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GAS PHASE CHEMICAL PHYSICS

UV Photofragment Spectroscopy and Electronic Energy Transfer on a Peptide Scaffold: The Case of Near-Degenerate UV Chromophores

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Sandia National Laboratories

75th International Symposium on Molecular Spectroscopy

Mini-symposium: Spectroscopy meets Chemical Dynamics

June 24th, 2022

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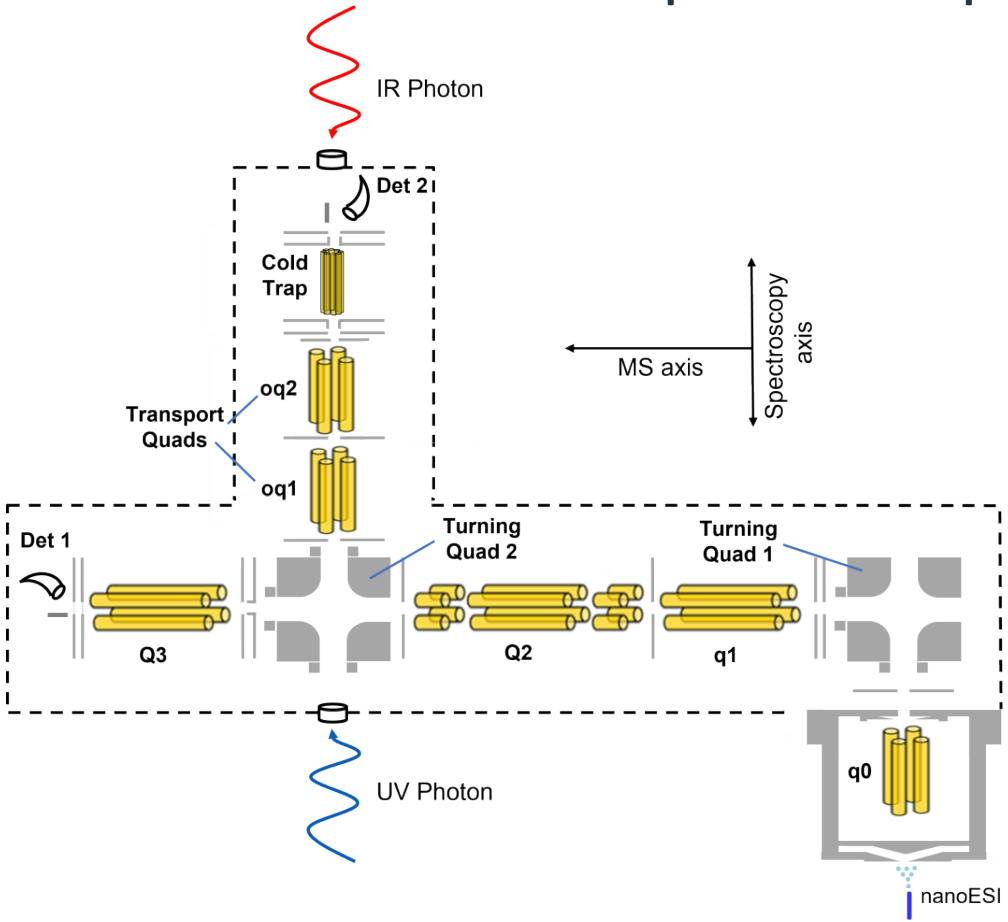
UV Photofragment Spectroscopy and Electronic Energy Transfer on a Peptide Scaffold: The Case of Near-Degenerate UV Chromophores

- Instrumental Methods
- Peptide Scaffold
- UV Spectra
- Photofragment Mass Spectra
- IR Spectra
- Summary

Instrumentation and Methods for Cold Ion Spectroscopy

- Nano-ESI
- Parent isolation in Q2
- Cooling of parent ions in cold trap
- IR and UV spectroscopy of cold ions in cold trap
- Parent knockout in Q3
- Photofragment analysis in Q3



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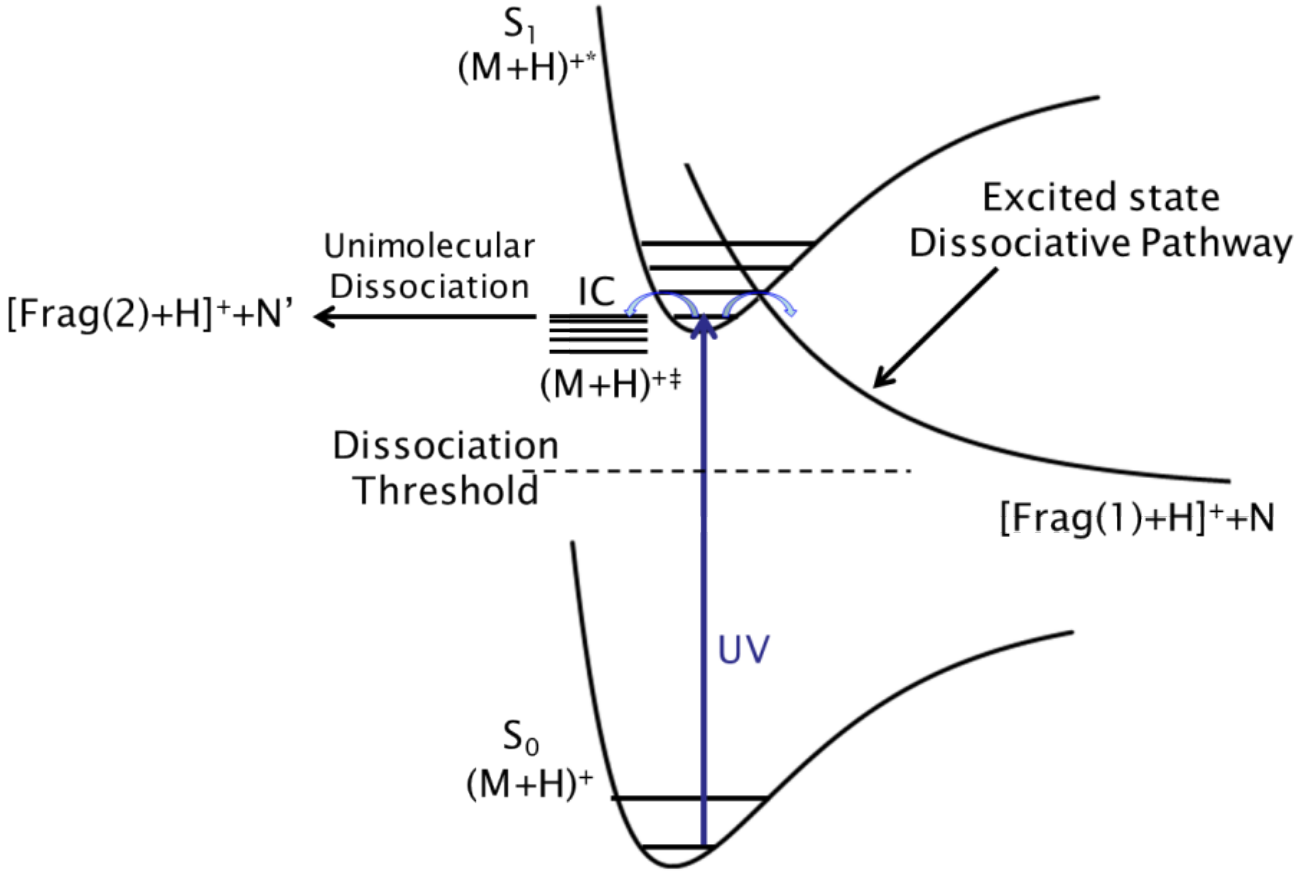
JG Redwine, ZA Davis, NL Burke, RA Oglesbee, SA McLuckey, TS Zwier. Int J Mass Spectrom, 2013.

UV Photofragment Spectroscopy on Cold Ions



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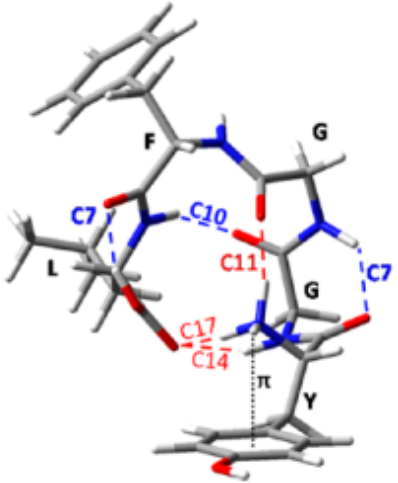
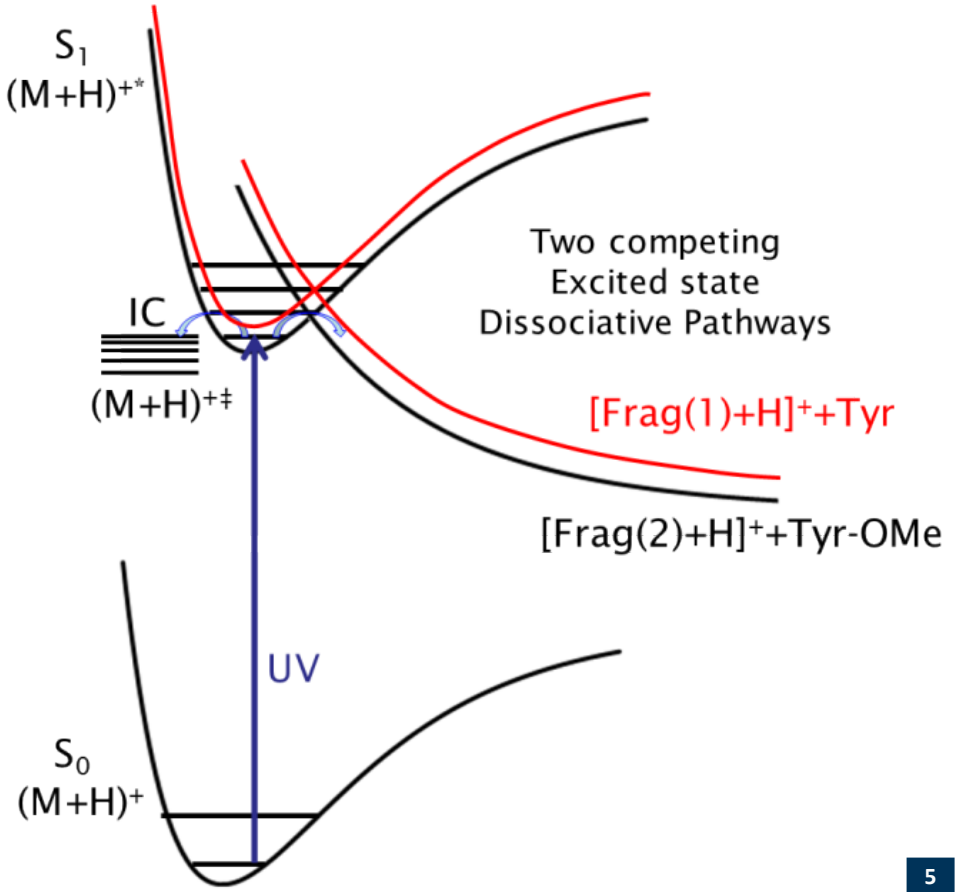
Electronic Energy Transfer between UV chromophores



- Well-defined, known starting geometry
- Excitation of single vibronic levels in either chromophore
- Collision-free probing of EET
- Close-lying excited states: Model for chromophore array (e.g., photosynthesis)



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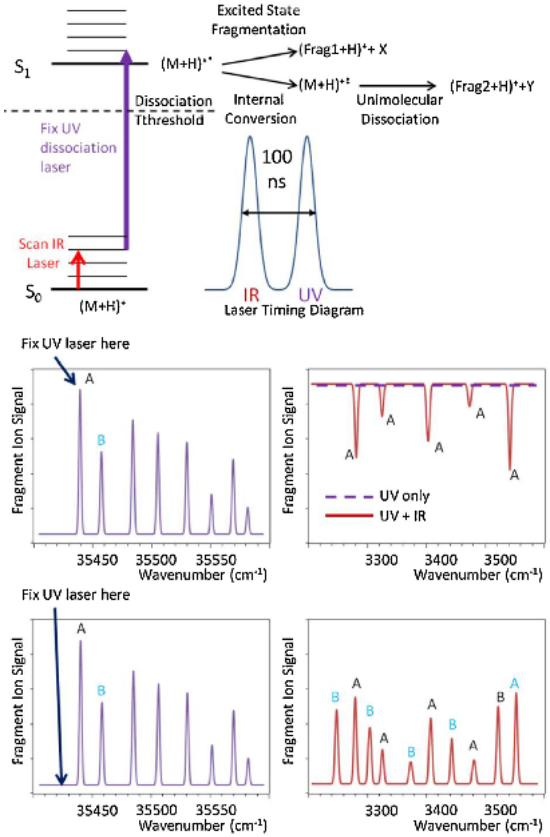
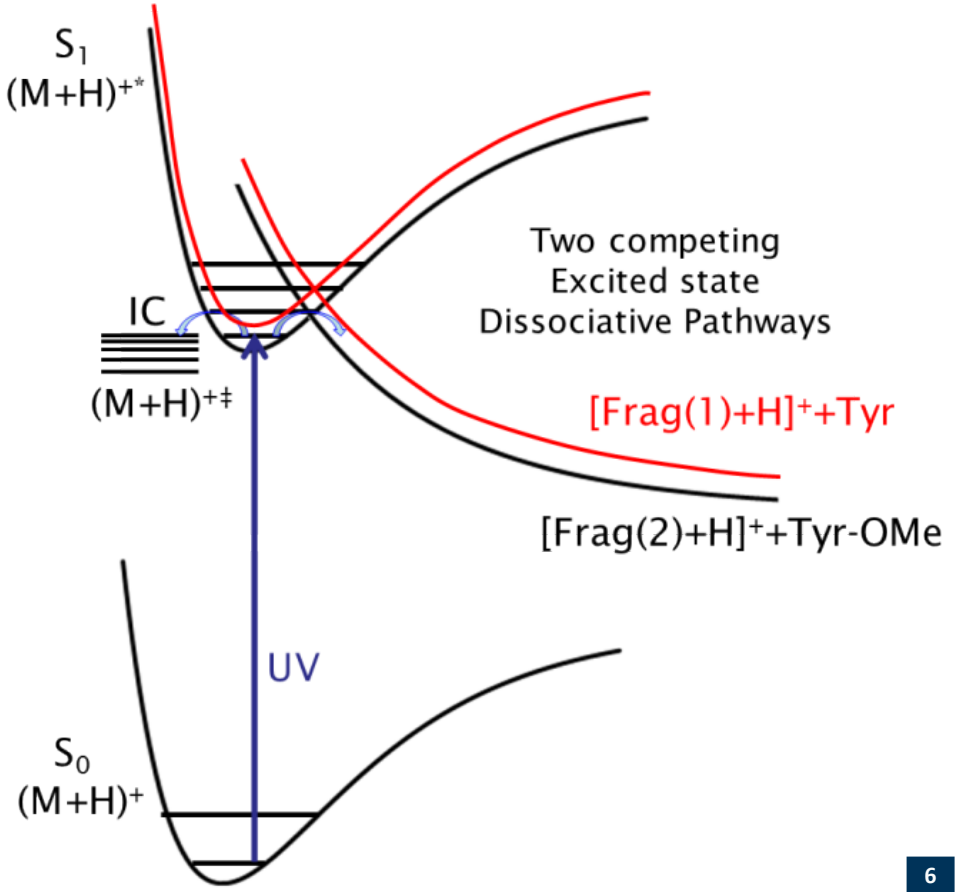
NL Burke, JG Redwine, JC Dean, SA McLuckey, TS Zwier. Int J Mass Spectrom, 2015.

IR-UV Ion Gain and Ion Dip Spectroscopy





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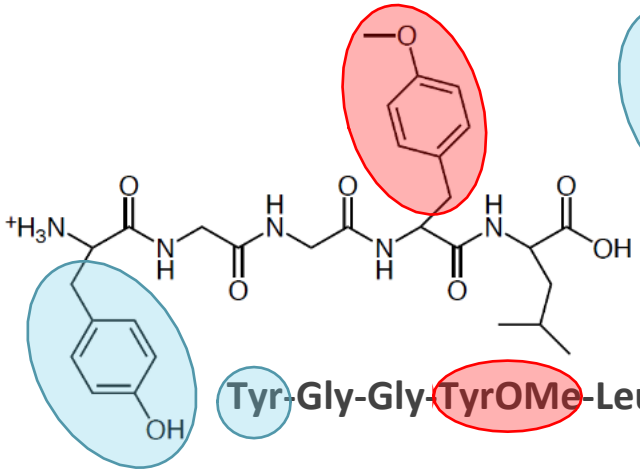
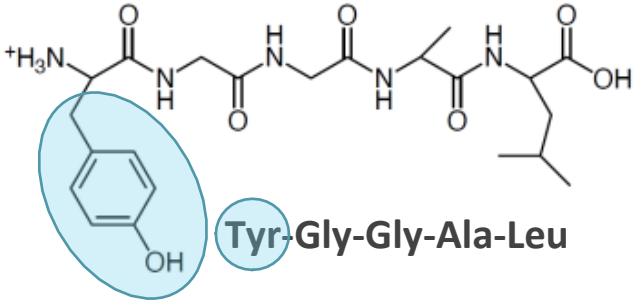
NL Burke, JG Redwine, JC Dean, SA McLuckey, TS Zwier. Int J Mass Spectrom, 2015.

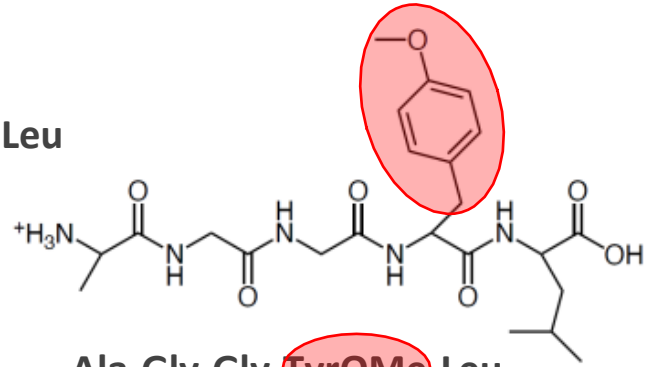
Peptide Scaffold: Tyrosine-OH and Tyrosine-OMe



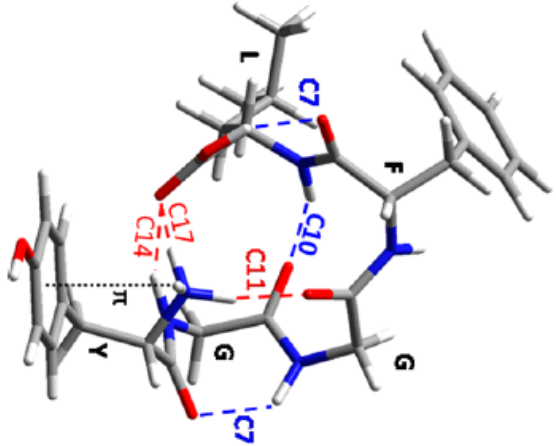
Tyr-Gly-Gly-TyrOMe-Leu

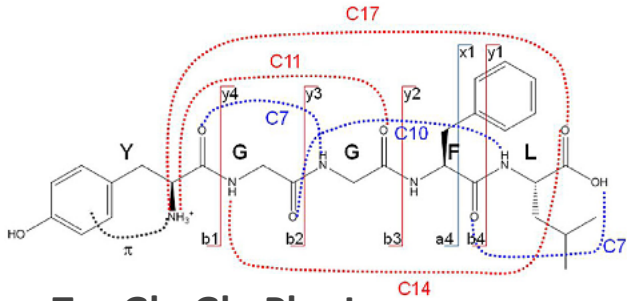


Tyr-Gly-Gly-Ala-Leu



Ala-Gly-Gly-TyrOMe-Leu





Tyr-Gly-Gly-Phe-Leu
YGGFL
Leu-enkephalin

NL Burke, JG Redwine, JC Dean, SA McLuckey, TS Zwier. Int J Mass Spectrom, 2015.

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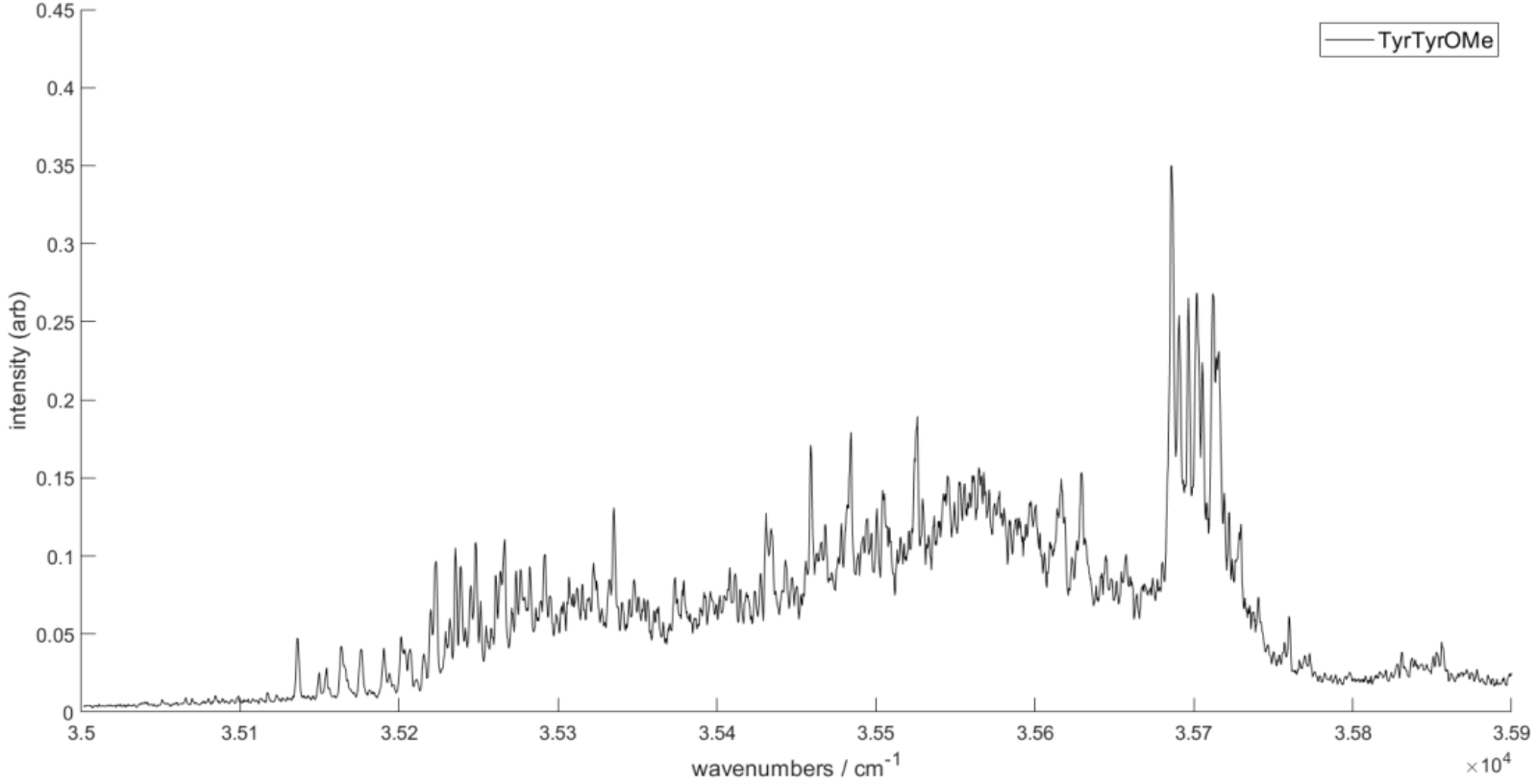
Ultraviolet Spectroscopy



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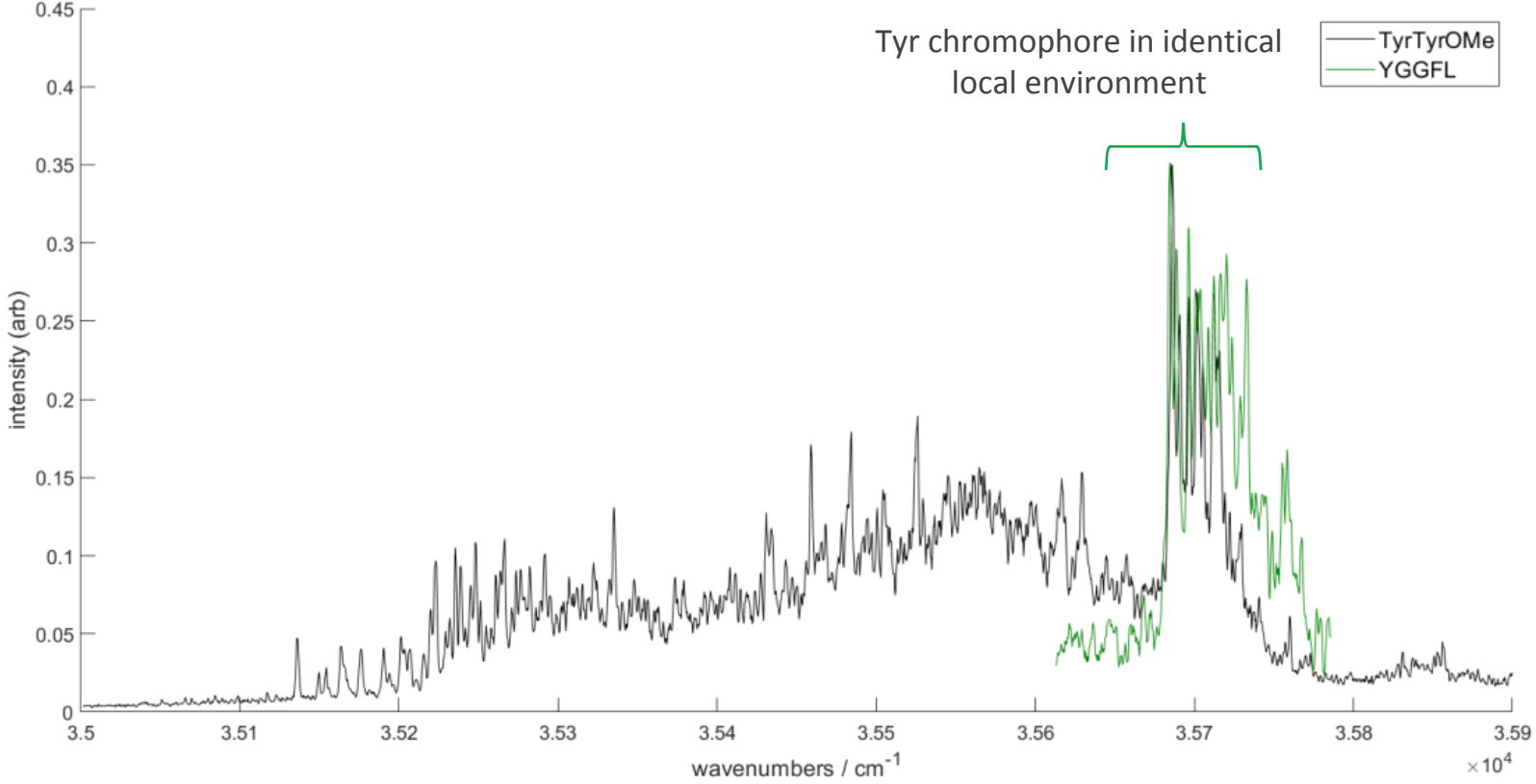
Ultraviolet Spectroscopy



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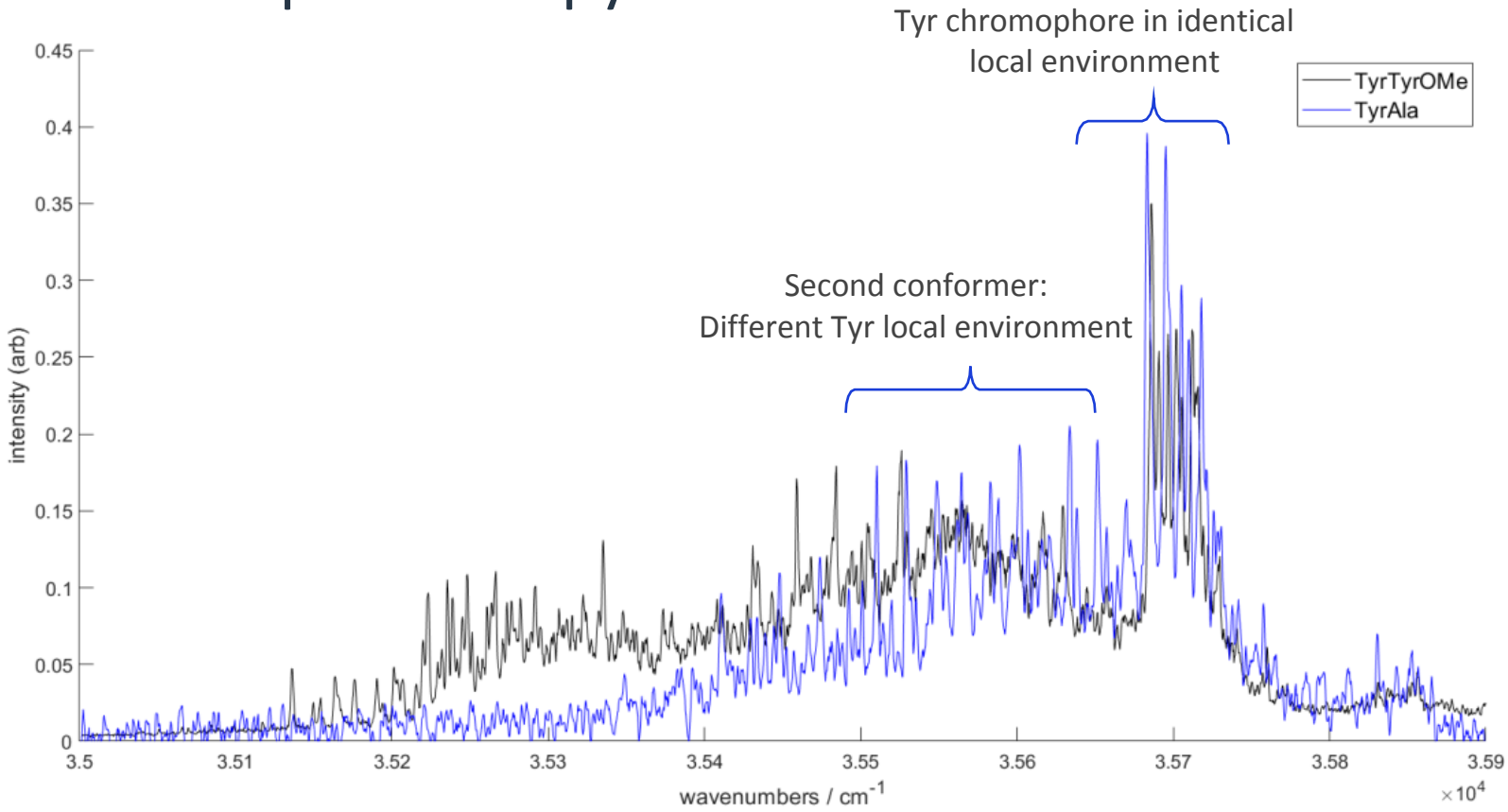
Ultraviolet Spectroscopy



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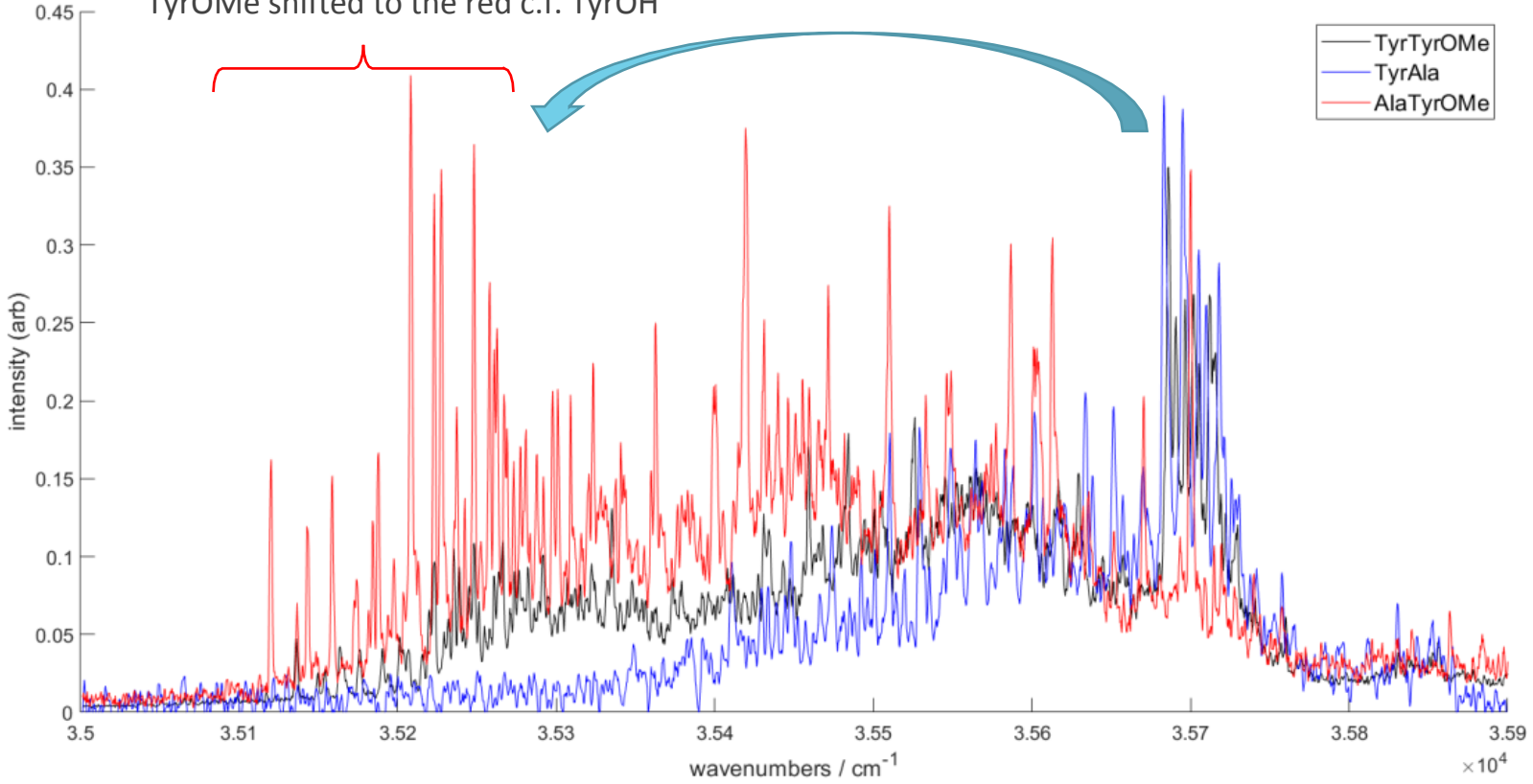
Ultraviolet Spectroscopy

TyrOMe shifted to the red c.f. TyrOH



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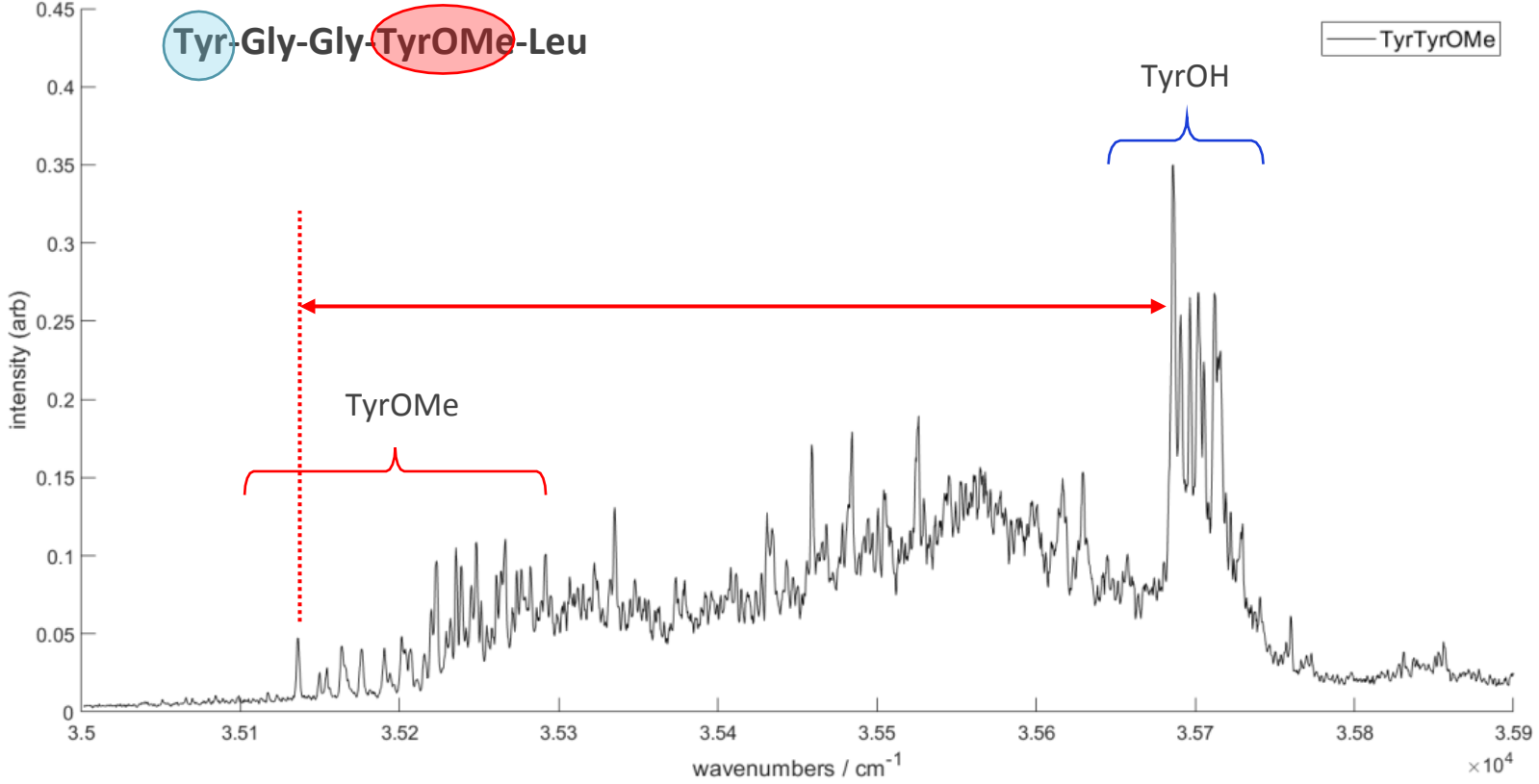
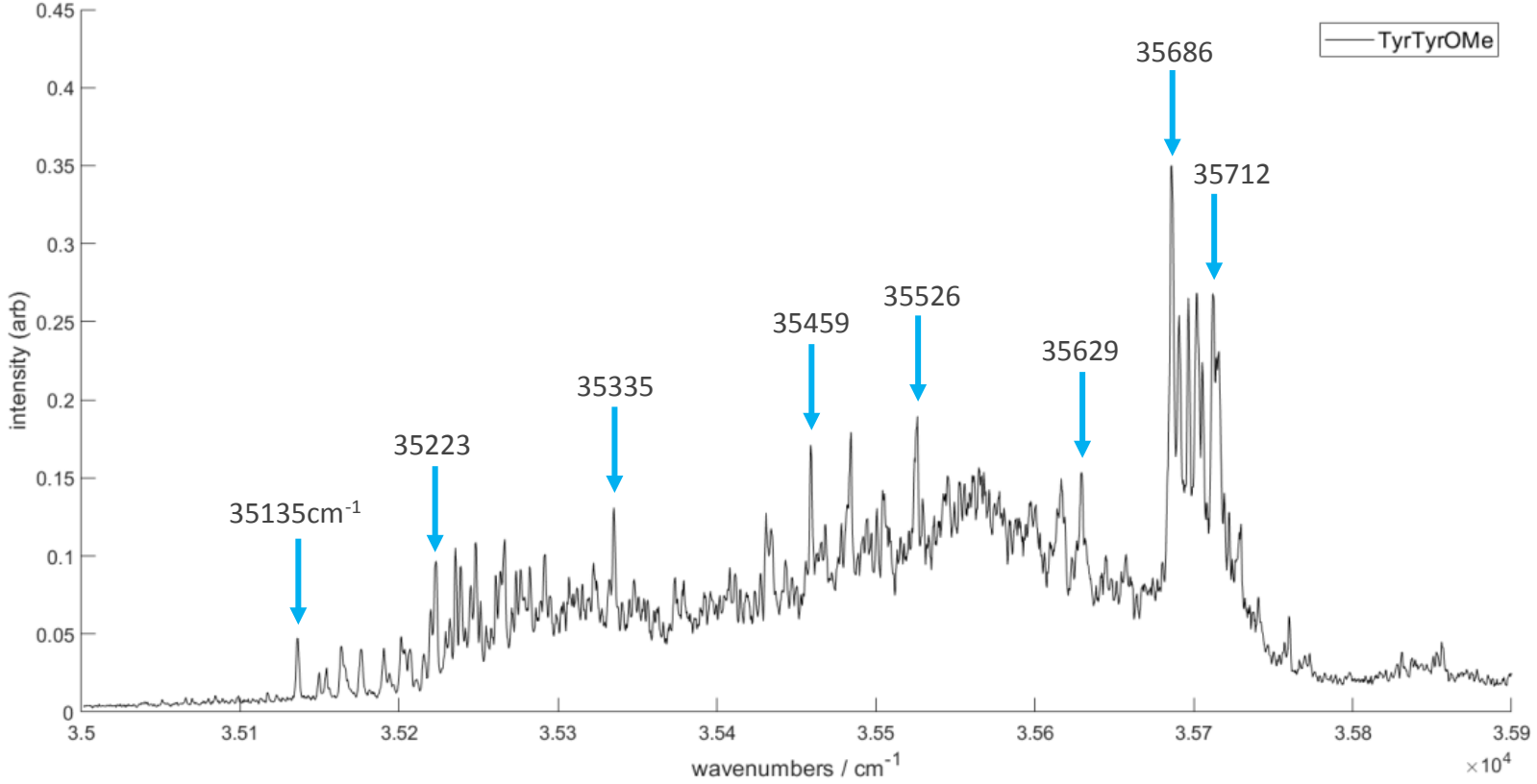
Ultraviolet Spectroscopy



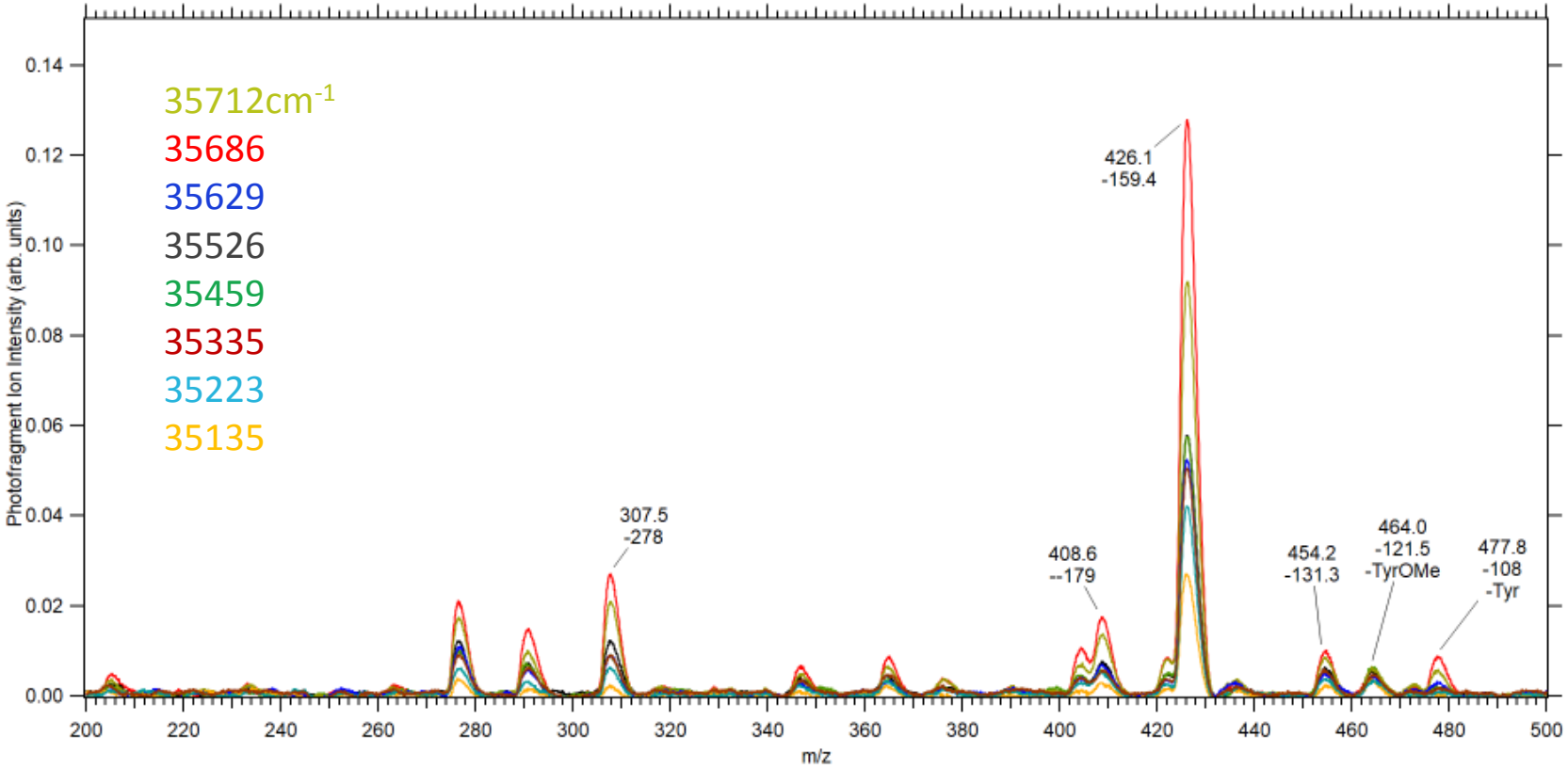
GAS PHASE CHEMICAL PHYSICS

Photofragment Mass Spectra – Tyr/TyrOMe



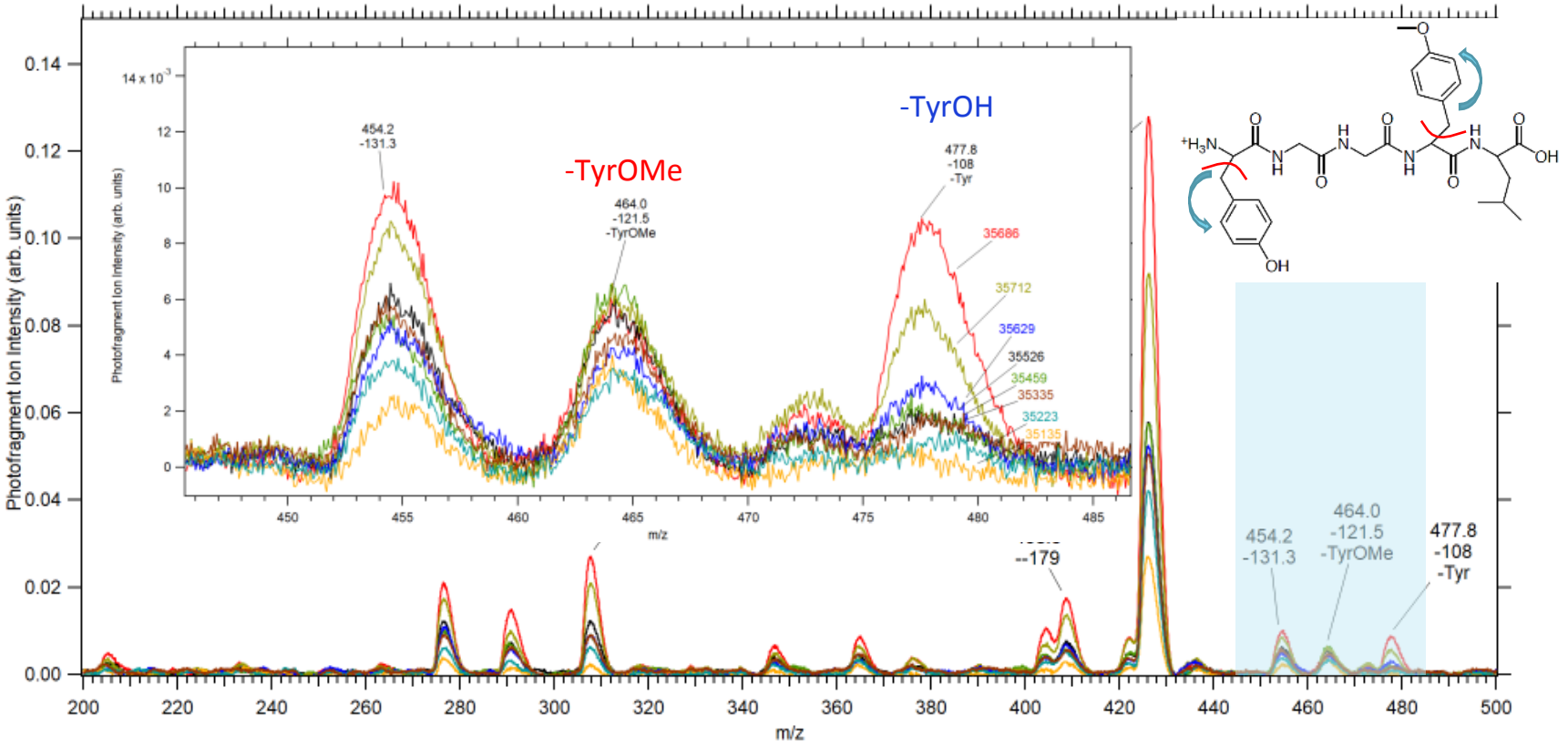
GAS PHASE CHEMICAL PHYSICS

Photofragment Mass Spectra – Tyr/TyrOMe



GAS PHASE CHEMICAL PHYSICS

Photofragment Mass Spectra – Tyr/TyrOMe

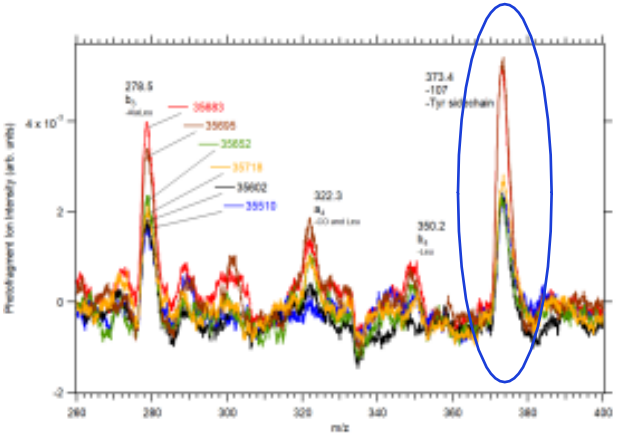


GAS PHASE CHEMICAL PHYSICS

Photofragment Mass Spectra – Tyr/TyrOMe Integrated Intensities

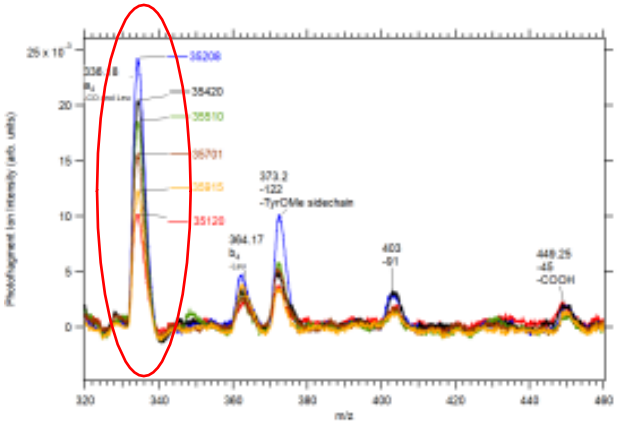
Photofragment Mass Spectra – Tyr/TyrOMe, Tyr/Ala, and Ala/TyrOMe

Tyr/Ala



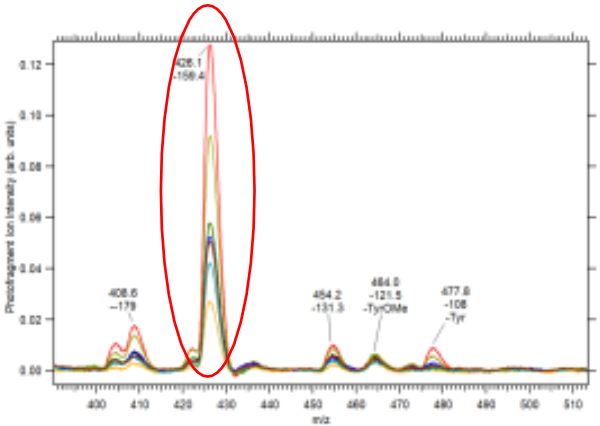
- Side chain loss dominates
- Only TyrOH

Ala/TyrOMe



- Hot ground state fragmentation dominates
- Only –TyrOMe side chain loss

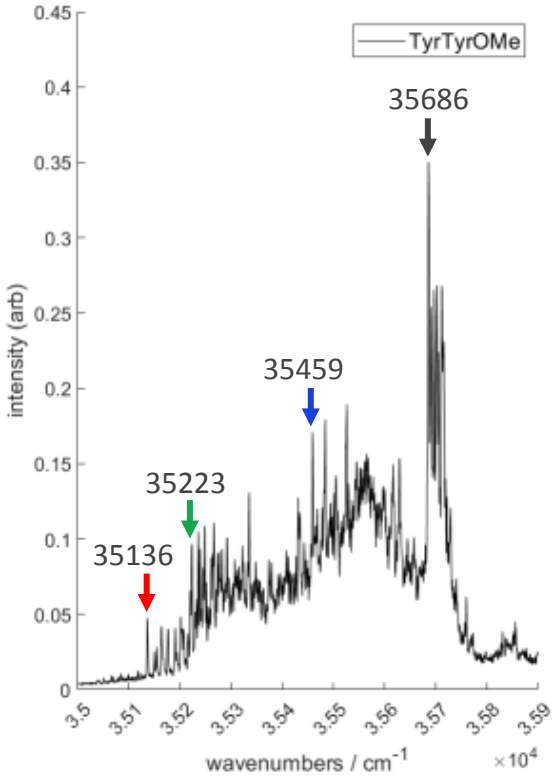
Tyr/TyrOMe

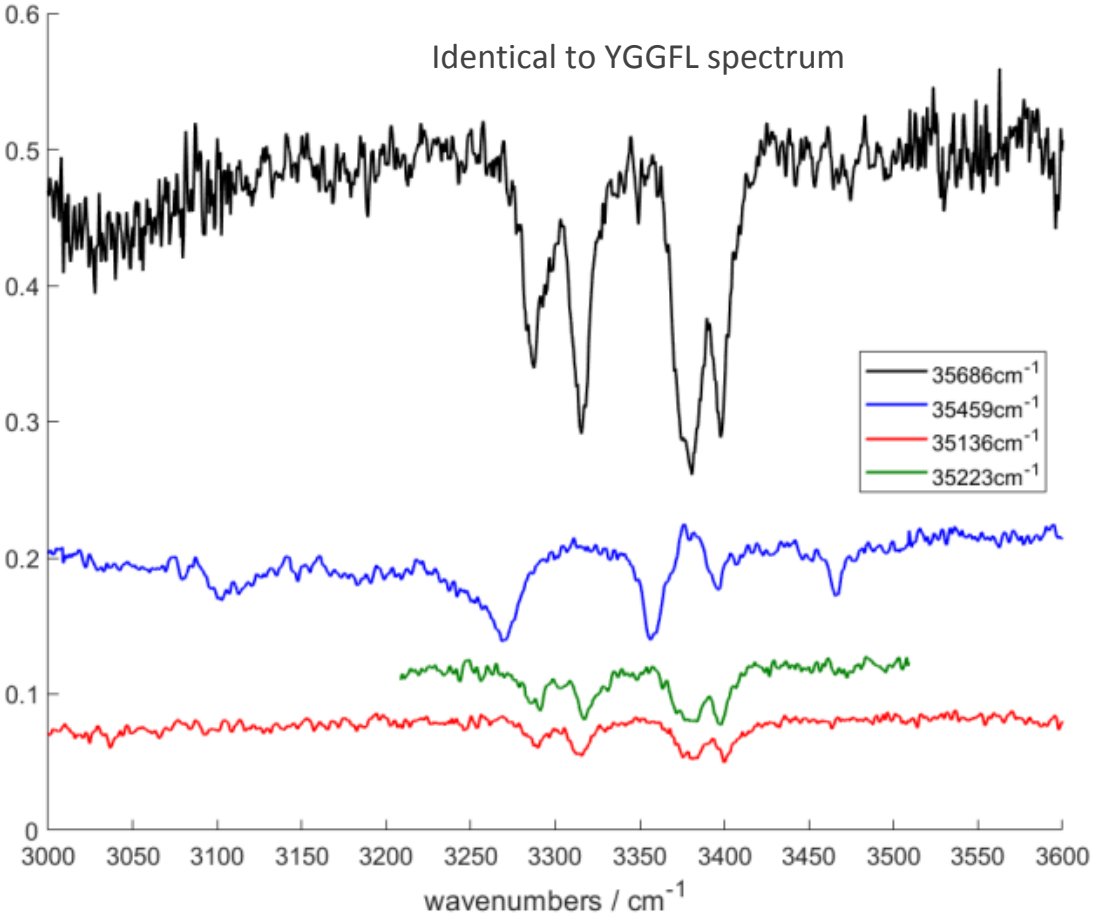


- Hot ground state fragmentation dominates
- Both side chain loss, λ dependent

GAS PHASE CHEMICAL PHYSICS

Infrared Spectroscopy – Tyr/TyrOMe





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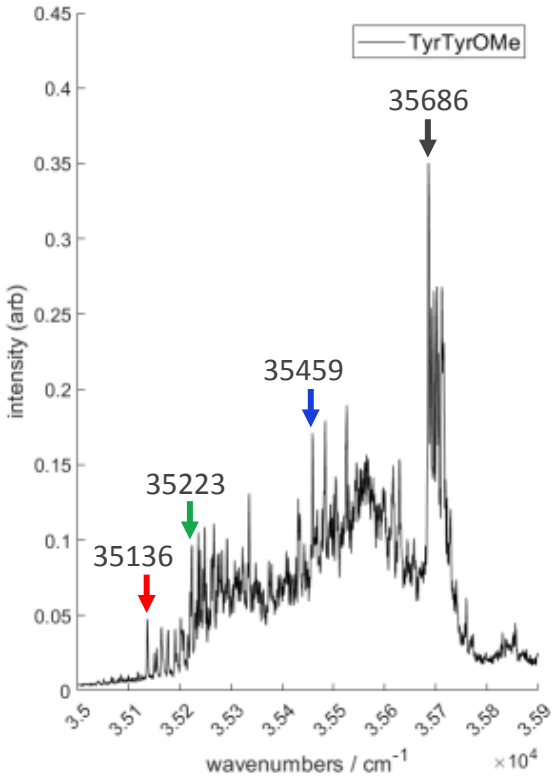
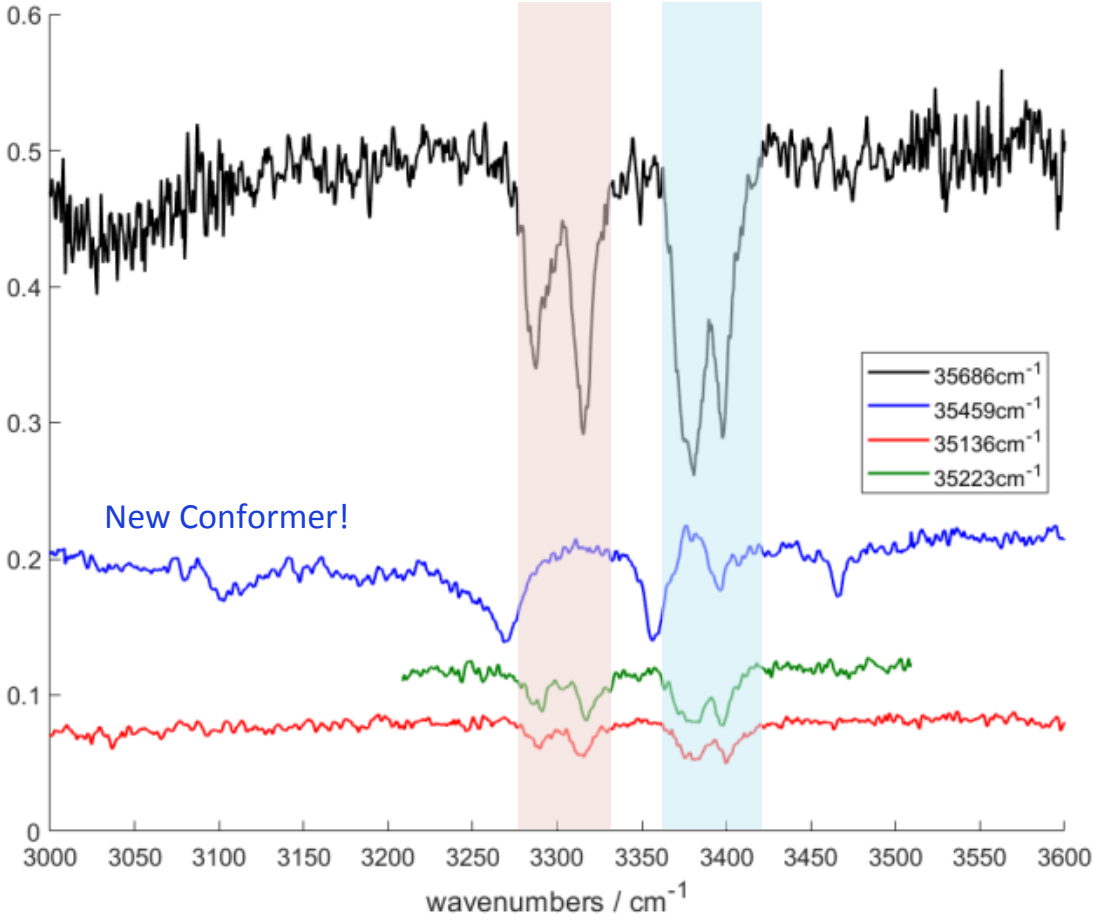
Infrared Spectroscopy – Tyr/TyrOMe





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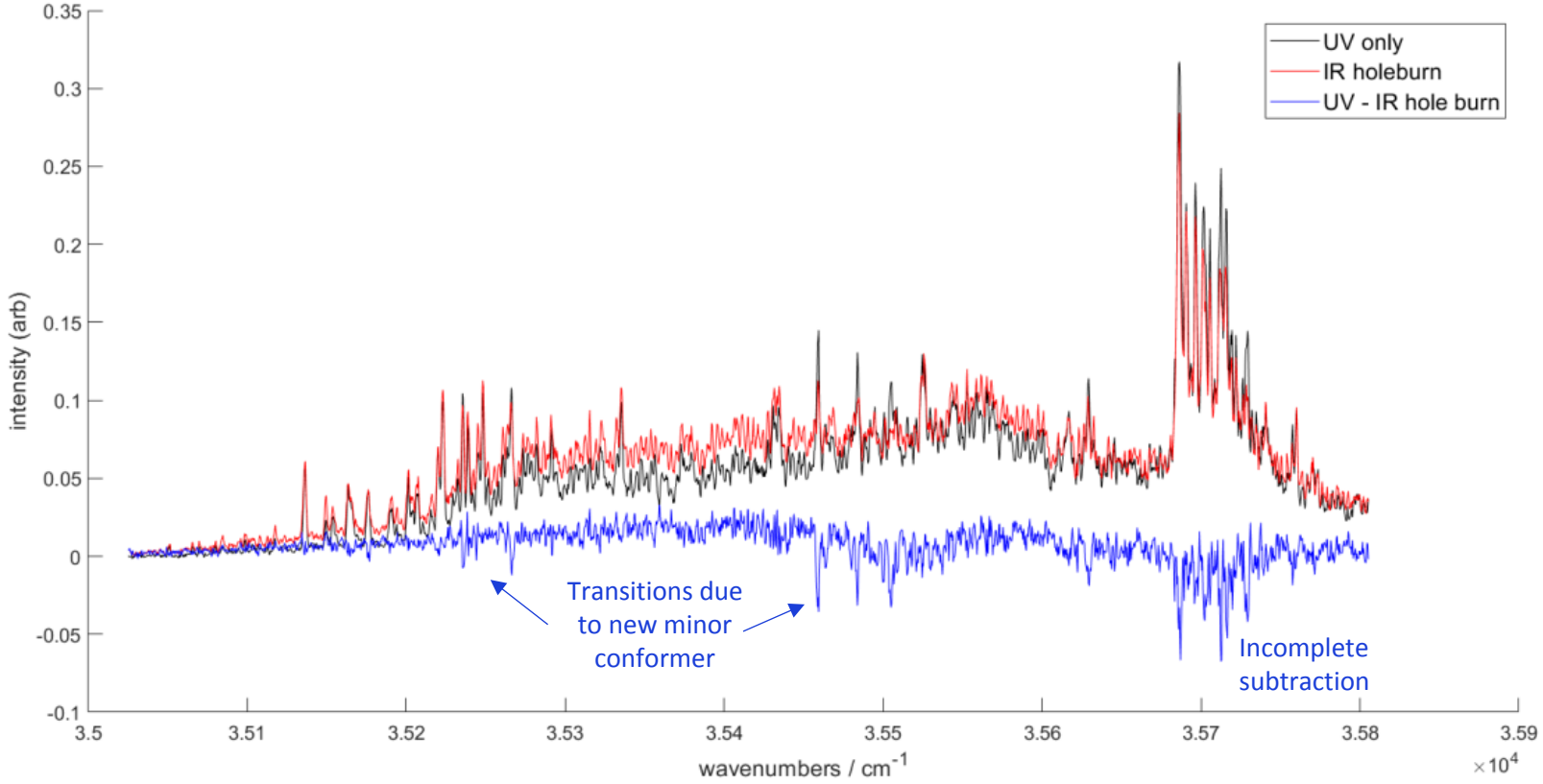
IR-UV Hole-burning – Tyr/TyrOMe



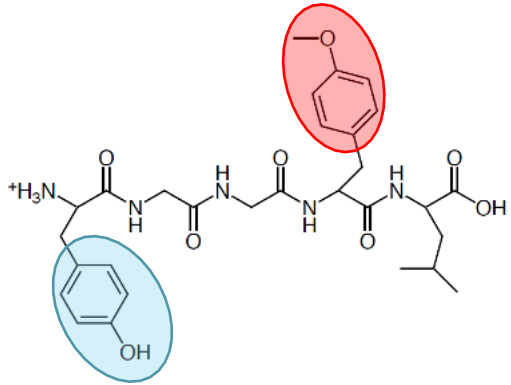
GAS PHASE CHEMICAL PHYSICS

Summary

- Tyr/TyrOMe peptide series has similar structure as previously studied YGGFL
- There are varying amounts electronic energy transfer observed.
- The TyrOMe-containing peptides may have faster internal conversion than YGGFL, Tyr/Ala.
- There is an additional Tyr/TyrOMe conformation confirmed by IR dip spectra

Future Work

- Excited state IR spectra
- Assign minor conformer
- Study TyrOMe/Tyr peptide series
- UV-UV hole burning
- Quantify single vibronic level EET rates



Insert TyrOMe/Tyr structure

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