

focal point review

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Far-Ultraviolet Spectroscopy in the Solid and Liquid States: A Review

Ultraviolet (UV) spectroscopy has long been used together with visible (Vis) spectroscopy to investigate electronic transitions of a molecule. Most studies of the electronic structure of molecules using UV spectroscopy have been carried out in the 190–380 nm region because commercial UV-Vis spectrometers are available only for that region. The wavelength region shorter than 190 nm is also very rich in information about the electronic states and

structure of a molecule, but the absorptivity is very high in this region, and thus, this region has been employed to investigate mainly the electronic states and structure of gas molecules. Because condensed-phase materials with high molecular density do not transmit much light in the shorter wavelength region of the UV, reflection spectroscopy has been used to observe spectra of solid samples in the wavelength region shorter than 190 nm. However, for liquid samples one cannot generally use either absorption spectroscopy or specular reflection spectroscopy. Accordingly, UV spectroscopy in this region for liquid samples has been a relatively undeveloped research area. To solve the above difficulties of UV spectroscopy in the

wavelength region shorter than 190 nm we have recently developed a totally new UV spectrometer based on attenuated total reflection (ATR) that enables us to measure spectra of liquid and solid samples in the 140–280 nm region. We will show that spectroscopy in the wavelength region shorter than 190 nm holds considerable promise not only in basic science but also in applications such as qualitative and quantitative analysis, on-line monitoring, environmental geochemical analysis, and surface analysis. The purpose of the present review paper is to report recent progress in UV spectroscopy of solid and liquid phases in the 140–280 nm region. In this review, we refer to the 120–200 nm region to as the far-UV (FUV) region. The term “vacuum

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UV region" is no longer appropriate for the 120–200 nm region because most recent spectrometers used in this region are not evacuated but instead incorporate a nitrogen purge. This review consists of eight parts: (1) introduction to FUV spectroscopy, (2) brief history of FUV spectroscopy, (3) development of new FUV spectrometers, (4) FUV studies of liquid water and aqueous solutions, (5) FUV spectra of organic molecules in the liquid states, (6) band assignments by quantum chemical calculations, (7) potential applications of FUV spectroscopy in liquid and solid states; and (8) future prospects of FUV spectroscopy.

Index Headings: Far-ultraviolet spectroscopy; FUV; Attenuated total reflection; ATR; Electronic structure; Electronic states; Water; Aqueous solutions; On-line monitoring.

INTRODUCTION TO FAR-ULTRAVIOLET SPECTROSCOPY

We first illustrate the characteristics and usefulness of far-ultraviolet (FUV) spectroscopy by discussing the absorption spectrum of water.¹ Figure 1 shows the spectrum of water from the infrared (IR) to the FUV region.² In this figure the intensity is shown in absorbance units assuming a path length of 100 nm based on literature data of molar

absorptivities.² In the IR region one can observe two major bands at about 2900 nm (3400 cm⁻¹) and 6200 nm (1650 cm⁻¹) assigned to H–O–H stretching and bending modes, respectively. Bands due to their overtones and combinations are observed in the near-infrared (NIR) region. The ultraviolet–visible (UV–Vis) region does not show significant absorption of water, but it is noted that the FUV region contains an absorption due to water at about 150 nm that is stronger by several orders of magnitude than the H–O–H stretching band. This band is called simply the first electronic transition ($\tilde{A} \leftarrow \tilde{X}$) of water because it arises from the electronic transition of the lowest energy site.³ Specifically, this band is assigned to the transitions from the 1b₁ (n orbital) to 4a₁ (σ^* orbital) and the 3s (Rydberg) orbital. The former is the transition regarding the valence electron (nonbonding lone-pair electrons of the oxygen atom), so that it reflects hydrogen bonding of water.⁴ On the other hand, the latter is the transition to the Rydberg series, often called molecular orbital (MO) Rydbergization.^{4,5} The radii of the electron orbitals of Rydberg states are several to several tens of times larger than those of the corre-

sponding ground state, so that the Rydberg states in condensed phases are sensitive to the effects of surrounding molecules.⁶ From the peak shifts of the $\tilde{A} \leftarrow \tilde{X}$ band due to phase transitions of water one can easily understand the fact that the first electronic transition of water varies with changes in hydrogen bonding and molecular density. The band is located at 168,^{7,8} 148–150,^{9–13} and 144^{13–15} nm for the gas, liquid, and solid states of water, respectively. The band moves to a shorter wavelength region with the increase in the strength of hydrogen bonding.

Since the hydrogen bonding of water varies with temperature and hydration by ions, inorganic molecules, and organic molecules, it has long been considered that the $\tilde{A} \leftarrow \tilde{X}$ band may provide a powerful way to explore the hydrogen bonding and hydration of water and may be useful in quantitative and qualitative analysis of aqueous solutions. However, the absorption of the $\tilde{A} \leftarrow \tilde{X}$ band is so intense that one could not observe the band maxima of liquid water and aqueous solutions until the recent development of an ATR-FUV spectrometer.^{9,16}

Quantitative and Qualitative Analysis of Aqueous Solutions Using the Foot Region of the $\tilde{A} \leftarrow \tilde{X}$ Band of Water. The first electronic transition of water extends to the 200 nm region, and many basic scientific studies and applications have been done with commercial UV–Vis spectrometers using the wings of this band.^{17–26} Here, we introduce our recent studies on quantitative and qualitative analyses of aqueous solutions using the long-wavelength wing of this band. Figure 2 depicts FUV–UV spectra in the 190–250 nm region of eight kinds of natural mineral water obtained at a local supermarket and pure water.²⁴ It is noted that the eight kinds of water samples can be discriminated unambiguously without any spectral pretreatment. It is well known that nitrate ions have a significant absorption band near 210 nm.²⁴ Among the eight kinds of natural mineral water samples, Alkali Ion, Rokko, and Tateyama are the top three in terms of the concentration of nitrate ions (0.94, 0.58, and 0.31 mg/100 mL, respectively), and thus they yield an intense absorption near 210 nm. This

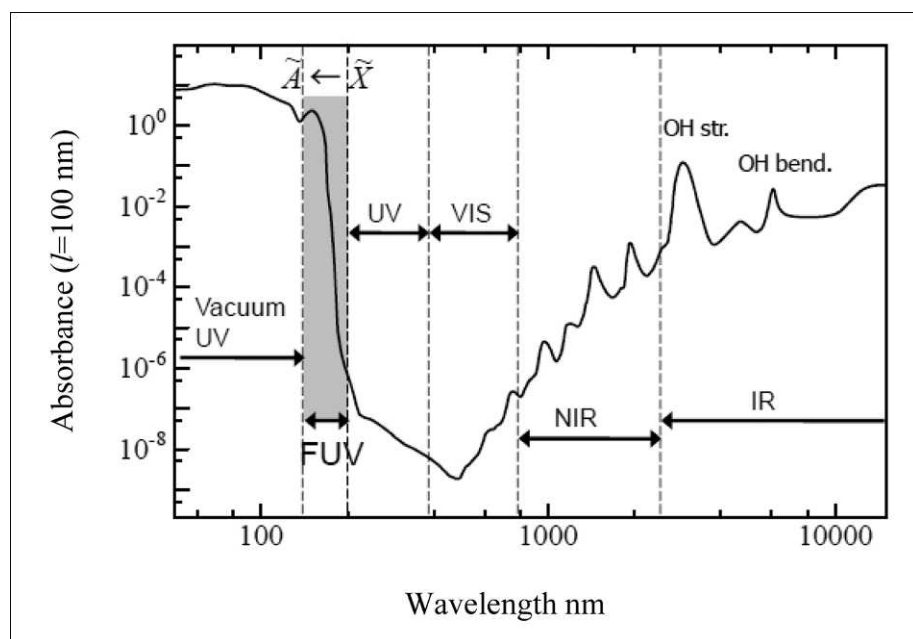


Fig. 1. The absorbance spectrum of water from the IR to FUV region, assuming a path length of 100 nm (from Ref. 2)

simple example shows the potential of the long-wavelength wing in qualitative analysis of aqueous solutions.

Figure 3 shows FUV-UV spectra of HCl aqueous solutions with a concentration range from 0 to 20 ppm.²⁴ The intensity at 190 nm varies clearly with the concentration. We developed a calibration model for predicting the concentration of HCl in the aqueous solutions by using a least squares method.²⁴ The correlation coefficient, r , and standard deviation, σ , of the model were 0.9987 and 0.18 ppm, respectively. The detection limit of this method for the determination of HCl in aqueous solutions was estimated to be 0.5 ppm. If one used a cell with a longer path length, one could expect a much better detection limit, i.e., 0.1 ppm. This is comparable with the detection limit of ion chromatography. Moreover, if one could employ a spectrometer having a stability of 0.001 absorbance units at 190 nm, the detection limit would become about 0.05 ppm. This is a good example demonstrating the usefulness of the long-wavelength wing region for the quantitative analysis of aqueous solutions.

The determination of HCl is very important in various fields such as environmental monitoring and process analyses.^{24,25,27} For example, in the washing and etching processes of semiconductors the concentration of HCl must be controlled precisely, and thus, it has become more and more important to monitor the exact concentration of HCl in an aqueous solution agent with a highly diluted concentration below 100 ppm.

We investigated the determination of NH_3 and H_2O_2 in aqueous solutions as NH_3 and H_2O_2 are important agents in the washing process of semiconductor wafer surfaces.²⁴ Figure 4A shows FUV-UV spectra of NH_3 and H_2O_2 solutions with a concentration of 100 ppm and Figs. 4B and 4C depict FUV-UV spectra of aqueous solutions containing both NH_3 and H_2O_2 .²⁴ The concentrations of NH_3 in Figs. 4B and 4C are 84 and 21 ppm, respectively, while those of H_2O_2 are varied over a concentration range of 0 to 96 ppm with an increment of 24 ppm. We used multiple linear regression (MLR) to

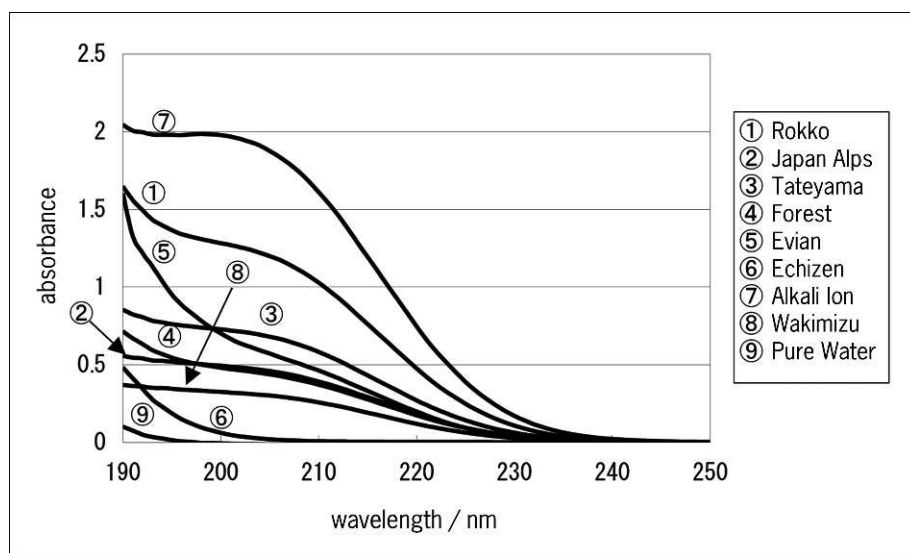


Fig. 2. FUV-UV spectra in the region of 190–250 nm of eight kinds of natural mineral water and pure water. (Reproduced with permission from Ref. 24. Copyright (2004) Society for Applied Spectroscopy.)

develop calibration models. The r and σ values for NH_3 and H_2O_2 were 0.9988 and 1.44 ppm, and 0.9999 and 0.50 ppm, respectively. The detection limit for the determination of NH_3 and H_2O_2 may be estimated to be 0.2 ppm for measurements made in a 1-cm cell. This study demonstrated that the long-wavelength wing is useful also for quantitative analysis of two-component systems.

Characteristics and Advantages of FUV Spectroscopy for the Study of Liquids and Solids. The characteristics of spectroscopy for liquid and solid studies in the FUV region may be summarized as follows:^{9–15,17–33}

- (1) In general, liquid and solid samples have very strong absorption in the 120–200 nm region. Many materials

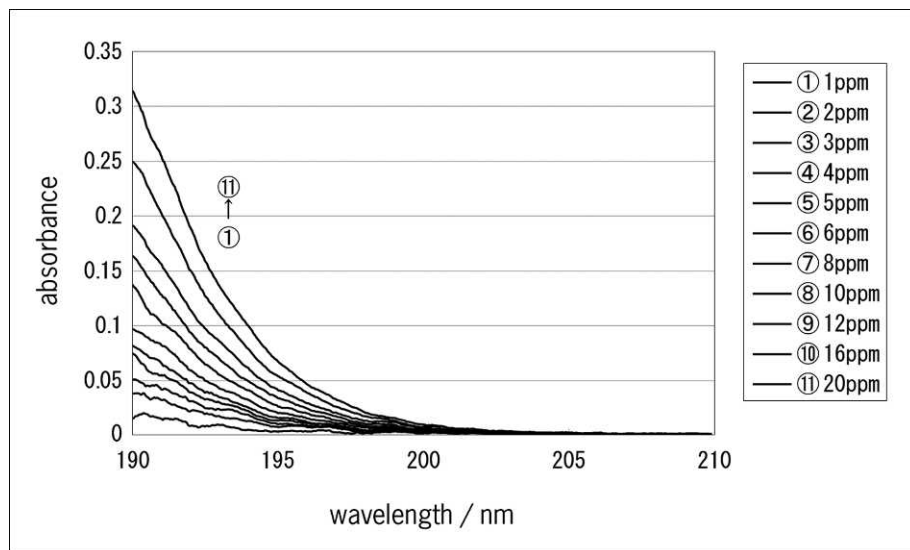


Fig. 3. FUV-UV spectra in the region of 190–210 nm of aqueous solutions of HCl at concentrations of 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0, 12.0, 16.0, and 20.0 ppm. (Reproduced with permission from Ref. 24. Copyright (2004) Society for Applied Spectroscopy.)

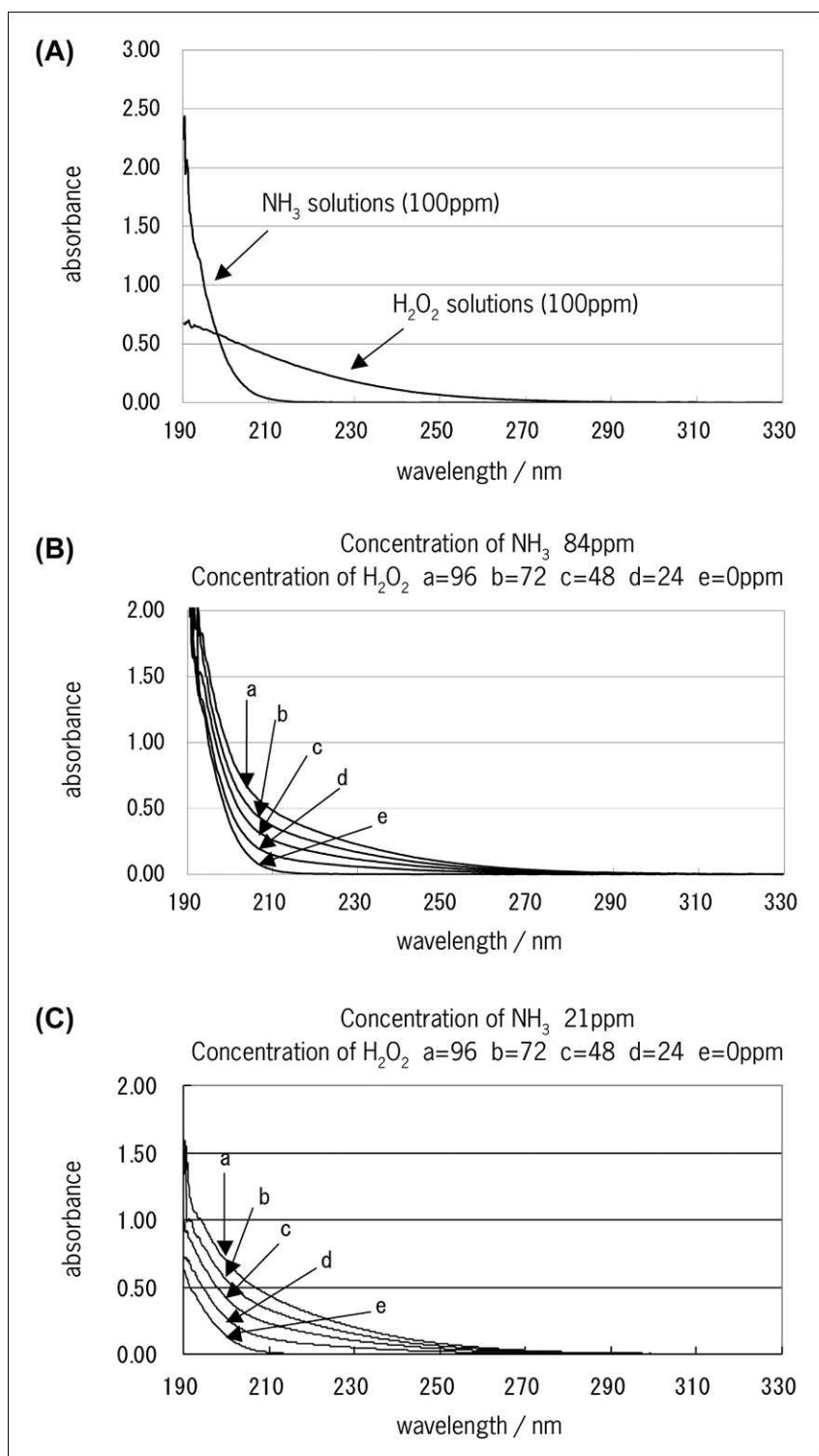


FIG. 4. (A) FUV-UV spectra in the 190–330 nm region of NH_3 and H_2O_2 solutions with a concentration of 100 ppm. FUV-UV spectra in the 190–330 nm region of aqueous solutions containing both NH_3 and H_2O_2 . Concentrations of NH_3 : (B) 84 ppm, (C) 21 ppm. Concentrations of H_2O_2 : (a) 96, (b) 72, (c) 48, (d) 24, and (e) 0 ppm. (Reproduced with permission from Ref. 24. Copyright (2004) Society for Applied Spectroscopy.)

that do not show a significant absorption in the region longer than about 200 nm yield intense absorptions in this region.

- (2) Spectroscopy in this region is concerned with the transitions between electronic energy levels including Rydberg states.
- (3) Water absorbs light strongly in the wavelength region shorter than 170 nm while it absorbs incident light poorly in the wavelength region longer than about 200 nm.
- (4) Oxygen in the air yields a very intense absorption, and thus, a spectrometer used in this region must be evacuated or purged with nitrogen gas.

FUV spectroscopy has the following advantages for liquid and solid studies:

- (1) One can explore electronic transitions and structure of a molecule. Unique information about the electronic transitions and structure of the molecule not available from ordinary UV spectroscopy can be extracted from FUV spectra.^{9,29–33}
- (2) It enables one to obtain information about Rydberg transitions of liquids.^{31–33} Many small molecules have a π – π^* transition in the FUV region, so that one can investigate π – π^* transitions by using FUV spectroscopy.
- (3) One can investigate hydrogen bonding and hydration of water, aqueous solutions, and organic molecules.^{9,30}
- (4) It is possible to apply FUV spectroscopy to qualitative analysis and discrimination analysis of various liquid and solid samples because each molecule shows a unique FUV spectrum, and FUV spectra are very sensitive to variations such as those in chemical bonding, molecular conformations, and molecular environments.^{17,20–24,26} The result in Fig. 2 is a good example of application of FUV spectroscopy to discrimination analysis.²⁴
- (5) FUV spectroscopy is very useful for highly sensitive quantitative analysis because almost all molecules give rise to strong absorption in the FUV region, and the intensity and wavelength of an FUV band are very sensitive to changes in concentration,

temperature, pH, and so on. One can see good examples of quantitative analysis by FUV spectroscopy in Figs. 3 and 4.²⁴ It is also possible to employ FUV spectroscopy for on-line analysis and process monitoring, as will be mentioned later.^{24,25,27}

Although FUV spectroscopy does have huge potential and the FUV region has long been considered a potentially fruitful area of research, the difficulty of obtaining such measurements due to high absorptivity in this region has prevented the development of FUV spectroscopy for liquid and solid phases. FUV spectroscopy for liquid and solid states has been the so-called “Sleeping Giant,” as near-infrared spectroscopy was in the past.³³ To wake up the giant it was necessary to develop FUV spectrometers based on totally new ideas.^{16,25} Thus, we have recently developed two types of FUV spectrometers; one is an ATR-FUV spectrometer that enables one to observe strong absorption bands in the FUV region without saturation,¹⁶ and another is a small portable FUV spectrometer for on-line analysis.²⁵ We will describe these FUV spectrometers later in some detail.

BRIEF HISTORY OF FAR-ULTRAVIOLET SPECTROSCOPY

For more than 50 years spectra of molecules in the gas phase in the FUV region have been studied.^{3,35-42} These studies revealed that various kinds of molecules have strong absorptions due to electronic transitions to low-lying Rydberg states in the FUV region until their vertical ionized energy (i.e., the transition energy between the electronic states with the same molecular structure (nuclear coordinate)). Many gas molecules with sufficient vapor pressure were subjected to FUV measurement, but we do not mention the history of FUV spectroscopy of gas molecules in detail here because it is outside the scope of this review. However, we will later describe several important examples of gas-phase FUV studies in relation to band assignments for FUV spectra of liquid and solid samples.

Many research groups tried to measure FUV spectra of liquid and solid

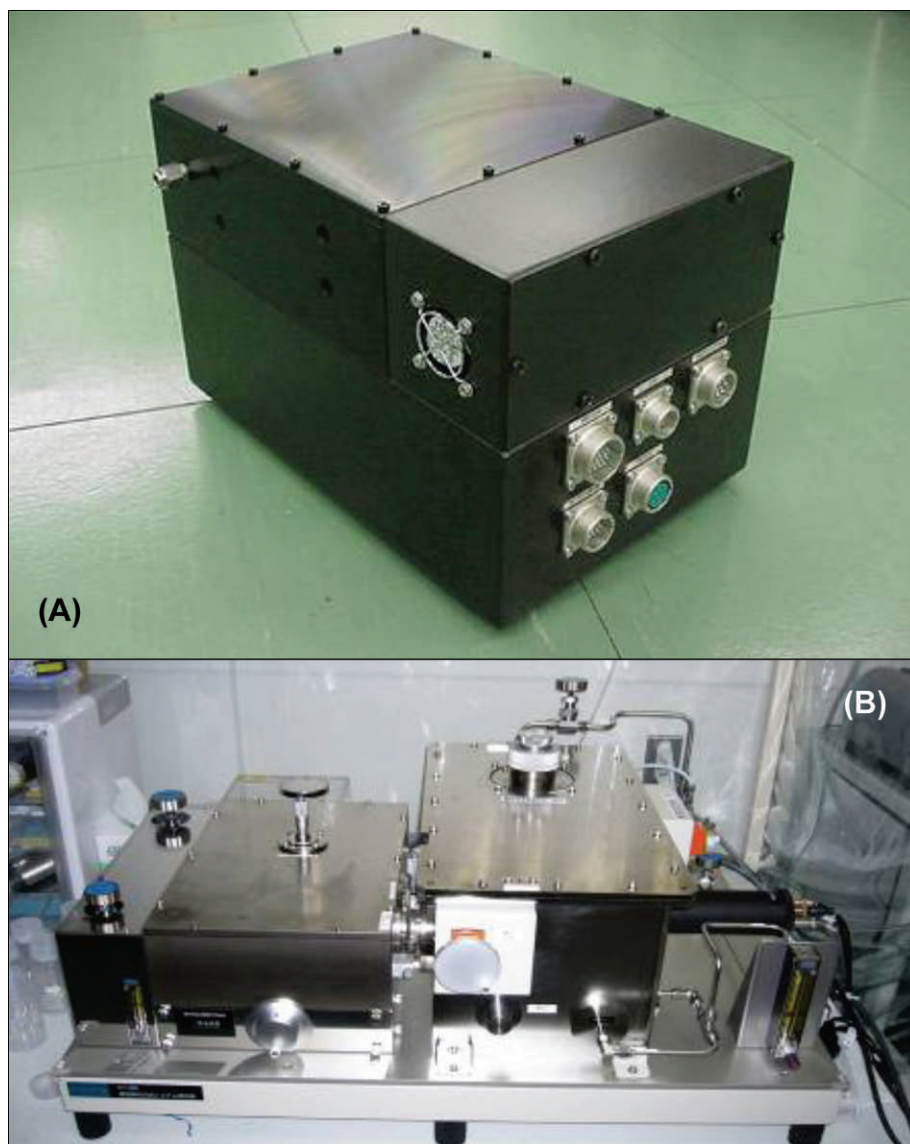


Fig. 5. (A) The compact FUV spectrometer. (B) The ATR-FUV spectrometer.

samples. For example, even in 1971 Rubloff et al.⁴³ investigated FUV spectroscopy of solids in the region of 6–36 eV (207–34 nm) using synchrotron radiation from an electron storage ring. Jung and Gress^{44,45} also used synchrotron radiation to measure transmission FUV spectra in the 115–207 nm (10.8–6.0 eV) region of CH₃OH and C₂H₅OH in liquid phases. They did not observe an absorption band at around 183 nm (6.76 eV) region, which corresponds to the $\tilde{A} \leftarrow \tilde{X}$ transition in the gas phase, but they assigned the first absorption band at 152 nm (8.16 eV) to the n-3s Rydberg excitation. Kuo et al.⁴⁶ mea-

sured FUV absorption spectra of CH₃OH in neat solid and rare gas mixtures.

As noted above, FUV spectra of water and aqueous solutions in the FUV region have been a matter of considerable interest for several years.^{11-15,17-21,47-54} Some research groups reported transmission spectra of water down to 155 nm (8.0 eV) or below upon preparing an extremely thin (<300 nm) water film.^{15,51} These techniques were not convenient and suffered from poor repeatability. Thus, instead, reflection spectra of water were measured in the wavelength region below 170 nm. When

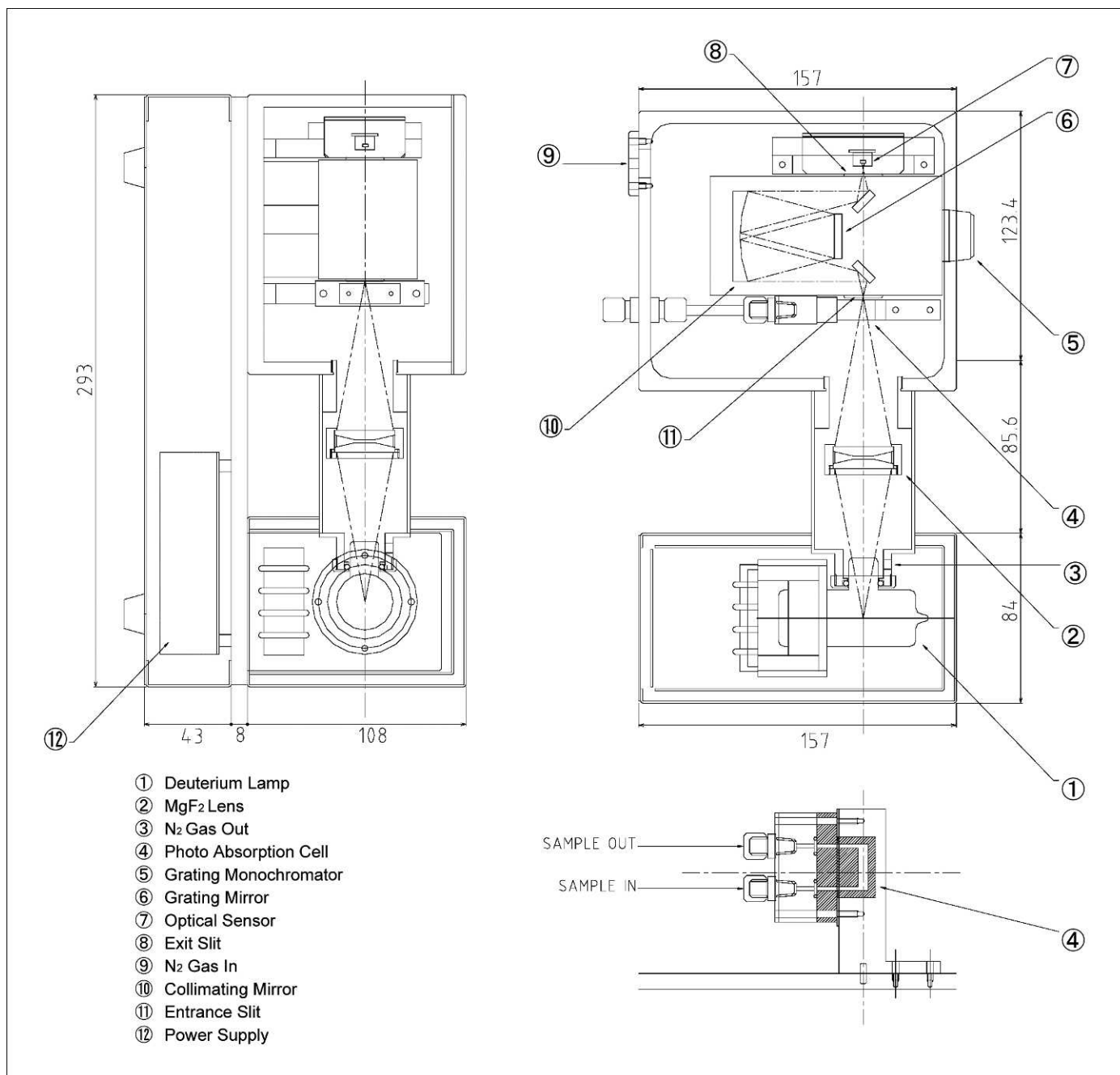


FIG. 6. Schematic diagram of the compact FUV spectrometer developed at Kwansei Gakuin University. (Reproduced with permission from Ref. 25. Copyright (2005) American Chemical Society.)

light reflects at a water surface, the reflectance is determined by the refractive index n , the absorption index k , and the angle of incidence. Painter et al.^{10,52–54} calculated the absorption spectra of water from reflection measurements, but poor sensitivity of the reflection measurements prevented the study of important questions such as how minute levels of

dissolved substances affect absorption bands of water.

Many FUV spectroscopy studies have been carried out for water, aqueous solutions, and liquids using the region of the long-wavelength wing near 190 nm because its intensity, position, and bandwidth are very sensitive to changes in hydrogen bonding and hydration of

water and aqueous solutions.^{17–21,24} For example, Quickenden and Irvin¹⁹ applied Urbach's rule,¹⁸ which assumes that the slope of the absorption edge is proportional to $\exp(-1/kT)$. Halmann and Platzner¹⁷ and Williams et al.²⁰ investigated temperature-dependent variations in the long-wavelength wing of water. Recently, Marin et al.²¹ studied

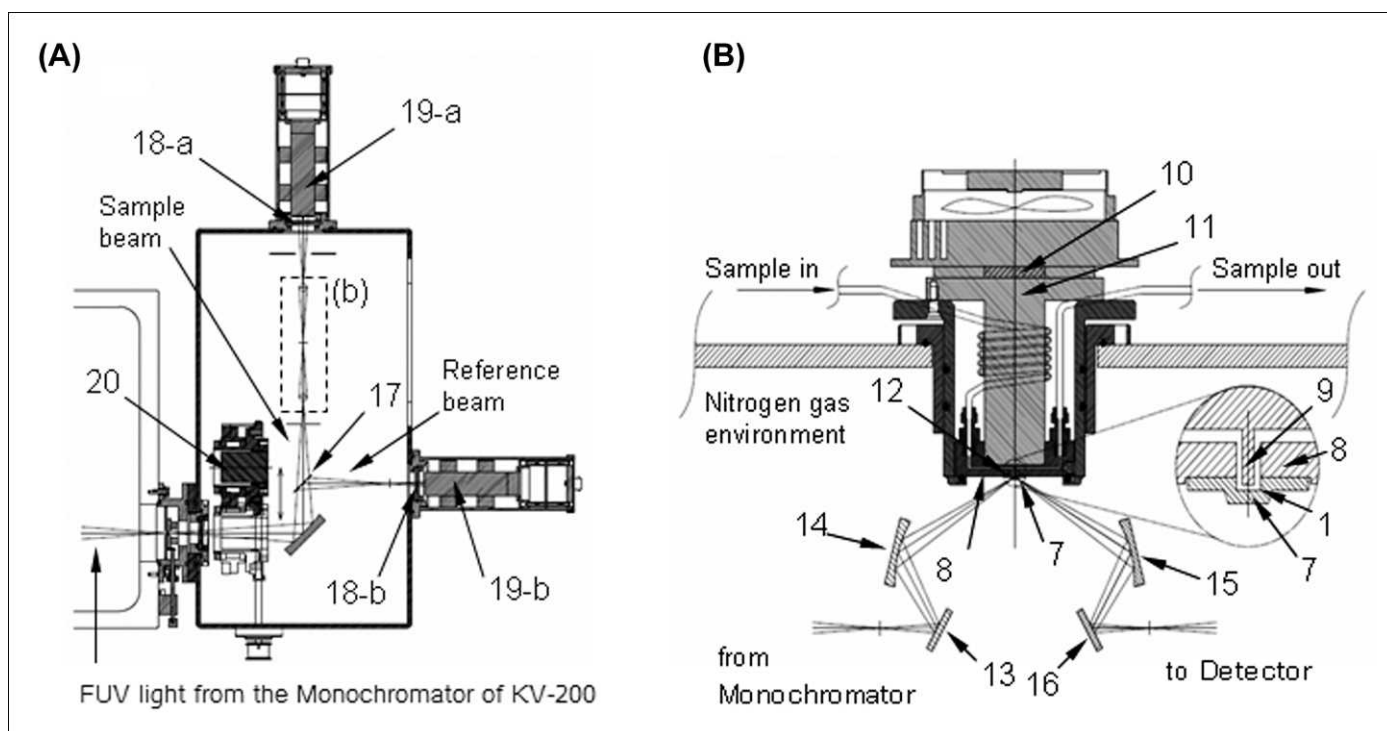


FIG. 7. Schematic diagram of the ATR-FUV spectrometer. (A) A portion of the custom design of the commercial KV-200 spectrometer. (B) Illustration of the flow cell between the IRE probe (7) and the fluorinated resin holder (8) enlarged from the area marked with the dashed rectangle in (A). (Reproduced with permission from Ref. 16. Copyright (2007) American Institute of Physics.)

the absorption edge of supercritical and subcritical water and D'Abramo et al.²² supported the experiment from theoretical calculations. Moreover, the first electronic transition of water induces ionization of water molecules. From the point of view of ionization mechanism, many experimental and calculation studies have been carried out.²⁰

The 190–250 nm region (FUV-UV region) has already been utilized for the determination of a variety of inorganic ions such as NO_2^- , NO_3^- , and Cl^- in aqueous solutions.^{26,55–60} It has also been used for the analysis of waste water,⁶⁰ spring water,²⁶ and mineral water.²⁴ Most of these analyses have been based on absorption bands of solutes such as NO_3^- rather than those of water. However, one must know that the $\tilde{A} \leftarrow \tilde{X}$ band of water and other bands due to substances such as NO_3^- overlap near 200 nm. We found that in KNO_3 solutions the long-wavelength wing of the water band show a longer wavelength shift with the increase in the KNO_3 concentration.²³

DEVELOPMENTS OF TWO NEW TYPES OF FUV SPECTROMETERS

To open up the possibility of liquid- and solid-state FUV spectroscopy for both basic science and applications we recently developed two types of FUV spectrometers with quite different designs.^{16,25} One is a compact spectrometer that enables us to measure spectra of liquid samples down to 180 nm with a simple N_2 gas purge (Fig. 5A, Fig. 6).²⁵ The size of the spectrometer is small, only 30 cm $\times$ 16 cm $\times$ 16 cm, including a UV light source, a grating, a photo-absorption cell, and an optical sensor. This spectrometer is useful particularly for on-line monitoring of aqueous solutions. The other is an ATR spectrometer that covers the wavelength range from 140 to 300 nm (Fig. 5B).¹⁶ In this spectrometer our technique uses the evanescent wave created through total reflection when light is passed through an internal reflection element (IRE) in contact with a sample. By using this instrument one can detect the whole first

electronic transition absorption band of water down to 140 nm.

A Compact FUV Spectrometer. Figure 6 shows a schematic of the compact FUV spectrometer.²⁵ FUV light from a deuterium lamp (1) is passed through a photo-absorption cell (4) and then dispersed with a reflection grating (6). The optical path length of the cell used was 0.5 mm and the transmittance of the UV radiation for an aqueous solution within the cell was ~ 0.45 at 180 nm. The deuterium lamp, which we used as the FUV light source, has a window made of MgF_2 for measurements made in the 180–220 nm region. The grating had 2400 lines/mm and the blazed wavelength was 250 nm. Since this spectrometer was designed for direct determination of industrial components in aqueous solutions in on-line monitoring, we paid much attention to detecting enough brightness in preference to the resolution of detectable wavelength.²⁵ A thin diamond film sensor was used as an optical sensor for the FUV spectrometer because of the bright FUV radiation. For

on-line monitoring we do not need very high resolution of wavelength because, in general, absorption bands of components in the FUV-UV region are broad and we employ the shoulders of their bands in the 180–220 nm region. Thus, we used our spectrometer with a 0.6 mm slit that enables us to measure the spectra with a bandwidth of ~ 5 nm.

The spectrometer is very small because we use a diamond film that is very small in size. A diamond film has optical sensitivity in the region from 150 to 220 nm and operates with a simple power supply circuit.^{61,62} Recently, diamond films have often been used to monitor the optical intensity of excimer lasers. However, to date little attention has been paid to their use as optical sensors for FUV spectrometry because the optical sensitivity of the sensor is not very high, although it is very small. The detector module of a diamond film has dimensions of 3 cm $\times$ 3 cm $\times$ 1 cm including an electric circuit. Commercial FUV spectrometers use a photomultiplier tube, which needs very high voltage operation and occupies a large volume. Furthermore, they need a large vacuum pump or a great deal of purge air. Our spectrometer requires only 0.1 L/min as the flow rate of N₂ gas blown into the measuring area.

This spectrometer was applied first to direct determination of peracetic acid (PAA), hydrogen peroxide, and acetic acid (AA) in disinfectant solutions by using their absorption bands in the 180–220 nm region.²⁵ The FUV method we proposed does not require any reagents or catalysts, a calibration standard, or a complicated procedure for the analysis. The detection limit for PAA using this new FUV spectrometer was evaluated to be 0.002 wt%, and the dynamic ranges of the measured concentrations were from 0 to 0.05 wt%, from 0 to 0.2 wt%, and from 0 to 0.2 wt% for PAA, H₂O₂, and AA, respectively.²⁵

The difference in the measurable shortest wavelength limit between this spectrometer and commercial UV-Vis spectrometers is only 10 nm (180 nm versus 190 nm), but this small difference makes a huge difference in sensitivity particularly for aqueous solutions because, in general, absorbance at 180 nm

of an aqueous solution is much larger than that at 190 nm (see Fig. 1).

An ATR-FUV Spectrometer. Higashi and coworkers designed and constructed a novel ATR based FUV spectrometer.¹⁶ In this spectrometer the design of a very small internal reflection element (IRE) probe has led to successful measurement of the entire $\tilde{A} \leftarrow \tilde{X}$ transition absorption band of water and aqueous solutions.

Figure 7 shows a schematic diagram of this instrument.¹⁶ Figure 7A depicts a portion of the custom design of a commercial FUV spectrometer (KV-200, Bunkou-Keiki, Hachioji, Japan). Figure 7B illustrates a flow cell unit formed between the sapphire IRE probe (7) and a fluorinated resin holder (8) enlarged from the area marked with a dashed line (part b) in Fig. 7A. The probe is fixed in place by the fluorinated resin holder (8), with the flow sample cell formed by a space between the fluorinated resin guide (9) and the aperture (1) of the probe. A liquid sample for measurement is drawn into the 2 mm diameter aperture in the IRE probe, and the scaled inner environment is purged and then filled with pure nitrogen or argon gas. To control the sample temperature over the range of 5–80 °C a Peltier element (10) is in contact with the probe holder (8) by a heat pipe (11).

Figure 8 depicts the developed IRE probe.¹⁶ 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. Materials such as sapphire with a higher refractive index than water have insufficient transmission, while those with sufficient transmission (e.g., MgF₂, CaF₂, and synthetic quartz) have lower refractive indices than water in the FUV region. Although sapphire lacks sufficient transmission in the wavelength region shorter than 160 nm, Higashi et al.¹⁶ 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 fact,

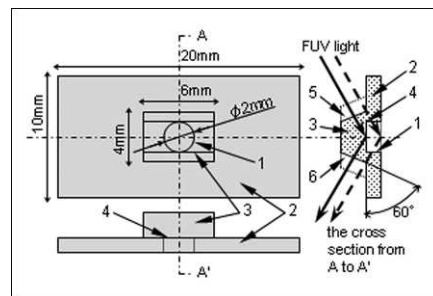


Fig. 8. Description of the ATR probe. It consists of a trapezoidal internal reflection element (IRE) and a rectangular base plate with a cylindrical aperture. The probe consists of an aperture positioned within a rectangular base plate and a small IRE, which fully seals the aperture through a heat-fused surface, resulting in good optical contact. Adhesives are not used to prevent sample contamination and residue from remaining in the device. The broken line shows the ordinary size of a small IRE without an aperture. (Reproduced with permission from Ref. 16. Copyright (2007) American Institute of Physics.)

the internal transmittance of vacuum UV grade of sapphire near 160 nm is more than 0.30 with a path length of 5 mm or less. We therefore used this material for the IRE with a single reflection and an angle of incidence of 60°.

The ATR probe consists of two parts; a trapezoidal IRE and a rectangular base plate with a cylindrical aperture (1). These two parts are integrated by an optical contact technique. The base plate sits on the same side of the IRE at which it comes into contact with the sample through the aperture at the interface surface (4). The IRE itself has both an incident surface (5) and an outgoing surface (6), which are not in contact with the sample. FUV light entering the incident surface perpendicularly strikes the interface surface and then perpendicularly exits the outgoing surface. The size of the IRE is very small, 4.0 $\times$ 6.0 $\times$ 2.0 mm³. When water is used as a sample, the penetration depth of the evanescent wave at 150 nm (9.3 eV) is about 20 nm. For this instrument, any kind of neat liquid or solution can be used as the sample. Solid samples can also be investigated but good contact between the IRE and a solid sample is required.

A 30 W deuterium lamp was used as the light source for the KV-200 spectrometer, which incorporated a diffrac-

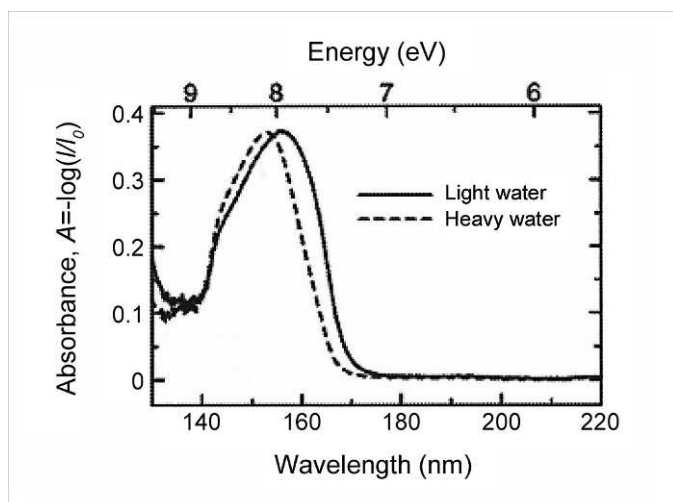


Fig. 9. ATR-FUV spectra of light and heavy water in the 140–220 nm region. (Reproduced with permission from Ref. 16. Copyright (2007) American Institute of Physics.)

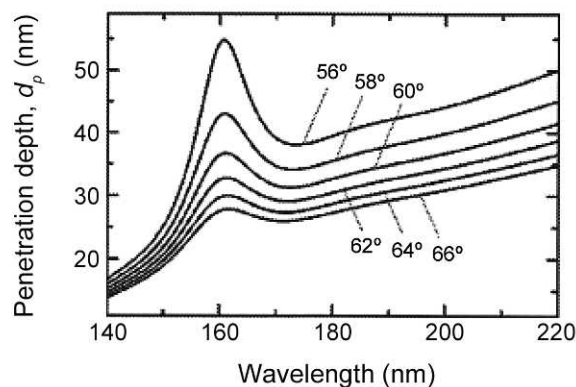


Fig. 10. Simulation of penetration depth of the evanescent wave in water for incident angles over the range of 56°–66°. (Reproduced with permission from Ref. 16. Copyright (2007) American Institute of Physics.)

tion grating with 2400 grooves/mm and a blazed wavelength of 150 nm. As depicted in Fig. 7A, the FUV light from the monochromator is split into a reference beam and a sample beam by a MgF₂ beam splitter. The reflected light and the reference beam finally pass through a synthetic quartz plate coated with sodium salicylic acid, which fluoresces. Fluorescence of each beam is then detected by a photomultiplier.

Attenuated total reflection FUV spectra of light and heavy water in the 140–220 nm (9–6 eV) region obtained using the above instrument are shown in Fig. 9.¹⁶ It is noted that the entire first electronic transition band of water can be detected by using the ATR-FUV spectrometer. It is interesting to note that the peak of D₂O lies at higher energy than that of H₂O. This shift is attributed to the difference in vibrational zero-point energy. The result in Fig. 9 reveals that the $\bar{A} \leftarrow \bar{X}$ band of water is located at about 156 nm; however, one must remember that refractive index is a function of wavelength. The penetration depth of the evanescent wave d_p is strongly dependent on the ratio of the refractive indices of the IRE, n_1 , and sample, n_2 , as follows:

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

Higashi et al.¹⁶ developed a simulation of penetration depth of the evanescent wave in water for incident angles over the range of 56°–66° as shown in Fig. 10. For this calculation, the reported refractive indices of water¹⁰ and sapphire⁶³ were substituted into Eq. 1.

A marked increase of the penetration depth happens at around 161 nm as shown in Fig. 10, as the refractive index of water has a maximum value over 1.65 between normal and anomalous dispersions at 159 nm (see Fig. 11A). Figure 11A shows the results of Painter and coworkers¹⁰ of the optical constants of water.¹⁶ The dash-dot line in Fig. 11A represents refractive index and the solid line depicts the absorption index of water. The refractive index n and the absorption index k have distinct maxima at 159 and 151 nm, respectively. Broken and solid lines in Fig. 11B show the calculated and measured results, respectively, of the ATR-FUV spectra at a variety of incident angles. It is noted that the peak wavelength of both the measured and calculated ATR spectra for different incident angles of $\theta = 56^\circ$ – 64° are closely matched at around 157 nm. The deviation of experimental and calculated results may be caused by the range of incident angles in the measuring beam focused on the IRE surface.

As mentioned above, the ATR-FUV spectra obtained by this device show a

specific distortion in the evanescent wave, but Higashi et al.¹⁶ demonstrated that calculations based on the Fresnel formula may be used to correct for this distortion

This spectrometer has been used for both basic research on hydrogen bonding and hydration of water and electronic transitions and structure of organic molecules such as alcohols and ketones and has been applied to qualitative and quantitative analysis and on-line monitoring, as will be described later.^{9,27,30–33}

ATR-FUV STUDIES ON LIQUID WATER AND AQUEOUS SOLUTIONS

Direct Observation of the Absorption Bands due to the First Electronic Transition of Liquid H₂O and D₂O.

The origin of the low-lying electronic transition band of water, $\bar{A} \leftarrow \bar{X}$, has still not been conclusively established. The peak energy of the $\bar{A} \leftarrow \bar{X}$ band of water shifts from 7.4 eV (168 nm) to 8.6 eV (144 nm) upon the phase transition from vapor to ice.^{8,13} In the case of liquid water, the observed peak energy is approximately 8.3 eV, which decreases on heating^{9,21} or on addition of a salt. As discussed above, the shift can be generally explained in terms of a change in the hydrogen bonding in water that accompanies the perturbation of the lone-pair valence bond edge. Moreover,

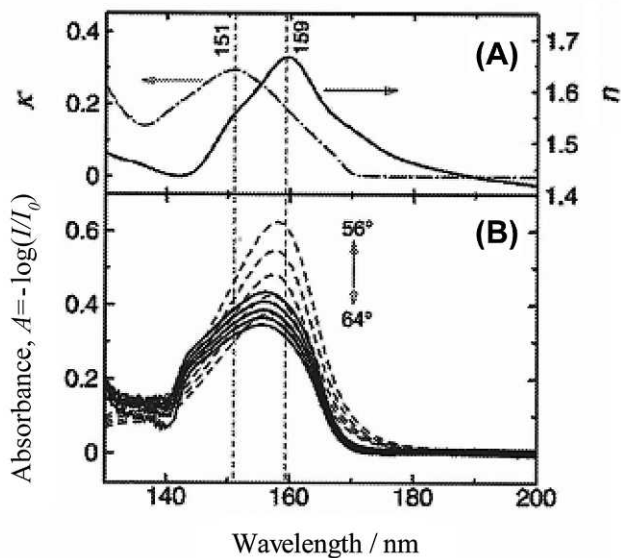


Fig. 11. (A) The refractive indices of water (dash dot line) and the absorption index (solid line) of water. (B) Broken and solid lines show the calculated and measured results, respectively, of the ATR-FUV spectra at a variety of incident angles. (Reproduced with permission from Ref. 16. Copyright (2007) American Institute of Physics.)

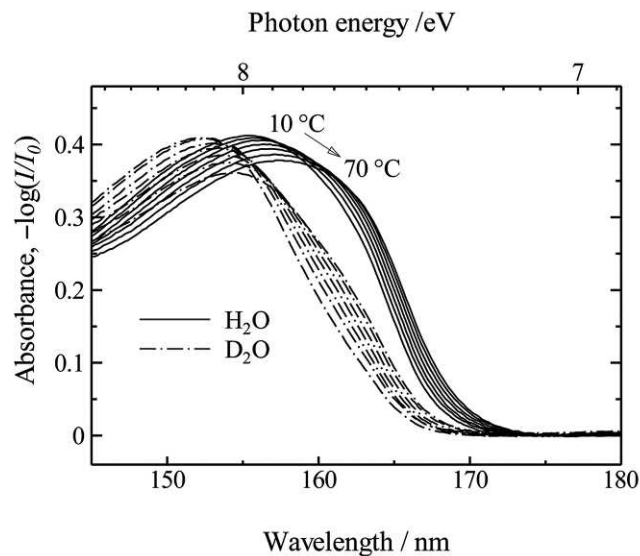


Fig. 12. ATR-FUV spectra of H_2O and D_2O at different temperatures. (Reproduced with permission from Ref. 9. Copyright (2008) American Institute of Physics.)

the shift of the absorption band of water may be attributed to solvation and Rydbergization effects or to molecular excitons.

The $\tilde{A} \leftarrow \tilde{X}$ band of water is so strong that it was difficult to measure the band maxima of the $\tilde{A} \leftarrow \tilde{X}$ band of liquid water and aqueous solutions. Therefore, the positions of the band maxima of liquid water and ice were determined by regular reflection measurements.^{11,52-54} Ikehata et al.⁹ have recently succeeded in the direct observation of the entire $\tilde{A} \leftarrow \tilde{X}$ absorption band, including the band maxima, by using the ATR-FUV spectrometer since the ATR geometry reduces the absorbance markedly in comparison to transmission measurements.

Figure 12 shows ATR-FUV spectra of H_2O and D_2O at different temperatures (10–70 °C).⁹ The maximum absorptions for all the D_2O spectra lie at higher energies than the H_2O spectra at the same temperature. Specifically, the band maxima at 20 °C are 155 and 152 nm for H_2O and D_2O , respectively. This difference is attributed to the difference in the vibrational zero-point energies. Marked red shifts are observed upon heating for

the spectra of H_2O and D_2O , and the peak intensities decrease on heating. According to a theoretical prediction by the Fresnel formula, the latter may be partly due to a change in the refractive index of water, which is a typical feature of ATR measurements. The ATR spectrum of water is not identical to its transmission spectrum. ATR spectra involve shifts not only in peak intensity but also in the wavelength. Ikehata et al.⁹ used the Kramers–Kronig transformation (KKT) and Fresnel formulas to separate the contributions of the absorption and refractive indices. Figures 13A and 13B display the calculated results of refractive index n for H_2O and D_2O , respectively.⁹ It can be seen from Fig. 13 that every spectrum of the optical indices shifts to the low-energy side on heating. The refractive index spectra (n) exhibit an anomalous dispersion region over 7.7 eV (161 nm) with a maximum value of 1.59. In this way, systematic measurements of the ATR-FUV spectra of H_2O and D_2O with heating from 10 to 70 °C and the analysis of KKT reveal that the $\tilde{A} \leftarrow \tilde{X}$ band of liquid water shifts to lower energy on heating. This result is in good agreement with the red

shift observed in the low-energy band tail of the $\tilde{A} \leftarrow \tilde{X}$ band.

Effect of Cations on the First Electronic Transition of Liquid Water. It is known that the energy of the $\tilde{A} \leftarrow \tilde{X}$ transition of water is characterized by thermodynamic cycles showing adiabatic electron affinity and solvation energy of internal (OH^-) and/or external anionic defects.^{20,64} The effect of anions on the long-wavelength edge of the $\tilde{A} \leftarrow \tilde{X}$ band of water has been analyzed from the viewpoint of the Urbach rule,^{19,20,23} while the effect of cations has not been investigated extensively. The effect of alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) on the first electronic transition ($\tilde{A} \leftarrow \tilde{X}$) of liquid water was investigated by ATR-FUV spectroscopy.³⁰

Figure 14 displays ATR-FUV spectra of 1 M alkali metal (Li, Na, K, Rb, and Cs) nitrate solutions and pure water measured at 25 °C.³⁰ The corresponding spectra of aqueous solutions of 1 M alkali metal bromides were also measured. A band at 6.1 eV is due to the $\pi-\pi^*$ transition of NO_3^- and that at 8.0 eV arises from the first electronic transition ($\tilde{A} \leftarrow \tilde{X}$) of water. Note that the spectral shapes of the $\pi-\pi^*$ transition band are

perfectly matched for all the cations, while the first transition band varies with the cations. The absorbance of the $\tilde{A} \leftarrow \tilde{X}$ band decreases with the addition of nitrate salts and with decreasing cation size. In addition, the peak energy increases slightly with the decrease in the cation size.

In Fig. 15A, the ATR absorbance, $-\log(I/I_0)$, where I and I_0 represent detected light intensities for sample solution and air, respectively, of the $\tilde{A} \leftarrow \tilde{X}$ band maxima of water is plotted against the reciprocal of the ionic radii of cations, R_c^{-1} .³⁰ Although the plots of the ATR intensities seem to have no correlation with R_c^{-1} , the nitrate and bromide show similar profiles. In Fig. 15B, the refractive indices measured with the D line of sodium (589 nm), n_D , of 1 M bromide and nitrate solutions are plotted against R_c^{-1} . Interestingly, the profiles in Fig. 15A are very similar to the plots of the refractive indices (Fig. 15B). Ikehata et al.³⁰ considered that the change in the absorption intensity of the $\tilde{A} \leftarrow \tilde{X}$ band is predominantly attributed to the refractive indices of the salt solutions. They confirmed the effect of refractive index on an ATR spectrum by a simple optical simulation based on the Fresnel equations. Simulated ATR spectra in the $\tilde{A} \leftarrow \tilde{X}$ band of water for samples with different refractive indices are shown in Fig. 16.³⁰ Optical constants of water and sapphire (IRE) were modeled by suitable functions of wavelength comparable to the reported values. It can be seen in Fig. 16 that a difference for the increase of 0.003 in the refractive index produces an increase of the ATR absorbance at the peak of the $\tilde{A} \leftarrow \tilde{X}$ band of approximately 0.005. It is becoming apparent that the differences of the ATR absorbance of the $\tilde{A} \leftarrow \tilde{X}$ band of water are predominantly due to the refractive indices of solutions.

Figure 17 shows peak energies (E) of the $\tilde{A} \leftarrow \tilde{X}$ band in ATR-FUV spectra of alkali metal nitrate and bromide solutions versus the reciprocal of the ionic radii of cations.³⁰ The solid lines in Fig. 17 are linear fits to the data obtained by fitting to the equation

$$E = aR_c^{-1} \Delta E \quad (2)$$

The intercepts, ΔE , show a significant difference between the nitrate and bro-

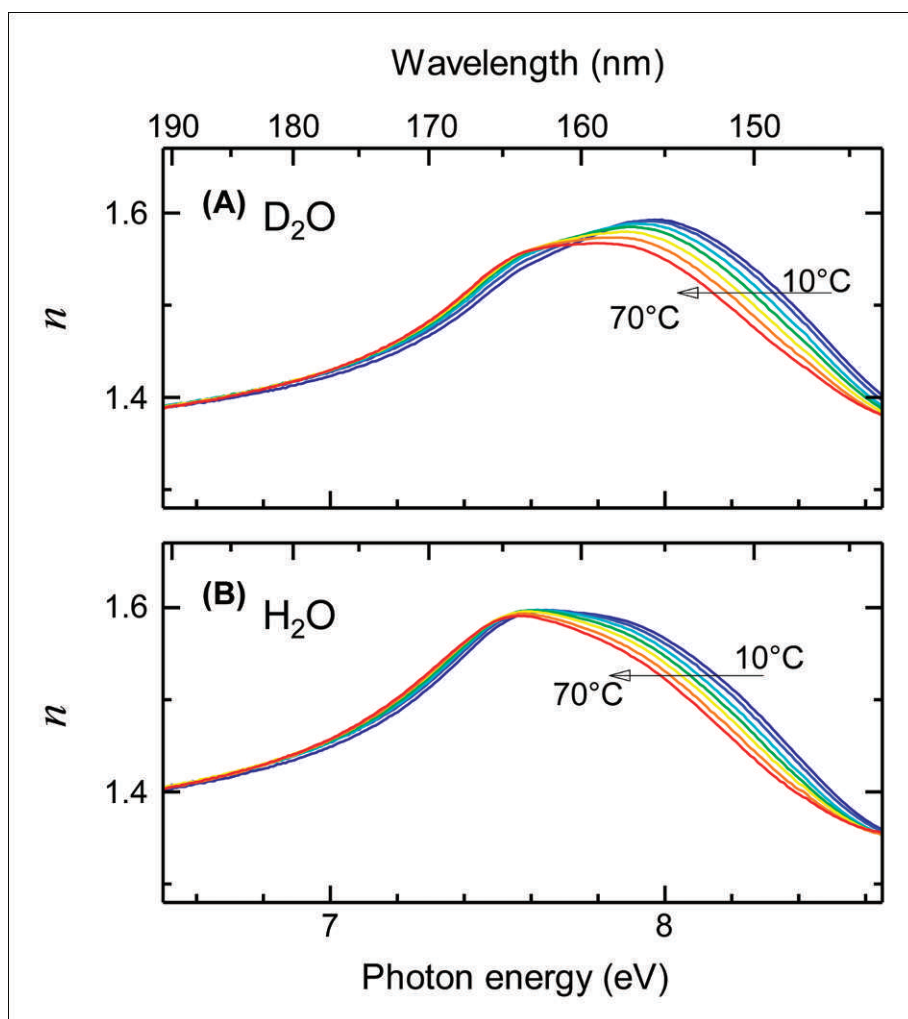


Fig. 13. Refractive indices n of (A) H_2O and (B) D_2O converted from the ATR-FUV spectra shown in Fig. 12 by the Kramers–Kronig transformation. (Reproduced with permission from Ref. 9. Copyright (2008) American Institute of Physics.)

mide solutions (Fig. 17). The slopes, a , attributed to the cations are approximately 0.04 for both the nitrate and bromide series. The Gibbs energies of solvation, ΔG , are proportional to R_c^{-1} of ions that interact via a Coulomb force and are also related to the $\tilde{A} \leftarrow \tilde{X}$ transition energy.⁶⁴ On the basis of an analogy between the linear relation in Fig. 17 and the Born equation,⁶⁵

$$\Delta G_{\text{Bom}} = q^2/2(1-1/\epsilon)R_c^{-1}$$

Ikehata et al.³⁰ suggested that the energy shift of the $\tilde{A} \leftarrow \tilde{X}$ transition due to the cations is also characterized by the solvation energy.

FUV SPECTRA OF ORGANIC MOLECULES IN THE LIQUID STATE

Band Assignments of FUV Spectra of Organic Molecules in the Liquid State. Several examples of the measurement of FUV spectra of organic molecules as pure liquids by using transmission methods were reported before the ATR-FUV method was introduced. However, unequivocal band assignments have never been established for FUV spectra of liquid organic molecules because of the following reasons.

- (1) The number of liquid organic molecules whose FUV spectra had been

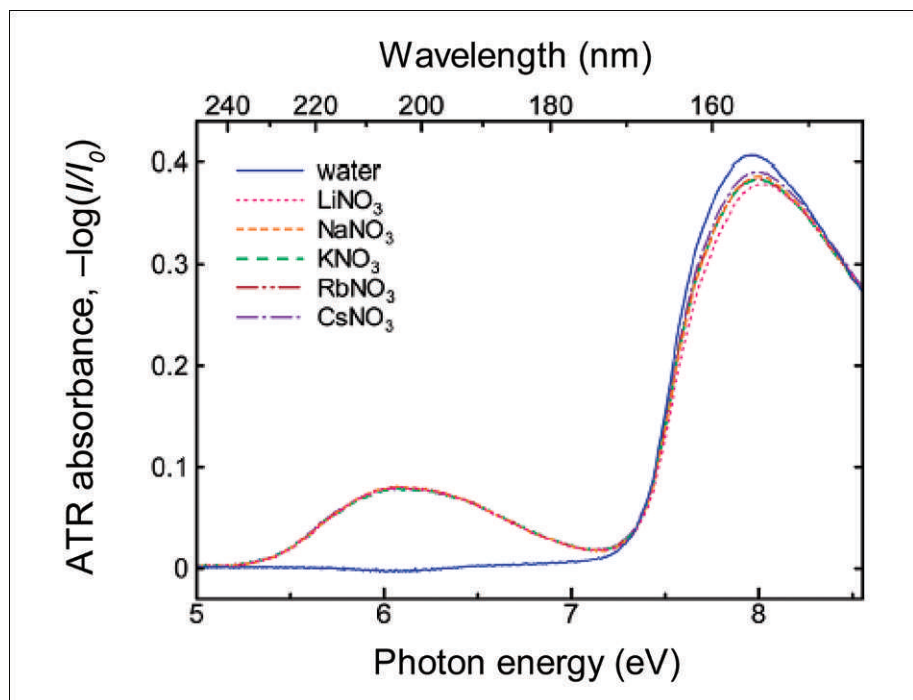


Fig. 14. ATR-FUV spectra of aqueous solutions of 1 M alkali metal nitrates measured at 25 °C. (Reproduced with permission from Ref. 30. Copyright (2010) American Chemical Society.)

measured was very limited. There has been no systematic study for FUV spectra of liquid organic molecules.

- (2) There have been only a few studies in which liquid-state spectra have been compared with the corresponding gas-phase spectra. An FUV spectrum changes markedly upon going from the gaseous to the liquid state. In the latter there are interactions such as hydrogen bonding and exchange repulsions between valence electrons of neighboring molecules.
- (3) In general, FUV spectra of liquid organic molecules are broad and their spectral structure is not clear because of the interactions mentioned above. Thus, it is not easy to determine the number of bands involved in what may appear to be a single broad band.

In order to develop band assignments of FUV spectra of liquid samples, first of all, one must measure FUV spectra of many basic compounds in the liquid phase such as *n*-alkanes, branched

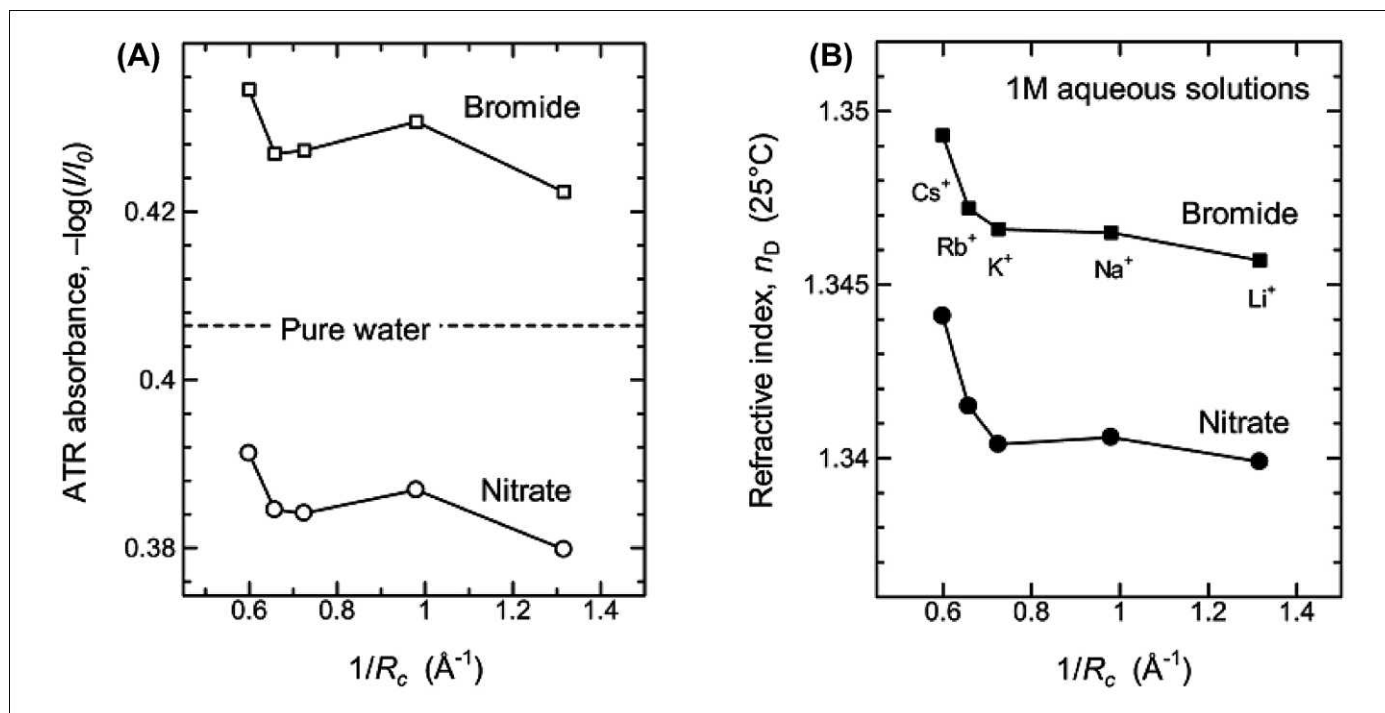


Fig. 15. (A) Plots of ATR absorbance, $-\log(I/I_0)$, of the $\tilde{A} \leftarrow \tilde{X}$ band maxima of water versus the inverse of the ionic radii of the cation, R_c^{-1} . (Reproduced with permission from Ref. 30. Copyright (2010) American Chemical Society.) (B) Refractive indices, n_D , of 1 M bromide and nitrate solutions versus the inverse of the ionic radii of the cations, R_c^{-1} . (Reproduced with permission from Ref. 30. Copyright (2010) American Chemical Society.)

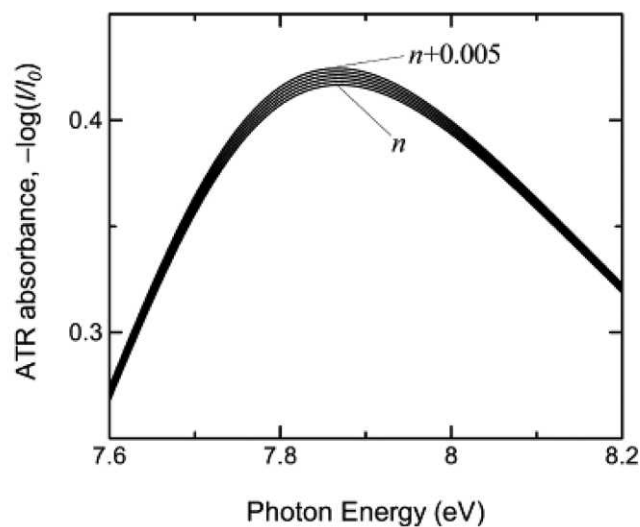


Fig. 16. Simulated ATR spectra in the $\tilde{A} \leftarrow \tilde{X}$ band of water for samples with different refractive indices. The refractive index of pure water, n , denotes reported values as a function of wavelength.¹⁰ (Reproduced with permission from Ref. 30. Copyright (2010) American Chemical Society.)

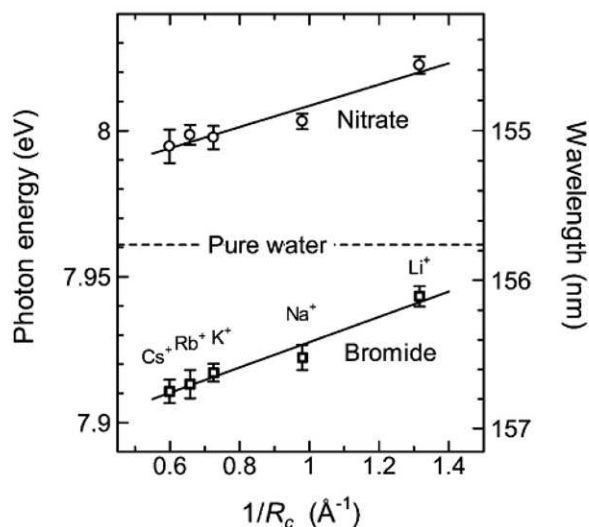


Fig. 17. Peak energies of the $\tilde{A} \leftarrow \tilde{X}$ band in the ATR-FUV spectra of alkali metal nitrates and bromides versus the inverse of the ionic radii of the cations. (Reproduced with permission from Ref. 30. Copyright (2010) American Chemical Society.)

alkanes, alcohols, ketones, and so on. For problem (3), it is very important to compare an FUV spectrum of a liquid sample with the corresponding gas-phase spectrum. In the meantime, it has become possible to predict electronic transitions of an organic molecule with the recent development of quantum chemical calculations. Thus even if the gas-phase spectrum is not available, one can compare a liquid spectrum with the corresponding gas-phase spectrum by using calculations at the level of an equation-of-motion coupled cluster model with single and double excitation (EOM-CCS(D)) or Becke's three-parameter hybrid density function in combination with the Lee–Yang–Parr correlation functional based on the Coulomb attenuating method (CAM-B3LYP).^{66,67}

As for problem (2) the FUV transitions have been studied for molecules in rare gas solid matrices, as liquids and as condensed gases.^{68,69} For example, the dependence of density of rare-gas matrices and liquids on the transition energies and spectral width has been discussed. However, such studies for realistic systems with strong interactions like organic molecules in pure liquids

have never been carried out. Therefore, by comparing systematically ATR-FUV spectra of a series of liquid organic molecules with results of quantum chemical calculations, one can establish band assignments in the FUV region.

In this section we report our recent studies on band assignments of ATR-FUV spectra of alkanes,³³ methanol,³¹ and ketones.³² For all the cases we compared obtained ATR-FUV spectra with the corresponding gas-phase spectra reported earlier by other research groups. For the band assignments of methanol we used deuteration effects and for those of ketones we tried quantum chemical calculations.

Band Assignments Based on Comparison of ATR-FUV Spectra of Liquid Organic Molecules with Corresponding Gas Spectra. Tachibana et al.³³ measured the ATR-FUV spectra of the several kinds of liquid normal and branched alkanes and investigated their band assignments and spectra–structure relationship. Figure 18 displays ATR-FUV spectra in the region of 8.55–6.53 eV (145–190 nm) of n -alkanes (C_nH_{2n+2} ; $n = 5$ –14) in the liquid phase.³³ It can be seen from Fig. 18 that all the alkanes investigated show a

broad feature near 8.3 eV and that the band shows a shift to the lower energy side with a significant intensity increase as the alkyl chain length increases. The inset in Fig. 18 depicts the second-derivative spectra in the 7.8–7.4 eV (155–175 nm) region. Note that there is a band near 7.7 eV.

In Fig. 19A the peak energy of the band near 8.3 eV is plotted against the number of carbon atoms for the n -alkanes.³³ It can be seen that there is a clear correlation between the peak energy and the number of carbon atoms. The plot can be fitted by a single-exponential curve and the curve converges to 8.1 eV.

Raymonda and Simpson³⁸ measured FUV spectra in the 11.5–7.1 eV region of n -alkanes ($n = 1$ –9) in the gas state by using a transmission method. They observed the corresponding band near 8.3 eV and a similar shift for the gaseous alkanes. According to these authors, the corresponding curve for the gaseous state converges to 8.1–7.8 eV. It is clear that a similar trend of the convergence value can be seen for both states.

In Fig. 19B plots of the peak energy of the band near 8.3 eV of n -alkanes ($n = 5$ –14) in the liquid state versus the

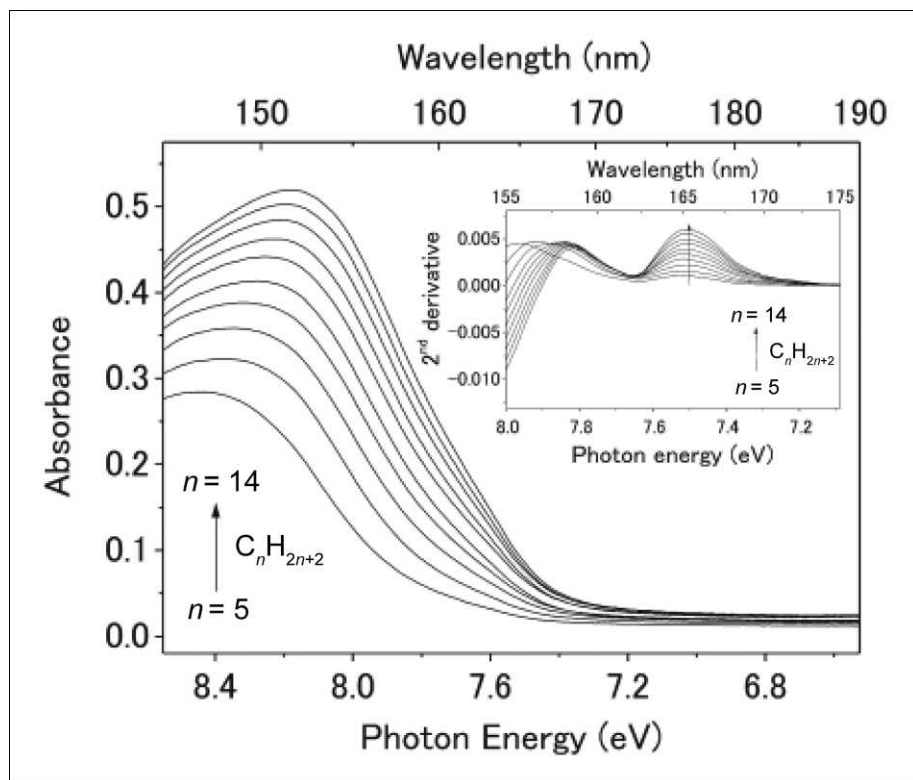


Fig. 18. ATR-FUV spectra in the region of 8.55–6.53 eV for n -alkanes (C_nH_{2n+2} ; $n = 5$ –14) in the liquid phase. (Reproduced with permission from Ref. 33. Copyright (2011) Society for Applied Spectroscopy.)

number of carbon atoms are compared with the corresponding plots of n -alkanes ($n = 1$ –8) in the gas state.³³ Of note in the plots shown in Fig. 19B is that the liquid alkanes give a similar trend to the gaseous alkanes. Therefore, Tachibana et al.³³ concluded that the peak near 8.3 eV of the liquid alkanes has the same origin as that of the gaseous alkanes.

In comparison with the proposed band assignments by Raymond and Simpson,³⁸ Au et al.,³⁹ and Costner et al.,⁷⁰ Tachibana et al.³³ have tentatively assigned the 8.3 eV band to the overlap of two bands due to the transition from the highest occupied molecular orbital (HOMO) to 3p and that from the HOMO-1 (the second highest occupied molecular orbital) to 3s.

Moreover, Tachibana et al.³³ estimated the absorptivity of the n -alkanes by use of the effective thickness, d_e , whose value is equal to the thickness of a transmission cell that would give the same intensity as an ATR measurement. It was found that there is a linear relationship between the absorptivity and the number of carbon atoms. Thus, it is very likely that the intensity increases with the increase in the total number of σ electrons. This result supports the above band assignments.

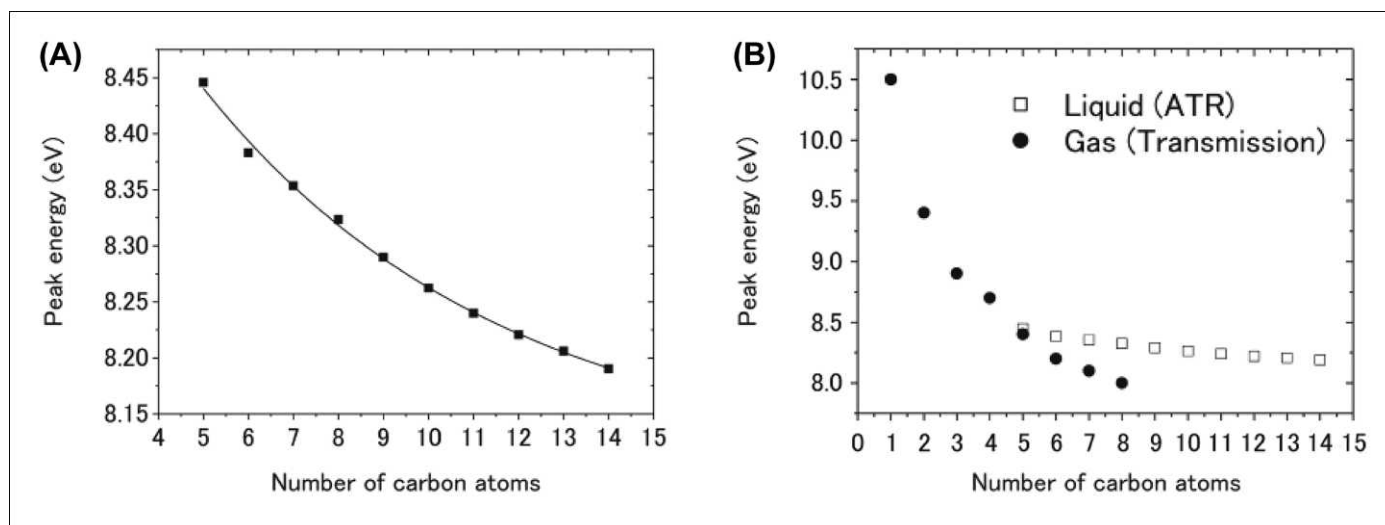


Fig. 19. (A) Plot of the peak energy of a band near 8.3 eV of n -alkanes ($n = 5$ –14) versus the number of carbon atoms. (Reproduced with permission from Ref. 33. Copyright (2011) Society for Applied Spectroscopy.) (B) Plot of the maximum of the band near 8.3 eV of n -alkanes ($n = 5$ –14) in the liquid state versus the number of carbon atoms and that of the maximum of a band observed in the same wavelength region of n -alkanes ($n = 1$ –8) in the gas state. The gas-state data were taken from Ref. 39. (Reproduced with permission from Ref. 33. Copyright (2011) Society for Applied Spectroscopy.)

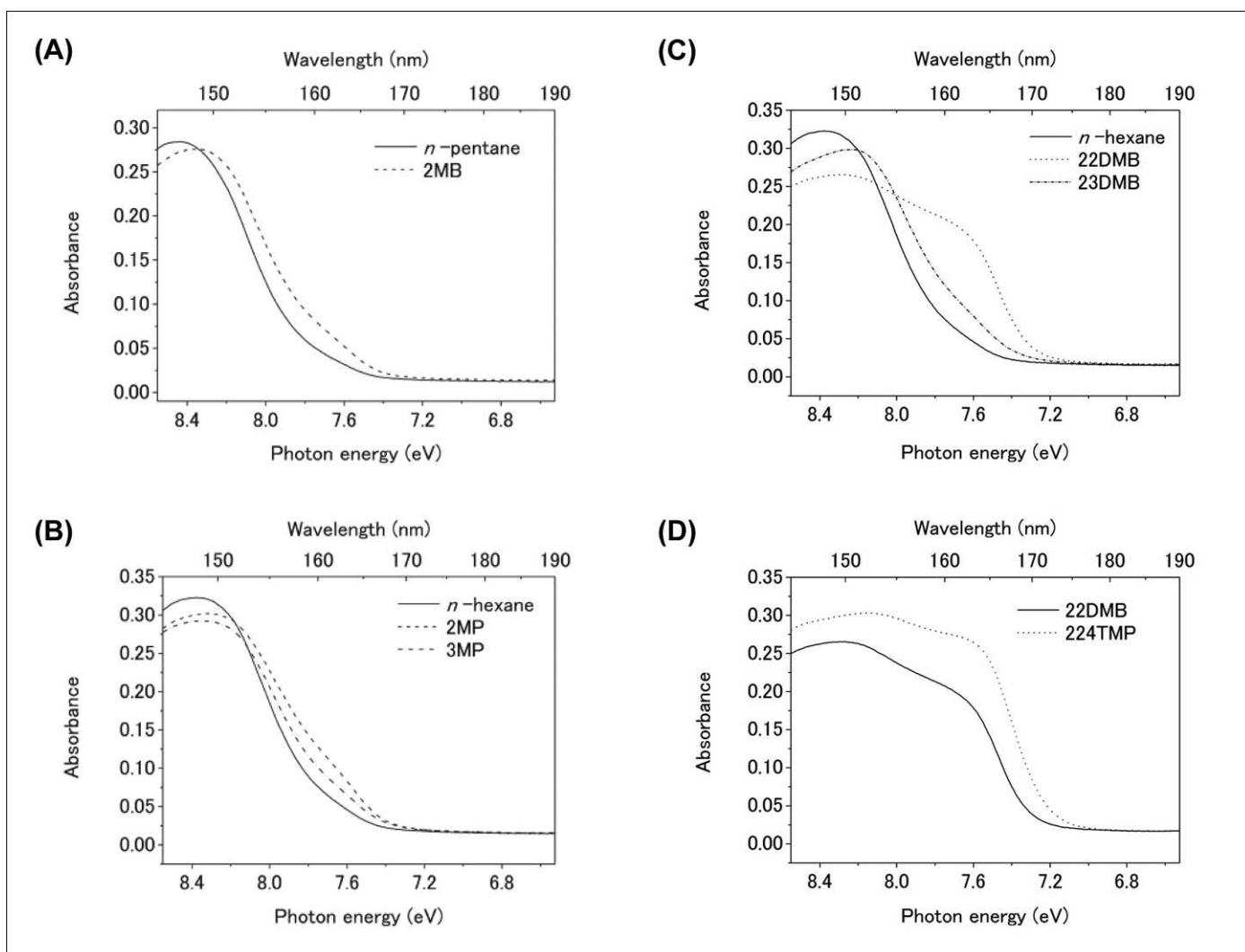


Fig. 20. ATR-FUV spectra of (A) *n*-pentane and 2 MB, (B) *n*-hexane, 2 MP, and 3 MP, (C) *n*-hexane, 2,2-dimethylbutane [22DMB], and 2,3-dimethylbutane [23DMB], and (D) 2,2,4-trimethylpentane [224TMP] in the liquid state. (Reproduced with permission from Ref. 33. Copyright (2011) Society for Applied Spectroscopy.)

Figure 20 shows ATR-FUV spectra of (A) *n*-pentane and 2-methylbutane [2MB], (B) *n*-hexane, 2-methylpentane [2MP], and 3-methylpentane [3MP], (C) *n*-hexane, 2,2-dimethylbutane [22DMB] and 2,3-dimethylbutane [23DMB], and (D) 2,2,4-trimethylpentane [224TMP] in the liquid state.³³ Note that *n*-pentane and 2MB have the same number of carbon atoms and *n*-hexane, and 2MP and 3MP also have the same number of carbon atoms. Also note that 22DMB and 23DMB have two branched alkyl groups with quaternary and tertiary carbon atoms, respectively, and 224TMP has a quaternary carbon. It can be seen from Figs. 20A and 20B that

the absorption maximum of the 8.3 eV band of the branched alkanes shows a lower energy shift and a shoulder near 7.7 eV becomes clear compared with the spectrum of the corresponding *n*-alkane with the same number of carbon atoms. Figures 20C and 20D reveal that the intensity of the band at 7.7 eV increases with the number of carbon atoms in the alkane without branches (*n*-hexane), that with tertiary (23DMB), and then those with quaternary carbon atoms (22DMB and 224 TMP). It is also noted that the more branched, the lower the energy of the 8.3 eV band. Tachibana et al.³³ assigned the 7.7 eV shoulder to the transition from HOMO to 3s. It is

inferred that the forbidden transition from HOMO to 3s becomes allowed by the decrease in symmetry upon going from the *n*-alkanes to the branched alkanes with a quaternary carbon.

A similar relation between FUV spectra and structure was observed for liquid ketones. Morisawa et al.³² investigated low-*n* Rydberg transitions of liquid ketones by using ATR-FUV spectroscopy. They proposed assignments for absorptions in the 8.55–6.20 eV (145–200 nm) region by comparing the spectra for the liquid phase with those measured in the gas phase.

Electronic transitions of acetone in the gas phase have been investigated by

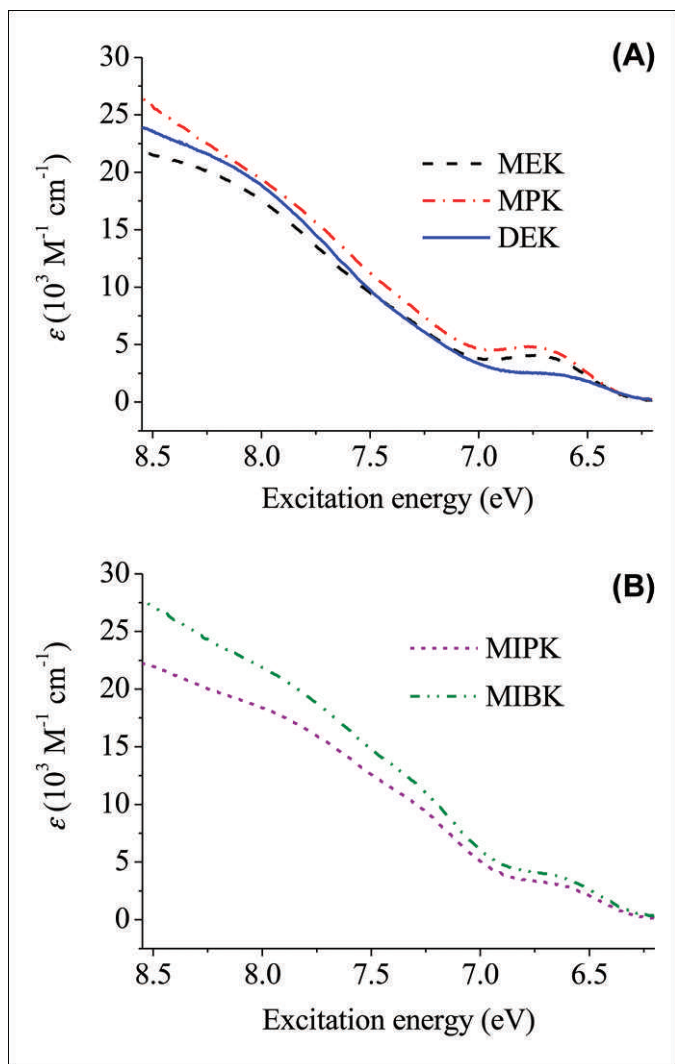


Fig. 21. FUV molar absorptivity (ϵ) spectra of (A) aliphatic ketones terminated by CH_3 (MEK, MPK, and DEK) and (B) branched ketones (MIBK and MIPK) in the liquid phase. (Reproduced with permission from Ref. 32. Copyright (2011) American Chemical Society.)

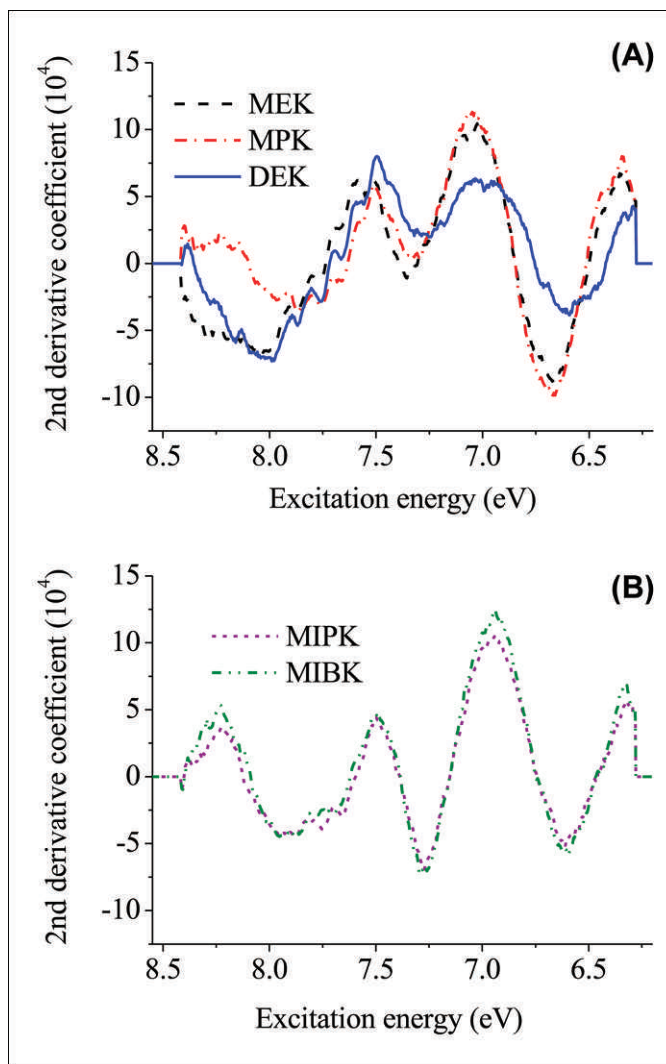


Fig. 22. Second derivatives of FUV- ϵ spectra of (A) aliphatic ketones terminated by CH_3 (MEK, MPK, and DEK) and (B) branched ketones (MIBK and MIPK) in the liquid phase. (Reproduced with permission from Ref. 32. Copyright (2011) American Chemical Society.)

using standard absorption,^{3,71–75} energy loss,^{74,76,77} and resonance-enhanced multiphoton (REMPI) spectroscopy.^{78–81} Several theoretical investigations have also been carried out on the vertical transition energy of acetone in the FUV region.^{81–83} These studies suggested the assignments for a few absorptions in the 7.45–4.38 eV region of acetone in the gas phase. Although the first electronic transition, the valence $n \rightarrow \pi^*$ transition, is a dipole-forbidden transition, it is observed in the UV region (5.4–3.8 eV) as an electrovibronic transition.³ In the FUV region, $n\text{-}3s$ Rydberg and $n\text{-}3p$

Rydberg transitions of acetone in the gas phase are observed at 6.35 and 7.4 eV, respectively, as strong and weak absorptions. As for other ketones in the gas phase, a strong absorption at around 6.3 eV and absorptions in the region of 7.5–7.0 eV are assigned to the $n \rightarrow 3s$ and $n \rightarrow 3p$ transitions, respectively, as strong and weak absorptions. As for other ketones in the gas phase, strong absorption at around 6.3 eV is assigned to the $n \rightarrow 3s$ transition, as discussed in the following paragraphs.

Figure 21A shows the molar absorptivity, ϵ , for FUV spectra of aliphatic

ketones terminated by CH_3 [methyl ethyl ketone (MEK), methyl *n*-propyl ketone (MPK), and diethyl ketone (DEK)] and Fig. 21B shows those of branched ketones [methyl *i*-propyl ketone (MIPK) and *iso*-butyl methyl ketone (MIBK)].³² It is noted that all the ketones show an absorption band at around 6.7 eV; however, the higher-energy regions of all ketones are significantly different from each other in their spectral shapes. The branched ketones (MIPK and MIBK) yield a clear shoulder near 7.3 eV.

Figures 22A and 22B display second

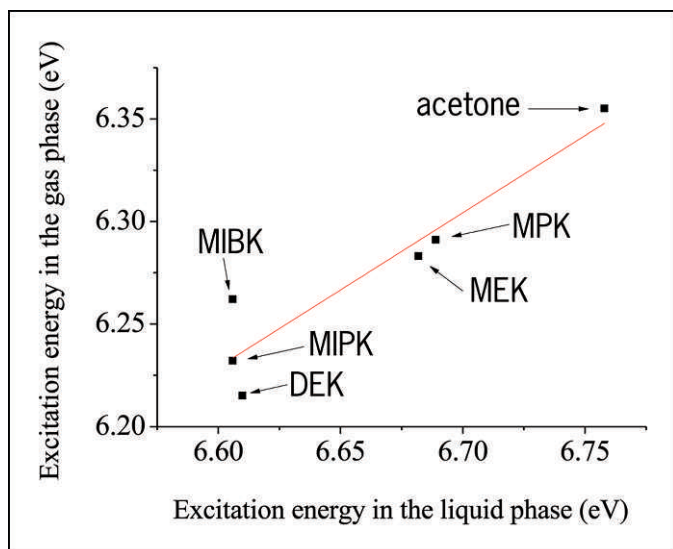


Fig. 23. Correlation between excitation energy of n -3s transition in the liquid phase and that in the gas phase. (Reproduced with permission from Ref. 32. Copyright (2011) American Chemical Society.)

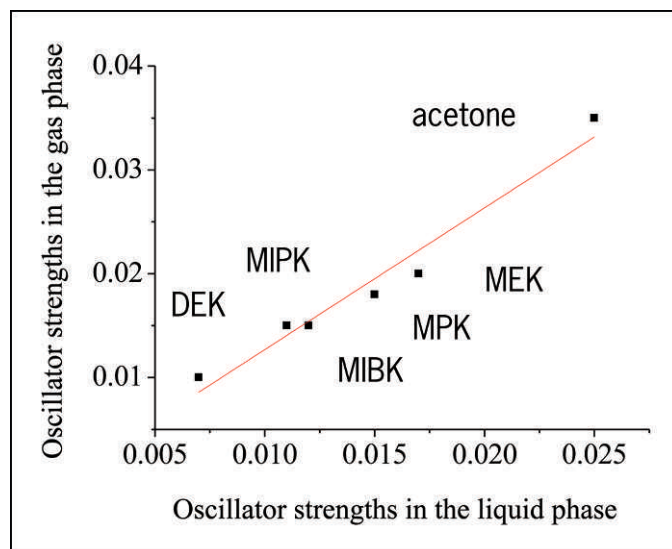


Fig. 24. Correlation between oscillator strength of the n -3s transition in the liquid phase and that in the gas phase. (Reproduced with permission from Ref. 32. Copyright (2011) American Chemical Society.)

derivatives of FUV- ϵ spectra of (A) aliphatic ketones terminated by CH_3 (MEK, MPK, and DEK) and (B) branched ketones (MIBK and MIPK) in the liquid phase.³² It can be seen from Figs. 22A and 22B that the aliphatic ketones show negative peaks near 8.0 and 6.7 eV whereas the branched ketones have another negative peak between them (7.3 eV). The peaks at around 6.7 and 8.5 eV are referred to as Band A and Band C, respectively, and the shoulder seen for the branched ketones is referred to as Band B.

Band A near 6.75 eV of the liquid-phase acetone is located at a slightly higher energy than the n -3s transition of the gas phase acetone (6.35 eV). Morisawa et al.³² investigated the correlations between the n -3s transition and Band A in terms of the 0-0 transition and the oscillator strength among all the investigated ketones as shown in Figs. 23 and 24. Based on the correlations, they suggested that Band A of the liquid phase is due to the n -3s transition as in the case of the gas phase.

Band assignments of Band B and Band C have not been carried out in the studies of gas-phase spectra. However, Band B appears even in the gas phase spectra because bands which appear clearly in the FUV spectra of branched

ketones in the liquid state are also observed in the gaseous state. Thus, we will discuss Band B and C by using quantum chemical calculations in a later section.

These studies have given a solid base to the band assignments of FUV spectra of organic molecules in the liquid phase and revealed the potential of ATR-FUV spectroscopy in investigating the molecular and electronic structure of molecules in the liquid state.^{32,33}

ATR-FUV Spectra of CH_3OH , CH_3OD , CD_3OH , and CD_3OD in the Liquid Phase. In the previous sections we showed that one can make assignments of FUV bands by measuring ATR-FUV spectra of a series of liquid organic molecules and comparing them with the corresponding gas-phase spectra. Alternatively one can make band assignments of FUV bands by using deuteration, which was commonly used in the early days of vibrational spectroscopy. Since zero-point vibrational energy is different between an electronic excitation state and its ground state, the deuteration effect appears in an excitation energy of the electronic transition. The effect occurs for molecules in both the gaseous and liquid states, so that one can compare the effect between them.

Morisawa et al.³¹ investigated ATR-

FUV spectra in the region of 145–220 nm of CH_3OH , CH_3OD , CD_3OH , and CD_3OD in the liquid phase. Cheng et al.⁴⁰ measured FUV spectra in the 107–220 nm region of CH_3OH , CH_3OD , CD_3OH , and CD_3OD in the gas phase by using a high-resolution spectrometer with synchrotron radiation. Based on the experimental results including those for the deuterated species together with time-dependent density functional theory (TD-DFT) calculations, they assigned three absorptions at around 183 nm (6.8 eV), 160 nm (7.7 eV), and 149 nm (8.3 eV) to the transitions between the ground state X^1A' and three excited states $1^1A''$ ($2a''$ -3s), $2^1A''$ ($2a''$ -3p), and $3^1A''$ ($2a''$ -3p'') or $3^1A'$ ($2a''$ -3p'), respectively.⁴⁰ Morisawa et al.³¹ called these three transitions, the A-X, B-X, and C-X transitions, respectively.

As to liquid phases, Jung and Gress^{44,44} and Kuo et al.⁴⁶ carried out interesting studies. The former group measured a transmission spectrum of liquid CH_3OH by use of a very thin cell with a path length of $1.0 \pm 0.5 \mu\text{m}$. They observed a broad absorption feature in the region from 6.8 eV (182 nm) to 10.8 eV (115 nm). However, it was difficult to determine absorption coefficients because of the uncertainty in the path length of the very thin cell and

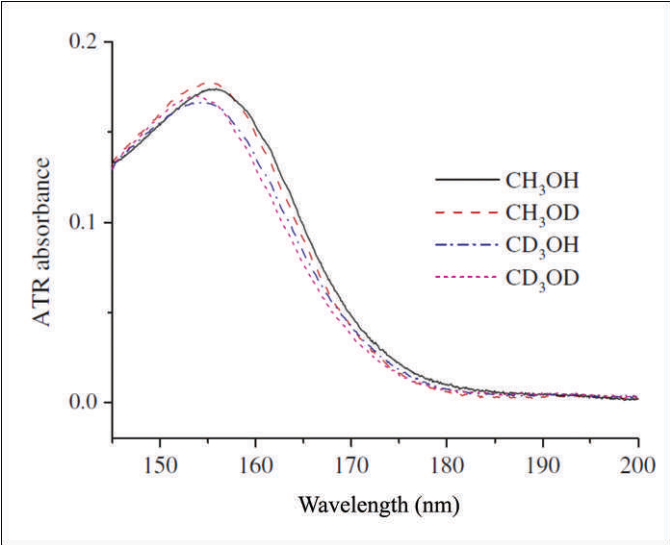


Fig. 25. ATR- FUV spectra of CH₃OH (solid line), CH₃OD (dashed line), CD₃OH (dot dashed line), and CD₃OD (short-dash line) in the pure liquid state in the region from 145 to 200 nm. (Reproduced with permission from Ref. 31. Copyright (2009) Elsevier.)

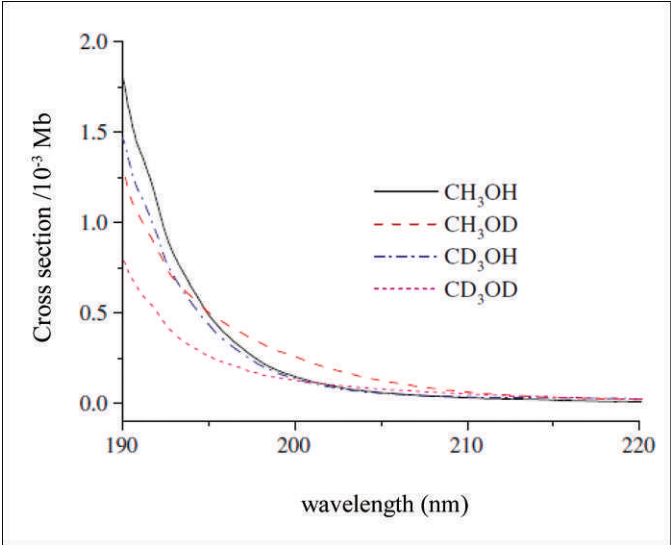


Fig. 26. Transmission FUV spectra in the region of 190–220 nm of CH₃OH (solid line), CH₃OD (dashed line), CD₃OH (dot dashed line), and CD₃OD (short-dashed line) in the pure liquid state. (Reproduced with permission from Ref. 31. Copyright (2009) Elsevier.)

TABLE I. The peak maximum region and band maximum (nm), HWHM of the longer wavelength side of the peak (nm), and oscillator strength in the ATR-FUV spectra of CH₃OH, CH₃DH, CD₃OH, and CD₃OD.³¹

Species	Peak maximum region	λ_{cent}	HWHM	f
CH ₃ OH	155.0–156.3	155.7	10.3	0.057
CH ₃ OD	154.7–155.6	155.2	10.0	0.056
CD ₃ OH	153.3–154.5	153.9	11.1	0.054
CD ₃ OD	153.0–154.3	153.7	10.6	0.053

TABLE II. Transition energies of acetone calculated in the present study (EOM-CCSD/aug-cc-pVDZ) and in previous studies by other groups.³²

		Exp. (gas phase)	EOM-CCSD/ aug-cc-pVDZ ^a		Previous results		
			energy	Osc. str.	EOM-CC/ POL1 ^b	CASPT2 ^c	EOM-CCSD/ 6-311(2+,2+)G ^{*,*}
1 ¹ A ₂	(n-π*)	4.49 ^c	4.49	0.0000	4.48	4.18	4.47
1 ¹ B ₂	(n-3s)	6.36 ^c	6.40	0.0314	6.39	6.58	6.42
2 ¹ A ₂	(n-3p)	7.45 ^c	7.43	0.0000	7.41	7.34	7.31
		7.36 ^f					
2 ¹ A ₁	(n-3p)	7.41 ^f	7.47	0.0001	7.45	7.26	7.41
2 ¹ B ₂	(n-3p)	7.45 ^f	7.60	0.0071	7.51	7.48	7.39
3 ¹ B ₂	(n-3d)	8.09 ^c	8.04	0.0414	7.95	8.04	7.82
3 ¹ A ₁	(n-3d)	7.8 ^c	8.24	0.0702	8.23	7.91	8.02
1 ¹ B ₁	(n-3d)	8.17 ^c	8.49	0.0160	8.43	8.20	8.11
4 ¹ B ₂	(n-3d)		8.76	0.0000	8.48	8.18	8.10
3 ¹ A ₂	(n-3d)		8.79	0.0000	8.44	8.09	8.08
4 ¹ A ₁	(π-π*)		9.21	0.2743	9.15	9.16	8.59
2 ¹ B ₁	(σ-π*)		9.29	0.0016	9.30	9.10	9.31
4 ¹ A ₂	(σ-π*)		9.47	0.0000	9.45		8.60

^a Ref. 32. ^b Ref. 78. ^c Ref. 77. ^d Ref. 79. ^e Ref. 71. ^f Ref. 76.

thus unequivocal band assignments were not made.

Attenuated total reflection FUV spectra in the region from 145 to 200 nm of CH₃OH, CH₃OD, CD₃OH, and CD₃OD in the liquid phase are shown Fig. 25.³¹ It is noted that the CH₃ and CD₃ species show significant differences in the peak position and the peak height. Table I summarizes the peak positions, band widths (HWHM; half width at half-maximum) and estimated oscillator strengths of the four species.³¹ The peak position shows a blue shift upon deuteration. The CD₃ substitution yields a greater shift (1.8 and 1.5 nm for CD₃OH and CD₃OD, respectively) than the OD substitution (0.5 and 0.2 nm for CH₃OD and CD₃OD, respectively). The oscillator strengths, f , decrease by the CD₃ substitution. The value of that for CH₃OH in the liquid phase was estimated to have the same order of f for the B–X and C–X transitions in the gas phase, but to be about ten times greater than that of the A–X transition in the gas phase.⁴⁰

According to Cheng et al.⁴⁰ the B–X and C–X transitions in the gas phase show a larger blue shift on CD₃ substitution than for OD substitution while the A–X transition shows a greater blue shift by the OD substitution than by the CD₃ substitution. Morisawa et al.³¹

found that for the liquid phase, the trends of isotope effects in the peak maximum region (Fig. 25) are similar to those for the B–X and C–X transitions of the gas phase spectrum. On the other hand, in the region of the long-wavelength wings of the strong band, the spectra of which are shown in Fig. 26,³¹ the trends are similar to that of the A–X transition. The oscillator strengths of the absorption near 155 nm of CH₃OH and its deuterated species in the liquid phase (Fig. 25) are similar to those of the B–X and C–X transitions in the gas phase, while the cross-section in this region (Fig. 26) decreases to 1/200 of that of the gas phase A–X transition.

From the above insight, Morisawa et al.³¹ have concluded that the first absorption peak in the ATR–FUV spectra originates from the interacting states between the A and B states because of identical symmetry of these states. These isotope effects may be used to help the assignments of the electronic absorption spectra of liquid organic molecules.

BAND ASSIGNMENTS BY QUANTUM CHEMICAL CALCULATIONS

An ATR–FUV Study on Low-*n* Rydberg Transitions of Liquid Ketones. In the previous section it was shown that a systematic comparison between gas-phase and liquid-phase spectra enables one to investigate band assignments in the FUV region. However, this method of band assignments requires gas phase spectra, which can be obtained only for molecules with significant vapor pressure. Thus, there is a significant limitation in this approach. Recently quantum chemical calculations have made marked progress, enabling precise prediction of electronic excitation energies.

Morisawa et al.³² carried out ab initio quantum chemical calculations of acetone. Table II compares the transition energies of acetone calculated by them with experimental results for acetone in the gas phase studied by photoabsorption⁷⁵ and REMPI^{80,81} spectra. Figure 27 displays the transition energies, oscillator strengths, and spectral simulations for (A) acetone, (B) MEK, (C) MPK, (D) DEK, and (E) MIPK calcu-

lated by EOM–CCSD/aug-cc-pv DZ together with their observed spectra.³² Based on the theoretical results, Morisawa et al.³² proposed the following assignments:

- (1) *A transition in the region of 6.4–6.3 eV; the $n \rightarrow 3s$ transition:* In this region there is an isolated transition from *n* to the excitation orbital, whose representation is *A*₁ for *C*_{2v} species (acetone and DEK) or *A'* for *C*_s species (MEK, MPK, and MIPK).
- (2) *Transitions in the region of 7.60–7.13 eV; the $n \rightarrow 3p$ transitions:* In this region there is a group of transitions containing three transitions from *n* to the orbitals, whose representations are *A*₁, *A*₂, and *B*₂ for the *C*_{2v} species or two of *A'* and *A''* for the *C*_s species.
- (3) *Transitions in the region of 8.9–7.8 eV; the $n \rightarrow 3d$ transition:* For acetone, there are five Rydberg transitions whose upper orbitals are the five 3d orbitals. For the other ketones, because of their similarity in strength and transition energy, they include the same kinds of transitions. Additional transitions should contain 4s or higher components.
- (4) There is a transition that has the strongest oscillator strength in this region, which is assigned to the $\pi \rightarrow \pi^*$ transition.

As can be seen from Fig. 27 the spectral simulation based on the result of the EOM–CCSD/aug-cc-pVDZ calculation reproduces Band A in the lower-energy region.

In the region of Band B, the $n \rightarrow 3p$ transition exists, but this transition has strong intensity only for molecules with low symmetry. This tendency is in good agreement with the fact that Band B appears clearly in the FUV spectra of branched ketones while it appears only weakly in the spectra of molecules with different carbon chains and can be seen only very weakly in the spectra of acetone and diethyl ketones with high symmetry.

Band C of liquid acetone is observed at 8.47 eV as a large broad absorption while the spectrum of gas-phase acetone shows a strong, broad, and complicated structured band in the region of 8.5–7.5

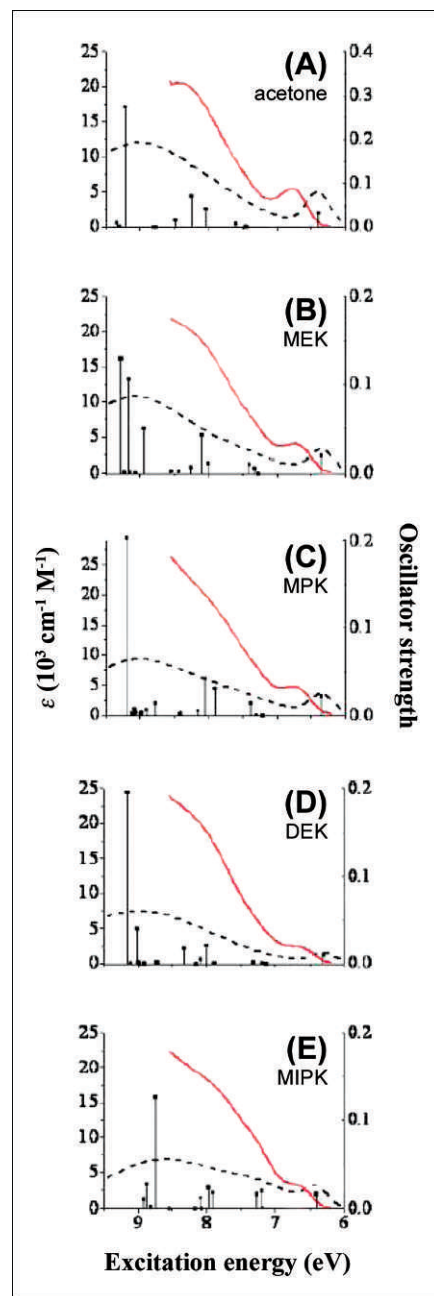


Fig. 27. Transition energies, oscillator strengths, and spectral simulations for (A) acetone, (B) MEK, (C) MPK, (D) DEK, and (E) MIPK calculated by EOM–CCSD/aug-cc-pVDZ. Stick diagram: Calculated transition energy and oscillator strength. Black line, simulated ϵ spectra; red line, observed spectra in the liquid phase. (Reproduced with permission from Ref. 32. Copyright (2011) American Chemical Society.)

eV with the most intense absorption peak at 8.10 eV. According to the theoretical studies conducted using CASPT2,⁸¹ EOM-CC,⁸² and EOM-CCSD,^{32,83} there are two components of the n-3d Rydberg state and the intensities of these transitions strongly depend on the methods of calculations, as discussed in Ref. 81.

Because the FUV spectra of liquid-phase ketones show no structured absorption and they heavily overlap each other, their detailed assignment is not easy. Therefore, Morisawa et al.³² discussed the intensity ratios between Band A and others for acetone. The area of Band B and Band C ($A_{\text{Band B+Band C}} = A_{\text{total}} - A_{\text{Band A}}$) is 9.0 times that of Band A for acetone in the liquid phase. Theoretical calculations based on CASPT2 and EOM-CC/POL1⁸² and the calculation by Morisawa et al.³² (EOM-CCSD/aug-cc-pVDZ) estimated the ratios of the total oscillator strength of n-3p and n-3d to n-3s of acetone to be 3.5, 4.5, and 4.3, respectively. The oscillator strength of the $\pi-\pi^*$ transition was calculated to be 21.5, 8.1, and 8.7 times stronger than that of n-3s by CASPT2,⁸¹ EOM-CC/POL1,⁸² and EOM-CCSD/aug-cc-pVDZ,³² respectively. Thus, the large intensity of Band C may be explained by the contribution of the $\pi-\pi^*$ transition directly as an overlapped absorption caused by a red shift from the gas phase as seen in the $\pi-\pi^*$ transition of amides^{84,85} or indirectly by intensity borrowing, for example, which results in the higher energy shift of Rydberg states in the liquid phase.³²

Morisawa et al.³² also made band assignment for other ketones and discussed the peak shift and broadening of the n-3s transition for acetone in the liquid phase as described below. In this way they investigated n-3p Rydberg transitions for acetone and other ketones in the liquid phase.

Investigations of Transition Energy of Liquid- and Gas-Phases by Polarizable Continuum Model Calculations. As described in the previous section, some FUV bands of ketones could be assigned to Rydberg states by referring to the band assignments in the gas phase.³² The assignments were confirmed by quantum chemical calculations. In this way there is clear

correlation between transitions in the liquid states and those in gas states; however, the transition energy shows a large shift of several thousand cm^{-1} between them.

Morisawa et al.³² reported that the energy of the n-3s Rydberg transition of acetone in the liquid phase shifts to the higher energy side by 0.39 eV from the corresponding position of the gas phase. The shift of 0.39 eV is significantly larger than that of the $n-\pi^*$ transition (0.05 eV).^{86,87} In the case of the $n-\pi^*$ transition the shift originates from a difference in the dipole-dipole interaction in the liquid phase between the ground and excited states of acetone.^{88,89} According to this theory, the larger blue shift in the n-3s transition than in the $n-\pi^*$ transition means that the 3s orbital should be more delocalized and nondirectional than the π^* orbital.

Quantum chemical calculations with a polarizable continuum model (PCM) are widely used to estimate transition energies in solvents. The advantage of PCM is that it allows solvent effects of electronic transitions to be calculated very easily; however, it cannot take into account direct interactions such as hydrogen bonding. Recently, Aidas et al.⁸⁶ reported the calculated result of the valence $n-\pi^*$ transition for neat liquid acetone and its aqueous solution by using a combined quantum mechanics/molecular mechanics (QM/MM) model coupled to classical molecular dynamics (MD) simulations and the PCM. Since Morisawa et al.³² focused on the n-3s Rydberg transition, they used TD-CAM-B3LYP to reproduce the transition energy of the Rydberg orbitals. Table III shows results of the calculation of TD-CAM-B3LYP/aug-cc-pVTZ for acetone in the gas phase and in the neat

liquid.³² The calculated results for the gas phase correspond well to the experimental results. The calculated gas-to-liquid energy shift of the n-3s Rydberg transition is estimated to be 0.22 eV. It reproduces the larger shift of the n-3s transition than the $n-\pi^*$ transition but it is a little smaller than the experimental results, as shown in Table III. The discrepancy between the shift observed in the FUV absorption spectra and that calculated with PCM should result from the neglect of intermolecular interactions, as Aidas et al. pointed out.⁹⁰

The higher energy shift of the Rydberg transition was observed for the n-3s Rydberg transition of water.⁹⁰ The shift of the band of the n-3s transition in acetone (0.4 eV) is smaller than that in water (approximately 1 eV).⁹ It is known that the shift in the n-3s transition of water depends on its temperature.⁹ This dependence means that the liquid structure is related to the spectral shift, which is attributed to the effect of hydrogen bonding. By analogy to water, the smaller shift in the liquid acetone indicates that the interaction between acetone molecules is (as expected) weaker than hydrogen bonding of water. A more detailed discussion should result after more data on the solvatochromism of the n-3s Rydberg transition is obtained.

APPLICATIONS OF FUV SPECTROSCOPY IN LIQUID AND SOLID STATES

As we already mentioned above, FUV spectroscopy holds considerable promise for a variety of applications from qualitative and quantitative analysis to on-line analysis and process monitoring. Here, we introduce two interesting examples of applications of FUV spectroscopy in liquid and solid phases.

TABLE III. Comparison of a gas-to-liquid shift between experiments and ab initio calculations using PCM for the $n-\pi^*$ and the n-3s Rydberg transition of acetone.³²

		Experiments			TD-CAM-B3LYP/aug-cc-pVTZ		
		gas	neat liq	shift	gas	neat liq	shift
1^1A_2	($n-\pi^*$)	4.43 ^a	4.51 ^b	0.08	4.43	4.60	0.17
1^1B_2	(n-3s)	6.36 ^a	6.75 ^c	0.39	6.39	6.62	0.22

^a Ref. 71.

^b Ref. 83.

^c Ref. 32.

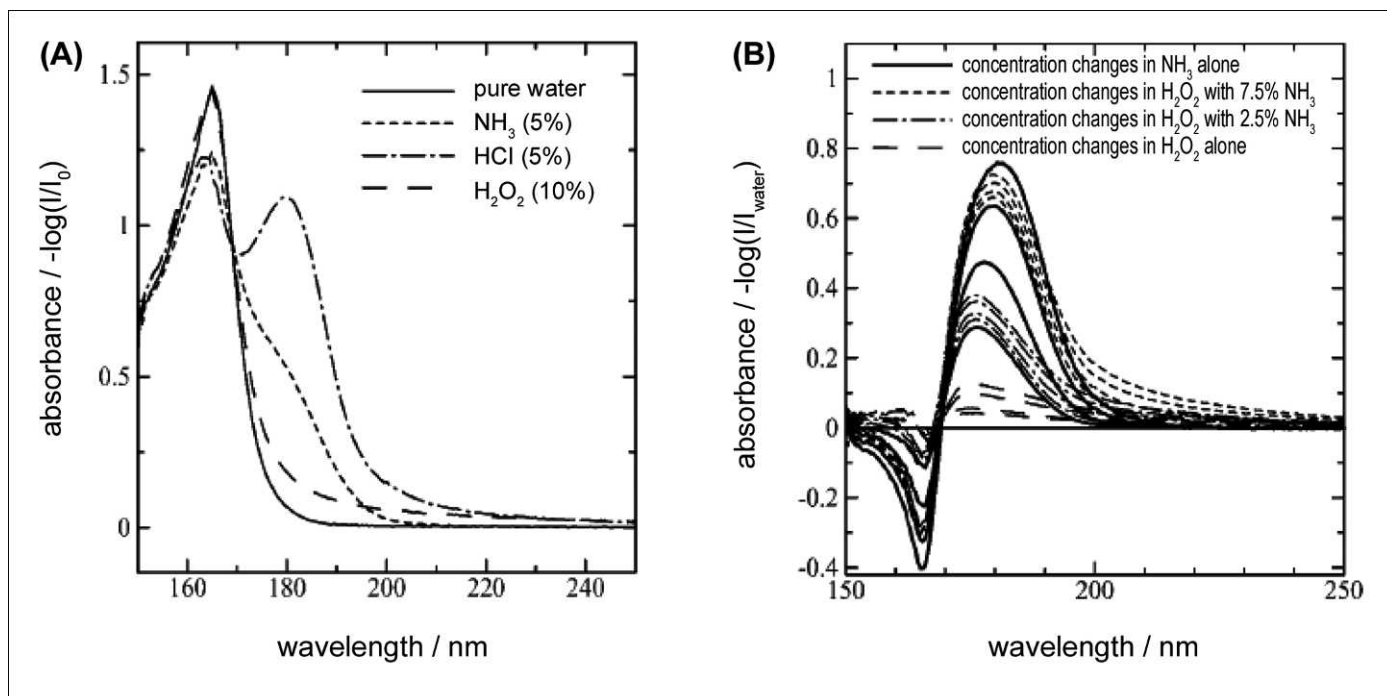


Fig. 28. (A) FUV-ATR spectra of pure water, 5% NH_3 , 5% HCl , and 10% H_2O_2 measured using a quartz ATR probe. (Reproduced with permission from Ref. 27. Copyright (2008) Society for Applied Spectroscopy.) (B) FUV-ATR spectra of NH_3 and H_2O_2 in aqueous solutions measured using a quartz ATR probe. Solid lines represent the spectra of NH_3 alone with different concentrations (0, 2.5, 5, 7.5, and 10%); long dashed lines depict the spectra of H_2O_2 alone with different concentrations (2.5, 5, 7.5, and 10%); dot-dash-dot lines represent the spectra of H_2O_2 (2.5, 5, 7.5, and 10%) in solutions with 2.5% NH_3 ; and short dashed lines describe the spectra of H_2O_2 with different concentrations (2.5, 5, 7.5, and 10%) including 7.5% NH_3 . (Reproduced with permission from Ref. 27. Copyright (2008) Society for Applied Spectroscopy.)

Monitoring the Quality of Semiconductor Wafer Cleaning Solutions using ATR-FUV Spectroscopy. ATR-FUV spectroscopy was employed for direct measurement of the concentrations of semiconductor wafer cleaning fluids such as SC-1 (aqueous solution of NH_3 and H_2O_2) and SC-2 (aqueous solution of HCl and H_2O_2).²⁷ The RCA (Radio Corporation of America) cleaning method has been extensively used in removing contaminants from silicon wafer surfaces in the semiconductor fabrication process.⁹¹ The method consists of oxidizing fluids such as NH_3 , H_2O_2 , and water, and HCl , H_2O_2 , and water. A mixture of 29% NH_3 , 31% H_2O_2 , and water with a (weight) ratio of 1:1:5 is called SC-1, and a 1:1:6 mixture of 36% HCl , 31% H_2O_2 , and water is called SC-2. Because the concentration of cleaning fluids changes within the cleaning process and affects the semiconductor fabrication yield, careful monitoring of the concentrations of these components is crucial to ensure

timely addition or replacement of cleaning fluid. Higashi et al.²⁶ demonstrated by using model fluids that ATR-FUV spectroscopy is very useful for this purpose.

Figure 28A shows FUV-ATR spectra of pure water, 5% NH_3 , 5% HCl , and 10% H_2O_2 measured using a quartz ATR probe with a 70° incidence angle.²⁷ A shoulder near 180 nm of 5% NH_3 aqueous solution is assigned to the $n \rightarrow \sigma^*$ transition of NH_3 and a peak at 180 nm of 5% HCl aqueous solution is due to the charge transfer to solvent (CTTS) of Cl^- . An aqueous solution of H_2O_2 shows a broader featureless absorption spectrum below 240 nm. Moreover, in each spectrum of these solutions a water band near 165 nm should be affected as the result of the addition of dissolved components. As a result, the three solution spectra can be readily discriminated.

Figure 28B depicts FUV-ATR spectra of various mixtures of NH_3 and H_2O_2 obtained by using the ATR spectrum of

pure water as a background.²⁷ Solid lines represent the spectra of NH_3 alone at different concentrations (0, 2.5, 5, 7.5, and 10%), long dashed lines depict the spectra of H_2O_2 alone at different concentrations (2.5, 5, 7.5, and 10%), dot-dash-dot lines represent the spectra of H_2O_2 (2.5, 5, 7.5, and 10%) in solutions with 2.5% NH_3 , and short dashed lines describe the spectra of H_2O_2 at different concentrations (2.5, 5, 7.5, and 10%) including 7.5% NH_3 . Higashi et al.²⁷ considered that the spectral variations observed in Fig. 28B arise from changes not only in the bands due to the solutes, but also from the $\tilde{A} \leftarrow \tilde{X}$ ($n \rightarrow \sigma^*$) transition band of water itself. It is noted that the absorption maxima around 180 nm shows a red shift with the increase in the concentration of NH_3 . This is because the water band is shifted to longer wavelengths by modification of the water molecule's hydrogen bonding.

Figures 29A and 29B depict calibration models for predicting the concen-

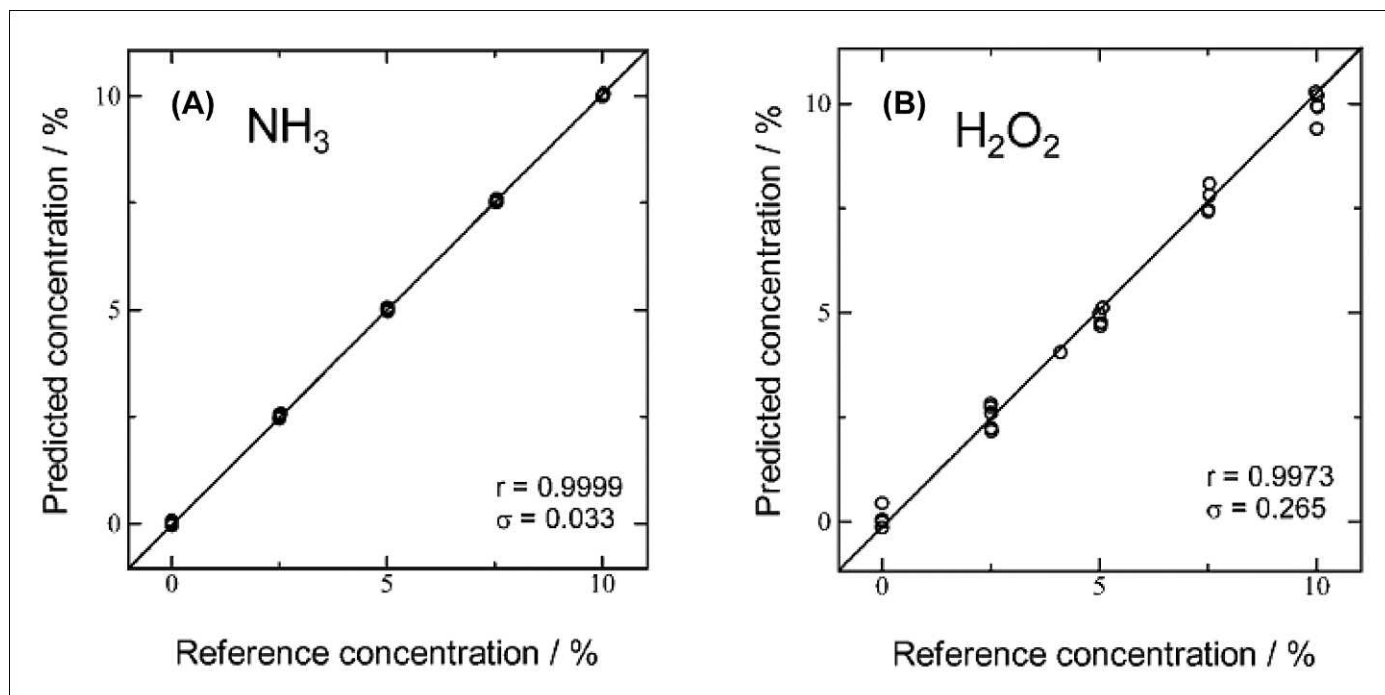


Fig. 29. (A) Calibration models for predicting the concentrations of NH_3 in aqueous solutions containing both NH_3 and H_2O_2 . (Reproduced with permission from Ref. 27. Copyright (2008) Society for Applied Spectroscopy.) (B) Calibration models for predicting the concentrations of H_2O_2 in aqueous solutions containing both NH_3 and H_2O_2 . (Reproduced with permission from Ref. 27. Copyright (2008) Society for Applied Spectroscopy.)

TABLE IV. Results of prediction. Two kinds of samples were tested to evaluate the developed calibration models for SC-1 and SC-2.²⁷

Mixture ratio Components	SC-1				SC-2			
	1: 1: 5		1: 1: 20		1: 1: 6		1: 1: 20	
	NH_3	H_2O_2	NH_3	H_2O_2	HCl	H_2O_2	HCl	H_2O_2
Prepared value	4.16	4.44	1.33	1.41	4.50	3.88	1.64	1.41
Measured value	4.16	5.00	1.10	1.94	4.55	3.54	1.62	1.27

trations of NH_3 and H_2O_2 in the aqueous solutions containing both NH_3 and H_2O_2 with the concentration ranges from 0 to 10% by using a multivariate analysis.²⁷ For NH_3 the correlation coefficient, r , is 0.9999 with a standard deviation, σ , of 0.033%, and the corresponding values calculated for H_2O_2 are 0.9973 and 0.265%, respectively. The large spectral changes due to NH_3 in the aqueous solutions contribute to determine the concentration of NH_3 more sensitively than that of H_2O_2 . The same procedure was repeated under the same conditions for HCl and H_2O_2 in SC-2, yielding corresponding values of 0.018% for HCl

and 0.178% for H_2O_2 . Table IV summarizes the results of prediction obtained when these calibration models are applied to test two kinds of samples of SC-1 and SC-2. Acceptable prediction accuracy for monitoring the cleaning process was obtained.

In this study, Higashi et al.²⁷ succeeded in increasing the absorption by increasing the penetration depth of the evanescent wave using quartz as the IRE in view of its low refractive index IRE.

Application of FUV Spectroscopy to Classification of Polymer Thin Films. Sato et al.²⁹ demonstrated the potential of FUV-UV spectroscopy in

the 120–300 nm region in the nondestructive 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; each film was about 10 μm in thickness). Figure 30A compares FUV-UV spectra in the 120–300 nm region of these samples, measured with a commercial FUV spectrometer (KV-201, Bunkoh-Keiki Co., Ltd.).²⁹ The three types of polymer films are clearly discriminated by their FUV-UV spectra.

The PE films show a broad feature in the wavelength region shorter than 170 nm and a weak absorption band near 185 nm. The former arises from the σ – σ^* transition of the C–C bonds of PE while the latter seems to be due to small alkyl branches of the PE films as will be discussed below.²⁹ Roughly speaking, a σ – σ^* transition is due to the transition from a bonding orbital to an antibonding orbital, and its energy is nearly equal to double the bonding energy. The σ – σ^* transitions of PVC and PVDC, which

have one and two C–Cl bonds in the polymer units, respectively, are shifted to a longer wavelength region because the transitions of the C–C bonds are affected by the existence of a C–Cl bond (Fig. 30).

Figure 30B compares FUV–UV spectra in the 120–300 nm region of pristine polymer films of (a) three kinds of PEs (high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE)) and (b) PVC.²⁹ It can be seen from Fig. 30B that HDPE, which has fewer alkyl branches than low-density PE, does not give rise to a shoulder near 185 nm while LDPE and LLDPE, which have alkyl branches, give rise to a shoulder at this wavelength. Therefore, Sato et al.²⁹ assigned the shoulder to the branches of the PE chains.

The bonding energy of a C–C bond changes with substituents on the C atoms, and thus the σ – σ^* transition is very sensitive to these substituents. Thus, the FUV spectra of substituted hydrocarbon compounds also change with the kinds and the number of substituents. In this way, FUV spectroscopy holds considerable promise as a nondestructive qualitative analysis method for polymers.

FUTURE PROSPECTS

As described in this review FUV spectroscopy of liquid and solid samples is a very promising research area from the standpoints of both basic science and applications. It is very likely that FUV spectroscopy will develop strongly in both areas. FUV spectroscopy is electronic spectroscopy and very rich in information about electronic states and structure of molecules. Thus far, electronic states and structure of liquid and solid phases have been investigated by using mainly the longer wavelength region ($\lambda > 190$ nm) simply because available commercial spectrometers do not measure shorter wavelengths. Only some exceptional materials such as rare gas liquids at low temperature have been subjected to FUV spectroscopy measurements to study electronic states and structure. ATR spectroscopy will likely become a general technique for exploring electronic transitions appearing in the 140–200 nm region. Many small

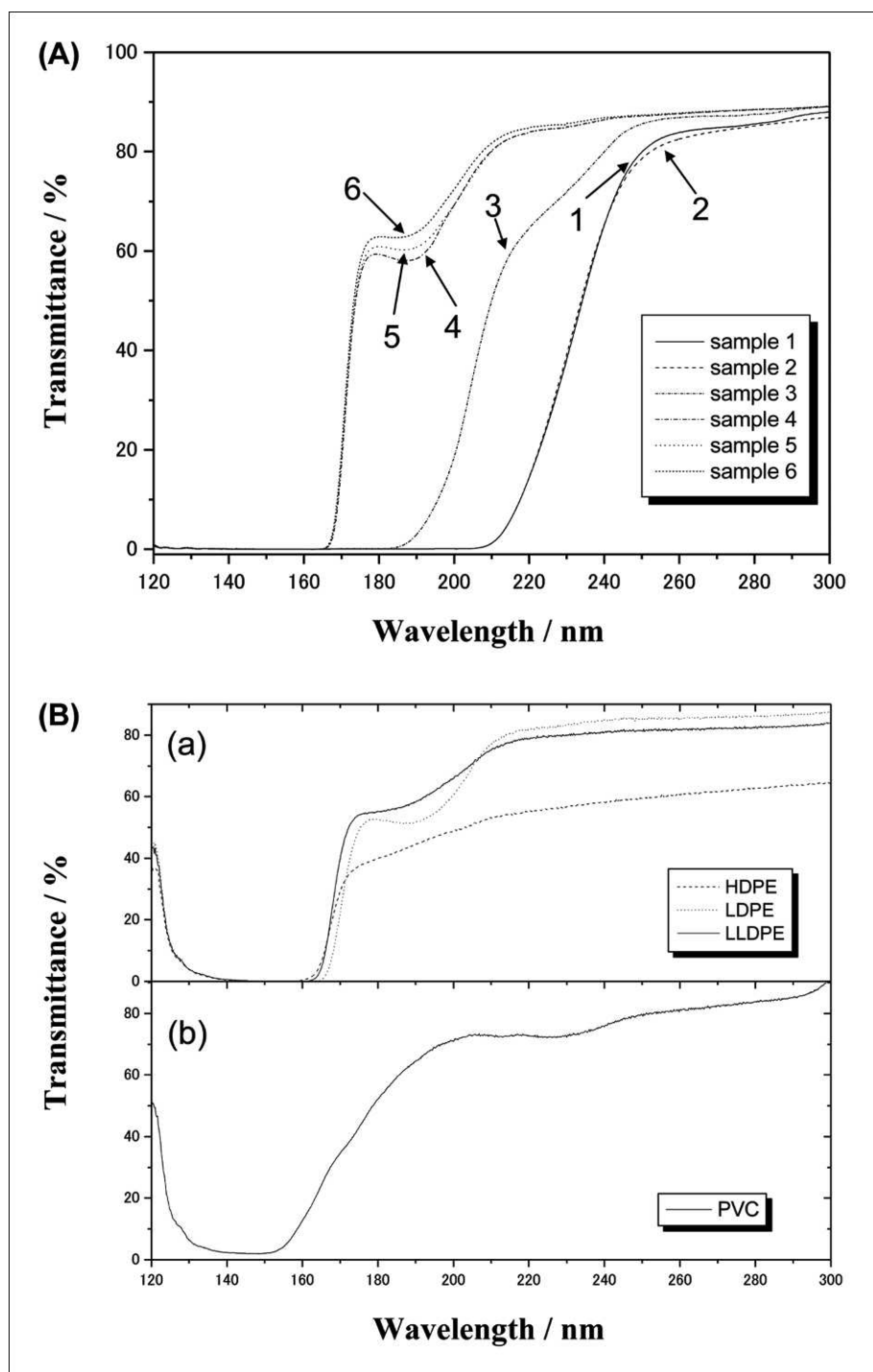


Fig. 30. (A) FUV spectra in the 120–300 nm region of polyvinylidene chloride (PVDC) films with different additives (Sample 1 and Sample 2), one polyvinyl chloride (PVC) film (Sample 3), and polyethylene (PE) films from three sources (Sample 4, Sample 5, and Sample 6). (Reproduced with permission from Ref. 29. Copyright (2007) Society for Applied Spectroscopy.) (B) (a) FUV spectra in the 120–300 nm region of three kinds of polyethylenes (high-density polyethylene, HDPE; low-density polyethylene, LDPE; and linear low-density polyethylene, LLDPE). (b) FUV spectrum of PVC. (Reproduced with permission from Ref. 29. Copyright (2007) Society for Applied Spectroscopy.)

molecules have a π - π^* transition in this region, so that ATR-FUV spectroscopy should give a huge amount of spectral data about π - π^* transitions of many molecules in liquid and solid phases. Of course, not only the data of the π - π^* transitions but also those of other transitions can be obtained. In particular, studies on Rydberg transitions are unique and important. All in all, ATR-FUV spectroscopy should open new areas of electronic spectroscopy of liquids and solids.

Attenuated total reflection FUV spectroscopy may be important not only in chemistry but also in physics. It may shed light on condensed-matter physics through electronic transition absorptions. Another notable point of ATR-FUV spectroscopy is that it is powerful in exploring ultra-thin surface films. It may also become a useful technique for surface structure, properties, and reactions.

An upcoming area of ATR-FUV spectroscopy is time-resolved ATR-FUV spectroscopy. We have recently started developing this new technique, which may open a novel research field of electronic spectroscopy, such as the investigation of radical reactions.

There are very wide areas of applications in FUV spectroscopy in liquid and solid phases. Notable advantages of FUV spectroscopy are its high sensitivity and selectivity that allow one to employ this technique for a variety of qualitative and quantitative analyses, discriminant analysis, and even on-line monitoring. Of note is that FUV spectroscopy is particularly useful for water and aqueous sample analysis. It is also noted that ATR-FUV spectroscopy is very suitable for surface analysis and is readily applicable to polymer thin films. The ATR-FUV method enables changes in the surface of thin films to be monitored, e.g., surface degradation. In the FUV applications, small FUV spectrometers that work only in limited spectral ranges may also be useful for particular purposes such as process analysis.

For both basic studies and applications further studies on band assignments in the FUV region are of particular importance. Extensive spectral data in this region are required to

establish the band assignments. Quantum chemical calculations should also play a very important role in band assignments.

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