

CH 154K: Advanced Physical Chemistry Laboratory  
Spectroscopy Primer

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Harshal Gupta

Lab Director: Ruth Shear

Department of Chemistry and Biochemistry

The University of Texas at Austin

## Introduction and Motivation

Spectroscopy is a powerful tool for determining the structures of atoms and molecules. It provides information about: 1) the electronic structures of atoms, i.e., how electrons are arranged around atomic nuclei, the energy levels of atoms, ionization potentials, etc., and 2) the electronic and geometrical structures of molecules, and other important physical properties such as the force constants of bonds (a measure of the stiffness of the bond); dissociation energies of molecules; vibrational frequencies, rotational frequencies, etc.

As you will infer from chapters 1 and 2 of this Primer, and learn from the suggested reading, spectroscopy *is* applied quantum mechanics. Therefore, some proficiency with quantum mechanics is required to understand the results of the experiments you will perform in the laboratory.

Now, a course on quantum mechanics and spectroscopy (CH 354L or CH 354) is a co-requisite, and not a prerequisite for the advanced physical chemistry laboratory (CH 154K). Most students have had a course in quantum mechanics by the time they take CH 154K. However, there are many who take it concurrently with the lab, and even the students who have taken quantum mechanics already, may need a refresher. This Primer is designed *to help you find what you may need* to analyse and interpret the data from the spectroscopy experiments in CH 154K. At present, quantum mechanics is treated implicitly, in the light of spectroscopy, and the reader is referred to the appropriate references (see the Suggested References list on page 16) to get the details. In several places, the student is led into conceptual questions that he or she must attempt to answer, and then learn about the topics under discussion from the suggested reading. Here, it must be pointed out that the **Suggested Reading** list towards the end is one of the most useful things in this Primer. The Primer provides you with a broad summary, but the devil lurks in the details. There are many different references, and you may find a couple that you like more than the others. So, be sure to check them out.

### *How to get the most out of this Primer*

1. Read over each chapter, and make a note of the **Suggested Reading** (cited in parentheses where needed) for each of the topics introduced.
2. Attempt to answer the questions that are raised, and then look up the appropriate references for the answer.
3. When you are *reading* about the topics in the **Suggested Reading**, have a pencil and some paper handy, so you can work things out on your own from time to time (unless you are good at working them out in your head). In other words, *read actively*.
4. Reason things out, ask questions of yourself. Try to see what something really means by putting it in simple terms. Make a note of your doubts, and be sure that you have tried your best to resolve them before you ask your TA or instructor.
5. Try to look at the big picture, and where your experimental results fit into it. If you have a broad idea, it is a bit easier to tackle the details. Do not ignore the

asides and caveats as they are there to lead you into the details. These are often either italicised, or begin with boldface font.

6. Make use of the appendices on **Basic Physics** and **Properties of Light**. You might find them handy (especially when you read through some of the references, and begin to analyse your data).

If you haven't done any spectroscopy experiments yet (or even if you have), you can start taking in the big picture by going over this short Primer.

Finally, it must be reiterated that this Primer is NOT a textbook. It is a guide that contains a brief overview of spectroscopy, and directs you to the appropriate references. It is intended as a buffer between the deceptive simplicity of instructional experiments, and the violence of quantum mechanics (when you do grab it by the horns – please excuse the pun). Humour aside, in writing this Primer, I hope that the student will get a broad introduction to spectroscopy, and will actually begin to develop an interest in it. This is the first time that such a Primer has been written as a supplemental aid to this course, and has therefore, not been “road tested”. I would greatly appreciate the feedback of my students and fellow instructors in improving this Primer and making it more useful to future groups of students.

Harshal Gupta  
February 2005

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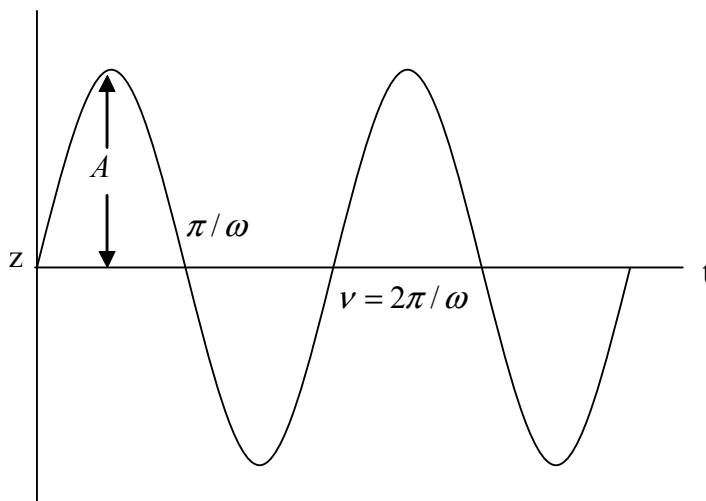
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## Chapter 1: Some Basic Concepts

Since spectroscopy is the study of the interaction of electromagnetic radiation (light) with matter, it is only natural to begin its study by reviewing briefly, the nature of electromagnetic waves and the kinds of interactions they may have with matter. In later chapters, we will see how spectroscopy can elucidate the structure of matter – atoms and molecules to the chemist.

### 1.1 Basic properties of Electromagnetic waves

Electromagnetic radiation can be thought of as *harmonic waves* originating at a source and propagating in straight lines (except in the cases of refraction, reflection, and diffraction\*). Electromagnetic (EM) waves are comprised of orthogonal (mutually perpendicular) *electric and magnetic fields* that oscillate, in much the same way as the physical displacements of a stretched string that is vibrating. It is the interaction of these oscillating fields with matter that gives rise to a spectrum.



**Fig. 1.1** A harmonic wave. Note that the number of oscillations per unit time is being measured.

A *harmonic wave* (Fig. 1.1) may be represented by a sine function,  $z = A \sin \omega t$ , where  $z$  is the *displacement* (say of the string or the electric field)  $A$  is the *amplitude*,  $\omega$  is the *angular frequency*, and  $t$  is the time. The angular frequency,  $\omega$  is related to the *frequency*,  $\nu$  by the expression  $\nu = \omega/2\pi$ . Thus, a harmonic wave in time is given by

$$z = A \sin \omega t = A \sin 2\pi \nu t \quad (1.1)$$

In other words, if one were to look at the wave at a fixed point in space, the wave would look like Fig 1.1, and be described by (1.1).

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\* This last case is thought to be a phenomenon resulting from reflection and interference. See reference (ii) in the Bibliography.

The frequency, as you may recall, is the number of oscillations per unit time. The SI unit of frequency is a Hertz (Hz), and has dimensions of  $s^{-1}$ . Note that I have ignored the *phase* of the wave in (1.1). In a more rigorous treatment, (1.1) would be written as  $z = A\sin(\omega t + \phi)$ , where  $\phi$  is the *phase* of the wave. Also, in talking about EM waves, we will generally consider only the electric field of the radiation and ignore the magnetic field (can you think of a reason for this?) that is travelling orthogonal to it. Thus, an electromagnetic wave is represented by

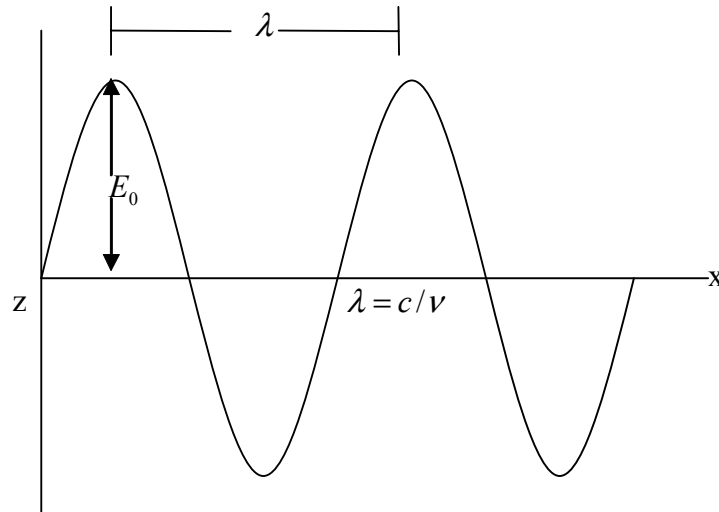
$$E = E_0 \sin \omega t = E_0 \sin 2\pi\nu t \quad (1.2)$$

where  $E$  is the electric field, and  $E_0$  is its amplitude.

Since EM waves are *travelling waves*, one really needs a description of the wave in terms of the spatial variation (a variation in space) of the displacement rather than the temporal variation (a variation in time) given in (1.1). Now, distance and time are related by  $x = ct$ , where  $x$  is the distance that the wave travels in time  $t$  at a speed  $c$  (the speed of light for EM waves). Using this in (1.2), gives

$$E = E_0 \sin\left(\frac{2\pi\nu x}{c}\right) \quad (1.3)$$

A travelling wave is shown in Fig. 1.2.



**Fig. 1.2** A travelling wave. Note that the cycles per unit length are being measured. Contrast with Fig. 1.1.

A travelling wave can also be characterised by its *wavelength*,  $\lambda$ . Wavelength and frequency are related by the well known expression

$$\nu\lambda = c \Rightarrow \lambda = \frac{c}{\nu} \quad (1.4)$$

From (1.3) and (1.4), we get:

$$E = E_0 \sin\left(\frac{2\pi x}{\lambda}\right) \quad (1.5)$$

Wavelengths are expressed in many different units that are *convenient* to work with (i.e., not too large or small) in a particular region of the EM spectrum (see Fig. 1.3). For example, wavelengths are given in  $\mu\text{m}$  in the infrared (IR) region, and in nm or  $\text{\AA}$  in the visible and UV regions.

Yet another useful way to characterise EM radiation is in terms of the *wavenumber*,  $\tilde{\nu}$ , which is *defined* as the inverse of the wavelength given in units of cm. i.e.,

$$\tilde{\nu} \equiv \frac{1}{\lambda} (\text{cm}^{-1}) \quad (1.6)$$

Thus,

$$E = E_0 \sin 2\pi\tilde{\nu}x \quad (1.7)$$

The wavenumber may be thought of as the spatial frequency of the wave (Fig. 1.2), i.e. the number of complete cycles per cm of radiation. In fact, as you may have inferred from (1.4) and (1.6), the wavenumber and the temporal frequency are directly proportional to each other through the following expression:

$$\nu = c\tilde{\nu} \quad (1.8)$$

where  $c$  is the speed of light in  $\text{cm s}^{-1}$ . In direct analogy with the temporal variation of the displacement of the wave, if one were to look at the wave at a particular time, the wave would look like Fig 1.2, and be described by (1.4)<sup>†</sup>.

**Note:** To avoid confusion between  $\nu$  and  $\tilde{\nu}$ , remember their respective units. The frequency is measured in Hz ( $\text{s}^{-1}$ ), and the wavenumber in  $\text{cm}^{-1}$ . However, spectroscopists often use the term “frequency” when they are talking about the wavenumber, especially in vibrational spectroscopy. This should not be a source of confusion, however, since the wavenumber and the temporal frequency are directly proportional as seen in equation (1.8).

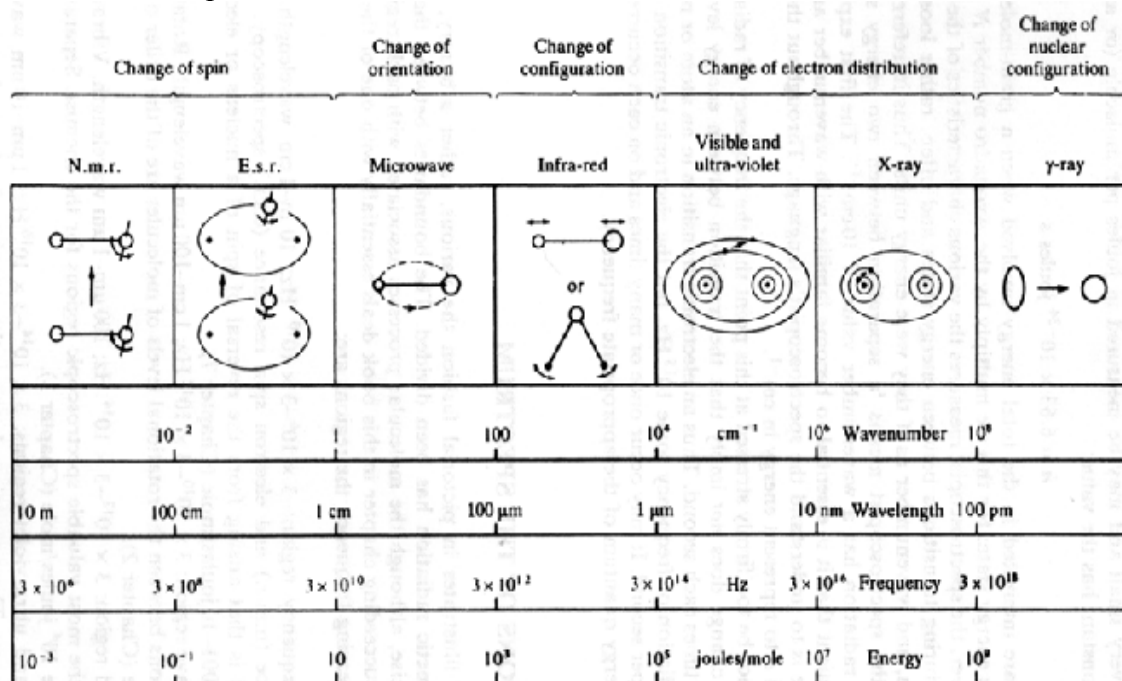
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<sup>†</sup> In fact, in order to take both the temporal and spatial variation into account, the equation for the EM wave equation is a combination of equations (1.1) and (1.4). See, for example, p. 3 of ref 6.

## 1.2 Regions of the Electromagnetic Spectrum

EM radiation can impart energy to atoms and molecules, and bring about several kinds of processes. These include changes in nuclear spin, changes in the orientation, configuration, and electron distribution of molecules, and changes in the nuclear configuration of molecules. The approximate regions into which the EM spectrum is divided and the processes associated with each of these regions is depicted pictorially in Fig. 1.3 (taken straight from reference 4). For details on each of these processes the reader is referred to the relevant references (refs 4 – 6). Notice that “white light” is only a very small part of the EM spectrum.

In this lab we will study only a few kinds of molecular spectroscopy, viz., rovibrational (rotational changes accompanying vibrational transitions), vibronic (vibrational changes accompanying electronic transitions), and electronic spectroscopy. However, it is worthwhile to be aware of the other kinds of spectroscopic techniques that are available to the chemist. Also, atomic spectroscopy though not explicitly mentioned here, will be discussed in chapter 3.



**Fig.1.3** The regions of the EM spectrum. Note the use of different units in the different ranges of the spectrum. ESR stands for Electron Spin Resonance and NMR for Nuclear Magnetic Resonance (see ref 4).

## 1.3 What is measured in a spectroscopy experiment?

We are familiar with the notion that electrons in atoms and molecules exist in one of many different *discrete* energy levels and states, and that energy is *quantised*. This is what is implied, for example, when one speaks of an electron in a particular orbital of an atom or a molecule. Similarly, the other types of energy of the molecule, viz., rotational, vibrational, nuclear-spin, etc. are also quantised, and molecules can exist in several



different types of energy levels (rotational, vibrational, etc.). A molecule may move from one level to another only by an abrupt change involving a finite amount – a *quantum* – of energy. In a spectroscopy experiment, this energy is usually supplied by EM radiation, i.e. the experimenter shines “light” on a sample of molecules, and records the resultant spectrum.

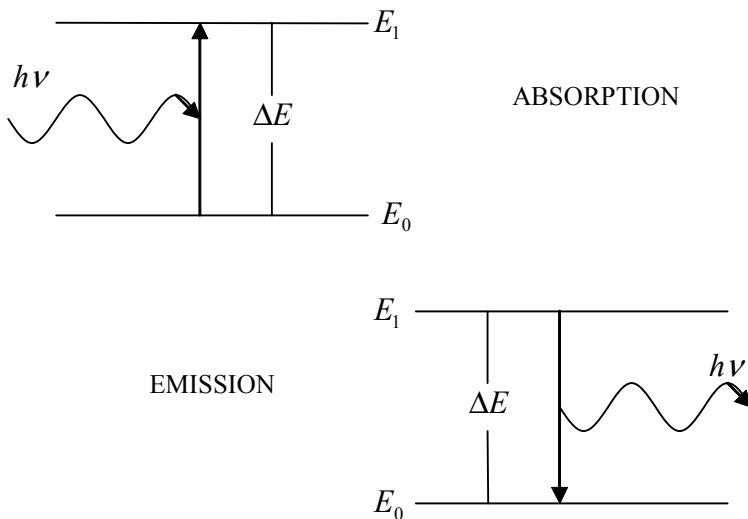
Take, for instance, two possible energy levels of a molecule, say two of its vibrational levels as shown in Fig. 1.4.  $E_0$  and  $E_1$  are the energies of the two levels. The subscripts 0 and 1 used to distinguish these levels are actually, *quantum numbers*, which have certain *physical interpretations* (look up quantum numbers from refs 1 – 3, and 5 – 7.). Transitions can occur between the two levels once the appropriate quantum of energy, viz.,  $\Delta E = E_1 - E_0$  is absorbed or emitted by this molecule. The absorbed or emitted energy is in the form of a *photon*, and the energy of this photon is:

$$\Delta E = h\nu = hc\tilde{\nu} \quad (1.9)$$

where  $h$  is Planck’s constant ( $\sim 6.63 \times 10^{-34}$  Js).

The frequency and the wavenumber of the radiation are then given by

$$\nu = \frac{\Delta E}{h} = \frac{E_1 - E_0}{h} \Leftrightarrow \tilde{\nu} = \frac{E_1 - E_0}{hc} \quad (1.10)$$



**Fig. 1.4** Absorption and emission. A photon of energy  $h\nu$  equal to the difference in the energies of the two levels is absorbed for excitation; a photon of the energy of the gap is released when the system relaxes to the lower level.

**Absorption spectra:** Equation (1.10) implies that if light of one frequency (*monochromatic radiation* – actually, this is not a single frequency, but a very narrow range of frequencies.),  $\Delta E/h$  is incident on the molecule, and then if the molecule is in

level  $0$ , it will absorb that radiation and make a transition to level  $1$ . A detector used to collect light after it has interacted with the molecule will record a diminished intensity of this light. On the other hand, if the molecule is exposed to a wide range of frequencies (*white light*), then all the other frequencies will be undiminished, and the detector will record a diminished intensity of the radiation that corresponds to the energy difference between the two levels. This situation corresponds to collecting an *absorption spectrum*.

***Emission spectra:*** The other scenario is that the molecule relaxes from level  $1$  to level  $0$ , and emits radiation of frequency  $\Delta E/h$ , and an emission spectrum is obtained.

When talking about absorption and emission spectra, one really talks about not one molecule, but a sample containing a large number of molecules, and one must keep things such as *Beer's Law*, and the *Boltzmann Distribution* in mind when interpreting the intensities of the lines observed in spectra. These issues are covered in detail in many of the suggested references (refs 4 – 6).

***From the above discussion, the important thing to realise is that in a spectroscopy experiment, one really measures the difference,  $\Delta E$ , between energy levels, and not the absolute energy of the atom or the molecule in a particular energy level.***

## Chapter 2: Spectroscopy and Quantum Mechanics

What are the rules that govern atoms and molecules and how they interact with EM radiation? How do the spectra of atoms and molecules provide information about their structures? The answer to the first question is dealt with in very rough strokes in this chapter. The reader should refine this picture from the suggested reading. The second question is addressed in the next chapter, again in rather crude terms.

**Achtung!** Despite the title, quantum mechanics is treated in implicit terms in this chapter. You should consult the appropriate references (1 – 3, and parts of the others) to hone your knowledge of this subject.

### 2.1 Atomic Energy Levels

The simplest system – atomic hydrogen is discussed in this section. For a more elaborate treatment, the reader is advised to consult ref 3.

#### 2.1.1 Bound States and Continuum States

The first major success for quantum mechanics was the explanation of the spectrum of the hydrogen atom. Experimentalists had already deduced from the laboratory spectrum of hydrogen that it had many states with well-defined *discrete* energies, and also, states with a *continuum* of energies. Heisenberg and Schrödinger, each with his independent conceptualisation of quantum mechanics, demonstrated that states with a finite average separation between the electron and proton have discrete energies. On the other hand, the states with an infinite average electron-proton separation have a (nearly<sup>‡</sup>) continuous range of energies. The former are called *bound states*, and the latter, *unbound states*. The discrete energies allowed for the hydrogen atom are found to obey the formula

$$E_n = -\frac{\xi}{n^2} \quad (2.1)$$

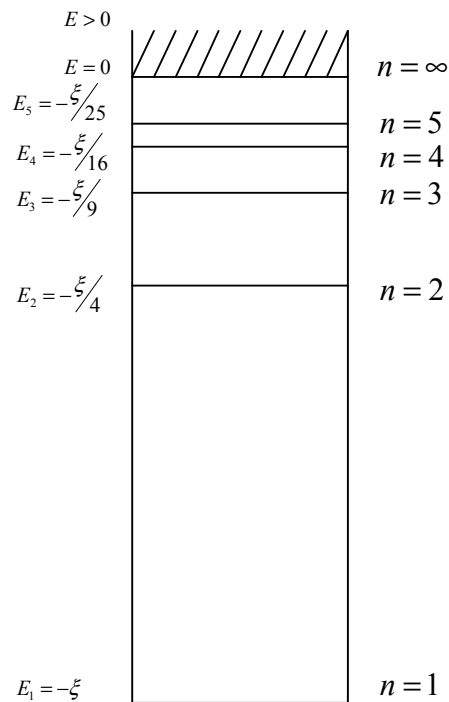
where  $\xi$  is a positive constant energy, and  $n = 1, 2, 3, \dots$  designate the energy levels. The allowed energies of a hydrogen atom are shown in figure 2.1. From equation 2.1, we can see that  $n = 1$ , yields the most negative energy  $E_1 = -\xi$ , which corresponds to the most strongly bound state of the hydrogen atom, commonly referred to as the *ground state*. If an atom in its ground state were imparted an energy greater than or equal to  $\xi$ , then the total energy of the atom would be positive or zero, and the electron and the proton would be infinitely separated (for this convention, take a look at your freshman physics textbooks. The zero of energy is taken to be at infinity, and the lower energies are therefore, negative.).

The state corresponding to  $n = 2$  has energy  $E_2 = -\frac{\xi}{4}$ , that to  $n = 3$  has energy  $E_3 = -\frac{\xi}{9}$ , and so on. Note that the larger the value of  $n$ , the closer the energy of that state to the zero

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<sup>‡</sup> This is known as the *correspondence principle* – the appearance of continuity in classical systems is really an illusion, because the separation between states is extremely small. You should look this up from one of the suggested references.

of the energy. Thus, the hydrogen atom has a ladder of energy levels. At any given time, the atom is found only on one of the steps of this ladder. It is never found with an energy that lies between these steps. It can, however, ascend or descend the steps of this ladder of energy levels.



**Fig. 2.1** Atomic energy levels of hydrogen. Note how the energy levels bunch together for large  $n$ .

A *spectral line* is a result of the transition of the atom from one energy level to another (cf. section 1.3, absorption and emission spectra). When the atom moves up the ladder, the situation corresponds to absorption of radiation, when it moves down the ladder, it corresponds to emission. You may investigate the emission spectra of hydrogen and sodium atoms in the lab).

**Exercise:** Determine the difference in energy between two steps (say,  $n = 4$  and  $n = 2$ ) of the ladder. You will use a relation similar to the answer you obtain here when you perform the experiment on the atomic emission of hydrogen and sodium. Look up the value of the constant  $\xi$  from one of the references listed in the suggested reading.

### 2.1.2 Transitions from bound states to continuum states

In the discussion in 2.1.1, we talked about the spectral transitions between bound states. What happens when a hydrogen atom jumps from one of the bound states to a continuum state? I will let you infer this from the discussion above. What is this process called? What is the process when a hydrogen atom relaxes from a continuum state to a bound state called? Looking at reference 3 may help. First, try to answer these questions on your

own, and then **definitely** look at reference 3 – you will come across many other interesting details as well.

**Caveats:** **1)** The above discussion was restricted to hydrogen, since it is the simplest atom. The concepts introduced also apply to atoms with many electrons. Consult the suggested references for details on these. In particular, note the differences between hydrogen and alkali metals on the one hand, and helium and alkaline earth metals on the other. If you are interested in knowing more about atomic spectra, and want to know the details of the spectra of the elements in the periodic table, you may want to consult some of the later chapters of reference 3. **2)** I have not talked about *selection rules* here, but in interpreting atomic spectra, one needs to worry about these. Selection rules are rules that determine whether a particular transition will occur.

## 2.2 Molecular Energy Levels

Having talked about atoms, we turn our attention to molecules. We look at three of the several different types of energies associated with molecules, viz., electronic, vibrational, and rotational energy, and see how these are described quantum mechanically. The changes in these energies are brought about by collisions or by the absorption or emission of radiation. Again, this is done in coarse terms, and that only in the context of diatomic molecules. The reader is advised to fine tune his or her knowledge from the suggested references.

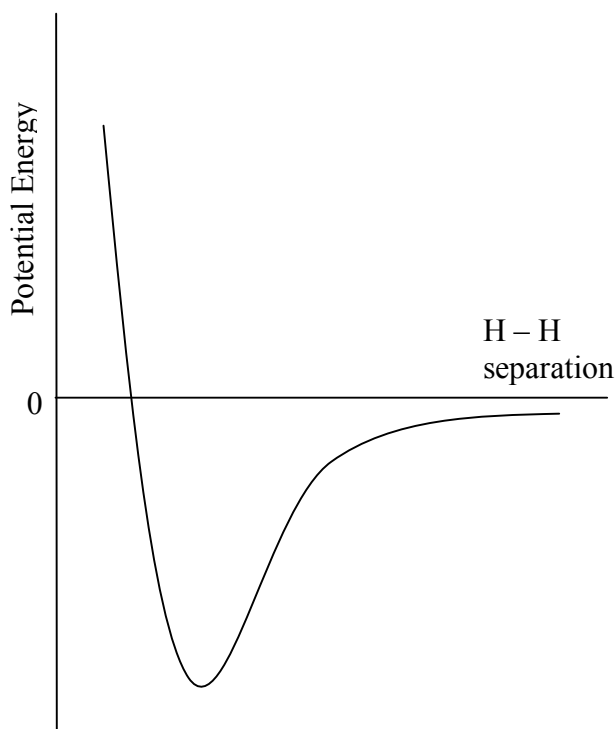
### 2.2.1 Electronic Energy Levels

What happens when two hydrogen atoms approach each other from a very large distance? If the velocity of each of these atoms is low enough<sup>§</sup>, they will form a hydrogen molecule. The basic physics of this process is the following. Each atom possesses an electric field due to the fact that it has an electron and a proton. Each atom is affected by the electric field of the other, and the electron distribution around it changes such that the net force between the atoms is attractive. When the atoms are far apart, then over time, only one of the electrons is between the two protons and the other electron is on the other side of the proton. The electron that is between the two protons acts to partially shield them from each other, but *on average*, in the region between them, the electric field due to the protons is somewhat stronger. This distorts the electron distribution in such a way that it is maximised in the region between the two protons, further screening the protons (and hence decreasing their mutual repulsion). The enhancement in the electron density between the two protons gives rise to attractive forces on the protons that act to *pull* them into this region. As the atoms come closer together, their electrons respond even more strongly to the two protons – the electron of atom A pulls on the proton of atom B, and the electron of atom B pulls on the proton of atom A. Now, the electrons are no longer possessed by either one of the atoms, but are *shared* by both atoms, i.e., proton A cannot tell the difference between electrons A and B (after all, they are both electrons!), and proton B cannot tell the difference between electrons A and B either! If the protons

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<sup>§</sup> Also, if there is a third atom to take away some of the energy from the collision – an exception to this occurs in the interstellar medium (the space between the stars), where a special kind of reaction called an ion-molecule reaction (a two-body collision) is responsible for molecule formation. See, for example, p. 24 – 27 of ref 10.

continue to come closer together<sup>\*\*</sup>, however, the probability that there is no electron density between them becomes large, and they repel each other. Figure 2.2 is a diagrammatic representation of the interaction of two hydrogen atoms to form a molecule. The curve in this figure is the potential energy of a hydrogen molecule in its ground state, plotted as a function of the internuclear (proton-proton) separation. Identify the regions described in the preceding discussion on this curve, i.e., when the hydrogen atoms are far apart, when they are closer together, and when they are so close that the electrostatic repulsion between them becomes large. At what point on the curve is the hydrogen molecule in its *equilibrium configuration*? In other words, where is the energy of this system minimized?



**Fig. 2.2** The interaction potential of two hydrogen atoms in the ground electronic state of a hydrogen molecule. Can you identify the various regions mentioned in the preceding discussion?

The electronic energy levels of a molecule are *qualitatively* similar to those of an atom in that there is a set of discrete energy levels. Transitions between the electronic energy levels occur with the absorption or emission of radiation, or through collisions. They are different from atomic energy levels, because the electron distribution in a molecule is different from that in an atom. But, there is another crucial difference between atomic and molecular systems. When the molecule is in an excited electronic level, the force of attraction between the atoms is different to when it is in the ground electronic level as a result of changes in the electron distribution. *Find out what happens to the attractive forces between the atoms of a molecule in excited electronic energy levels. Do they weaken, or do they strengthen? What does this mean for molecules? From the discussion*

<sup>\*\*</sup> This is what happens in the interior of stars – hydrogen atoms moving at very high speeds (comparable to that of light) collide to form helium – a process called *nuclear fusion*.

in this paragraph, and from your own research from one of the suggested references, what may happen to a molecule in highly excited electronic levels? What wavelengths of light are responsible for this process?

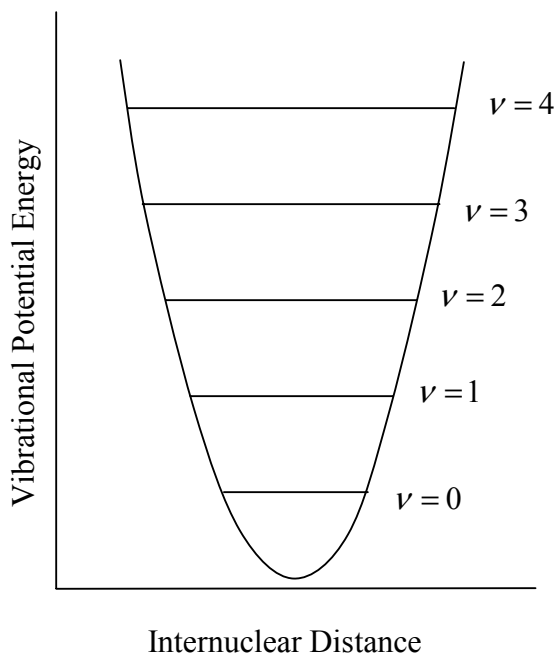
Yet another difference that may have become apparent to the astute reader is that molecules may have other types of energy besides electronic energy. This is discussed in the next two sections.

### 2.2.2 Vibrational Energy Levels

Molecules possess vibrational energy by virtue of the motion of their *nuclei* (atoms) about their equilibrium positions. As is the case for electronic energy levels, the vibrational energy levels of a molecule are also governed by quantum mechanics. The vibrational energy of a molecule in the first approximation is given by

$$E_{\nu} = K \left( \nu + \frac{1}{2} \right) \quad (2.2)$$

where  $K$  is a positive constant energy, and  $\nu = 0, 1, 2, 3, \dots$  is the *vibrational quantum number*. This expression for the energy comes from the description of a bond as a *harmonic oscillator*, much like a spring that is displaced by a *small amount* from its equilibrium position. Again, you should consult the references (in particular, ref 5) in the suggested reading list to learn about this model, and the *anharmonic oscillator* model (which is closer to the behaviour of real molecules).



**Figure 2.3** The allowed vibrational energy levels of a molecule in the harmonic oscillator approximation. Note how the levels are equally spaced. Is this true for a real molecule? Why or why not?

Figure 2.3 shows the vibrational energy levels of a molecule in the harmonic oscillator approximation. Note that even in its ground vibrational level,  $v = 0$ , the molecule still possesses some energy – the *zero-point* energy. What does this mean for molecules? Are they ever still? What is the quantum mechanical explanation for this zero-point motion? Notice the spacing of the vibrational energy levels. According to equation 2.2, they are equally spaced. Is this true for a real molecule? If not, what are the implications of the unequal spacings?

The vibrational potential energy described above is for a diatomic molecule. For a polyatomic molecule, the vibrational energy is the sum of the vibrations of the form given in equation 2.2, with different values of the constant  $K$ . As in the case of electronic energy levels, transitions from one vibrational level to another result from collisions, or the absorption and emission of radiation.

**Important:** It must be emphasised again, that the harmonic oscillator model described above is only a first approximation, and like any other first approximation, is a useful starting point. The vibrational energy levels of a real molecule behave differently from this, and the *anharmonic* oscillator (Morse oscillator) is a better description of the vibrational motion of a real molecule. *You should look up the latter from one of the suggested references.* It should also be pointed out, that the harmonic oscillator model holds only at the *bottom* of the vibrational potential energy well, and deviates significantly from a real vibrational potential well at larger internuclear separations.

### 2.2.3 Rotational Energy Levels

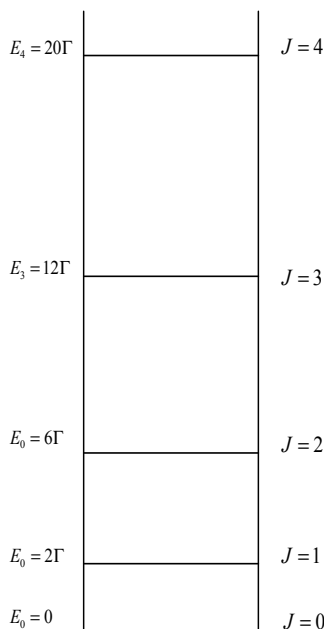
Molecules possess rotational energy due to end-over-end rotations. Classically, a rigid body can rotate with any energy that can be changed in a continuous manner. For example, if you roll a piece of chalk (a round cylinder) on the floor, it should be intuitively obvious that you can impart any rotational velocity – and hence, any rotational kinetic energy to it. In other words, you can set the chalk rolling as quickly or as slowly as you like. However, since molecules are quantum systems, their rotational energies can have only certain allowed values given by

$$E_J = \Gamma J(J+1) \quad (2.3)$$

where  $\Gamma$  is a constant specific to the molecule, and  $J = 0, 1, 2, \dots$  is the *rotational quantum number*. The value of  $\Gamma$  depends upon the masses of the atoms and their internuclear separation. Once again, note that equation 2.3 is a first approximation to the rotation of a molecule, and comes from the *rigid rotator* model, in which it is assumed that the molecule is rigid, and cannot change its shape as it is rotating. For a real molecule, other effects must be taken into account. Can you think of any? From the suggested references, look up the model which better describes the rotation of a real molecule.



The ladder of rotational energy levels is shown in figure 2.4. After looking at this figure, and going through the associated reading, mull over and attempt to answer the questions posed below. There is a lot to swallow here, but if you are systematic, and go over the suggested references, reading actively, you will have an easier time mastering the concepts.



**Fig. 2.4** Allowed energies of a diatomic molecule approximated by a rigid rotator.

What do you notice about the spacing of these energy levels? Note that these energy levels have a family of *degenerate* states. From a quantum mechanics or spectroscopy text, find out the *degeneracy* of the rotational levels of a rigid rotator. Why is  $E = 0$  allowed for a rigid rotator? Does this violate the uncertainty principle?

**Note:** As in the case of atoms, certain selection rules must be applied when analysing the transitions between different energy levels of molecules. Look these up from the suggested references (refs 5 and 6).

**Jargon:** *Energy levels, states, and degeneracy.* In the discussion above, the words *state* and *level* have been used seemingly interchangeably. However, there is a distinction between the two. The following sentence should make this clear. An energy *level* may contain one or more *states*. Also, the states of a molecule may be *degenerate*, that is, they have the same energy. Energy levels may have within them, several degenerate states. For example, the  $2p$  orbital of the O atom in its ground configuration has three degenerate states –  $2p_x$ ,  $2p_y$ , and  $2p_z$ . The distinction between states and levels will become clear once you learn about orbitals and quantum numbers from the suggested reading (refs 3 and 5).

### 2.2.4 Relative Ordering of Molecular Energy Levels

The total energy of the molecule is the sum of its electronic, vibrational, and rotational energies, and depends on the particular electronic state, vibrational state, and rotational state that the molecule happens to be in. Each electronic state has a ladder of vibrational energy levels, which in turn contain a family of rotational levels. Transitions take place from a particular electronic + vibrational + rotational state to another. The energy of each state is the sum of the energies of each part. The three types of energies are said to form a *rovibronic manifold*. Two of the experiments in CH 154K, deal with *rovibrational* and *vibronic* spectroscopy. Based on the wavelength of radiation associated with each type of transition (Fig 1.3), can you deduce the relative ordering of energy levels? In other words, what type of transition – electronic, rotational, or vibrational – takes the most energy? Which takes the least?

## Chapter 3: Interpretation of Spectra – Atomic and Molecular Structure

Spectroscopists can deduce the “structure” of an atom or a molecule from its energy spectrum by using the principles of quantum mechanics. The word *structure* is in quotation marks, because it describes not only the geometric structure of the system under study, but also, the probability distributions of electrons around the nucleus of an atom, and around the nuclei of molecules – the electron configurations of atoms and molecules (note that atoms do not have well defined boundaries, and one can only talk about the *probability distributions* of electrons, because this is what comes out of the use of the Schrödinger equation. Hence, one talks of an *electron cloud* around a nucleus, because electrons are delocalised in space – a consequence of the so-called *wave-particle duality*).

What information is contained in a spectrum? How does one infer the structure of an atom or a molecule from its spectrum? The basics of this are introduced here.

### 3.1 Spectral Information

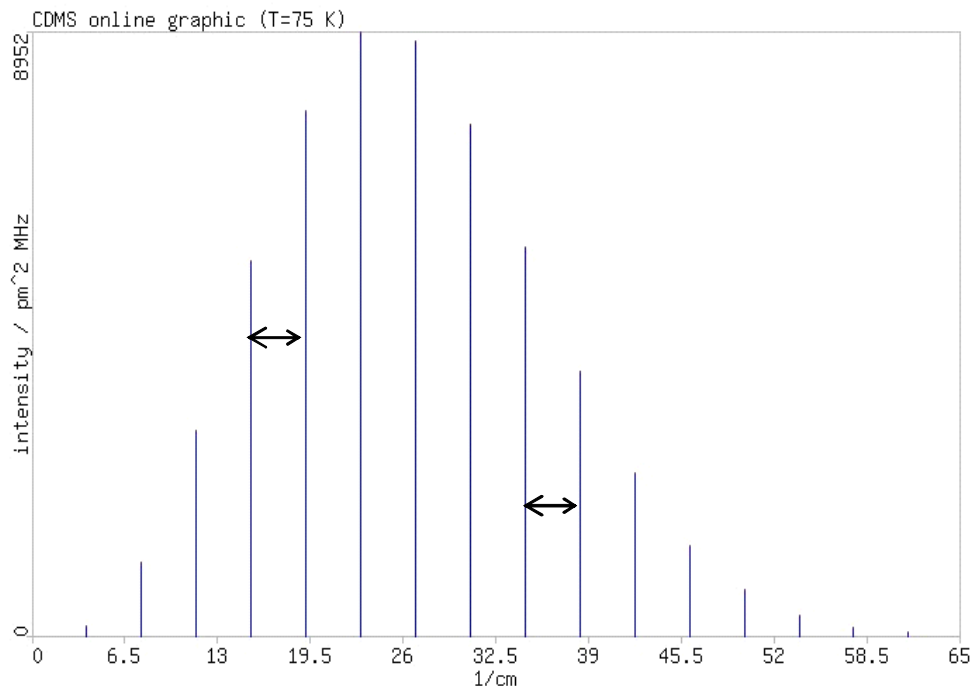
#### 3.1.1 Line Positions and Intensities

***Positions of Spectral Lines:*** As mentioned in section 2.1.1, a *spectral line* is a result of the transition of the system (atom or molecule) from one energy level to another, as it absorbs or emits EM radiation in the process. An energy spectrum is most commonly obtained in the form of some *intensity* as a function of the wavelength (or wavenumber, or frequency). Thus, the wavelength at which a spectral line occurs indicates the energy,  $\Delta E$ , of that transition (see chapter 1, if you haven’t already, for relations between the wavelength and the energy).

***Intensities of Spectral Lines:*** The intensity of a spectral line is an indication of the *probability* of a particular transition – the more intense a line, the more likely the transition. It also tells you something about the *populations of states*, that is, the number of molecules in excited energy levels relative to those in the ground energy level. Suppose that a transition to level C from levels A and B is equally likely, then if level A has more molecules than level B, then the transition from A to C will be stronger than that from level B to C. The third type of information that can be obtained from the intensities of the lines in a spectrum is the *path length* or the *optical depth* of a sample, that is, the number of particles that are in the path of a beam of light passing through a sample (review Beer’s Law, absorbance, and transmittance from refs 4 and 5).

#### 3.1.2 Patterns and Regularities in a Spectrum

In the spectroscopy experiments you will perform in this lab, you will often look for patterns, and regularities in the spectrum of the atoms or molecules you will analyse. The following example serves to illustrate this process. Suppose you collect a microwave spectrum of CO in its ground vibrational state ( $v = 0$ ) at 75K, and it looks like Figure 3.1.



**Fig. 3.1** The rotational spectrum of CO in its ground vibrational level at 75K. The arrows indicate the spacing between two adjacent lines. The length of each arrow is  $2B$ . The plot was generated on the website of the Cologne Database of Molecular Spectroscopy (cdms.de).

There are several *equally spaced lines* with a distribution of intensities. Each of these lines corresponds to a difference in energies between two states (the transitions between states are governed by the appropriate selection rules). These lines are then *assigned* with the appropriate quantum numbers, which in turn are fit to an analytic relation (for example, equation (2.3)). Usually, it is an *extension* of relations like (2.3) known from quantum mechanics. For rotational spectra, the spacing between adjacent lines corresponds to two times the *rotational constant* of the molecule. The rotational constant is given by

$$B = \frac{h}{8\pi^2 I_b c} \quad (3.1)$$

where  $I_b$  is the *moment of inertia* of the molecule. Recall that the moment of inertia is given by

$$I_b = \mu r^2 \quad (3.2)$$

where  $r$  is the internuclear distance,  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the *reduced mass* of the molecule (and the two masses are obviously the masses of the two atoms that make up the molecule).

Hence, we can determine the bond length of the molecule by solving for  $r$ . For polyatomic molecules, there are three moments of inertia (true for any three dimensional object), and hence, one obtains three rotational constants from the spectrum which must be analysed to obtain the bond lengths and bond angles.

The example above illustrates a typical spectroscopic analysis, in which one obtains a certain physical quantity from the spectrum, and uses it to derive other parameters of the molecule using well established relationships from quantum mechanics. You may perform several experiments in which you will do just this. In addition to the structure of the molecule, you will also determine other important parameters, such as the force constant (a measure of the “stiffness”) of the bond, the *anharmonicity* of the bond, and its dissociation energy. The details of these will become clear as you analyse your data from the experiments.

*Thus, the recognition of patterns and regularities in a spectrum is central to spectroscopy.*

*Question:* How does a spectrum such as the one shown in Fig. 3.1 relate to the models (and extensions thereof) that were discussed in chapter 2? Look up one of the suggested references (refs 1 – 5) to find out.

### 3.2 Instrumentation and Associated Details

Look these up from the suggested readings. In particular, see chapter 1 of ref 4 from the suggested reading.

#### Bibliography

- (i.) Parts of this Primer are adapted from refs 3, 4, 5, 6 and 10 listed in the Suggested Reading.
- (ii.) Born, M., and Wolf, E. *Principles of Optics*, 4<sup>th</sup> ed. p. 16.; Pergamon Press, 1970.
- (iii.) Herzberg, G. *Molecular Spectra and Molecular Structure: Volume I, Spectra of Diatomic Molecules*; Krieger Publishing Co. 1991 (Reprint).

#### Suggested Reading

The following references (except refs 6, 9, and 10) are on reserves in the Chemistry library.

**A. Basic Quantum Mechanics:** There are several books dealing with this subject, and you may already have a favourite. But, these are some books I would recommend if this is your first skirmish with the subject. Note that the ubiquitous Atkins book is nowhere in this list!

1. Levine, Ira, N. *Physical Chemistry*, 5<sup>th</sup> ed.; McGraw-Hill, 2001.
2. Levine, Ira, N. *Quantum Chemistry*, 5<sup>th</sup> ed.; Prentice Hall, 1999.

3. Herzberg, G. *Atomic Spectra and Atomic Structure*, 2<sup>nd</sup> ed.; Dover Publications, 1944. Old school, but chapter 1 contains an excellent introduction to quantum mechanics in the light of spectroscopy. Lots of spectra and energy level diagrams tie together theory and observations quite well. Also includes a good discussion of quantum numbers.

**B. Spectroscopy:** Again, many books, but the ones I would suggest are the following.

4. Banwell, C.N., McCash, E.M. *Fundamentals of Molecular Spectroscopy*, 4<sup>th</sup> ed.; McGraw-Hill 1994. Good introduction for the beginner; mathematics is kept to a minimum, and illustrations abound. Stress on the practical aspects of spectroscopy. However, some of the theory is not so great (e.g., discussion of orbitals is misleading and *dead wrong* in places!). Use with due caution. I would recommend reading chapters 1 through 3. For the rest of the material I suggest looking at references 3, and 5.

5. Harris, D.C., Bertolucci, M.D., *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*, Corrected 1<sup>st</sup> ed.; Dover Publications, 1989. An excellent book aimed at the beginning student of spectroscopy, but also goes into many advanced topics. Does not assume a lot of background knowledge, and contains a brief review of quantum mechanics. Also contains an extensive discussion of group theory (people who have had inorganic chemistry will recognize this, but even those who haven't might enjoy it too). Besides, Dan Harris is a hoot! Be sure to read his preface to this book.

6. Bernath, P.F. *Spectra of Atoms and Molecules*; Oxford University Press, 1995. Good book, but assumes knowledge of quantum mechanics, and has few illustrative examples. The examples are in the form of problems that the student must work out. Not many people appreciate this approach. However, there are some masochists out there who just might.

7. Herzberg, G. *Molecular Spectra and Molecular Structure: Volumes I, II, and III*; Krieger Publishing Co. 1991 (Reprint). For specialists and researchers; you might find the examples and illustrations to be enlightening.

8. White, J.M. *Physical Chemistry Laboratory Experiments*; Prentice Hall, 1975. From our own Dr White, this is a good little book, and covers the theory behind the experiments quite well.

**C. Recreational Books dealing with Spectroscopy:**

9. Barrow, Gordon M. *The Structure of Molecules: An Introduction to Molecular Spectroscopy*; W.A. Benjamin, 1963. Old school, and what a book! The only reason I list this as a recreational book, is because it is so much fun to read! Definitely check it out if you can. Only 156 pages thick, this book is a rare read!

10. Hartquist, T.W., Williams, D.A. *The Chemically Controlled Cosmos: Astronomical Molecules from the Big Bang to Exploding Stars*; Cambridge University Press, 1995. This book is an interesting read, and deals with the two exciting fields of astrochemistry and molecular astrophysics. Talks about how chemistry plays a delicate role in controlling the evolution of certain astronomical environments.

## Appendix A: Basic Physics

### Correspondence between linear and rotational motion (adapted from ref 6)

	<i>Linear Motion</i>	<i>Rotational Motion</i>
<i>Position</i>	Distance, $x$	Angle, $\theta$
<i>Velocity</i>	Velocity, $v = \frac{dx}{dt}$	Angular velocity, $\omega = \frac{d\theta}{dt}$
<i>Acceleration</i>	Acceleration, $a = \frac{dv}{dt} = \frac{d^2x}{dt^2}$	Angular acceleration, $\alpha = \frac{d^2\theta}{dt^2}$
<i>Mass</i>	Mass, $m$	Moment of Inertia, $I = mr^2$
<i>Momentum</i>	$p = mv$	Angular momentum $L = I\omega$
<i>Kinetic Energy</i>	$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$	$E = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$
<i>Force (Newton's 2<sup>nd</sup> Law)</i>	Force, $F = ma = \frac{dp}{dt}$	Torque, $\tau = I\alpha = \frac{dL}{dt}$

**Coulomb's Law:** The electrostatic force between two charges,  $q_1$  and  $q_2$ , separated by a distance  $r$  is given by

$$F = \frac{1}{4\pi\epsilon_0} \frac{q_1q_2}{r^2}$$

Note: This force can be attractive or repulsive depending on the sign of the charges.

**Electric field:** The electric field due to a charge,  $q$ , at any point a distance  $r$  away from the charge is given by

$$E = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2}$$

**Electric Dipole Moment:** An electric dipole is a system of two equal and opposite charges separated by a distance,  $d$ , and has a vector quantity called the dipole moment associated with it. The electric dipole moment is given by

$$\vec{\mu} = q\vec{d}$$

As you will discover from your reading of the suggested material, the dipole moment is extremely important in spectroscopy.

For a review of the basic physics behind the quantities summarised here, you should consult your freshman physics textbooks. The more advanced reader may wish to consult *Classical Mechanics* by Herbert Goldstein, and *Classical Electrodynamics* by J.D. Jackson.

## Appendix B: Properties of Light

The following table (adapted from ref 5) summarises the properties of light that are important to the spectroscopist. You should look up the conversion factors between the various units from the suggested references (ref 5, in particular).

<i>Relationship</i>	<i>Symbols</i>	<i>Common units</i>
$\lambda\nu = c$	$\lambda$ wavelength $\nu$ frequency $c$ speed of light	nm, Å, μm Hz (s <sup>-1</sup> ) 2.99792458x10 <sup>10</sup> cm s <sup>-1</sup> in vacuum
$\tilde{\nu} = \frac{1}{\lambda}$	$\tilde{\nu}$ wavenumber	cm <sup>-1</sup>
$E = h\nu = hc\tilde{\nu}$	$E$ energy	J, cal, kcal, erg, eV
$p = \frac{E}{c}$	$p$ momentum	kg m s <sup>-1</sup>
$A = \epsilon cl$	$A$ absorbance $\epsilon$ molar absorptivity $l$ light path length	Dimensionless L mol <sup>-1</sup> cm <sup>-1</sup> cm
$A = \log\left(\frac{I_0}{I}\right)$	$I_0$ incident light intensity $I$ emergent light intensity	J m <sup>-2</sup> s <sup>-1</sup>
$T = \frac{I_0}{I}$	$T$ transmittance	Dimensionless
$\%T = 100T$	$\%T$ percent transmittance	Dimensionless