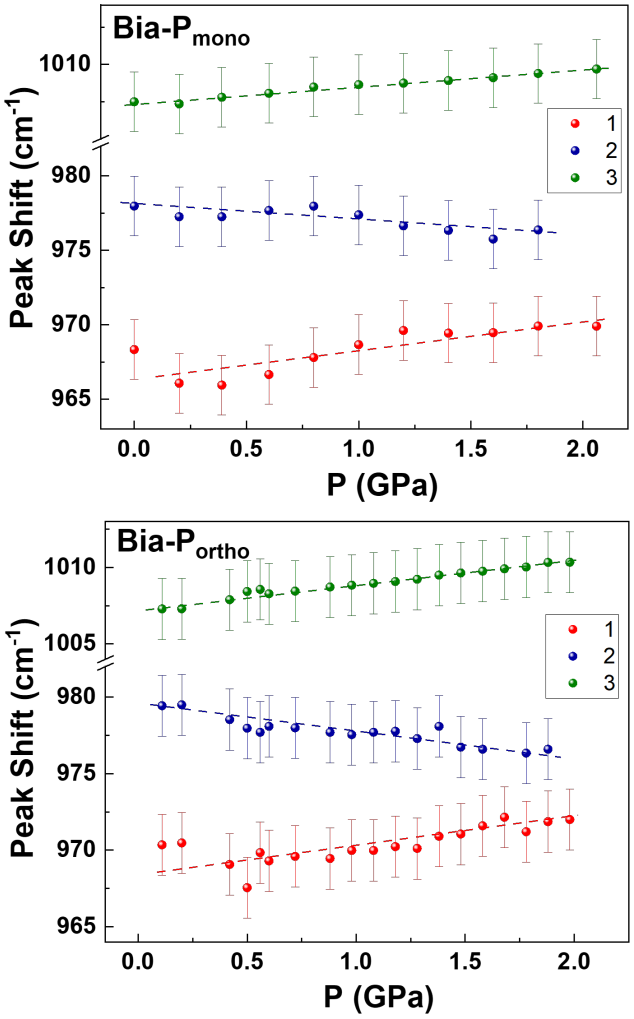
Stark contrast between phonon modes

LIESST effect at lowest T

PRESSURE DEPENDENCE

Evolution of Phonon modes in Infrared

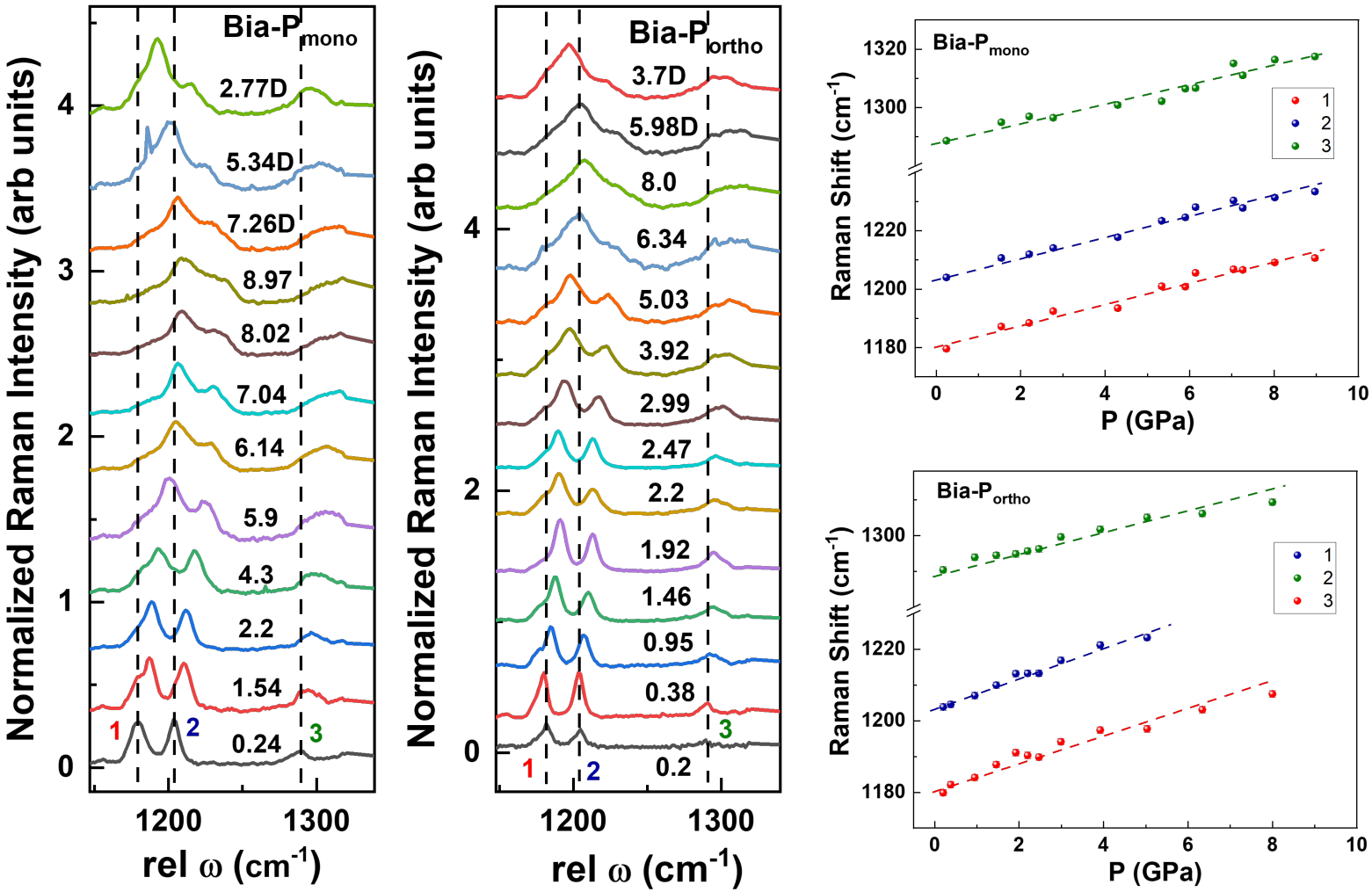




- Negative Grüneisen parameter for some phonon modes.
- With pressure even though modes associated with ligands change to the values of LS, no spin-transition is observed for Bia-P_{ortho}

PRESSURE DEPENDENCE

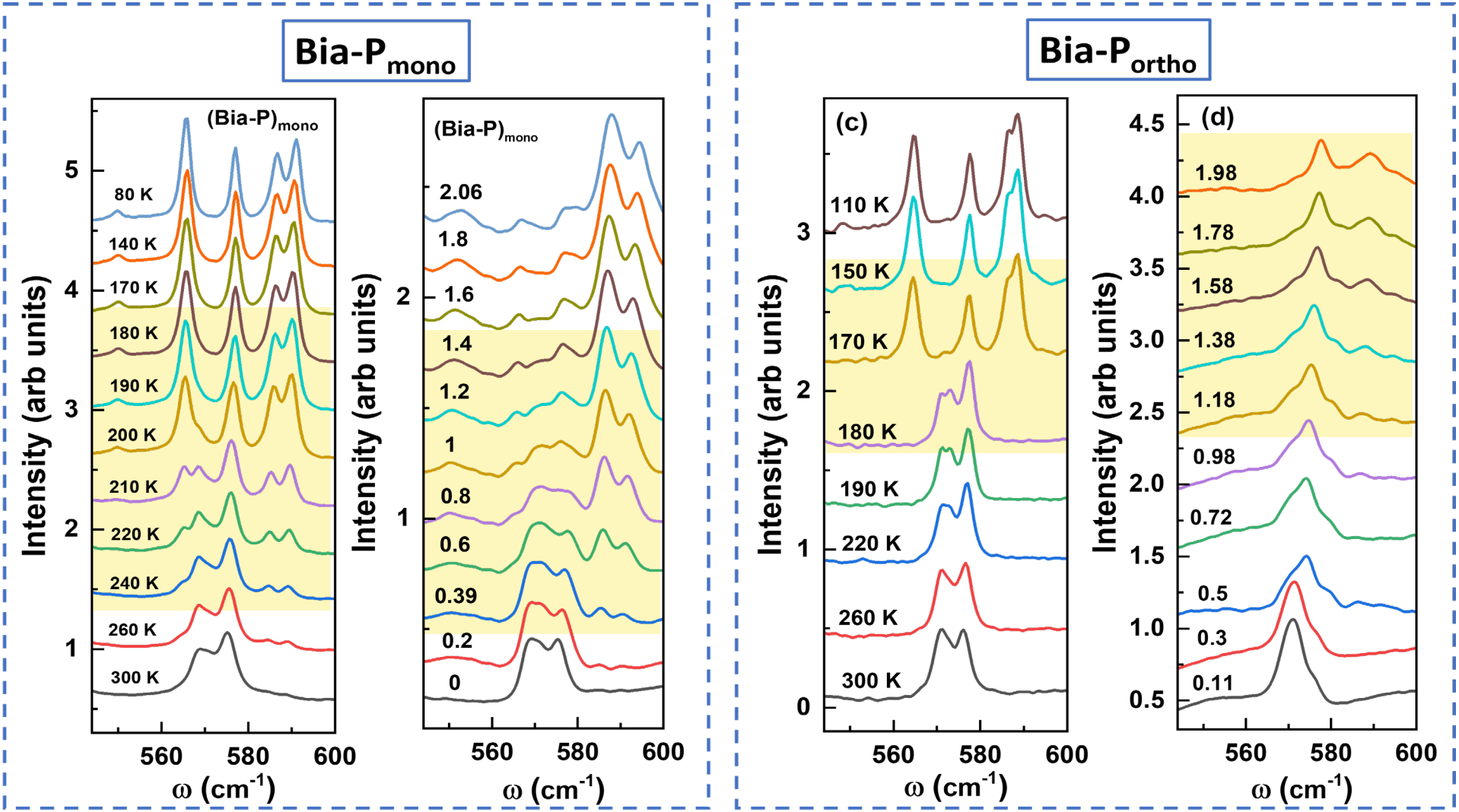
Evolution of Phonon modes in Raman



- With decompression most phonon modes in both the polymorphs return to their ambient state.
- No LIESST effect observed for the samples in the LS state, induced by pressure.

PRESSURE DEPENDENCE

Comparison with temperature for Infrared

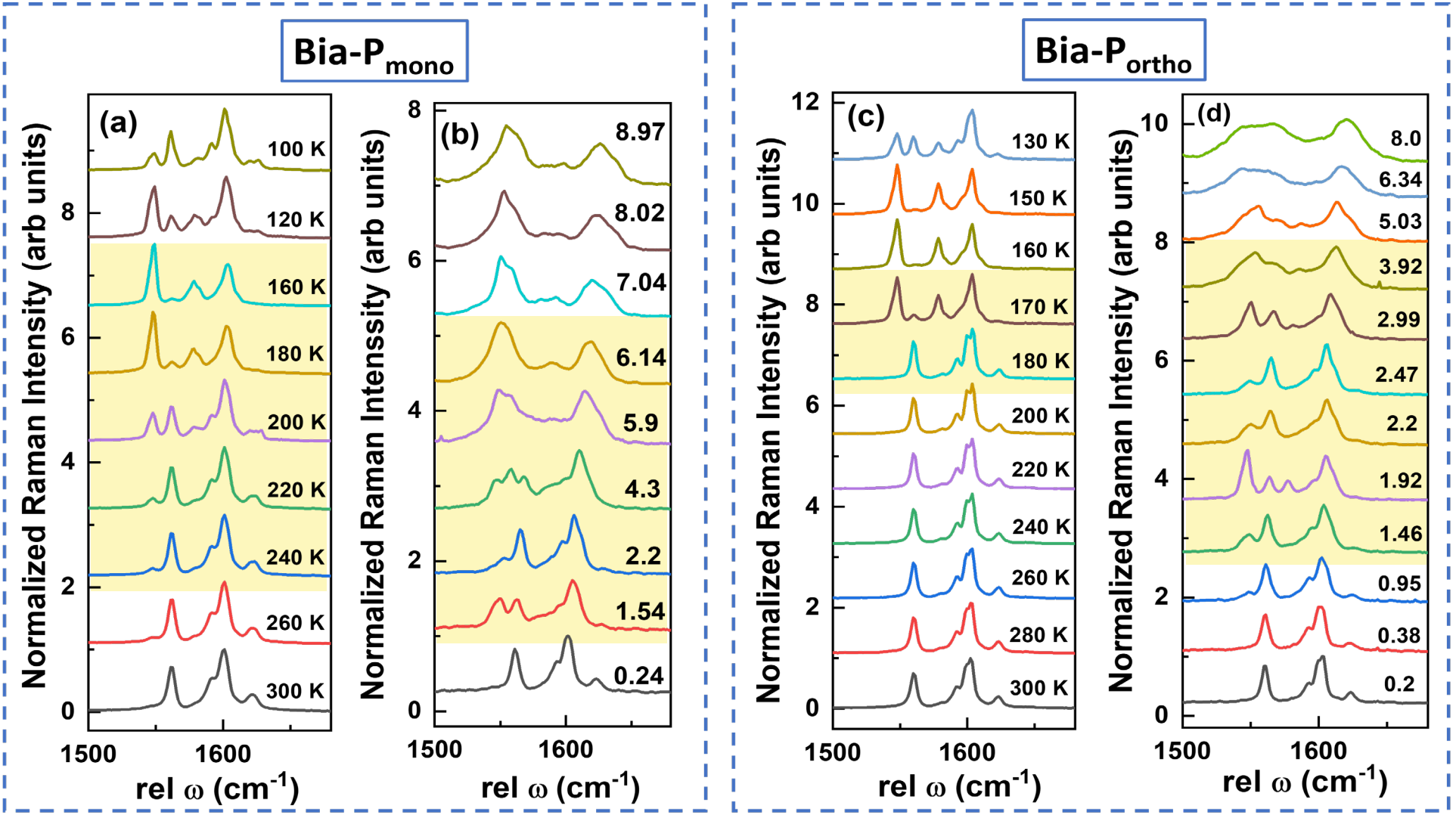


Nearly a full Transition

Partial Transition (superstructure ?)

PRESSURE DEPENDENCE

Comparison with temperature for Raman

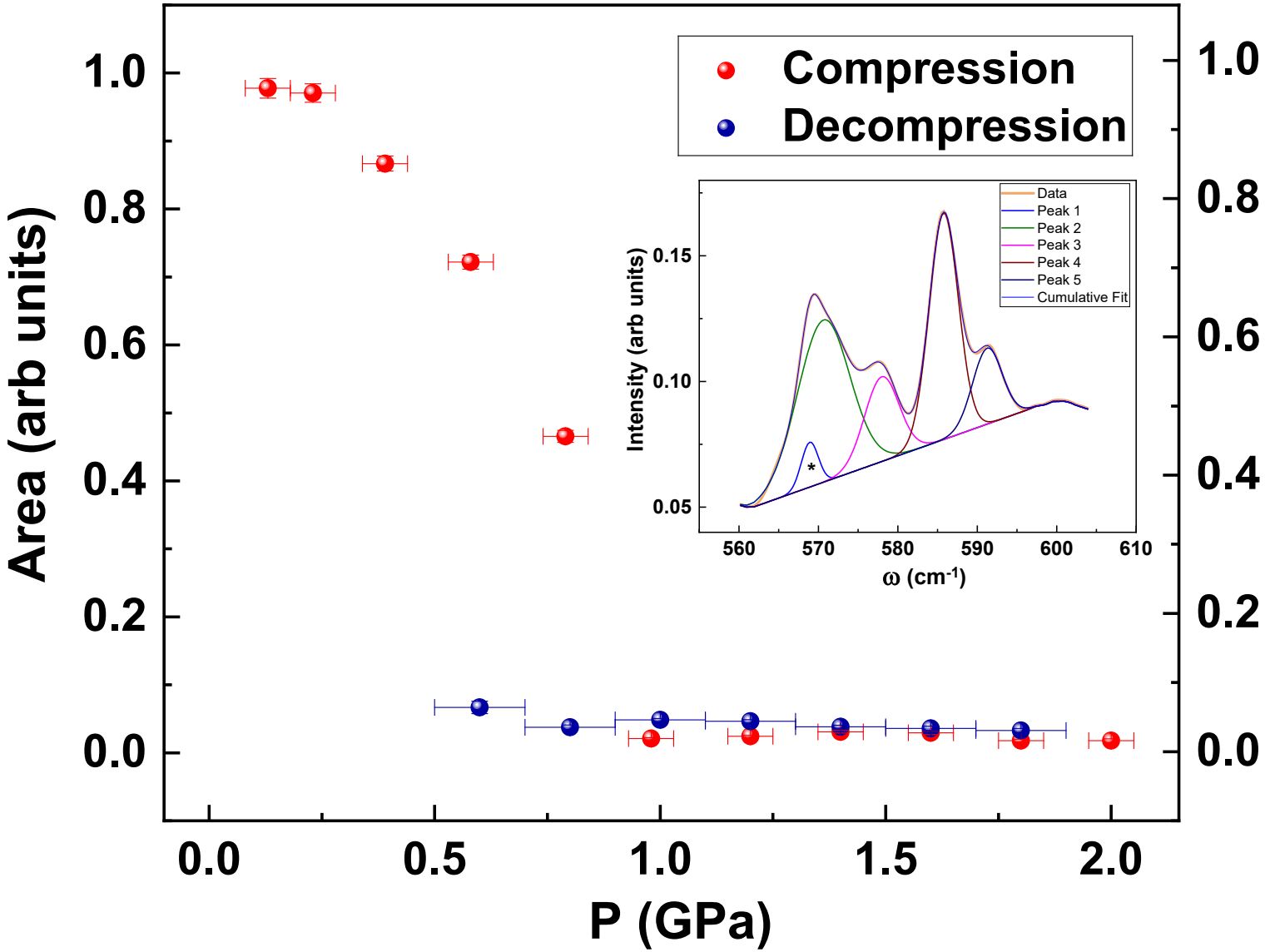


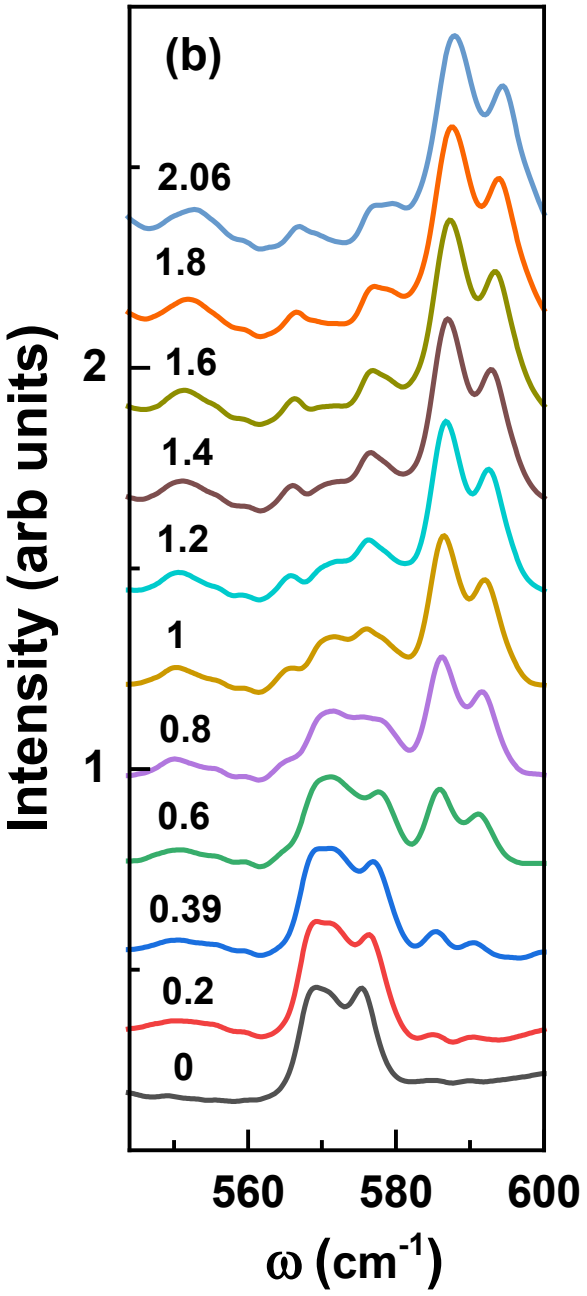
Full Transition in Bia-P$_{mono}$

Partial Transition in Bia-P$_{ortho}$ even at higher pressures

PRESSEURE HYSTERESIS

Bia-P_{mono}





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FUTURE WORK:

Manuscript

Preperation of a manuscript based on the present results under progerss.

DFT

Using SIESTA for first principles calculations and identification of the phonon modes.

Vibrational Entropy:

Pressure evolution of vibrational entropy.

LIESST in IR:

Investigation of LIESST effect by using a laser in an IR setup.

ACKNOWLEDGEMENTS

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Yves-Laurent Mathis

SMIS :

Francesco Capitini

Tasso Springer

Fellowship

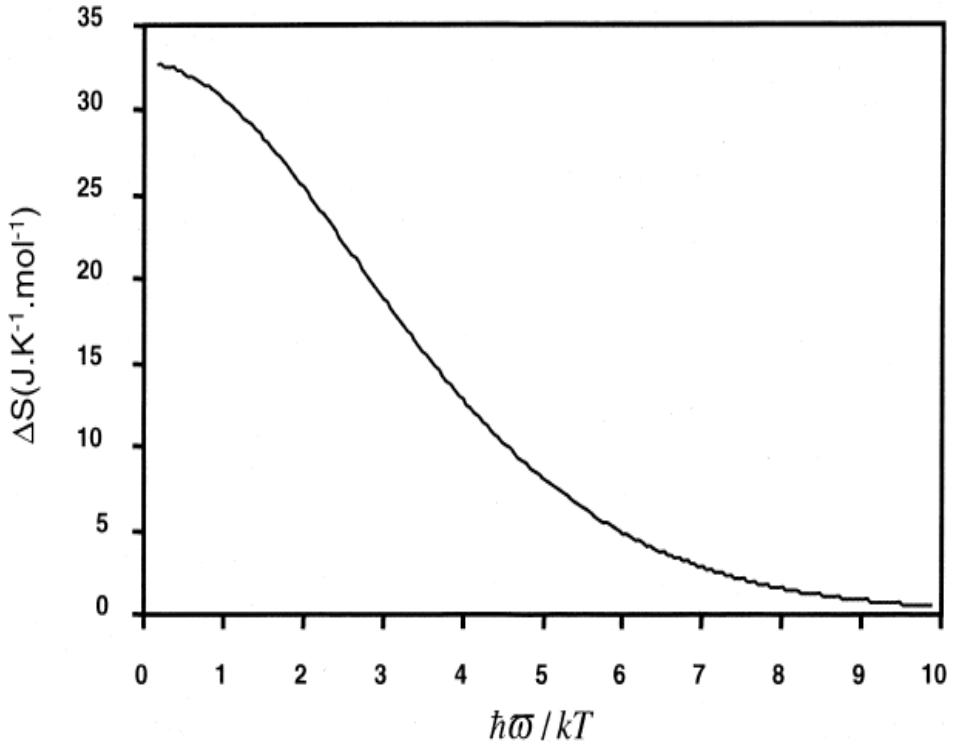
THANK YOU FOR YOUR ATTENTION !

FRAGEN ?

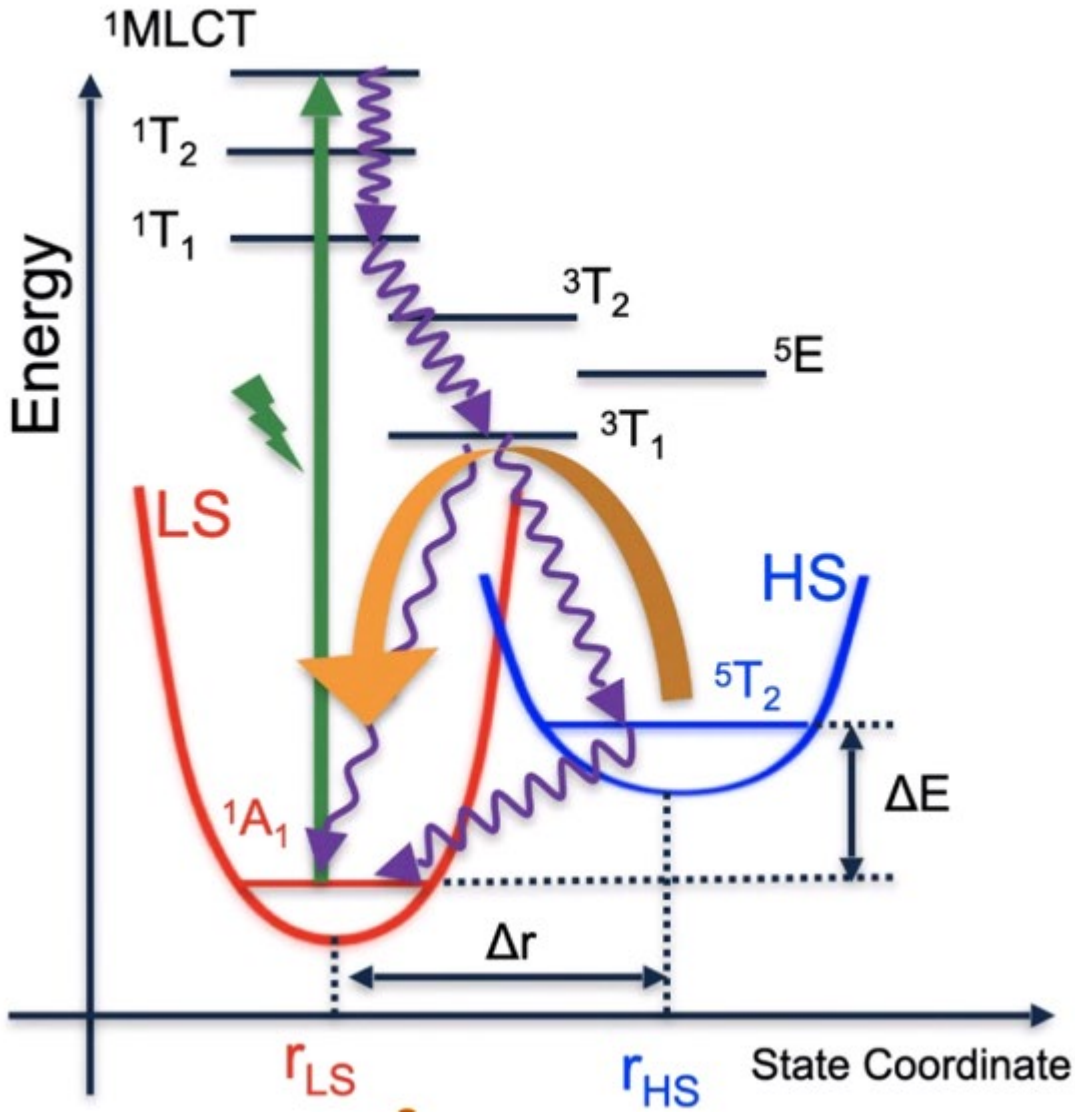
EXTRA SLIDES

VIBRATIONAL CONTRIBUTION TO ENTROPY

-
- =



A. Bousseksou et al. Chemical Physics Letters 318 (2000) 409–416


¹MLCT
¹T₂
¹T₁
³T₂
⁵E
³T₁
Energy
LS
HS
⁵T₂
¹A₁
ΔE
Δr
r_LS
r_HS
State Coordinate

ASSIGN MULLIKEN SYMBOLS

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	h = 4
A_1	Γ_1	1	1	1	1	z
B_1	Γ_2	1	-1	1	-1	x, R_y
B_2	Γ_3	1	-1	-1	1	y, R_x
A_2	Γ_4	1	1	-1	-1	R_z

- Rule 1:

  (Labels)

Dimensionality	Designation
1-D symmetric to principal C_n axis	A
1-D anti-symmetric to principal C_n axis	B
2-D	E
3-D	T

- Rule 2: Subscripts and superscripts

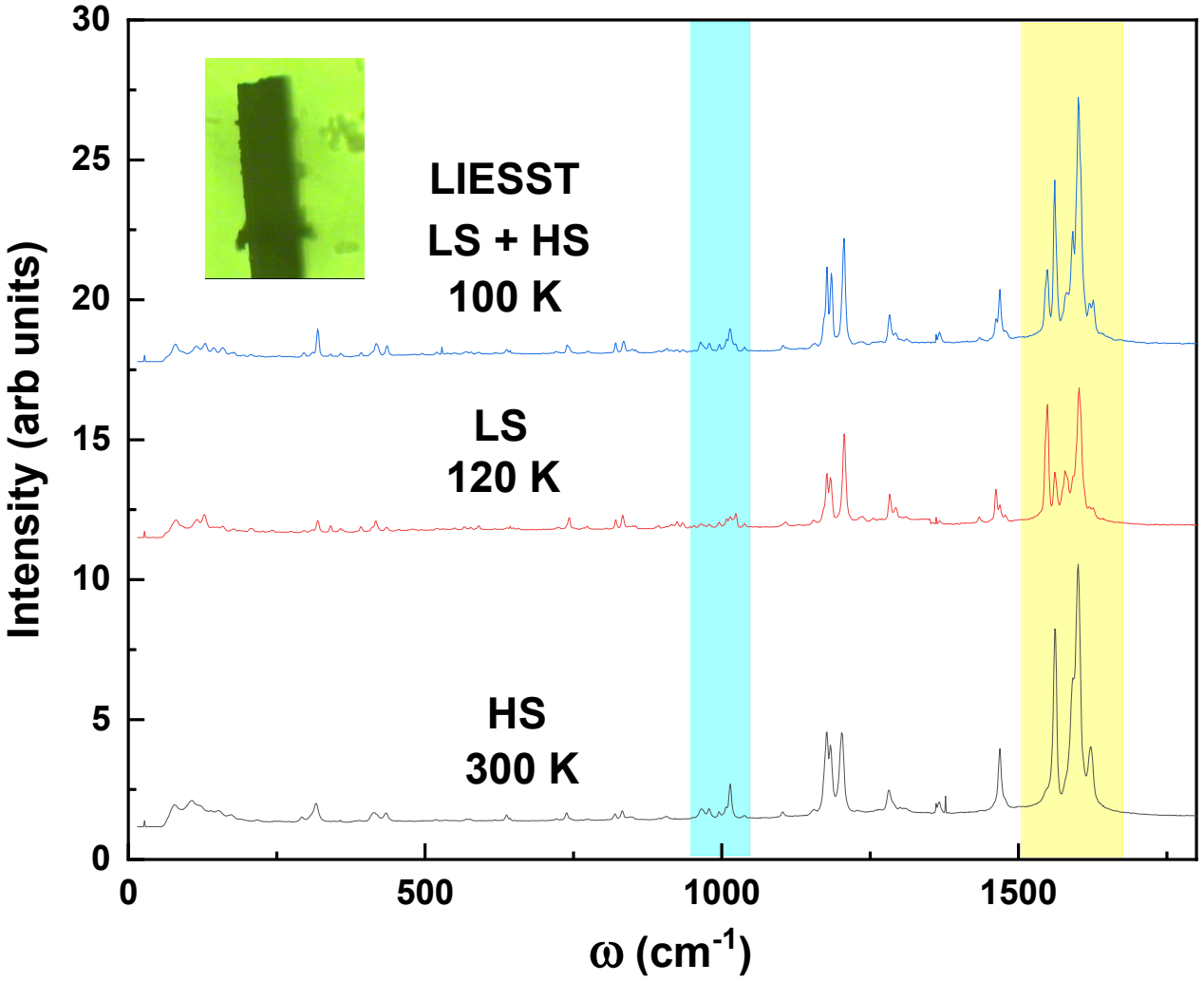
  1 = symmetric to σ_v or C_2; 2 = anti-symmetric to σ_v or C_2 ; g = symmetric to inversion center;

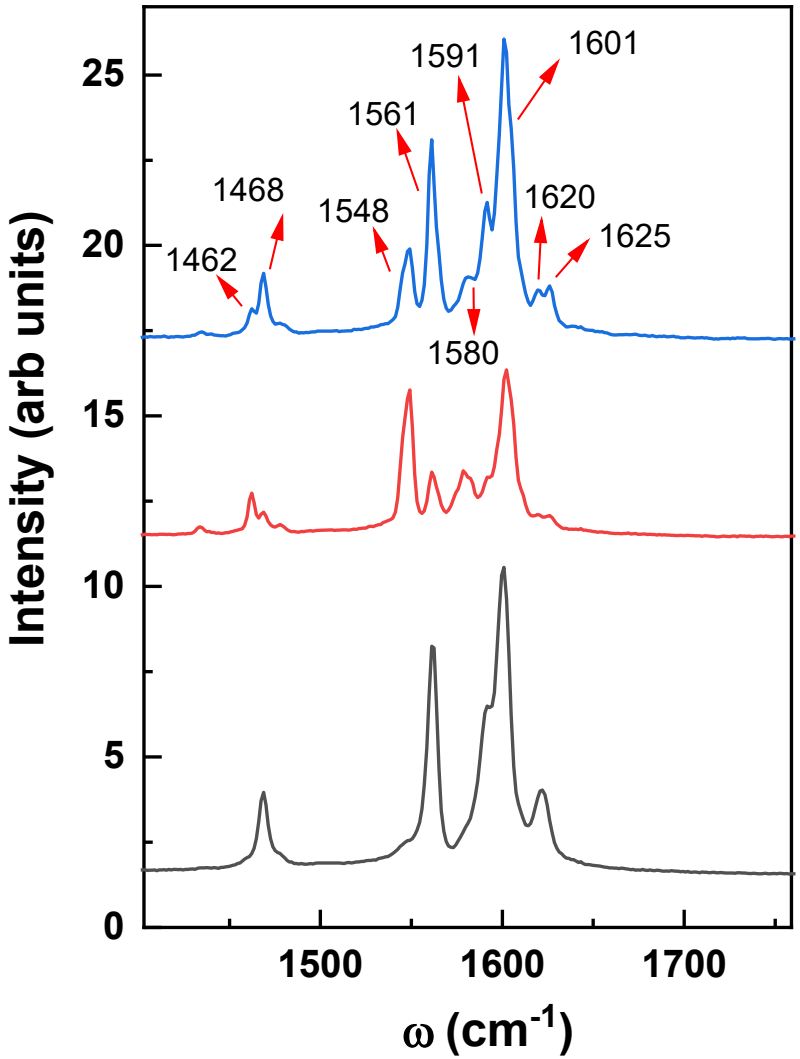
  u = anti-symmetric to inversion center; ‘ = symmetric to σ_h ; “ = anti-symmetric to σ_h

OUTLINE

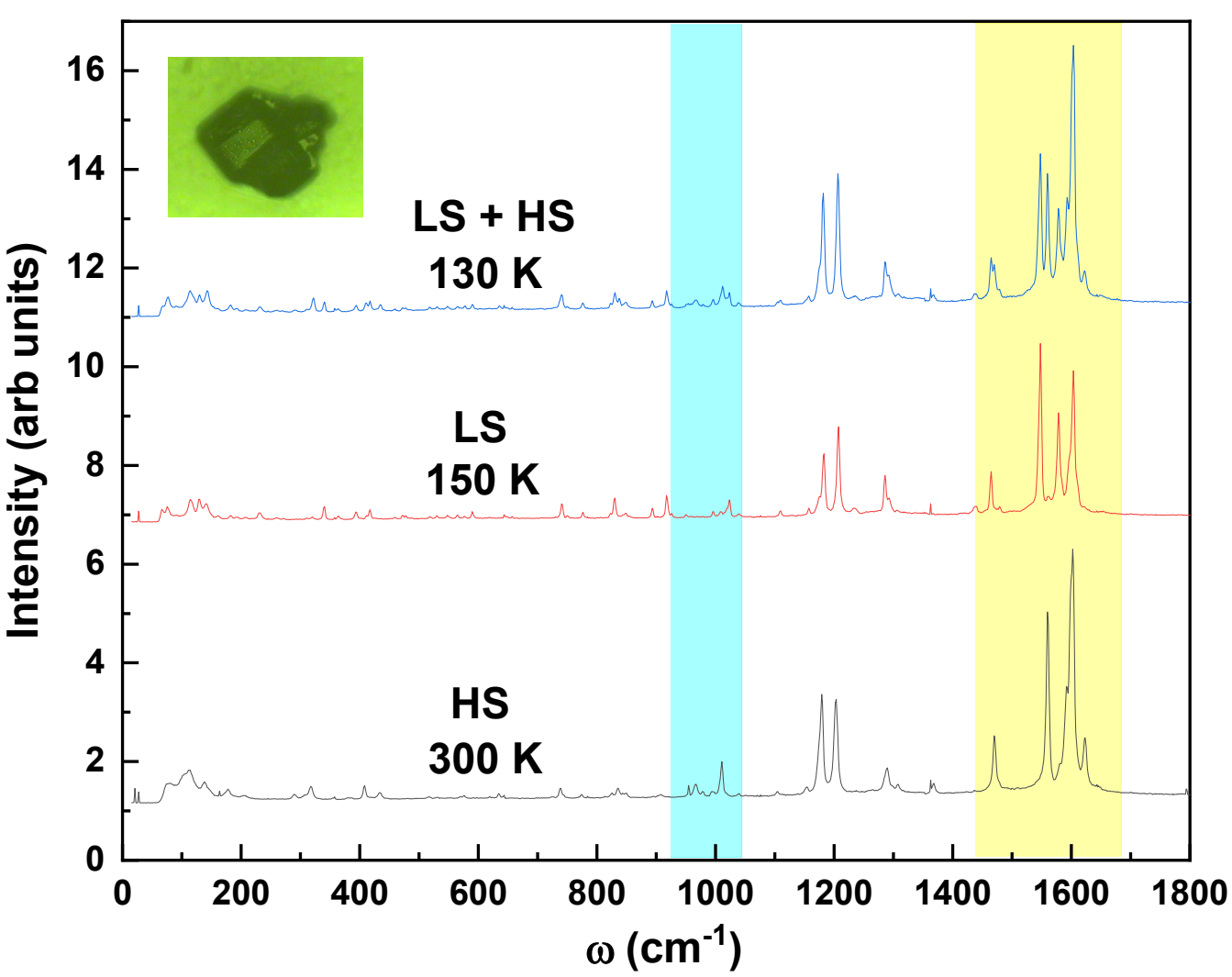
1. Introduction
2. Infrared spectra’s as a function of temperature
3. Infrared spectra’s as a function of pressure
4. Raman spectra as a function of temperature
5. Raman spectra: LIESST effect
6. Future Work

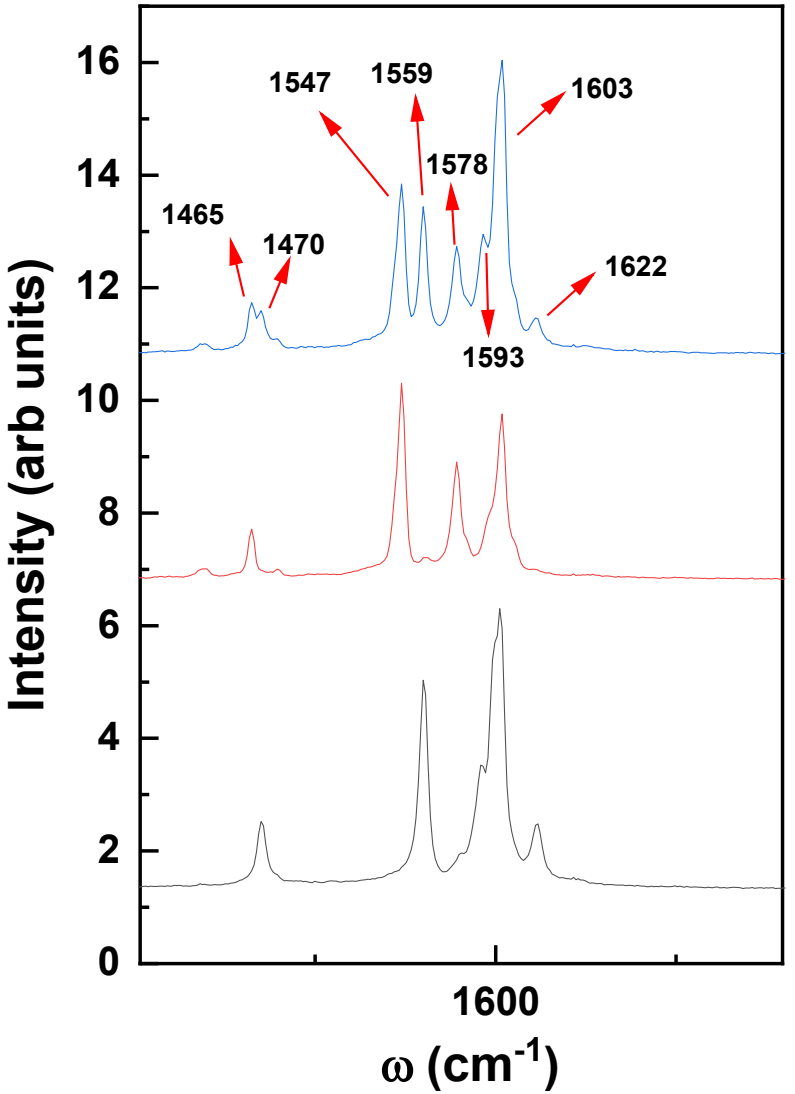
MONO


LIESST
LS + HS
100 K
LS
120 K
HS
300 K
Intensity (arb units)
ω (cm-1)
0
5
10
15
20
25
30
0
500
1000
1500


1462
1468
1548
1561
1580
1591
1601
1620
1625
Intensity (arb units)
ω (cm-1)
0
5
10
15
20
25
1500
1600
1700

ORTHO


LS + HS
130 K
LS
150 K
HS
300 K
Intensity (arb units)
ω (cm-1)
0
2
4
6
8
10
12
14
16
0
200
400
600
800
1000
1200
1400
1600
1800


1547
1559
1603
1578
1465
1470
1622
1593
Intensity (arb units)
ω (cm-1)
0
2
4
6
8
10
12
14
16
1600