芳香族ポリアミド逆浸透膜の振動分光解析

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Vibrational Spectroscopic Analysis of
Aromatic Polyamide Reverse Osmosis Membranes

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[Abstract] Model systems of aromatic polyamide based reverse osmosis (RO) membranes were constructed by molecular dynamics simulation and their hydrogen bond network was investigated via clustering based on the first hydrogen shell around each functional group. The clustering information was used with the "Weight-Averaged Anharmonic Vibrational Analysis" method developed by us to obtain the IR difference spectra of RO membranes at various moisture conditions. Computational results were verified by comparing with experimentally obtained IR spectra. A peak at approximately 2700 cm^{-1} was assigned to the O-H stretch in the carboxyl group and is thought to provide crucial information on the composition and ionization state of RO membranes.

[Introduction] Reverse osmosis (RO) membranes are the most widely used technology in desalination plants to remove salt from sea and brackish water. Commercially, most RO membranes are those based on aromatic polyamides such as in panel a) of Fig. 1, which have a high salt rejection rate of over 99 %.[1] One of the main challenges currently facing such membrane is fouling, i.e. particles attaching to the membrane surface, which greatly increases operational cost, inhibiting further spread of desaltation technology. Attempts to overcome this proved to be difficult, because the filtering mechanism and structure of RO membranes is poorly understood. Infrared (IR) spectroscopy is a robust experimental method that can characterize material structure. Recently, our group has demonstrated with sphingomyelin[2] and nylon systems,[3] that experimental IR spectra and computational quantum mechanics can be combined to reveal details of microscopic material structure. In this work, the "Weight-Averaged Anharmonic Vibrational Analysis"[2,3] method is further used to calculate highly accurate IR spectra of RO aromatic membranes at a low computational cost. Water moisture effect on the IR spectrum of RO membranes is investigated, and verified by experimental results.

[Methods] Simulation systems of RO membrane bulk are constructed from up to 32 polyamide chains ($C_{195}H_{142}N_{32}O_{40}$), such as shown in panel a) of Fig. 1, with varying amount of water to represent different humidity conditions. A modified AMBER96 force field is used for the polyamide chains, while TIP3P is used for water molecules. Molecular dynamics simulation is conducted with the LAMMPS package.
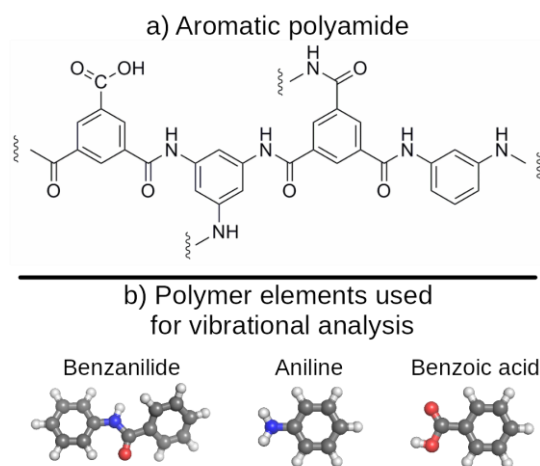

Fig. 1. a) An example of aromatic polyamide structure. b) Elements of the polyamide membrane used during vibrational analysis.

To reduce computational cost, only the IR difference spectra between RO membranes at different humidity are targeted. Therefore, only functional groups sensitive to water need to be investigated. In the case of model RO membrane, hydroxyl, carboxyl, carbonyl and amine functional groups are selected. Polyamide chains are accordingly divided into elements, as shown in panel b) of Fig. 1. For each element, a cluster type is assigned by considering other elements with hydrogen bonds between the functional groups within the first hydration shell.

Electronic structure calculations are done with Gaussian09 for the 70 most populous cluster types. The structures are optimized using the B3LYP functional with 6-31++G** basis set for the functional groups and water, and 6-31++G* for the remaining atoms. VQDPT2[4] calculations are conducted to obtain anharmonic frequencies for each cluster type. The IR spectrum of a RO membrane at a specific humidity is obtained by summing the frequencies of all cluster types with their volume density as weight.

[Results and Discussion] Figure 2 displays both computed and experimental IR difference spectra between RO membranes at high and low humidity. The positions and frequency shifts of amide I, amide II and amide bond N-H stretch modes show a good match. The overall shape of region above 3000 cm^{-1} is also similar, but inconsistencies remain because of the difficulty of accurately reproducing the IR spectrum of water.

The most acute inconsistency belongs to the O-H stretch mode of carboxyl group, indicated by a) in Fig. 2, were both the peak (~ 2700 cm^{-1}) and dip are much smaller in the experimental results. This indicates that the amount of hydrogen bonds where the carboxyl group acts as a donor is overestimated in current computation, which can be attributed to the deprotonation of carboxyl that is not taken into account in the current model. This carboxyl O-H stretch peak it thought to provide valuable information about the ionization of the RO membrane, and further work will be done to clarify its precise meaning.

[References]

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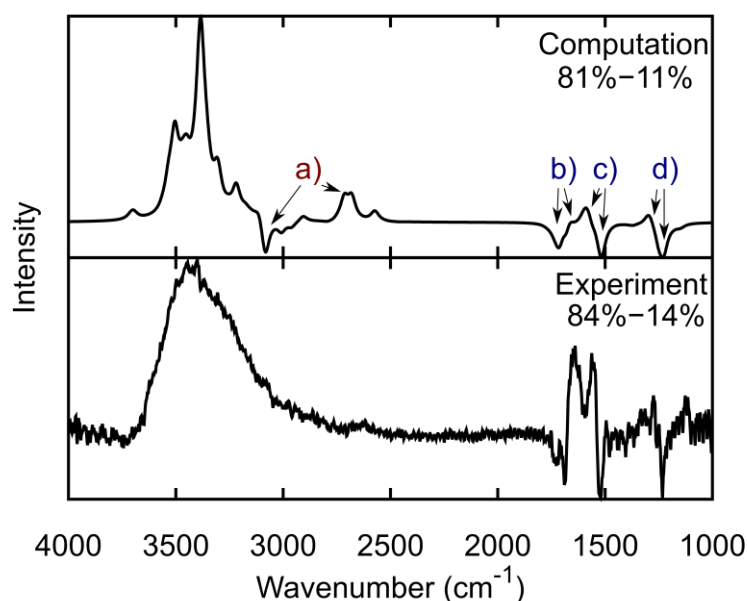[4] K. Yagi, *et al. J. Chem. Phys.* **140**, 084113 (2014).

Fig. 2. Computational and experimental IR difference spectra, where the percentages in the graph show the relative humidity of the RO membranes used. The O-H stretch of benzoic acid is indicated by a) in the computation graph, while amide I, amide II and amide bond N-H stretch are indicated by b), c) and d), respectively. The dips and peaks correspond to the absence and presence of hydrogen bonds with water.