

Vibrational Solvatochromism from First-Principles: SolEFP Method

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Ab initio theoretical model for simple vibrational probes

Introduction

- ▶ Vibrational lineshape and band position is deeply related to molecular dynamics and structural changes
 - ▷ Thorough understanding of vibrational solvatochromism is crucial!
- ▶ Accurate theoretical model is needed!
 - ▷ interpretation of experimental spectra require simulations
 - ▷ all of the proposed approaches are **semi-empirical**
 - ▷ here we propose **fully first-principles theory** of vibrational solvatochromism
- ▶ Frequency shift is described in terms of coarse-grained models[1,2]

$$\Delta\omega_j \simeq \left\{ \frac{1}{2M_j\omega_j} \left(\frac{\partial^2}{\partial Q_j^2} - \sum_i \frac{g_{ijj}}{M_i\omega_i^2} \frac{\partial}{\partial Q_i} \right) \right\} U(\mathbf{Q})$$

- ▷ Solute-solvent interaction potential $U(\mathbf{Q})$ is approximately partitioned into physically well-defined components[3]

Coulomb electrostatics

Distributed solvatochromic multipole moments (SolCamm)[2]

$$\Delta\omega_j^{\text{Coul}} \approx \sum_x \left\{ l^{(x)} \phi + L_a^{(x)} \phi_a + \frac{1}{3} \Lambda_{ab}^{(x)} \phi_{ab} + \frac{1}{15} \lambda_{abc}^{(x)} \phi_{abc} + \dots \right\}$$

Exchange-repulsion

EFP Repulsion energy

$$E_{\text{ex}} \approx \sum_{i \in A} \sum_{j \in B} \left[-4 \sqrt{\frac{-2 \ln |S_{ij}|}{\pi}} \frac{S_{ij}^2}{R_{ij}} - 2S_{ij} \left(\sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - 2T_{ij} \right) + 2S_{ij}^2 \left(- \sum_{J \in B} \frac{Z_J}{R_{iJ}} - \sum_{I \in A} \frac{Z_I}{R_{Ij}} + 2 \sum_{l \in B} \frac{1}{R_{il}} + 2 \sum_{k \in A} \frac{1}{R_{kj}} - \frac{1}{R_{ij}} \right) \right]$$

Polarization

Distributed polarizability derivatives wrt normal coordinates

$$\Delta\omega_j^{\text{pol}} \approx -\frac{1}{2} \mathbf{a}_j \cdot \mathbf{F}, \text{ where } \mathbf{a}_j = \mathbf{F}^T \cdot [\mathbf{D}^{-1} \Delta_j \mathbf{D}^{-1}] - \Phi_j^T \cdot [\mathbf{D}^{-1} + (\mathbf{D}^{-1})^T]$$

N-methylacetamide

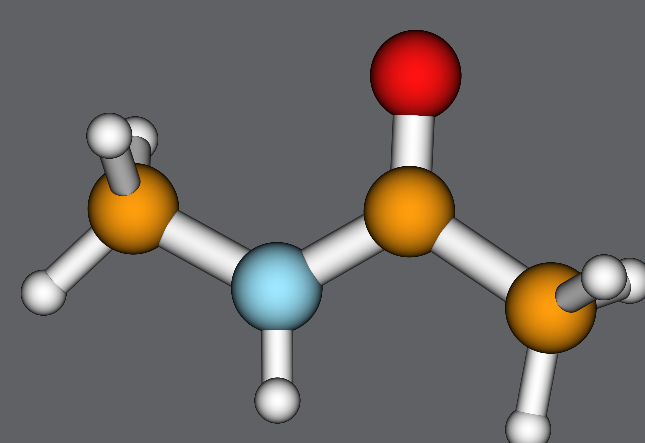


Figure: Probe: amide I mode

Performance of SolEFP

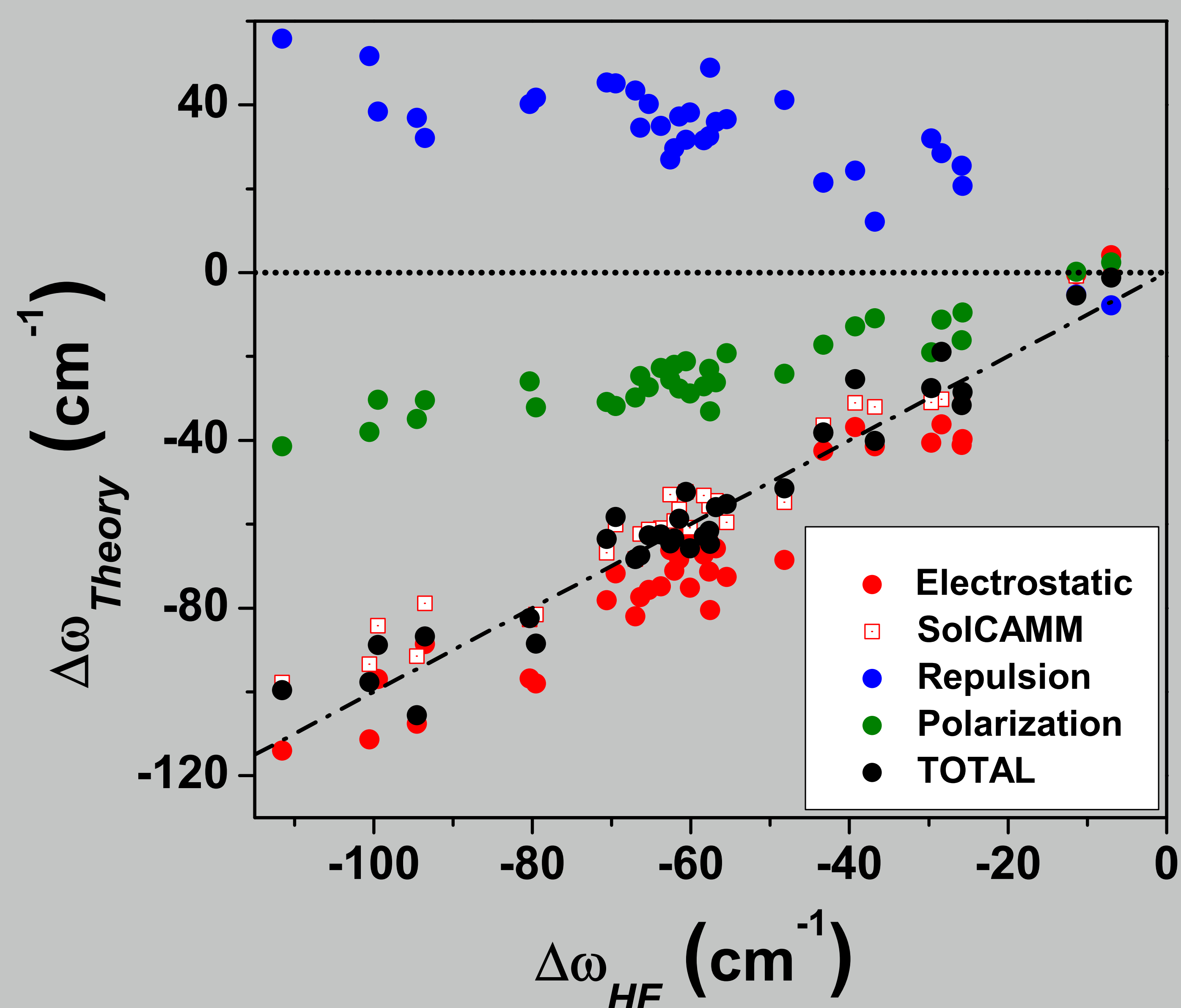
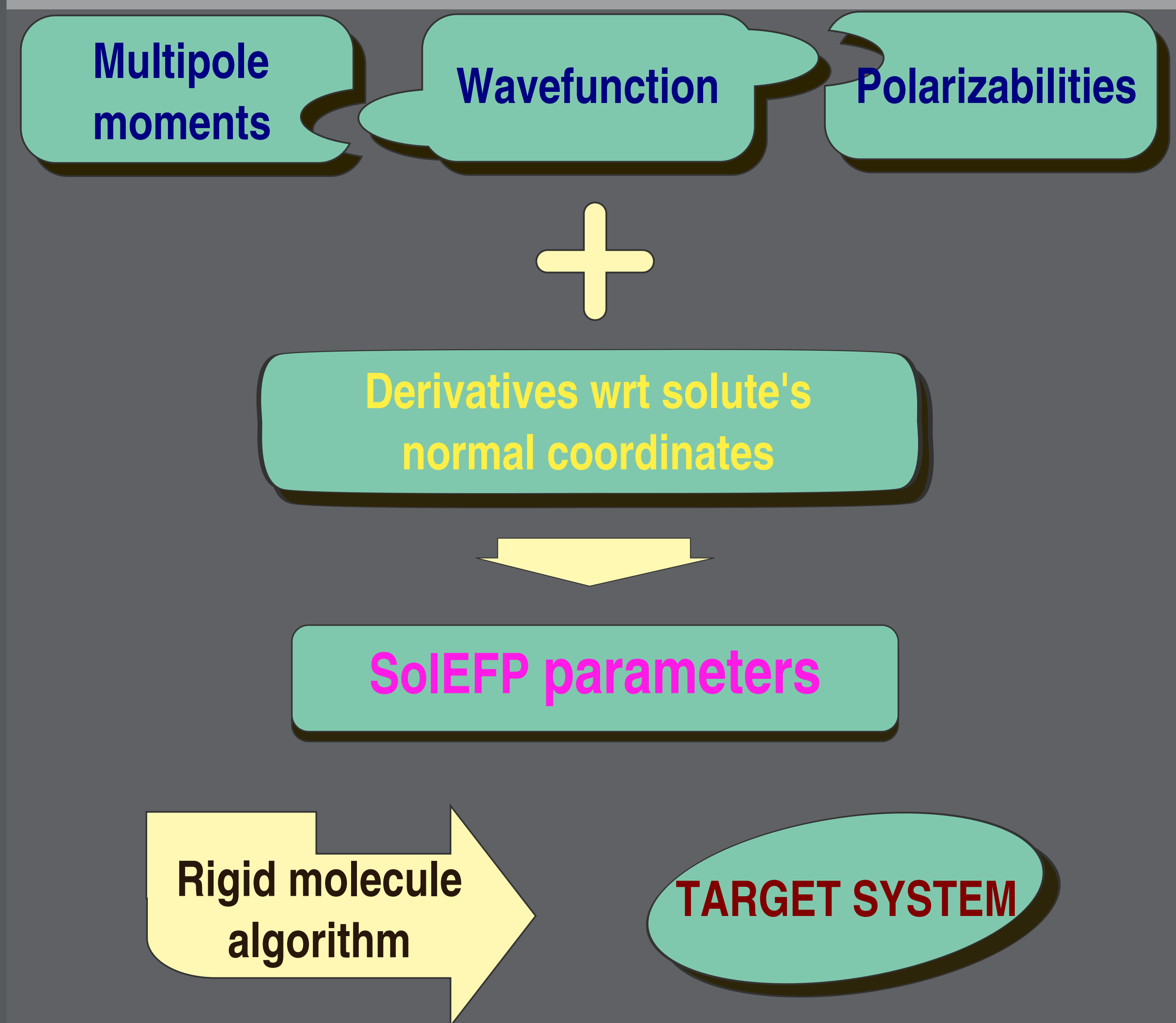


Figure: Amide I mode frequency shifts of *N*-methylacetamide (NMA) in water clusters

SolEFP model overview



Onsager test of solvatochromic operator

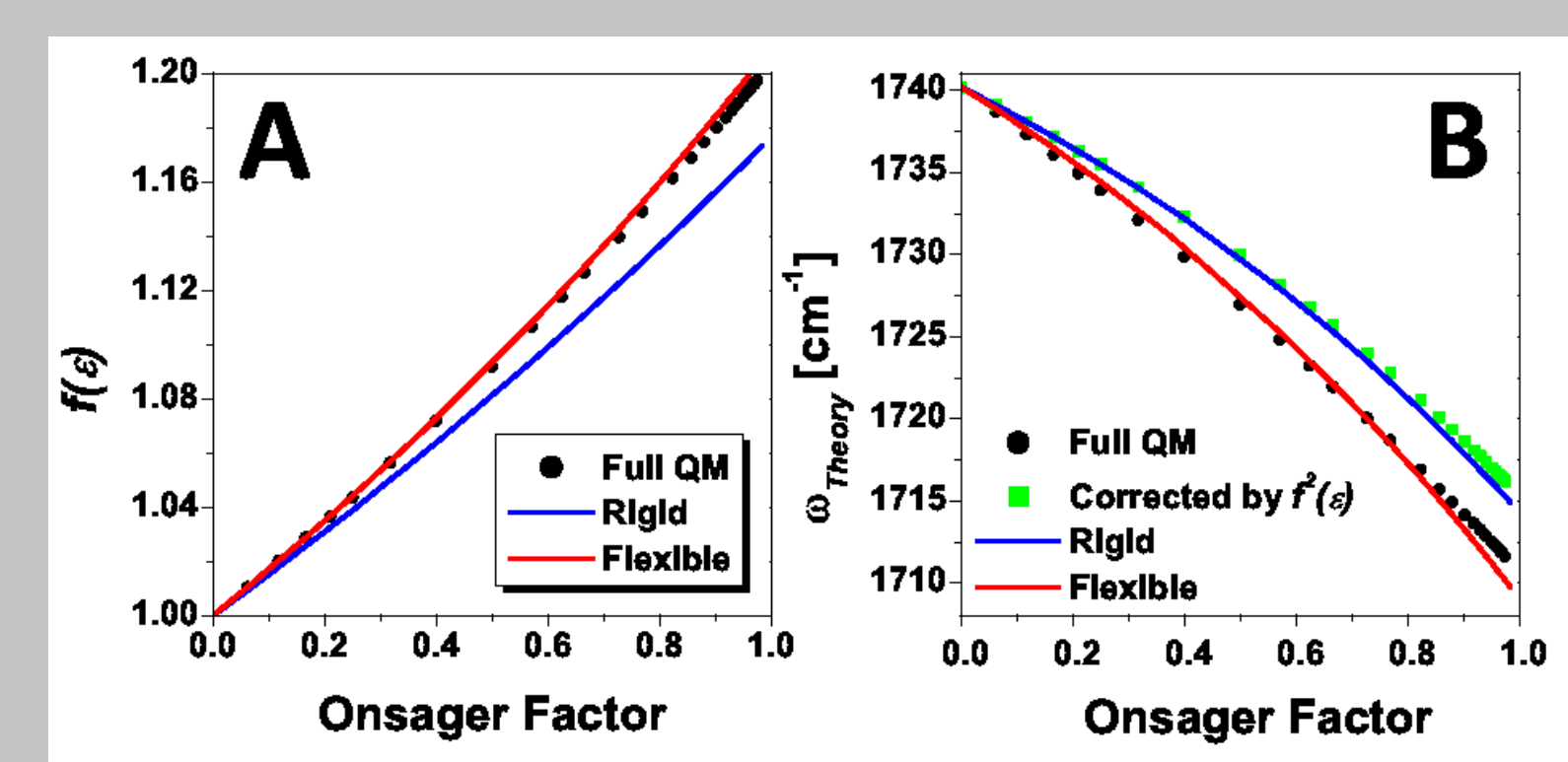


Figure: NMA in spherical cavity

Distance dependence

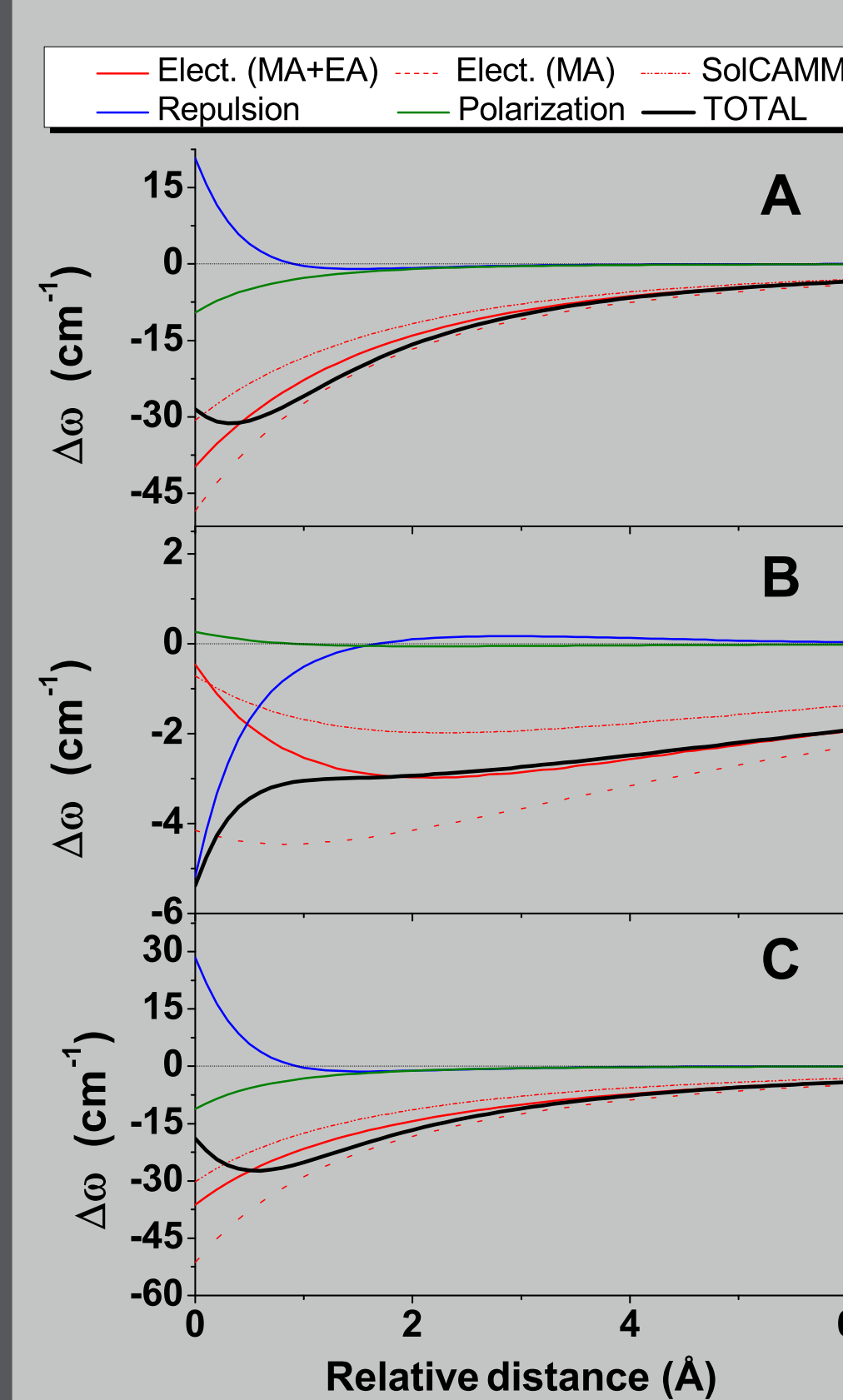


Figure: NMA-water molecule scans

Many-body effects

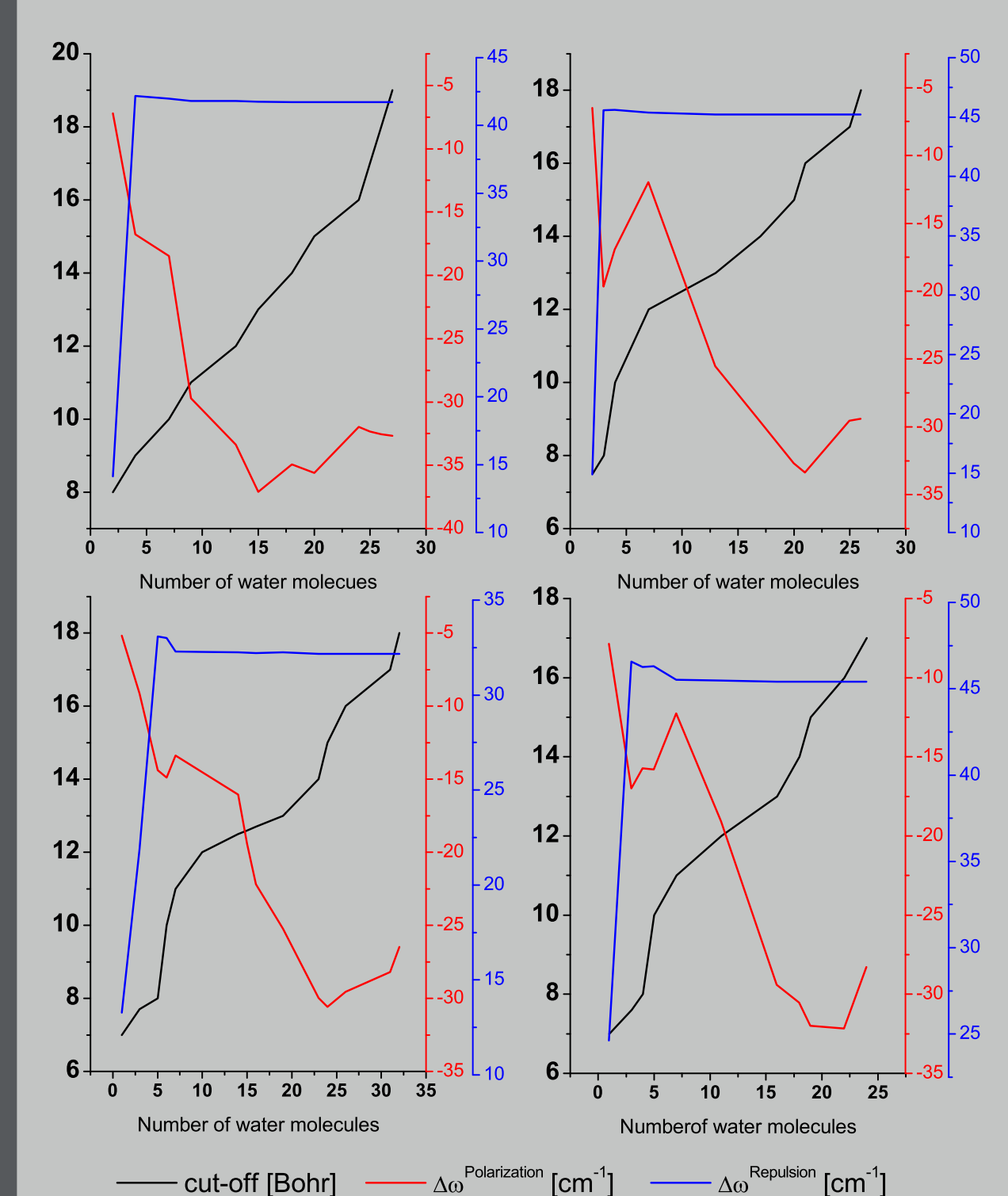


Figure: Polarisation and repulsion: Four NMA-H₂O_{n=27-32} clusters.

Conclusions

- ▶ Accurate for NMA-water systems at Hartree-Fock level
- ▶ Repulsive potential contributes to **large blue-shift**!
- ▶ Polarization is **red-shifting** and highly non-additive!
- ▶ Limitation: applicable to small, quite rigid fragments
- ▶ **Future**: include *electron correlation effects*, apply to MD

References

- [1] M. Cho, *J. Chem. Phys.*, 130, 094505 **2009**
- [2] B. Błasiak, H. Lee, M. Cho, *J. Chem. Phys.*, 139, 044111 **2013**
- [3] M. S. Gordon, L. Slipchenko, H. Li, J. H. Jensen, *Annu. Rep. Comput. Chem.*, 3, 177 **2007**