The Quest for Absolute Chirality

The Quest for Absolute Chirality

New Zealand INSTITUTE for Advanced Study

CTCP Centre for Theoretical Chemistry and Physics

MARSDEN FUND
TE PŪTEA RANGAHAU A MARSDEN

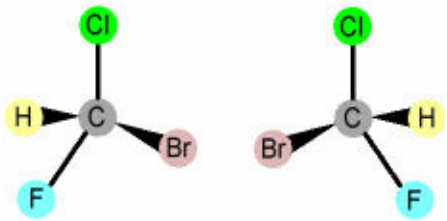
Acknowledgment

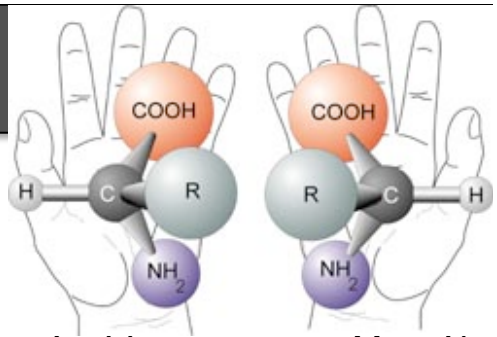
Massey University

James Cook Fellowship, Royal Society NZ , Alexander von Humboldt Foundation

T. Saue (Toulouse), B. Compton (Tennessee), G. Rauhut (Stuttgart), V. Barone (Pisa), P. Lazzeretti (Modena), Ch. Chardonnet (Paris), R. Berger & S. Nahrwold (Darmstadt), J. Crassous (Rennes), P. Botschwina (Göttingen), V. Flambaum (Sydney), M. G. Kozlov (Petersburg), M. Ilias (Sweden), J. Thyssen, R. Bast, J. Gierlich, A. Kuehn, Ch. Thierfelder, D. Figgen, J. K. Laerdahl, A. Borschevsky, A.-L. Deppenmeier, K. Beloy

Structural Chirality





(Greek: *kheir* ⟶ Hand)

- A molecular structure is called **chiral** *if and only if* it does not have an *axis of improper rotation* S_n (that is, an n-fold rotation followed by a reflection in the plane perpendicular to this axis), *inversion center* or *plane of symmetry* which maps the molecule onto itself. (NB: *a chiral molecule is not necessarily asymmetric, that is completely devoid of any symmetry elements, as it can have, for example, rotational or permutation symmetry*).

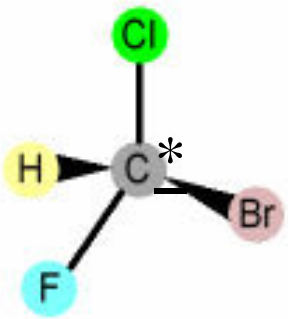
- A simplified rule applies to tetrahedrally bonded carbon: if all four substituents are different, the molecule is chiral.

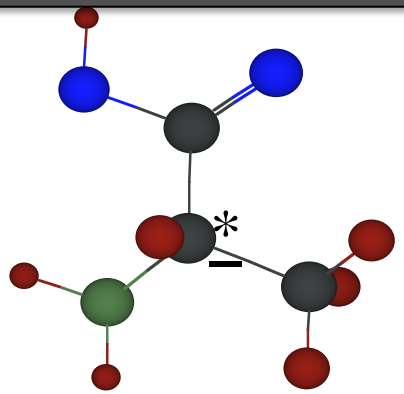
- **Point chirality** centers around a single atom.

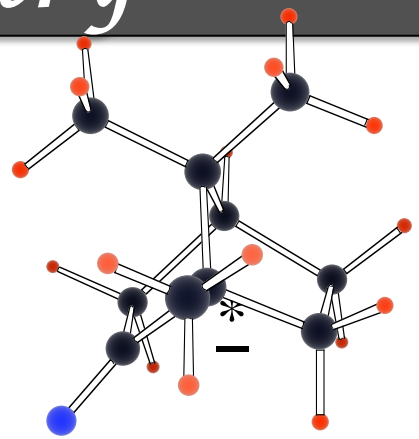
- **Molecular Chirality** is not a quantum mechanical observable.

Chiral Forms in Chemistry

Point chirality:



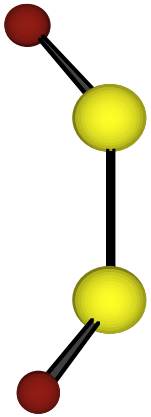


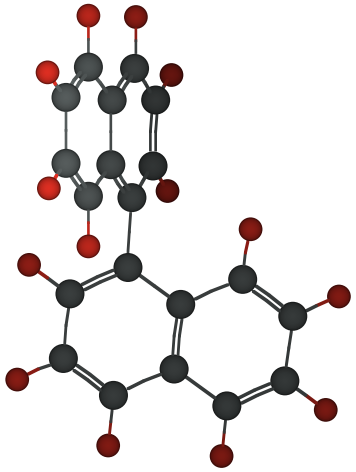


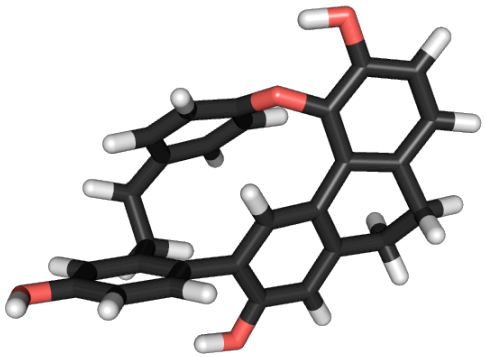
Camphor

Axial and planar chirality:

Axis or plane of chirality - an axis or plane about which a set of substituents is held in a spatial arrangement which is not superimposable on its mirror image.

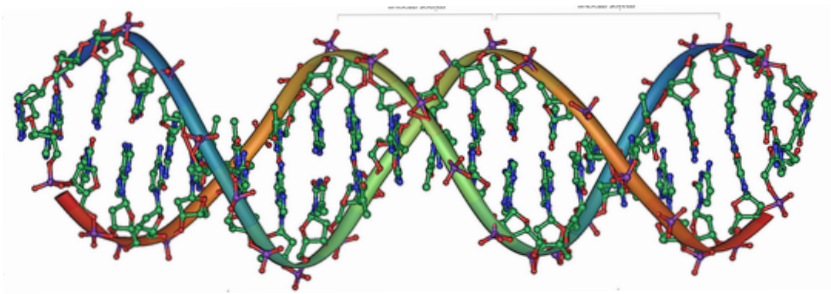


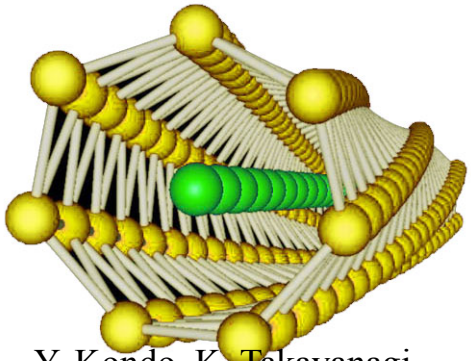




Cavicularin

Some molecules with helical (extended axial) chirality:



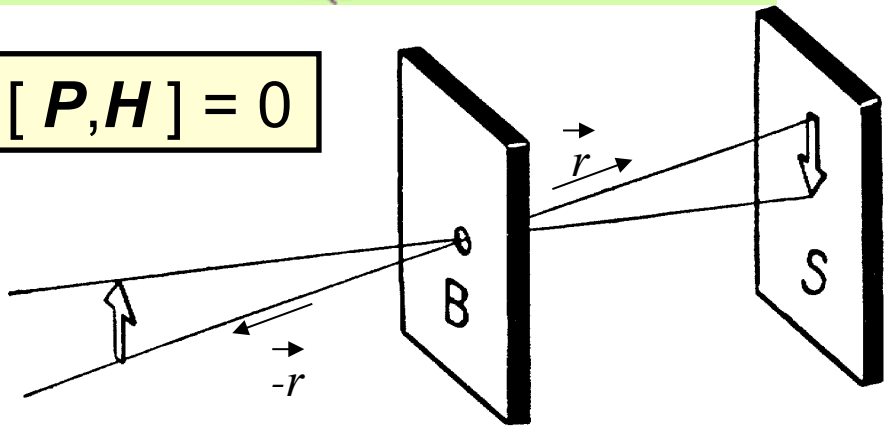


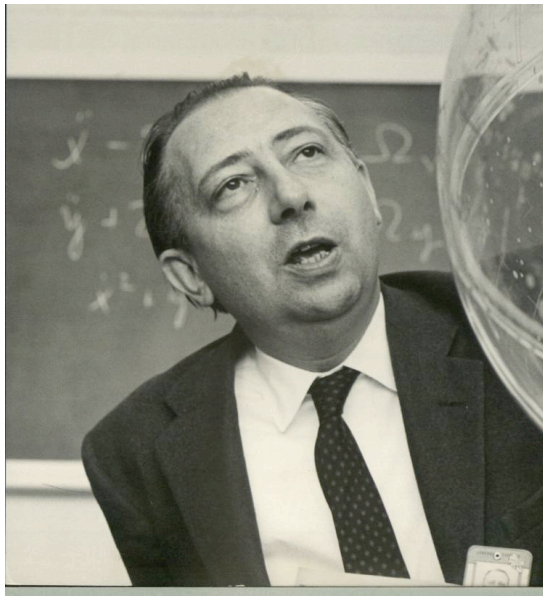
Y. Kondo, K. Takayanagi, *Science* 289, 606 (2000).

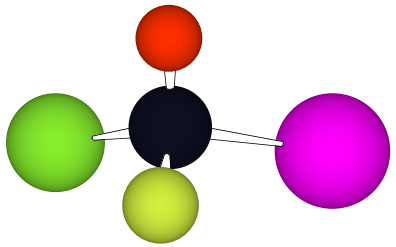
The Principle of Parity Conservation

Reflectional Symmetry

$$\boldsymbol{P}:\ \Psi_L \rightarrow \Psi_D\ ,\ \ [\,\boldsymbol{P},\boldsymbol{H}\,] = 0$$

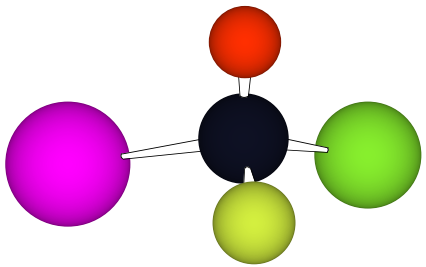


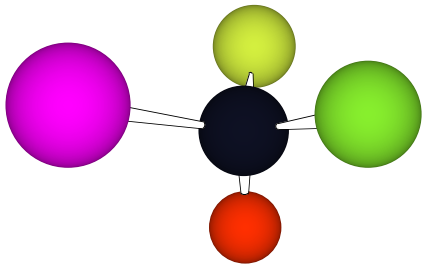




$$\vec{r} = (x,y,z) \xrightarrow{\ \boldsymbol{P}\ } -\vec{r} = (-x,-y,-z)$$

$$\sigma(y,z) \searrow \quad (-x,y,z) \quad \nearrow \varphi_x(180^o)$$





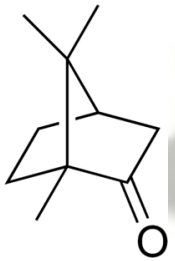
Inversion in 3D space

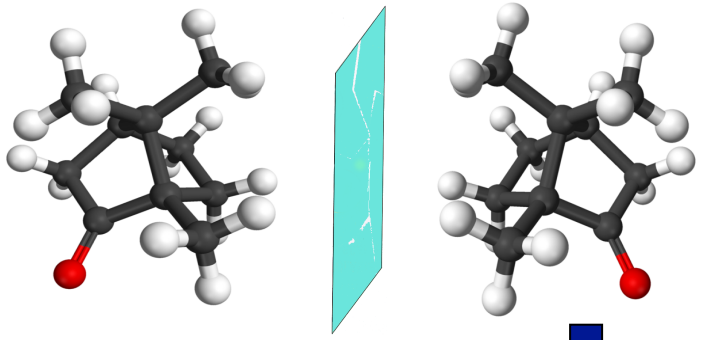
E.Wigner, *Z. Phys.* 43, 624 (1927)

Parity Conservation: Consequences

Camphor $C_{10}H_{16}O$

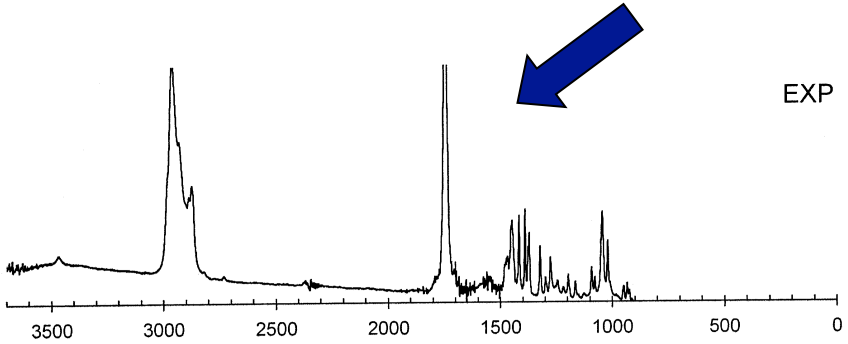
Cinnamomum camphora

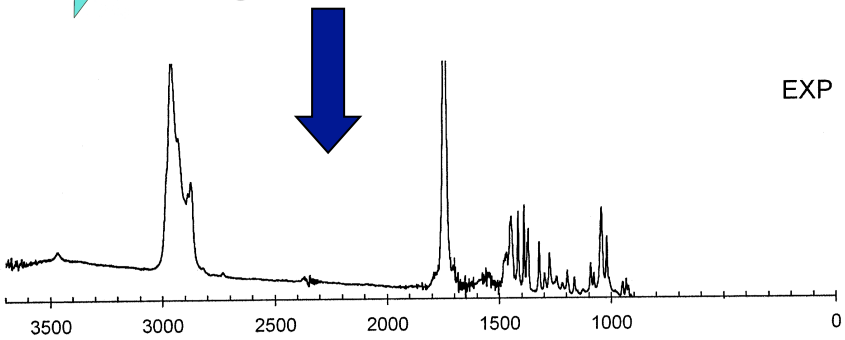




d-camphor

l-camphor





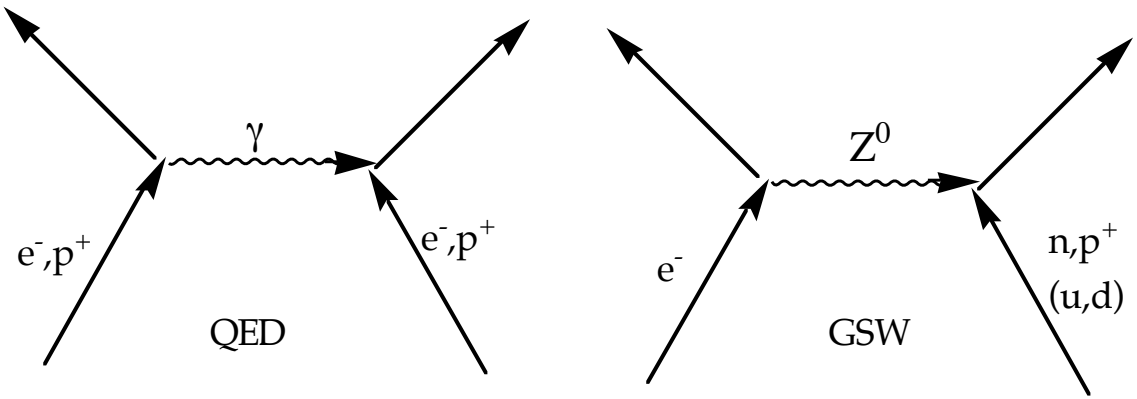
Mirror image symmetry is perfect
Same spectroscopic properties for $|L\rangle$ and $|R\rangle$ in an achiral environment

identical IR spectra

Breaking Mirror Image Symmetry

at the microscopic level

$$\left[P, H_{eN}^{PNC}\right] \neq 0$$

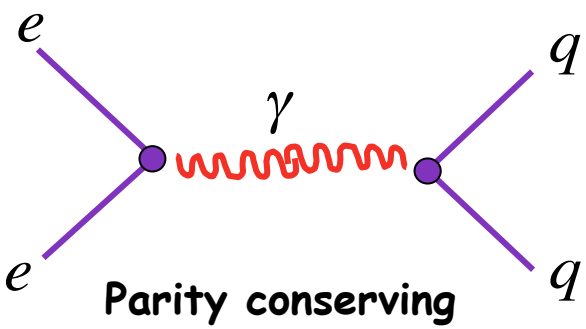


Bouchiat-Hamiltonian: $$H_{eN}^{PNC} = \frac{G_F}{4mc\sqrt{2}} \sum_{i,n} Q_{W,n} \{\boldsymbol{\sigma}_i \boldsymbol{p}_i, \rho_n(\boldsymbol{r}_{in})\}_+$$

G_F= 1.16637 x 10^{-11} MeV^{-2} = 2.22255 x 10^{-14} a.u.

Lee Yang Weinberg Salam Glashow

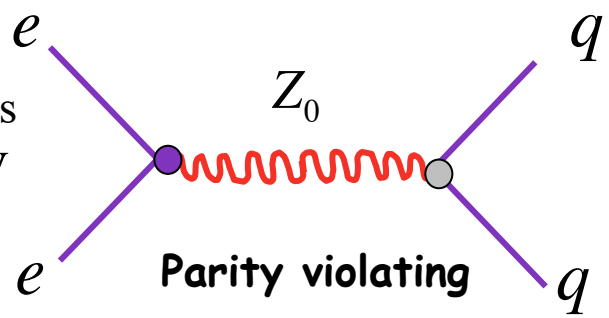
Electroweak Electronic Structure Theory



PV, PNC

Z_0 carries handedness

$M_Z = 91.188$ GeV



W.Greiner, B.Müller, *Gauge Theory of Weak Interactions*, Springer, Heidelberg, 1996.
J.Sapirstein, in *Relativistic Electronic Structure Theory. Part I. Fundamentals*, ed. P.Schwerdtfeger, Elsevier, 2002; pg.352.
F. Halzen, A. D. Martin, *Quarks & Leptons*, Wiley, New York (1984).
J. S. M. Ginges, V. V. Flambaum, *Phys. Rep.* 397, 63 (2004).

$$\gamma_5 = \gamma^5 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} = i\gamma^1\gamma^2\gamma^3\gamma^0$$

Bilinear Covariants:			
$\bar{\psi} = \psi^\dagger \gamma^0$	Scalar	$\bar{\psi}\psi$	+ under P, boson spin 0
$\gamma^\mu = (\beta, \beta\vec{\alpha})$	**Vector**	$\bar{\psi}\gamma^\mu\psi$	− under P, boson spin 1, e.g. $P : \vec{r} \rightarrow -\vec{r}$
	Tensor	$\bar{\psi}\sigma^{\mu\nu}\psi$	boson spin 2
	Axial Vector	$\bar{\psi}\gamma^5\gamma^\mu\psi$	+ under P, boson spin 1, e.g. $P : \vec{L} \rightarrow \vec{L}$
	Pseudoscalar	$\bar{\psi}\gamma^5\psi$	− under P, boson spin 0 $(\vec{L} = \vec{r} \times \vec{p})$

V-A Coupling: $\frac{1}{2}\gamma^\mu(c_V^p - c_A^p\gamma^5)$, c_V^p, c_A^p vertex factors for a particle

$$\hat{H}_{PV} = \frac{G_F}{\sqrt{2}} \sum_N \left[c_1^N \bar{\psi}_e \gamma^\mu \gamma^5 \psi_e \bar{\psi}_N \gamma^\mu \psi_N + c_2^N \bar{\psi}_e \gamma^\mu \psi_e \bar{\psi}_N \gamma^\mu \gamma^5 \psi_N + H_{ee} \right]$$

$G_F = 1.16637 \times 10^{-11}$ MeV^{-2} = 2.22255×10^{-14} a.u.

$$c_1^p = \tfrac{1}{2}\left(1 - 4\sin^2\theta_W\right) \approx 0.02 \quad , \quad c_1^n = -\tfrac{1}{2} \quad , \quad c_2^p = -c_2^n = \tfrac{1}{2} g_A \left(1 - 4\sin^2\theta_W\right) \approx 0.05$$

0.2397(13)

time-like component (A_e, V_N):

$$\Rightarrow \hat{H}_1 \cong \frac{G_F}{\sqrt{2}}\gamma^5\left[Zc_1^p\rho_p(r) + Nc_1^n\rho_n(r)\right] \xrightarrow{\rho_p(r)\approx\rho_n(r)} \hat{H}_1 \cong \frac{G_F}{2\sqrt{2}} Q_W \rho(r)\gamma^5$$

Weak charge $\quad Q_W = -N + Z\left(1 - 4\sin^2\theta_W\right) \approx -N \quad , \quad \int \rho(r) d^3r = 1$

Nuclear spin-dependent part,
space-like component (V_e, A_N):

$$\hat{H}_2 \cong \frac{G_F}{\sqrt{2}}\vec{\alpha}\left[c_2^p \sum_p \vec{\sigma}_p + c_2^n \sum_n \vec{\sigma}_n\right]\rho(r)$$

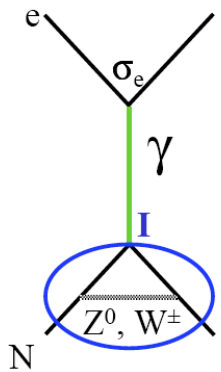
$$\Rightarrow \boxed{H_{PV} = \frac{G_F}{2\sqrt{2}} \underbrace{\sum_{i,M} Q_{W,M}\gamma_i^5 \rho_M(\vec{r}_{iM})}_{\text{NSI}} + \frac{G_F}{\sqrt{2}} \sum_{i,M}\left(f_{NC} + f_{HF} + f_A\right) \underbrace{\vec{\alpha}_i \vec{I}_M \rho_M(\vec{r}_{iM})}_{\text{NSD}} + \ldots}$$

$$f_{NC} = c_2^N \frac{1/2 - K_M}{I_M(I_M+1)} \quad , \quad f_{HF} = \kappa_{HF}/I_M \quad , \quad f_A = \kappa_A \frac{K_M}{I_M(I_M+1)}$$

$$K_M = (-1)^{I-l+1/2}(I_M + 1/2) \quad , \quad \kappa_{HF} = -\tfrac{1}{3} Q_W \frac{\alpha\mu_N}{m_p R_M}$$

anapole moment: $\kappa_A = \propto \mu A^{2/3}$

J. S. M. Ginges, V. V. Flambaum, *Phys. Rep.* 397, 63 (2004).
V. F. Dmitriev, V. B. Telitsin, *Nucl. Phys. A* 674, 168 (2000).



The Nonrelativistic Formalism (Schrödinger Picture)

The unitary transformation from the Dirac- to the Schrödinger picture:

$$H_{tr} = UHU^{-1}, \quad U^{FW} = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \\ -\frac{1}{\sqrt{1+XX^\dagger}} X & \frac{1}{\sqrt{1+XX^\dagger}} \end{pmatrix}$$

$$X = \left(2\mathrm{mc}^2 + E - V\right)^{-1} c\boldsymbol{\sigma p}, \quad \varphi_S = X\varphi_L$$

1) Diagonal perturbation operators f:

$$\begin{pmatrix} V - E + f & c\boldsymbol{\sigma p} \\ c\boldsymbol{\sigma p} & -2\mathrm{mc}^2 + V - E + f \end{pmatrix} \begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = 0$$

Substitution of V by $V+f$ in the power series leads to the following expression for the Pauli-series through a FPFW transformation (in atomic units):

$$\tilde{H}_+ = V + f + \frac{1}{2c^2}\left(c\boldsymbol{\sigma p}\right)^2 - \frac{1}{8c^4}\left[c\boldsymbol{\sigma p}, \left[c\boldsymbol{\sigma p}, V + f\right]\right] - \frac{1}{8c^6}\left(c\boldsymbol{\sigma p}\right)^4 + \ldots \quad \Longrightarrow \quad f^S = f + \frac{1}{8c^2}\Delta f + \ldots$$

Neglect of these higher order terms leads to the so-called picture change error which becomes important for heavy elements.

2) Off-diagonal perturbation operators f, e.g. by $\gamma^5 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$:

$$\begin{pmatrix} V - E & c\boldsymbol{\sigma p} + f \\ c\boldsymbol{\sigma p} + f & -2\mathrm{mc}^2 + V - E \end{pmatrix} \begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = 0$$

$$\tilde{H}_+ = V + \frac{1}{2c^2}\left(c\boldsymbol{\sigma p} + f\right)^2 - \frac{1}{8c^4}\left[c\boldsymbol{\sigma p} + f, \left[c\boldsymbol{\sigma p} + f, V\right]\right] - \frac{1}{8c^6}\left(c\boldsymbol{\sigma p} + f\right)^4 + \ldots \quad \Longrightarrow \quad f^S = \frac{1}{2mc}\left[\boldsymbol{\sigma p}, f\right]_+ + \ldots$$

$$\longrightarrow \quad H_{eN}^{PNC} = \frac{G_F}{4mc\sqrt{2}} \sum_{i,M} Q_{W,n} \left\{\boldsymbol{\sigma}_i \boldsymbol{p}_i, \rho_M(\boldsymbol{r}_{iM})\right\}_+$$

Bouchiat-Hamiltonian

Preliminary Results for the Anapole Moment

Victor V. Flambaum

Miroslav Ilias

Kyle Beloy

Anastasia Borschevsky

$$H^a_{PV} = \frac{G_F}{\sqrt{2}} \sum_{i,M} \kappa_M \frac{\vec{\alpha}_i \vec{I}_M}{I_M} \rho_M(\vec{r}_{iM})$$

diatomic molecule MX, Hund's case b), $^2\Sigma$ state, preferably light nucleus X with I=0:

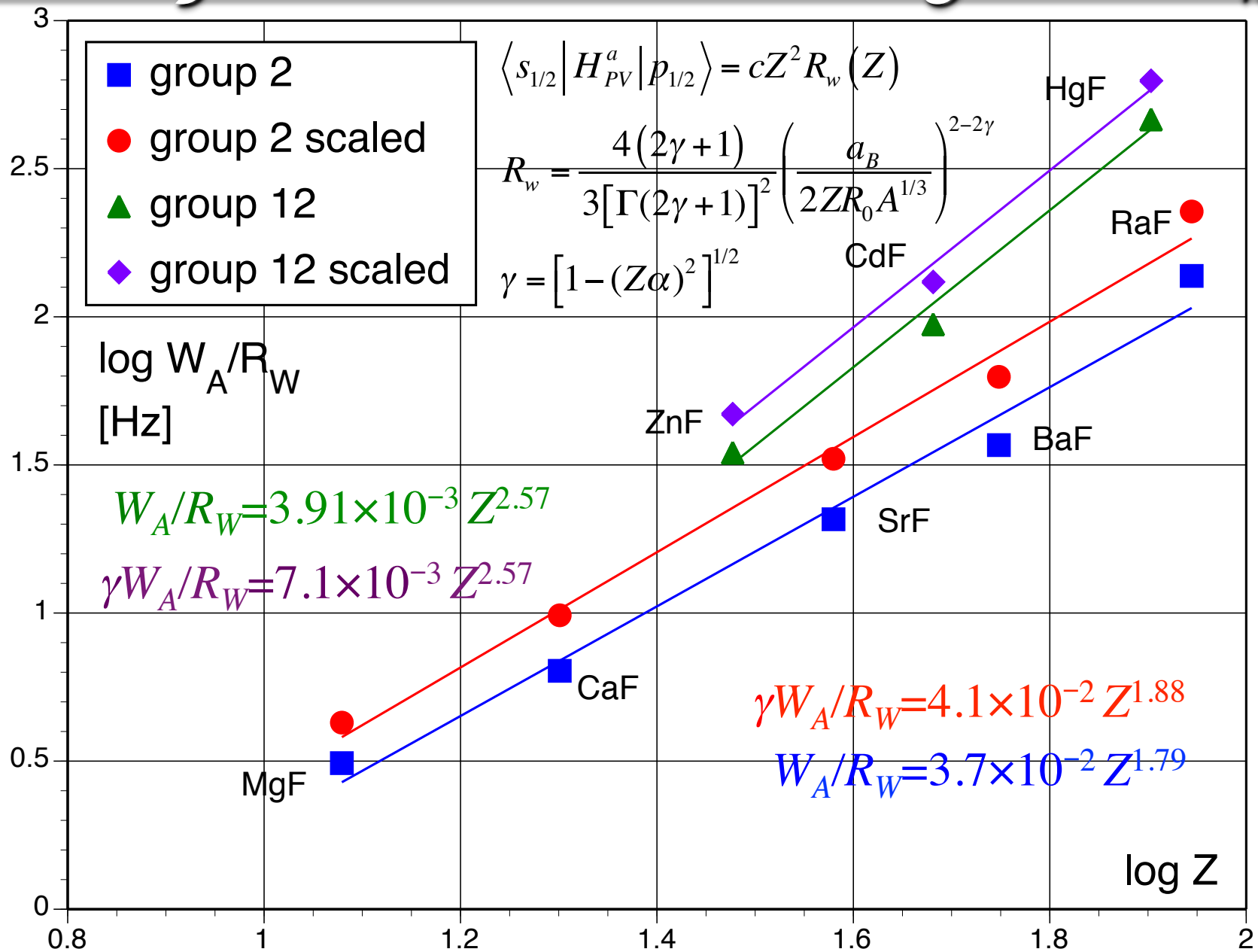
$$\hat{H}^{eff}_{PV} \cong \kappa_M W_A \frac{\left(\vec{n} \times \vec{S}\right)\vec{I}_M}{I_M}$$

DHF results, Gaussian nucleus, kinetic balance

Molecule	W_A [Hz]	γW_A [Hz]	Previous results [Hz]
MgF	3.8	4.9	
CaF	8.0	10.6	
SrF	40.7	51.8	65 (DeMille 2008)
BaF	112.9	146.0	135 (Nayak 2009, DF); 160 (Nayak 2009, CI); 164 (DeMille 2008); 111 (Kozlov 1997, RECP+SCF); 107 (Kozlov 1997,RECP+RASSCF); 181 (Kozlov 1997,RECP+SCF+EO).
RaF	1364	1641	1360 (Berger 2010, HF+spin. pol.)
YbF	527	596	729 (DeMille 2008) 484 (Titov 1996, RECP+SCF)
ZrN	60.0	68.5	99
LaO	149	180	222 (DeMille 2008)
MgBr	-8	-16	18 (DeMille 2008)
HgF	3025	3162	

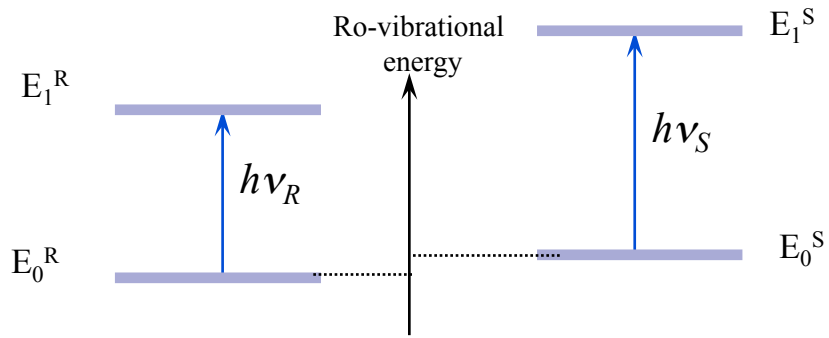
γ=1-2 (from atomic RPA+Brückner, V. Dzuba)

Anapole Moment Z-Scaling with R_W



Parity Violation in Chiral Molecules

1975: Due to parity violation, two enantiomers do not have the same absorption spectrum (first time suggested in 1975 by V. S. Letokhov: *Phys. Lett.* 53A, 275 (1975))



$$\nu_R \neq \nu_S$$

$$\Delta\nu_{PV} = \nu_R - \nu_S \neq 0$$

1976 : Proposition to search for parity violation effect in CHFClBr spectrum [O.N. Kompanets et al., *Opt. Commun.* 19, 414 (1976)]

CHFClBr

Experimental attempts to measure PV in chiral molecules:

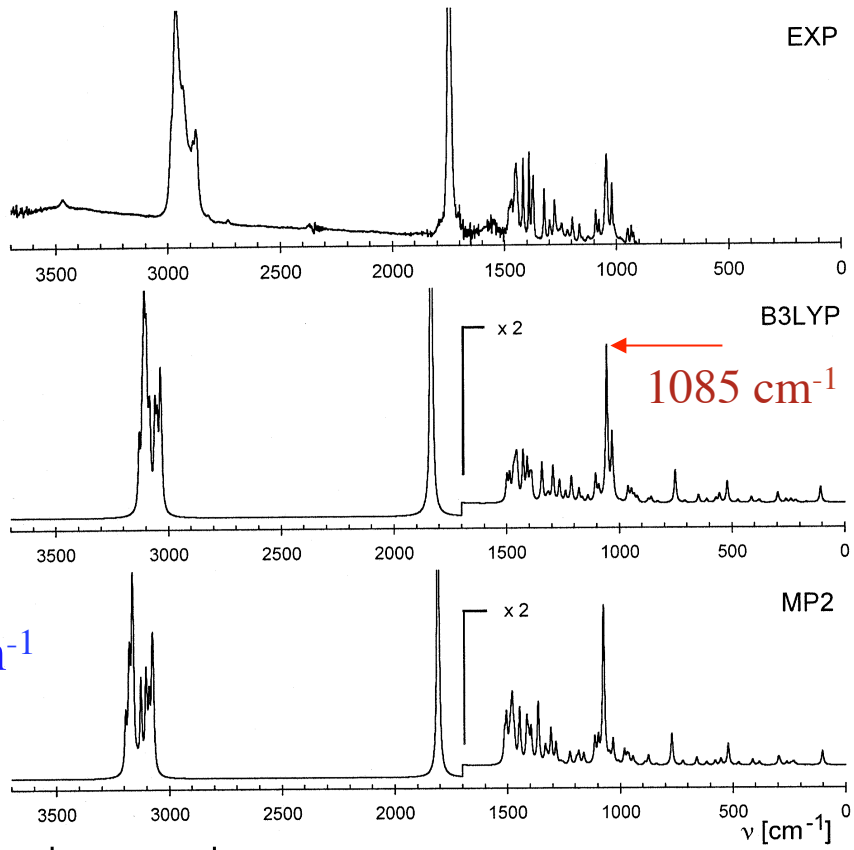
Vib-Rot Spectroscopy:	Ch.Chardonnet, Ch.J.Bordé, C. Daussy (Paris)
Mössbauer/NMR Spectroscopy:	R.N.Compton (Tennessee)
Dynamics in excited electronic states:	M.Quack (Zürich)
Spin-spin Coupling:	Dmitry Budker (Berkeley)
Electronic Spectroscopy	Melanie Schnell (Hamburg)

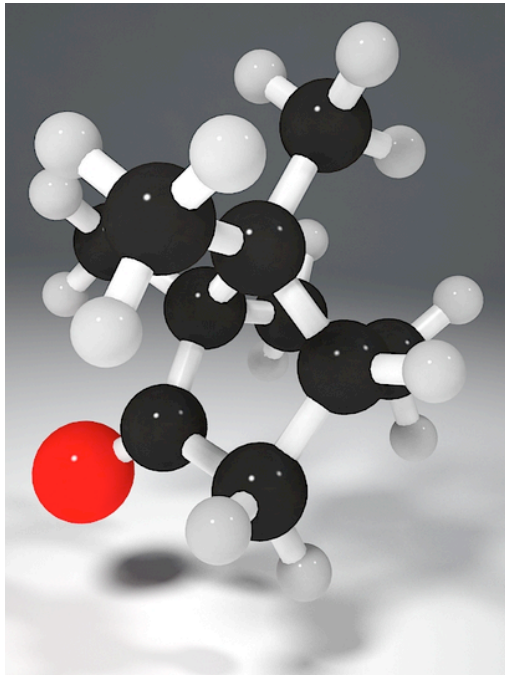
Reviews on Parity Nonconservation in Chiral Molecules

- P. Schwerdtfeger, in *Computational Spectroscopy*, J. Grunenberg (ed.), Wiley (2010); pgs. 201-221.
- B. Darquié, C. Stoeffler, S. Zrig, J. Crassous, P. Soulard, P. Asselin, T. R. Huet, L. Guy, R. Bast, T. Saue, P. Schwerdtfeger, A. Shelkovnikov, C. Daussy, A. Amy-Klein, C. Chardonnet, *Chirality* 22, 870-884 (2010).
- M. Quack, J. Stohner, M. Wileke, *Annu. Rev. Phys. Chem.* 59, 741 (2008).
- J. Crassous, Ch. Chardonnet, T. Saue, P. Schwerdtfeger, *Org. Biomol. Chem.* 3, 2218–2224 (2005).
- R. Berger, in *Relativistic Electronic Structure Theory. Part 2: Applications*, P. Schwerdtfeger (ed.), Elsevier, Amsterdam, 2004, pgs. 188-288.
- J. Crassous, F. Monier, J.-P. Dutasta, M. Ziskind, C. Daussy, C. Grain and C. Chardonnet, *ChemPhysChem* 4, 541–548 (2003).
- M. Quack, *Angew. Chem. Int. Ed.* **41**, 4618–4630 (2002).
- C. Chardonnet, C. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, C. J. Bordé, in *Parity violation in atomic physics and electron scattering*, B. Frois and M.A. Bouchiat (eds.), World Scientific, New-York, 1999, pgs. 325–355.
- M. Quack, *Angew. Chem. Int. Ed. Engl.* **28**, 571–586 (1989).

First attempt to measure PNC effects in Chiral Compounds

First exp. attempt: E. Arimondo, P. Glorieux, T. Oka, *Opt. Commun.* 23, 369 (1977). 9.22 μm R(28) CO_2 laser line for the vibrational excitation of *d*- and *l*-camphor: Negative outcome: $\Delta\nu < 300$ kHz





1 Hz = 3.3×10^{-11} cm^{-1}
= 4.0×10^{-13} kJ/mol
= 4.1×10^{-15} eV

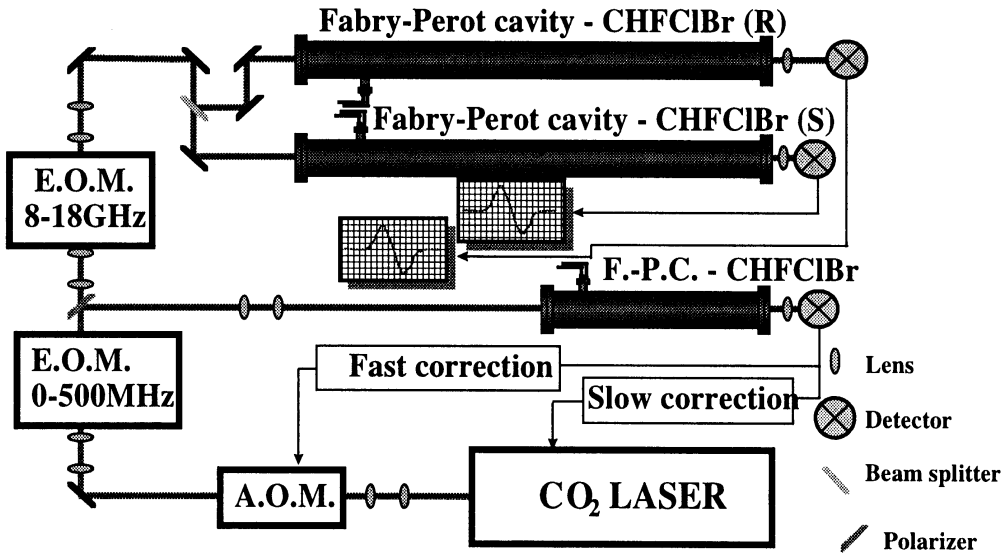
$\longrightarrow |\Delta\nu/\nu| < 10^{-8}$ (theoret: $|\Delta\nu/\nu| = 10^{-19}$)

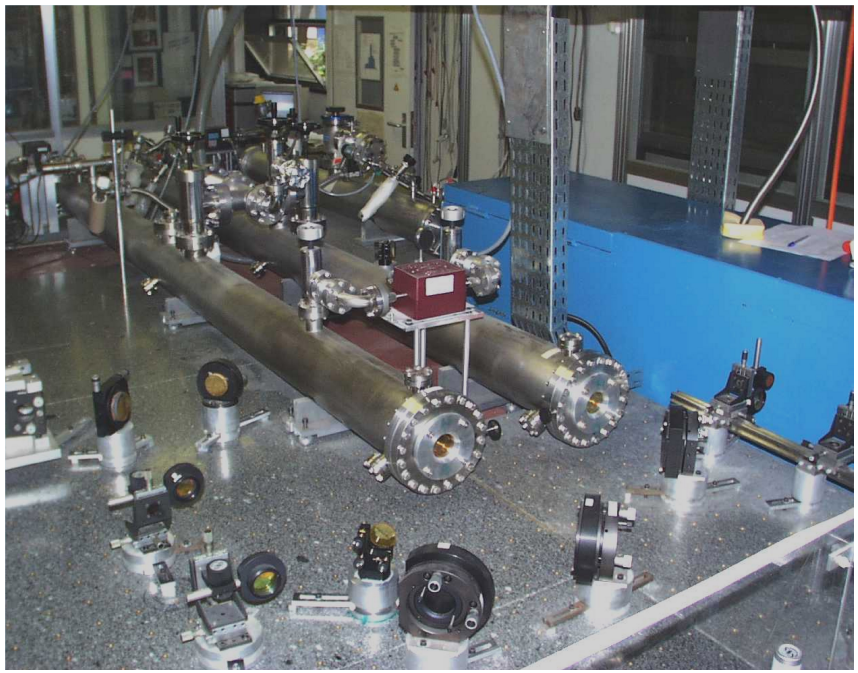
P.Schwerdtfeger, A.Kühn, R.Bast, J.K.Laerdahl, F.Faglioni, P.Lazzeretti, *Chem. Phys. Lett.* 383, 496 (2004)

Nonlinear Laser Spectroscopy on Vibrational Transitions in CHFClBr *and* CHFCII *- The Paris Experiments 1999/2000*

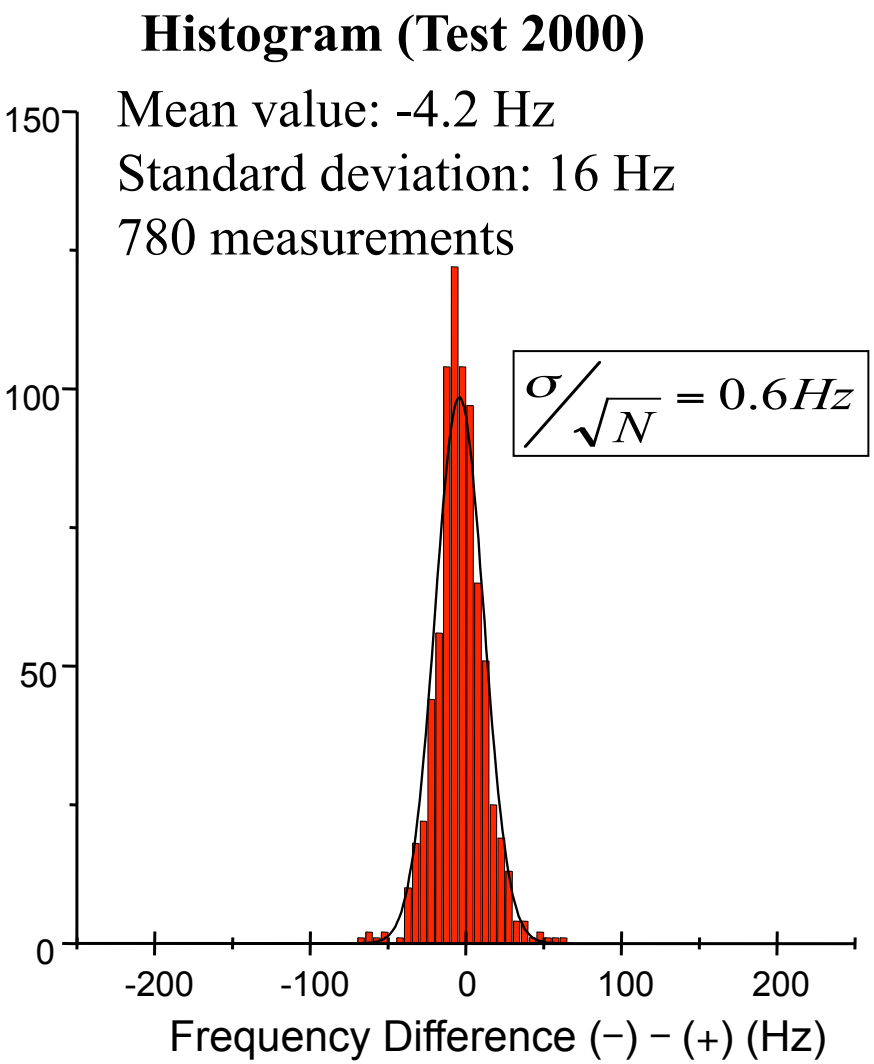
Ch. Chardonnet and co-workers (Paris)

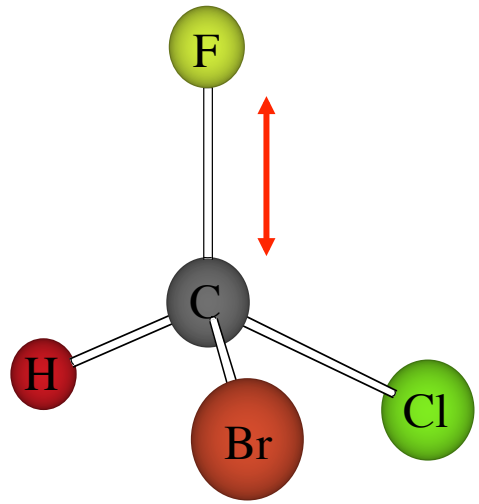
Last experiments done by Ch. Daussy et al., *Phys. Rev. Lett.* 83, 1554 (1999); M. Ziskind et al, *Eur. Phys. J. D* 2, 219 (2002): Strong ν_4 CF stretching mode which matches the R(14)-branch of the 9.4 μm CO_2 laser band (1071 cm^{-1}). Resolution: a few Hz.

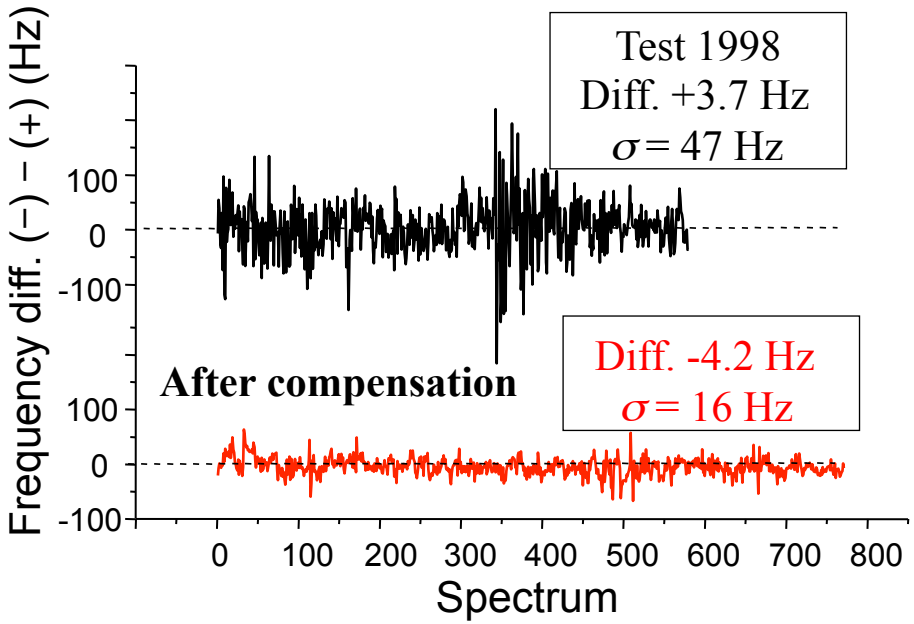




Results for CHFClBr







C. Daussy et al., *Phys. Rev. Lett.* 83, 1554 (1999)
M. Ziskind et al., *Euro. Phys. J. D* 20, 219 (2002)

CHFClBr - Results

Anharmonic Vibrational Analysis

Quartic *q*-FF, aug-cc-pvtz basis sets for all atoms, VPT

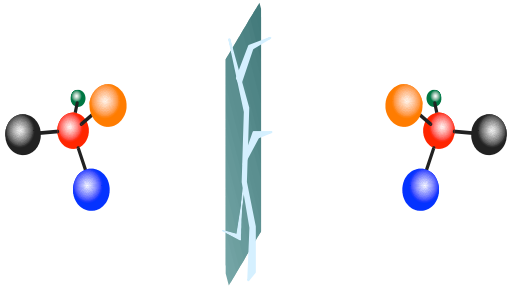
Property	Mode	MBPT2 Harmonic	MBPT2	B3LYP	PW91	CCSD(T) +AH+BSI	Exp.
E_{ZPVE}		4668.5	4621.6	4494.1	4352.7	4585.4	-
$\nu^{(1)}$	CH str	3185.8	3053.6	3011.6	2930.9	3032.8	3025.5
$\nu^{(2)}$	FCH bend	1339.4	1309.4	1293.7	1238.0	1304.6	1306.2
$\nu^{(3)}$	(Cl,Br)CH bend	1246.5	1224.1	1185.3	1137.5	1214.3	1202.8
$\nu^{(4)}$	CF str	1093.5	1065.3	1047.2	1008.2	1073.6	1077.2
$\nu^{(5)}$	CCl str	808.7	793.5	731.1	712.8	779.4	787.0
$\nu^{(6)}$	CBr str	682.6	675.1	636.2	620.6	661.9	663.6
$\nu^{(7)}$	FCCl bend	431.7	427.4	413.6	404.4	421.7	425.2
$\nu^{(8)}$	FCBr bend	319.7	316.4	302.9	293.7	312.4	313.0
$\nu^{(9)}$	ClCCl bend	228.9	227.2	215.1	209.0	222.9	223.6
rms			10.2	20.8	58.7	4.2	-

G. Rauhut, V. Barone, P. Schwerdtfeger, *J. Chem. Phys.* 125, 054308 (2006).
Exp. Values from A. Beil, H. Hollenstein, O. L. Monti, M. Quack, J. Stohner, *J. Chem. Phys.* 113, 2701 (2000).

C-F *Stretching frequencies for chiral methane derivatives*

from Dirac-Hartree-Fock results

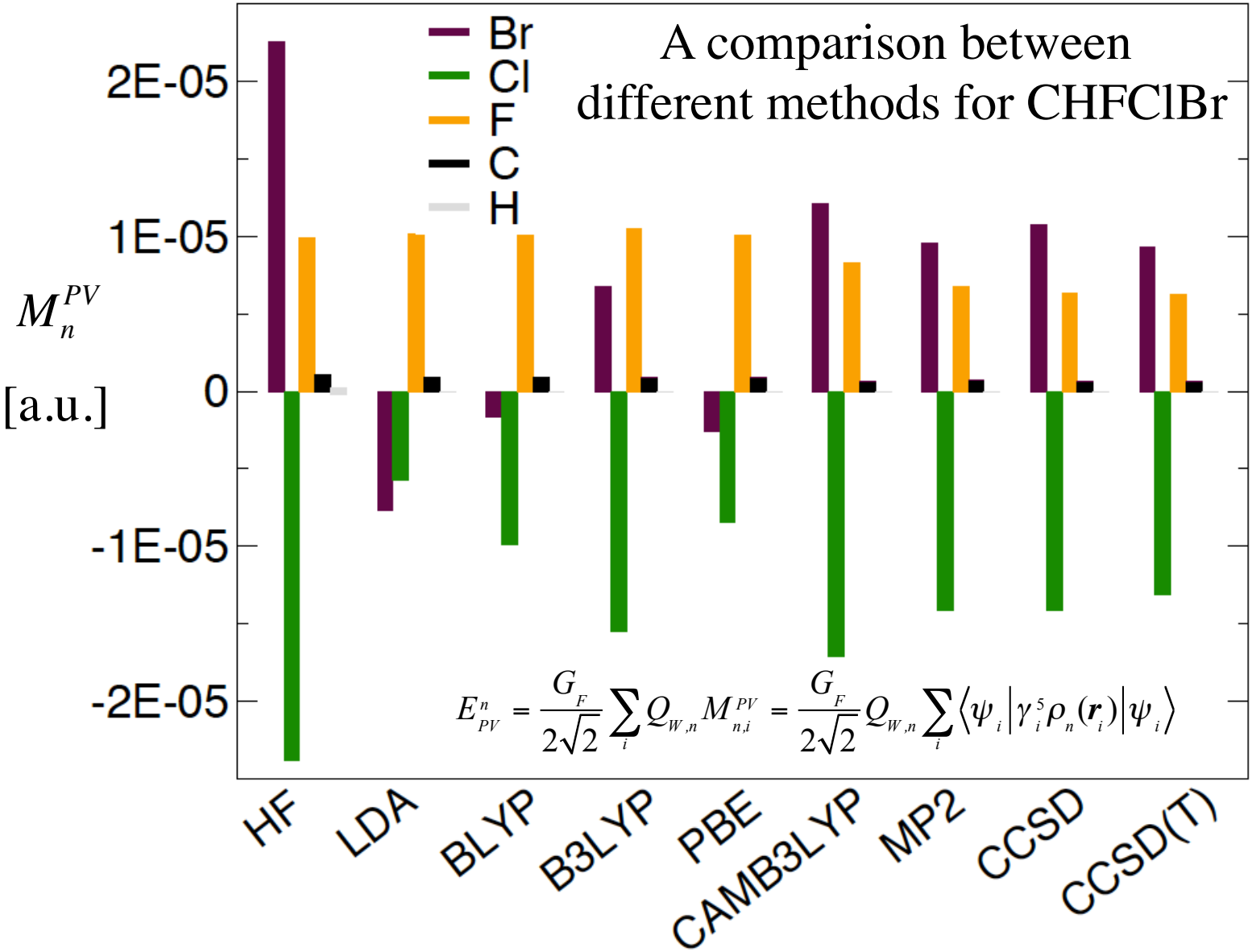
1 Hz = 3.3×10^{-11} cm^{-1}
= 4.0×10^{-13} kJ/mol
= 4.1×10^{-15} eV



	ω_e (GHz)	$x_e\omega_e$ (GHz)	ω_{PV} (mHz)	ν_{PV} (mHz)	ΔE_{PV} (mHz)
CHFClBr					35.0
C-F	36,000	270	0.9	-1.0	
C-Cl	25,900	54	-2.4	-3.5	
C-Br	21,500	57	0.2	0.5	
CHFBrI					1047
C-F	35,300	280	15.7	-17.9	
C-Br	22,800	18	-55.3	-90.0	
C-I	18,300	6	0.2	3.9	
CHClBrI					659
C-Cl	24,600	120	7.6	-19.5	
C-Br	21,600	9	-33.6	-39.5	
C-I	16,700	3	-1.6	-0.9	

J.K.Laerdahl, P.Schwerdtfeger, H.M.Quiney, *Phys. Rev. Lett.* 84, 3811 (2000)
P. Schwerdtfeger, J.K.Laerdahl, C. Chardonnet, *Phys. Rev. A* 65, 042508 (2002)

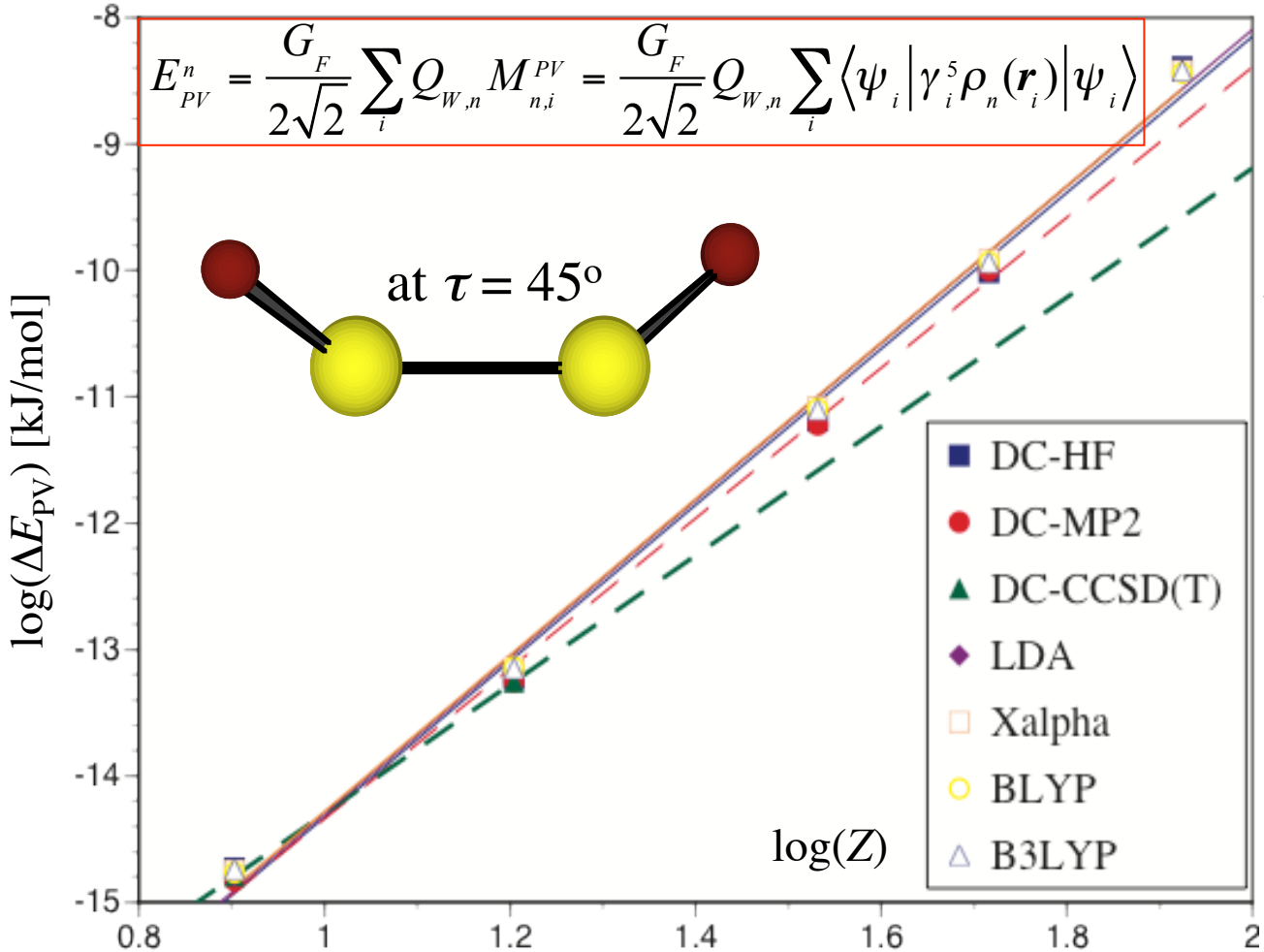
The chiral center does not yield max PV



Moving towards heavier elements: the Z^5-scaling law

DHF and DKS calculations on H_2O_2, H_2S_2, H_2Se_2, H_2Te_2, and H_2Po_2

$$E_{PV}^{n} = \frac{G_F}{2\sqrt{2}} \sum_i Q_{W,n} M_{n,i}^{PV} = \frac{G_F}{2\sqrt{2}} Q_{W,n} \sum_i \langle \psi_i | \gamma_i^5 \rho_n(\boldsymbol{r}_i) | \psi_i \rangle$$



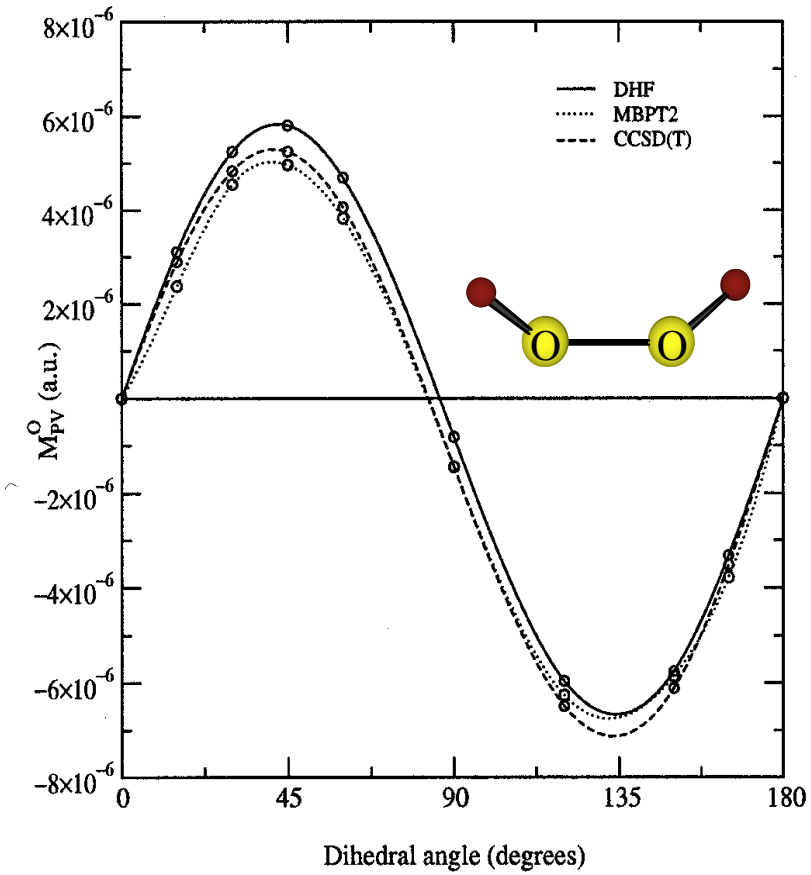
$$\Delta E_{PV} = cZ^{\gamma}$$

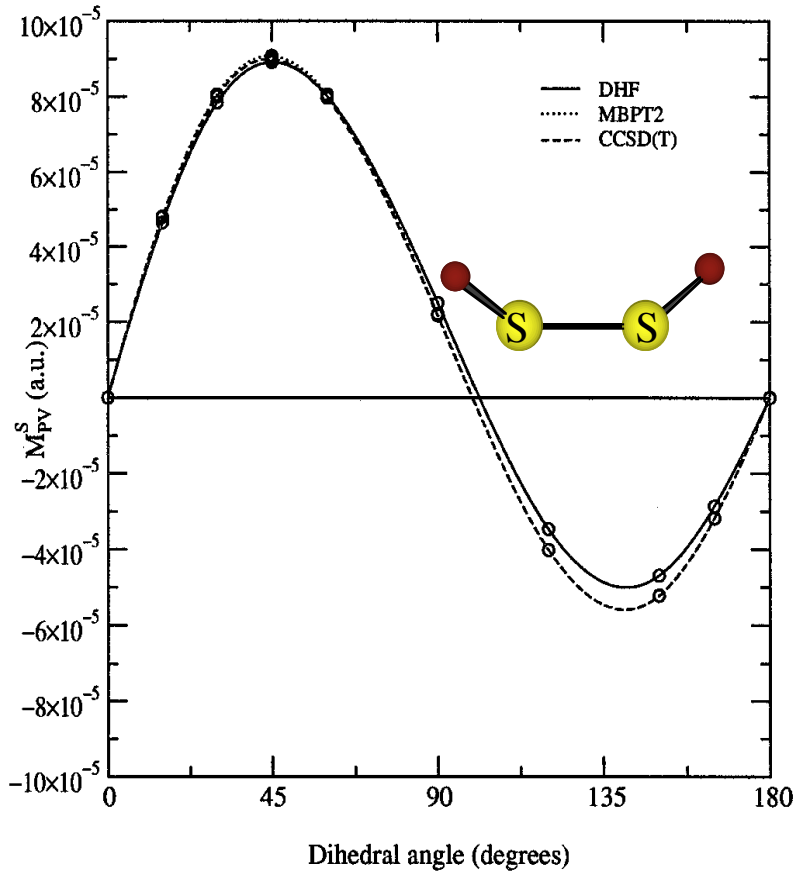
Method	c [kJ/mol]	γ
HF	3.1×10^{-21}	6.18
MP2	5.1×10^{-21}	5.95
LDA	3.1×10^{-21}	6.21
Xα	3.4×10^{-21}	6.19
BLYP	3.4×10^{-21}	6.18
B3LYP	3.5×10^{-21}	6.17
CCSD(T)	3.9×10^{-20}	5.11

only two values

J. K. Laerdahl, P. Schwerdtfeger, *Phys. Rev. A* 60, 4439 (1999). J. Thyssen, J. K. Laerdahl, P. Schwerdtfeger, *Phys. Rev. Lett.* 85, 3105 (2000); J. N.P. van Stralen, L. Visscher, C. V. Larsen, and H. J. Aa. Jensen, *Chem. Phys.* 311, 81 (2005).
More detailed analysis see: R. Bast, A. Koers, A. S. P. Gomes, M. Iliaš, L. Visscher, P. Schwerdtfeger, T. Saue, *Phys. Chem. Chem. Phys.* 13, 864 (2011).

Dependence on the HXXH torsional angle



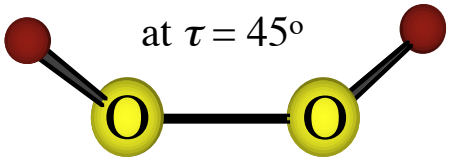


Chirality $\not\rightleftarrows$ Nonzero E_{PV}

How accurate is DHF?

+ Basis set convergence, Electron correlation, missing Breit +QED interactions, V_e-A_e Coupling

$$E_{PV}^{n} = \frac{G_F}{2\sqrt{2}} \sum_i Q_{W,n} M_{n,i}^{PV} = \frac{G_F}{2\sqrt{2}} Q_{W,n} \sum_i \langle \psi_i | \gamma_i^5 \rho_n(\boldsymbol{r}_i) | \psi_i \rangle \longrightarrow \Delta_{cor} M_n^{PV} = \left. \frac{\partial E_{cor}}{\partial \lambda} \right|_{\lambda=0}$$



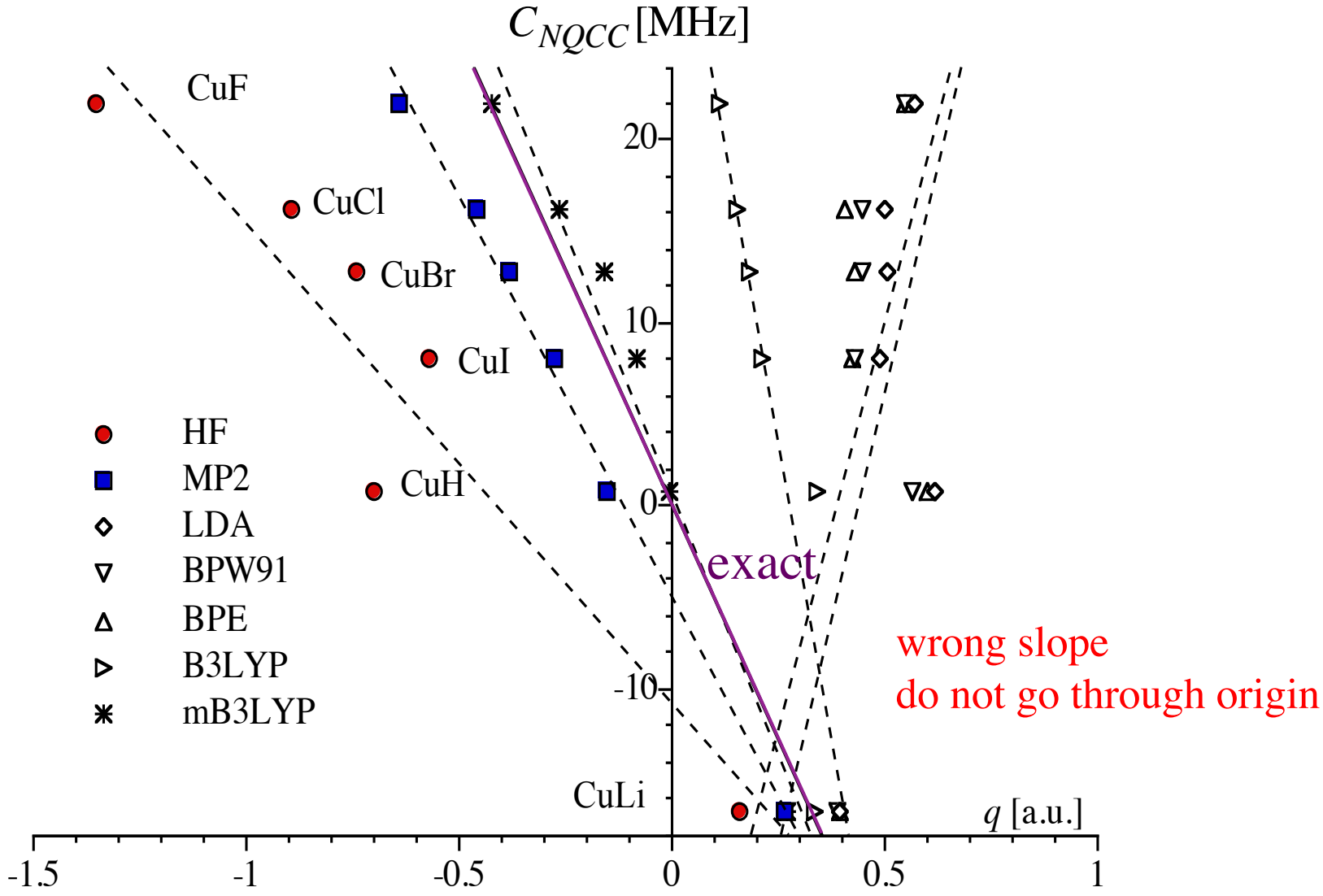
$M_{n=O}^{PV}$ λ	DHF	KR-MP2	KR-CCSD(T)
0.1	4.313×10^{-5}	3.651×10^{-5}	3.836×10^{-5}
0.01	5.895×10^{-6}	5.044×10^{-6}	5.330×10^{-6}
0.001	5.801×10^{-6}	4.963×10^{-6}	5.245×10^{-6}
0.0002	5.801×10^{-6}	4.963×10^{-6}	5.246×10^{-6}
analytic	5.801×10^{-6}	-	-

Compare to real λ: ~ -10^{-14} to -10^{-12} (!)

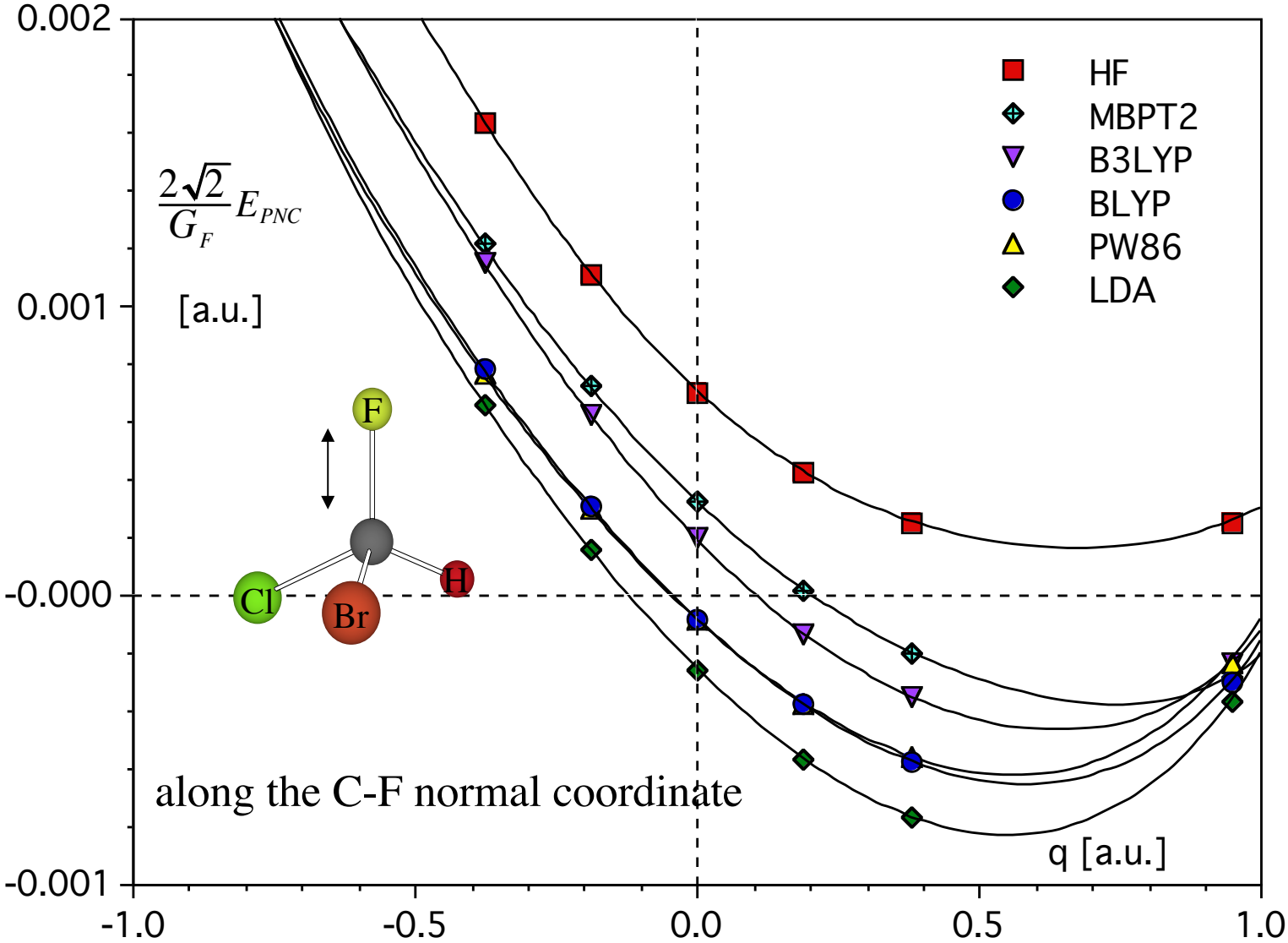
J.Thyssen, J.K.Laerdahl, P.Schwerdtfeger, *Phys. Rev. Lett.* 85, 3105 (2000).

Worst case scenario for DFT

Cu EFG vs. measured NQCC for copper halides (^{63}Cu)

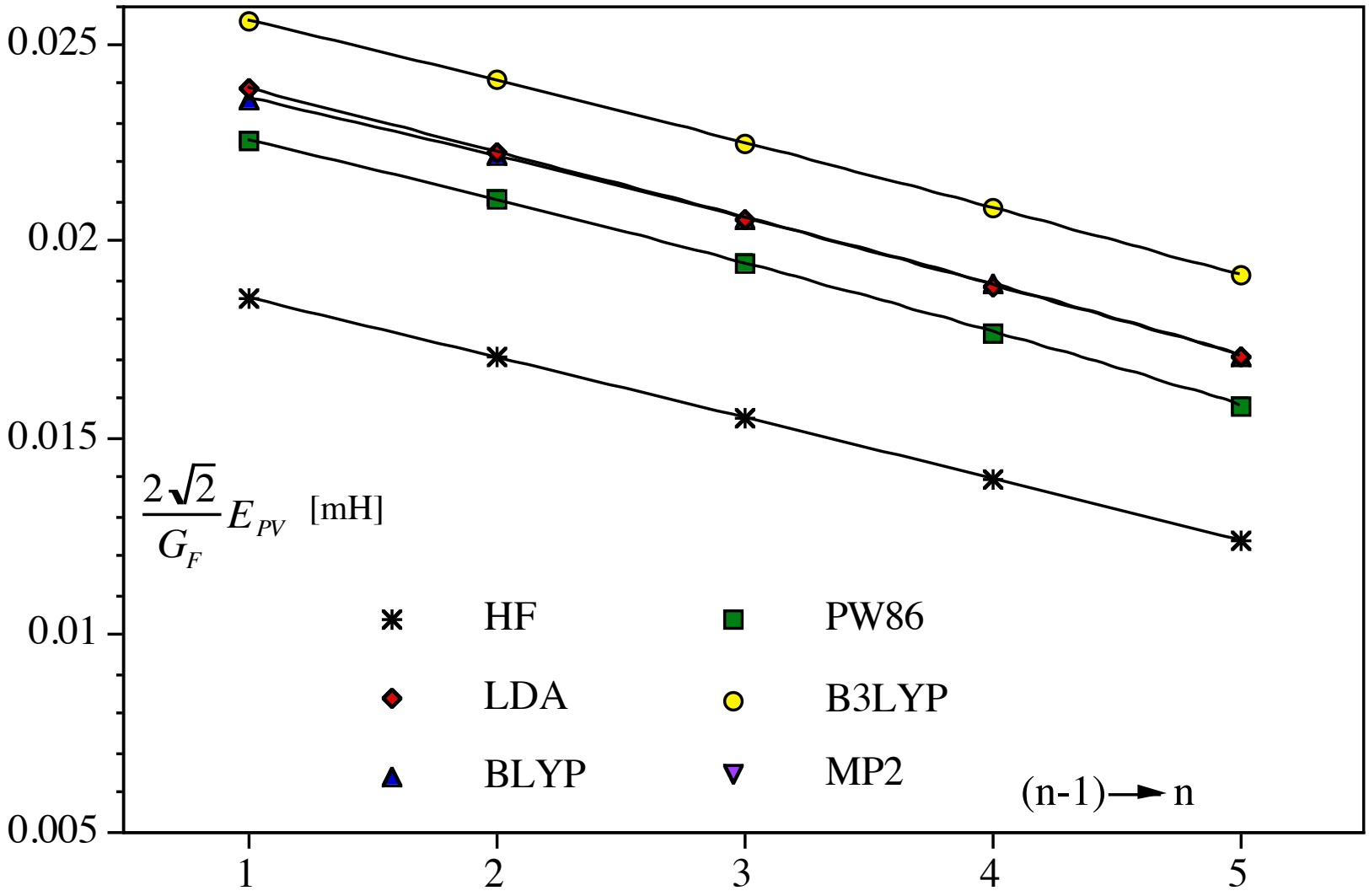


How accurate is DFT for PV?



P. Schwerdtfeger, T. Saue, J. N. P. van Stralen, L. Visscher, *Phys. Rev. A* 71, 012103 (2005).

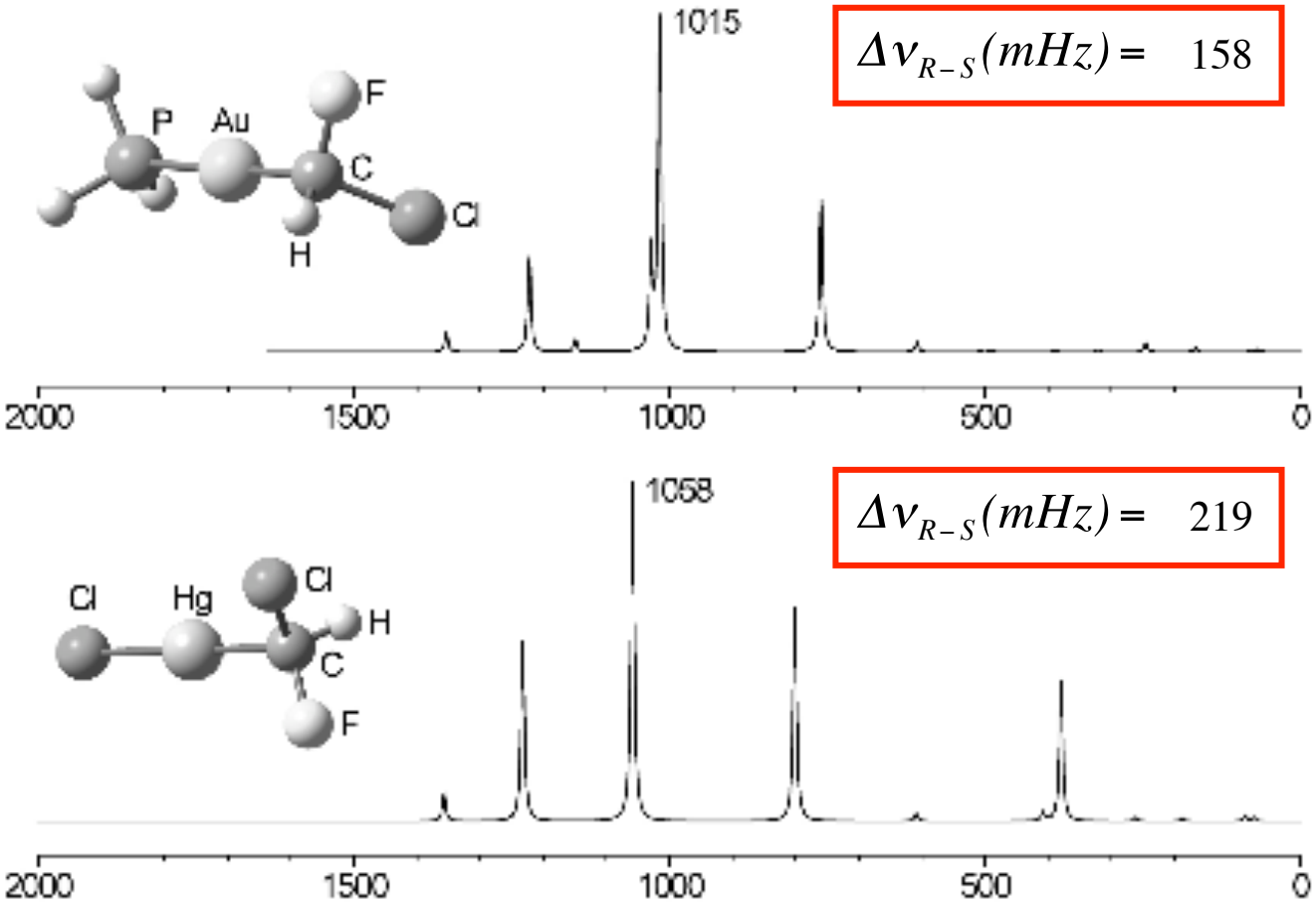
NB: Vibrational Transitions remain basically unaffected



The Search for a better candidate: Using the Z^5-law

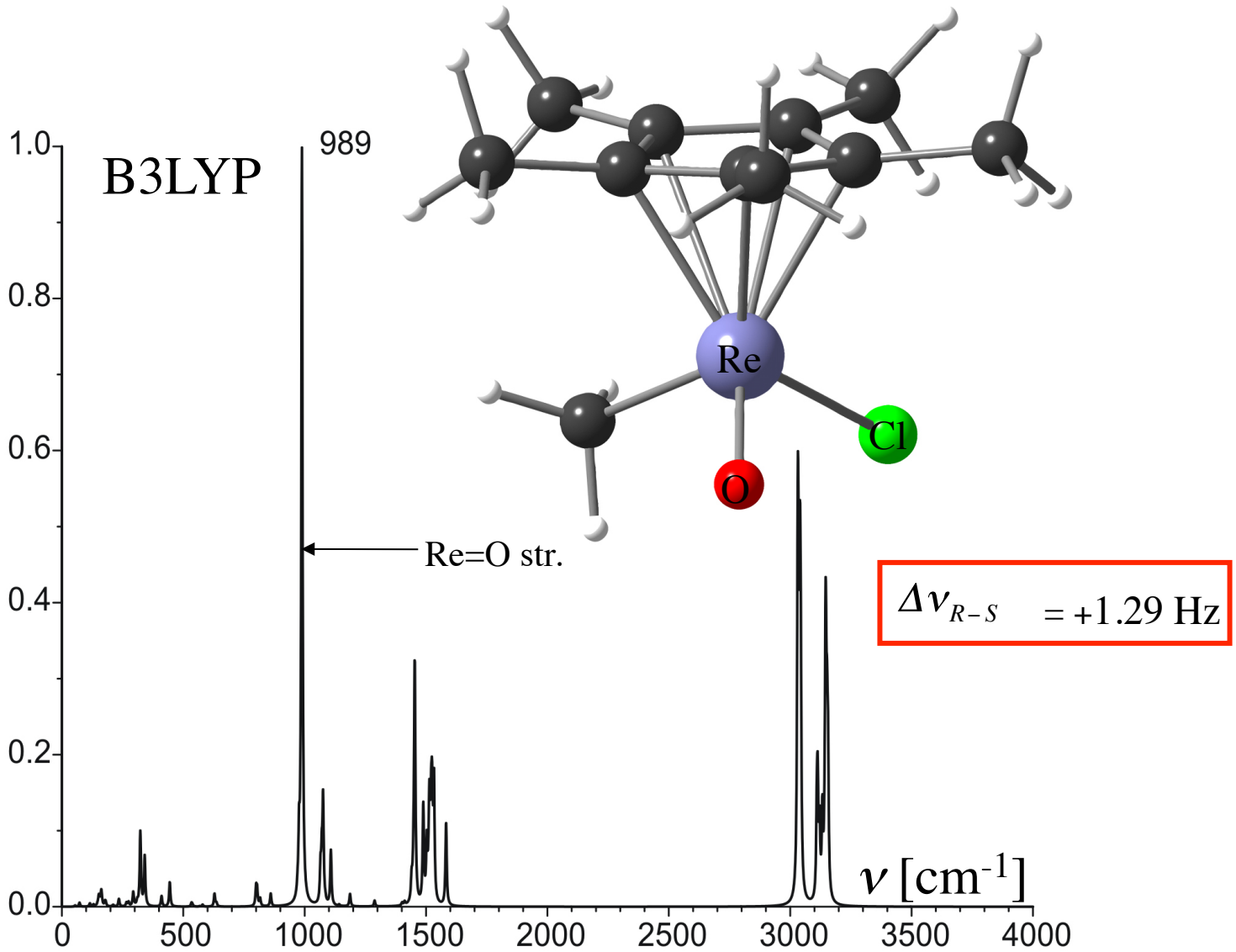
Moving towards the 1 Hz accessible region

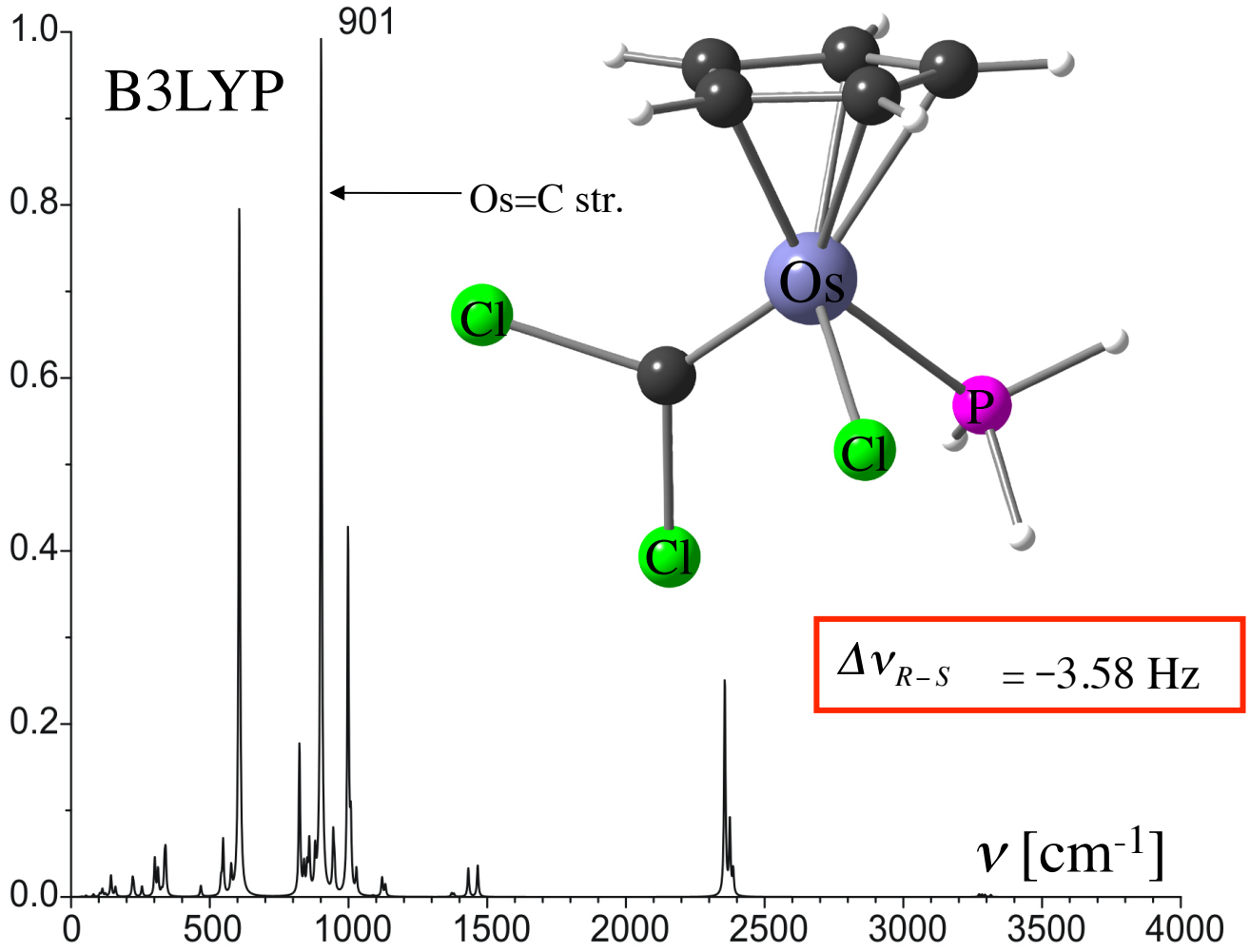
R. Bast, P. Schwerdtfeger, *Phys. Rev. Lett.* 91, 023001-1-3 (2003).



➡ Two orders of magnitude improvement (NB: 2 *mHz* for CHFClBr)

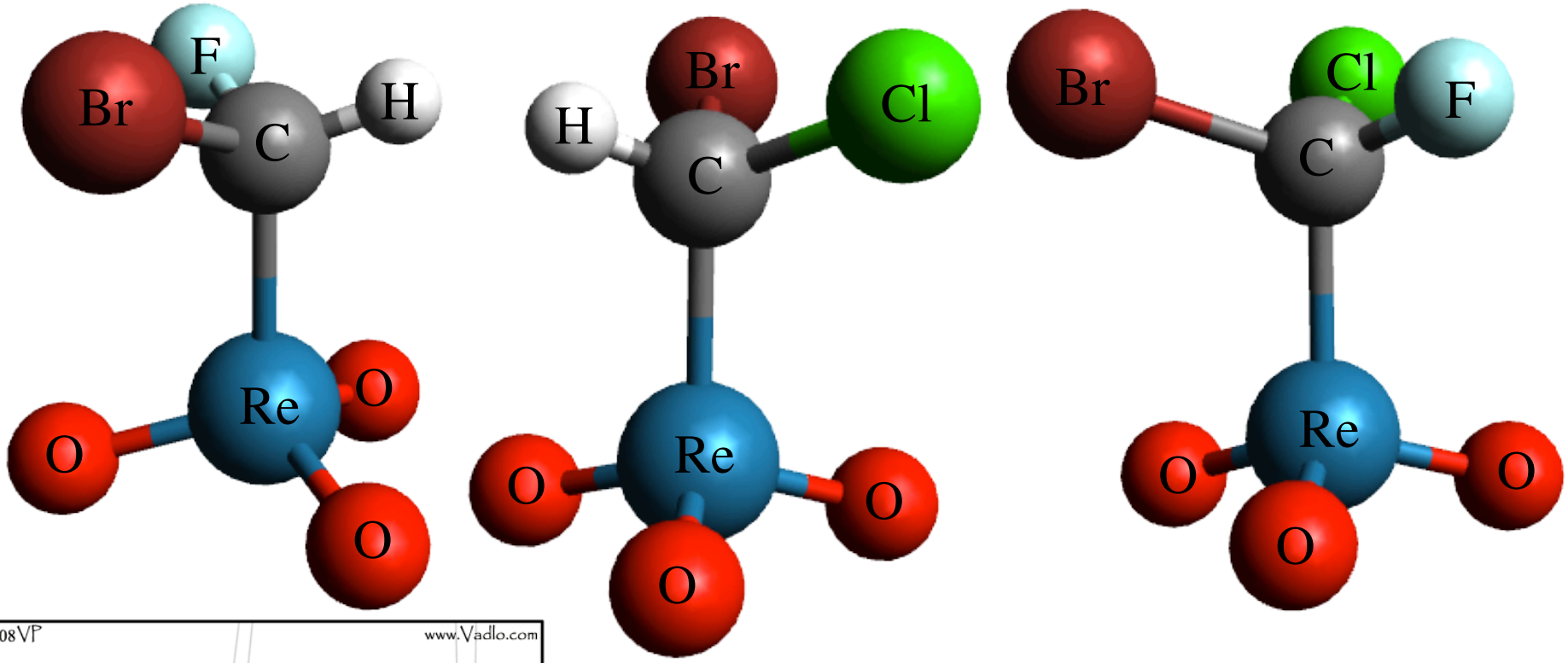
The Search for a better candidate: Stable Compounds

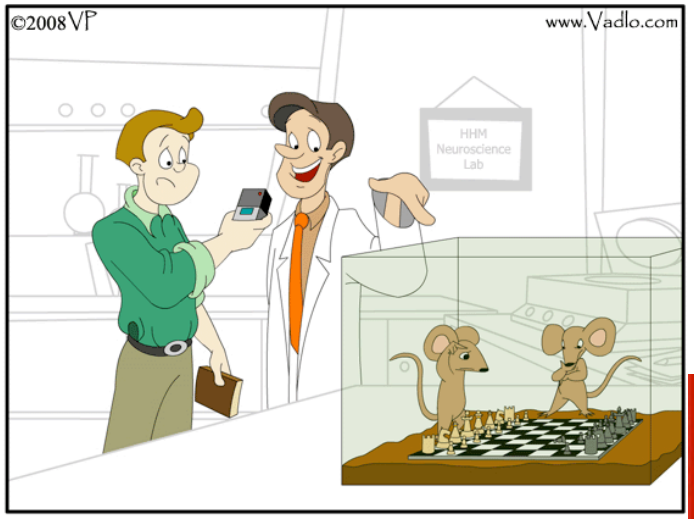




P. Schwerdtfeger, R. Bast, *J. Am. Chem. Soc.* 126, 1652-1653 (2004).
F. De Montigny, R. Bast, A. S. Pereira Gomes, G. Pilet, N. Vanthuyne, C. Roussel, L. Guy, P. Schwerdtfeger, T. Saue, J. Crassous, *Phys. Chem. Chem. Phys.* 12, 8792-8803 (2010).

New chiral methyl-trioxorhenium compounds





This is our director's pet project.

The French - New Zealand collaboration

Jeanne Crassous (Rennes):

to be synthesized

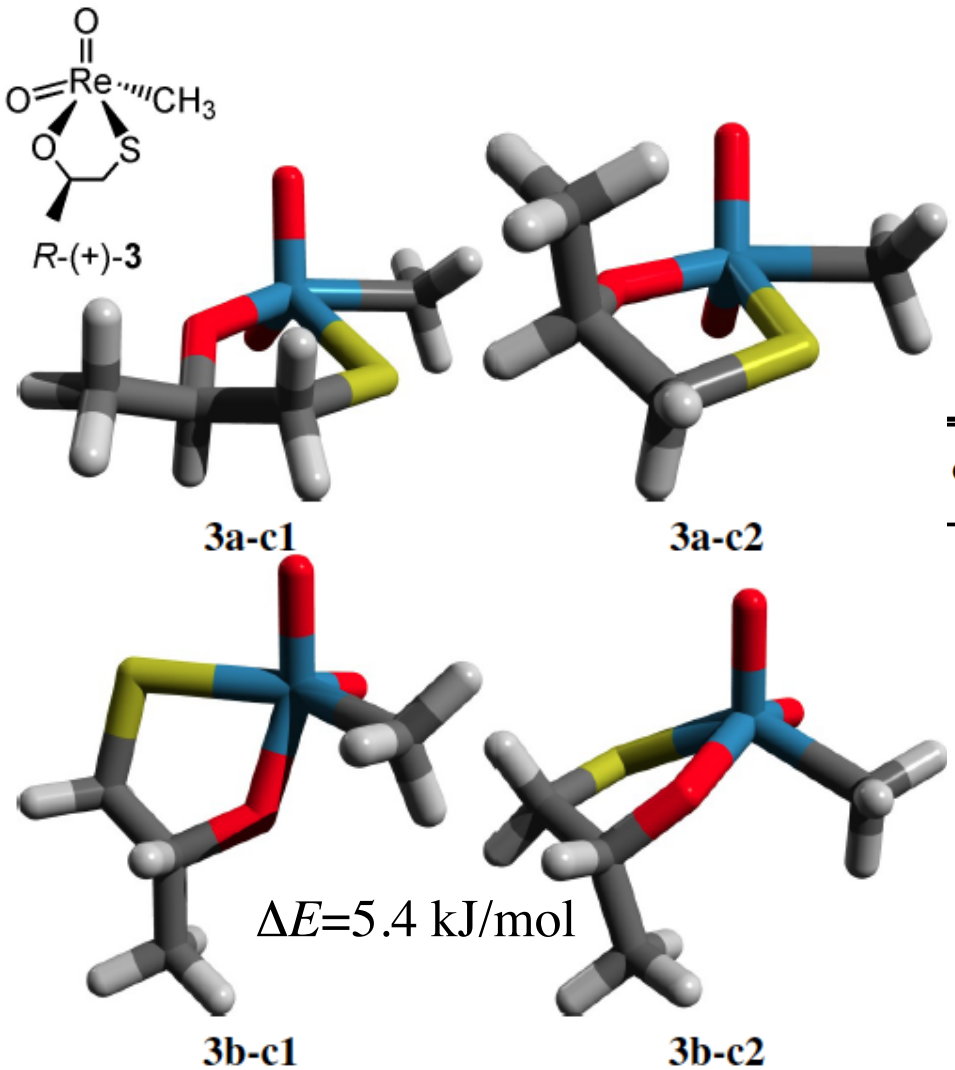
CTCP Centre *for* Theoretical Chemistry *and* Physics

Université Paul Sabatier TOULOUSE III

UNIVERSITÉ DE RENNES 1

LPL Laboratoire de physique des lasers

A very recent paper from the Crassous group



Calculated reduced masses (in amu), vibrational transition frequencies (in cm^{-1}) of the anti-symmetric and symmetric Re=O stretches for the conformers 3a-c1 and 3a-c2, with corresponding Dirac-Coulomb Hamiltonian PV fundamental transition frequency differences $\Delta\nu_{0\rightarrow1}$ (in Hz).

Conformer	Mode	Method	Red. mass	Harmonic	Fundamental	PV shift
3a-c1	asym	HF	14.2074	1106	1102	–0.211
		B3LYP	15.7268	986	982	0.078
		PBE	15.8522	951	944	0.195
	sym	HF	8.7326	1174	1165	0.344
		B3LYP	12.8095	1022	1010	0.150
		PBE	14.8015	980	968	0.036
3a-c2	asym	HF	15.2424	1106	1102	0.219
		B3LYP	15.7515	985	981	–0.119
		PBE	15.8566	950	944	–0.271
	sym	HF	8.4859	1175	1165	–0.056
		B3LYP	7.2491	1021	1010	–0.170
		PBE	13.1114	979	966	–0.084

N. Saleh, S. Zrig, T. Roisnel, L. Guy, R. Bast, T. Saue, B. Darquié, J. Crassous, Phys. Chem. Chem. Phys. Xx. Xx-xx (2013).

New candidates: NWHClI *etc.*

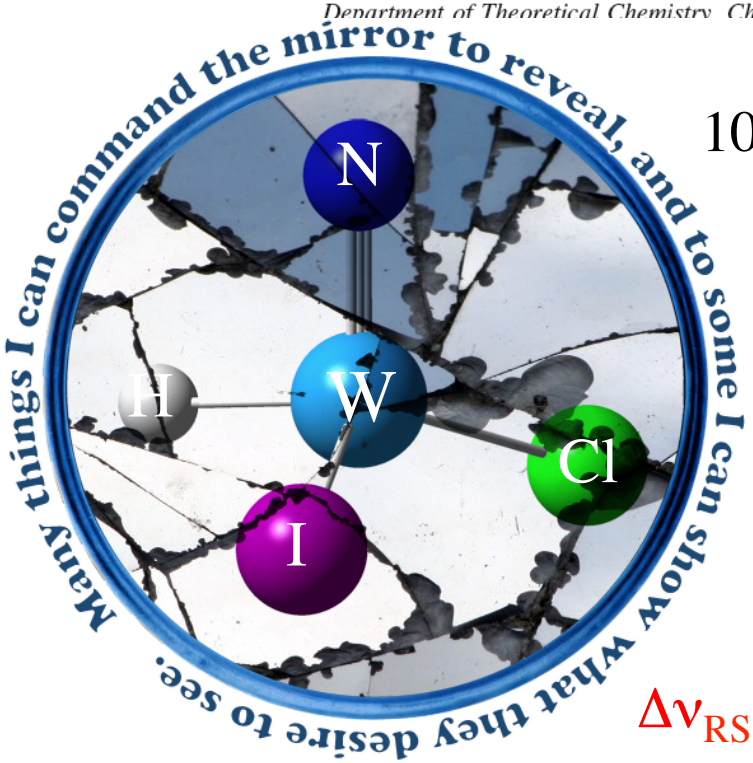
A Combined Theoretical and Experimental Study of Simple Terminal Group 6 Nitride and Phosphide N≡MX$_3$ and P≡MX$_3$ Molecules

Xuefeng Wang and Lester Andrews*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

Roland Lindh, Valera Veryazov, and Björn O. Roos

Department of Theoretical Chemistry, Chemical Center, University of Lund, POB 124, 2-221 00 Lund, Sweden



1078 cm^{-1}

$\Delta\nu_{RS}$= 0.71 Hz

Molecule	ΔE_{PV} [Hz] DKS-B3LYP
R-NWHFCl	7.8
R-NWHFBr	-15.1
R-NWHFI	-49.8
R-NWHClBr	-54.2
R-NWHClI	-138.4
R-NWHBrI	-84.7
S-NWFClBr	-24.0
S-NWFClI	-61.3
S-NWFBrI	-37.6
S-NWClBrI:	-0.4

Other possibilities: PWXYZ, AsWXYZ, NUXYZ etc.

D. Figgen, A. Koers, P. Schwerdtfeger, *Angew. Chem. Int. Ed.* 49, 2941 (2010).

Nuclear Spin dependent PNC: NMR Spectroscopy

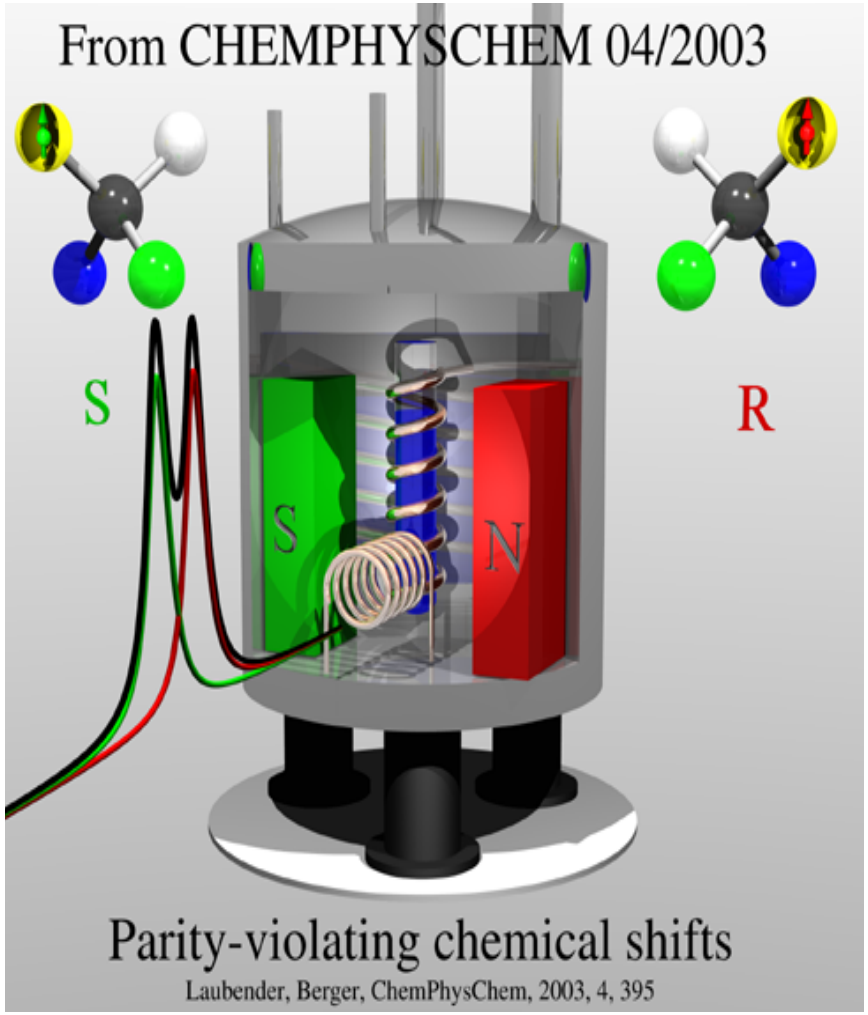
J.R.Robert, A.L.Barra, *Chirality* 13, 699 (2001); G. Laubender, R.Berger, *ChemPhysChem* 4, 395 (2003)

What molecule?

-Nuclear spin I=1/2 (for I>1/2 line broadening due to the NQM

- One or more heavy atoms because of Z-scaling: ^{187}Os ($\Delta\nu$ = 10 Hz), ^{183}W($\Delta\nu$ = 2 Hz), ^{117,119}Sn ($\Delta\nu$ = 3.5 Hz)

For Os NMR: see R. Benn et al., *J. Am. Chem. Soc.* 111, 8754 (1989)



Problems:

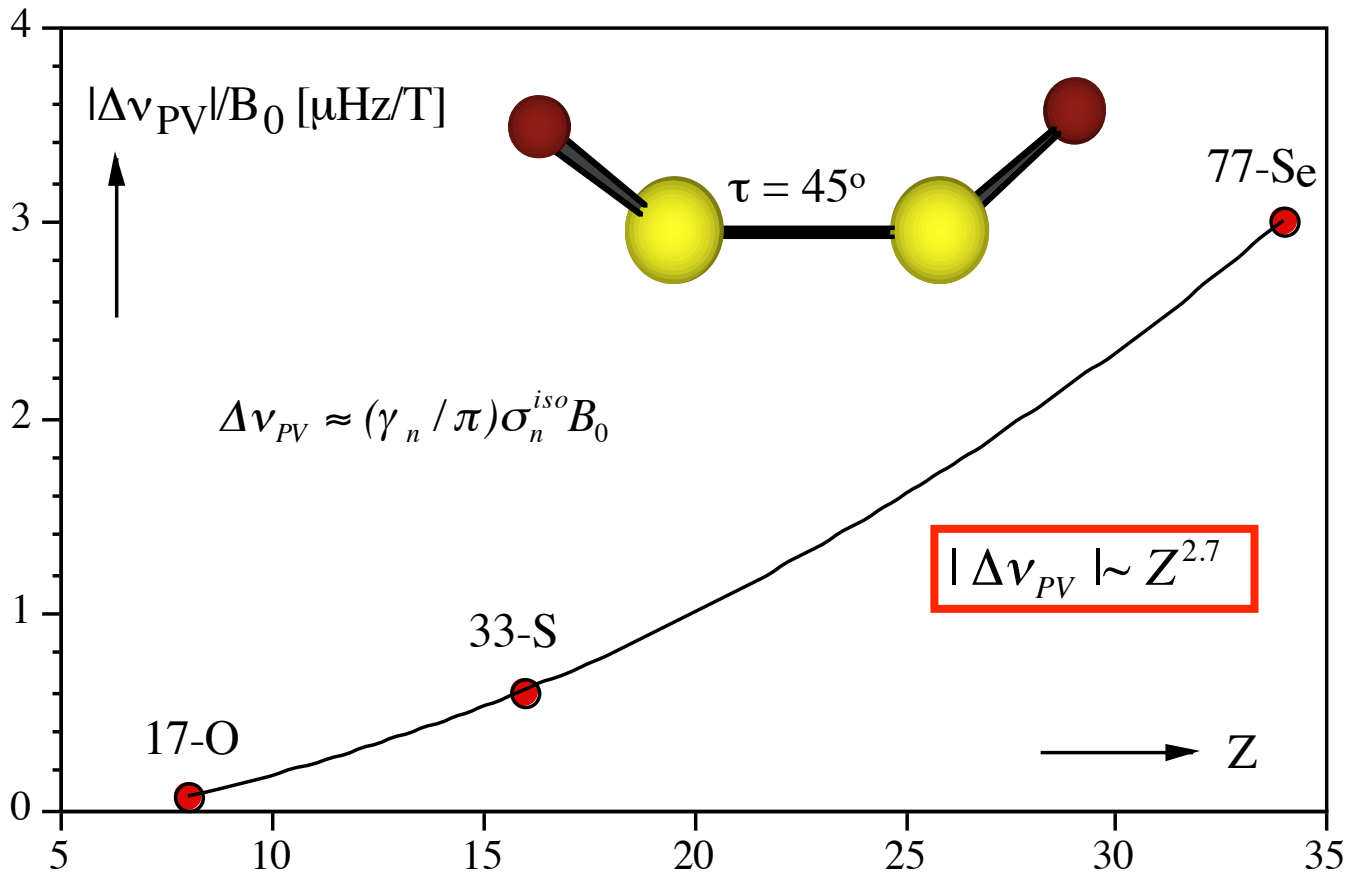
- PV chemical shift contribution ~ ***B***

$\longrightarrow$ large magnetic fields

Current B_0 for a 900 MHz NMR: 21.1 T

- High-resolution gas-phase NMR (10 mHz)
- Low Z-scaling behaviour.
  - enhancement due to relativistic effects?
  - Not beyond the mHz range at 20 T?

G. Laubender, R.Berger, *ChemPhysChem* 4, 395 (2003)
A. Soncini, F. Faglioni, P. Lazzeretti, *Phys. Rev. A* 68, 033402 (2003).



Lazzeretti: Magnetic fields of 10^5 T needed !
Wiesenfeld: For 205-Tl NMR ~ 100 μHz/T
A.L.Barra, F.B.Robert, L.Wiesenfeld, *Phys. Lett.* 115, 443 (1986)

ZORA-BLYP calculations for NWHClI

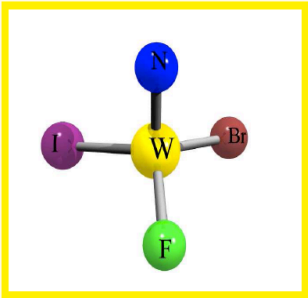
S. Nahrwold, R. Berger, P. Schwerdtfeger, *to be published*.

$$\sigma_{ab}^{PV} = \frac{\partial^3 E}{\partial B_a \partial I_b \partial \lambda^{PV}} \Rightarrow \sigma_{ab}^{PV} = \sigma_{ab,dia}^{PV} + \sigma_{ab,para}^{PV} + \sigma_{ab,SO}^{PV}$$

B=11.7 Tesla used

^{183}W NMR parameters in NWXYZ

molecule	$\Delta\nu^{pv}/\mu$Hz	$\Delta\nu_p^{pv}/\mu$Hz	$\Delta\nu_{so}^{pv}/\mu$Hz	$\Delta\nu$/kHz	δ/ppm
NWBrClF	−9.09	1.15	−10.24	22.4	1070
NWBrClI	0.398	2.578	−2.179	43.9	2090
NWBrFI	−16.7	4.8	−21.4	32.7	1560
NWClFI	−25.9	3.6	−29.6	28.5	1360
NWHBrCl	−94.1	−43.4	−50.8	42.2	2010
NWHBrF	−176	−74	−102	29.0	1380
NWHBrI	−196	−96	−101	51.6	2460
NWHClF	−88.4	−41.8	−46.6	24.2	1150
NWHClI	−293	−139	−154	47.4	2260
NWHFI	−363	−152	−210	34.3	1640



The PC NMR parameters are calculated with respect to the reference compound WO_4^{2-}, i.e. $\Delta\nu = \nu - \nu\left(WO_4^{2-}\right)$ and $\delta = \Delta\nu/\nu\left(WO_4^{2-}\right)$.

PNC in Nuclear Spin-Spin Coupling

V. Weijo, P. Manninen, J. Vaara, *J. Chem. Phys.* 123, 054501 (2005)

in CHFBrI: $J(^{19}F^{127}I)$= 66.2 Hz, $J_{PNC}(^{19}F^{127}I)$= 7.2 nHz

Optical detection of NMR J-spectra at zero magnetic field

M.P. Ledbetter [a,*], C.W. Crawford [b], A. Pines [b,c], D.E. Wemmer [b], S. Knappe [d], J. Kitching [d], D. Budker [a,e]

[a] *Department of Physics, University of California, Berkeley, CA 94720-7300, USA*
[b] *Department of Chemistry, University of California, Berkeley, CA 94720, USA*
[c] *Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[d] *Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA*
[e] *Nuclear Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

ARTICLE INFO

Article history:
Received 30 January 2009
Revised 24 March 2009
Available online xxxx

Keywords:
Atomic magnetometers
Zero-field NMR
Microfluidics
Scalar coupling

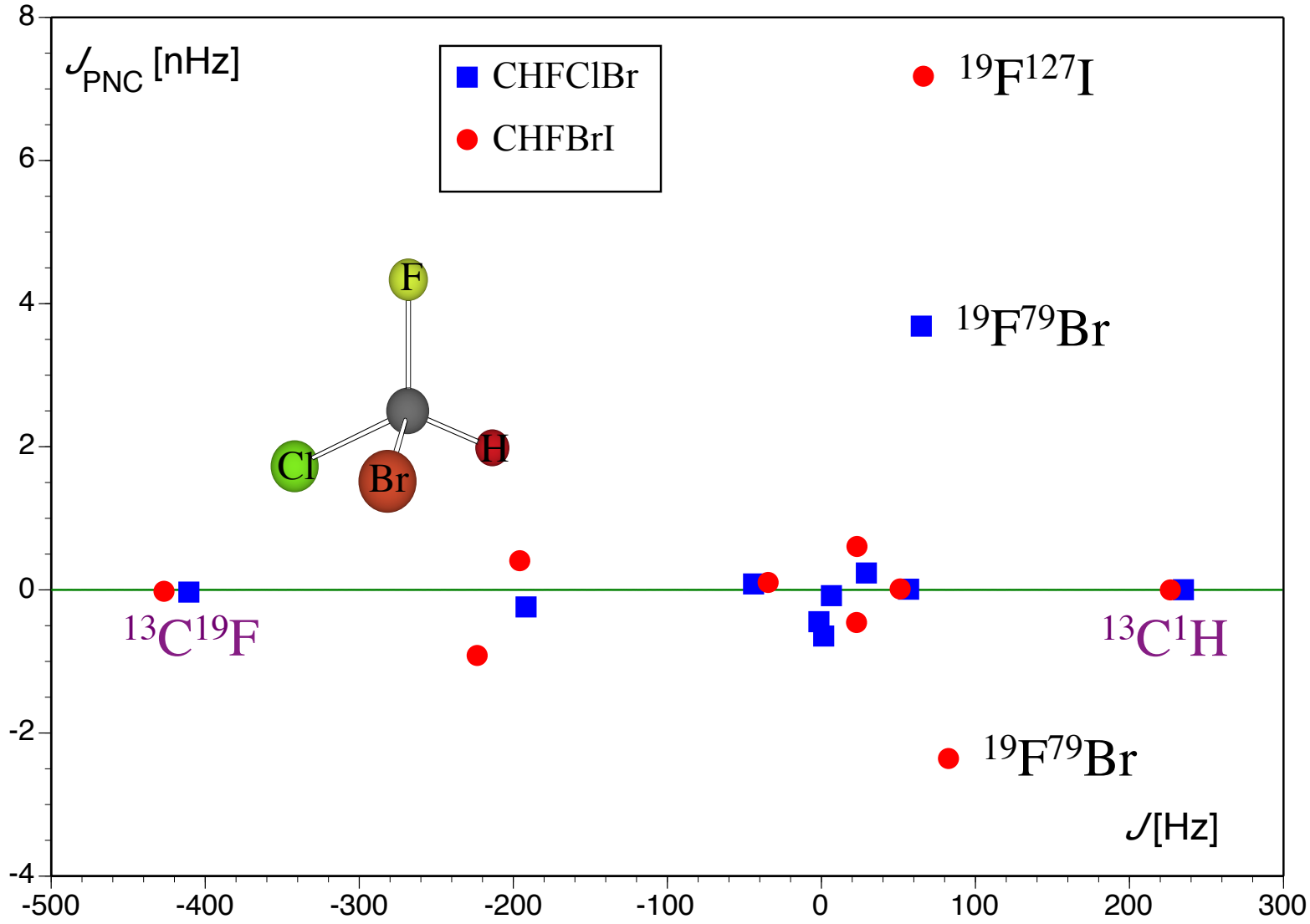
ABSTRACT

Scalar couplings of the form $J\mathbf{I}_1 \cdot \mathbf{I}_2$ between nuclei impart valuable information about molecular structure to nuclear magnetic-resonance spectra. Here we demonstrate direct detection of J-spectra due to both heteronuclear and homonuclear J-coupling in a zero-field environment where the Zeeman interaction is completely absent. We show that characteristic functional groups exhibit distinct spectra with straightforward interpretation for chemical identification. Detection is performed with a microfabricated optical atomic magnetometer, providing high sensitivity to samples of microliter volumes. We obtain 0.1 Hz linewidths and measure scalar-coupling parameters with 4-mHz statistical uncertainty. We anticipate that the technique described here will provide a new modality for high-precision "J spectroscopy" using small samples on microchip devices for multiplexed screening, assaying, and sample identification in chemistry and biomedicine.

© 2009 Elsevier Inc. All rights reserved.

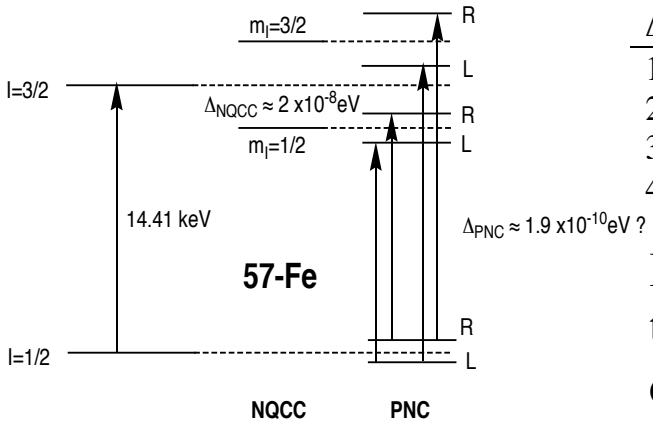
→ 1 μHz resolution possible

Simply going for the largest *J* coupling constant?



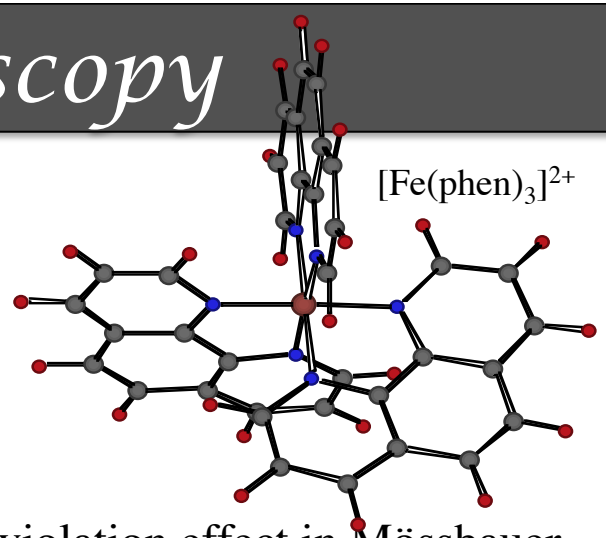
B3LYP results from V. Weijo, P. Manninen, J. Vaara, *J. Chem. Phys.* 123, 054501 (2005)

Mössbauer Spectroscopy



Ground state? (TDDFT/PW91, ADF)

ΔE (eV)	singlet	triplet	quintet
1	1.98	1.87	3.01
2	2.00	1.88	
3	2.01	1.90	
4	2.12	1.95	



In closed-shell systems parity violation effect in Mössbauer transitions are suppressed significantly:

Consider the Dirac bispinor Ψ,

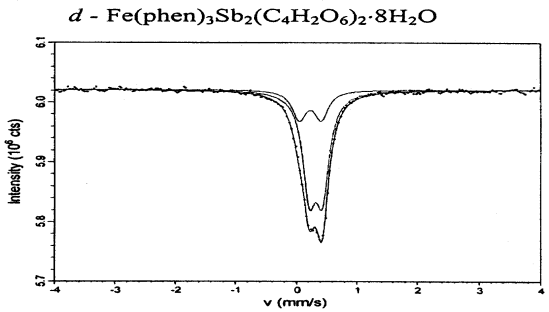
$$\Psi^K = K\Psi, \quad K = -i\sigma_2 C = \gamma^1\gamma^3 C, \quad K^\dagger K = 1, \qquad [K,D] = 0$$

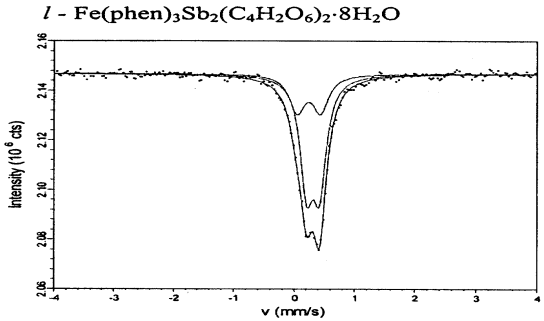
with K being time reversal Kramers operator. K commutes with the γ^5 Matrix but anticommutes with the α_i-matrices in the Dirac equation. Hence we obtain:

$$< \Psi^K | H^1_{pv} | \Psi^K > = < \Psi | H^1_{pv} | \Psi > \quad \text{and}$$
$$< \Psi^K | H^2_{pv} | \Psi^K > = - < \Psi | H^2_{pv} | \Psi >$$

where $$H = \underbrace{\frac{G_F}{2\sqrt{2}} \sum_{i,n} Q_{W,n} \gamma_i^5 \rho_n(\vec{r}_i)}_{H^1_{PV}} - \underbrace{\frac{G_F}{\sqrt{2}} \sum_{i,n} \lambda_n (1 - 4\sin^2\theta_W) \vec{\alpha}_i \vec{I}_n \rho_n(\vec{r}_i)}_{H^2_{PV}} + \ldots$$

→ **Open-shell systems are needed !**





A. S. Lahamer, S. M. Mahurin, R. N. Compton, D. House, J. K. Laerdahl, M. Lein, P. Schwerdtfeger, *Phys. Rev. Lett.* 85, 4470 (2000).

Conclusions

- High resolution vibrational spectroscopy has perhaps the best chance for success (CHFClI, CDFClI, (XY)Se=O, (XYZ)W≡N).
- NMR experiments are currently underway (Tennessee, Berkeley), it looks more promising now.
- PNC in electronic transitions are also currently investigated.
- Theoretical calculations need to become more precise in order to confirm future experimental work (Breit interactions).
- The search for suitable chiral molecules (thermodynamically stable and in the right frequency range) including heavy elements is less than trivial. Currently no simple lego-PV model available. We started on chiral uranium compounds.
- Effects have to be in the > 1 Hz range, also more optimistic estimates of the Paris group for future high resolution experiments are moving towards 10-100 mHz.
- Future prospects: Trapped molecules at ultracold temperatures (1 mK and below), lasers which operate between 1-20 μm.

Thank You!