

# Vibrational Solvatochromism Studies of Amide I mode of N-Methylacetamide

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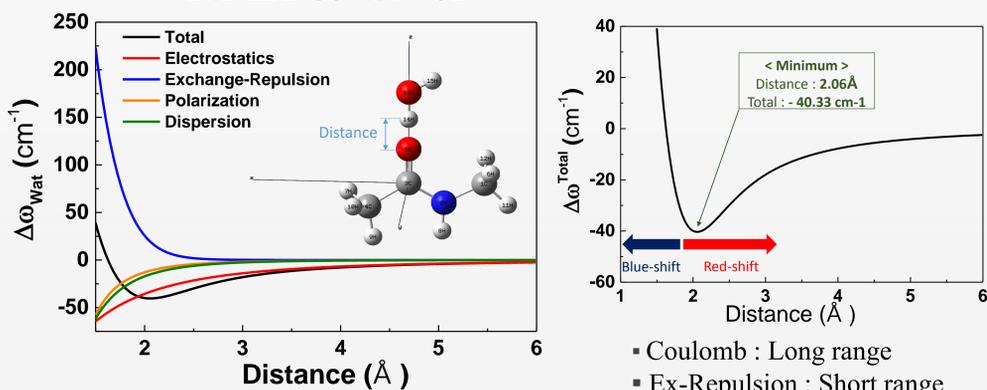


## Abstract

Vibrational solvatochromism is the frequency changes in the vibrational absorption spectrum due to molecular surrounding changes. To study the environment of a molecule, we often use properly chosen chromophores. We'll discuss carbonyl IR probe among chromophores. The first thing considered in carbonyl IR probe is Amide I mode, which occurs naturally in proteins and it means the vibrations of the peptide group. The frequency shifts from SolEFP (vibrational solvatochromism theory based on effective fragment potential) can be used to predict amide vibrational frequency shifts for any configuration of NMA (N-Methylacetamide) and water. We can also investigate how the frequency changes with the distance and rotation of neighboring water molecules. In addition, ion(Na<sup>+</sup>) and NMA systems will be discussed and compared with the results of quantum chemical vibrational analysis.

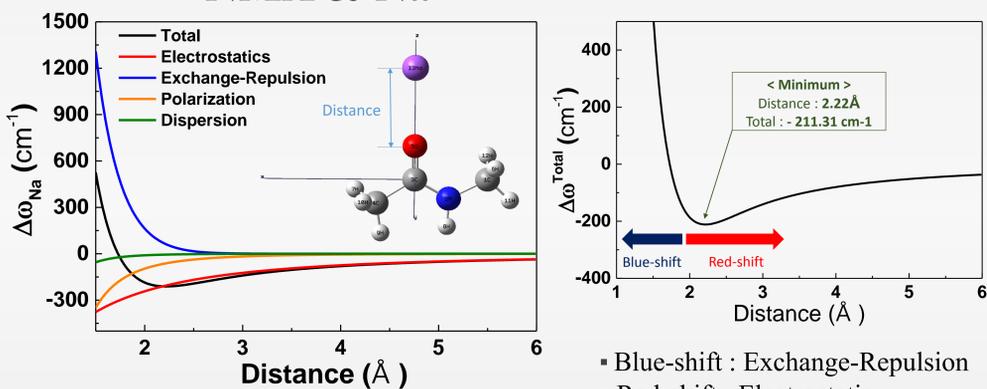
## SolEFP Method

### NMA & water



- Coulomb : Long range
- Ex-Repulsion : Short range
- Induction : Medium range
- Dispersion : Short range

### NMA & Na<sup>+</sup>



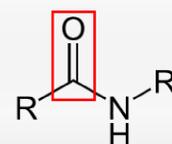
- Blue-shift : Exchange-Repulsion
- Red-shift : Electrostatic

1.7 Å	Total	Electrostatics	Repulsion	Polarization	Dispersion
Water	-15.3	-50.18	99.96	-29.48	-35.6
Na <sup>+</sup>	37.44	-312.84	572.9	-196.37	-26.25

- Because of the charge, the point at which peak shift appears is more than five times larger due to electrostatic.
- In the case of Na<sup>+</sup> since the charge is concentrated in the middle, the partial charge is large.
- Overestimate

## Amide I mode

- The first consideration in Carbonyl IR Probe was the naturally occurring amide I mode in protein, which is mostly the vibration of the peptide group.
- Amide I mode has been studied for a long time in terms of vibrational solvatochromism, because it can be used to investigate protein structure and dynamics.



## SolEFP - Frequency shift

$$\Delta\omega^{\text{SolEFP}} = \underbrace{\Delta\omega^{\text{Coul}} + \Delta\omega^{\text{Ind}}}_{\Delta\omega^{\text{Electric}}} + \underbrace{\Delta\omega^{\text{Disp}} + \Delta\omega^{\text{Ex-Rep}} + \Delta\omega^{\text{CT}}}_{\Delta\omega^{\text{Non-Electric}}}$$

- It only relies on the monomer properties.
- SolEFP method is applicable to large systems.

## Weak Coupling Approximation

### Weak coupling approximation frequency shift

$$\Delta\omega_j = \frac{1}{2M_j\omega_j} \left\{ \sum_i g_{ijj} \delta Q_i + \frac{\partial^2 U}{\partial Q_j^2} \right\}$$

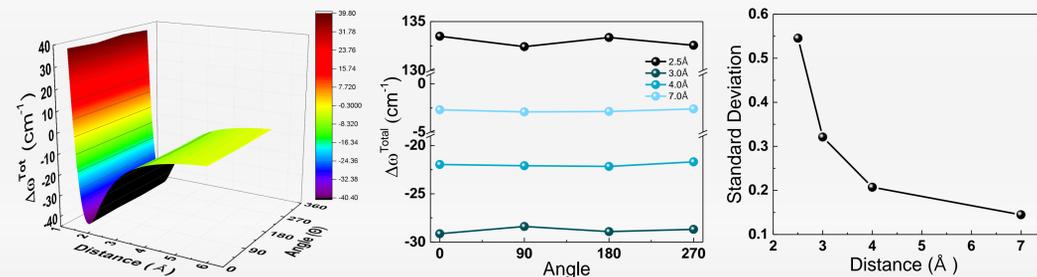
### Structural distortion of the *i* th normal coordinate

$$\delta Q_i = -\frac{1}{M_i\omega_i^2} \frac{\partial U}{\partial Q_i} = \delta Q_i^{\text{Coul}} + \delta Q_i^{\text{Ex-Rep}} + \delta Q_i^{\text{Ind}} + \delta Q_i^{\text{Disp}} + \delta Q_i^{\text{CT}}$$

- Weak coupling approximation is approximation for vibrational modes that are fairly local in character such as C=O stretches.
- In the coarse-grained models of the vibrational solvatochromism, the solvation induced vibrational frequency shift is related to the gas phase geometrical change of the solute due to solvation.
- Thus it can be seen from the equation that the structural deformation during the solvation affects all the interaction energy components.

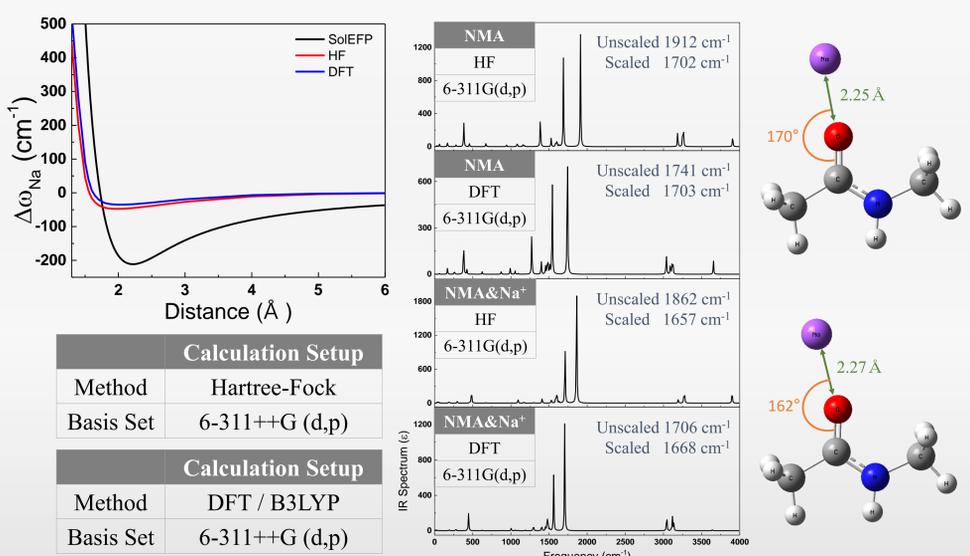
## Δω Depending on Angle and Distance

### Using rotation matrix, rotate 15H about the z-axis



- The change of frequency shift according to the angle change becomes smaller as the distance increases. That is, as the distance increases, the effect of the angle is small. This is the same for other factors.

## Quantum Chemical Vibrational Analysis



## Reference

- [1] Buckingham, A. D. *Trans. Faraday Soc.* **1960**, *56*, 753–760
- [2] B. Błasiak, M. Cho, *J. Chem. Phys.*, **2014**, *140*, 164107
- [3] B. Błasiak, M. Cho, *J. Chem. Phys.*, **2015**, *143*, 164111

## Conclusion

- Vibrational solvatochromism should be treated as a qualitative tool for analyzing vibrational frequency shifts of amide I mode in aprotic and weakly polar solvents.
- The solshift method describes the vibrational solvatochromism well by polar solvents such as water, but there is room for improvement because it does not adequately describe the solvatochromism by ion.

## Acknowledgements

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