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Far-ultraviolet spectroscopy of solid and liquid states: characteristics, instrumentation, and applications

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Recently, far-ultraviolet (FUV) spectroscopy, which is the spectroscopy of wavelengths in the region 140–200 nm, of solid and liquid states has received significant attention as a novel spectroscopic method. FUV spectroscopy provides new possibilities for studying electronic structures and transitions in almost all types of molecules, from water to polymers. It also shows great promise for a variety of applications. It is well known that wavelengths below 200 nm are rich in information regarding the electronic structure and states of molecules. However, absorptivity is so high in the FUV region, that it has not been employed to investigate solids and liquids. Another problem for FUV region analysis was the instrumentation: FUV spectrometers required vacuum evacuation. Moreover, it was difficult to find applications for FUV spectroscopy. Recently, we introduced the attenuated total reflection (ATR) technique to FUV spectroscopy, which overcomes these issues. ATR-FUV spectroscopy enables the measurement of FUV spectra for solid and liquid samples, establishing a new spectroscopic research area. Using ATR-FUV spectroscopy, electronic transitions that cannot be observed with ordinary UV spectroscopy (200–380 nm) are accessible; Rydberg transitions are just one example. FUV spectroscopy has been demonstrated to have unique and versatile applications. A variety of extensive application studies are now in progress, ranging from applications to fundamental science, such as studies of hydrogen bonding, hydration, and adsorption of water and aqueous solutions, to practical applications such as online, geochemical, environmental, and polymer film analyses. This review provides an introduction to, and brief history of, FUV spectroscopy, and describes the development of new FUV spectrometers, studies on electronic structure and transitions, its various applications, and future prospects.

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1. Introduction

Recently, far-ultraviolet (FUV) spectroscopy of the condensed phase has received keen interest because it not only provides novel information about the electronic structure and transitions in a variety of molecules, from simple molecules such as water, alcohols, and alkanes, to functional materials, polymers, and biological materials, but also offers various new applications such as qualitative and quantitative analyses, online monitoring, material analyses, geochemical and environmental analyses, and surface plasmon resonance (SPR).^{1–29} One of the more important features of FUV spectroscopy is that most molecules without an absorption at wavelengths >200 nm show intense absorptions in the FUV region; water, *n*-alkanes, and aliphatic alcohols are good examples. Light with a wavelength shorter than that of visible light (<380 nm) and longer than that of X-ray (>10 nm) is considered

UV light.^{1,30–55} In this review, the wavelength region of 120–200 nm is referred to as the FUV region. The term “vacuum UV region” (VUV) is no longer relevant to the 120–200 nm region because most modern spectrometers operating in this region do not use vacuum evaporation systems, but nitrogen gas-purged systems. The region of 200–300 nm is named the deep UV (DUV) region.^{1,35} This review is partly concerned with studies in the DUV region. The purpose of this review is to report recent progress in liquid and solid-state FUV spectroscopy, from the development of new instrumentation to its applications. The applications covered include not only basic science, such as studies on electronic transitions and structure, but also practical applications.

1.1 Brief history of FUV spectroscopy

Spectroscopy in the FUV region has a long history.^{1–3,30–34,36–66} For more than 50 years, gas-phase FUV spectra of molecules have been investigated using vacuum-evaporated spectrometers.^{1–3,30–34,36–54} These studies revealed that a variety of molecules have strong absorptions in the FUV region due to electronic transitions between low-lying Rydberg states and their vertical ionized energy. Studies on Rydberg states

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stretch back to the 1960s.^{1–3,33,34,43–51,55–57} In 1974, Robin³² assigned a few bands produced by gas-phase propane to transitions, including Rydberg states, based on term value analysis. Many other research groups, including Raymonda and Simpson,³⁶ Barnes and Simpson,³⁷ Robin and Kuebler,³⁸ and Kaya and Nagakura,³⁹ studied the FUV spectra of *n*-alkanes,³⁶ acetone,^{37,38} amides,³⁹ and many other molecules. Recently, Au *et al.*⁴⁰ carried out more detailed studies on gaseous *n*-alkanes and assigned a peak in the region 10.6–8.5 eV and a shoulder in the region 9.8–8.0 eV to Rydberg transitions. Cheng *et al.*⁴¹ investigated the FUV spectra of CH₃OH and its deuterated derivatives in the gas phase. They proposed band assignments for three absorptions at around 183 nm (6.8 eV), 160 nm (7.7 eV), and 149 nm (8.3 eV) based on the experimental results, including those of deuterated species, using time-dependent density functional theory (TD-DFT) calculations.

FUV spectroscopic studies of molecules in the condensed phase also date back more than 40 years,^{1,2,42–68} although examples are much fewer than those of molecules in the gas phase. The FUV spectra of water were investigated using transmission measurements of an extremely thin water film (2.850 Å thick)^{56,57} or water reflection measurements.^{59–61} However, these studies suffered from poor reproducibility and inconvenient measurement methods. Measurements of FUV spectra of some solids have been performed using synchrotron radiation.^{42–44} The existence of Rydberg transitions was suggested for a few liquid and solid samples. For example, Weiss *et al.*⁵⁷ indicated the existence of a Rydberg state in the

Langmuir–Blodgett film of Ca-arachidate in the solid state using X-ray spectroscopy.

As can be seen, FUV spectroscopy has a long history and has produced significant results regarding electronic transitions and structure, mainly in the gaseous state. However, FUV spectroscopic studies of condensed matter have been far behind for three main reasons: (1) most molecules have very high absorptivity in the FUV region; (2) FUV instrumentation has significant operational difficulties (*e.g.* an FUV spectrometer must be vacuum-evaporated or nitrogen gas-purged); and (3) it was difficult to identify practical applications. To solve these problems in FUV spectroscopy, we recently developed an attenuated total reflection (ATR)-FUV spectrometer. The development of the ATR-FUV spectrometer signified the advent of a new research area in spectroscopy. The emergence of ATR-FUV spectroscopy has created huge possibilities in FUV spectroscopy of the condensed phase.

1.2 Uniqueness and advantages of FUV spectroscopy in liquid and solid studies

FUV spectroscopy is a unique type of electronic spectroscopy, which can provide specific information about electronic transitions and structure that ordinary UV spectroscopy (200–380 nm) cannot.^{1–3} For example, FUV spectroscopy allows us to investigate the Rydberg transitions of liquids and solids,^{10,12,16,24} as well as electronic transitions involving σ electrons in a variety of molecules and π – π^* transitions in molecules such as amides and nylons.^{16,24} Another distinction is that, in contrast to the ordinary UV region (200–380 nm),



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(2) development of new spectrometers such as portable NIR imaging systems, (3) proposal of new spectral analysis methods such as moving window PLS (4) experimental and quantum chemical calculation studies of spectra, and (5) a variety of applications from basic molecular science to practical applications. Prof. Ozaki has received many awards including the Tomas Hirschfeld Award (1998), the Science and Technology Award of the Japanese Government (2005), the Gerald Birth Award and the Bomen–Michelson Award. Also he is a fellow of the Royal Society of Chemistry, Japan Chemical Society, and the Society for Applied Spectroscopy.



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water has a very intense absorption at around 150 nm due to the $\tilde{A} \leftarrow \tilde{X}$ transition.^{6,8}

1.3 Recent advances in FUV spectroscopy

Recent developments in FUV spectroscopy include the development of FUV spectrometers,^{6,9,20,21} studies on electronic structure and transitions in organic and inorganic molecules and polymers,^{10,11,15,16,24} and a variety of applications, such as those for water and aqueous solution analyses,^{14,19,21,51,69} industrial processes,^{5,7,9,21,69} and SPR in the FUV region.²⁸ It is worthy of note here that the introduction of quantum chemical calculation to FUV spectroscopy has enhanced usefulness of FUV spectroscopy in exploring the electronic structure of molecules.

Thus far, we have developed five kinds of FUV spectrometers:^{6,9,20,21} three ATR-FUV spectrometers and two transmittance FUV spectrometers.^{6,21} One is a portable FUV spectrometer designed for online monitoring of aqueous solutions.⁹ Another is a time-resolved transmittance FUV spectrometer.²⁰ Some of these spectrometers cover both the FUV region (140–200 nm) and DUV region (200–300 nm), referred to as FUV-DUV spectrometers. In this review, these FUV-DUV spectrometers are discussed in section 2. Besides ATR-FUV spectrometers some research groups use synchrotron radiation to measure the transmittance spectra of condensed materials.^{42–44} However, it is clear that ATR-FUV spectrometers are much simpler than synchrotron radiations.

ATR-FUV spectra have recently been studied extensively for water,^{6,8} aqueous solutions,^{11,17–19} alcohols,^{5–10} *n*- and branched alkanes,^{12,13,15} ketones,¹² and amides¹⁶ in the condensed phase, and nylons²⁴ and TiO₂^{22,23,25} in the solid phase. The assignment of absorption bands, electronic transitions, and structure was investigated for the above molecules by comparing experimental results with quantum chemical calculations.

The FUV spectra of alkanes and related molecules have provided new insight into Rydberg states and transitions involving electrons in the condensed phase (see section 3.1 for more details). The FUV spectra of amides in the liquid phase and nylons in the solid phase were also investigated.^{16,24} For amides, it was revealed, by combining the experimental results and the results of quantum chemical calculations, that the major band for simple amides, such as formamide and *N*-methyl formamide, appears at around 190 nm, arising mainly from the $\pi \rightarrow \pi^*$ transition, but with several types of Rydberg transitions also coexisting in the vicinity (see section 3.2 for more details).^{16,24} The introduction of the ATR-FUV spectrometer has opened a new avenue for water research. Ikehata *et al.*¹¹ explored the effects of cations on the first electronic transition, $\tilde{A} \leftarrow \tilde{X}$, of liquid water by ATR-FUV spectroscopy. They found that the peak energy of the $\tilde{A} \leftarrow \tilde{X}$ band of water, which showed a marked red shift with decreasing hydrogen bond strength, decreased with increasing cation size. Goto *et al.*¹⁸ studied the cationic effects on the $\tilde{A} \leftarrow \tilde{X}$ transition of water using lanthanide cations. Goto *et al.*²⁶ also explored the structure of water on a thin film of aluminum

using ATR-FUV spectroscopy (see section 4.1 for more details). Using FUV spectroscopy, qualitative and quantitative analyses of spring water are also possible (see section 4.2 for more details).

As mentioned above, FUV spectroscopy holds considerable promise for a variety of applications, from qualitative and quantitative analyses to online analysis and process monitoring. For example, Higashi *et al.*⁵ applied ATR-FUV spectroscopy to monitor the quality of semiconductor wafer-cleaning solutions, achieving direct measurement of the concentrations of fluids such as SC-1 (aqueous solution of NH₃ and H₂O₂) and SC-2 (aqueous solution of HCl and H₂O₂) (see section 5.1 for more details).⁵

Sato *et al.*⁷ demonstrated the utility of FUV-DUV spectroscopy in the 120–300 nm region in the non-destructive classification of commercial food wrap films (polyethylene (PE) films from three sources, two polyvinylidene chloride (PVDC) films with different additives, and one polyvinyl chloride (PVC) film).

More recently, Tanabe *et al.*^{22,23,25} studied the electronic states of TiO₂ and TiO₂ modified with metal nanoparticles (Pt, Pd, and Au) using the ATR-FUV-DUV spectrometer. They found that the deposition of metal nanoparticles changed the spectral shape and intensity, indicating variations in the electronic state and photocatalytic activity of TiO₂ (see section 6 for more details). The application of FUV spectroscopy is almost endless. Recently, it has been applied to studies of biological materials, polymer nanocomposites, ionic liquids and even biological tissues, and geological and environmental materials. Moreover, basic studies to develop FUV-SPR is underway.²⁸

2. Instrumentation

2.1 ATR-FUV spectrometer

Absorption intensities are so strong in the FUV region, particularly for liquids and solids, that FUV light cannot even penetrate a thin film. Our group (Higashi *et al.*⁶) designed and constructed an ATR-based FUV spectrometer. The ATR method allows spectral measurement similar to that of transmittance spectra, but with a very short optical path length. Thus, compared to transmittance spectroscopy, the ATR method has significant merits both in terms of quantitative measurements and easy handling of liquid or solid samples with strong absorption.⁶

A schematic of the ATR-FUV instrument developed is shown in Fig. 1.⁶ Fig. 1(A) illustrates a portion of the custom-designed commercial KV-200 FUV spectrometer (Bunkou-Keiki, Tokyo, Japan), while Fig. 1(B) shows an ATR probe with a temperature control system; a flow cell unit is formed between the sapphire internal reflection element (IRE) probe (7) and a fluorinated resin holder (8) enlarged from the area marked with a dashed line (part b) in Fig. 1(A). A liquid sample for ATR measurement is drawn into the 2 mm-diameter aperture (1) in the IRE probe. Air in the sealed instrument is purged with pure nitrogen gas,

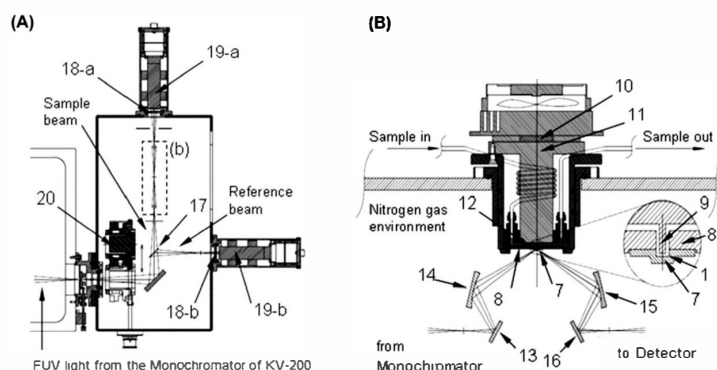


Fig. 1 Schematic diagram of the ATR-FUV spectrometer. (A) Originally designed semi-double beam part for the commercial KV-200 spectrometer. (B) The ATR probe with a temperature control system. From ref. 6 (1) aperture, (2)–(6) not shown here, see Fig. 1 in ref. 6, (7) ATR IRE probe, (8) a fluorine resin holder, (9) a fluorine resin guide, (10) a Peltier element, (11) a heat pipe, (12) a thermal sensor, (13)–(16) attached mirrors, (17) a MgF_2 beam splitter, (18a) and (18b) a synthetic quartz plate, (19a) and (19b) a photomultiplier, (20) a polarizing element.

while the sample can be handled in air, representing one of the advantages of this instrument.

The light source used was a 30 W deuterium lamp. The FUV light from the monochromator is split into reference and sample beams by a MgF_2 beam splitter (Fig. 1(B)). The reflected light and reference beam finally pass through a synthetic quartz plate coated with sodium salicylic acid, which fluoresces. The fluorescence of each beam is then detected by a photomultiplier.

Sample preparation and measurement in ATR-FUV spectroscopy is relatively easy. In most cases of liquid and solid samples, what one has to do is just to put samples on an ATR prism in air. For some solid samples special care may be needed. See ref. 8.

Fig. 2 shows the ATR-FUV spectra of light and heavy water at 145–220 nm (9–6 eV) measured over a temperature range of

10–70 °C using the above instrument.⁸ It is worth noting that the whole first electronic transition band of water can be detected by using the ATR-FUV spectrometer, and that the peaks attributed to D_2O always lie at higher energy than those of H_2O .^{6,8} This shift is attributed to the difference in vibrational zero-point energy between H_2O and D_2O . The result in Fig. 2 reveals that the $\bar{A} \leftarrow \bar{X}$ band of H_2O is located at about 156 nm, and that the $\bar{A} \leftarrow \bar{X}$ peak shifts to a longer wavelength with an increase in temperature and decrease in peak intensity. Thus, a decrease in the hydrogen bond strength in water causes a redshift in the water peak and a decrease in intensity.

ATR spectroscopy has long been used in infrared (IR) spectroscopy. It has disadvantages as well as advantages.^{2,3,6} The disadvantage of ATR spectroscopy is that ATR spectra include not only absorption but also the refractive index. The advantages and disadvantages in ATR-FUV spectroscopy are basically the same as those in ATR-IR spectroscopy except for the selection of the ATR prism material as will be discussed later.^{2,3,6} It should be remembered that an ATR spectrum is not identical to the corresponding transmittance spectrum. The penetration depth of the evanescent wave, d_p , is dependent on the refractive indices of the IRE, n_1 , and sample, n_2 , as follows:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2/n_1)^2}} \quad (1)$$

ATR spectra include not only absorption, but also the refractive index. The Kramers-Kronig transformation (KKT) and the Fresnel formulas should be employed to separate the contributions of the absorption and refractive indices. For more detailed discussion concerning ATR correction in the FUV region, refer to ref. 8.

Higashi *et al.*⁶ simulated the penetration depth of the evanescent wave in water for incident angles over the range of 56°–66° taking the reported refractive indices of water and sapphire into eqn (1). A marked increase in the penetration depth happens at around 161 nm, as the refractive index of water has

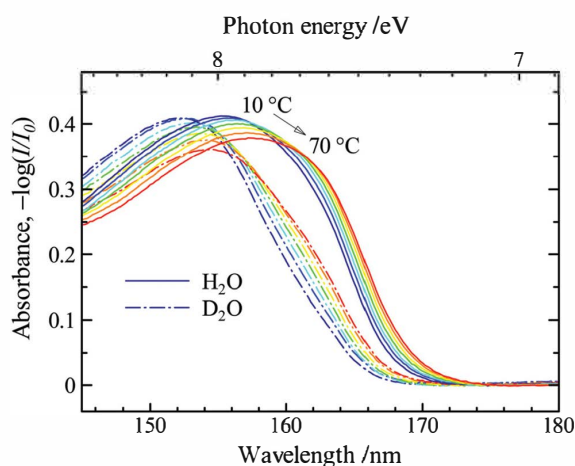


Fig. 2 ATR-FUV spectra (ATR absorbance) of H_2O and D_2O measured over a temperature range of 10–70 °C. From ref. 8.

a maximum value over 1.65 between normal and anomalous dispersions at 159 nm. The ATR-FUV spectra obtained by this device show a specific distortion in the evanescent wave, but Higashi *et al.*⁶ revealed that calculations based on the Fresnel formula may be used to correct for this distortion. One of the difficult points in ATR-FUV spectroscopy is the selection of IRE materials. The IRE used with the ATR technique must fulfill two important conditions. One is that the refractive index of the IRE must be greater than that of the sample material, and another is that the IRE material must have sufficient transmission in the measured wavelength range. For the FUV region (140–200 nm), there seemed no ideal IRE material that fulfills both conditions. Although sapphire lacks sufficient transmission in the wavelength region shorter than 160 nm, Higashi *et al.*⁶ used it because if the path length through the IRE is made short enough, the material should be able to yield at least some absorption spectra.

In an actual ATR measurement, refractive indices of both IRE and sample should be considered. For example, the refractive index of TiO₂ (~2.5) is larger than that of sapphire IRE (~1.8). Therefore, total reflection does not occur between them. However, even under such conditions, our instrument can measure spectra reflecting the optical properties of samples such as TiO₂ and ZnS. The details are discussed in ref. 29.

We also constructed a time-resolved ATR-FUV spectrometer (Fig. 3) for the investigation of radical species in a chain reaction in order to measure the transient absorption spectra for stable and radical species at 170–185 nm.²⁰ In order to probe a chemical reaction, in particular, a chain reaction, both the product and the reactant should be observed. Typical reactants do not have absorptions in the UV-VIS region, but do in the FUV region.

The developed time-resolved ATR-FUV spectrometer is based on a nanosecond transient absorption spectrometer.²⁰ White light from a laser-driven Xe lamp source was utilized as the probe light, because a stable tunable laser was not available in this wavelength region. A solar blind-response photomultiplier with a homemade preamplifier was employed to detect the probe light. This system is highly suited to monitor-

ing transient species created by the photodissociation of phenol and tryptophan.²⁰ We also developed a portable and highly sensitive FUV spectrometer for online monitoring. This instrument is outlined in section 5.1.

3. Characteristic FUV spectra and electronic structure and transitions studied using the spectra of various organic molecules

Before we introduced ATR-FUV spectroscopy, there were several important FUV studies on condensed materials such as water, alcohols, and TiO₂.^{3,42–45,54,56,57} Most of them have been carried out by using synchrotron radiation.^{3,42–44} By using FUV spectroscopy Costner *et al.*⁵⁶ indicated the existence of Rydberg transitions in liquid alkanes based on the intensities of the tails near 175 nm of strong bands in the 170–200 nm region measured by a transmission method by which the peak positions could not be observed owing to the strong bands. The Rydbergization of the valence type anti-bonding orbital of water in the condensed phase was reported by Chergui and Schwentner.⁵⁴

Jung and Gress^{43,44} measured the FUV spectra of CH₃OH and C₂H₅OH in the 115–207 nm region by a transmission method using synchrotron radiation. They could not observe an absorption band at around 183 nm, which corresponds to the A–X transition in the gas phase, so they assigned the first absorption band at 152 nm to the n–3s Rydberg excitation. Moreover, a thin cell of 1.0 (±0.5) μm was used, and thus it was impossible to estimate the absorption cross section correctly.

We measured the FUV spectra of various kinds of molecules in the condensed phase using the ATR-FUV spectrometer, namely alcohols,¹⁰ *n*- and branched alkanes,^{12,13,15} ketones,¹² amides,¹⁶ and nylons.²⁴ From these spectra, we studied the following: (1) characteristic bands, (2) band assignments, and (3) electronic structure and transitions. For band assignments and the studies on the electronic structure and transitions we used quantum chemical calculations, which have progressed remarkably in the last two decades. One of the most important findings from our series of FUV spectroscopy studies on various organic molecules was the existence of confined Rydberg transitions in liquid and solid phases.

Fig. 4(a)–(g) display the ATR-FUV spectra of *n*-alkanes (C_mH_{2m+2}, *m* = 5–9);¹³ C₆H₁₄ isomers;¹³ CH₃OH, CH₃OD, CD₃OH, and CD₃OD;¹⁰ four linear and two branched ketones;¹² five amides,¹⁶ and five nylons including *N*-methyl acetamide,²⁴ respectively. ATR-FUV spectroscopy enables one to collect FUV spectra for any kind of molecule in the condensed phase. In contrast to the DUV region, almost all molecules show bands in the FUV region. Comparison of the spectra in Fig. 4 led us to conclude that common bands near 150 nm are assignable to alkyl groups. Ketones, amides, and nylons show characteristic bands at 175–195 nm, 190–220 nm, and 190–210 nm, respectively.

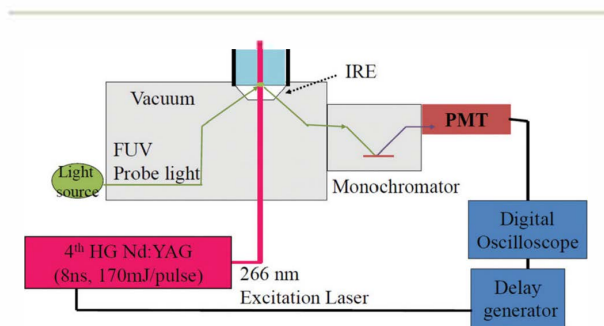


Fig. 3 A schematic diagram of the time-resolved attenuated total reflectance far-ultraviolet spectrometer. From ref. 20.

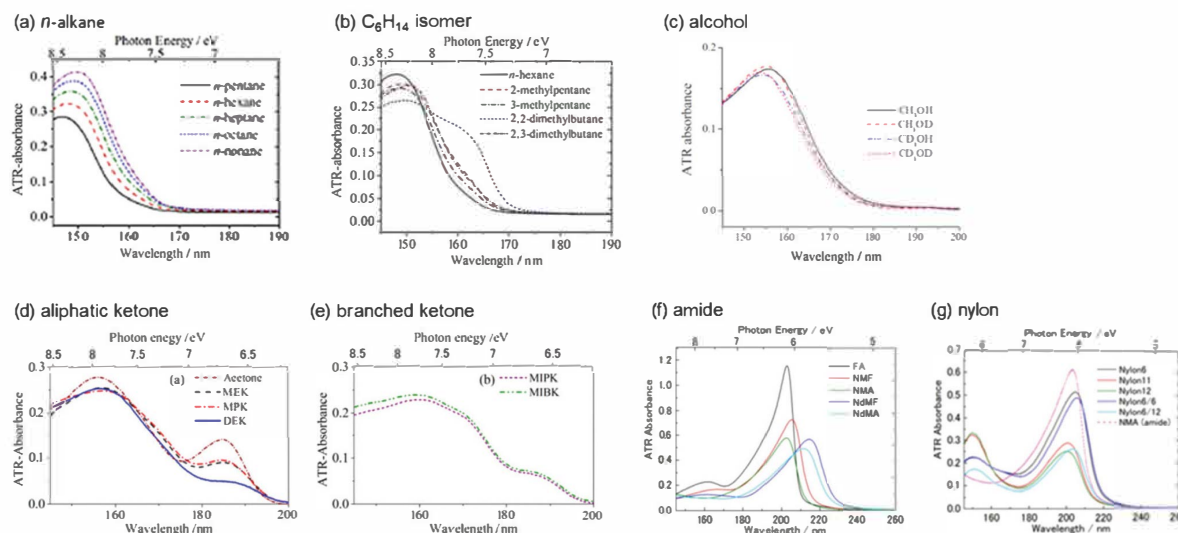


Fig. 4 ATR-FUV spectra of (a) *n*-alkanes (C_mH_{2m+2} , $m = 5-9$) (from ref. 15), (b) C_6H_{14} isomers in the liquid phase (from ref. 15), (c) CH_3OH (solid), CH_3OD (break), CD_3OH (dot break) and CD_3OD (short break) in the liquid state (from ref. 10), (d) four aliphatic-ketones and (e) two branched ketones (from ref. 12), (f) FA, NMF, NMA, NdMF, and NdMA in the liquid phase (from ref. 16), and (g) nylon 6, nylon 11, nylon 12, nylon 6/6, nylon 6/12, and liquid NMA in a cast film (from ref. 24).

The FUV spectra of *n*-alkanes (Fig. 4(a)) yield a broad feature near 150 nm. This band has a lower energy shift and significant increase in intensity as the alkyl chain length increases. Quantum chemical calculations revealed that the band around 150 nm for *n*-alkanes was due to the σ -Rydberg $3p_y$ transition and its red shift was caused by the destabilization of the σ orbital and the stabilization of the Rydberg $3p$ level, which is enhanced as the carbon chain increases.¹² The n -3s, n -3p, and n -3d Rydberg transitions were investigated for linear and branched ketones in the liquid phase (Fig. 4(d) and (e)). The liquid phase spectra were compared with those of the gas phase, and the bands observed at 175–200 nm and 160–175 nm showed strong correlations with the molecular structure of the investigated ketones and were assigned to the n -3s and n -3p Rydberg transitions, respectively.

Investigation of the FUV spectra of amides in the liquid phase was also of interest because valence-Rydberg coupling was expected in their π - π^* transitions and direct interactions *via* hydrogen bonding affect the excited states.¹⁶ It was shown, with the aid of quantum chemical calculations, that the amide band at ~ 190 nm was mainly due to the π - π^* transition, and that several types of Rydberg transitions also existed in its vicinity. The valence-Rydberg coupling of the π - π^* transition was more significant than the n - π^* transition.¹⁶

Nylons are also very interesting targets for FUV spectroscopy because they contain both alkane chains and amide groups, and therefore, their FUV spectra have features of both alkanes and amides.²⁴

In this review, we outline FUV spectroscopy and quantum chemical calculation studies of alkanes and nylons.

3.1. *n*- and branched alkanes

Fig. 5 displays the calculated spectra in the region 9.5–6.5 eV (130–190 nm) of *n*-alkanes (C_mH_{2m+2} , $m = 5-9$) by TD-DFT/aug-cc-pVTZ.¹² The calculated spectra are in good agreement with the observed FUV spectra in terms of the redshift of the main peak with a significant increase in intensity corresponding to increased alkyl chain length, although the calculations overestimate the peak positions by about 0.5 eV. A convoluted spectrum of *n*-hexane, with peaks in the region 9.5–6.5 eV, is shown in Fig. 6.¹² Notably, many transitions have significant

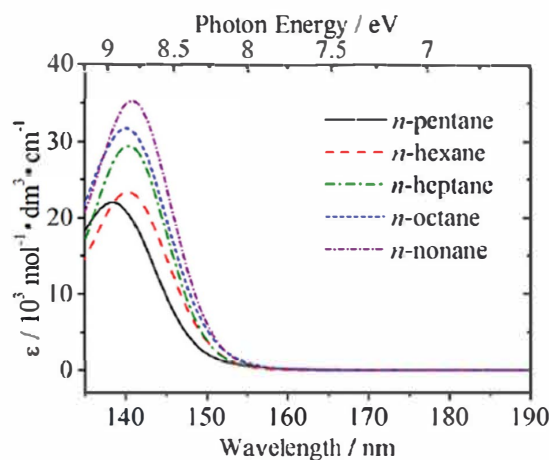


Fig. 5 Calculated FUV spectra of *n*-alkanes in the region of 140–190 nm (C_mH_{2m+2} , $m = 5-9$). From ref. 15.

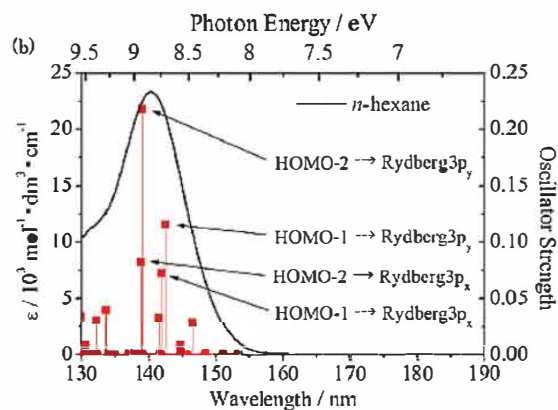


Fig. 6 Theoretical FUV spectra in the region of 130–190 nm of *n*-hexane calculated by TD-DFT. Band assignments are shown. From ref. 15.

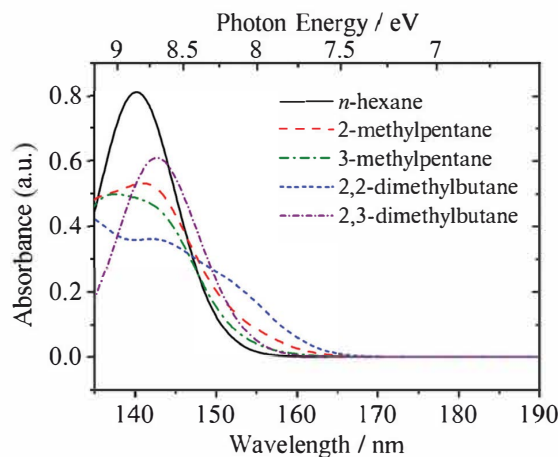


Fig. 7 Calculated FUV spectra in the region of 135–190 nm of *n*-hexane, 2MP, 3MP, 2,2-DMB, and 2,3-DMB. From ref. 15.

contributions to an absorption band at around 9 eV. According to calculations, the most intense peak is attributed to the transition from HOMO-2(σ) to Rydberg $3p_y$ (hereafter denoted as T1).¹² All *n*-alkanes investigated have similar transition natures to that of T1, although the energy level of HOMO-2(σ) interchanges with HOMO-3(π) at $m = 7$ (*n*-heptane). A transition from HOMO-1(π) to Rydberg $3p_y$ is the second most intense transition (T2), while other transitions, namely σ -Rydberg $3p_x$ and σ -Rydberg $3p_x$, also contribute to this broad band.

To investigate the effects of branching of the carbon chain on excitation spectra, the FUV spectra of *n*-hexane, 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB) were obtained.¹² Fig. 4(b) shows that, in the spectra of all branched alkanes, the band at ~ 8.3 eV (~ 150 nm) has a lower energy shift and that the intensity of the shoulder at ~ 7.7 eV (~ 160 nm) increases remarkably in the order: alkanes without branches < tertiary carbon < quaternary carbon.

The TD-DFT spectra of *n*-hexane, 2MP, 3MP, 2,2-DMB, and 2,3-DMB are depicted in Fig. 7.¹² The calculated spectra reproduced the experimental spectra well in terms of both the peak shift and the change in the intensity of the higher energy band. Increase in the intensity of the lower-energy band and the lower-energy shift in the branched alkanes were also well recognized in the calculated spectra.

In addition, branched alkanes with a relatively high symmetry (C_{2v} and C_{2h}), such as 3-MP and 2,3-DMB, had only a weak shoulder near 7.6 eV, whereas those with a relatively low symmetry (C_s), such as 2-MP and 2,2-DMB, had very clear shoulders. Morisawa *et al.*¹² inferred that the forbidden transition from $\sigma(a_g)$ to $3s$ becomes allowed in response to the decrease in symmetry that occurs on going from *n*-alkanes to branched alkanes with lower symmetry.

3.2. Nylons

Morisawa *et al.*²⁴ investigated the FUV spectra of five kinds of nylons, namely nylon 6, nylon 11, nylon 12, nylon 6/6, and nylon 6/12, whose chemical structures are shown in Fig. 8.

Fig. 9 shows normalized ATR-FUV spectra with the intensity of the peak near 200 nm from these nylons and liquid *N*-methylacetamide (NMA) in a cast film.²⁴ All nylons had two intense features near 150 and 200 nm, which were assigned to alkane and amide moieties, respectively. The intensity of the 150 nm band increased in the order: nylon 6 < nylon 6/6 < nylon 6/12 < nylon 11 < nylon 12, which is the same as the order of increasing number of CH_2 groups. TD-DFT calculations were carried out for the monomer units of nylons 6, 11, and 12 in order to interpret the ATR-FUV spectra of nylons; Fig. 10 shows the calculated spectra of these model compounds in a vacuum.²⁴ The calculated spectra yielded bands near 140 and 170 nm. Taking into account that TD-DFT provides higher transition energies than the experimental results, and that we did not consider the effects of the surroundings, we assigned these bands to those observed near 150 and 200 nm, respectively.

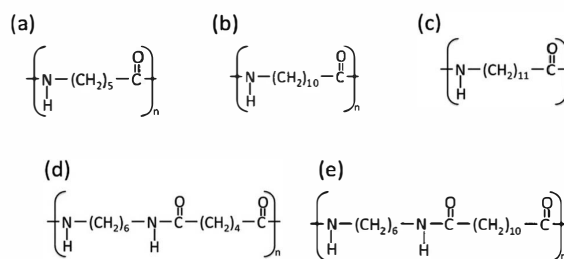


Fig. 8 Chemical structures of (a) nylon 6, (b) nylon 11, (c) nylon 12, (d) nylon 6/6, and (e) nylon 6/12. From ref. 24.

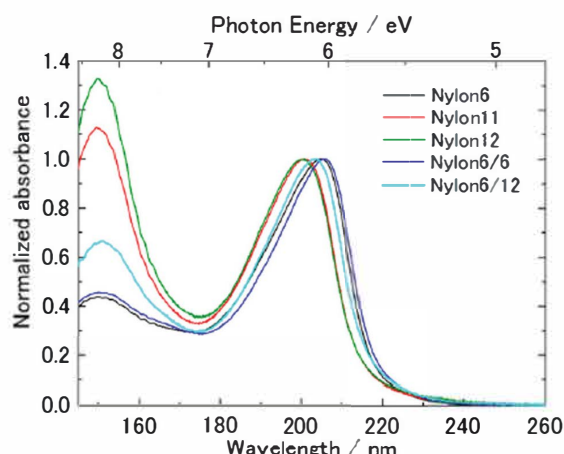


Fig. 9 Normalized ATR-FUV spectra with the intensity of the peak near 200 nm of the five kinds of nylon and liquid *N*-methylacetamide (NMA). From ref. 24.

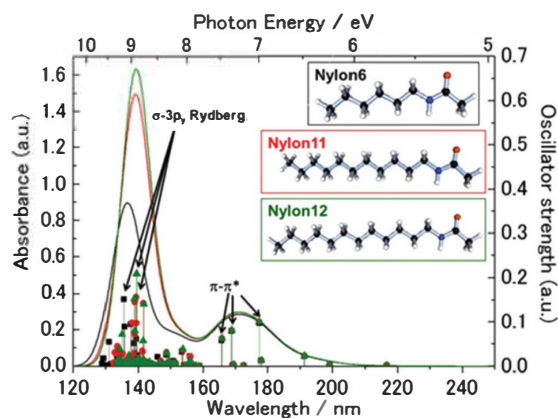


Fig. 10 Calculated FUV-DUV spectra with bars and their convolution of model compounds of nylon 6, nylon 11, and nylon 12 under vacuum. Band assignments are shown. TD-DFT calculations for monomer units of nylon 6, nylon 11, and nylon 12 were carried out. From ref. 24.

Morisawa *et al.*²⁴ assigned the 150 and 200 nm bands to the σ -Rydberg 3p and π - π^* transitions of nylons, respectively. The Rydberg transitions are delocalized over the hydrocarbon chains, while the π - π^* transitions are relatively localized to the amide group. The shift of the π - π^* absorption peak to longer wavelengths in nylon 6, nylon 6/6, and nylon 6/12 may be caused by hydrogen bonding. Therefore, Morisawa *et al.*²⁴ explored the effects of hydrogen bonding using monomer, dimer, and trimer models. Fig. 11 depicts the structures of nylon 6 and nylon 6/6 trimer models with the calculated transition dipole strengths. Hydrogen bonds were perfectly constituted by inverting alternate chains in the α -form of the nylon 6 model, while in the α -form of nylon 6/6 the progressive shear structure was adopted. These trimer models represented the

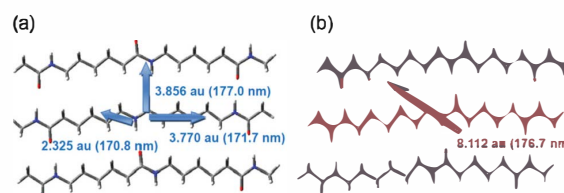


Fig. 11 Computational trimer models of hydrogen bonded systems for (a) nylon 6 and (b) nylon 6/6 with the transition dipole strengths. From ref. 24.

hydrogen-bonded system of the unit cell regarding the π - π^* transitions. The π - π^* transitions in nylon 6/6 were delocalized by being coupled with each other, and the oscillator strengths were accumulated at the lowest state, while in nylon 6, the π - π^* transitions were localized and the oscillator strengths were distributed to more than one state. In this way, the FUV spectroscopy studies on nylon provided new insight into the electronic structure and hydrogen bonding in nylons.

4. FUV spectroscopy studies of water and aqueous solutions

ATR-FUV studies of water and aqueous solutions have been carried out, from fundamental studies such as those on the nature of the first electronic transition of water, to applications such as water quality analysis. Ikehata *et al.*⁸ studied the origin of low-lying electronic transition bands in water using the ATR-FUV spectrometer. They succeeded in direct observation of the absorption bands of the first electronic transition in liquid H_2O and D_2O by ATR-FUV spectroscopy. By measuring the temperature-dependent spectra of water in the temperature range 10–70 °C, Ikehata *et al.* provided solid evidence for the redshift of the first absorption band of liquid water upon heating. Ikehata *et al.* and Goto *et al.*¹⁸ investigated cationic effects on the $\tilde{A} \leftarrow \tilde{X}$ transition of liquid water. Goto *et al.*¹⁹ reported the electronic transitions of amino acids in aqueous solutions. Furthermore, the pulse laser photolysis of aqueous ozone in the microsecond range was studied using time-resolved FUV spectroscopy.²¹ Goto *et al.*²⁶ investigated the surface effects of alumina on liquid water by using variable angle ATR-FUV (VA-ATR-FUV) spectroscopy. In this section, the ATR-FUV spectroscopy study of water on an aluminum thin film, and the qualitative and quantitative analyses of spring water samples by FUV-DUV spectroscopy, are reviewed.

4.1 Investigation of surface effects of alumina on the electronic state of water by variable angle ATR-FUV spectroscopy

Goto *et al.*²⁶ investigated the effects of the alumina surface on the $\tilde{A} \leftarrow \tilde{X}$ transition using variable angle ATR-FUV spectroscopy. The first electronic transition ($\tilde{A} \leftarrow \tilde{X}$ transition) band of water (H_2O and D_2O) was observed at around 8.45 eV for H_2O and 8.53 eV for D_2O , as shown in Fig. 12. For these spec-

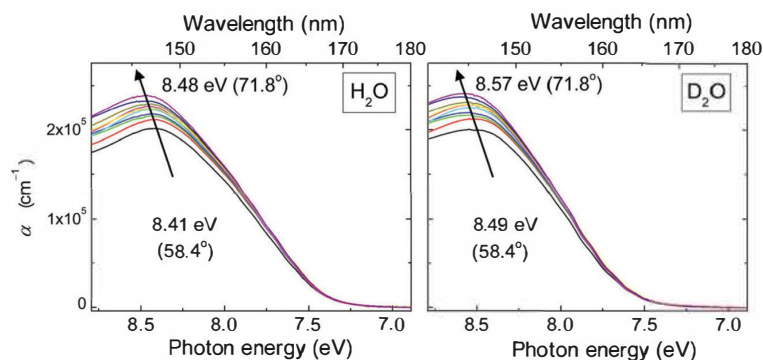


Fig. 12 FUV absorption spectra of H₂O (left) and D₂O (right) with various incident angles shown in parentheses. From ref. 26.

tral measurements, water was put on an α -alumina IRE, and therefore, the obtained spectra were affected by the surface condition of alumina. It is known that the physical properties of interfacial water (density, viscosity, *etc.*) are distinctively different from those of bulk water. As the incident angles of the probe light increase from 58.4° to 71.8°, the $\tilde{A} \leftarrow \tilde{X}$ band maxima are blue-shifted from 8.41 to 8.48 eV for H₂O and 8.49 to 8.57 eV for D₂O. Variable angle spectra were analyzed by the alternating least-squares (ALS) method, assuming that water consisted of bulk water and a 2 nm-thick interfacial water layer. Fig. 13 shows the normalized $\tilde{A} \leftarrow \tilde{X}$ bands of H₂O in the bulk and interfacial phases. Reported bands for solid H₂O in hexagonal crystals (*I_h*) and amorphous phases are also shown for comparison.⁷⁰ The $\tilde{A} \leftarrow \tilde{X}$ band of the interfacial water was markedly blue-shifted and red-tailed compared with bulk water. The difference in the electronic state of interfacial water from the bulk water was mainly due to the hydrogen bond structure and energy affected by the alumina surface.

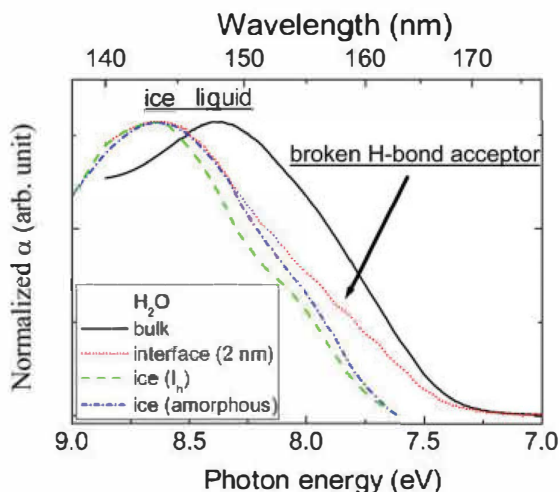


Fig. 13 Normalized $\tilde{A} \leftarrow \tilde{X}$ bands of bulk and interfacial H₂O in the liquid state determined by the present experiment and those of *I_h* and amorphous ice states obtained from ref 70. From ref. 26.

4.2 Qualitative and quantitative analyses of spring water samples by FUV-DUV spectroscopy

Mitsuoka *et al.*¹⁴ demonstrated an interesting example of the geochemical and environmental application of FUV spectroscopy. They measured the FUV-DUV spectra in the 190–280 nm region of spring water samples collected in the Awaji-Akashi area, Tanba area, and Rokko-Arima area of Hyogo Prefecture in Japan (Fig. 16). As can be deduced from the map in Fig. 14, these three areas have quite different geological features. The map shows the geological outline and sampling points.

Fig. 15 shows FUV-DUV transmission spectra in the region 170–300 nm for Na₂SO₄ (5 mM), NaNO₃ (10 mM), NaCl (50 mM), and MgCl₂ (50 mM) solutions, and ultra-pure water (UPW), along with their first derivative spectra.¹⁴ The spectra in Fig. 15 were collected by a KV-200 FUV spectrometer (Bunkoh-Keiki, Co., Ltd, Hachioji, Japan) and used to analyze the FUV-DUV spectra of spring water samples as shown in Fig. 16(a)–(c).¹⁴ It can be seen from Fig. 15 that NaNO₃ solution yields a strong band at around 200 nm, arising from its π - π^* transition, the Na₂SO₄ solution gives a very steep band starting at around 190 nm, and the NaCl and MgCl₂ solutions give rather gradual bands beginning at around 200 nm. The first derivative spectra revealed clear differences around 190 nm between the spectra of the Na₂SO₄ solution and those of the NaCl and MgCl₂ solutions.

Fig. 16(a)–(c) show the FUV-DUV spectra of spring water collected from the Awaji-Akashi area (island area, southern part), Tanba area (northern mountain area), and Rokkou-Arima area (middle east mountain area).¹⁴ It can be clearly seen that the three areas afforded quite distinct spectra. In this review, we will only discuss the spectra in Fig. 16(a). It is noted in Fig. 16(a) that areas A02 and A05 show saturated features in their spectra. The spring water samples from these two areas contained large amounts of NO₃[−] and Cl[−] ions, due to the samples coming from sedimentary lithology near the seashore, which contains many ions from seawater. Area A04 was far from the sea, with its spring water arising from granitic lithology; thus, A04 did not yield an intense band in Fig. 16(a).

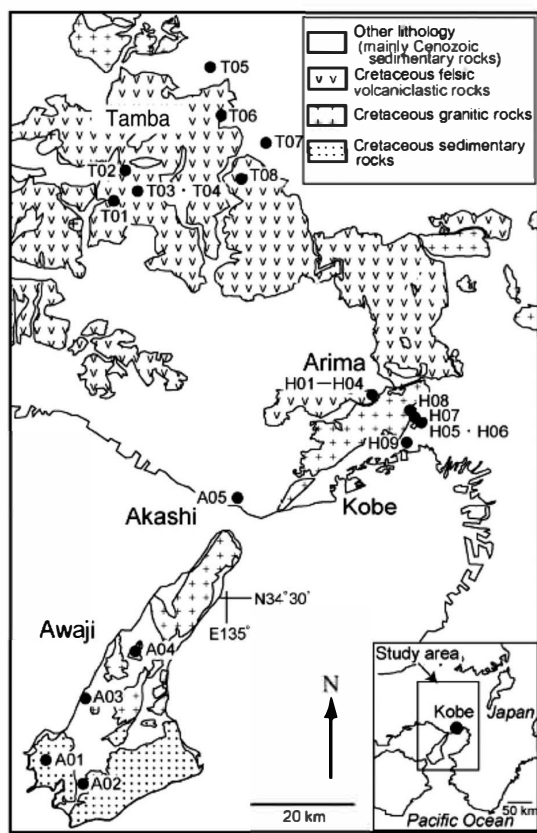


Fig. 14 A geological outline map of Hyogo Prefecture, Japan, showing the places where the spring water samples were collected. Awaji area (A01–A05). Arima area (H01–H09). Tamba area (T01–T08). The geological map was modified from the geological survey of Japan (2009). From ref. 14.

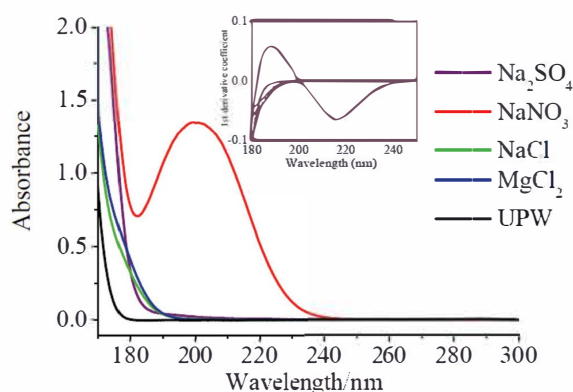


Fig. 15 FUV spectra in the 170–300 nm region of Na_2SO_4 (5 mM), NaNO_3 (10 mM), NaCl (50 mM), and MgCl_2 (50 mM) solutions, and ultra-pure water (UPW). Inset: first derivative in the 180–250 nm region of the spectra. From ref. 14.

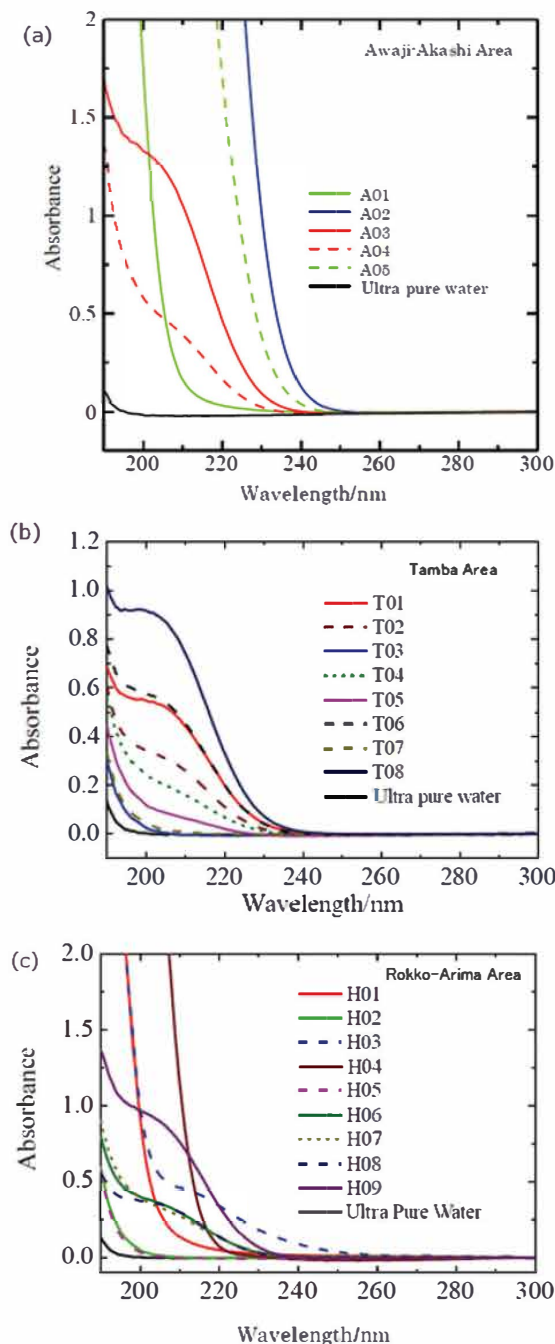


Fig. 16 (a) FUV-DUV spectra in the 190–300 nm region of spring water of Awaji area (A01, A02, A03, A04, A05) (see, Fig. 14) and ultra-pure water. From ref. 14. (b) FUV-DUV spectra in the 190–300 nm region of spring water of Tamba area (T01, T02, T03, T04, T05, T06, T07, T08) (see Fig. 14) and ultra-pure water. From ref. 14. (c) FUV-DUV spectra in the 190–300 nm region of spring water of Arima area (H01, H02, H03, H04, H05, H06, H07, H08, H09) (see, Fig. 14) and ultra-pure water. H01, H02, H03 and H04 belong to the Arima Hot spring. Others belong to the Rokko area. From ref. 14.

These results revealed that the spring water in the Awaji-Akashi area varied largely with local geology. Mitsuoka *et al.*¹⁴ also showed that the quantitative analysis of components in spring water can be performed using chemometrics as well as FUV-DUV spectroscopy. Thus, FUV-DUV spectroscopy emerges as a simple tool for monitoring spring water. FUV-DUV spectroscopy can be utilized for various water analyses, including environmental assessment.

5. Industrial and practical applications of FUV spectroscopy

Industrial and practical applications of FUV spectroscopy have been limited in comparison with other spectroscopic methods as this spectral region has been inaccessible using routine measuring techniques due to the strong absorption of oxygen in air. Moreover, the observed absorptivity is extremely strong in the FUV region, such that it is difficult to measure full absorption spectra without saturation. However, compared with other spectroscopic methods, FUV spectroscopy has the advantages of non-destructive analysis, easy sample preparation, high sensitivity, and simple spectral analysis.^{1–3} Thus, FUV spectroscopy holds considerable promise as a unique analytical method, not only for aqueous solutions,^{6,8,11,17,18,21} but also for organic and inorganic compounds, such as polymer films²⁶ and semiconductors.^{22,23,25,29}

FUV-DUV spectroscopy in the region 190–280 nm has long been utilized as a highly sensitive and simple method for qualitative and quantitative analyses of liquid water and aqueous solutions.^{4,69,71–73} UV spectrometers can be used in this region. Notably, various kinds of ions show a strong band in this region; for example, it is well known that NO₃[–] yields an intense band near 200 nm due to π – π^* transition^{69,71–73} and halogen ions give rise to a CTTS (charge transfer to solvent) band around 170–225 nm.^{69–72} Ferree and Shannon⁶⁹ reported the quantitative analysis of nitrogen compounds in waste water by utilizing the NO₃[–] absorption near 200 nm. Higashi and Ozaki⁴ applied FUV-DUV spectroscopy to the 190–280 nm region for the qualitative analysis of various commercial mineral waters. Various types of mineral waters could be classified clearly based on the observed bands arising from the π – π^* transition of NO₃[–] and the CTTS transitions of halides.

FUV spectroscopy (including the shorter wavelength region of DUV spectroscopy) has found the following industrial and practical applications:^{1–3}

(1) quantitative and qualitative analyses of aqueous solutions including mineral water, spring water, and waste water.^{11,14,19,21}

(2) Monitoring semiconductor water-cleaning solutions⁹ and disinfectant solutions.⁵

(3) Quantitative and qualitative analyses and classification of polymer thin films.⁷

(4) Monitoring of radical species in semiconductor water-cleaning solutions.²¹

(5) Measuring the physical properties of semiconductor materials such as TiO₂.^{22,23,25,29}

(6) SPR in the FUV region makes SPR-FUV sensors possible.²⁸

In this review, we introduce our studies on the direct measurement of peracetic acid, hydrogen peroxide, and acetic acid in disinfectant solutions.⁵

5.1 Direct measurement of peracetic acid, hydrogen peroxide, and acetic acid in disinfectant solutions

Higashi *et al.*⁵ proposed a rapid and highly selective FUV-DUV spectroscopic method for the simultaneous determination of peracetic acid (PAA), hydrogen peroxide, and acetic acid (AA). Since the proposed method utilized the 180–220 nm region, we developed a portable and highly sensitive FUV spectrometer that enabled the measurement of spectra down to 180 nm. The proposed method does not require any reagents, catalysts, calibration standards, or complicated procedures for analysis. The only preparation procedure required is the dilution of H₂O₂ with pure water to a concentration lower than 0.2 wt% in the sample solutions.

PAA has been used extensively for sterilization since concerns about the environmental spread of infectious agents have grown and the need for so-called cold sterilization has increased.^{74–76} The accurate determination of PAA is required to monitor the PAA levels in disinfectant solutions and to adjust the concentration through the addition of concentrated PAA solution. However, no applicable method has yet achieved a rapid, continuous, selective, and sensitive measurement for the online monitoring of PAA disinfectant solutions.

A PAA solution was prepared from H₂O₂ in the presence of an acid catalyst, typically H₂SO₄.⁵ The equilibrium state is shown in the following equation:



Thus, industrial PAA solutions always contain significant amounts of H₂O₂. The analysis of PAA solutions requires high selectivity and little cross-reaction with co-existing H₂O₂ and AA. Higashi *et al.*⁵ attempted to use FUV-DUV spectroscopy to monitor PAA, H₂O₂, and AA in disinfectant solutions. For this purpose, they build a new portable FUV-DUV spectrometer.⁵ The instrument is very compact, being only 30 cm × 16 cm × 16 cm in size, and includes a UV light source, a grating mirror, a photoabsorption cell, and an optical sensor. Due to the large absorbance of aqueous solutions in the measured region, the optical path length of the cell used was 0.5 mm. A deuterium lamp with a transparent window made of MgF₂ in the spectral region 180–220 nm was used as the UV light source. To determine the PAA in disinfectant solutions, we did not require very high wavelength resolution and, thus, focused on detecting sufficient brightness in preference to resolving detectable wavelengths. To achieve bright UV radiation, we utilized a thin diamond film sensor as an optical sensor in the FUV spectrometer, which also contributed to the miniaturization of the spectrometer.

Commercial FUV spectrometers need a large vacuum pump or a great deal of purging gas, such as nitrogen or argon, to remove the oxygen from its large optical measuring area. This was the fatal weak point for the online use of these FUV-DUV spectrometers in process analyses. However, our FUV-DUV spectrometer was very small and suitable for online use. The flow rate of N_2 gas blown into the measuring area was only 0.1 L min^{-1} .

Fig. 17 shows absorption spectra in the region 190–290 nm of (a) an aqueous solution of AA with a concentration of 1.7 wt%, (b) an aqueous solution of H_2O_2 with a concentration of 0.2 wt%, and (c) a diluted PAA disinfectant solution with concentrations of 0.86, 0.23 and 0.22 wt% for PAA, H_2O_2 , and AA, respectively.⁵ The spectra in this figure were measured using a commercial spectrometer (Shimadzu UV-visible spectrophotometer, UV-2550). Fig. 18 shows their second-derivative spectra.⁵

The concentrations of PAA and H_2O_2 in disinfectant solutions were usually within the ranges 0.15–0.2 wt% and

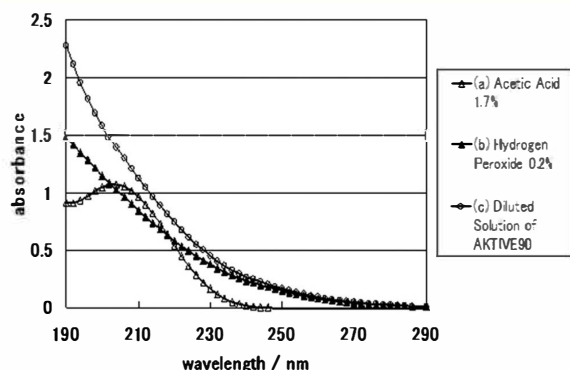


Fig. 17 FUV-DUV absorption spectra of (a) aqueous solution of AA with a concentration of 1.7 wt%, (b) an aqueous solution of H_2O_2 with a concentration of 0.2 wt%, and (c) diluted PAA disinfectant solution (AKTIVE90) with concentrations of 0.86, 0.23, and 0.22 wt% for PAA, H_2O_2 and AA, respectively. From ref. 5.

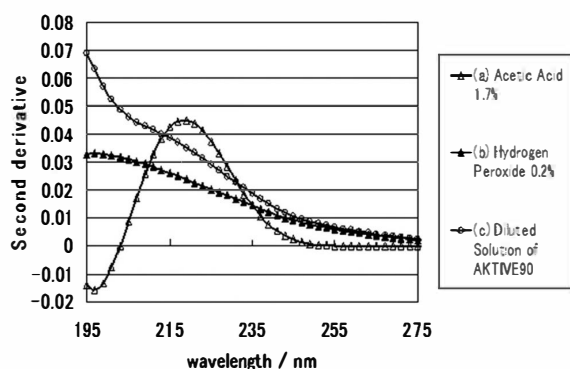


Fig. 18 Second derivative spectra of FUV-DUV absorption spectra shown in Fig. 23. From ref. 5.

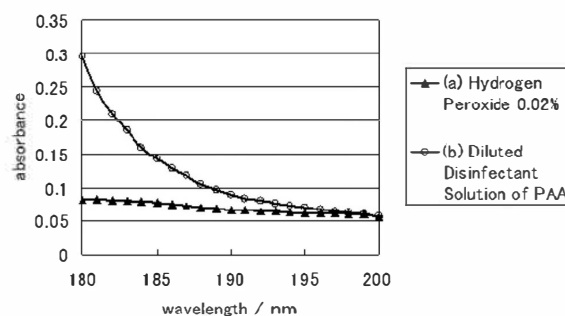


Fig. 19 FUV absorption spectra of (a) an aqueous solution of H_2O_2 with a concentration of 0.02 wt%, and (b) diluted disinfectant solution of PAA with concentrations of 0.01, 0.02 and 0.05 wt% for PAA, H_2O_2 and AA, respectively. From ref. 5.

0.5–2.0 wt%, respectively. However, in diluted disinfectant solutions, the characteristic absorption band of PAA emerged below 190 nm due to a decrease in H_2O_2 absorption intensity with the dilution of disinfectant solutions, while the intensity of the PAA absorption remained below 190 nm (Fig. 19). Fig. 20 depicts the absorption spectra at 180–200 nm of (a) an aqueous solution of H_2O_2 with a concentration of 0.02 wt%, and (b) a diluted disinfectant solution of PAA with concentrations of 0.01, 0.02, and 0.05 wt% for PAA, H_2O_2 , and AA, respectively.⁵

Using 19 types of spectral data, shown in Fig. 20 and Table 1, we developed calibration models.⁵ There was good agreement between spectral analysis and titration methods for all measured concentrations of the three species. Correlation coefficients and standard errors in predictions of PAA, H_2O_2 , and AA concentrations were 0.969 and 0.002 wt%, 0.997 and 0.003 wt%, and 0.967 and 0.01 wt%, respectively.⁵ We concluded from this result that it is possible to perform online monitoring of PAA concentration in a disinfectant solution with an accuracy of 0.002 wt%.

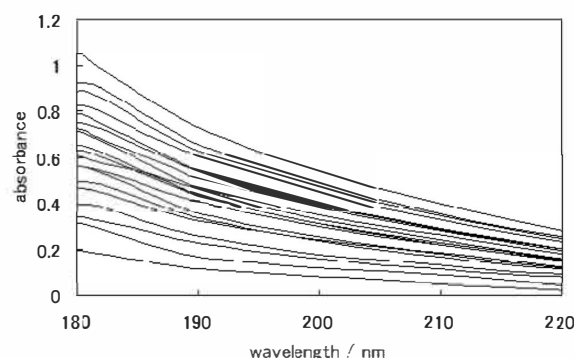


Fig. 20 FUV absorption spectra of the 19 types of sample solutions containing PAA, H_2O_2 and AA in differing concentrations. These spectra were used to construct calibration models. From ref. 5.

Table 1 Concentrations of PAA, H₂O₂ and AA in 19 sample solutions used to develop calibration models. Concentrations were calculated by multiplying dilution ratios with concentrations measured by titration before dilution. From ref. 5

Sample No.	Concentrations [wt%]		
	PAA	H ₂ O ₂	AA
1	0.020	0.105	0.095
2	0.022	0.149	0.067
3	0.019	0.128	0.050
4	0.019	0.059	0.052
5	0.019	0.104	0.098
6	0.019	0.082	0.073
7	0.019	0.082	0.067
8	0.017	0.152	0.137
9	0.018	0.128	0.115
10	0.016	0.130	0.119
11	0.011	0.134	0.149
12	0.011	0.107	0.101
13	0.012	0.087	0.034
14	0.013	0.040	0.083
15	0.013	0.039	0.033
16	0.005	0.021	0.131
17	0.003	0.021	0.017
18	0.005	0.111	0.017
19	0.004	0.068	0.063

6. FUV and DUV spectroscopy of TiO₂ and metal-modified TiO₂: the consistent relationship between electronic state and photocatalytic activity

Semiconductor materials such as TiO₂ have attracted much attention due to their photocatalytic activities and potential as next-generation solar cell materials.^{77–82} They function under irradiation with light of higher energy than their band-gap energy.⁸¹ For example, the band-gap energy of anatase TiO₂ is about 3.2 eV, and thus, anatase TiO₂ works as a photocatalyst under UV (≤ 400 nm), DUV, and FUV light. Many other semiconductor materials, such as zinc sulfide (ZnS), also have strong absorption in these regions. Their photo-induced functions are caused by charge-separation in the semiconductors; *i.e.*, electron excitations from the valence band into the conduction band with corresponding hole generation in the valence band.

Therefore, knowledge about electronic states in semiconductors is important, not only for fundamental understanding, but also in material design. In this section, FUV and DUV spectroscopy studies of TiO₂ and metal-modified TiO₂ are reviewed.

6.1 FUV-DUV spectra of TiO₂

A synchrotron radiation spectroscopy can measure the refractive spectra of TiO₂ over a wide wavelength range, including the FUV region, with strong spectral intensity as shown in Fig. 21.⁸³ Hosaka and co-workers reported the reflectance of anatase TiO₂ single crystal spectra in the 3–15 eV region in

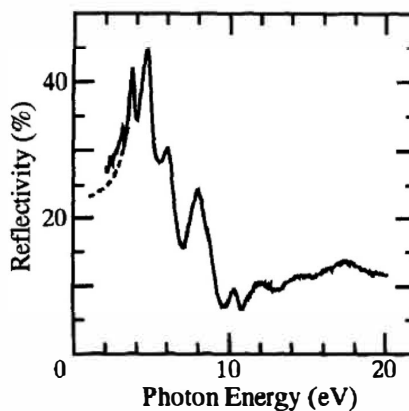


Fig. 21 Reflection spectra of an anatase TiO₂ single crystal measured by synchrotron radiation spectroscopy. From ref. 83.

1996. They assigned the measured bands based on theoretical calculations.

The absorbance index, α , of TiO₂ in the DUV region (200–300 nm) is about 10^6 – 10^7 cm⁻¹.⁸² Thus, it is difficult to measure the transmission spectra of TiO₂. In 2011, Sérgio's group reported the FUV-DUV transmission spectra of the TiO₂ film using the synchrotron radiation spectrometer.⁶⁸ However, as they reported, reliable data was limited to the DUV region (>200 nm) because of the effects of H₂O (Fig. 22). They achieved spectral measurements by the transmission method by adopting very thin films prepared by reactive magnetic sputtering.

Fig. 23a and b–e show FUV-DUV spectra measured by using an ATR-FUV-DUV spectrometer and SEM images of anatase TiO₂ nanoparticles of different sizes.²³ The FUV-DUV spectra have three small bands at ~ 160 , 200, and 260 nm. Sérgio's spectra also had very weak and broad absorption bands at ~ 200 and 260 nm (Fig. 25(a)). They assigned these two bands to the $e_g(\sigma) \rightarrow t_{2g}(\sigma^*)$ and $t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ transitions, respectively, based on the molecular orbital energy level diagrams and calculated band structures reported by other groups.^{84,85} Considering these previously reported experimental and theoretical results, the band at ~ 160 nm in Fig. 26(a) was assigned to the $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$ transition, as shown in the inset of Fig. 23(a). It should be noted that the spectra of TiO₂ nanoparticles are easily measured by the ATR-FUV-DUV spectrometer, which is a much simpler system than conventional methods such as synchrotron radiation spectroscopy.

As shown in Fig. 23(a), the spectral intensity of the 40 nm diameter TiO₂ nanoparticles (green line) was larger than that of the 200 nm diameter TiO₂ nanoparticles (blue line). The spectral intensity of TiO₂ with a 5 μ m secondary particle diameter (red line) was similar to that of smaller TiO₂. According to the SEM images shown in Fig. 23(b) and (c), the original particle diameter of 5 μ m secondary particle diameter TiO₂ was several dozen nanometres. Therefore, it can be said that spectral intensity is strongly dependent on particle size; small

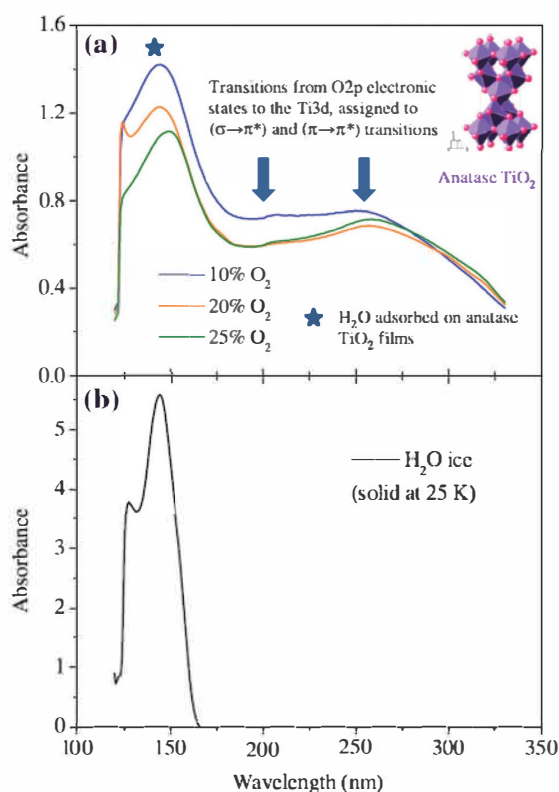


Fig. 22 Transmission spectra of (a) TiO_2 thin films and (b) H_2O (solid at 25 K) single crystal measured by synchrotron radiation spectroscopy. From ref. 68.

nanoparticles have greater spectral intensity than larger nanoparticles. This may be due to the differences in the amount of material in the evanescent field (*i.e.*, the measurable field). In the present case, the penetration depth was approximately <50 nm and, thus, the amount of 40 nm diameter TiO_2 in the evanescent wave range (Fig. 23(f)) was larger than that of 200 nm diameter TiO_2 (Fig. 23(g)).

6.2 Electronic state changes in TiO_2 upon metal nanoparticle deposition

It is well known that loading TiO_2 with metal nanoparticles improves its photocatalytic activity.^{86–91} This is because deposited metal nanoparticles work as a photo-excited electron sink, and enhance the photo-induced charge-separation efficiency. The FUV-DUV spectrometer can detect variations in the electronic state resulting from metal nanoparticle depositions.

The FUV-DUV spectra of TiO_2 and TiO_2 with metal (Au, Pd, and Pt) nanoparticles were measured under conditions where the metal nanoparticle diameter was several nanometres and the amount of deposited metal nanoparticles was ~ 0.04 wt%. Fig. 24(a) depicts a TEM image of Au nanoparticles on TiO_2 .²² As shown in Fig. 24(b), upon the deposition of metal nano-

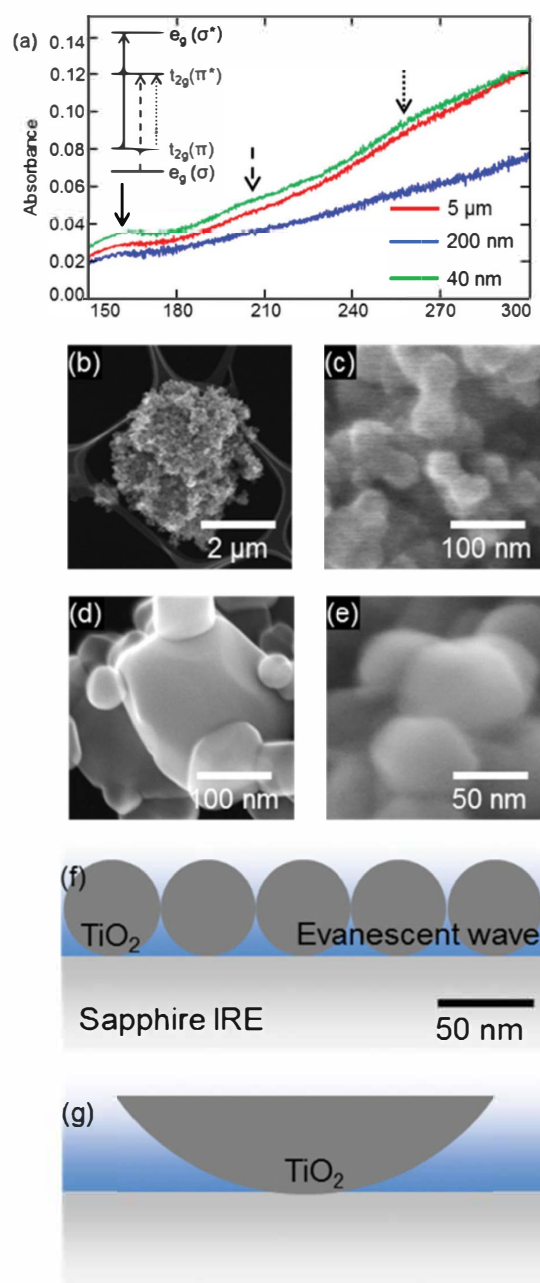


Fig. 23 (a) Typical FUV-DUV spectra of TiO_2 nanoparticles. (b–e) SEM images of TiO_2 nanoparticles with (b, c) 5 μm secondary particle diameter, (d) 200 nm diameter, and (e) 40 nm diameter. (f, g) Outline figures of TiO_2 nanoparticles in the evanescent fields for (f) 40 nm and (g) 200 nm diameters. From ref. 23.

particles, the spectral intensity in the longer wavelength region (approximately 270–300 nm) decreased, while that in the shorter wavelength region (approximately 150–180 nm) increased.²² In addition, the degree of spectral change strongly

depended on the type of metal nanoparticle used. Pt nanoparticles caused the largest change in spectral intensity, while Au nanoparticles had little effect. The work functions of TiO_2 , Au, Pd, and Pt are 4.0, 4.7, 4.9, and 5.7 eV, respectively. Considering these work functions, a larger work function in modifying metals can be said to result in larger FUV-DUV spectral changes.

In order to discuss the degree of spectral changes, the integrated intensity ratio of spectral intensity in the longer wavelength region (270–300 nm) to that of the shorter wavelength region (150–180 nm) was calculated. Fig. 24(c) plots these ratios against the difference in work function between TiO_2 and each metal,²² demonstrating a strong positive correlation between the intensity ratio and work function.

Tanabe *et al.*²² discussed the origins of the spectral changes during metal nanoparticle deposition. When TiO_2 is in contact with a metal with a higher work function than its own, TiO_2 electrons flow into the said metal, until both Fermi levels become equal. As a result, the number of electrons at relatively high-energy levels in TiO_2 , which can be excited by relatively long wavelength light, decreases. Such electron transfers results in suppression of the absorption intensity in the longer wavelength region. However, as noted above, by depositing metal nanoparticles on TiO_2 , the nanoparticles work as an electron sink for photo-excited electrons, and the charge-separation efficiency of TiO_2 is enhanced. This enhancement of charge-separation efficiency means that more electrons can be excited and more UV light can be absorbed, leading to an increase in spectral intensity in the shorter wavelength region. This process may also occur in the longer wavelength region, but the overall change in spectral intensity is affected both by this enhancement and the decrease in the number of electrons. The positive relationship between the degree of spectral changes and the work function of metals (Fig. 24(c)) indicates that the larger work function difference between TiO_2 and metal results in increased electron inflow from TiO_2 to the metal, and thus, a larger enhancement of the charge separation.

These electronic state changes should affect the photocatalytic activity. Actually, the photocatalytic activity of each sample strongly depended on the work function of the modified metal, as shown in Fig. 24(d). The photocatalytic activity is estimated based on the photodegradation reaction of methylene blue, $1 - I/I_0$, where I_0 and I are the absorbance values of methylene blue aqueous solution at 665 nm before and after UV light irradiation, respectively.²² It should be noted that there was also a strong positive correlation in Fig. 24(d), as shown in the case of Fig. 24(c). These results indicate that larger electron transfer and charge separation enhancement lead to higher photocatalytic activity.

6.3 Effects of metal sizes and shapes on photocatalytic activity

The photocatalytic activity of TiO_2 modified with metal nanoparticles is affected not only by the kind of modified metal, but also by the metal sizes and shapes.²⁵ The FUV-DUV

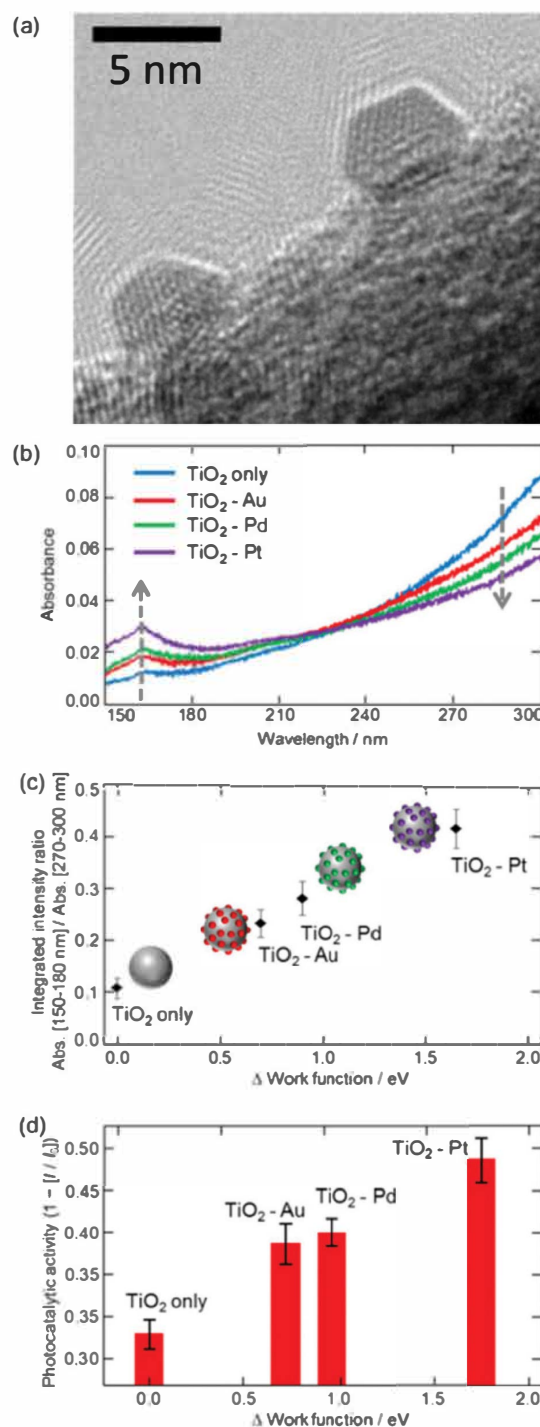


Fig. 24 (a) A TEM image of Au nanoparticles on TiO_2 . (b) FUV-DUV spectra of TiO_2 only (blue) and TiO_2 with Au (red), Pd (green), and Pt (purple) nanoparticles. (c) Integrated intensity ratio of the 150–180 nm region and the 270–300 nm region plotted versus the difference in the work function between TiO_2 and each metal. (d) Photocatalytic activity of each material. From ref. 22.

spectra of TiO_2 modified with metal nanoparticles also reflects the differences in size and shape of the metal nanoparticles.

Fig. 25a depicts the FUV-DUV spectra of TiO_2 only and TiO_2 -Au nanoparticles of 5, 10, 20, and 60 nm diameters.²⁵ SEM images of the Au nanoparticles are depicted in Fig. 25(b-e),

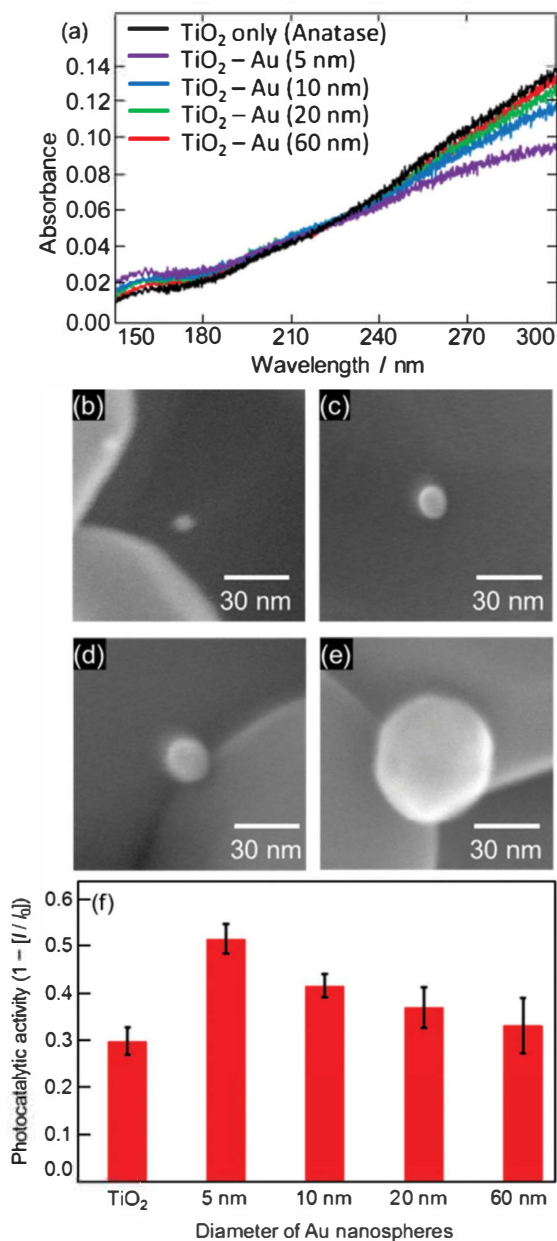


Fig. 25 (a) FUV-DUV spectra of TiO_2 only (black) and TiO_2 with Au nanoparticles with 5 (purple), 10 (blue), 20 (green), and 60 nm (red) diameters. (b-e) SEM images of (b) 5, (c) 10, (d) 20, and (e) 60 nm diameter Au nanoparticles. (f) Photocatalytic activity of each material. From ref. 25.

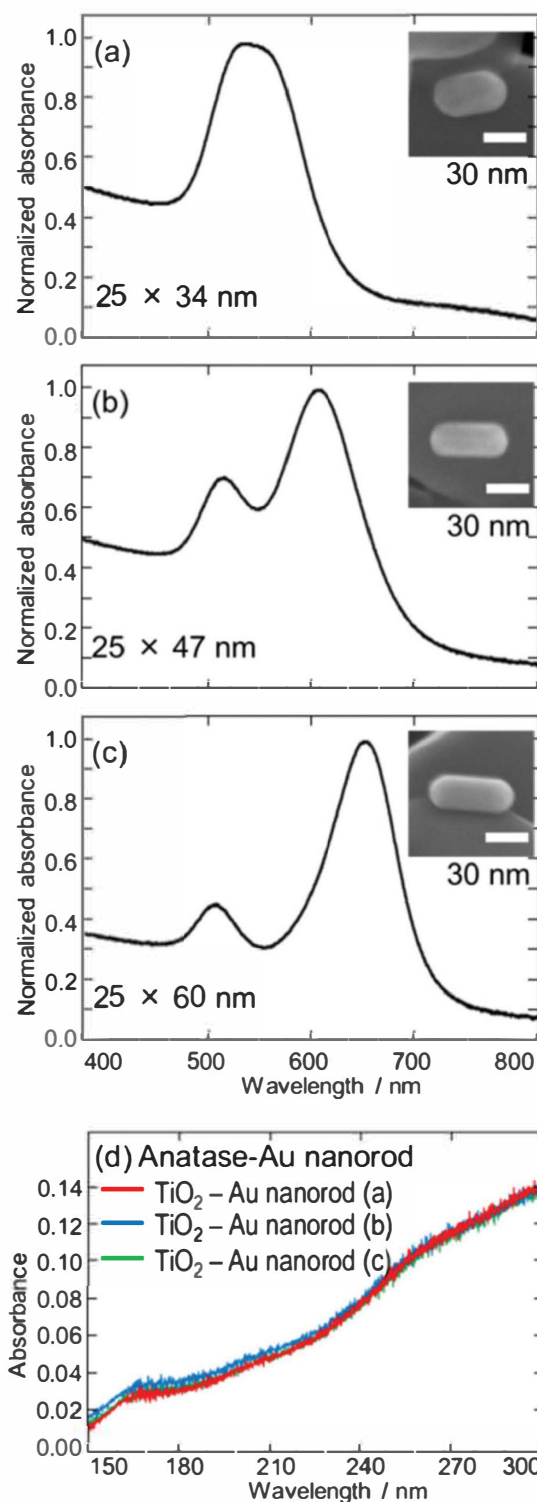


Fig. 26 (a-c) Visible absorption spectra and (inset) SEM images of Au nanorods with 25 nm diameter $\times$ (a) 34, (b) 47, and (c) 60 nm lengths. (d) FUV-DUV spectra of TiO_2 with Au nanorods of different shapes. From ref. 25.

and the number of deposited Au nanoparticles is almost the same (3.8×10^{10} on 1 g TiO_2). In all cases, upon the deposition of Au nanoparticles, the spectral intensity in the longer wavelength region decreased and that in the shorter wavelength region increased, as also observed in Fig. 24(b). It can be seen from Fig. 25(a) that smaller Au nanoparticles induced larger spectral changes, indicating that smaller Au nanoparticles had a large effect on the electronic states of TiO_2 . Even when the number of deposited Au nanoparticles was regulated so that the weights of Au were almost the same (1.3×10^{-4} g on 1 g TiO_2), the degree of spectral alternation was still increased consistently with decreasing Au nanoparticle size. The photocatalytic activity, determined from the photodegradation reaction rate of methylene blue, was also consistent with the amount of spectral changes, as shown in Fig. 25(f).

Subsequently, the effects of Au nanoparticle shapes were discussed. Fig. 26(a–c) exhibits the visible absorption spectra and the SEM images of Au nanorods with various aspect ratios. All nanorods had 25 nm diameters, and lengths of 34, 47, and 60 nm, with corresponding aspect ratios of 1.36, 1.88,

and 2.40, respectively. Fig. 26(d) shows the FUV-DUV spectra of TiO_2 with these three kinds of Au nanorods.²⁵ No obvious significant difference was present among these three spectra. Fig. 27(a) compares the visible absorption spectra of Au nanospheres and Au nanocubes of almost the same size (~ 60 nm diameter or length), and Fig. 27(b) shows the FUV-DUV spectra of TiO_2 with these two nanoparticles.²⁵ Again there was no remarkable spectral change. These results indicated that the electronic states of TiO_2 with Au nanoparticles depended more strongly on the Au particle size rather than Au shape. There was also no significant change in photocatalytic activity among TiO_2 samples with three kinds of Au nanorods, and between TiO_2 -Au nanospheres and TiO_2 -Au nanocubes.

The results illustrated in this section clearly demonstrate the potential of FUV-DUV spectroscopy as a novel investigation method for the electronic states of semiconductor materials such as TiO_2 and metal-modified TiO_2 . The electronic states revealed by the FUV-DUV spectra had strong effects on photocatalytic activity, and gave insight into the relationship between the electronic states and photocatalytic activities depending on various factors, such as the type of metal and the modified particle size, and may lead to the development of highly efficient optical materials, such as photocatalysts and solar cells.

7. Conclusions and future prospects

FUV spectroscopy is one of the old spectroscopy techniques, but it was mainly used for the gas phase. The introduction of ATR techniques has brought about a renaissance in FUV spectroscopy. Nowadays one can investigate any kind of molecules by using ATR-FUV spectroscopy. Spectra in the FUV region are very rich in information about electronic states and molecular structure. A number of molecules do not have absorptions in the DUV region, but do in the FUV region. Previously, it was difficult to observe the electronic transitions of solid and liquid samples in the FUV region. ATR-FUV spectroscopy comprises a new avenue for electronic spectroscopy. It has provided novel information about transitions involving electrons, π - π^* transitions and Rydberg transition, and a variety of molecules, such as alcohols, ketones, amides, and nylons, have been shown to have Rydberg transitions in the region 140–200 nm. In these studies, combination with quantum chemical calculations has played an important role. ATR-FUV spectroscopy allows us to investigate the electronic states in TiO_2 and related materials very easily, and has shown promise in applications in various fields. Of particular note are its applications to semiconductor materials. We have studied the relationship between the electronic states and the photocatalytic activity of TiO_2 and metal-modified TiO_2 . ATR-FUV spectroscopy is unique and useful in various kinds of water research, in terms of both basic science and practical applications. As basic studies of water and amino acids, we investigated the $\tilde{A} \leftarrow \tilde{X}$ transitions of liquid water and, for example, the cationic effect on the transitions of amino acids in

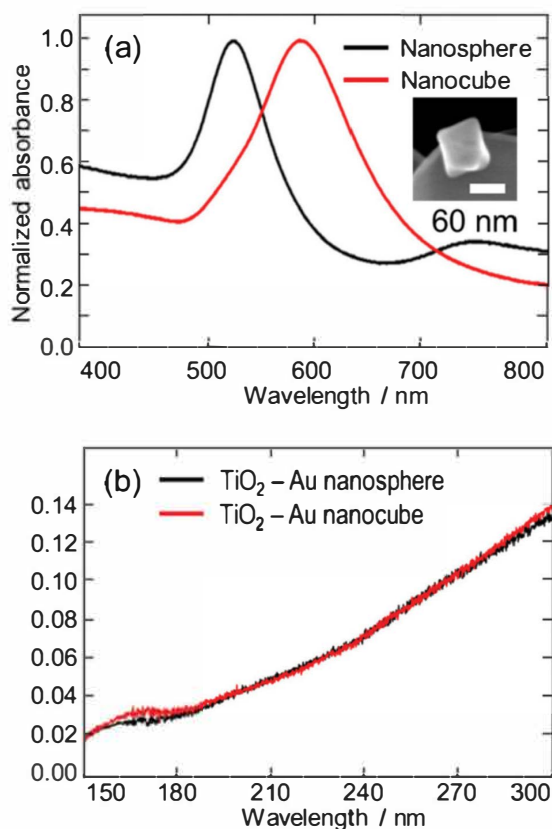


Fig. 27 (a) Visible absorption spectra of (black) Au nanospheres with 60 nm diameter and (red) Au nanocubes with the corresponding size. The inset is a SEM image of the Au nanocube. (b) FUV-DUV spectra of TiO_2 with (black) Au nanospheres and (red) Au nanocubes. From ref. 25.

aqueous solutions. The application studies of water, such as quantitative analysis of mineral water and spring water, were carried out using an original compact spectrometer. It was revealed that time-resolved FUV-DUV spectroscopy is useful for monitoring radicals in aqueous solutions.

Sato *et al.* reported the potential of FUV-DUV spectroscopy in polymer film research. FUV-DUV spectroscopy can be utilized for identification, classification, quantitative and qualitative analyses, and assessing the physical properties of polymers in a non-destructive manner for both bulk materials and thin films.

There are several promising areas for FUV spectroscopy, summarized as follows:

(1) further development of a combination of FUV-DUV spectroscopy and quantum chemical calculations is highly important for providing further insight into electronic transitions and structure.

(2) Time-resolved FUV spectroscopy when the FUV region is undeveloped. This method could be used for photochemical reactions in the FUV region.

(3) Development of compact FUV-DUV spectrometers for online and inline analysis. Water and aqueous solutions have very steep tails in the 170–200 nm region. This tail is useful in the quantitative analysis of aqueous solutions. For industrial applications, further development of compact FUV-DUV spectroscopy is needed.

(4) ATR-FUV spectroscopy is powerful for exploring ultrathin surface films, such as polymers. It may become a useful technique to provide information on surface structure, properties, and reactions.

(5) The FUV, DUV, and UV regions are seamless, so that spectral measurement of the whole FUV-DUV-UV region becomes increasingly important. For example, we recently studied the FUV-DUV-UV spectra of polymer nanocomposites containing graphene. The polymer shows bands in the FUV region while graphene yields bands in the DUV-UV region. Thus, by measuring the whole region, we can explore the electronic structure at the same time under similar experimental conditions.

(6) Geochemical and environmental chemistry applications of FUV-DUV spectroscopy may be important, because the FUV-DUV spectra of spring water samples reflect the geology of the source and environmental changes in water.

(7) Development of FUV-DUV SPR sensors, which use aluminum in their films, is very much expected because they have higher sensitivity than Vis SPR sensors. Moreover, the former has surface-selectivity and material-selectivity.

(8) FUV-DUV spectroscopy may be important not only in chemistry, but also in physics. It may shed light on condensed matter physics through electronic transition absorptions.

(9) It should be noted that there is marked progress in optical materials in the FUV region. These developments in the optical devices should further develop FUV spectroscopy.

All in all, we believe FUV spectroscopy has a bright future as a reborn spectroscopy technique for basic science and applications. In the near future it may become routine practical spectroscopy.

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