

Perfluoroalkanes Remain on Water Surface even after Volatilization: Affinity Analysis of Fluorinated Solvent with Water Surface

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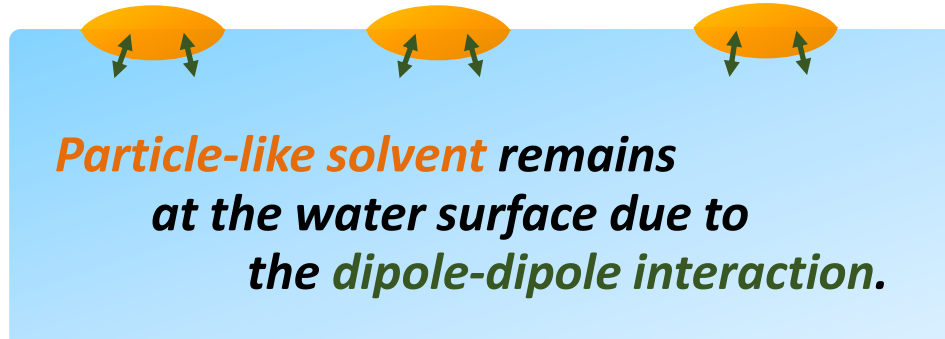
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Abstract (up to 200 words).

Perfluoroalkyl (R_f) compounds are known to have a poor solubility for most solvents except fluorinated solvents, which is known as a fluorophilic property. In Langmuir (L) film studies of R_f compounds, fluorinated solvents such as perfluoro-*n*-alkanes are generally used as a good solvent for depositing a sample monolayer on the water surface. On the other hand, a single R_f chain with a short length such as $C_6F_{13}-$ is known to exhibit a totally different character from a condensed matter to have a strong affinity to a water molecule on the water surface via the dipole-dipole interaction, which is known as the dipole interactive (DI) property. On considering the DI property, the solvents of perfluoro-*n*-alkanes would remain on water for a long time, which may disturb the formation of L film on water. In the present study, details of a liquid layer of perfluoro-*n*-alkanes on water are investigated by using infrared external reflection (IR ER) spectrometry. Although the perfluoro-*n*-alkanes are highly volatile, the relevant vibration bands did not disappear even after two hours, which means that they remain on the water surface. Fortunately, however, the remained solvent, C_6F_{14} , has been found no disturbing factor for preparation of L films. (198 words)

Keywords (up to 10): organofluorine compounds, fluorophilic property, air/water interface, infrared active surface modes, liquid particle, stratified dipole-arrays (SDA) theory, perfluoro benzene

Graphical abstract



Introduction

Perfluoroalkyl (R_f)-containing materials are known to exhibit a poor affinity not only to aqueous solutions, but also to organic solvents. In fact, R_f compounds are generally insoluble in both aqueous and organic solvents; whereas they are exceptionally soluble in fluorinated solvents [1],[2]. This indicates that R_f compounds are both hydrophobic and oleophobic and belong to the third group called "fluorous" or "fluorophilic" (Fig. 1a) [1],[2]. The fluorous property is positively used in synthetic organic chemistry. By introducing an R_f group into a catalyst, for example, a product and the catalyst can easily be separated by liquid-liquid extraction using fluorinated and organic solvents [2]. Introduction of an R_f group into a reactant as a fluorous tag is another useful technique in synthetic chemistry [3],[4], which is also based on the good affinity between the R_f group and fluorinated solvents.

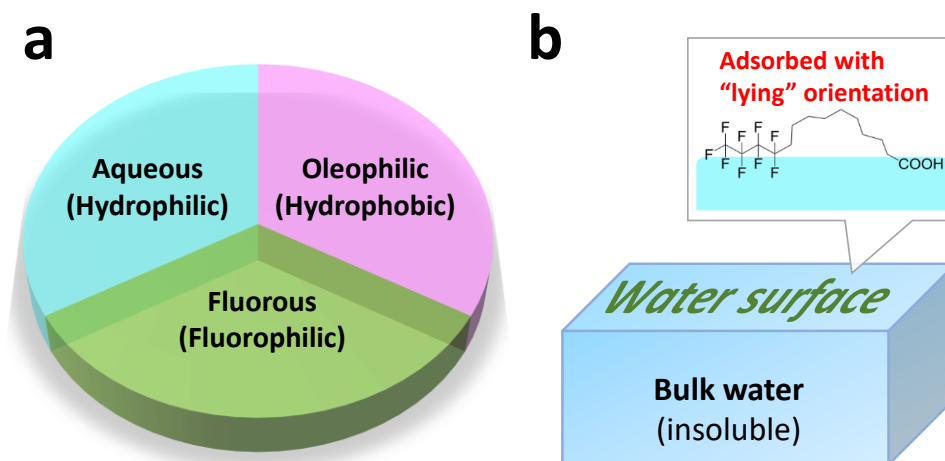


Fig. 1 a) Three groups explaining the affinity of compounds. b) Good affinity of a single R_f chain to the water surface revealed in a previous study of fatty acids having a short R_f chain. (2-column)

In monolayer studies of R_f compounds on water, fluorinated solvents are needed as a good solvent for spreading the R_f compounds on the water surface [5],[6], since the R_f compounds are mostly insoluble in non-fluorinated organic solvents, e.g., chloroform. In a former study, for example, perfluoro-*n*-hexane (C_6F_{14}) was used as the spreading solvent for preparing Langmuir monolayer films (L films) of perfluoro-*n*-eicosane ($C_{20}F_{42}$) and perfluoro-*n*-tetracosane ($C_{24}F_{50}$) [6]. In another study of a $C_{20}F_{42}$ L film, a mixed solution of 1,1,2-trichlorotrifluoroethane ($CFCl_2-CH_2Cl$) and perfluoro-*n*-pentane (C_5F_{12}) was used as the solvent [5]. Since the molecular interactive force of perfluoro-*n*-alkanes is due to the dipole-dipole interaction (i.e., the orientation effect [7]) induced by the large permanent dipole moment along the C–F bond [8],[9],[10], high solubility of the long perfluoro-*n*-alkane in an R_f solvent is readily understood by solvation due to the dipole-dipole interaction. In this manner, R_f solvents are necessary as a good solvent for monolayer studies using R_f compounds.

We have to be careful, on the other hand, about R_f solvents on the water surface: a short linear R_f groups such as C_4F_9- and $C_6F_{13}-$ are known to be interacted with the surface water molecules via the surface-specific dipole-dipole interaction known as the dipole-interactive (DI) force [9],[11],[12],[13]. The DI property is specifically found between a short R_f chain having a “single”-molecular character and a molecular water such as water vapor [12]. In other words, a single R_f chain exhibits an unusual character having “a good affinity to a molecular water.” The dangling OH groups are known to exist at the water surface by SFG spectroscopic studies [14]-[16], which indicates that molecular water-like species should be involved about the water surface, which is totally different from bulk. This implies that the water surface exhibits a similar character to a molecular water. An L film of fatty acids having a short R_f chain (C_4F_9- and $C_6F_{13}-$) is a good example, in which R_f chains have a characteristic lying molecular orientation (Fig. 1b)

[9],[11],[17],[18]; whereas those having a longer R_f chain ($C_8F_{17}-$ and $C_{10}F_{21}-$) spontaneously aggregate resulting in a standing molecular orientation, which were revealed by surface potential measurements combined with surface pressure-surface area ($\pi-A$) measurements [9],[11]. In short, a single R_f chain with a weak aggregating property specifically shows the DI property with the water surface. Hence, we are now interested in a case that an R_f solvent of perfluoro-*n*-alkane is spread on the water surface. In the case of a normal hydrocarbon solvent, the solvent evaporates with time leaving nothing on water. The R_f solvent, however, would remain on water for a long time due to the DI property, which may be inappropriate for preparing L films of R_f -containing amphiphilic compounds on water. Since R_f -containing compounds requires an R_f solvent as a good solvent, this is an experimental dilemma.

In the present study, an evaporation process of an R_f solvent, C_6F_{14} , C_7F_{16} , C_8F_{18} and C_9F_{20} , on the water surface is investigated by using infrared external reflection (IR ER) spectroscopy. Due to the poor solubility of the R_f solvents in water [1],[2], they were readily laid on the water surface. IR ER measurements were carried out by using both s- and p-polarizations, by which not only molecular interaction, but also the molecular orientation was discussed on the surface selection rule (SSR). Although the spectral intensity of R_f solvents runs down quickly with time, the weakened IR bands did not disappear, and they remained for more than 2 hours irrespective of the R_f chain length. Of interest was that the IR ER spectra on water did not obey the SSR, and a characteristic band was commonly found in both s- and p-polarized spectra. In our recent study, we revealed that not only the normal modes of a molecule, but also the surface modes of phonon have to be considered for understanding IR spectra of the perfluoro-*n*-alkanes, which are induced by the large dipole moment [19]. In addition, the surface modes were found to be useful for discussing “morphology” of the thin liquid layers [19], which would also be crucial in the present

case, i.e., the R_f solvents on water. By considering the selection rule of the surface mode, the spectral characters of the IR ER spectra on water are discussed, and the aggregation state of the R_f solvents on water has been revealed, which explains the mechanism of the long-term stay of the R_f solvents on water. As discussed later, however, the remaining solvent, C_6F_{14} , has eventually been found not a disturbing factor for the preparation of an L film.

Materials and Methods

Chemicals. Perfluoro-*n*-hexane (C_6F_{14} ; bp = 59°C) with a purity of 95%, perfluoro-*n*-octane (C_8F_{18} ; bp = 104°C) with a purity of 98% and perfluoro-*n*-nonane (C_9F_{20} ; bp = 125°C) with a purity of 97% were purchased from Sigma-Aldrich (St. Louis, MO, USA). Perfluoro-*n*-heptane (C_7F_{16} ; bp = 82°C) with a purity of 98% was purchased from PCR Research Chemicals, Inc. (Gainesville, FL, USA). They were used as is without further purification.

Pure water for the subphase was obtained by a Millipore (Molsheim, France) Elix UV-3 pure-water generator connected to a Yamato (Tokyo, Japan) Autopure WT100U water purifier, which is a compatible model with Milli-Q. The water showed an electric resistivity of 18.2 MΩ cm at least. The surface tension showed 72.5 mN m⁻¹ at 25°C, which was measured by using Kyowa Interface Science Co., Ltd. (Saitama, Japan) DropMaster, DM-501Hy.

Preparation of a liquid layer of perfluoroalkanes on water. A liquid layer of an R_f solvent on the water surface for IR ER measurements was prepared on a USI System (Fukuoka, Japan) FSD-220 LB trough. The water surface area was 27300 mm². For IR ER measurements, an R_f solvent with a volume of 120 μL was gently put on the water surface by using a micro syringe. The liquid volume gives the film thickness of ca. 4 μm in theory, if the solvent does not volatilize at all.

For comparison, an IR ER spectrum of an L film of a very long compound of perfluoro-*n*-tetracosane ($C_{24}F_{50}$; mp = 188°C) was also measured. The sample was purchased from Sigma-Aldrich, which was dissolved in a good solvent of C_6F_{14} for the L film preparation. The surface pressure was measured by the Wilhelmy method using a paper plate ($1 \times 1 \text{ cm}^2$). The temperatures of the water subphase and ambient air were both fixed at 25°C.

IR ER measurements. The main bench of the IR ER measurements was a Thermo Fischer Scientific (Madison, WI, USA) Nicolet 6700 FT-IR spectrometer. The FT-modulated IR ray at 60kHz was led out of the spectrometer, and it was passed through a HINDS Instruments (Hillsboro, OR, USA) wire-grid polarizer made of ZnSe for controlling the polarization. The polarized IR ray was directly introduced onto the liquid layer on water with the angle of incidence of 80° , and the reflected ray was led to an MCT detector through a BaF_2 lens (Fig. 2). To obtain a spectrum with a better signal-to-noise (SN) ratio, the wavenumber resolution was set to 8 cm^{-1} . To avoid distortion of the baseline of IR ER spectra caused by changing water level due to evaporation [20], the measurements were carried out while adding water as needed. IR ATR spectra were measured with the same condition as those used in a previous study [19].

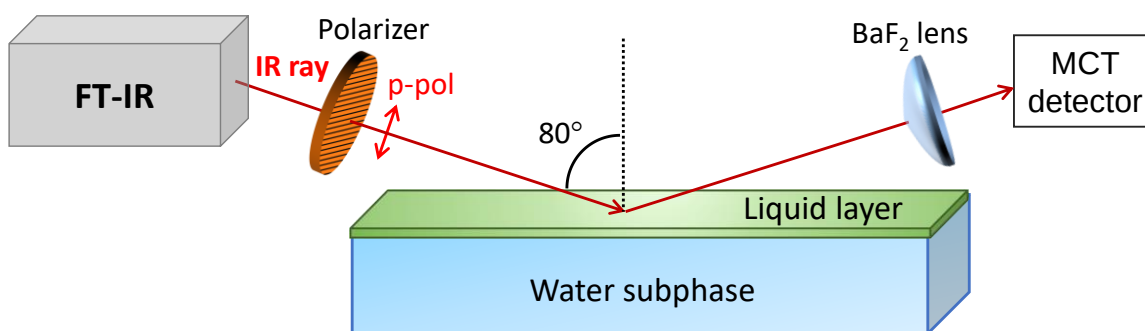


Fig. 2 Schematic image of IR ER measurements of a liquid layer of a perfluoroalkane. (2-column)

Results and Discussion

Evaporation process of a liquid layer of R_f solvent on the water surface. Fig. 3b presents time-dependent IR ER spectra of a liquid layer of C₆F₁₄ on water, which were measured by using the p-polarized light with the angle of incidence of 80°. The top spectrum entitled “0–8 min” shows the time-averaged spectrum in the first 8 minutes immediately after dropping the sample during 1000 times accumulations. For comparison, an IR ATR spectrum of bulk C₆F₁₄ (thick and water-free) is presented in Fig. 3a. Compounds having a linear (unbranched) R_f group represented by perfluoro-*n*-alkanes show strong bands in the C–F stretching vibration region (1350–1100 cm⁻¹) [21],[22], and three bands at 1234, 1205 and 1147 cm⁻¹ are prominent for the ATR spectrum (Fig. 3a). The band at 1147 cm⁻¹ is assigned to the CF₂ symmetric stretching vibration ($\nu_s(\text{CF}_2)$) band, which is useful as a marker band of the molecular packing of R_f chains [8],[9],[23],[24]. In the first ER spectrum (0–8 min), the $\nu_s(\text{CF}_2)$ band appears at 1153 cm⁻¹, which is clearly higher than that of the ATR spectrum by 6 cm⁻¹. This shift is fairly large, even if an apparent shift induced by an electromagnetic effect [25],[26] is taken into account. This indicates that the molecular packing of C₆F₁₄ becomes significantly looser [24] after being spread on the water surface.

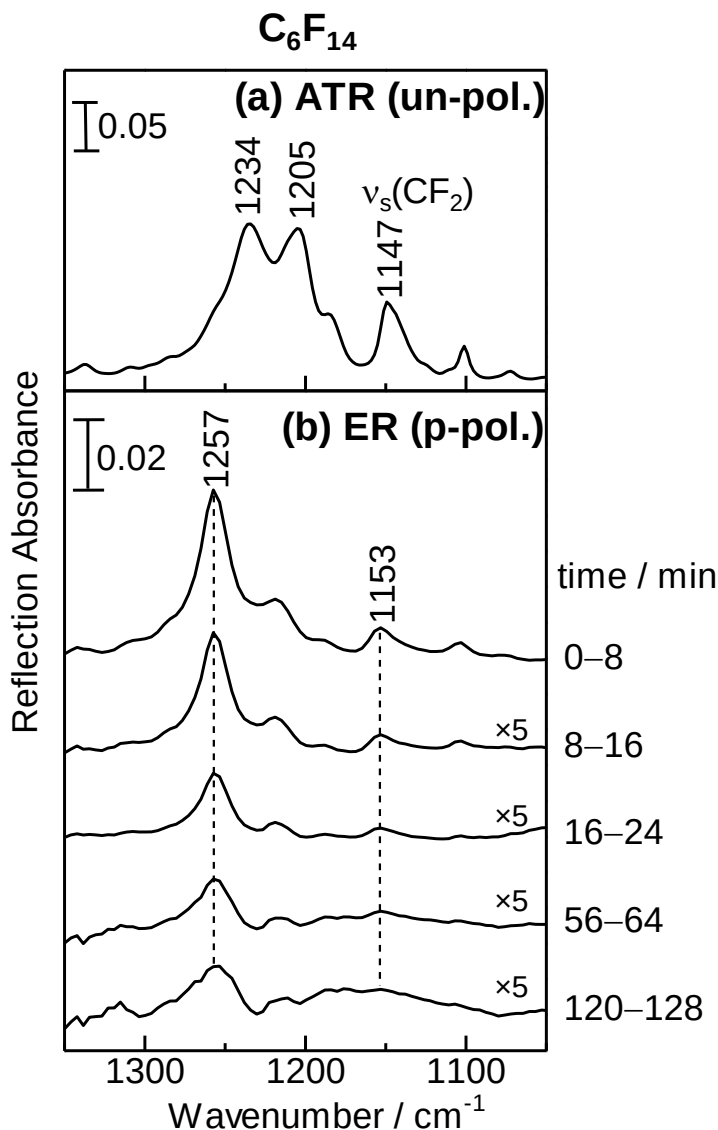


Fig. 3 a) IR ATR spectrum of C₆F₁₄ in bulk liquid. b) Time dependent IR p-polarized ER spectra of the liquid film of the same compound spread on water. **(1-column)**

Of another note is that two bands at 1234 and 1205 cm⁻¹ of the bulk sample disappear for the liquid layer, and instead a new band develops at 1257 cm⁻¹. In a previous study, similar spectral changes were found on a Ge surface, on which complete volatilization was allowed. In a similar discussion, the bands at 1234 and 1257 cm⁻¹ are assigned to the bulk TO (transverse optic) mode and the surface mode (Berreman's mode) that is close to the bulk LO (longitudinal optic) mode,

respectively [19], which indicates that the liquid layer on water has a very small thickness. In fact, the bands in the first spectrum (0–8 min) gradually decreased during the accumulations, which means that the thickness was getting smaller with time.

Since the boiling point of C_6F_{14} (59°C) is comparable to that of chloroform (61°C), C_6F_{14} is expected to fully evaporate in a few minutes leaving nothing on water as found for chloroform. On the Ge-made ATR prism, as expected, C_6F_{14} disappeared quickly after putting it on the prism [19]. On the water surface, on the other hand, the bands at 1257 and 1153 cm^{-1} still remain in the second spectrum (8–16 min) without changing the band position, although the intensity becomes ca. 5 times weaker than the first one (Fig. 3b). As a matter of fact, those bands remain for more than 120 minutes, which is extraordinarily long period of time compared to the case on the Ge surface. This strongly suggests that C_6F_{14} remains as a result of interaction with the water surface.

As discussed above, the $\nu_s(CF_2)$ band of the liquid film of C_6F_{14} on water appears at a higher position than that of the corresponding bulk liquid, which indicates that the molecular packing in the liquid layer is looser than that in bulk. This implies that the molecules on water are not aggregated because of the DI character, which results in a “lying molecular orientation” as schematically presented in Fig. 1b [9],[11] as discussed in the next section.

Molecular orientation analysis of perfluoro-*n*-alkanes in the liquid layer on water:

Polarization dependent IR ER spectral measurements. Fig. 4 presents an IR ER spectrum of a C_6F_{14} liquid layer on water measured by using the s-polarized light (orange line) with the angle of incidence of 80°, which is the averaged spectrum in the first 8 minutes. A similar spectrum of the black dashed line obtained by the p-polarized light (top one in Fig. 3b) is overlaid on the s-polarized one. To discuss these spectra, the SSR of IR ER spectroscopy on a thin film in the three-

layer system (air/film/substrate) is referred as follows for the angle of incident of 80° that is higher than the Brewster angle of the air/water interface (54.5°) [20],[25]-[30].

- a. **p-polarization measurements:** the horizontal component of a transition moment gives a “positive” band, while that of the vertical one gives a “negative” band.
- b. **s-polarization measurements:** *only “negative” bands appear* corresponding to the horizontal component of the transition moment. The vertical component gives no band.

Judging from these SSRs, the molecular orientation can be discussed by the sign of the band. In our present case using the s-polarized light, however, all the bands appear with the “positive” sign, and the spectral shape is nearly the same as the p-polarized one, which cannot be understood simply by the SSR.

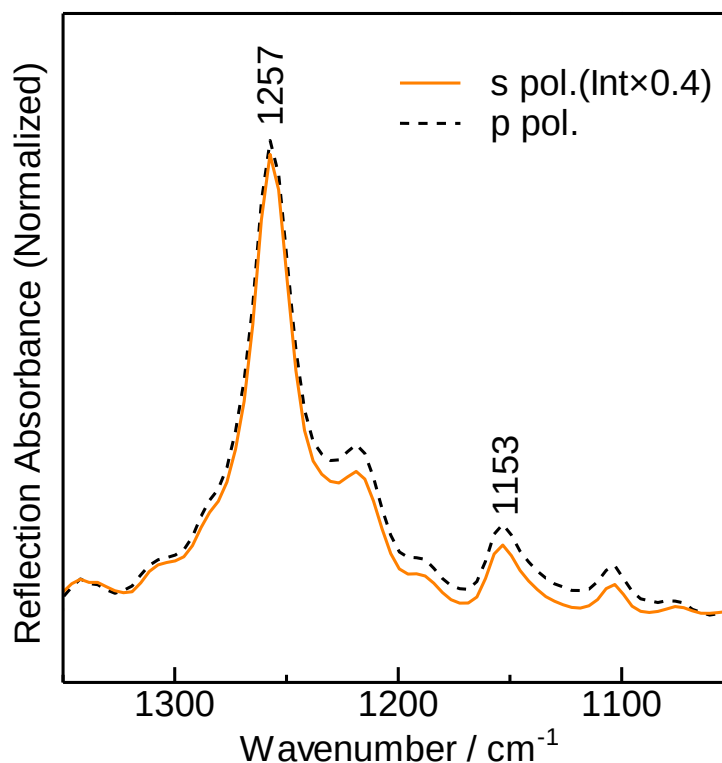


Fig. 4 IR ER spectra of a C_6F_{14} liquid film on water measured by using s-polarized (orange line) and p-polarized light (black dashed line). **(1-column)**

Since the sample liquid film is floated on the water surface, the optical system may be out of schemes of the normal ER spectroscopy considering an insoluble thin film involved in the three-layer system of air/film/substrate. The liquid film would have two possibilities: large film thickness and a strong molecular interaction with the water surface, which makes the layer boundary unsharp. Fortunately, however, the former possibility, a large film thickness, can be excluded because the spectrum has the “surface mode” at 1257 cm^{-1} , which appears only for a very thin thickness [19]. On the other hand, the other possibility still remains: an unsharp layer boundary is generated because of the layer mixing at the water surface.

To discuss this possibility, an L film of a longer and involatile perfluoro-*n*-alkane, $\text{C}_{24}\text{F}_{50}$, is measured as the reference sample, which is known to have a “smooth” surface and “parallel” thickness with a standing molecular orientation [5],[6]. To prepare the L film, C_6F_{14} was used as the solvent, and the solution was spread on water. After 10 minutes for the volatilization of solvent, the L film was compressed with a barrier to obtain a π -*A* isotherm (Fig. S1), which reproduced the former one [5],[6]. The reproducibility indicates that the smooth and parallel monolayer is readily obtained. When the monolayer of $\text{C}_{24}\text{F}_{50}$ at 10 mN m^{-1} is measured by using the s- and p-polarized IR light, in fact, normal ER spectra are obtained as shown in Fig. 5b except the band at 1256 cm^{-1} . The apparent bands at 1209 and 1153 cm^{-1} are known to respond to the chain length, and these band positions are surely attributed to $\text{C}_{24}\text{F}_{50}$ [6].

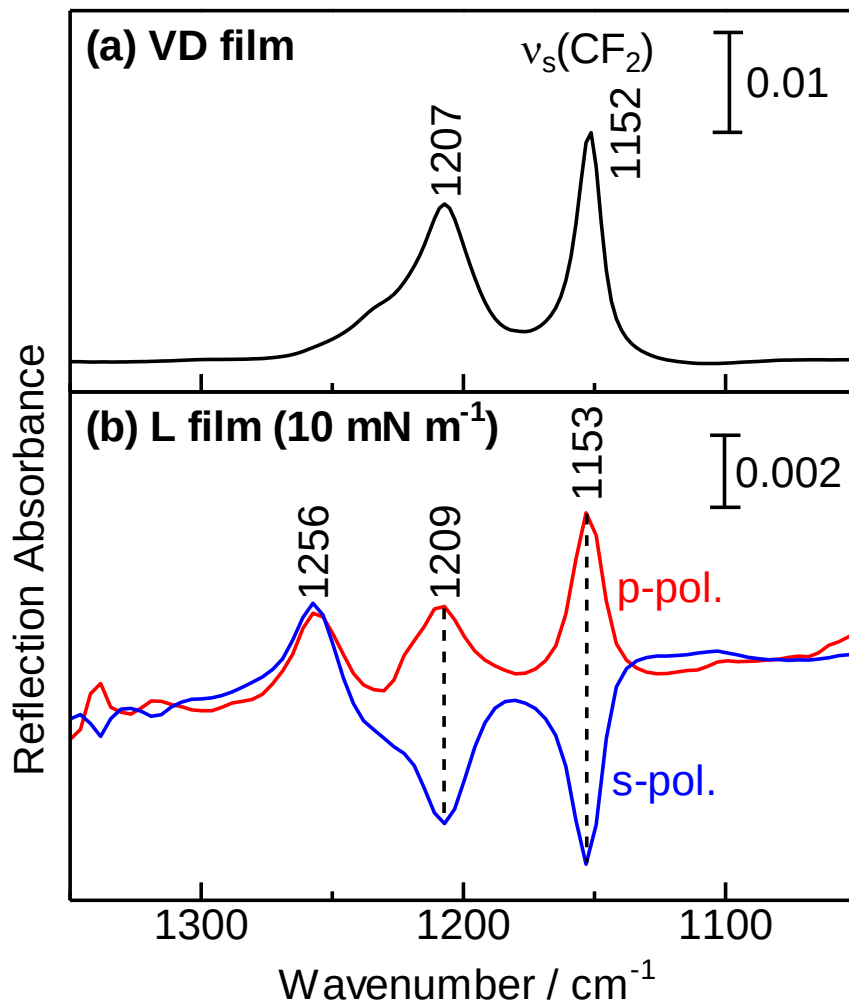


Fig. 5 (a) IR transmission (Tr) spectrum of the vapor deposited (VD) film of C₂₄F₅₀ on a Si substrate. (b) IR ER spectra of C₂₄F₅₀ L film on water using s- (blue) and p-polarized light (red).
(1-column)

The band at 1153 cm⁻¹ is assigned to the $\nu_s(\text{CF}_2)$ mode, whose transition moment is almost perpendicular to the molecular axis [21]. On the other hand, the band at 1209 cm⁻¹ is a little complicated and a simple assignment to a specific mode is difficult [31]. According to our former analysis on p-polarized multiple-angle incidence resolution spectrometry (pMAIRS)[26],[32],[33], however, the transition moment of this band is nearly parallel to the film surface, and the band is roughly assigned to the CF₂ anti-symmetric stretching vibration ($\nu_a(\text{CF}_2)$) mode. Therefore, the

sign of both bands found in the s- and p-polarizations in Fig. 5b agrees with the perpendicularly standing molecular orientation of the $C_{24}F_{50}$ molecules in the film. In this manner, our ER measurements proved to have no problem for discussing the $C_{24}F_{50}$ monolayer on water.

Then, what is the reason for the abnormal positive peak at 1256 cm^{-1} ? A hint is found in the spectrum of a vapor-deposited (VD) film of $C_{24}F_{50}$ on a Si substrate (Fig. 5a). The VD film having no solvent (C_6F_{14}) misses the band at 1256 cm^{-1} , which straightforwardly implies that the band is attributed to C_6F_{14} , and not to $C_{24}F_{50}$. To summarize the discussion so far, the unusual positive peak at 1256 cm^{-1} indicates that C_6F_{14} molecules are not in a smooth and parallel layer.

In addition, the band at 1256 cm^{-1} remains for a long time in a similar manner to the liquid layer of the pure solvent (C_6F_{14} having no $C_{24}F_{50}$) as found in Fig. 3b. Two possibilities are thus considered: the solvent is 1) deeply involved in the $C_{24}F_{50}$ film layer making the film loosely packed, and 2) the solvent is trapped at the water surface. If the molecular interaction between $C_{24}F_{50}$ and the solvent, i.e., solvation, is dominant, the possibility 1) is expected. On the other hand, if the DI property is dominant rather than the solvation, the C_6F_{14} molecules would be removed from the film of $C_{24}F_{50}$ by the DI property with the water surface, which satisfies the possibility 2). Since the $C_{24}F_{50}$ L film has a highly packed structure with the perpendicularly standing molecular orientation[5],[6], the possibility 1) would thus be excluded.

To experimentally confirm this assumption, the L film was transferred onto a Si substrate by the Langmuir-Blodgett (LB) technique. A dried LB film can exclude the effect of DI, which can discriminate the two possibilities. First of all, both p- and s-polarized IR ER spectra in Fig. S2 have no band of C_6F_{14} at 1256 cm^{-1} , which concludes that the solvent is preferentially associated with water, and it does not remain in the $C_{24}F_{50}$ L film, which readily denies the possibility 1).

Here, another question should be considered: Why the remaining R_f -solvent of C_6F_{14} on water does not disturb the formation of the L film? To reveal the reason, we consider another question: How does C_6F_{14} molecules remain on/in the water surface? The key band is the solvent band at 1256 cm^{-1} that corresponds to the surface mode found in both s- and p-polarizations (Fig. 5b). The polarization-independent surface mode is also available at the last moment of evaporation in the time-dependent IR ATR spectra of C_6F_{14} “on the Ge prism” [19], which indicates that the remained liquid continuous film is broken to be of minute particles as schematically presented in Fig. 6a [19]. In the same manner, the solvent molecules at the water surface are not in a continuous film, but as many particles. Some organic solvents are known to form particles with a lens-shape on the water surface [34]. In a similar manner, the R_f solvent should remain as lens-shaped particles as a result of a balance between the dipole-dipole interaction with the water surface and the fluororous property of C_6F_{14} molecules (Fig. 6b), which should not disturb the formation of the L film. This scheme also explains the reason why the spectrum in Fig. 4 does not obey the SSR of ER. In Fig. 3b, the band at 1257 cm^{-1} is found in the first ER spectrum (0-8 min), which indicates that the particles are formed at a very early stage.

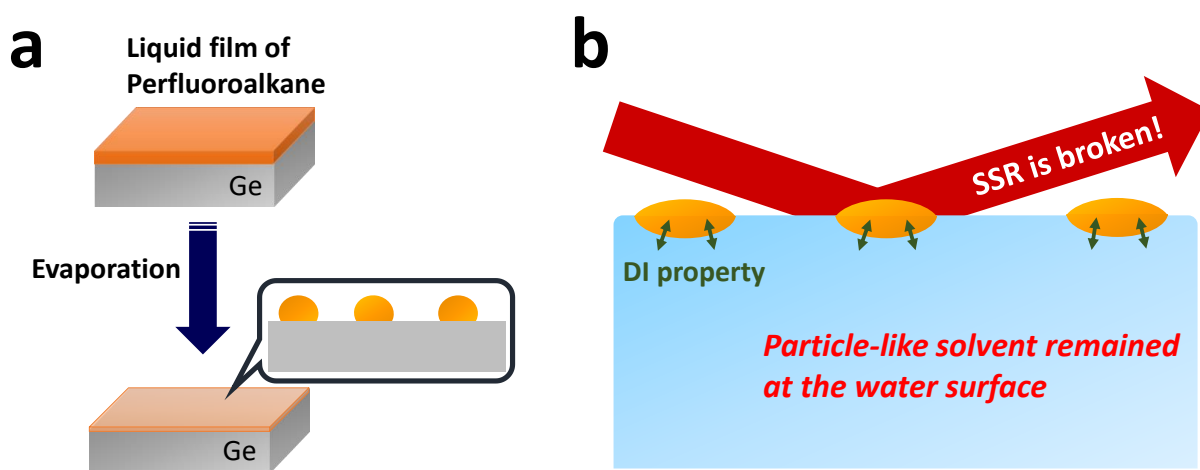


Fig. 6 Schematic image of a) the evaporation process of a liquid film of the R_f solvent on a Ge surface and b) the R_f solvent remained on the water surface. **(2-column)**

Chain length dependence of R_f solvents and the mechanism of the long-term stay on water.

Similar IR ER measurements on water were carried out for other perfluoro-*n*-alkanes having different chain length of C_7F_{16} , C_8F_{18} and C_9F_{20} , which are all liquid at an ambient temperature. In the lower panel of Fig. 7, averaged IR ER spectra in the first 8 min (0–8 min) are presented, and IR ATR spectra of bulk liquid are presented in the upper panel. A similar spectral change between the upper and lower panels to that of C_6F_{14} (Fig. 3) is found irrespective of the even-odd number of the chain length. Therefore, all the R_f solvents commonly have a particle-like morphology at the water surface at the last moment of evaporation, and they are not fully evaporated even after 120 min and they still remain on water as found for C_6F_{14} .

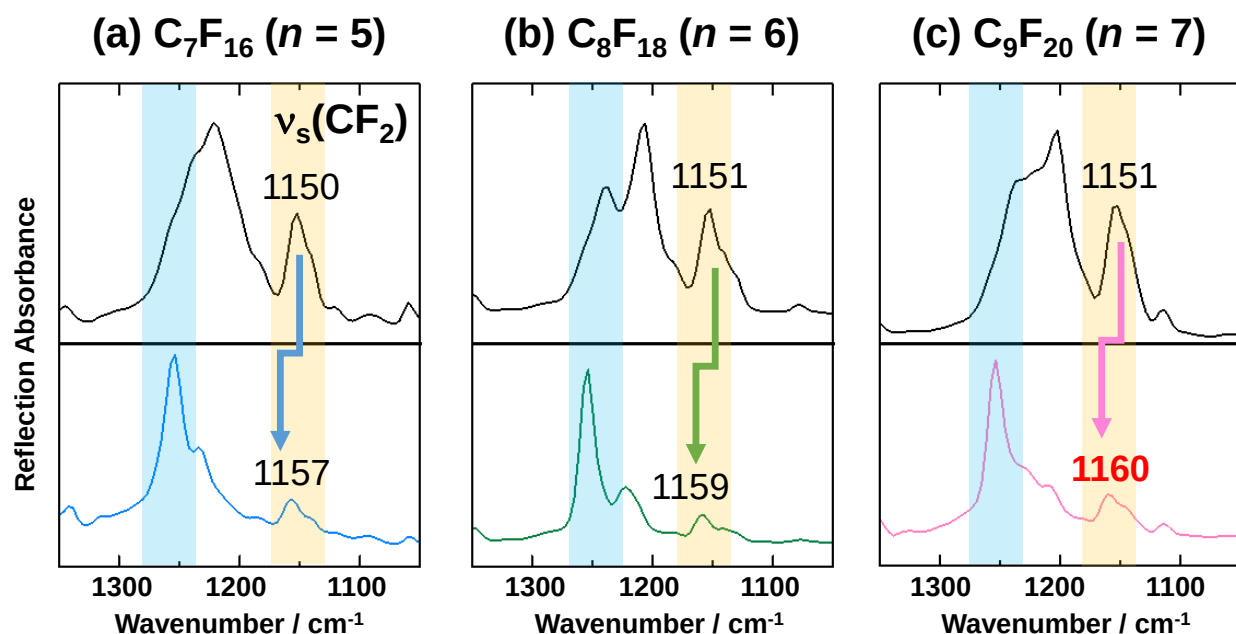


Fig. 7 IR ATR spectra of the R_f solvents in bulk (upper) and IR ER spectra of those on water (lower): (a) C_7F_{16} , (b) C_8F_{18} and (c) C_9F_{20} . **(2-column)**

Next, the molecular packing in the liquid particles is discussed by using the $\nu_s(CF_2)$ band, which is a good marker of molecular packing of R_f chains [8],[9],[23],[24]. According to the

stratified dipole-arrays (SDA) theory, the aggregating property of R_f chains ($CF_3(CF_2)_n-$) depends on the number of CF_2 units, n : R_f chains with $n \geq 7$ spontaneously aggregate; whereas shorter R_f chains remain to have single-molecular characters [9],[11]. This theory is true of the case on a solid surface as found in the previous paper: the time-dependent IR ATR spectra of C_9F_{20} ($n = 7$) showed no band shift even at the last moment of evaporation; whereas C_6F_{14} , C_7F_{16} and C_8F_{18} ($n = 4-6$) showed a clear higher wavenumber shift [19].

“On water,” on the other hand, the higher wavenumber shift of the $\nu_s(CF_2)$ band is found even for C_9F_{20} (Fig. 7c), which means that the molecular packing in the particles on water becomes looser than that in bulk liquid, which does not obey the SDA rule. Since the SDA theory does not consider atmosphere of water, the looser packing found on water should be induced by the dipole-dipole interaction with surrounding water molecules, which disturbs the spontaneous aggregation of perfluoro- n -alkane molecules. In this manner, the SDA molecular packing is a result of a balance of the molecular aggregation and the DI force when the molecules are on water. The strong DI force is thus considered a driving force to make the R_f solvent on the water surface for a long time (Fig. 6b).

Finally, we note that hexafluoro benzene (C_6F_6) having no permanent dipole moment also remains on water for more than 120 minutes, which is monitored by the C–C stretching vibration bands (Fig. S3). As mentioned above, particle-like strong IR absorber yields a surface-mode band of phonon or polariton. In fact, a weak absorber, C_6F_6 , having no permanent dipole exhibits no surface mode as expected, and only a band shift is found for the C–C stretching vibration band by about 10 cm^{-1} (Fig. S3). Therefore, the staying mechanism of C_6F_6 on water is different from that of perfluoro- n -alkanes. As a matter of fact, C_6F_6 has a weak quadrupole because of the symmetric molecular structure [35]–[37], and this dielectric polarization can interact with the water surface

like DI. In addition, C_6F_6 has a molecular orbital, which can also be interacted with a water molecule: the π orbital of C_6F_6 and the lone pair of oxygen of a water molecule [38]. To reveal the staying mechanism of C_6F_6 on the water surface in more detail, quantum chemical calculation would be required for quantitative discussion.

Conclusion

In the present study, a liquid layer of perfluoro-*n*-alkanes (R_f solvents) on the water surface has been investigated by using infrared external reflection (IR ER) measurements. The R_f solvents used in this study with a high volatility exhibited a rapid decrease of spectral intensity with time. At the last stage of the evaporation, however, a minute amount of R_f solvents was found to stay on the water surface for more than 120 minutes. The surface modes active in both s- and p-polarized IR ER spectra have revealed that the R_f solvents remain as discontinuous particles, not as a continuous thin film. In addition, the molecular packing in the particles is looser than that in a bulk sample, which is induced by the dipole interactive (DI) force of the surrounded water molecules. Since the water surface exhibits a similar property to molecular water, the particles are localized at the surface and are not dispersed in bulk. In this manner, the dipole-dipole interaction has proved to be key to understand the remained R_f solvent on the water surface for a long period of time as well as the molecular packing.

It is worth noting that the long-staying character of solvent on water is not found for non-fluorine organic solvents represented by chloroform. Thanks to this character, chloroform efficiently evaporates leaving nearly nothing on water. Since the molecular interactive character of chloroform is mostly driven by London's dispersion force that is a function of the molecular polarizability only (not on the dipole moment) [7], chloroform is recognized again to have much weaker interaction with the water surface than an R_f solvent.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/xxx>

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Supplementary material

Perfluoroalkanes Remain on Water Surface even after Volatilization: Affinity Analysis of Fluorinated Solvent with Water Surface

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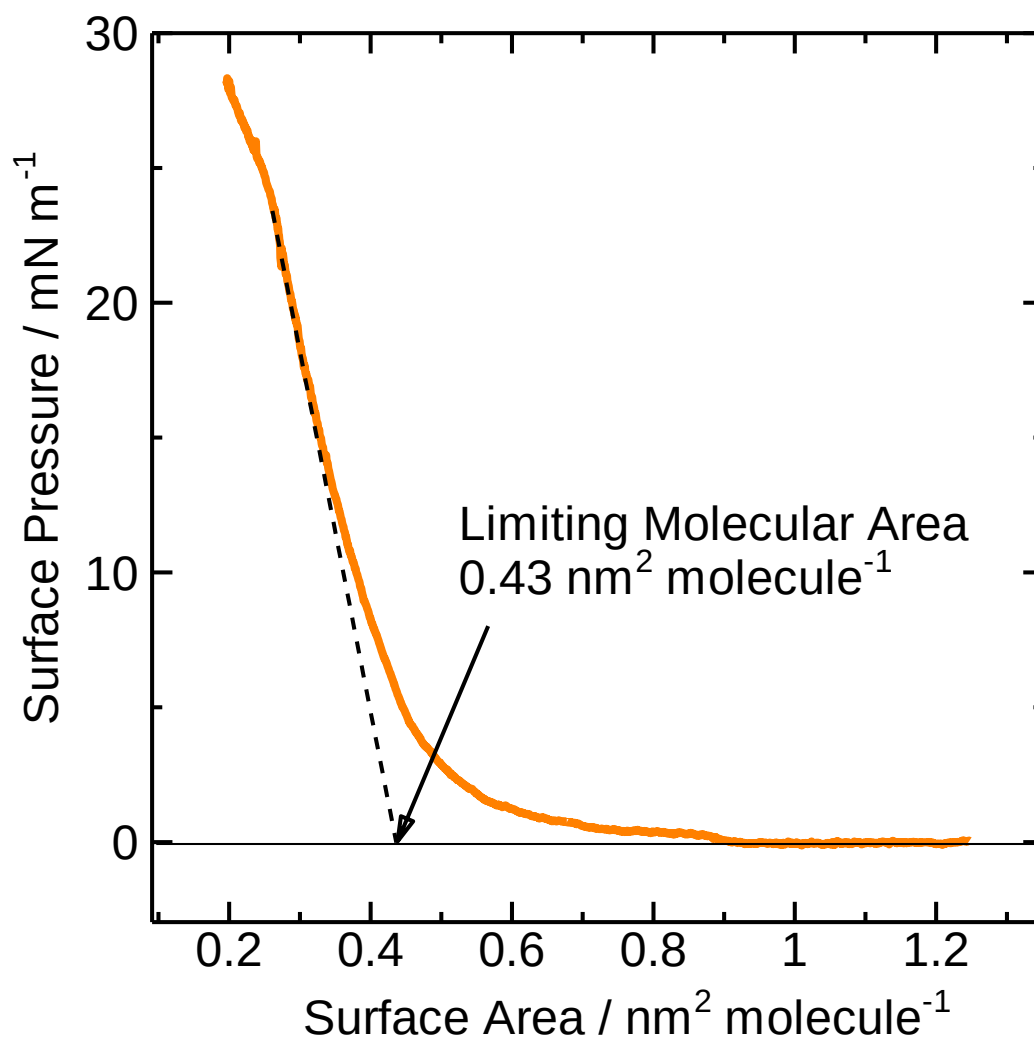


Fig. S1 π -A isotherm of a C₂₄F₅₀ L film prepared by spreading a solution dissolved in C₆F₁₄.

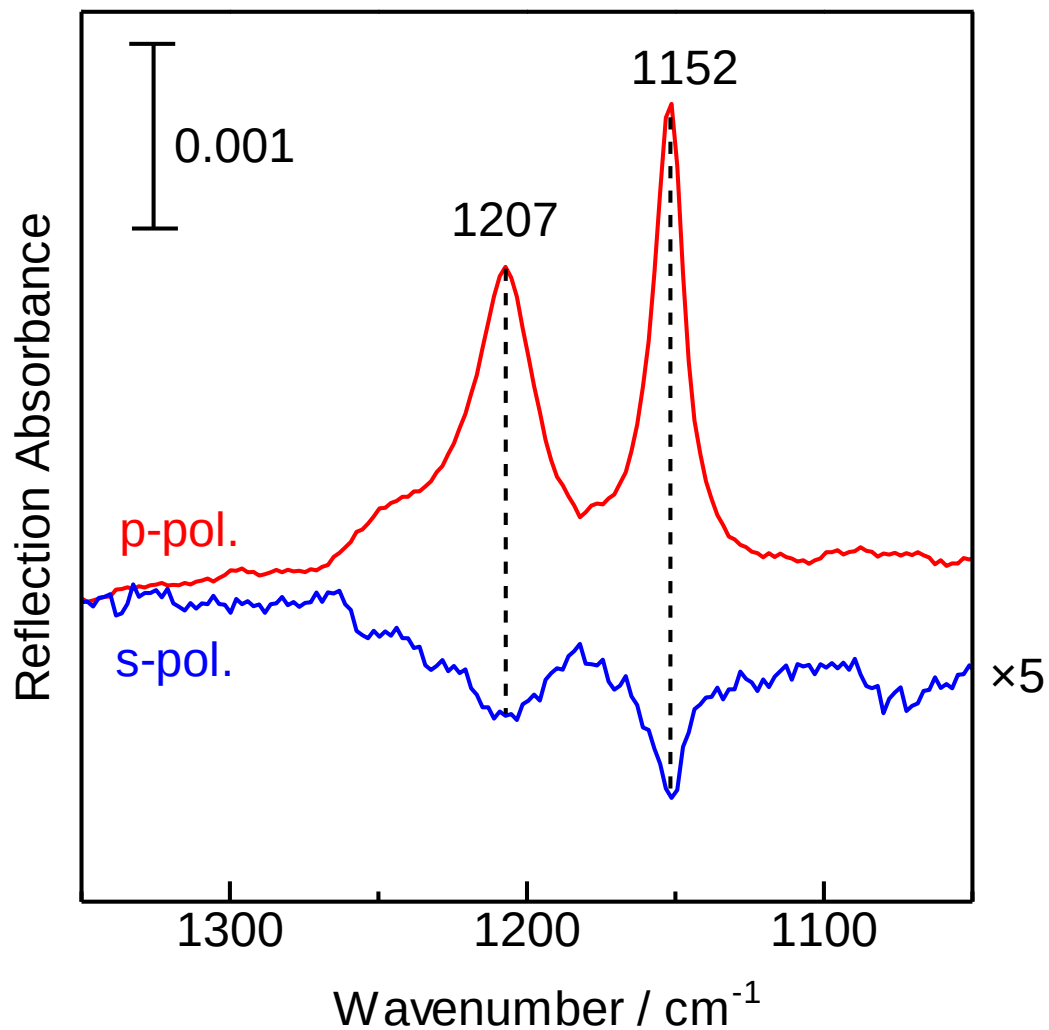


Fig. S2 IR ER spectra of a $\text{C}_{24}\text{F}_{50}$ LB film deposited on a Si substrate measured by using s- and p-polarized light with an angle of incidence of 80° .

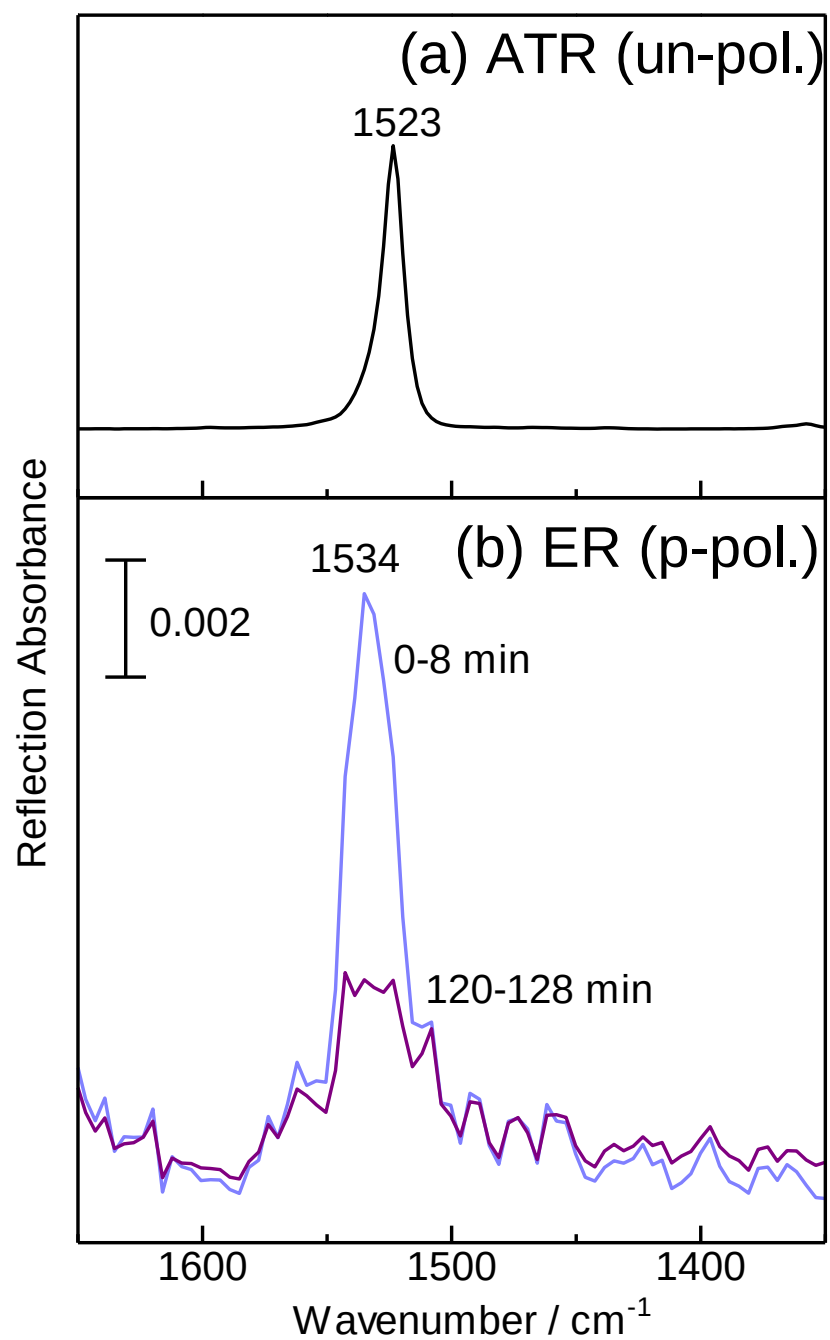


Fig. S3 (a) IR ATR spectrum of hexafluorobenzene (HFB), and (b) time dependent IR ER spectra of an HFB liquid layer on water.