Supporting Information for:
Molecular Fingerprints of Hydrophobicity at Aqueous Interfaces from Theory and Vibrational Spectroscopies

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Sample characterization

Thin BN nanoplatelets aqueous dispersions were purchased from Sigma Aldrich (at a concentration of 20 mg/ml) and all the other concentrations investigated here were obtained by evaporation of the dispersion directly in the measurement cell under a nitrogen-purged environment. The cell was periodically weighted to measure the amount of evaporated solvent and to calculate the effective concentration of the BN nanoplatelets dispersion. Three concentrations have been measured, corresponding to 20 mg/ml, 50 mg/ml and 100 mg/ml. These three concentrations have been identified as low water-, medium water- and high water- content regions for the BN nanoplatelets-water dispersions.

The size distribution of a diluted BN nanoplatelets aqueous dispersion (2 mg/L) was analyzed by Dynamic Light Scattering (DLS) using a DynaPro NanoStar (Wyatt Technology, Santa Barbara, CA), with a 658 nm laser. The measurements were performed in disposable 50-µL cuvettes (Eppendorf, Germany) and reflect the average of ten five-second acquisitions. The intensity autocorrelation function was converted to a hydrodynamic radius based on the Stokes-Einstein equation using a regularization method employed in the Dynamics software (version 7.0.3, Wyatt Technology, Santa Barbara, CA). Three separately prepared suspensions of the BN nanoplatelets were analyzed.

DLS analysis showed a heterogeneous size distribution with two particle size fractions of the BN nanoplatelets, when suspended in water. There was a major size fraction (90%) with a 140 nm radius and a minor size fraction (10%) with a 1500 nm radius, which can be due either to aggregation or to the production process of the BN nanoplatelets. The thickness of the thin BN nanoplatelets is about 2.4 nm, as measured in Ref. 1.

THz absorption spectroscopy

THz absorption spectra of thin BN nanoplatelets aqueous dispersions were recorded in the frequency range from 50 to 240 cm⁻¹ by FTIR absorption spectroscopy at room temperature. THz-FTIR measurements were performed using a Bruker Vertex 80v spectrometer equipped with a mercury arc lamp as source and a liquid helium-cooled bolometer from Infrared Laboratories as detector. The samples were placed in a temperature-controlled liquid transmission cell from Harrick with z-cut quartz windows and a 25 µm-thick Kapton spacer. 64 scans with a resolution of 2 cm⁻¹ were averaged for each spectrum. The spectra were smoothed with a 3 points-wide moving average.

All spectra were obtained by subtracting from the absorption of the BN nanoplatelets aqueous dispersion, the signal of the corresponding amount of dry BN in the considered dispersion. In fact, the frequency-dependent absorption coefficient of each dispersion with respect to that of the dry BN (Δα(ν)) can be expressed by using Lambert-Beer’s law as:
\[
\Delta \alpha(\nu) = \frac{(\alpha_{\text{sample}} - \alpha_{\text{dryBN}})}{x_w} = \frac{1}{d \cdot x_w} \ln \left( \frac{I_{\text{dryBN}}(\nu)}{I_{\text{sample}}(\nu)} \right)
\]  (1)

where \(d\) is the sample thickness, \(x_w\) is the molar fraction of water in each dispersion, \(\alpha_{\text{sample}}(\nu)\) and \(\alpha_{\text{dryBN}}(\nu)\), \(I_{\text{sample}}(\nu)\) and \(I_{\text{dryBN}}(\nu)\) are the absorption coefficients and the transmitted intensities of a BN nanoplatelets aqueous dispersion and of the dry BN in the dispersion at a fixed concentration, respectively.

The exact sample layer thickness was determined by recording the etalon fringes of the empty cell before every measurement, while the sample layer thickness of each dispersion was estimated by the volume of each dispersion obtained by evaporation in the sample cell. During each series of measurements the sample compartment of the spectrometer was continuously purged with technical grade dry nitrogen to minimize air humidity.

To analyze the different spectral contributions of hydration water in the system, for each BN aqueous dispersion a model of the form was used:

\[
\Delta \alpha = n_{HF} \alpha_{HF} + \sum_{n=1}^{N} L_n
\]  (2)

where \(\alpha_{HF}\) accounts for the contribution of the broad librational band of water centered at about 700 cm\(^{-1}\). This term were subsequently scaled by \(n_{HF}\) as a fit parameter.

The additional positive contributions arise from a small number of resonances due to hydration water, which can be described by damped harmonic oscillator (DHO) line shapes of the form

\[
L_n(\tilde{\nu}) = \frac{a_n w_n^2 \tilde{\nu}^2}{4 \pi^3 \left[ \frac{\tilde{\nu}^2 w_n^2}{\pi^2} + \left( \tilde{\nu}_{d,n}^2 + \frac{w_n^2}{4 \pi^2} - \tilde{\nu}^2 \right)^{2} \right]}
\]  (3)

where \(a_n\), \(w_n\) and \(\tilde{\nu}_{d,n}\) are the amplitude, the damping width and the center frequency of the \(n^{th}\) damped harmonic oscillator mode, respectively. Note, that \(\tilde{\nu}_{d,n}\) is the apparent center frequency of the damped resonance. For the unperturbed oscillator frequency \((\tilde{\nu}_{0,n})\) the following relationship holds: \(\tilde{\nu}_{0,n} = \sqrt{\tilde{\nu}_{d,n}^2 + \frac{w_n^2}{4 \pi^2}}\).

A low-frequency DHO with an unperturbed center frequency of about 60 cm\(^{-1}\) (and a width between 115 and 150 cm\(^{-1}\), depending on the considered concentration) was also employed for all the concentrations investigated here to describe the Debye relaxations extending from the GHz frequency range into the THz region, as previously done for different water systems.

The results of the fits for the hydration water in the investigated BN aqueous dispersions at different concentrations are shown in Fig.S1 and are listed in the following table.
Table S1. Spectral parameters of the hydration water in BN aqueous dispersions at different water content (concentration), obtained by fitting a set of unperturbed harmonic oscillators to the differential absorption spectra. The statistical 2σ error is given in brackets.

The linewidths of the resonances have been fixed in the final fitting procedure to the values obtained in a full free parameters fit and similarly to Ref. 4. As a comparison, we report the parameters for bulk water at room temperature obtained with the same fitting procedure from Ref. 5: $\tilde{\nu}_0=181(2)$ cm$^{-1}$ and $w=537(3)$ cm$^{-1}$.

| water content (concentration) | $\tilde{\nu}_{d,n}$ [cm$^{-1}$] | $\tilde{\nu}_{0,n}$ [cm$^{-1}$] | $w_n$ [cm$^{-1}$] |
|------------------------------|-------------------------------|-------------------------------|-----------------|
| low (100 mg/ml)              | 142(2)                        | 159(2)                        | 440             |
| medium (50 mg/ml)            | 146(2)                        | 162(2)                        | 440             |
|                              | 190(4)                        | 197(4)                        | 330             |
| high (20 mg/ml)              | 157(1)                        | 176(1)                        | 490             |
Figure S1. Absorption spectra of BN nanoplatelets aqueous dispersions at different concentrations (top panel: 100 mg/ml, low water content; middle panel: 50 mg/ml, medium water content; bottom panel: 20 mg/ml, low water content). Each spectrum (black line) was modeled as a sum of damped harmonic oscillator (red line), as described in the text. The individual harmonic oscillators are color-coded using the same color for similar center frequencies.
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