Ionization Measurement and Spectroscopy of ThS and ThS^+

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Applications

- Fundamental interest of actinides
  - Few existing studies,
  - 5*f* electron roles unclear
- Relativistic theory assessment
  - Experimental data to evaluate performance of ECPs
- Actinide “hard versus soft” chalcogen ligand properties
  - Comparison with ThO
- Advanced separation processes
  - Relevant to nuclear fuel technology

Previous Work

Heavy molecules & ions studied in the gas phase by the Heaven group:

ThN, ThO, ThF, HfO, HfS, UO, UF, UO_2

Mass spectrometry gas phase actinide study with DFT calculations (Pereira *et. al.*)

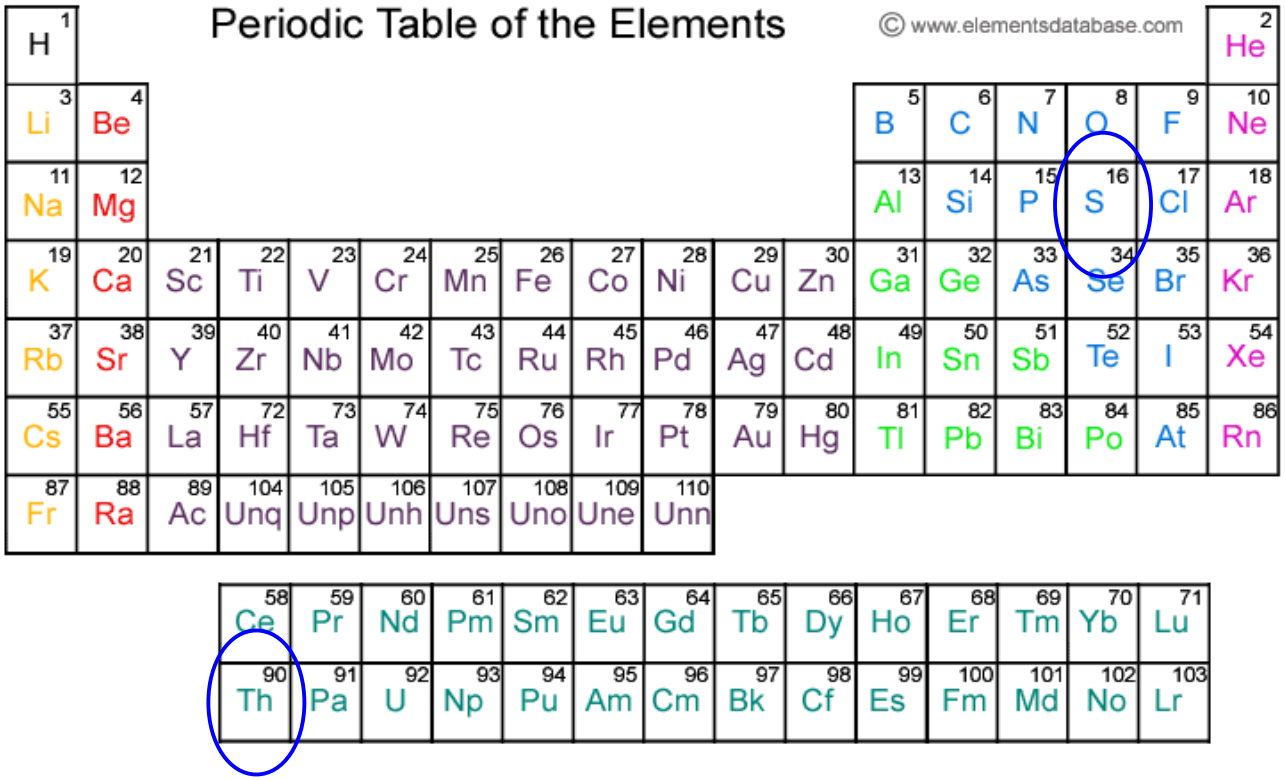
$D_0(ThS^+)$ = 5.7(1) eV, IP (ThS) = 6.7(2) eV

Matrix-isolated study of ThS with DFT calculations (Liang & Andrews)

X $(^1\Sigma^+)$ $\Delta G_{1/2}$ = 474.7 cm^{-1} , $^3\Delta$ state predicted at 3200 cm^{-1}

Barker, B. J., Antonov, I. O., & Heaven, M. C. (2012) *Journal of Molecular Spectroscopy, 275*
Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006). *J Chem Phys, 125*(13)
Liang, B., & Andrews, L. (2002) *The Journal of Physical Chemistry A, 106*(16)
Pereira, C. C., Marsden, C. J., Marcalo, J., & Gibson, J. K. (2011) *Phys Chem Chem Phys, 13*(28)

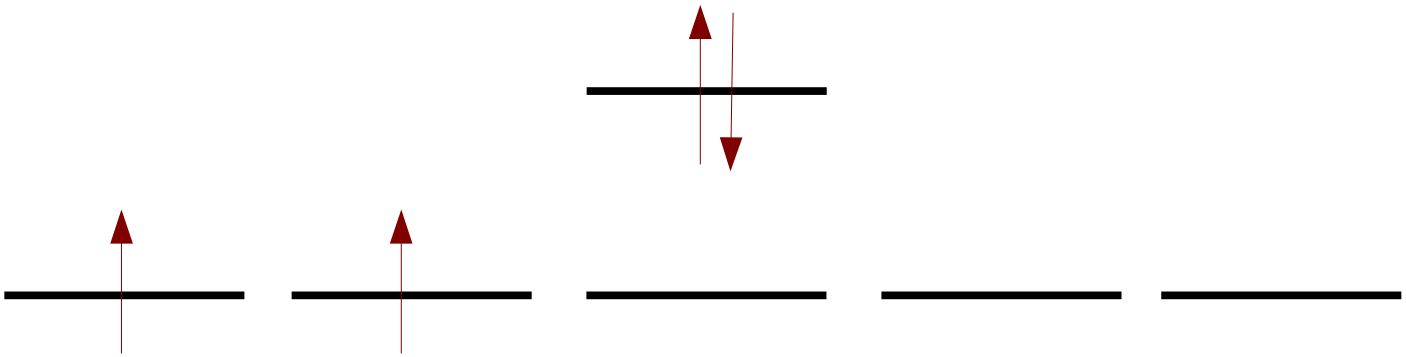
Outline



- Experimental details
- Spectral results for ThS/ThS$^+$
- Computational results (CASSCF/MRCI/SO, (R)CCSD(T))
- Comparison of properties to ThO/ThO$^+$, HfS/HfS$^+$, HfO/HfO$^+$
    - All numbers reported are in units of cm^{-1} unless otherwise noted.

Outline

Th: [Rn]$6d^2 7s^2$



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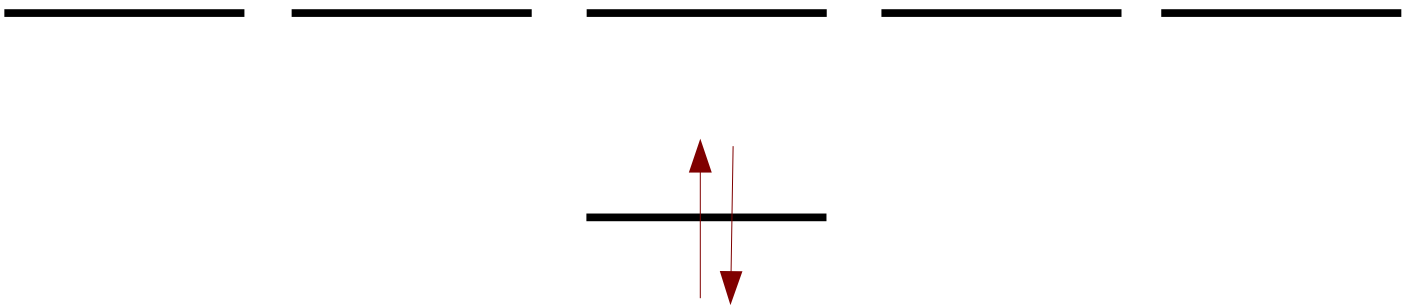
Outline

Th^{2+}: $[Rn]7s^2$ ← S^{2-}

$^1\Sigma^+$



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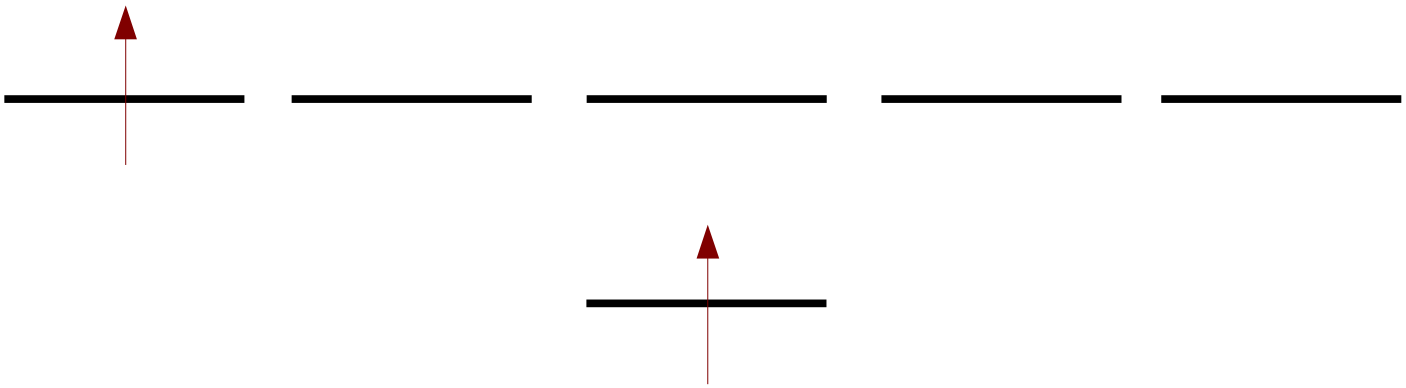
Outline

Th^{2+*}: [Rn]6d7s ← S^{2-}

$^3\Delta_{1,2,3}$, $^1\Delta_1$



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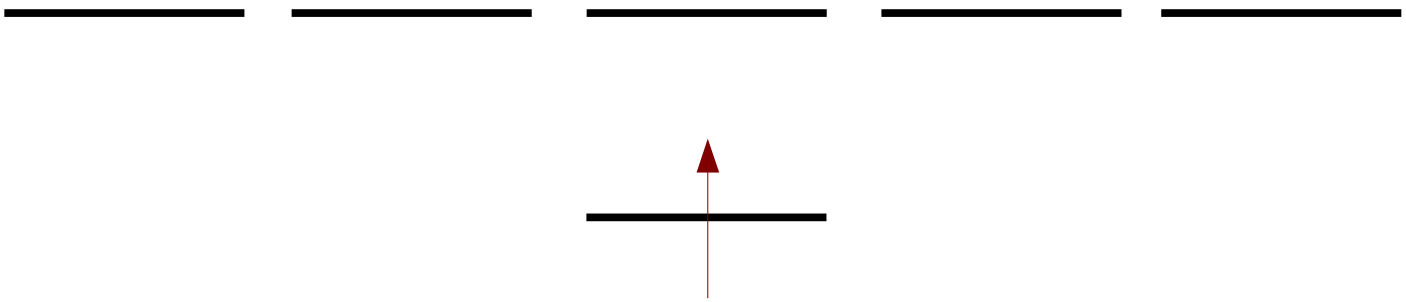
Outline

Th^{3+}: [Rn]7s ← S^{2-}

$^2\Sigma^+$



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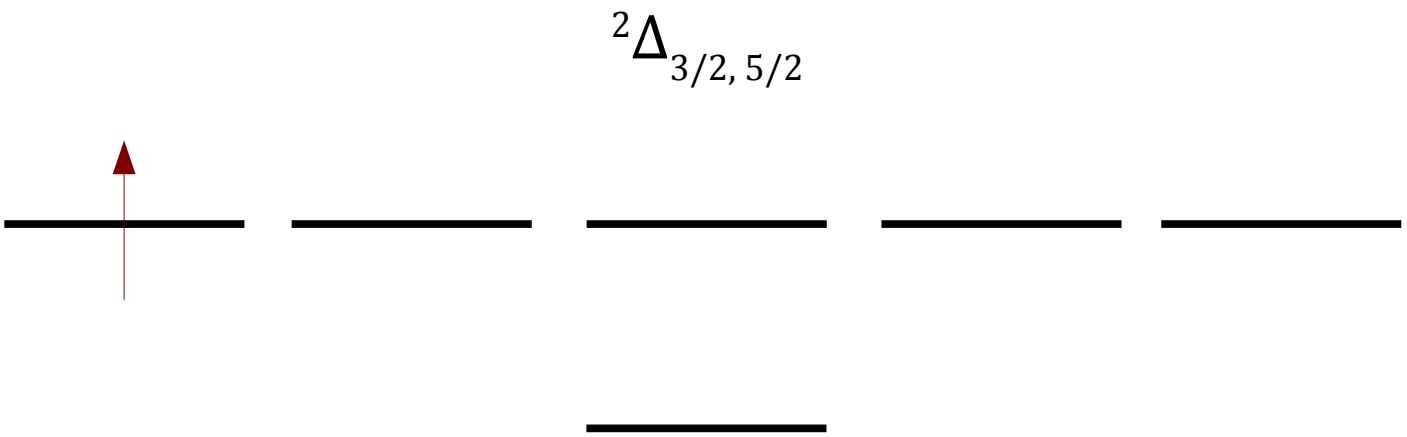
Outline

Th^{3+*}: [Rn]6d ← S^{2-}



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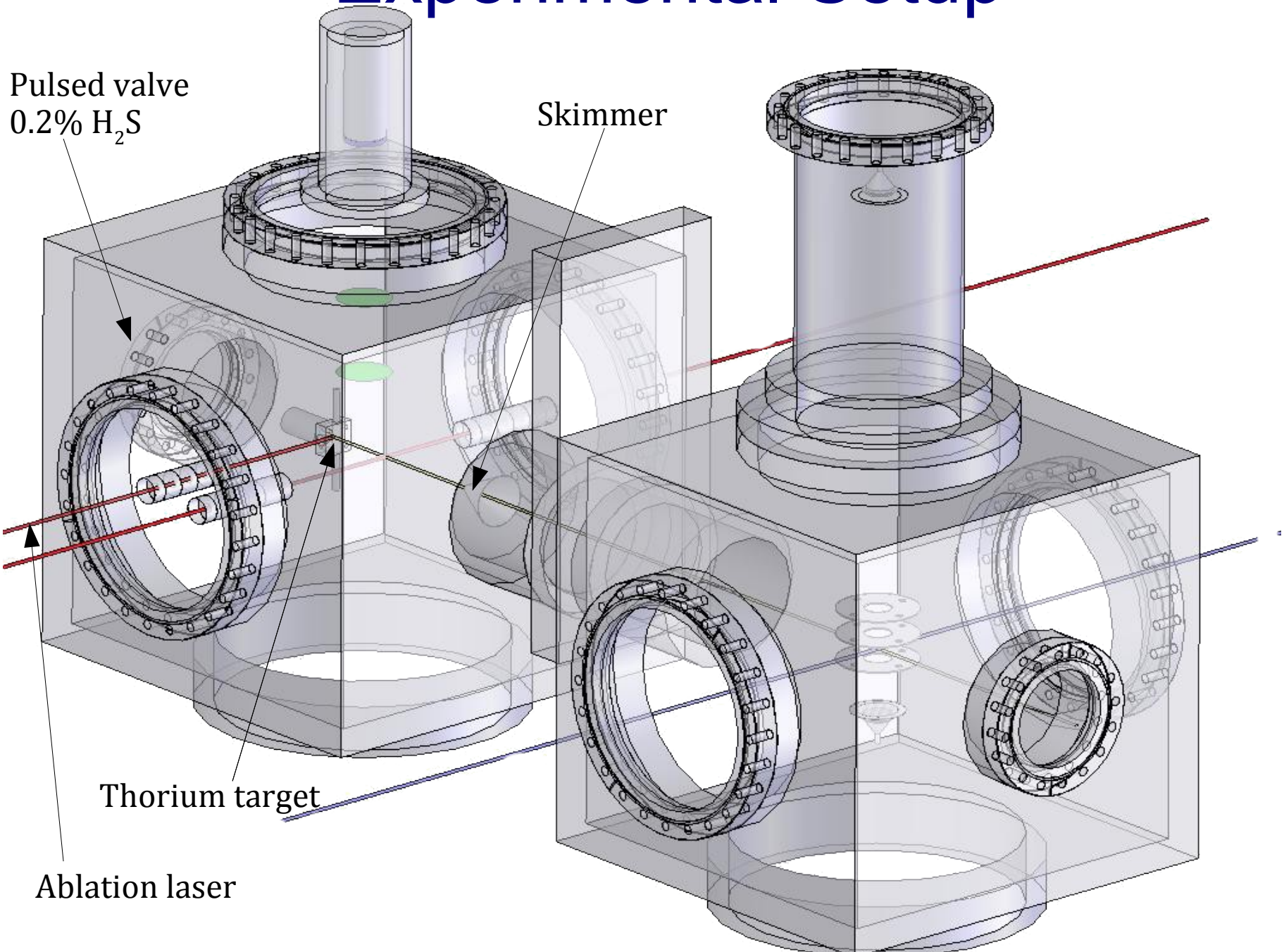
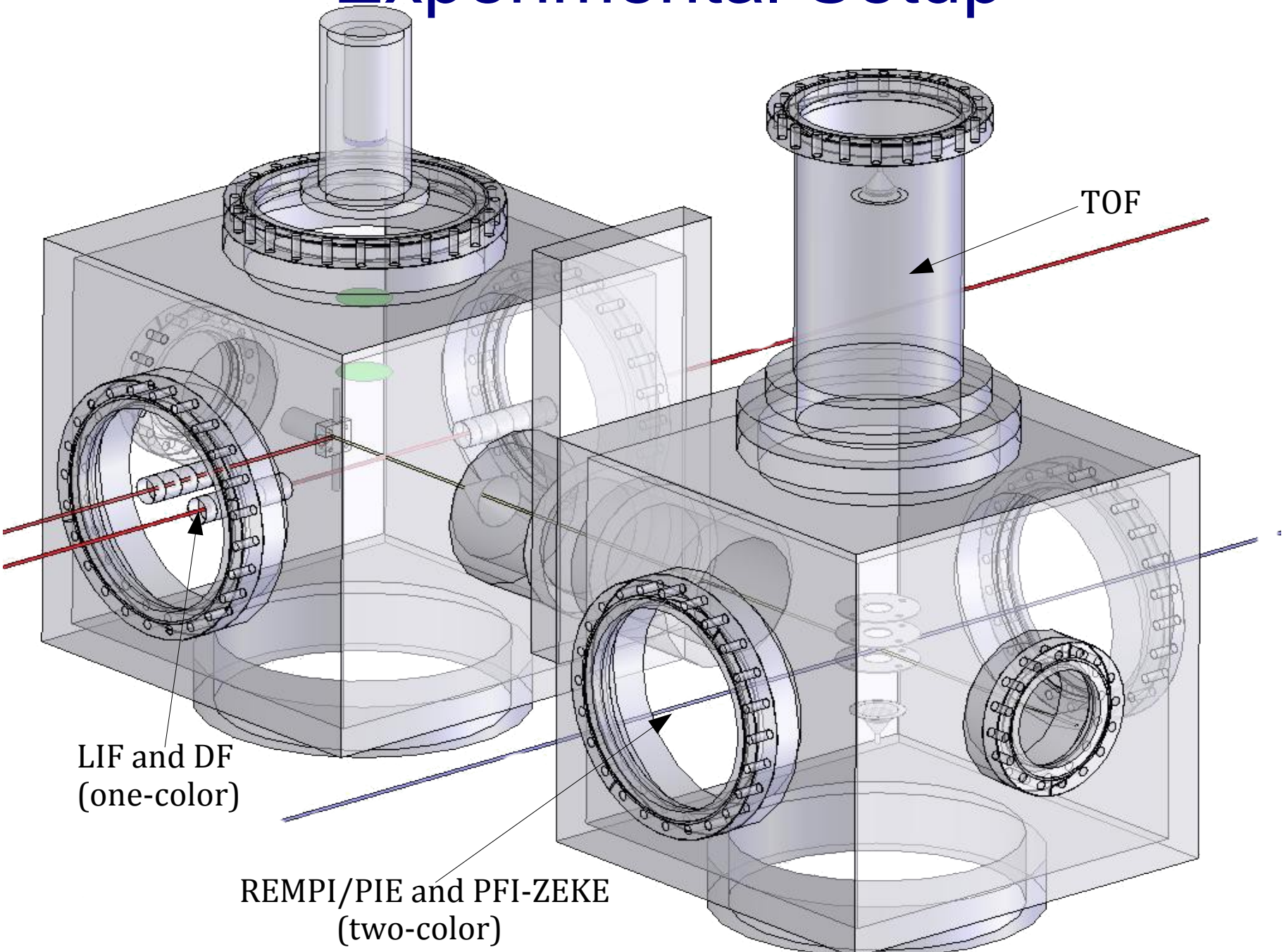
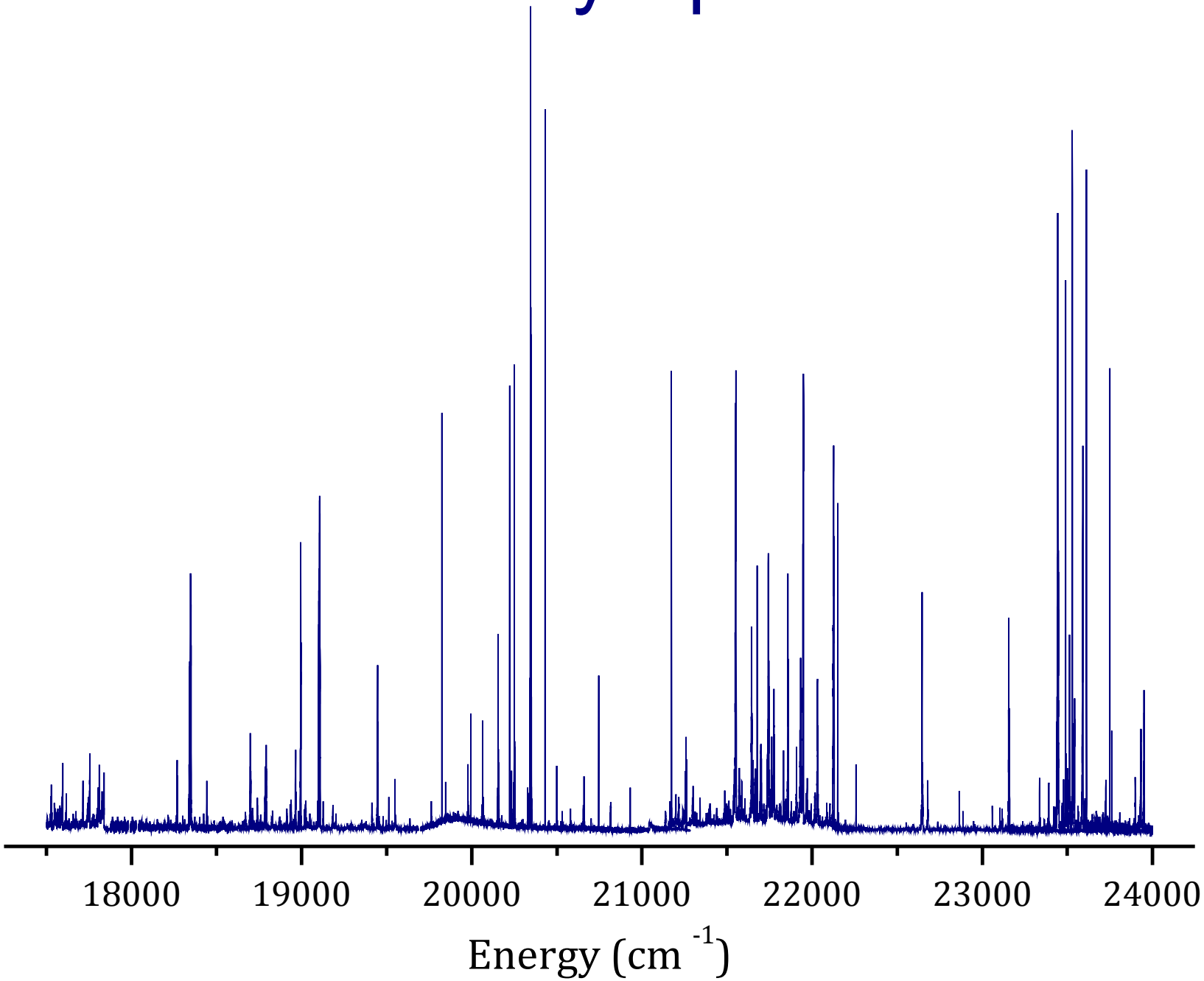
Experimental Setup



Experimental Setup



LIF Survey Spectrum



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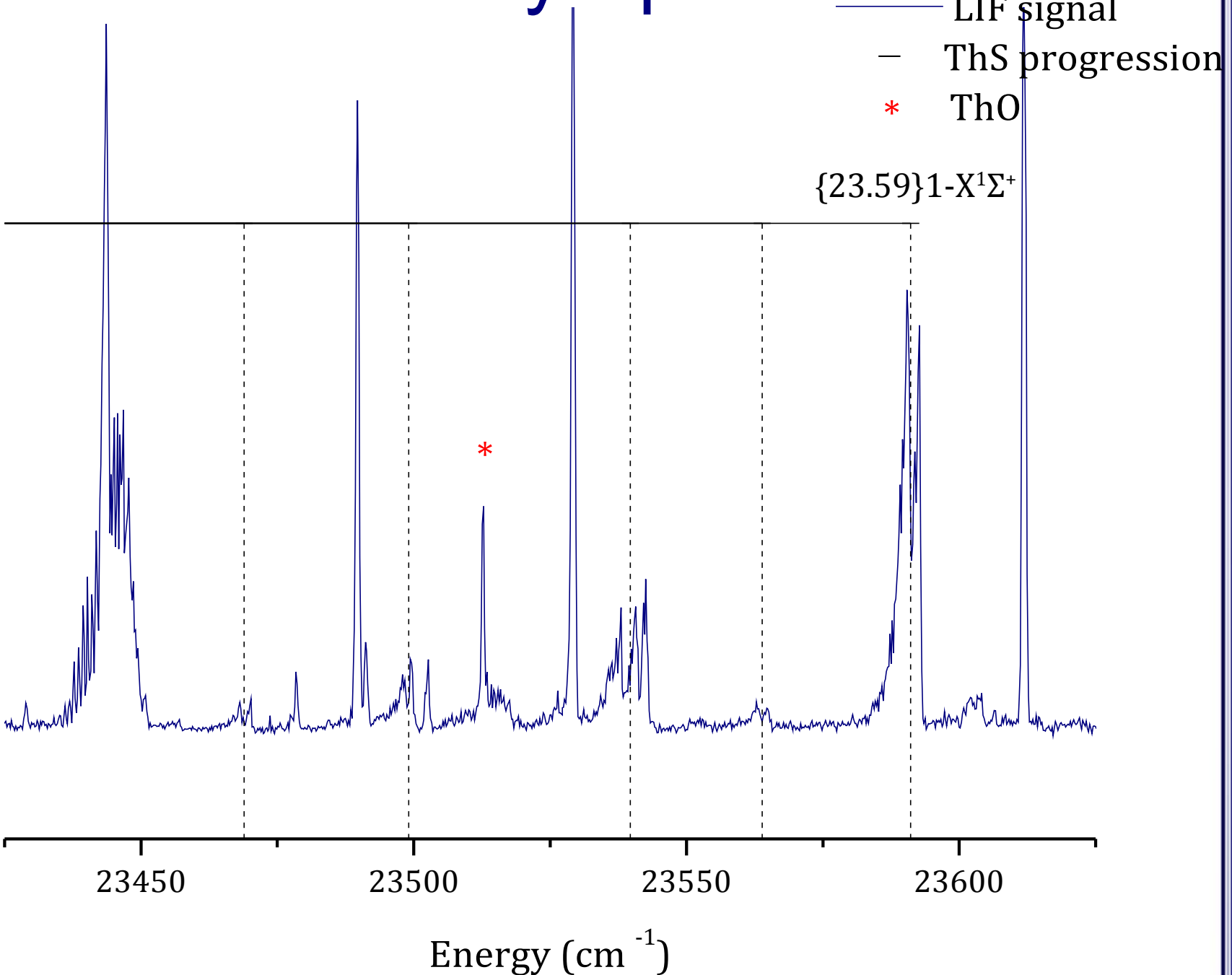
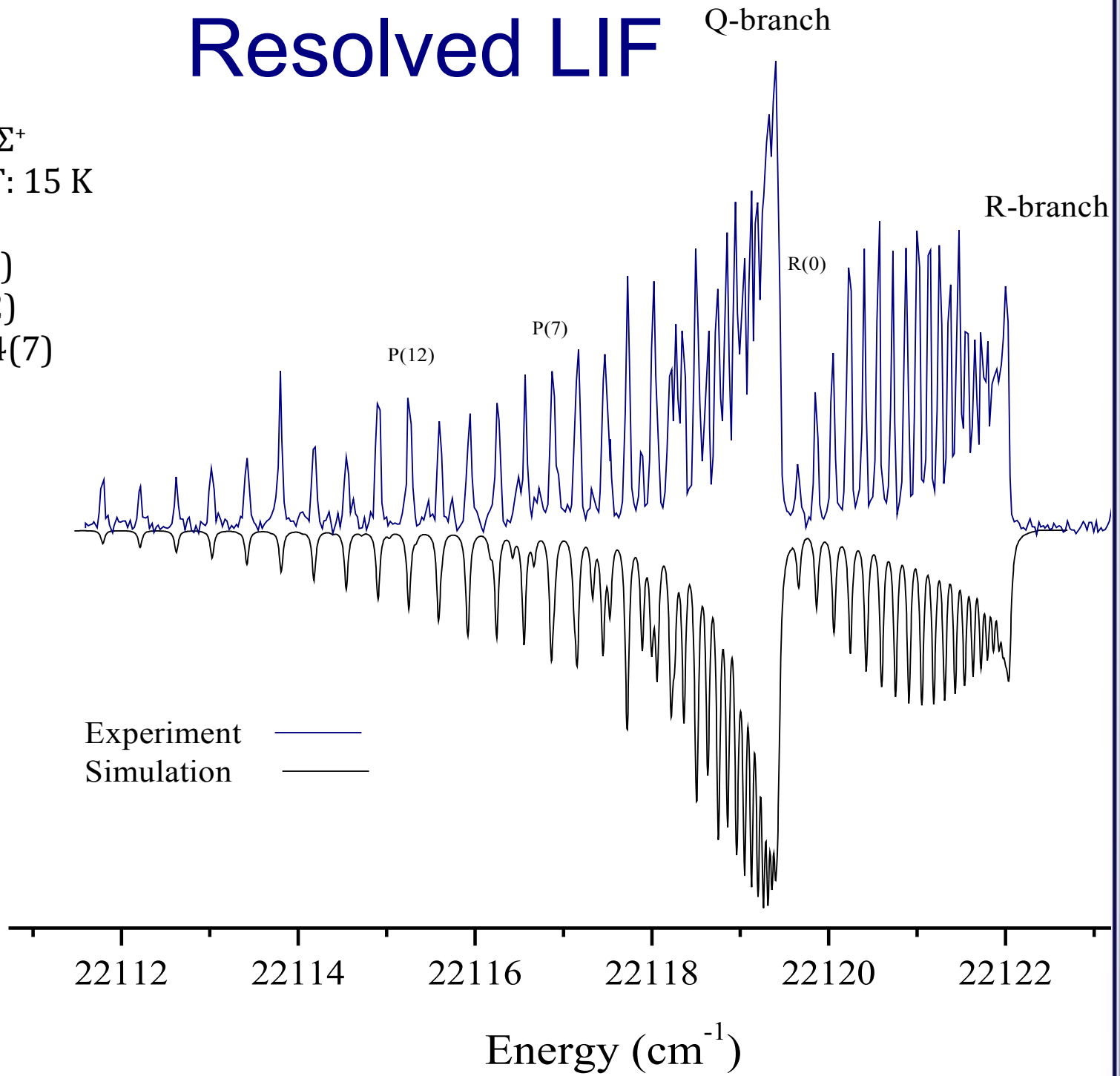


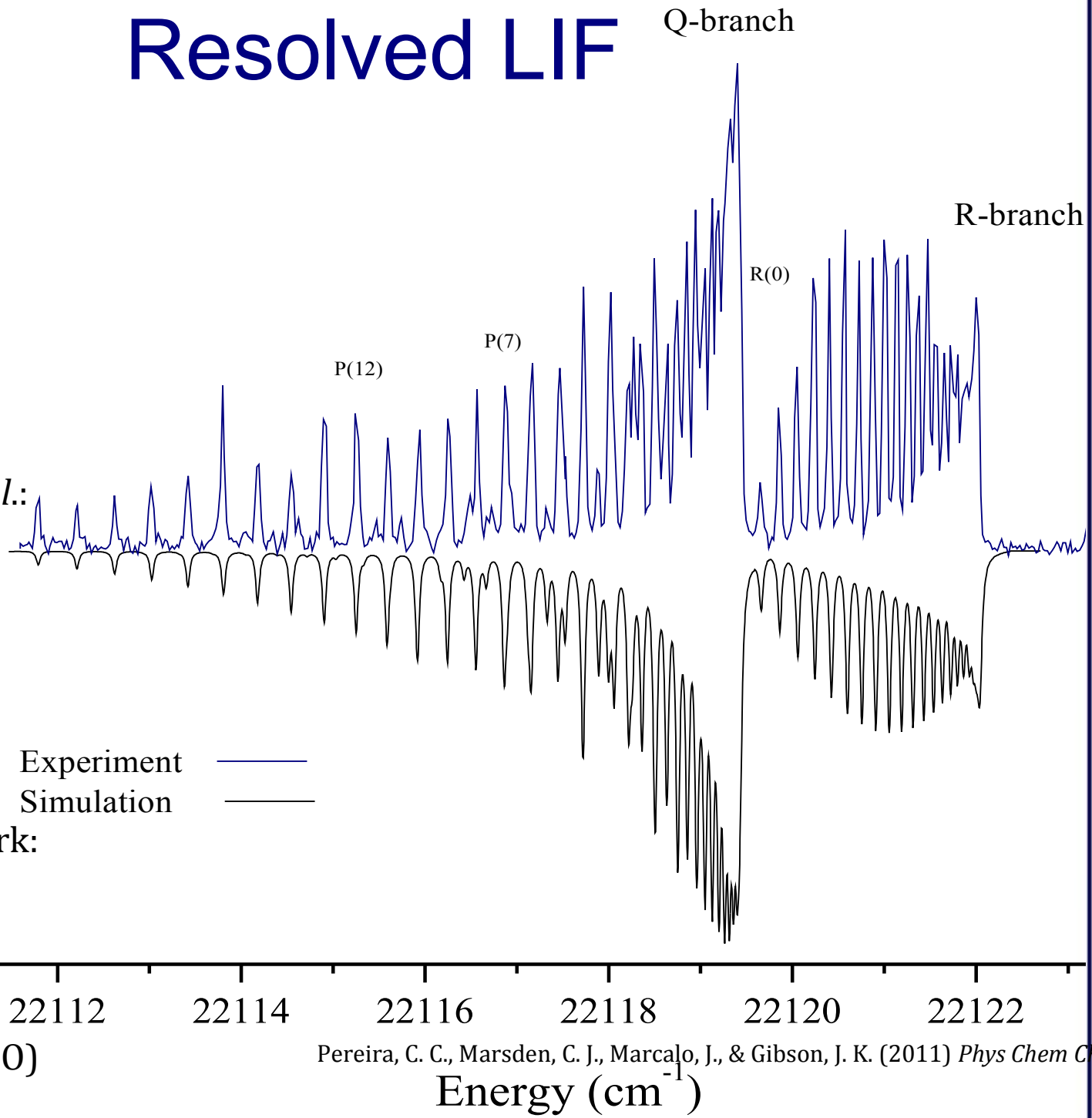
Resolved LIF

[22.13]1 - $X^1\Sigma^+$
Simulation T: 15 K

B'' = 0.111(2)
B' = 0.106(2)
q' = 0.00014(7)



Resolved LIF



B'' = 0.111(2)

From Pereira *et al.*:
B'' =
0.1123
(B3LYP)
0.1106
(MPW1PW91)

From current work:
B'' =
0.1115
(RCCSD(T))
0.1114
(CASSCF/MRCI/SO)

Pereira, C. C., Marsden, C. J., Marcalo, J., & Gibson, J. K. (2011) *Phys Chem Chem Phys, 13*(28)

Molecular Constants from LIF Data

State	Origin	B	q ($\cdot 10^{-3}$)
$X^1\Sigma^+$	0.0	0.111(2)	0
{18.26}1	18259.0(3)	0.104(2)	0
{18.53}1	18529.4(3)	0.106(2)	1.6(1)
{18.69}1	18689.5(3)	0.104(2)	1.9(2)
{21.54}1	21543.0(3)	0.103(2)	0.21(3)
{21.94}1	21938.8(3)	0.103(2)	0.8(3)
{22.02}1	22024.8(3)	*	*
[22.12]1	22117.5(3)	0.106(2)	0.14(7)
{23.15}1	23148.7(3)	*	*
{23.59}1	23585.9(3)	0.105(2)	0.8(4)

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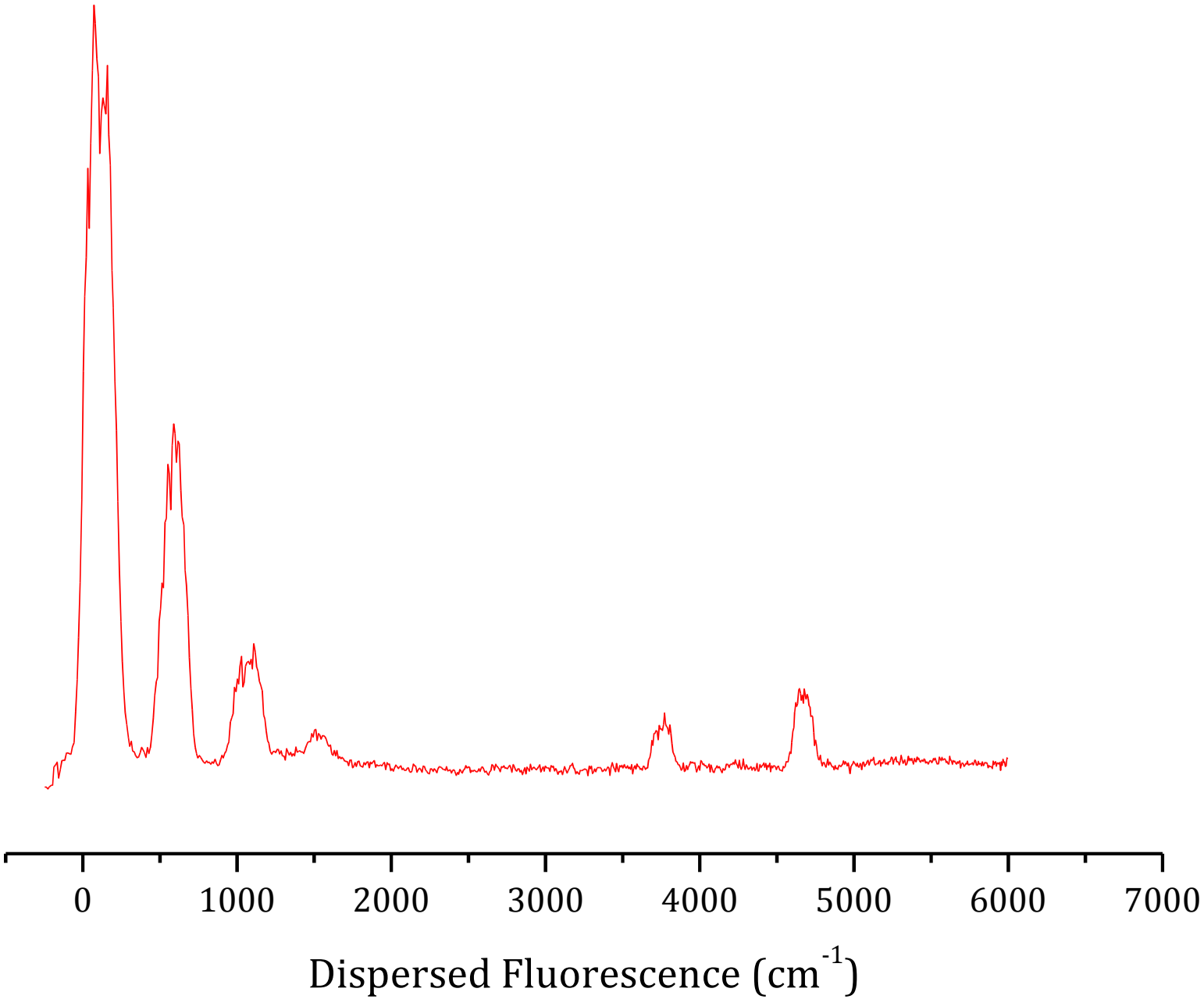
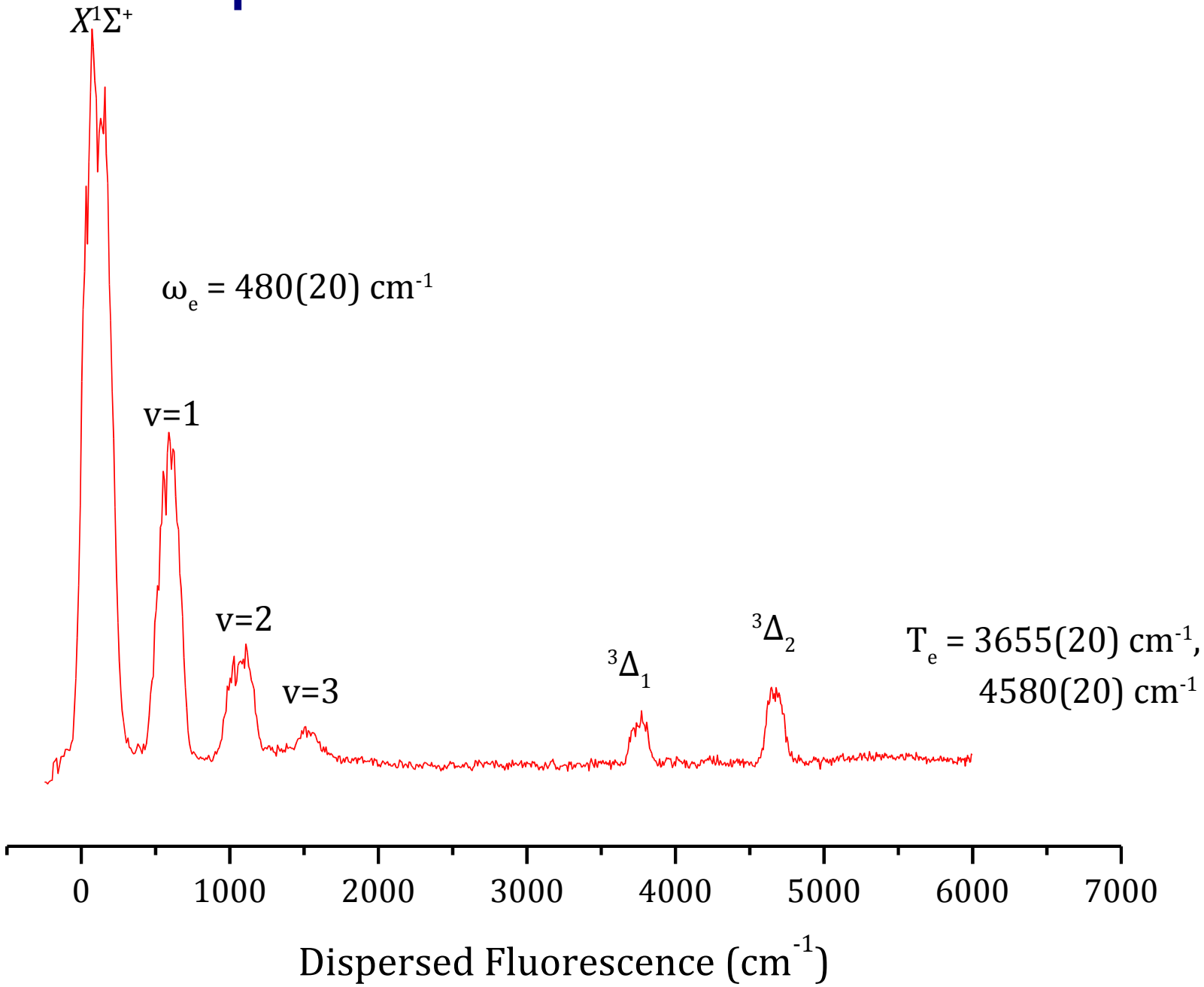
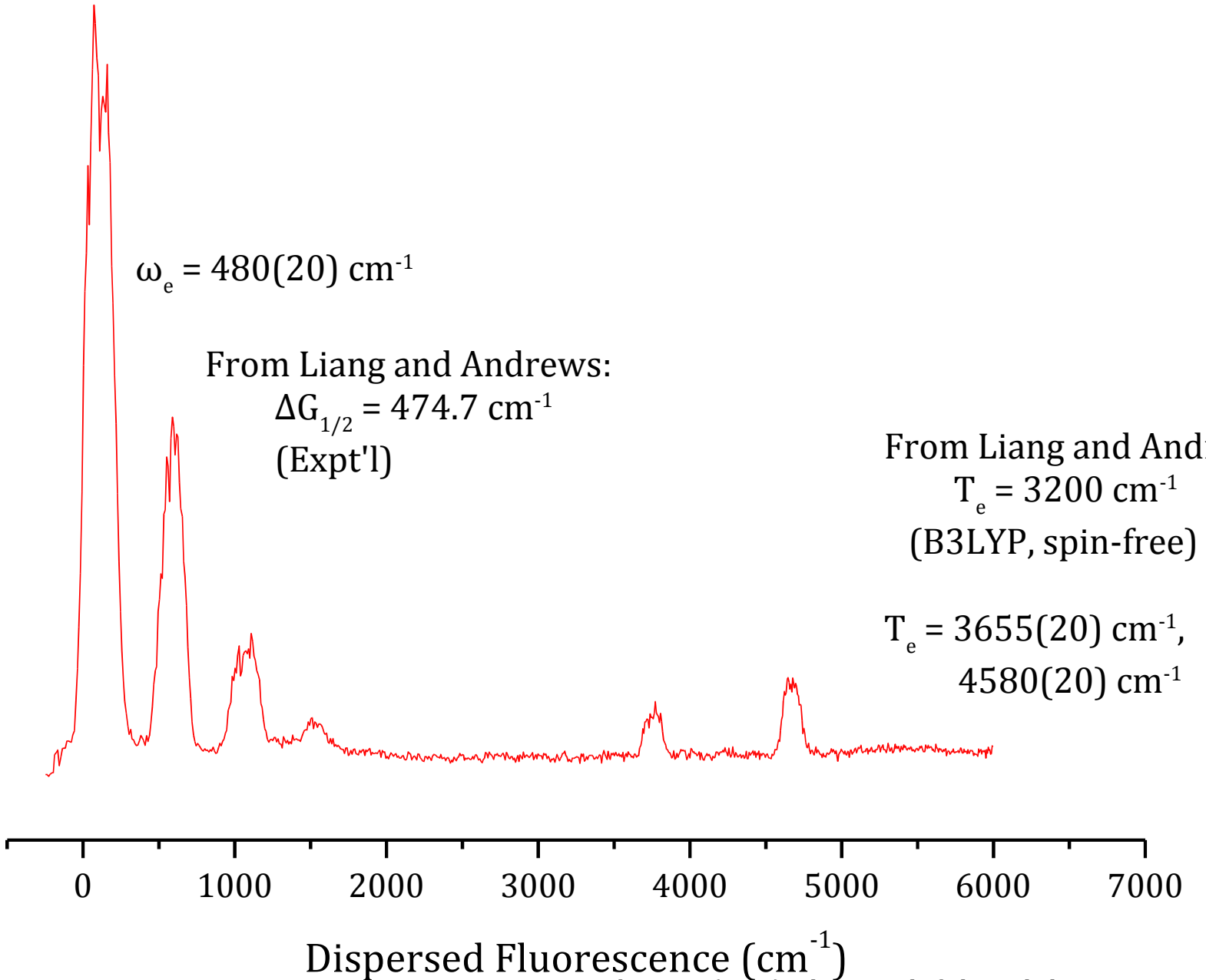
Dispersed Fluorescence



Dispersed Fluorescence

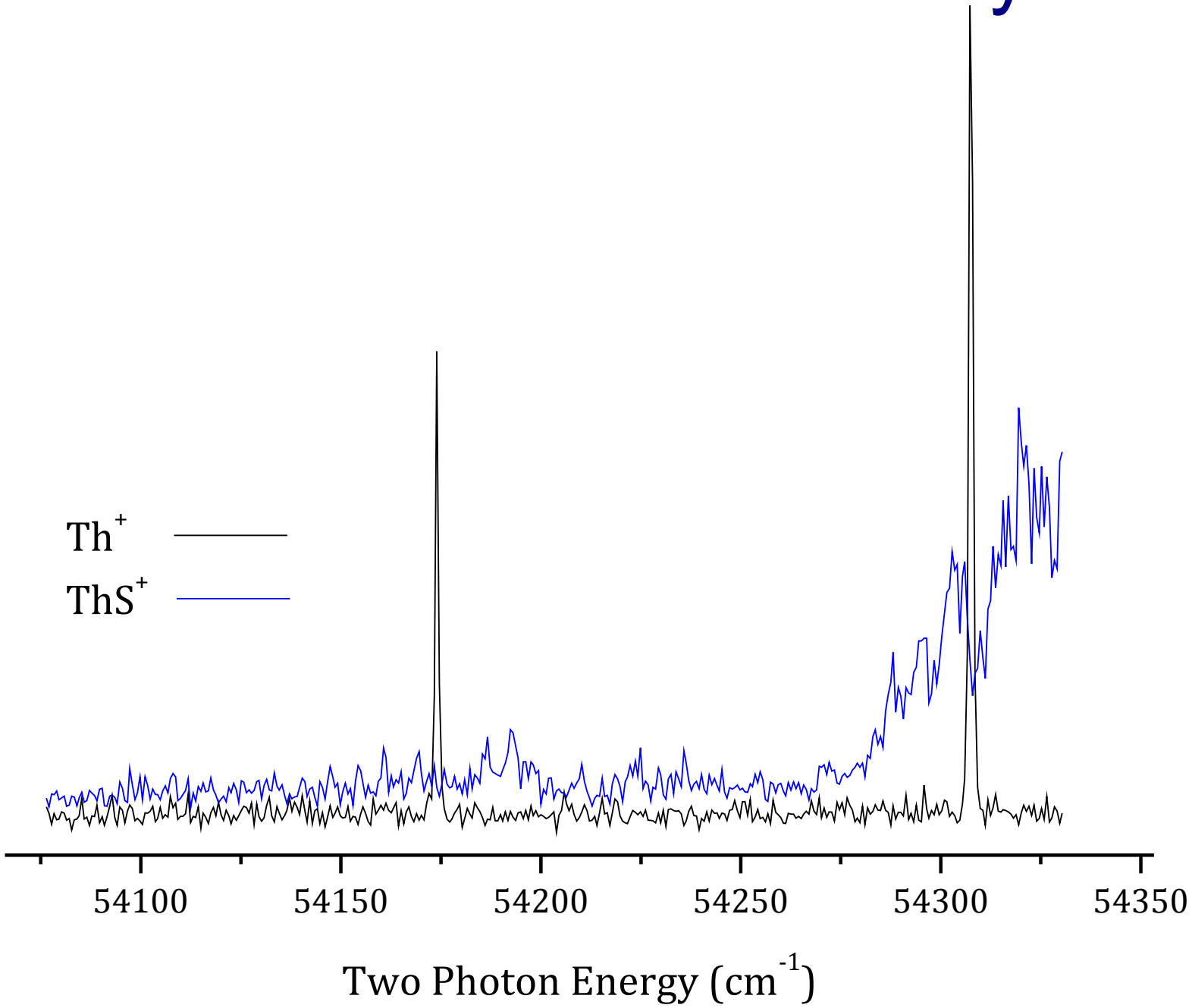


Dispersed Fluorescence



Liang, B., & Andrews, L. (2002) *The Journal of Physical Chemistry A, 106*(16)

Photoionization Efficiency



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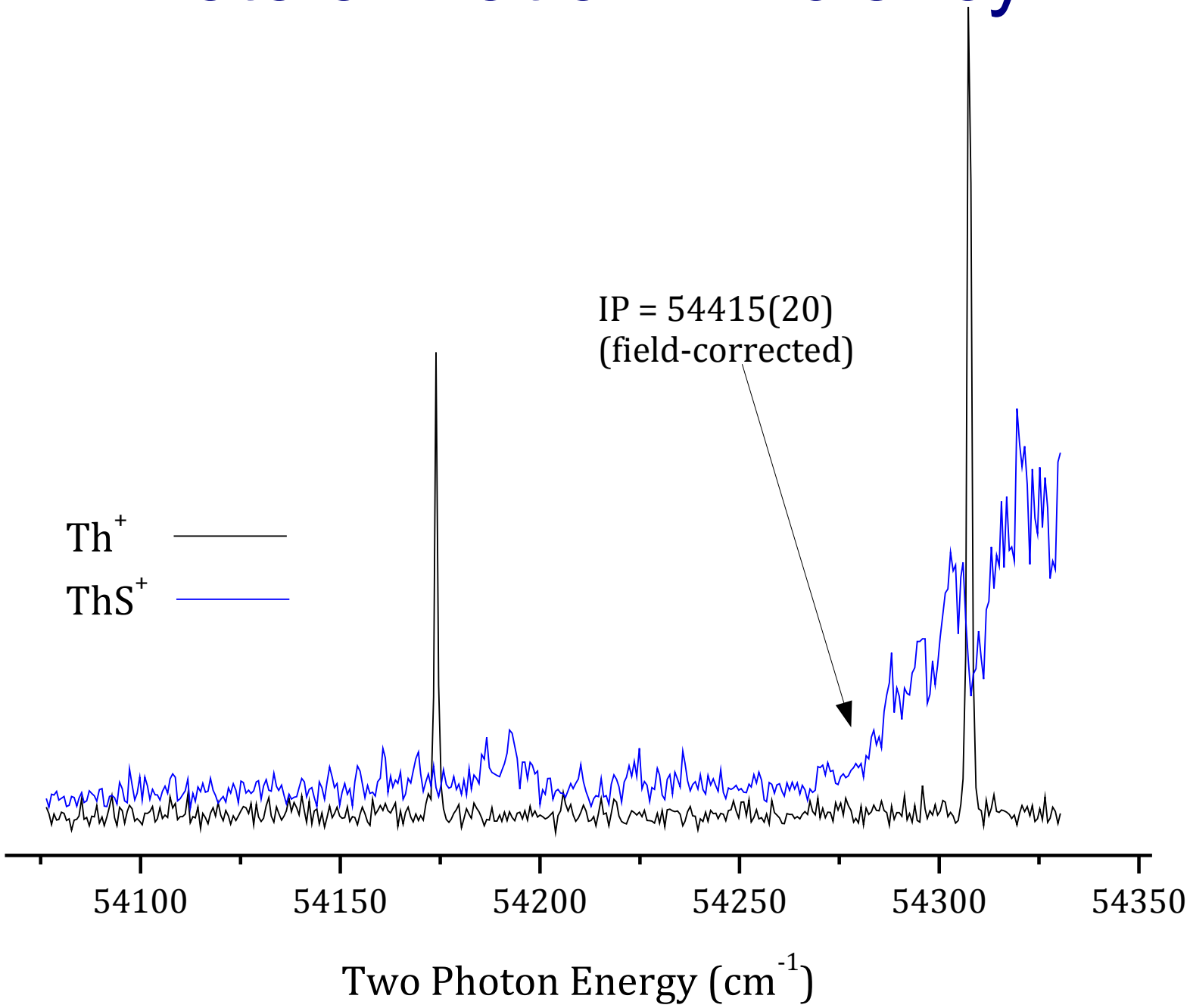
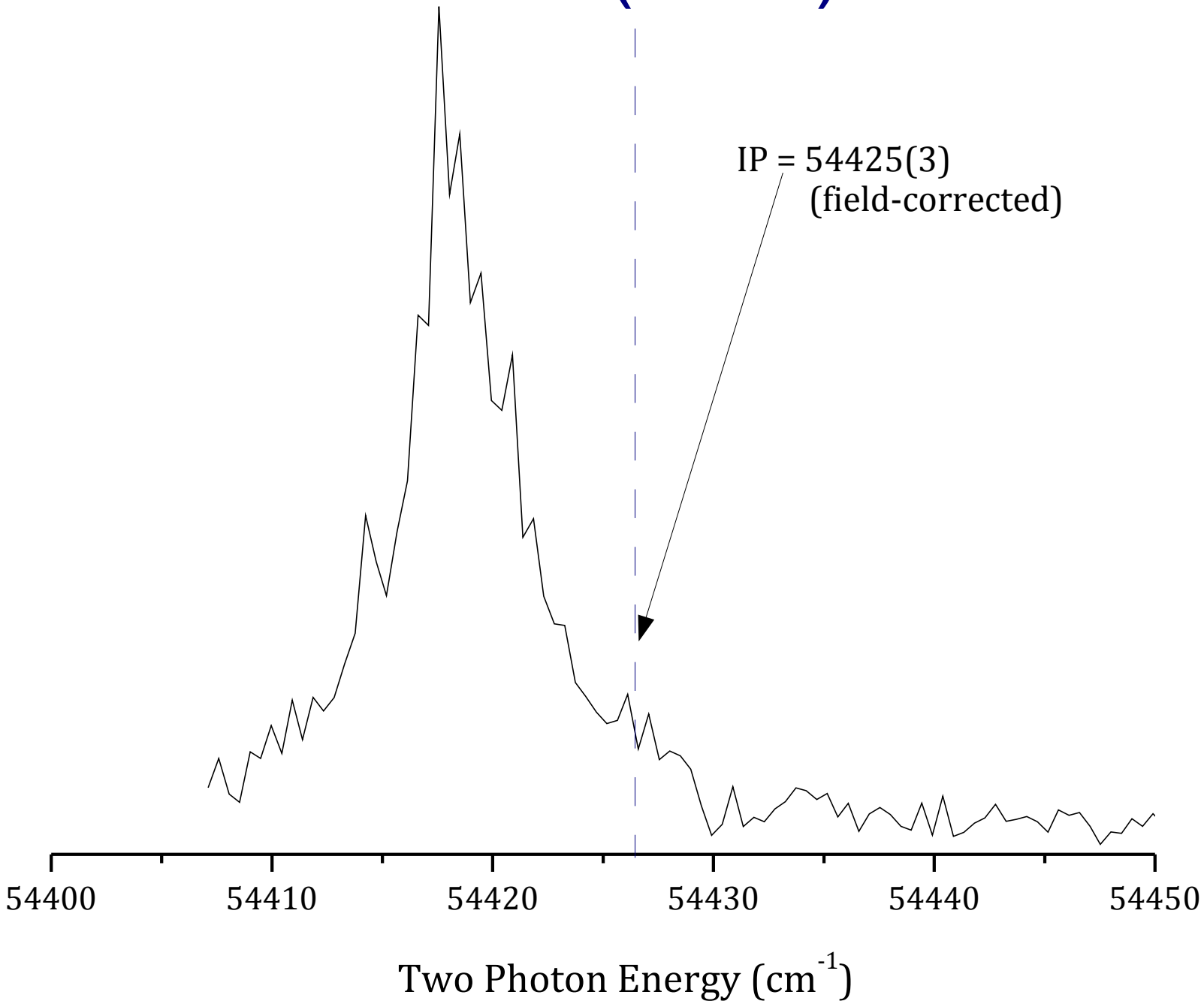


PFI-ZEKE (ThS^+)


IP = 54425(3)
(field-corrected)
54400
54410
54420
54430
54440
54450
Two Photon Energy (cm-1)

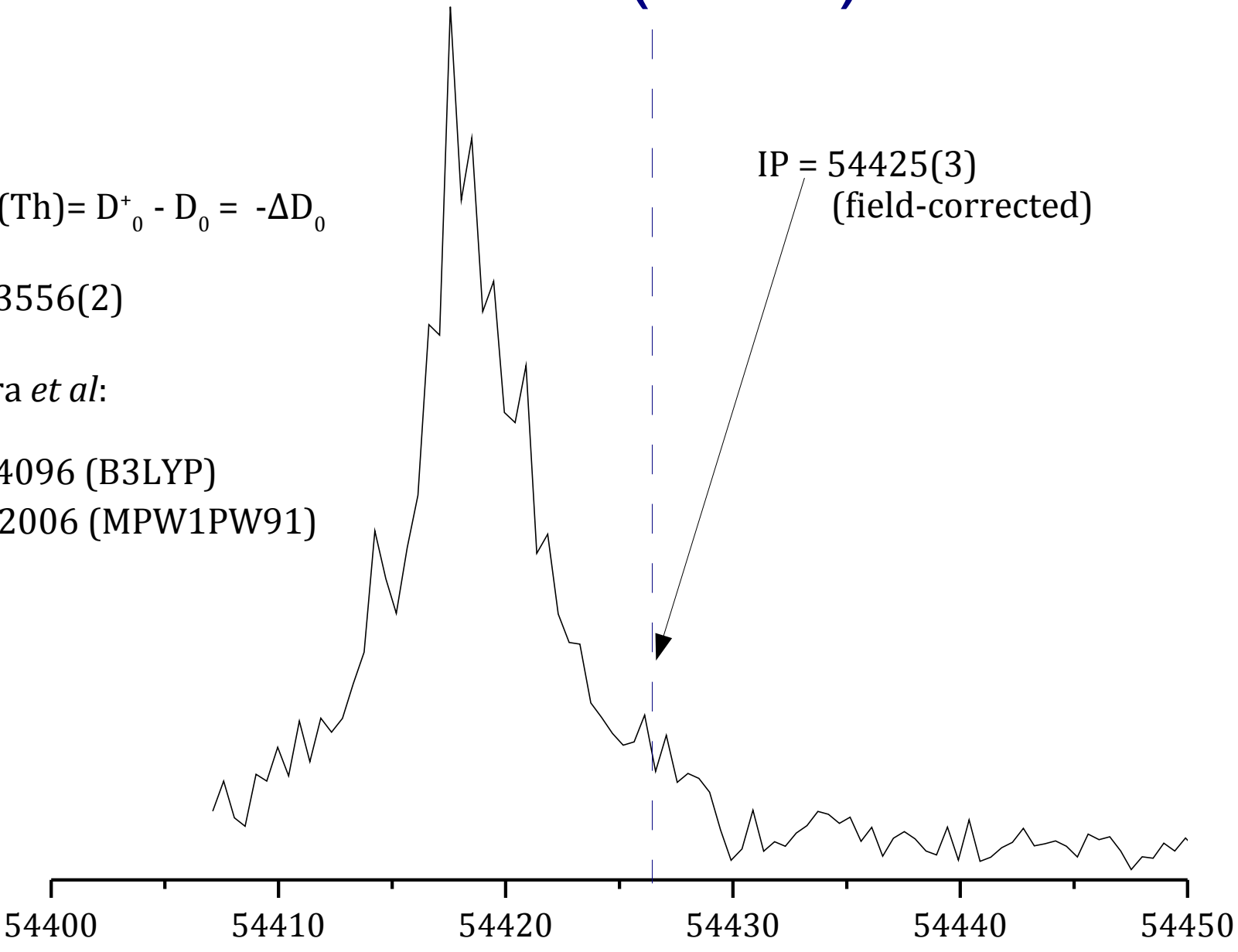
PFI-ZEKE (ThS^+)

IP(ThS) - IP(Th)= D^+_0 - D_0 = $-\Delta D_0$

ΔD_0 = -3556(2)

From Pereira *et al*:

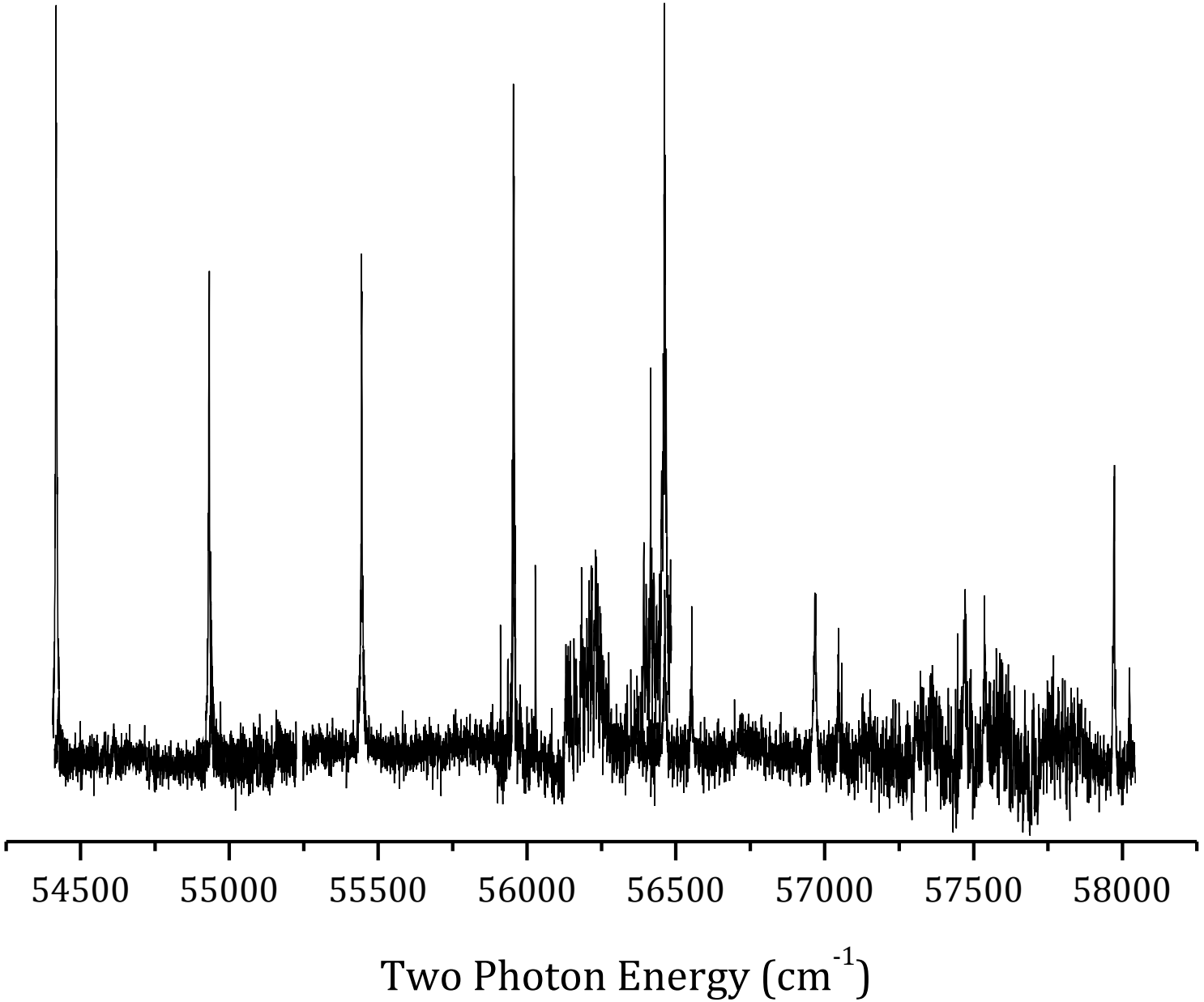
ΔD_0 = -4096 (B3LYP)
= -2006 (MPW1PW91)



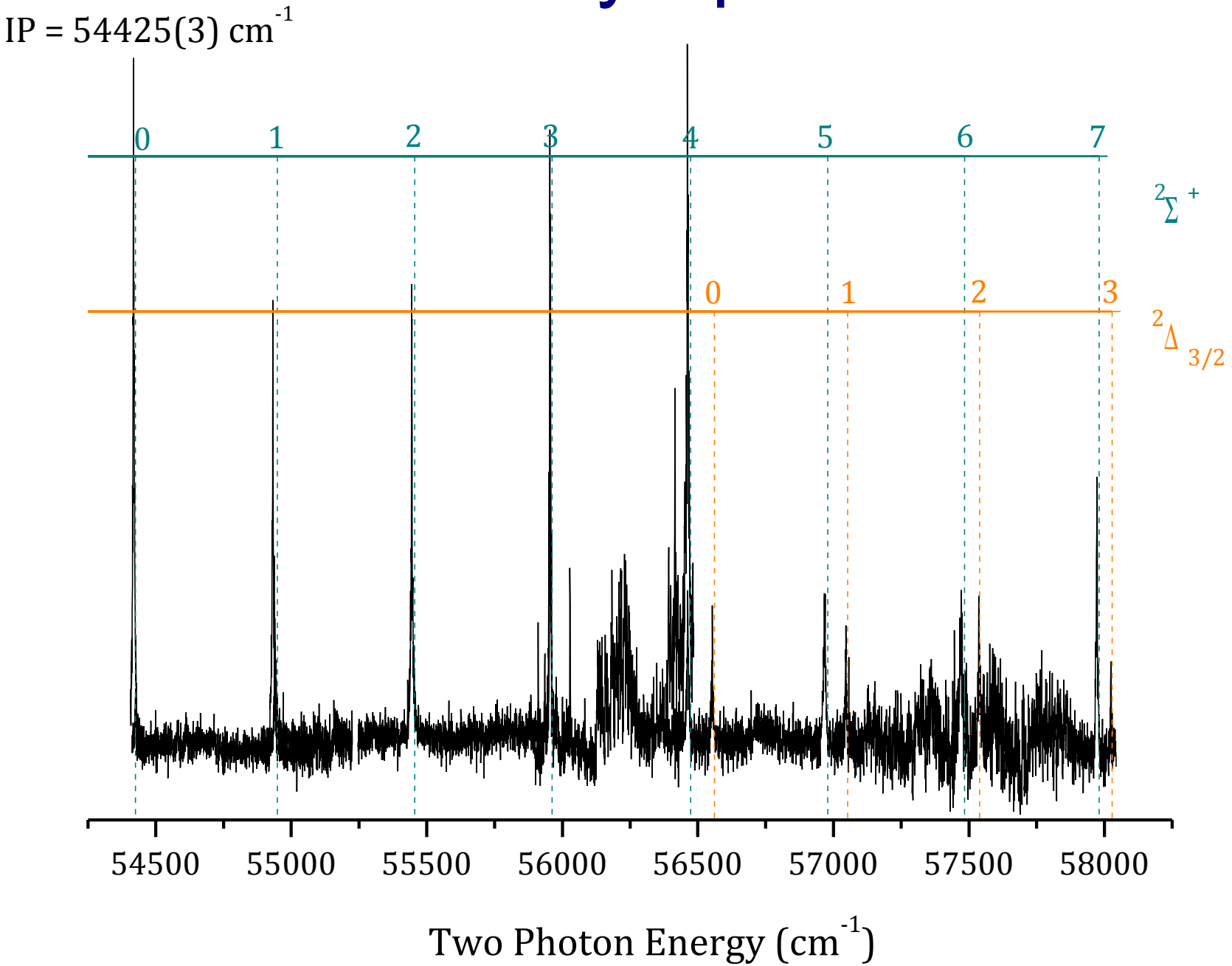
Pereira, C. C., Marsden, C. J., Marcalo, J., & Gibson, J. K. (2011) *Phys Chem Chem Phys, 13*(28)

ZEKE Survey Spectrum

IP = 54425(3) cm^{-1} (from {23.59}1 state)



ZEKE Survey Spectrum



ThS^+ State Energies

Vibronic state	T_e	State: ω_e, $\omega_e x_e$
$^2\Sigma^+_{v=0}$	0.0	$^2\Sigma^+$: 517(2), 1.2(3)
$^2\Sigma^+_{v=1}$	523(3)	
$^2\Sigma^+_{v=2}$	1030(3)	
$^2\Sigma^+_{v=3}$	1537(3)	
$^2\Sigma^+_{v=4}$	2048(3)	
$^2\Delta_{3/2,\,v=0}$	2136(3)	$^2\Delta_{3/2}$: 489(4), **
$^2\Sigma^+_{v=5}$	2554(3)	
$^2\Delta_{3/2,\,v=1}$	2627(3)	
$^2\Sigma^+_{v=6}$	3059(3)	
$^2\Delta_{3/2,\,v=2}$	3115(3)	
$^2\Sigma^+_{v=7}$	3556(3)	
$^2\Delta_{3/2,\,v=3}$	3603(3)	

Calculations

ThS					ThS$^+$				
State	T_e	ω_e	B_e	r_e (Å)	State	T_e	ω_e	B_e	r_e (Å)
$X^1\Sigma^+$	0 (0)	477 (479)	0.1074 (0.1079)	2.363 (2.358)	$X^2\Sigma^+$	IP= 53709 (53928)	502 (508)	0.1114 (0.1115)	2.321 (2.318)
$^3\Delta_1$	3940	454	0.1047	2.394	$^2\Delta_{3/2}$	2499	479	0.1084	2.353
$^3\Delta_2$	4856 (4923)	453 (457)	0.1048 (0.1052)	2.393 (2.388)	$^2\Delta_{5/2}$	4730	487	0.1087	2.350
$^3\Delta_3$	5811	455	0.1050	2.391	$^2\Pi_{1/2}$	8803	475	0.1063	2.375
					$^2\Pi_{3/2}$	10313	472	0.1063	2.375

CASSCF/MRCI/SO calculations using an ECP and basis sets for Th from Cao and Dolg[a]. Parenthesis indicate CCSD(T) (RCCSD(T) for the ion) method. For S, the aug-cc-pVTZ basis set was used.

[A] Cao, X., M. Dolg, H. Stoll, *J. Chem. Phys. 118, 487* (2003)

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$X^1\Sigma^+$	0 (0) 0	477 (479) 480(20)	0.1074 (0.1079) 0.111(2)	2.363 (2.358)	$X^2\Sigma^+$	IP= 53709 (53928) 54425(3)	502 (508) 517(2)	0.1114 (0.1115)	2.321 (2.318)
$^3\Delta_1$	3940 3655(20)	454	0.1047	2.394	$^2\Delta_{3/2}$	2499 2136(3)	479 489(4)	0.1084	2.353
$^3\Delta_2$	4856 (4923) 4580(20)	453 (457)	0.1048 (0.1052)	2.393 (2.388)	$^2\Delta_{5/2}$	4730	487	0.1087	2.350
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Experimental value.

[A] Cao, X., M. Dolg, H. Stoll, *J. Chem. Phys. 118, 487* (2003)

Properties

	IP	$^3\Delta_1$ $^2\Delta_{3/2}$	$^3\Delta_2$ $^2\Delta_{5/2}$	SO energy	B_e
[a]ThO	53254	5316.6	6127.9	811.3	0.3326(6)
[a]ThO$^+$	-	2933.7	5814.4	2880	0.3450(6)
ThS	54425(3)	3655(20)	4580(20)	925(28)	0.111(2) [0.1074]
ThS$^+$	-	2136(3)	[4730]	2594	[0.1114]

Brackets denote calculated values.

a. Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006) *J Chem Phys, 125(13)*

Properties

	IP	ω_e	$(\omega_e^+/\omega_e)^2$	ΔD_0	B_e
[a]ThO	53254	895.77	1.137	-2385.09	0.3326(6)
[a]ThO$^+$	-	954.97	-	-	0.3450(6)
ThS	54425(3)	480(20)	1.16(10)	-3556(2)	0.111(2) [0.1074]
ThS$^+$	-	517(2)	-	-	[0.1114]

Brackets denote calculated values.

a. Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006) *J Chem Phys, 125(13)*

Properties

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[a]ThO$^+$		954.97			0.3450(6)
ThS	54425(3)	480(20)	1.16(10)	-3556(2)	0.111(2) [0.1074]
ThS$^+$		517(2)			[0.1114]
[b,c]HfO	63760	974.09	1.081	-8807.77	0.386537(7)
[c]HfO$^+$		1013			0.403(5)
[d]HfS	61933	526.848	1.109	-6685.71	0.13336(4)
[d]HfS$^+$		554.9			0.130(8)

a. Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006) *J Chem Phys, 125(13)* b. Jonsson, J., Edvinsson, G., and Taklif, A. G. (1995) *J Mol Spec, 172*
c. Merritt, J. M., Bondybey, V. E., Heaven, M. C. (2009) *J Chem Phys, 130* d. Barker, B. J., Antonov, I. O., & Heaven, M. C. (2012) *J Mol Spec, 275*

Conclusions

Electronic spectra have revealed rotational and vibrational parameters for ThS as well as state energies for the lowest electronic level of the neutral molecule. Ionization spectra confirm theoretical predictions, and two vibronic progressions of the cation have been characterized. Rotational structure for the ion could not be obtained.

Results from previous works concerning the molecule are validated, especially with regard to QR-DFT studies. Calculations illustrate very good agreement between theory and experiment.

ThS properties are consistent with other heavy diatomic molecules, indicating only minor changes in bonding character moving from 2^{nd} to 3^{rd} row monatomic ligands for Th.

Acknowledgments

Dr. Ivan Antonov, for substantial calculation and experimental assistance

Dr. Michael Heaven & the Heaven group for moral and technical support:

Michael Sullivan, Kyle Mascaritolo, Dr. Jiande Han,

Dr. Keith Freel

U.S. Department of Energy grant, DE-FG02-01ER15153

Cherry Emerson Center for Scientific Computing

Parameters

	$^3\Delta_1$ $^2\Delta_{3/2}$	$^3\Delta_2$ $^2\Delta_{5/2}$	SO energy	r_e (Å)
[a] HfO	9230.77	10152.31	921.54	1.285
HfO^+	[8175]			
[b] HfS	6631.2	7596.6	965.4	2.191
[b] HfS^+	5187(3)	7986(3)	2754	2.215
[c] ThO	5316.6	6127.9	811.3	1.881
ThO^+	2933.7	5814.4	2880	1.360
ThS	3655(20)	4580(20)	925	2.363
ThS^+	2136(3)	[4730]	2594	2.321

a. Jonsson, J., Edvinsson, G., and Taklif, A. G. (1995) *Journal of Molecular Spectroscopy, 172*
b. Barker, B. J., Antonov, I. O., & Heaven, M. C. (2012) *Journal of Molecular Spectroscopy, 275*
c. Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006) *J Chem Phys, 125(13)*

ThS^+, ThO^+, HfS^+

State	v	T_e (cm^{-1})		
		ThO^+	HfS^+	ThS^+
$^2\Sigma^+$	0	(IP=53254)	(IP=61933)	(IP=54428)
	1	950	552	511
	2	1895	1101	1022
	3	-	1648	1534
	4	-	2191	2039
	5	-	2732	2546
	6	5627	3270	3049
	7	6547	3805	3551
$^2\Delta_{3/2}$	0	2934	5265	2132
	1	3846	5791	2626
	2	-	6313	3115
	3	5657	6832	3682

Goncharov, V., Kaledin, L. A., & Heaven, M. C. (2006). *J Chem Phys, 125*(13)
Barker, B. J., Antonov, I. O., & Heaven, M. C. (2012) *Journal of Molecular Spectroscopy, 275*