3. Electronic spectroscopy and vibrational spectroscopy

[Purpose]

You will derive the electronic energy of atoms and the vibrational energy of diatomic molecules as well as their structural parameters by measuring the atomic and molecular spectra. You will also learn how to handle light sources and spectrometers.

[Principle]

Atoms and molecules have their eigenstates, which are the states of the discrete levels of observables such as energy or angular momentum. The energy of an atom is expressed as the sum of the electronic energy E_e and the translational kinetic energy of the center of gravity of the atom E_{trans}

$$E = E_e + E_{trans} \qquad (1)$$

For the hydrogen atom and hydrogen-like ions (atomic nuclei with one electron) such as He^+ and Li^{2+}, E_e is expressed by the solution to the Schrödinger equation $H\Psi = E_e\Psi$,

$$E_e(n) = \frac{-\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} \qquad (2)$$

where $\mu = m_e m_n/(m_e + m_n)$ is a reduced mass, m_e and m_n are the electron and nuclear mass, respectively, Z is an atomic number, ε_0 is a vacuum permittivity, e is an elementary charge and h is Planck constant.

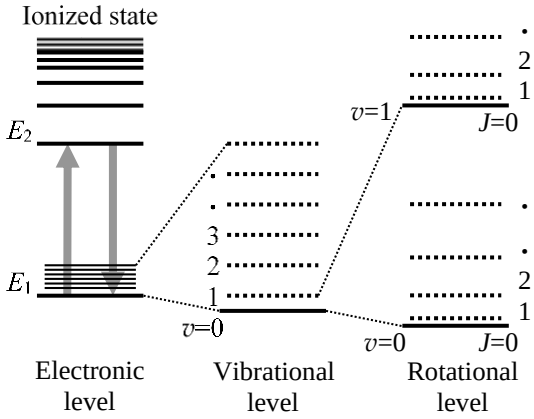

Fig. 1 Energy level diagram for molecule.

The electron energies E_e have discrete values. For hydrogen-like ions, E_e are solely quantized by the principal quantum number n. For atoms with two or more electrons, E_e are quantized by n, the azimuthal quantum number l, magnetic quantum number m_l, and the spin quantum number s. In addition to E_e, molecules also have vibrational and rotational energies, which are the relative motions of the nucleus. Figure 1 shows a schematic of the electronic, vibrational, and rotational energy states of molecules.

When atoms or molecules are irradiated with light having a photon energy $h\nu$ and the photon energy is equal to the energy difference of the eigenstates, the light is absorbed by the atoms or molecules, occurring the transition from a lower-energy state such as a ground state (E_1) to a higher-energy state (excited state, energy E_2) (Fig. 1, upward arrow). In contrast, atoms and molecules in the excited state emit light with a certain probability and transit to a more stable state (Fig 1, downward arrow). The wavelength λ of the light emitted from or absorbed by atoms and molecules has the following equation with their energies.

$$h\nu = \frac{hc}{\lambda} = E_2 - E_1 \qquad (3)$$

Here, ν and c are the frequency and velocity of light, respectively. Therefore, the eigenvalues, the energies of atoms and molecules can be determined from the emission and absorption spectra.

《Atomic spectra》

The emission spectra of atoms represent the emission intensities as a function of wavelength. When atoms are excited in a flame or a discharge tube, the emission was observed with the electronic transitions of the atoms from the excited states to the ground state. The wavelength of the emission (i.e., the position of the emission line) is specific to each element. In this experiment, you will obtain the emission spectra of atoms by using a discharge tube.

A discharge tube consists of a vacuum tube containing a gaseous sample and electrodes attached to the upper and lower sides of the vacuum tube. When a high voltage is applied across the electrodes, electrons are emitted from one of the electrodes. They are accelerated and collide with the atoms of the gaseous sample, generating atoms in the electron-excited state. These atoms are in excited states with different quantum numbers, and all of them rapidly lose their energy through emission or other phenomena and transit to a more stable state.

The emission wavenumber $\tilde{\nu}$ and wavelength λ of the hydrogen atom is expressed by the Rydberg formula.

$$\tilde{\nu} = \frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \tag{4}$$

Here, $\tilde{\nu}$ is the inverse of λ, R_{H} is the Rydberg constant, and m and n are positive integers where $m < n$. By comparing the Rydberg formula with the equation for energy (E_n) in quantum mechanics, you will find that the Rydberg constant is expressed by the atomic number, reduced mass, and other physical constants.

Atomic spectra are also used for qualitative and quantitative analyses because the emission and absorption wavelengths in the spectra are specific to the elements. In the spectrum of sunlight from a spectrometer, you will see hundreds of dark lines over the broad emission spectrum of visible light. The wavelength of the dark lines was first recorded by Fraunhofer, and hence these lines are called Fraunhofer lines. Dark lines are generated when the black body radiation from the high-temperature solar core is absorbed by the atoms in solar atmosphere. Therefore, the composition of solar atmosphere can be determined by comparing the wavelengths of the Fraunhofer lines with the absorption lines of the elements.

《Vibrational-rotational spectra》

Figure 2 shows the vibrational-rotational energy and spectrum of a diatomic molecule. As shown in the figure, sets of spectral lines (rotation lines) positioned at almost regular intervals are observed in some infrared absorption spectra of gaseous samples. Such spectra are called the vibrational–rotational spectra. In the spectra of molecules at thermal equilibrium, rotation lines are observed because the molecules are distributed in many excited states.

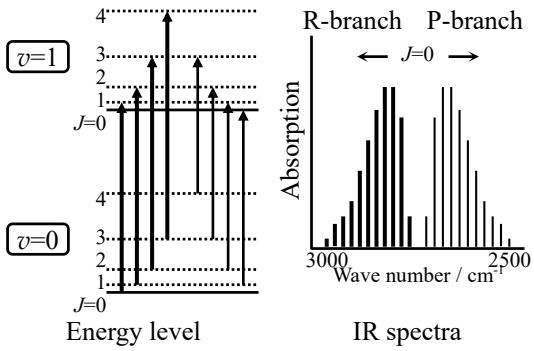

Fig. 2 Vibration-rotation energy levels and infrared absorption spectra.

The approximation equation for the vibrational-rotational energy $E(v, J)$ of diatomic molecules in units of wavenumber is given by

$$F(v,J) = \frac{E(v,J)}{hc} = \tilde{\nu}_0\left(v + \frac{1}{2}\right) + B_v J(J+1) \tag{5}$$

v=0, 1, 2..., J=0, 1, 2...

The first and second terms on the right-hand side are the vibrational and rotational energies, and v and J are the vibrational and rotational quantum numbers, respectively.

The wavenumber of molecular vibration in the first term $\tilde{\nu}_0$ is given by

$$\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_m}} \tag{6}$$

where $\mu_m = \frac{m_1 m_2}{m_1 + m_2}$ is a reduced mass of diatomic molecule and k is a force constant between two atoms (see Fig. 3).

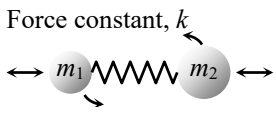

Fig. 3 Vibration-rotation model for diatomic molecule.

The term B_v in the second term of Eq. (5) is the rotational constant of the molecule with a vibrational quantum number v. In quantum mechanics, B_v is given by

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right) \tag{7}$$

where B_e is the rotational constant of the molecule at equilibrium (i.e., the state without molecular vibration) and α_e is the vibrational-rotational coupling constant, which indicates the degree of change in rotational energy due to molecular

vibration. Using the moment of inertia I_e, B_e is expressed by

$$B_e = \frac{h}{8\pi^2 c I_e} = \frac{h}{8\pi^2 c \mu_m r_e^2} \quad (8)$$

where r_e is the interatomic distance at the equilibrium structure.

By substituting Eq. (7) into Eq. (5), the wavenumbers of the absorption lines in the *P*-branch (transition from *J* to *J*−1) and *R*-branch (transition from *J* to *J*+1) are given by

$$\tilde{\nu}_P(J) = \frac{E(1,J-1) - E(0,J)}{hc} = \tilde{\nu}_0 - (2B_e - 2\alpha_e)J - \alpha_e J^2 \quad (9a)$$

$$\tilde{\nu}_R(J) = \frac{E(1,J+1) - E(0,J)}{hc} = \tilde{\nu}_0 + 2B_e - 3\alpha_e + (2B_e - 4\alpha_e)J - \alpha_e J^2 \quad (9b)$$

where *J*=0, 1, 2...

In Fig. 2, thin and thick lines correspond to the *P*- and *R*-branches, respectively. When *J* increases, the spectral lines in the *P*-branches shift to the low-frequency side and the lines in *R*-branches shift to the high-frequency side. Therefore, structural parameters such as the interatomic distance can be determined by measuring the positions of the spectral lines and using Eqs. (8) and (9).

[Preparation before experiments]

You will submit the report of four quizzes just before the experiment in Day 1. The quizzes are:

1. What are the electronic and vibrational spectra?
2. Summarize the general features of a spectrometer.
3. Write down the equation of a vibrational wavenumber $\tilde{\nu}_0$ in diatomic molecules.
4. What is a rotational constant?

[Laboratory apparatus, instruments, and reagents]

《On laboratory bench》			
Ultraviolet-visible spectrometer (common use)	,	Optical fiber (common use)	
PC for controlling spectrometer (common use)	,	PC for analysis	1
Hydrogen discharge tube (common use)	,		

[Experimental procedures]

Carry out Experiments A and B on Day 1 and Experiment C on Day 2.

<u>A. Observation of emission spectra of hydrogen atom</u>

1. Read through [Notes] before starting the experiment. [Notes] are listed in the next page.
2. Turn on the ultraviolet-visible (UV-Vis) spectrometer and personal computer (PC) used for controlling the spectrometer.
3. Turn on the hydrogen discharge tube.
4. According to the manual of the spectrometer, confirm the wavelength resolution of the UV-Vis spectrometer using the spectral line H_α at approximately 656 nm. Adjust the experimental condition such as numbers of scan and an observing time in a single-shot in the data accumulation.
5. Observe the spectral lines of the hydrogen atom with both high-and low-intensity peaks as follows: Move the optical fiber away from the light source to obtain a spectrum in which a high-intensity peak does not saturate. Then, bring the optical fiber close to the light source to obtain a spectrum in which a low-intensity peak is clearly observed. Save the results of the two cases.
6. Determine the wavelength for the peak position using the PC, convert it into the wavelength in vacuum (λ_{vacuum}), and calculate the wavenumber $\tilde{\nu}$ and vibrational frequency ν. λ_{vacuum} can be calculated using $\lambda_{vacuum} = n\lambda_{air}$, where λ_{air} is the wavelength in air and n is the refractive index of air (=1.0003). ν can be calculated using $\lambda_{vacuum}\nu = c$, where c is the speed of light.
7. Plot the wavenumber of each spectral line against the inverse of the square of the integer n ($1/n^2$). Use an

appropriate quantum number to confirm that the plots fit a straight line. Calculate the slope of the line by the least-squares method to determine the Rydberg constant.

8. Calculate the ionization potential of the hydrogen atom using the Rydberg constant you determined in step 7.

B. Observation of sunlight

1. Direct the end of the optical fiber connected to the UV-Vis spectrometer towards the window to observe the spectrum of sunlight. Find the Fraunhofer lines using the PC and record the wavelength.
2. Convert the wavelength into that in vacuum and calculate the wavenumber $\tilde{\nu}$.
3. If weather conditions are poor, carry out the observation the next day.
4. Collect the absorption wavelengths in the atomic spectra of various elements, identify the elements corresponding to the Fraunhofer lines, and analyze the composition of the solar atmosphere.

C. Observation of vibrational spectra of diatomic molecule

1. Get a chart of vibration spectra for diatomic molecules from the staff member and analyze the spectra as follows.
2. Assign the absorption lines in the *P*-branch (transition from J to $J-1$) and *R*-branch (transition from J to $J+1$). Assume that $m = -J$ for the *P*-branch and $m = J+1$ for the *R*-branch (refer to Fig. 2).
3. Calculate the intervals between adjacent absorption lines $\Delta\tilde{\nu}(m)$.
4. Plot $\Delta\tilde{\nu}(m)$ against m and draw a straight line using the least-squares method. Calculate B_e and α_e from the slope and m-intercept of the line, respectively.
5. Calculate $\tilde{\nu}_0$, r_e, and k from Eqs. (6), (8), and (9a), respectively.

[Notes]

1. The ultraviolet-visible spectrometer is a precision instrument and may become unable to produce reliable results if the angles of the diffraction grating and mirrors inside the spectrometer are changed. Do not disturb the spectrometer with any impact, such as by dropping it.
2. The inside of the optical fiber is made of glass and therefore fragile. Do not fold the optical fiber to a radius of 10 cm or smaller.
3. Turn off the hydrogen discharge tube when it is not used because its lifetime is limited. During discharge, a high voltage is applied in the tube, increasing its temperature; take care to avoid burns and electrical shock and do not touch any parts other than the power switch.

[Appendix]

《Principle of spectrometer》

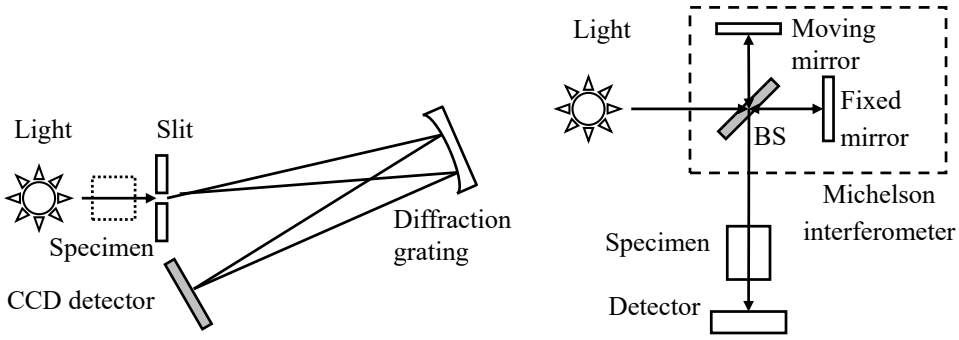

Fig. 4 Wavelength dispersive (left) and Fourier-transform (right) infrared spectrometers.

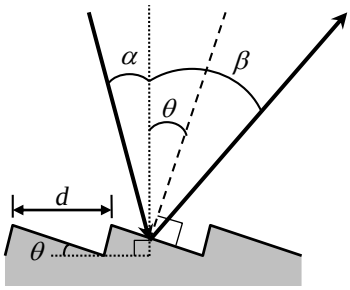

Fig. 5 Structure of diffraction grating.

Spectrometers are instruments used to measure the spectrum of light. Figure 4 shows a schematic of a spectrometer.

Dispersive spectrometers shown in Fig. 4 (left) are used to measure atomic spectra. Light from a light source enters an incident slit and reaches a spectroscopic element. A diffraction grating (see Fig. 5) used as the spectroscopic element disperses white light into beams of rainbow colors similarly to prisms. The dispersed light is converted into electrical signals by a detector and is observed as a spectrum. To measure emission spectra, a light-emitting material is placed at the position of the light source. To measure absorption spectra, a sample is placed between the light source and the spectrometer.

In contrast, Fourier transform spectrometers shown in Fig. 4 (right) are generally used to measure infrared absorption spectra. Incident light from a light source passes through a Michelson interferometer and reaches a sample. The light passing through the sample is converted into electrical signals by a detector. The signals are imported into a PC, subjected to Fourier transform, and shown as a spectrum.

《Principle of light dispersion》

Diffraction gratings are a spectroscopic element based on the interference of light and are fabricated by making hundreds or thousands of sawtooth parallel grooves per millimeter on metal (*e.g.*, Al) thin films. Light diffracted at the planes of adjacent grooves interferes constructively when the following relation holds.

$$N\lambda = d(\sin\alpha + \sin\beta) \qquad N = 1, 2, 3, \cdots \tag{10}$$

where d is the spacing of the grooves on the diffraction grating, and α and β are the angles of the incident light and emitted light with respect to the normal line of the grating plane, respectively. The term N is an integer called the order and is usually assumed to be equal to 1. The angle between the groove and grating planes (called the blaze angle) is θ, and the condition for geometric reflection at a groove plane is given by $\theta = (\beta - \alpha)/2$. Therefore, light with a wavelength that satisfies Eq. (11) interferes constructively.

$$\lambda = 2d\sin\theta\cos\left\{\frac{(\alpha+\beta)}{2}\right\} \tag{11}$$

When white light is incident to the diffraction grating, violet light is observed for a large β. The color changes to blue, green, yellow, orange, and red with decreasing β. When the diffraction grating is rotated in the spectrometer, the angle of the incident light to the diffraction grating varies, which changes the dispersion angle of light and the wavelength of the detected light. In this experiment, the spectrometer is fixed and the dispersed light is detected in two dimensions by a charge-coupled device (CCD) detector.

Fourier transform detectors use a Michelson interferometer instead of the spectroscopic element. Infrared light from a source enters an interferometer and is split into two beams at a beam splitter (BS). One passes through the BS and travels toward a fixed mirror and the other is reflected at the BS and travels towards a movable mirror. The two beams are reflected at the mirrors and overlap, then pass through a sample and are collected at a detector. When the difference between the distances from the BS to the fixed and movable mirrors is half the difference in optical path $\delta/2$, the beams reflected at the two mirrors have a difference in optical path of δ, making the synthetic waves interfere either constructively or destructively. δ can be varied by moving the movable mirror. The intensity of the detected light (integrated over the entire wavelength range) $I(\delta)$ is a function of δ and is given by

$$I(\delta) = \int_{-\infty}^{\infty} B(\nu)\left\{1 + \cos\left(2\pi\frac{\delta}{\lambda}\right)\right\} d\nu \tag{12}$$

$B(\nu)$ expresses the relationship between the intensity and wavelength of the light that has reached the detector. Here, $I(\delta)$ is divided into the δ-independent term (I_1) and δ-dependent term [$I_2(\delta)$] as follows.

$$I(\delta) = \int_{-\infty}^{\infty} B(\nu)d\nu + \int_{-\infty}^{\infty} B(\nu)\cos\left(2\pi\frac{\delta}{\lambda}\right)d\nu = I_1 + I_2(\delta) \qquad (13)$$

By multiplying the measured $I_2(\delta)$ with a cosine function and integrating the product with respect to δ (Fourier transform), we obtain $B(\nu)$ given by

$$\int_{-\infty}^{\infty} I_2(\delta)\cos\left(2\pi\frac{\delta}{\lambda}\right)d\delta = B(\nu) \qquad (14)$$

$I_2(\delta)$ is called the interference curve (interferogram). When a sample is placed at the position of the sample holder in Fig. 4 (right) and $I_2(\delta)$ is similarly measured, $B(\nu)$ for the light, including that absorbed by the sample, can be obtained. By comparing this $B(\nu)$ with that obtained without the sample, we determine the absorption spectrum.

[Checklist]

1. Do you understand the conversion among the wavelength, wavenumber, and vibrational frequency of light and the relationships among these factors and energy?
2. Emission spectra are classified into several spectral series according to m in Eq. (4). Do you know the names of the spectral series for m = 1–3?
3. Do you understand how to calculate the ionization potential from Eq. (4)?
4. Do you understand how to derive Eq. (4) from Bohr's atomic model and quantization conditions?
5. What are Fraunhofer lines? What information may be derived from Fraunhofer lines?
6. Why does the fine structure shown in Fig. 2 appear in the vibrational spectrum of diatomic molecules?
7. What information (parameters) for diatomic molecules can be obtained by analyzing the fine structure shown in Fig. 2?

[References]

Atkins' Physical Chemistry (Oxford University Press) provides the atomic and molecular spectroscopy (rotational, vibrational and electronic spectroscopy) as well as the quantization of vibrational and rotational motions. The latest version is the 11th edition. However, you can access the almost same contents in the former editions. The following references in Japanese contain the instructions and details of the experiments.

[1] The Chemical Society of Japan (ed.), 5th Edition of Chemistry Laboratory Course, Spectroscopy I, Maruzen Co., Ltd. (2005) (in Japanese).

[2] M. Nakata, Quantum Chemistry – Basic Concept, Chapter 16, Tokyo Kagaku-Dojin (1995) (in Japanese).

[3] The Chemical Society of Japan (ed.), Chemistry Handbook – Basic Edition, Revised 4th Edition, Maruzen Co., Ltd. (1993) (in Japanese).

[4] M. Ogasawara, M. Seo, A. Tada, and H. Hattori (ed.), New Physical Chemistry Laboratory, 2nd Edition, Sankyo Publishing Co., Ltd. (1998) (in Japanese).