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ELECTROMAGNETIC SPECTRUM:

Scientists have found that many types of wave can be arranged together like notes on a piano keyboard, to form a scale.

X-RAYS:

X-rays are very high frequency waves, and carry a lot of energy. They will pass through most substances, and this makes them useful in medicine and industry to see inside things. X-rays are given off by stars, and strongly by some types of nebula.

When we use X-rays, we make them by firing a beam of electrons at a "target". If we fire the electrons with enough energy, X-rays will be produced.
Uses:

- X-rays are used by doctors to see inside people. They pass easily through soft tissues, but not so easily through bones.

- We send a beam of X-Rays through the patient and onto a piece of film, which goes dark where X-Rays hit it.

- This leaves white patches on the film where the bones were in the way.

- Lower energy X-Rays don't pass through tissues as easily, and can be used to scan soft areas such as the brain.

- Sometimes a doctor will give a patient a "Barium Meal", which is a drink of Barium Sulphate. This will absorb X-rays, and so the patient's intestines will show up clearly on a X-Ray image.

- X-Rays are also used in airport security checks, to see inside your luggage. They are also used by astronomers - many objects in the universe emit X-rays, which we can detect using suitable radio telescopes.

**Ultra-Violet :**

Ultra-Violet light is made by special lamps, for example, on sun beds. It is also given off by the Sun in large quantities. We call it "UV" for short.

Uses:

- Uses for UV light include getting a sun tan, detecting forged bank notes in shops, and hardening some types of dental filling. You also see UV lamps in discos, where they make your clothes glow.
- This happens because substances in washing powder "fluoresce" when UV light strikes them.

- When you mark your possessions with a security marker pen, the ink is invisible unless you shine a UV lamp at Ultraviolet rays can be used to kill microbes.

- Hospitals use UV lamps to sterilise surgical equipment and the air in operating theatres. Food and drug companies also use UV lamps to sterilise their products.

- Suitable doses of Ultraviolet rays cause the body to produce vitamin D, and this is used by doctors to treat vitamin D deficiency and some skin disorders.

Infra-red:

Infra-red waves are just below visible red light in the electromagnetic spectrum ("Infra" means "below"). You probably think of Infra-red waves as heat, because they're given off by hot objects, and you can feel them as warmth on your skin. Infra-Red waves are also given off by stars, lamps, flames and anything else that's warm - including you.

Uses:

- Infra-red waves are called "IR" for short. They are used for many tasks, for example, remote controls for TVs and video recorders, and physiotherapists use heat lamps to help heal sports injuries. Because every object gives off IR waves, we can use them to "see in the dark".

- Night sights for weapons sometimes use a sensitive IR detector (other types, called "image intensifiers", use visible light). Remember the film, "Predator"?

- Apart from remote controls, one of the most common modern uses for IR is in the field of security. "Passive Infra-Red" (PIR) detectors are used in burglar alarm systems, and to control the security lighting that many people have fitted outside their
houses.

- These detect the Infra-Red emitted by people and animals. You've probably seen TV programmes in which police helicopters track criminals at night, using cameras which can see in the dark.

- These cameras use Infra-Red waves instead of "ordinary" light, which is why people look bright in these pictures.

**Doppler Line Broadening:**

**Lorentzian versus Maxwellian:**

Natural broadening, which is governed by a Lorentz distribution, is converted into Doppler broadening, which is assumed to be characterized by a Maxwell distribution, when the atoms are set into motion by placing them in contact with a heat reservoir and, due to the linear relation between velocity and frequency shift, the latter will also be governed by a Maxwell distribution.

If, in the absence of Doppler broadening, there is only natural radiation broadening, it is unclear how the contact with a heat reservoir converts a Lorentzian into a Maxwellian distribution.

**Widths of spectral lines:**

**Real spectral lines are broadened because**

- Energy levels are not infinitely sharp.
- Atoms are moving relative to observer.

**Three mechanisms determine profile φ(ν):**

- Quantum mechanical uncertainty in the energy E of levels with finite lifetimes.
The natural width of a line (generally very small).

Collisional broadening. Collisions reduce the effective lifetime of a state, leading to broader lines. High pressure.

More collisions (eg. stars). – Doppler or thermal broadening, due to the thermal (or large-scale turbulent) motion of individual atoms in the gas relative to the observer.

**Natural width:**

**Uncertainty principle:**

- Energy level above ground state with energy E and lifetime $\Delta t$, has uncertainty in energy: $\Delta E \Delta t \sim h$.
- A photon emitted in a transition from this level to the ground state will have a range of possible frequencies, $\Delta \nu \sim \frac{\Delta E}{h} \cdot \frac{1}{2\pi \Delta t}$.

**Doppler Half-Width:**

If the damping coefficient happens to be the ratio of the natural radiation damping constant to the fine structure constant, $\frac{4\pi \ h \nu^2}{3 \ mc^2}$.

**Pressure broadening:**

The first test for collisional effects is the prediction of helium–O₂ broadening and shifting coefficients of the spectral lines in the A-band spectrum.

These coefficients represent the linear dependence of the line widths and shifts on the, in this case, helium density. The broadening coefficients have been determined experimentally, and are reported in the literature.

The line shift coefficients, however, were too small to determine accurately. The effect of line-mixing on the line widths is expected to be negligible, since there is no...
significant overlap between spectral lines at the relatively low pressures for which the experiments were carried out (0.26 atm O$_2$ partial pressure and a range of 0.13–0.52 atm helium pressure).

If line-mixing is neglected, the spectrum becomes a sum of Lorentz lines. The pressure broadening and shifting coefficients can be defined.

We define the coefficients $\gamma_k$ for the kth spectral line in units of cm$^{-1}$ atm$^{-1}$ for comparison with the experiment (k corresponds to a set of quantum numbers $N$, $F$, $J$ of the transition).

**Pressure-dependent absorption strengths:**

A comparison between theory and experiment will put the line-mixing incorporated in the current theory to the test. One tests the formalism, the helium–O$_2$ interaction potentials, and especially the off-diagonal elements in the relaxation matrix.

For this comparison, one should look at the spectrum to find out where line-mixing becomes most apparent.

**X-ray Spectra:**

**Introduction:**

X-rays are KeV photons. Atomic X-rays are emitted during electronic transitions to the inner shell states in atoms of modest atomic number. These X-rays have characteristic energies related to the atomic number, and each element therefore has a characteristic X-ray spectrum.

In this experiment you will use a high resolution solid-state X-ray detector to record the characteristic spectra of several elements, repeat the pioneering work of Moseley relating X-ray energies to atomic number, and also explore the use of X-rays as a diagnostic tool for sample identification.

The X-rays detector is a reverse biased PiN diode.
The X-ray is photoelectrically absorbed and the liberated electron loses energy in the silicon by creating electron-hole pairs @ 3.6 eV per pair. Recall that in a p-n junction the majority carriers diffuse across the interface creating an electric field that sweeps any excess charge out of the depletion zone.

THE EXPERIMENTAL METHODS OF X-RAY SPECTROSCOPY:

The experimental techniques necessary for the study of X-ray spectra are essentially of two parts. On the one hand there must be some means of dispersing the spectrum so as to separate the various wavelengths and, of course, to measure these wavelengths, and on the other hand it is necessary to know the relative intensities of the various wavelengths.

Hence the modern methods of X-ray spectroscopy involve the use of crystals or of ruled gratings for dispersion together with photographic or ionisation methods for intensity measurements.

CRYSTAL METHODS:

It was seen in Chapter 6 that a crystal behaves as a diffraction grating for X-rays and, since diffraction angles depend on wavelength, the phenomenon provides a means of dispersing an X-ray spectrum.

In practice the actual methods used are based firmly on the concept of reflection from lattice planes, and in these methods X-rays are reflected from a crystal face, which will, of course, be parallel to a family of lattice planes.

\[ 2d_{hkl} \sin \theta = \lambda \]

X-ray satellites:

- The nature and properties of many classes of x-ray satellites, unlike those of the main lines, remain at present unclear.

- In addition to the importance of solving these problems for x-ray spectroscopy, a
careful study of satellites allows one apparently to obtain valuable information on the ionization mechanism of the inner shells of atoms, on the phenomena accompanying this process, and also on the behavior of electrons in a solid.

An attempt is made in this paper to study the properties and to explain the nature of some types of satellites; this attempt is based on the concept of auto-ionization of the atom when the number of inner electrons changes.

The x-ray spectrum emitted by the sample is produced by simple electronic transitions, which allow more straightforward interpretations than those of the Auger spectra.

When only considering the electric dipole vector of radiation, x-ray emission from an excited ion is governed by simple rules of selection ($\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$).

The effects of relaxation and electronic reorganization in other molecular orbitals attendant upon the creation of the initial vacancy, and also in the final state after the x-ray has been emitted, are ignored.

Since other orbitals are assumed unaffected, this approach is also called the ‘frozen orbital’ approximation.

An x-ray emission line (or diagram line) resulting from a transition between two levels in the energy-level diagram is frequently accompanied by satellites lines (or non-diagram lines), i.e., x-ray lines whose energies do not correspond to the difference of two energy levels of the same atom.

The term ‘satellite’ means weak lines close to the strong parent (or diagram) lines.

Particle induced x-ray emission (PIXE) spectra, electron probe microanalysis (EPMA) x-ray spectra, or x-ray fluorescence (XRF) spectra of materials exhibit intensity modifications of satellite lines from one compound to another.

The satellite lines are classified into three groups by its origin:
1) Multivacancy satellites.
2) Charge-transfer satellites for late transition-metal compounds.
3) Molecular-orbital splitting satellites (Kawai, 1993).

- The Kα lines usually show high-energy satellite lines, corresponding to the existence of a specific number (i) of ‘spectator’ vacancies in the layer L, which affect the subsequent transitions.

- These peaks can be identified generally as KαL^1, and they appear on the side of higher energies of the main line Kα₁,₂.

- This kind of satellite lines are called multivacancy satellites lines, and among them we find the double ionization caused by KαL^1 (or simply KαL): when 1s and 2p vacancies are created simultaneously, the 2p vacancy has a relatively long life-time compared to that of the 1s vacancy.

**Double and triple vacancy satellite lines in Al Kα at higher:**

- At higher energies than Kα₁,₂ we find the satellite spectrum KL^1 consisting of lines (in increasing order of energy value) Kα’, Kα₃ and Kα₄.

- At even higher energies we can also observe satellite lines by triple ionization (KL^2), called Kα₅ and Kα₆. In this section, we present the results of our measurements for these lines of multiple vacancies for pure aluminum and alumina (Al₂O₃), with XRF and EPMA.

- The KL^2 satellites are the highest order of ionization obtained by bombarding with photons and electrons, and they have even lower intensities than KL^1.

- which presents the experimental intensities of the Al Kα spectrum on a logarithmic scale to facilitate its appreciation.
Satellite lines produced by charge transfer:

- The effect of charge transfer is important in the compounds formed by the last transition metals. Usually, in these compounds, the 3d orbital is the outermost.

- Then there is the ligand energy level (e.g. in NiF₂, the level of F 2p) which is a few eV below of 3d of the main atom.

- So if there was a vacancy in the 1s level of the transition element, the 3d level is far deeper than the valence bond.

- This situation is quite unstable, so some electrons from the decay of the F 2p level to the level of Ni 3d (Kawai, 1993).

Photoelectron spectroscopy:

- The locations of peaks in the XPS spectrum indicate both the presence of specific elements and their respective oxidation states. Furthermore, the binding energy of core electrons is very sensitive to the chemical environment of the corresponding element.

- When the same atom is bonded to a different chemical species, this leads to a change in the binding energy of its core electrons. The variation of binding energy results in a shift of the corresponding XPS peak.

- This effect is termed as chemical shift, which can be applied to study the chemical status of all elements in the surface.

- Therefore, XPS is also known as electron spectroscopy for chemical analysis (ESCA). The intensity of photoelectron peak varies with the surface concentration of the corresponding element, allowing quantitative determination of the composition of the surface.

- There are different X-ray sources. Non-monochromatic sources utilise the Kα radiation from Aluminium (Al) and Magnesium (Mg).
The energy of AlKα lines is 1486.6 eV and MgKα 1253.6 eV[66]. When the X-ray source is non-monochromatic, the output consists of a broad continues distribution (Bremsstrahlung radiation) with much higher intensity at characteristic line Kα1,2 and there are weaker satellite lines Kα3,4 and Kβ.

1qAl Kα radiation can be monochromatic by using quartz crystals.

This allows the energy spread of the exciting radiation to be significantly reduced. At the same time, all satellite lines and the Bremsstrahlung radiation are removed, producing a cleaner spectrum with reduced background intensity.

\[ E_B = hU - E_{\text{kin}} - e\phi_{\text{sp}} \]

Thus at binding energy close to zero, the closely-spaced valence band appear and with increasing binding energy the increasingly tightly-bound core levels.

The core levels have variable intensities and widths and non-s-levels are doublets. The doublets arise through spin-orbit (\( j-j \)) coupling.

Two possible state characterized by the quantum number \( j \) \( (j=I+s) \) arise when \( I>0 \) as shown in table 1.

Finally the decay of core holes resulting from photoemission can give rise to Auger electron.

**Scanning Electron Microscopy (SEM):**

The scanning electron microscopy (SEM) provides the investigator with a highly magnified image of the surface that is very similar to what one expects if one could actually see the surface visually.

The resolution of the SEM can approach a few nm and it can operate at magnifications from 10x – 1000000x.
Absorption and Emission of Radiation by an Atomic Oscillator:

INTRODUCTION:

In 1904 J.J. Thompson (1857–1939) proposed a static model of the atom, and in 1911 E. Rutherford (1871–1937) proposed a dynamic model of the atom. It was hoped that any atomic phenomena could be explained by Newton’s mechanics and Maxwell’s electrodynamics.

However, two big problems remained unsolved. According to Maxwell’s electrodynamics, each accelerated charged particle (such as an electron in Rutherford’s model of the atom) inevitably emits electromagnetic radiation and therefore collapses into the nucleus.

EMISSION OF ELECTROMAGNETIC RADIATION:

Emission of electromagnetic radiation results from electromagnetic fields emitted by accelerated electric charges or generally from dynamic electric and magnetic fields (Poynting vector).

We view the atom as a system consisting of a nucleus, with charge $Q$, and one particle, with charge $q$ and mass $m$, moving in a circular orbit within a radius $r$ at an angular velocity $\Omega$. This is Rutherford’s “planetary” model of the atom\(^{(9,10)}\).

The driving force is only the external force $f_{\text{ext}}$, and the equation of motion is the Abraham–Lorentz equation of motion \(m(\vec{v} - \dot{\vec{r}}) = f_{\text{ext}}\).

ABSORPTION OF ELECTROMAGNETIC RADIATION:

Absorption of electromagnetic radiation\(^{(40)}\) of one dipole in the $x$ axis results from the work of $f_x$ $dx = f_x \, v_x \, dt = f_x \, \partial x/\partial t \, dt = p_x \, dt$ done on the charge $q$ by the driving force $f_x$. 

\[(\text{ext}) f = \text{v} \times v \]
EMISSION AND ABSORPTION SPECTRA:

- The emission and absorption of light (transfer of energy & momentum) takes place in a particular manner. All forms of electromagnetic radiation interact with matter in the process of emission and absorption.

- The radiation propagates in a wavelike fashion but in an interaction the radiation behaves as a concentration of energy (photons) moving at the speed of light.

- Most of the chemical and optical properties of a substance are dependent upon the outer most bound electrons in atoms. Each electron is usually in its ground state (the lowest energy state).

- Only when an atom absorbs sufficient and specific energy can the atom absorb the energy and the electron move to a well defined higher energy state (excited state). The electrons and nucleus of an atom form a system with total energy $E$.

- The total energy for an individual electron is simply the sum of its kinetic energy and the potential energy of the system of the electron bound to the nucleus.

- The total energy has a set of discrete energy levels and so emission and absorption can only take place when the change in energy is equal to the difference between two energy levels.

RESONANT ABSORPTION:

Shows a schematic diagram of a set of discrete electronic energy levels for an electron bound to an atom. When white light passes through a material such as a gas, then photons with an energy equal to a difference between two energy levels of the gas atoms can be absorbed to produce excited atoms. This process is called resonant absorption.
SPONTANEOUS EMISSION:

Excited atoms will spontaneous lose energy by emitting a photon whose energy is equal to the difference in energy between the two energy levels. This process is called spontaneous emission.

THE SPECTRAL LINES VARY IN INTENSITY IN AN EMISSION SPECTRUM:

- This is because not all transitions from higher energy levels to lower ones occur with equal probabilities. Some transitions are actually forbidden.

- The brightest spectral lines correspond to the transitions that occur most often, that is, they have the highest probability of occurring.

- A spectral line is very weak when the transition has a low probability of occurring.

ATOMIC EXCITATION:

There are three main mechanisms by which atoms may be excited to higher energy levels.

COLLISIONS:

Atoms that collide with each other can transfer their kinetic energy into electron energy of either or both of the colliding atoms.

The excited atoms will than lose its excitation energy by emitting one or more photons as they returns to its ground state.

RESONANT ABSORPTION:

The absorption by an atom of a photon of light whose energy is equal to the energy required to raise an electron to a higher energy state. When white light (all wavelengths in visible spectrum present) passes through hydrogen gas, the photons whose energy corresponds to the difference in energy levels of hydrogen are absorbed.
The excited hydrogen atoms immediately lose energy by radiating energy in random directions.

**INTRODUCTION:**

The purpose of this book is to present a unified account of the exciting developments in the field of quantum electronics which have occurred during the last two decades. Following introductory chapters on electromagnetism and quantum mechanics, the basic processes involving the interaction of radiation and atoms are discussed in some detail.

**Planck's radiation law:**

The more important fundamental laws and facts of physical science have all been covered, and these are so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote.

**FRANCK-HERTZ EXPERIMENT:**

The Frank-Hertz experiment was one of the first to show that atoms can only accept energy in a packet or quantum, i.e., there exist discrete energy levels within atoms.
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