The Importance of Relativistic DFT-GIAO Calculations of NMR Parameters of Methyl Halides

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Overview

1. Introduction
2. Theory
3. Results
4. Conclusions
5. Acknowledgments

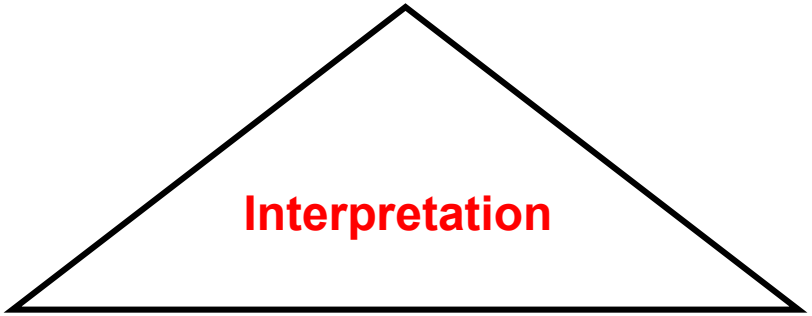
Aim and scope of work

Theoretical support in analysis of NMR spectra of compounds containing „heavier nuclei”

1. **Heavy Nuclei on Light Atom (HALA)**
2. **Models: HX, CH_3X where X is F, Cl, Br and I**
3. **ADF 2014.01, Slater-Type Orbitals (STO)**

Tools: ADF 2014.01 (and earlier)

Molecules
(structure, nuclear shielding)



Experimental

NMR spectrum

Theory
structure/NMR
parameters

Symbiosis of experiment and theory

Theoretical calculations[a]

1. *Geometry optimization*
2. *DFT (BLYP, B3LYP, ...)*
3. *Basis sets: DZ, DZP, TZP, TZ2P, QZ4P*

Simple HX and CH_3X: where X = F, Cl, Br and I

4. NMR calculations: GIAO nuclear shieldings:

Nonrelativistic (NR)

Scalar ZORA

Spin-orbit ZORA

5. Comparison of theory with experiment

[a] ADF, Some NR results obtained with G'09

Harmonic vs anharmonic frequencies (modeling IR/Raman spectra)

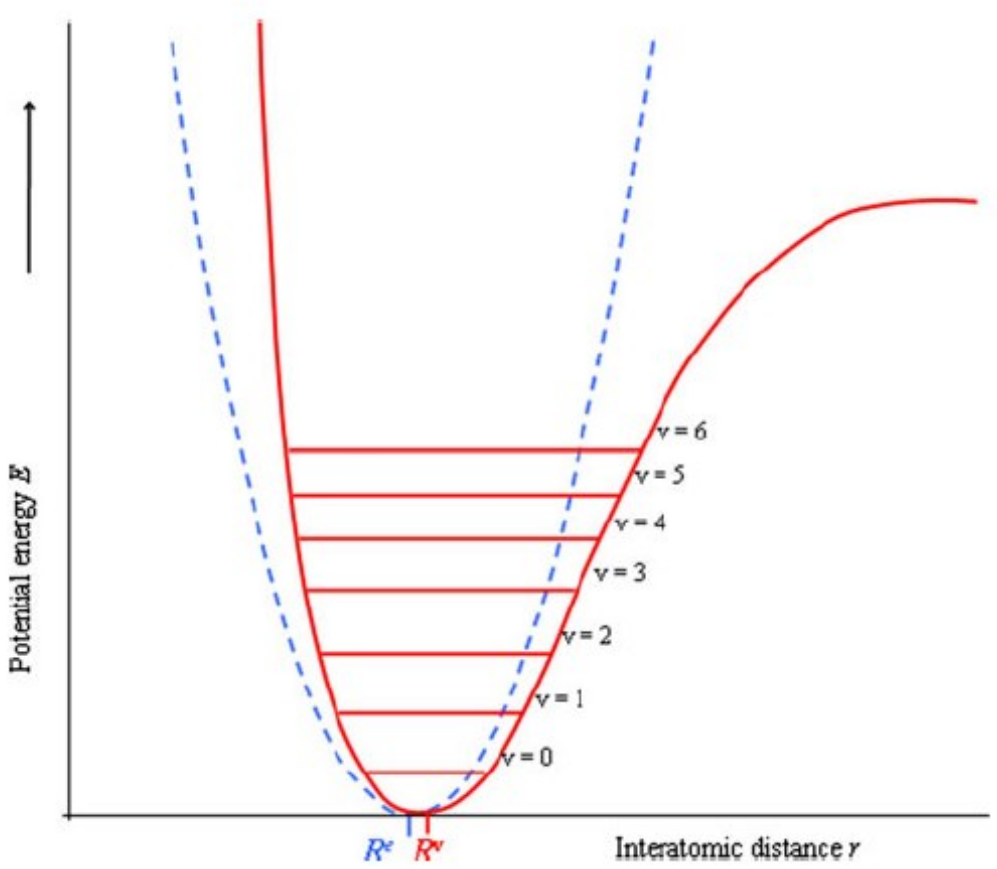


Fig. 1 Schematic representation of the potential energy surface of two interacting atoms using harmonic (*dashed line*) *vs* anharmonic (*solid line*) approximations

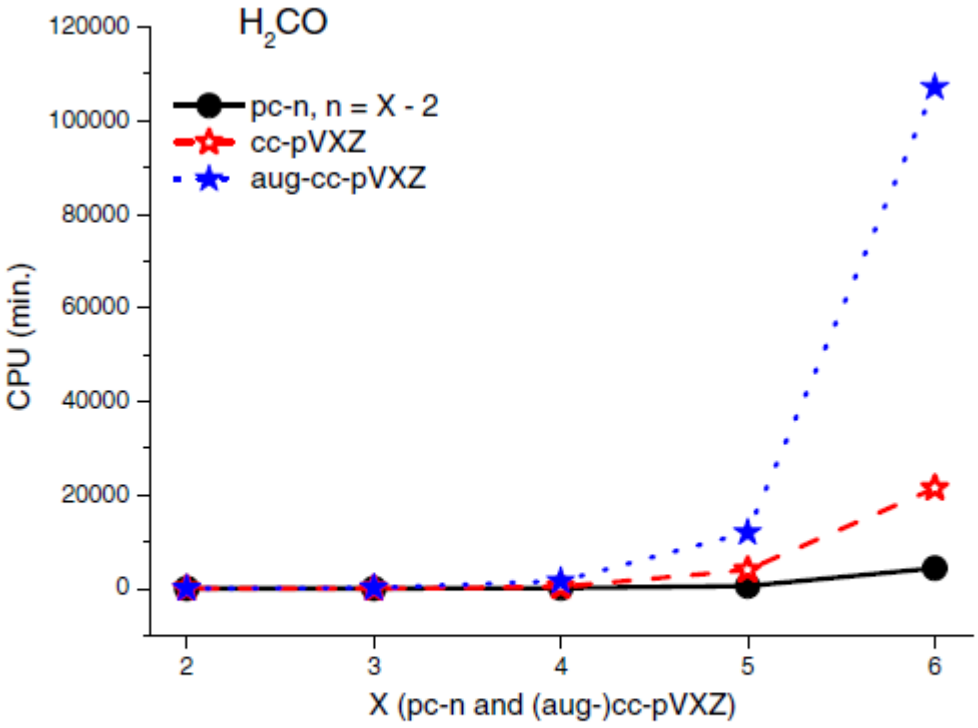


Fig. 3 CPU time (min) dependence on the type and size of basis set for formaldehyde VPT2 calculation with pc-*n*, cc-pVXZ and aug-cc-pVXZ basis sets

VPT2 model (in G'09) for ZPVC + TC

Calculation of nuclear shieldings (ppm): CH3X, X = F, Cl, Br and I

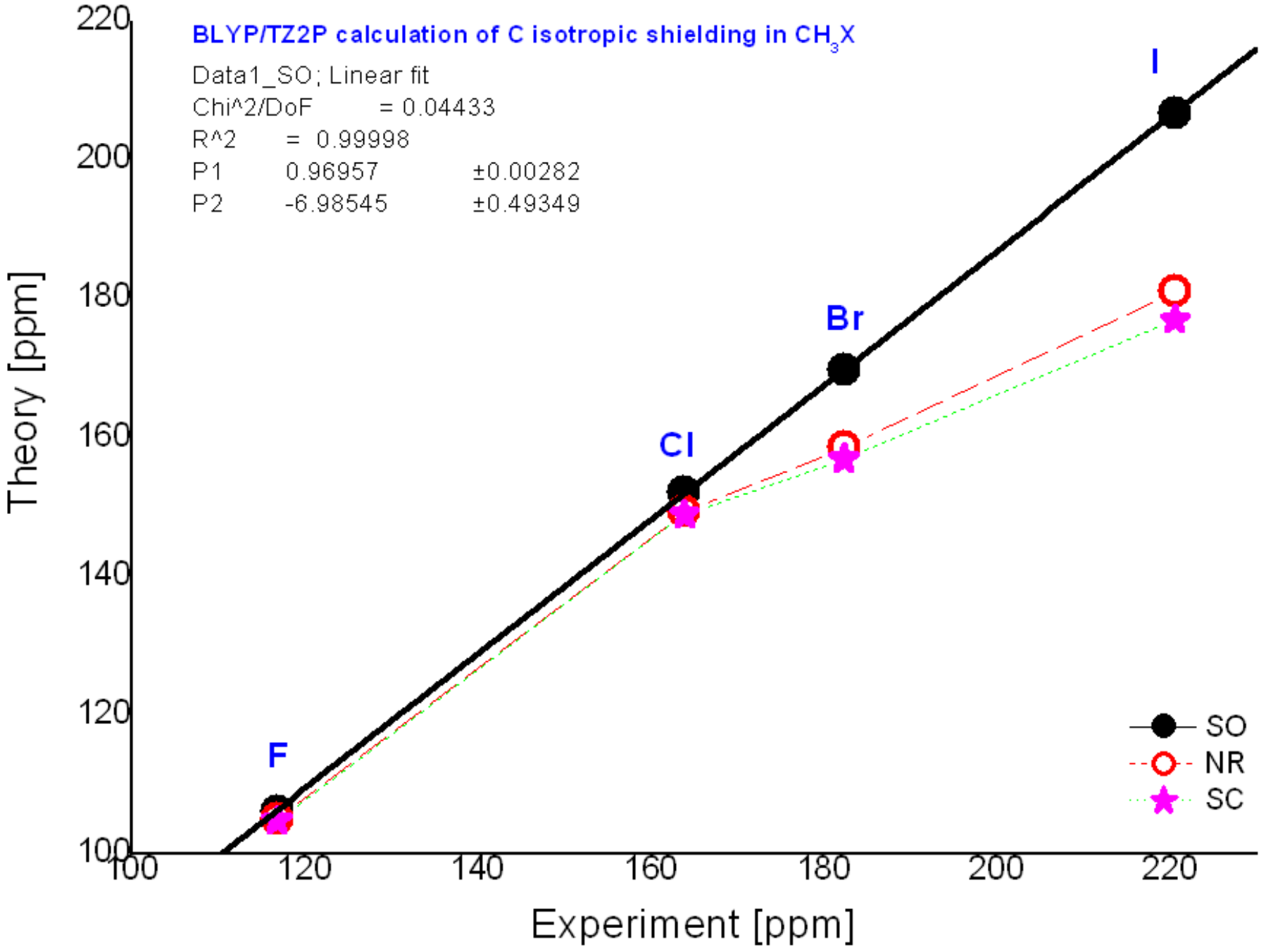
	ZORA						ZORA		
Method	SO			Scalar				NR	
Methyl Iodide	C	H	I	C	H	I	C	H	I
Exp.	220.72	28.78							
Exp.	220.59	28.75							
BHandHLYP	216.43	29.84	5040.83	185.34	29.71	4126.56	189.42	29.79	4178
B3LYP	210.35	29.94	4847.41	180.61	29.67	3955.77	184.68	29.75	4023.8
mPW1PW	212.03	29.89	4941.94	184.33	29.64	4055.67	188.36	29.71	4118.62
PBE0	213.09	29.82	4959.9	185.69	29.57	4076.22	189.72	29.65	4137.74
OPPBE0	213.41	29.88	4985.93	188.56	29.62	4109.76	192.45	29.69	4175.3
B1PW91	211.69	29.9	4954.9	184.44	29.65	4070.27	188.47	29.72	4132.51
KT2	214.07	29.83	4879.42	187.58	29.49	4025.57	191.4	29.58	4087.17
BP86	207.91	29.86	4785.51	180.45	29.55	3918.02	184.51	29.64	3990.21
BLYP	206.81	29.96	4698.83	177.02	29.65	3822.94	181.08	29.73	3900.78
Re							178.00	29.54	447.80
Rv at 0K							174.85	28.93	445.48
Rv + Temp							174.75	28.92	445.38
ZPVC							-3.15	-0.61	-2.32
TC							-0.10	-0.01	-0.10
ZPVC+TC							-3.25	-0.62	-2.42

Structure: Gaussian 09 Rev. D.01; B3LYP/C,H,X Def2-TZVPPD (gas)

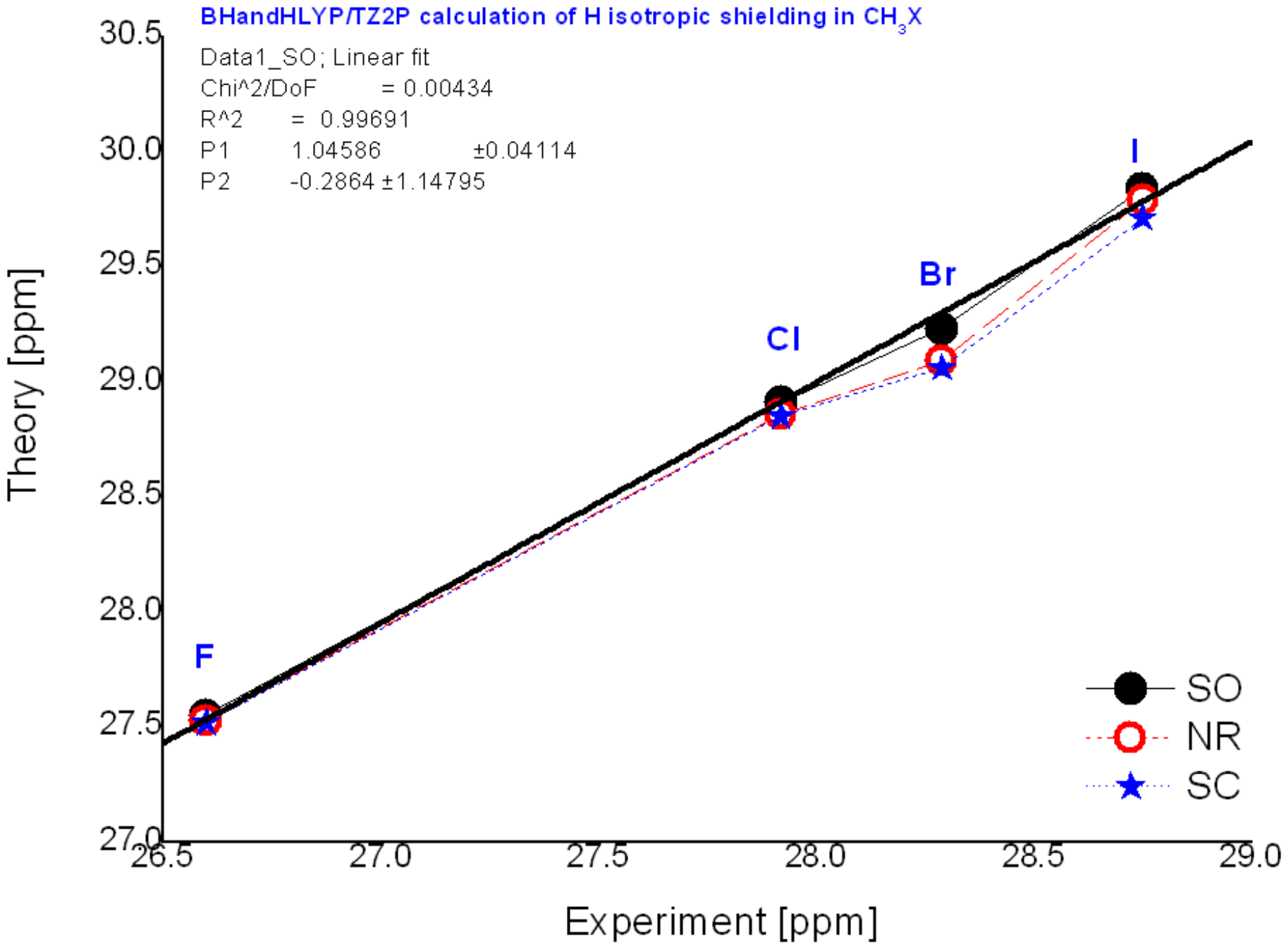
NMR: ADF 2014.01; unscalled NonRelativistic and Relativistic DFT/TZ2P

ZPVC+TC from G09, VPT2

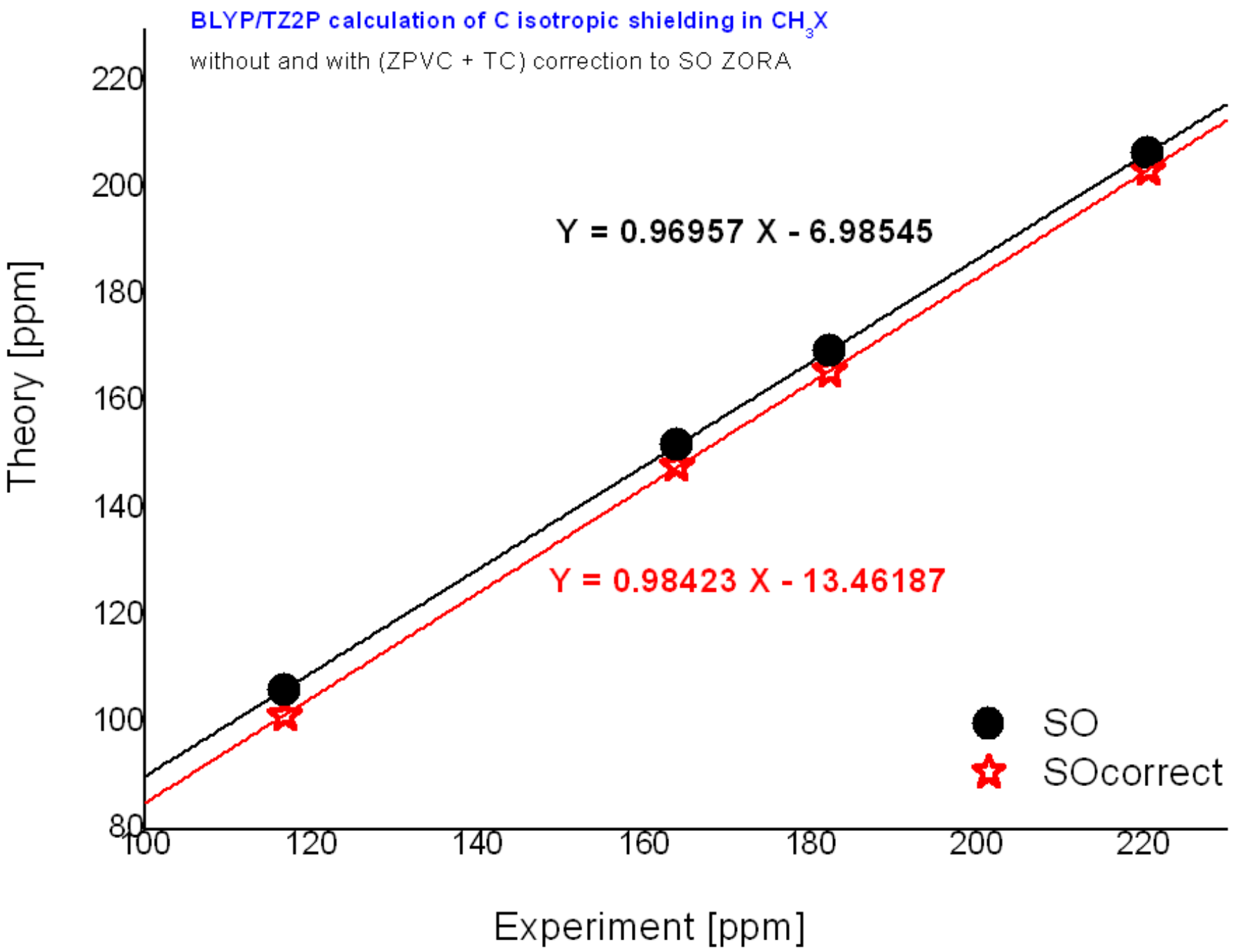
^{13}C nuclear shieldings (ppm): CH_3X, X = F, Cl, Br and I



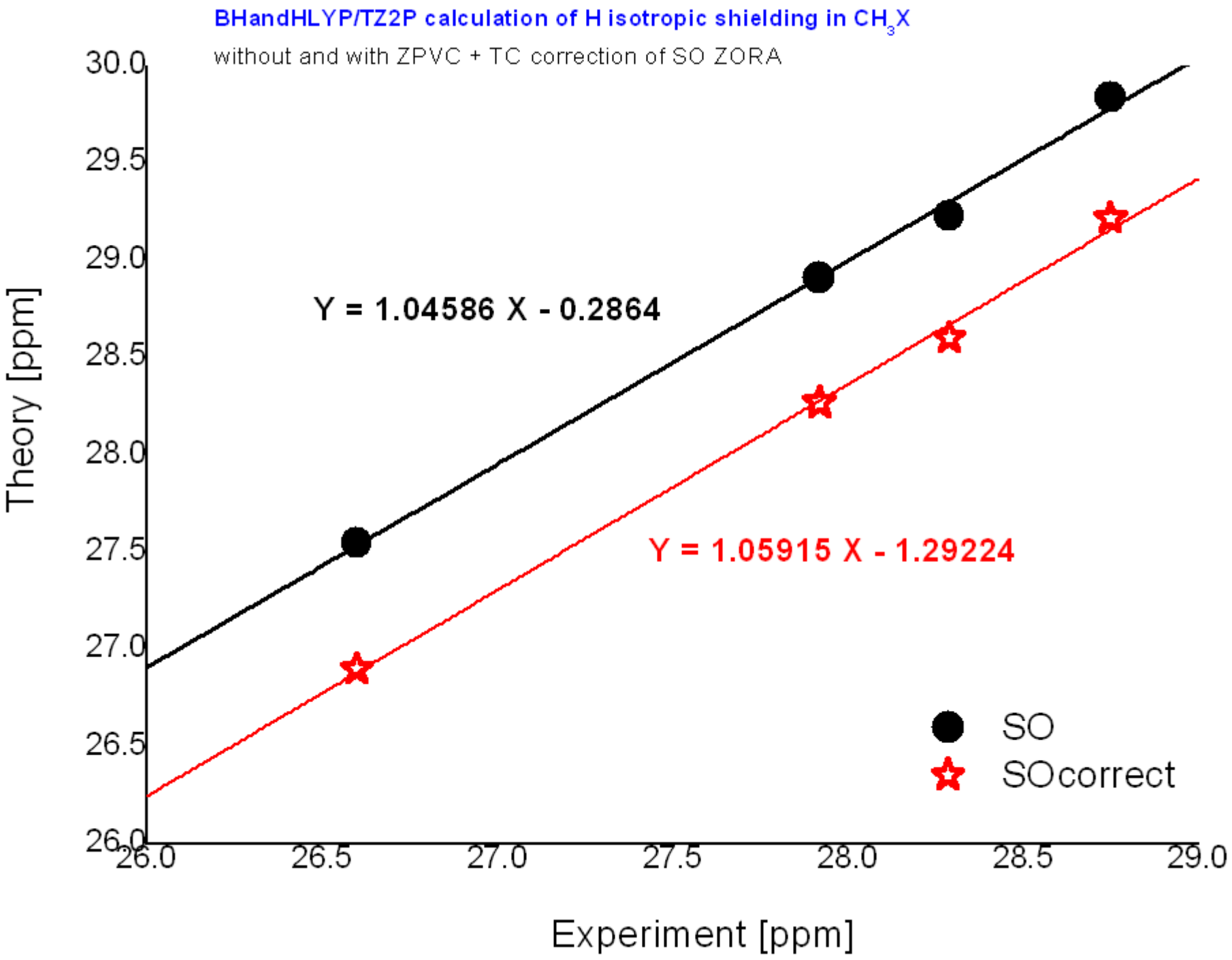
^{1}H nuclear shieldings (ppm): CH_3X, X = F, Cl, Br and I



^{13}C nuclear shieldings (ppm): CH_3X, X = F, Cl, Br and I



^{1}H nuclear shieldings (ppm): CH_3X, X = F, Cl, Br and I



Conclusions:

Recommendations for RelativisticZORA NMR calculations:

ADF (no parallel calculations !): DFT/TZ2P Spin-orbit ZORA

(?) ZPVC & TC: VPT2 (in Gaussian 09)

Results are improved (in comparizon to NR data)

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Thank You for Your Attention