

## Why Understanding Solvent Softness Matters?

- Extension of Pearson's concept of hard and soft acids and bases (HSAB) to solution implies that *chemically hard solvents tend to dissolve hard solutes and soft solvents dissolve soft solutes*
- Several aspects of solution chemistry have been attributed to solvent hardness and softness, e.g.:
  - (1) In aqueous-organic solvent mixtures, the sulfates of "soft"  $\text{Cd}^{2+}$  tend to become **less soluble** with increasing water content, whereas sulfates of "harder" 3d cations like  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  show the **opposite trend**
  - (2) The relatively **hard chloride** salts of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  show **higher solubility** with increasing water content, whereas the **softer bromide** salts show **opposite trend**
  - (3) In **soft acetonitrile**, metal cation complexes of N-phenylaza-15-crown-5 show stability order  $\text{Ca}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+} > \text{Ag}^+$ , but **opposite order** in **harder methanol**
  - (4) Phenol alkylation by 3-bromopropene produces mostly **allyl phenyl ether** in "harder" **acetone** and mostly **o-allyl phenol** in "softer" **benzene or toluene**
  - (5) Sodium phenolate alkylation by 3-chloropropene gives near **100% O-alkylation** in **ethanol** and only **22% O-alkylation** in **phenol**
  - (6) Substitutions of soft/hard groups on ionic liquids (ILs) imparts a drastic change to their viscosity, enthalpy of vaporization and the ion conductivities
  - (7) The hardness/softness of ions of ILs directly controls the solubility of materials like polymers in them.

## Quantification of Solvent Softness

## Empirical Scales of Solvent Softness/Hardness

- A number of solvent softness scales have been developed based on the measurements of infrared or Raman spectral shifts, half-wave potentials, reaction enthalpies, second-order rate constants and fluorescence shifts *etc.*
- The  **$\mu$ -scale** of solvent softness proposed by **Marcus** is based on the difference between Gibbs energies of transfer for "soft"  $\text{Ag}^+$  vs "hard"  $\text{Na}^+$  and  $\text{K}^+$ :

$$\mu = \frac{\Delta_{tr}G^\circ(\text{Ag}^+) - 0.5[\Delta_{tr}G^\circ(\text{Na}^+) + \Delta_{tr}G^\circ(\text{K}^+)]}{100 \text{ kJ mol}^{-1}}$$

- $\mu$ -scale quantifies the relative softness of a solvent
- For **hard solvents**  $\mu$  is **negative** and **soft solvents** have **positive value of  $\mu$**

## Electronic Structure Methods

- **Chemical hardness ( $\eta$ )** is defined in the realm of conceptual density functional theory (DFT) and global **chemical softness ( $S$ )** is the inverse of hardness:

$$\eta \equiv \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)}$$

Where  $E$  is the energy of system containing  $N$  electrons.

- $\eta$  is approximated in terms of the ionization potential,  $I$ , and electron affinity  $A$ :

$$\eta \approx I - A$$

- These quantities can be calculated through total energies of **neutral ( $E_N$ )**, **cationic ( $E_{N-1}$ )** and **anionic ( $E_{N+1}$ )** species of the optimized molecular geometry

$$I = E_{N-1} - E_N$$

$$A = E_N - E_{N+1}$$

- An alternative method is provided by Koopman's theorem, according to which, the chemical hardness is defined in terms of frontier molecular orbitals energies:

$$\eta \approx \text{Gap} = E_{LUMO} - E_{HOMO}$$

## Orbital Overlap Distance and Chemical Softness

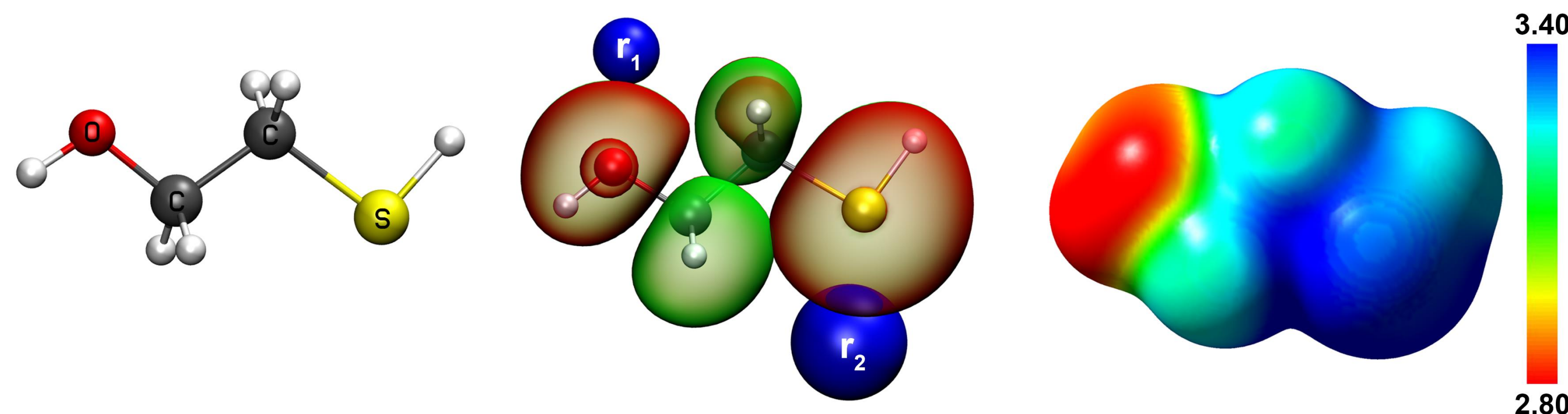
- The **Orbital Overlap Distance  $D(\vec{r})$**  quantify whether the orbitals at a given point are compact or diffuse
- It is constructed from the Orbital Overlap Range Function  $EDR(\vec{r}; d)$  which quantifies the extent to which an electron at point  $\vec{r}$  in a calculated wave function overlaps over distance " $d$ "<sup>2-3</sup>

$$EDR(\vec{r}; d) = \int d^3\vec{r}' g_d(\vec{r}, \vec{r}') \gamma(\vec{r}, \vec{r}')$$

$$g_d(\vec{r}, \vec{r}') \equiv \rho^{-1/2}(\vec{r}) \left( \frac{2}{\pi d^2} \right)^{3/4} \exp\left(-\frac{|\vec{r} - \vec{r}'|^2}{d^2}\right)$$

$$D(\vec{r}) = \arg \max_d EDR(\vec{r}; d)$$

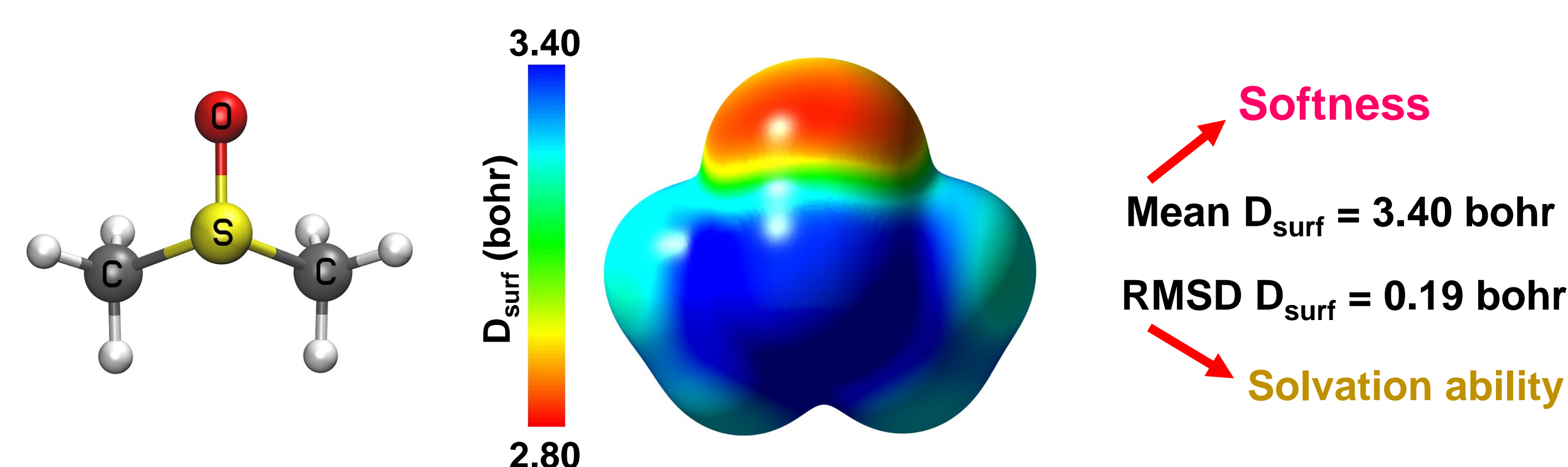
- **Compact, chemically stable atoms** tend to have overlap distances smaller than **chemically soft, unstable atoms**



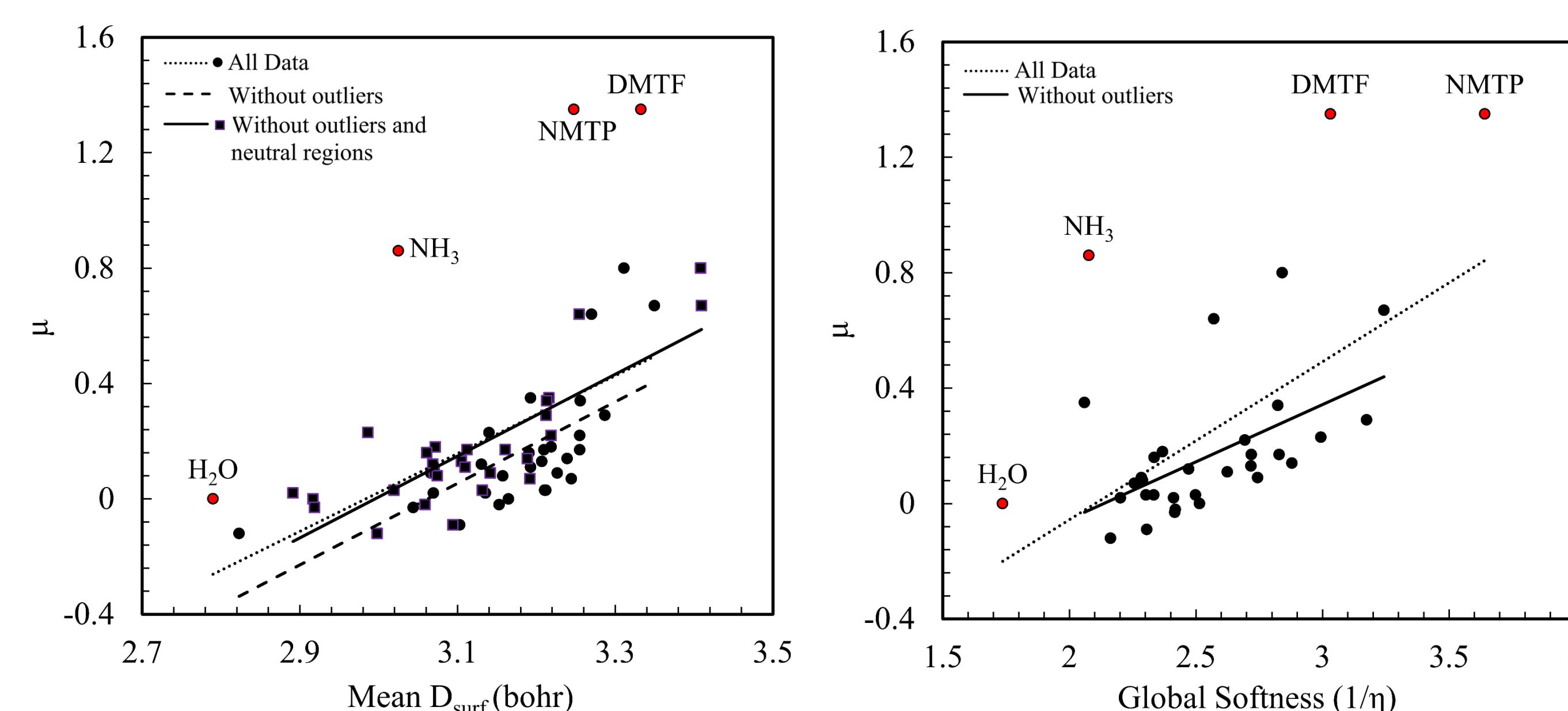
(Left) Optimized geometry (Middle) Green and red surfaces are representative occupied orbitals HOMO and HOMO-1. Blue surfaces are the test function plotted at 80% of its maximum value  $D(\vec{r}_1) = 2.9$  bohr and  $D(\vec{r}_2) = 3.4$  bohr (Right) Plot of  $D(\vec{r})$  on 0.001 e/bohr<sup>3</sup> electron density surface ( $D_{\text{surf}}$ ).

Correlation between mean  $D_{\text{surf}}$  and  $\mu$ -scale of Softness

- We used the mean value of  $D(\vec{r})$  plot on 0.001 e/bohr<sup>3</sup> electron density surface (**Mean  $D_{\text{surf}}$** ) to fit the empirical  $\mu$ -scale of softness
- **RMSD  $D_{\text{surf}}$**  can be used to characterize the solvating ability of solvents

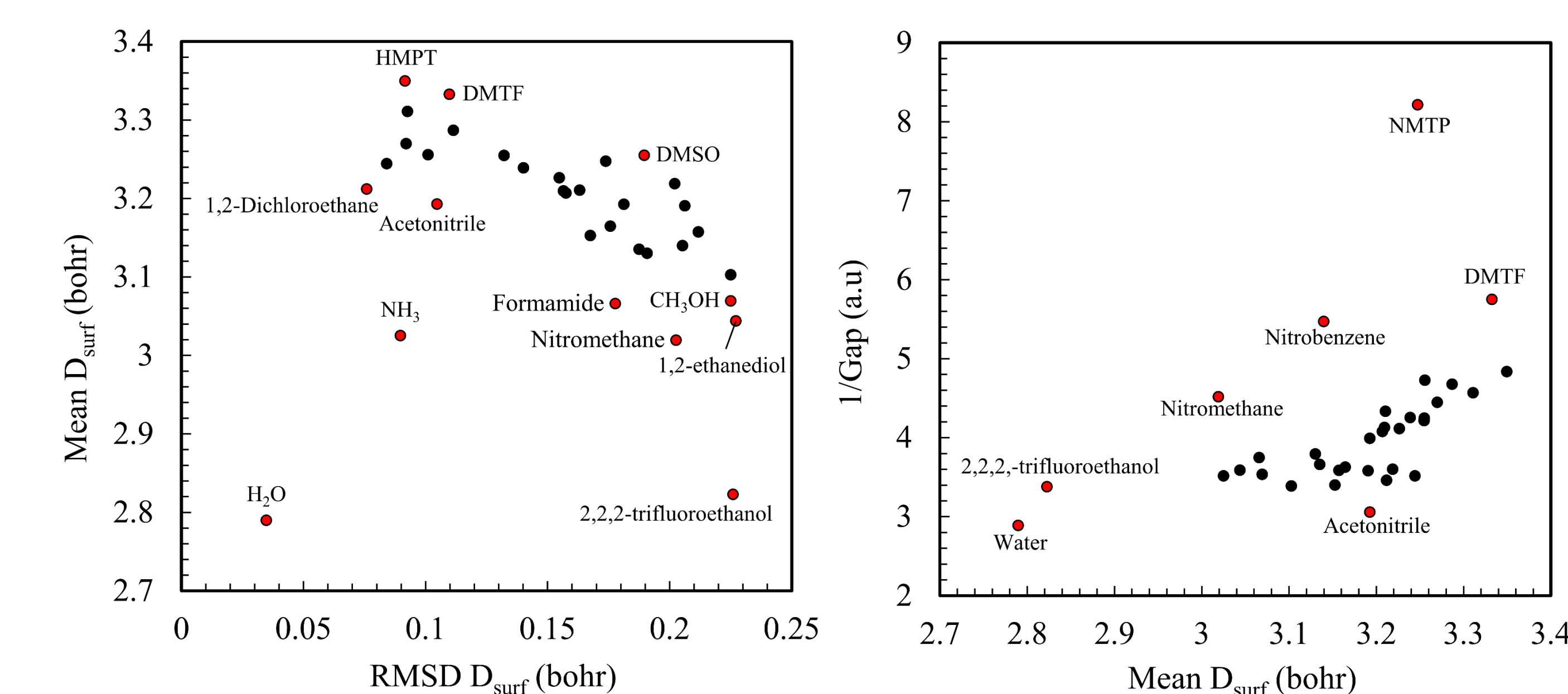


- Fitting **Mean  $D_{\text{surf}}$**  to the empirical  $\mu$ -scale of softness gives excellent correlation and compliments the findings of global softness.



- Linear fits of experimental Marcus  $\mu$  parameter to  $D_{\text{surf}}$ , global softness  $1/\eta$  and HOMO-LUMO Gap. Fits are performed for the 34 solvents in Table I of Ref. [1].  
A = All data, B = Without outliers, C = Without outliers,  $D_{\text{surf}}$  on charged areas only.

Method	Data	Equation	R <sup>2</sup>	MAE
$D_{\text{surf}}$	A	$\mu = 1.349 D_{\text{surf}} - 4.026$	0.209	0.230
	B	$\mu = 1.413 D_{\text{surf}} - 4.325$	0.445	0.126
	C	$\mu = 1.418 D_{\text{surf}} - 4.249$	<b>0.659</b>	<b>0.244</b>
$1/\eta$	A	$\mu = 0.397(1/\eta) - 0.848$	0.292	0.194
	B	$\mu = 0.547(1/\eta) - 1.150$	0.331	0.170
$1/\text{Gap}$	A	$\mu = 0.277(1/\text{Gap}) - 0.891$	0.531	0.176
	B	$M = 0.214(1/\text{Gap}) - 0.687$	0.294	0.123



## Applications to ionic liquids

- We used the obtained best linear fitting model to predict the  $\mu$  values for selected ionic liquids (ILs)
- **Anionic part plays fundamental role** to control the softness of ionic liquid.
- Ionic liquids having [Br] and [Cl] as anions have large value of  $\mu$
- **RMSD  $D_{\text{surf}}$  increases with decrease in Mean  $D_{\text{surf}}$**  where ionic liquids having hard anions and small  $\mu$  values shows large RMSD  $D_{\text{surf}}$ .

Ionic Liquid	Mean $D_{\text{surf}}$ (bohr)	RMSD $D_{\text{surf}}$ (bohr)	Predicted $\mu$
$[\text{N}_{1116}][\text{Br}]$	3.373	0.123	<b>0.536</b>
$[\text{C}_2\text{py}][\text{Br}]$	3.350	0.157	<b>0.503</b>
$[\text{N}_{1116}][\text{Cl}]$	3.338	0.082	<b>0.486</b>
$[\text{emim}][\text{Br}]$	3.337	0.178	<b>0.484</b>
$[\text{mPhim}][\text{Br}]$	3.332	0.168	<b>0.478</b>
$[\text{C}_2\text{py}][\text{Cl}]$	3.302	0.106	<b>0.436</b>
$[\text{mPhim}][\text{Cl}]$	3.292	0.126	<b>0.421</b>
$[\text{emim}][\text{Cl}]$	3.290	0.133	<b>0.419</b>
$[\text{N}_{1116}][\text{MeSO}_4]$	3.221	0.178	<b>0.321</b>
$[\text{mPhim}][\text{MeSO}_4]$	3.175	0.176	<b>0.255</b>

## Acknowledgment

- National Science Foundation Award DMR-1505343
- TCU CSE Graduate Student Research Fund (GSRF)

## References

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