

Two- and four-component relativistic calculations of parity violation effects in molecules

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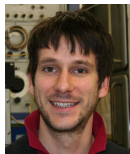
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Infrared ultra high resolution spectroscopy (Paris)



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C. Chardonnet



C. Daussy



C. Stoeffler

Fourier-transform infrared and microwave spectroscopy (Paris, Lille)



P. Asselin

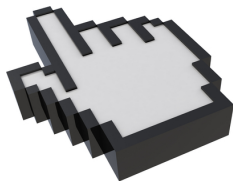


P. Soulard



T. Huet

Outline: parity violation (PV) in relativistic framework



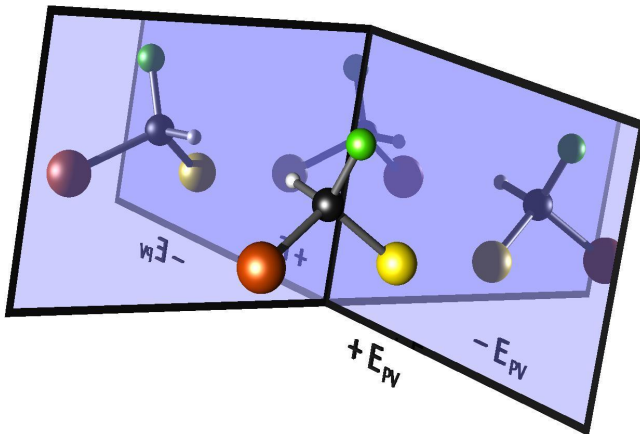
- relativistic interaction Hamiltonian
 - calculation of PV shifts in vibrational transitions
 - search for a suitable molecule for experimental observation of PV
 - projection analysis of the PV energy
 - electron chirality density
 - PV energy gradient
 - perspectives
-
- other theory groups working on PV: R. Berger, P. Lazzeretti, P. Manninen, M. Quack, P. Schwerdtfeger, J. Stohner

Left or right



- mirror-image symmetry is broken
- universe is “left-handed”
- biomolecular homochirality (*D*-sugars, *L*-aminoacids)
- replication/docking/... is easier in a homochiral environment

Chiral molecule in front of two mirrors



$$\hat{P}|\psi(\vec{r})\rangle = |\psi(-\vec{r})\rangle \quad \hat{P}|\psi^S\rangle = |\psi^R\rangle \quad \hat{P}|\psi^R\rangle = |\psi^S\rangle \quad \hat{P}^2 = \hat{I}$$

Loss of symmetry means loss of degeneracy

enantiomers related by parity operation

$$\hat{P}|\psi^{\text{R}}\rangle = |\psi^{\text{S}}\rangle$$

PV Hamiltonian changes sign under parity operation

$$\hat{P}^{-1}\hat{H}_{\text{PV}}\hat{P} = -\hat{H}_{\text{PV}}$$

expectation values differ by sign

$$\begin{aligned}\langle\psi^{\text{R}}|\hat{H}_{\text{PV}}|\psi^{\text{R}}\rangle &= \langle\hat{P}\psi^{\text{R}}|\hat{P}^{-1}\hat{H}_{\text{PV}}\hat{P}|\hat{P}\psi^{\text{R}}\rangle \\ &= -\langle\psi^{\text{S}}|\hat{H}_{\text{PV}}|\psi^{\text{S}}\rangle\end{aligned}$$

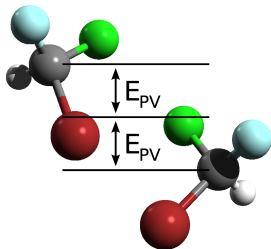
PV energy difference is twice the expectation value

$$\Delta E_{\text{PV}} = 2|\langle\psi|\hat{H}_{\text{PV}}|\psi\rangle|$$

PV energy difference

$$E_{\text{PV}} = \langle \Psi | \hat{H}_{\text{PV}} | \Psi \rangle$$

$$\hat{H}_{\text{PV}} = \frac{G_{\text{F}}}{2\sqrt{2}} \sum_A Q_{\text{w}}^A \sum_i \gamma_i^5 \rho^A(\vec{r}_i)$$



- $G_{\text{F}} = 2.22255 \times 10^{-14} E_{\text{h}} a_0^3$
energy difference obtained through perturbation theory
- Q_{w}^A : weak charge of nucleus A
scales roughly as number of neutrons
- γ^5 matrix couples large and small components

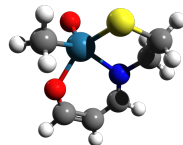
$$\gamma^5 = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

- ρ^A : normalized nuclear charge density
provides natural partitioning in atomic contributions
- E_{PV}^A scales as Z_A^5
we are interested in for heavy nuclei and relativistic treatment

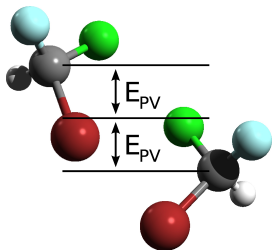
Heavy elements dominate

$$E_{\text{PV}}^A = \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i \langle \psi_i | \gamma_i^5 \rho^A(\vec{r}_i) | \psi_i \rangle$$

nucleus A	$\langle \psi_i \gamma_i^5 \rho^A(\vec{r}_i) \psi_i \rangle$ (in 1.0×10^{-3} a.u.)	Q_{w}^A	E_{PV}^A (in $1.0 \times 10^{-15} E_{\text{h}}$)
H	-0.00011	0.07	-0.00000
H	-0.00012	0.07	-0.00000
H	+0.00005	0.07	+0.00000
H	+0.00005	0.07	+0.00000
H	-0.00023	0.07	-0.00000
H	-0.00003	0.07	-0.00000
H	+0.00016	0.07	+0.00000
H	+0.00016	0.07	+0.00000
H	+0.00002	0.07	+0.00000
H	-0.00032	0.07	-0.00000
C	-0.00127	-5.57	+0.00006
C	-0.00082	-5.57	+0.00004
C	-0.01484	-5.57	+0.00065
C	+0.00521	-5.57	-0.00023
C	-0.00807	-5.57	+0.00035
C	+0.00655	-5.57	-0.00029
O	+0.01010	-7.42	-0.00059
O	+0.05418	-7.42	-0.00316
S	+0.19781	-14.84	-0.02307
N	+0.06501	-6.49	-0.00332
Re	+3.06542	-106.57	-2.56703
total			-2.59659



PV energy difference



$$E_{\text{PV}} = \frac{G_{\text{F}}}{2\sqrt{2}} \sum_A Q_{\text{w}}^A \sum_i \langle \psi_i | \gamma_i^5 \rho^A(\vec{r}_i) | \psi_i \rangle$$

- a priori we do not know which enantiomer is lower in energy (although qualitative models exist)
- we cannot say in general that *D*-sugars and *L*-aminoacids are lower
- nodal surface that changes sign is often very close to the nucleus

1-electron Dirac equation

$$\begin{bmatrix} VI_{2 \times 2} & c(\vec{\sigma} \cdot \vec{p}) \\ c(\vec{\sigma} \cdot \vec{p}) & (V - 2mc^2)I_{2 \times 2} \end{bmatrix} \begin{bmatrix} \psi^{\text{L}} \\ \psi^{\text{S}} \end{bmatrix} = E \begin{bmatrix} \psi^{\text{L}} \\ \psi^{\text{S}} \end{bmatrix}$$

$$c(\vec{\sigma} \cdot \vec{p})\psi^{\text{L}} + (V - 2mc^2)I_{2 \times 2}\psi^{\text{S}} = E\psi^{\text{S}}$$

relation between large and small components

$$\psi^{\text{S}} = \frac{1}{2m} B(E) (\vec{\sigma} \cdot \vec{p}) \psi^{\text{L}}$$

energy-dependent factor

$$B(E) = \left[1 + \frac{E - V}{2mc^2} \right]^{-1}$$

nonrelativistic limit

$$\lim_{c \rightarrow \infty} c\psi^{\text{S}} = \frac{1}{2m} (\vec{\sigma} \cdot \vec{p}) \psi^{\text{L}}$$

$$\hat{H}_{\text{PV}} = \sum_A \hat{H}_{\text{PV}}^A \quad E_{\text{PV}} = \sum_A E_{\text{PV}}^A$$

$$\begin{aligned} E_{\text{PV}}^A &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i \langle \psi | \gamma_i^5 \rho^A(\vec{r}_i) | \psi \rangle \\ &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i [\langle \psi^{\text{L}} | I_{2 \times 2} \rho^A(\vec{r}_i) | \psi^{\text{S}} \rangle + \langle \psi^{\text{S}} | I_{2 \times 2} \rho^A(\vec{r}_i) | \psi^{\text{L}} \rangle] \end{aligned}$$

using

$$\lim_{c \rightarrow \infty} c \psi^{\text{S}} = \frac{1}{2m} (\vec{\sigma} \cdot \vec{p}) \psi^{\text{L}}$$

nonrelativistic limit of the interaction Hamiltonian

$$\lim_{c \rightarrow \infty} c \hat{H}_{\text{PV}}^A = \frac{1}{2m} \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i [I_{2 \times 2} \rho^A(\vec{r}_i), (\vec{\sigma}_i \cdot \vec{p}_i)]_+$$

relativistic Hamiltonian

$$\hat{H}_{\text{PV}}^A = \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i \gamma_i^5 \rho^A(\vec{r}_i)$$

Hamiltonian including the nuclear spin dependent term

Hamiltonian so far

$$\hat{H}_{\text{PV}} = \frac{G_{\text{F}}}{2\sqrt{2}} \sum_A \sum_i \gamma_i^5 Q_{\text{W}}^A \rho^A(\vec{r}_i)$$

Hamiltonian including the nuclear spin dependent term

$$\hat{H}_{\text{PV}} = \frac{G_{\text{F}}}{2\sqrt{2}} \sum_A \sum_i \left[\gamma_i^5 Q_{\text{W}}^A \rho^A(\vec{r}_i) - 2\lambda_A (1 - 4\sin^2 \theta_{\text{W}}) \vec{\alpha}_i \cdot \vec{I}_A \rho^A(\vec{r}_i) \right]$$

- first term modifies energy eigenvalues
- second term modifies NMR parameters
- we will not consider the second term in this talk

Experimental techniques

we are still waiting for the first successful experiment on molecular PV

- vibrational spectroscopy
- Mössbauer spectroscopy
- NMR spectroscopies
- optical rotation
- electronic excitation spectra
- spectroscopy on laser-cooled molecules

PV in vibrational spectroscopy

- select suitable molecule
- select suitable vibrational coordinate Q
- PV energy depends on Q

$$E_{\text{PV}} = E_{\text{PV}}(Q)$$

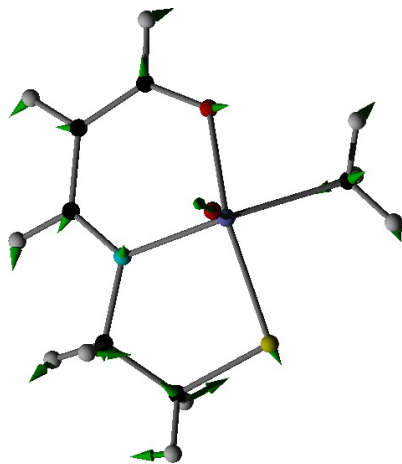
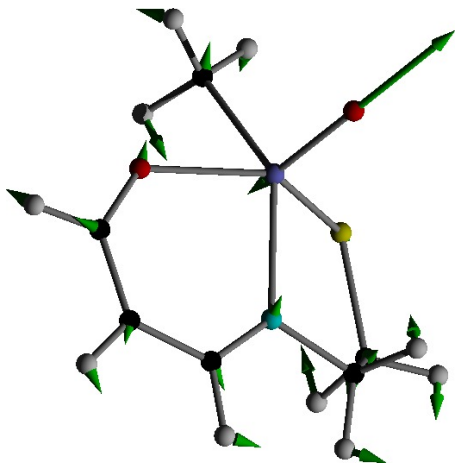
- PV vibrational transition frequency difference for $0 \rightarrow n$ transition:

$$\Delta E_{\text{PV};0 \rightarrow n} = 2\langle n | E_{\text{PV}}(Q) | n \rangle - 2\langle 0 | E_{\text{PV}}(Q) | 0 \rangle$$

- we can expand $E_{\text{PV}}(Q)$ in Q :

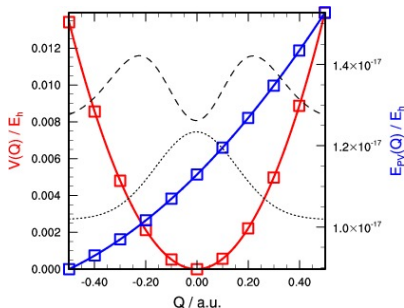
$$E_{\text{PV}}(Q) = E_{\text{PV}}^{[0]} + E_{\text{PV}}^{[1]}Q + \frac{1}{2}E_{\text{PV}}^{[2]}Q^2 + \dots$$

- vibrational spectroscopy experiment does not probe $E_{\text{PV}}^{[0]}$



computational protocol

- optimize structure
- obtain harmonic force field
- perturb molecule along a selected mode
- calculate energy at these displaced geometries
- calculate $\langle \hat{H}_{PV} \rangle$ at these displaced geometries
- calculate shift for $0 \rightarrow n$ transition

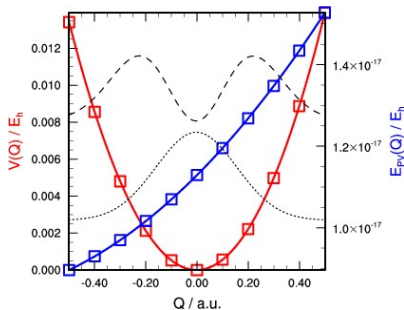


methods

- structure and force field:
ECP B3LYP, def2-TZVPP basis
- single-point energy and property calculations:
DC Hamiltonian or X2C Hamiltonian, HF or KS, dedicated even-tempered basis

approximations

- Born–Oppenheimer approximation
- electron correlation is approximated (exchange–correlation)
- Dirac–Coulomb Hamiltonian or X2C Hamiltonian (relativistic treatment crucial)
- assume that wavefunction is dominated by one electron occupation (self-consistent field)
- we follow normal modes: uncoupled picture
- no environment (molecule alone in the universe)



- fit polynomials to $P(Q)$ and $V(Q)$

$$E_{\text{PV}}(Q) = E_{\text{PV}}^{[0]} + E_{\text{PV}}^{[1]}Q + \frac{1}{2}E_{\text{PV}}^{[2]}Q^2 + \dots$$

- Numerov–Cooley procedure

$$\Delta E_{\text{PV};0 \rightarrow n} = 2\langle n | E_{\text{PV}}(Q) | n \rangle - 2\langle 0 | E_{\text{PV}}(Q) | 0 \rangle$$

- perturbational approach

$$\Delta E_{\text{PV};0 \rightarrow n} \approx n \frac{\hbar}{\mu\omega_e} \left[E_{\text{PV}}^{[2]} - \frac{1}{\mu\omega_e^2} E_{\text{PV}}^{[1]} V^{[3]} \right]$$

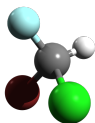
- perturbational approach works well
- good for analysis
- can offer error estimates
- we do not probe $E_{\text{PV}}^{[0]}$ in the vibrational experiment
- there can be cancellation or enhancement

Search for the ideal candidate

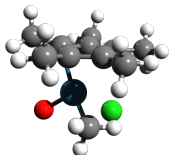
- experimental setup aiming at resolving 10 mHz

- contain one or more heavy atoms near the stereochemical center
- intense band within the CO₂ laser operating range (850–1120 cm⁻¹)
- separable in stable enantiomers
- not bulky (sensitivity of experiment determined by the partition function)
- avoid nuclei with quadrupole moment (avoid large hyperfine structure)
- allow supersonic expansion (sublimate without decomposition)
- gram-scale

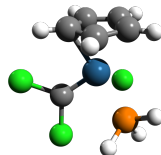
Some studied molecules



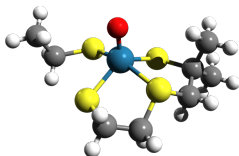
C-F stretch
HF: 0.002 Hz



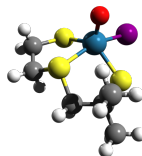
Re=O stretch
HF: -2.077 Hz
B3LYP: -2.386 Hz



Os=C stretch
HF: -3.085 Hz
B3LYP: -1.152 Hz

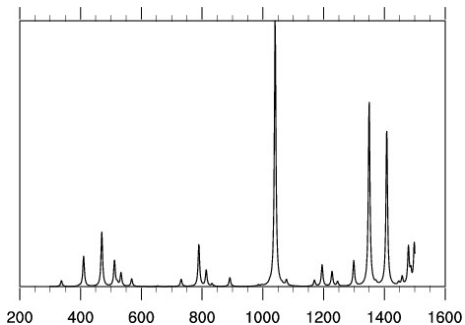
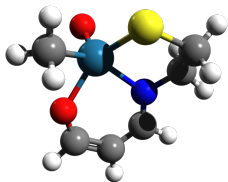


Re=O stretch
HF: -1.585 Hz
B3LYP: -0.102 Hz

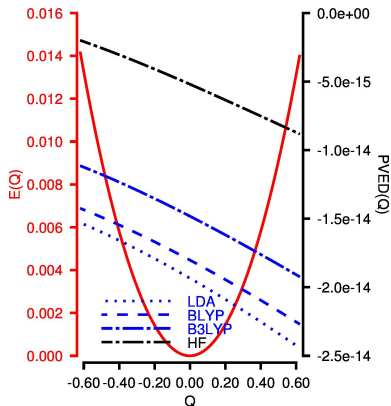


Re=O stretch
HF: +0.157 Hz
B3LYP: -0.069 Hz

$C_5H_7NOS-ReOMe$



C₅H₇NOS-ReOMe

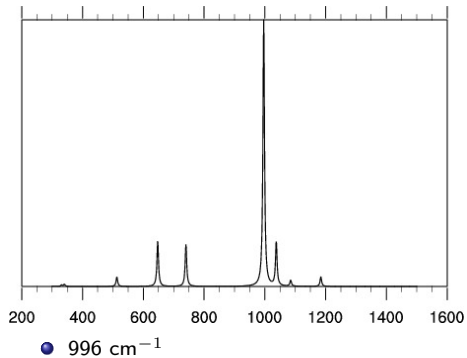
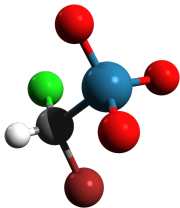


method	harmonic	anharmonic
LDA	-0.672	-0.753
BLYP	-0.582	-0.656
B3LYP	-0.482	-0.554
HF	-0.279	-0.341

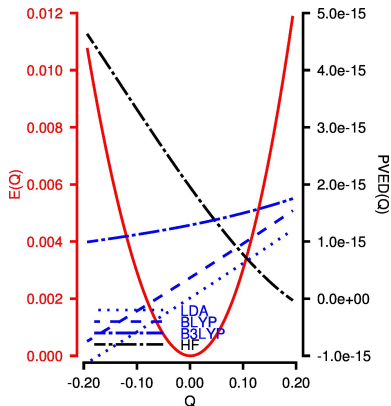
method	$E_{PV}^{[1]}$	$E_{PV}^{[2]}$
LDA	-24.5	-8.5
BLYP	-22.7	-7.3
B3LYP	-21.8	-6.1
HF	-18.6	-3.5

* All numbers in Hz (all DC Hamiltonian).

CHClBrReO3



CHClBrReO3



method	harmonic	anharmonic
LDA	+0.040	-0.088
BLYP	+0.044	-0.082
B3LYP	+0.112	+0.070
HF	+0.453	+0.708

method	$E_{PV}^{[1]}$	$E_{PV}^{[2]}$
LDA	+19.8	+5.2
BLYP	+19.4	+5.7
B3LYP	+6.1	+14.8
HF	-42.5	+58.1

* All numbers in Hz (all DC Hamiltonian).

Projection analysis

SCF expectation value is a sum of orbital contributions

$$E_{\text{PV}}^A = \langle \Phi | \hat{H}_{\text{PV}}^A | \Phi \rangle = \sum_i \langle \psi_i | \hat{H}_{\text{PV}}^A | \psi_i \rangle$$

we can expand the molecular orbitals $|\psi_i\rangle$ in a set of fragment orbitals $|\phi_j\rangle$

$$|\psi_i\rangle = \sum_j |\phi_j\rangle \langle \phi_j | \psi_i \rangle + |\text{pol}\rangle = \sum_j |\phi_j\rangle c_{ji} + |\text{pol}\rangle$$

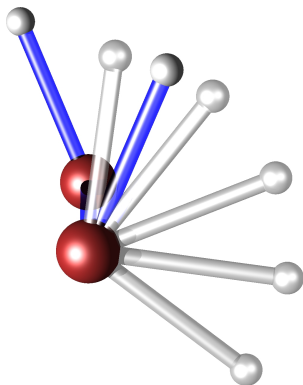
c_{ji} can be determined from a system of linear equations

$$\langle \phi_k | \psi_i \rangle = \sum_j \langle \phi_k | \phi_j \rangle c_{ji}$$

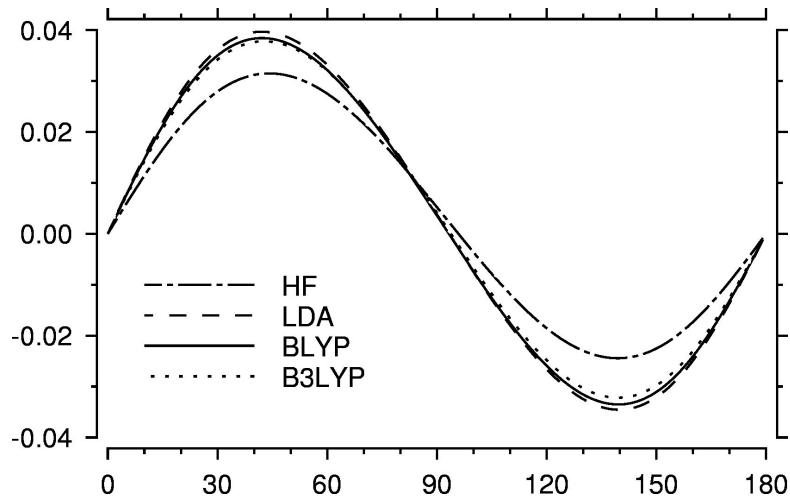
$$E_{\text{PV}}^A = \sum_{ijk} \langle \phi_j | \hat{H}_{\text{PV}}^A | \phi_k \rangle c_{ji}^* c_{ki} + \langle \text{pol} |$$

- we choose the fragment orbitals to be the occupied orbitals of the individual atoms
- we can distinguish intra- and interatomic contributions

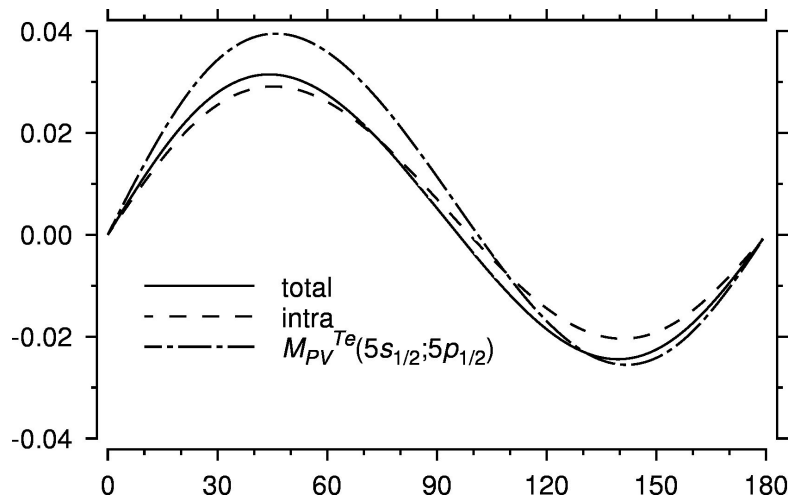
Projection analysis: classic series H_2X_2



Projection analysis: reduced contribution in H_2Te_2



Projection analysis: individual contributions in H_2Te_2



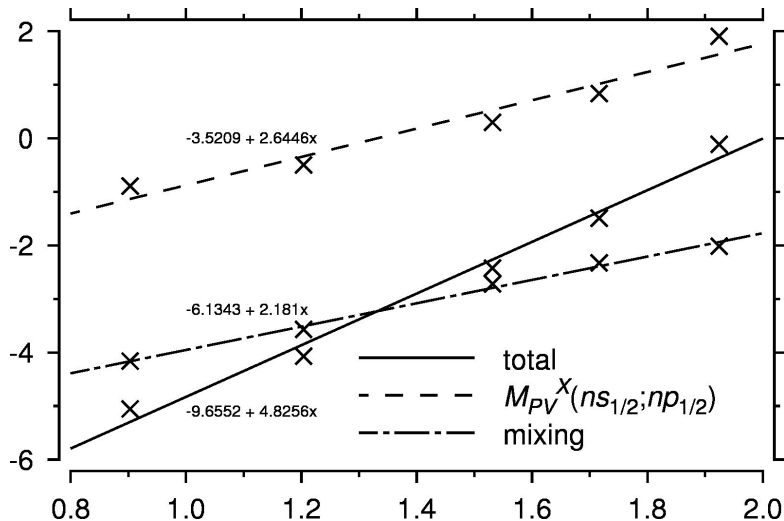
Projection analysis

$$\psi = \begin{bmatrix} \psi^{\text{L}\alpha} \\ \psi^{\text{L}\beta} \\ \psi^{\text{S}\alpha} \\ \psi^{\text{S}\beta} \end{bmatrix} = \begin{bmatrix} R^{\text{L}}(r)\chi_{\kappa, m_j}(\theta, \phi) \\ iR^{\text{S}}(r)\chi_{-\kappa, m_j}(\theta, \phi) \end{bmatrix}$$

- R^{L} and R^{S} are the large and small radial functions
- χ_{κ, m_j} are the 2-component angular functions

$$\begin{aligned} \sum_{jk} \langle \phi_j^X | \gamma^5 \rho^X | \phi_k^X \rangle &= i \langle R_j^{\text{L};X} | \rho^X | R_k^{\text{S};X} \rangle_r \langle \chi_{\kappa_j, m_j}^X | \chi_{-\kappa_k, -m_k}^X \rangle_{\theta, \phi} \\ &\quad - i \langle R_j^{\text{S};X} | \rho^X | R_k^{\text{L};X} \rangle_r \langle \chi_{-\kappa_j, m_j}^X | \chi_{\kappa_k, -m_k}^X \rangle_{\theta, \phi} \end{aligned}$$

Projection analysis: scaling



Electron chirality density

can we visualize the contribution from one atom?

$$E_{\text{PV}}^A = \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i \langle \psi_i | \gamma_i^5 \rho^A(\vec{r}_i) | \psi_i \rangle$$

contribution is a sum of weighted integrals

$$\begin{aligned} E_{\text{PV}}^A &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \sum_i \int d\vec{r} \psi_i^\dagger(\vec{r}) \gamma_i^5 \psi_i(\vec{r}) \rho^A(\vec{r}_i) \\ &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \int d\vec{r} \gamma^5(\vec{r}) \rho^A(\vec{r}) \end{aligned}$$

$\gamma^5(\vec{r})$ has been introduced in the NR framework by Hegstrom
particularly simple in the relativistic framework (κ span L, λ span S)

$$\gamma^5(\vec{r}) = \sum_{\kappa\lambda} \left[\chi_\kappa^\dagger(\vec{r}) \chi_\lambda(\vec{r}) D_{\lambda\kappa} + \chi_\lambda^\dagger(\vec{r}) \chi_\kappa(\vec{r}) D_{\kappa\lambda} \right]$$

Electron chirality density

$$\gamma^5(\vec{r}) = \sum_{\kappa\lambda} \left[\chi_{\kappa}^{\dagger}(\vec{r}) \chi_{\lambda}(\vec{r}) D_{\lambda\kappa} + \chi_{\lambda}^{\dagger}(\vec{r}) \chi_{\kappa}(\vec{r}) D_{\kappa\lambda} \right]$$

$$E_{\text{PV}}^A = \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \int d\vec{r} \gamma^5(\vec{r}) \rho^A(\vec{r})$$

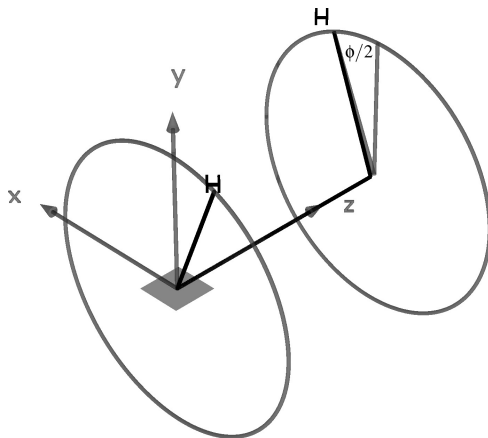
approximation: point charge nucleus (difference typically 10%)

$$\begin{aligned} E_{\text{PV}}^A &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \int d\vec{r} \gamma^5(\vec{r}) \delta^3(\vec{r} - \vec{R}_A) \\ &= \frac{G_{\text{F}}}{2\sqrt{2}} Q_{\text{w}}^A \gamma^5(\vec{R}_A) \end{aligned}$$

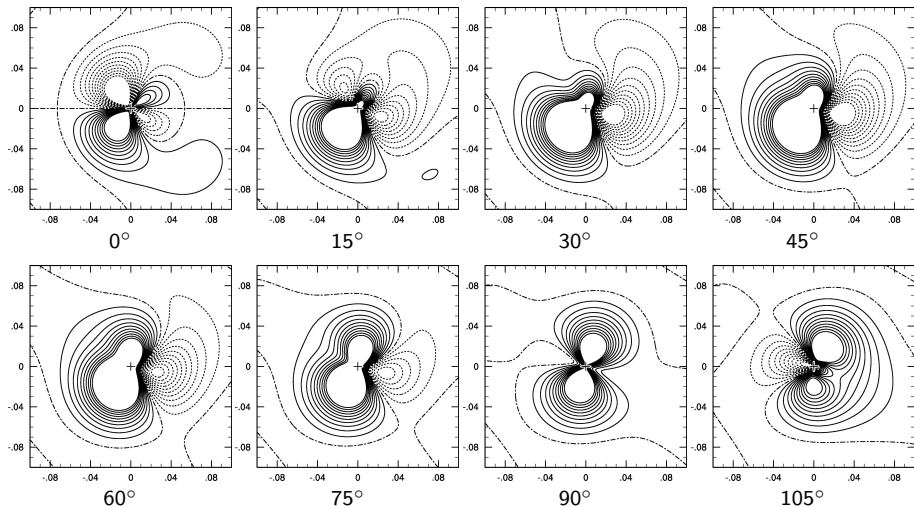
observations

- knowledge of $\gamma^5(\vec{R}_A)$ is enough for qualitative understanding
- atomic nature
- it must have positive and negative regions and nodal surfaces
- if we understand derivatives of $\gamma^5(\vec{R}_A)$ we understand the PV vibrational shift

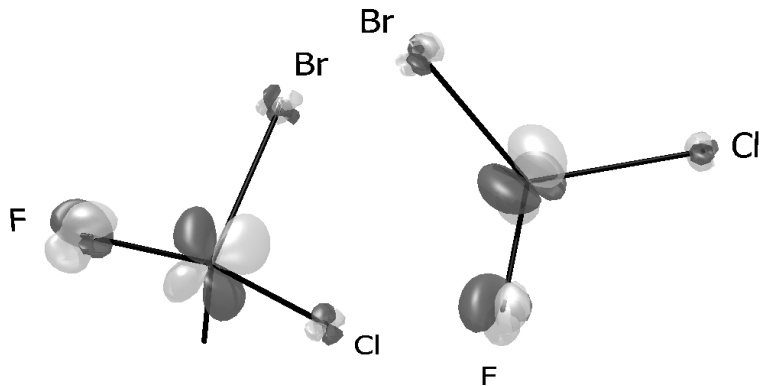
Electron chirality density in H_2Te_2



Electron chirality density in H_2Te_2

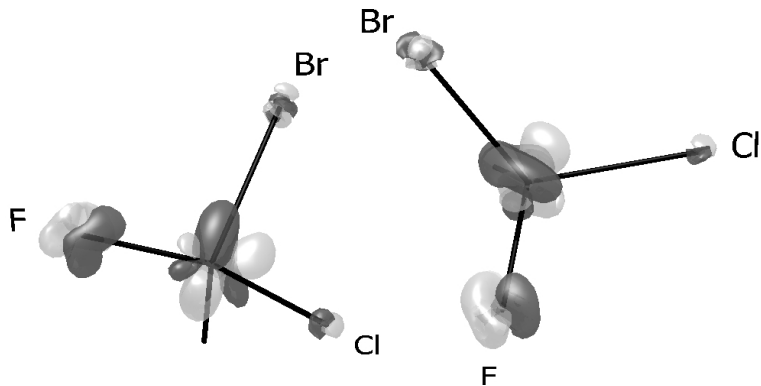


CHFCIBr electron chirality density isosurface



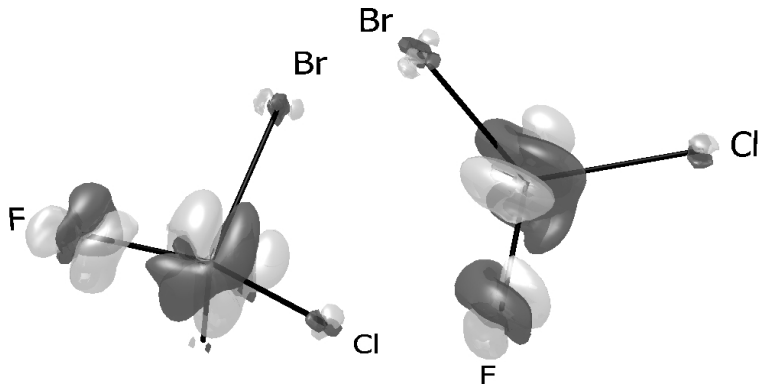
- CHFCIBr molecule from two angles

CHFCIBr electron chirality density isosurface



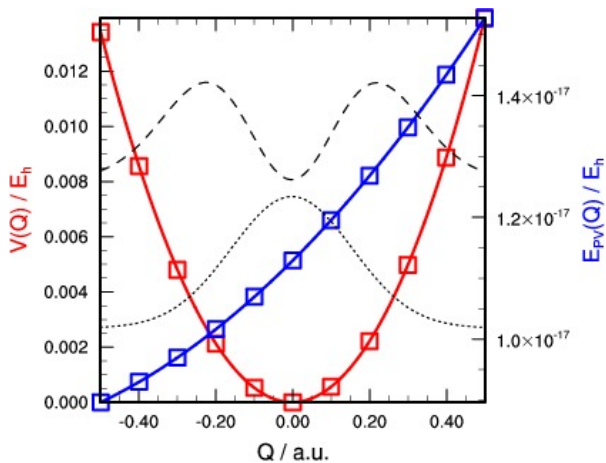
- first derivative with respect to C–F stretching normal coordinate

CHFCIBr electron chirality density isosurface



- second derivative with respect to C–F stretching normal coordinate

PV energy gradient



PV energy gradient

$$\hat{H}_{\text{PV}} = \sum_A \hat{H}_{\text{PV}}^A \quad E_{\text{PV}} = \sum_A E_{\text{PV}}^A$$

$$\hat{H} = \hat{H}_0 + \sum_A f_A \hat{H}_{\text{PV}}^A$$

$$E_{\text{PV}}^A = \left. \frac{dE}{df_A} \right|_{\{\vec{f}_K\}=0} = E^{f_A} = E^f$$

$$\vec{g}_B = \vec{R}_B - \vec{R}_{B,0}$$

$$\frac{d}{dg_{B,i}} E_{\text{PV}}^A = \left. \frac{d^2 E}{dg_{B,i} df_A} \right|_{\{\vec{f}_K\}=0, \{\vec{g}_K\}=0} = E^{g_{B,i} f_A} = E^{gf}$$

PV energy gradient

$$E = v_{\mathbf{n}-\mathbf{n}} + v_{\mathbf{n}-\mathbf{ext}} + h_{\kappa\lambda} D_{\lambda\kappa} + V_{\kappa\lambda} D_{\lambda\kappa} + \frac{1}{2} G_{\kappa\lambda}(\mathbf{D}) D_{\lambda\kappa}$$

$$F_{\kappa\lambda} = h_{\kappa\lambda} + V_{\kappa\lambda} + G_{\kappa\lambda}(\mathbf{D})$$

$$E^f = V_{\kappa\lambda}^f D_{\lambda\kappa} = \langle \chi_{\kappa} | \hat{H}_{\text{PV}}^A | \chi_{\lambda} \rangle D_{\lambda\kappa}$$

$$E^{gf} = V_{\kappa\lambda}^{gf} D_{\lambda\kappa} + h_{\kappa\lambda}^g D_{\lambda\kappa}^f + G_{\kappa\lambda}^g(\mathbf{D}) D_{\lambda\kappa}^f - S_{\kappa\lambda}^g W_{\lambda\kappa}^f$$

$$W_{\lambda\kappa}^f = (\mathbf{DFD})_{\lambda\kappa}^f$$

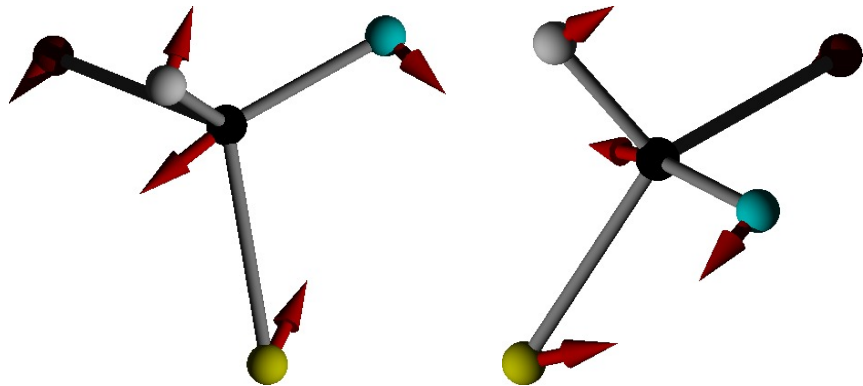
$$(\mathbf{DFD})^f = \mathbf{D}^f \mathbf{F} \mathbf{D} + \mathbf{D} \mathbf{F}^f \mathbf{D} + \mathbf{D} \mathbf{F} \mathbf{D}^f$$

PV energy gradient

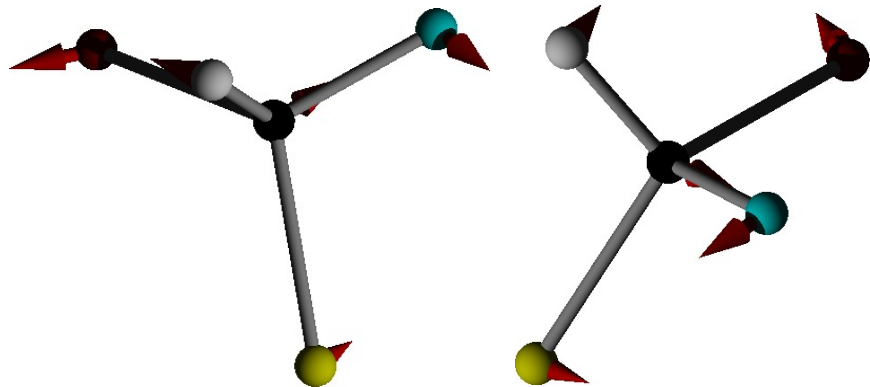
Example: CHFCIBr molecule

$$E^{gf} = \begin{bmatrix} E^{C_x,C} & E^{C_x,H} & E^{C_x,F} & E^{C_x,Cl} & E^{C_x,Br} \\ E^{C_y,C} & E^{C_y,H} & E^{C_y,F} & E^{C_y,Cl} & E^{C_y,Br} \\ E^{C_z,C} & E^{C_z,H} & E^{C_z,F} & E^{C_z,Cl} & E^{C_z,Br} \\ E^{H_x,C} & E^{H_x,H} & E^{H_x,F} & E^{H_x,Cl} & E^{H_x,Br} \\ E^{H_y,C} & E^{H_y,H} & E^{H_y,F} & E^{H_y,Cl} & E^{H_y,Br} \\ E^{H_z,C} & E^{H_z,H} & E^{H_z,F} & E^{H_z,Cl} & E^{H_z,Br} \\ E^{F_x,C} & E^{F_x,H} & E^{F_x,F} & E^{F_x,Cl} & E^{F_x,Br} \\ E^{F_y,C} & E^{F_y,H} & E^{F_y,F} & E^{F_y,Cl} & E^{F_y,Br} \\ E^{F_z,C} & E^{F_z,H} & E^{F_z,F} & E^{F_z,Cl} & E^{F_z,Br} \\ E^{Cl_x,C} & E^{Cl_x,H} & E^{Cl_x,F} & E^{Cl_x,Cl} & E^{Cl_x,Br} \\ E^{Cl_y,C} & E^{Cl_y,H} & E^{Cl_y,F} & E^{Cl_y,Cl} & E^{Cl_y,Br} \\ E^{Cl_z,C} & E^{Cl_z,H} & E^{Cl_z,F} & E^{Cl_z,Cl} & E^{Cl_z,Br} \\ E^{Br_x,C} & E^{Br_x,H} & E^{Br_x,F} & E^{Br_x,Cl} & E^{Br_x,Br} \\ E^{Br_y,C} & E^{Br_y,H} & E^{Br_y,F} & E^{Br_y,Cl} & E^{Br_y,Br} \\ E^{Br_z,C} & E^{Br_z,H} & E^{Br_z,F} & E^{Br_z,Cl} & E^{Br_z,Br} \end{bmatrix}$$

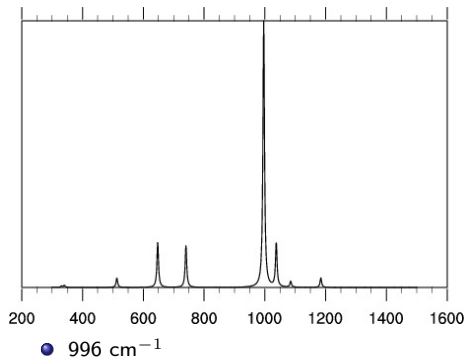
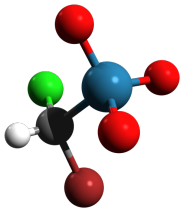
CHFCIBr: E_{pV}^{Br} gradient



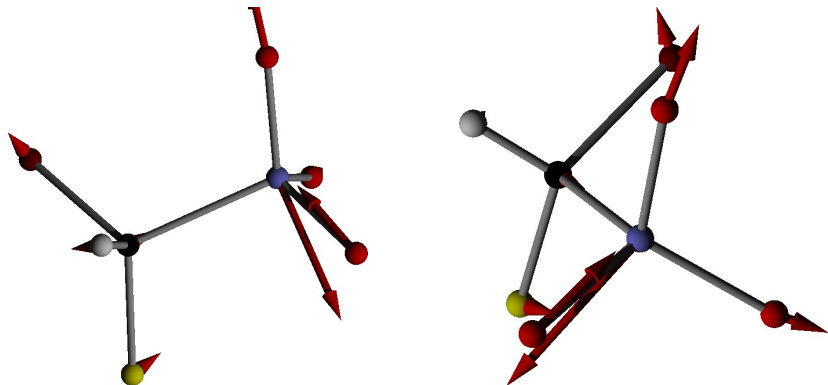
CHFCIBr: E_{pV}^{Cl} gradient



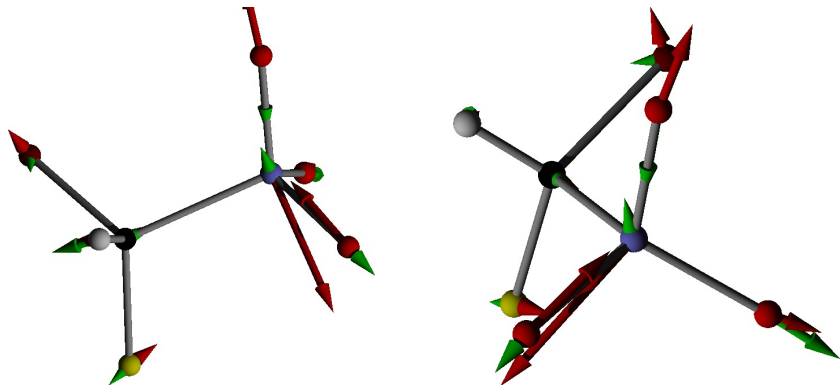
CHClBrReO3



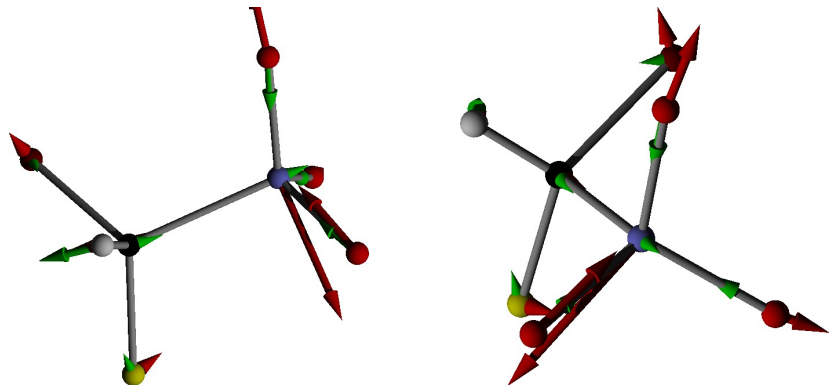
CHClBrReO₃: PV energy gradient



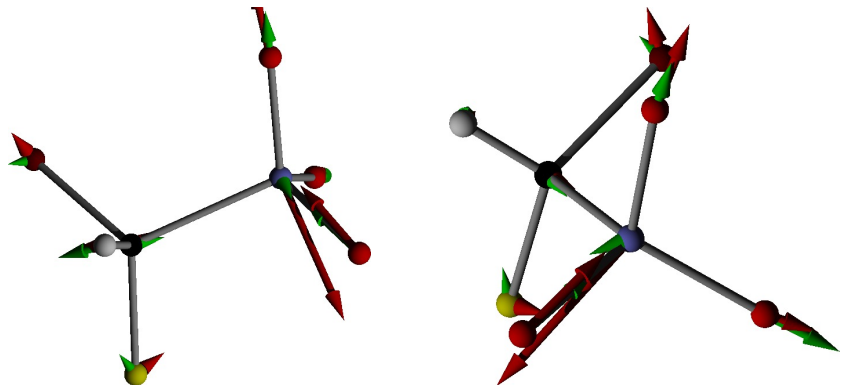
CHClBrReO₃: PV gradient and vibrational mode 13



CHClBrReO₃: PV gradient and vibrational mode 15



CHClBrReO₃: PV gradient and vibrational mode 14



Conclusions and perspectives

- PV is highly challenging for experiment and theory
- Re complexes are promising candidates
- we see large sensitivity on molecular structure elements
- we see large sensitivity on choice of method (functional)
- we need to invest in higher-level methods and push the computational machinery to the limit
- analysis tools will help us to develop models for the PV vibrational shift
- PV gradient and Hessian (to come) may point us to the right way

