Accurate Molecular Orientation Analysis by IR pMAIRS Considering the Refractive Index of the Thin Film Sample

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Abstract: Infrared p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) is a powerful tool for analyzing the molecular orientation in an organic thin film. In particular, pMAIRS works powerfully for a thin film with a highly rough surface irrespective of degree of the crystallinity. Recently, the optimal experimental condition has comprehensively been revealed, with which the accuracy of the analytical results has largely been improved. Regardless, some unresolved matters still remain. A structurally isotropic sample, for example, yields different peak intensities in the in-plane and out-of-plane spectra. In the present study this effect is shown to be due to the refractive index of the sample film, and a correction factor has been developed using rigorous theoretical methods. As a result, with the use of the correction factor, organic materials having atypical refractive indices such as perfluoroalkyl compounds ($n = 1.35$) and fullerene ($n = 1.83$) can be analyzed with high accuracy comparable to a compound having a normal refractive index of ca. 1.55. With this improved technique, we are also ready for discriminating an isotropic structure from an oriented sample having the magic angle of 54.7°.

Keywords: p-polarized multiple-angle incidence resolution spectrometry (pMAIRS), Molecular orientation analysis, Isotropic thin film, Fullerene, Perfluoroalkyl compound

Introduction

Structural characterization of an organic thin film is a key to develop an electronic device, since the molecular orientation and stacking play a dominating role in the device performance.[1-6] Infrared (IR) spectroscopy is most suitable for the purpose thanks to the quantitative reproducibility and the high sensitivity for a monolayer-level sample. In addition, IR spectra reveal molecular information irrespective of the crystallinity of the film that is an advantage of using pMAIRS when compared to the X-ray and electron diffraction techniques. IR pMAIRS is thus quite powerful for studying a liquid-crystalline and polymer thin films.[7-11] Some IR bands such as the C–H out-of-plane deformation vibration of an aromatic ring[12-16], the CH_2 scissoring vibration and the band progression of an alkyl chain[17] exhibit an apparent correlation with the crystal structure of the film, with which the structural characterization can readily be performed on an FT-IR bench in a laboratory.

To reveal the molecular orientation in a thin film, transmission (Tr) and reflection-absorption (RA) spectrometries have conventionally been employed[17] in a cooperative manner, since the two techniques have mutually independent (orthogonal) surface selection rules to each other. The orientation analysis based on this combination technique, however, requires theoretical calculations on electrodynamics on a flat- and parallel-layers model, which needs optical constants a priori. Therefore, the combination technique has rarely been employed for a practical analysis,[17-19] which is commonly true of other analytical techniques represented by the attenuated total reflectance (ATR) technique.

To overcome this situation, IR p-polarized multiple angle incidence resolution spectrometry (pMAIRS)[20-22] is quite useful. pMAIRS yields in-plane (IP) and out-of-plane (OP) spectra from an identical sample, as if both measurements were performed on a normal-incidence transmission geometry. Note that the IP and OP spectra have the same shape as that of Tr and RA spectra, respectively. Since the identically same sample area is used for both IP and OP spectra, the dichroic ratio, $A_{\mathrm{IP}}/A_{\mathrm{OP}}$, is impervious to the surface roughness of the sample up to several hundreds of nanometers, which is a great benefit of using pMAIRS as compared to other analytical techniques such as spectroscopic ellipsometry,[23-26] which is largely influenced by the roughness. Once the dichroic ratio of pMAIRS spectra is obtained, the uniaxial orientation angle, ϕ, can simply be calculated as:[22]

$$\phi = \tan^{-1}\sqrt{\frac{2A_{\mathrm{IP}}}{A_{\mathrm{OP}}}}, \tag{1}$$

when the “optimal angle set” is employed for the measurements, since the optical constant of the substrate has already been taken into account in the optimization process.[27] Here, the angle is an average one over a wide area of the film with an assumption of the uniaxial orientation having the optical axis perpendicular to the film surface.

Here, we have to note, however, that for quantitative analysis of using pMAIRS, the following two approximations are required:

1) The absorbance (ordinate) scale is common to both OP and IP spectra.

2) The refractive index of the sample is nearly 1.5.

Since absorbance is proportional to $(\boldsymbol{\mu} \cdot \boldsymbol{E})^2$, $A_{\mathrm{IP}}/A_{\mathrm{OP}}$ is represented as:

$$\frac{A_{\mathrm{IP}}}{A_{\mathrm{OP}}} = \left(\frac{\mu_x E_x}{\mu_z E_z}\right)^2 , \tag{2}$$

where $\boldsymbol{\mu}$ and $\boldsymbol{E}$ are the transition dipole moment and the electric field at the dipole, respectively. Therefore, the first approximation is interpreted as that E_x/E_z equals to unity. Since the electric field intensity depends on an optical interface, however, some corrections may be needed. A theoretical correction is difficult, unfortunately, because the OP measurement employs a concept of a virtual longitudinal-wave,[21] which is difficult to treat on electrodynamics. Regardless, if a thin film having a perfectly isotropic structure ($\mu_x = \mu_z$) is measured, E_x/E_z should experimentally be revealed, which can be used for the intensity correction.

In our previous study[27] on the optimization of the angle set, poly(2-perfluorobutyletyl acrylate) (C4FA; Chart 1)[28] is employed as an ideally isotropic sample, since it is gel-like liquid in an ambient temperature. In the present study, this sample is conveniently used for the correction.

As for the second approximation, in the present study, we have found a theoretical route to incorporate the refractive index into the correction. To check the correction, a fullerene (C_{60}) thin film is used, since it has a high refractive index of ca. 1.8,[29] and it has an ideally isotropic structure in the film because of the spherical molecular shape. Before the correction, in fact, the isotropic thin film exhibits the IP and OP spectra with the same shape, but they have different intensities from each other as presented in Figure 1, due to the influence of the high refractive index.

The present study thus reveals the residual issue of “the corrections due to the thin film layer.” As a result, pMAIRS has become a very accurate and reliable technique for quantitatively determining the molecular orientation. With this technique, a wide variety of organic thin films can be a good analytical target for pMAIRS irrespective of the surface flatness and the crystallinity.

Fundamentals of molecular orientation analysis by IR spectroscopy

An infrared spectrum reflects the complex relative electric permittivity, $\tilde{\varepsilon}$, which can be discussed via the corresponding complex refractive index, $\tilde{n} = n + \mathrm{i}k$, of an analyte because of $\tilde{\varepsilon} = (n + \mathrm{i}k)^2$. In fact, when the optical interface can be ignored (for example, the KBr pellet technique), the absorbance is proportional to the absorption index, α ($\alpha \equiv 4\pi k/\lambda$, λ is the wavelength).

Since the isotropic extinction coefficient, k_{iso}, is correlated with the x, y, and z components as:

$$k_{\mathrm{iso}} = \frac{1}{3}\left(k_x + k_y + k_z\right), \tag{3}$$

then the perpendicular ($k_x = k_y = 0$) and parallel ($k_x = k_y$ and $k_z = 0$) orientation to the surface can be represented within a uniaxial system by:

$$k_z = 3k_{\mathrm{iso}} \quad \text{and} \quad k_x = \frac{3}{2}k_{\mathrm{iso}}, \tag{4}$$

respectively. Here, subscripts of x and y are along the surface-parallel direction; whereas

z corresponds to the surface normal. Therefore, for an orientation angle of θ, an ellipsoidal representation is available:

$$k_x = k_y = \frac{3}{2} k_{\mathrm{iso}} \sin^2\theta \qquad \text{and} \\ k_z = 3k_{\mathrm{iso}} \cos^2\theta \,. \tag{5}$$

As a result, the orientation angle is given by:

$$\theta = \tan^{-1}\sqrt{\frac{2k_x}{k_z}} \left(= \tan^{-1}\sqrt{\frac{2\mu_x^2}{\mu_z^2}} \right). \tag{6}$$

If $2k_x/k_z$ is obtained experimentally, the orientation angle can readily be calculated in place of using $2\mu_x^2/\mu_z^2$, which is used in the present study as follows.

Optical parameters in pMAIRS

When pMAIRS spectra are measured by using the optimal angle set, the IP and OP spectra ideally depend on the transverse and longitudinal optic (TO and LO) energy-loss functions,[30] respectively.[27] In fact, according to Itoh et al.,[31] analytical expressions of pMAIRS spectra are represented by eq. 7.

$$A_{\mathrm{IP}} = \frac{8\pi d_2}{\lambda}\left[h_x^{\mathrm{IP}}\,\mathrm{Im}(\tilde{\varepsilon_x})\right] = \frac{8\pi d_2}{\lambda} h_x^{\mathrm{IP}}\,(2n_x k_x)$$
$$A_{\mathrm{OP}} = \frac{8\pi d_2}{\lambda}\left[h_{\mathrm{z}}^{\mathrm{OP}}\,\mathrm{Im}\left(-\frac{1}{\tilde{\varepsilon_z}}\right)\right] = \frac{8\pi d_2}{\lambda} h_{\mathrm{z}}^{\mathrm{OP}} \frac{2n_z k_z}{\left({n_z}^2 + {k_z}^2\right)^2} \qquad (7)$$

Here, $\mathrm{Im}(\tilde{\varepsilon_x})$ and $\mathrm{Im}(-1/\tilde{\varepsilon_z})$ are TO and LO energy-loss functions,[30] respectively, where $\tilde{\varepsilon}$ is the permittivity of the thin film having a thickness of d_2. Note that the coefficient ratio, $h_x^{\mathrm{IP}}/h_{\mathrm{z}}^{\mathrm{OP}}$, is directly influenced by E_x/E_z, which is determined by the angle set and the refractive index of substrate.[27, 31]

Now, let us consider the following two approximations, which should work well for many organic materials: 1) $n^2 \gg k^2$, and 2) n has no anisotropy and no anomalous dispersion (i.e., $n_x = n_z \equiv n$). The first approximation means a weak absorption of light at the wavelength. On this condition, the anomalous dispersion of the real part of the refractive index becomes small, which makes the second approximation acceptable. With these conditions, eq. 7 can be simplified to have eq. 8.

$$A_{\mathrm{IP}} \approx \frac{8\pi d_2}{\lambda} h_x^{\mathrm{IP}}\,(2nk_x)$$
$$A_{\mathrm{OP}} \approx \frac{8\pi d_2}{\lambda} h_{\mathrm{z}}^{\mathrm{OP}} \frac{1}{n^4}(2nk_{\mathrm{z}}) \qquad (8)$$

After this simplification, the IP and OP spectra simply depend on k_x and k_z, respectively, as well as the common real part of *n*. Therefore, the ratio of the two equations becomes quite simple form (eq. 9).

$$\frac{A_{\mathrm{IP}}}{A_{\mathrm{OP}}} = \frac{n^4 h_{\mathrm{x}}^{\mathrm{IP}} k_x}{h_{\mathrm{z}}^{\mathrm{OP}} k_{\mathrm{z}}} = \frac{n^4 H k_x}{k_{\mathrm{z}}} \quad \left(H \equiv \frac{h_{\mathrm{x}}^{\mathrm{IP}}}{h_{\mathrm{z}}^{\mathrm{OP}}} \right) \tag{9}$$

Here, $H \equiv h_x^{\mathrm{IP}} / h_{\mathrm{z}}^{\mathrm{OP}}$ is a newly introduced parameter to make the equation visually clearer. This equation can be deformed to be:

$$\frac{k_x}{k_{\mathrm{z}}} = \frac{A_{\mathrm{IP}}}{n^4 H A_{\mathrm{OP}}}. \tag{10}$$

In this manner, k_x / k_z can be obtained from pMAIRS spectra for the orientation analysis as shown by eq. 10, if *H* and *n* are available a priori.

Therefore, the orientation angle is given by:

$$\theta = \tan^{-1} \sqrt{\frac{2A_{\mathrm{IP}}}{n^4 H A_{\mathrm{OP}}}}. \tag{11}$$

Since H is driven by E_x / E_z, H is a “substrate-specific parameter.” If an ideally isotropic thin film can be measured, as mentioned above, H can also experimentally be obtained, since $k_x/k_z = 1$ holds for the isotropic sample. By putting $k_x/k_z = 1$ into eq. 10, n^4H can thus simply be obtained by using the isotropic sample (eq. 12).

$$n^4H = \left(\frac{A_{\mathrm{IP}}}{A_{\mathrm{OP}}}\right)_{\mathrm{isotropic}} \tag{12}$$

Once we have the correction factor of n^4H, the orientation analysis using the pMAIRS dichroism on the substrate is made very accurate.

Experimental

The standard sample of poly(2-perfluorobutyletyl acrylate) (C4FA; Chart 1) was provided by courtesy of Daikin Industries, Ltd. (Osaka, Japan) as mentioned in a previous paper.[27]

The spin-coated thin films of C4FA were prepared on a substrate at 2000 rpm. The IR transparent substrates with a size of 40 × 20 mm^2 were made of Ge (the refractive index of the substrate, n_{sub} = 4.0), Si (n_{sub} = 3.4), ZnSe (n_{sub} = 2.4) and $\mathrm{CaF_2}$ (n_{sub} = 1.4). A thin film of fullerene ($\mathrm{C_{60}}$) with a thickness of 50 nm was prepared on a substrate at an evaporation rate of 3.0 nm min^{-1} under a base pressure of 10^{-4} Pa. The substrate was kept at an ambient temperature during the evaporation process. IR pMAIRS spectra were measured with the optimal angle set (see Table 1). The experimental details are referred to literature. [27,32]

RASULTS AND DISCUSSION

C4FA involves both C−H and C−F groups in the side chain (see Chart 1). Since the C−F stretching vibration modes have a strong absorption coefficient due to the large dipole moment, a large band shift between IP and OP spectra is found,[27] which is called the TO-LO splitting[33] or Berreman's effect[34] due to a large anomalous dispersion of n. This situation is not good for the present study, since eq. 8 is based on a weak-absorption approximation. In contrast, the C−H stretching vibration (ν(C−H)) bands exhibit a weak absorption, and thus the dispersion of n can be ignored. Therefore, the ν(C−H) bands are used for the determination of n^4H.

Figure 2a – d are pMAIRS spectra in the ν(C−H) region of the C4FA thin film deposited on the Ge, Si, ZnSe and CaF_2 substrates, respectively. All the spectra show that both IP and OP spectra have a common band shape, which implies an isotropic structure in the thin film. The intensity ratio between IP and OP spectra, however, varies a lot depending on the substrate, which is induced by the variance of H. In addition, the OP bands are larger than the IP ones, which is opposite to the pMAIRS spectra of a C_{60}

thin film, in which the IP bands are larger (Figure 1). This reflects the difference of the refractive indices of C4FA ($n = 1.35$)[27,35] and C_{60} ($n = 1.83$).[29] In this manner, the correction using n^4H is necessary.

To estimate the coefficient of H, the intensity ratio of $A_{\mathrm{IP}}/A_{\mathrm{OP}}$ is read from Figure 2. With the refractive index of 1.35 for C4FA, H is thus obtained by using eq. 12, which is listed in Table. 1. As shown in Table 1, the Ge, Si, and ZnSe substrates have similar H values about 0.14, but only the CaF_2 substrate has a largely different value. This is understandable when we remember that pMAIRS was originally developed for a film on a low-refractive index substrate.[20]

Table 2 shows the correction factors of n^4H on the substrates of Ge and CaF_2 calculated for representative organic compounds having different refractive indices: C_{60} ($n = 1.83$),[29] poly(3-hexylthiophene) (P3HT; $n = 1.60$),[36] polyethylene (PE; $n = 1.52$)[37] and polytetrafluoroethylene (PTFE; $n = 1.35$).[35] When the Ge substrate is chosen (see column 3), the value of n^4H is relatively near 1.0 for P3HT and PE. With this lucky situation, eq. 1 has been used thus far with no serious problem. For an organic thin film having an abnormal refractive index, such as C_{60} and PTFE, the pMAIRS spectra should be corrected by using n^4H. In a similar manner, when a low-refractive-index substrate represented by CaF_2 is used (column 4), the correction factor is adequately necessary.

The accuracy of the obtained correction factors of n^4H are checked by using the same C_{60} evaporated thin film used for Figure 1. Figure 3 presents the corrected pMAIRS spectra, in which the OP spectrum is multiplied by n^4H ($n = 1.83, H = 0.15$). Since C_{60} has a spherically symmetric molecular structure, IP and OP bands are expected to give the same band intensities as each other. In fact, the IP and OP spectra are apparently identical to each other in terms of both shape and intensity, which proves that the correction factor is quantitatively reliable and useful.

Conclusion

To achieve an accurate quantitative molecular orientation analysis in an organic thin film, pMAIRS is found to require a correction factor that depends on an optical interface. The factor has been deduced based on electrodynamics, which has readily been calculated for some organic thin films deposited on representative substrates having various refractive indices. As expected theoretically, the factor is found to depend on the refractive indices of both sample thin film and substrate. The reason why a film having a normal refractive index about 1.5 deposited on a high refractive-index substrate needs no correction has been clearly revealed. This means that many organic thin films deposited on a Ge or Si substrate do not need the correction applied and can be continued to be recorded in the same manner as before. When the film is prepared on a low refractive-index substrate such as CaF_2, the correction factor is definitely needed. If a thin film having an abnormal refractive index, represented by fullerene and perfluoroalkyl compounds, is measured, the correction based on the refractive index of the compound improves the accuracy of the analytical results. With this technique, a thin film having a random molecular orientation yields identical band intensity for the IP and OP spectra. Even if an “oriented” sample with the orientation angle of 54.7° is available, it is impossible to have all the transition moments having the same orientation angle, which means that some bands must have a “non-unity” intensity ratio between the IP and OP spectra. In this manner, pMAIRS enables us to strictly discriminate an isotropic sample from an oriented sample.

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Figure captions:

Figure 1 pMAIRS spectra of a C_{60} evaporated thin film deposited on a Ge substrate with no correction. The red and blue lines correspond to IP and OP spectra, respectively.

Figure 2 pMAIRS spectra of C4FA thin films spin-coated on different substrates: Ge (a), Si (b), ZnSe (c), and CaF_2 (d). The dichroic ratio between IP and OP spectra, $A_{\mathrm{IP}}/A_{\mathrm{OP}}$, is calculated by using the ν(C−H) band height at ca. 2970 cm^{-1}.

Figure 3 Corrected pMAIRS spectra of a C_{60} evaporated thin film deposited on a Ge substrate: the OP spectrum is multiplied by n^4H $(n = 1.83, H = 0.15)$. The red and blue lines correspond to IP and OP spectra, respectively.

Table 1 The substrate-specific parameter of *H* calculated for representative substrate materials: Ge, Si, ZnSe, and CaF_2.

Substrate	Refractive index	Angle set and step[27]	*H*
Ge	4.0	9° − 44°; 5°	0.15
Si	3.4	9° − 44°; 5°	0.14
ZnSe	2.4	9° − 44°; 5°	0.11
CaF_2	1.4	8° − 38°; 6°	0.21

Table 2. The correction factor of $\boldsymbol{n^4 H}$ calculated for some organic compounds having various refractive indices measured on different substrates of Ge and CaF_2.

Sample	Refractive index, *n*	$n^4 H_{\mathrm{Ge}}$	$n^4 H_{\mathrm{CaF_2}}$
C_{60}	1.83[29]	1.68	2.52
P3HT	1.60[36]	0.98	1.47
PE	1.52[37]	0.82	1.23
PTFE	1.35[35]	0.50	0.75

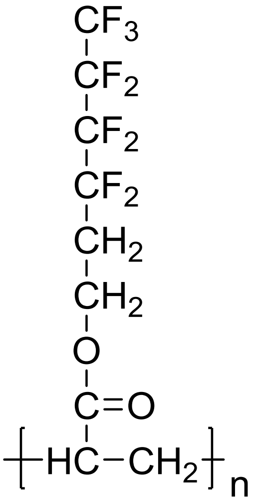

Chart 1 Chemical structure of poly(2-perfluorobutylethyl acrylate), C4FA.

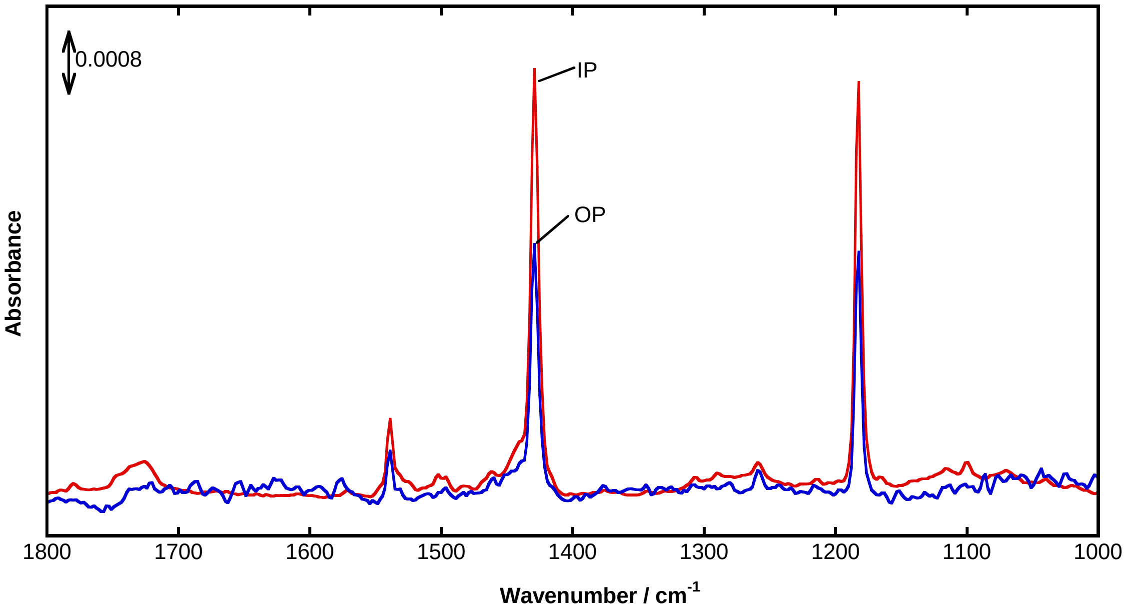

Figure 1 N. Shioya et al.

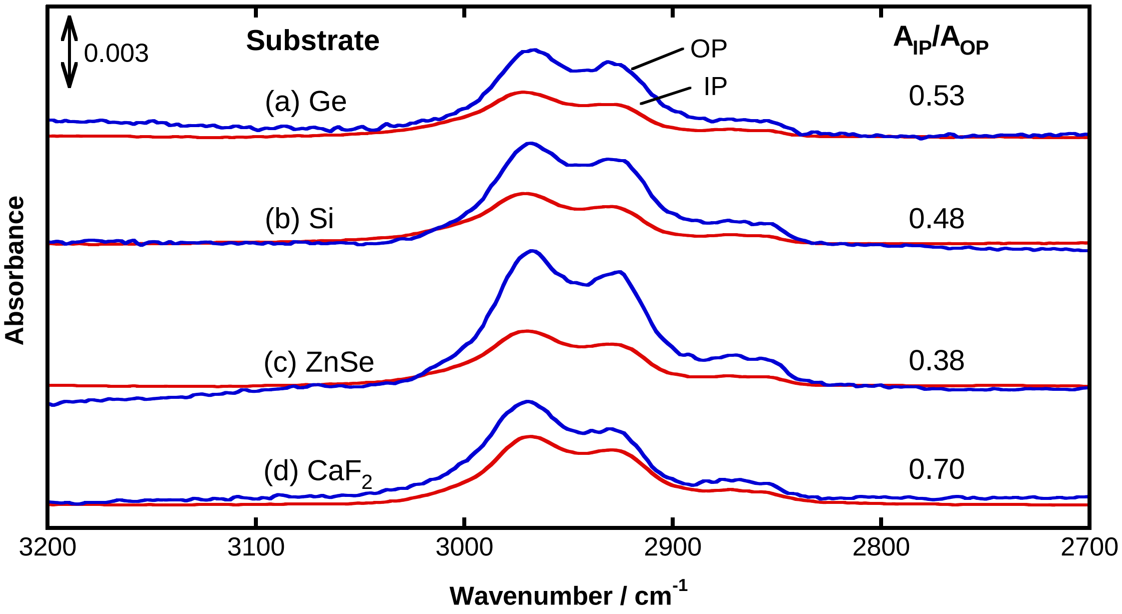

Figure 2 N. Shioya et al.

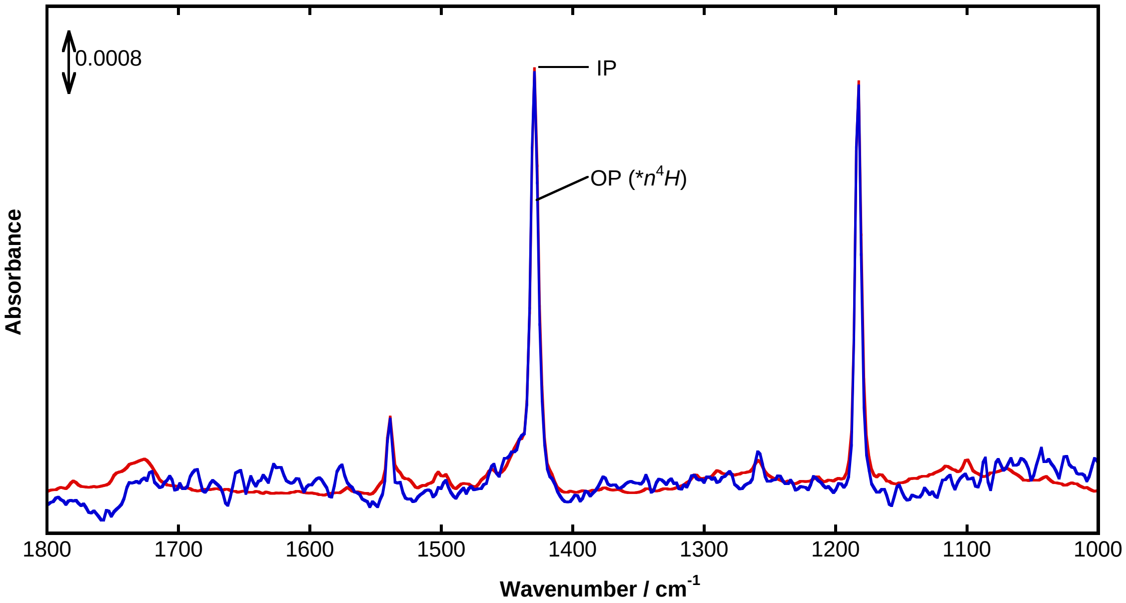

Figure 3 N. Shioya et al.