Elucidating the mechanism of selective ion adsorption to the liquid water surface

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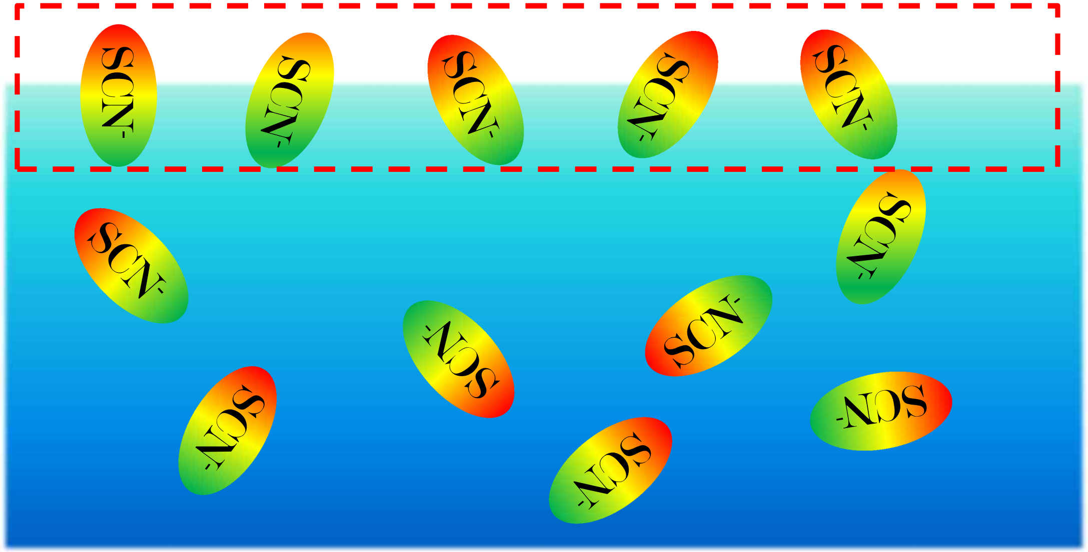
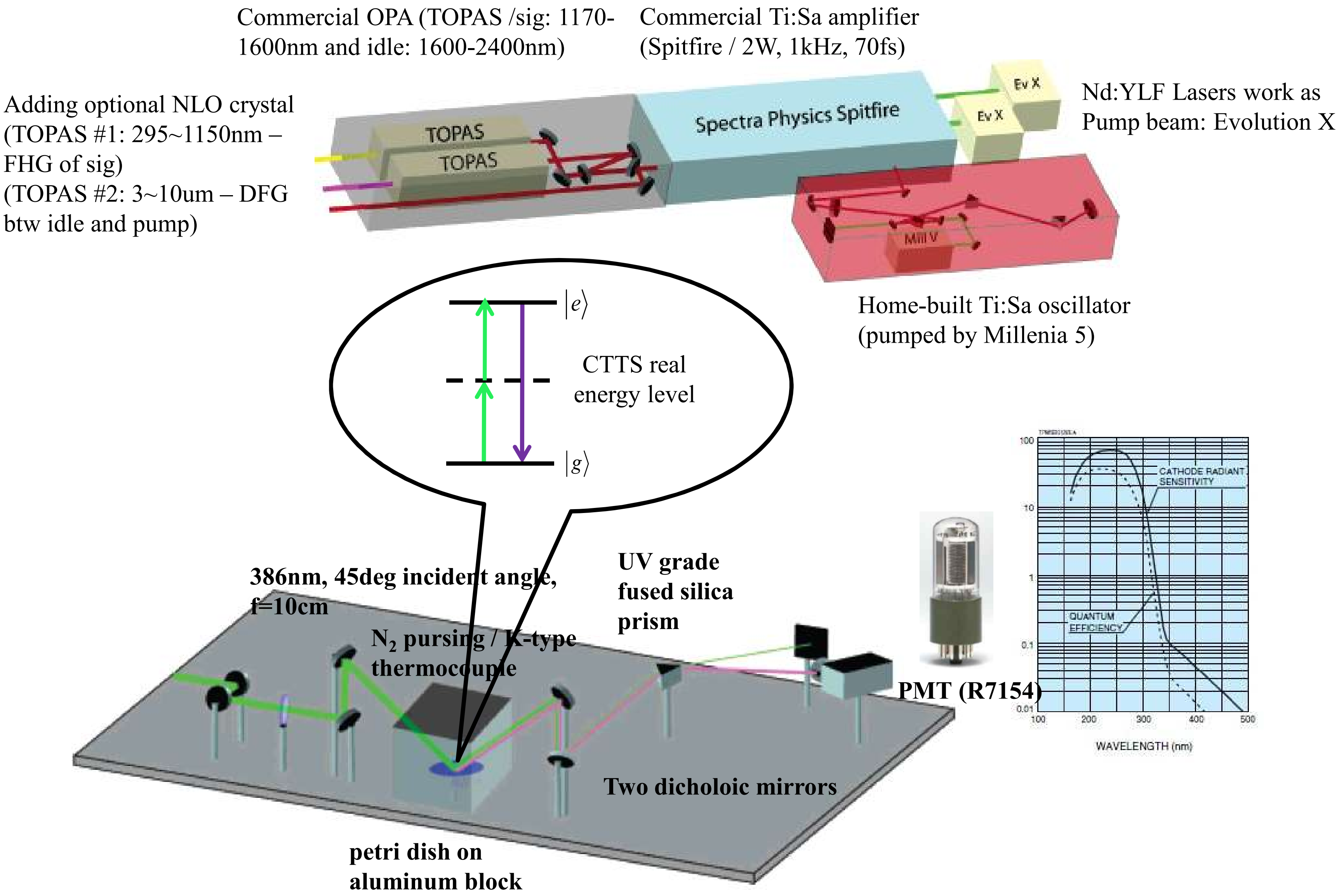
Edited by Michael L. Klein, Temple University, Philadelphia, PA, and approved November 28, 2011 (received for review October 4, 2011)

Proc. Natl. Acad. Sci. USA, 109, 701-705 (2012).



SHG system based on fs Laser (Saykally Group)



Resonant SHG response from charge-transfer-to-solvent

*Charge-transfer-to-solvent : release of a electron from anion (usually halide ions) occurred by photochemical reaction

¶ General pathways : Chem. Rev. 70, 59–93 (1970).

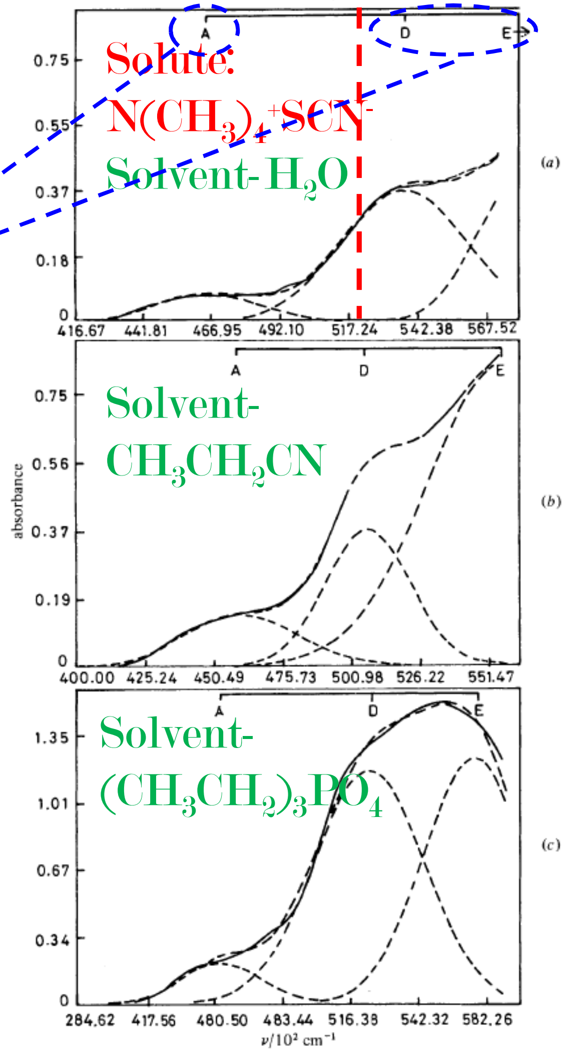
1) Radical formation

$$X_{aq}^{-} \xrightarrow{h\nu} X_{aq}^{-*} \longrightarrow (X_{aq}\cdot + e^{-})_{aq}$$

2) Direction release

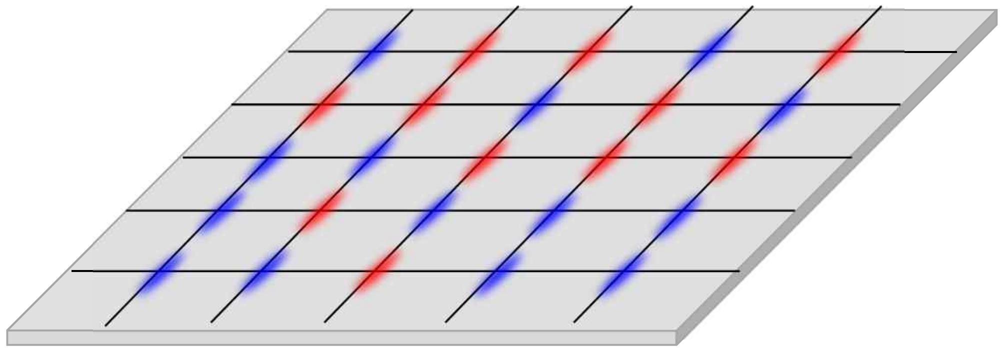
$$X_{aq}^{-} \xrightarrow{h\nu} X_{aq}\cdot + e_{aq}^{-}$$

Absorption band is sensitively dependent on surrounding molecules



Surface adsorption model – Langmuir adsorption

* Originated from adsorption of atoms or molecules on solid substrates

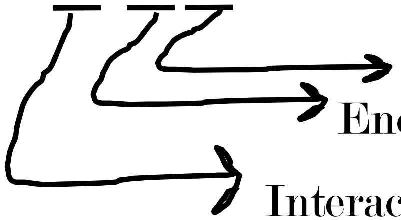


S: total number of binding sites

: occupied site (S_1)

: Vacancy (S_o=S- S_1)

$$r_{ad} = k_{ad} P S_o$$



In equilibrium, $r_{de} = k_{de} S_1 = k_{ad} P S_0 = k_{ad} P(S - S_1)$

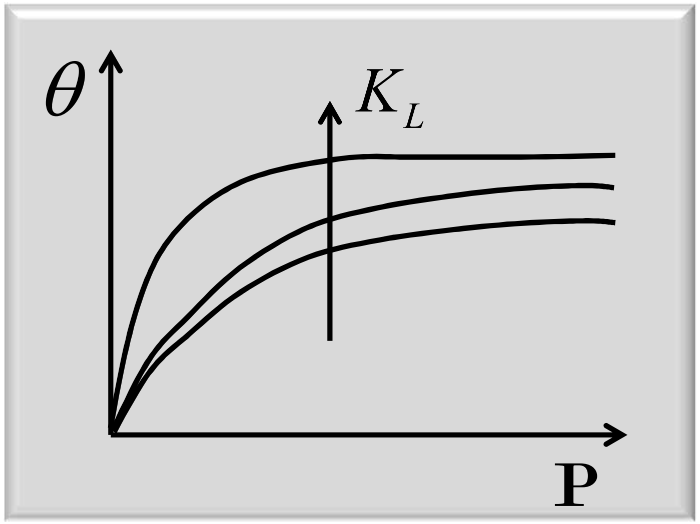
Surface adsorption model – Langmuir adsorption

$$r_{de} = k_{de}S_1 = k_{ad}PS_0 = k_{ad}P(S - S_1)$$

By rewriting $\frac{S_1}{S} = \theta$ (fraction of coverage) and $\frac{k_{ad}}{k_{de}} = K_L$ (Langmuir constant)

$$\Rightarrow \; [\theta = \frac{PK_L}{1 + PK_L}]$$: **Langmuir adsorption equation**

Typical Langmuir isotherm curve



***In the solution, P can be replaced by concentration, c.**

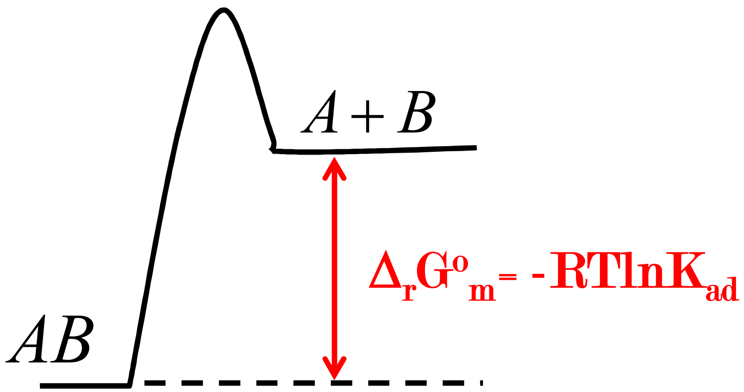
$$\Rightarrow \; [\theta = \frac{cK_L}{1 + cK_L}]$$

Thermodynamic quantities: How to deduce ΔG and ΔS ?

*Like a chemical reaction, binding of adsorbent can be represented as,

$$AB \underset{Ads}{\overset{Des}{\rightleftarrows}} A + B$$

Butt, H.J.; Graf, K.; Kappl,M.
Physics and Chemistry of Interfaces (2006).



where the adsorption equilibrium constant K_{ad} is,

$$K_{ad} = \frac{k_{de}}{k_{ad}} = \frac{S_o P}{S_1} = K_L^{-1} \Rightarrow \theta = \frac{cK_L}{1 + cK_L} = \frac{c}{K_{ad} + c}$$

Experimental result of SCN⁻ ion adsorption

*Fitting equation of SHG intensity can be represented as following procedure,

$$I_{SHG} \propto \left|\chi_{eff}^{(2)}\right|^2 = \left|[\hat{e}(\omega_{SH})\cdot \overleftrightarrow{L}(\omega_{SH})]\cdot[\overleftrightarrow{\chi}^{(2)} : [\hat{e}(\omega_F)\cdot \overleftrightarrow{L}(\omega_F)]^2]\right|^2$$

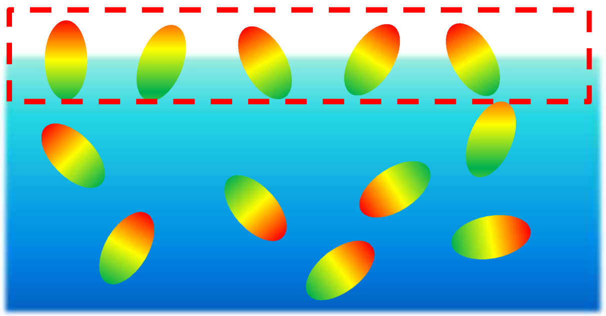
Lower with increasing temperature, but negligible.

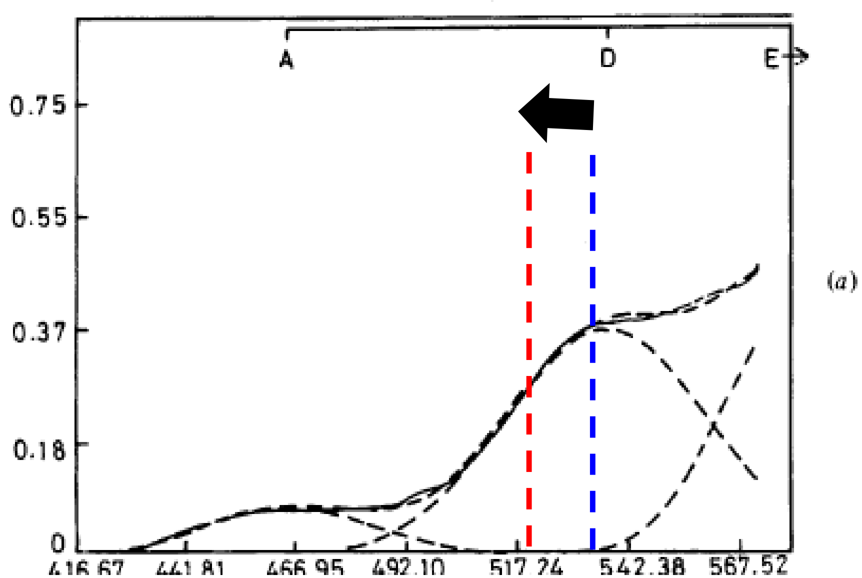
$$\Rightarrow \quad \chi^{(2)}_{ijk} = N_s \sum_{\xi,\eta,\zeta} \alpha^{(2)}_{\xi\eta\zeta} \langle (\hat{\xi}\cdot\hat{i})(\hat{\eta}\cdot\hat{j})(\hat{\zeta}\cdot\hat{k}) \rangle$$

$$, \alpha^{(2)}_{\xi\eta\zeta} = \alpha^{(2)}_{NR} + \sum_q \frac{\alpha_q(T)}{\omega_{IR} - \omega_q + i\Gamma_q}$$

Spectral peak shifts to low frequency.

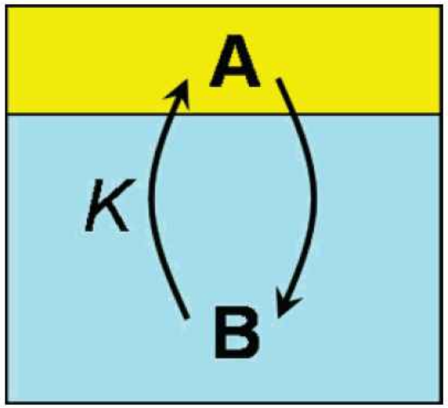
$$\Rightarrow \quad I_{SHG} = \left|A(T)S_o\theta + B\right|^2 = \left|A(T)S_o \frac{c}{K_{ad}+c} + B\right|^2$$





Experimental result of SCN^- ion adsorption

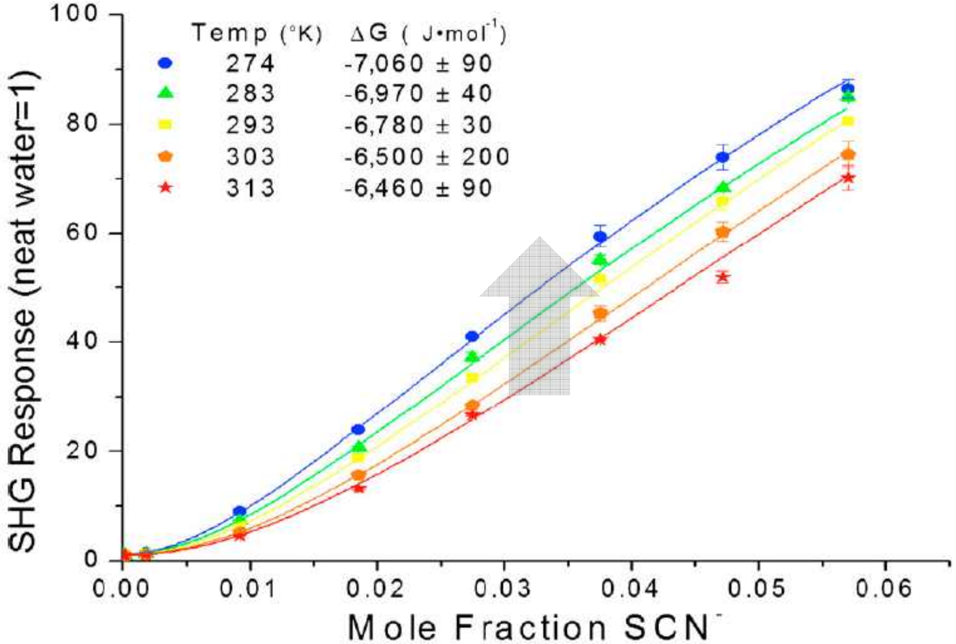
Exchange between a solute and a solvent molecule



$$A_S + B_B \rightleftharpoons A_B + B_S$$

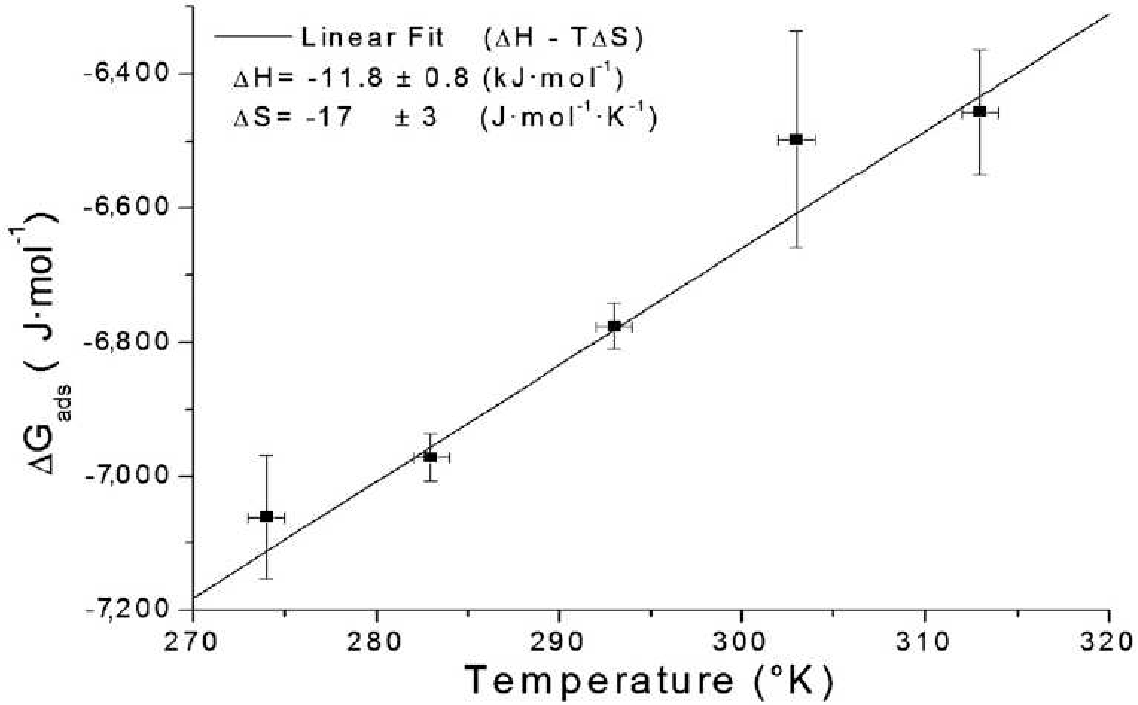
$$AC + B \underset{\text{Desorption of water}}{\rightleftharpoons} A + C + B \underset{\text{Adsorption of solute}}{\rightleftharpoons} A + BC$$

$$N_S = \frac{N_S^{max} \times C}{C + 55.5\ \text{M} \times \exp(\Delta G_{ads}/RT)}$$



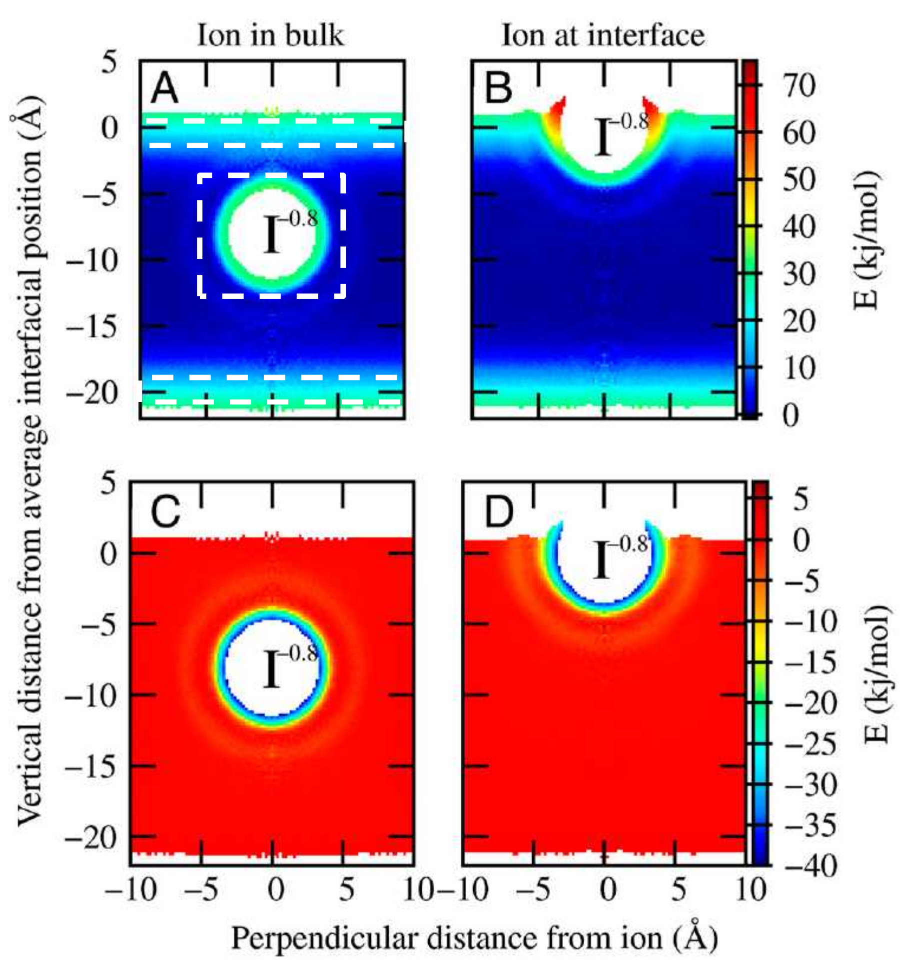
Experimental result of SCN^- ion adsorption

$$\Delta_r G^o_m = -RT\ln K_{ad} = \Delta_r H - T\Delta_r S$$



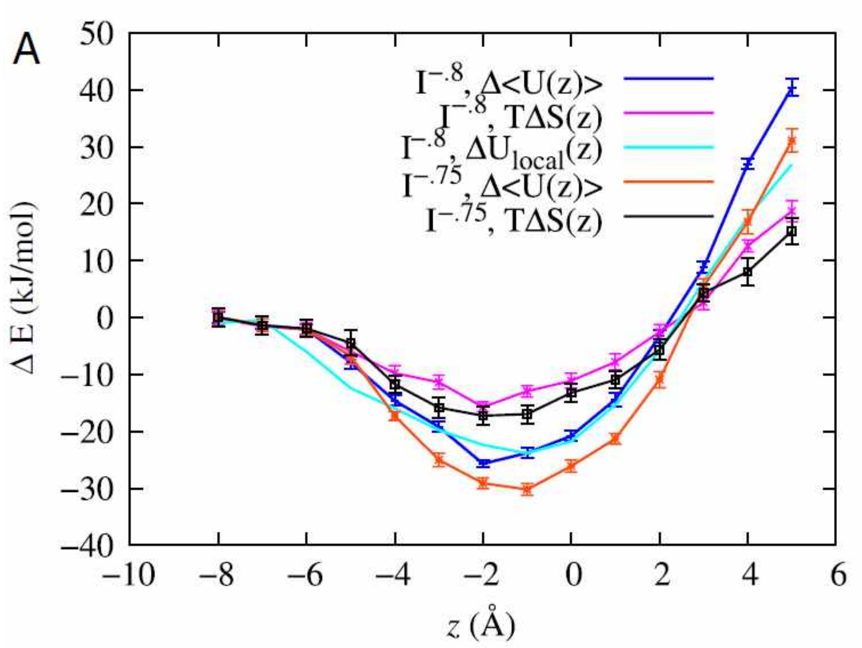
Experimentally measured Gibbs free energy and entropy were both negative.

Prediction from the simulation – interaction E of water

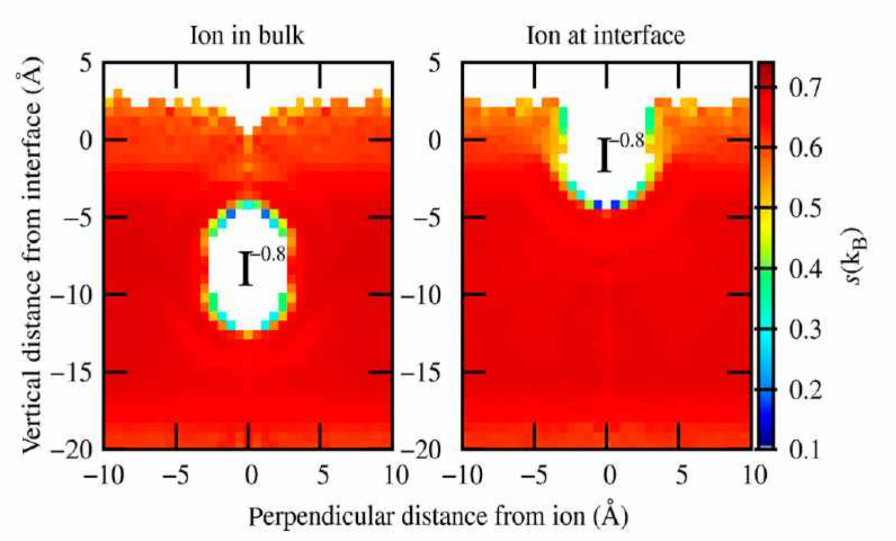


$$\varepsilon(\mathbf{r};z) = \varepsilon^{(\mathrm{ion})}(\mathbf{r};z) + \frac{1}{2}\varepsilon^{(\mathrm{solv})}(\mathbf{r};z)$$

$$U_{\mathrm{local}}(z) = \bar{\varepsilon}_{\mathrm{coord}} n_{\mathrm{coord}}(z) + \bar{\varepsilon}_{\mathrm{surf}} n_{\mathrm{surf}}(z) + \bar{\varepsilon}_{\mathrm{bulk}} n_{\mathrm{bulk}}(z)$$

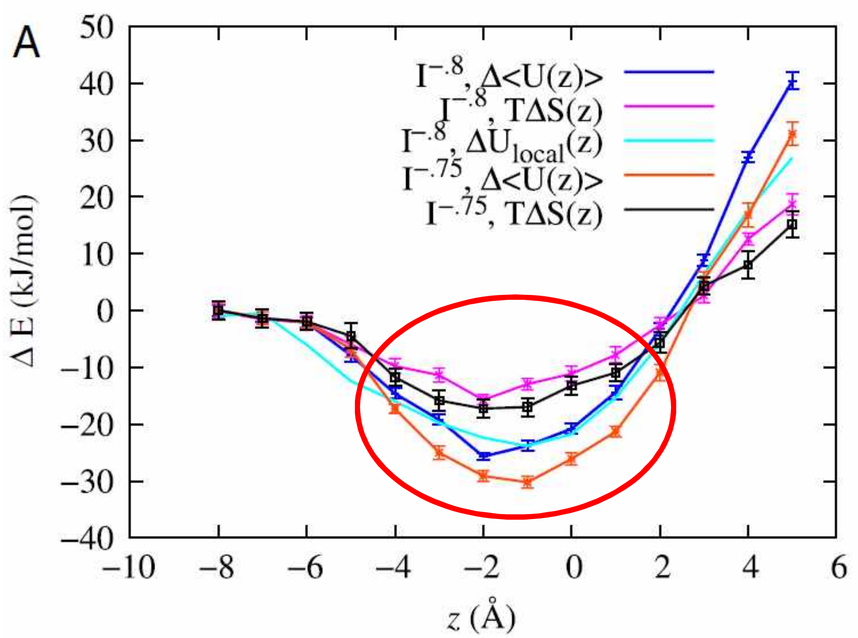


Prediction from the simulation – Estimation of the entropy



$$H = S / k_B = \ln \Omega = -\sum_j P_j \ln P_j$$

$$s(\mathbf{r}) = -k_B \int d\cos\theta \, p(\cos\theta; \mathbf{r}) \ln p(\cos\theta; \mathbf{r})$$



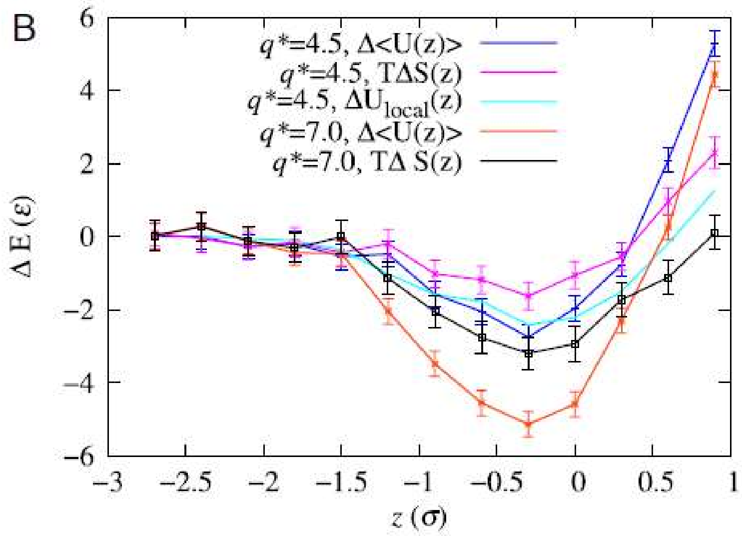
Summary

*Surface adsorption of thiocyanate ions were observed by SHG signal from CTTS process.

*Measured thermodynamic parameters, $\Delta_r H$ and $\Delta_r S$ are both negative.

*From the simulation, it was suggested that $\Delta_r H$ and $\Delta_r S$ of the system have minimum at several angstrom below the Gibbs dividing surface.

Prediction from simulation – interaction E of water



$$\Phi_{12}(r,\theta_1,\theta_2,\phi) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu_1\mu_2}{4\pi\epsilon_0 r^3}\left(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right)$$