Recent computational results in Tromsø and Toulouse

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my PV background and commitment

- 2002 undergrad project in Peter's group
  calculations with the DIRAC code
- 2004–2008 Ph.D. in Trond's group
  DIRAC calculations and development (NMR parameters)
- 2008–2011 post-doc in the group of Kenneth Ruud
- since October 2011: CR2 in Toulouse

what theoretical chemistry can do for PV

- calculate effect (pre-screening)
- know the approximations and limits
- develop better methods

$$\beta' mc^2 + V I_{4\times 4} + c(\vec{\alpha}\cdot\vec{p})\psi = E\psi$$

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

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

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

$$H_{\mathsf{PV}} = \sum_A H^A_{\mathsf{PV}}$$

$$E^A_{\mathsf{PV}} = \frac{G_{\mathsf{F}}}{2\sqrt{2}} Q^A_{\mathsf{w}} \sum_i \langle\psi_i|\gamma_5 \rho^A(\mathbf{r}_i)|\psi_i\rangle$$

$$= \frac{G_{\mathsf{F}}}{2\sqrt{2}} Q^A_{\mathsf{w}} \sum_i \left[\langle\psi^{\mathsf{L}}_i|I_{2\times 2}\rho^A(\mathbf{r}_i)|\psi^{\mathsf{S}}_i\rangle + \langle\psi^{\mathsf{S}}_i|I_{2\times 2}\rho^A(\mathbf{r}_i)|\psi^{\mathsf{L}}_i\rangle\right]$$

$$\lim_{c\to\infty} cH^A_{\mathsf{PV}} = \frac{1}{2m}\frac{G_{\mathsf{F}}}{2\sqrt{2}} Q^A_{\mathsf{w}} \sum_i [I_{2\times 2}\rho^A(\mathbf{r}_i), (\vec{\sigma}\cdot\vec{p})]_+$$

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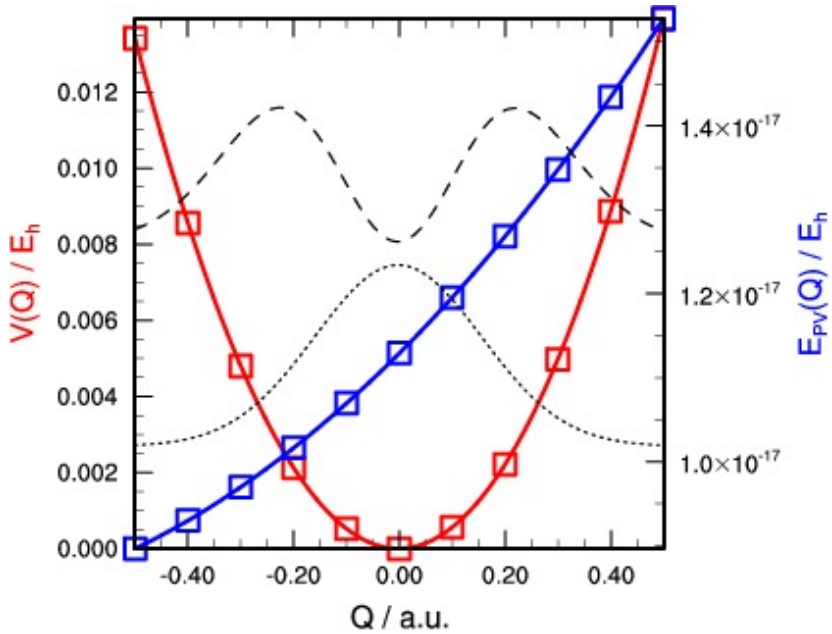
computational protocol

- optimize structure
- obtain harmonic force field
- perturb molecule along a selected mode
- calculate energy at these displaced geometries
- calculate $E_{\mathsf{PV}} = P^{[0]}$ at these displaced geometries (slow)
- calculate $\Delta P_{0 \to n}$



approximations

- Born–Oppenheimer approximation
- electron correlation is approximated
- relativity is approximated (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)

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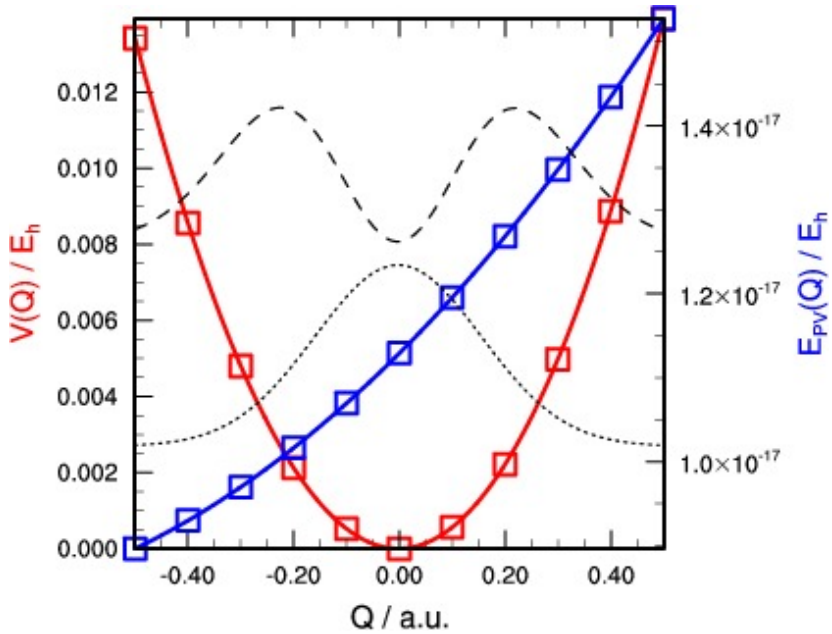

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- fit polynomials to $P(Q)$ and $V(Q)$

$$P(Q) = P^{[0]} + P^{[1]}Q + \frac{1}{2}P^{[2]}Q^2 + \cdots$$

- Numerov–Cooley procedure

$$\Delta P_{0\to n} = 2(P_n - P_0); \qquad P_n = \langle n|P(Q)|n\rangle$$

- perturbational approach

$$\Delta P_{0\to n} \approx n\frac{\hbar}{\mu\omega_e}\left[P^{[2]} - \frac{1}{\mu\omega_e^2}P^{[1]}V^{[3]}\right]$$

- good for analysis
- can offer error estimates
- we do not probe $P^{[0]}$ in the vibrational experiment
- we have models for rationalizing $P^{[0]}$
- very little is known about $P^{[1]}$ and $P^{[2]}$
- there can be cancellation or enhancement
- perturbational approach works well

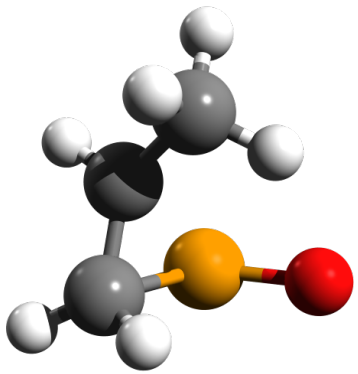
how do we calculate P and V?

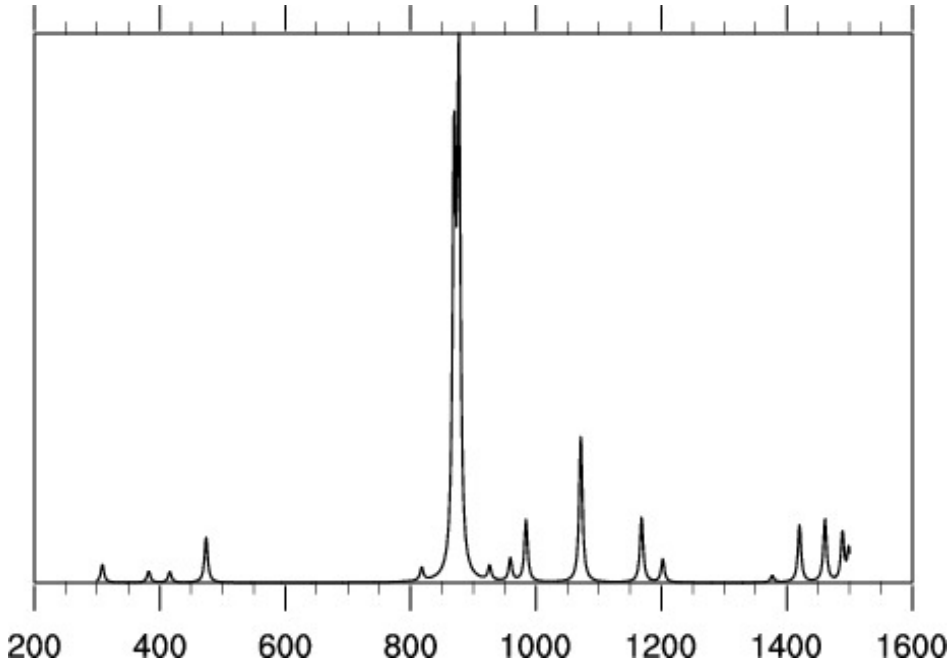
- we calculate V using density functional theory (DFT) approximations
- we calculate P using DFT approximations or Hartree–Fock theory

how reliable are the DFT approximations (functionals)?

- using more and more sophisticated functionals does not guarantee to approach the experimental result
- wave-functional based methods can be systematically improved but they are currently not available for the property under study

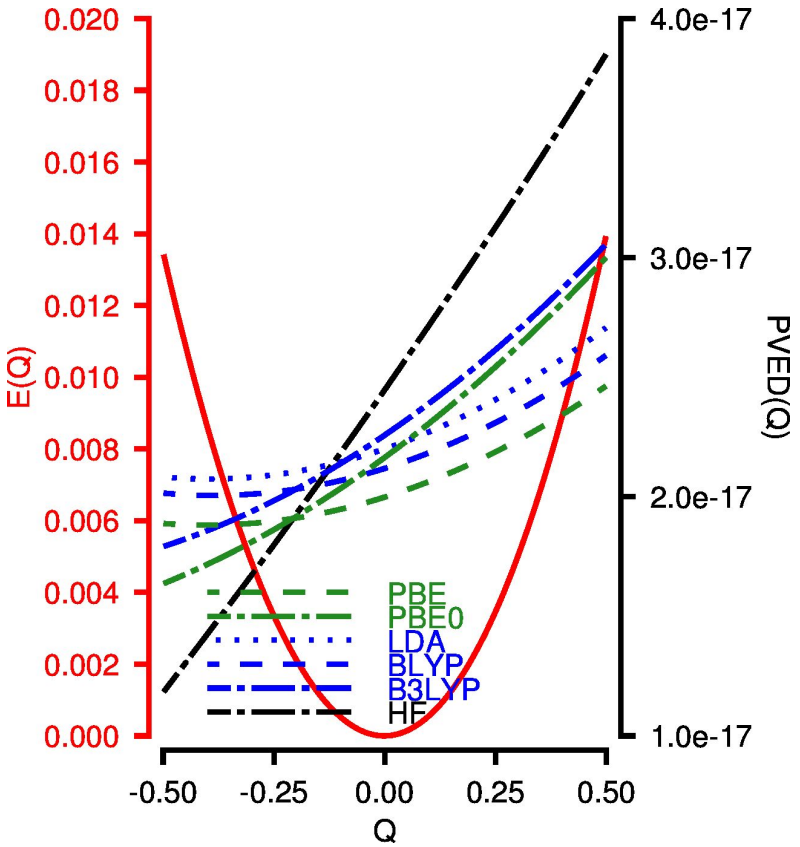
C_3H_6SeO





- 1168 cm^{-1}

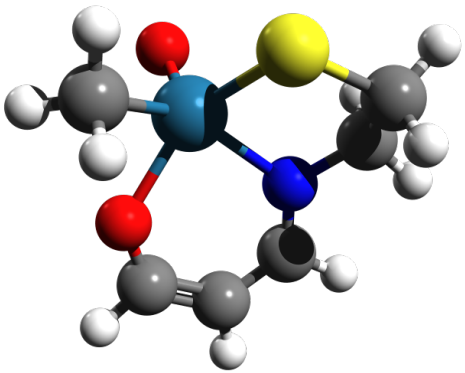
C_3H_6SeO

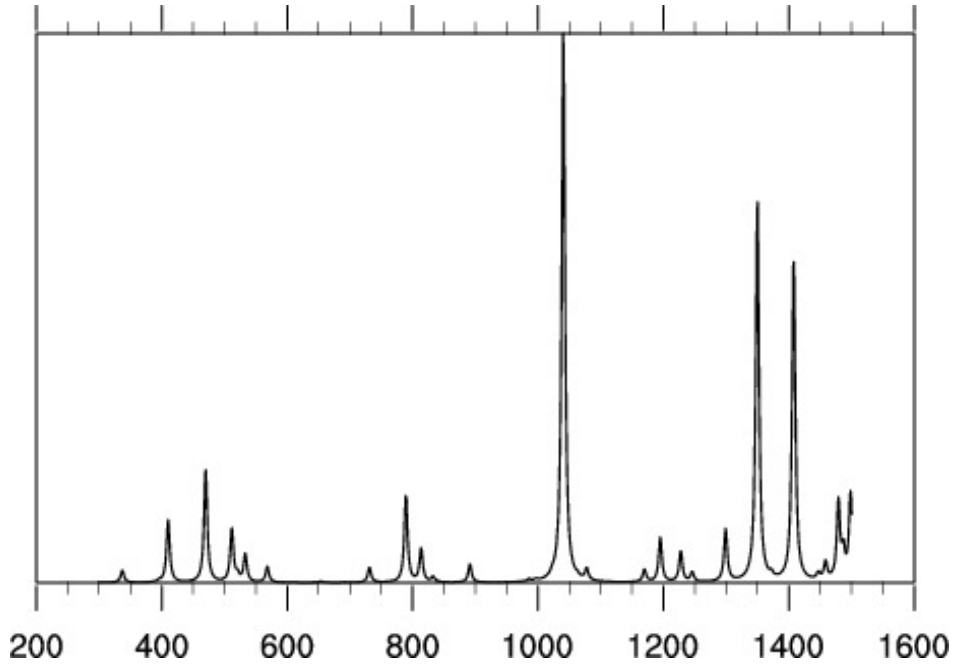


method	harmonic	anharmonic
LDA	+0.0025	+0.0024
BLYP	+0.0024	+0.0023
B3LYP	+0.0022	+0.0020
PBE	+0.0023	+0.0022
PBE0	+0.0020	+0.0018
HF	+0.0009	+0.0005

* All numbers in Hz (all DC Hamiltonian).

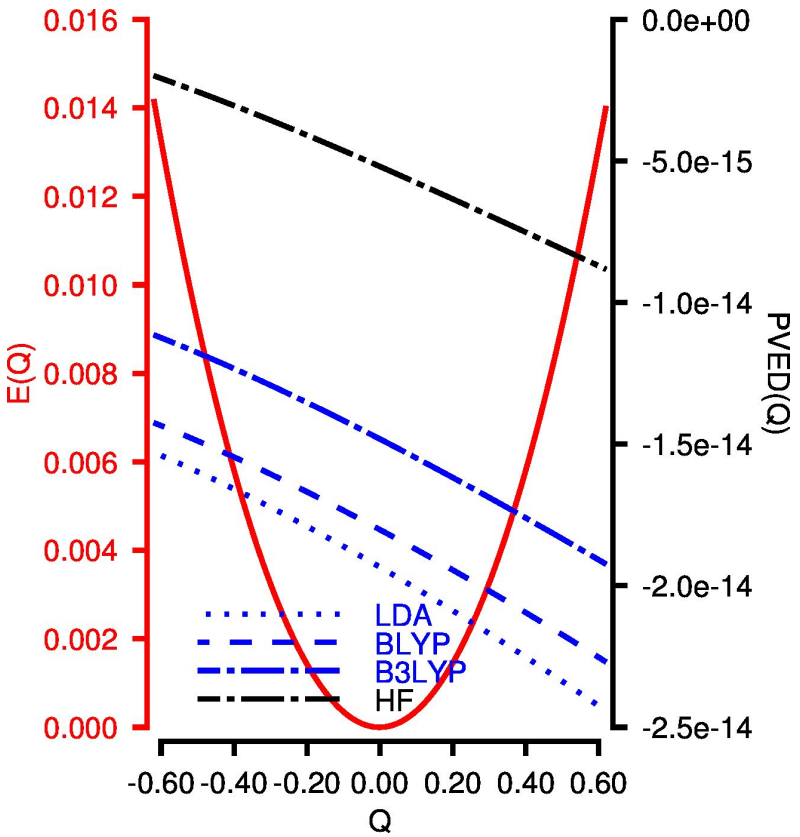
C_5H_7NOS-ReOMe





- 1227 cm^{-1}

C_5H_7NOS-ReOMe

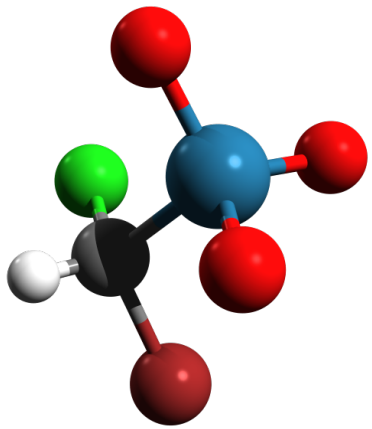


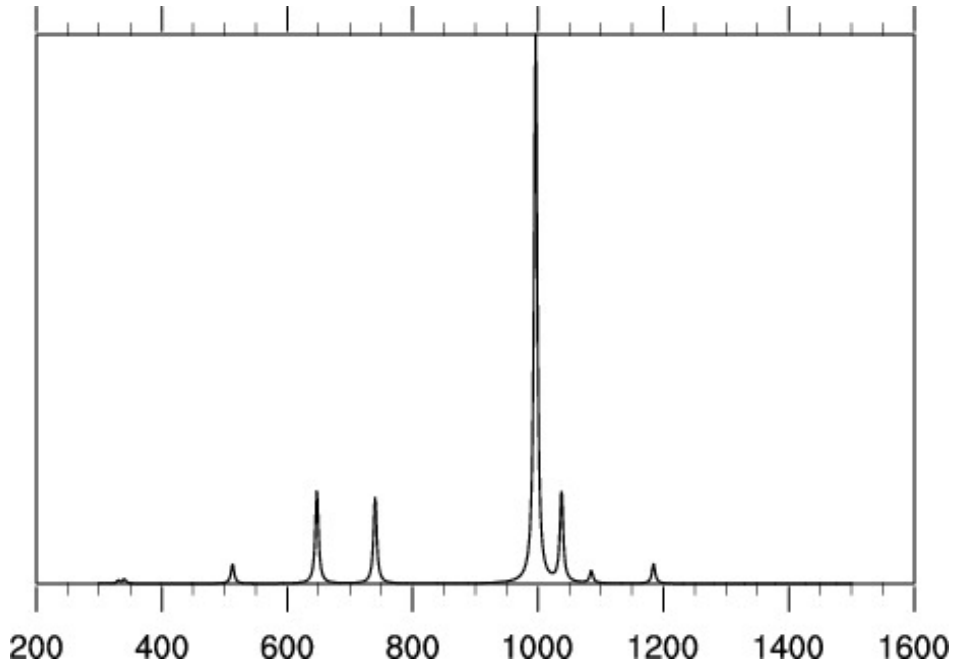
method	harmonic	anharmonic
LDA	–0.672	–0.753
BLYP	–0.582	–0.656
B3LYP	–0.482	–0.554
HF	–0.279	–0.341

method	$P^{[1]}$	$P^{[2]}$
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).

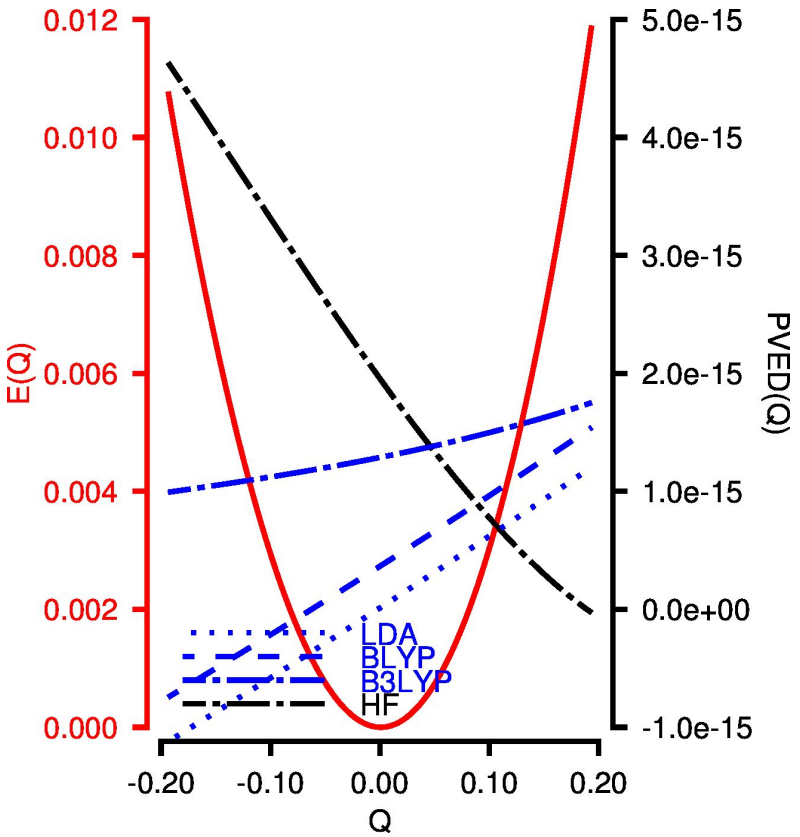
CHClBrReO3





- 996 cm^{-1}

CHClBrReO3

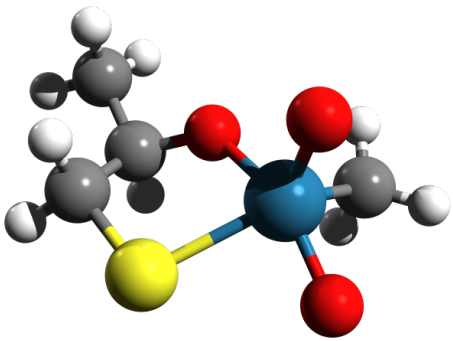


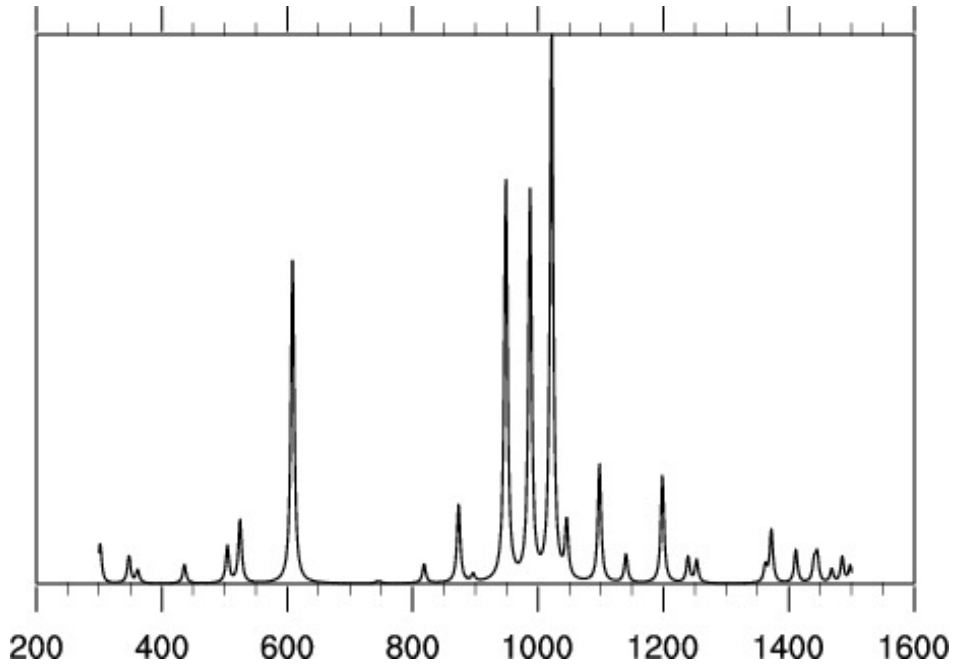
method	harmonic	anharmonic
LDA	+0.040	−0.088
BLYP	+0.044	−0.082
B3LYP	+0.112	+0.070
HF	+0.453	+0.708

method	$P^{[1]}$	$P^{[2]}$
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).

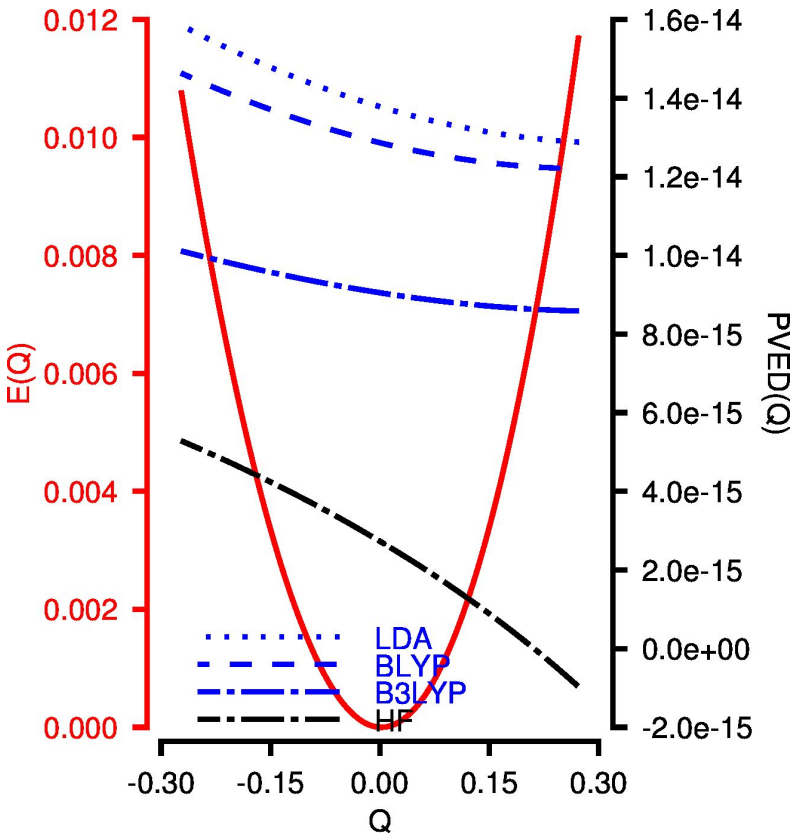
C_3H_6OS–ReO_2Me (isomer 1)





- 987 cm^{-1}

C_3H_6OS–ReO_2Me (isomer 1)

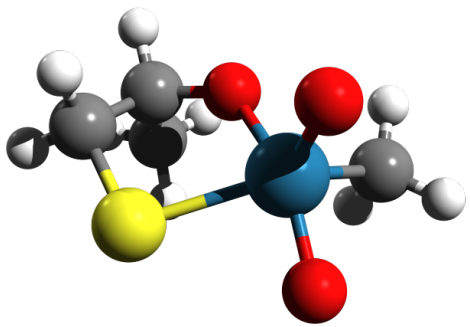


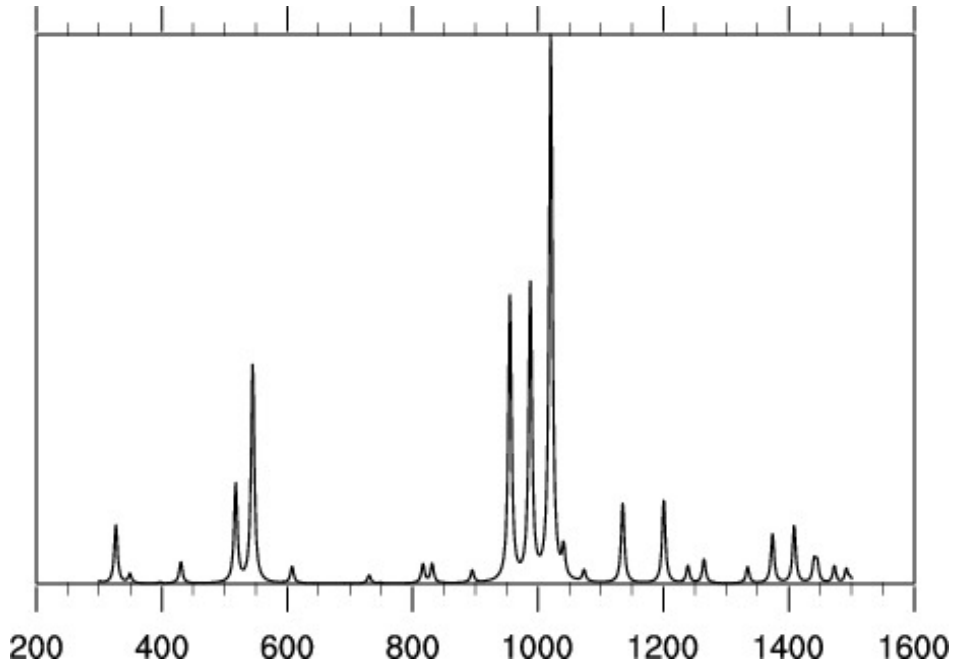
method	harmonic	anharmonic
LDA	+0.778	+0.933
BLYP	+0.739	+0.865
B3LYP	+0.399	+0.479
HF	–0.749	–0.409

method	$P^{[1]}$	$P^{[2]}$
LDA	–18.2	+52.1
BLYP	–14.9	+49.4
B3LYP	–9.6	+26.9
HF	–36.3	–48.2

* All numbers in Hz (all DC Hamiltonian).

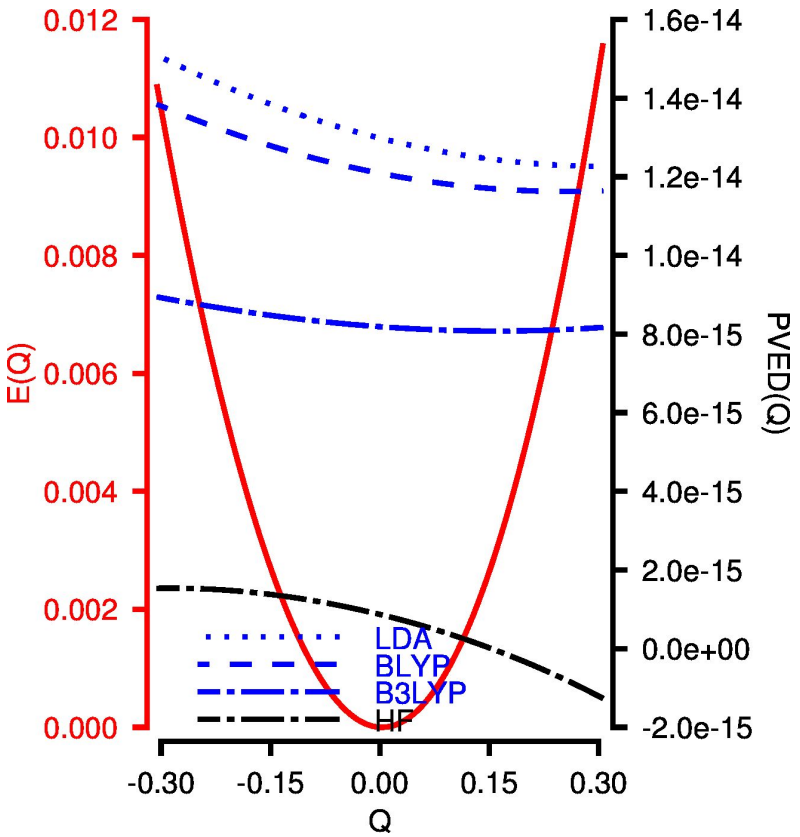
C_3H_6OS–ReO_2Me (isomer 2)





- 988 cm^{-1}

C_3H_6OS–ReO_2Me (isomer 2)

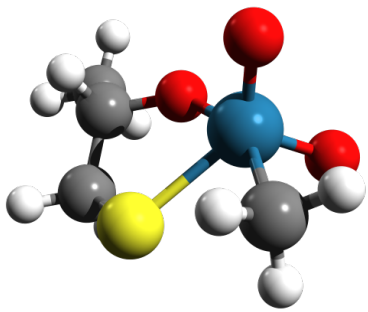


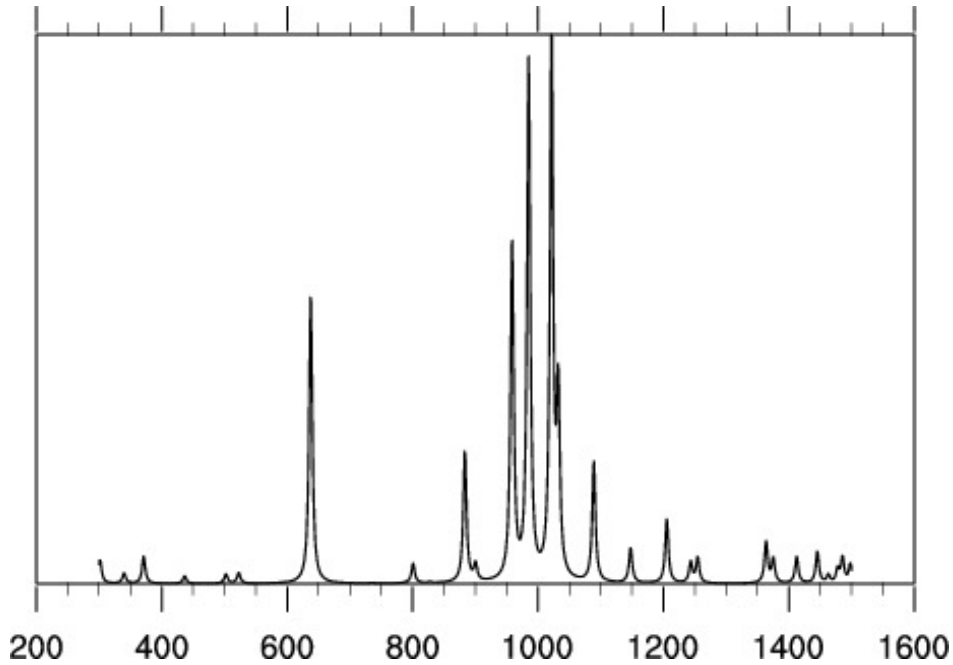
method	harmonic	anharmonic
LDA	+0.923	+1.053
BLYP	+0.870	+0.969
B3LYP	+0.494	+0.528
HF	–0.957	–0.816

method	$P^{[1]}$	$P^{[2]}$
LDA	–15.3	+49.0
BLYP	–11.9	+46.1
B3LYP	–4.4	+26.4
HF	–14.8	–49.1

* All numbers in Hz (all DC Hamiltonian).

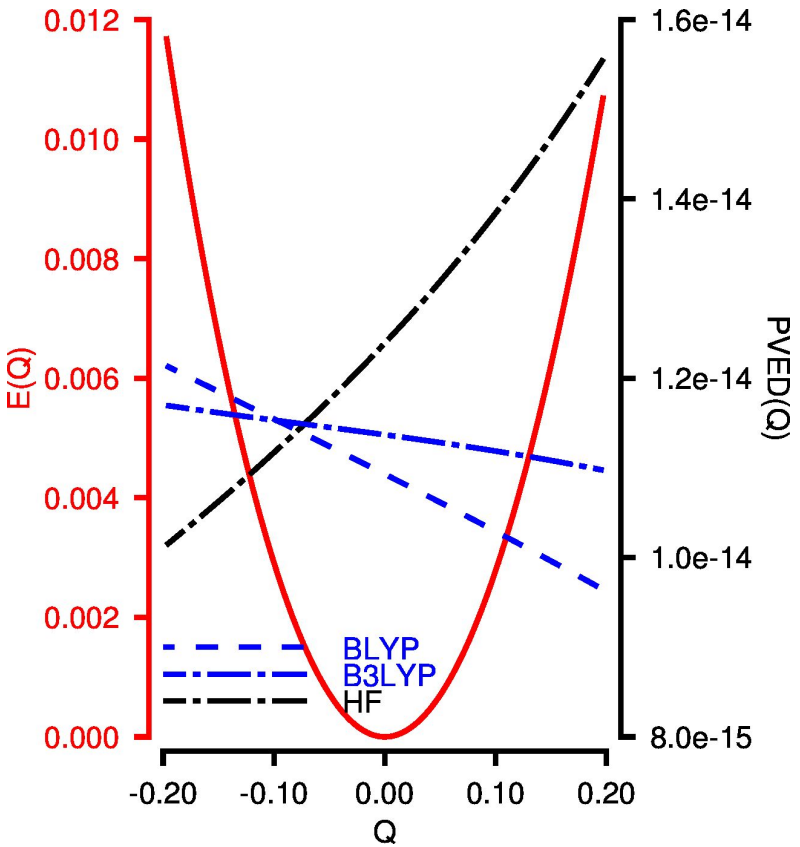
C_3H_6OS–ReO_2Me (isomer 3)





- 985 cm^{-1}

C_3H_6OS–ReO_2Me (isomer 3)



method	harmonic	anharmonic
BLYP	–0.056	–0.162
B3LYP	–0.047	–0.077
HF	+0.602	+0.828

method	$P^{[1]}$	$P^{[2]}$
BLYP	–20.5	–7.6
B3LYP	–5.5	–6.4
HF	+43.4	+75.2

* All numbers in Hz (all DC Hamiltonian).

conclusions

- we obtain significant PV shifts for all studied Re complexes
- we see large sensitivity on molecular structure elements
- we see large sensitivity on choice of method (functional)
- lacking higher-level methods we cannot judge the quality of our results
- we need to develop higher-level methods and push the machinery to the limit