The PFI-ZEKE spectroscopy study of HfS^+ and the ionization energy of HfS

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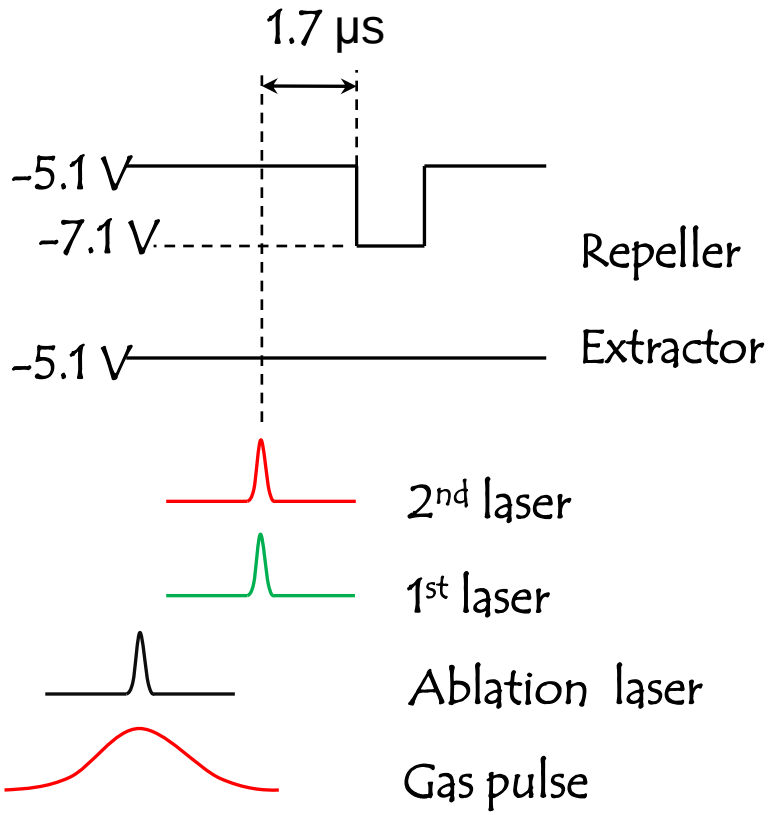
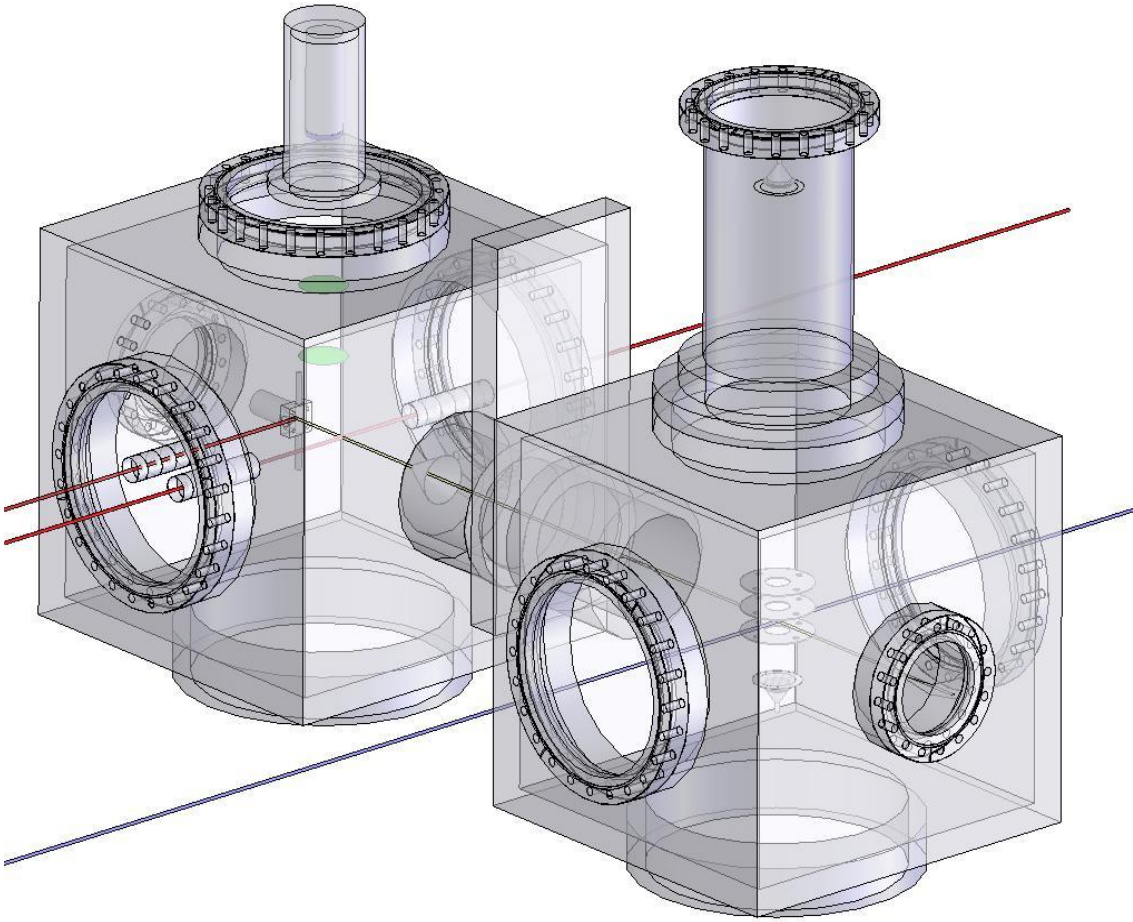
Why HfS and HfS^+?

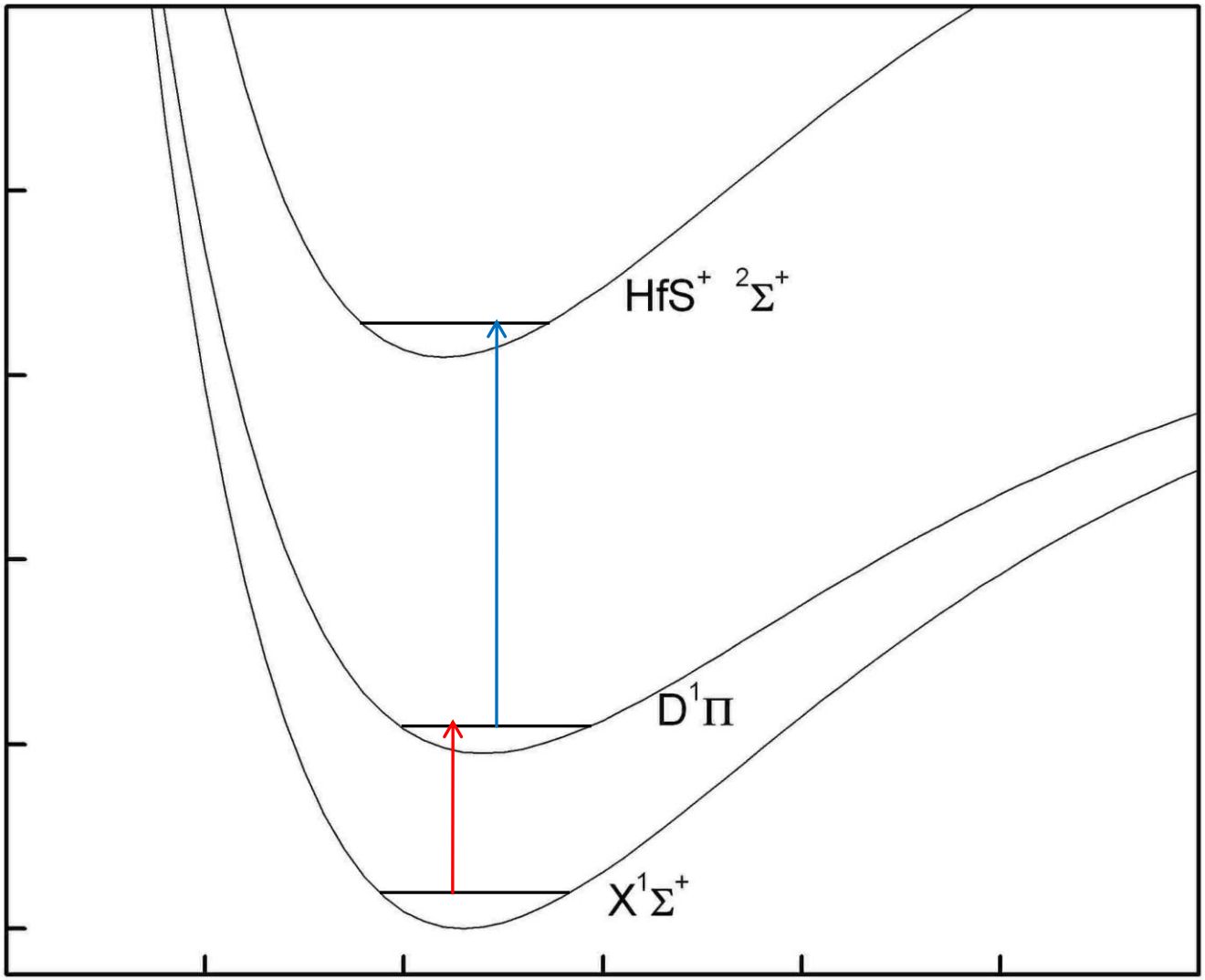
- MeS (Me=Ti, Zr) were found in cold star spectra
- Hf compounds are isoelectronic to Th compounds
- In ThO and HfO bond shortens and weakens when ionized. How does change of ligand affect that?

Experimental setup





Excitation scheme for HfS PFI-ZEKE



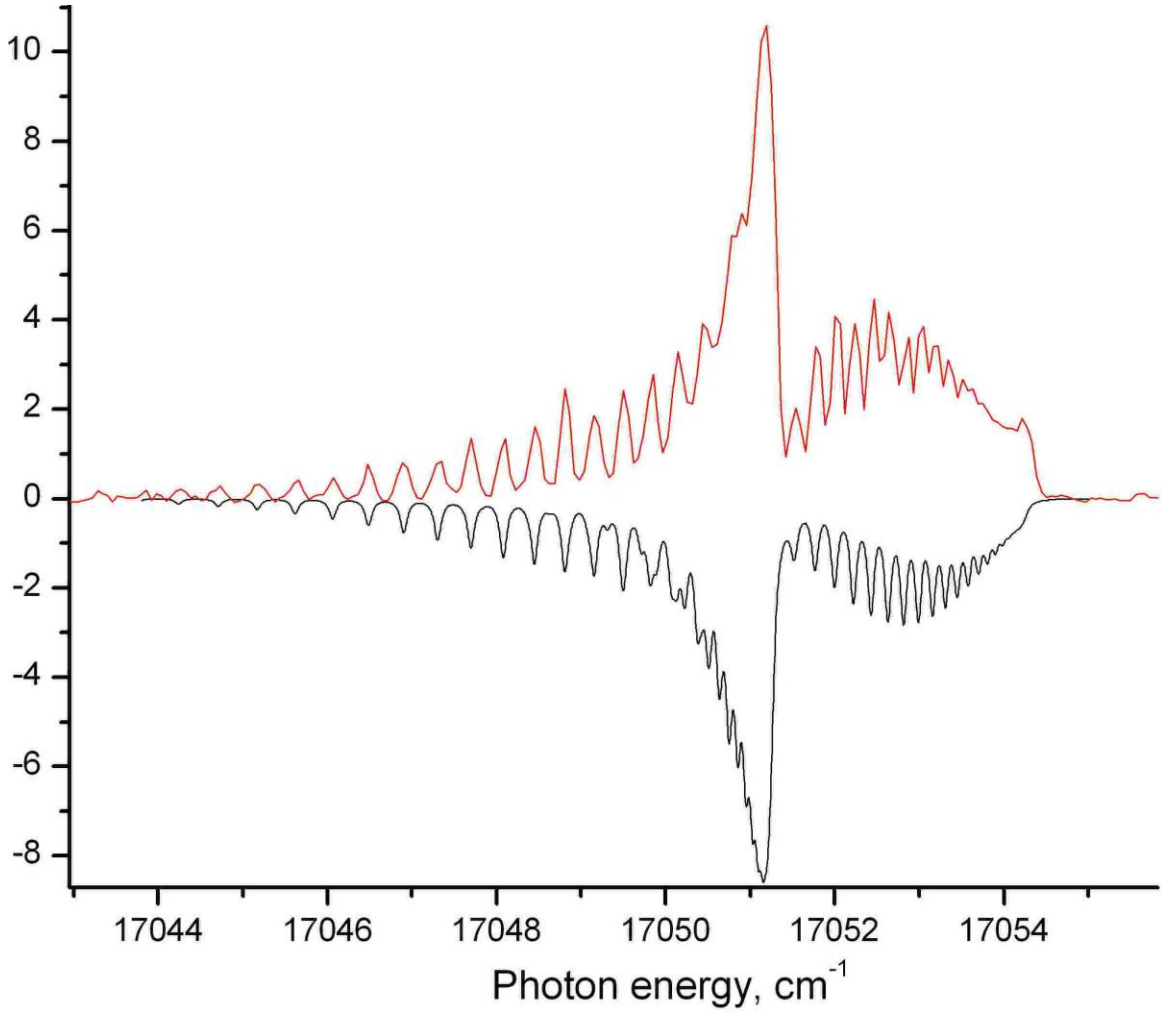
LIF of (0,0) band of $D^1\Pi - X^1\Sigma^+$

T_{rot}=15K

Experimental data

Simulation

Molecular constants from
Jonsson, J., Edvinson, G. and
Taklif, A.G., *Phys. Scr.*, **50**, 661 (1994)



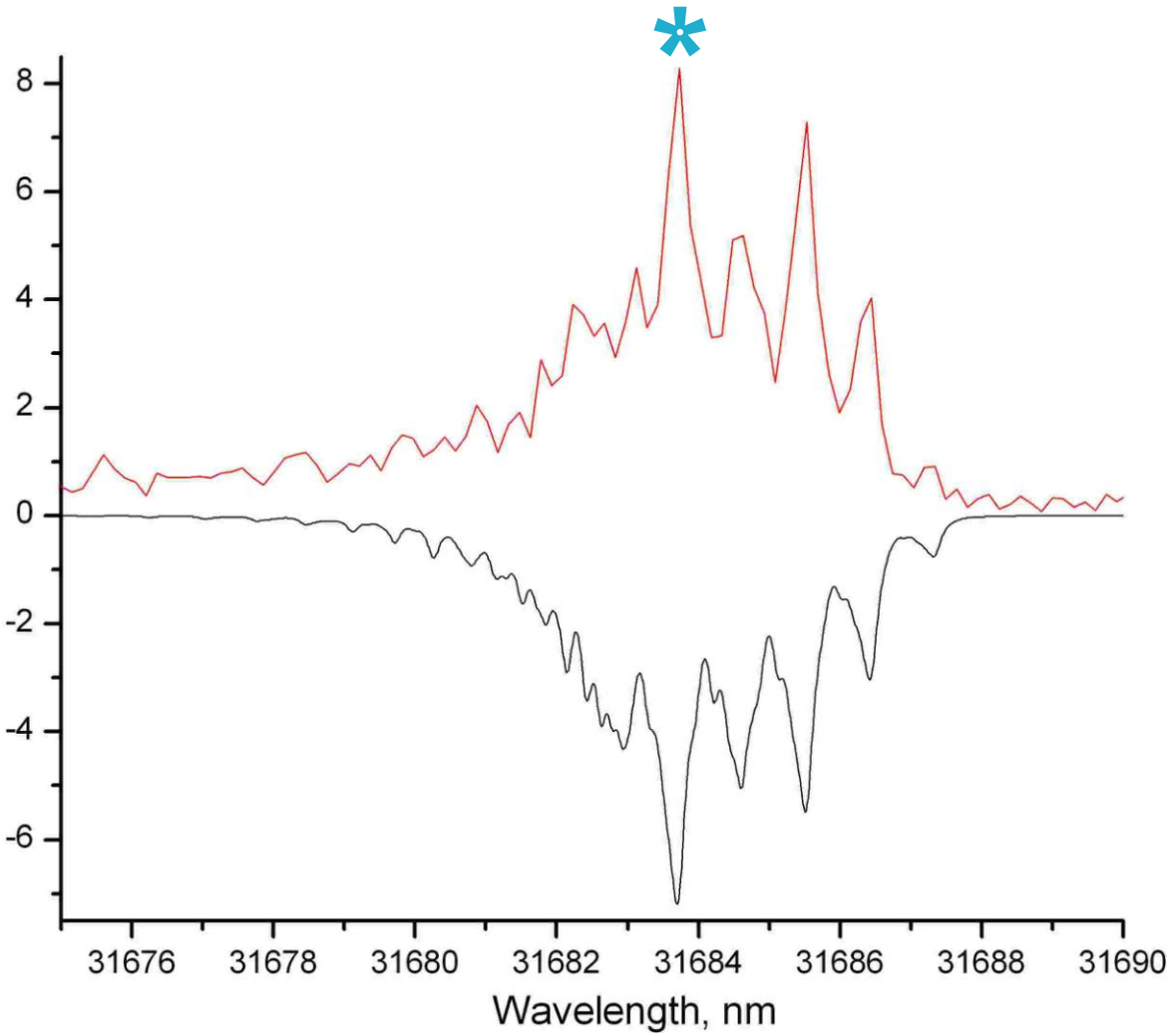
LIF of the (4–0) [31.6] $^1\Pi$–$X^1\Sigma^+$ transition

Hf isotope ratio:

^{176}Hf = 5.206%
^{177}Hf = 18.606%
^{178}Hf = 27.297%
^{179}Hf = 13.629%
^{180}Hf = 35.100%

Isotope shift

$\Delta E=(1-\rho)\upsilon\Delta G_{\upsilon+1/2}$

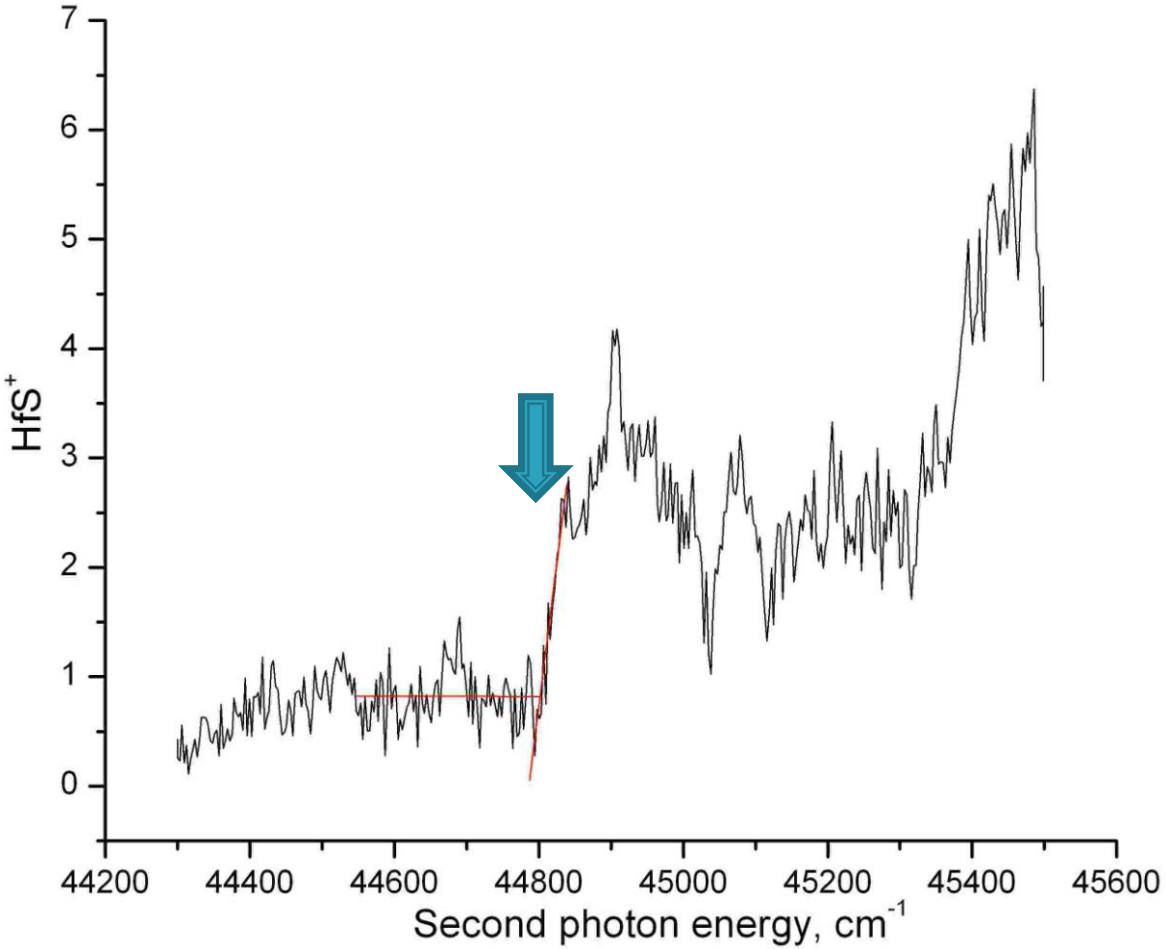


PIE spectrum of HfS

Pump laser tuned to bandhead of 0–0 $D^1\Pi$–$X^1\Sigma^+$ transition at 586.225 nm

$\Delta E = 6*(F(V/cm))^{1/2} \approx 100\ cm^{-1}$

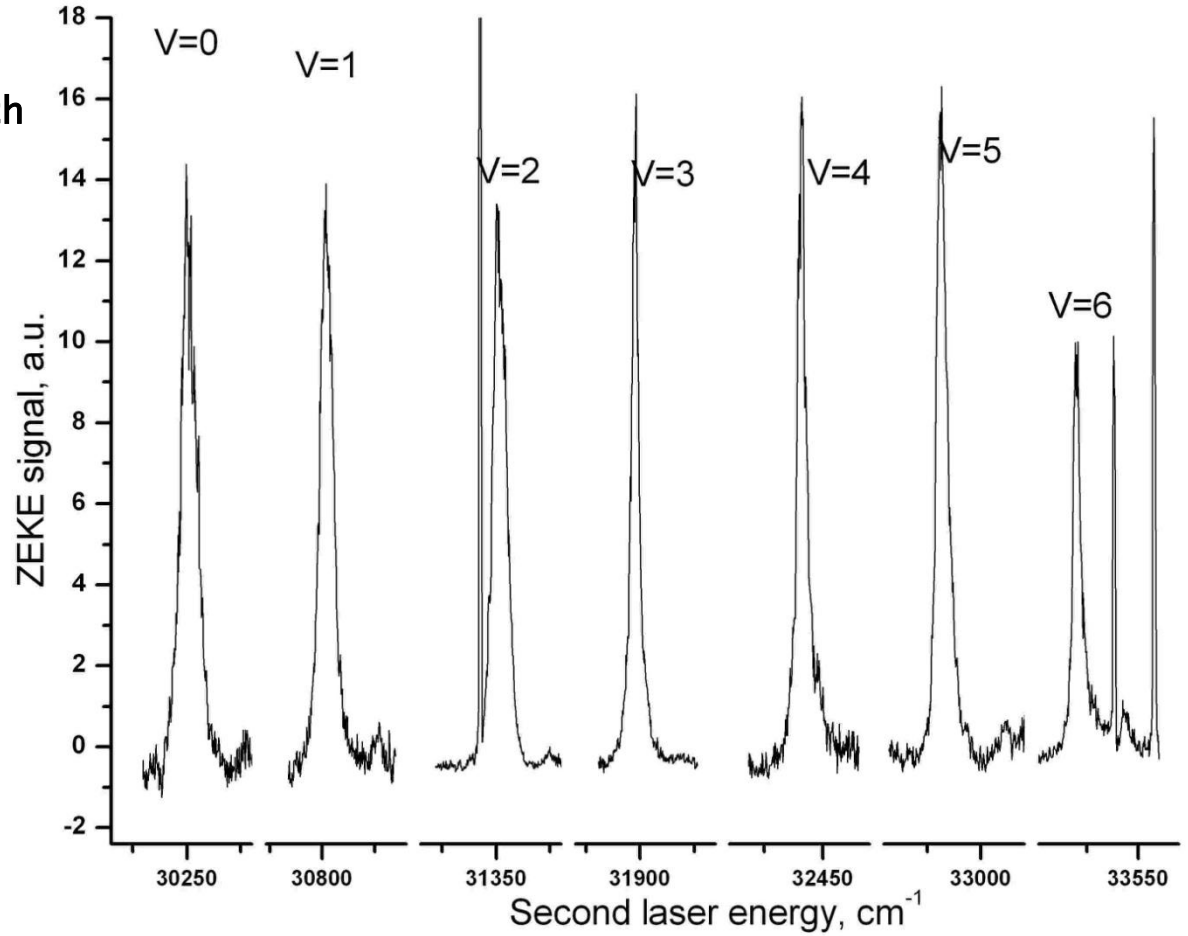
$IP = 61930(40)\ cm^{-1}$



PFI–ZEKE of HfS^+ ($X^2\Sigma^+$) v=0–6

Pump laser tuned to Q-branch of $[31.6]^1\Pi$–$X^1\Sigma^+$ of ^{180}Hf at 31683.7 cm^{-1}

Transitions to v=0–18 of $X^2\Sigma^+$, v=0–8 of $^2\Delta_{3/2}$ and v=0–2 of $^2\Delta_{5/2}$ states were observed



Rotationally resolved PFI-ZEKE of HfS^+ ($X^2\Sigma^+$) at v=0

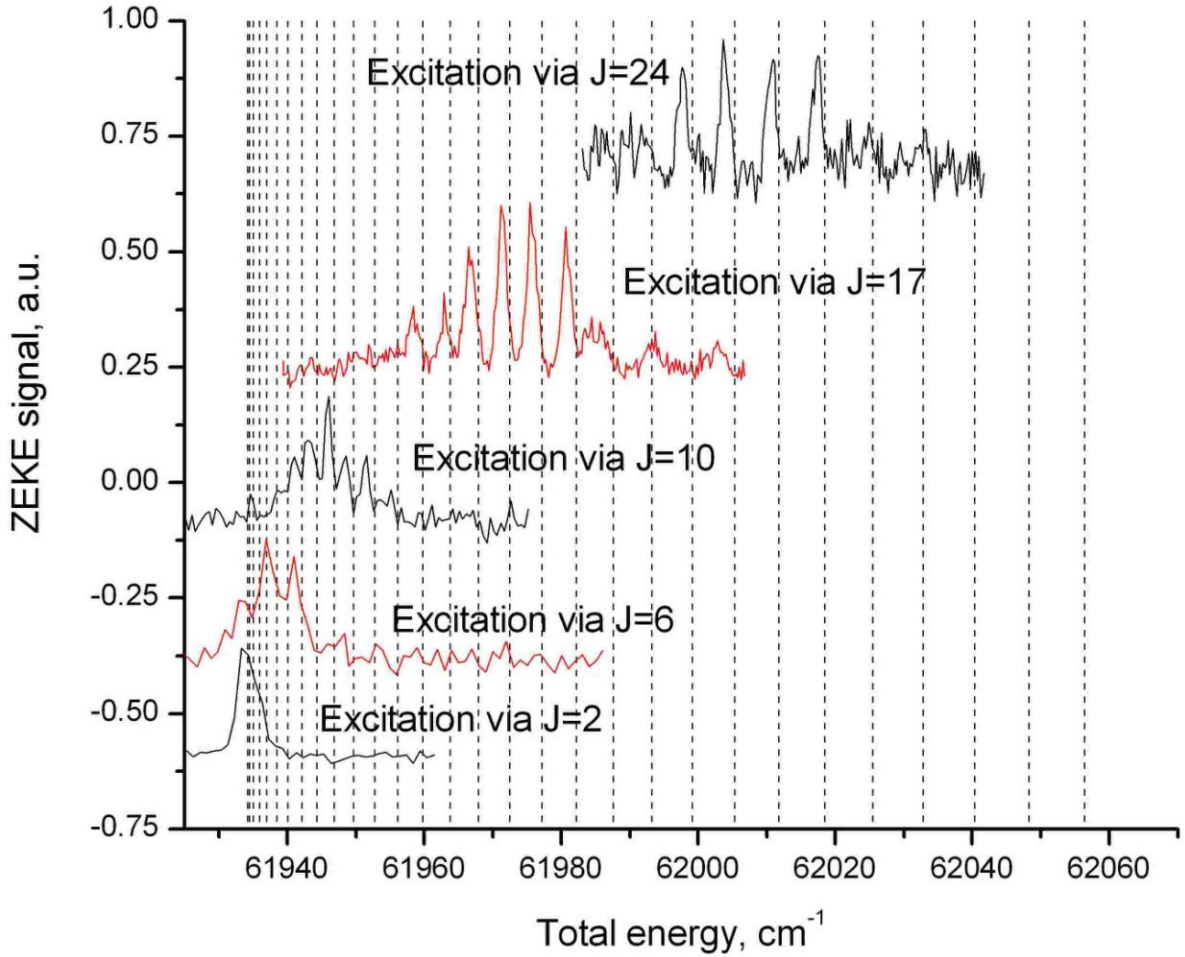
Pump laser tuned to P-lines of $D^1\Pi$-$X^1\Sigma^+$

$\Delta J \leq 0$ propensity observed

Accurate IP=61933(2) cm^{-1} determined from excitation via J=2 curve

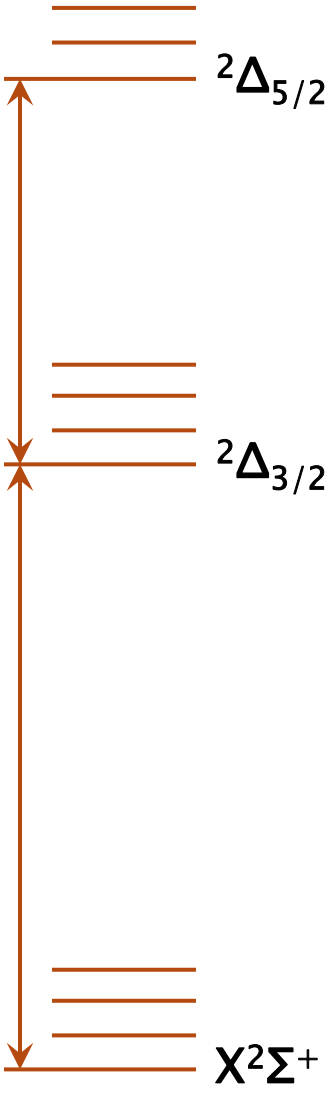
B^+=0.139(4) cm^{-1}

No rotational data for v≥0 and for electronically excited states



Molecular constants of HfS^+ $X^2\Sigma^+$, $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ states

	HfS $^1\Sigma^+$	HfS+ $^2\Sigma^+$	HfS+ $^2\Delta_{3/2}$	HfS+ $^2\Delta_{5/2}$
V observed	-	0-18	0-8	0-2
T_0 (IP for HfS), cm^{-1}	61933(2)	0	5267(2)	8017(2)
ω_e, cm^{-1}	526.8480(12)	555.0(1)	529.4(2)	528.5(6)
$\omega_e\chi_e$, cm^{-1}	1.23453(21)	1.414(2)	1.579(4)	1.0(6)
B_0, cm^{-1}	0.13336(4)	0.139(4)	-	-
r_0, Å	2.1567(7)	2.10(1)	-	-



Comparison of HfS/HfS^+, HfO/HfO^+ and ThO/ThO^+ properties

	HfS/HfS^+	HfO/HfO^+	ThO/ThO^+
ΔD_0	- 0.8537 eV	- 1.092 eV	- 0.3 eV
$(\omega_e^+/\omega_e)^2$	1.110	1.092	1.137
Δr_0	- 0.05 Å	- 0.038 Å	- 0.033 Å

Conclusions

- PFI-ZEKE method was used to study the HfS^+
- Spectra were recorded and molecular constants measured for $X^2\Sigma^+$, $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ states of HfS^+
- IP(HfS)=61933(2) cm^{-1}
- $\Delta J \leq 0$ propensity in rotational PFI-ZEKE observed
- Hf-S bond becomes shorter and weaker after ionization. Same behavior was found before for Hf-O and Th-O bond.