# Vibrational solvatochromism of CN and SCN probes revisited

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We directly confront experiment and our solvatochromism first-principles theory combined with molecular dynamics for CN probes. We found that H-bonding introduces strong vibrational response due to exchange-repulsion potential slope wrt normal coordinate. We also found that solvatochromic induction effects are highly delocalized.

## Introduction

- $\blacktriangleright$  Small vibrational probes like CN, SCN and N<sub>3</sub> have been extensively used to probe local electric fields in molecular systems [1]
- electrostatic in aqueous environment [1]
- comparison with experiment at that time



Figure: Solvatochromism of Me(S)CN probe across various solvents.

 $oldsymbol{lpha}_j \ = \ -rac{1}{M_j \omega_j} \sum_i rac{g_{ijj}}{M_i \omega_i^2} \left( rac{\partial oldsymbol{lpha}_0}{\partial Q_i} 
ight),$ 

## **Ensemble average frequency shifts**

## **Frequency shifts: distributions**

#### Induced solvatochromic moments



Figure: Decomposition of CN stretch frequency shifts for MeSCN dissolved in various solvents



Figure: Distributions of electrostatic and repulsion CN stretch frequency shifts for MeSCN





Figure: Upper graphs: total solvatochromic moments vs electrostatic frequency shifts; *lower graphs:* distributions of induced moments

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**Electrostatic solvatochromism of MeSCN CN stretch** 

### Conclusions

- H-bonding interaction induces sharp blue-shifts which are direct manifestation of Pauli principle!
- Such repulsive contribution cannot be linked with electric fields by any means
- Consequence: electric field measurements based on electrostatic callibration of CN IR probes in *H*-bonding environments are erroneous! To correctly measure the field strength one needs first to substract exchange-repulsion solvatochromism to obtain pure electrostatic shifts
- Induction effect cannot be neglected. However, solvatochromic polarization cannot be easily extracted from molecular total solvatochromic moments since it is highly local CN and SCN probes exhibit very similar solvatochromic responses

#### To understand solvatochromism





Figure: Solvatochromic transition potential in vacuum (MP2/6-311++G\*\*)

Figure: Induced localized solvatochromic dipoles (RHF/6-311++G\*\*)

## References

[1] H. Kim, M. Cho, *Chem. Rev.*, 113, 5817 **2013** B. Błasiak, H. Lee, M. Cho, J. Chem. Phys., 139, 044111 2013 2 [3] B. Błasiak, M. Cho, J. Chem. Phys., 140, 164107 2014

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