MCDHF calculations of the first and the second ionization potential of thorium

Maxime Brasseur

CompAs workshop Lisbon

UMONS
University of Mons

Faculty
of Science

Table of contents

Interest of Thorium

- Measure two first ionization potentials (IP) in Thorium 232 with a in-gas laser ionization technique at KUL
- Thorium (229) used for nuclear clock
- First ionization potential :
  - Measure first ionization potential : 50 868.41(2) cm^{-1} (50 868.139 cm^{-1} NIST)
  - Calculations with different approaches, Weigand. A. et al. (2014) : 50 572.127 cm^{-1}, 50814.099 cm^{-1} and 50491.47 cm^{-1}
- Second ionization potential :
  - Measure second ionization potential : 95 982-99 208 cm^{-1} (97 593,1 cm^{-1} NIST)
  - Weigand. A. et al. (2014) : 100 093,4-100 819,3 cm^{-1}

General procedure

- $H_{DC} = \sum_{i=1}^{N} h_{D_i}$ with $h_{D_i} = c\vec{\alpha} \cdot \vec{p_i} + (\beta - 1)c^2 + V(r_i)$ ($\alpha^j = \gamma^0\gamma^j$ and $\beta = \gamma^0$)

- Each electron: $h_D\varphi = E\varphi \rightarrow \varphi(r,\theta,\phi) = \frac{1}{r}\begin{pmatrix} P_{n,\kappa}(r)\chi_{\kappa,m}(\theta,\phi) \\ iQ_{n,\kappa}(r)\chi_{\kappa,m}(\theta,\phi) \end{pmatrix}$ where $P_{n,\kappa}(r)$ and $Q_{n,\kappa}(r)$ are large and small radial part, respectively.

- $P_{n,\kappa}(r)$, $Q_{n,\kappa}(r)$? → solve MCDHF equations (Self-Consistent Field method)

- CI: $\Psi(P,J,M) = \sum_{r=1}^{n_c} c_r\,\Phi(\gamma_r,P,J,M)$

Active set (AS) approach

1. Optimisation step (solving MCDHF equations):
    - Reference CSFs (single or multi-reference) build by angular coupling of spectroscopic orbitals
    - Consider layers of correlation orbitals and allow one or more excitations from spectroscopic orbitals to the orbitals in the AS
    - Optimise orbitals that are not yet optimised
2. Configuration interaction step:
    - No longer solve MCDHF equations, consider more layers of correlation orbitals with the Relativistic Configuration Interaction program

Model A

Th I :

Optimisation:

- MR : $6d^2 7s^2, 6d^3 7s, 6d^4$ ⇒ 21 CSFs;
- VV1: SD {MR} → {7s,6p,6d,5f,5g} ⇒ 291 CSFs;
- VV2: SD {MR} → {7s, 6(p-g)} ⇒ 971 CSFs;
- VV3: SD {MR} → {7(s-g)} ⇒ 3102 CSFs;
- VV4: SD {MR} → {8(s-g)} ⇒ 6730 CSFs

RCI:

- CV: S {6s,6p}→ MR ⇒ 6756 CSFs;
- CC: SD {6s,6p}→ MR ⇒ 6858 CSFs

Th II :

Optimisation:

- MR : $6d7s^2, 6d^2 7s, 6d^3$ ⇒ 10 CSFs;
- VV1: SD {MR} → {7s,6p,6d,5f,5g} ⇒ 61 CSFs;
- VV2: SD {MR} → {7s, 6(p-g)} ⇒ 188 CSFs;
- VV3: SD {MR} → {7(s-g)} ⇒ 584 CSFs;
- VV4: SD {MR} → {8(s-g)} ⇒ 1258 CSFs

RCI:

- CV: S {6s,6p}→ MR ⇒ 1275 CSFs;
- CC: SD {6s,6p}→ MR ⇒ 1332 CSFs

IP1 MR	IP1(1)	IP1(2)	IP1(3)	IP1(4)	IP1(CV)	IP1(CC)	Exp	NIST	Weigand
40 498.4	41 484.8	41 704.9	47 808.1	48 260.6	48 253.2	47 831.6	50 868.4	50 868.1	50 814.1

Model B

Th I :

- MR: $6d^2 7s^2, 6d^3 7s, 6d^4, 5f^2 6d7s, 5f^2 6d^2, 5f^2 7s^2 \Rightarrow$ 128 CSFs;
- Same active set

Th II :

- MR: $6d7s^2, 6d^2 7s, 6d^3, 5f^2 7s, 5f^2 6d \Rightarrow$ 29 CSFs;
- Same active set

IP1 MR	IP1(1)	IP1(2)	IP1(3)	IP1(4)	IP1(CV)	IP1(CC)	Exp	NIST	Weigand
41 553.0	42 017.2	42 157.0	48 281.3	48 907.6	47 923.4	46 860.0	50 868.4	50 868.1	50 814.1

Model C

Th I :

- MR: $6d^2 7s^2, 6d^3 7s, 6d^4, 5f^2 6d7s, 5f^2 6d^2, 5f^2 7s^2, 5f6d^2 7p, 5f6d7s7p, 5f7s^2 7p \Rightarrow$ 254 CSFs;
- Same active set

Th II :

- MR: $6d7s^2, 6d^2 7s, 6d^3, 5f^2 7s, 5f^2 6d, 5f6d7p, 5f7s7p \Rightarrow$ 52 CSFs;
- Same active set

IP1 MR	IP1(1)	IP1(2)	IP1(3)	IP1(4)	IP1(CV)	IP1(CC)	Exp	NIST	Weigand
44 592.3	48 010.8	48 093.7	48 424.6	49 236.2	47 330.7	45 591.0	50 868.4	50 868.1	50 814.1

Model D

Th I :

- MR: $6d^2 7s^2, 6d^3 7s, 6d^4, 5f^2 6d7s, 5f^2 6d^2, 5f^2 7s^2, 5f6d^2 7p, 5f6d7s7p, 5f7s^2 7p$ ⇒ 254 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g};
- VV2: SD {MR} → {7s, 7p, 6(d-h)};
- VV3: SD {MR} → {7(s-h)};
- VV4: SD {MR} → {8(s-h)};
- VV5: SD {MR} → {9(s-h)};
- VV6: SD {MR} → {10(s-h)};
- CV: S {6s,6p}→ MR
- CC: SD {6s,6p}→ MR ⇒ 210 849 CSFs

Th II :

- MR: $6d7s^2, 6d^2 7s, 6d^3, 5f^2 7s, 5f^2 6d, 5f6d7p, 5f7s7p$ ⇒ 52 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g};
- VV2: SD {MR} → {7s, 7p, 6(d-h)};
- VV3: SD {MR} → {7(s-h)};
- VV4: SD {MR} → {8(s-h)};
- VV5: SD {MR} → {9(s-h)};
- VV6: SD {MR} → {10(s-h)};
- CV: S {6s,6p}→ MR
- CC: SD {6s,6p}→ MR ⇒ 27 890 CSFs

IP1 MR	IP1(1)	IP1(2)	IP1(3)	IP1(4)	IP1(5)	IP1(6)	IP1(CV)	IP1(CC)	Exp
44 592.3	48 010.8	48 202.9	48 519.0	49 327.3	49 394.2	49 406.2	47 789.8	46 306.4	50 868.4

0.02%

Model E

Th I :

- MR: $6d^2 7s^2, 6d^3 7s, 6d^4, 5f^2 6d7s, 5f^2 6d^2, 5f^2 7s^2, 5f6d^2 7p, 5f6d7s7p, 5f7s^2 7p$ ⇒ 254 CSFs;
- VV1-VV6 : SDTQ {MR} → active set ($n_{max} l_{max} = 10h$)
- CV: S {6s,6p}→ MR ⇒ 2 939 952 CSFs reducing to 157 258CSFs

Th II :

- MR: $6d7s^2, 6d^2 7s, 6d^3, 5f^2 7s, 5f^2 6d, 5f6d7p, 5f7s7p$ ⇒ 52 CSFs;
- VV1-VV6: SDTQ {MR} → active set ($n_{max} l_{max} = 10h$)
- CV: S {6s,6p}→ MR ⇒ 28 424 CSFs

IP1 MR	IP1(1)	IP1(2)	IP1(3)	IP1(4)	IP1(5)	IP1(6)	IP1(CV)	Exp	NIST
44 592.3	48 017.6	48 210.5	48 538.8	49 324.3	49 390.4	49 402.4	47 786.7	50 868.4	50 868.1

Model F

Th I :

- CV1: SrD {MR} → {8(s-h)} ⇒ 2 490 400 CSFs
- CV2: SrD {MR} → {9(s-h)} ⇒ 4 500 614 CSFs
- CV3: SrD {MR} → {10(s-h)} ⇒ 7 104 787 CSFs

Th II :

- CV1: SrD {MR} → {8(s-h)} ⇒ 324 348 CSFs
- CV2: SrD {MR} → {9(s-h)} ⇒ 584 962 CSFs
- CV3: SrD {MR} → {10(s-h)} ⇒ 922 492 CSFs

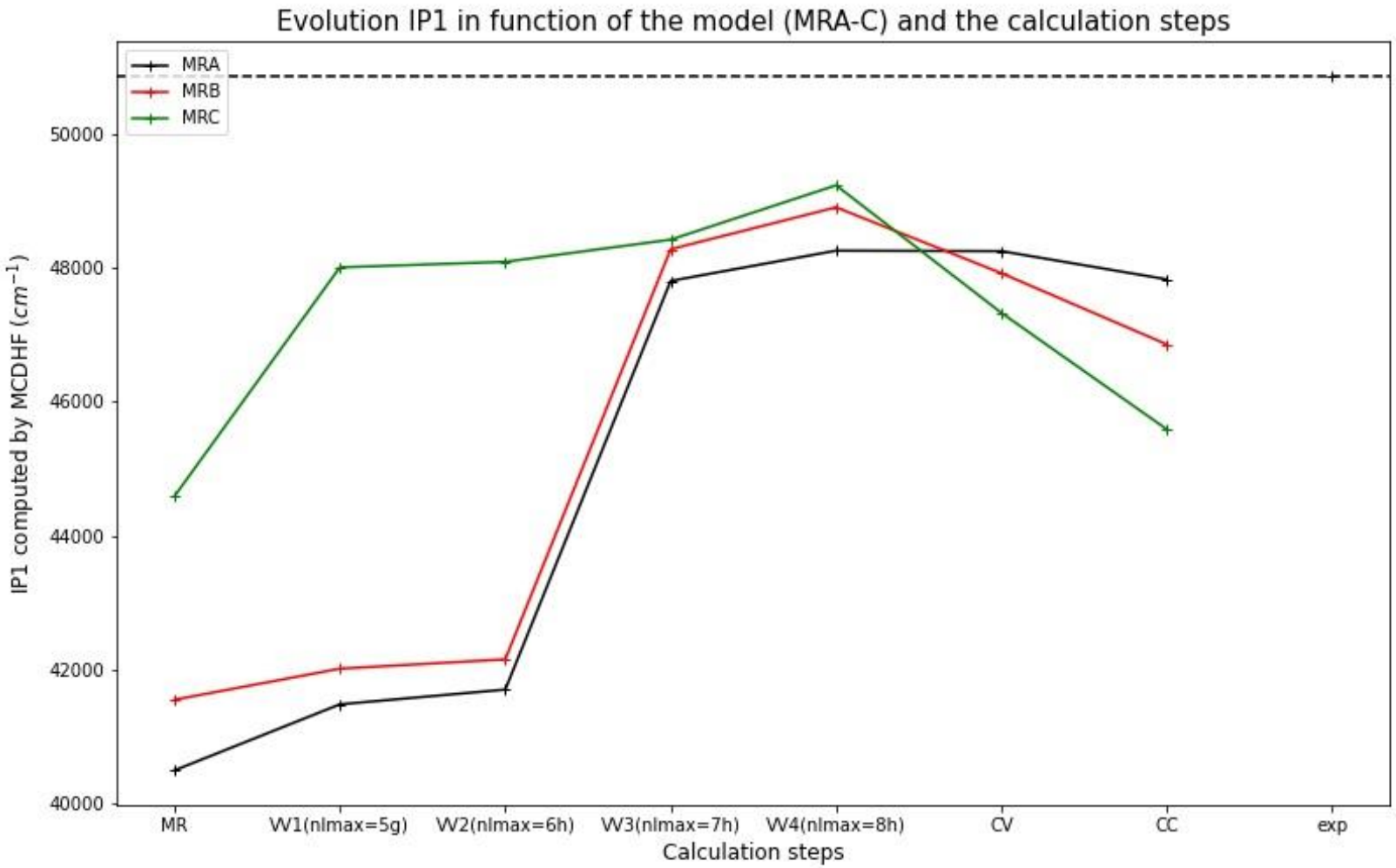
VV4(8) (model D)	SrD(8) (model F)	VV5(9) (model D)	SrD(9) (model F)	SrD(10) (model F)	Exp	NIST
49 327.3	49 519.7	49 394.2	50 144.8	In progress	50 868.4	50 868.1

Some graphs

Number of configurations

	Th I	Th II
MRA	3	3
MRB	6	5
MRC	9	7

Increase MR, tend to the experimental value until the CV and CC correlations

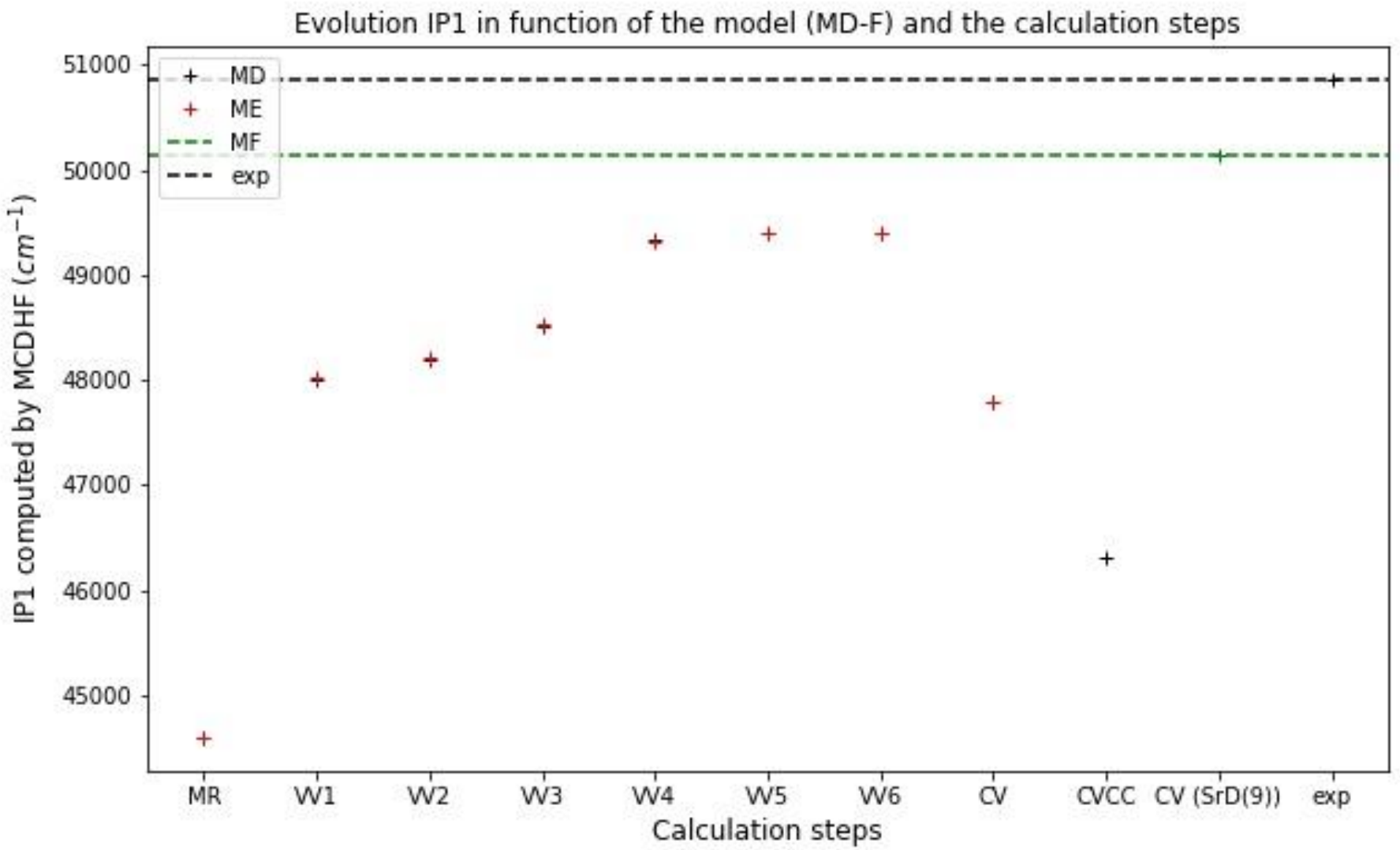


First ionization potential

MD : SD
ME : SDTQ
MF : CV (SrD)

Not significant differences between MD and ME

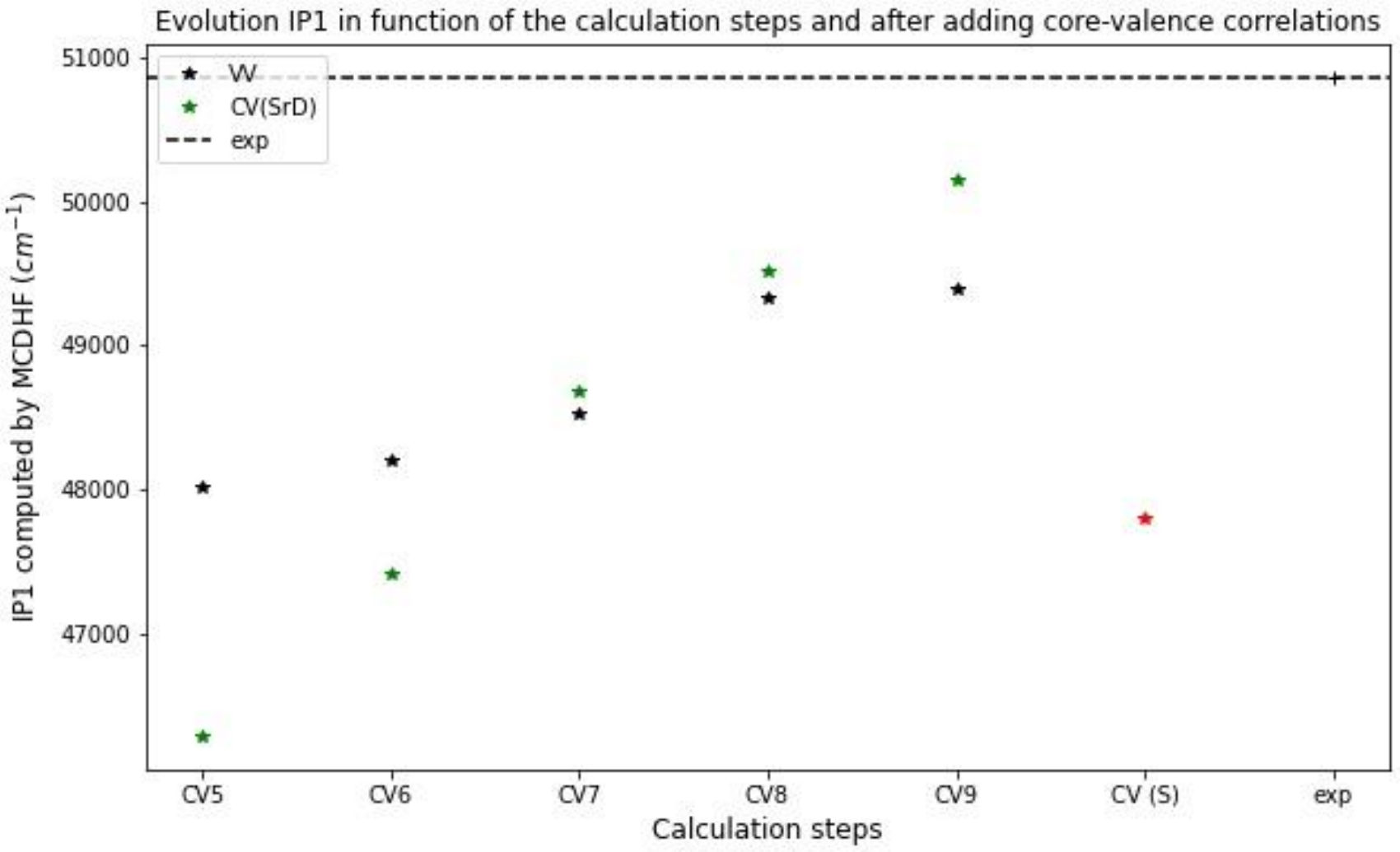
Improvement with SrD



First ionization potential

- CV(S): S {6s,6p} → MR
- CV9: SrD {MR} → {9s, 9p, 9d, 9f, 9g, 9h}

Improvement of the IP1 value after adding CV correlations through SrD excitations



Model A

Th II :

- MR: $6d7s^2, 6d^27s, 6d^3, 5f^27s, 5f^26d, 5f6d7p, 5f7s7p \Rightarrow$ 52 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g} ⇒ 131 CSF
- VV2: SD {MR} → {7s, 7p, 6(d-h)} ⇒ 589 CSFs;
- VV3: SD {MR} → {7(s-h)} ⇒ 1712 CSFs;
- VV4: SD {MR} → {8(s-h)} ⇒ 3859 CSFs;
- VV5: SD {MR} → {9(s-h)} ⇒ 6892 CSFs;
- VV6: SD {MR} → {10(s-h)} ⇒ 10 881 CSFs;
- CV: S {6s,6p}→ MR ⇒ 12 085 CSFs
- CC: SD {6s,6p}→ MR ⇒ 27 890 CSFs

Th III :

- MR: 5f6d, 5f7s⇒ 5 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g} ⇒ 14 CSF
- VV2: SD {MR} → {7s, 7p, 6(d-h)} ⇒ 48 CSFs;
- VV3: SD {MR} → {7(s-h)} ⇒ 119 CSFs;
- VV4: SD {MR} → {8(s-h)} ⇒ 248 CSFs;
- VV5: SD {MR} → {9(s-h)} ⇒ 423 CSFs;
- VV6: SD {MR} → {10(s-h)} ⇒ 644 CSFs;
- CV: S {6s,6p}→ MR ⇒ 659 CSFs
- CC: SD {6s,6p}→ MR ⇒ 1136 CSFs

IP2 MR	IP2(1)	IP2(2)	IP2(3)	IP2(4)	IP2(5)	IP2(6)	IP2(CV)	IP2(CC)	Exp
99 802.7	100 474.6	100 444.9	100 406.7	100 839.8	100 874.0	100 880.8	109 572.0	114 570.8	95 982-99 208

0.007%

Second ionization potential

Model B

Th II :

- CV1: SrD {MR} → {8(s-h)} ⇒ 324 348 CSFs
- CV2: SrD {MR} → {9(s-h)} ⇒ 584 962 CSFs
- CV3: SrD {MR} → {10(s-h)} ⇒ 922 492 CSFs
- CV(5d6s6p) : 2 005 456 CSFs
- CC: SD {MR} → {10(s-h)} ⇒ 3 002 179 CSFs

Th III :

- CV1: SrD {MR} → {8(s-h)} ⇒ 35 177 CSFs
- CV2: SrD {MR} → {9(s-h)} ⇒ 61 591 CSFs
- CV3: SrD {MR} → {10(s-h)} ⇒ 95 355 CSFs
- CV(5d6s6p) : 207 857 CSFs
- CC: SD {MR} → {10(s-h)} ⇒ 507 530 CSFs

VV4(8)	VV5(9)	VV6(10)
100 839.8	100 874.0	100 880.8

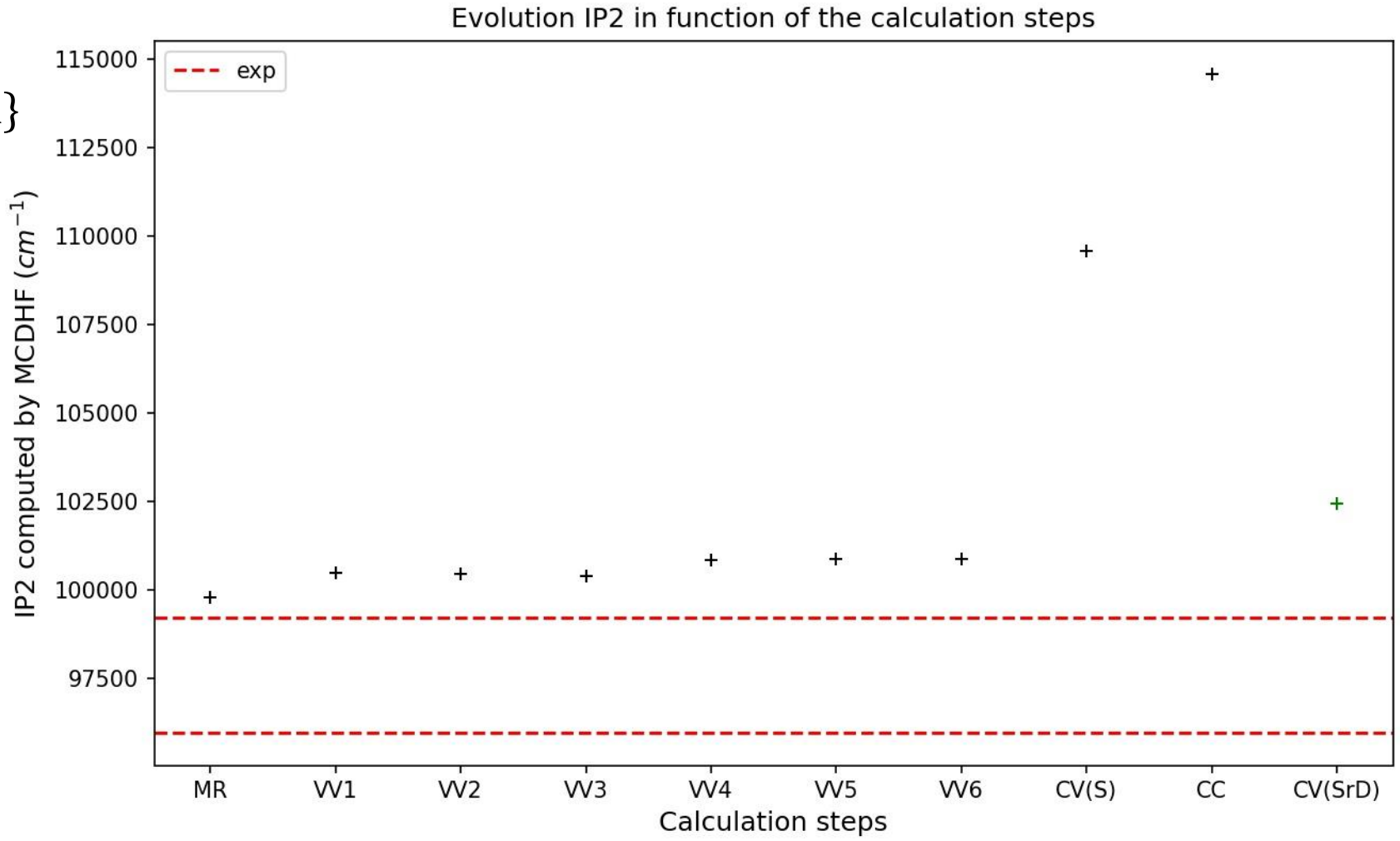
IP2(CV(S))	SrD(8)	SrD(9)	SrD(10)	CV(5d6s6p)	CC(SD)	Exp	NIST	Weigand
109 572.0	101 898.1	102 359.0	102 426.5	96 719.4	102 190.9	95 982- 99 208	97 593,1	100 093,4- 100 819,3

0.07%

❖ CV(SrD):

SrD {MR} →

{10s, 10p, 10d, 10f, 10g, 10h}

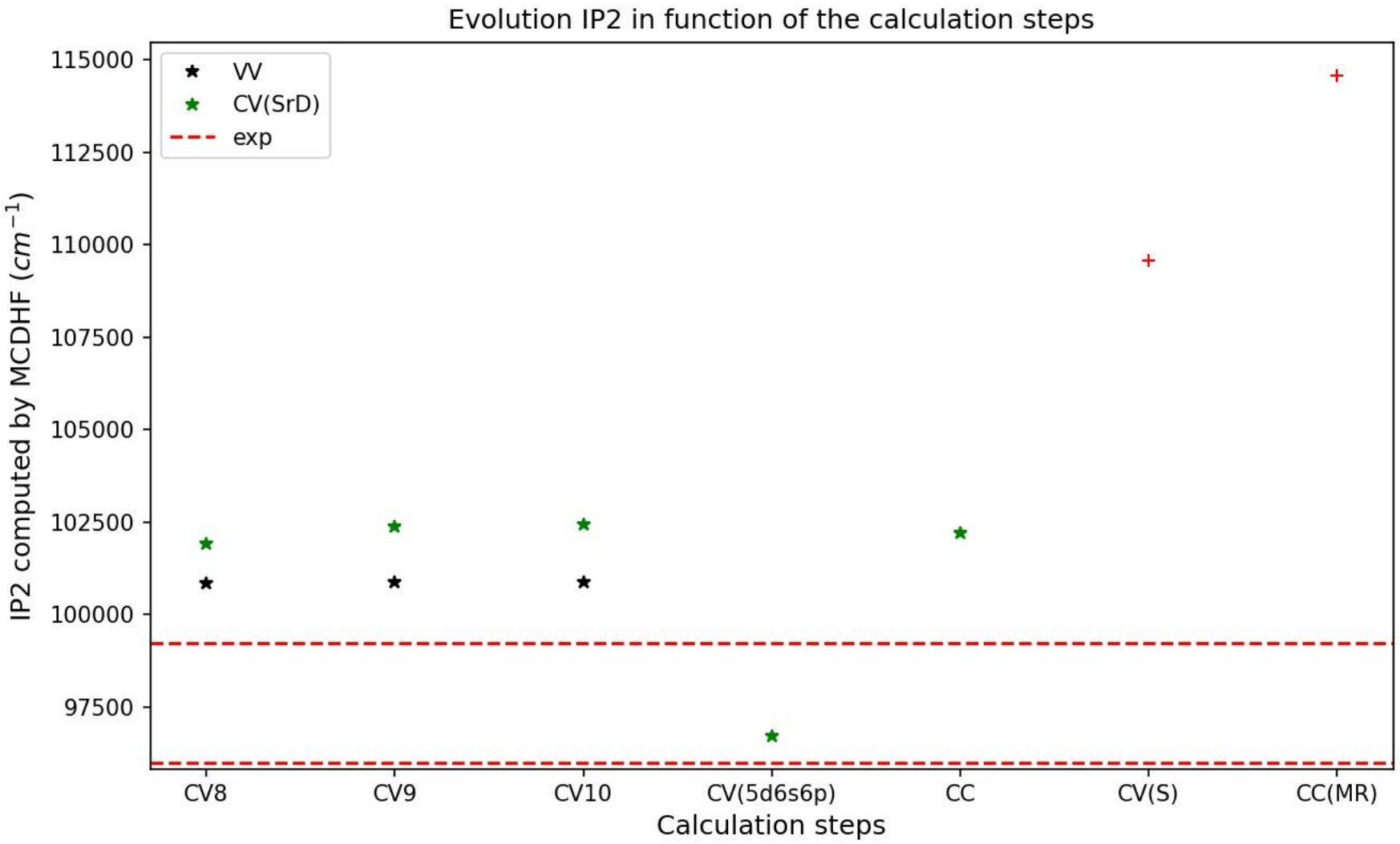


Second ionization potential

❖ CV(S): S {6s,6p}→ MR

Outlook:

- CC with one hole in 5d (size too huge)



Conclusion

First ionization potential

- By increasing the MR, the calculated value tends to the experimental one but the CV and CC correlations cause divergence
- We decide to increase the active set in VV correlations which improve the IP1 value but not enough and complicate to reproduce CV and CC correlations
- CV correlations with SrD to {(8-9)s, (8-9)p, (8-9)d, (8-9)f, (8-9)g, (8-9)h} improve the IP1 value.

Outlook: Assume could reproduce experimental value by increasing active set but calculation size becomes significant

Conclusion

Second ionization potential

- Same strategy than computation of first ionization potential (VV+SrD)
- As in the first ionization potential, by considering SrD excitations for CV correlations, can improve the IP_2 value

Outlook: by considering more correlations in CC with two holes (one in 6s and/or in 6p and/or in 5d orbitals) but the calculation size becomes very huge.

Bibliography

- Atomic Spectra Database *NIST, 2009*. Available at: https://www.nist.gov/pml/atomic-spectra-database (Accessed: 03 April 2024).

- Grant. I. P. Relativistic Quantum Theory of Atoms and Molecules. *Springer*, New-York, 799 p, 2007.

- Weigand. A. et al. Relativistic Small-Core Pseudopotentials for Actinium, Thorium, and Protactinium, *The Journal of Physical Chemistry A*, 118(13), pp. 2519–2530.