# First-Principles Theory of Vibrational Solvatochromism

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## SolEFP model (Solvatochromism theory based on effective fragment potentials)

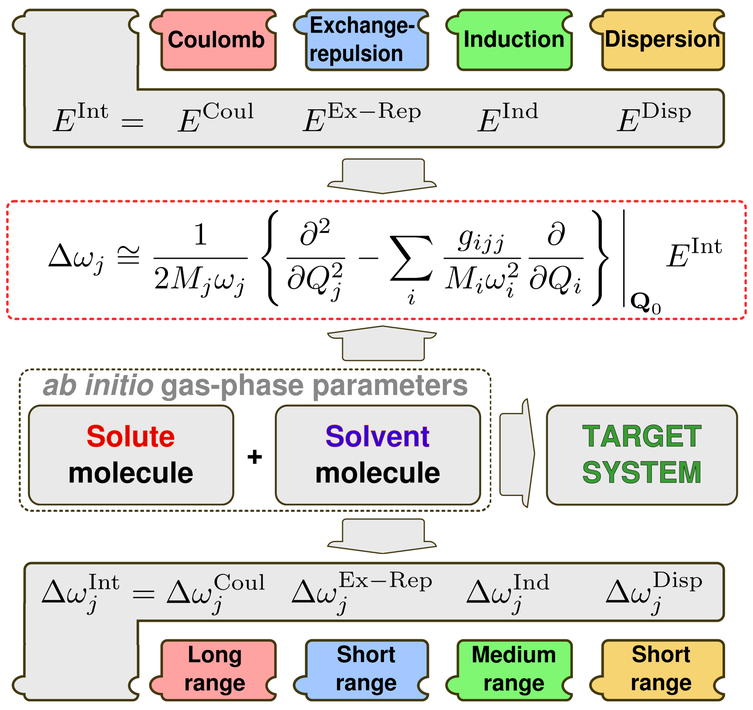
### Why do we need this?

- Accurate and efficient model of vibrational solvatochromism is very important for understanding and interpreting the 1D and 2D IR spectra
- Many IR probes have been systematically used to probe local molecular environments. However, despite the widely acknowledged opinion, their vibrational solvatochromism *is not* understood well enough

### What is new in our approach?

- Previous models are based strictly on Coulombic interactions between IR probe and environment (solvent) molecule. Based on our theory, a variety of other interactions is also included
- Our model is derived from first-principles and is universal for any type of local vibrational mode and solvent molecule. Previous (empirical) models generally suffer from lack of transferability and versatility because they always have to be *adjusted* to some benchmark data

### How does it work?

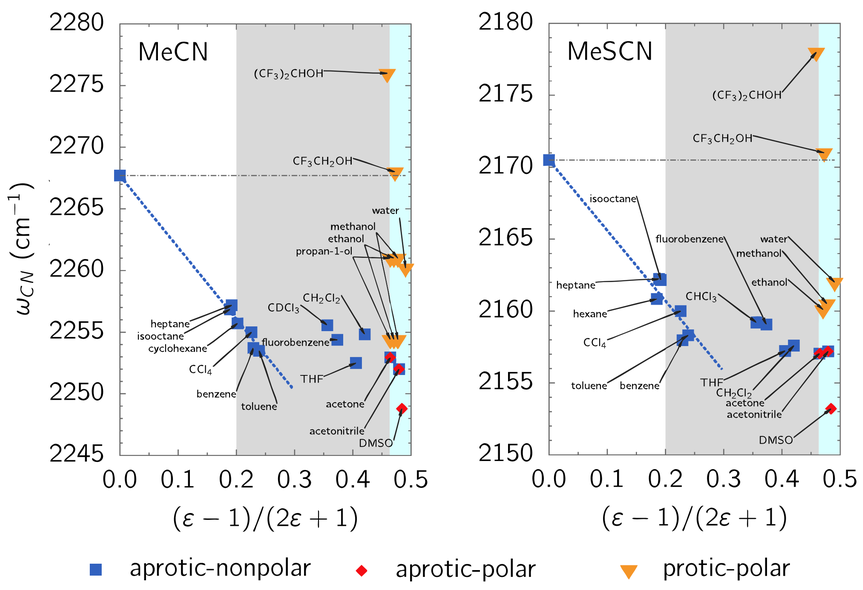


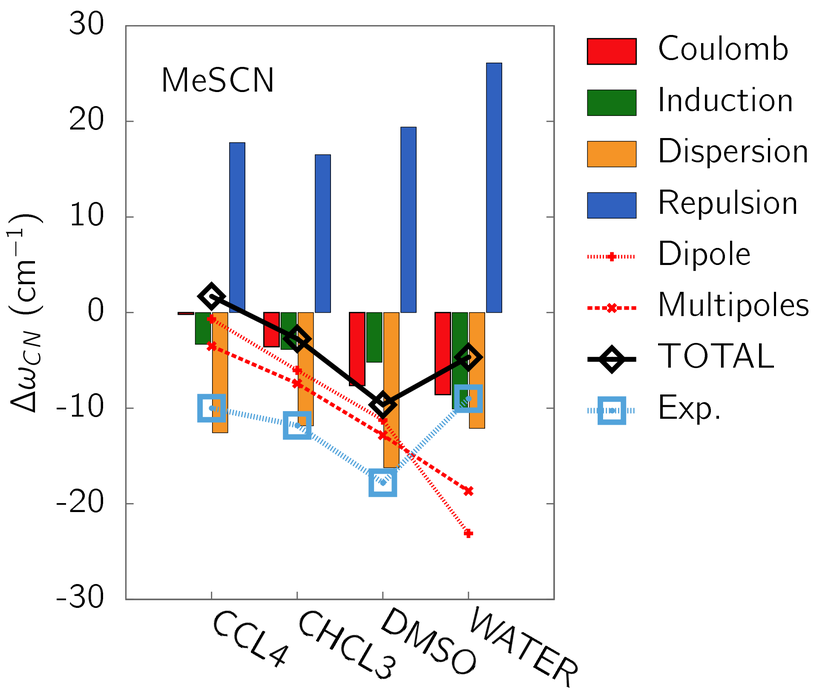

### Frequency shifts in reality

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?

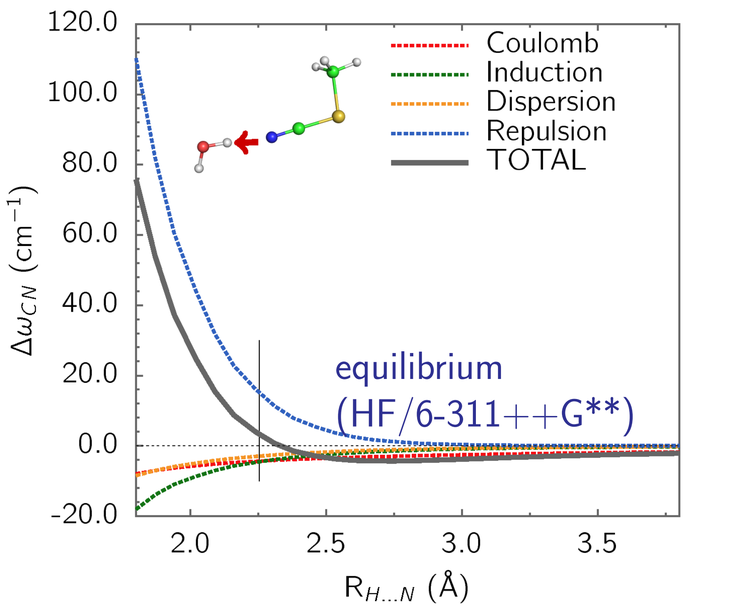
### SolEFP + molecular dynamics simulation vs reality

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



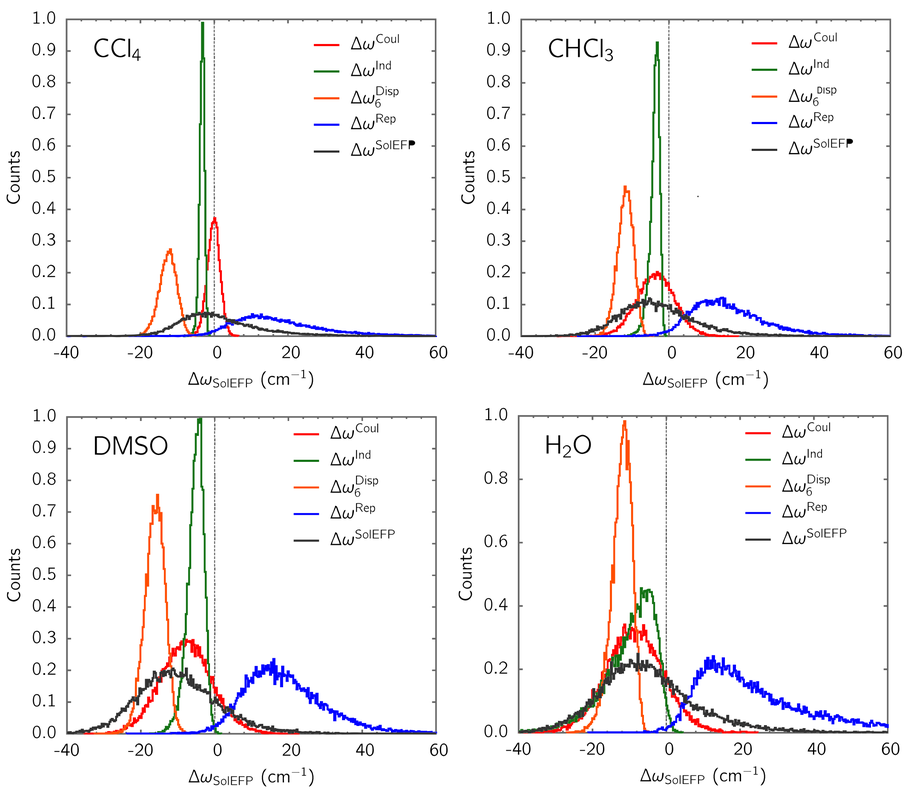



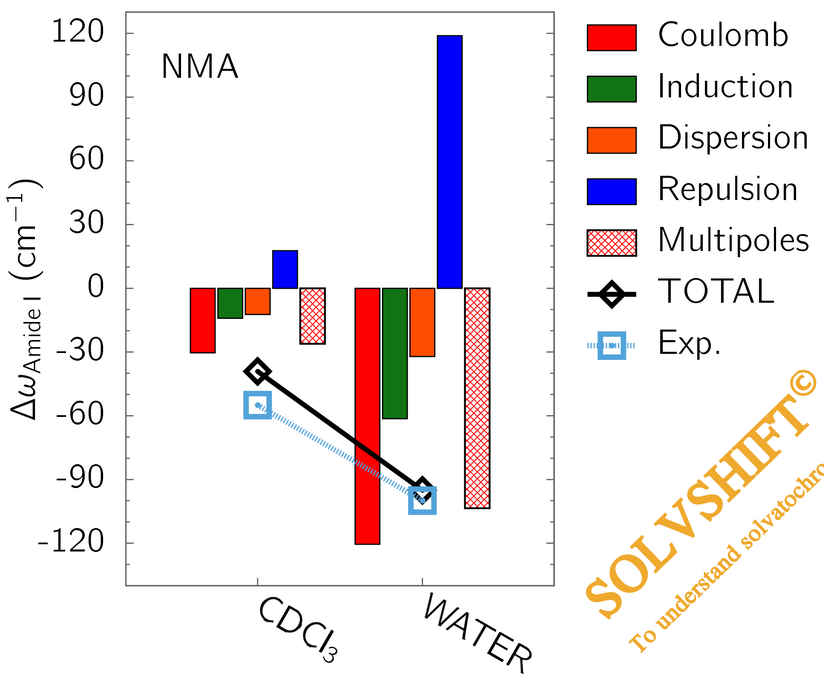

### Model H-bonded complex studies

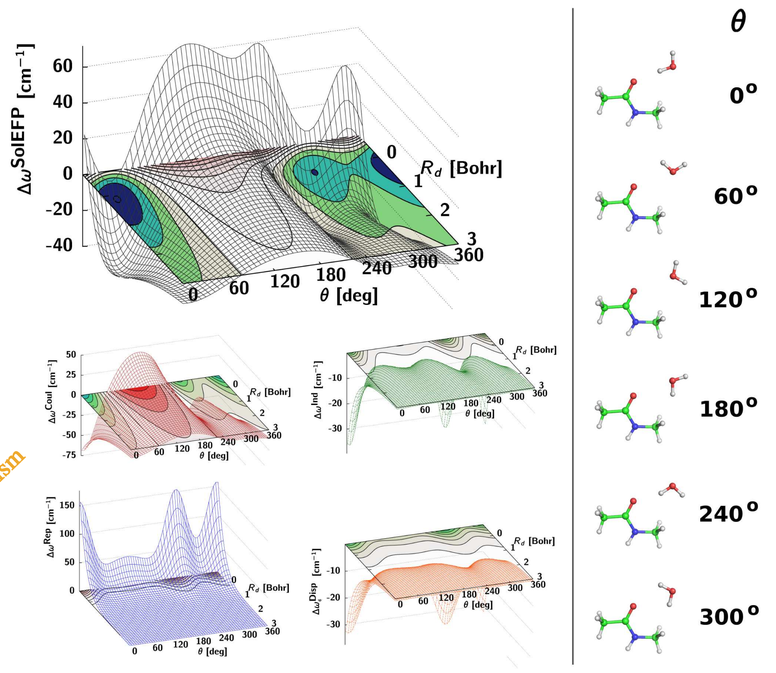



### Distributions of frequency shifts

From MD/SolEFP method for MeSCN in various solvents (CN stretch mode)

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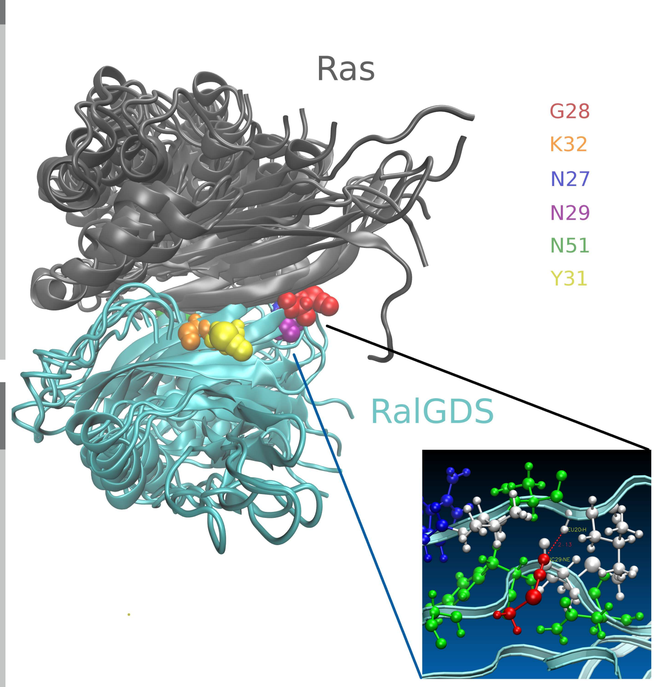
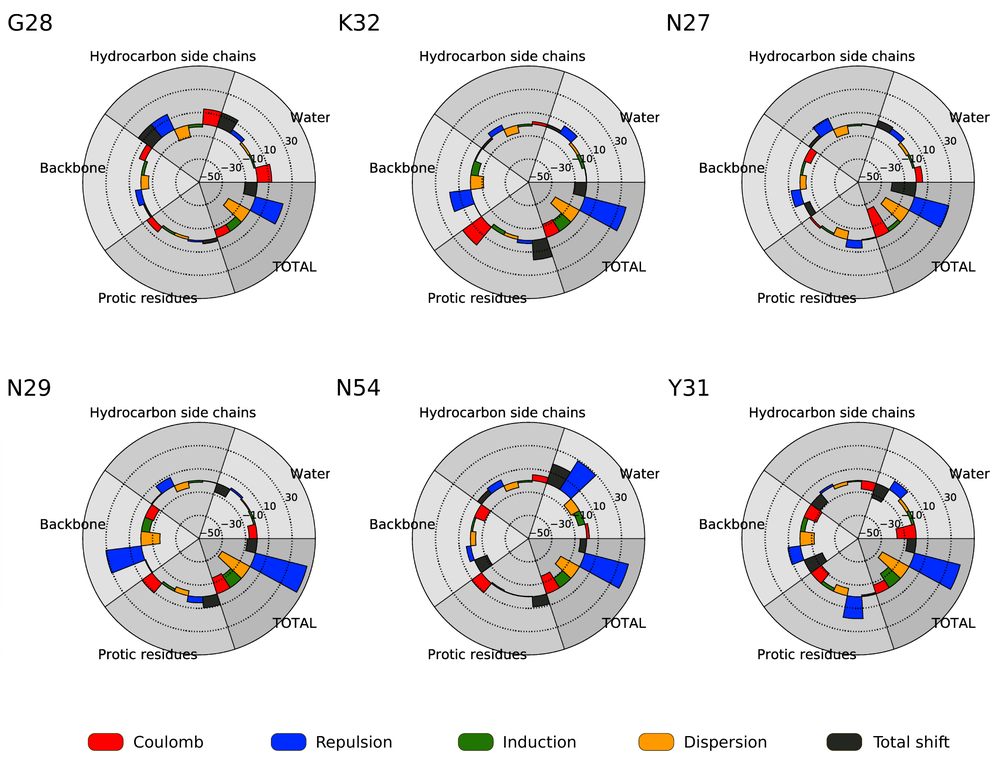
### Frequency shifts of CN stretch mode at the protein interface

We have observed 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.




### What is it for? / Plans

- Modeling 1D and 2D IR spectra
- Probing interaction energies in biomolecules by using IR spectroscopy
- Future: test SolEFP model for more systems; include rigorously charge-transfer and study vibrational solvatochromism due to ions

### References

[1] H. Kim, M. Cho, *Chem. Rev.*, 113, 5817 **2013**

[2] A. W. Ritchie, L. J. Webb, J. Phys. Chem. B, *In press* **2015**

[3] B. Błasiak, M. Cho, *J. Chem. Phys.*, 140, 164107 **2014**

[4] B. Błasiak, M. Cho, *Submitted* **2015**



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