Infrared Spectra of Water Isotopes(H_2O, HDO, and D_2O Molecules) in Hydrophobic Poly(vinylidene fluoride)

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FTIR spectra of water isotopes H_2O, HDO, and D_2O in hydrophobic polymer solid have been first observed on poly(vinylidene fluoride) (PVDF), although the similar spectra had been measured in solid nitrogen and other inactive-gas solids by the matrix-isolation method. The spectra of H_2O and D_2O reveal that water molecules exist as a monomeric species in PVDF and does not take dimer or cluster structures. This restricted isolated water state in PVDF originates from the rather strong intermolecular interaction between the water molecules and the hydrophobic polymer.

Water is an important hydrogen-bonding substance for the living, and so the nature of water forming hydrogen-bonding had been studied comprehensively.[1] The physical states of water in various environments are also an important research problem. There are many studies on the structure of water itself and the related environmental systems.[2-7] We have recently studied the infrared spectra of water sorbed into polymers.[8] In connection with this study, we have made a study of the water isotopes in a hydrophobic polymer, in which water molecules exist as a isolated monomeric species.

In this paper we present the result of infrared spectroscopic study on H_2O, HDO, and D_2O sorbed into hydrophobic poly(vinylidene fluoride).

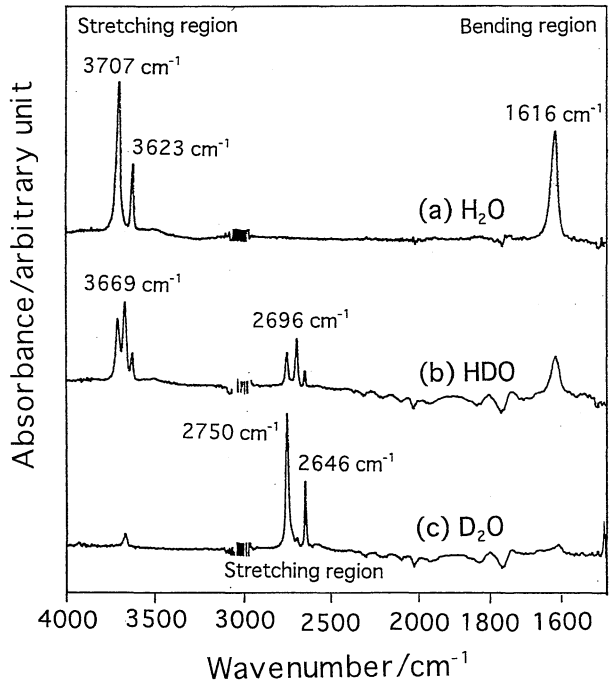

Figure 1. FTIR spectra of H_2O, HDO, and D_2O isotopes in PVDF.

Poly(vinylidene fluoride) (PVDF), Kyner pellet of Kureha company, was used. Films with ca. 0.8 mm thickness were made by the melt-and-pressed procedure. After drying 1 week at ca. 1 Pa, these films were conditioned in the atmosphere of relative humidity (RH) 65% of H_2O, D_2O, and HDO, and water was sorbed into them. The equilibrium mixtures of H_2O and D_2O were used to obtain HDO. Thus three kinds of films, which sorbed H_2O, D_2O, and HDO, were prepared. The water contents of these films were ca. 0.03 w%. The infrared spectra were measured with a Perkin-Elmer System 2000 FTIR instrument at 25 ℃. The spectrum of sorbed water was obtained by the subtraction procedure, in which the spectrum of polymer at RH 0% was subtracted from that of polymer at RH 65%. The experimental details were described in Ref.8.

The FTIR spectra of H_2O, HDO, and D_2O in PVDF were shown in Figure 1. The spectra of water sorbed into hydrophobic PVDF gave the sharp and well-separated absorbance bands. The spectrum of H_2O shows two sharp OH-stretching ν(OH) bands of 3706 cm^{-1} and 3688 cm^{-1}, and a bending δ ($\angle$HOH) band of 1616 cm^{-1}, corresponding to 3 fundamental bands of normal-modes for free H_2O molecule. The spectrum of D_2O in PVDF also shows the two OD-stretching bands at the frequency region lower than 1 / 1.414 times due to the isotope-exchange effect from H to D atom. The $\angle$DOD bending band δ ($\angle$DOD), however, could not detected because of the intensity of strong PVDF bands. In contrast with these two spectra, the spectrum of HDO (the premature of H_2O and D_2O) in PVDF shows quite different feature, i.e., two triplet bands at the both regions of ν (OH) region and ν (OD) region for H_2O and D_2O, respectively. Two peaks of both sides in each triplet band region have the same frequencies of those in the spectra of H_2O and D_2O in PVDF, respectively. Therefore, the middle peak of each triplet may be attributed to the pure band of HDO in PVDF. There are 3 kinds of water states for the spectrum of HDO in PVDF according to the equilibrium of the exchange-reaction among three isotopes. For the spectrum of D_2O in PVDF, a small content of HDO formation is observed: this may attributed to the equilibrium of the same exchange-reaction between the

Table 1. Observed band-frequencies and their band assignments of H_2O, HDO, and D_2O in PVDF

	Water in PVDF Present study			Water in vapor Ref. 9		
	ν_a (cm^{-1})	ν_s (cm^{-1})	δ (cm^{-1})	ν_a (cm^{-1})	ν_s (cm^{-1})	δ (cm^{-1})
H_2O	3707	3623	1616	3756	3652	1595
HDO	3669	2696	-[a]	-	2719	1402
D_2O	2750	2646	-[a]	2789	2666	1179

[a] Non-detectable due to PVDF bands.

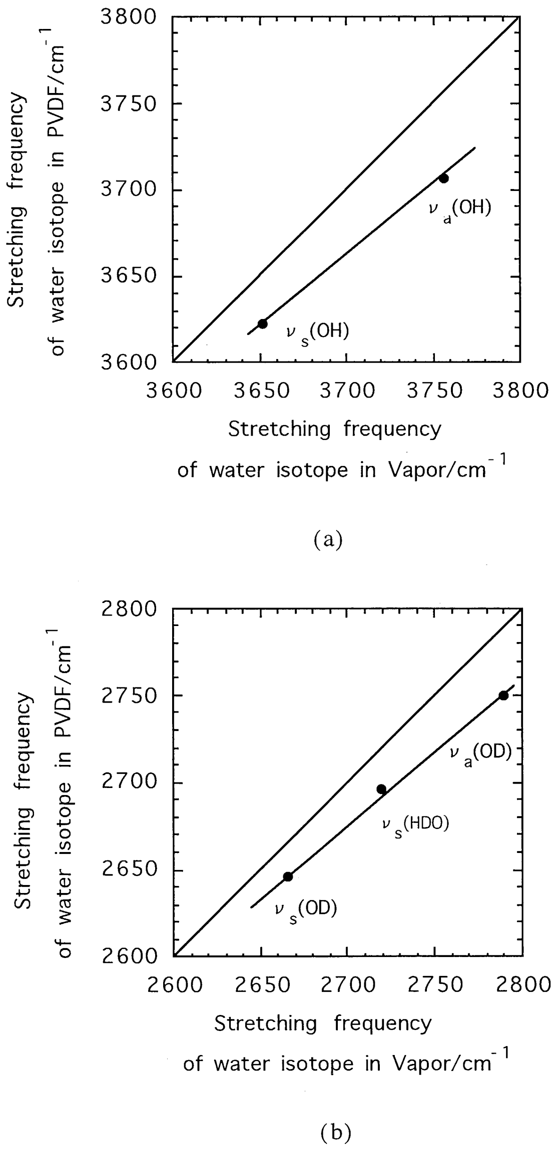

Figure 2. Relation of observed band-frequencies between two kinds of water molecules in PVDF and in vapor. (a) The OH stretching frequency region of 3600 ~ 3800 cm^{-1} and (b) the OD stretching frequency region of 2600 ~ 2800 cm^{-1}.

D_2O and the contaminated H_2O in humidity used for the present study. Eventually FTIR spectra of 3 isotopes of water have been observed for the first time at a room temperature in the hydrophobic polymer solid, although these spectra had been observed by the FTIR spectroscopy of the Matrix-Isolation method in solid nitrogen and so on.

Observed frequencies of these bands and their assignments were also summarized in Table I, in comparison with the referenced data of water vapor H_2O, HDO, and D_2O in literature.[9] Water isotopes sorbed into PVDF gave the frequency values shifting to lower positions for the bond stretching band; $\Delta\nu_a$ = 49 cm^{-1} (from $\Delta\nu_a$ = 3756 cm^{-1} in vapor to $\Delta\nu_a$ = 3707 cm^{-1} in PVDF) and $\Delta\nu_s$ = 29 cm^{-1} (from $\Delta\nu_s$ = 3652 cm^{-1} in vapor to $\Delta\nu_s$ = 3623 cm^{-1} in PVDF) for H_2O isotope; $\Delta\nu_a$ = 39 cm^{-1} and $\Delta\nu_s$ = 20 cm^{-1} for D_2O isotope. Moreover, for the frequency lowering-shift of HDO isotope, $\Delta\nu_a$ = 23 cm^{-1} is also a reasonable value. While, for the bending band of water isotopes in PVDF gave the higher-frequency shift. Figure 2 shows the relation of their frequencies between two kinds of water in PVDF and in vapor. The straight line joining these data points locates on the position under the diagonal line for (a) the OH and (b) the OD stretching frequency regions, respectively. And the deviation of this line from the diagonal line, i.e., the distance between two lines may reflect the dimensions of intermolecular interactions between water molecules and PVDF polymer. The distance of ~ 20 cm^{-1} indicates the rather strong intermolecular interaction between the water molecules and even hydrophobic PVDF polymer, in compared with that between the water molecules and the solid nitrogen or other inactive gas.[10,11]

In conclusion, FTIR spectra of water isotopes H_2O, HDO, and D_2O in hydrophobic polymer solid were observed for the first time in PVDF at a room temperature, although the similar spectra had been measured in solid nitrogen and other inactive-gas solids by the matrix-isolation method. The spectra reveal that water molecules exist as a monomeric species in PVDF, but do not take the free rotation motion. This restricted isolated water state in PVDF originates from the rather strong intermolecular interaction between the water molecules and the hydrophobic polymer.

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