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Low Polarity Water, a Novel Transition Species at the Polyethylene-Water Interface

Edward M Kosower* and Galina Borz*

Abstract

The bridge between water repelling and water-attracting regions is here recognized as low polarity water, a novel "neutral" form of water; its identity as a dipole-dipole water dimer supported by spectroscopic evidence of its presence in thin films of water on a polyethylene surface. . High resolution (0.5 cm^{-1}), low signal energies (Sg 100) and short scans (0.1 s) are used to ensure that all peaks are detected. The thin films may be trapped between two polyethylene windows, affirming the low polarity of this water; the spectra of the trapped films ("sandwich") are similar to those from a subtraction procedure. Use of the "sandwich" is a new and useful technique in surface studies. In general, intermediate forms might bridge incompatibility between different regimes, from sets of molecules (chemistry, physics) to sets of organisms (biology, sociology). Thin films of water on polyethylene also display strong and transient peaks of water oligomers (cyclic pentamer, cyclic hexamers (chair and boat), bicyclic hexamers (books 1 and 2) and tricyclic hexamers (prism) that have been previously identified in thin films of water on a silver halide surface.

1 Introduction

Hydrophobic character, a property of non-polar molecules and their aggregates, is manifested by the exclusion of water (or other polar materials), and thus leads to separate regions for the two molecular types. This apparently simple outcome has

parallels in the effect of hydrophobic character on protein structure, on the behavior of liquid mixtures, and on other aspects of chemical and biological interactions[1-3]. One of the most significant structural questions is that of the interface between hydrophobic and polar regions; its identity has challenged molecular science over many years. We herein reveal the surprising nature of water at the interface.

Hydrophobic hexane arranged like crystalline PE interacts repulsively with water according to molecular dynamics (MD) calculations[4]. In contrast, the idea is strengthened by MD calculations[5] for the approach of hydroxide ion to a surface water generated by the GROMOS program. Others have used sum-frequency scattering to analyze the molecular arrangements around an oil droplet[6] and the surface of nonpolar liquids[7]. In no case was a detailed structure of the region given.

2 Results and Discussion

We began with a novel formulation of the water contact layer at the hydrophobic molecule-water interface (HWI). We reasoned that the water molecules would be arranged so as to minimize their net dipole moment next to the hydrophobic PE. The first arrangement has apposed bond dipoles, with a pair of OH bonds emerging from the plane formed by the two OH bonds carrying the dipoles. (Figure 1a, dipole moment 0.21 D with no attempt to minimize) *The first arrangement has a small net dipole and should be an appropriate low polarity neighbor for the polyethylene surface.* The apposed bond dipoles should lead to a low transition dipole and thus low absorption intensity for some of the vibrations.

After we had devised our HWI water model, a search for dipole-dipole dimers turned up a drawing of water (Figure 1b) [8] based on dipole-dipole attraction in water (and methanol) that was similar to ours and is illustrated together with a calculation of the IR spectrum for our model (Figure 1a). The purpose of the drawing was to explain the interactions involved in the elution process of chromatography.

The second arrangement for the water dimer has always been chosen in the literature and includes a hydrogen bond connecting the two water molecules (dipole moment 2.70 D). We expanded the choice to an apposed pair of water dimers as a minimal water combination meant to diminish the overall dipole moment (Figure 1c, dipole moment 1.07 D). The arrangement will be discussed below.

The polyethylene films always carried a film of water of which some must be low polarity water. We acquired spectra, normally using 100 successive 0.1 s scans (signal, Sg 100, resolution 0.5 cm^{-1}) of a polyethylene cell containing 1 μL of water. The modest interaction between water molecules with apposed dipoles implies that the bands would be located at the "usual" bending frequency for water, i.e. 1643 cm^{-1} obtained by using the standard resolution (4 cm^{-1}), a conclusion supported by the experimental results.

A procedure for extracting spectra has steps:

1. Select pairs of successive spectra (#n and #n+1) and carry out a subtraction, either (n+1) − n or n- (n+1).

2. Examine the difference spectra for number of peaks, heights, and location.

3. The spectra obtained are those of low polarity water (LPW) because (a) this should be the major species near hydrophobic surfaces and (b) fluctuations would more likely with less polar species. We present the spectra for the wavelength range of the bending region 1637- 1645 cm^{-1}.

The high resolution spectra reveal that **there are indeed** some bending peaks for water with diminished absorbance in the difference between two *successive* spectra, indicative of decreased transition dipoles for the species lost or gained. Figure 2a shows 10 successive spectra of the bending region (1637-1645 cm^{-1}). Figure 2b shows plots of the low polarity water (LPW) on polyethylene (PE). Three LPW spectra are shown in Figure 2c and six additional LPW spectra are given in Figure 2d both on stretched PE (SPE). Three or four maxima appear in all of the spectra with many peaks having absorbances of less than 0.2.

To test more realistic ideas for the surface water, we have constructed models with two layers of water of each type placed over a hydrophobic surface represented by two n-hexane molecules (to simulate PE). The two types may be termed (a) low-polarity water (LPW) and (b) "polar water" made from four pairs of hydrogen-bonded water dimer. Calculations were carried out at the DFT-B3LYP-6-31G* level using the Spartan Parallel Suite (version 1.20) for each type of model. The calculated IR spectra are shown with the structural models.

The LPW model (Figure 3a) is formed by two rows of 4 dipole-dipole dimer pairs. The distances between the side-by-side pairs are fixed so that they are approximately 4.6 Å apart. The individual pairs were adjusted to make them fit as well as possible the structure of a single dipole-dipole dimer pair. The low

calculated dipole moment (0.77 D) supports compatibility with the PE surface.

The "polar water" model (Figure 3b) is composed of four water dimer pairs, each

connected by a hydrogen bond. These are placed in two layers separated by about

4.0-4.1 Å. No attempt was made to optimize the positions of the hydrogens. The

calculated dipole moment (4.06 D) indicates that the affinity for the PE surface

would be modest.

The assignment is tested by the presence of a 4-(or 6-)band spectrum at 3140 cm^{-1},

which we had previously associated with the low absorbance band between 1637

and 1645 cm^{-1}. This region is shown in Figure 4a for the LPW spectra shown in

Figure 2d. In addition, calculations for a dipole-dipole dimer (with or without n-

hexane) show that there are two peaks in the mid IR, one very weak peak between

1600-1700 cm^{-1} and one much stronger peak between 1750 and 1850 cm^{-1}.

Since stretched polyethylene (SPE) has been used to orient molecules for the study

of their (UV-visible) spectroscopic properties, we tried SPE as a substrate for

water. By virtue of the research described above, we could readily identify LPW

as a significant component of the surface water on SPE, as shown in Figures 2c

and 2d. Comparison of Figures 2b and 2d suggest that there is some more definite

division into groups for the SPE. The explanation for this result may be

understood on the basis of the surface changes[9] on stretching in which islands of

organized lamellae are isolated among hills of amorphous PE.

Some of the maxima and the corresponding absorbances for the LPW spectra are

listed in Table 1. First, only two of the 72 absorbances are above 0.25 in value,

values that appear to support the expectation that the LPW has a weak absorption

in this region. Second, there are at least four maxima, in agreement with absorption due to a water dimer (++, +-, -+, and - - with respect to the bending vibrations). Third, the maxima are remarkably consistent, almost all the same in each column of the Table within the resolution used (0.5 cm^{-1}). Fourth, the spectra derived from a pressed pair of polyethylene windows are similar to those from the subtractions of successive spectra. Fifth, the stronger absorption predicted from the calculations of the dimer pairs are present in the range from 1750-1850 cm^{-+}. Sixth, the region near 3140 cm^{-1} contains a complex set of 4 or 6 bands that we believe to be associated with the LPW spectrum. The combination of experiment and calculation provides strong support for the identification of the dipole dipole dimer as the important constituent of the vicinal layer of water on polyethylene. In addition, the attraction of OH$^-$ ion for the water-nonpolar surface[5] is readily explained by its association with the end OH groups of the dipole dipole dimer.

In addition to the low intensity peaks that we have described above, there are a number of stronger bands that require some discussion of their origin. A precursor on the path to a better understanding of the HWI was our recognition of unique infrared peaks for water oligomers, a process that occurred in four stages. Using thin film infrared spectroscopy (TFIS), the first stage was the discovery of peaks for six water oligomers using a resolution of 4 cm^{-1} and naming the peaks "marker peaks" [10,11]. The second stage was the realization that these peaks derived their intensity from resonance among a set of identical oligomers excited by low energy phonons as calculated for cyclic pentamers in the gas phase[12]. The third stage was

the switch from "regular" resolution (4 cm^{-1}) to a higher resolution (0.5 or 1 cm^{-1})
producing dramatic spectra of the water oligomers. The fourth stage was the use of
polyethylene as cell windows producing spectra that seemed sharper and closer to
the peaks of the "pure" oligomers, such as the boat form of the cyclic hexamer and
the prism form of water hexamer. The identification of six oligomers has been
reported elsewhere[10] but many more have been analyzed theoretically[13]. We can
present here only two examples in which strongly absorbing oligomers are
associated with an LPW spectrum for the ranges, 1500 to 1575 and 1640 to 1730
cm^{-1}. (Figures 5a,b) The overall spectrum for a typical run is shown in Figure 6.
Many of the oligomer peaks of water films on polyethylene are shorter lived (0.1 s
or less) than those on AgX substrates, but in one exception, the cyclic pentamer
had a lifetime of more than 1s. Some of the oligomers on AgX (AgBr-AgCl)
lasted for as long as 1 s and were useful as a "lifetime tag" for identifying species-
related peaks[10]. The electrostatic field on the AgX surface may stabilize the
oligomers. This interesting phenomenon will be explored later.

3 Conclusions

Polyethylene (PE) has a surface with hydrophobic character. Nevertheless, a thin
water film is bound to the surface. This is now explained by the presence of an
intermediate neutral species, low polarity water (LPW), a dipole dipole dimer,
rather than an unstructured vapor[3]. No mention of this novel form of was made in
a recent analysis of the theory of water[14], and we have briefly considered the
dimers of water trimer (μ 1.07 D) or water pentamer (μ 0.927 D), oligomers with
relatively low dipole moments. In both cases, planar forms can be generated by

enough energy (800 cm^{-1} for the pentamer) to produce the marker peak

absorbances but are probably not compatible with hexane on a local scale due to

the tetrahedral orientations needed for oxygen bonding. The role of LPW in the

behavior of such species as cell membranes and channels remains to be studied.

The use of the "sandwich" is a new and useful technique in surface studies. In

general, intermediate forms might bridge incompatibility between different

regimes, from sets of molecules (chemistry, physics) to sets of organisms (biology,

sociology).

4 Experimental Methods

Spectra (usually 100 in a run) were acquired with a Bruker Vertex 70 using mostly

low signal strength (Sg, 100) and short scan times (0.1 s) as explained in our

previous papers, [10, 11, 15,16] using a Bruker Equinox 55/S. The polyethylene cells

were made from LDPE film purchased in a supermarket. Sections of the film

larger than the passage through the cell holder were cut and scotch-taped to a card

labeled with the information for the experiment. A polypropylene probe tip was

taped to the inside of the cell so that samples could be later introduced. A

background was taken before the cell was placed on the holder and a spectrum of

the cell was acquired after placement, revealing the adsorbed water. A 1 μL

sample of water was introduced into the cell as a guarantee that water vapor was

available for deposition on the surfaces. Spectra were converted from Opus format

to Origin 6.1 for display, subtraction and labeling. Computations were carried out

on a Macintosh Pro equipped with 28 GB RAM using the Spartan program[17],

version 1.20. The H-bonded water dimer dipole moment has been reported. [18] The

use of stretched PE in vibrational spectroscopy was first described in detail in

1981. [19] A need for detailed understanding of water structures in connection with

drug design has been outlined in a recent review.[20]

Acknowledgements

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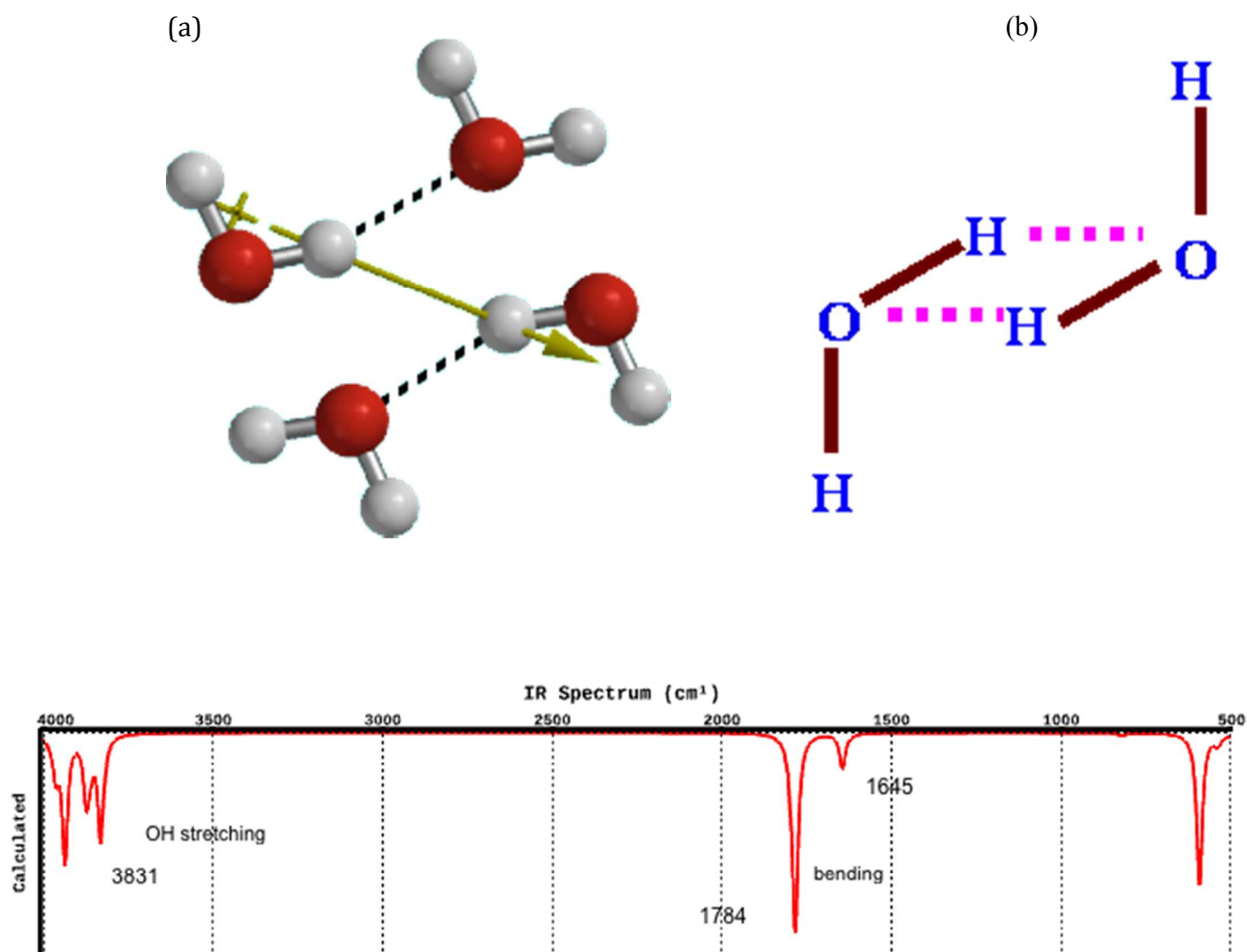[19] J. G. Radrlsrewskl, J. Michl, *J. Phys. Chem.* **1981**, *85*, 2934-2937.

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End Notes

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Author's Notes
E.M.K. conceived the project and wrote the mss. G.B. carried out the experiments
and the data work up.

(a)

(b)

Figures 1a and 1b. (a). Two pairs (left and right) of water molecules arranged with the dipoles apposed. Hydrogen bonds connect the pairs. The net dipole for the combination is calculated as 0.21 D. (b) A formula sketch for a dipole-dipole dimer used for explaining elution in chromatography (reprinted with permission of the copyright owners)
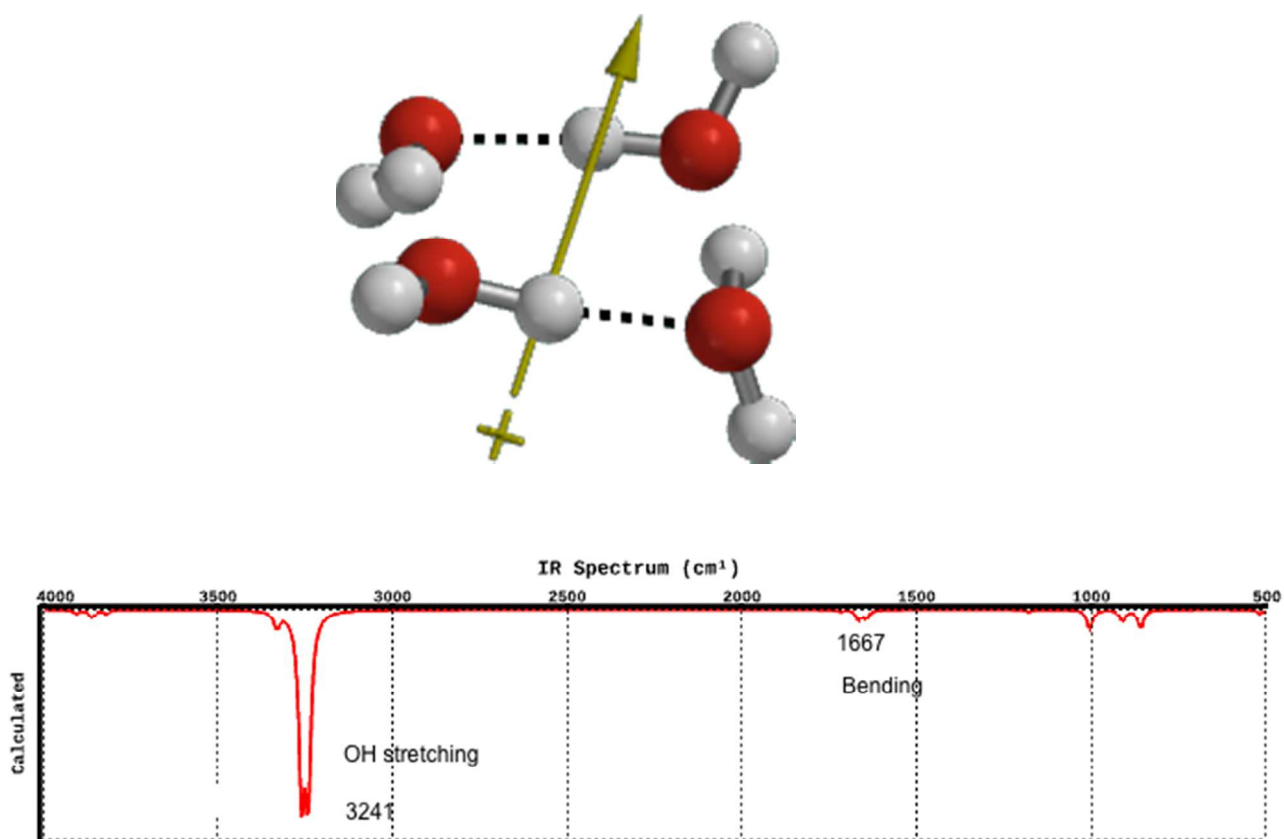
Figure 1c. Two pairs of hydrogen-bonded water dimers with opposite directions for donor-acceptor hydrogen bonds. The net dipole is calculated as 1.07 D.
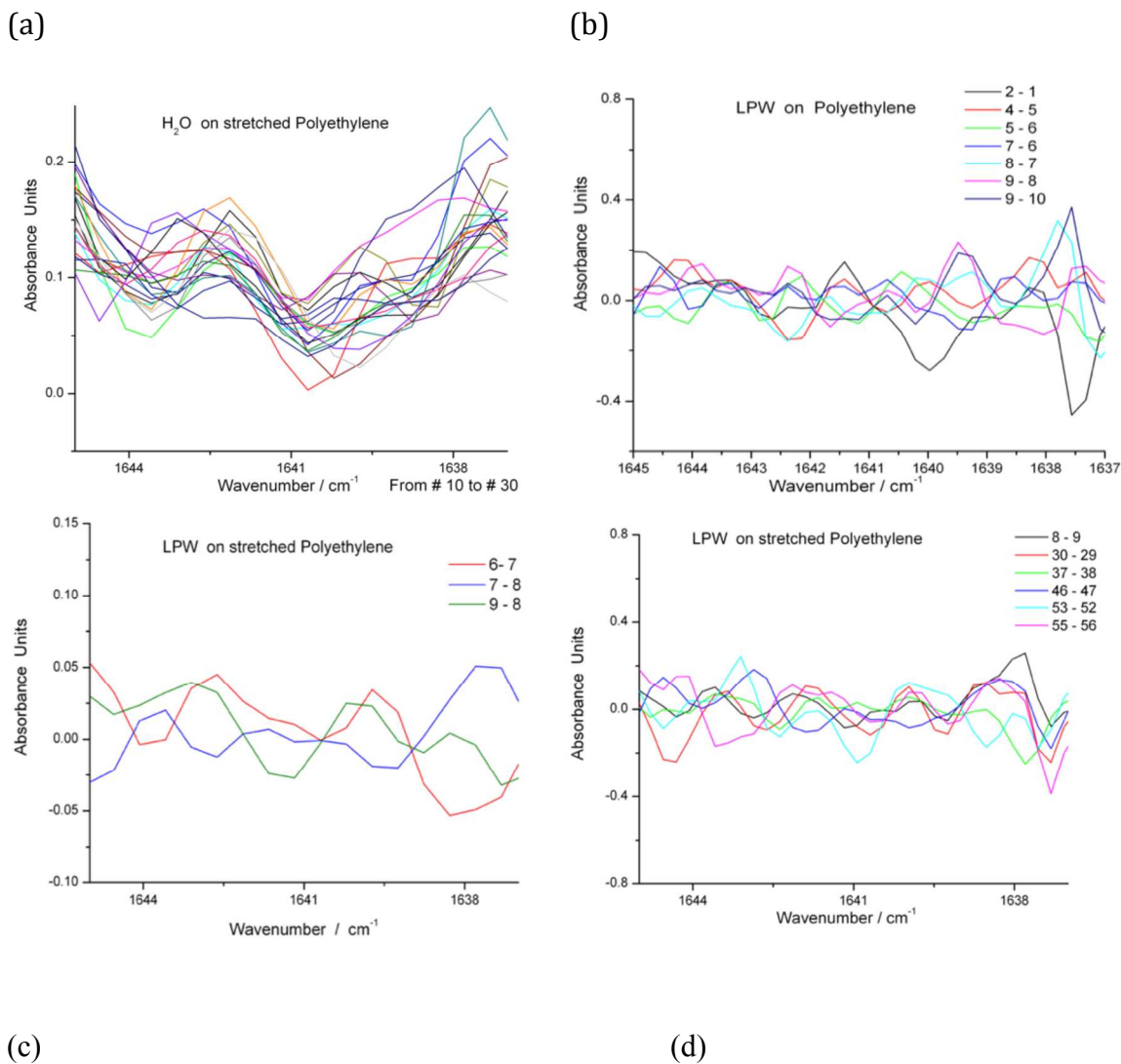
(a)

(b)

(c)

(d)

Figure 2 (a) Absorbance spectra of water on polyethylene (PE) in the water bending region (1637- 1645 cm^{-1}). Spectra #10-30 are displayed (b) Subtraction spectra for low polarity water (LPW) on PE (c) A few LPW spectra on stretched PE (SPE). (d) A set (8-9, 30-29, 37-38, 46-47, 53-52 and 55-56) of 6 LPW spectra with approximately 4 peaks (1637- 1645 cm^{-1}) from water spectra on SPE.

(a)　　　　　　　　　　　　　　(b)

IR Spectrum (cm¹)

OH stretching
3136-3773

2953

2568

1808-1639, 1592, 1569.1448-1051

bending, 10 in last

(a)

IR Spectrum (cm¹)

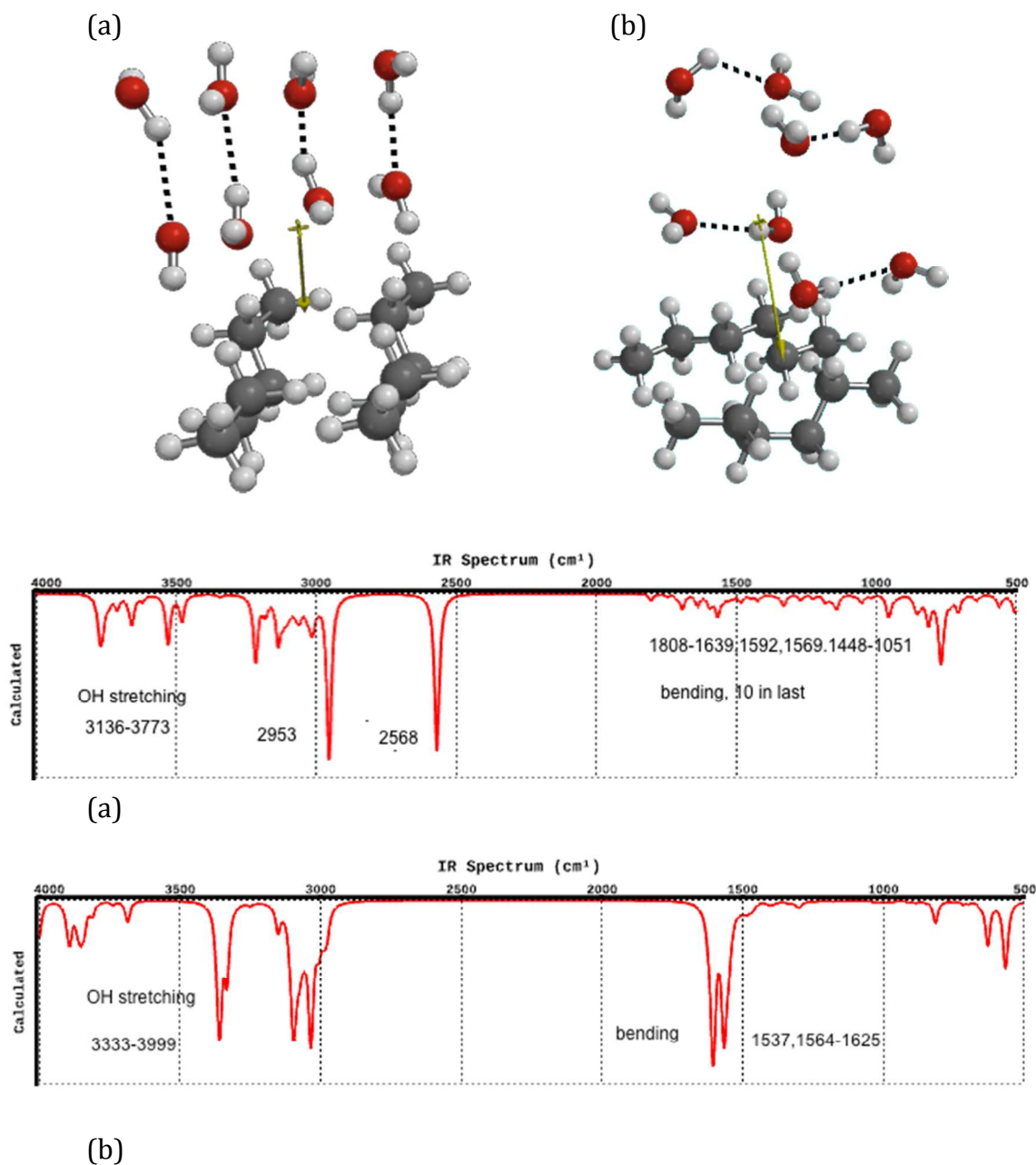OH stretching

3333-3999

bending

1537,1564-1625

(b)

Figure 3 (a). Molecular structure for an LPW model composed of 8 water molecules, grouped as 4 dipole-dipole pairs, over a pair of n-hexane molecules. The calculated dipole moment is 0.77 D. The calculated IR spectrum is shown above. The longest wavelength O-H stretching bands are 2568 and 2953 cm^{-1}. There are many bending bands from 1808 -1051 cm^{-1}. Most of these bands are relatively weak. (b) Molecular structure of 8 water molecules, grouped as 4 pairs of H-bonded water dimers, over a pair of n-hexane molecules. The calculated IR spectrum is shown above. The dipole moment is calculated as 4.06 D. The longest wavelength O-H stretching bands are 3353 and 3359 cm^{-1}. There are many bending bands at 1537 -1625 cm^{-1}. Several of these bands are moderate in strength.
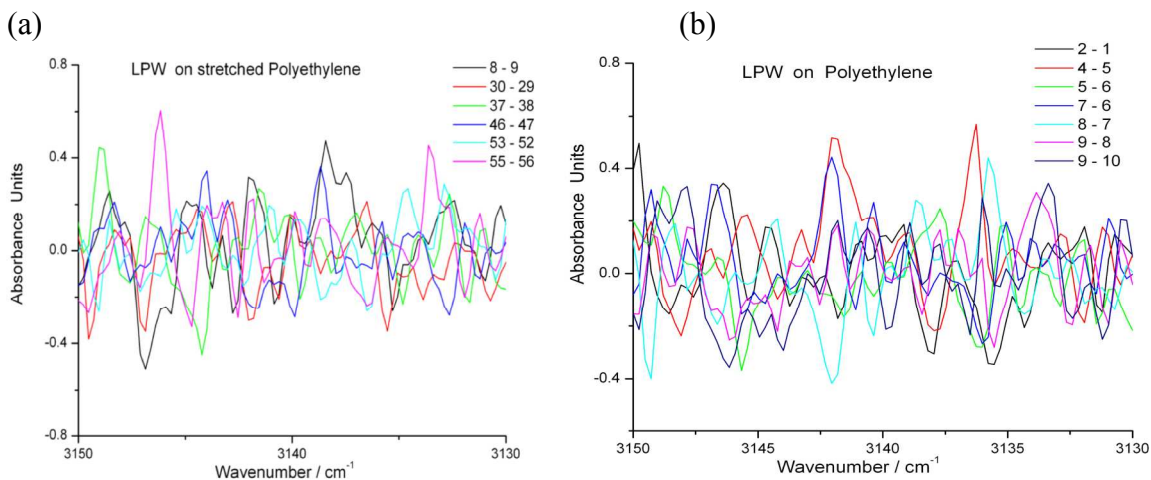
(a)

(b)

Figure 4 (a) The 3140 cm^{-1} region of a series of LPW spectra for a thin film of water on SPE in the wavelength region for asymmetric OH stretching between 3130 and 3150 cm^{-1} derived from the subtractions shown in Figure 2d (b) The 3140 cm^{-1} region of a series of LPW spectra for a thin film of water on PE in the wavelength region for asymmetric OH stretching between 3130 and 3150 cm^{-1} derived from the subtractions listed in the Figure (2-1, 4-5, 5-6, 7-8, 8-7, 9-8, 9-10).
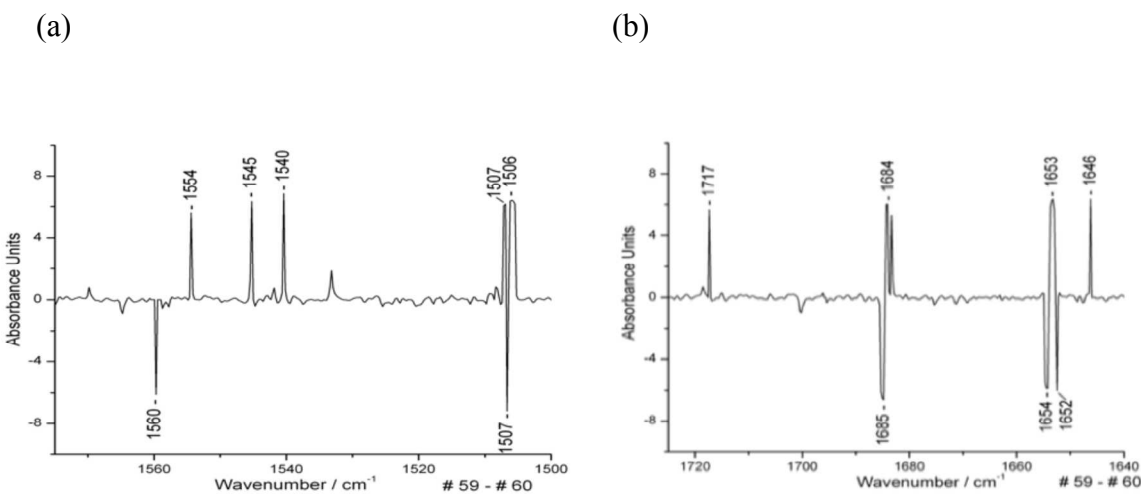
(a)　　　　　　　　　　　　　　　　(b)

Figure 5 (a) A set of oligomer peaks between 1500 and 1575 cm^{-1} for the LPW spectrum obtained by the subtraction of spectrum #60 from spectrum #59. Some of the oligomers have been previously identified: 1506, book 1, 1540, cyclic hexamer chair form, 1540 and 1554, unknown, 1560, cyclic hexamer, boat form. (b) A set of oligomer peaks between 1640 and 1730 cm^{-1} for the LPW spectrum obtained by by the subtraction of spectrum #60 from spectrum #59. Some of the oligomers have been previously identified: 1648, unknown, 1653, prism, 1684, bag 2? and 1717, cyclic pentamer.
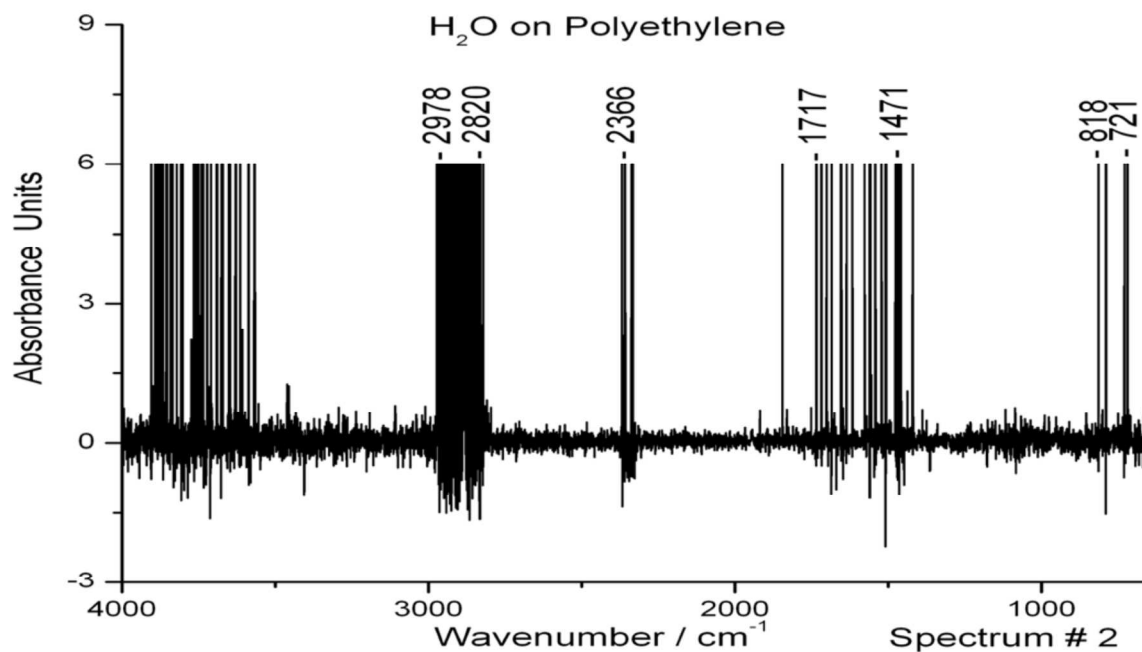
Figure 6 Spectrum #2 from a series for a thin film of water on polyethylene (PE) for the wavelength region between 650 and 4000 cm^{-1}. The absorptions largely due to the polyethylene of the cell are marked (2820-2976 and 1471 cm^{-1}) along with a water oligomer, the pentamer, at 1717 cm^{-1} and CO_2 complexes near 2366 cm^{-1}. Of the 13 unmarked oligomers with absorbance of 6, 6 have been identified. 2 more tentatively, and 5 are unknown.

Table 1 Maxima and Absorbances in Wavelength Range 1637 – 1645 cm^{-1}

Spec A-B	λ_U	Abs$_1$	λ_2	Abs$_2$	λ_3	Abs$_3$	λ_4	Abs$_4$	λ_5	Abs$_5$	λ_6	Abs$_6$
PE^a												
2-1	1638.3	.0620	1639.3	.0661	1641.4	.1525	1642.4	.0255	1643.6	.0788	1644.8	.1908
4-5	1637.3	.1110	1638.3	.1701	1640.0	.0811	1641.4	.0842	1643.4	.0803	1644.3	.1603
5-6	1637.8	.0133	1638.5	.0207	1640.5	.1132	1642.1	.0969	1643.6	.0749	1644.6	.0212
7-6	1637.6	.0739	1638.5	.0933	1640.7	.0824	1641.7	.0532	1642.3	.0567	1643.3 1644.5	.0662 .1330
8-7	1637.8	.3181	1639.3	.1138	1640.2	.0886	1641.7	.0164	1643.8	.0504	-	-
9-8	1637.3	.1346	1639.5	.2337	1640.7	.0402	1642.4	.1348	1643.8	.1449	1644.8	.0313
9-10	1637.6	.3720	1639.5	.1885	1640.7	.0219	1642.4	.0677	1643.1	.0509	1643.8 1644.6	.0801 .0593
SPE^b												
8-9	1637.0	.2504	1639.7	.0364	1640.5	-.0062	1642.1	.0702	1643.6	.1009	-	-
30-29	1637.8	.0735	1638.5	.1244	1640.0	.1033	1641.9	.1073	1643.4	.0709	-	-
37-38	1638.5	.0009	1640.0	.0545	1640.9	.0302	1641.7	.0516	1643.6	.0423	1644.8	-.0012
46-47	1638.0	.1285	-	-	1641.2	.0030	1642.9	.1630	-	-	1644.6	.1468
53-52	1638.0	.0264	-	-	1640.0	.1214	1641.7	.0677	1643.1	.2432	1644.1	.0387
55-56	1638.3	.1428	1640.0	.0770	1641.4	.0783	1642.1	.1118	-	-	1644.1	.1514

a PE, polyethylene b SPE, stretched polyethylene
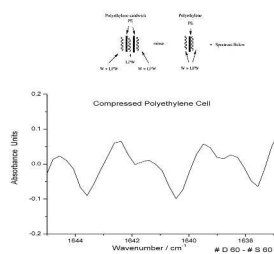
Table of Contents Picture

Table of Contents Figure. Polyethylene sandwich or single window cell: Dark bars represent polyethylene (PE) windows (double or single) of cell. Wavy lines are water (W) and low polarity water (LPW). Subtraction of the single window spectrum from the double window spectrum leaves the LPW spectrum as illustrated in the Figure.