First-Principles Discrete Model of the Vibrational Solvatochromism based on Effective Fragment Potentials

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SolEFP model

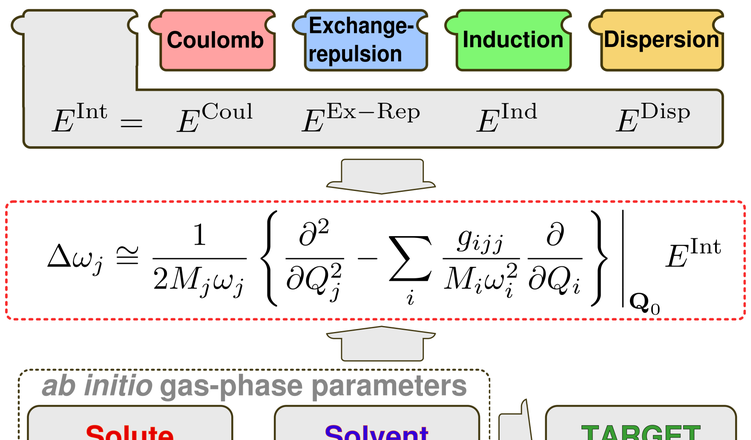
Why do we need this?

- Accurate and efficient model of vibrational solvatochromism is indispensable for interpreting the IR spectra
- Despite the widely acknowledged opinion, vibrational solvatochromism of many IR probes *is not* understood well enough

What is new in our approach?

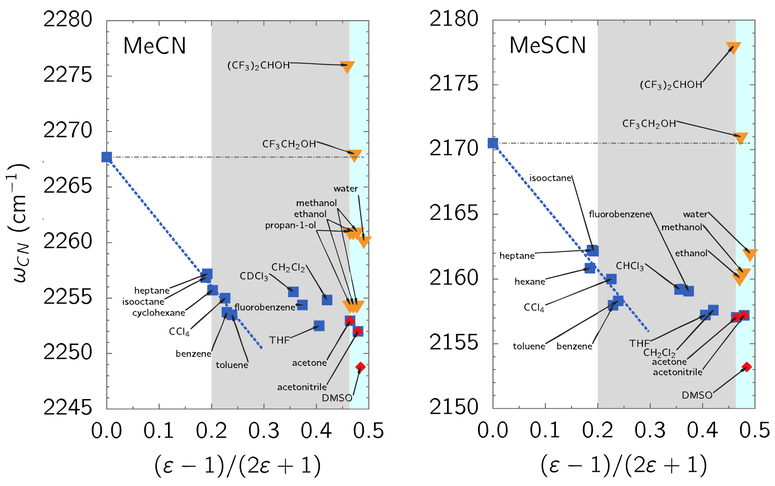
- Previous models are based on Coulombic interactions. Based on our theory, a variety of other interactions is also included
- Our model [1] is derived from first-principles. Previous models generally suffer from lack of versatility because they always have to be *adjusted* to benchmark data

How does it work?



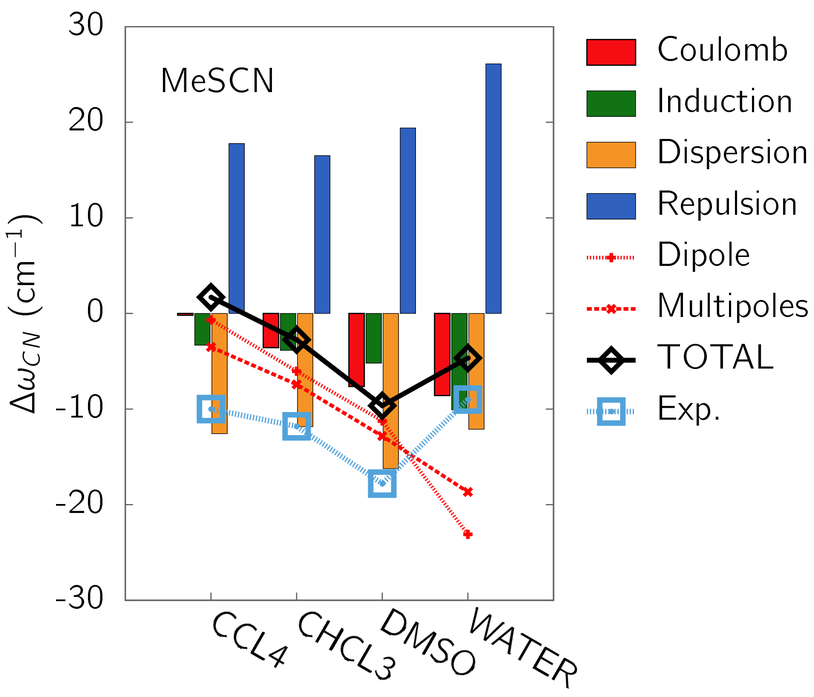
Frequency shifts in reality

The origins of experimental frequency shifts of nitrile (CN) stretch mode in various solvents are not fully understood, in fact. Particularly, where does the blue shift in protic solvents come from? Electrostatics? Something else? [2]



SolEFP/Amber vs reality

While amide I mode in N-methylacetamide [1] (NMA) can be well described by electrostatics, CN stretch mode in methyl thiocyanate (MeSCN) cannot. [2] Hydrogen bonds lead to substantial exchange-repulsion blue shifts. Multipole-based models incorrectly predict opposite trend in water.

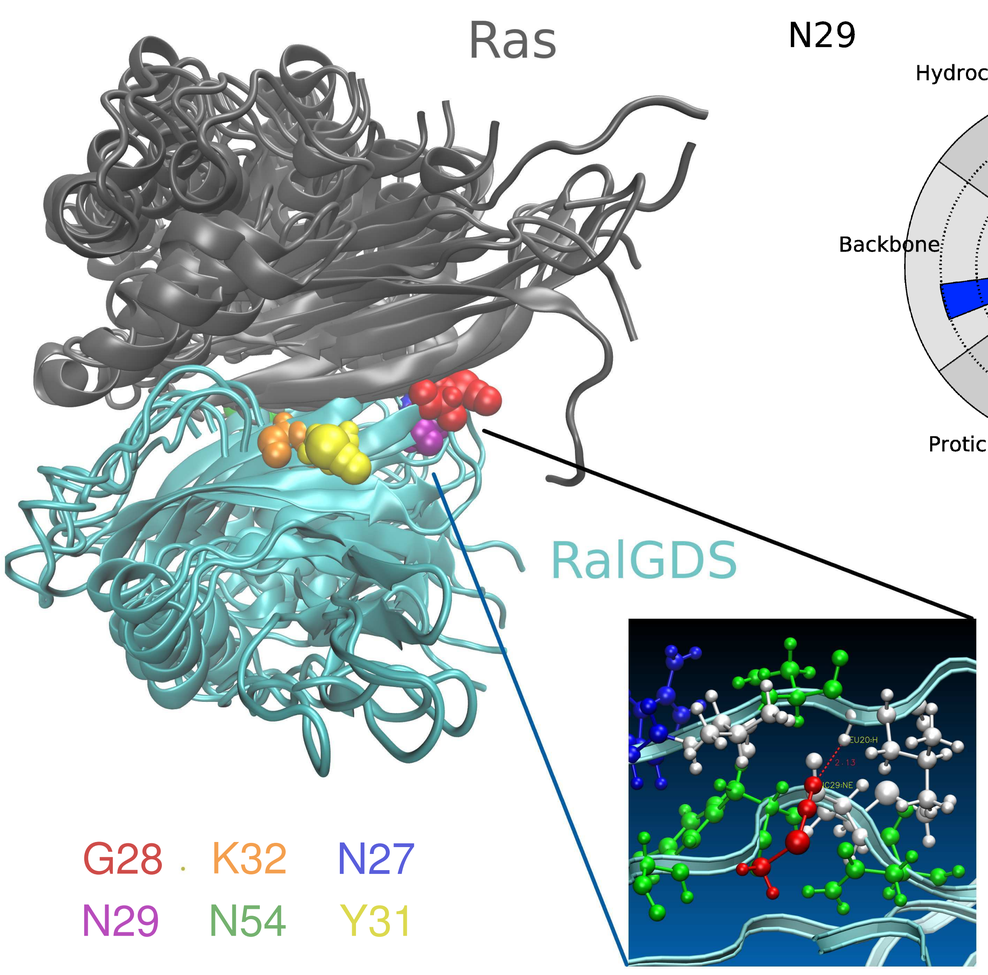


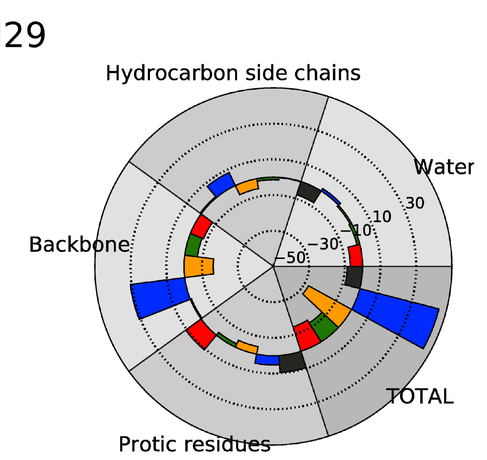
Non-electric field effects

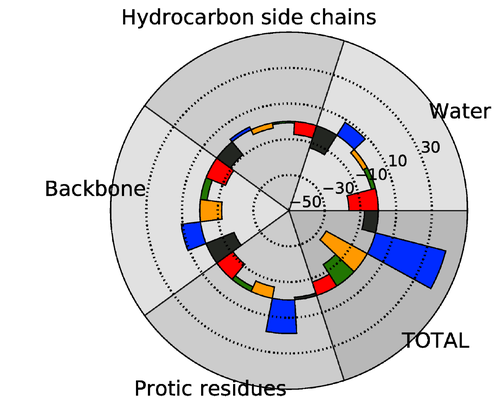
In hydrogen bonding environments, the vibrational solvatochromism of widely used IR probes has to account for exchange-repulsion effects. Dispersion is also an important contribution. [1-2]

$$\Delta\omega_j^{\mathrm{Ex-Rep}} = \frac{4}{M_j\omega_j}\sum_i G_i \sum_{a\in A}\sum_{b\in B}\frac{S_{ab}}{r_{ab}}\left[\frac{\partial S_{ab}}{\partial Q_i} + \ldots\right]$$

$$\Delta\omega_j^{\mathrm{Disp}} = \frac{1}{4\pi M_j\omega_j}\sum_i G_i \sum_{a\in A}\sum_{b\in B}\times \frac{\partial}{\partial Q_i}\int_0^\infty \mathrm{Tr}\,\left[\boldsymbol{\alpha}_a\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_b\cdot\mathbf{T}\right]d\Omega + \ldots$$







Frequency shifts of CN stretch mode at the protein interface

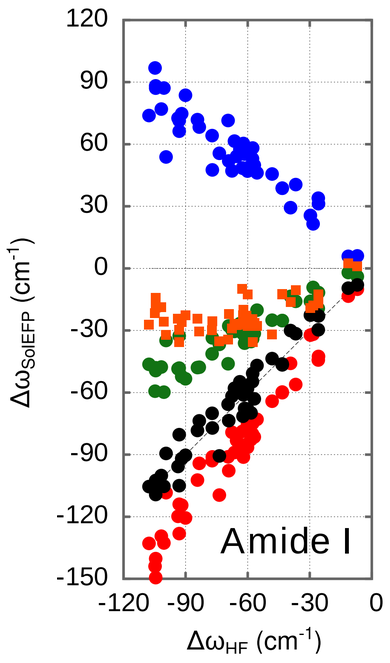
We have observed [2] that not only H-bonding can contribute to strong specific frequency shifts but also *steric contacts* between IR probe and environment. In particular, spatial confinement inside protein induces frequency shifts which cannot be correctly described by electrostatics.

SOLVSHIFT©

To understand solvatochromism

NMA-water clusters

Validation



Summary

- Our model accounts for electrostatic and exchange-repulsion effects
- We can qualitatively predict experimental data
- Studies based on Coulombic approximation need to be re-investigated
- We need to improve accuracy of our model and MD simulation protocol

Acknowledgements

This work was supported by grant IBS-R023-D1. We thank Wrocław Centre for Networking and Supercomputing for providing high quality computational resources.

References

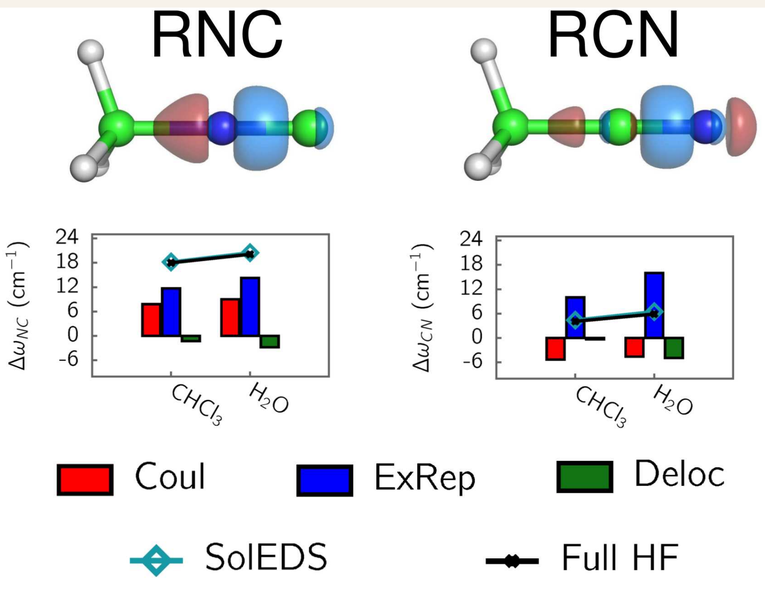
[1] B. Błasiak, M. Cho, *J. Chem. Phys.*, 143, 164111 **2015**.

[2] B. Błasiak, A. W. Ritchie, L. J. Webb, M. Cho, *Phys.Chem.Chem.Phys.*, In Press **2016**.

[3] M. Maj, C. Ahn, B. Błasiak, K. Kwak, H. Han and M. Cho, *Under revision*, **2016**.

Future: apply SolEFP to new IR probes [3]

$$\frac{\partial\boldsymbol{\mu}}{\partial Q} = -\iiint\frac{\partial\rho}{\partial Q}\mathbf{r}\cdot d\mathbf{r} + \sum_x Z_x\frac{\partial\mathbf{r}_x}{\partial Q}$$



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