

# Ubiquity of Micron-Thick Interface along a Quartz-Water Boundary

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## Supporting information

### 1. The partition function for converting the vibrational spectroscopy to thermodynamic properties

A partition function links the microscopic properties of a system and its macroscopic ones. If we deal with the canonical system, the form of the partition function will be given by:

$$Z = \sum_i e^{-\beta E_i} \quad (i = 1, 2, 3, \dots) \quad (1)$$

This equation depends on the temperature and the energies of the microstates, where  $E_i$  is the energy of each microstate (i) and  $\beta = \frac{1}{\kappa_B T}$ . Where  $\kappa_B$  is the Boltzmann constant, and T is the temperature in Kelvin.

The energies of the microstates are determined by thermodynamic variables, such as the number of particles and the volume, and by microscopic properties, such as the mass of the particles composing the system. From a model of the microscopic constituents of the system, one can calculate the energy of the microstates, the partition function, and then the thermodynamic properties of the system using the Boltzmann factor:

$$P_i = \frac{1}{Z} e^{-\beta E_i} \quad (2)$$

$P_i$  is the probability that the system occupies a microstate  $i$ . The partition function then acts as a normalizing constant, making the sum of the probabilities equal to 1. From this step, one can calculate the thermodynamic value of the total energy. If the system is divided into  $N$  subsystems having negligible interaction energies, the partition function is written as the product of the partition functions  $z_i$ , of each subsystem:  $Z = \prod_i^N z_i$  (3)

Therefore, the partition function is the sum of the energy states of the system. If the different forms of energy in the system are independent from each other, the total energy can be written as a sum of all these energies:

$$E_{tot} = E_n + E_{el} + E_{trans} + E_{vib} + E_{rot} \quad (4)$$

Where  $E_n$  is the nuclear energy,  $E_{el}$  the electronic energy,  $E_{trans}$  the energy of translation,  $E_{vib}$  the energy of vibration and  $E_{rot}$  the energy of rotation. In this way, the energy levels of the molecules are quantified and:  $E_{el} > E_{vib} > E_{rot} > E_{trans}$  [1, 2].

The partition function is then written as the product of the partition functions of each energy forms in the system:

$$Z_{tot} = Z_n \cdot Z_{el} \cdot Z_{trans} \cdot Z_{vib} \cdot Z_{rot} \quad (5)$$

For water, the nuclear and electronic partition functions ( $E_n, E_{el}$ ) are equal to 1 [3]. Additionally, the first order of  $E_{rot}$  is negligible, and the translational energy is not quantified frequently [1]. As a result, the vibrational energy, which we measure in FTIR, is the dominant contribution to the calculation of the partition function.

The total energy is the sum of the energies of the microstates multiplied by their probability, and it relates to the partition function as follows:

$$\langle E \rangle = \sum_j E_j P_j = \frac{1}{Z} \sum_j E_j e^{-\beta E_j} = - \frac{1}{Z} \frac{\delta}{\delta \beta} Z(\beta, E_1, E_2, \dots) = - \frac{\delta \ln Z}{\delta \beta} \quad (6)$$

Which can be written as:

$$\langle E \rangle = \kappa_B T^2 \frac{\delta \ln Z}{\delta T} \quad (7)$$

Since the Helmholtz energy is equal to  $F = E - TS$ , then it becomes:

$$F = -\kappa_B T \ln Z \quad (10)$$

Finally, the Gibbs free energy (G) can be obtained from:  $G=F+PV$ , and this yields:

$$G = -\kappa_B T \ln (Z) + \kappa_B T V \left( \frac{\ln (Z)}{\delta V} \right) \quad (11)$$

As a result, the partition function enables to calculate how much the Gibbs free energy changes when the vibrational energy changes. The partition function that we use in this study is the same as Bergonzi et al.'s [4, 5], which is derived from Griffith and Scheraga's [6], and Néméthy and Scheraga's [7]. It can be expressed in the following form:

$$Z = \sum_{N_i} g \left[ \prod_{i=1}^3 [f_{i,inter} \exp(-E_i/RT)]^{N_A x_i} \prod_{i=1}^3 [f_{i,intra} \exp(-E_i/RT)]^{N_A x_i} \right] \quad (11)$$

Where  $g$  describes the different populations of water absorbing the infrared radiation, and  $f_i$  are the weighting factors of each infrared mode.

The fraction of each population was obtained by decomposing the OH stretching band into three Gaussian components. The  $g$  factor is calculated from these three populations as:

$$g = \frac{N_A}{N_{NW}! N_{IW}! N_{MW}!} \quad (12)$$

Where  $N_{NW} = N_A x_{NW}$ ,  $N_{IW} = N_A x_{IW}$ , and  $N_{MW} = N_A x_{MW}$ .

NW is the network water (see the main text for details on the three populations), IW the intermediate water, and MW the multimer water;  $N_A$  is the Avogadro number and  $N_i = N_A x_i$  with  $\sum N_i = N_A$  are the number of each species per mole of water;  $x_i$  is the mole fraction of each species.

The weighting factors  $f_i$  are assigned to the three intermolecular factors  $f_{i,inter}$ , one for each of the three populations, and identically for the three intramolecular factors  $f_{i,intra}$ :

$$f_{i,inter} = \left[ 1 - \exp(-h\nu_i^{(T)}/\kappa_B T) \right]^{-3} \left[ 1 - \exp(-h\nu_i^{(L)}/\kappa_B T) \right]^{-3} \quad (i = 1, 2, 3) \quad (13)$$

$$f_{i,intra} = \left[ 1 - \exp(-h\nu_i^{(S)}/\kappa_B T) \right]^{-3} \left[ 1 - \exp(-h\nu_i^{(B)}/\kappa_B T) \right]^{-3} \quad (i = 1, 2, 3) \quad (14)$$

$\nu_i^{(S)}$  the wavenumber assigned to the OH stretching mode, while the  $\nu_i^{(B)}$  the wavenumber attributed to the bending mode. In this way, it is crucial to measure the wavenumbers of each mode experimentally and not calculate them to adjust the results with the reference values. In addition, it is necessary to experimentally obtain the fraction of each of the three populations and insert these parameters as an input of the model. These parameters were obtained from the micro FTIR measurements presented in the manuscript.

The population of NW ( $n_h \sim 4$ ) is considered as the fundamental level, i.e.  $E_{NW} = 0$ . The energy assigned to the level of IW is the energy required to transform a bond  $O - H \cdots O$  of ice in a free OH bond, estimated for liquid water equal to  $E_H = 23.3 \text{ kJ.mol}^{-1}$  [4, 8-10]. Finally, the energy allocated to the energy level of the MW population must be a combination of the energies required to break 2, 3, and 4 hydrogen bonds with this form  $E_{MW} = x_2 2E_H + x_1 3E_H + x_0 4E_H$ . However, the fractions of the 2-, 1- and 0-linked populations contained in the MW fraction are not well-defined separately in the literature. That is why Bergonzi et al. assumed that in MW, the molecules create 2 hydrogen bonds at maximum. This hypothesis is verified by different studies [11-14]. Therefore, the energy assigned to the MW population is the energy required to break 2 hydrogen bonds and is equal to  $2E_H$ .

As a result, the partition function can be calculated entirely from the experimental data. But, in our case, the connectivity, libration and bending bands were not recorded because of the quartz container. Consequently, we use the reference values of Bergonzi's measurements for these three modes of water molecules as a function of temperature, linearly extrapolated when working beyond the range (-10° to +90°C) explored in Bergonzi et al.

## **References**

1. Biéumont, É., *Spectroscopie moléculaire: Structures moléculaires et analyse spectrale*. 2008: De Boeck Supérieur.
2. Poilblanc, R., *Spectroscopies infrarouge et Raman*. 2006.
3. Martin, J., J. Francois, and R. Gijbels, *First principles computation of thermochemical properties beyond the harmonic approximation. I. Method and application to the water molecule and its isotopomers*. The Journal of chemical physics, 1992. **96**(10): p. 7633-7645.

4. Bergonzi, I., et al., *Gibbs free energy of liquid water derived from infrared measurements*. Physical Chemistry Chemical Physics, 2014. **16**(45): p. 24830-24840.
5. Bergonzi, I., et al., *Oversolubility in the microvicinity of solid–solution interfaces*. Physical Chemistry Chemical Physics, 2016. **18**(22): p. 14874-14885.
6. Griffith, J. and H. Scheraga, *Statistical thermodynamics of aqueous solutions. I. Water structure, solutions with non-polar solutes, and hydrophobic interactions*. Journal of Molecular Structure: THEOCHEM, 2004. **682**(1-3): p. 97-113.
7. Némethy, G. and H.A. Scheraga, *Structure of water and hydrophobic bonding in proteins. I. A model for the thermodynamic properties of liquid water*. The Journal of Chemical Physics, 1962. **36**(12): p. 3382-3400.
8. Marechal, Y., *The hydrogen bond and the water molecule: The physics and chemistry of water, aqueous and bio-media*. 2006: Elsevier.
9. Eisenberg, D., *Kauzmann, The structure and properties of water*. 1969, Oxford University Press, Oxford.
10. Schuster, P., G. Zundel, and C. Sandorfy, *The Hydrogen Bond: Theory*. Vol. 1. 1976: North-Holland.
11. Luzar, A., *Resolving the hydrogen bond dynamics conundrum*. The Journal of Chemical Physics, 2000. **113**(23): p. 10663-10675.
12. Stillinger, F.H. and A. Rahman, *Improved simulation of liquid water by molecular dynamics*. The Journal of Chemical Physics, 1974. **60**(4): p. 1545-1557.
13. Swiatla-Wojcik, D., *Evaluation of the criteria of hydrogen bonding in highly associated liquids*. Chemical Physics, 2007. **342**(1-3): p. 260-266.
14. Thaomola, S., A. Tongraar, and T. Kerdcharoen, *Insights into the structure and dynamics of liquid water: A comparative study of conventional QM/MM and ONIOM-XS MD simulations*. Journal of Molecular Liquids, 2012. **174**: p. 26-33.