SIMULATION OF IR ABSORPTION SPECTRA FOR N-ALKANETHIOL SAM MODELS

Antonius Ghanim

Dr. Lloyd Bumm, Soumya Bhattacharya, Mitchell Yothers

University of Oklahoma

Physics REU

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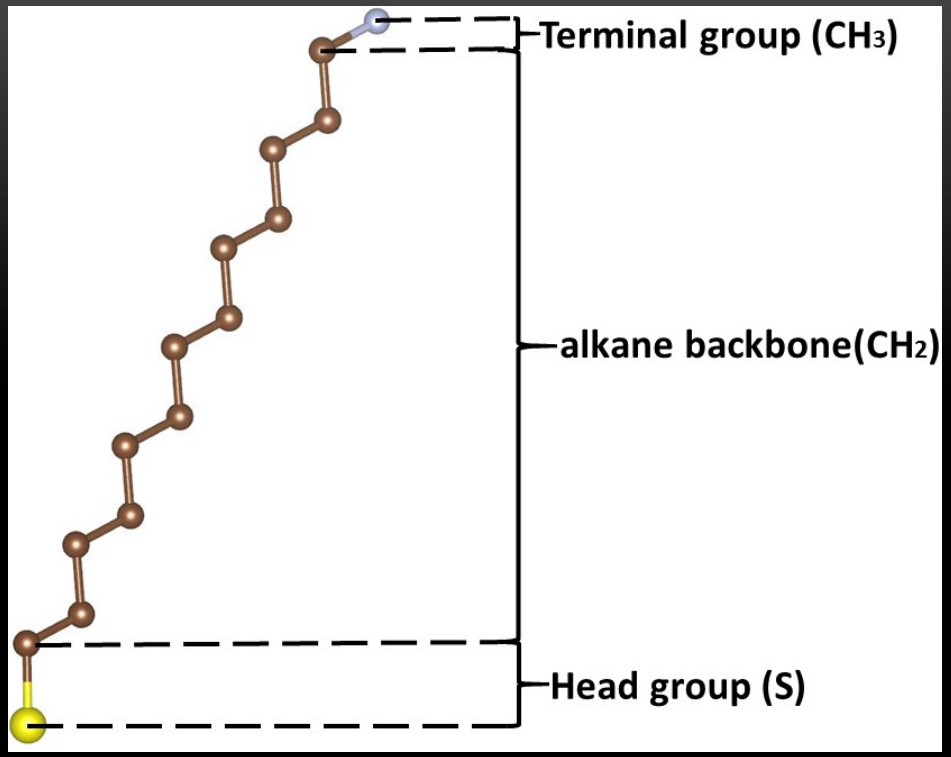
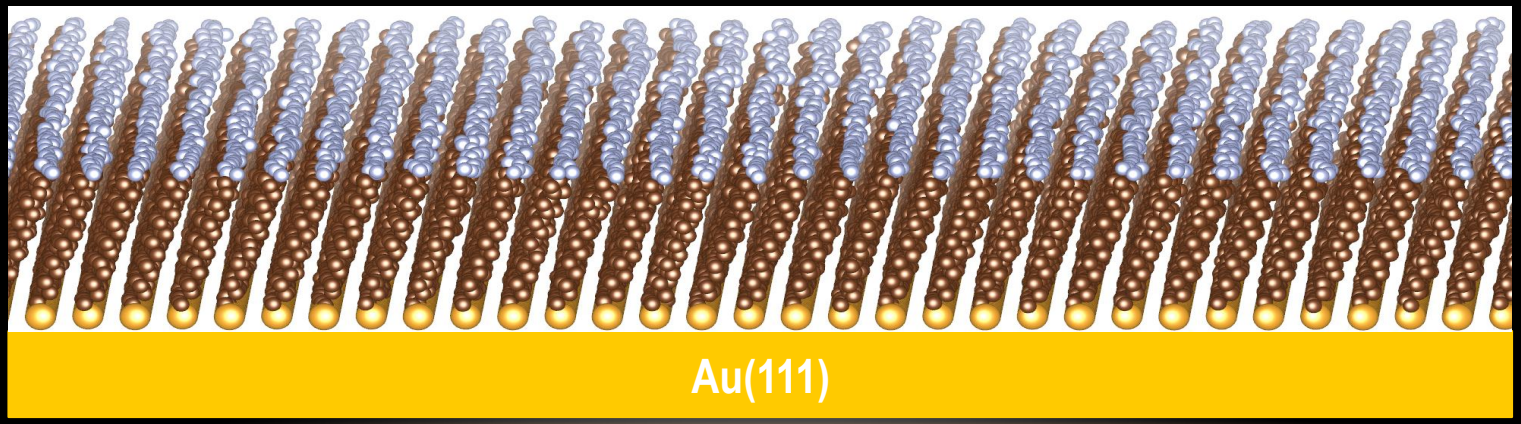
SELF-ASSEMBLED MONOLAYERS

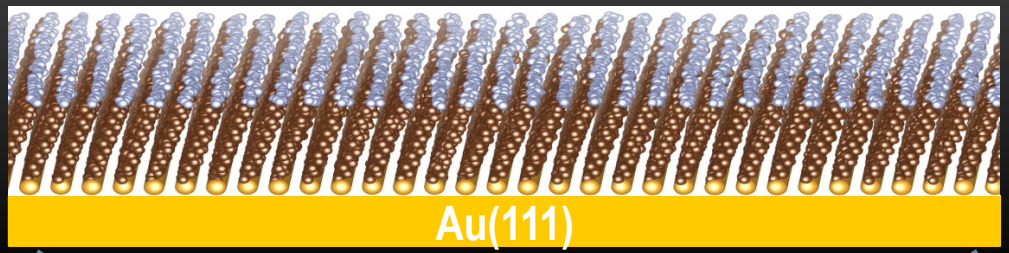
- n-alkanethiol on gold
- Sulfur attracted to gold surface
- Van der Waals interactions form layer

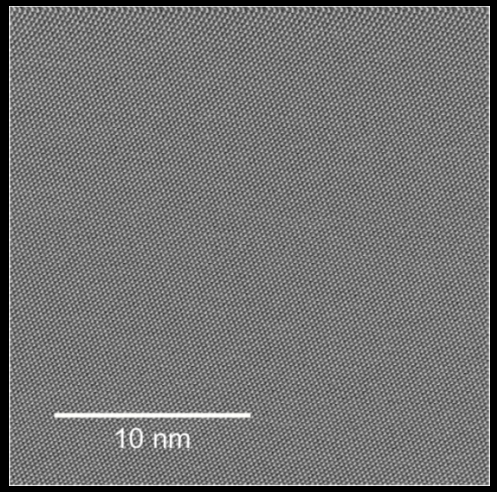


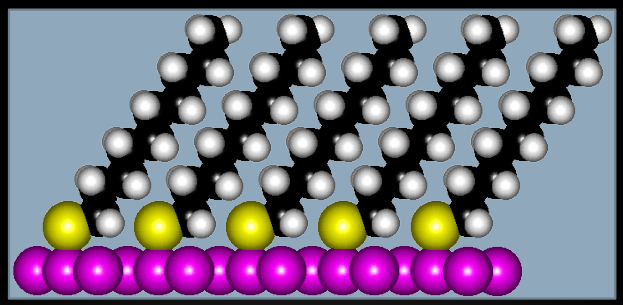


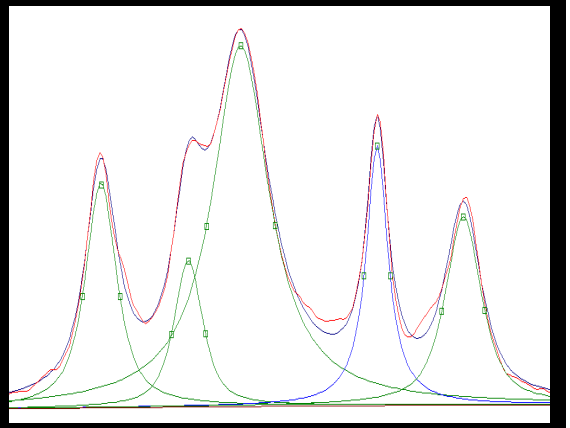
Figures made by Soumya Bhattacharya

SYSTEM









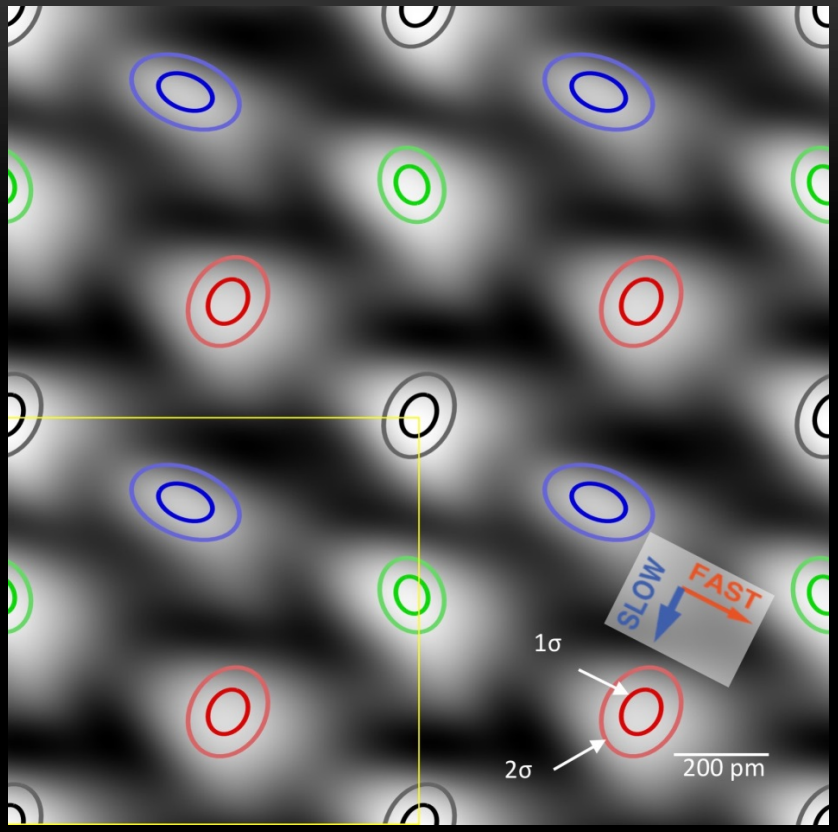
STM Experiment

Molecular Dynamics Modeling

IR Spectrum Simulation

EXPERIMENT

- Scanning Tunneling Microscope (STM) topographic image
- Result suggests…
- Purpose: To find an optimized MD model for the 4-molecules basis surface structure

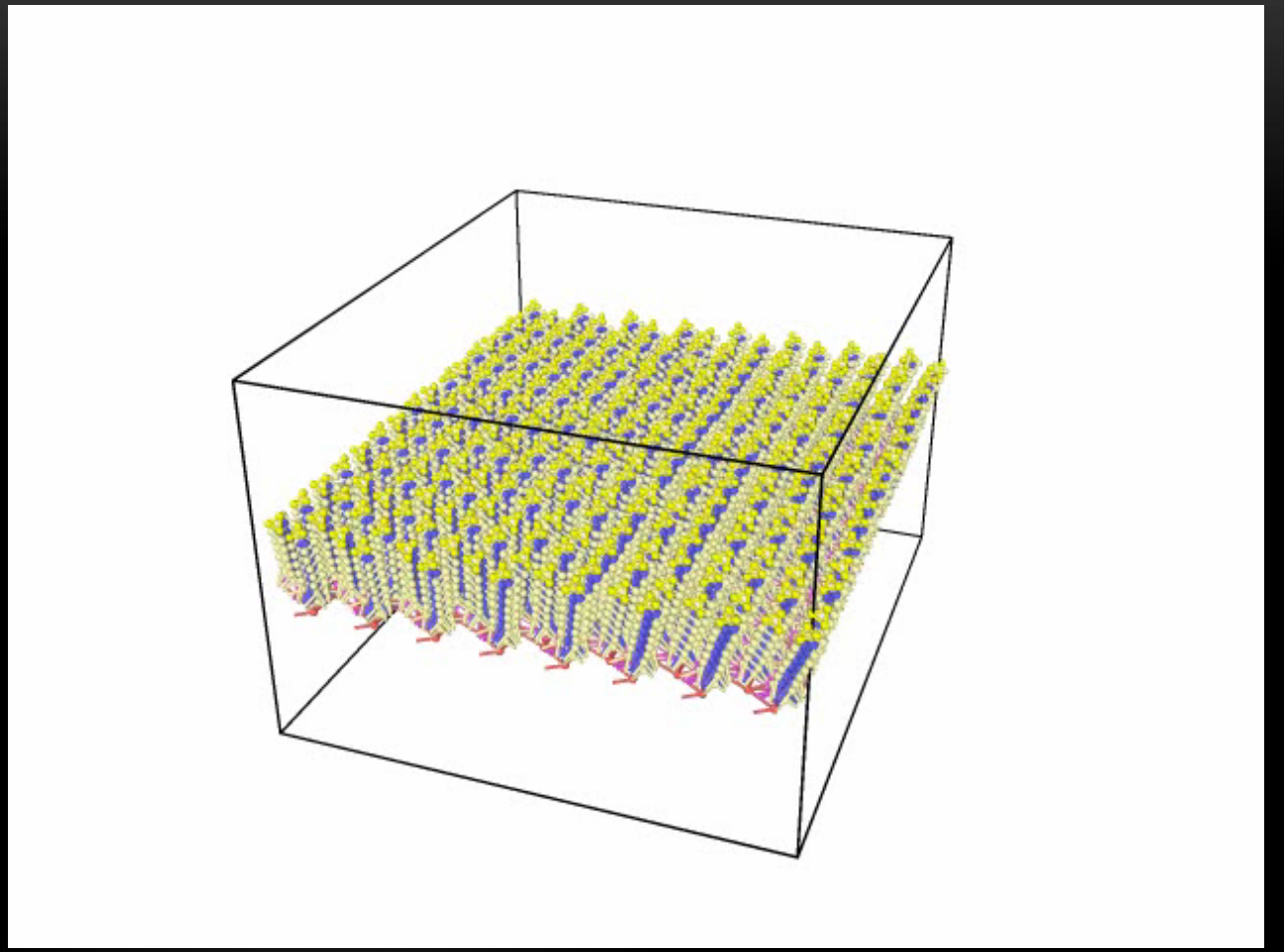


The fig. shows a 4-molecules basis surface structure of 1-decanethiol on Au(111)

STM image and analysis by Mitchell Yothers

MOLECULAR DYNAMICS

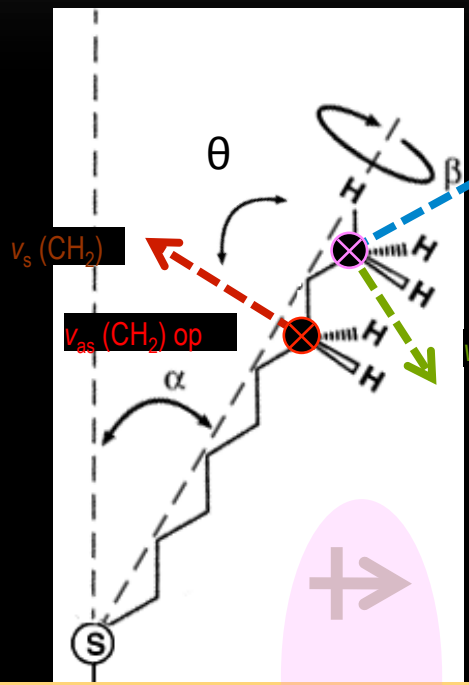
- Uses classical mechanics
- Produces *x,y,z* data for each atom for each time step
- To find a reason for the observed pattern



INFRARED REFLECTION ABSORPTION SPECTROSCOPY (IRRAS)

$$I \alpha \cos^2(\theta)$$

- Mid infrared light (600 – 4000 cm^{-1})
- Probes molecular vibrations (stretching and bending)
- Measures normal component of transition dipole



IR light striking surface at grazing incidence (~86°)

IR light reflected from surface

perpendicular dipoles reinforced by image dipole

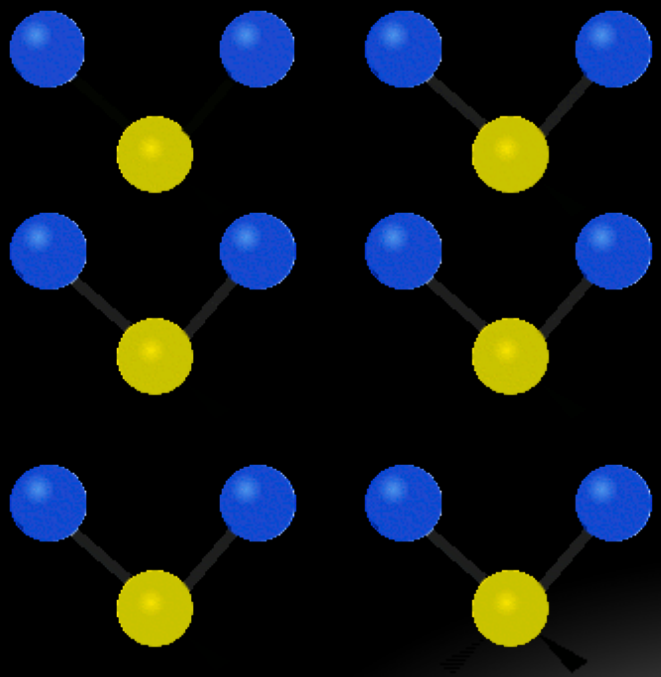
parallel dipoles are suppressed by quadrupole formed with the image dipole

figure: Love, J. C. et al. *Chem. Rev.* **2005**, 105, 1117

INTENSITIES

- In-plane symmetric vibration (a)
- In-plane asymmetric vibration (b)
- Out of plane symmetric vibration (c)

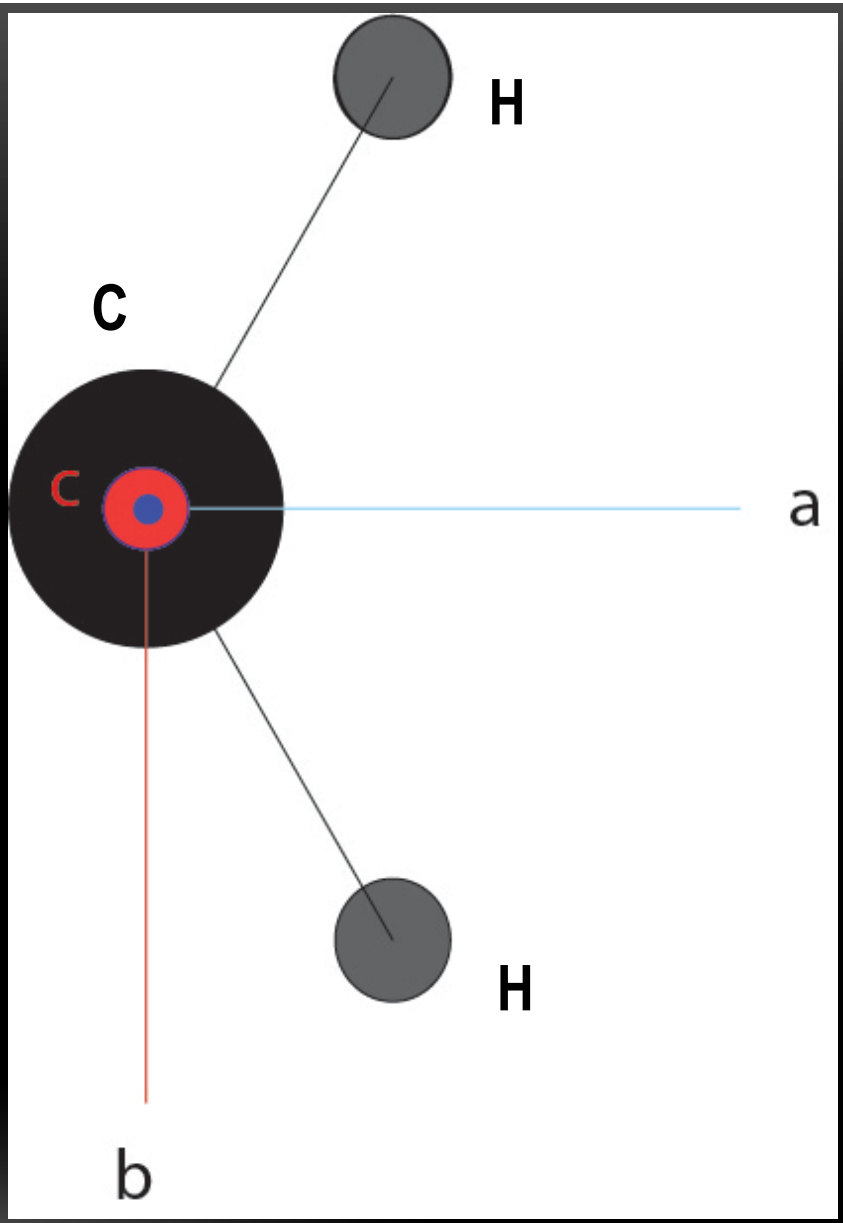
Symmetric Asymmetric



IP Stretching

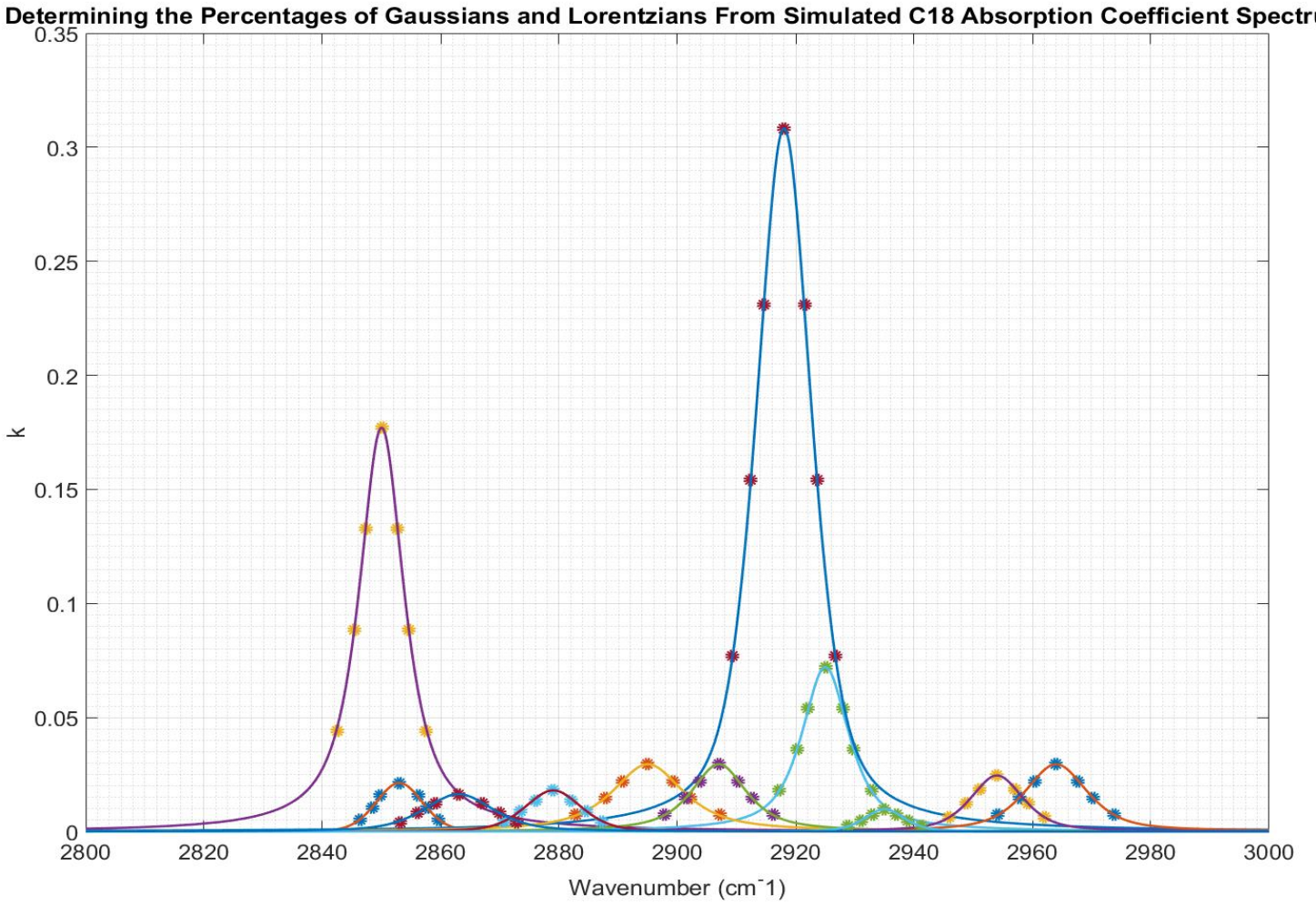
OP Wagging

IP Bending

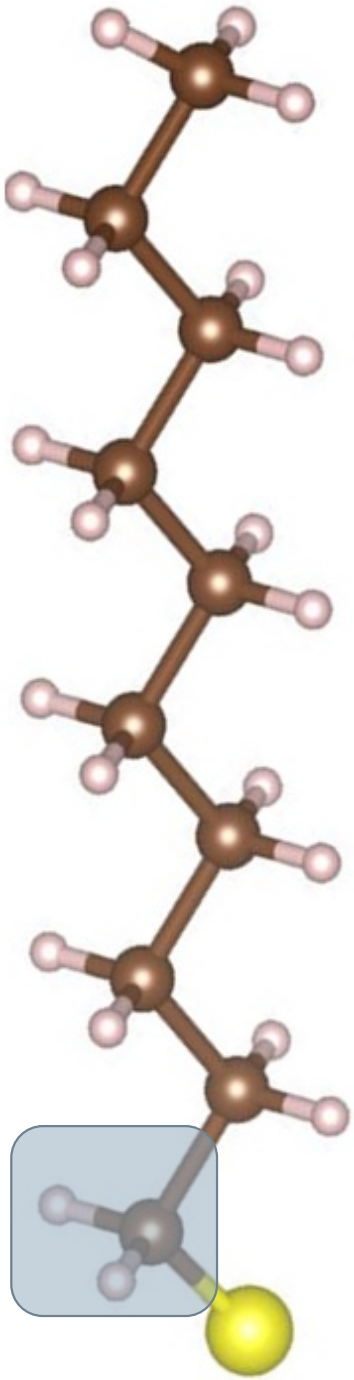


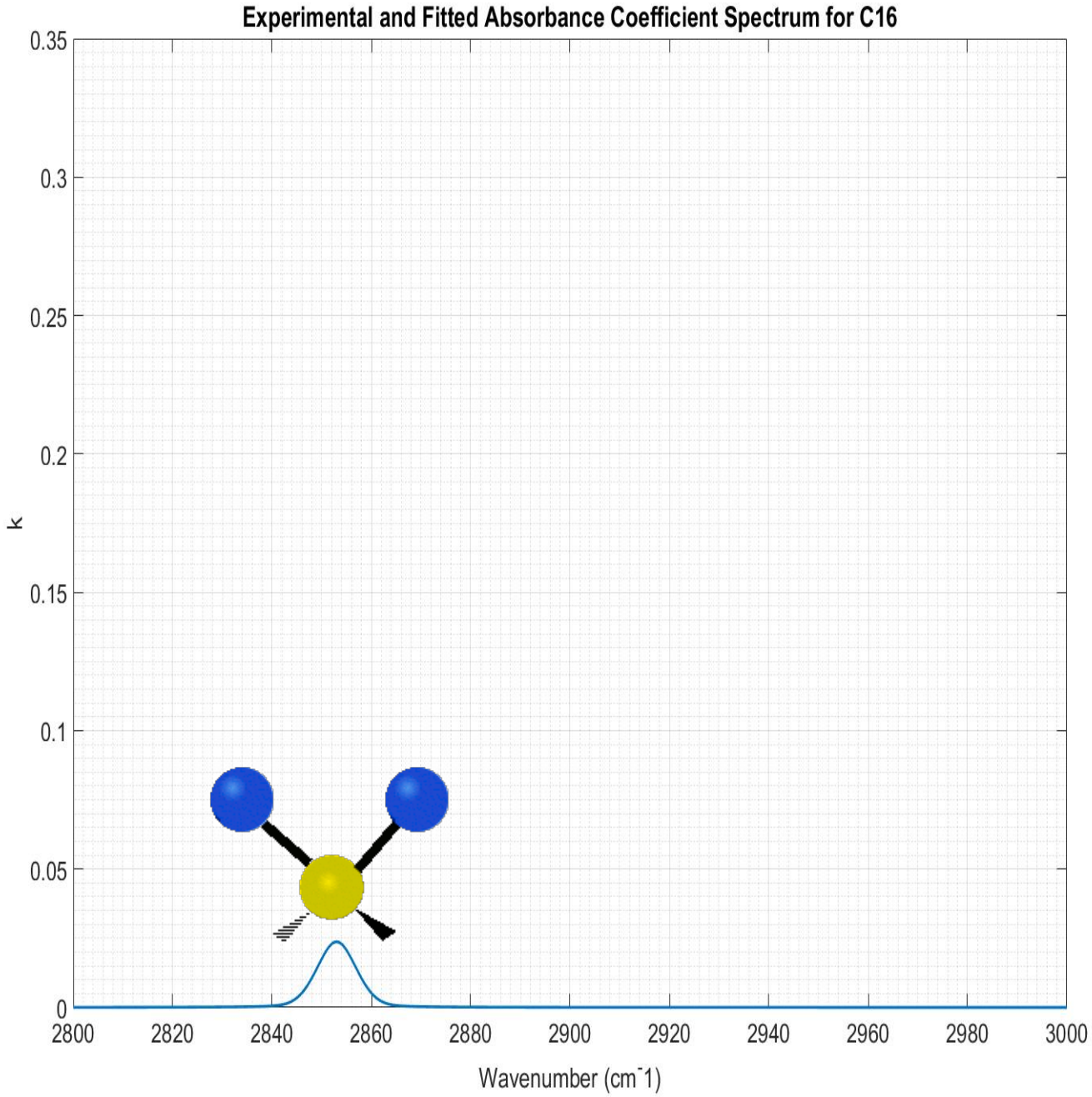
Animation Source: Wikipedia
https://en.wikipedia.org/wiki/Molecular_vibration

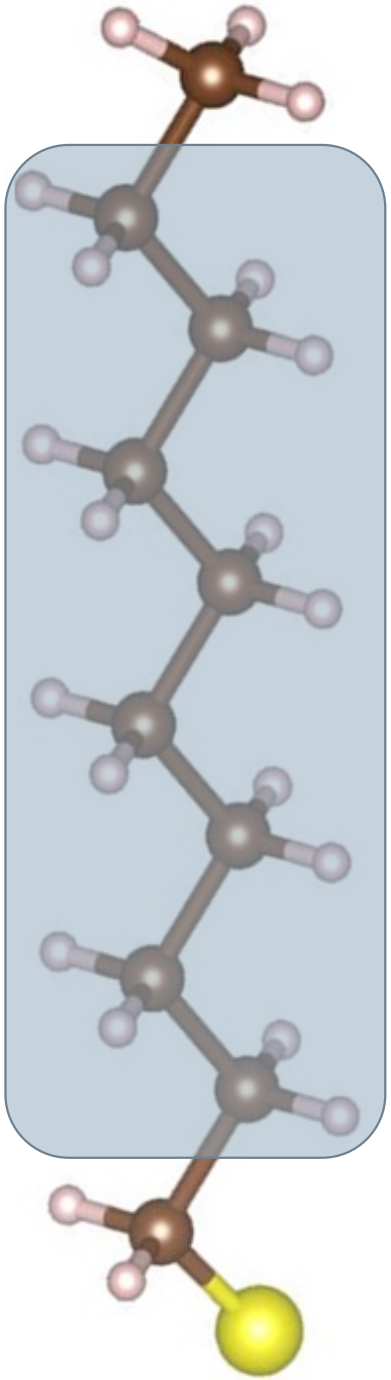
$$I \alpha | E \bullet p |^2$$

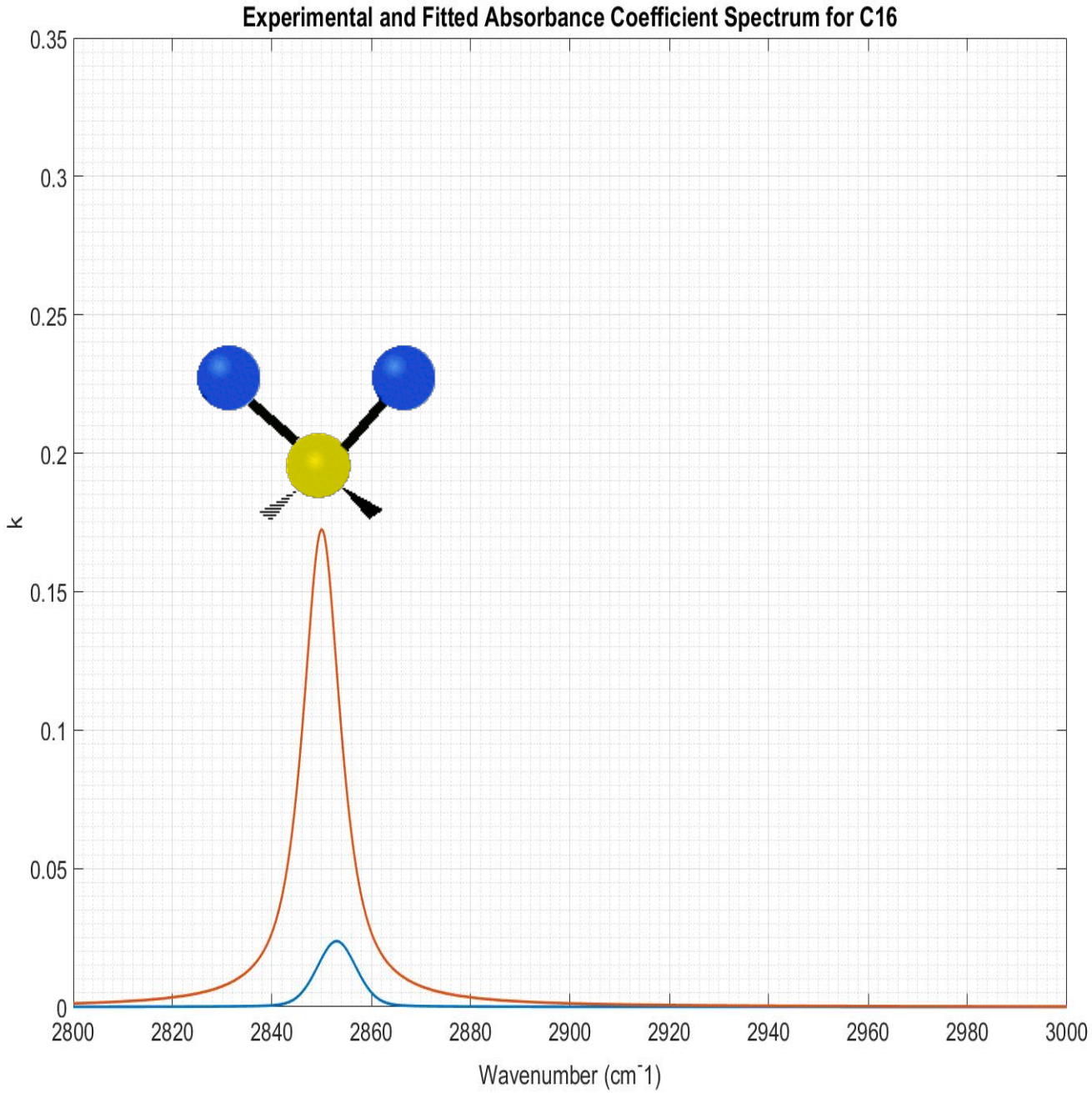


- Measurements of widths at ¼ peak, ½ peak and ¾ peak.
- Fit a superposition of Gaussian-Lorentzian with percentage as variable.




Experimental and Fitted Absorbance Coefficient Spectrum for C16
k
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2800
2820
2840
2860
2880
2900
2920
2940
2960
2980
3000
Wavenumber (cm¯1)

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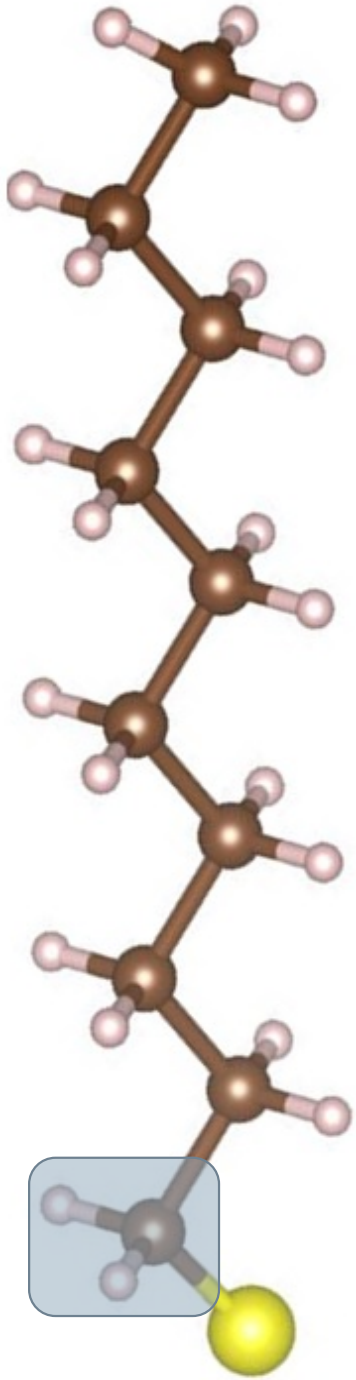

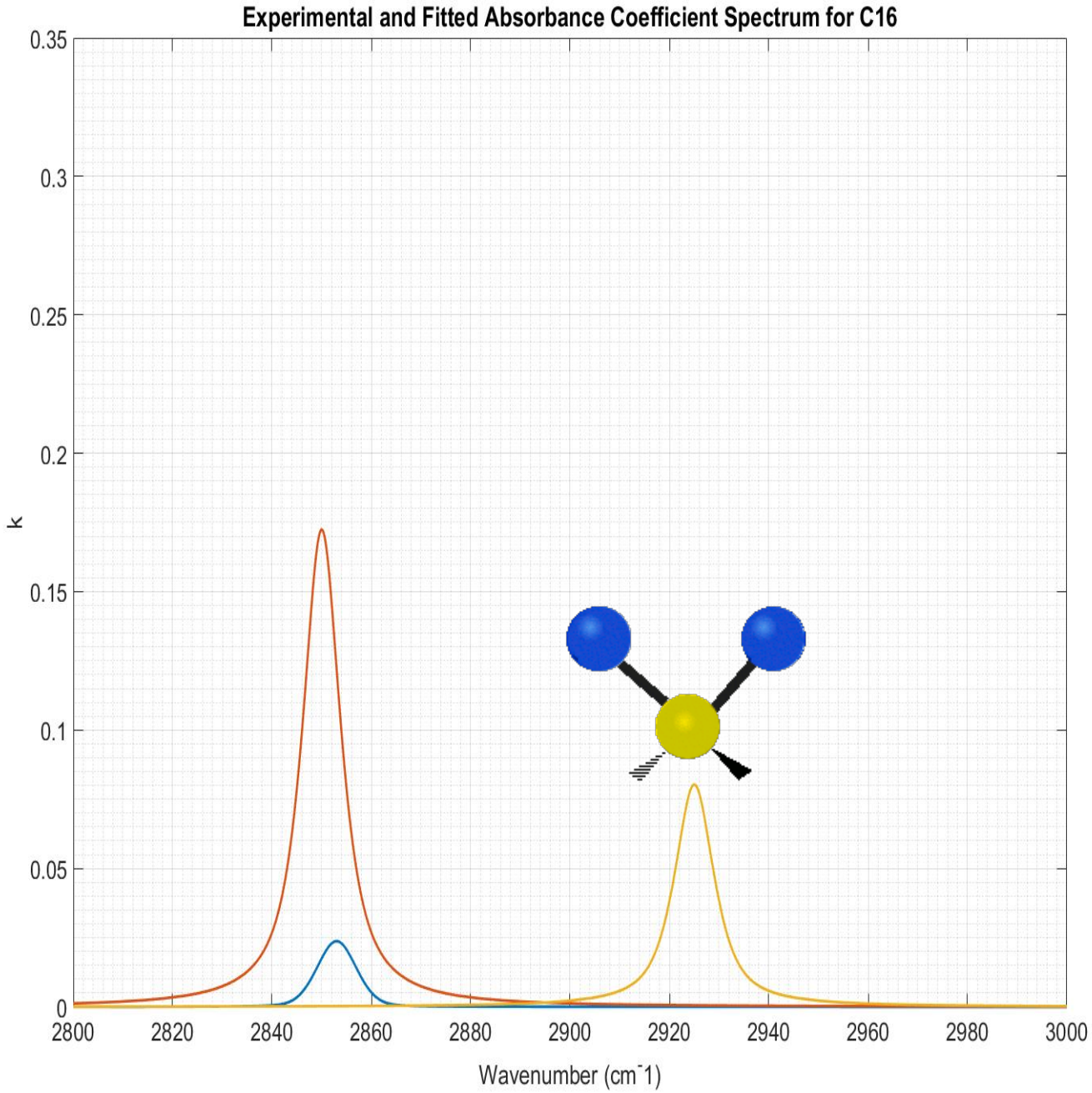
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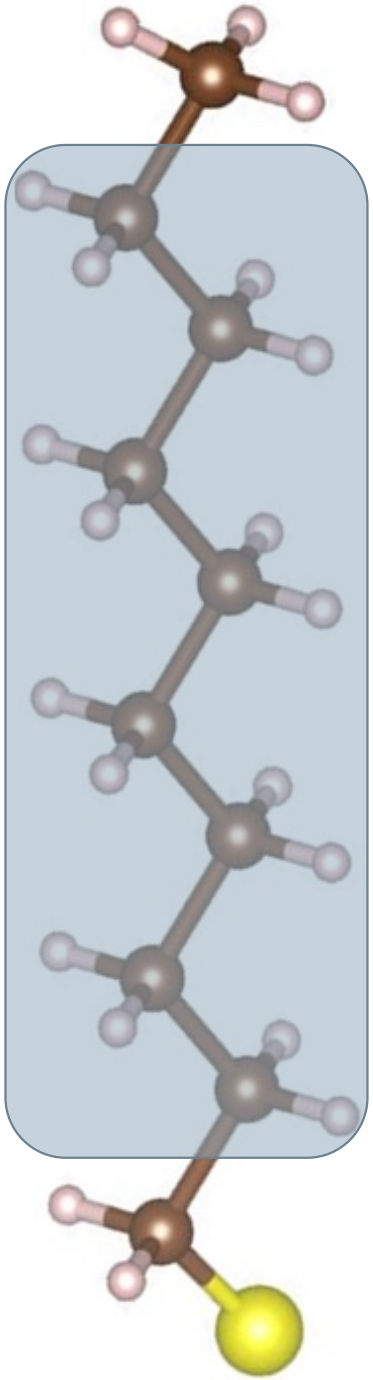
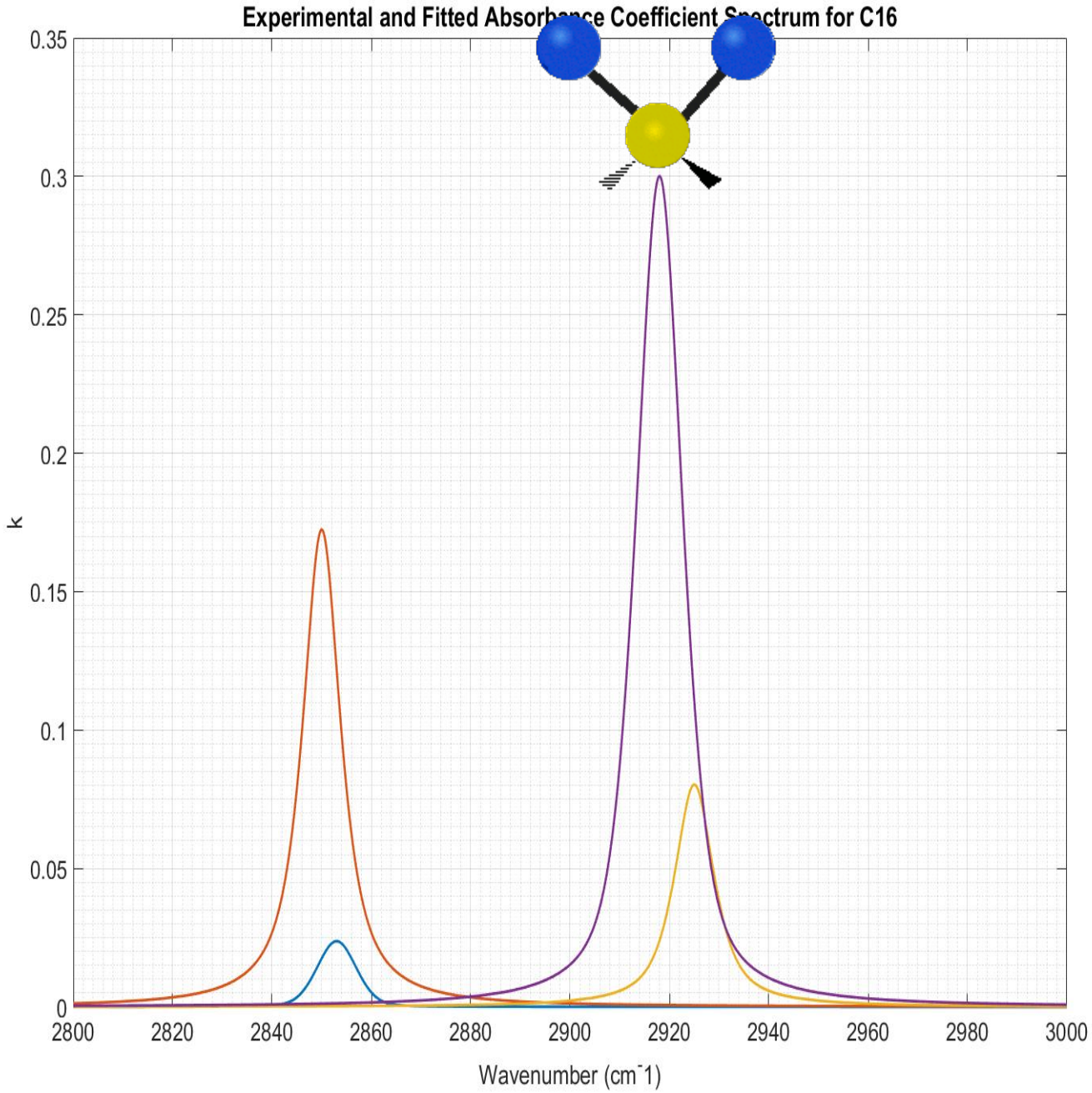
Wavenumber (cm-1)

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0.05
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0.35
2800
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2840
2860
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2900
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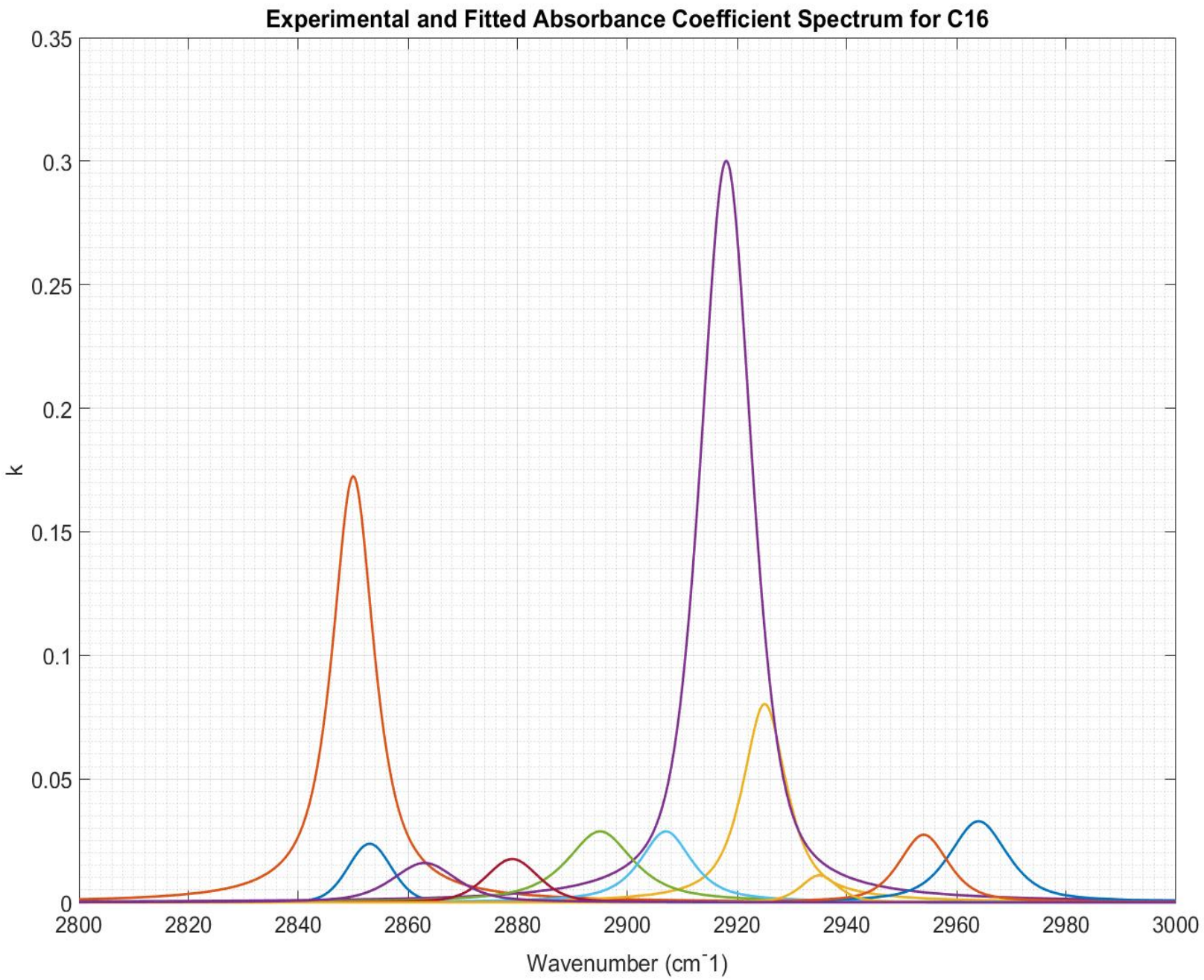
2940
2960
2980
3000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0.2
0.15
0.1
0.05
0
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2880
2900
2920
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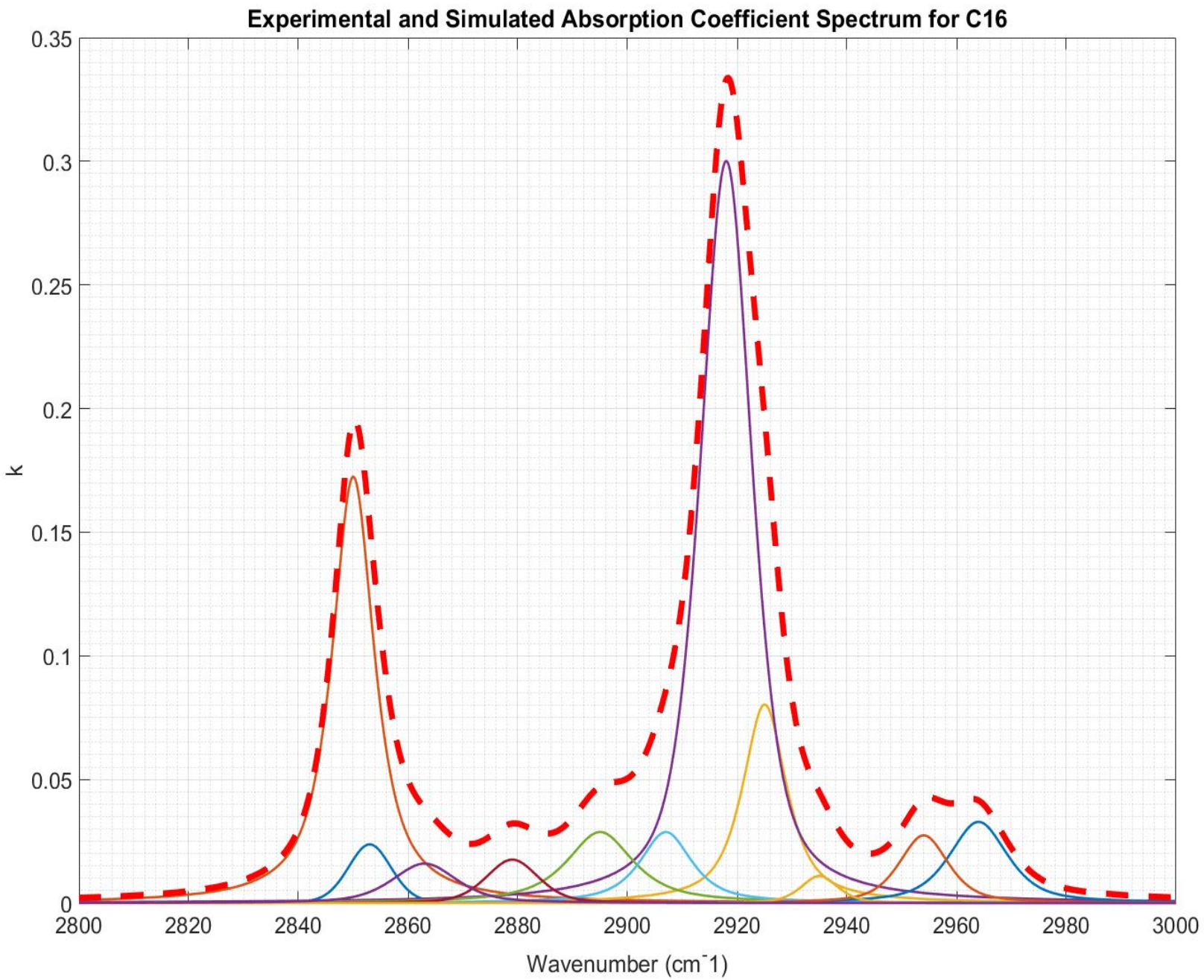
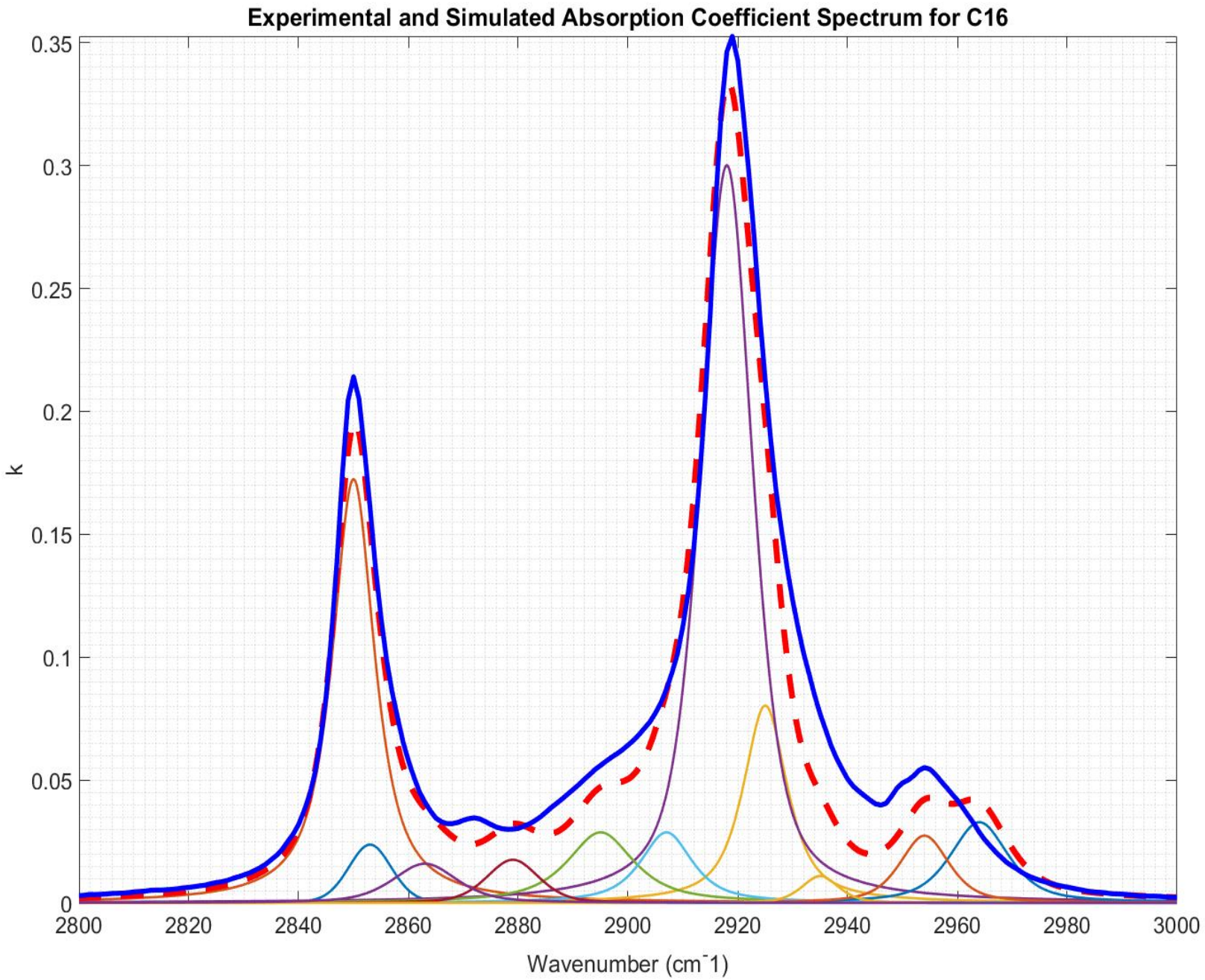
2980
3000
Wavenumber (cm¯1)


Experimental and Simulated Absorption Coefficient Spectrum for C16
k
Wavenumber (cm-1)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
2800
2820
2840
2860
2880
2900
2920
2940
2960
2980
3000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0.2
0.15
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0.05
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2860
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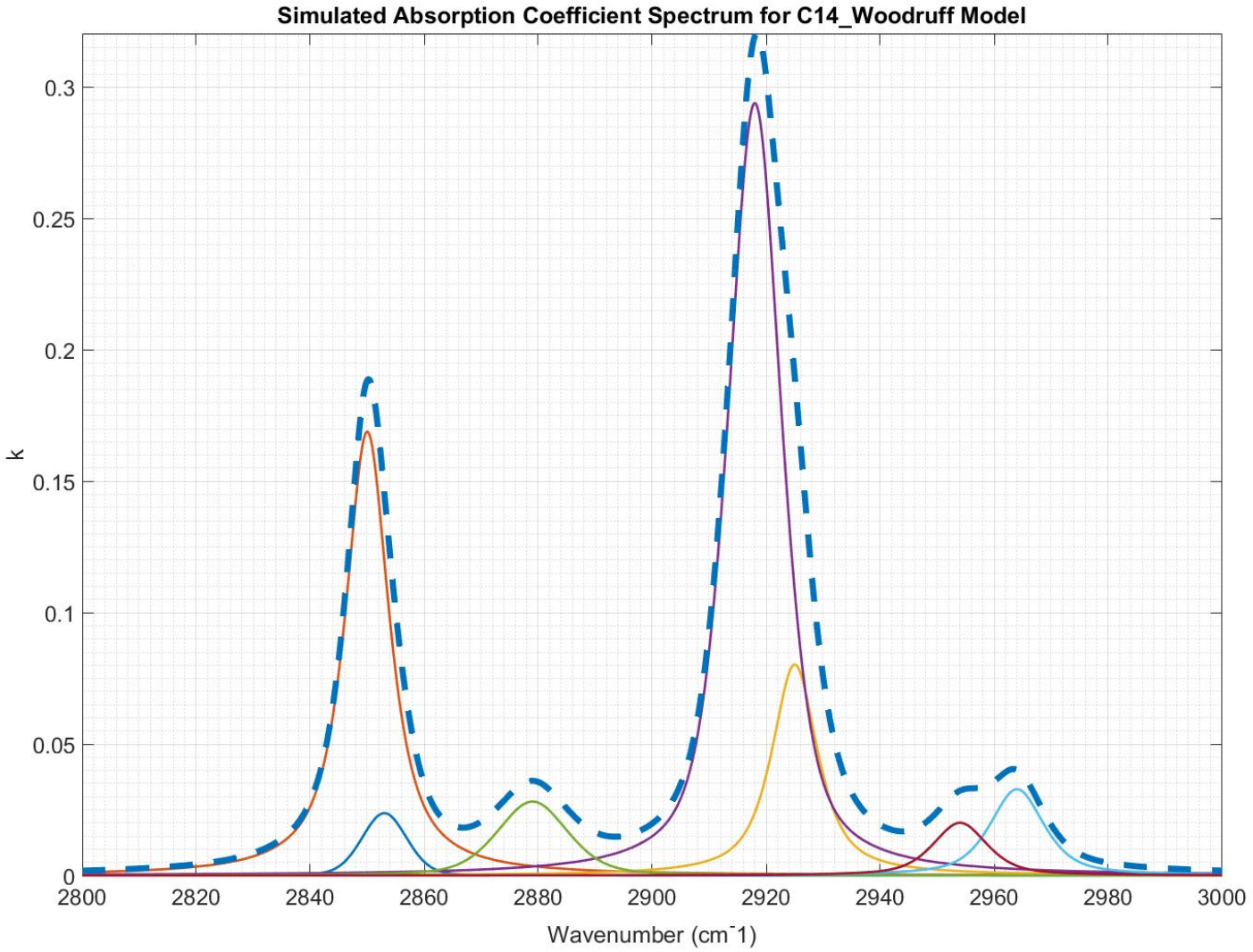
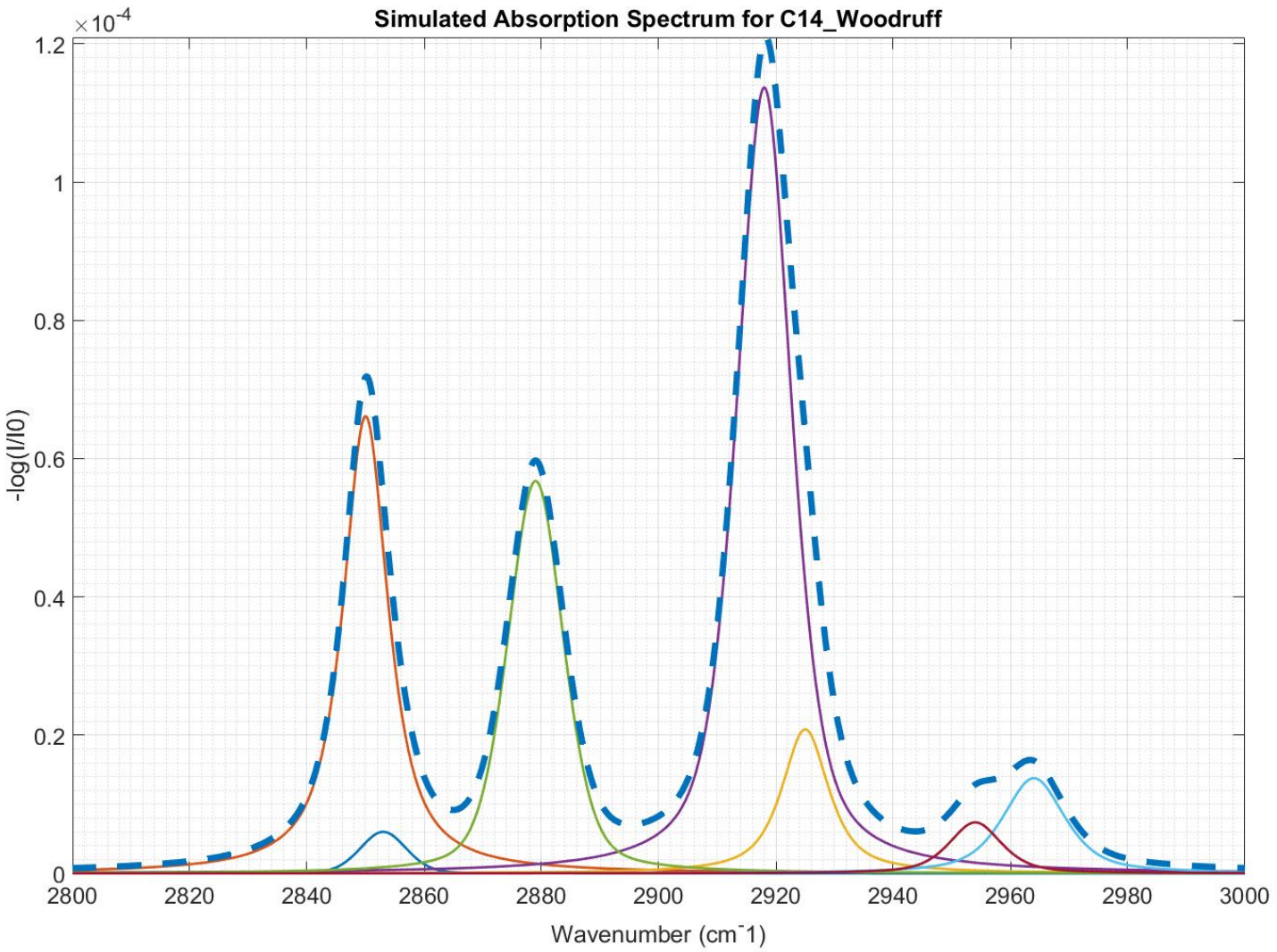
2920
2940
2960
2980
3000



Beer-Lambert Law for Isotropic systems

$$A = -\log\left(\frac{I}{I_0}\right)$$

$$\frac{I}{I_0} = e^{-4\pi k \nu t}$$


Simulated Absorption Spectrum for C14_Woodruff
×10^-4
1.2
1
0.8
0.6
0.4
0.2
0
-log(I/I0)
2800
2820
2840
2860
2880
2900
2920
2940
2960
2980
3000
Wavenumber (cm^-1)

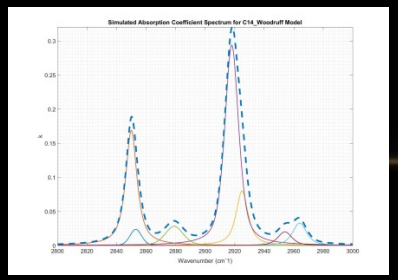
CONCLUSION

SAM Literature

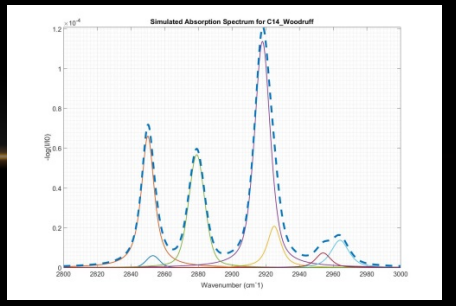
Molecular Dynamics data

CODE

Absorption Coefficient Spectrum



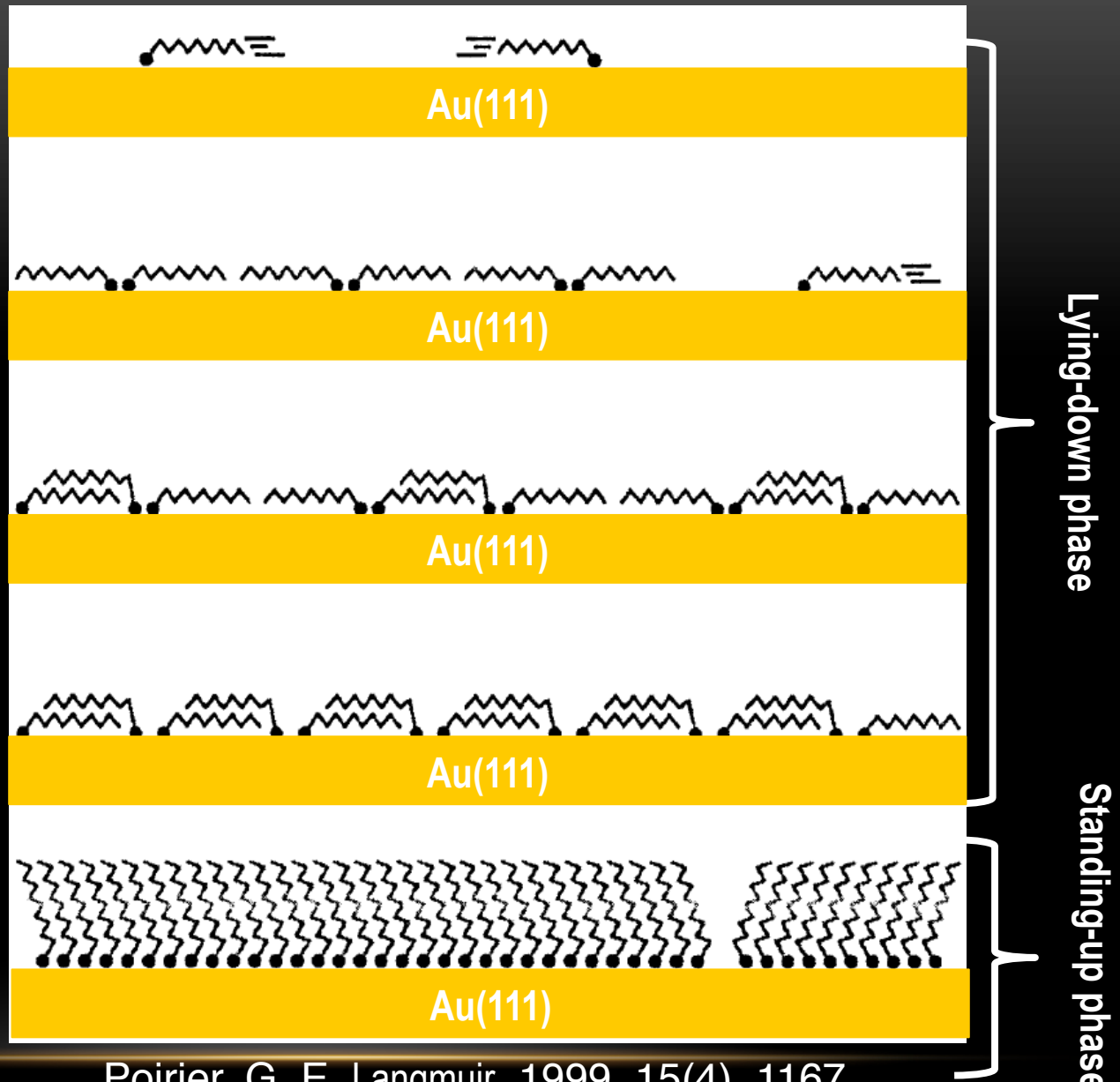
Absorption Spectrum



ACKNOWLEDGEMENTS

- Dr. Lloyd Bumm, Soumya and Mitchell
- REU Program
- Dr. Strauss, Dr. Abbott and Rishabh
- Chris's mom

Gold diggers be like…



Poirier, G. E. Langmuir, 1999, 15(4), 1167