Supplementary materials : Physisorption and desorption of H_2, HD and D_2 on amorphous solid water ice. Effect on mixing isotopologue on statistical population of adsorption sites

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Calculation details

The demonstration of eq. (7) in the main article needs some development detailed here. Notation of the article will be simplified.

We consider two species a and b, with a common set of adsorption sites. The state density is given by g. These energies are simply shifted for the two species:

$$\begin{aligned} g_a(E) &= g(E-\Delta_a) \\ g_b(E) &= g(E-\Delta_b) \end{aligned} \tag{1}$$

For a single specie, energy states population $P_a(E)$ follows the Fermi-Dirac distribution for given T and μ_a:

$$P_a(E) = g_a(E)/(1+e^{-(E-\mu_a)/k_bT}) \tag{2}$$

When the two species a and b are in competition, the common set of adsorption sites is shared, and effective states density is reduced by the population of the other.

$$\begin{aligned} P_a(E) &= g'_a(E)/(1+e^{-(E-\mu_a)/k_bT}) \\ \text{with} \quad g'_a(E) &= g_a(E) - P_b(E+\Delta_b-\Delta_a) \end{aligned} \tag{3}$$

and

$$\begin{aligned} P_b(E) &= g'_b(E)/(1+e^{-(E-\mu_b)/k_bT}) \\ \text{with} \quad g'_b(E) &= g_b(E) - P_a(E+\Delta_a-\Delta_b) \end{aligned} \tag{4}$$

Inserting eq.(4) in eq.(3), we obtain

$$P_a(E) = \frac{g\left(E-\Delta_{Da}\right) - \dfrac{g\left(E-\Delta_a\right) - P_a\left(E\right)}{1+e^{\dfrac{\mu_b - E + \Delta_a - \Delta_b}{k_bT}}}}{1+e^{\dfrac{\mu_a - E}{k_bT}}} \tag{5}$$

Setting the reduced values, $m=\mu/k_bT$, $\delta=\Delta/k_bT$ and $\varepsilon = E/k_bT$, this leads to

$$P_a(E) = g(E-\Delta_a) \Bigg/ \frac{1-\dfrac{1}{1+e^{m_b-\delta_b-\varepsilon+\delta_a}} + e^{m_a-\varepsilon}}{1-\dfrac{1}{1+e^{m_b-\delta_b-\varepsilon+\delta_a}}} \tag{6}$$

This expression can be simplified:

$$P_a(E) = \frac{g(E-\Delta_a)}{1+e^{m_a-\varepsilon}+e^{\delta_b-\delta_a+m_a-m_b}} \tag{7}$$

The expression for specie b is the same, inverting a and b.

The case of $n+2$ species can be treated the same way. Let's take species a and b taken separately, but both sharing there adsorption site g with a finite number n of other species. We suppose that their population can be written:

$$p_a(E) = \frac{g(E-\Delta_a)}{1+e^{(\mu_a-E)/k_bT}+e^{m_a-\delta_a}\sum\limits_{i=1}^{n} e^{\delta_i-m_i}} \tag{8}$$

and similarly for p_b.

$$p_b(E) = \frac{g(E-\Delta_b)}{1+e^{(\mu_b-E)/k_bT}+e^{m_b-\delta_b}\sum\limits_{i=1}^{n} e^{\delta_i-m_i}} \tag{9}$$

We can remark that (8) and (9) are verified in the particular case of equation (7) with $\sum\limits_{i=1}^{n} e^{\delta_i-m_i} = e^{\delta_b-m_b}$.

Considering that this two species have now to share their adsorption sites, this leads to equations (3) and (4). We can follow the development used previously for these two equations. We set the short notation $\Sigma = \sum\limits_{i=1}^{n} e^{\delta_i-m_i}$.

$$P_a(E) = g(E-\Delta_a) \Bigg/ \frac{1-\dfrac{1}{1+e^{m_b-\delta_b-\varepsilon+\delta_a}+e^{m_b-\delta_b}\Sigma} + e^{m_a-\varepsilon} + e^{m_a-\delta_a}\Sigma}{1-\dfrac{1}{1+e^{m_b-\delta_b-\varepsilon+\delta_b}+e^{m_b-\delta_b}\Sigma}} \tag{10}$$

This expression can be simplified:

$$P_a(E) = g(E-\Delta_a) \Bigg/ \left(1+\frac{\left(e^{m_a-\varepsilon}+e^{m_a-\delta_a}\Sigma\right)\left(1+e^{m_b-\delta_b-\varepsilon+\delta_a}+e^{m_b-\delta_a}\Sigma\right)}{e^{m_b-\delta_b-\varepsilon+\delta_a}+e^{m_b-\delta_b}\Sigma}\right)$$

then, remarking that

$$\left(e^{m_a-\varepsilon}+e^{m_a-\delta_a}\sum\right)=e^{m_a-m_b-\delta_a+\delta_b}(e^{m_b-\delta_b-\varepsilon+\delta_a}+e^{m_b-\delta_b}\sum)$$

we obtain

$$P_a(E)=g(E-\Delta_a)/ \\ (1+e^{m_a-m_b-\delta_a+\delta_b}(1+e^{m_b-\delta_b-\varepsilon+\delta_a}+e^{m_b-\delta_b}\sum))$$

and finally

$$P_a(E)=g(E-\Delta_a)/ \\ (1+e^{m_a-\varepsilon}+e^{m_a-\delta_a}(e^{\delta_b-mb}+\sum) \tag{11}$$

The terms concerning specie b can now be include in the sum, to obtain the same equation that equation (8). This shows that population of molecules a sharing their adsorption site with a finite number n of other species, only shifted in energy, can be written:

$$p_a(E)=\frac{g(E-\Delta_a)}{1+e^{(\mu_a-E)/k_bT}+e^{(\mu_a-\Delta_a)/k_bT}\times\sum_{i=1}^{n}e^{(\Delta_i-\mu_i)/k_bT}} \tag{12}$$