
Introduction

This thesis is based on a number of experimental investigations in the field of laser spectroscopy that were carried out at two different institutes. The work began at the Royal Institute of Technology in Sweden in the period 2003-2005, focusing on the technique of laser-induced breakdown spectroscopy (LIBS). Thereafter a number of studies were performed with the Amsterdam extreme ultraviolet (XUV) laser setup, starting with Rydberg-valence state interactions in the nitrogen molecule. Afterwards it proceeded to the characterization of the so-called “heavy Rydberg states” in the H^+H^- composite.

In the following sections of this chapter a few key concepts of the experiments will be explained, as an introduction to the chapters contained in this thesis.

Experimental: the XUV laser setup

The majority of the experimental work presented in this thesis (Chapters 1 to 5) has been performed in the extreme ultraviolet (XUV) region of the spectrum. A review on the nature of XUV light and a historical perspective on its applications in spectroscopy can be found in [1]. The presently used instrument, the Amsterdam narrowband and tunable extreme ultraviolet laser facility, and its applications to gas-phase atomic and molecular spectroscopy has been described in a number of PhD thesis at the Vrije Universiteit [2]. Some of its main characteristics will be detailed briefly below.

The tunable, narrowband XUV laser source is based on harmonic upconversion. To achieve this, narrowband visible radiation is generated in a pulse-dye laser (PDL) pumped by the second harmonic of a Nd:YAG laser. The visible radiation is frequency doubled using a nonlinear crystal (BBO, KDP). The resulting ultraviolet (UV) output is

guided by dichroic mirrors (that filter the remnant of visible light) into a vacuum chamber. The XUV radiation is generated by a third harmonic generation (THG) process; this is achieved by focusing the UV light in an inert gas (Xe, Kr) [3, 4]. The need of a windowless vacuum system arises as XUV radiation is absorbed in all materials below 110 nm, and at these wavelengths the use of cells sealed off by some optical material is prohibited. The solution is to use a pulsed gas jet as non-linear medium [5]. The pulsed gas jet, in combination with differential pumping provides a solution because the density of inert gas in the focus of the UV laser can be made large without having too much absorption for the generated XUV radiation, as the molecular density is restricted to the small path length across the molecular jet close to the nozzle. The differential pumping provides the conditions of vacuum outside the THG region, and the XUV radiation is not absorbed and can propagate into another (differentially pumped) vacuum chamber to be used for spectroscopy experiments. The efficiency of the tripling process is rather low (10^{-6} - 10^{-7}) and therefore there is a strong remnant beam of UV light that travels collinearly to the XUV beam generated.

The physics of the harmonic generation is well understood [3, 6, 7, 8, 9], and following the notation of [3], the equation that governs the frequency generation process, in terms of the component i of the polarization and the susceptibility tensor is:

$$\begin{aligned} P_i &= \varepsilon_0 \chi_{ij}^{(1)} E_j + P_{NL} \\ &= \varepsilon_0 \left(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l \right) \end{aligned} \quad (1)$$

where $\chi_{ij}^{(1)}$ is the linear susceptibility, $\chi_{ijk}^{(2)}$ is responsible for the frequency doubling generation and $\chi_{ijkl}^{(3)}$ is responsible for the third harmonic generation. In isotropic homogeneous media (such as a gas jet) a reversal in the sign of E_j and E_k must cause a reversal in the sign of P_i . This condition results in $\chi_{ijk}^{(2)} = 0$. This means that in a gas jet it is not possible to generate the second harmonic of the initial frequency. Note that the above equation describes harmonic conversion in the perturbative regime (i.e. field densities of $< 10^{12}$ W/cm²); these conditions are typically met in a setup with nanosecond pulsed laser systems. The amount of XUV light produced by these means is low because it relies on a third-order perturbative process while the material density in the focus (gas-phase) is low: hence the conversion efficiency is 10^{-6} or less.

The bandwidth achieved in the XUV range is determined by that of the incident visible pulsed laser beam. For a Gaussian beam (the ideal case) the XUV-bandwidth is $\Delta\nu_{XUV} = \sqrt{6}\Delta\nu_{vis}$, but in practical cases the bandwidth is slightly larger. In a scanning experiment the wavelength can be calibrated in the visible domain by on-line monitoring the Doppler-limited absorption spectrum of I_2 in an absorption cell; XUV frequencies relate to the visible by the exact relation $\nu_{XUV} = 6\nu_{vis}$.

The used excitation scheme is resonantly enhanced multiphoton ionization, combined with a time-of-flight detection system (REMPI-TOF). The XUV+UV radiation is perpendicularly intersected by a pulsed molecular beam. The XUV photon is resonantly absorbed by the molecules in the beam (H_2 , N_2) and the UV photon excites the molecule (non-resonantly) further above the ionization energy. The generated ion is detected by a time-of-flight spectrometer that allows for mass identification. This scheme is particularly useful to study isotope effects.

In the experimental scheme described above, the spatial and temporal overlap (within 1 ns) of the XUV and UV laser pulses is assured by the THG process. However, in Chapters 4 and 5 a slightly different experimental approach is used: only the XUV photons are selected and the UV photon necessary for the non-resonant ionization is provided by the frequency doubled output of a second PDL. In this case, the XUV frequency was kept constant, and the UV frequency was tuned. The XUV radiation was kept fixed to an intermediate state of the H_2 molecule that has a short lifetime (> 0.5 ns), and therefore careful alignment and precise triggering was necessary to achieve spatial and temporal overlap of the two laser pulses.

Rydberg states

Most of this thesis work deals with Rydberg states, and in the following paragraphs some basic ideas about them will be explained. Rydberg states are excited states of the molecule (or atom) for which the energy of the states can be expressed as:

$$E_n = IE_{ion} - \frac{R_m}{(n - \mu_l)^2} \quad (2)$$

where n is called the principal quantum number having positive integer values, μ_l is the quantum defect, which is a characteristic of a partic-

ular Rydberg series and it depends on the orbital angular momentum quantum number l of the Rydberg electron. R_m is the mass-scaled Rydberg constant taking into account the finite mass of the nucleus $R_m = R_\infty \left(\frac{M}{m_e + M} \right)$ where $R_\infty = 109\,737.318 \text{ cm}^{-1}$, M is the mass of the molecule (or atom) and m_e is the mass of the electron. IE_{ion} is the ionization energy of the neutral molecule (or atom) and is called the Rydberg series limit.

In a pure Coulombic potential, classical mechanics gives the orbit of the electron as ellipses, and the quantum defect is related on how much the electron penetrates the core [10]. Due to the $\frac{l(l+1)}{r^2}$ centrifugal potential, in the higher l states the electron does not penetrate the core as much, and therefore the quantum defect becomes smaller when the l values increase. Also, the mean radius of the orbit is proportional to the principal quantum number squared. In atomic units [11]:

$$\langle r \rangle_{n^*,l} = \frac{n^{*2}}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^{*2}} \right] \right\}$$

where Z is the charge of the ion core ($Z = 1$ for neutral molecules) and $n^* = n - \mu_l$ is the effective quantum number. This means that even for rather “low” quantum numbers ($n \sim 10$), the size of the radius of the orbit is rather large. When the electron is at such a large distance, the core electrons shield the excited electron of the charge of the nucleus, so that the electric potential provided by the core is similar to that of a hydrogen atomic ion. Therefore the energy dependence is hydrogen-atom like ($-1/n^2$), but the principal quantum number $n^* = n - \mu_l$ takes into account (via the quantum defect) the deviation from a purely Coulombic potential.

Electronic Rydberg series can converge to excited rotational or vibrational states of the ion and even to electronically excited states of the ion. In the high energy regions (close to the series limit), it becomes crowded with Rydberg series converging to the various limits. In most cases, Rydberg-Rydberg state interactions occur. Such high- n value electronic Rydberg series are observed in Chapters 4 and 5 for the H_2 molecule. In Chapters 1, 2 and 3, low- n Rydberg states of N_2 were studied. In the latter cases, the Rydberg states were heavily perturbed by neighboring valence states. In Chapter 4, a different Rydberg series is studied: a Rydberg series of the H^+H^- ionic pair. In this series, the Rydberg electron is substituted by an H^- composite particle, and in

spite of being a different type of state altogether, the energy spacing of the levels and its quantum mechanical treatment still follows the simple eq. (2), but with a new R_m value defined [12].

The description of Rydberg states, as well as the interactions between them and with other bound states and the continua above them, are the main subject of quantum defect theory (QDT) [10, 13].

Rydberg-valence state interactions

Rydberg-valence interactions and perturbations arise whenever the approximations (in most cases the Born-Oppenheimer (BO) approximation) used to derive wave functions associated with these states are not sufficiently accurate. In the BO approximation an approximate Hamiltonian of the system (H^{BO}) is built, and its orthonormal solutions (ϕ_j^{BO}) obey:

$$\begin{aligned}\langle \phi_i^{BO} | H^{BO} | \phi_i^{BO} \rangle &= E_i^{BO} \\ \langle \phi_i^{BO} | H^{BO} | \phi_j^{BO} \rangle &= 0\end{aligned}$$

The total Hamiltonian of the system can be written as $H^T = H^{BO} + H^{negl}$ and the H^{negl} is a neglected term in the BO approximation [11]. In most cases, the interactions are local and they involve only two states (sometimes three). This means that the matrix element:

$$\langle \phi_i^{BO} | H^T | \phi_j^{BO} \rangle = \langle \phi_i^{BO} | H^{negl} | \phi_j^{BO} \rangle \neq 0 \quad (3)$$

where the term neglected (H^{negl}) in the H^{BO} Hamiltonian couple the different ϕ_j^{BO} states to each other. In principle it is possible to express any exact solution (Ψ_i) of the total Hamiltonian (H^T) as an (infinite) expansion of the approximated BO functions:

$$\Psi_i = \sum_j c_{ij} \phi_j^{BO}$$

If one term of the expansion is sufficient, this means that the BO approximation is reasonable. In the work presented in Chapters 1, 2 and 3, the states have to be expressed as expansions of two and sometimes three terms of the BO expansion.

Usually these interactions (perturbations) are detected in terms of irregularities in the quantum level structure, as the spacing between

recorded spectral lines becomes irregular. We also investigate the interactions in terms of constructive and destructive interference effects, affecting the intensities of the lines in the spectrum. The quantum interference effect manifest itself by the intensity borrowing phenomenon and unusual predissociation J -dependence of the linewidths.

The first three chapters deal with Rydberg-valence interaction between states, and specially *homogeneous* and *heterogeneous* interactions. Homogeneous interactions are those where $\Delta\Omega = 0$ with Ω the value of the projection of the total angular momentum (exclusive of nuclear spin) J_z of the molecule onto the internuclear axis. It fulfills $\Omega = \Lambda + \Sigma$, where Λ is the value of the projection of the total electronic orbital angular momentum L_z onto the internuclear axis, and Σ is the value of the projection of the total electron spin S_z onto the internuclear axis. Both Σ and Λ values are (in most cases) labels of the eigenfunction. A heterogeneous perturbation is characterized by $\Delta\Omega = \pm 1$. The homogeneous interactions dealt with here are of electrostatic nature, and therefore $\langle \phi_i^{BO} | H^{negl} | \phi_j^{BO} \rangle = H_{ij} = \text{constant}$ [11]. The important feature in heterogeneous interactions is that the interaction matrix element depends on the quantum number J . The total angular momentum quantum number J remains defined (because J^2 commutes with H^T), and therefore the selection rule common to all perturbations is $\Delta J = 0$.

Laser induced breakdown spectroscopy

In laser-induced breakdown spectroscopy (LIBS), the idea is to focus a powerful pulsed laser onto a target, ablating the surface of this target and creating a *plume* of plasma. This plasma emits light as the excited atoms (and molecules) decay to their ground states. The main goal is to record this emission spectrum and determine the composition of the original target. Apart from being able to know which elements are present in the target, the objective is to quantify the elemental abundance. Normally one uses samples of known composition to calibrate the setup.

The calibration is done by determining the relationship between the light intensity measured and the amount of various elements present in the sample. In the calibration process, standard samples with known chemical composition are measured. After selecting the standards, it

is necessary to select the spectral lines to use for the analysis of the element of interest (the analyte). The desirable situation for spectral lines used to detect the concentration of the analyte is that the total (integrated) intensity of the line varies linearly with the concentration of the element. In reality it is found that this intensity versus concentration curve is not linear for all concentrations. At high concentrations of the analyte, re-absorption in the cooler, outer parts of the plasma takes place, diminishing the intensity of some (more sensitive) lines. Therefore, a high sensitivity spectral line must be used for low concentrations, while a low sensitivity line should be used for high concentrations. For the purposes of detection, it means that different lines should be used for calibration for different concentration ranges. Therefore a pre-existent knowledge of the range of concentrations to be measured in the sample must be established before LIBS studies take place.

Another major drawback of this detection system is what is called the “matrix effect”. The matrix is the composition of the substance in which the analyte is found. Usually, the matrix refers to the major component or base element (for example, iron in steel). The introduction of additional elements into the sample in large amounts ($> 5\%$) can affect the slope of the calibration curve. This is called interelement effect or matrix effect. In many cases the matrix effect is independent of the spectral line, i.e. the same matrix effect on many different spectral lines of the same element in a given matrix can be found. The phenomenon is not well understood from a physical point of view [14]. For the purposes of detection, this means that for each specific study, the target’s main composition should be known, in order to perform a calibration based on reference samples of the same matrix composition.

What makes the LIBS detection system attractive is the fact that it can be used in harsh environments, such as inside melting furnaces of metals. Or in places where a fast selection of the target is important, such as a scrap metal yard, where the value of the different pieces of metal depends greatly on their specific composition. The paper presented here was part of a project together with Stena Metall AB, a metal recycling company present in Stockholm, in which the aim was to assess the possibility to use LIBS to discriminate between metallic pieces to be recycled according to their composition. This work was used for the initiation of a study on a larger scale: “Laser-Induced Breakdown Spectroscopy for Advanced Characterization and Sorting of Steel Scrap

(LCS)” (EU Research Programme of the Research Fund for Coal and Steel, Grant Agreement Number: RFSR-CT-2006-00035). The goal of the latter project was to industrially evaluate the use of LIBS for scrap analysis and sorting.

Outline of this thesis

Chapter 1 is an introduction to the problems and challenges that must be dealt with when studying the spectrum of molecular nitrogen. From a general perspective, it describes the contribution of the Amsterdam XUV laser facility to the understanding of the complex N_2 energy levels and their interactions. This chapter also serves as an introduction to the next two chapters.

Chapter 2 is about Rydberg-valence states interacting and perturbing each other. In this Chapter one exemplary case, prototypical for the entire N_2 spectrum, is investigated in detail. The Rydberg state $o^1\Pi_u(v = 1)$ is perturbed (homogeneous perturbation) at low- J values by the valence state $b^1\Pi_u(v = 9)$ and at high- J values by the $b'^1\Sigma_u^+(v = 6)$ valence state (heterogeneous perturbation). The $o^1\Pi_u(v = 1) \sim b^1\Pi_u(v = 9)$ mixing is so pronounced that it has led in the past to incorrect assignment of the spectral lines. The mixing of states gives rise to effects of quantum interference on the oscillator strength of the observed lines.

Chapter 3 deals with the perturbations of the Rydberg complex $3p\pi_u c^1\Pi_u(v = 2)$ with other valence singlet states and with triplet states. The perturbations with the singlet valence state $b'^1\Sigma_u^+(v = 7)$ results in a strong Λ -doubling between the e and f states of the $c(v = 2)$ and a P/R branch intensity anomaly for the $b' - X(7, 0)$ band. Strong local perturbations in energy and line width of the $c(v = 2)$ are attributed to a heterogeneous perturbation of the $C^3\Pi_u(v = 17)$ state.

Chapter 4 is about the first spectral observation of a series that was baptized “heavy Rydberg series”, a short for Rydberg series in a heavy Bohr atom. A heavy Bohr atom is a hydrogen atom where the electron is replaced by a H^- composite-like “particle”, forming the ion-pair $H^+ + H^-$. The remarkable result is that the energy dependence of the heavy Rydberg series is similar to that of a “regular” (electronic)

Rydberg series, but with rescaling of the Rydberg constant due to the difference in mass between the electron and the H^- .

Chapter 5 deals with the characterization of the heavy Rydberg series excitation and observation mechanism, the “complex resonances”. The linewidths and line positions of the heavy Rydberg series are analyzed. The resulting quantum defects are related to the line positions using an (over-simplified) quantum defect theory model.

Chapter 6 deals with using laser-induced breakdown spectroscopy detection system to measure the trace amounts of nickel, copper and other metals in steel targets. As an example of an industrial application, the concentration of copper in scrap metals is studied, which is an important factor to determine the quality of the samples to recycle. Another application of the LIBS method is the study of the nickel and copper concentrations in a sample of iron-rich magma.