
FUNDAMENTALS OF ATOMIC AND MOLECULAR SPECTROSCOPY IN INSTRUMENTAL ANALYSIS

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ABSTRACT

Atomic and molecular spectroscopy plays a pivotal role in instrumental analysis, providing essential insights into the structure and behavior of atoms and molecules. This fundamental field explores the interaction between matter and electromagnetic radiation, enabling the identification and quantification of chemical species with remarkable precision and accuracy. In this abstract, we present a comprehensive overview of the principles underlying atomic and molecular spectroscopy, including spectroscopic techniques such as absorption, emission, and scattering. Additionally, we delve into the theoretical foundations of spectroscopic phenomena, including electronic transitions, vibrational and rotational motions, and the application of quantum mechanics to elucidate spectral patterns. Furthermore, the importance of spectroscopy in various fields, such as environmental monitoring, pharmaceutical analysis, and material science, is highlighted. As a critical component of modern instrumental analysis, mastering the fundamentals of atomic and molecular spectroscopy is essential for researchers, analysts, and scientists seeking to explore and manipulate the microscopic world of atoms and molecules.

Keywords: atomic, molecular spectroscopy

INTRODUCTION

Molecular spectroscopy is the scientific discipline that investigates how molecules behave in response to electromagnetic radiation. The term "electromagnetic radiation" refers to any type of radiation in which the electric field and the magnetic field both undergo simultaneous changes. Light is a very well-known example of electromagnetic energy in its physical manifestation. There are a number of different ways to define electromagnetic radiation, including energy, intensity, frequency, and wavelength.

$$E = hv$$

The pioneering work of Albert Einstein and Max Planck, who each explained the photoelectric phenomena and the emission of light by a blackbody radiator, can be traced back to the time when it was discovered that the energy of electromagnetic radiation is related to its frequency. This discovery may be traced back to the time when it was made. When Planck's constant is used, the proportionality formula can be reduced to the form of an equality.

We can determine the speed of electromagnetic radiation by multiplying the frequency by the constant c . This gives us the square root of the speed ($c = \lambda\nu$). By inserting the solution into the previously presented formula for the wave length, we should be able to determine the frequency.

$$E = hc/\lambda$$

Because of this, the amount of energy carried by electromagnetic radiation diminishes as its wavelength grows longer. Longer wavelengths of electromagnetic radiation carry less energy than shorter wavelengths. Radiation of electromagnetic waves with short wavelengths is likely to have a high energy content.

List electromagnetic spectrum radiation from high to low energy. Include atom and molecule processes for each radiation type

Atoms and molecules both have the ability to either take in or give off electromagnetic energy. After absorbing a sufficient amount of radiation, a species will go through a transition from its ground state to an excited state, which will have a higher energy level. The emission of photons occurs whenever a species transitions from an excited state to a ground state. In the field of analytical chemistry, the primary applications of spectroscopy are, first, the identification of species and, second, the quantification of species.

Recording a species' absorption or emission as a function of frequency or wavelength can be used to generate a spectrum, which is a representation of the strength of absorbance or emission as a function of wavelength. This can be used to identify the species in question. The spectral features of a molecule can act as a molecular fingerprint, which can then be used to identify the molecule. The value of a species' spectrum as a tool for identifying substances grows with the level of specificity it possesses. Some spectroscopic techniques, such as nuclear magnetic resonance (NMR) spectroscopy, are very helpful for identifying chemicals, whereas other approaches generate spectra that are all rather similar and, as a result, are less effective. NMR spectroscopy is one example of this. Some of the methods that provide extremely distinctive spectra, such as nuclear magnetic resonance (NMR) spectroscopy, are more suitable to analysing and assigning structures than others, such as infrared spectroscopy. Because different molecules emit distinctly different infrared spectra, a computer can be used to compare the spectrum of the unknown drug to a database of spectra of known compounds in order to locate the one that is the most similar. If the spectrum of the unknown item is already stored in the library, then identifying it won't be difficult at all.

A standard curve can be used in conjunction with spectroscopy to determine the concentration of a species. This is accomplished by comparing the absorbance or intensity of the emission to the curve. We are going to focus our attention for the time being on taking measurements of the quantitative absorbance.

Take for instance the sample shown in Figure 1 as an example; through it, there will be transmission of light of a particular wavelength. In the process of determining the potency of a radiation source (P_0) using a sample that does not contain the absorbing species of interest (also known as a "blank"). After that, the quantity of radiation (P) that is able to pass through the sample is measured.

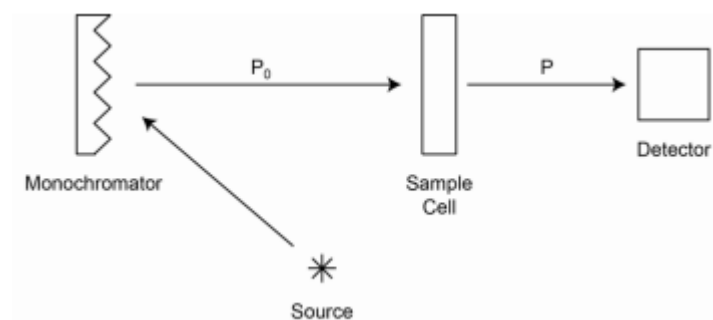


Figure 1. Spectrophotometer Block Diagram

The ratio P/P_0 is the percentage of the incident radiation that the sample was able to block; it is represented by the symbol T . This value may be found in the table below.

$$T = P/P_0 \quad \text{and} \quad \%T = (P/P_0) \times 100$$

When there is a high absorbance, P falls, which results in less light being able to pass through the sample and reaching the detector.

Beer's Law

It is possible to change the absorbance of a sample by modifying the concentration (c) of the sample. It goes to reason that when concentration rises, a greater amount of radiation will be absorbed, which will result in a greater level of absorption. Because of this, there is a direct correlation between the two concepts of concentration and absorbance.

The distance of the route is another factor to consider (b). As the route length gets longer, there will be a greater number of molecules in the path of the radiation beam, which will cause the absorbance to go up. As a consequence, the level of focus decreases as the length of the trip increases.

When the concentration as well as the length of the route are given in moles per litre. The third factor is the molar absorptivity, which is more often known as the extinction coefficient. This factor, which is measured in centimetres in some areas of research, is an extinction coefficient. When determining the concentration of a sample using spectroscopic methods, one of the steps involves selecting a certain wavelength of radiation to shine on the sample. You probably already know this from your own experience, but various chemical species absorb different frequencies of light in varying amounts. The molar absorptivity of a species can be thought of as a measurement of how well that species absorbs light of a certain wavelength. When a species absorbs electromagnetic radiation, it shifts from its resting state, which is known as its ground state, into a condition that is more energetically stimulated. This process is referred to as an excitation transition, and it is important to note that each and every excitation transition has an associated probability. It is appropriate to have a conversation about the various forms of energy that are capable of being converted within a chemical species. Some shifts can be tolerated or even welcomed more readily than others. High molar absorptivities are a telltale sign of a transition that is either highly preferred or strongly allowed. Transitions that are only slightly preferred or allowed are characterised by their modest molar absorptivities. The molar absorptivity is directly proportional to the absorbance value. Because of this, the absorbance and the molar absorptivity are directly proportional to one another in a one-to-one connection.

During the experiment in which a spectrum (recording the absorbance as a function of wavelength) is recorded for a material that needs to be identified, the concentration and path length are held constant throughout the entirety of the spectrum. A spectrum is a plot that displays the relative molar absorptivity of a species as a function of wavelength. The only thing that varies across wavelengths is the molar absorptivity, hence this is the only variable that can be used to describe the spectrum.

The Beer-Lambert law, often known as Beer's Law, can be stated as an equation, which demonstrates that absorbance is proportional to concentration, route length, and molar absorptivity. This equation can also be referred to as Beer's Law.

$$A = \epsilon bc$$

Instrumental Setup of a Spectrophotometer

There are five primary components that make up a spectrophotometer: the source, the monochromator, the sample holding, the detector, and the readout device. The majority of spectrophotometers that are used nowadays are connected to a computer, and the majority of these computers are used to control the spectrophotometers. The data that was obtained by the detector is typically exhibited in some form on the computer screen.

Radiation sources

It should go without saying that the source must totally cover the spectrum region that is being monitored, but it's worth mentioning nevertheless. Additionally, the source possesses a high power or intensity, which indicates that it releases a significant number of photons into the environment. A lower detection threshold is associated with a higher signal-to-noise ratio. This is due to the fact that every detector picks up signal in addition to background noise. The reliability of the source is the second essential feature to look for. The instability of the power output of a source can magnify background noise and bring mistake into comparisons between reference values and samples that have not been checked.

Create a graph with the y axis representing the relative brightness of the light coming from an incandescent bulb, and the x axis representing the wavelength of the light. The blackbody radiation plot is a tried-and-true method, yet it still works. Display, on the same graph, the output of a radiation source that operated at a higher temperature.

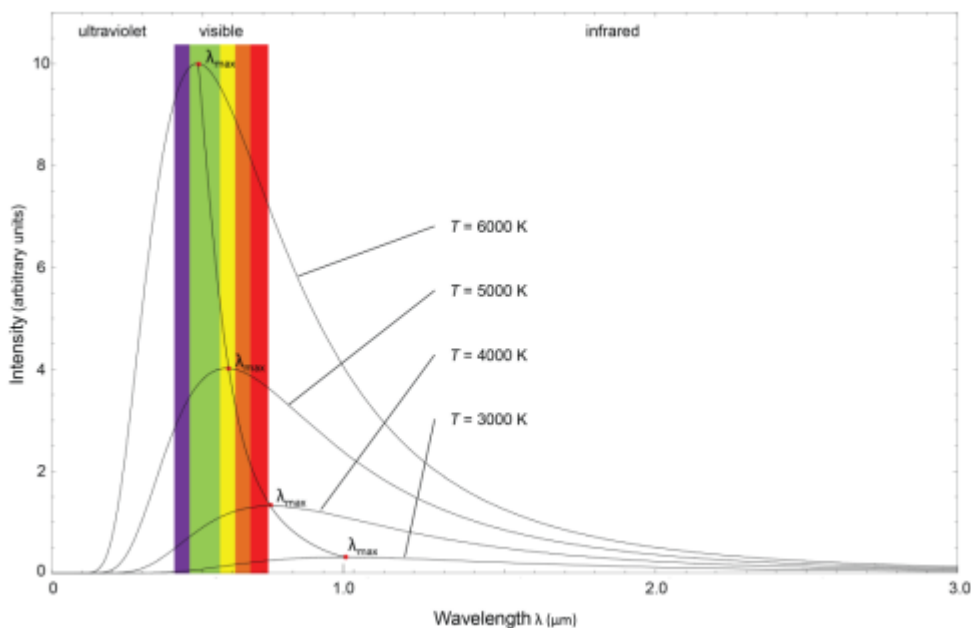


Figure 2. Blackbody radiation output at various temperatures

Indicated in Figure 2 is the peak power or intensity of the radiation emitted by a blackbody radiator when measured at a specific wavelength. The intensity lessens as the wavelength is shorter but increases as it gets longer. The output of a blackbody radiator is proportional to the temperature. As the temperature rises, the peak wavelength of greatest intensity moves towards the ultraviolet region of the electromagnetic spectrum, as can be seen in Figure 2.

REVIEW OF LITERATURE

Kevin Lehmann (2016) such is the case with her description of what it is like to spend weeks at a time on top of a distant mountain studying the night sky or with her account of the Australian bushfires that destroyed the Mount Stromlo Observatory in the year 2003. The fundamental concepts that are introduced in PHYSICS TODAY chapters on neutron-capture techniques that produce elements other than iron and the several nucleo-synthetic burning stages that occur throughout a star's lifetime should not provide any challenges for the readers of the magazine. Readers who do not have a good background in physics and astronomy, on the other hand, might need to skip around from chapter to chapter in order to piece together a logical image.

Rita Kakkar(2015)The term "spectroscopy" refers to the scientific study of how various substances respond when exposed to electromagnetic radiation. Analysing substances molecule by molecule and atom by atom is a frequent analytical procedure. Analysing the spectra of individual atoms and molecules is another application of this technology for gaining knowledge about them. The fast developing field of spectroscopic applications has been very beneficial to many other fields, including the research of energy, the processing of chemicals, the preservation of the environment, and even medicine. This book is intended to serve as an introduction to the study of spectroscopy. The usage of mathematics has been kept to a minimum throughout the text, with the exception of instances in which it was unavoidable. The fundamental concepts and practical applications of spectroscopy are explored in great detail throughout this book.

Additionally, the author delves into issues such as time-dependent perturbation theory, laser action, and the uses of Group Theory in the interpretation of spectra.

Brian K. Taylor (2023) Because of its straightforward explanations and affordable price, this book serves as an excellent introduction for people in a variety of fields, including students, researchers, and professionals. Because of the demographic of its readership, this book is not suitable for use in advanced chemistry classes either as a primary or supplementary resource for the subject matter. This material, on the other hand, is helpful for educators who seek to present spectroscopy to students at a more fundamental level. The book's straightforward writing style, comprehensive examples, and concise nature make it an excellent resource for independent study. You can finish reading it from beginning to end in a matter of days or weeks. The tone of the author is captivating, and after finishing the piece, the audience will feel as though they have a solid understanding of the topic at hand.

G. Pichler(2014) We will go over the findings of our most recent research on heavy alkali vapour absorption and emission using high-intensity light-emitting diodes manufactured by NICHIA, LUMILED, and OSRAM. These diodes produce a lot of light. When it comes to doing very accurate absorption tests, having access to narrow-band continuous light sources, such as those that UV LEDs and LEDs in the visible spectral range can supply, is absolutely necessary. In a traditional configuration for absorption, high resolution scanning monochromators were utilised with all-sapphire cells and heat-pipe oven cells. In addition to the self-broadened alkali resonance lines, we also investigated the molecular bands and the diffuse bands of alkali dimers. Additionally, a number of applications, most notably in the field of dentistry, will be offered as examples.

D. W. Ball(2018) An introduction to atomic and molecular spectroscopy is provided in this book, as one may infer from the book's title. The relationship between spectroscopy and quantum physics is discussed in greater detail in the Preface. This is supported by the Table of Contents, which reveals that around half of the chapters deal with quantum mechanics and that similarly only approximately half of the chapters deal with spectroscopy in an explicit manner. This book is very well written and makes no assumptions about the reader's prior understanding of quantum physics or spectroscopy. Neither quantum mechanics nor spectroscopy are the only fields that include challenging mathematical concepts.

Dennis W Lindle(2019) In order to fulfil a stringent deadline for publication, these proceedings have been put together in an unofficial capacity. The participants' contributions to the manuscripts were provided in an extremely diverse range of formats, ranging from formally typeset texts to copies of the speakers' transparencies. We are grateful to the speakers who were able to promptly get their manuscripts ready after the session. Not only do these sessions detail tried-and-true procedures and approaches, but they also provide a look into the future of this rapidly evolving field. We anticipate that researchers and practitioners working in this field will find these proceedings to be an invaluable resource.

Dietmar Kolb(2016) The concept that everything in the cosmos is composed of extremely minute particles called "atrons" has been floating around for quite some time. In the middle of the 19th century, spectroscopy was developed, which allowed for the identification of a great many essential characteristics of atoms. In spite of this, it wasn't until the development of quantum physics approximately sixty years ago that scientists were able to

get a more in-depth understanding of the atomic structure. This article, which comes from the theoretical physics working group, is an attempt to provide some background for the revolutionary breakthroughs that have taken place over the course of history in our understanding of atomic structure. These developments have occurred in our ability to predict the behaviour of subatomic particles.

Bobby Antony(2016)A worldwide consortium known as the Virtual Atomic and Molecular Data Centre (VAMDC) Consortium federates atomic and molecular datasets by means of an e-science infrastructure and an organisation to support this activity. Data that are needed for the interpretation of astronomical spectra and for modelling in many different branches of astrophysics are handled by approximately 90 percent of the inter-connected databases. Recently, the VAMDC Consortium has integrated databases from the plasma community and the radiation damage community. Additionally, the VAMDC Consortium has been pushing the publication of data from Indian institutes. This article provides a description of the organisational structure of the VAMDC Consortium, which aims to provide the most effective distribution of atomic and molecular data for the sake of scientific study. It should be emphasised that the VAMDC Consortium strongly recommends that writers of research papers utilising data make citations to the appropriate databases in addition to the original experimental and theoretical works.

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Mario V. Freamat(2012)The purpose of this article is to provide a description of a more advanced undergraduate lab that demonstrates molecular spectroscopy by measuring the vibrational energy separation between nitrogen molecules when they are in the gas phase. We show students how they can investigate the quantized vibrational potential of neutral and ionised N₂ by utilising a simple and affordable AC discharge tube and a handheld spectrometer to detect and analyse the radiative collisional processes that occur in the gas. In this experiment, we illustrate how students can research the quantized vibrational potential of neutral and ionised N₂.

JaanLaane(2019)The majority of what we know about atoms, molecules, and the fundamental properties of matter has been gleaned from spectroscopy over the course of the last century or so. Twenty chapters highlighting the pioneering work of these scholars in the field of molecular spectroscopy were written by researchers who are known around the world. In these chapters, the most recent developments in spectroscopic theory and technique, as well as innovations in apparatus, are discussed in detail. There is a broad range of topics that are discussed. Lasers are used in a significant portion of the research; nevertheless, their applications range widely, including sub-femtosecond spectroscopy, the

investigation of art and archaeological relics, and the study of viruses. Work on biological systems is discussed in three chapters, and the physics of lasers is treated in three parts in the book. The most recent advancements in microwave techniques, cavity ringdown spectroscopy, surface-enhanced Raman spectroscopy, and two-dimensional correlation spectroscopy are discussed here. The book not only demonstrates the adaptability of spectroscopy, but it also contains chapters on issues such as molecular dynamics, electronic excited states, symmetry applications, and neutron scattering.

Ingolf V. Hertel(2015) Following a concise introduction in Section 5.1, we will go more deeply into rotational (microwave) and vibrational (infrared) spectroscopy in Sections 5.2 and 5.3, respectively, and supplement our understanding with brief excursions into FTIR and IR action spectroscopy. When the discussion moves to the spectroscopy of electronic transitions (VIS, UV, and VUV), a number of cutting-edge methods for modern molecular spectroscopy are discussed. In the following section (5.6), you will learn all there is to know about Raman spectroscopy, an important subfield of spectroscopy that falls somewhere in the between of electronic and vibrational spectroscopy. In Section 5.5.4, we demonstrate the incredible potential of modern high resolution spectroscopy by illustrating how it can be used to analyse larger molecules and even biologically relevant compounds. This helps to emphasise the breadth of applications for this technology. In this final section, Section 5.8, we will provide an overview of photoelectron spectroscopy

OBJECTIVES

1. To study atomic and molecular spectroscopy
2. To study molecular spectroscopy

RESEARCH METHODOLOGY

If the energy of the input photon is strong enough, an electron from an inner shell can be propelled into an empty orbital and moved there. Two distinct types of resonances have been seen in the electron energy loss and photoabsorption spectra of molecular inner-shell excitations. The first type of Rydberg state occurs when the inner-shell boundaries are approached by the Rydberg state. At lower energies, one may observe conspicuous features that are either vibrationally organised or otherwise apparent. They are not comparable to any characteristics of the photoabsorption spectrum of the isoelectronic atom in any way. As a result, they have to be attributed to the excitation of an electron in a molecule that is located in the lowest empty orbital, which is comparable to an electron in an atomic inner shell. For example, the initial Kr inner shell excitation is represented by the $3d \rightarrow 5p$ transition, while in HBr it is a $3d \rightarrow 4p\sigma^*$ transition. The characterization of the kinetics of this excitation is placed in context by the previous paragraph, which describes an experimental investigation of core-excited HF.

Core-excited species of light elements, which are defined as those with a low charge number Z , are able to undergo non-radiative decay in their most basic form by emitting a single electron. This phenomenon, which is also known as resonant Auger decay, is often divided into the two groups described below. In the so-called participator Auger decay, the electron that was stimulated during the step of absorption is the one that fills the void left in the inner shell. A single gap can be found in one of the valence orbitals in the final state, just as there is in the state that is produced by direct ionisation. It is usual for the participant Auger process to leave a signature that consists of an enhancement of the valence photoemission line. The excited electron is a "bystander" in the process that is

referred to as the spectator Auger decay. The direct procedure that would lead to the end state with two valence shell holes is severely hindered by a model consisting of a single particle. Figure 3 shows a schematic representation of these two potential decay methods, together with the usual Auger decay process that results in doubly charged ions. Both of these mechanisms result in doubly charged ions.

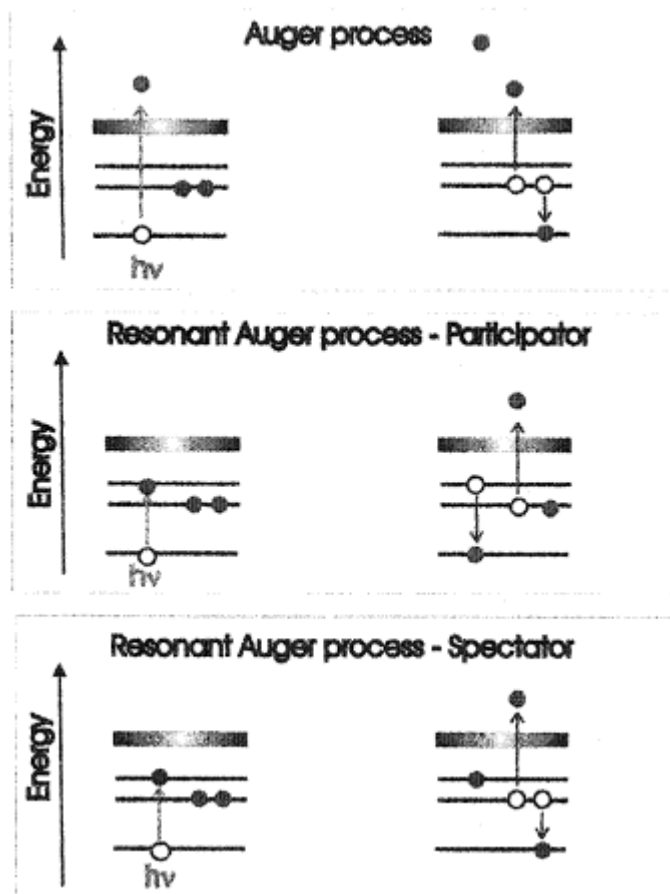


Figure 3. Loss of Normal, Resonant, and Spectator Auger Activity

Resonant Cross

When the core of a molecule is excited, a transitory intermediate state is produced. This state can be conceptualised as an evolving nuclear wavepacket that exists on the potential energy surface of the electronic hole. Relaxation is caused by the oscillations of the vacuum as well as the interaction caused by the Coulomb force. The timeframe is in agreement with the presence of the core-hole. $1/\Gamma_d$. Researchers have been able to build and analyse experiments to test coherence between excitation and decay beyond what can be represented by a simple two-step description. This has been made possible by adding the resonant Auger process into a unified theory of resonant inelastic X-ray scattering (RIXS), which has allowed them to design the theory. These coherent effects are made abundantly clear by the equation that describes the cross section

$\sigma(E, \omega)$ in the RIXS formalism.

Radiation that has already arrived, which is denoted by a spectral function $\Phi(\omega, \Gamma)$, operator D is what causes a dipole transition to occur after an initial state $|i\rangle$, with authority

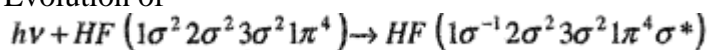
Consequently, to a state that is located halfway in between $|\Psi_d\rangle$. Because the core-hole only exists for a short period of time, the radiation that is produced as a result is a coherent superposition of the eigenstates that are excited by the core $|c\rangle$. As a direct consequence of the Coulomb interaction, this state will, in due course, decay to a lower energy level denoted by the operator $Q|f\rangle$, of energy E_f . A representation of the process in its entirety can be seen in the cross section.

$$\sigma(E, \omega) = |F^2|^2 \Phi(\omega - E - (E_f - E_i), \Gamma_f),$$

$$\hbar\omega_f = E_i - E_f,$$

Result and discussion

Experiments involving high-frequency had to be carried out at beamline 8.0.1 because beamline 10.0.1 did not have the necessary photon energy range (which was between 674 and 694 eV). The Evolution of



was set off by light with a photon resolution of 0.2 eV that was linearly polarised. The spectra of absorption were examined in order to understand how the rate of Auger decay would be affected by a detuning of £2 from the resonance maximum located at 687 eV. The hemispherical analyzer SES-200 was utilised in order to carry out the electron energy study. This analyzer was calibrated to the 40 eV pass energy that was discussed in Chapter 3. In just a few moments, we will discuss the rationale behind our decision to maintain the detection angle at 90 degrees relative to the plane of polarisation of the incident radiation. The purpose of this experiment was to see how the HF resonant Auger spectra changed as a function of the oxygen concentration. Because the core-excited state is placed so far below the first Rydberg states, the spectrum of the total ion yield can be seen in Figure 43. This molecule is a good answer for such investigations because of the location of the core-excited state. Because of this, the study of a broad spectrum of detuning is possible, and it does so without the additional complication of extra excitations. The accumulation period was prolonged with O in order to compensate for the weakening of the oscillator that occurred further away from the absorption maximum.

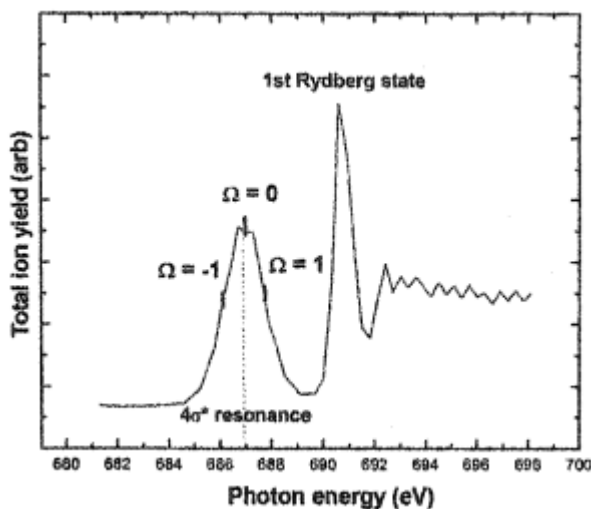


Figure 4. Between 674 and 692 eV in Total Ion Yield for HF

Auger spectra are produced when valence electrons are ejected from molecules, and as a general rule, these spectra are more complex than those produced by atoms. However, in the case of HF, a reliable assignment may be obtained by establishing a correlation between the lines in the conventional Auger spectrum and the energy levels of Ne^{*}. This correlation can be found by looking at the spectrum. This is due to the fact that the spectrum of HF radiation is sufficiently similar to that of the isoelectronic atom neon. This relationship, which is valid for the resonant Auger spectrum, will be utilised in the ensuing explanation of the decay of the core-excited HF. The involved states are listed in Table 1, together with their respective energy, intensities, and estimated asymmetry parameters. These states are active (P) and passive (S). The Auger spectra that were acquired are presented in Figure 5.

Table 1. Auger Spectra of Core-Excited High-Frequency Radiation: Contributing States

Final state	Decay	E (eV)	parameter
${}^2\Pi(1\pi^{-1})$	P	689.88	0.25
${}^2\Sigma^+(3\sigma^{-1})$	P	685.9	-0.15
${}^2\Delta(1\pi^{-2}\sigma^*)$	S	661.67	-0.57
${}^2\Pi(3\sigma^{-1}1\pi^{-1}\sigma^*)$	S	660.48	0.25
${}^2\Sigma^+(1\pi^{-2}\sigma^*)$	S	659.87	1.20

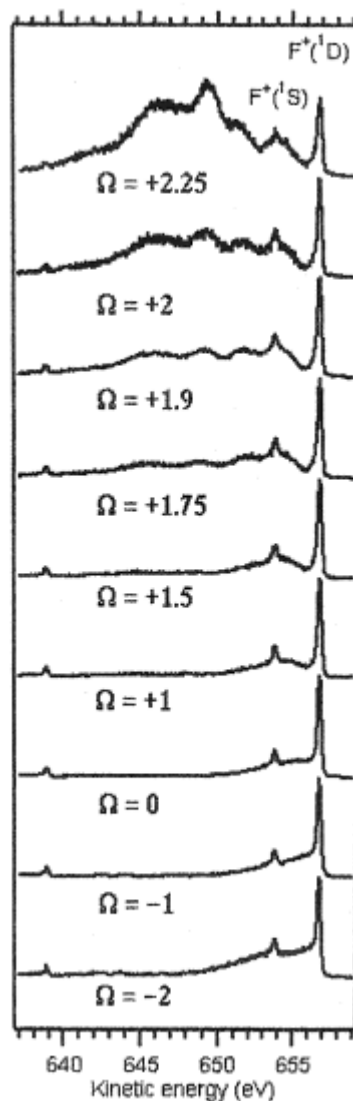


Figure 5. Resonant Auger Decay Spectra of the $1\sigma^{-1}4\sigma^*$ Excited state of the core far from the absorption maximum for a variety of narrow band detunings. The peaks of each spectrum have been normalised to the same value.

CONCLUSION

In conclusion, the study of atomic and molecular spectroscopy plays a crucial role in instrumental analysis, enabling scientists and analysts to gain valuable insights into the properties and behavior of atoms and molecules. Through the interaction of matter with electromagnetic radiation, spectroscopic techniques offer a powerful means of identifying and quantifying various chemical species, even in trace amounts. From the basics of absorption, emission, and scattering processes to more advanced techniques such as NMR, UV-Vis, IR, and Raman spectroscopy, these methods provide a wealth of information about the structure, composition, and dynamics of matter.

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