This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2022-11661C

GAS PHASE CHEMICAL PHYSICS

Double Resonance Studies of the Structures and Dynamics of Cryo-cooled Peptide Ions

Casey D. Foley[1], Kendrew Au[1], Etienne Chollet[2], Matthew A. Kubasik[2], and Timothy S. Zwier[1]
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[2]Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT, USA

40 Years of Gas Phase Laser Spectroscopy: An On-going Story

September 6th, 2022

Sandia National Laboratories

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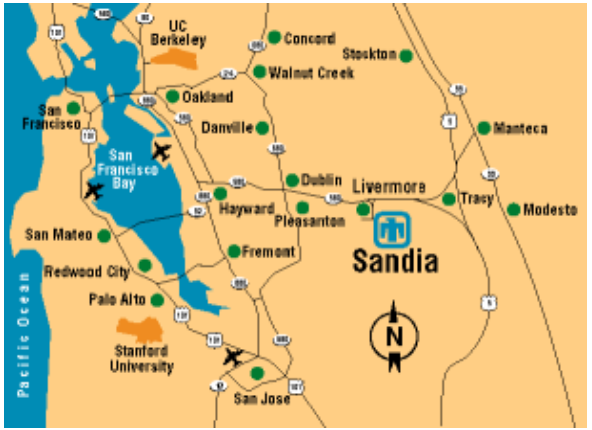
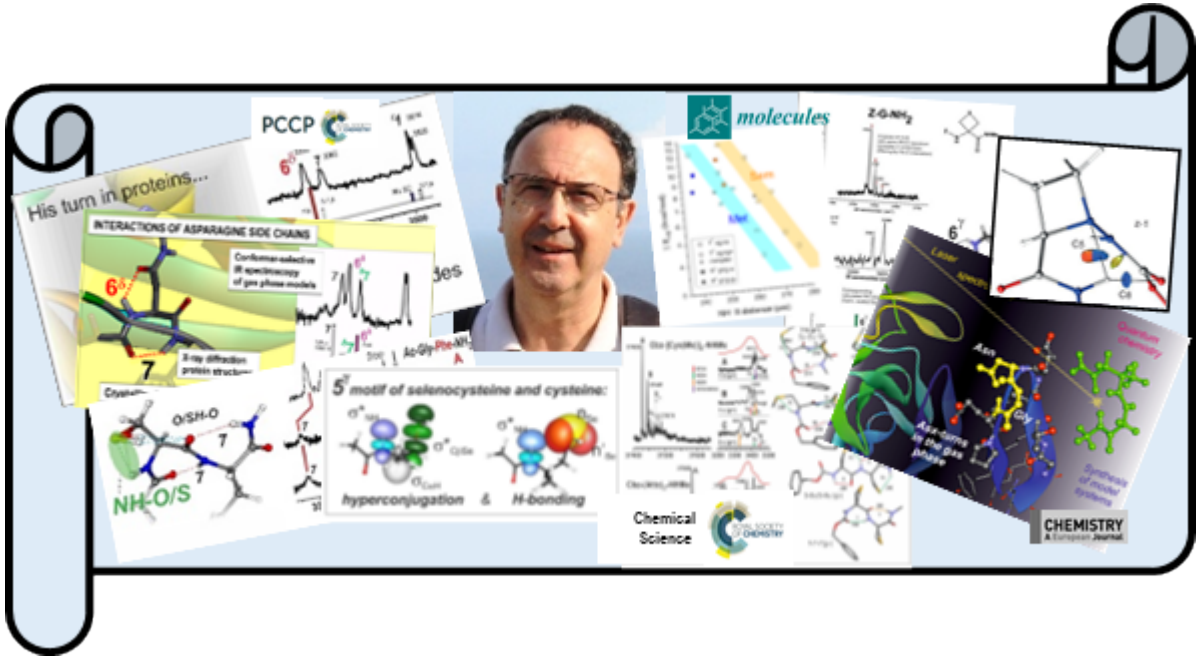
Livermore, California



Gas Phase Chemical Physics
Sandia National Laboratories
Livermore, CA

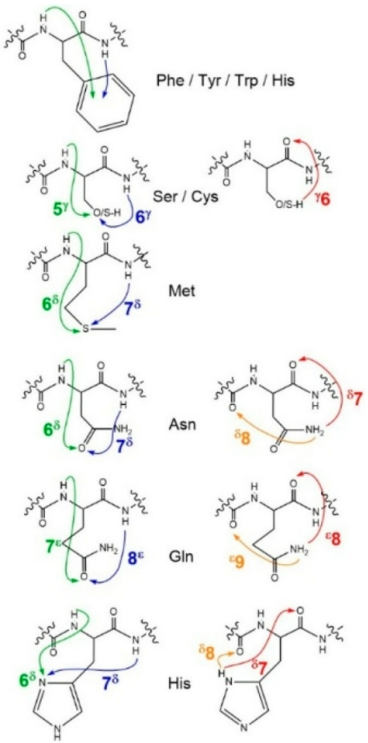
GAS PHASE CHEMICAL PHYSICS

Single-Conformation Laser Spectroscopy of Neutral Peptides

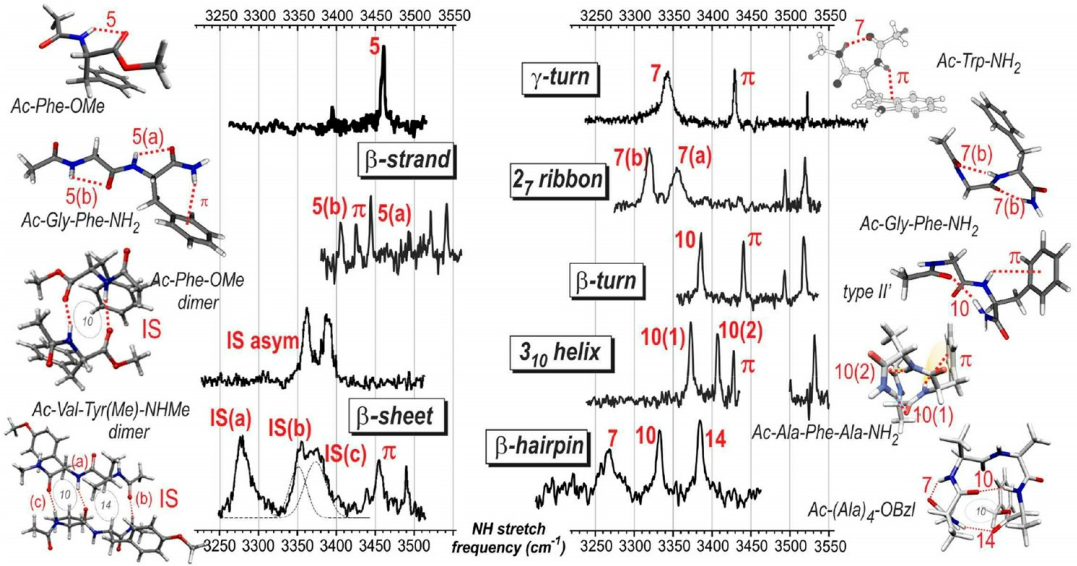


GAS PHASE CHEMICAL PHYSICS

Single-Conformation Laser Spectroscopy of Neutral Peptides



Backbone-side chain interactions



Secondary structures

E. Gloaguen, M. Mons, K. Schwing, M. Gerhards, Chem. Rev. 2020 **120**, 12490-12562.
DOI: (10.1021/acs.chemrev.0c00168)

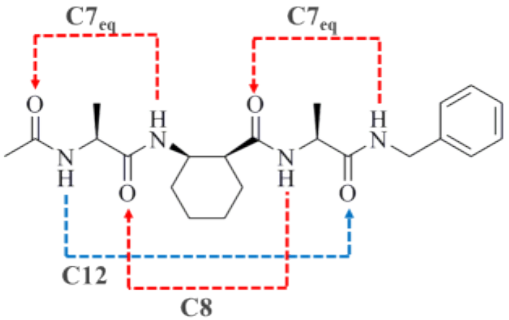
GAS PHASE CHEMICAL PHYSICS

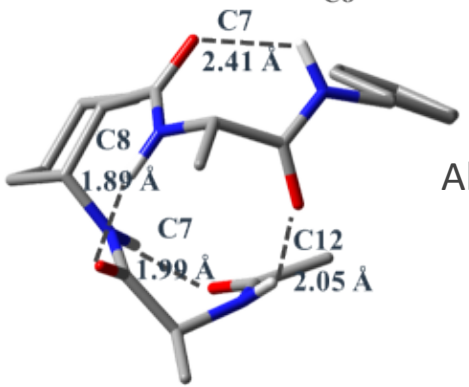
Synthetic Foldamers

α/β/α with cyclically constrained β-peptide

Dr. Soo Hyuk Choi
Yonsei University

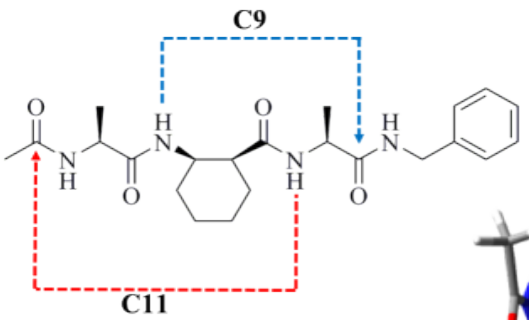
Tetra-amide H-bonded cycle



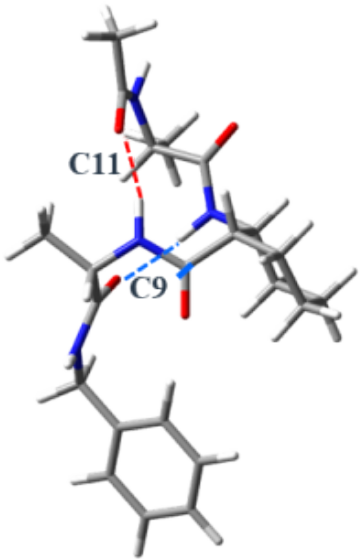


All 4 NH groups
in H-bonds

9/11 mixed helix former



Just 2 H-bonds.
Start of mixed helix



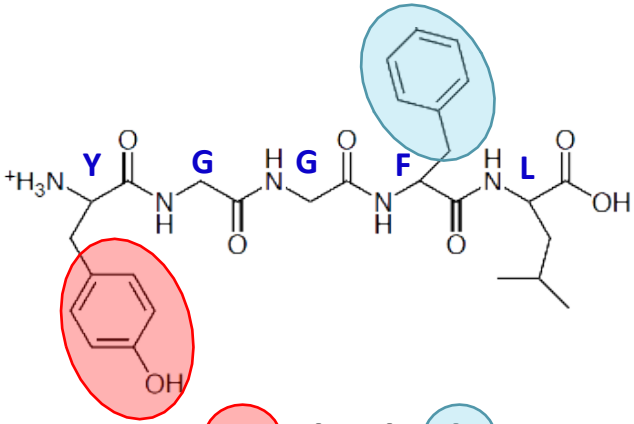
GAS PHASE CHEMICAL PHYSICS

K.N. Blodgett et al., J. Phys. Chem. A **122**, 3697-3710 (2018)

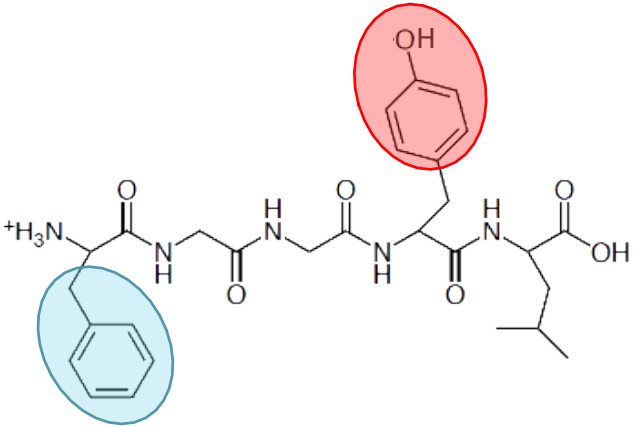
Cryo-cooled Ions

Peptide Scaffold: YGGFL vs. FGGYL

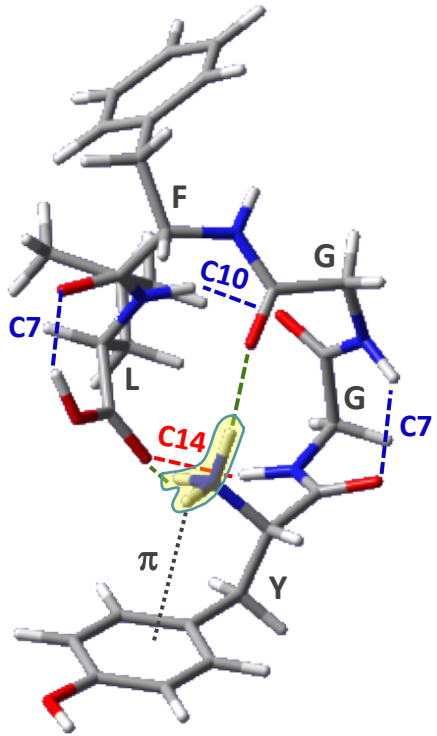
- Effect of Charge
- Larger H-bonded network



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



Phe-Gly-Gly-Tyr-Leu
FGGYL



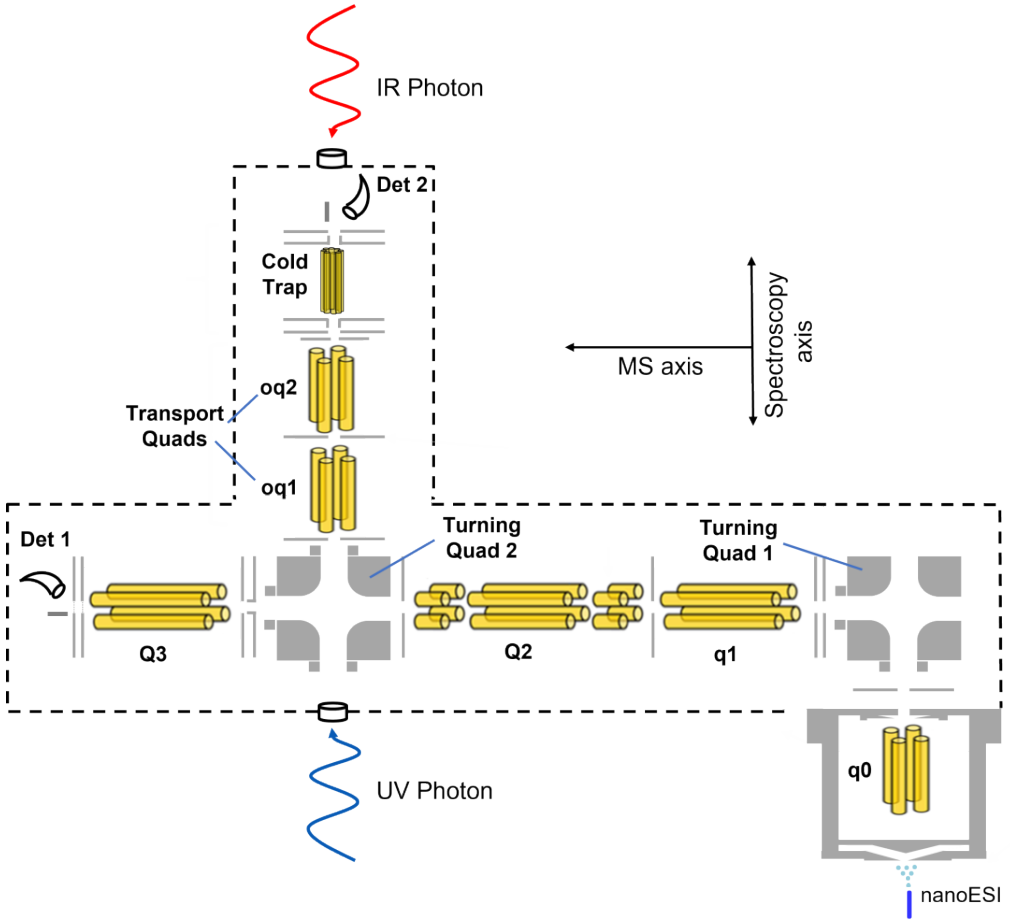
Tyr-Gly-Gly-Phe-Leu
YGGFL
Leu-enkephalin

GAS PHASE CHEMICAL PHYSICS

NL Burke, JG Redwine, JC Dean, SA McLuckey, TS Zwier, *Int J Mass Spectrom*, **378**, 196 (2015).

Instrumentation and Methods for Cold Ion Spectroscopy

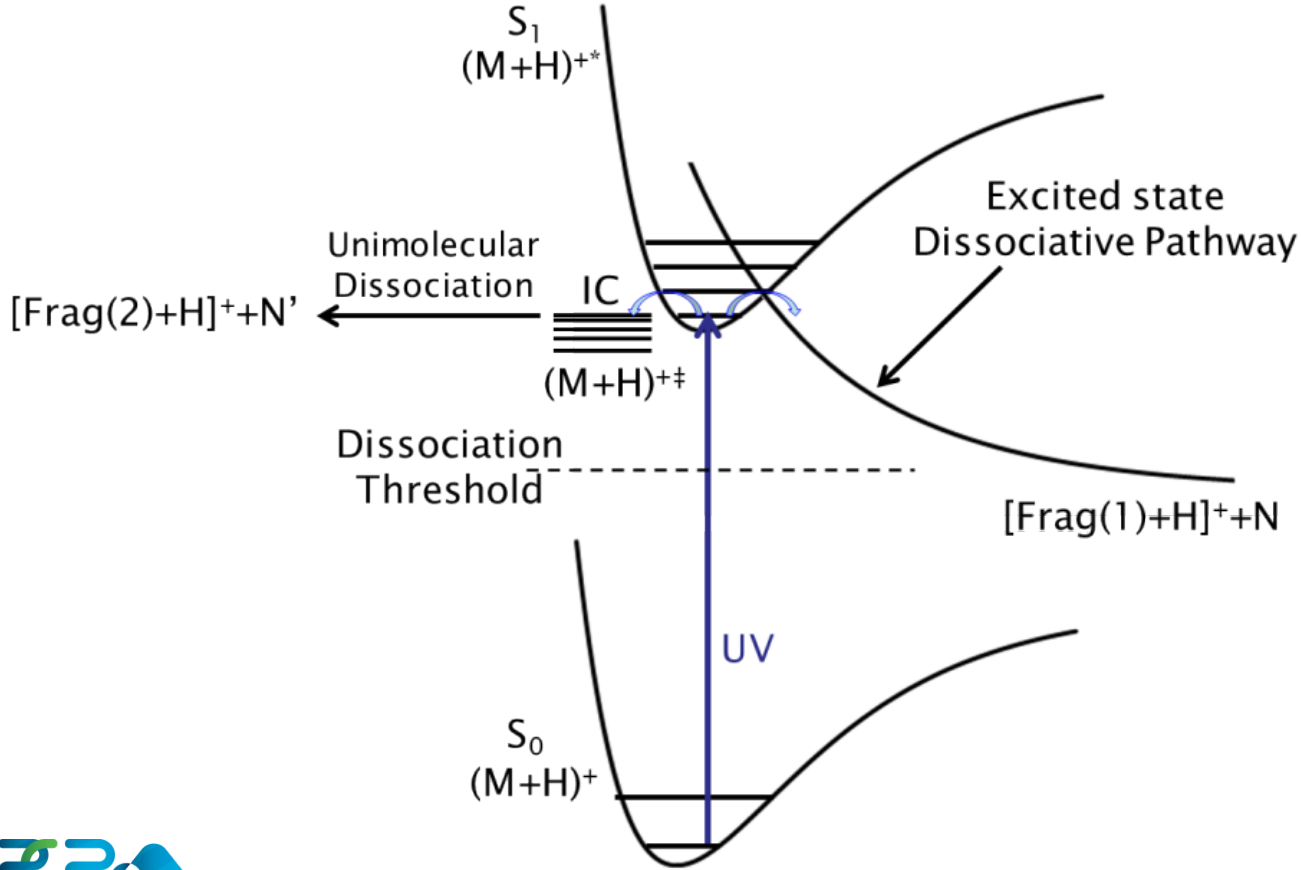
- Nano-ESI
- Parent isolation in Q2
- Cooling of parent ions in cold trap
- IR and UV spectroscopy of cold ions in cold trap
- Fragment scanned out up to parent mass
- Photofragment analysis in Q3



GAS PHASE CHEMICAL PHYSICS

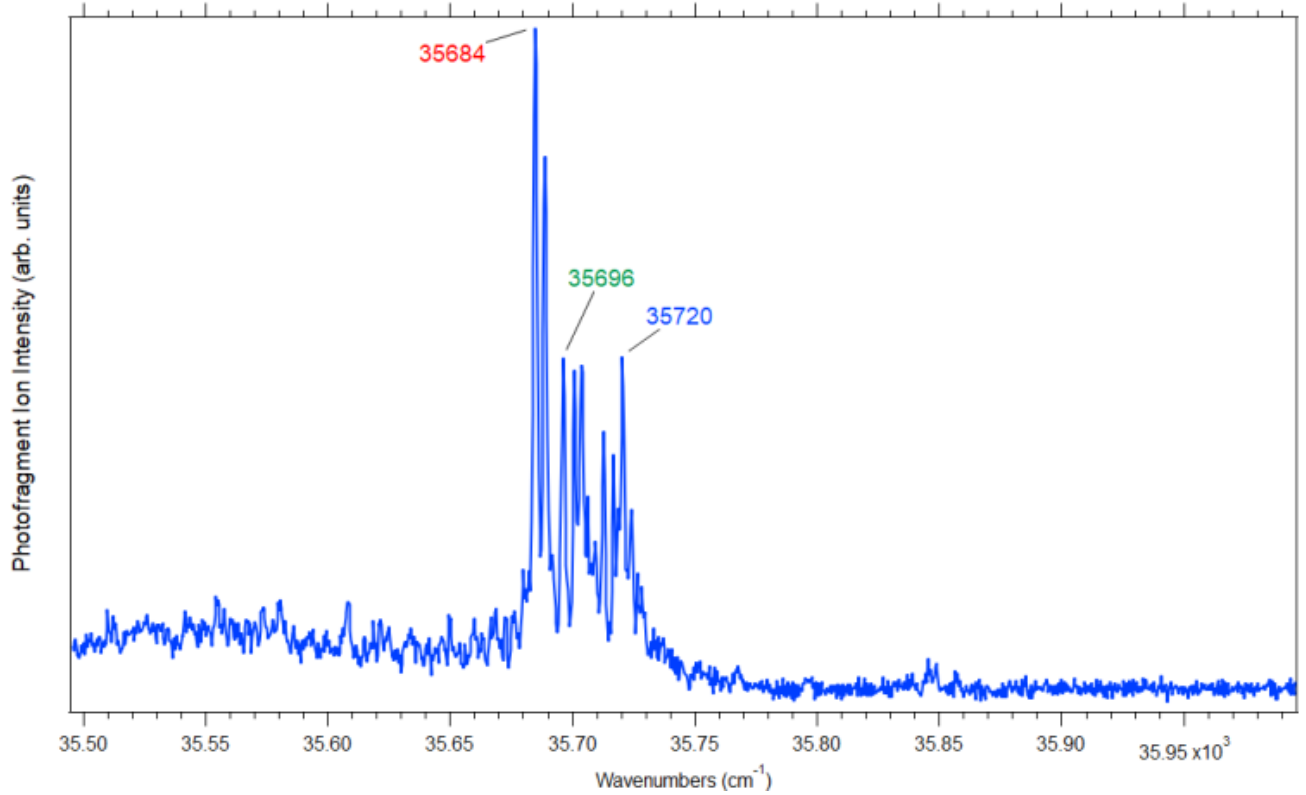
JG Redwine, ZA Davis, NL Burke, RA Oglesbee, SA McLuckey, TS Zwier. Int J Mass Spectrom, 2013.

UV Photofragment Spectroscopy on Cold Ions



GAS PHASE CHEMICAL PHYSICS

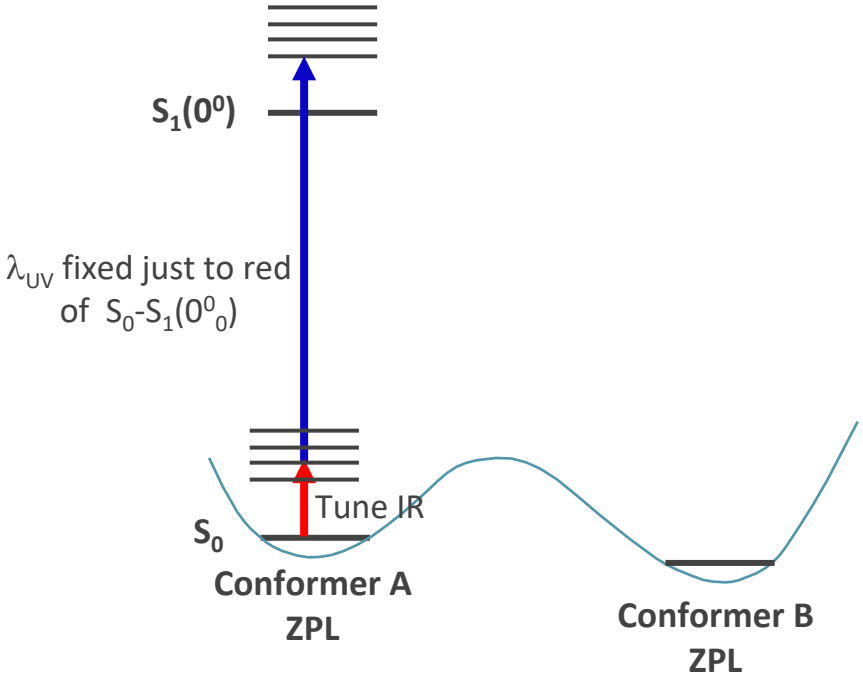
UV Photofragment Spectrum of [YGGFL+H]$^+$

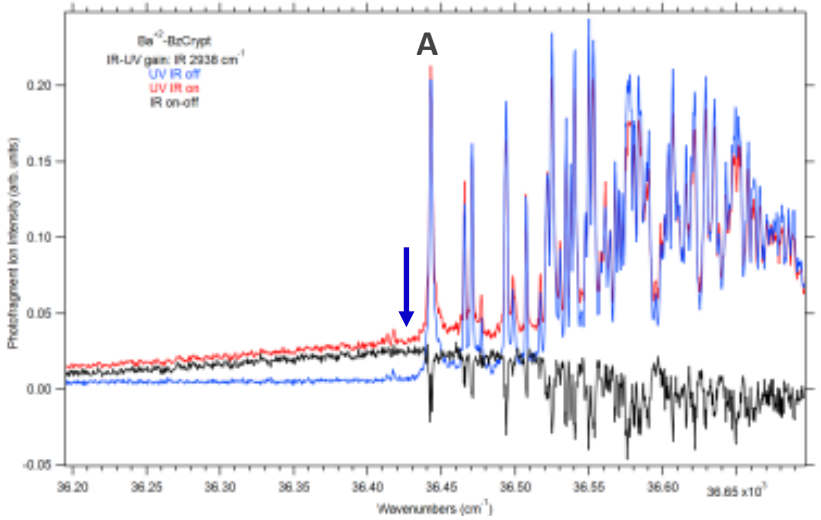


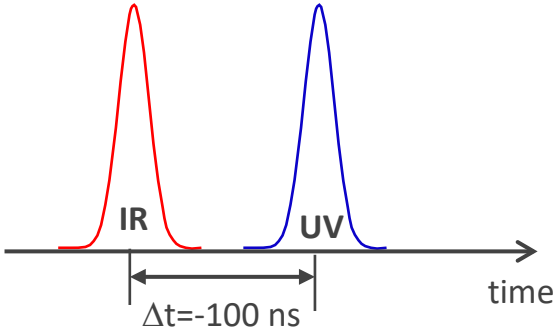
GAS PHASE CHEMICAL PHYSICS

IR-UV Ion Gain Spectroscopy:

IR Spectra in the Ground State

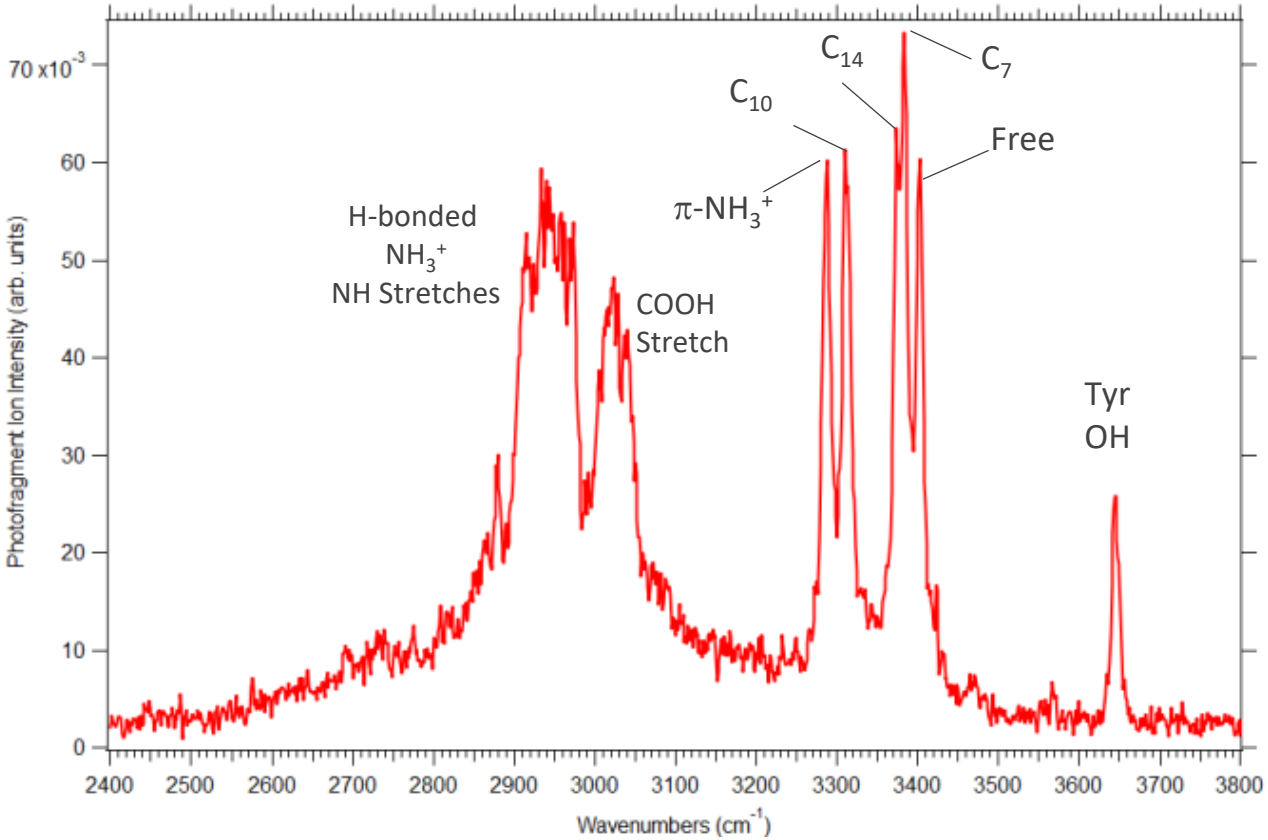


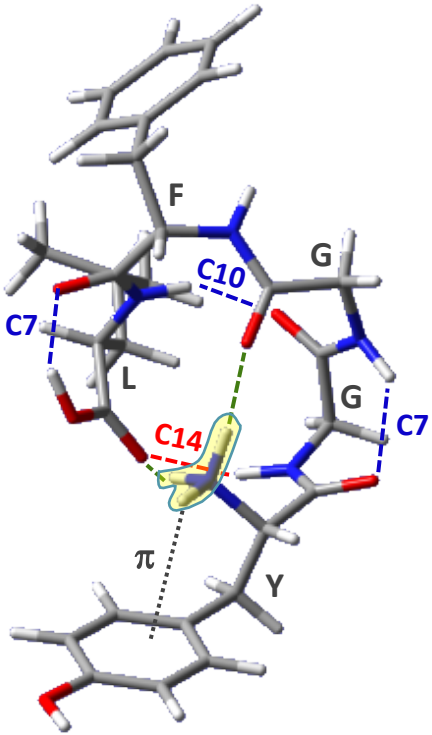




GAS PHASE CHEMICAL PHYSICS

YGGFL IR-UV Ion Gain Spectroscopy



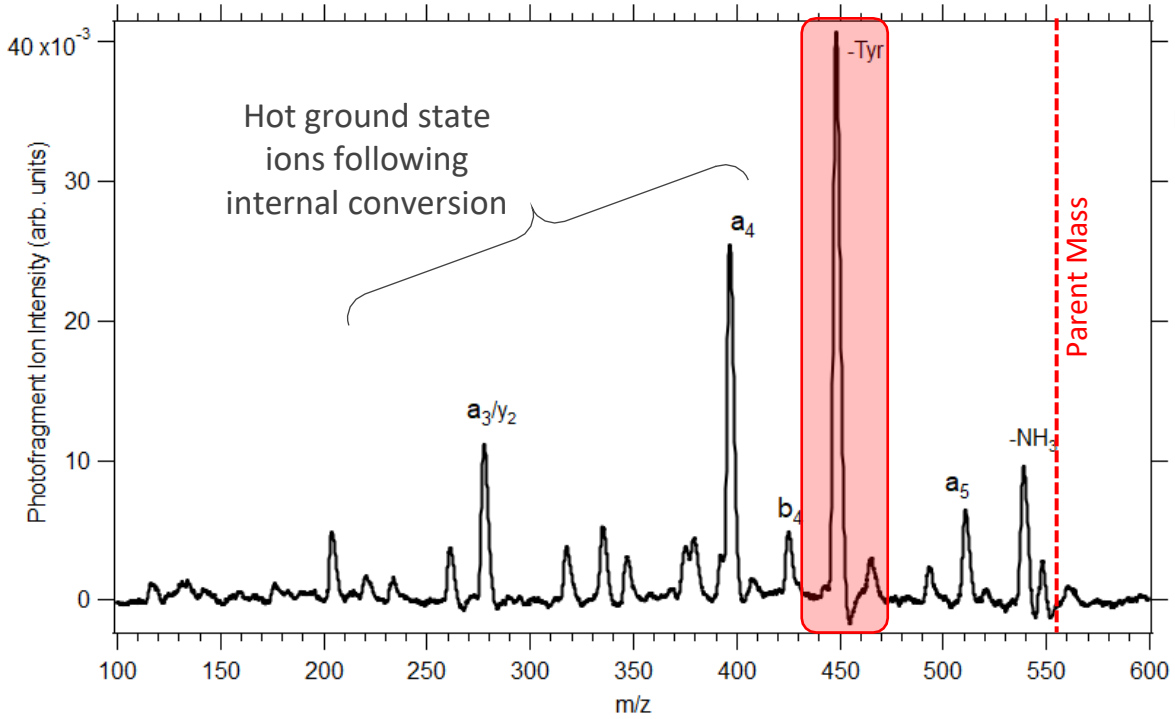


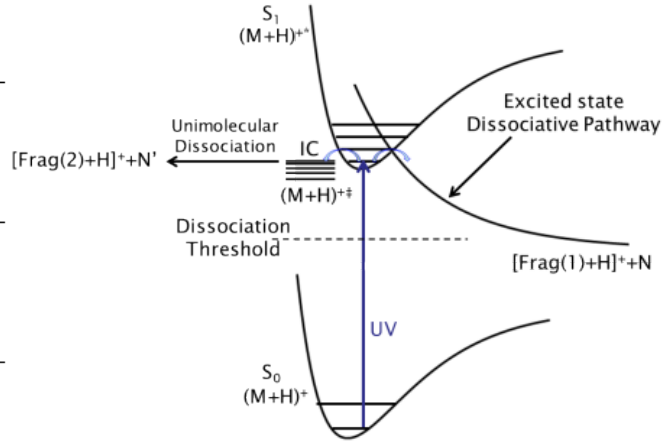
Assigned Structure for
$[YGGFL+H]^+$

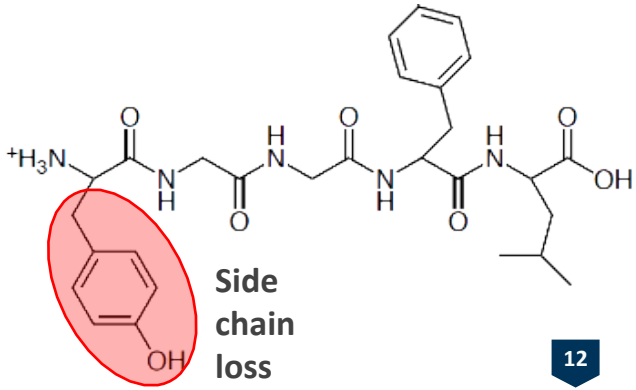
GAS PHASE CHEMICAL PHYSICS

NL Burke, JG Redwine, JC Dean, SA McLuckey, TS Zwier, *Int J Mass Spectrom*, **378**, 196 (2015).

Cryo-cooled [YGGFL+H]$^+$ UV photofragment mass spectrum







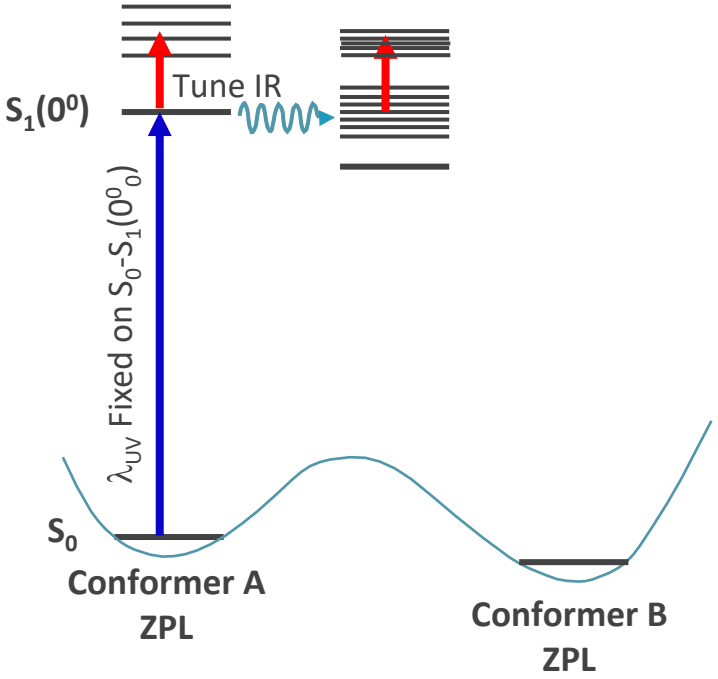
Side chain loss

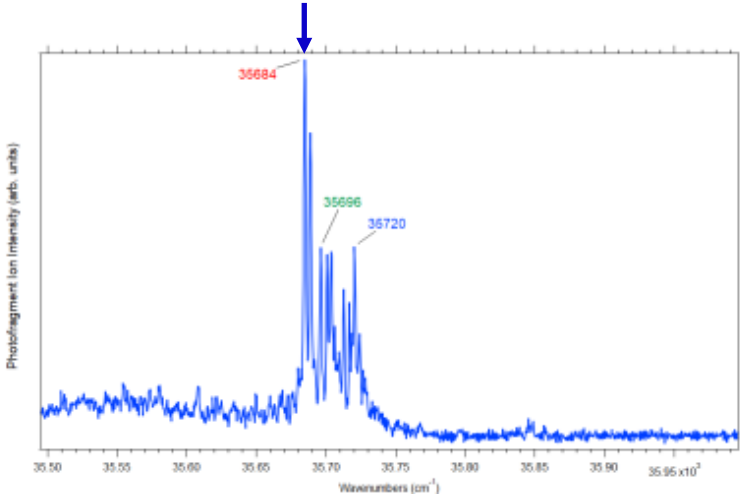
- CID-like ions: Hot grd state fragment ions
- Side-chain loss: Excited state process

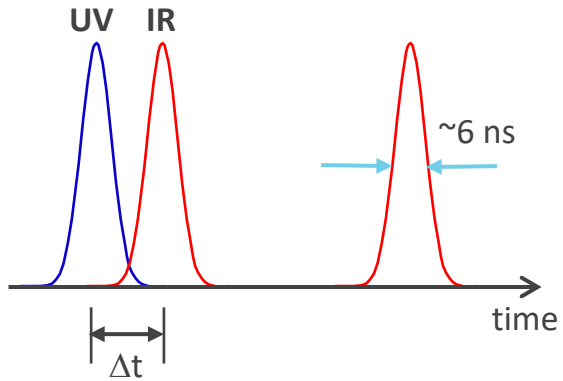
GAS PHASE CHEMICAL PHYSICS

UV-IR Ion Gain Spectroscopy:

Single Conformation spectroscopy in the Excited State

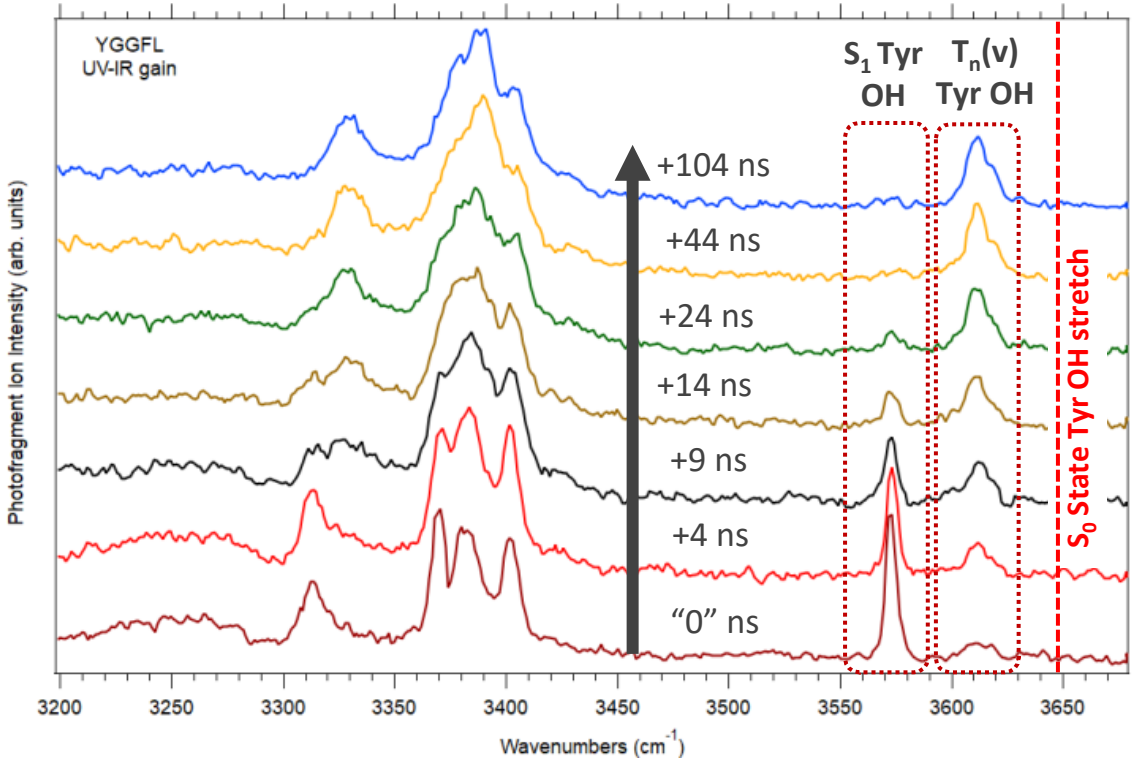


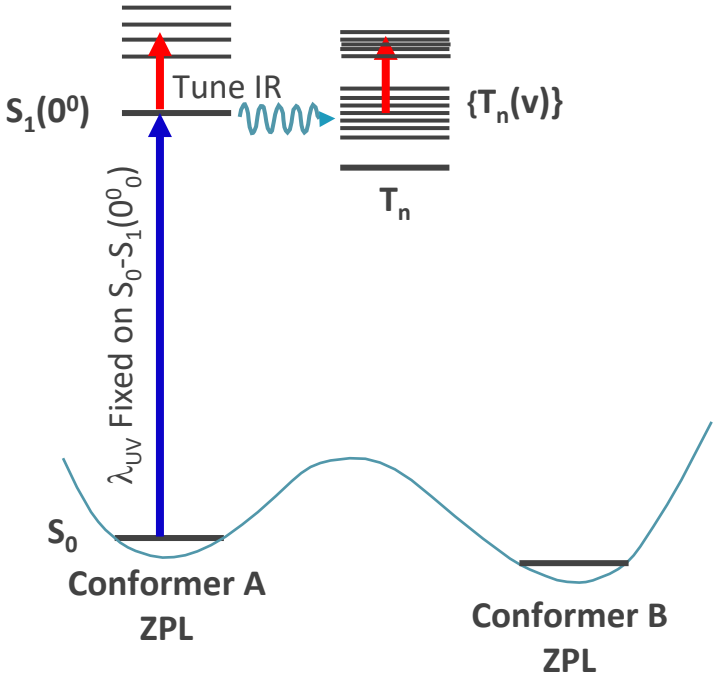




GAS PHASE CHEMICAL PHYSICS

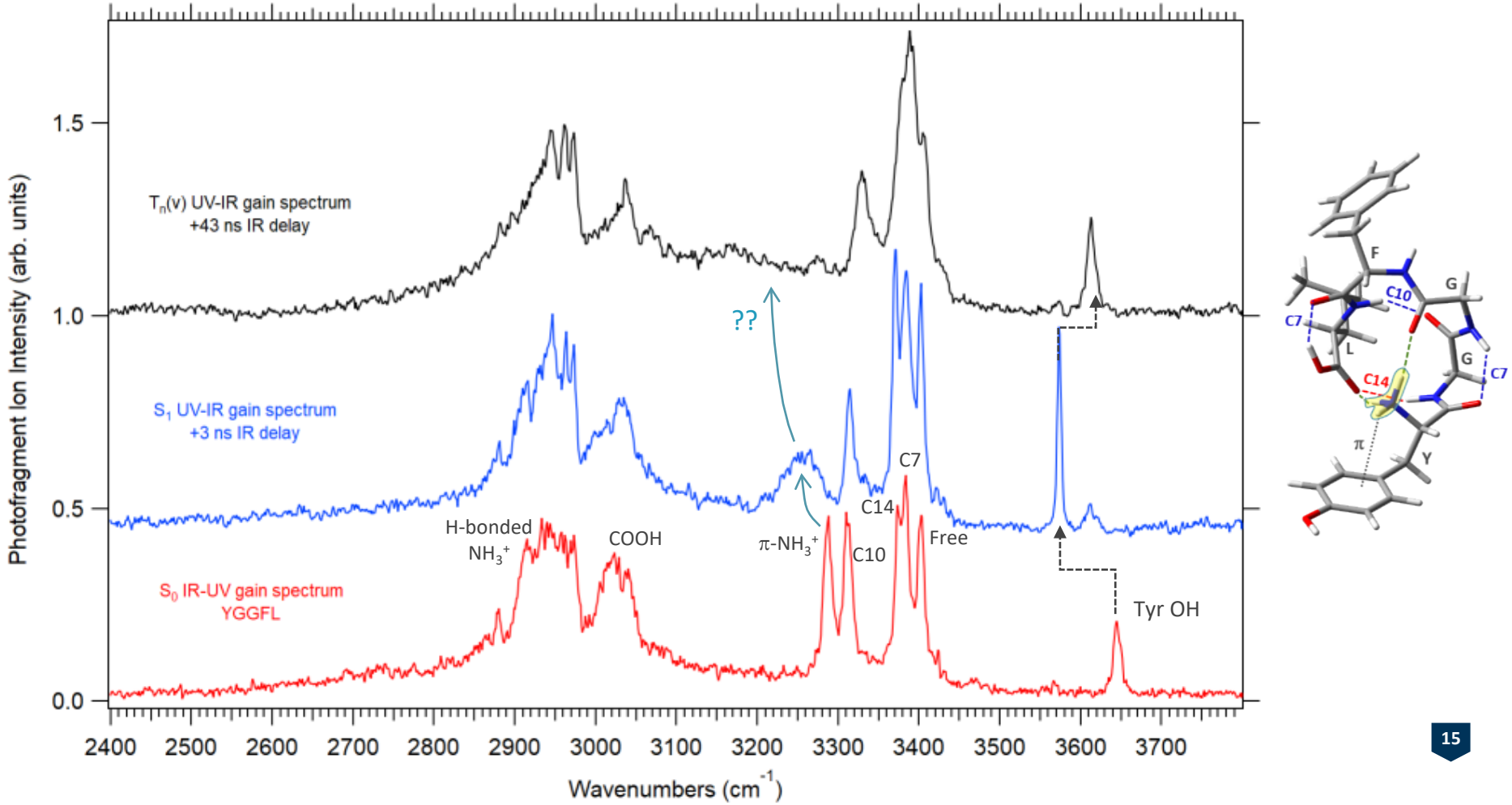
YGGFL UV-IR gain spectra



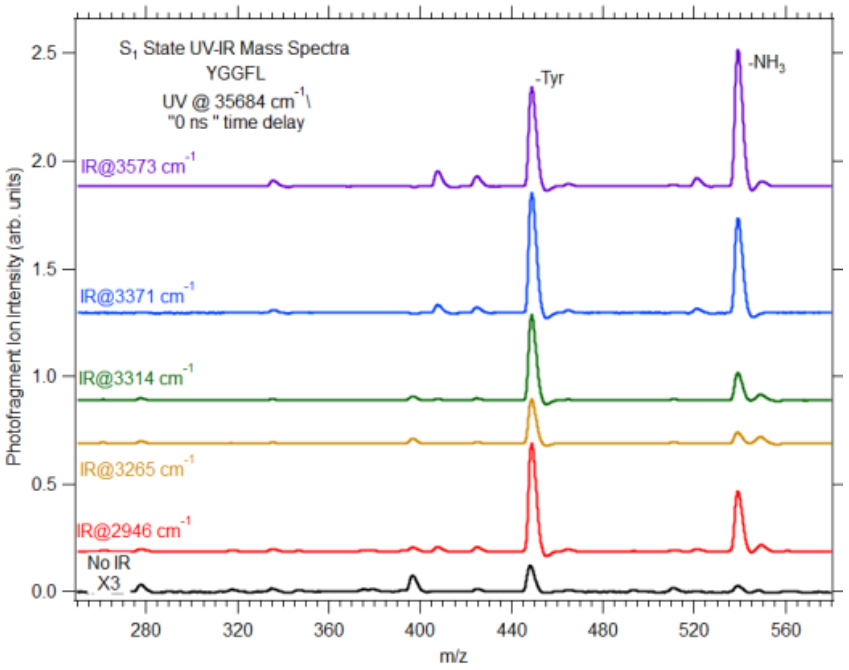


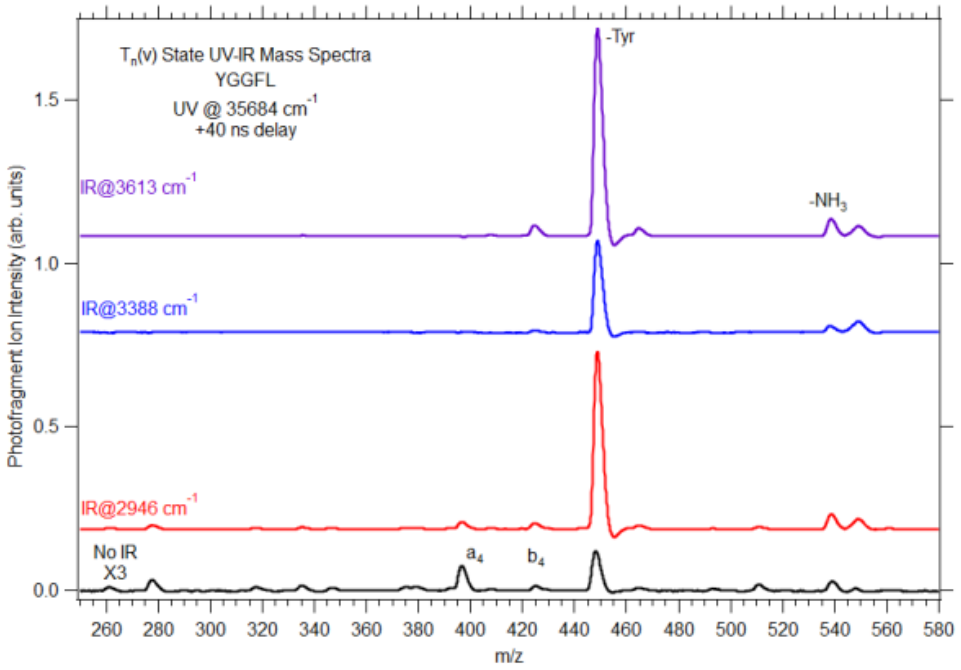
GAS PHASE CHEMICAL PHYSICS

[YGGFL+H]$^+$ Electronic State Dependence of IR spectra



YGGFL IR-induced Photofragments out of S_1, T_n





$\pi\pi^*$ singlet state of Tyr:

- Loss of Tyr side chain
- Loss of NH_3 => ET involved

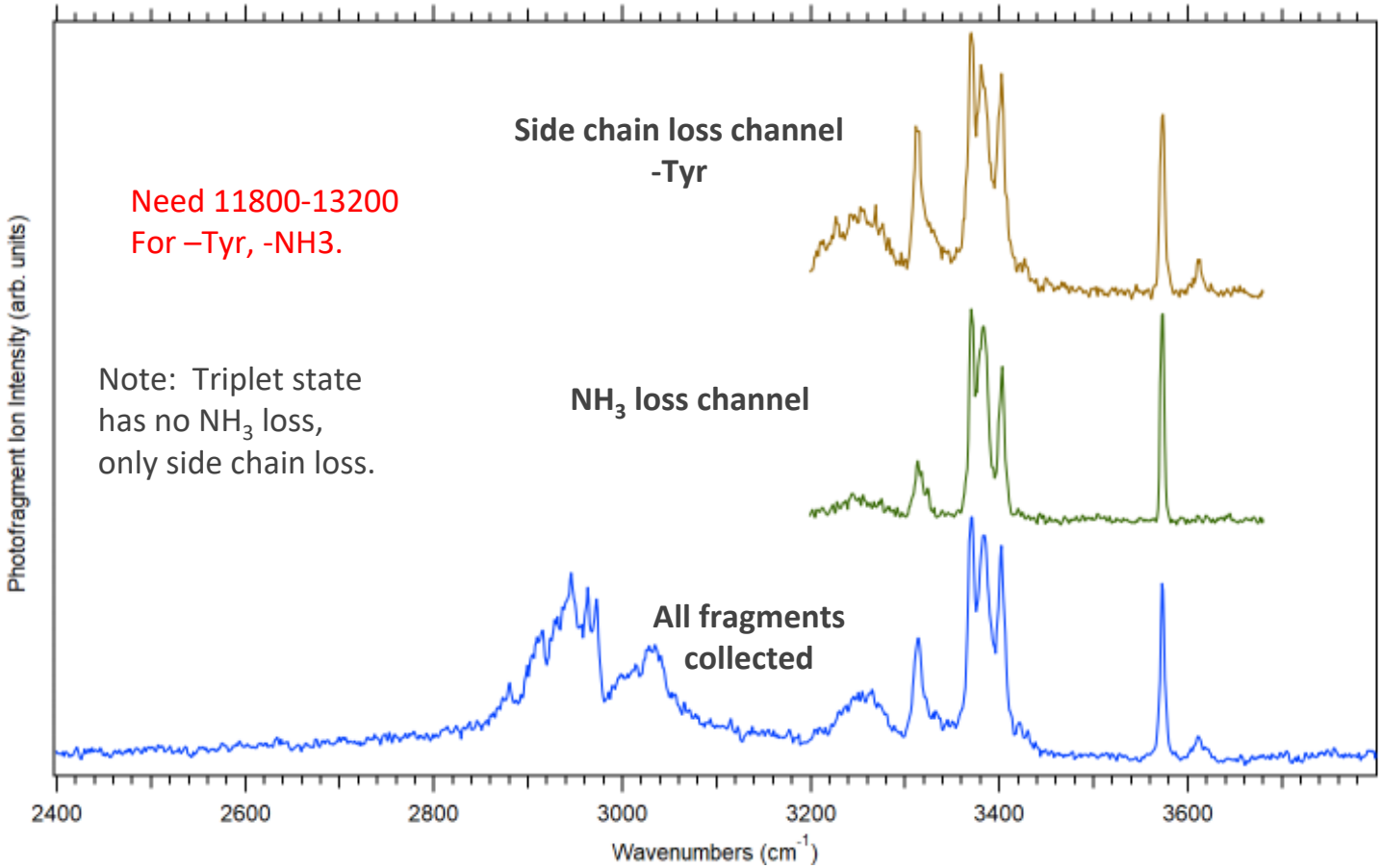
} In competition

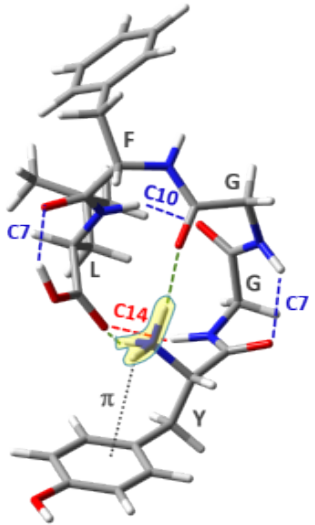
- $\frac{\phi_{NH3}}{\phi_{Tyr}}$ non-monotonic in λ_{IR}

Triplet state(s) of Tyr:

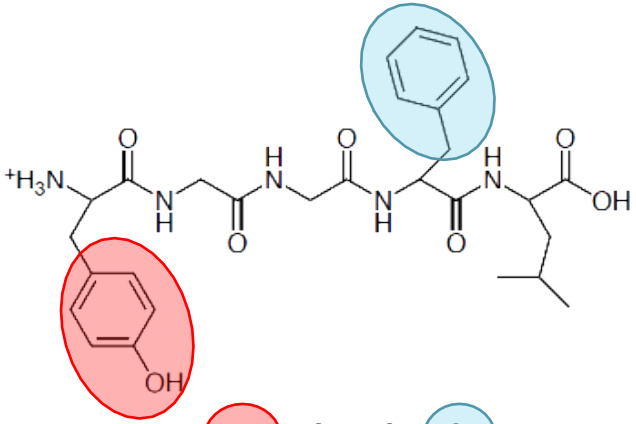
- Loss of Tyr side chain dominates
- No loss of NH_3 => ET suppressed or side chain enhanced?

[YGGFL+H]$^+$ Mass-resolved S_1 state IR spectra

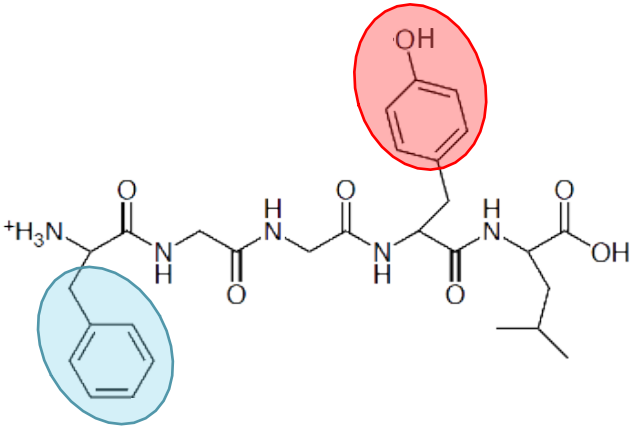




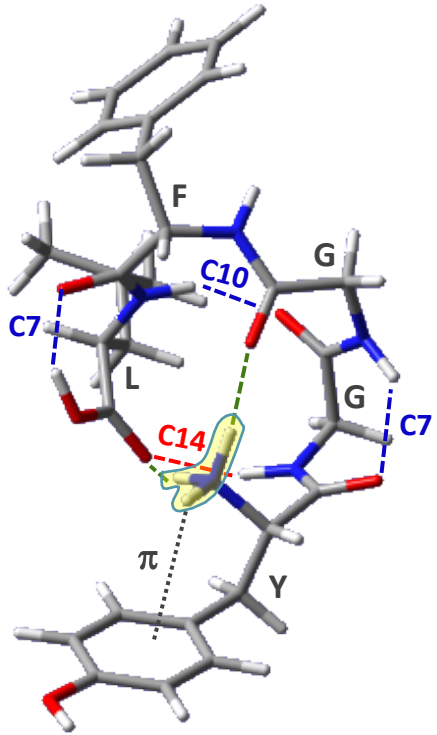
Peptide Scaffold: YGGFL vs. FGGYL



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



Phe-Gly-Gly-Tyr-Leu
FGGYL

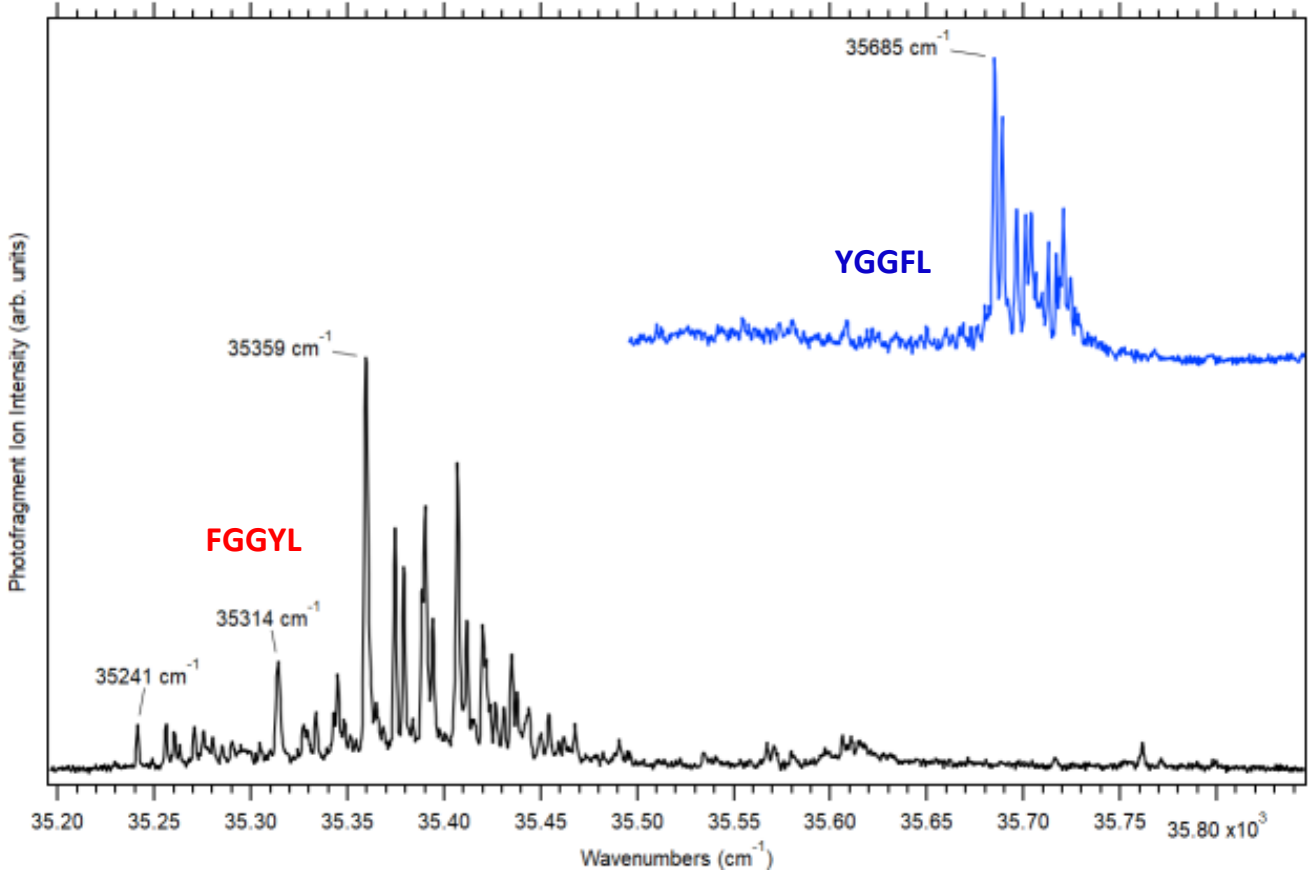


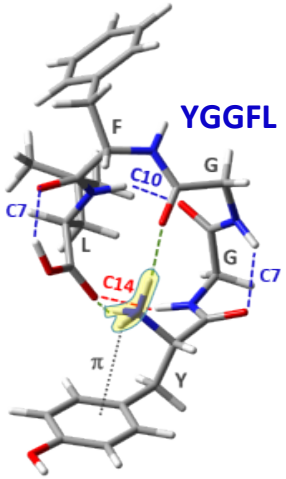
Tyr-Gly-Gly-Phe-Leu
YGGFL
Leu-enkephalin

GAS PHASE CHEMICAL PHYSICS

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

FGGYL vs YGGFL: UV photofragment spectra



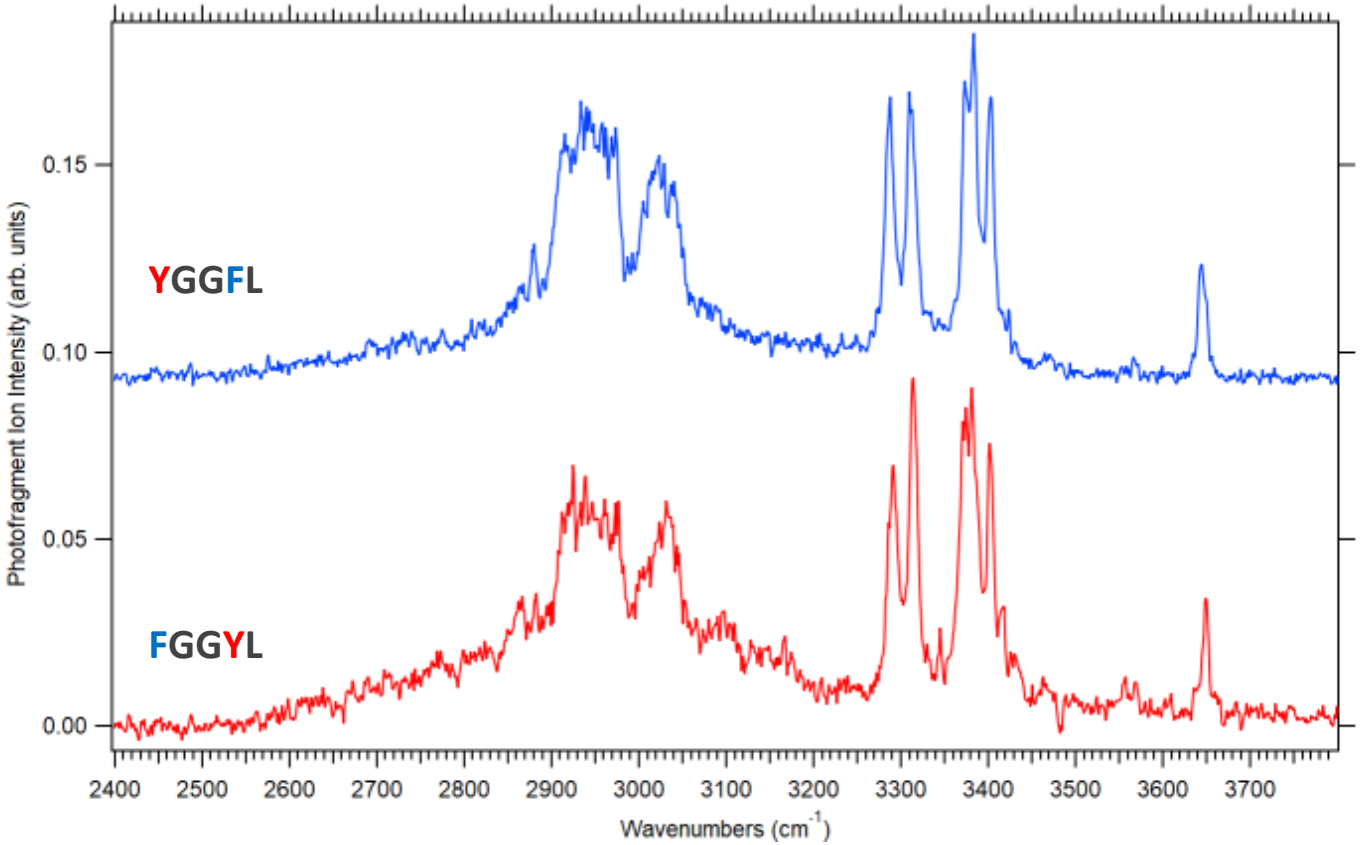


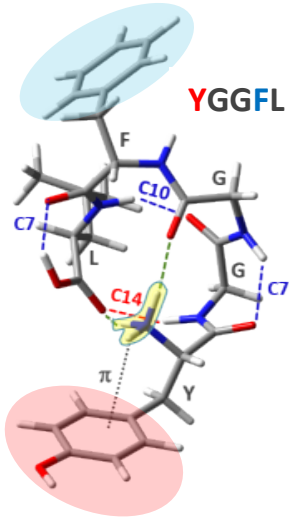
FGGYL ??

- Is the YGGFL structure maintained in FGGYL?

GAS PHASE CHEMICAL PHYSICS

FGGYL vs YGGFL: IR-UV gain spectra

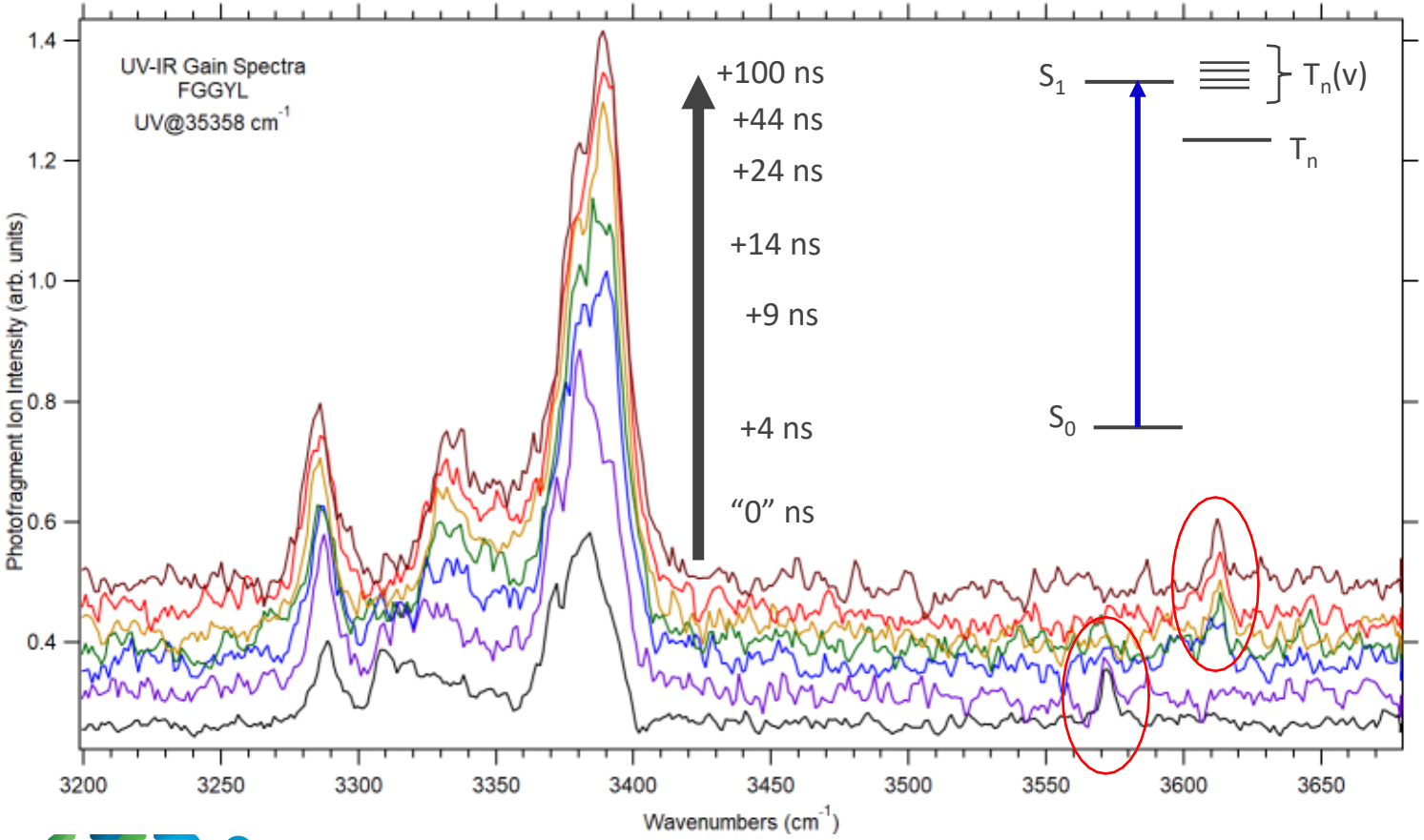




FGGYL

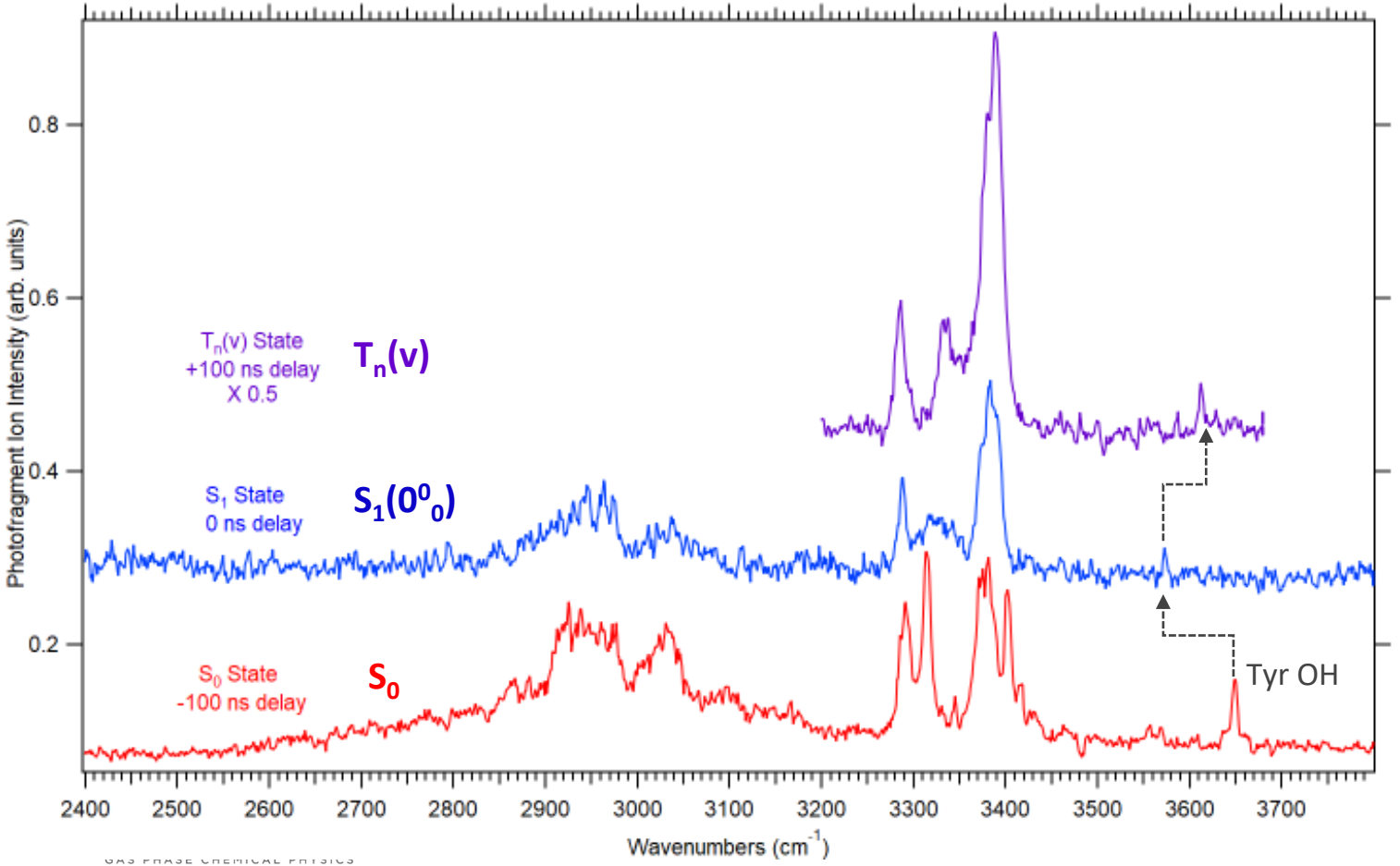
GAS PHASE CHEMICAL PHYSICS

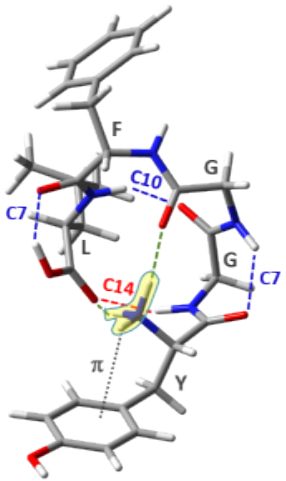
[FGGYL+H]$^+$ IR Time Delay Profile



GAS PHASE CHEMICAL PHYSICS

[FGGYL+H]$^+$ Electronic State Dependence of IR spectra

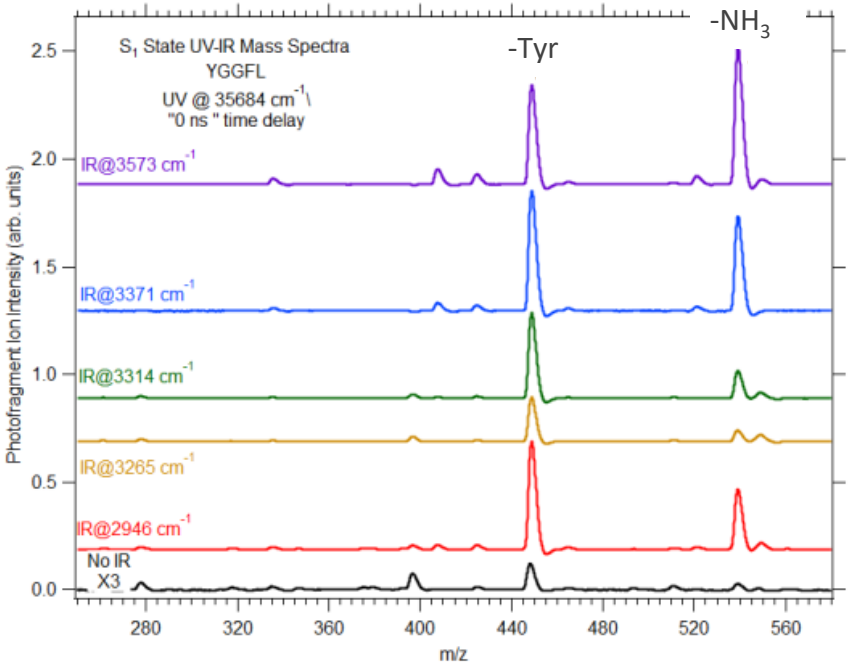




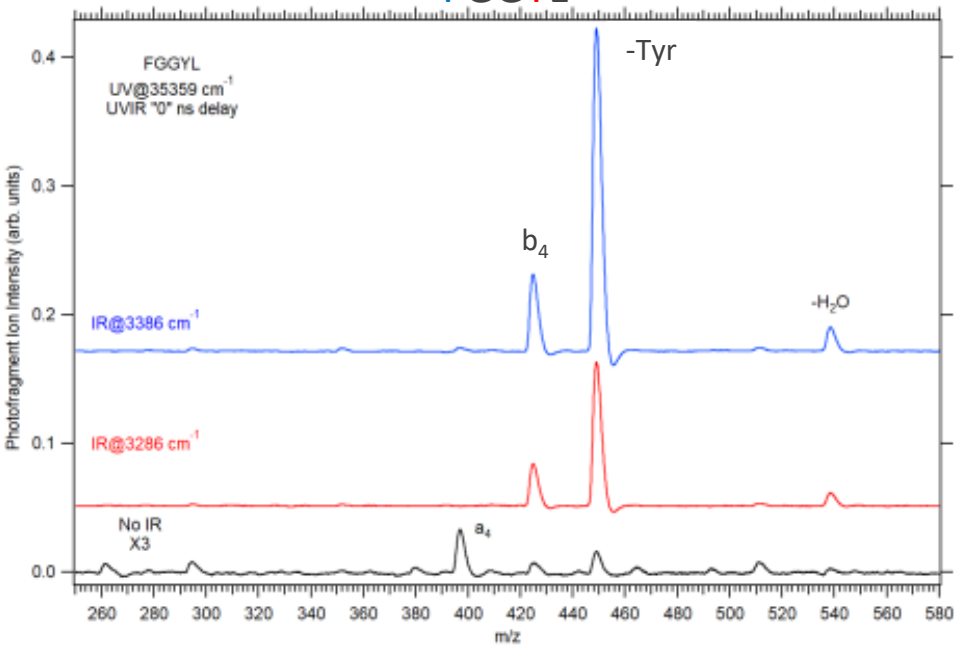
Change to FGGYL

IR-induced Photofragments out of S_1

YGGFL



FGGYL



ππ* singlet state of Tyr(1):

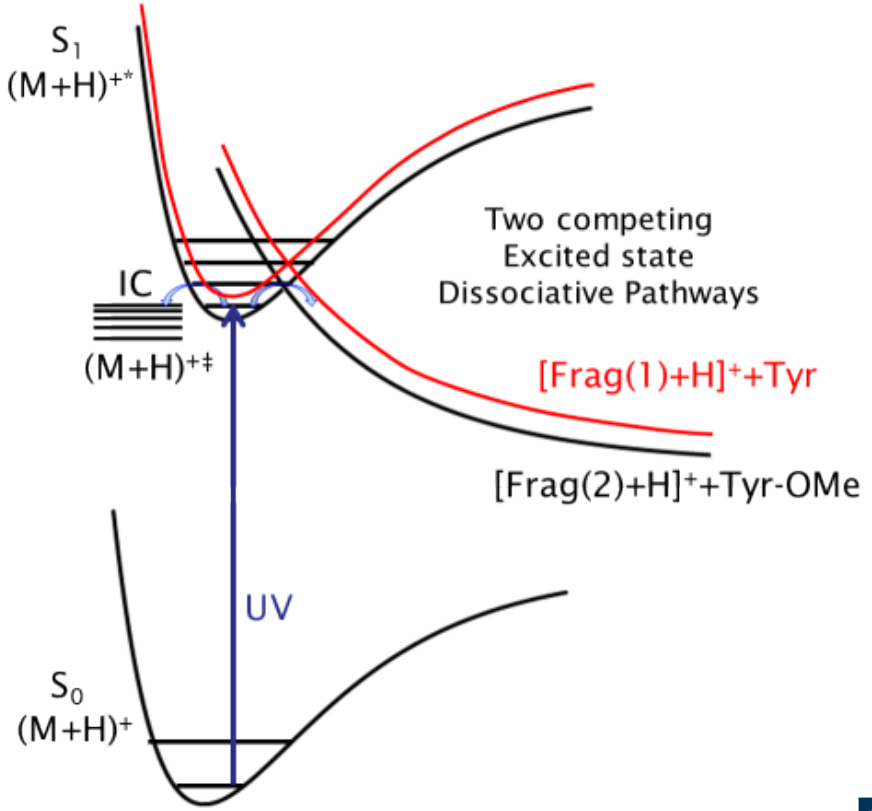
- Loss of Tyr side chain
- Loss of NH_3 => ET involved } In competition
- $\frac{\phi_{NH3}}{\phi_{Tyr}}$ non-monotonic in λ_{IR}

ππ* singlet state of Tyr(4):

- Loss of Tyr side chain
- **No** Loss of NH_3 => ET channel turned off
  Tyr remote from NH_3^+
- Is b_4 related to proton conduit?

Electronic Energy Transfer
between near-degenerate UV chromophores

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

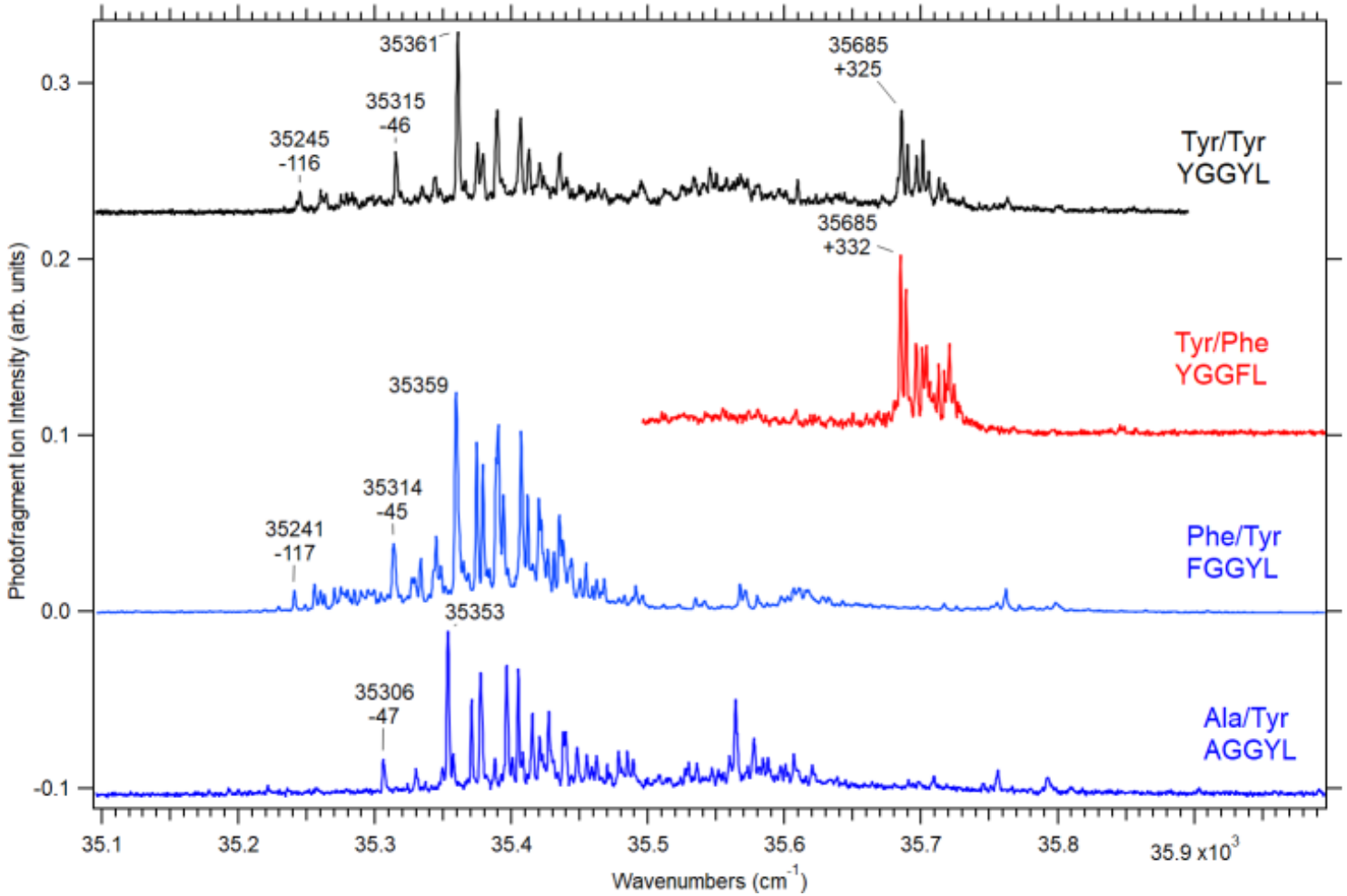


GAS PHASE CHEMICAL PHYSICS

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

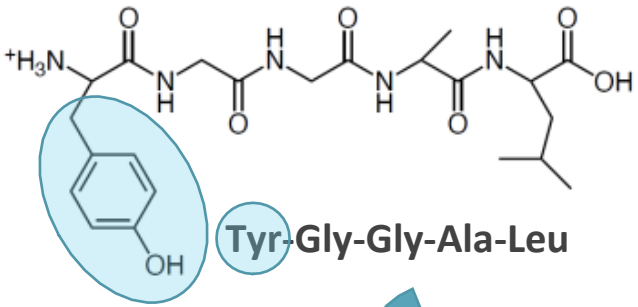
YGGYL Bichromophore c.f. YGGFL and FGGYL

- OH orientation
- Phe rotamers
- Tyr rotamers
- Leucine rotamers

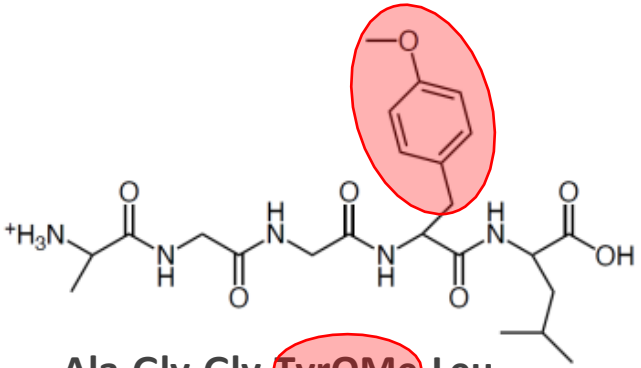


GAS PHASE CH

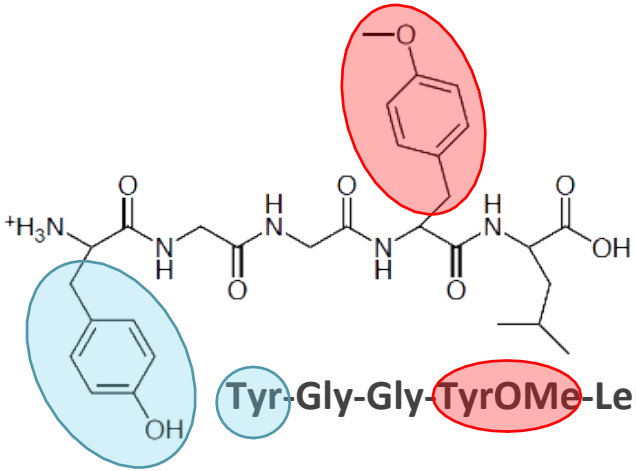
Peptide Scaffold: Tyrosine-OH and Tyrosine-OMe



Tyr-Gly-Gly-Ala-Leu



Ala-Gly-Gly-TyrOMe-Leu



Tyr-Gly-Gly-TyrOMe-Leu

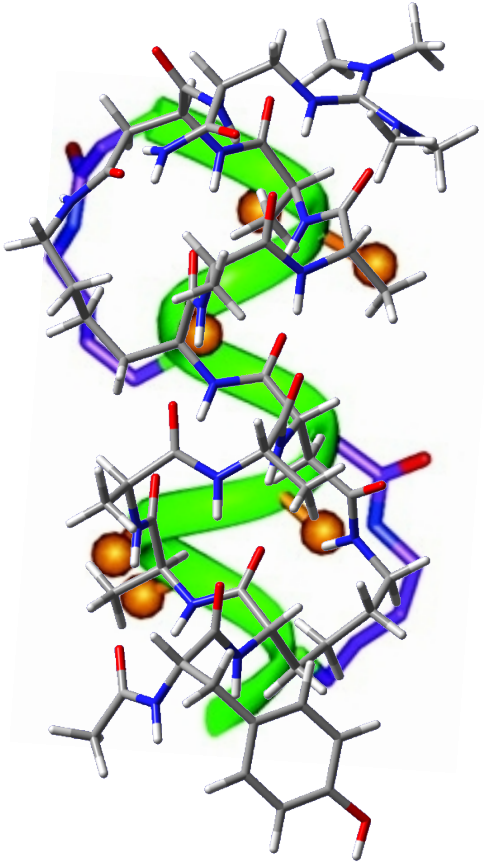
GAS PHASE CHEMICAL PHYSICS

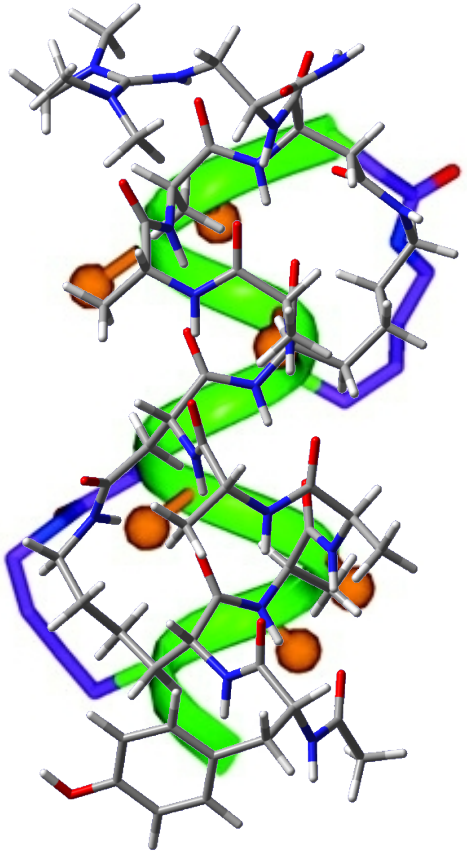
Stapled α-helices as Scaffolds to study Electronic Energy Transfer

Timothy Hill

David Fairlie

LL
Fully
RH
α-Helix





DD
Fully
LH
α-Helix

GAS PHASE CHEMICAL PHYSICS

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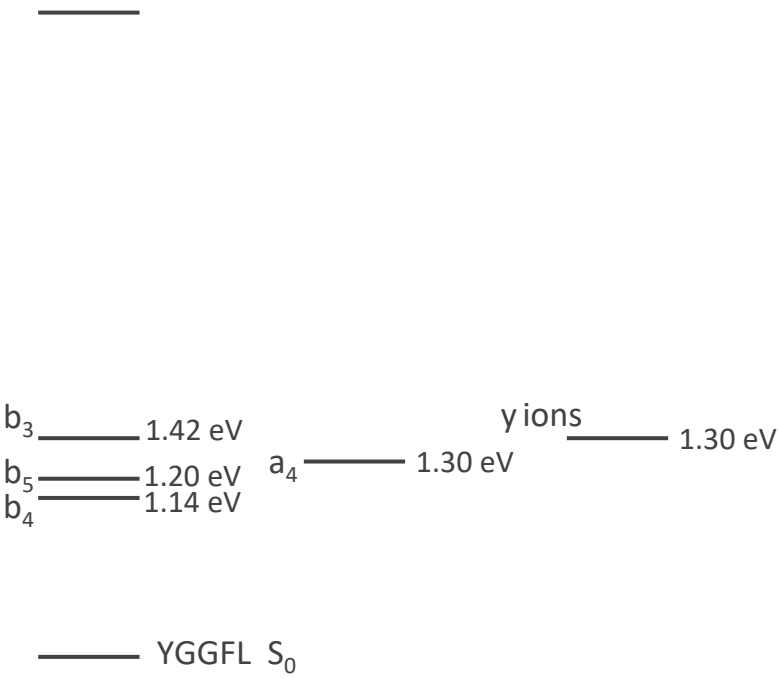
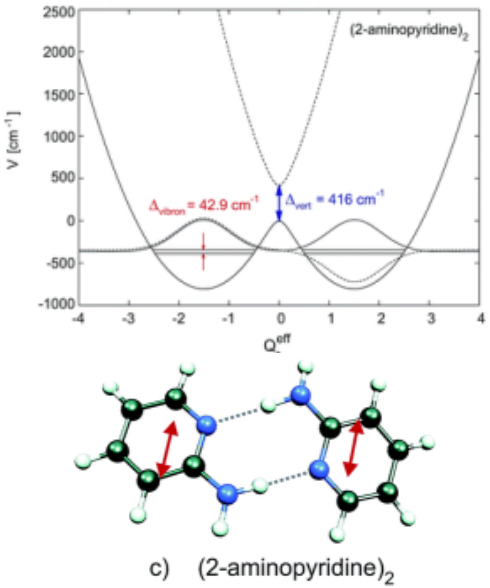
GAS PHASE CHEMICAL PHYSICS



J. Laskin, JPCA **2006**, *110*, 8554

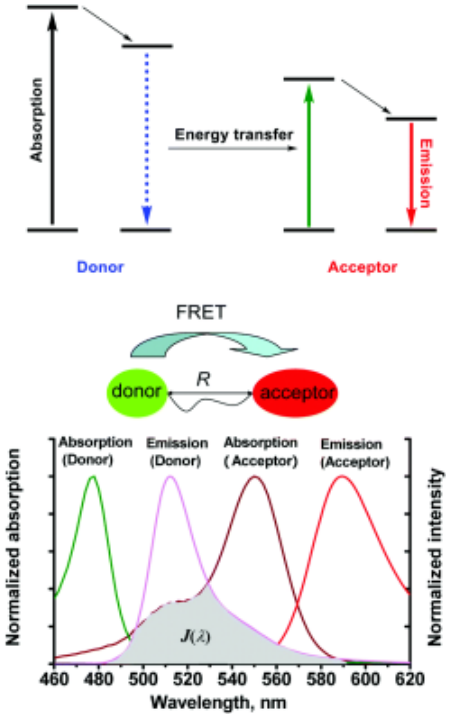
Resonant Energy Transfer



Excitonic coupling

- 2 identical chromophores in symmetric positions
- Chromophores 'touching'

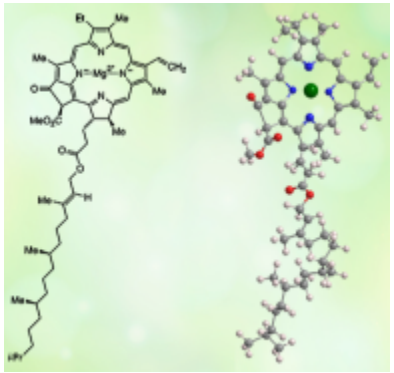
***Chem. Sci.**, 2015,**6**, 6059-6068*

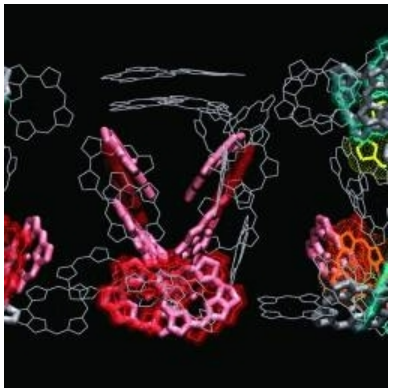


FRET

- Well-defined Donor-acceptor
- Large ΔE
- Large R (20-60 Å): Weak coupling

*Chem. Soc. Rev., 2020, **49**, 5110-5139*





Photosynthetic Reaction Center (PSII)

- Many near-identical chromophores spaced over range of distances.
- Different local environments.
- Exquisite efficiency, directed EET.

01/21/2019 ACS Molecule of the Week

GAS PHASE CHEMICAL PHYSICS