of several types: photovoltaic, photoconductive, photoelectromagnetic, and photoemissive, of which the principal detector is the photomultiplier.

The performance of the above detectors is a function of many parameters, such as temperature, chopping frequency, field of view, detector area, and so forth, and the performance is specified in numerous ways. One common performance criterion is the spectral D^* (dee star). The spectral response, as indicated by the spectral D^*, for several of the above mentioned detectors is indicated at the bottom of Fig. 2.3. The difference in performance caused by changing the temperature from 195 to 295°K for lead sulphide and indium antinomide is indicated.

More detailed discussions of sources and detectors are available in standard texts (4, 5) and in chapter 3 of this volume.

2.4.3 Types of Spectra

The energy distribution in any material is fundamentally a question of the relative positions of all particles at a given time. The total energy of the system can be expressed as the sum of four different types of energy: translational, rotational, vibrational, and electronic. Because different amounts of energy are required to cause transitions within each of these different energy types, evidence for a transition will occur in a specific part of the spectrum.

Translational energy need not be considered here because it is generally very small and is not quantized, and the space available for this type of motion is unrestricted and usually undefined. The other three types of energy are limited in space to the size of the molecule, and are truly quantized.

Rotational energy is the kinetic energy of rotation of a molecule as a whole in space, and transitions between the rotational energy levels which produce rotational spectra require only small amounts of energy. Consequently, pure rotational transitions may be observed in the mid- and far-infrared and microwave regions, where the energy is very low and insufficient to cause or result from vibrations or electronic transitions.

Vibrational energy is involved with the movement of atoms relative to each other about a fixed position. Transitions here require greater amounts of energy than for rotations, and consequently evidence for such vibrational transitions occur in the mid and near infrared regions. However, because the energy necessary to cause vibrations is greater than that necessary to cause rotations, vibrational transitions are always accompanied by rotations in the situation where the material is free to rotate (as in gases).

Electronic energy is the energy required to cause the electrons about individual atoms, or located in bonds, to adopt a different configuration, and this requires even larger amounts of energy. Therefore, evidence for this type of transition is observed predominantly in the visible, ultraviolet, and x-ray regions. Again, the energy required is more than sufficient to cause vibrational and rotational transitions as well, and so evidence for these transitions appear together with those of electronic transitions. The energy levels, energy level diagrams and the transitions between these levels will be discussed in somewhat more detail below (see Section 2.6).

The spectral range between the ultraviolet and microwave, which corresponds to the energy transitions between electronic, vibrational, and rotational levels, can be considered to be the range where electromagnetic energy truly interacts with matter, and consequently they are the regions where most information about the nature of a material can be obtained from a study of the electromagnetic energy which has interacted with it. As a result, this is the range that is of prime interest for remote sensing purposes in the present discussion.

In regions of higher energy in the spectrum, such as the "ray" region (gamma, x-ray, and cosmic), the energy is sufficient to disrupt matter, causing electrons to be completely lost to the system or for bonds to be broken and molecules to fragment. In regions of lower energy, the longwave region—radar, radio, and audio—the interaction with matter is frequently quite feeble or transient and is quite often a consequence of macroscopic effects. Although these latter two regions yield extremely powerful data in remote sensing applications, (for example, from γ-ray spectroscopy and x-ray fluorescence of the lunar surface) discussion of these techniques lies outside the scope of the present treatment.

2.5 QUANTUM DESCRIPTIONS

It is necessary to adopt a quantum view for the interaction of electromagnetic energy with matter

because, whereas the large objects of our ordinary experience move according to Newton's classical laws of motion, the small objects that make up atoms and atomic systems (the electrons and nuclei) move according to the principles of quantum mechanics.

2.5.1 Description of Matter

The quantum mechanical description of an atom or atomic system is made in terms of a wave function, or state function, which is usually designated by Ψ.

A characteristic state (also called an eigenstate, or a stationary state) is one that corresponds to a perfectly defined energy for the system, and a system may have many such states, which are usually different in energy. When two or more states have the same energy, those states are said to be degenerate.

The basic task of quantum mechanics is to determine methods of finding the wave functions for a given atom or atomic system, and the performance of this task involves obtaining solutions for the Schrodinger equation. As stated earlier, the Schrodinger equation is not strictly derivable, and should be considered to be the counterpart in quantum mechanics of Newton's $f = ma$ in classical mechanics.

The Schrodinger wave equation has the general form

$$\nabla^2 \psi + \frac{8\pi^2 m}{h}(E - U)\psi = 0$$

for a particle of mass m, where ψ is the wave function, h is Planck's constant, E is the eigenvalue, and U is a potential function.

The details of solving the equation are, except for the simplest systems, usually quite complicated; but the results are extremely important and easily understood, and most remote sensing concepts are based on such results.

It turns out that acceptable solutions to the Schrodinger equation are only possible if the energy, E, has certain definite discrete values. These values are the eigenvalues and are, in fact, the characteristic energy levels of that particular system. Because every system has a different arrangement of the energy values or energy levels, the arrangement of energy levels for any system—or

material—completely characterizes that system.

Information about any system in a remote sensing situation is only available as a consequence of the system changing from one of these characteristic energy levels to another, and such a change is called a transition. Such transitions most often take place as a result of absorption or emission of electromagnetic radiation. The various types of energy levels will be discussed in the next section.

2.5.2 Description of Interaction of Energy with Matter

Of particular interest in remote sensing of geology is the study of the interaction of energy with solids. They, in particular, may be characterized in terms of their optical constants, n, and k, the refractive index and extinction coefficients, respectively, which are functions of wavelength for a given material. The magnitude of the refractive index indicates the speed with which electromagnetic energy passes through the material, while the effect of the extinction coefficient is to introduce an exponential damping to the electromagnetic wave as it traverses the material.

The usefulness of the quantum mechanical approach is that it allows the stationary states of a system to be determined. These time independent stationary states are, in fact, the only allowed energy levels which the system can adopt. Such energy levels may be plotted to yield an energy level diagram that can be most useful in visualizing the transitions that produce features in a spectrum.

Once a system occupies a particular stationary state or energy level, it will remain in that state indefinitely until something causes it to change, thus causing a transition to another allowed energy level.

At present, we are primarily interested in those interactions that alter the energy content of the material, and the frequency-intensity relationship of the radiation, and so basically we are concerned with absorption and emission of electromagnetic radiation.

If we consider a system that is in the process of changing from one stationary state (energy level) to another, the state function during the transition is given by a linear combination of the two stationary states involved. This intermediate state function is called a coherent state, and the essential difference between a coherent and stationary state is that the energy of the stationary state is well defined while that of the coherent state is not.

The quantum mechanical description of, for example, a radiating system may be given as follows: During a transition from one energy level (E_1) to another (E_2), the system enters a coherent state and oscillates sinusoidally with a frequency (ν) determined by the energy difference between the two energy levels, that is

$$E_1 - E_2 = h\nu$$

Such a sinusoidal oscillation is accompanied by an oscillating electromagnetic field that constitutes the radiation.

Before electromagnetic radiation can interact with matter, there must be some way in which the matter can interact with either the electric or magnetic field of the radiation. In most transitions of interest in remote sensing situations, the interaction takes place between the electric field and matter. However, matter does react with the magnetic field and a great deal of very valuable information concerning a material is available as a result. For example, radiation in the microwave and radio frequency regions is used to study very low energy transitions that result from the reorientation of nuclear and electron spins when subjected to an applied magnetic field, as in the case of nuclear and electron spin resonance studies.

In order for the electric field of electromagnetic energy to interact with matter, the system must have a charge distribution that changes when the system makes the transition from the initial to the final state. Two stationary states may be induced to become coherent, or an induced transition may take place, due to the fact that when electromagnetic energy falls on a system, the oscillating field of the electromagnetic radiation may disturb the potential energy of the system in just the correct way to allow the transition. The electric field of the radiation, in fact, oscillates at the point occupied by the system with a frequency ν. Then the electric field in the x direction, E_x, can act on the dipole component μ_x to produce a change in the energy $E_x \mu_x$. This term adds to the potential energy of the system and consequently is responsible for causing the transition to take place.

2.6 ENERGY LEVELS

In most geological remote sensing situations the energy detected passes through the terrestrial atmosphere, and so it is necessary to have some understanding of the spectral behavior of gases as well as solids. Gases differ from solids because they possess the ability to rotate. The discussion here will be limited to the energy levels and the transitions between them in molecules, except for a brief treatment of crystal field effects on ions in solids.

The total energy of a system is made up of the sum of three distinct types of energy—rotational, vibrational, and electronic—and each of these forms will be discussed separately below.

2.6.1 Rotational Energy Levels

These are only introduced because of their relevance to the atmospheric gases, and to illustrate the concept of discrete energy levels between which transitions occur to produce features in a spectrum.

The rotation of a gas molecule can be described in terms of its angular momentum, I, defined as

$$I = \Sigma_i m_i r_i^2$$

where m_i is the mass of the ith particle and r_i is its perpendicular distance from an axis of rotation. There are three principal axes of rotation (designated a, b, and c) whose origin is the center of gravity of the system, and the moments of inertia about these axes are designated I_a, I_b, and I_c.

Any gas molecule can be classified into one of four general types, depending upon the relationship between the values of its three principal moments. The molecule is called linear when $I_a = I_b$, and $I_c = 0$; a spherical top when $I_a = I_b = I_c$; a symmetric top when $I_a = I_b \neq I_c$; and an asymmetric top when $I_a \neq I_b \neq I_c$.

The energy levels for a linear or symmetric top are very simply calculated because only one quantum number, designated J, is required to specify the rotational state, and the energy of the levels are given by

$$E_{ROT} = \frac{h}{8\pi^2 cI} J(J + 1)$$

where J can take any integral value; that is, $J = 0, 1, 2, 3$, and so forth.

Fig. 2.4 shows an energy level diagram calculated using this approach where the allowed transitions between the levels are indicated by vertical
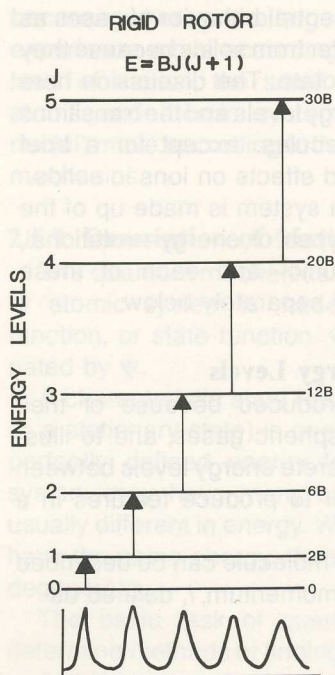
RIGID   ROTOR

$$E = BJ(J + 1)$$

FIGURE 2.4. Rotational energy level diagram. The energy levels were calculated using a rigid-rotor model, where $B = \dfrac{h}{8\pi^2 cI}$ is the rotational constant. The appearance of spectra produced as a result of transitions between these levels is included at the bottom.

arrows, and the form of the resultant spectrum is illustrated immediately below. The treatment for symmetric and asymmetric top molecules is more complex, and their treatment should be pursued through standard works on the subject, for example, King (6, 7).

2.6.2 Vibrational Energy Levels

The forms of the vibrations and the values of the permitted energy levels of a material are determined by the number and type of the constituent atoms, their spatial geometry, and the magnitude of the binding forces between them. The vibrations of a molecule consist of very small displacements of the atoms from their equilibrium positions.

In a molecule composed of N atoms there are $3N$ possible modes of motion because each atom has three degrees of freedom. Of these modes of motion, three constitute translations, and three constitute rotations of the molecule as a whole (except for linear molecules where there are only two rotations) and so there are $3N$-6 (or $3N$-5 for

linear molecules) possible independent types of vibrations.

The general motions of a system of atoms can be analyzed in terms of a set of internal coordinates. There is one particular such set called "normal coordinates," which is especially convenient for describing molecular vibrations, and indeed this set is necessary for carrying out quantum mechanical treatments. One particular value of the normal coordinate treatment is that the symmetry of the molecule allows great simplifications to be made in the computational process.

The energy levels of a linear harmonic oscillator are given by

$$E_v = (v + \tfrac{1}{2})\, h\nu ,$$

where ν is the classical frequency of the system, and v is the vibrational quantum number which may take any integral value, that is, $v = 0, 1, 2 \ldots$, and so forth. For a molecule with many classical frequencies, the energy is given by $E = (v_1 + \tfrac{1}{2})\, h\nu_1 + (v_2 + \tfrac{1}{2})h\nu_2 + \cdots + (v_{3N-6} + \tfrac{1}{2})h\nu_{3N-6}$.

The bands that occur in a spectrum as a result of transitions between vibrational energy levels are referred to as fundamentals, overtones, or combination tones. Fundamentals occur as a result of a transition from the ground state, where the value of all quantum numbers v_i is zero, to a state where all are zero except one, and its value is unity, that is, $v_i = 1$. This is, then, the fundamental of the ith vibrational mode, and features due to fundamental vibrations typically occur in the mid and far infrared regions of the spectrum, all at wavelengths longer than 3 μm. An overtone occurs when the transition is from the ground state to one in which $v_i = 2$, while all other quantum numbers remain zero. Combination tones occur when a transition takes place from the ground level (all $v_i = 0$) to a level whose energy is determined by the sum of two or more fundamental or overtone vibrations, that is, to a level where

$$E_v = (v_1 + \tfrac{1}{2})h\nu_1 + (v_2 + \tfrac{1}{2})\, h\nu_2$$

where v_1 and $v_2 \neq 0$. Features due to overtone and combination zones typically appear between 1.1 and 5 μm. The energy levels, normal coordinates, and spectrum resulting from the indicated transitions are shown in Fig. 2.5. More complete discussions of the vibrational process are available in
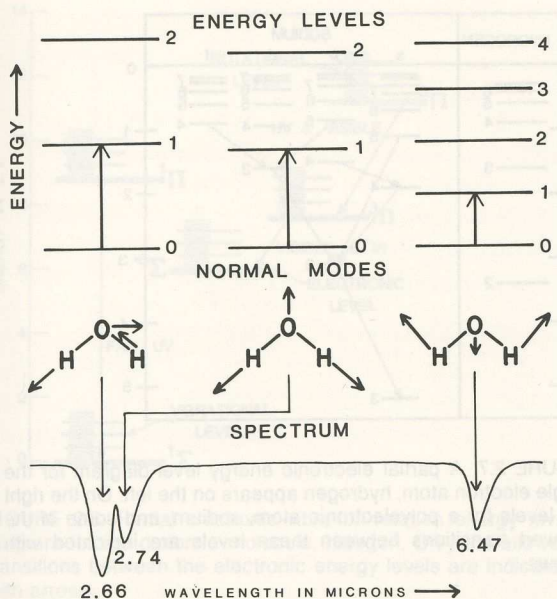
FIGURE 2.5. Vibrational energy level diagram for water, in which the levels of the three fundamental (v_3, v_1, and v_2) vibrations are separated horizontally. A representation of the form of these normal modes is illustrated diagrammatically near the center, and the appearance of the infrared absorption spectrum corresponding to the transitions from the ground to the first excited states is included at the bottom.
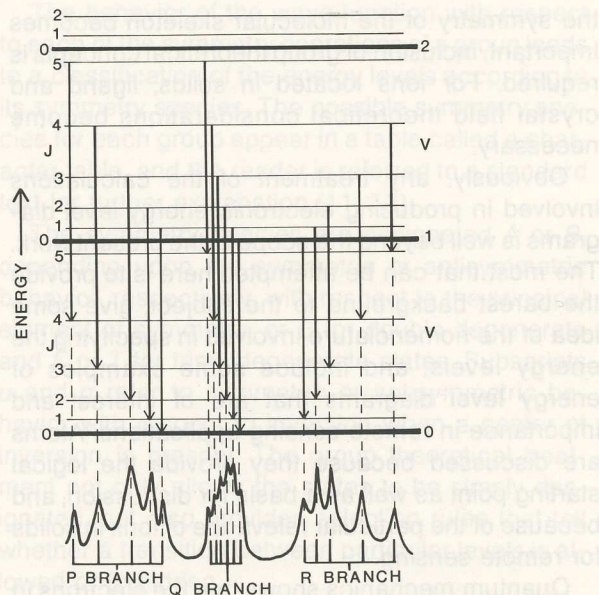

FIGURE 2.6. Vibration-rotation energy level diagram showing the allowed transitions (indicated with arrows) between the various energy levels. The resultant spectrum is shown below, displaying the typical P, Q, and R branches.

standard text books, that is, Wilson (8), Herzberg (9), and Barrow (10).

2.6.3 Vibration-Rotation Energy Levels

Normally, both the vibrational and rotational energy will change simultaneously because the amount of energy required to cause a vibrational transition is much more than sufficient to cause rotational transitions. Consequently, gas spectra usually consist of a large number of lines extending to both higher and lower frequencies from the frequency of the vibrational transition. These are due to the familiar P, Q, and R branches in vibrational gas spectra. The P branches appear at lower frequencies, R branches at higher frequencies and Q branches occur near the center. This is illustrated in Fig. 2.6.

Gas spectra of different molecules have quite different appearances, depending upon which selection rules apply in the particular case. Detailed studies of the associated rotational bands in the PQR branches can yield information on the moments of inertia of a molecule in both the ground and excited states.

2.6.4 Electronic Energy Levels

The subject of electronic energy levels is both extensive and complex because the treatment varies widely depending upon the nature of the material being considered.

In performing remote sensing, one encounters diatomic (O_2, N_2, CO, and so forth) and polyatomic (H_2O, CO_2, N_2O, and so forth) atmospheric gases, complex molecular organic materials (principally vegetation), and solid inorganic substances (rocks and soils). From a geological standpoint, much excellent data is available as a result of transitions between the electronic energy levels of ions embedded in inorganic solids. These transitions provide extremely valuable, though indirect, information concerning the bulk material. Consequently, remote sensing involves a consideration of the energy levels in many different types of matter.

An exact solution to the Schrodinger equation can only be obtained for an atom with a single electron. Solutions for polyelectronic atoms are achieved by making various approximations, such as ignoring the effects of the inner shell electrons.

For polyatomic molecules, consideration of the electronic states involves excursions into valence-bond and molecular-orbital theory, and, because

the symmetry of the molecular skeleton becomes important, inclusion of group theoretical concepts is required. For ions located in solids, ligand and crystal field theoretical considerations become necessary.

Obviously, any treatment of the calculations involved in producing electronic energy level diagrams is well beyond the scope of the present work. The most that can be attempted here is to provide the barest background to the subject, give some idea of the nomenclature involved in specifying the energy levels, and include some examples of energy level diagrams that are of interest and importance in remote sensing applications. Atoms are discussed because they provide the logical starting point as well as a basis for discussion, and because of the particular relevance of ions in solids for remote sensing.

Quantum mechanics shows that the electrons in an atom can only occupy specific quantized orbits, and these can be specified in terms of three quantum numbers, designated n, the principal quantum number; L, the angular momentum quantum number; and m, the magnetic quantum number. For polyelectronic atoms a fourth quantum number, m_s, the spin quantum number is required. For the hydrogen atom, the electronic levels can be specified by just the principal quantum number (n), and the values of the levels are given by

$$E_{ni} = \frac{R}{n_i^2}$$

where R is a constant determined by the mass and the charge of the electron. The energy levels of hydrogen are shown on the left side of Fig. 2.7.

The spectroscopic designation of an electronic energy level for most polyatomic atoms can be given in terms of a quantum number L (corresponding to the individual electron angular momentum quantum number l) and a quantity called the multiplicity. States for which $L = 0, 1, 2, 3$, and so forth, are designated S, P, D, F, and so forth, while the multiplicity is defined as $2S + 1$, where S is the resultant spin. Since S can take ½, or whole integral values, $2S + 1$ takes values, 1, 2, 3, and so forth. The electronic state is then designated ^{2S+1}L. When the value of $2S + 1$ is 1, 2, 3, 4, and 5, the states are called singlet, doublet, triplet, quadruplet, or quintet states.
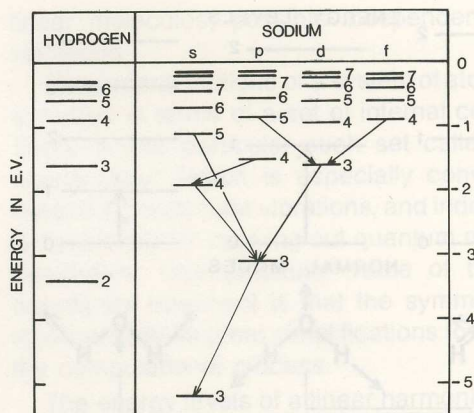

FIGURE 2.7. A partial electronic energy level diagram for the single electron atom, hydrogen appears on the left. On the right the levels for a polyelectronic atom, sodium, and some of the allowed transitions between these levels are indicated with arrows.

A partial energy level diagram for sodium is shown on the right-hand side of Fig. 2.7.

As distinct from atoms, many molecules and all diatomics possess the ability to both vibrate and rotate, and consequently vibrational and rotational energy levels are superimposed on each electronic energy level. Because the energy involved in an electronic transition is much greater than that required for vibrational and rotational transitions, the electronic transitions are always accompanied by vibrational, and where possible, by rotational transitions. Consequently, diatomic electronic spectroscopy is a particularly fruitful area for obtaining detailed information on moments of inertia and potential energy functions of the states involved. A partial energy level diagram for the diatomic molecule N_2 appears in Fig. 2.8.

For some polyatomic molecules, an electronic transition may be essentially located in a specific localized bond or group, such as in the $>C = O$ group, and in such a situation the analysis can be similar to that for diatomic molecules. For others, in particular the aromated hydrocarbons, the various electronic states are designated in terms of the states of the π electrons.

However, in general, the electronic states of polyatomic molecules are best described in terms of the state of the molecule as a whole for a given assignment of electrons in individual orbitals. The total electronic wave function must have a symmetry that is compatible with the symmetry of the molecular skeleton, and so it is the symmetry behavior that
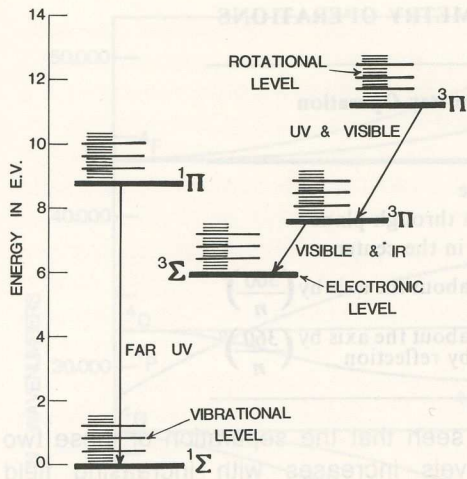
FIGURE 2.8. Partial electronic-vibration-rotation energy level diagram for the diatomic molecule, nitrogen. Only the allowed transitions between the electronic energy levels are indicated with arrows.

best describes the electronic states of a polyatomic molecule.

In order to have some feeling for the meaning of the symbols assigned to these states, it is necessary to briefly consider some aspects of symmetry groups. Such concepts are at least equally important in considering the vibrational motions of polyatomic molecules. The advantage of the symmetry group approach is that it allows hundreds of thousands of molecules to be classified into a small number of groups according to the number and nature of their symmetry elements. All molecular symmetries can be treated in terms of just five symmetry elements, and these elements can be explained in terms of the symmetry operation involved. The symmetry elements, the symbols designating them, and the corresponding symmetry operations are listed in Table 2.1.

It is found that only a relatively few combinations of these symmetry elements occur, and each combination of the elements is called a group. They are called either symmetry point groups or symmetry space groups. The point groups are so named because under all operations of the group, some point in the molecule remains fixed. Symmetry space groups are usually appropriate for crystals, and they are so called because translations are allowed (that is, no point remains fixed) where the entire unit cell is translated by an operation to another completely equivalent position in the crystal.

The behavior of the wave function with respect to each of the symmetry operations of a group leads to a classification of the energy levels according to its symmetry species. The possible symmetry species for each group appear in a table called a character table, and the reader is referred to a standard text for further explanation (11, 12).

The symmetry species are designated A or B, depending upon the symmetric or antisymmetric behavior, respectively, with respect to the principal element of symmetry, or E for double degenerate and F or T for triply degenerate states. Subscripts u and g refer to symmetric or antisymmetric behavior with respect to inversion when a center of inversion is present. The group theoretical treatment not only allows the states to be simply designated, but also provides selection rules that tell whether a transition between particular levels is allowed or forbidden.

As mentioned above, for remote sensing of geological materials, one of the more important considerations is that of the electronic energy levels of an ion in a solid. When an atom is embedded in a crystal lattice, either as a constituent or an impurity, one or more of its electrons may be shared by the solid as a whole, and is not associated with any particular atom. The energy levels of such electrons become smeared into regions called valence or conduction bands of the solid as a whole, and the atom becomes an ion. The bound electrons of the ion have quantized energy states associated with them.

In the case of rare earth atoms, the unfilled shells involve the deep-lying $4f$ electrons, which are well-shielded from outside influences; thus their energy levels remain essentially unchanged when embedded in a solid.

In the transition elements (for example, Ni, Cr, Fe, and so forth) however, it is the $3d$ shell electrons that primarily determine the energy levels, and these electrons are not shielded, so their energy levels are greatly perturbed by the external field of the crystal. In such a case it is the symmetry of the surrounding electric field that designates the energy levels.

In the spherical potential of the free ion, the $5d$ orbitals have identical energy levels, that is, they are fivefold degenerate, and the effect of applying a surrounding field is to resolve this degeneracy by changing the energies of some of the orbitals relative to others. However, the new energy states

TABLE 2.1.   SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

Symbol	Symmetry Element Description	Symmetry Operation
E	Identity	No change
σ	Plane of symmetry	Reflection through plane
i	Center of symmetry	Inversion in the center
C_n	Axis of symmetry	Rotation about the axis by $\left(\dfrac{360}{n}\right)^{\circ}$
S^n	Rotation-Reflection axis	Rotation about the axis by $\left(\dfrac{360}{n}\right)^{\circ}$ followed by reflection

must be compatible with the symmetry of the imposed field and, consequently, the energy levels are specified in terms of the symmetry species of the applied crystal field.

The way in which the degenerate energy levels of the isolated ion are resolved by application of a crystal field (called crystal field splitting) is indicated in Fig. 2.9 for the simplest case of an ion with only a single d electron, such as is the case for the Ti^{3+} ion. The five-fold ^2D level of the free ion, shown on the left, is split into a doubly degenerate ^2E_g and a triply degenerate ^2T_g level under the influence of an octahedral field, and

it can be seen that the separation of these two energy levels increases with increasing field strength.

A more complex, but only partial energy diagram appears in Fig. 2.10 for a d^5 ion, such as Mn^{2+}. The energy levels of the free ion are shown (where the states are designated using nomenclature appropriate for a polyelectronic atom) on the left-hand side, and the energy levels adopted as a function of field strength for an octahedral field on the right. It will be noted that the totally symmetric ^6S state is not split.

The energy levels for the same ion in different crystal fields are greatly different. Consequently, in observing transition between the energy levels of the ions in crystals, one obtains particularly useful information about the type of material in which the ion is contained, and even though this information is somewhat indirect, it is among the most powerful techniques available for remote sensing of solids.
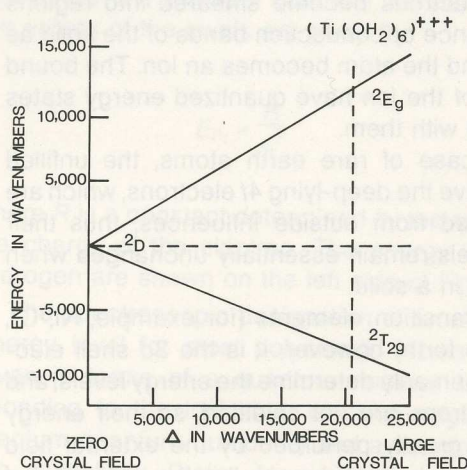
2.7 REQUIREMENTS FOR REMOTE SENSING

The basic concept for remote sensing is that information about the object or target is contained in the electromagnetic radiation passing from the object to the observer, and it is this radiation that forms the communication link. The information is present in the form of a wavelength-intensity relationship, and when this is presented for more than one wavelength, and the wavelengths are ordered, it constitutes a spectrum.

The essential elements of a remote sensing system are the generation, interaction with the object, transmission, collection and wavelength separation, and the detection and recording of electro-

FIGURE 2.9. The electronic energy level diagram for a metal ion with a single d electron. The effect of increasing the strength of an octahedral crystal field on the ^2D state is illustrated. The five-fold degenerate ^2D state is split into a doubly degenerate ^2E_g and a triply degenerate $^2T_{2g}$ state, and their separation increases with increasing field strength. The position of the levels for the Ti^{3+} ion in the complex $(Ti(H_2O)_6)^{3+}$ is indicated by the vertical dotted line. A transition ^2E_g $^2T_{ig}$ will produce a spectral feature at about 20,400 cm⁻¹.