Raman Spectra of Carbon Chains (Polyyne)

Jorge Alarcón Ochoa

1. Benchmarking: Most Accurate Level of Theory
   - Most Accurate Combinations (xc/basis)
2. Trends of the LO Mode
   - LO Mode vs. Chain Size
3. Raman Spectrum of Polyyne
   - Full Spectrum of all Chains
4. Open Sourcing

What is the most accurate level of theory?

- We begin by calculating the Raman spectra for model compounds in order to find the most accurate level of theory for our work.
- DFT offers on average an accuracy of 1% for Raman intensities (we want this or better).
- Keep in mind that good parameters for Raman studies are not ”good” in general. Sometimes basis sets that predict good raman frequencies are bad at describing other structural parameters (i.e. equilibrium geometries, energies).
- We test combinations of four of the most widely used exchange correlation functionals(B3LYP, BLYP, PBE0, BP91) and the basis sets available in **NWCHEM**.

Acetylene

Exchange Functional	Basis Set	LO Mode (cm^{-1})
b3lyp	3-21GSP	1948.73
b3lyp	aug-pc-0	2000.71
blyp	pcS-0	1972.22
pbe0	3-21GSP	1974.33
pbe0	pcemd-2	1972.89
bp91	6-311G	1989.42
bp91	pcS-0	1967.50

The LO mode for an acetylene molecule is expect to be around 1974 cm^{-1}.

1-Hexene and Benzene

Exchange Functional	Basis Set	Mode (cm^{-1})
blyp	pcs0	1643.41
pbe0	3-21GSP	1682.76
bp91	pcs0	1651.53

1-Hexene has mode corresponding to the Monoalkyl C=C stretch between 1638 and 1650 cm^1.

Exchange Functional	Basis Set	Mode (cm^{-1})
blyp	pcs0	977.49
pbe0	3-21GSP	969.20
bp91	pcs0	986.42

Benzene has mode corresponding to unsubtituted aromatic ring breathing at 992 cm^1.

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Polyyne

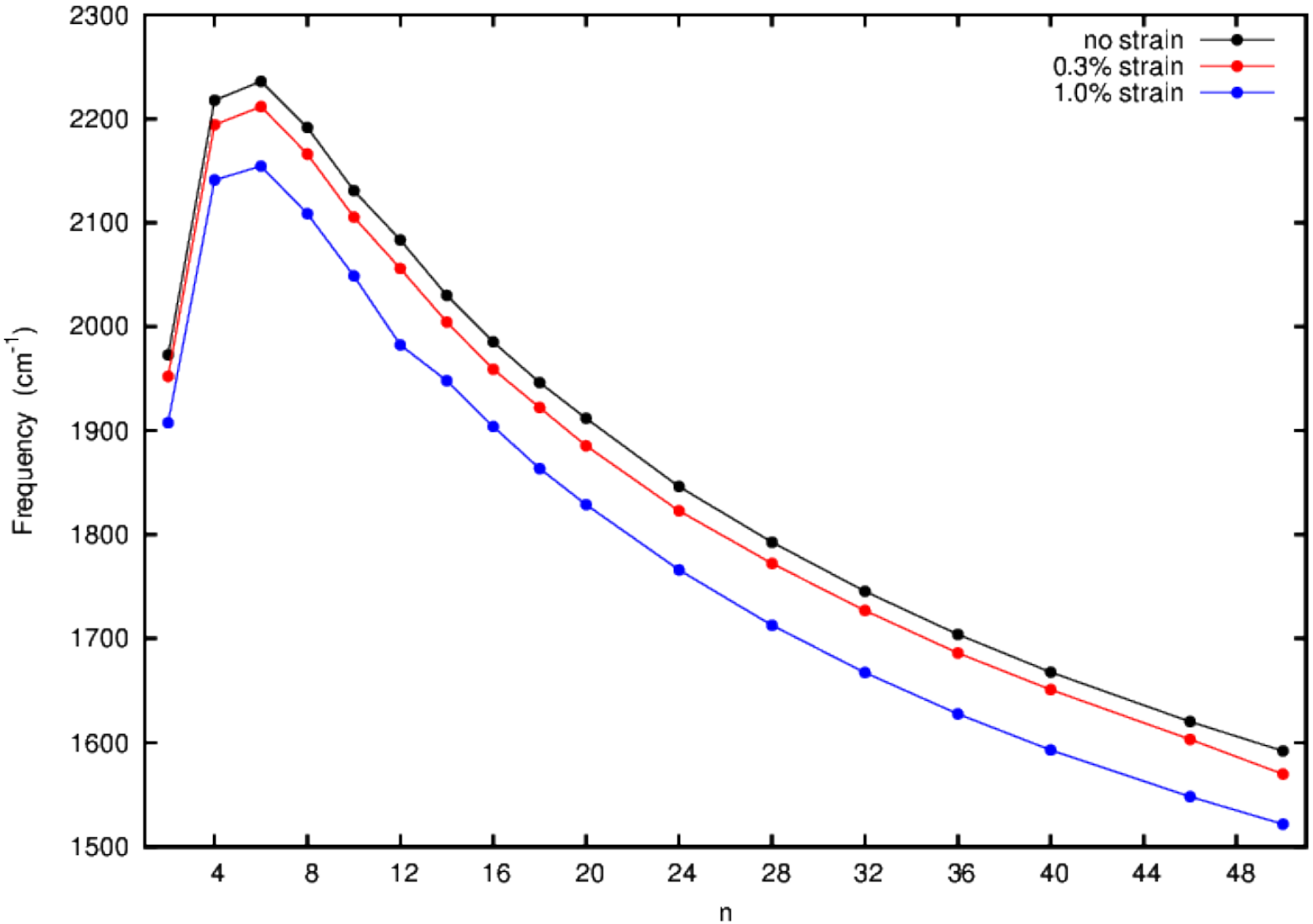
Our carbon chains are made up of alternating triple and single bonds and are capped at the ends by hydrogen.

This is for example C_{10}, which is made up of 5 repeating -C≡C- units.

Longitudinal Optic Mode

The LO mode corresponds to in phase alternation between compression/expansion of the triple bonds and expansion/compression of the single bonds. The LO mode was identified by visualizing of the vibrational frequencies with the aid of the software package **avogadro**.

LO vs. Size

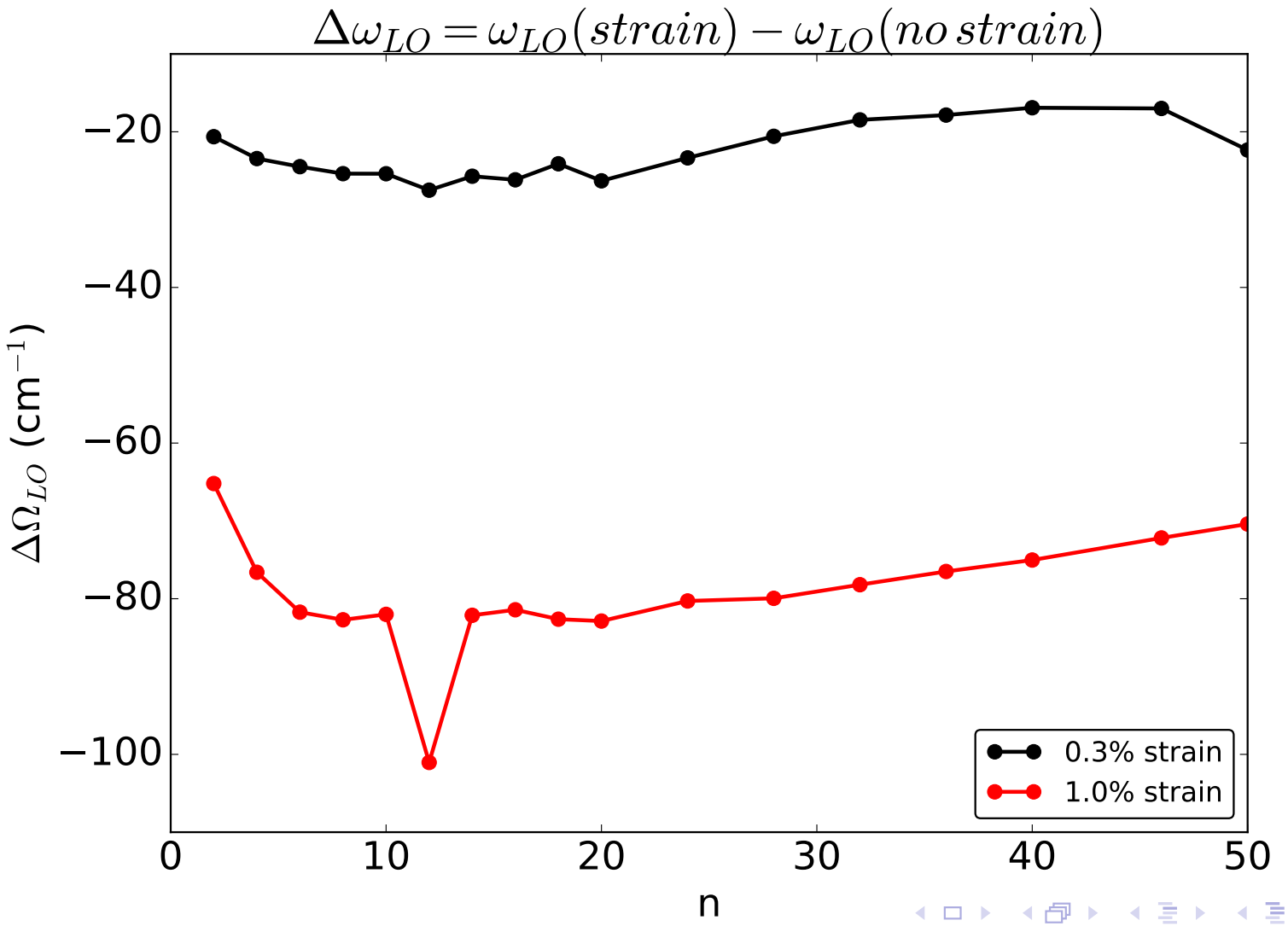

no strain
0.3% strain
1.0% strain
Frequency (cm^{-1})
n
2300
2200
2100
2000
1900
1800
1700
1600
1500
4
8
12
16
20
24
28
32
36
40
44
48

Remarks

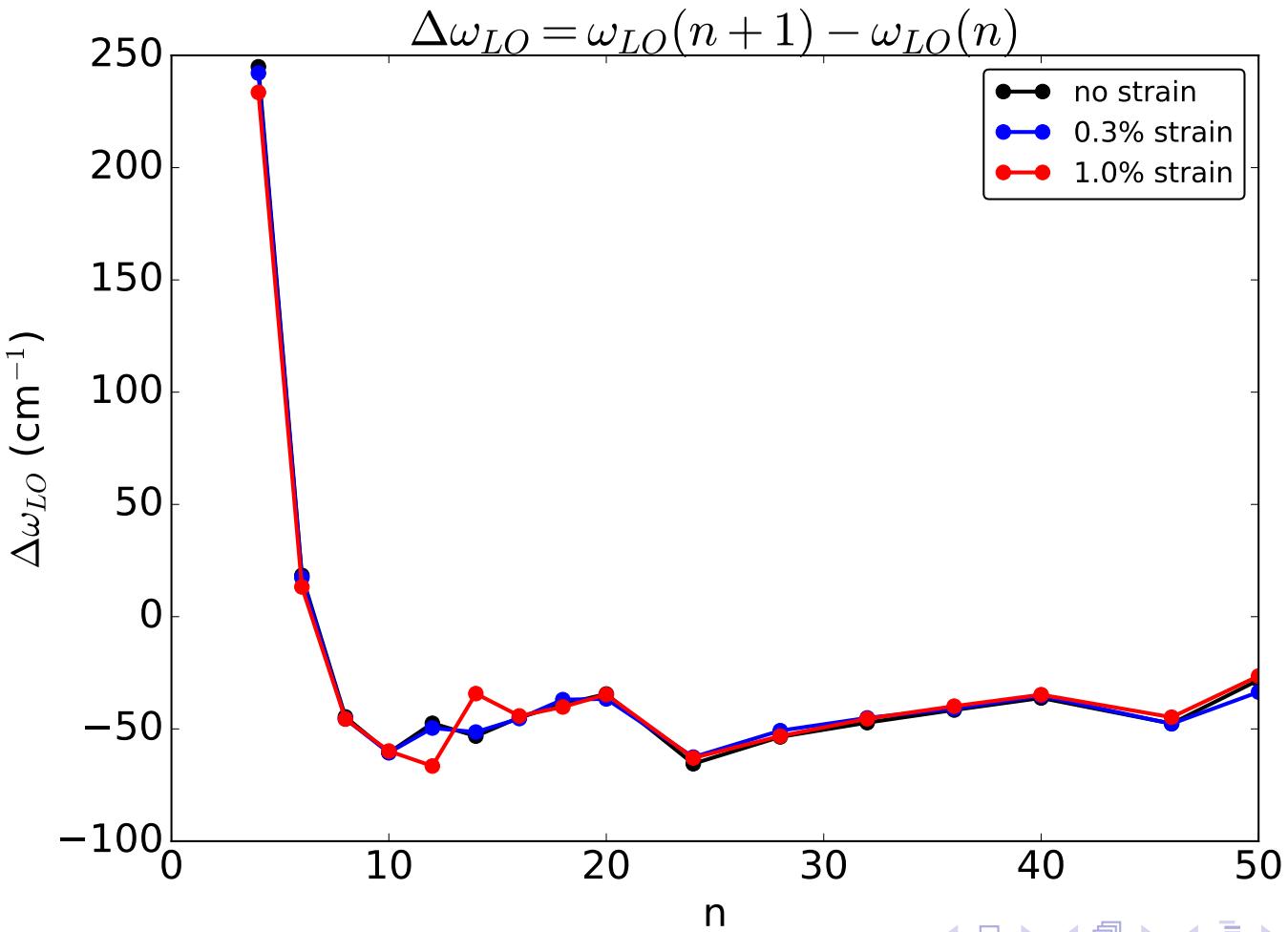
For large chains (≥ 36) there is an appearance of an LO-like mode in which each half of the chain has an LO -like vibrational pattern.

These appear in the range of 1800's cm^{-1}. The change in the frequency of this LO-like mode follows the patterns for the actual LO mode with respect to strain and size.

Change in the LO Mode Frequency upon Strain



Change in the LO Mode Frequency with Growing Chain size



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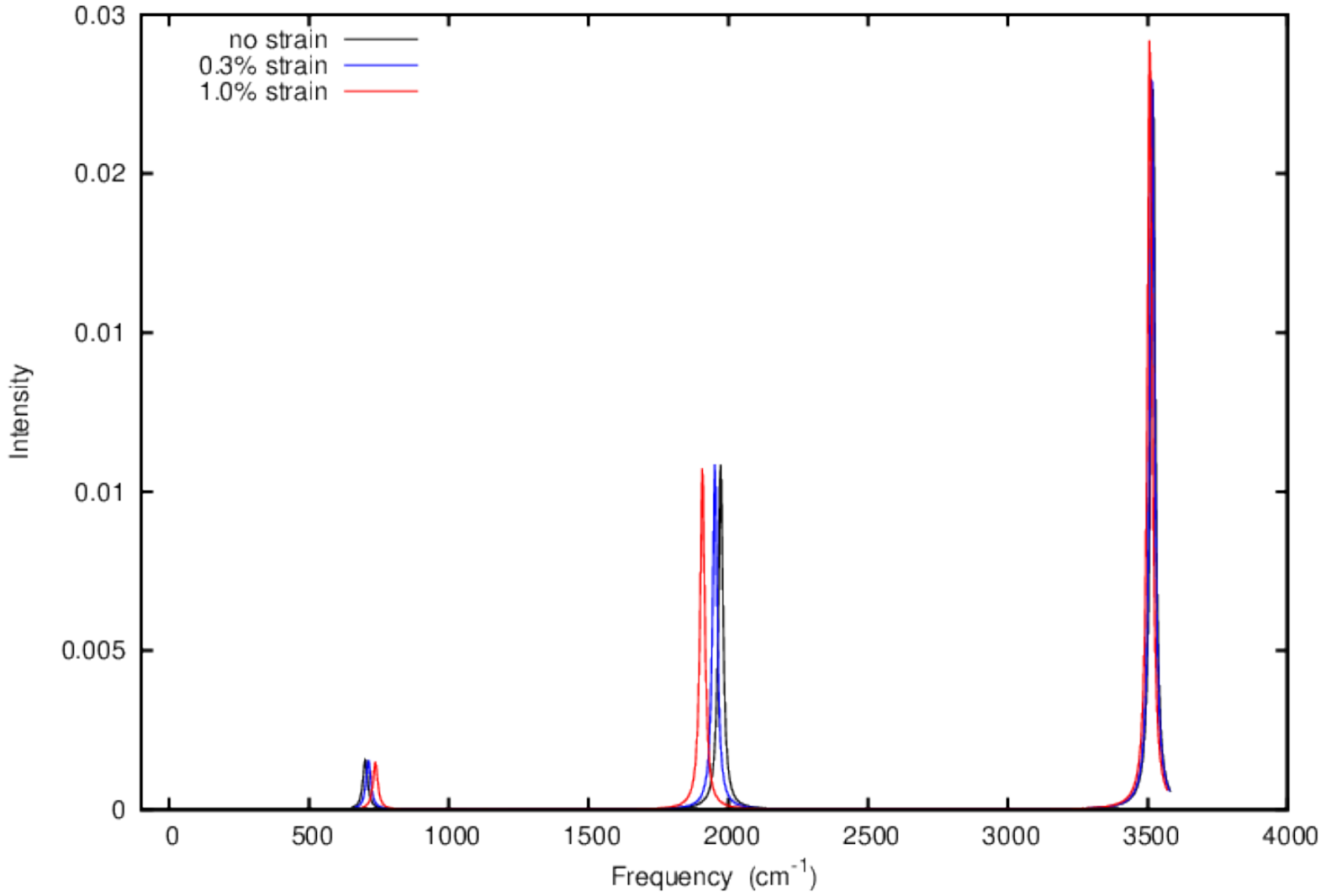
Key Features

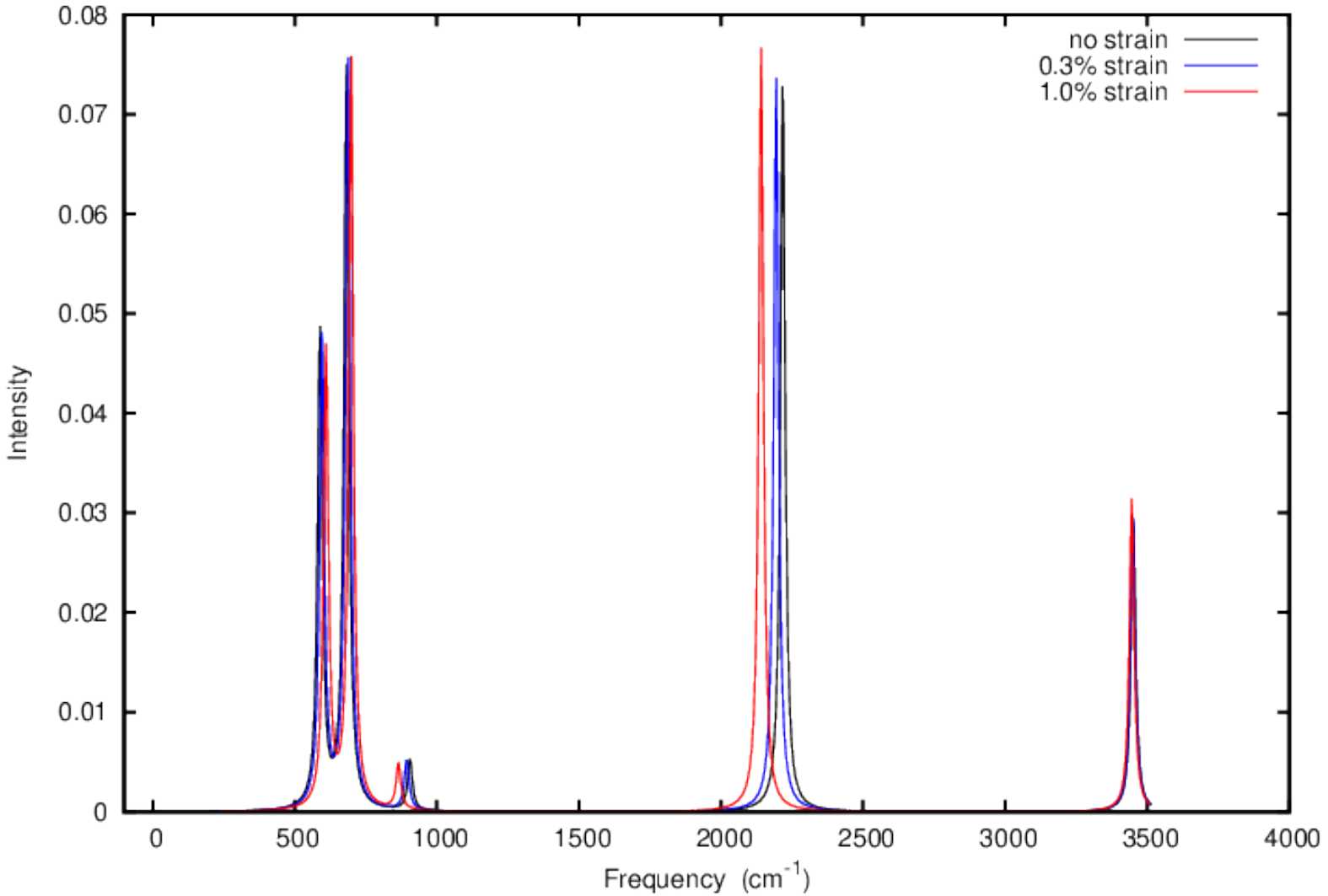
Most often there are four clusters of peaks for the a given spectrum.

- Low frequencies (0-100 cm^{-1}): wagging of the chain.
- Mid frequencies (1000-LO cm^{-1}): Single bond stretching/compressing.
- LO and LO-like (LO-2000's cm^{-1}): Alternating stretching/compressing of single and triple bonds.
- High frequencies (3000's cm^{-1}): Alternating stretching/compressing of single and triple bonds with off-phase vbrations of the terminal hydrogens.

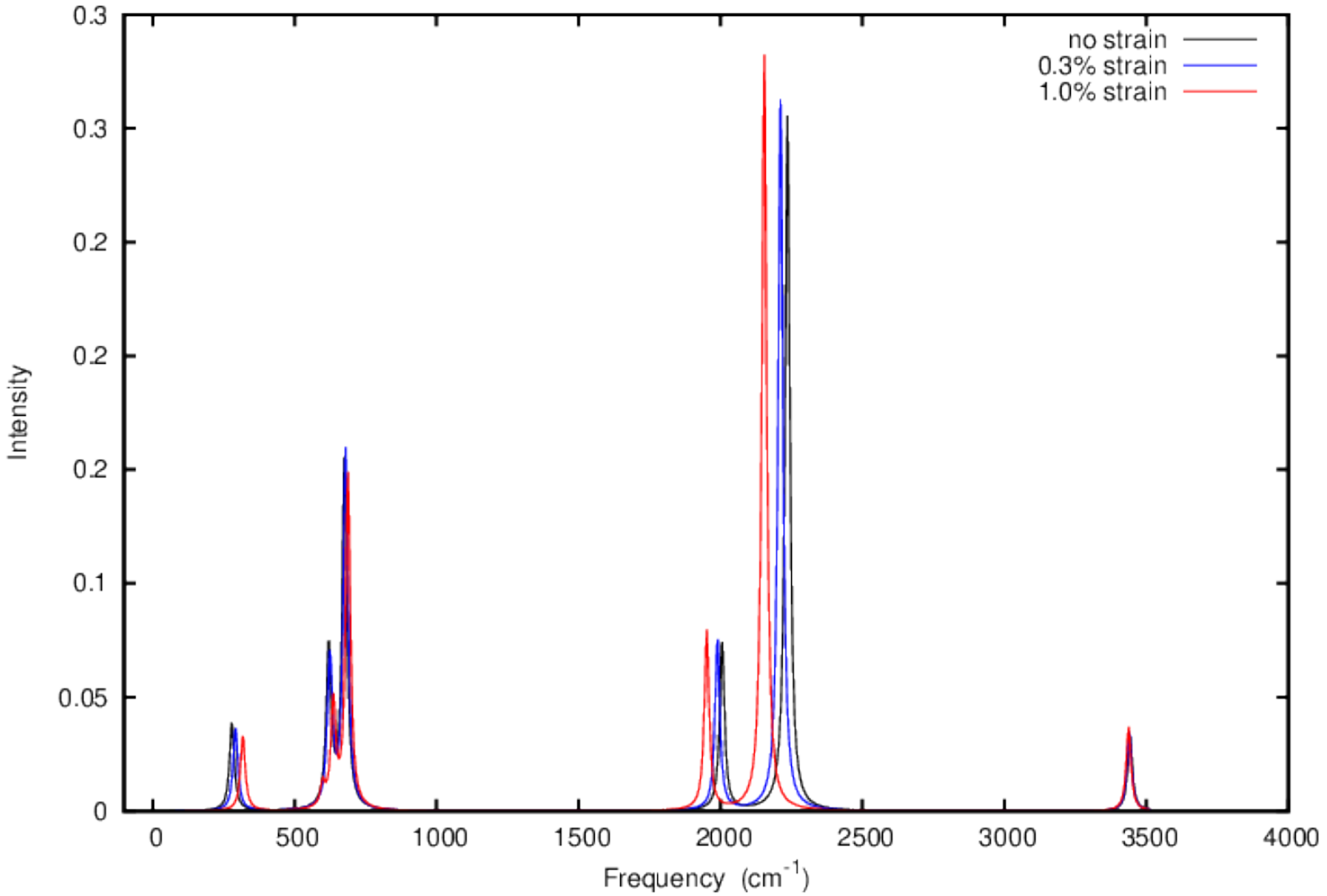
C_2


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
0.03
0.02
0.01
0.01
0.005
0
0
500
1000
1500
2000
2500
3000
3500
4000

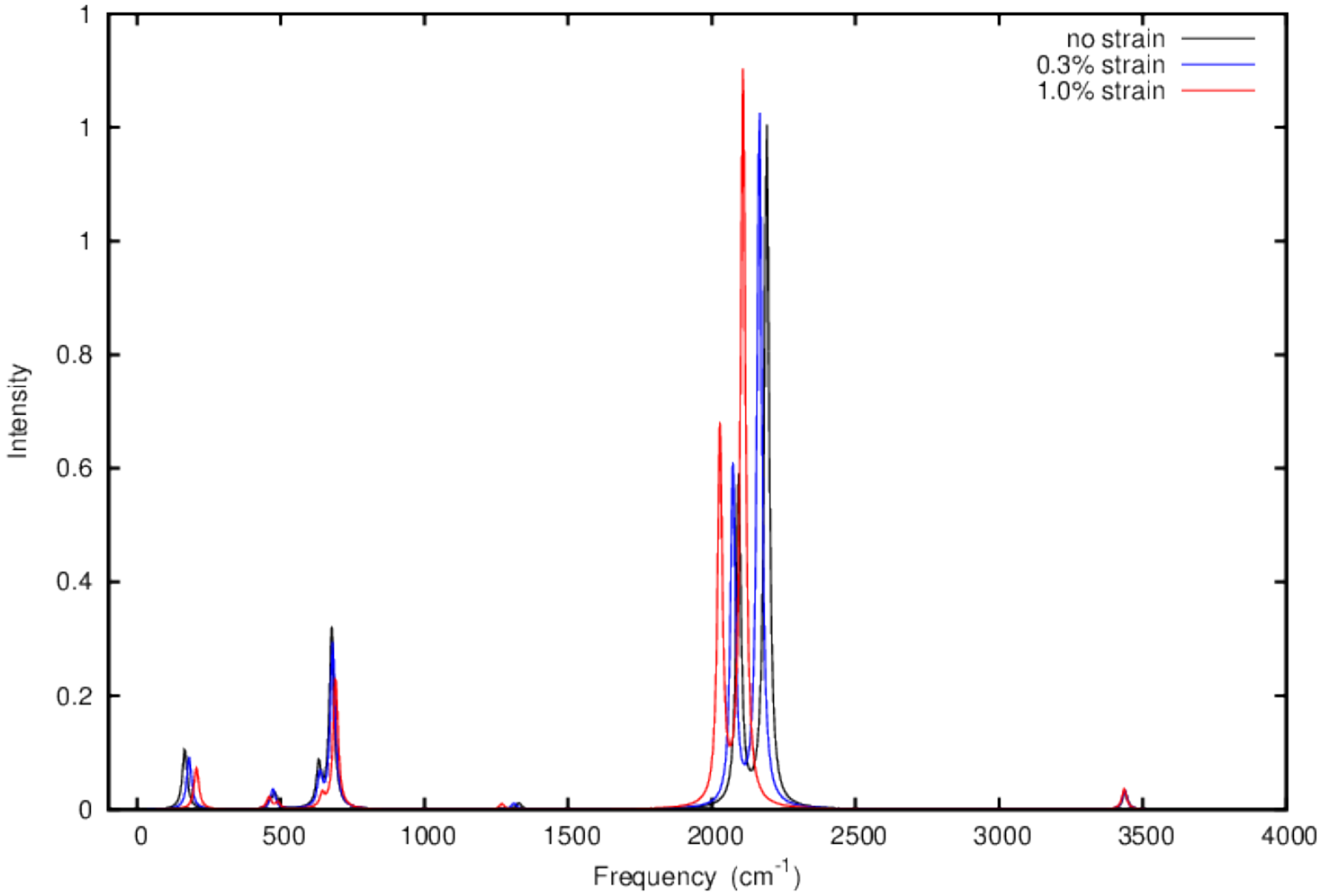
C_4


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
500
1000
1500
2000
2500
3000
3500
4000

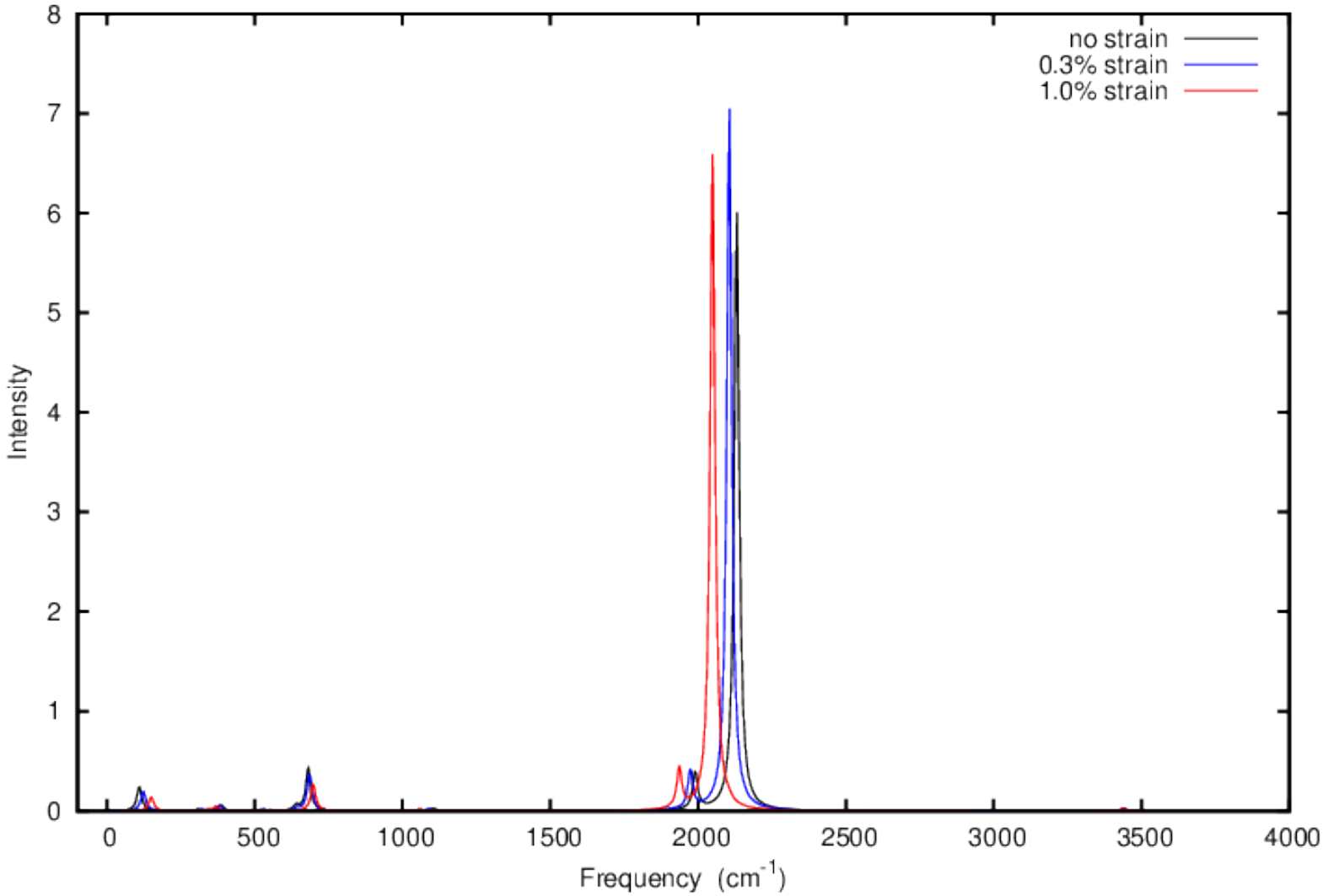
C_6


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
0
0.05
0.1
0.2
0.2
0.2
0.3
0.3
0
500
1000
1500
2000
2500
3000
3500
4000

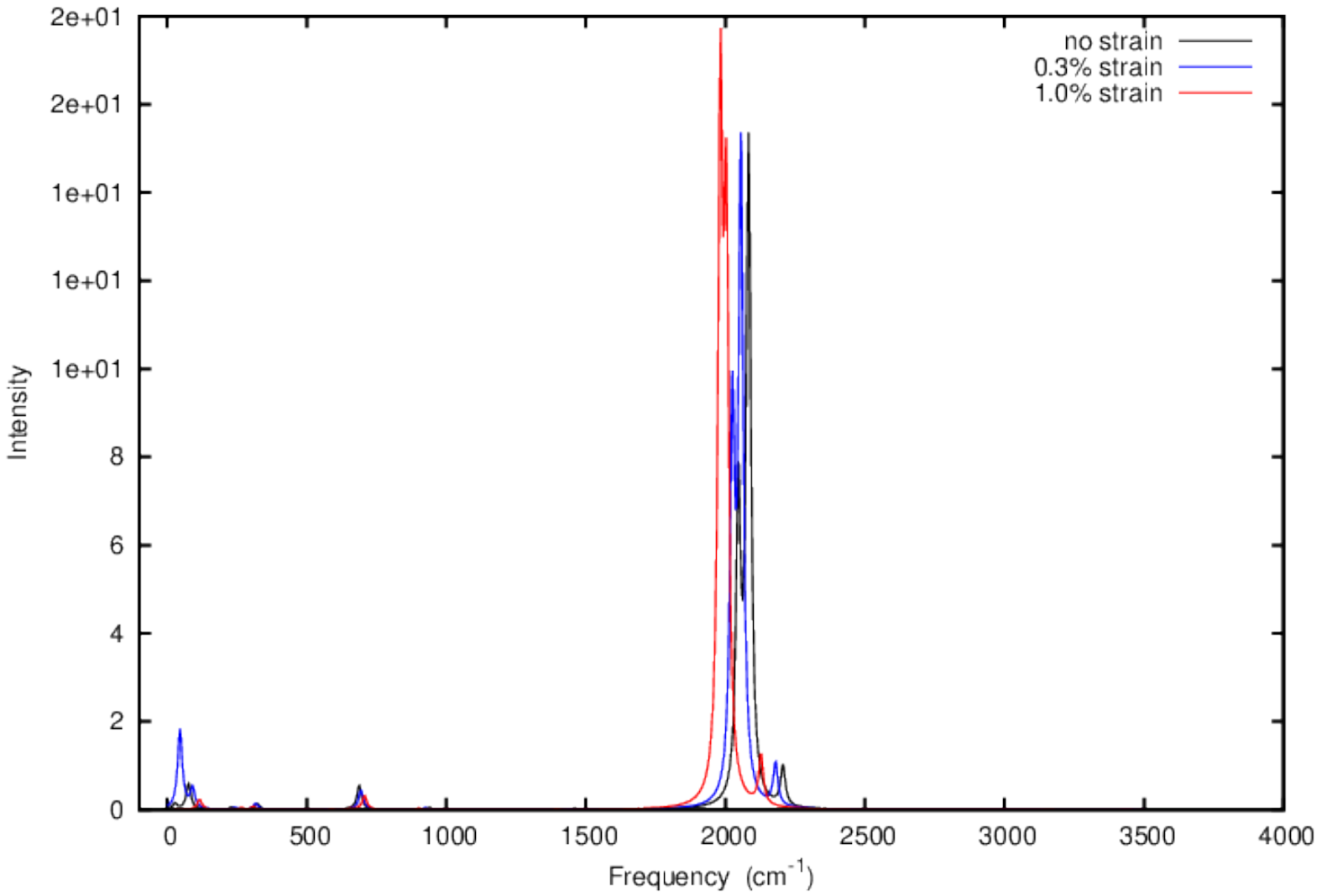
C_8


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
0
0.2
0.4
0.6
0.8
1
1
1
0
500
1000
1500
2000
2500
3000
3500
4000

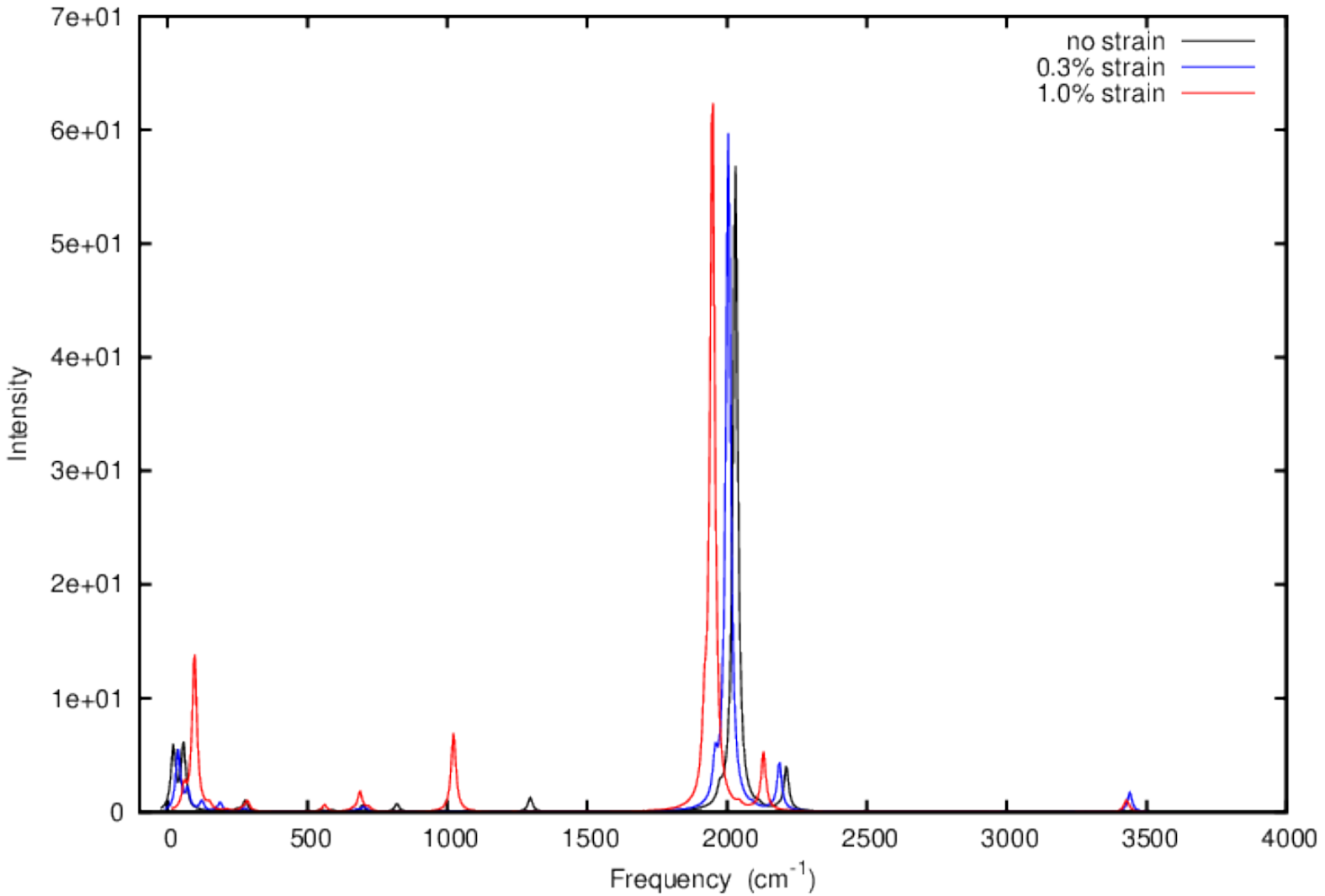
C_{10}


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
0
1
2
3
4
5
6
7
8
0
500
1000
1500
2000
2500
3000
3500
4000

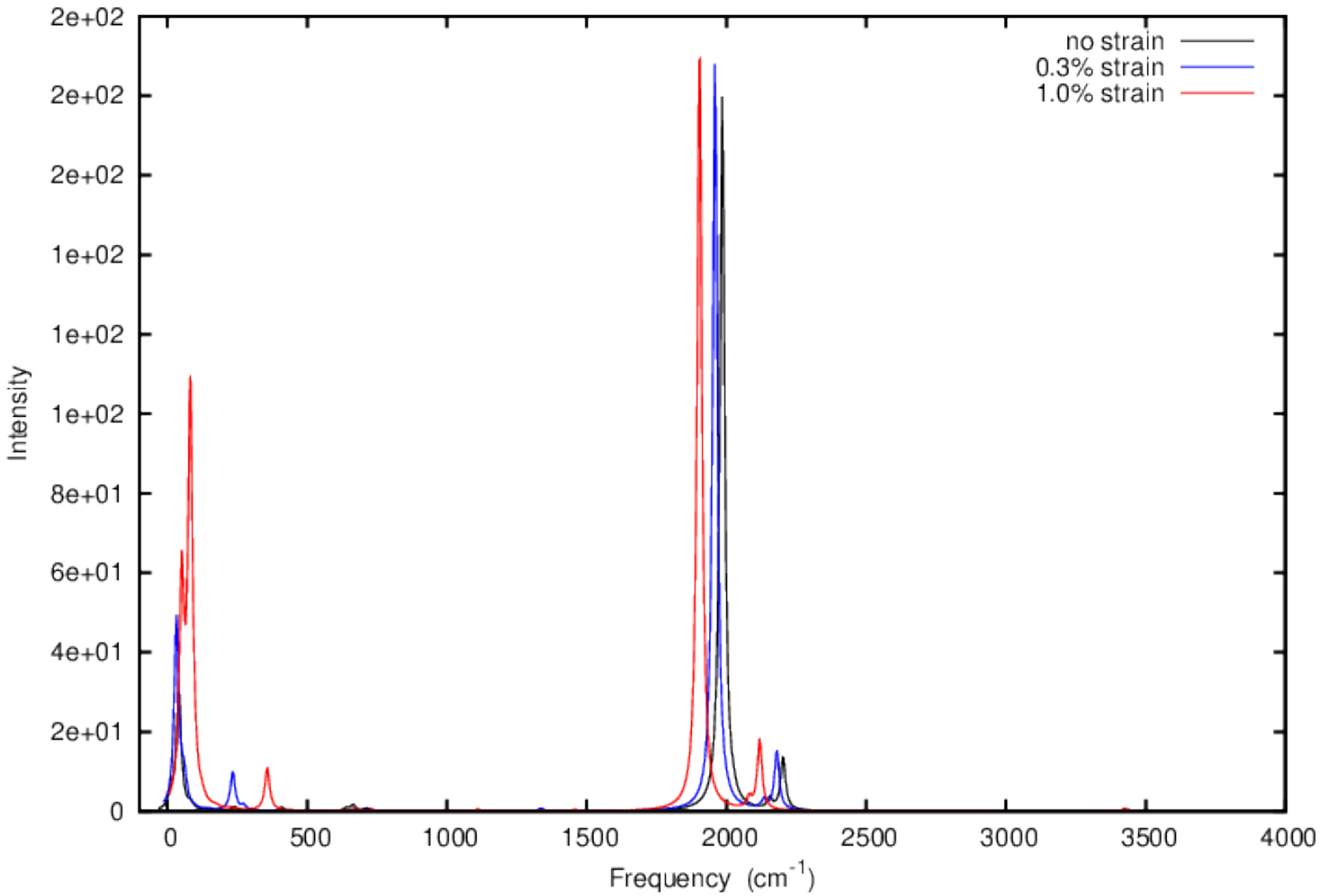
C_{12}


2e+01
2e+01
1e+01
1e+01
1e+01
8
6
4
2
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
4000
Frequency (cm-1)
no strain
0.3% strain
1.0% strain

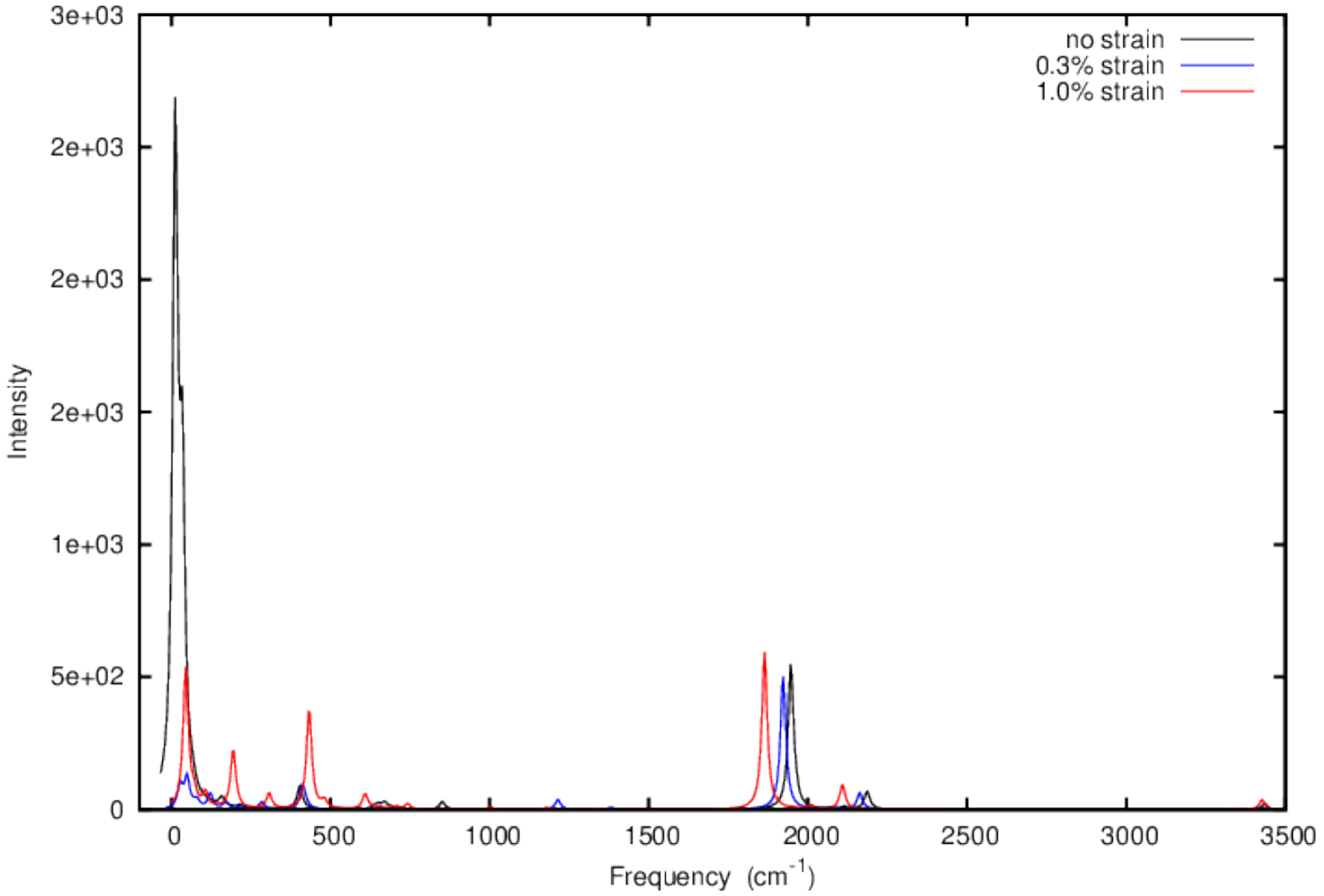
C_{14}


7e+01
6e+01
5e+01
4e+01
3e+01
2e+01
1e+01
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
4000
Frequency (cm-1)
no strain
0.3% strain
1.0% strain

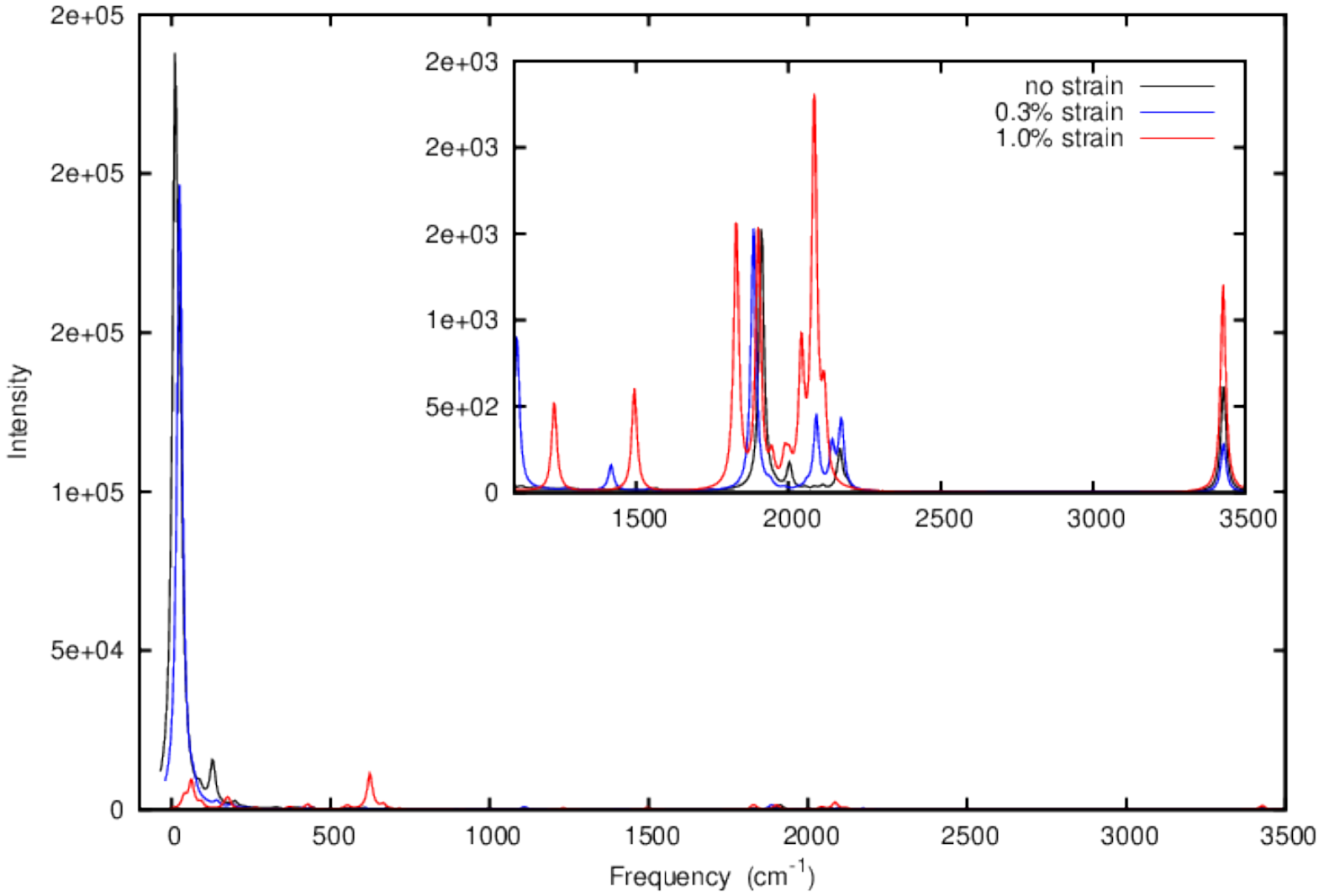
C_{16}


no strain
0.3% strain
1.0% strain
Intensity
Frequency (cm^{-1})
2e+02
2e+02
2e+02
1e+02
1e+02
1e+02
8e+01
6e+01
4e+01
2e+01
0
0
500
1000
1500
2000
2500
3000
3500
4000

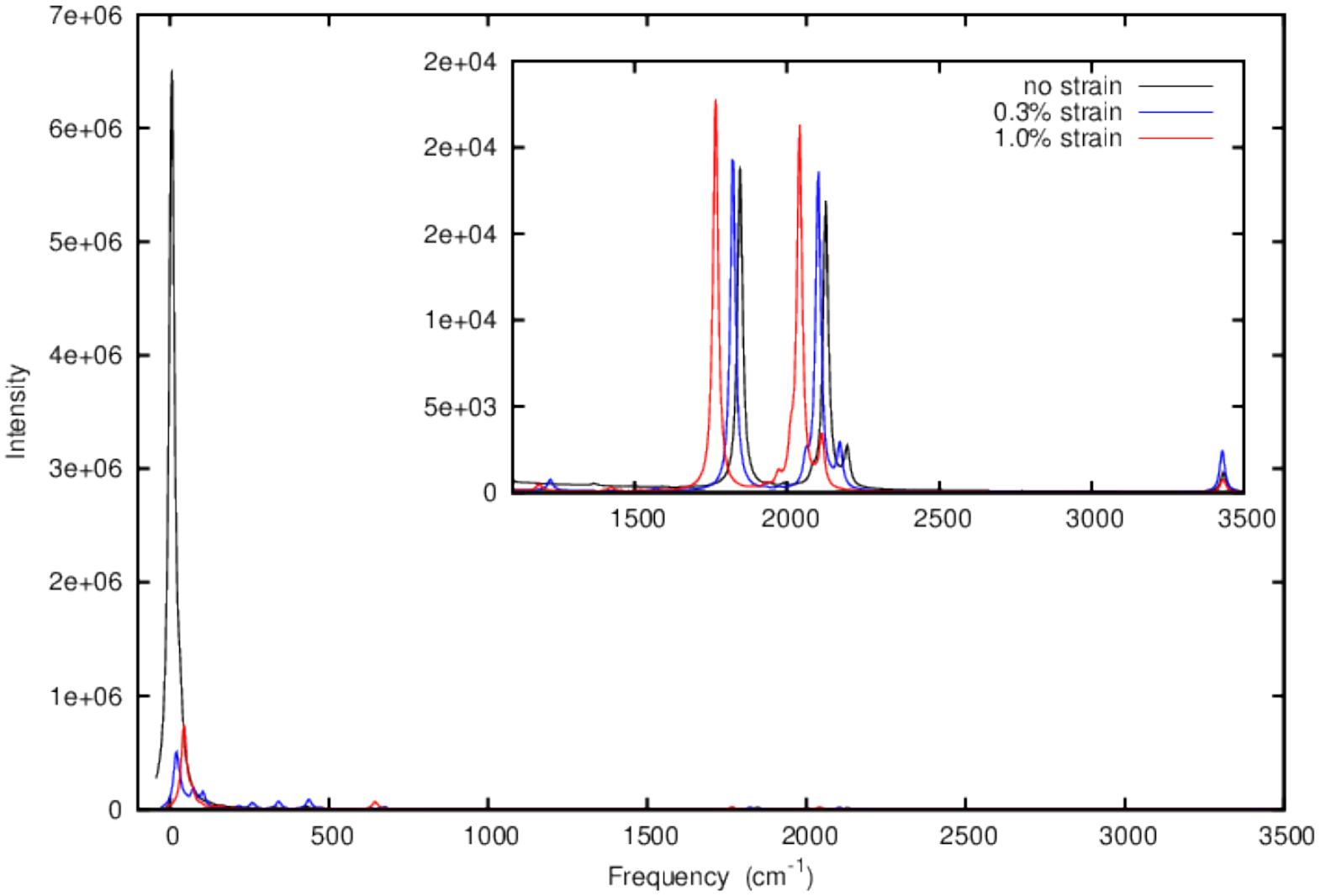
C_{18}


3e+03
2e+03
2e+03
2e+03
1e+03
5e+02
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
no strain
0.3% strain
1.0% strain

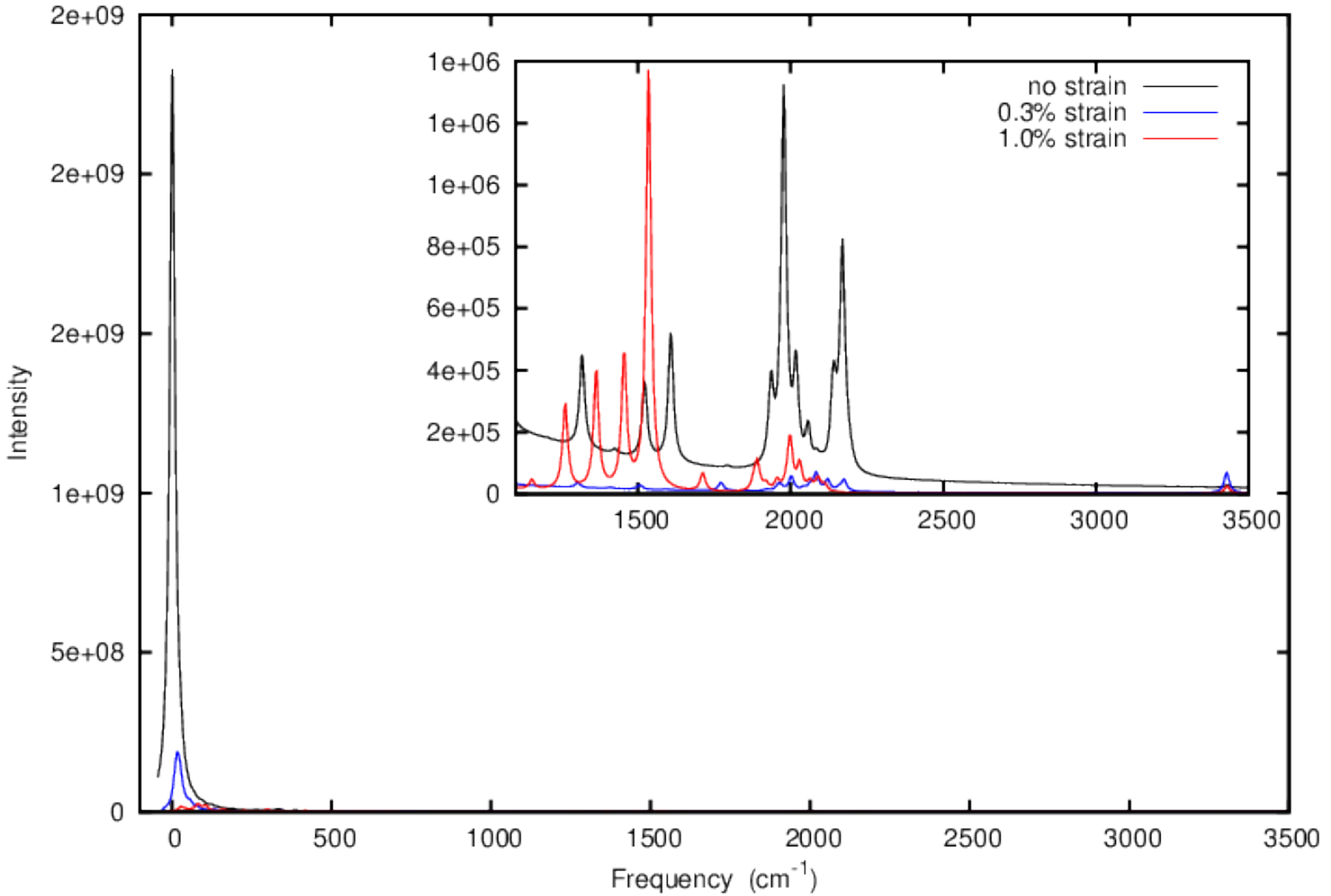
C_{20}


2e+05
2e+05
2e+05
1e+05
5e+04
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
2e+03
2e+03
2e+03
1e+03
5e+02
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

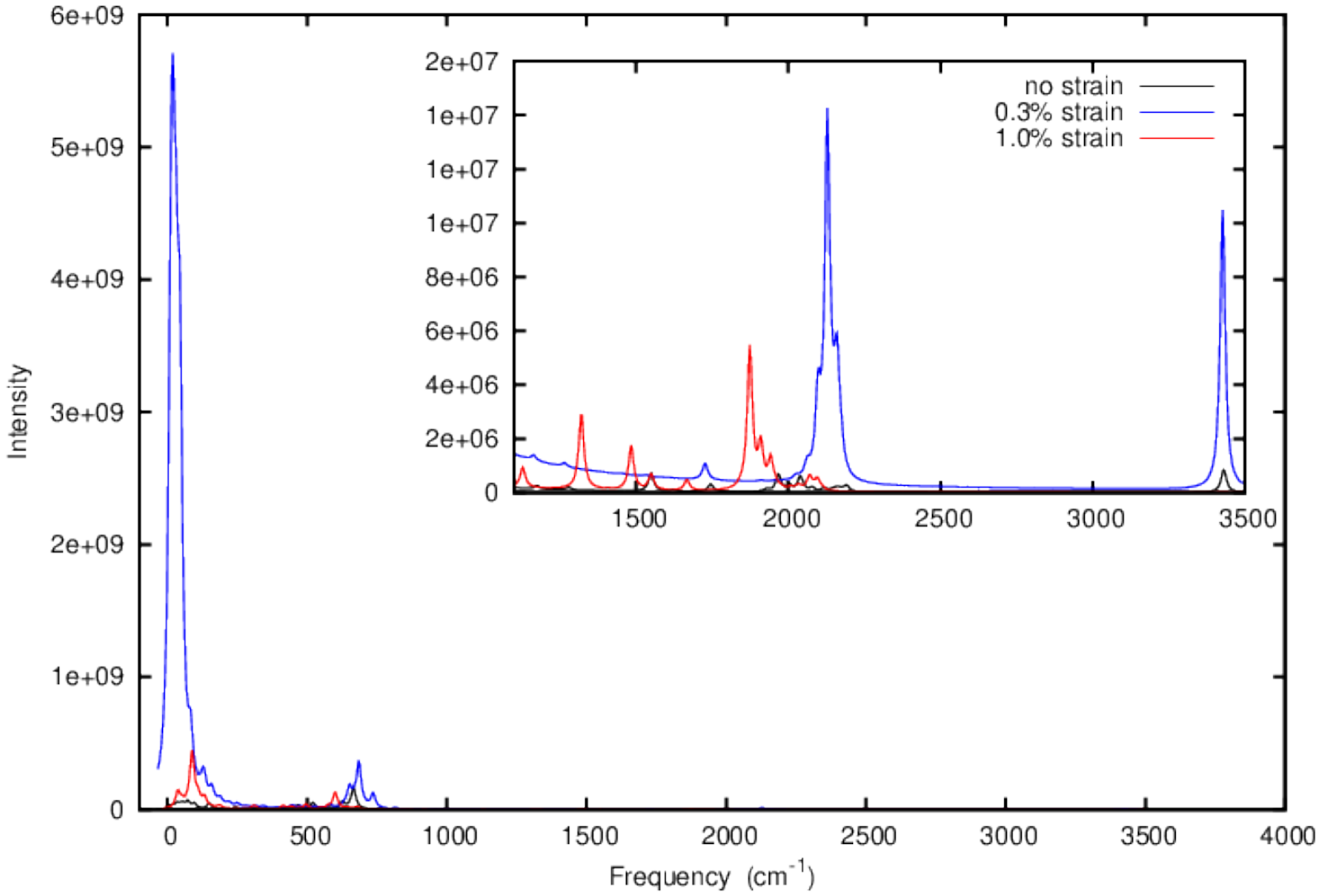
C_{24}


7e+06
6e+06
5e+06
4e+06
3e+06
2e+06
1e+06
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
2e+04
2e+04
2e+04
1e+04
5e+03
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

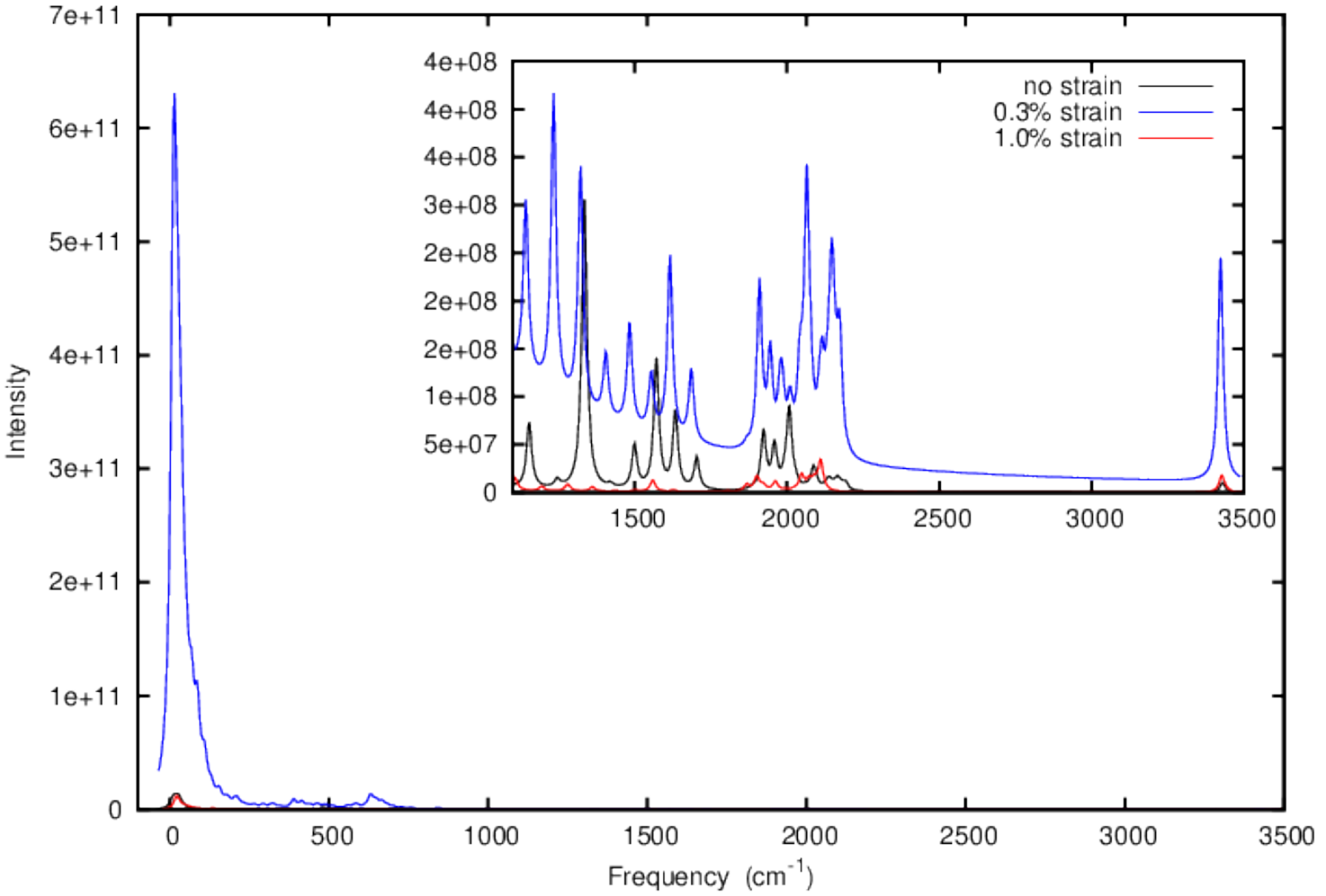
C_{28}


2e+09
2e+09
2e+09
1e+09
5e+08
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
1e+06
1e+06
1e+06
8e+05
6e+05
4e+05
2e+05
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

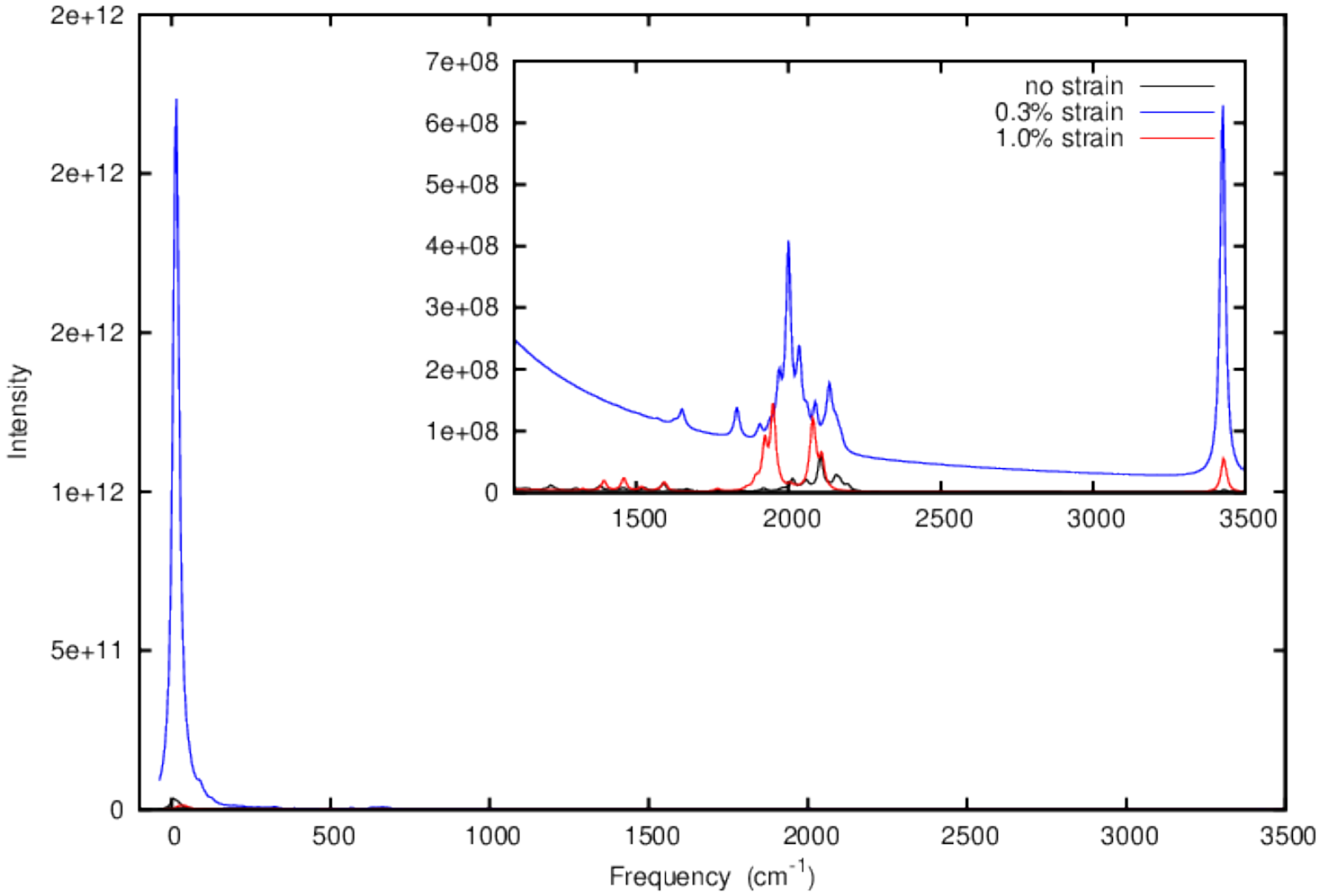
C_{32}


6e+09
5e+09
4e+09
3e+09
2e+09
1e+09
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
4000
Frequency (cm-1)
2e+07
1e+07
1e+07
1e+07
8e+06
6e+06
4e+06
2e+06
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

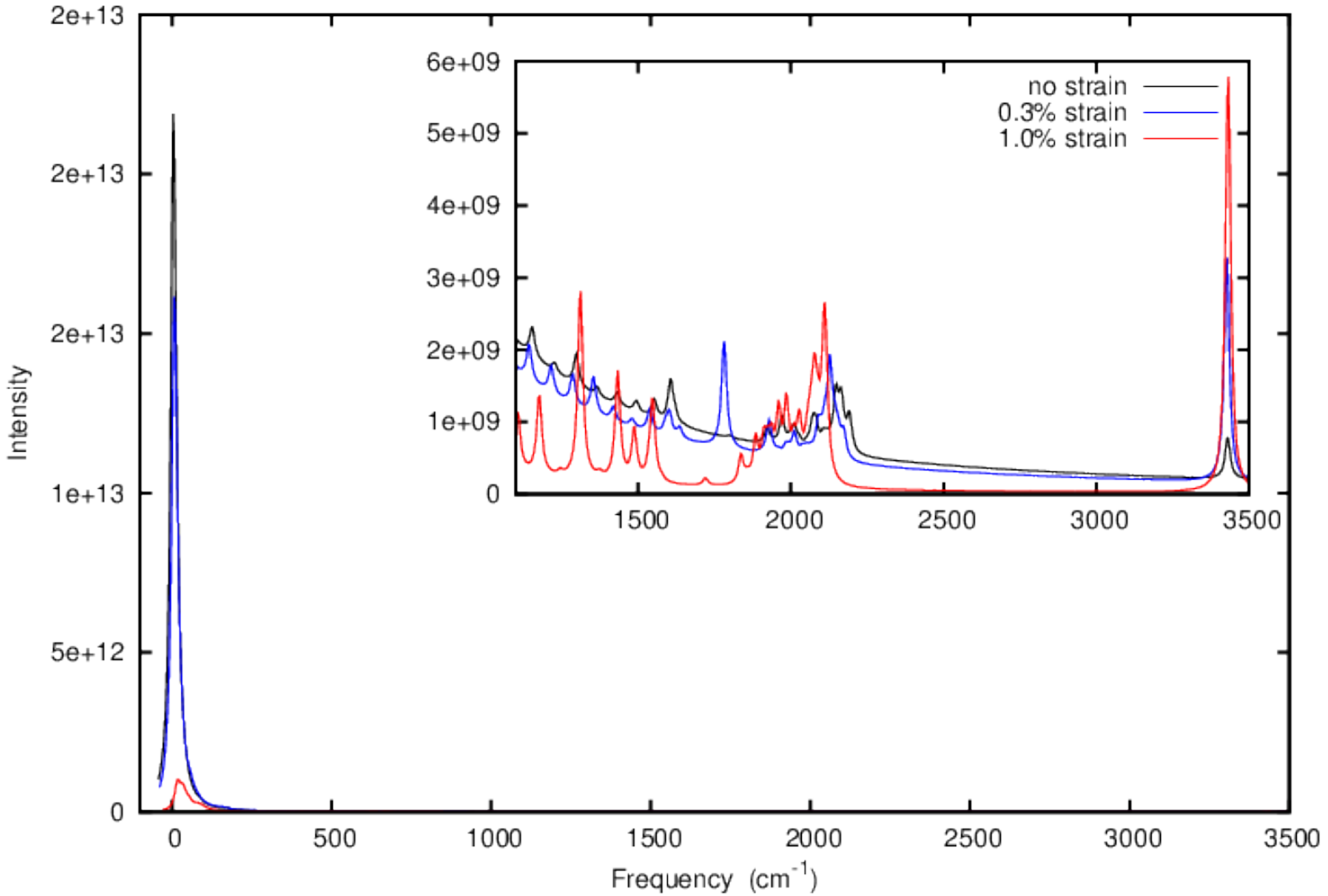
C_{36}


Intensity
Frequency (cm^{-1})
no strain
0.3% strain
1.0% strain
7e+11
6e+11
5e+11
4e+11
3e+11
2e+11
1e+11
0
0
500
1000
1500
2000
2500
3000
3500
4e+08
4e+08
4e+08
3e+08
2e+08
2e+08
2e+08
1e+08
5e+07
0
1500
2000
2500
3000
3500

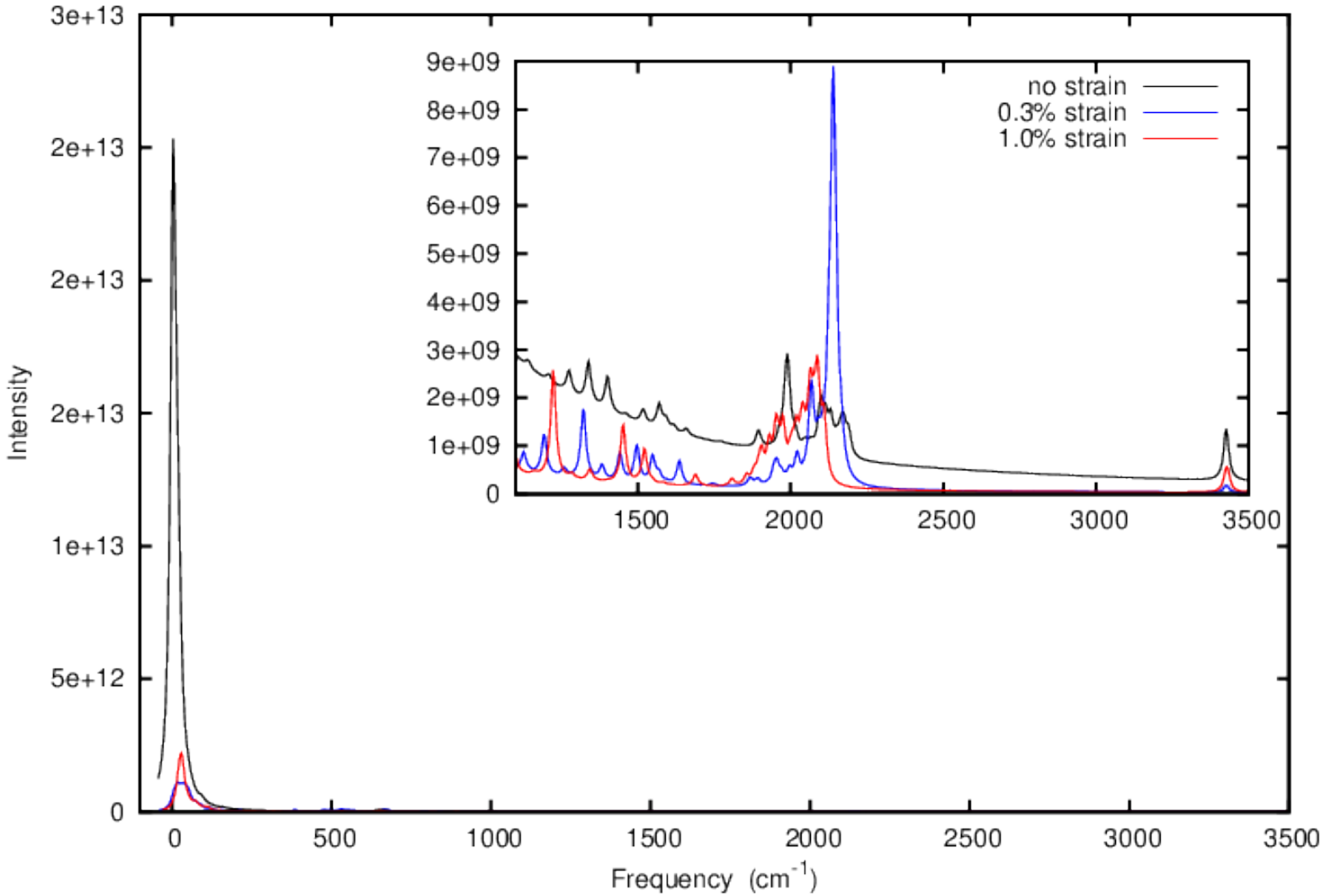
C_{40}


2e+12
2e+12
2e+12
1e+12
5e+11
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
7e+08
6e+08
5e+08
4e+08
3e+08
2e+08
1e+08
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

C_{46}


2e+13
2e+13
2e+13
1e+13
5e+12
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
6e+09
5e+09
4e+09
3e+09
2e+09
1e+09
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

C_{50}


3e+13
2e+13
2e+13
2e+13
1e+13
5e+12
0
Intensity
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)
9e+09
8e+09
7e+09
6e+09
5e+09
4e+09
3e+09
2e+09
1e+09
0
1500
2000
2500
3000
3500
no strain
0.3% strain
1.0% strain

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Thank you

Calculations done with **NWCHEM-6.5** in the Stampede Supercomputer (XSEDE Scholar Program - TG-TRA140037).

Code available at:

`https://github.com/alejandrox1/carbon_clusters`