Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for: Multiresolution Continuous Wavelet Transform for Studying Coupled Solute-Solvent Vibrations from Ab-Initio Molecular Dynamics

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1 Amide Modes Analysis from QM Clusters

In Fig. 1 the amide I, II, III and IV modes composition obtained from the Hessian based analysis are presented. This normal modes analysis has been performed on the NMA cluster including the closest water molecules to the NMA oxygen and $N-H$ hydrogen.

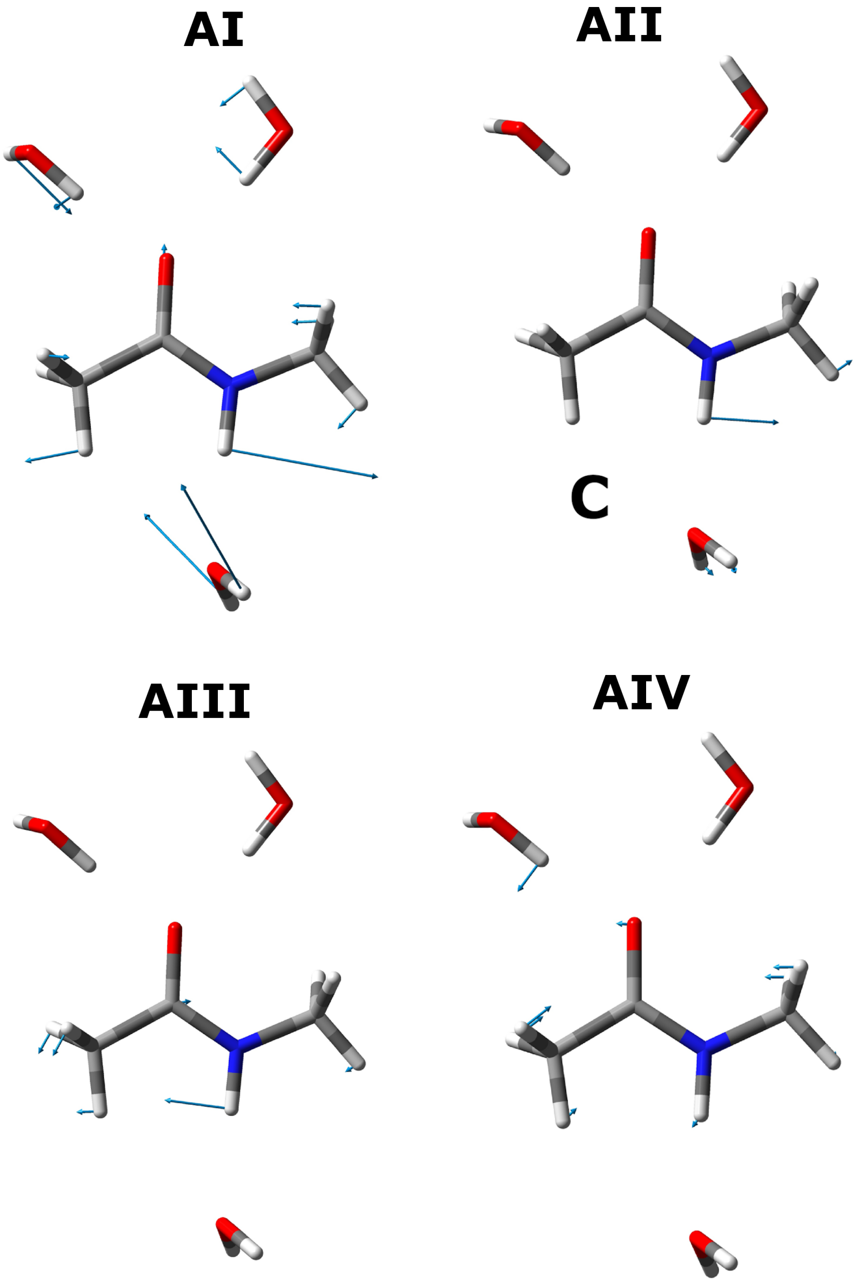

Figure 1. NMA cluster amide modes from Hessian based analysis.

2 Vibrational Spectra of Amide Bands from Fourier Transform

The Fourier transforms of the modes velocity autocorrelation functions obtained from Analysis 1 are performed.

The Fourier power spectrum in Fig. 2 shows a well-separated amide I mode in agreement with the nicely isolated mode described in the previous section. The amide I band presents two main peaks at 1606 cm^{-1} and 1612 cm^{-1} surroundend by other minor peaks at both the sides. This fact confirms a dynamical and very sensible to the environment nature of the mode for which a unique representative frequency value is not enough. The nature of this splitting can be attributed to different interactions with the environment, in particular concerning specific interactions such as hydrogen bonds as already supposed.[1,2]

Also in the full QM clusters calculations (data not shown) we found two frequency values associated to the mode at 1569 and 1588 cm^{-1} (anharmonic values) and of 1613 cm^{-1} and 1621 cm^{-1} (anharmonic values) for the QM/MM cluster.

The typical red shift of the mode in water solution is so nicely reproduced in both the analyses from AIMD and in the cluster calculations, indeed comparing our results with the experimental ones,[3] an almost quantitative agreement with the typical band red-shift that is around 100 cm^{-1} compared to the gas phase[4] is found.

We show the amide II power spectrum in Fig. 2. The mode has been successfully separated and appears as a defined band with the main peak at 1514 cm^{-1} and a small shoulder at 1517 cm^{-1}. Another important peak is found at 1500 cm^{-1}. The typical amide II blue shift observed experimentally in water solution is reproduced although not quantitatively, indeed a blue shift of 80 cm^{-1} (relative to the gas phase) should be observed.[3] The lack of a significant amide II blue shift could be due to the fact that the solute is described at QM level, and surrunding waters at MM level of theory. Indeed the the interaction between the amide hydrogen with the nearest water molecule is poorly described because the water oxygen is described only by a partial negative charge and not by an explicit treatment of the electronic density therefore this causes a poor representation of the hydrogen bond interaction.

The amide II obtained from the QM cluster calculation shows a significant quantitative agreement with the experiment, indeed the anharmonic value is at 1568 cm^{-1}. In the

QM/MM cluster, once obtained the ad hoc parameters for the van der Waals wall-depth to describe in a correct way the H(amide)-O(wat) interaction, we have reproduced a blue shift comparable with experimental one, with an anharmonic value of 1562 cm^{-1}.

The band observed in Fig. 2 presents two main peaks around 1254 and 1273 cm^{-1}. On average it is centered at 1265 cm^{-1} with a blue shift of 10 cm^{-1} in respet to the gas phase.[4] A qualitative reproduction of the blue shift is obtained but it is not quantitative. As the amide II band, the experimental blue shift, which is of about 58 cm^{-1} is difficult to reproduce. Our cluster calculations resemble more to the expermental value, indeed we find an amide III band at 1306 cm^{-1} for the QM cluster and 1295 cm^{-1} for the QM/MM one (anharmonic values).

A very good agreement with the experimental value[1,3] is found for the amide IV mode, indeed, as we can see from the spectrum in Fig. 2, the band is centered at 630 cm^{-1}, while the experimental value is at 632 cm^{-1}. Also in the clusters we find a good agreement (although it is understimated), with anharmonic values of 615 and 616 cm^{-1} for the QM and QM/MM clusters, respectively.

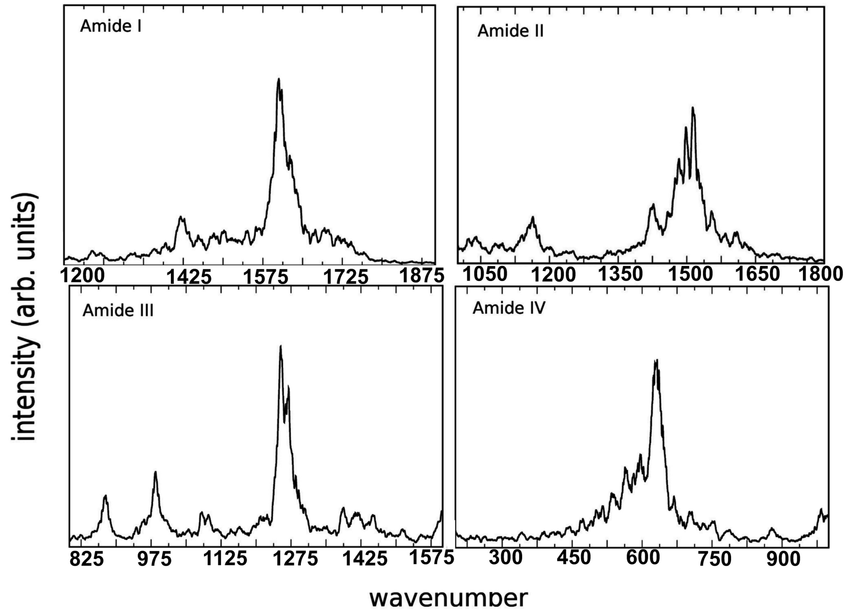

Figure 2. The amide modes Fourier power spectra obtained from AIMD of NMA in water solution.

Table 1. Half width half maximum comparison for experimental (from Ref. 4 for the steady state, and from Ref. 5 for the time-resolved) and computed amide mode bandwidths. All the values are in wavenumber.

	Amide I	Amide II	Amide III
Experiment (steady state)	∼30	∼30	∼20
Experiment (time-resolved)	∼75	-	-
This work (wavelet analysis)	∼125	∼130	∼70
This work (FT)	∼35	∼40	∼18

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