Feature Article

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Development of a New Measurement Method Using the Concept of Virtual Light

Takeshi Hasegawa

The physical properties of materials do not have a one-on-one relationship with the structure of a single molecule, because the molecular arrangement plays an important role. For a detailed analysis of molecular arrangement, it is necessary to know the direction of each functional group, the so-called molecular orientation. Recently, I constructed a measurement theory assuming virtual longitudinal-wave light as a method to clarify the molecular orientation using infrared spectroscopy. This measurement was realized in physical light by focusing attention on a new function of a classical formula called regression.

Introduction

One of the interest factors in spectroscopic measurement science is that it allows broad access to various fields such as molecular science, hardware development, and spectral analysis. The purpose of spectroscopic measurement is to reveal the interaction between molecules and light and present it as a spectrum. However, the ways that molecules and light interact vary widely according to the arrangements and collective states of molecules.

This is not limited to spectroscopic measurement. For example, let us think about the reactivity of magnesium oxide (MgO). MgO is typical basic oxide in terms of high school-level chemistry, i.e. it is dissolved by reaction with HCl, which is an acid. However, this is the case where MgO is a single molecule, or a solid where the molecular arrangement is not considered. If it is possible to cut the “crystal” of MgO successfully and create a surface where there are only ordered oxygen present, such a surface would not react with HCl at all. In this way, considerations about molecular arrangements are important for understanding chemistry.

Interactions between light and molecules are also significantly affected by molecular arrangements. For example, compare a randomly arranged state of stearic acid (molten state) with crystalline stearic acid. Not only changes in the number of molecular vibration frequencies but also different spectra according to spectrum measurement directions are observed. In particular, a crystalline state makes the resulting spectrum dependent on the measurement direction. This is known as a spectrum that reflects structural anisotropy.

In the recent nano-tech boom, intended functions are often achieved by the method of “arranging in specific order” and these are designed/synthesized functional molecules. In other words, structural anisotropy becomes a bridge between a single molecule and macro physical properties. Therefore, detailed investigations into structural anisotropy have been recognized as one of the fundamental technologies, a key part of modern nanotechnology.

This article introduces the construction of a new spectroscopic analysis method for clarifying structural anisotropy (i.e. molecular orientation). This is notably a unique example of the achievement starting from creating a new concept.

Thin Films with Strong Molecular Orientation

The thin films mentioned here are ultra thin films of nanometer-scale thickness, i.e. a thickness of a few molecular layers. In particular, a thin film with a thickness of a single molecular layer is called monomolecular film. This article focuses on how to create a Self-Assembled Monolayer (SAM) and Langmuir-Blodgett film (LB film)[1].

SAM is a method for covering a solid with a monomolecular film by binding molecules covalently to a solid substrate such as gold via a thiol group and joining the molecules to the solid substrate. On this occasion, molecules self-assemble through a hydrophobic interaction, etc. As a result, a thin film with a relatively high molecular density and orientation is formed with a thickness of just a single molecule. Because thiol and gold react only when they are in contact, the SAM film can be very easily formed by just immersing the metal into the solution.

On the other hand, LB films are produced by taking out a single molecular film formed on the surface of water to a solid substrate. To form a film on the water surface, it is necessary to prepare molecules which cause Langmuir adsorption at the boundary face between air and water. Amphipathic compounds are suitable for this because they contain both a hydrophilic group and a hydrophobic group in a single molecule. Stearic acid shown in Figure 1 is a typical amphipathic compound. Though it causes Langmuir adsorption on the water surface, the molecules spread in a disorderly manner and do not show arrangements immediately after they are dissolved in an organic solvent and dropped onto the water surface. When an intermolecular force is applied by reducing the film area, however, the molecular packing is improved and each molecular chain spreads to form a trans-zigzag structure. Unlike SAM, molecules are condensed by applying an external pressure, and thus the density of film molecules and degree of condensation can be controlled freely for LB films. Also, LB films have potential as device materials, in that several layers can be accumulated.

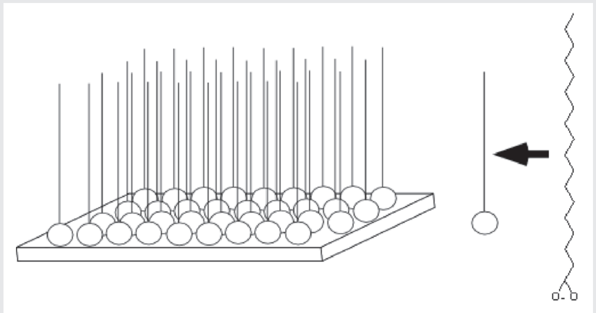
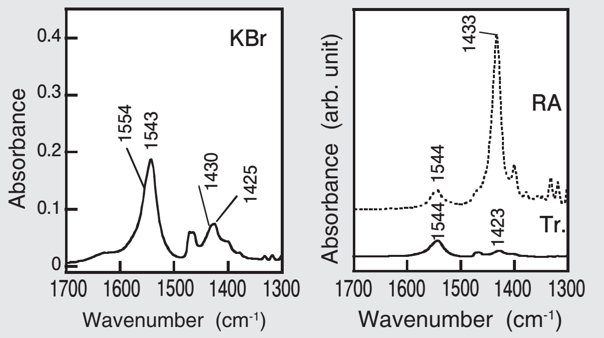


Figure 1 Schematic Diagram of the Metal-stearate Monolayer LB Film

Infrared Spectroscopic Analysis for Thin Films

Infrared spectroscopy is an extremely potent analytical method for obtaining molecular information in units of functional groups. Figure 2 shows the infrared spectra of cadmium stearate. Figure 2 (a) is measured by the KBr tablet method*1, and Figure 2 (b) is the transmission spectrum and reflection absorption (RA) spectrum of a 5-layer LB film[1,2]. Because the KBr tablet spectrum shows the state of random orientational ordering of sample molecules, it can be said to be a spectrum which reflects only absorptivity[1] i.e. excluding orientational factors. In the LB film spectrum, on the other hand, molecules are arranged in order, i.e. the spectrum reflects the information on the molecular orientation as well as absorptivity.



(a) KBr Tablet Method

(b) 5-layer LB Film
Reflection absorption (RA; Au substrate) and Transmission (TR.; Ge substrate) spectra

Figure 2 Infrared Spectra of Cadmium Stearate

In the infrared spectral measurement, the strongest absorbance is given when the electric field vector of infrared rays and the orientation of the group vibration (to be exact, vibration transition moment) become parallel[3]. For example, when a measurement is performed by normal incidence against the film, the electric field perpendicular to the direction of light is parallel to the film surface. As a result, “vibrations parallel to the film surface” are visible in the spectrum. In the RA method, on the other hand, a perpendicular electric field is formed on the film surface, because a metal is arranged on the substrate. Therefore, “vibrations perpendicular to the film surface” are visible in the spectrum. It can be said that the transmission method and RA method are surface analysis methods that are complementary to each other.

If the same thin film can be analyzed by both the infrared transmission and infrared RA methods, the orientational ordering of each group’s vibrations can be estimated from the comparison of two spectra[4]. Because the group vibration can be often estimated from the orientation of the molecular binding axis, the orientational ordering of the functional group of molecules can also be read.

However, the transmission method and RA method require a transparent plate and metal surface respectively for infrared rays. Thus, two types of substrates with

*1: A measurement method prepared by grinding down the sample and KBr (potassium bromide) crystal together in a mortar, putting them into a mold, pressing them while drawing a vacuum as necessary, and forming a transparent tablet.

totally different physical and chemical properties must be used. Now, the actual target for analysis is a thin film with a thickness of a single molecule. If such a thin film is directly placed on substrates with different properties, it is subjected to the differing actions of the substrates, i.e. a comparison of the "same" thin film is impossible.

In order to clarify the structural anisotropy of thin films spectroscopically, there are other representative methods such as the polarized light ATR method[5] and external reflection method[6]. In all cases, however, it is indispensable to know the optical constants of the substrates and film and to analyze permittivity. To resolve such problems, it might be advisable to put the whole thing in perspective and consider a new measurement method from the ground up.

Virtual Light Measurement and an Idea Allowing such Measurement

The transmission measurement method by normal incidence itself is an excellent method that facilitates the quantitative analysis of the obtained spectrum, because it enables selective measurement of vibrations parallel to the film surface and is with a relatively simple optical system. The RA method is also an excellent method being complementary with the transmission measurement method, but has two disadvantages. One is that the substrates are limited to metals and the other is that the scale used for band strength is different from that of the transmission method. However, an advantage of RA method, which uses metals, of forming an "electric field perpendicular to the film surface" near the boundary face would be useful if being achieved with another method.

The simplest idea for this is the optical system as shown in Figure 3[7]. Hereinafter, considerations are made for a special light which has an electric field vector parallel to the propagation direction of the light. Actually, it is impossible to create such a longitudinal wave light regularly in the infrared region, thus, this may be compared to "pie in the sky!" However, if it is possible to measure with this "virtual light", the information on molecular vibrations perpendicular to the film surface must be obtained by the normal incidence transmission method. Because the optical system for normal incidence transmission is the same as that of the usual transmission method, it would be possible to compare spectra using the same scale, and the information on both parallel and perpendicular to the film vibrations is not mixed as in the ATR or external reflection spectrum on a nonmetal substrate[8]. Since it is impossible to create virtual light in actuality, this idea seems to be impossible. However, it was found that theoretically, this could be avoided.

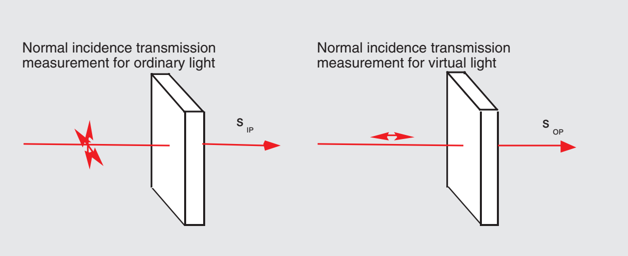


Figure 3 Schematic Diagram of Normal Incidence Transmission Measurement for Ordinary Light and Virtual Light
The arrows show the image of electric field vectors.
S_{IP} : Transmitted light intensity which has an electric field vector parallel to the film surface (in-plane direction)
S_{OP} : Transmitted light intensity which has an electric field vector perpendicular to the film surface (out-of-plane direction)

The idea for enabling virtual light measurement was found in a most unlikely place. It is a regression formula. The regression formula means "prediction formula." It is widely used in various fields including science. In the spectral analysis field, it can be also introduced as the expansion formula of the Lambert-Beer law. To be more specific, it is often used as the formula for using the entire spectral data on the measurement of the object containing several chemical species through multiple wavelengths. The simplest formula can be expressed as follows[1].

$$\mathbf{A}=\mathbf{CK}+\mathbf{U}_{\mathbf{d}} \cdots\cdots \quad (1)$$

Where **A** is a bundle of spectra, and **C** is a matrix in which concentration information is stored. **K** is the spectra for pure elements, which is equal to the multiple wavelength version of the molar absorptivity. Therefore, this formula can be considered to be an expansion of the Lambert-Beer law. The key point is that term $\mathbf{U}_{\mathbf{d}}$ which cannot be described by **C** is added. In fact, only this addition can be said as being substantially different from ordinary equations. The detailed explanation of this formula is omitted here. In brief, however, even if **A** includes the part that cannot be explained well by **C**, the other part, $\mathbf{A}\text{-}\mathbf{U}_{\mathbf{d}}$ can be expressed as **CK**.

Though this $\mathbf{U}_{\mathbf{d}}$ term normally has stored only a minute amount such as spectral noise, $\mathbf{U}_{\mathbf{d}}$ is not necessarily a minute amount in terms of the logic mentioned above. As long as $\mathbf{U}_{\mathbf{d}}$ has a random property toward **C**, this regression formula will function successfully and bring out the measurement amount equivalent to $\mathbf{A}\text{-}\mathbf{U}_{\mathbf{d}}$.

Multiple-Angle Incidence Resolution Spectroscopy (MAIRS)

What has been mentioned above can be over interpreted again as follows. It is alright to make a theoretical formula only for a part of the measurement amount ($\mathbf{A}$-$\mathbf{U}_d$) and leave the other ($\mathbf{U}_d$). As a matter of course, such an outrageous idea cannot be applied without limitation. It can be used only when a theoretical formula can be made using the **CK** style (i.e. linear combination). Though there are restrictions, such a method of theory construction is unprecedented. Since it is very interesting, I would very much like to make it a new measurement theory.

Fortunately, this idea is linked successfully to the above-mentioned virtual light measurement. As shown in Figure 4, when an oblique incidence transmission measurement is performed, "part" of the transmitted light intensity can be expressed as a linear combination of transmitted light intensity $\mathbf{s}_{IP}$ and $\mathbf{s}_{OP}$ (equivalent to **K**) in Figure 3. Thus, if the weighting factor (equivalent to **C**) in the event of linear combination can be constructed theoretically, $\mathbf{s}_{IP}$ and $\mathbf{s}_{OP}$ can be obtained from the measurable **A**. In other words unmeasurable $\mathbf{s}_{OP}$ can be obtained as if it was measured directly. In order to measure **A**, several single-beam measurements should be performed with different incidence angles, which can be performed with FT-IR.

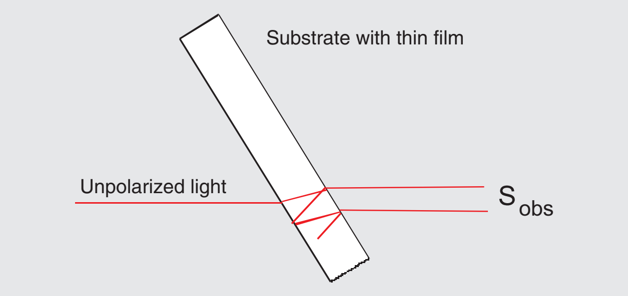


Figure 4 Image of Oblique Incidence Transmission Measurement

In a stroke of good fortune, I was able to successfully construct the theory for the part corresponding to **C** (**R** in Formula (2) and Formula (3)). As a result, both $\mathbf{s}_{OP}$ and $\mathbf{s}_{IP}$ could be obtained, which cannot be obtained with the other methods. Though the detailed explanation is omitted here, the basic formula is shown below[7].

$$\mathbf{S}=\mathbf{R}\begin{pmatrix}\mathbf{s}_{IP}\\ \mathbf{s}_{OP}\end{pmatrix}+\mathbf{U}_d \cdots\cdots (2)$$

$$\mathbf{R}=\left(\frac{4}{\pi}\right)^2\begin{pmatrix}1+\cos^2\theta_j+\sin^2\theta_j\tan^2\theta_j & \tan^2\theta_j\\ \vdots & \vdots\end{pmatrix} \cdots\cdots (3)$$

However, what is measured actually is not an absorbance spectrum, but a single-beam spectrum. Therefore, **A** has been changed to **S**. θ is the incidence angle measured from the normal direction of the substrate, and index j indicates several times of measurements with different incidence angles.

After **S** was obtained from the actual measurement, the incidence angle used for measurement is assigned in Formula (3) to make matrix **R**, and then the following formula is calculated based on Formula (2). This is referred to as the compromise solution calculation.

$$\begin{pmatrix}\mathbf{s}_{IP}\\ \mathbf{s}_{OP}\end{pmatrix}=\left(\mathbf{R}^T\mathbf{R}\right)^{-1}\mathbf{R}^T\mathbf{S} \cdots\cdots (4)$$

This measurement method was named Multiple-angle Incidence Resolution Spectroscopy (MAIRS) [9]. Because the peculiar concept of virtual light is used in this measurement, the results obtained from this method are also peculiar. The following are the representative results.

1. The result equivalent to a reflection absorption spectrum can be obtained in the transmitted light system.
2. Both normal incidence transmission spectrum and reflection absorption spectrum can be obtained from the same sample.
3. The result equivalent to a polarized spectrum can be obtained without using a light polarizer.
4. The orientational ordering of molecules can be analyzed without using any optical constant.

Figure 5 shows the results of the World's first infrared MAIRS measurement[7]. It is a result of measurement of a cadmium stearate 5-layer LB film formed on a germanium substrate (nonmetal). The results are well related to the transmission and RA spectra in **Figure 2**. Only this MAIRS method can derive the result equivalent to a RA spectrum on the nonmetal surface[10-12].

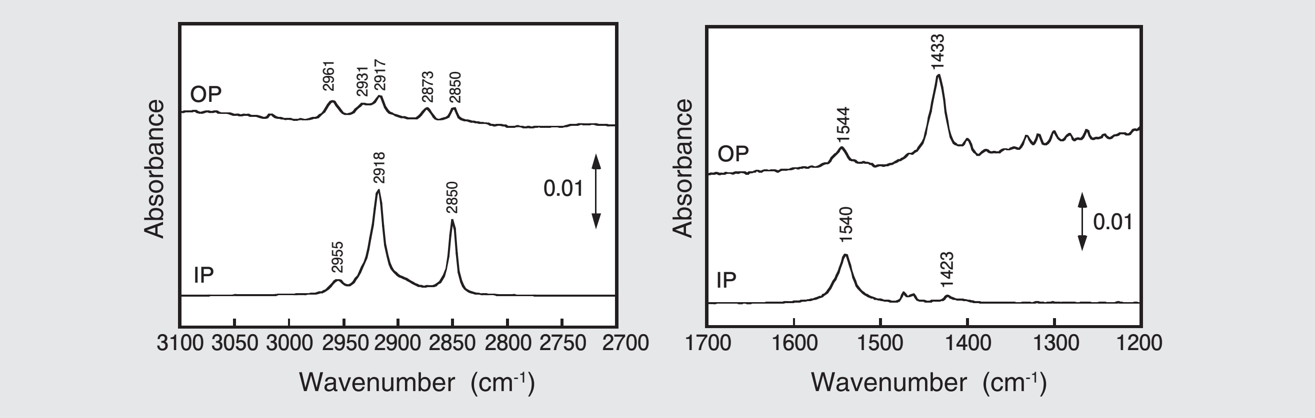


Figure 5 The World's First Infrared MAIRS Spectra
The sample is cadmium stearate 5-layer LB film formed on the Ge substrate (double-sided). OP and IP indicate a vibration spectrum in the out-of-plane and in-plane directions respectively.

Conclusion

I have been researching with the aim of "finding a new measurement method that creates a new scientific field." I always like to construct methods incorporating new concepts as much as possible, rather than improvement or combinations of existing methods. Research into the MAIRS method achieved together along with the creation of a new concept were not made pointedly. I think that they were accomplished through a completely open-minded, "Joy and Fun" spirit. This method itself has further unknown potential and I'm going to widen the new scientific field with this method, taking advantage of its unique functions.

(Publication members have responsibility for the translation)

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Takeshi Hasegawa

Tokyo Institute of Technology
Graduate School of Science and Engineering
Department of Chemistry
Associate professor
Also holds the post of “Structural function and measurement analysis”, JST PRESTO
Ph.D. in Science