An Introduction to Spectroscopy and Quantum Structure

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By

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For Emma, Milla, Gabriela, and Agatha

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FOREWORD

Spectroscopy is our most powerful tool for determining the structures and properties of atoms and molecules. This textbook provides a basic, undergraduate level introduction to several aspects of this broad field of study. In this book, we will explore several of the analytical spectroscopic techniques commonly employed in modern scientific laboratories, while at the same time investigating the underlying chemistry and physics that gives rise to the shapes and properties of molecules. The material presented in this book represents the basis of our understanding of matter. Given this and the fact that spectroscopy has become a vital tool for most areas of chemistry, it is essential that scientists and engineers learn about its principles and applications early in their scientific career.

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THE ZEROTH CHAPTER:
THE BASICS

This chapter outlines key concepts of spectroscopy and structure. It is intended to provide a foundation upon which to build an understanding of spectroscopic processes and how these relate to a quantum mechanical model of matter. Some students might find it beneficial to revisit this chapter as they progress through the later content.

0.1 – The Definition of Spectroscopy

Spectroscopy is the study of the interactions between matter and light. When a photon interacts with an atom or a molecule, it can induce a transition between discrete quantum states in the sample. This can occur via one of three processes: (1) absorption, (2) emission, or (3) scattering. Normally, these processes are represented with arrows on an energy level diagram as is shown in **Figure 0.1**.

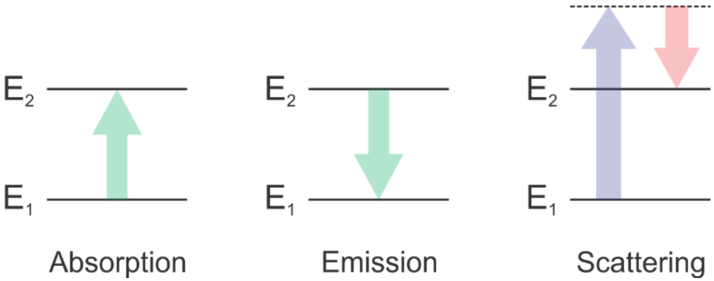

Figure 0.1 The three processes via which light can induce spectroscopic transitions; photon absorption, photon emission, and photon scattering. The photon loses energy in the scattering process that is shown here.

In **Figure 0.1**, energy level #2 (E_2) is higher in energy than energy level #1 (E_1). In general, energy level diagrams like those shown in **Figure 0.1** have low energy states towards the bottom of the page and high energy states towards the top of the page. These diagrams are very useful for describing spectroscopic transitions and we will make use of them often in this textbook. When light is absorbed, its energy and angular momentum are transferred to the atom or molecule. Conversely, when light is emitted, the atom or molecule relaxes to a lower energy state. An atom or molecule that has undergone a change in energy level is said to have undergone a ***transition*** between quantum states. We can summarize the absorption, emission, and scattering processes shown in **Figure 0.1** as follows:

Absorption:	The angular momentum and the energy of the photon are absorbed, and the atom or molecule adopts a higher energy state.
Emission:	An atom or molecule that is in a high energy state emits a photon to relax to a lower energy state. Energy and angular momentum are conserved.
Scattering:	A photon scatters off a molecule, thus changing the quantum state of the molecule. If the molecule gains energy, the photon loses a complementary amount of energy. If the molecule loses energy, the photon gains a complementary amount of energy. Energy and angular momentum are conserved.

****

Example 0.1. Transition Energy

If a molecule has one energy level at $E_1 = 3.5$ J and another energy level at $E_2 = 4.1$ J, what is the energy of the photon that is released in the emission process whereby the molecule relaxes from E_2 to E_1?

Answer:

Conservation of energy dictates that the energy lost by the molecule must be accounted for by the energy of the emitted photon. Thus, the energy of the nascent photon must be:

$$E_{photon} = E_2 - E_1 = (4.1 - 3.5)\ \text{J} = 0.6\ \text{J}$$

****

While somewhat over-simplified, these definitions of absorption, emission, and scattering give the gist of what we observe in spectroscopic experiments. By measuring the energy differences between quantum states in matter, we probe the quantum energy level structure. Since this energy level structure arises from the kinetic and potential energies of the nuclei and electrons in the atom or molecule, spectroscopic measurements provide information about the motions and positions of the particles in the system that is being studied. **Chapter 1** provides a more detailed description of the various quantum states of atoms and molecules, including a discussion of spectroscopic theory, atomic spectroscopy, and molecular orbital theory. **Chapter 2** discusses rotational motion and energy level structure. **Chapter 3** describes vibrational motion and a model for combined rotation and vibration. In **Chapter 4**, we will explore the process of Raman scattering and see how this can be used to determine molecular structures and properties. **Chapter 5** describes electronic energy level structure and combined rotational-vibrational-electronic (*i.e.*, rovibronic) transitions. In **Chapter 6**, we explore photoelectron spectroscopy whereby the emission of electrons is employed as a signal of light absorption. Finally, **Chapter 7** describes the basic principles behind nuclear magnetic resonance (NMR) spectroscopy. In all cases, it will be our goal to develop an algebraic expression of quantum state energy for the rotational, vibrational, electronic, and nuclear spin (NMR) processes, and relate these models to the observed spectrum using an energy level diagram.

0.2 – What is a spectrum?

A ***spectrum*** plots a response as a function of a continuous variable. For example, consider the three-tone A-minor chord, which is composed of the notes A, C, and E. If we play the notes A (220.00 Hz), C (261.63 Hz), and E (329.63 Hz), and record the sound intensity as a function of frequency, we produce the audio spectrum shown in **Figure 0.2**.

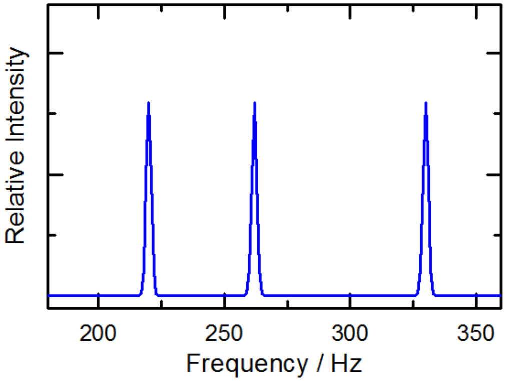

Figure 0.2 The audio spectrum of an A-minor chord. The spectrum plots sound intensity as a function of sound wave frequency.

We can acquire atomic and molecular spectra by recording the intensity of absorption, emission, or scattering of light as a function of its frequency. In doing so, we measure the frequency of light required to induce a transition between quantum states. This occurs because light carries energy, as well as angular and linear momentum; we will learn more about this in Chapter 1. For now, we will just focus on the energy that light carries. The key relationship between the energy of the light and its frequency, which was proposed by Max Planck, is given in equation (0.1).

$$E = h\upsilon \tag{0.1}$$

In equation 0.1, **E** is the energy of the light wave, **ν** (Greek letter *nu*) is the frequency of the light wave, and ***h*** is a scaling factor that is known as Planck's constant. The fact that the light energy is described by its frequency multiplied by a constant indicates that light energy is discrete (rather than continuous). We know these discrete packets (*aka* quanta) of light energy by their common name, ***photons***. Planck’s energy expression is one of the most important in quantum theory and we will discuss it further in Chapter 1. In considering the interaction between light and matter, we find that when a photon's energy is exactly equal to the energy gap between quantum states in an atom or molecule, the light can be absorbed, and the atom or molecule can undergo transition to the higher energy state. If the energy of the photon is not exactly equal to the energy gap between quantum states in the atom or molecule, the light is not absorbed by the molecule. Instead, the light can be scatter and usually it just passes through the sample (*i.e.*, the sample is transparent to that frequency of light). Thus, by monitoring the absorption of light by a sample of molecules as a function of the frequency (or wavelength) of the light waves, we generate an absorption spectrum wherein each absorption feature (*aka* peak or line) corresponds to a transition energy (*viz*. the gap between quantum states). This process is summarized in **Figure 0.3**.

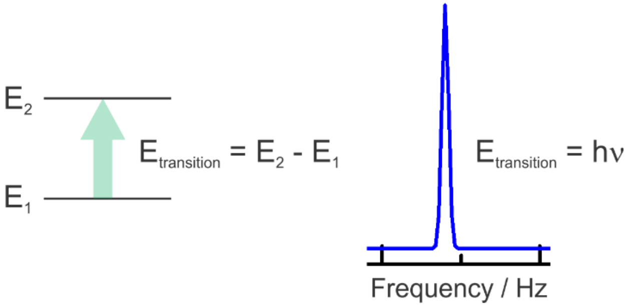

Figure 0.3 (Left) The transition energy between two quantum states of energies E_1 and E_2. (Right) The transition measured by absorption spectroscopy has an energy $E_{transition} = h\nu$.

****

Example 0.2 – Transition Frequency

A molecule has energy levels $E_2 = 2.0 \times 10^{-20}$ J and $E_1 = 1.0 \times 10^{-20}$ J. Planck's Constant is $h = 6.62607004 \times 10^{-34}$ J·s. What is the transition frequency in terahertz (THz = 1×10^{12} Hz).

Answer:

As was the case in example 0.1, we can take the difference between the energy levels to determine the energy of the transition:

$$E_{transition} = E_2 - E_1 = (2.0 \times 10^{-20}\ \text{J}) - (1.0 \times 10^{-20}\ \text{J}) = 1.0 \times 10^{-20}\ \text{J}$$

Having determined the transition energy, we can use Planck's energy expression to calculate the frequency of light required to induce the transition. Rearranging equation (0.1) yields:

$$\nu = E / h = 1.0 \times 10^{-20}\ \text{J} / 6.62607004 \times 10^{-34}\ \text{J·s} = 1.5 \times 10^{13}\ \text{Hz}$$

Since the solution was requested in units of THz, we must convert by dividing the frequency by 1 × 10^{12}, which yields a final answer of 15 THz.

****

0.3 – Energy Level Expressions

The energy levels of an atom are determined, to a first approximation, by the motions of its electrons. Molecular energy levels are determined by the relative rotational and vibrational motion of the nuclei in addition to the electronic motions in the molecule. There is also an inherent property of nuclei known as ***nuclear spin***, which is analogous to ***electron spin***, which must also be taken into consideration in our development of quantum energy structure. We will examine these phenomena in detail in **Chapters 1-7**. For now, it is useful to begin developing an understanding of quantum energy level structure and how this relates to spectroscopic measurements by simply stating that quantum state energies are a sum of the energies associated with each individual atomic or molecular motion:

$$E_{Total} = E_{Electronic} + E_{Vibrational} + E_{Rotational} + E_{Nuclear\,Spin} \quad (0.2)$$

Typically, spectroscopists write these energy contributions is a short-hand notation:

$$E_{Electronic} \equiv T_e$$

$$E_{Vibrational} \equiv G(v)$$

$$E_{Rotational} \equiv F(J)$$

Depending on how accurately we wish to describe the energy contributions, we will employ algebraic energy level expressions such as:

I. Vibrational energy:

Ia; 1st approximation: $G(v) = \omega_e\left(v + \tfrac{1}{2}\right)$

Ib; 2nd approximation: $G(v) = \omega_e\left(v + \tfrac{1}{2}\right) - \omega_e x_e\left(v + \tfrac{1}{2}\right)^2$

II. Rotational energy:

IIa; 1st approximation: $F(J) = BJ(J + 1)$

IIb; 2nd approximation: $F(J) = BJ(J+1) - D[J(J+1)]^2$

III. Rotational-vibrational energy, $S(v,J) = G(v) + F(J)$:

IIIa; 1st approximation: $S(v,J) = \omega_e\left(v+\frac{1}{2}\right) + BJ(J+1)$

IIIb; 2nd approximation:

$$S(v,J) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2$$
$$+BJ(J+1) - D[J(J+1)]^2$$

These energy level expressions combine as we would expect, and they are composed of variables (*e.g.*, v and J) and constants (*e.g.*, B, D, ω_e, and $\omega_e x_e$). The variables in these equations are known as ***quantum numbers***; they describe the state of the quantum system. The constants in these equations are related to the physical properties (*e.g.*, bond length, bond strength) of the quantum system. Consequently, if we know the values of the constants in these equations - or the physical properties which give rise to these constants - we can predict transition frequencies. Alternatively, we can measure transition frequencies and reverse-engineer the molecular constants by fitting to an appropriate model.

****

Example 0.3 – Calculating Transition Frequencies from Molecular Constants

The rotational constant of carbon monoxide, $^{12}C^{16}O$, is B = 57.8983 GHz. Calculate the frequency for the transition between the J = 0 rotational energy level and the J = 1 energy level.

Answer:

We must first realize that the question is asking us to calculate the rotational transition between the J = 0 and J = 1 quantum states of $^{12}C^{16}O$. Since we are only given the B constant, we must use the first approximation (given above) to determine the energies of the two rotational levels:

Since $E_{Rotational} = F(J) = BJ(J+1)$ and $E = h\nu$ (*i.e.*, energy and frequency are linearly related), we can report the rotational energies in units of GHz:

$$F(0) = B(0)(1) = 0 \text{ GHz}$$
$$F(1) = B(1)(2) = 2B = 2(57.8983 \text{ GHz}) = 115.7967 \text{ GHz}$$

Therefore, $\Delta F = F(1) - F(0) = \nu_0 = 115.7967$ GHz

In general, $\nu_J = F(J+1) - F(J) = 2B(J+1)$

****

It is worth noting that, due to Planck's relation ($E = h\nu$), transition energies are often reported with units of frequency. Moreover, since the speed of light can be expressed in terms of its wavelength and frequency (*i.e.*, $C = \lambda\nu$), it is also common to report transitions with units of wavelength. It is also common practice for spectroscopists to employ units of ***wavenumber*** (inverse wavelength with units of cm^{-1}) where:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(cm)} = \frac{10^7}{\lambda(nm)} \qquad (0.3)$$

****

Example 0.4 – Determining Molecular Constants from Transition Frequencies

Carbon monoxide, $^{12}C^{16}O$, exhibits a transition between the J = 4 and J = 5 rotational energy levels at ν_2 = 578.93 GHz. Calculate the rotational constant.

Answer:

As described above, we can develop a general description of rotational transitions (to a first approximation) by realizing $\nu_J = F(J+1) - F(J) = 2B(J+1)$. Thus,

$$\nu_4 = F(4+1) - F(4) = 2B(4+1) = 10B = 578.93 \text{ GHz}$$

We can then isolate the unknown B value to yield:

$$B = (578.93 / 10) \text{ GHz} = 57.893 \text{ GHz}$$

****

The same procedure outlined above can be applied to any spectroscopic transition. To properly analyze a spectrum, we must correctly assign quantum numbers. We will learn how to do this in due course.

****

Example 0.5 – Determining Molecular Constants from Transition Frequencies

If molecule AB has a harmonic vibrational constant equal of ω_e = 200 cm^{-1}, what is the energy gap between the v = 0 and v = 1 levels [*i.e.*, G(1) - G(0)]?

Answer:

The vibrational energy for the v = 0 and v = 1 levels (to a first approximation) is:

$$G(0) = 200\times(0+\tfrac{1}{2}) = 100 \text{ cm}^{-1}$$
$$G(1) = 200\times(1+\tfrac{1}{2}) = 300 \text{ cm}^{-1}$$

Therefore, the energy gap between vibrational levels is:

$$\Delta G = G(1) - G(0) = 200 \text{ cm}^{-1}$$

****

– 1 –

THE FIRST CHAPTER: SPECTROSCOPIC THEORY

1.1 – What do we measure?

Absorption spectra measure the colours (or wavelengths, or frequencies) of light absorbed by a sample. Usually this is done by using a “broad band” light source consisting of many different colours of light to excite the sample. The light that is transmitted (*i.e.*, that passes through the sample) can then be dispersed using a prism or grating, and the colours that were absorbed can be observed as intensity dips in the broad band spectrum. There are different variants of this process, such as Laser Induced Fluorescence (LIF), which monitors light emission following absorption of laser light, and Resonance Enhanced Multi-Photon Ionization (REMPI), which monitors ion formation following absorption of light, but the basic principle is the same. ***Emission spectra*** are recorded by measuring the light emitted by excited molecules when they relax to lower energy states. This, too, is usually accomplished by dispersing the emitted light.

Each different type of atom or molecule has a characteristic spectrum because each different type of matter has a characteristic quantum energy level structure. Absorption and emission of light is the process by which matter transitions between these different energy levels. Spectra must, therefore, be different for each different type of matter. The energy levels themselves arise from the internal motions of the atoms and molecules. We can relate the transition energy to the frequency of the absorbed/emitted light with equation (1.1)

$$\Delta E = E_2 - E_1 = h\nu \tag{1.1}$$

Planck’s constant, h, named after Max Planck, is a physical constant that reflects the size of ***quanta*** (the smallest subdivisions of a quantity) in quantum mechanics. It has a value of $h = 6.626\ 070\ 04 \times 10^{-34}$ J·s. As we will see, spectroscopy and quantum mechanics are intimately related. In fact, spectroscopy may be thought of as applied quantum mechanics. Alternatively, we may view quantum mechanics as the model by which we can explain spectroscopic observations.

1.2 – ...And from these Patterns

Interpreting spectra in terms of quantum mechanical models allows us to learn about the energetic and geometric structure of the atom or molecule in question, as well as about atomic or molecular properties. For example, spectroscopic studies can provide information on:

- The relative positions of atoms in molecules
- Bond strengths / force constants
- Potential energy curves & surfaces
- Dynamic behaviour (*e.g.*, energy disposal in molecular reactions)

We can also use statistical treatment to determine the thermodynamic and kinetic properties of ensembles of molecules. This field of study is called statistical mechanics. Of course, we are not limited to the information provided by the colour of the absorbed, emitted, or scattered light. Spectra also record intensity as a function of wavelength (or colour, or frequency). The intensity patterns contained in spectra provide information on:

- Concentrations of chemical species (macroscopic)
- Populations of energy levels (microscopic)
- Molecular properties such as dipole moments & polarizability
- Selection rules, which are related to wave function symmetry.

We will explore all these concepts, but before we do it is important that we have a good understanding of the nature of light.

1.3 – A Light Discussion of Wave Theory

Light is an ***electromagnetic wave*** that travels through vacuum with a speed of c = 299,792,458 m/s. Light consists of oscillating electric and magnetic fields, whose planes of oscillation are perpendicular to one another and to the light's direction of travel. Light is usually described by one of three properties:

Frequency (ν)	The number of oscillations of the electric or magnetic field per unit time. Measured in cycles/s (*i.e.*, s^{-1} = Hz).
Wavelength (λ)	The distance over which one oscillation occurs (usually reported in μm or nm).
Wavenumber ($\bar{\nu}$)	The inverse of wavelength, or the number of oscillations per unit distance (usually reported in cm^{-1}).

Figure 1.1 schematically shows the concept of wavelength and oscillation period, which is inversely related to the wave frequency. The properties of light may be related with the following equations:

Frequency & wavelength: $c\ (m/s) = \nu\ (Hz) \times \lambda\ (m)$ (1.2)

Frequency & wavenumber: $c\ (m/s) \times \bar{\nu}\ (m^{-1}) = \nu\ (Hz)$ (1.3)

Wavenumber & wavelength: $\bar{\nu}\ (m^{-1}) = 1 / \lambda\ (m)$ (1.4)

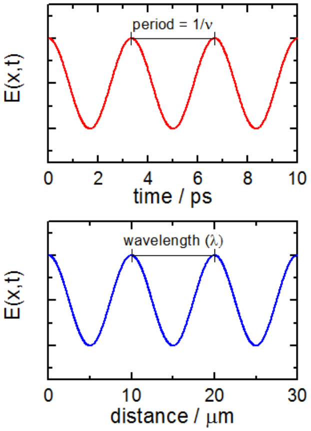

Figure 1.1. (Top) The electric field of a light wave viewed at a fixed point in space. The period of oscillation (*i.e.*, peak-to-peak spacing) is inversely related to frequency. (Bottom) The electric field of a light wave viewed at a fixed point in time. The distance over which one oscillation occurs (*i.e.*, peak-to-peak spacing) is known as the wavelength, λ.

Because atoms and molecules are composed of charged particles (electrons and protons), they are susceptible to electric fields. Thus, it is important for us to have a cursory knowledge of the oscillating electric field behaviour of light. In the mid-1800s, James Clerk Maxwell published a series of equations, now known as **Maxwell's equations**, which demonstrated that electricity, magnetism, and light are all manifestations of the electromagnetic field phenomenon. For our purposes, the most important result describes the temporal behavior of light's electric field:

$$E(x,t) = E_0 cos\left(\frac{2\pi\nu}{c}x - 2\pi\nu t + \phi_0\right) \qquad (1.5)$$

Where $\boldsymbol{x}$ is position, $\boldsymbol{t}$ is time, ν is frequency, $\boldsymbol{c}$ is the speed of light, and φ_0 is a phase factor that defines the angle.

****

Example 1.1 – Converting to wavenumber

What is the wavenumber of light which has a wavelength of $\lambda = 500$ nm? Report the answer in cm^{-1}.

Answer:

From equation 1.4 we find $\bar{\nu}$ (nm^{-1}) = 1 / λ (nm). To convert to cm^{-1}, we must realize that there are 10^7 nm per cm. Therefore,

$$\bar{\nu} \text{ (in cm}^{-1}) = 10^7 / \lambda \text{ (in nm)} = 10^7 / 500 = 20{,}000 \text{ cm}^{-1}$$

****

1.4 – The Quantum Theory of Light

Although the wave theory of light provides an excellent description of many observations with great accuracy, two (very important) observations cannot be explained by classical theory. These troubling observations are: (1) **black-body radiation** and (2) **the photoelectric effect**. The explanation of these observations led to the birth of quantum mechanics and earned separate Nobel Prizes for both Max Planck and Albert Einstein.

1.4.1 Black-body Radiation

Black-body radiation is the observation that a hot solid object emits light with an intensity distribution (as a function of wavelength or frequency) that is independent of the nature/composition of the hot material. The intensity distribution depends only on the temperature of the sample. Black-body radiation is associated with applications ranging from infrared imaging to incandescent light bulbs. By the late 19th century, scientists had carefully measured intensity distributions for a wide range of temperatures and found distributions like those shown in **Figure 1.2**.

The best theory of the late 19th century predicted that light intensities should become infinitely large at shorter wavelength (which is obviously wrong!). This failure of classical theory was termed ***the ultraviolet catastrophe***. The key assumption of this theory (and, in fact, the reason for the ultraviolet catastrophe) was that energy could be absorbed or emitted in any increment (*i.e.*, that light energy is a continuous property). Max Planck demonstrated that if light energy was absorbed in finite increments which depend linearly on the frequency, that the same classical derivation gave the distribution law:

$$I(v,t) = \frac{2\pi h v^3}{c^2}\frac{1}{e^{hv/kT}-1} \tag{1.6}$$

Where the Boltzmann constant, $k = 1.3806504 \times 10^{-23}$ J/K. Planck found that if the scaling factor (h) was given a value of $6.62607004 \times 10^{-34}$ J·s, his distribution law had nearly exact agreement with experiment.

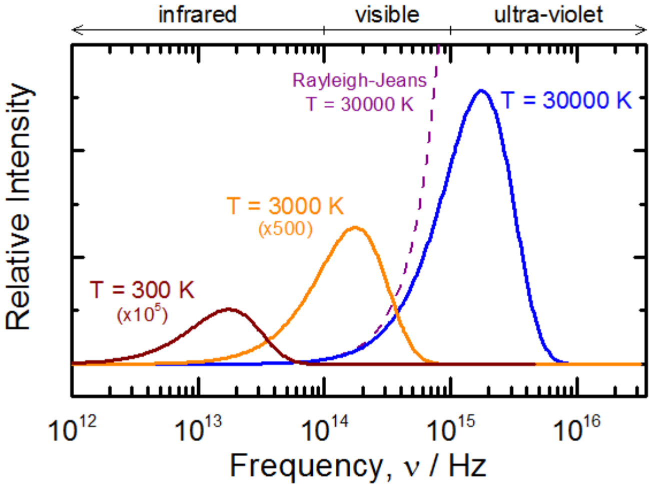

Figure 1.2. The observed intensity distribution for black-body radiation at (red curve) T = 300 K, (orange curve) T = 5,000 K, and (blue curve) T = 20,000 K. The prediction by the classical Rayleigh-Jeans Law for emission at T = 20,000 K is overlaid as a purple dashed curve.

1.4.2 The Photoelectric Effect

Another phenomenon that could not be explained by 19th century physics was the ***photoelectric effect***. When the surface of certain metals (contained in a vacuum) is illuminated, electrons are emitted. The emitted electrons can be collected using a positively charged electrode to measure the current. If a negatively charged grid/mesh is placed between the metal surface and the collecting electrode, we can determine the kinetic energy of the emitted electrons by applying a negative voltage to the grid and measuring the voltage required to repel the electrons (*i.e.*, shut off the current). This process is summarized below in **Figure 1.3**.

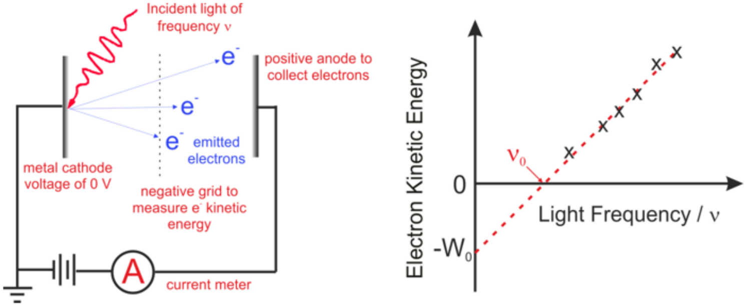
Incident light of frequency ν
positive anode to collect electrons
e⁻
e⁻
e⁻ emitted electrons
metal cathode voltage of 0 V
negative grid to measure e⁻ kinetic energy
A
current meter
Electron Kinetic Energy
0
-W₀
ν₀
Light Frequency / ν

Figure 1.3. (Left) The experimental set-up used to measure the photoelectric effect. (Right) Typical experimental observation of electron kinetic energies (eKEs) as a function of light frequency.

In studying the photoelectric effect, we observe the following:

i. There is essentially **no delay between when the light arrives and when the electrons are ejected**. This indicates that electron emission is not a thermal process because there’s no time for heating and transfer of thermal energy.

ii. **As the light intensity increases, the number of ejected electrons also increases**, but the maximum kinetic energy (KE_{max}) of the electrons is unaffected. This indicates that the energy imparted by the light does not depend on the amplitude of the light (contrary to the view that light is a wave).

iii. The **maximum kinetic energy, KE_{max}, of the ejected electrons increases when the light's frequency is increased**, but KE_{max} does not depend on the light's intensity. This indicates that the energy content of the light depends on the frequency of the wave rather than the wave amplitude.

iv. Each metallic material has **a characteristic threshold frequency, ν_0, below which no electrons are ejected**, regardless of the light's intensity. This indicates that a threshold energy known as the ***work function***, W, must be overcome to induce emission of photoelectrons.

It was Albert Einstein that explained the photoelectric effect. He demonstrated that the energy associated with light of frequency, ν, was discrete, occurring in tiny bundles (*i.e.*, quanta) of size:

$$\varepsilon(\nu) = h\nu \qquad (1.7)$$

Einstein called these quanta of light *photons*. Note that Planck's constant, h, also appears in equation 1.7. We can determine Planck's constant from the slope of the curve that is plotted in **Figure 1.3**. The threshold frequency, ν_0, for electron ejection indicates that each metal has a characteristic minimum energy that must be overcome to liberate electrons. This corresponding energy (*i.e.*, the work function, W), is equal to:

$$W = h\nu_0 \qquad (1.8)$$

The observations of the phenomena of black-body radiation and the photoelectric effect are not consistent with the wave description of light. Instead, these observations suggest that light is composed of quantized particles (*i.e.*, photons). Still, to describe properties of light (*e.g.*, reflection, refraction, propagation), electromagnetic radiation must be described as a wave. Thus, we say that light has a ***wave-particle duality***, since it has the characteristics of both particles and waves.

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Example 1.2 – Photoelectron Kinetic Energy

The bulk work function of copper is W = 4.7 eV. If light of wavelength $\lambda = 200$ nm interacts with the surface of metallic copper, what is the