Atomic structure calculations in neutral and singly-ionized thorium

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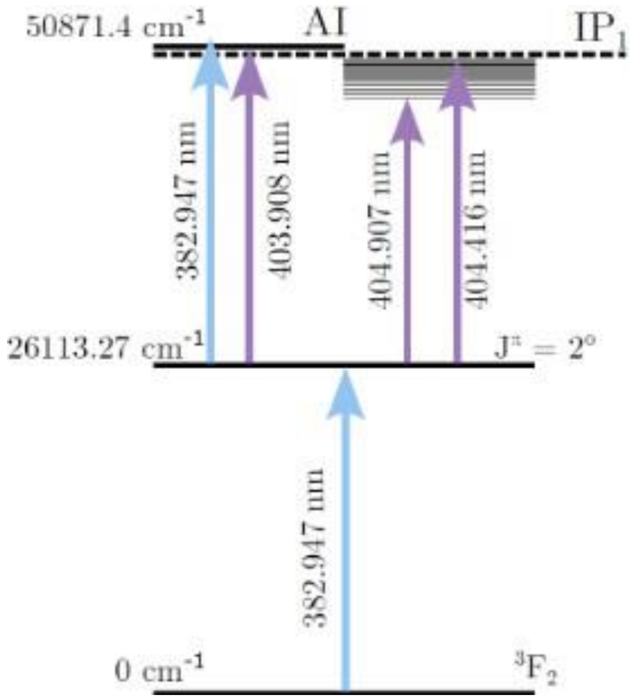
Table of contents

- Measure two first ionisation potentials (IP) with a technics in-gas laser ionisation

- To measure first ionisation potential, second step excites the level with a measured energy of 26 113.27 cm^{-1}(KUL)

⇨ Designation is not known → HFR+CPOL method



- Measure first ionisation potential : 50 867(2) cm^{-1} and 50 868.41(2) cm^{-1} (50 868.139 cm^{-1} NIST)

- Calculations with other methods (Weigand. A. et al., 2014) : 50 572.127 cm^{-1}, 50814.099 cm^{-1} and 50491.47 cm^{-1}

- Calculations with MCDHF method

General procedure

- Solve $H\Psi = E\Psi$ where $H = \sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_i + V(r_i)\right)$ (central field approximation)

- $H_i\varphi_i = E_i\varphi_i \rightarrow \varphi_i(r_i, \theta_i, \phi_i, s_i) = \frac{1}{r_i}P_{n_i l_i}(r_i)Y_{l_i}^{m_i}(\theta_i, \phi_i)\sigma_{m_{s_i}}(s_i)$

- Slater determinant: $\Psi(q_1, \ldots, q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(q_1) & \ldots & \varphi_N(q_N) \\ \ldots & \ldots & \ldots \\ \varphi_N(q_1) & \ldots & \varphi_N(q_N) \end{vmatrix}$

- $P_{n_i l_i}(r_i)$? → solve Hartree-Fock equations (Self-Consistent Field method)

- HF equations obtained by varationnal principle on the average energy of a configuration

Core polarisation correction

- Valence electron correlations represented by configuration interactions (CI) and other correlations by core-polarisation potential

- Quinet et al (1999, 2002): pseudo potentiel have one-body and two-body part :

  - $V_{P1} = -\frac{1}{2}\alpha_D \sum_{i=1}^{N} \frac{r_i^2}{(r_i^2+r_c^2)^3}$ and $V_{P2} = -\alpha_D \sum_{i>j} \frac{\vec{r_i}\cdot\vec{r_j}}{\left[(r_i^2+r_c^2)(r_j^2+r_c^2)\right]^{3/2}}$

  - α_D: dipole polarisability; r_c: ionic core radius

Slater-Condon method

- Consider CI: $\Psi_k = \sum_b y_k^b \psi_b$, where $\sum_b (y_k^b)^2 = 1$

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

Designation of the level of interest

Wavelength (nm)	Intensity	Lower level (even parity)			Upper level (odd parity)	
		$E(cm^{-1})$	Designation	J	$E(cm^{-1})$	J
382.838	14000	0	$6d^27s^2\ ^3F$	2	26113.269	2
445.80	4000	3687.987	$6d^27s^2$	2	26113.269	2
506.166	600	6362.396	$6d^37s\ ^5F$	2	26113.269	2
449.357	330	3865.474	$6d^27s^2\ ^3P$	1	26113.269	2
698.603	220	11802.932	$6d^37s\ ^5P$	2	26113.269	2
1321.715	220	18549.405	$6d^37s$	2	26113.269	2
688.883	160	11601.030	$6d^37s\ ^5P$	1	26113.269	2
530.831	120	7280.123	$6d^27s^2$	2	26113.269	2
822.768	120	13962.520	$6d^37s$	1	26113.269	2
975.401	61	15863.888	$6d^37s$	2	26113.269	2
1348.495	35	18699.623	$5f7s^27p\ ^3F$	2	26113.269	2
1562.015	35	19713.031	$6d^37s\ ^3F$	3	26113.269	2
486.479	18	5563.142	$6d^37s\ ^5F$	1	26113.269	2
430.098	16	2869.259	$6d^27s^2\ ^3F$	3	26113.269	2
537.168	14	7502.288	$6d^37s\ ^5F$	3	26113.269	2
1326.133	11	18574.610	$6d^37s$	1	26113.269	2
1461.591	11	19273.281	$6d^37s$	2	26113.269	2
1650.123	9	20054.771	$6d^37s\ ^3F$	2	26113.269	2
2203.502	3	21575.037	$6d^37s$	2	26113.269	2
2213.077	1	21594.673	$6d^37s\ ^1F$	3	26113.269	2

Wavelength (nm)	Intensity	Lower level (odd parity)		Upper level (even parity)	
		$E(cm^{-1})$	J	$E(cm^{-1})$	J
685.487	20	26113.269	2	40697.412	2 or 3
1199.960	19	26113.269	2	34444.598	2
1765.889	11	26113.269	2	31774.594	3
649.706	7	26113.269	2	41500.618	3

Transitions in NIST which depopulate and populate level 26 113.269 cm^{-1}

→ some lack of data
→ cannot identify clearly a designation

Comparisons between the highest transitions which depopulate the level 26 113.27 cm^{-1} available in NIST with the corresponding HFR+CPOL transitions

Designation of the level of interest

- Consider 4 configurations in each parity, $< r_{6p} >= 1.884\ a_0$ and α = 10.26 a_0^3 (Fraga. S. et al., 1976)

- Optimise energy level $(J^\pi = 2^o)$ with the experimental value 26 113.27 cm^{-1} and 26 113.268 cm^{-1} $(g_J = 0.980)$ in NIST

- We did it for 7 levels optimising average energies of $6d^27s7p$ and $5f6d^27s$:

Even parity	Odd parity
$6d^27s^2$	$6d^27s7p$
$6d^37s$	$6d^37p$
$6d^4$	$6d7s^27p$
$5f6d^27p$	$5f6d^27s$

Energy (cm^{-1})	24850.0	25080.9	26154.2	26431.4	27288.3	27440.1	27948.8	26113.27 (exp)
Landé g-factor	1.238	1.026	1.231	1.078	1.103	0.973	1.050	0.980

Energy (cm^{-1})	Ab initio composition in LS coupling						Presence (%)	
							$6d^27s7p$	$5f6d^27s$
24850.0	15.1%	$6d^27s7p(^1D)^3D$	7.9%	$5f6d^27s(^3F)^5P$	6.7%	$5f6d^27s(^3F)^3P$	48.8	30.5
25080.9	19.7%	$6d^27s7p(^3F)^3F$	10.9%	$6d^37p(^4F)^3F$	8.2%	$6d^27s7p(^3F)^3F$	43.5	31.3
26154.2	11.9%	$5f6d^27s(^3F)^3P$	10.1%	$6d^37p(^4F)^3D$	8.4%	$5f6d^27s(^1D)^3D$	38.8	38.2
26431.4	28.2%	$6d^27s7p(^1D)^3F$	4.8%	$6d^27s7p(^3F)^3D$	4.5%	$6d^37p(^4P)^5D$	48.9	24.8
27288.3	16.1%	$5f6d^27s(^3F)^3P$	13.2%	$5f6d^27s(^3P)^5F$	7.1%	$6d^37p(^4F)^3D$	28.6	51.9
27440.1	36.5%	$5f6d^27s(^3F)^5P$	19.9%	$6d^27s7p(^3P)^5P$	7.9%	$6d^37p(^4P)^5P$	41.5	42.9
27948.8	13.8%	$6d^27s7p(^1D)^3F$	13.6%	$5f6d^27s(^3P)^5F$	4.7%	$6d^27s7p(^1D)^3P$	33.9	43.9

$\Rightarrow$ Important mixing

Designation of the level of interest

Most intense transitions (NIST)

Wavelength (nm)	Intensity	$E(cm^{-1})$	Designation	J
382.83	14000	0	$6d^27s^2\ ^3F$	2
445.80	4000	3687.987	$6d^27s^2$	2
506.16	600	6362.396	$6d^37s\ ^5F$	2
449.35	330	3865.474	$6d^27s^2\ ^3P$	1
698.60	220	11802.932	$6d^37s\ ^5P$	2
1321.71	220	18549.405	$6d^37s$	2
688.88	160	11601.030	$6d^37s\ ^5P$	1
530.83	120	7280.123	$6d^27s^2$	2
822.76	120	13962.520	$6d^37s$	1

25 080.9 → 26 113.27

Wavelength (nm)	A (s^{-1})	E (cm^{-1})	$\|CF\|$	Expected
382.94	4.74E+07	0	0.3522	0
792.34	4.62E+06	13492.4	0.0792	3440.2
459.01	1.29E+06	4327.1	0.0238	4327.1
552.62	7.30E+05	8017.6	0.014	3720.5
630.26	4.99E+05	10246.8	0.0619	10923.1
446.57	5.70E+04	3720.5	0.0011	17847.7
658.32	4.02E+04	10923.1	0.0005	10246.8
1209.86	1.87E+04	17847.7	0.013	8017.6
441.05	1.15E+03	3440.2	0	13492.4

26 431.4 → 26 113.27

Wavelength (nm)	A (s^{-1})	E (cm^{-1})	$\|CF\|$	Expected
382.94	1.65E+07	0	0.2358	0
432.17	4.63E+06	3440.2	0.0983	3440.2
446.58	2.03E+06	3720.5	0.0387	4327.1
552.62	1.61E+06	8017.6	0.045	3720.5
459.01	8.98E+05	4327.1	0.0189	10923.1
630.26	3.21E+05	10246.8	0.0263	17847.7
792.34	2.16E+05	13492.4	0.0158	10246.8
658.33	1.80E+05	10923.1	0.008	8017.6
1209.86	9.43E+04	17847.7	0.0323	13492.4

Designation of the level of interest

27 288.3 → 26 113.27

Wavelength (nm)	A (s^{-1})	E (cm^{-1})	$\|CF\|$	Expected
382.94	8.02E+06	0	0.1153	0
441.05	4.28E+06	3440.2	0.0381	3440.2
446.57	3.14E+06	3720.5	0.0573	4327.1
459.01	2.03E+06	4327.1	0.0461	3720.5
552.62	7.62E+05	8017.6	0.0205	10923.1
1209.86	9.48E+04	17847.7	0.0368	17847.7
792.34	8.41E+04	13492.4	0.0061	10246.8
658.33	7.60E+04	10923.1	0.0051	8017.6
630.26	3.12E+04	10246.8	0.0056	13492.4

27 440.1 → 26 113.27

Wavelength (nm)	A (s^{-1})	E (cm^{-1})	$\|CF\|$	Expected
382.94	3.58E+06	0	0.0835	0
446.57	1.82E+06	3720.5	0.0621	3440.2
459.01	8.16E+05	4327.1	0.0224	4327.1
441.05	5.78E+05	3440.2	0.0074	3720.5
792.34	4.07E+05	13492.4	0.0618	10923.1
630.26	1.77E+05	10246.8	0.0583	17847.7
658.33	4.12E+04	10923.1	0.0037	10246.8
552.62	2.95E+03	8017.6	0.0001	8017.6
1209.86	1.52E+03	17847.7	0.0015	13492.4

27 948.8 → 26 113.27

Wavelength (nm)	A (s^{-1})	E (cm^{-1})	$\|CF\|$	Expected
446.57	1.15E+07	3720.5	0.2268	0
459.00	4.14E+06	4327.1	0.0694	3440.2
382.94	3.81E+06	0	0.0464	4327.1
552.62	6.52E+05	8017.6	0.019	3720.5
441.05	7.30E+04	3440.2	0.0007	10923.1
792.33	5.50E+04	13492.4	0.0042	17847.7
658.32	4.13E+04	10923.1	0.0022	10246.8
630.06	2.01E+04	10246.8	0.0024	8017.6
1209.83	3.99E+03	17847.7	0.0015	13492.4

Designation of the level of interest

Level of interest computed in our method at energy 26 431.4 cm^{-1} ($J^{\pi} = 2^{\circ}$)

Other confirmations :

1. Ratio between the two most intense transitions from NIST : 3.5

2. Ratio between the two most probable transitions from our calculations : 3.56

3. Designation : $27.4\%\ \ 6d^27s7p(^1D)^3F + 4.8\%\ \ 5f6d27s(^1D)^3D + 4.8\%\ \ 6d^27s7p(^3F)^3D$

$6d^27s7p$	$5f6d^27s$	$6d^37p$	$6d7s^27p$
44.50%	33.56%	18.24%	0.04%

4. Designation of ground state ($J=2^e$): $77.1\%\ \ 6d^27s^2(^3F)^3F + 13.1\%\ \ 6d^27s^2(^1D)^1D + 2.7\%\ \ 6d^37s(^2F)^3F$

Model A

Th I :

- MR : $6d^27s^2, 6d^37s, 6d^4 \Rightarrow$ 21 CSFs;
- VV1: SD {MR} → {7s,6p,6d,5f,5g} ⇒ 291 CSFs;
- VV2: SD {MR} → {7s, 6p, 6d, 6f, 6g} ⇒ 971 CSFs;
- VV3: SD {MR} → {7s, 7p, 7d, 7f, 7g} ⇒ 3102 CSFs;
- VV4: SD {MR} → {8s, 8p, 8d, 8f, 8g} ⇒ 6730 CSFs;
- CV: S {6s,6p}→ MR ⇒ 6756 CSFs;
- CC: SD {6s,6p}→ MR ⇒ 6858 CSFs

Th II :

- MR : $6d7s^2, 6d^27s, 6d^3 \Rightarrow$ 10 CSFs;
- VV1: SD {MR} → {7s,6p,6d,5f,5g} ⇒ 61 CSFs;
- VV2: SD {MR} → {7s, 6p, 6d, 6f, 6g} ⇒ 188 CSFs;
- VV3: SD {MR} → {7s, 7p, 7d, 7f, 7g} ⇒ 584 CSFs;
- VV4: SD {MR} → {8s, 8p, 8d, 8f, 8g} ⇒ 1258 CSFs;
- 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

First ionisation potential

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: $6d^27s^2, 6d^37s, 6d^4, 5f^26d7s, 5f^26d^2, 5f^27s^2, 5f6d^27p, 5f6d7s7p, 5f7s^27p$ ⇒ 254 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g};
- VV2: SD {MR} → $\{7s, 7p, 6d, 6f, 6g, 6h\}$;
- VV3: SD {MR} → $\{7s, 7p, 7d, 7f, 7g, 7h\}$;
- VV4: SD {MR} → $\{8s, 8p, 8d, 8f, 8g, 8h\}$;
- VV5: SD {MR} → $\{9s, 9p, 9d, 9f, 9g, 9h\}$;
- VV6: SD {MR} → $\{10s, 10p, 10d, 10f, 10g, 10h\}$;
- CV: S {6s,6p}→ MR
- CC: SD {6s,6p}→ MR ⇒ 210 849 CSFs

Th II :

- MR: $6d7s^2, 6d^27s, 6d^3, 5f^27s, 5f^26d, 5f6d7p, 5f7s7p$ ⇒ 52 CSFs;
- VV1: SD {MR} → {7s,7p,6d,5f,5g};
- VV2: SD {MR} → $\{7s, 7p, 6d, 6f, 6g, 6h\}$;
- VV3: SD {MR} → $\{7s, 7p, 7d, 7f, 7g, 7h\}$;
- VV4: SD {MR} → $\{8s, 8p, 8d, 8f, 8g, 8h\}$;
- VV5: SD {MR} → $\{9s, 9p, 9d, 9f, 9g, 9h\}$;
- VV6: SD {MR} → $\{10s, 10p, 10d, 10f, 10g, 10h\}$;
- 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

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 157 258 CSFs

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 :

- CV: SrD {MR} → {8s, 8p, 8d, 8f, 8g, 8h} ⇒ 2 490 400 CSFs

Th II :

- CV: SrD {MR} → 8s, 8p, 8d, 8f, 8g, 8h ⇒ 324 348 CSFs

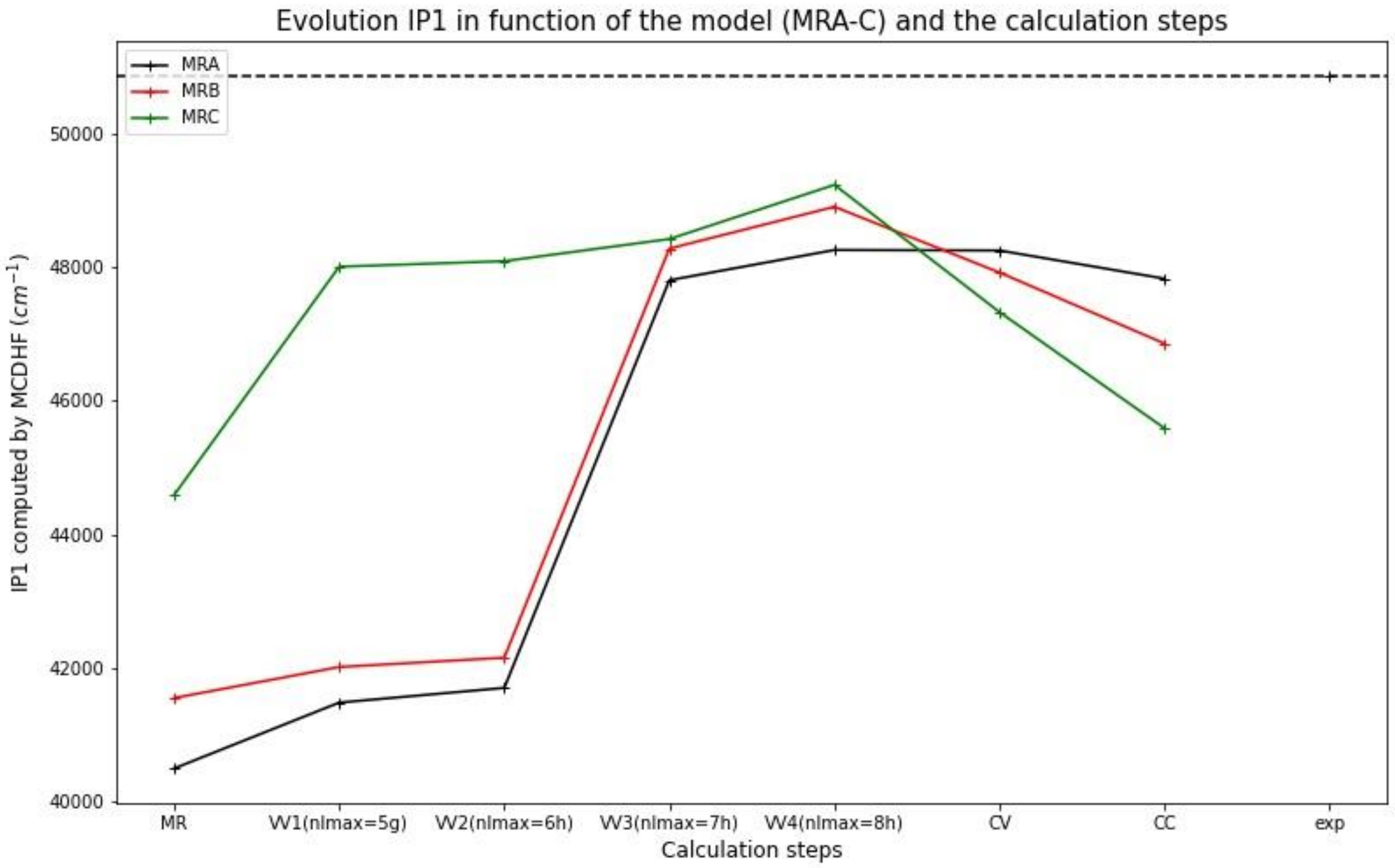
IP1(4) (model E)	IP1(SrD4) (model F)	IP1(SrD5) (model F)	Exp	NIST
49 327.3	49 519.7	In progress	50 868.4	50 868.1

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

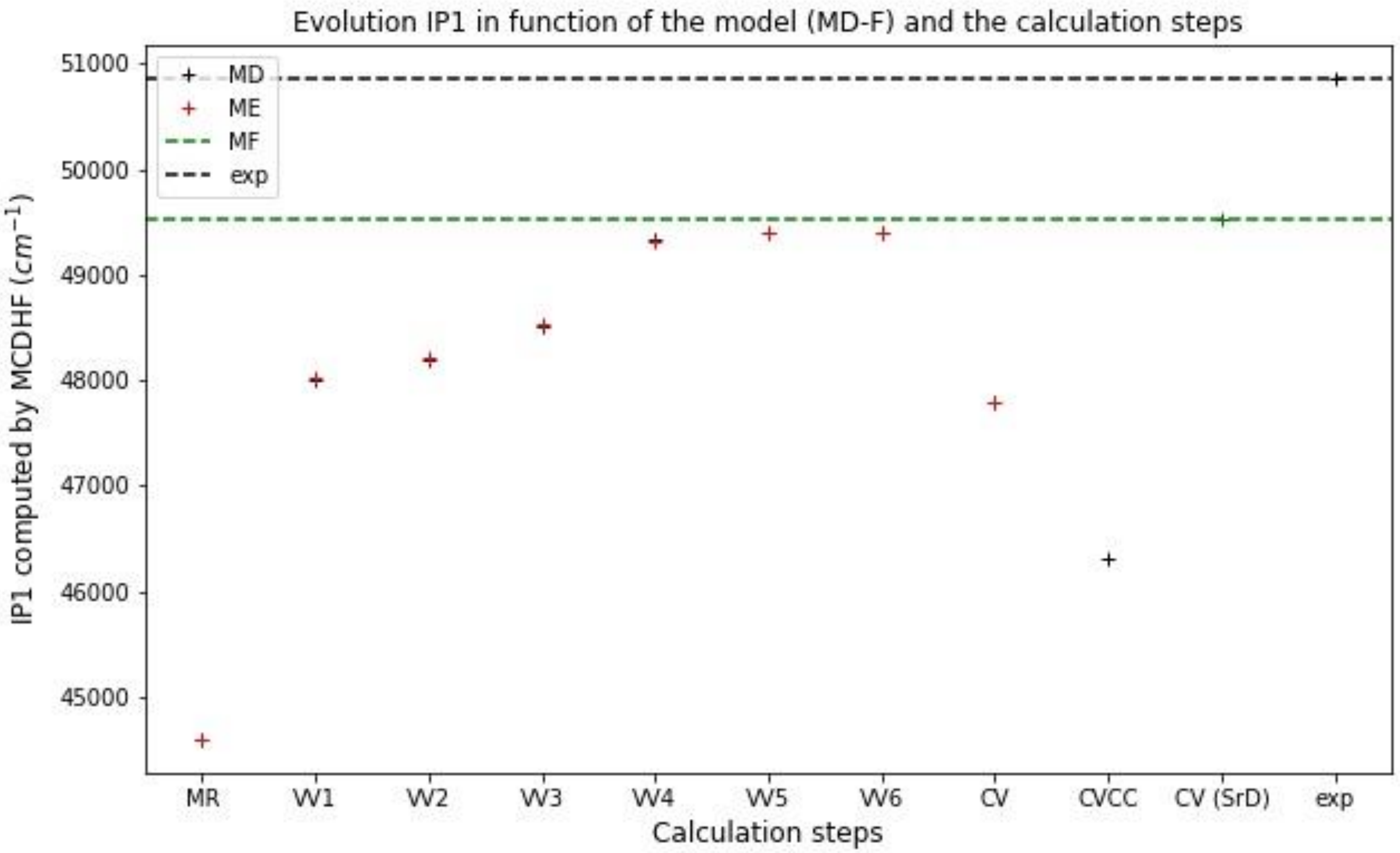


First ionisation potential

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

Not significant differences between MD and ME

Improvement with SrD



Conclusion

Designation

- Use HFR+CPOL to identify a designation of the level $26\,113.27\mathrm{cm}^{-1}$

•Not obvious due to some lack of data and significant mixing but there are some

convergence points which tend to this designation : $21.0\%\ \ 6d^27s7p(^1D)^3F + 7.0\%\ \ 6d^37p(^4F)^3D + 4.8\%\ \ 6d^37p(^2P)^3P$

- The level of interest is computed in our method at 26 431.4 cm^{-1}

First ionisation 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 $\{8s, 8p, 8d, 8f, 8g, 8h\}$ improve the IP1 value. Assume could reproduce experimental value by increasing active set but calculation size becomes significant

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