A new method for scaling harmonic frequencies to match experiment

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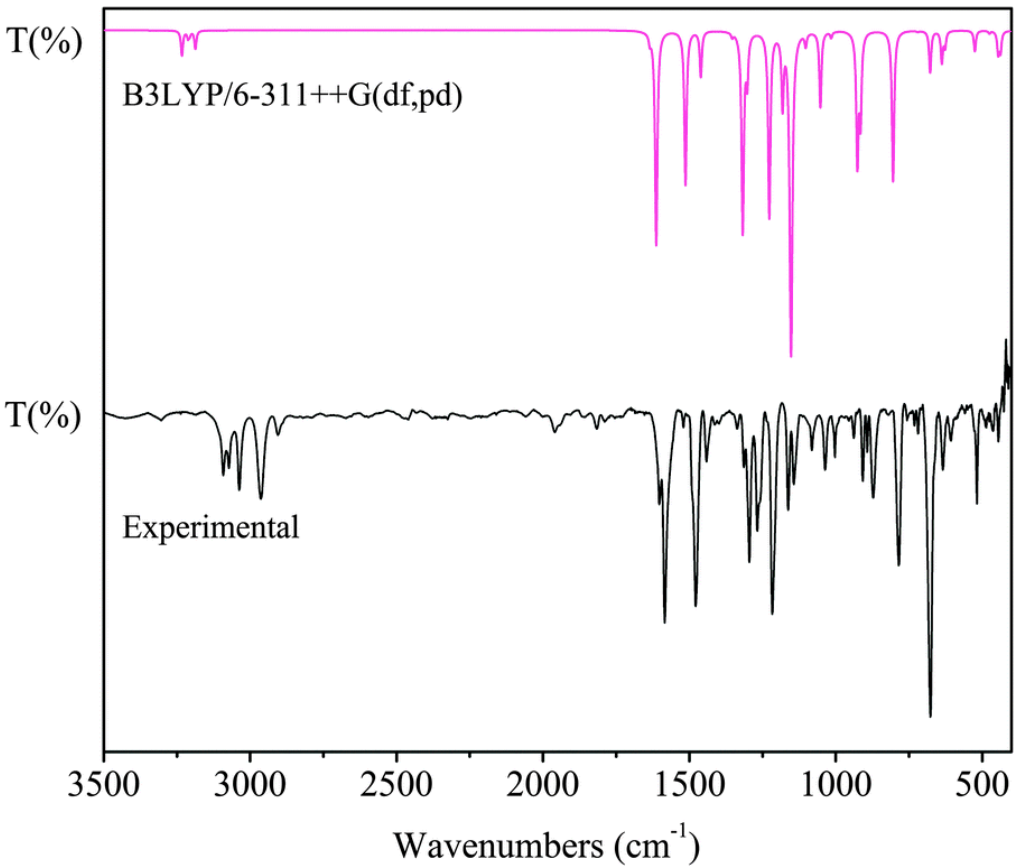
What's the problem?

Want to be able to accurately model IR spectra

Harmonic normal mode analysis is (relatively) cheap, easily implemented, widely available, but...

What's the problem?



Pàez-Jerez *et al.*, *New J. Chem.*, 2015, **39**, 4445-4451

Harmonic frequency correction models

Are errors due to harmonic approximation or level of *ab initio* theory?

Usual approach:

- Who knows? Who cares? Just scale frequencies to match experiment.
- Different scaling factors required for each level of theory
- Some indications that different scaling factors required for different frequency ranges

Harmonic frequency correction models

Are errors due to harmonic approximation or level of *ab initio* theory?

Our approach:

- Disentangle anharmonicity and methodological incompleteness errors
- Using a library of high quality analytic potential energy surfaces
- Calculate anharmonic frequencies that agree with experiment, get exact harmonic frequencies and anharmonicities for 'free'

Linear correction model

Harmonic frequency scaling model:

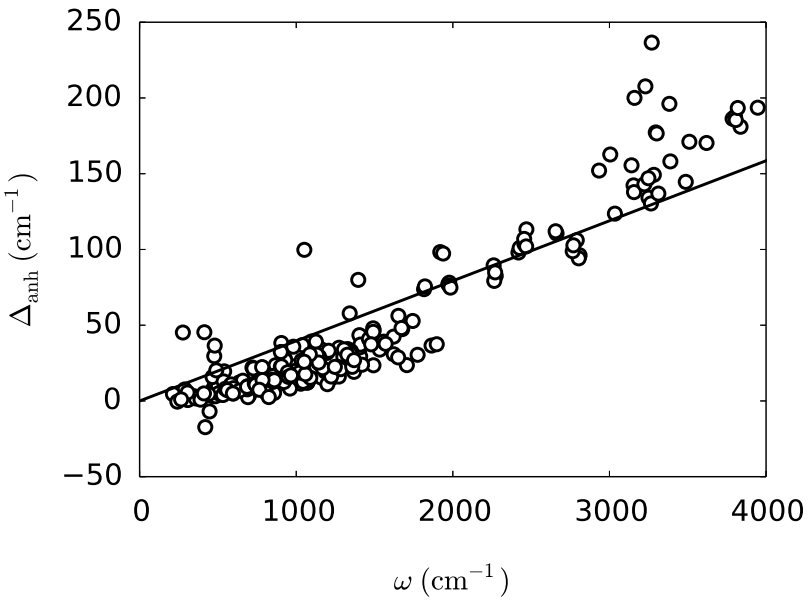
$$\nu \approx \lambda\omega$$

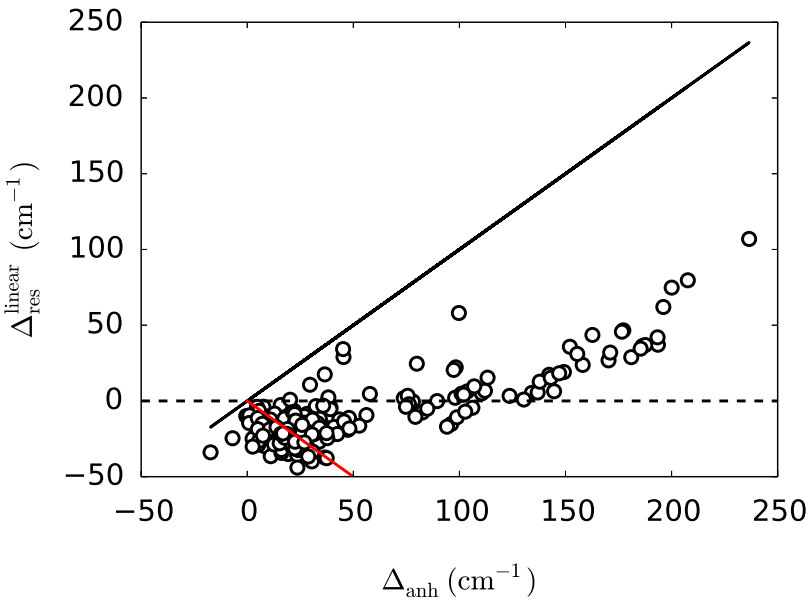
ν = anharmonic frequency, ω = harmonic frequency, λ = scaling factor.

Can be recast as linear correction model:

$$\begin{aligned} \nu &\approx (1 - c_1)\omega \\ &\approx \omega - c_1\omega \\ \omega - \nu &\approx c_1\omega \\ \Delta_{\text{anh}} &\approx c_1\omega \end{aligned}$$

Linear correction model





Polynomial correction model

Reminder: linear correction model

$$\begin{aligned} \nu &\approx \omega - c_1\omega \\ &\downarrow \\ \Delta_{\mathrm{anh}} &\approx c_1\omega \end{aligned}$$

Easily generalized to polynomial correction model:

$$\begin{aligned} \nu &\approx \omega - c_1\omega - c_2\omega^2 \\ &\downarrow \\ \Delta_{\mathrm{anh}} &\approx c_1\omega + c_2\omega^2 \end{aligned}$$

Quadratic correction model

During fitting process, $c_1 \approx 0$.

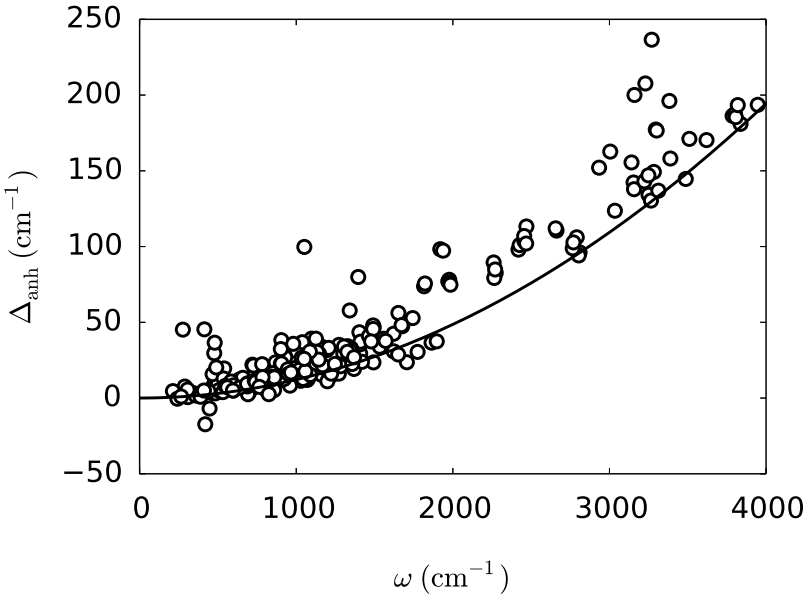
Setting $c_1 = 0$ gives quadratic correction model:

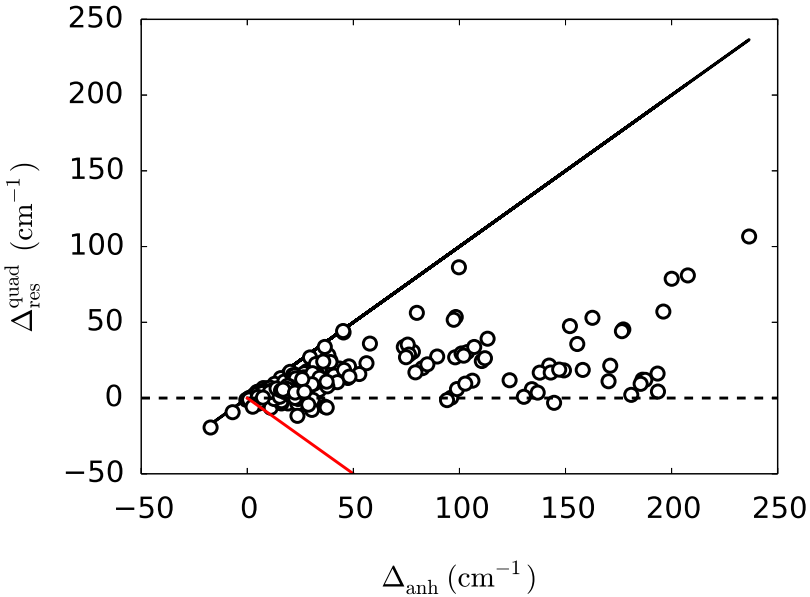
$$\Delta_{\mathrm{anh}} \approx c_2 \omega^2$$

Also apply "no overcorrection" condition:

$$\nu_{\mathrm{approx}} > \nu$$

Quadratic correction model for ZPVE calculations





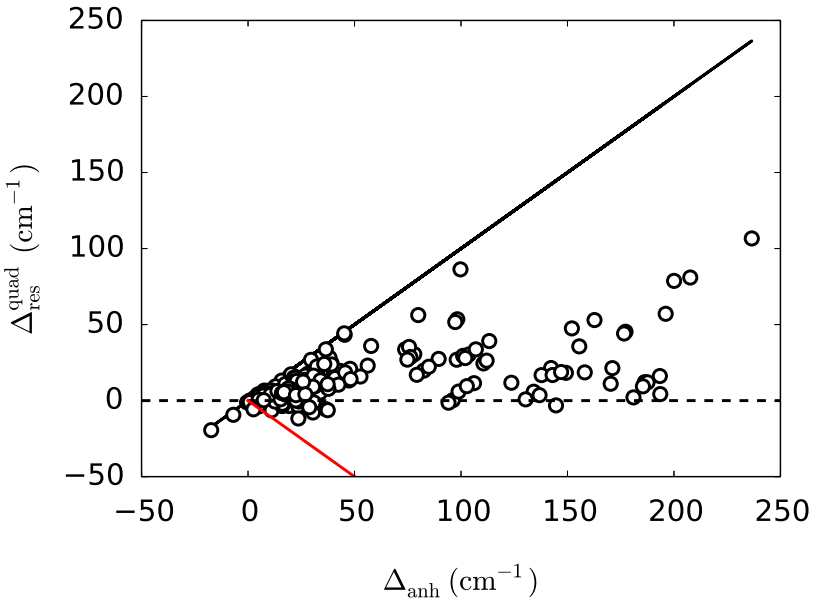
Mean absolute error: 13.3 cm^{-1}

Methodological incompleteness error

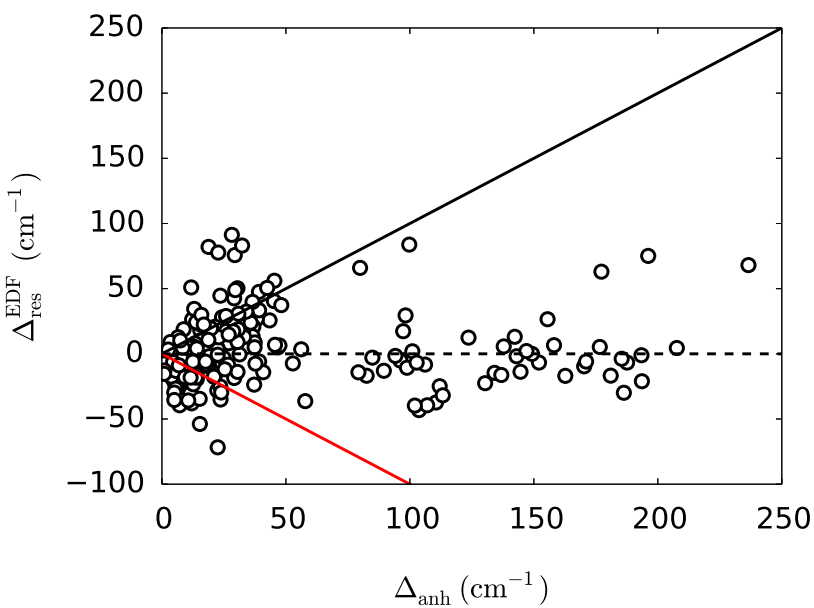
Can't usually obtain exact harmonic frequencies

Are DFT frequencies good enough?

Exact



DFT (EDF/cc-pVTZ)



Take-home messages

- DFTs model 'medium-range' intramolecular interactions poorly

- DFTs model covalent bonding reasonably

- Quadratic correction model will improve DFT stretching frequencies but *not* exacerbate problems with bends and torsions.

- Quadratic correction model for fundamental frequencies:

$$\nu \approx \omega - 0.00001215\ \omega^2$$

- Halve the coefficient if scaling frequencies for ZPVE calculations