The Spectroscopy of UF and UF^+

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Motivation

Spectra of gas-phase uranium fluoride have been obtained for the first time by LIF, REMPI, and ZEKE techniques.

Actinide compounds have unique bonding characteristics in which the role of *f*-electrons is not thoroughly understood.

Spectroscopic results are benchmarked against high-level computational efforts.

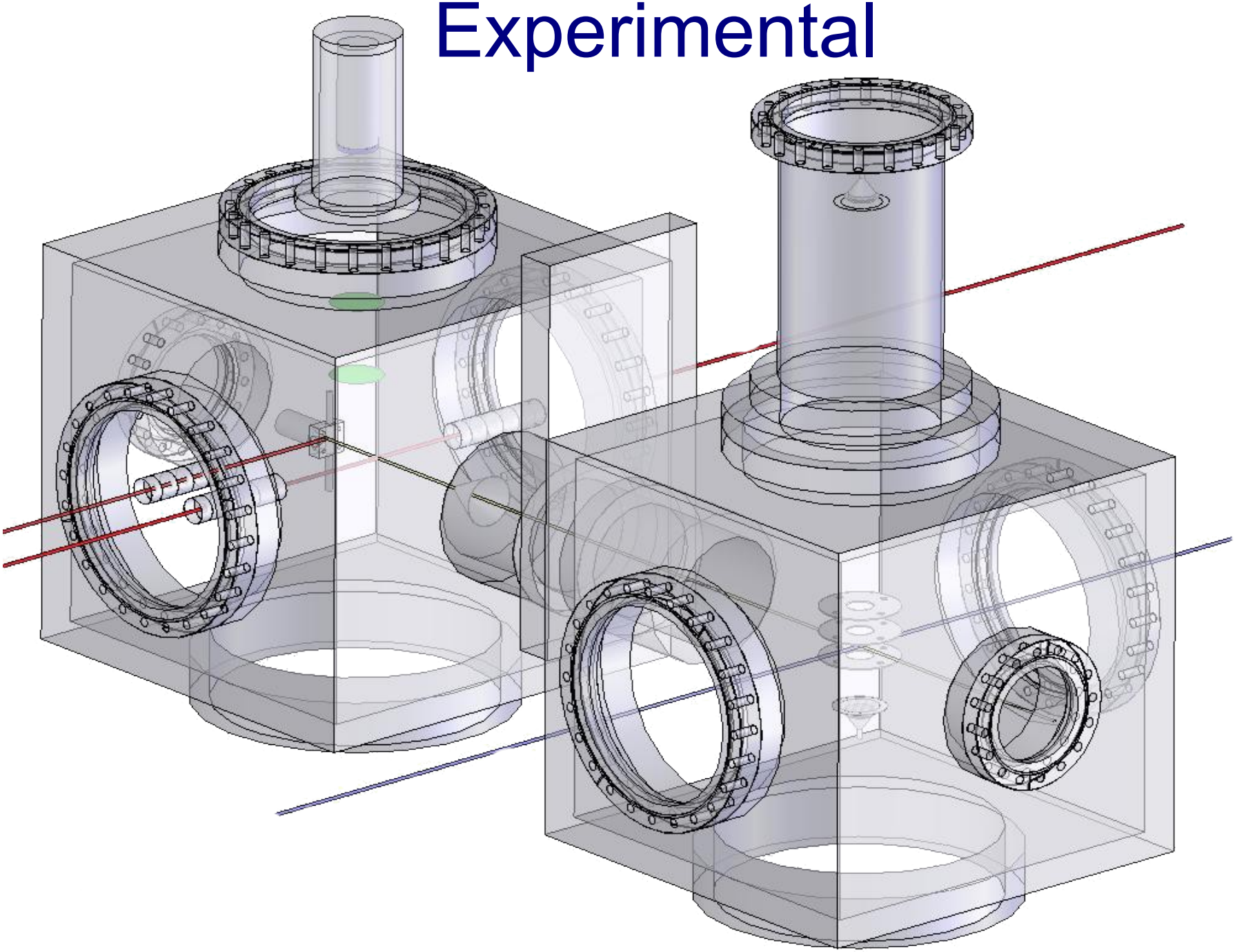
Some Related Studies

- L. Kaledin and M. Heaven, *J. Mol. Spec.* **185** (1997)
  Electronic spectroscopy of UO
  - Proposed LFT application to actinides

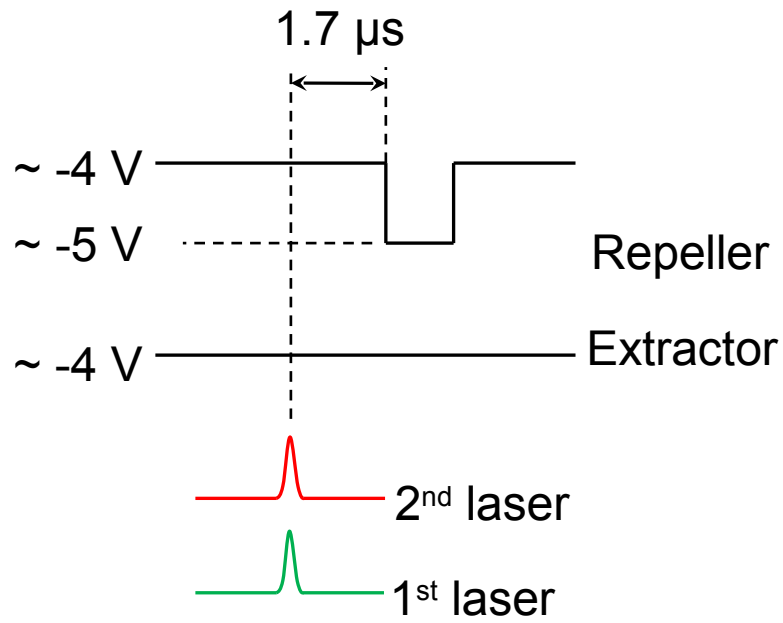
- R. Hunt *et al.*, *Inorg. Chem.* **33** (1994)
  Matrix IR spectra of the products from F_2, ClF, and Cl_2 reactions with pulsed-laser evaporated uranium atoms
  - Similar setup but Ar(s) is insufficient

- D. G. Fedorov *et al.*, *J. Chem. Phys.* **118** (2003)
  An *ab initio* study of excited states of U and UF
  - CASCI with SO-MCQDPT at aug-cc-VTZ level

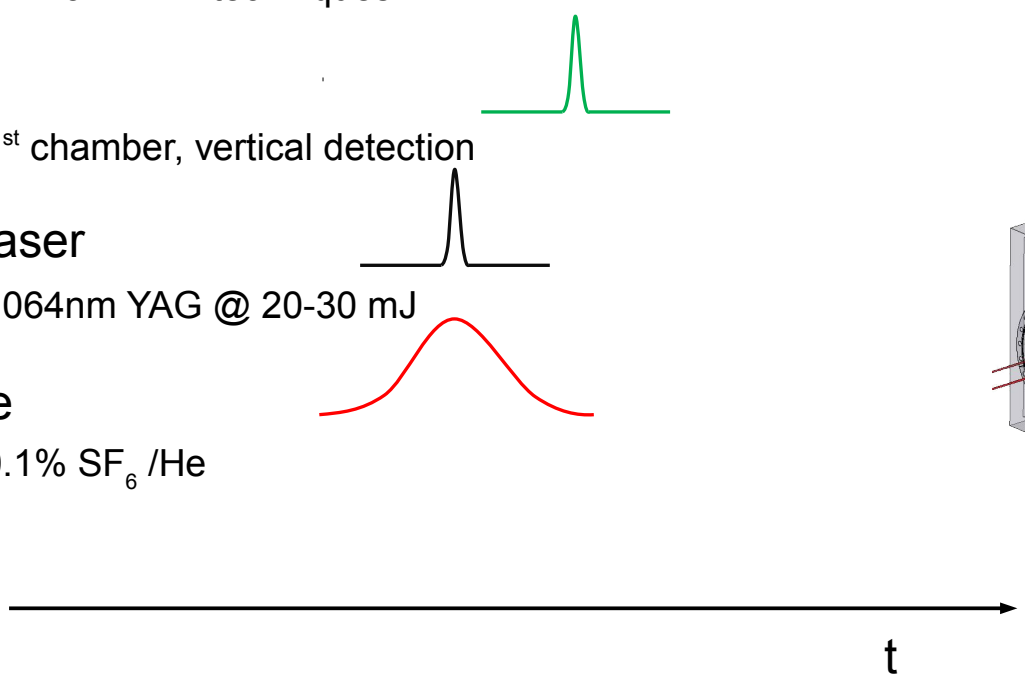
Experimental

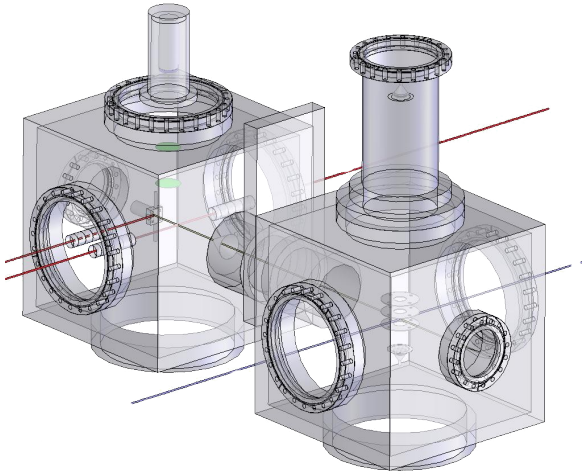


Experimental



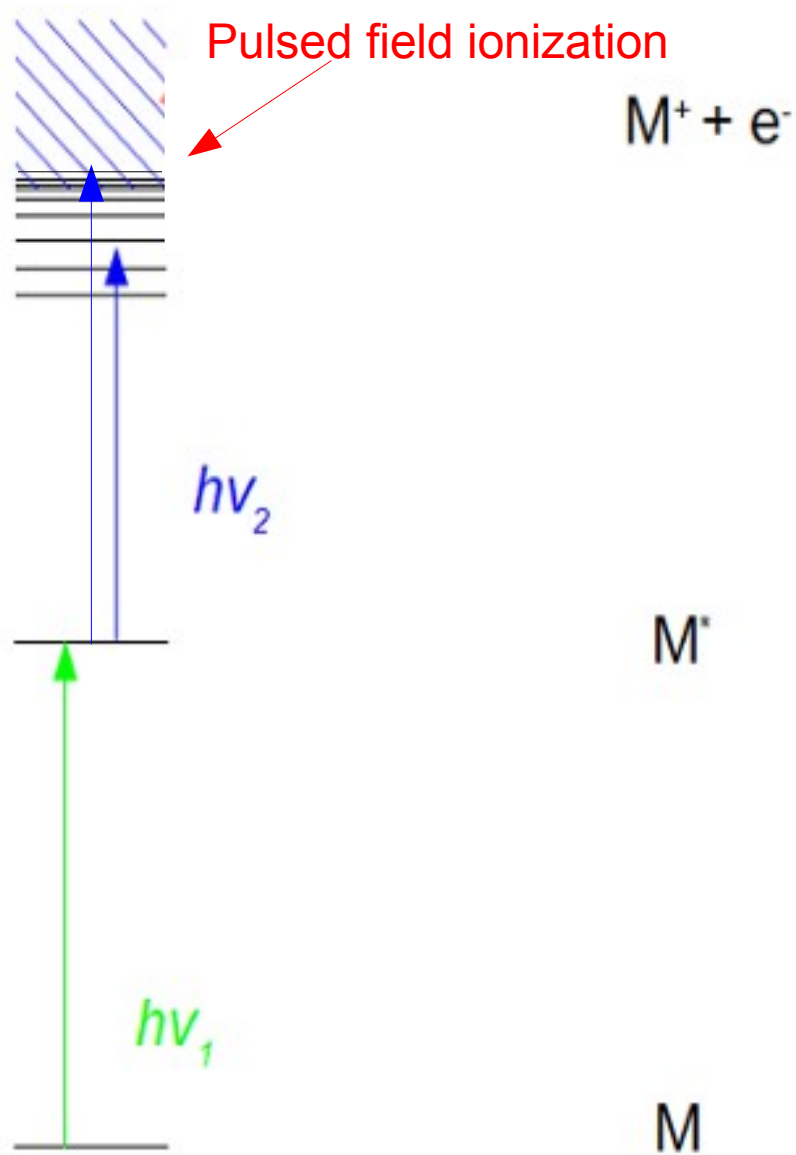
- Pulsed-field ionization
  Near-zero field
- REMPI or ZEKE lasers
  1+1' or 1+1/2 techniques
- LIF laser
  1st chamber, vertical detection
- Ablation laser
  1064nm YAG @ 20-30 mJ
- Gas pulse
  0.1% SF_6 /He



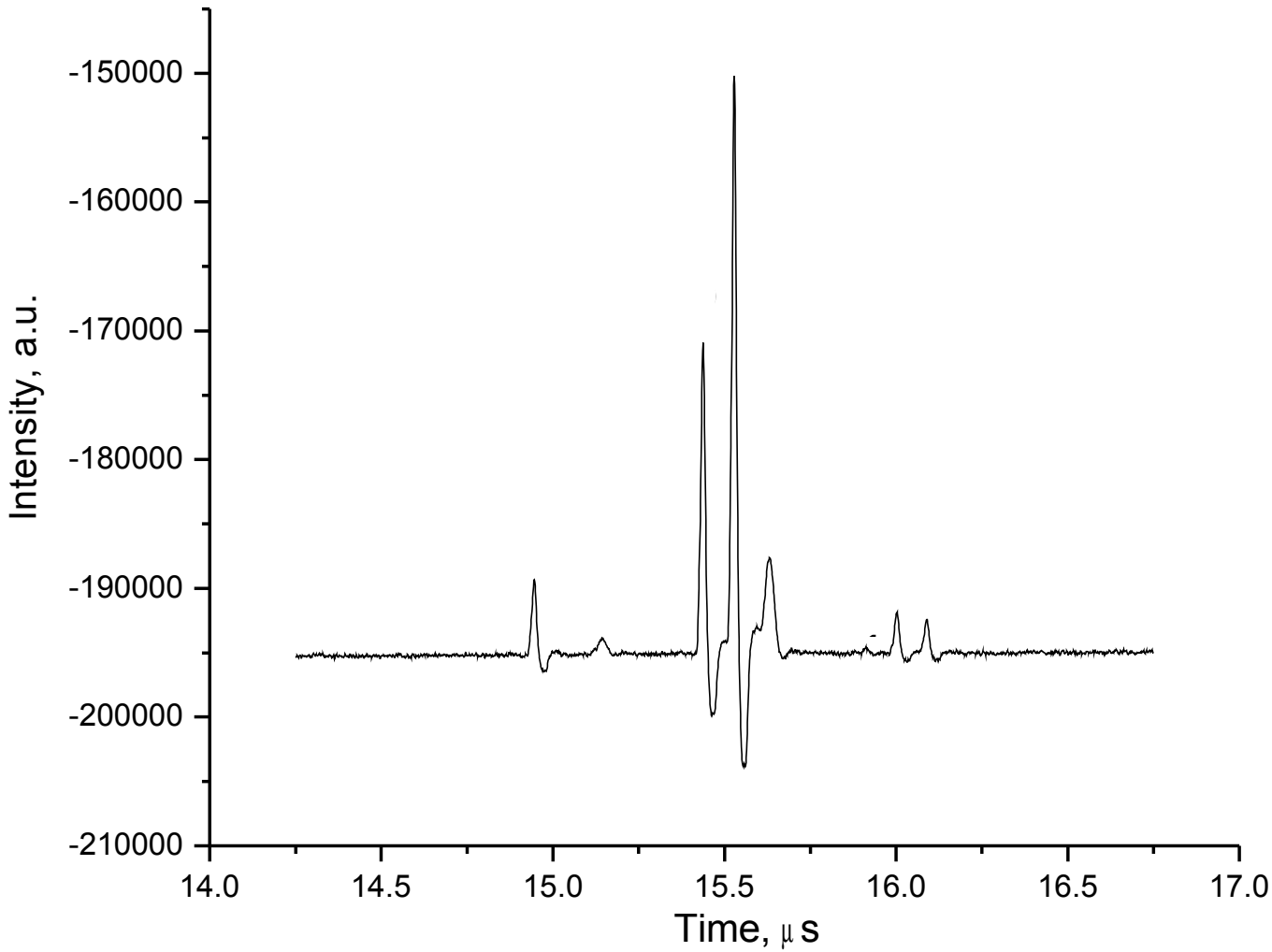


PUFI-ZEKE

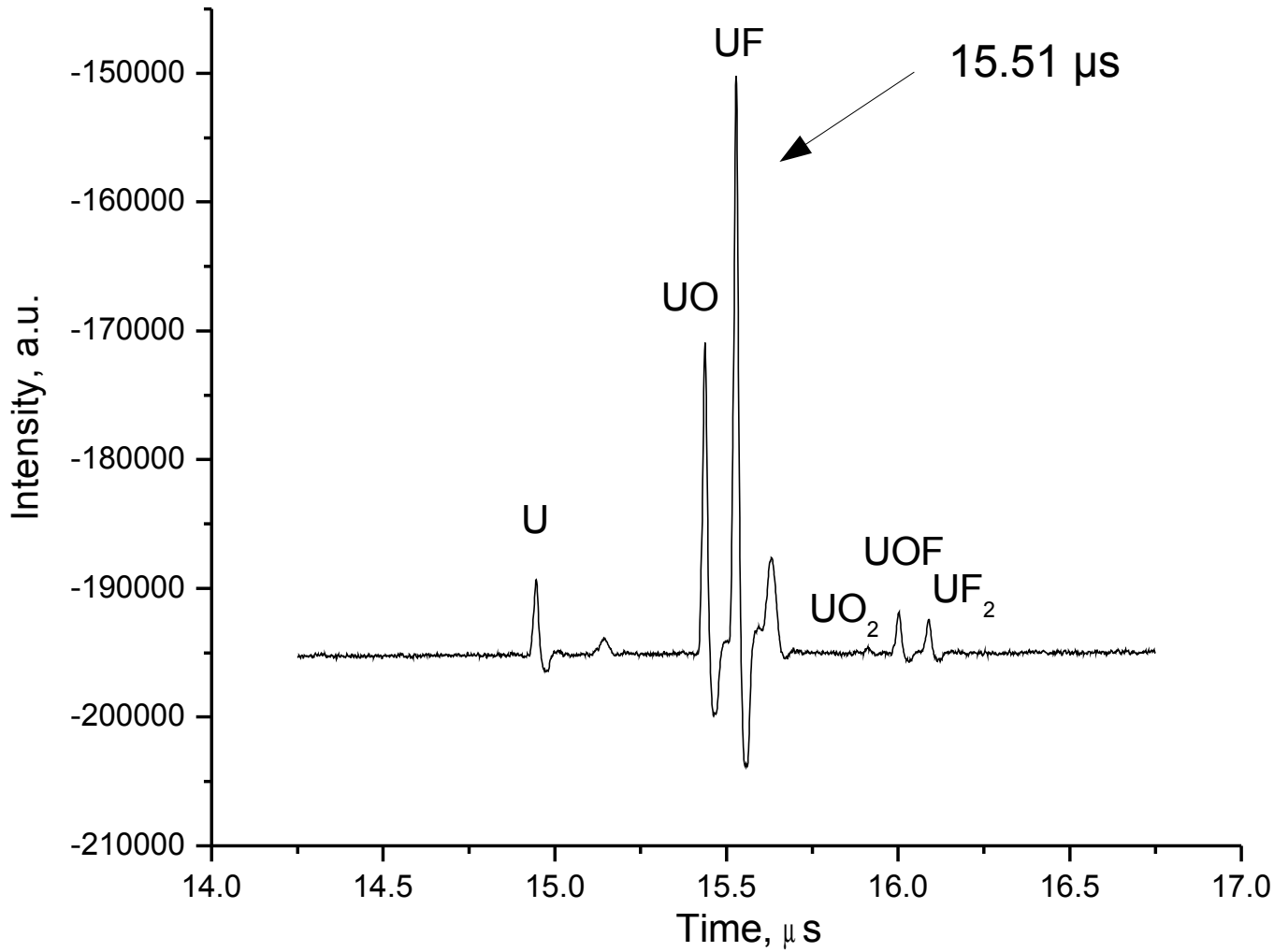
- Two-photon excitation to Rydberg levels
- Ionization by pulsed external field
- Detection of low KE electrons after several µs



Photoionization TOF Mass Spectrum

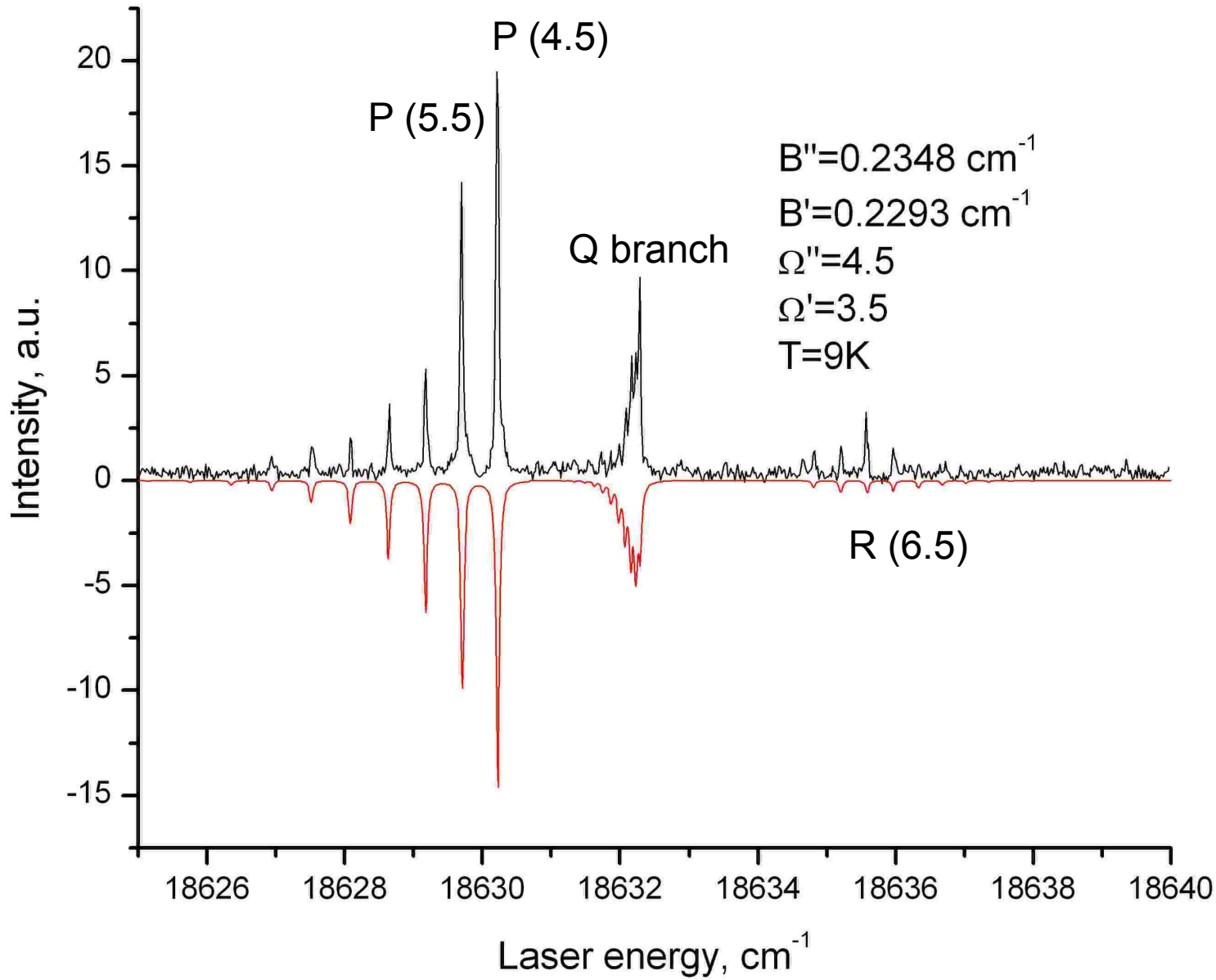


Photoionization TOF Mass Spectrum

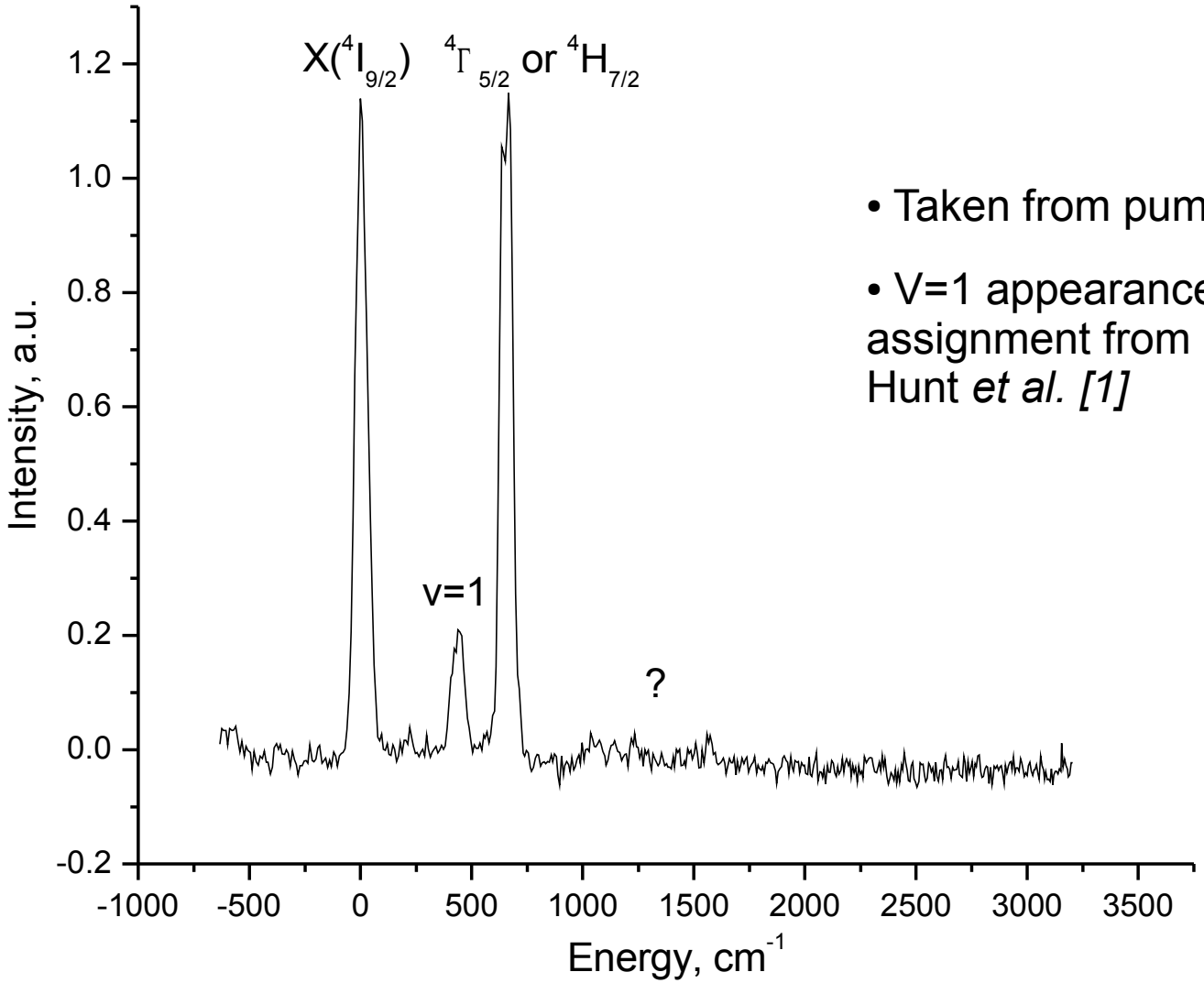


Temporal gates enable facile REMPI probe to find two-photon ionizing resonances, confirmed to belong to UF states

LIF Spectrum



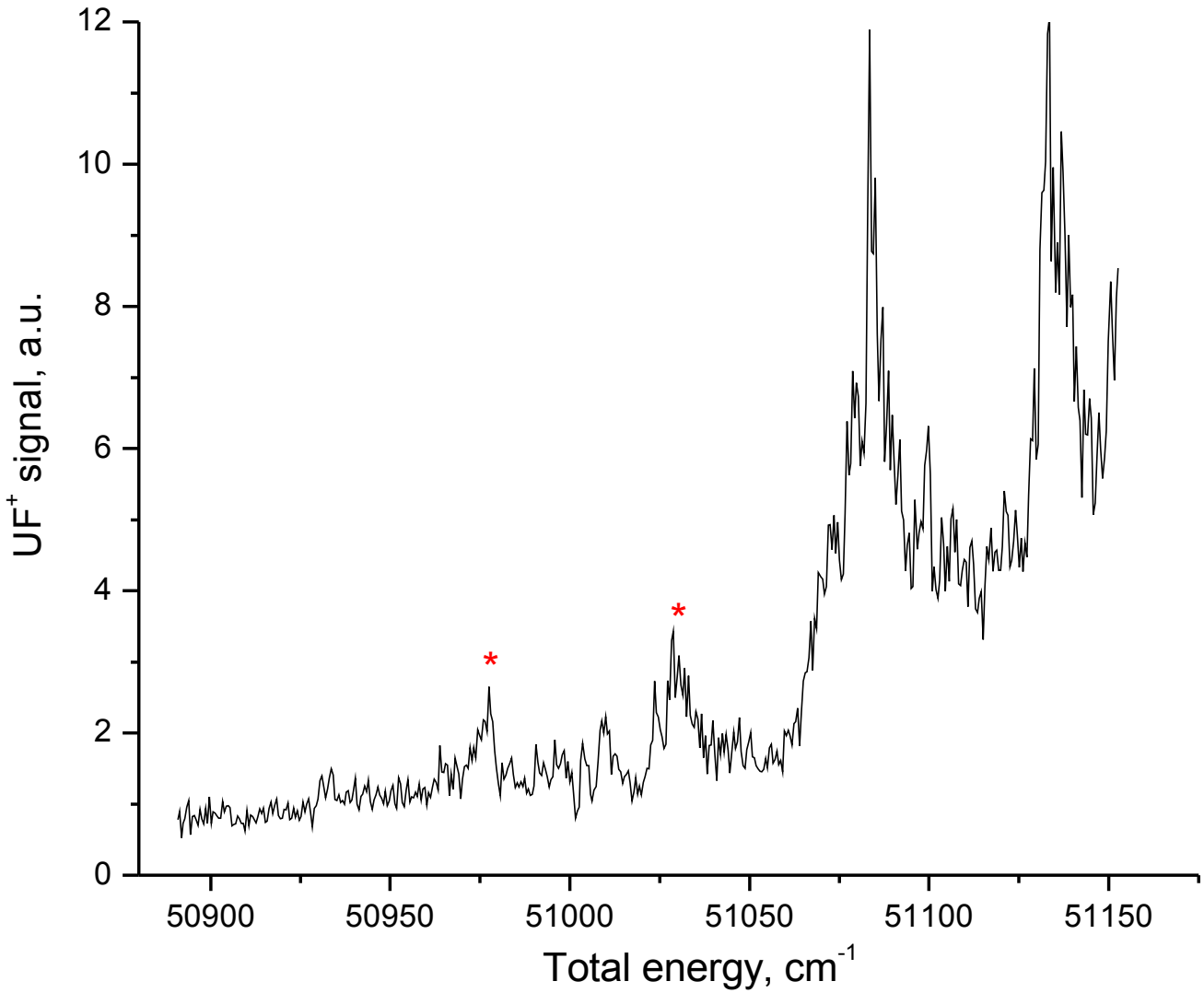
Dispersed Fluorescence Spectrum



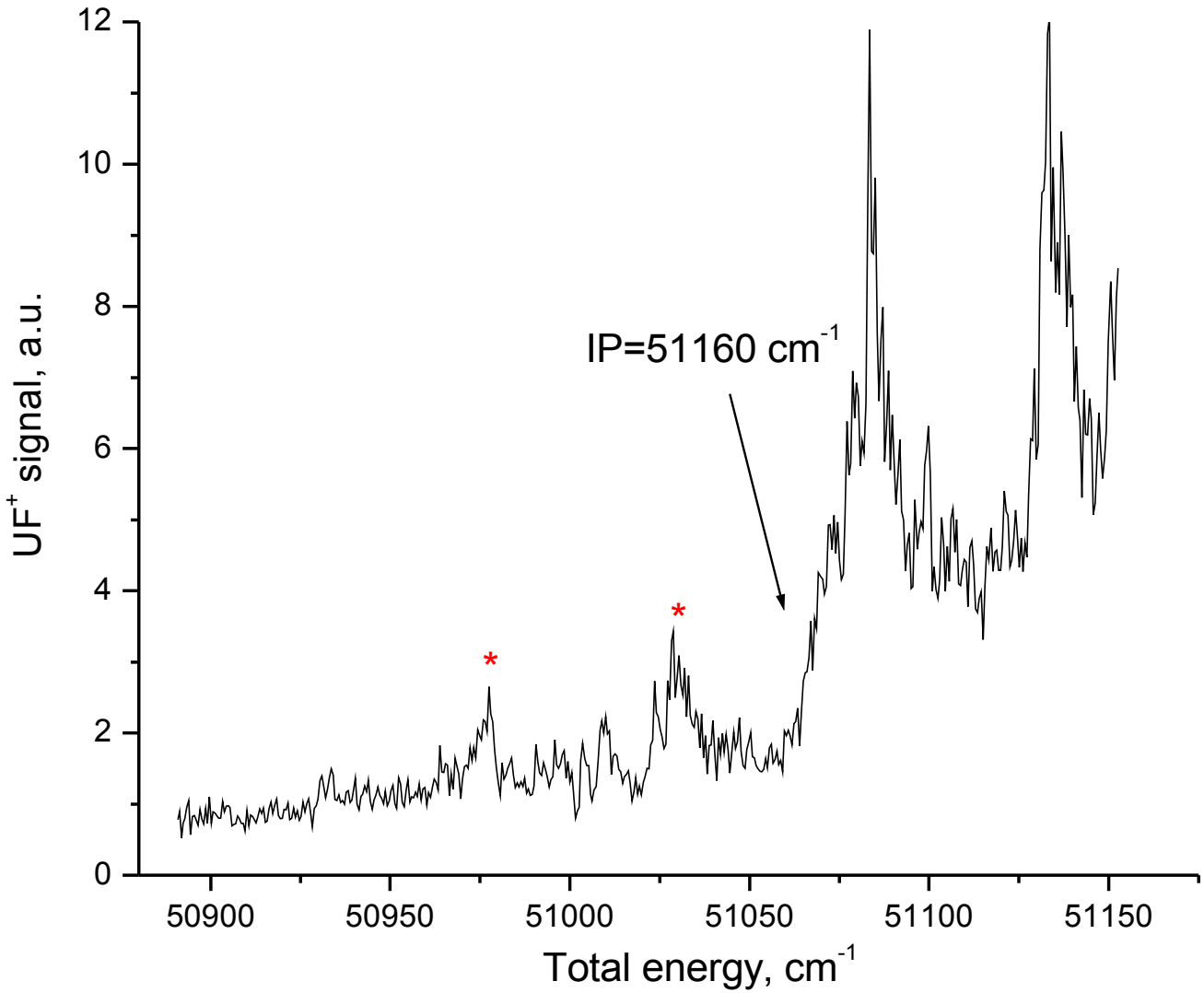
- Taken from pump of Q-line
- V=1 appearance confirms assignment from Hunt *et al. [1]*

[1] R. Hunt *et al.*, *Inorg. Chem.* (1994)

PIE-determined IP



PIE-determined IP



Resolved Ground State (UF^+)

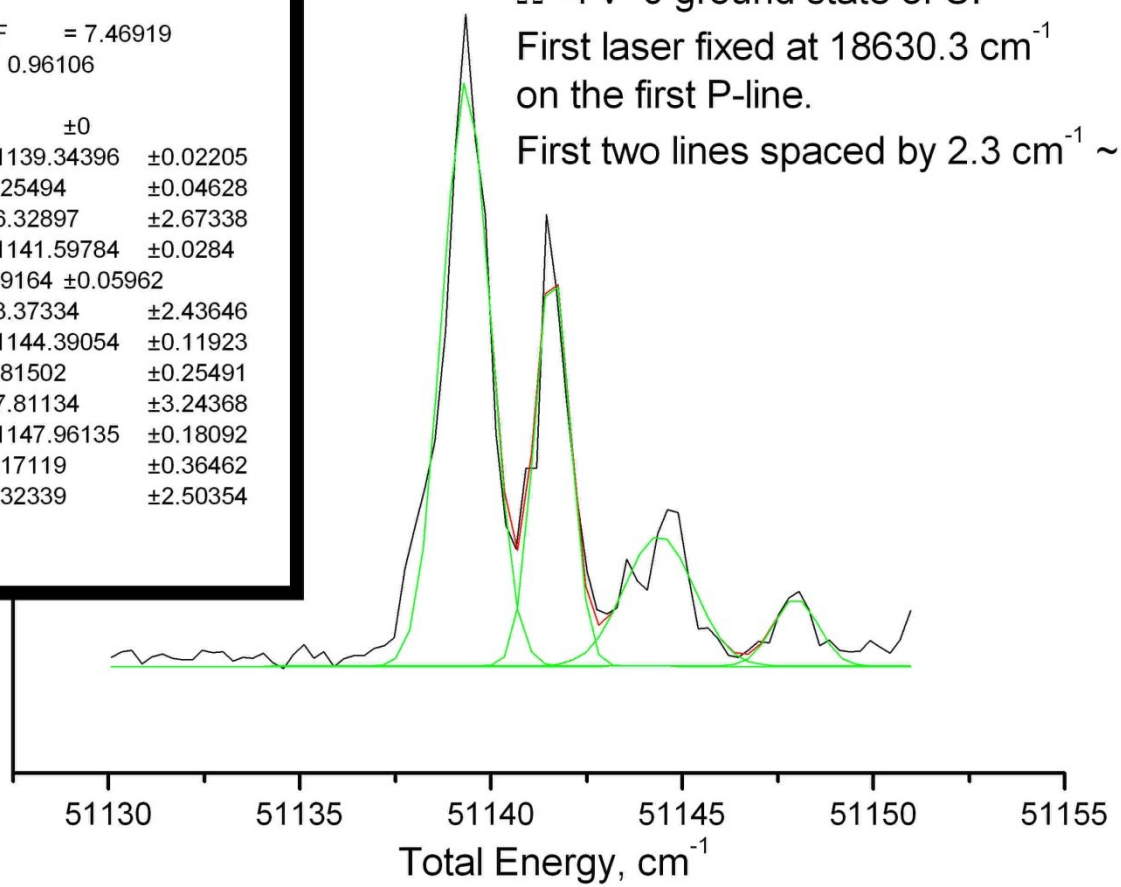
Data: A11112304CH1I_D
Model: Gauss

Chi^2/DoF = 7.46919
R^2 = 0.96106

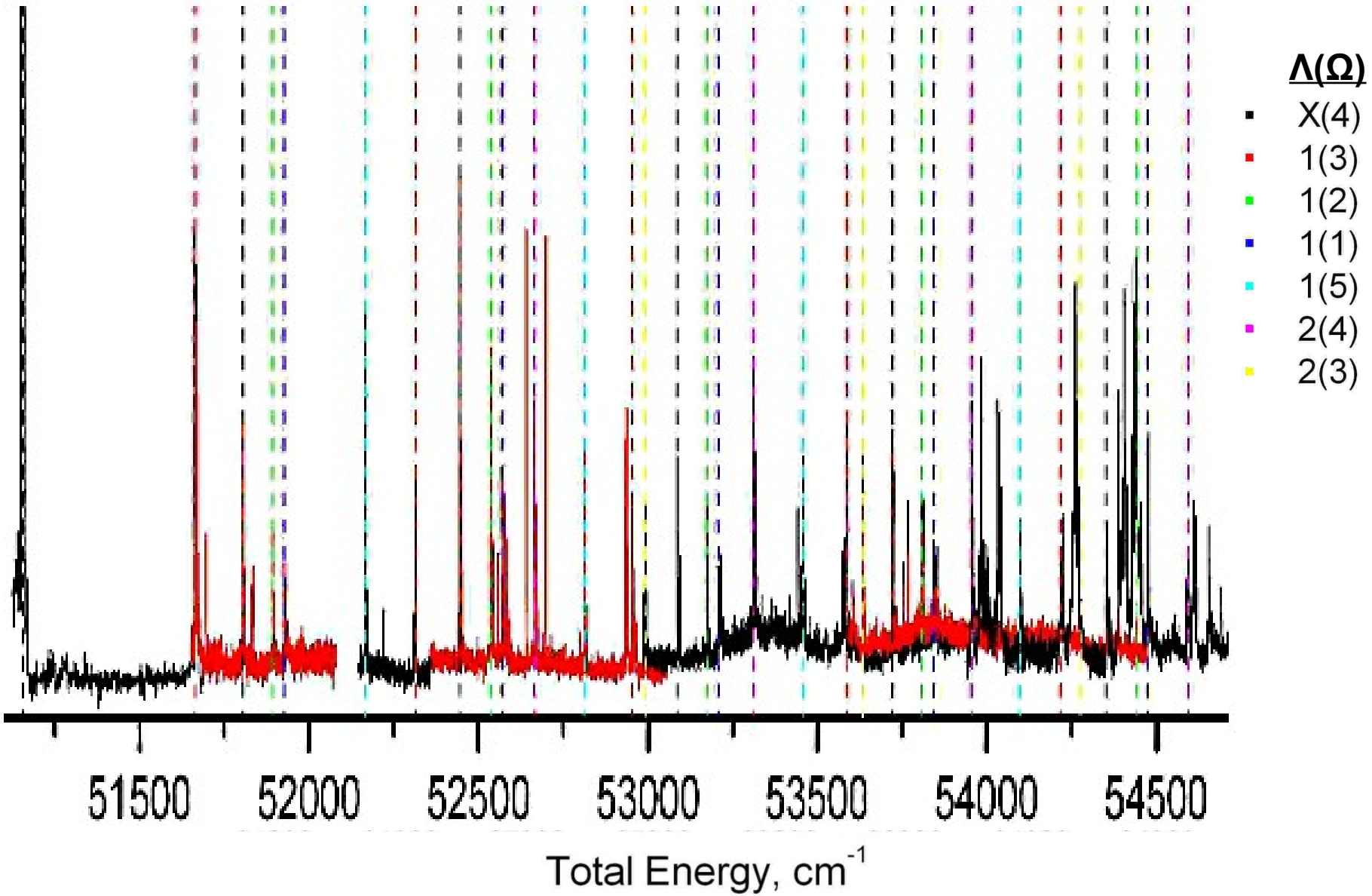
y0	0	±0
xc1	51139.34396	±0.02205
w1	1.25494	±0.04628
A1	86.32897	±2.67338
xc2	51141.59784	±0.0284
w2	0.9164	±0.05962
A2	43.37334	±2.43646
xc3	51144.39054	±0.11923
w3	1.81502	±0.25491
A3	27.81134	±3.24368
xc4	51147.96135	±0.18092
w4	1.17119	±0.36462
A4	9.32339	±2.50354

IP = 51137(1) cm^{-1}

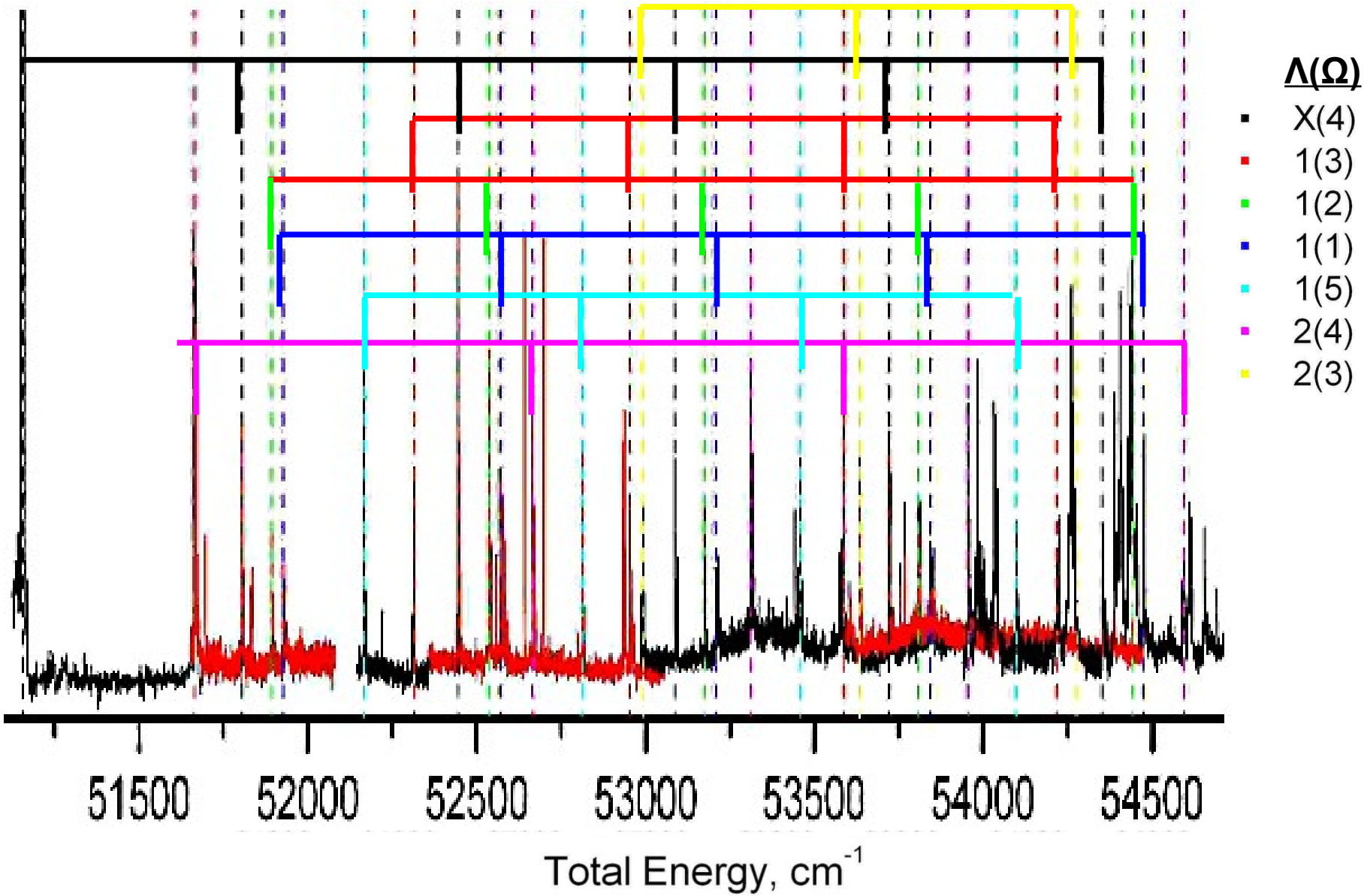
Ω=4 v=0 ground state of UF^+
First laser fixed at 18630.3 cm^{-1}
on the first P-line.
First two lines spaced by 2.3 cm^{-1} ~ 10 B



ZEKE Survey


Λ(Ω)
X(4)
1(3)
1(2)
1(1)
1(5)
2(4)
2(3)
51500
52000
52500
53000
53500
54000
54500
Total Energy, cm-1

ZEKE Survey


Λ(Ω)
X(4)
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2(3)
51500
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52500
53000
53500
54000
54500
Total Energy, cm-1

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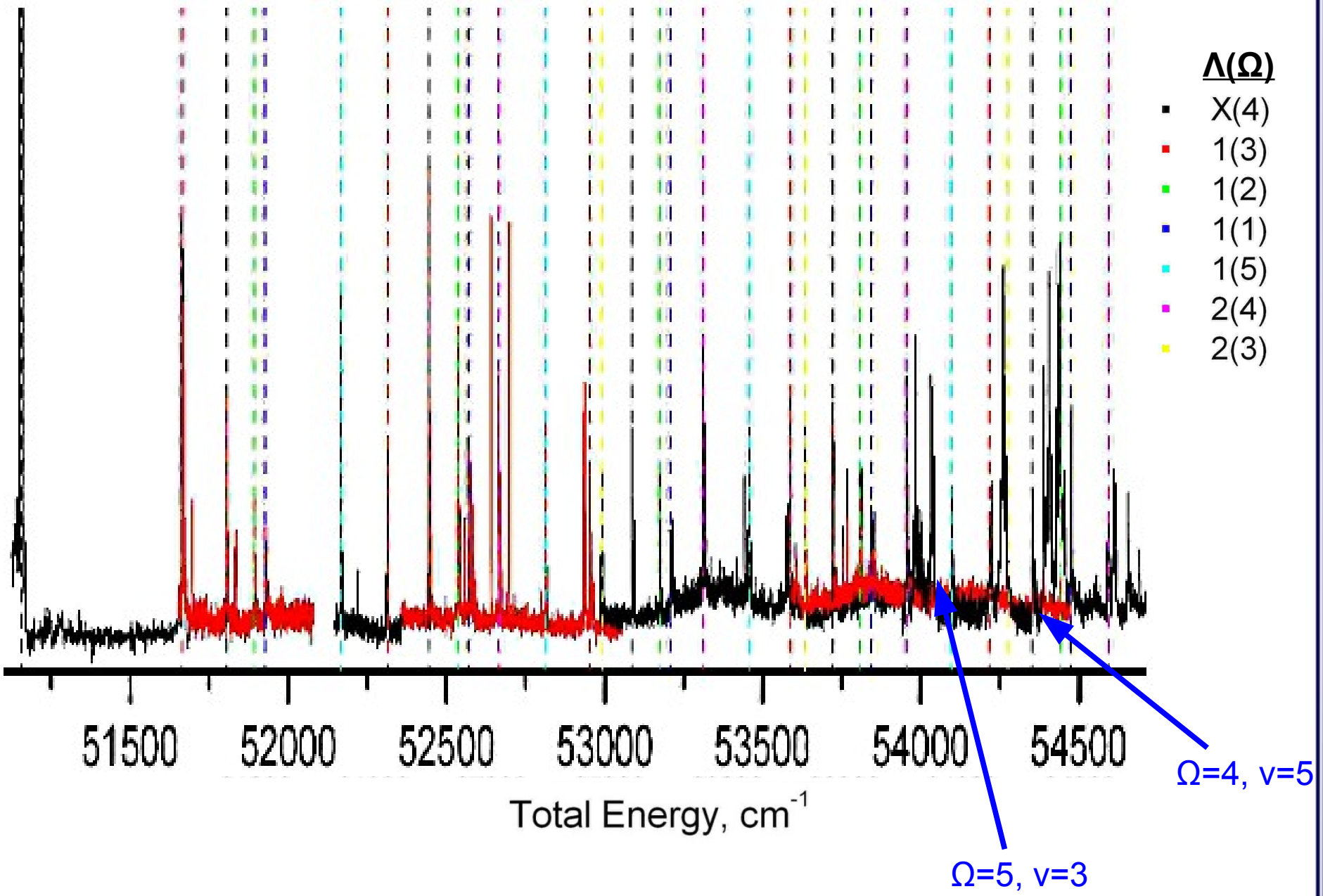

Λ(Ω)
X(4)
1(3)
1(2)
1(1)
1(5)
2(4)
2(3)
51500
52000
52500
53000
53500
54000
54500
Total Energy, cm-1
Ω=4, v=5
Ω=5, v=3

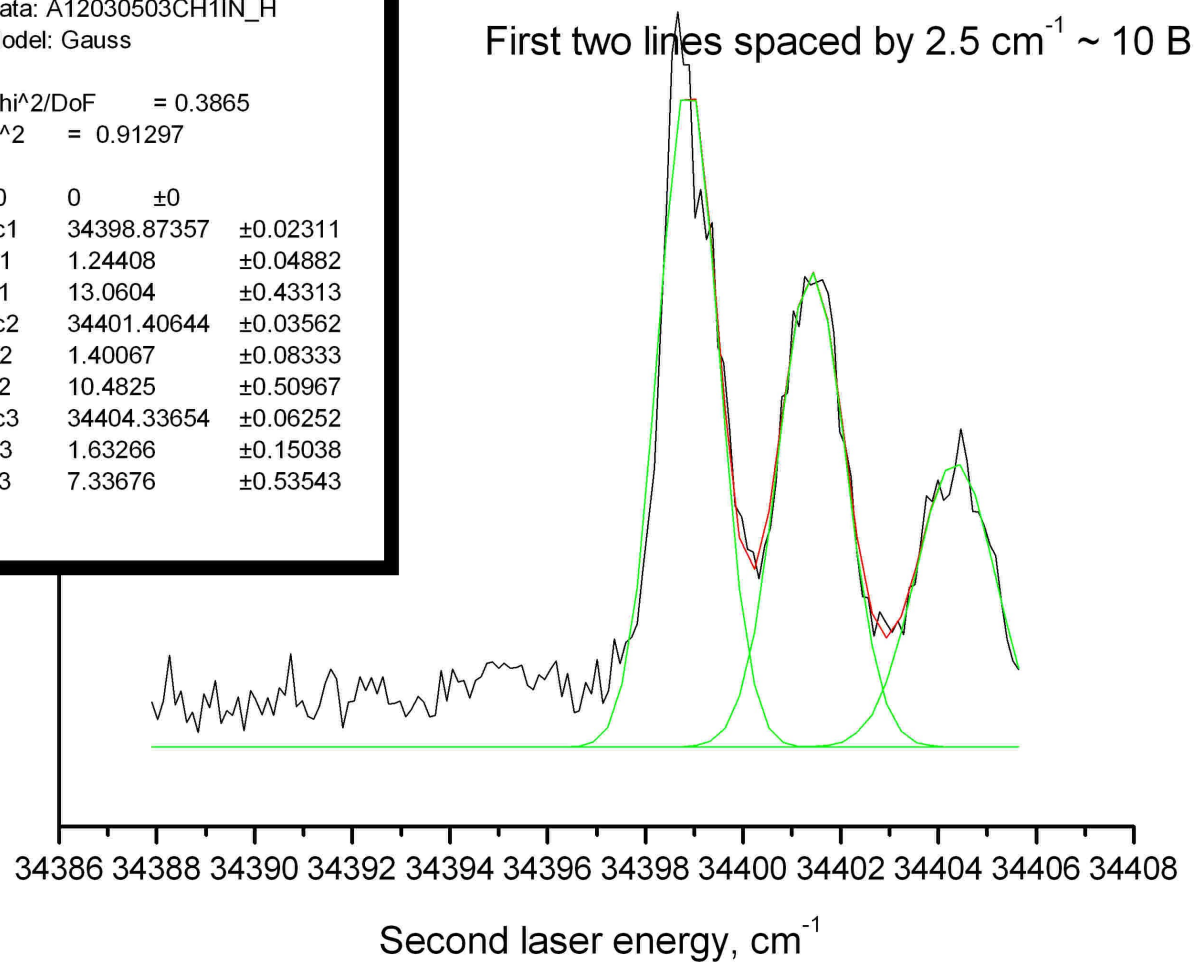
Resolved Excited State (UF^+)

Data: A12030503CH1IN_H
Model: Gauss

Chi^2/DoF = 0.3865
R^2 = 0.91297

y0	0	±0
xc1	34398.87357	±0.02311
w1	1.24408	±0.04882
A1	13.0604	±0.43313
xc2	34401.40644	±0.03562
w2	1.40067	±0.08333
A2	10.4825	±0.50967
xc3	34404.33654	±0.06252
w3	1.63266	±0.15038
A3	7.33676	±0.53543

Ω=4 v=5 ground electronic state of UF^+
First laser fixed at 19953 cm^{-1}.
First two lines spaced by 2.5 cm^{-1} ~ 10 B

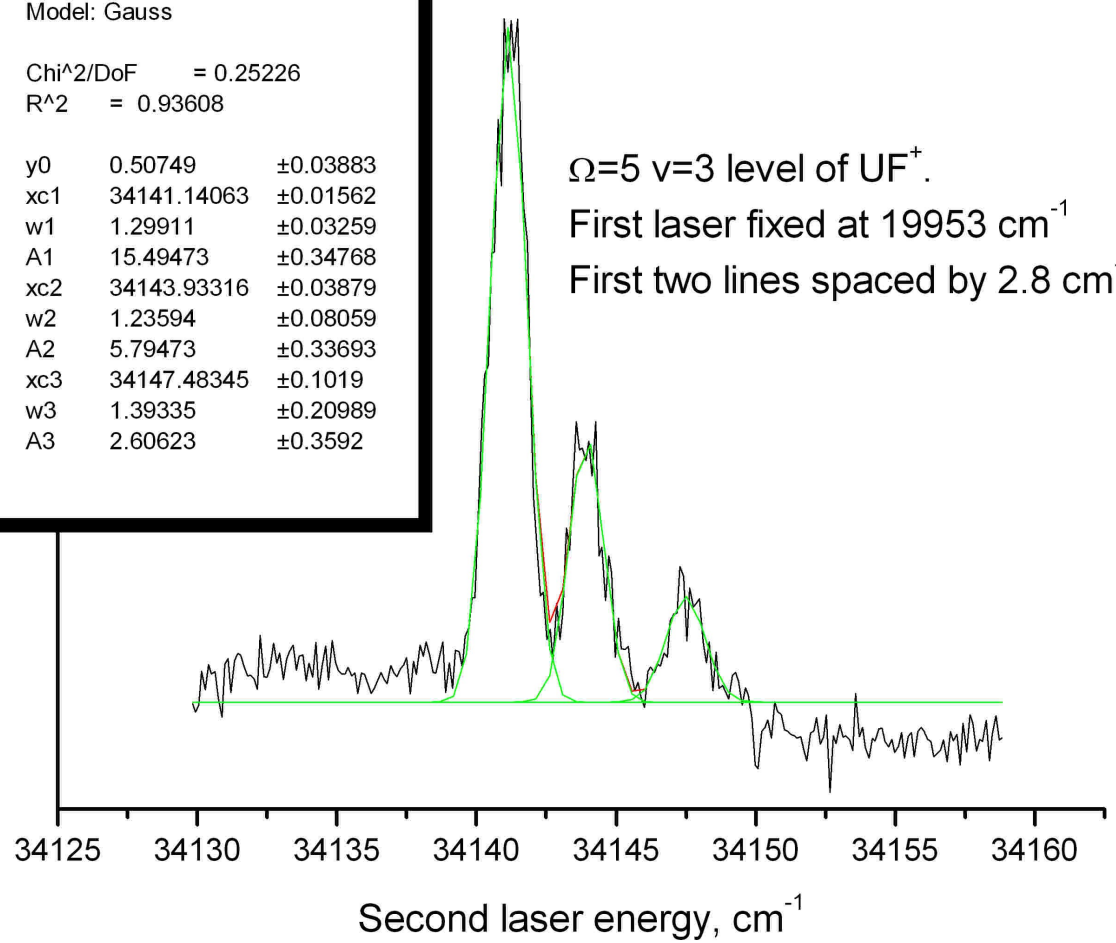


Resolved Excited State (UF^+)

Data: A12030504CH1IN_H
Model: Gauss

Chi^2/DoF = 0.25226
R^2 = 0.93608

y0	0.50749	±0.03883
xc1	34141.14063	±0.01562
w1	1.29911	±0.03259
A1	15.49473	±0.34768
xc2	34143.93316	±0.03879
w2	1.23594	±0.08059
A2	5.79473	±0.33693
xc3	34147.48345	±0.1019
w3	1.39335	±0.20989
A3	2.60623	±0.3592



Ω=5 v=3 level of UF^+.

First laser fixed at 19953 cm^{-1}

First two lines spaced by 2.8 cm^{-1} = 12 B

UF^+ Parameters and Term Energies

Λ(Ω)	ω_e	$\omega_e\chi_e$	Ω	B	T_e
X(4)	653.21	2.3235	4	0.24	0
1(3)	652.94	3.1358	3	0.24	511.821
1(2)	645.96	1.7450	2	0.24	738.836
1(1) and 1(?)	645.62	1.7170	1, (?)	0.24, (?)	771.718
1(5)	651.81	2.3085	5	0.245	1011.263
2(4)	648.36	1.4980	4	0.24	1512.147
2(2), 2(1)			2, 1		1780.388
2(3)	643?		3	0.24	1835.555
3(3)			3		3067.
1(6)			6		3232.
2(5)			5		3321.

All values in cm^{-1}.

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All values in cm^{-1}.

f^2s^2?

UF^+ versus UO

Λ(Ω)	UF^+ T_e	UO T_e [1]
X(4)	0	0
1(3)	511.821	651.12
1(2)	738.836	958.66
1(1)	771.718	-
1(5)	1011.263	1043.00
2(5)	3321.	-
2(4)	1512.147	2096.00
1(6)	3232.	4469(5)
3(3)	3067.	1941.48

[1] Kaledin, L. and Heaven, M. *J. Mol. Spec.* (1997)

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f^2s^2 for UF^+?

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2(5)	3321.	-
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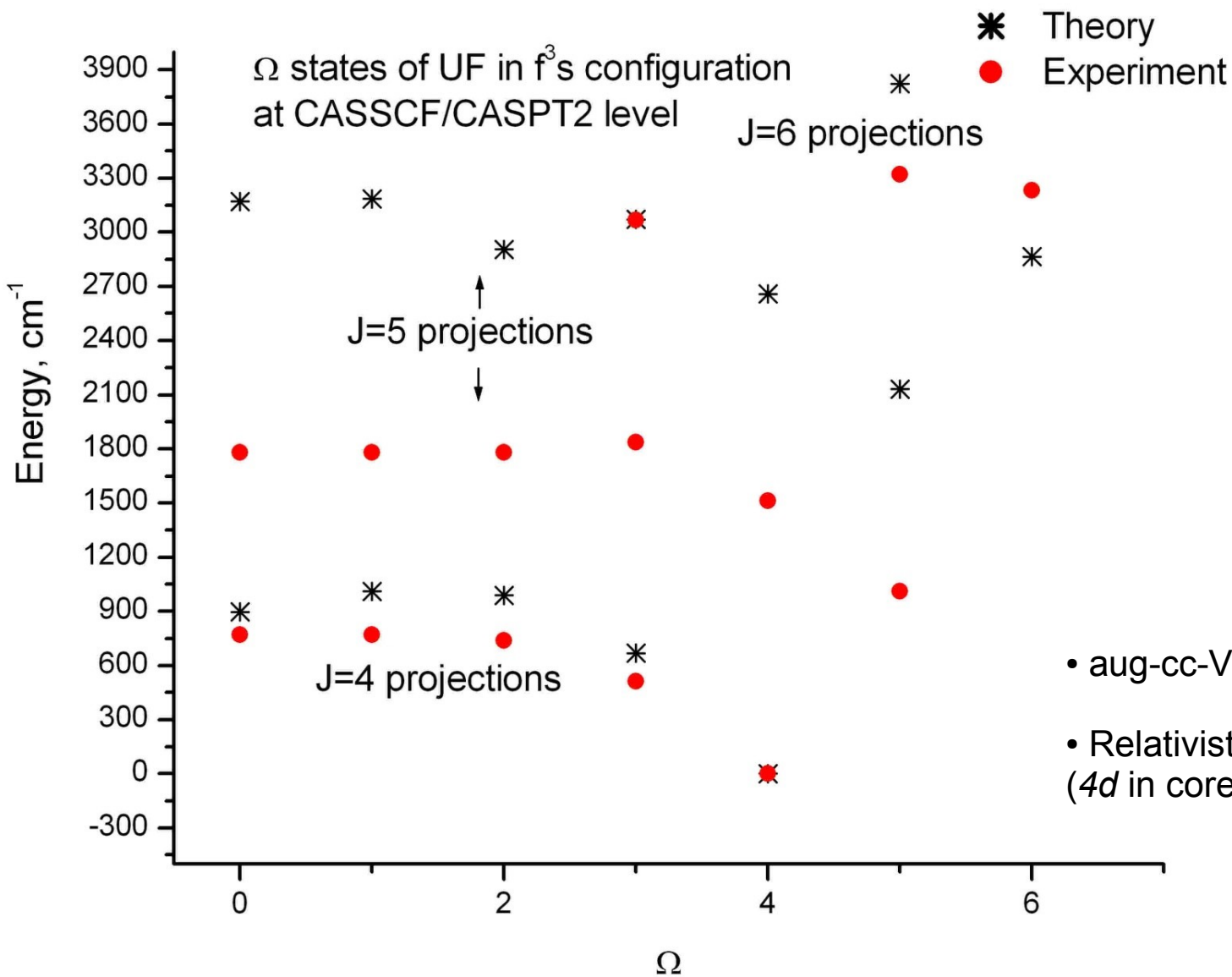
3(3)	3067.	1941.48

3(4) state not observed!

[1] Kaledin, L. and Heaven, M. *J. Mol. Spec.* (1997)

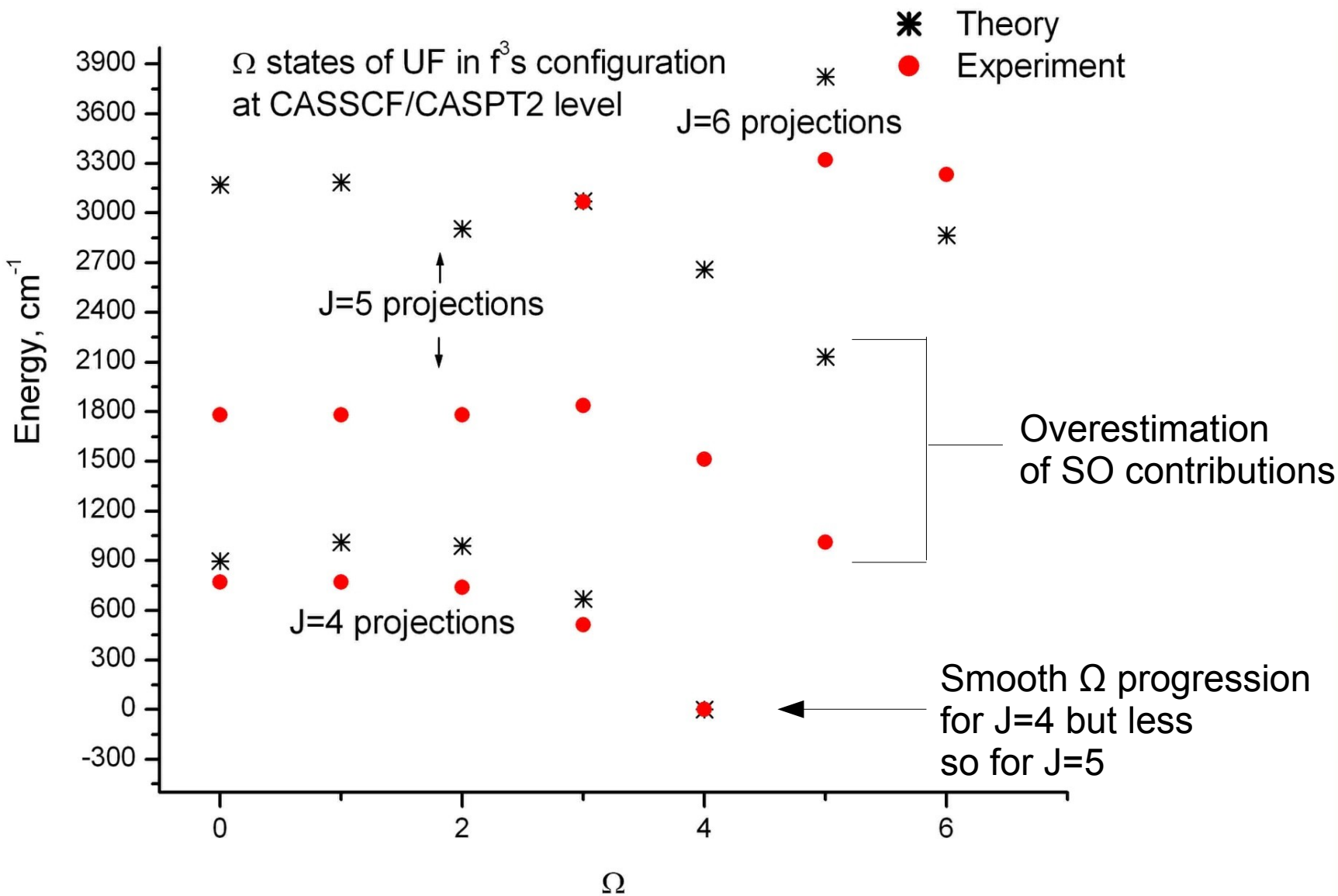
CASSCF/PT2 Calculations



- aug-cc-VTZ basis
- Relativistic PP on U (*4d* in core) [1]

[1] Dolg, M. and Cao, X. *J. Phys. Chem. A.* (2009)

CASSCF/PT2 Calculations



Future Work

- Complete assignment of UF^+ states
- Calculations encompassing f^2s^2 configuration and alternate PP sizes
- Investigate additional actinide compounds with 3rd row *p*-block elements

Acknowledgments

- Michael Heaven's research group (Ivan, Kyle, Jiande, Sullivan, Keith) and Xiaohong Wang

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