Supporting Information

Structural Evolution of Water-in-Propylene Carbonate Mixtures Revealed by Experimental Raman Spectroscopy and Molecular Dynamics

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Table of Contents

Spectral Preprocessing

   To account for small baseline shifts that occurred between replicates, the Raman spectra were aligned to a common baseline by taking the average of the final 50 intensity values (3750–3850 cm^{-1}) in each spectrum where there are no spectral features. The average value was then subtracted from the intensity of the corresponding spectrum. Following this baseline alignment, the average of the replicates was acquired. The O-H stretching region of the Raman spectra following the baseline adjustment and averaging of replicates is depicted in Figure S1.
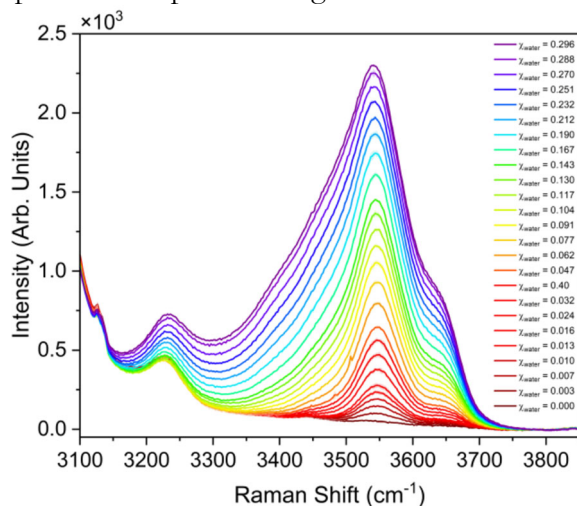

Figure S1. Raman spectra in the O-H stretching region for propylene carbonate with increasing water concentrations (red χ_{water} = 0 to violet χ_{water} = 0.296). Spectra are plotted as the average of two replicates following baseline adjustment and the standard deviation is plotted as shading.

   Due to overlap with the intense C-H stretching modes that originate from PC, the O-H stretching region has a steeply sloped baseline and is convoluted with the C-H stretching mode from PC at 3220 cm^{-1}. To deconvolute the spectral contributions of water and propylene carbonate in the O-H stretching region, an intensity normalization and subtraction of the pure propylene carbonate spectrum is performed. For the intensity normalization, a scaling factor, f, is calculated for each of the water concentrations studied. This is accomplished by dividing the intensity of the symmetric CH$_2$ stretching peak (2938 cm^{-1}) in the specific water + PC spectrum by the intensity (at the same peak position) in the pure PC spectrum. The entire pure PC spectrum was then scaled by the resulting ratio

and subtracted from the corresponding water + PC spectrum. This process is carried out mathematically for $\chi_{water} = 0.296$ as follows:

$$f = \left(\frac{I_{\chi = 0.296}\left(2938 \ cm^{-1} \right)}{I_{\chi = 0}\left(2938 \ cm^{-1} \right)} \right)$$

$$Corrected \ Spectrum = I_{\chi = 0.296} - \left(f \cdot I_{\chi = 0} \right)$$

Figure S2 demonstrates the result of scaling the pure PC spectrum to the intensity of the $\chi_{water} = 0.296$ spectrum as well as the resulting difference ("corrected") spectrum.
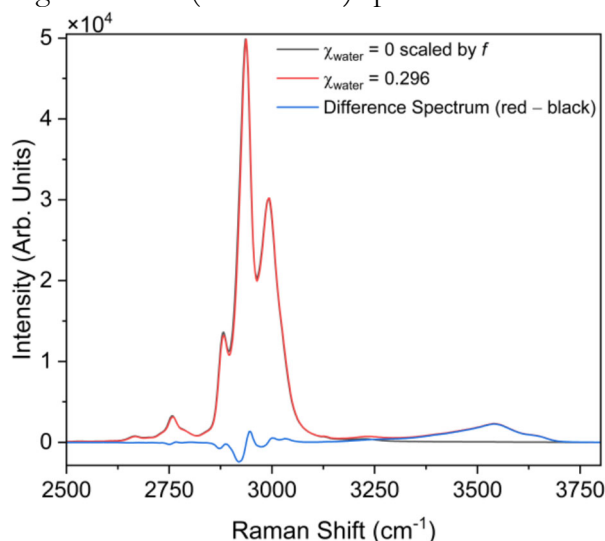

Figure S2. Raman Spectrum of PC + $\chi_{water} = 0.296$ (red), Pure PC ($\chi_{water} = 0$) scaled by the calculated scaling factor, f (black), and the resulting spectrum obtained from their subtraction (blue). Subtraction carried out to remove spectral contributions of pure PC from the O-H stretching region.

The symmetric CH_2 stretching peak was chosen as the reference point because it is the most intense peak in each of the individual spectra and because the scaling factor obtained using this peak is approximately the average scaling factor obtained when the same process was carried out using the symmetric CH_3 and asymmetric CH_2 stretching peaks as the reference point. After the intensity normalization and subtraction procedure, the spectral contributions from pure PC in the O-H stretching region have been removed. The resulting O-H stretching bands originating from water are plotted in the main article (Figure 1).

Raman Gaussian Deconvolution

To characterize the hydrogen bond structure of water as a function of its concentration in PC, the O-H stretching region was fit using a Gaussian deconvolution procedure in Origin Pro 2023. The deconvolution was carried out for 12 of the 25 total spectra, which includes the mole fractions $\chi_{water} =$ 0.007, 0.013, 0.024, 0.040, 0.062, 0.091, 0.117, 0.143, 0.190, 0.232, 0.270, and 0.296. The Fit Peaks (Pro) function in Origin Lab was used to parametrize and carry out the Gaussian fitting for the O-H stretching region between 3073 and 3847 cm^{-1} in each of the 12 spectra. The first step in the parametrization process is defining a baseline for the curve by choosing anchor points along the baseline and an appropriate function to connect the anchor points, effectively fitting the baseline of the data. The wavenumber values 3077, 3096, 3814, and 3843 cm^{-1} were chosen as anchor points for all spectra that were fit. These anchor points were then connected by a linear function. Following this, initial values for the Gaussian peak positions were chosen based on Origin Lab's built-in peak-finding function. Once the initialization parameters were set, the Gaussian fitting was carried out until a chi-squared convergence tolerance of 1×10^{-6} was reached. All parameters of the fit were allowed to vary freely apart from the baseline and the peak position of the highest frequency Gaussian. The decision to set the position of the highest frequency Gaussian to a constant value was made after the $\chi_{water} =$ 0.143, 0.190, 0.232, 0.270, and 0.296 spectra were initially fit without fixing this parameter. In these fits, the peak position of this Gaussian remained approximately constant, only changing by $\pm$ 0.2 cm^{-1}, which is much smaller that the resolution of the Raman instrument. Therefore, the position of this band was set as a fixed parameter for all subsequent fittings. The fit result of the highest water concentration spectrum was used to determine the constant value of the peak position to be 3642.85 cm^{-1}. The lowest frequency band in the O-H stretching region did not have a high enough intensity to carry out the fitting (did not converge within 500 iterations) until the concentration χ_{water} = 0.091 was reached, therefore only the seven highest concentration spectra were able to be fit to four

total bands. The lower water concentration spectra are only fit to three bands. In Figure S3, the O-H stretching region of the Raman spectra are plotted with the fit result overlaid on the corresponding spectrum. Table S1 contains the converged parameters for all deconvoluted spectra.
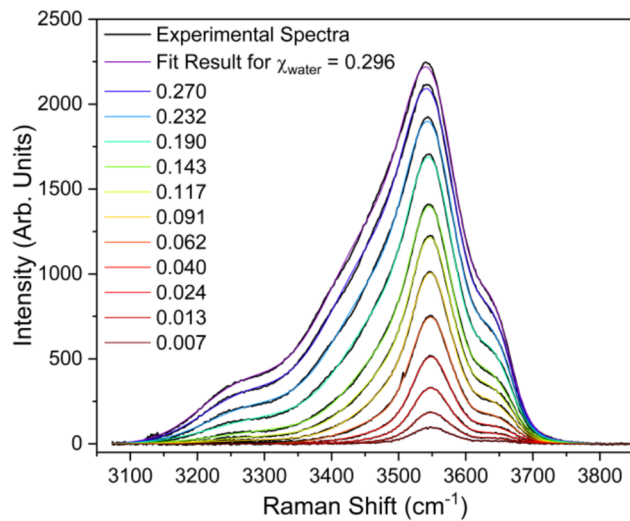

Figure S3. Result of Gaussian fitting to the O-H stretching Raman spectra of PC as a function of increasing water concentration. Experimental spectra are plotted in black and calculated (fit) results are in color.

Table S1. Peak center (cm⁻¹), area, intensity (arb. units), and full-width-half-max (FWHM) values obtained from the Gaussian fits of the O-H stretching region in the Raman spectra of the PC/water mixtures.

χ_{water}	Center (cm⁻¹)	Area	Max. Intensity	FWHM
Peak 1				
0.091	3331.549	5871.516	24.767	222.712
0.117	3329.720	10168.207	45.819	208.482
0.143	3313.961	15339.471	72.718	198.169
0.190	3292.773	25583.312	132.021	182.046
0.232	3274.531	30960.326	184.085	158.000
0.270	3266.546	40439.966	248.489	152.887
0.296	3261.367	46670.106	295.524	148.359
Peak 2				
0.007	3548.494	2272.982	12.437	171.694
0.013	3543.662	5779.104	42.771	126.935
0.024	3540.814	12003.970	77.994	144.588
0.040	3537.119	23089.416	132.327	163.920
0.062	3528.579	40341.990	219.315	172.805
0.091	3526.457	68049.167	397.876	160.673
0.117	3523.554	96854.100	541.741	167.956
0.143	3520.025	128609.003	681.587	177.263
0.190	3509.432	182358.176	899.519	190.451
0.232	3495.311	223349.016	1042.904	201.190
0.270	3485.685	266098.194	1207.844	206.966
0.296	3480.473	299576.228	1326.595	212.147
Peak 3				
0.007	3548.535	5596.160	83.026	63.320
0.013	3549.036	9158.259	141.291	60.893
0.024	3548.803	16421.794	250.442	61.600
0.040	3548.677	25529.054	380.962	62.954
0.062	3548.473	37362.355	534.077	65.720
0.091	3548.915	42541.617	624.894	63.955
0.117	3548.901	48777.053	700.712	65.395
0.143	3548.627	54480.111	758.554	67.471
0.190	3549.084	68665.483	878.296	73.446
0.232	3549.617	89078.920	1024.946	81.647
0.270	3550.014	105598.410	1134.446	87.446
0.296	3550.152	115507.264	1194.283	90.859
Peak 4				
0.007	3642.851	869.162	11.494	71.036
0.013	3642.851	2051.773	25.740	74.885
0.024	3642.851	3372.969	42.166	75.148
0.040	3642.851	4657.074	61.421	71.230
0.062	3642.851	7091.936	98.528	67.620
0.091	3642.851	11228.184	149.198	70.699
0.117	3642.851	13517.129	185.393	68.495
0.143	3642.851	14812.833	214.231	64.957
0.190	3642.851	19628.678	295.670	62.366
0.232	3642.851	25542.695	386.414	62.099
0.270	3642.851	30208.874	458.577	61.886
0.296	3642.851	32249.766	492.302	61.541

To aid in the assignment of the deconvoluted O-H stretching bands, isotopic dilution spectra (10% HOD in D_2O) were deconvoluted in the same manner of the H_2O spectra. The HOD spectrum for the highest D_2O concentration is plotted in Figure S4 along with the deconvoluted Gaussian bands. Table S2 contains the converged parameters for the deconvoluted $\chi_{water} = 0.23$ spectrum.
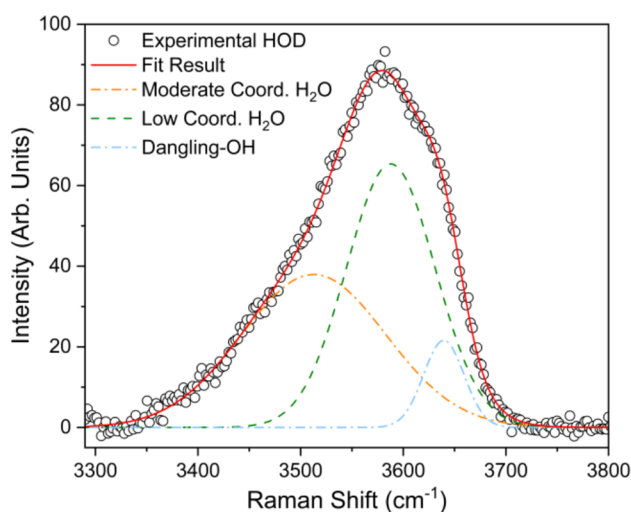

Figure S4. Gaussian deconvolution results for the isotopic dilution experiment where $\chi_{water} = 0.23$. Experimental data is plotted in black circles and the fit plotted as a red solid line. Dashed lines represent Gaussian bands used to fit experimental spectra.

Table S2. Peak center (cm^{-1}), area, intensity (arb. units), and full-width-half-max (FWHM) values obtained from the Gaussian fitting of the O-H stretching region in the Raman spectra of the isotopically diluted PC/D_2O mixtures.

Peak	Center (cm^{-1})	Area	Max. Intensity	FWHM
2	3512.755	6689.334	37.935	165.656
3	3587.795	7074.990	65.350	101.707
4	3639.476	1066.919	21.581	46.443

Attenuated Total Reflectance (ATR)-FTIR Spectra

ATR-FTIR spectra were taken to complement the Raman spectra of dilute water in PC. The ATR-FTIR spectra of the O-H stretching region for a selection of concentrations matching those in the Raman spectra are plotted in Figure S5. The χ_{water} = 0.013 and 0.223 spectra were deconvoluted in the same manner as the Raman spectra. The results are plotted in Figure S6 to demonstrate the evolution of the deconvoluted bands with water concentration. Table S3 contains the converged parameters for the deconvoluted χ_{water} = 0.013 and 0.223 ATR-FTIR spectra.
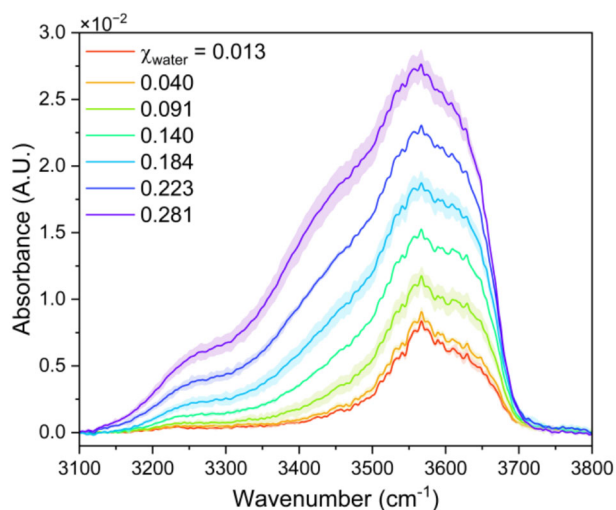
Figure S5. O-H stretching region in the ATR-FTIR spectra of increasing concentrations of water in PC. The spectra are an average of two trials and the standard deviation is included as shading around the solid line.
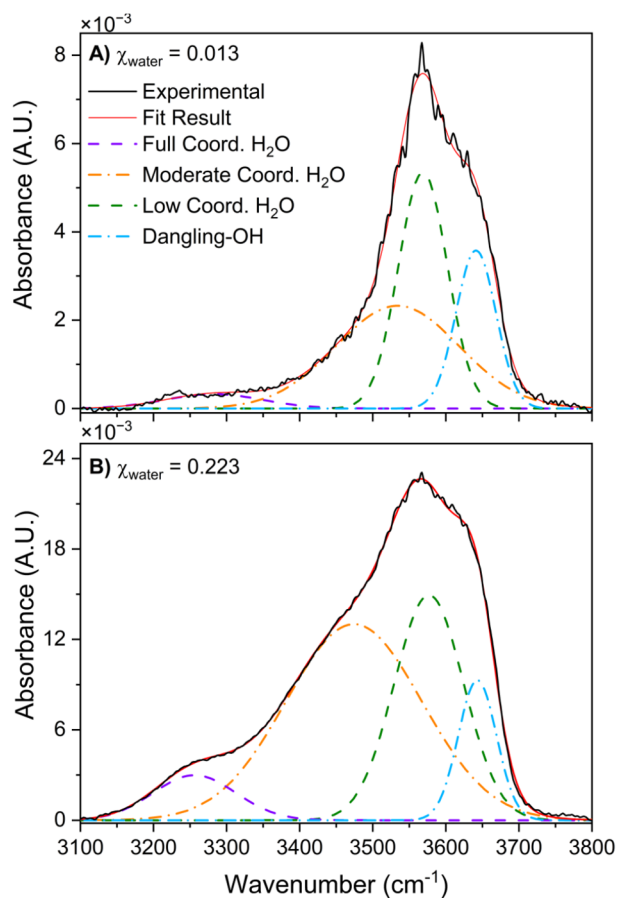
Figure S6. Gaussian deconvolution of experimental ATR-FTIR O-H region for water concentrations χ_{water} = 0.013 (A) and 0.223 (B). Experimental (black) and fit (red) spectra are plotted with solid lines. Dashed lines represent Gaussian bands used to fit experimental spectra.

Table S3. Peak center (cm⁻¹), area, intensity (arb. units), and full-width-half-max (FWHM) values obtained from the Gaussian fits of the O-H stretching region in the ATR-FTIR spectra of the PC/water mixtures.

χ_{water}	Center (cm⁻¹)	Area	Max. Intensity	FWHM
Peak 1				
0.013	3282.312	0.055	0.0003	156.755
0.223	3256.119	0.426	0.003	133.945
Peak 2				
0.013	3533.883	0.493	0.002	198.987
0.223	3474.114	3.033	0.013	218.946
Peak 3				
0.013	3568.560	0.449	0.005	78.881
0.223	3576.849	1.785	0.015	112.215
Peak 4				
0.013	3641.142	0.246	0.004	64.631
0.223	3643.126	0.609	0.009	61.600

Raman Ester Band Analysis

The symmetric and asymmetric ester group stretching bands from PC are reported to occur at 959 and 1228 cm^{-1}, respectively in Raman spectra.[1] Here, we observe these bands at 952.79 and 1224.31 cm^{-1} in the VV polarized Raman spectrum of pure PC. These bands are analyzed in order to determine bulk PC structure as a function of water concentration. The Raman spectra showing the ester bands for the χ_{water} = 0 (pure PC) and χ_{water} = 0.296 solutions are plotted in Figure S7. Both the VV and VH polarized responses are included for determination of the non-coincidence effect (NCE). The NCEs for the symmetric ester band when χ_{water} = 0 and 0.296 are 0.39 and 0.32 cm^{-1}, respectively. The NCEs for the asymmetric ester band when χ_{water} = 0 and 0.296 are -0.31 and -0.32 cm^{-1}, respectively. Peak positions for the symmetric and asymmetric polarized bands were determined through Gaussian fitting and the results are included in Table S4.
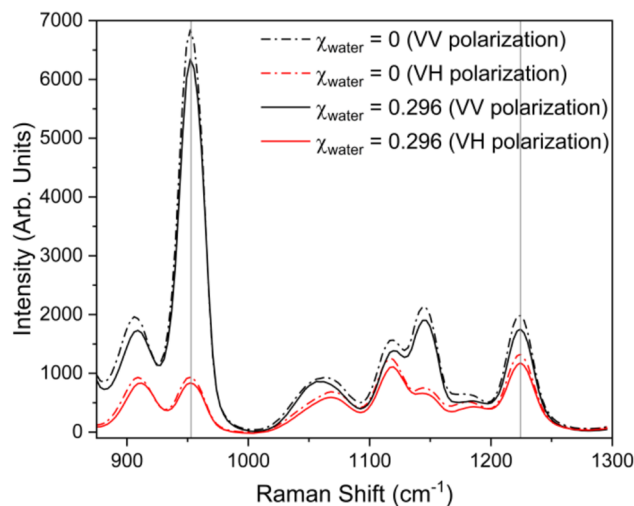

Figure S7. Raman spectra of the symmetric and asymmetric ester stretching bands of PC for the χ_{water} = 0 (dashed lines) and χ_{water} = 0.296 solutions (solid lines). The VV (black) and VH (red) polarized spectra are both included. Gray reference lines are plotted at the peak positions of the symmetric (952.8 cm^{-1}) and asymmetric (1224.3 cm^{-1}) VV polarized ester bands in the χ_{water} = 0 spectrum.

Table S4. Peak center (cm^{-1}), area, intensity (arb. units), and full-width-half-max (FWHM) values obtained from the Gaussian fitting of the ester stretching bands in the Raman spectra of the PC/water mixtures.

Spectrum	Center (cm^{-1})	Area	Max. Intensity	FWHM
Symmetric Ester Band				
χ_{water} = 0 (VV pol.)	952.791	163119.432	6611.649	23.177
χ_{water} = 0 (VH pol.)	952.404	24148.932	890.051	25.489
χ_{water} = 0.296 (VV pol.)	953.288	152857.135	6161.320	23.307
χ_{water} = 0.296 (VH pol.)	952.971	22265.168	818.978	25.540
Asymmetric Ester Band				
χ_{water} = 0 (VV pol.)	1224.306	41129.143	1673.639	23.086
χ_{water} = 0 (VH pol.)	1224.625	26213.472	1060.907	23.212
χ_{water} = 0.296 (VV pol.)	1224.731	35800.864	1463.143	22.987
χ_{water} = 0.296 (VH pol.)	1225.048	22665.846	925.767	23.0005

Electric field fluctuation decomposition

In the main text, we have used the distribution of electric fields along the O-H bond of a water molecular as a map to the Raman line shape. We have found that these distributions are naturally decomposed into two sub-populations depending on whether the tagged O-H bond is donating a hydrogen bond to another water molecule or not. Using the same geometric definition for a hydrogen bond as discussed in the main text, these decomposed distributions are shown in Figure S8 for a range of water concentrations.
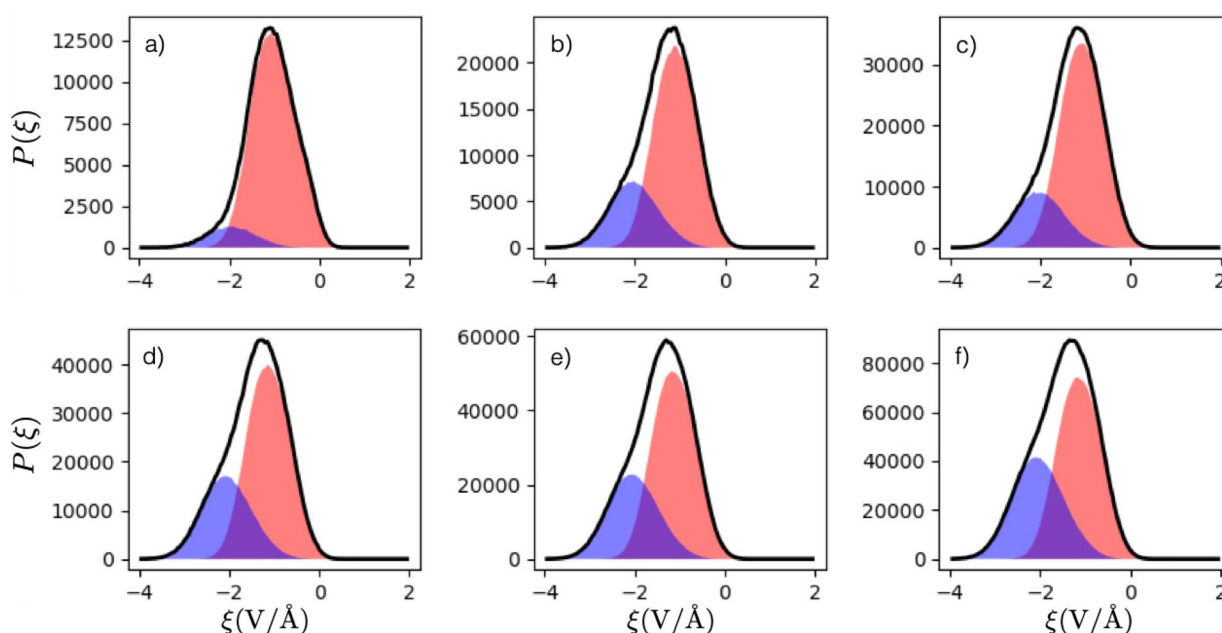

Figure S8. Electric field distributions for water solutions with χ_{water} = a) 0.04, b) 0.08, c) 0.12, d) 0.16, e) 0.19, and f) 0.22 computed from the molecular dynamics simulations discussed in the main text. Shaded regions highlight sub populations for O-H oscillators that are donating a hydrogen (blue) or not (red) to another water molecule.

References

(1) Janz, G. J.; Ambrose, J.; Coutts, J. W.; Downey, J. R. Raman Spectrum of Propylene Carbonate. *Spectrochim. Acta Part Mol. Spectrosc.* **1979**, *35* (2), 175–179. https://doi.org/10.1016/0584-8539(79)80181-6.