

Non-Coulombic solvatochromism of nitrile and thiocyanate infrared probes – frequency shift nature revisited

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Abstract: Vibrational solvatochromism of CN and SCN IR probes was widely understood to be mostly electrostatic in nature. In this study we show for the first time, that vibrational response of those probes is far more complex and repulsion interaction cannot be neglected for protic solvents. In particular, one cannot extract solvatochromism information based on spatial distribution of electric fields around the probes when they are interacting via H-bonds with environment because of the direct manifestation of Pauli principle. However, solvatochromism in aprotic solvents is well described by electrostatics.

Key words: infrared spectroscopy, vibrational probes, vibrational solvatochromism, interaction energy.

1. INTRODUCTION

Solvatochromism of small vibrational infrared (IR) probes have been widely used to probe local molecular environments when either dissolved in bulk liquid or inserted in biomolecules and bioorganic materials. [1] One of the most direct and easy-to-measure observables related with probe-environment interaction is the vibrational frequency change with respect to reference state upon perturbation in the environment. Therefore, understanding the underlying mechanisms of frequency shifts is absolutely crucial to interpret changes of experimental spectra.

Since some correlations of vibrational frequencies and electrostatic potential or field were generally observed for many vibrationally localized oscillators [1], the great majority of theoretical and experimental studies was focused on electrostatic interaction between IR probe and its environment, concluding that this is the dominant factor governing vibrational solvatochromism. In effect, the probes like nitriles (CN), thiocyanates (SCN) and azides (N₃) have been extensively used to probe electrostatic potentials and fields based on vibrational frequency shifts. In stark contrast, we showed recently that non-electrostatic repulsive interaction between probe and surrounding molecules induces *very large blueshifts* for *N*-methylacetamide amide I mode solvated by water. [3] However, no other studies were undertaken to confront this repulsive interaction with experimental data.

In this study, we analyze simple model systems: methyl nitrile and methyl thiocyanate dissolved in various solvents of varying polarity and proticity. Next, we partition the frequency shifts by applying our solvatochromism model [2-3] to molecular dynamics (MD) simulation trajectories and extract the frequency shift components due to electrostatics and repulsion.

2. RESULTS

To obtain the scope of the solvatochromic shift patterns across various solvents we plot the vibrational absorption frequencies of CN stretches in MeCN and MeSCN against dielectric strength of a medium described by Onsager factor, $(\epsilon-1)/(2\epsilon+1)$, where ϵ is dielectric constant of a pure solvent. [2]

It is strikingly evident that the vibrational solvatochromism of MeSCN probe in bulk solution can be divided into 3 major categories (the same pertains to MeCN):

- i. Solvents with no permanent dipole moment and not forming any specific interactions with CN groups. There is

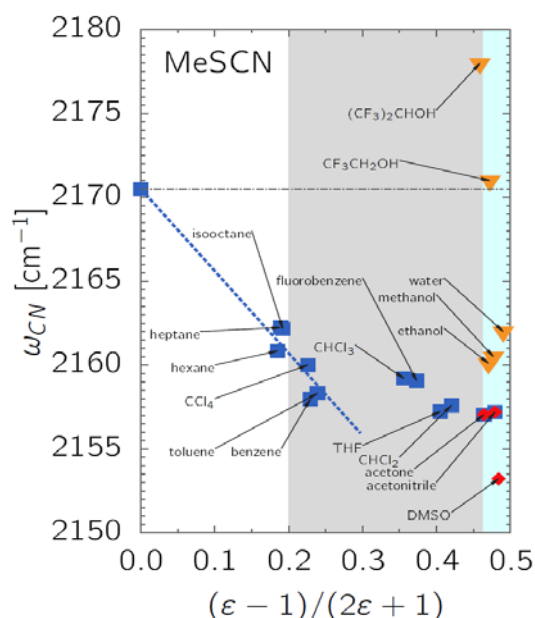


Figure 1. Experimental CN stretch frequencies of MeSCN dissolved in various solvents. Gas-phase state is assumed to be the reference state in this work.

a linear relationship between frequency and Onsager factor according to Kirkwood-Bauer-Magat formula;

- ii. Solvents with small permanent dipole moment and not forming any specific interactions with CN groups. For those systems one observes a deviation from a continuum response theory towards higher frequencies;
- iii. Solvents with large permanent dipole moment and forming specific (H-bonding) interactions with CN groups.

In this case, the deviation is even more pronounced, leading to considerable blue shifts.

To probe the origins of observed anomalies from simple electrostatic model we analyzed the frequency shifts for MeCN and MeSCN CN stretches in CCl_4 , CHCl_3 , DMSO and H_2O solutions at room temperature. It can be noticed that the decomposition is very complicated (Figure 2), though there is substantial offset between modelled and experimental values (about

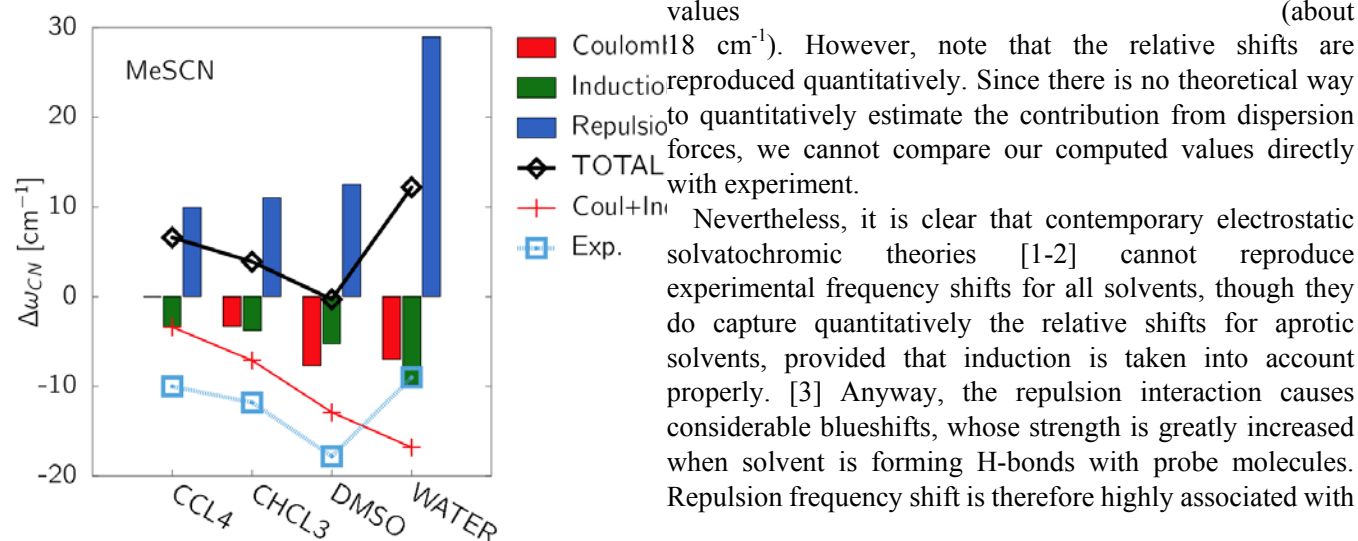


Figure 2. Decomposition of CN stretch frequency shifts for MeSCN in various solvents.

the strength of specific solute-solvent interactions. Since solvent molecules approach closer to the probe, the repulsive energy slope increases resulting in the increase of repulsion frequency shifts. [3] Note also that, at the current state of our knowledge, induction frequency shifts are the only electrostatic contributions to vibrational solvatochromism for MeSCN probe dissolved in CCl₄.

3. CONCLUSION

In this study, we showed that vibrational response of (S)CN IR probes is far more complicated as it was conjectured before and *one cannot*, in general, extract the solvatochromism from the distribution of electrostatic potentials around the probe if the probe fragment interacts with environment through *hydrogen bonds*. This is because the repulsion-induced blueshifting pattern is the direct manifestation of Pauli principle. In contrast, electrostatic interaction is sufficient to describe solvatochromism in aprotic solvents, provided that induction effects are included. See our Poster for more details.

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