Synopsis

The study of electronic structure of transition-metal containing diatomic molecules shed light on the role played by the $d$ electrons in a molecular bond. However, this presents a serious challenge for both theorist and experimentalist because of the complex electronic structure arising from the partial occupation of open $d$ orbital. Due to the presence of the unpaired $d$ electrons in the transition metals, the molecules containing these metals tend to have high density of excited electronic states with high-spin and orbital angular momenta. Configuration interactions between these excited states result in local and global perturbations, which are often responsible for many misinterpretations of the spectra. The study of the bonding trends of the transition-metal containing diatomic molecules provide a benchmark for the theoretical chemists to test the validity of their approximations and accordingly develop robust theoretical methods capable of accurately describing the electronic structure and geometry of larger systems. Over the past decades, significant progress has been made towards understanding the nature of the chemical bond in transition-metal containing diatomic molecules [1]. On the theoretical front, new and improved methods for electronic structure calculations have been developed. These \textit{ab initio} calculations account for configuration interaction, electron correlation, exchange and relativistic effects in their treatment which are very important for the molecules containing transition metal atoms [2]. However, on the experimental front, the study of diatomic molecules has been benefitted from the numerous developments made in the recent past. Prior to the development of lasers and molecular beam techniques, emission or absorption spectra recorded on photographic plate served as the main source of spectroscopic data. Conventionally, the metals were vaporized in high temperature ovens, and were allowed to react with various gases to form the desired molecular species [3].
Thus due to the high temperature conditions necessary for metal vapour production, the obtained molecular spectra were often complex and congested which many times led to misleading assignments [4-6]. The application of laser radiation sources in the 1970’s led to revolutionary developments in the field of molecular spectroscopy. The high spectral resolution and sensitivity brought about by the advent of laser sources allowed investigation of subtle and intricate structures present in the spectra of molecules, even at very low concentrations. The development of experimental technique of laser ablation followed by supersonic expansion, creating a molecular beam of refractory material at low temperature wherein most of the population remained in few rotational levels of the ground state, simplified the spectra dramatically. This simplified spectra led to an unambiguous assignment of character of the ground and excited electronic states [7] which is very important for understanding the nature of the transition metal-main group element bond.

This thesis presents the experimental study of electronic structure of two diatomic molecules lanthanum hydride (LaH) and zirconium nitride (ZrN) in the gas phase using laser-induced fluorescence (LIF) spectroscopy. Transition-metal containing diatomic molecules play an important role in many fields, such as catalysis [8], organometallics [9], surface science [10], and astrophysics [11]. The lanthanide hydrides have recently attracted much interest due to their use in semiconducting and magnetic materials [12,13]. Lanthanide metals are also being considered as materials for hydrogen storage [14]. It is therefore important to study small lanthanide hydrides to extend our knowledge of hydrogen chemistry of these compounds. The diatomic transition metal nitrides are simple model systems for fixation of nitrogen in industrial, inorganic, and biological systems [15,16]. Transition metal nitrides also have astrophysical importance and so far have not been detected in the stellar atmospheres, partly due to the lack of precise
spectroscopic data required for their meaningful search in the complex stellar spectra. Radiative lifetimes of neutral lanthanum (La I) atom are also included in this thesis. Transition probability data is useful for determination of elemental abundances in stellar atmosphere, validating the atomic structure calculations and also for understanding of the radiative properties of La I needed for few applications like that in the lighting industry.

In the present work, both LaH and ZrN molecules are produced at low temperature in pulsed supersonic free-jet apparatus. A rotating and translating metal rod is ablated with the third harmonic beam (354.7 nm, ~10–15 mJ/pulse) of a Nd: YAG laser focused to ~1 mm² spot. The laser produced metal plasma reacted with 2% ammonia seeded in He gas emerging from a pulse valve under a backing pressure of 275 kPa. The products of the reaction are expanded into vacuum, cooling the internal degrees of freedom of the molecules and are probed at right angle to the supersonic expansion axis about 50 mm downstream of the nozzle by a XeCl excimer pumped pulsed tunable dye laser. The resulting laser-induced fluorescence is imaged on an entrance slit of a monochromator equipped with a Peltier cooled photomultiplier tube. An output signal from the photomultiplier is amplified by a 1 GHz bandwidth amplifier, integrated by a gated integrator and stored on to a computer. Transition wavenumbers are calibrated by using a laser wavelength calibration facility of the dye laser utilizing neon optogalvanic spectral lines as well as by known atomic lines appearing in the spectra with an absolute precision of ~0.1 cm⁻¹. The molecular constants such as rotational constant, bond length, vibrational frequency, term energy are determined by using nonlinear least-squares fitting procedure of the observed transition wavenumbers to the energy level expression of the involved electronic states. The spectra are also fitted and simulated using Pgopher program [17].

The thesis is organized in six chapters. Chapter 1 presents a brief introduction and a theoretical background required to understand the electronic structure of a molecule with
special emphasis on the diatomic molecule [18-22]. This chapter contains an introduction to Born-Oppenheimer approximation which separates electronic and nuclear motions. The information on rotational and vibrational structure of diatomic molecules is presented. Electronic structure of diatomic molecules including different angular momenta, molecular term symbols, Hund’s coupling cases, spin-orbit components, parity and perturbation in the spectra of diatomic molecules is discussed in detail. This chapter, thus, provides both the introduction as well as theoretical background required to understand the work presented in the subsequent chapters.

Chapter 2 describes the experimental setup and the methodologies used in the present work. Production of a wide variety of metal-containing molecules of refractory nature and clusters became possible after the development of “Smalley source” in 1981[23]. The capability of the pulsed laser to vaporize elements of refractory nature in conjunction with supersonic expansion in free-jet allows formation of exotic species in the beam. Supersonic expansion is a well-known technique for cooling the internal degrees of freedom of molecules thereby simplifying the spectrum. This chapter describes the experimental setup which involves laser vaporization source, pulse valve, supersonic free-jet, tunable laser, fluorescence imaging and detection system, signal processing and data collection system. The classic technique of laser spectroscopy called Laser-Induced Fluorescence (LIF) is used in the present work. LIF spectra are recorded in two formats: fluorescence excitation spectrum and wavelength resolved fluorescence (WRF) or dispersed fluorescence (DF) spectrum. A fluorescence excitation spectrum is recorded by scanning the tunable dye laser frequency and recording the fluorescence intensity through the monochromator which is used as a broad band filter. The monochromator is set at the fixed wavelength corresponding to the strongest fluorescence terminating either to a ground or an excited state. However, wavelength resolved or dispersed fluorescence
spectroscopy involves the scanning of monochromator set at high-spectral resolution while the laser frequency fixed to a selected transition to a particular ro-vibronic level. The fluorescence excitation spectra provide information about the lower and upper electronic states involved in the transition. However, the resolved fluorescence spectra provide information about the vibrational structure of ground state and the wealth of information on low-lying electronic states. These techniques are discussed in detail. This chapter thus provides the consolidated view of experimental techniques used in the present work.

Chapter 3 presents the study of ground and high-energy excited electronic states of LaH molecules. The rotationally-resolved excitation spectra provided information on symmetry and molecular constants of the ground and the excited electronic states. Prior to this work there was no direct confirmation of ground state symmetry of LaH molecule, which is essential for understanding the bonding in the molecule. Bacis and Bernard were the first to report the electronic spectra of LaH in the hallow cathode discharge source [24], a hot source where the excited electronic states are populated. They identified $^3\Phi_4$-$^3\Delta_3$, $^3\Phi_3$-$^3\Delta_2$, $^1\Delta$-1$\Pi$, and $^1\Sigma$-1$\Pi$ electronic transitions [25] and assigned $^3\Delta$ to be the ground state based on the erroneous ab initio calculations on isovalent ScH [4] and their observation of transitions originating from $^3\Delta$ state. Later, high level ab initio calculations by Das and Balasubramanian [26] which include relativistic and electron correlation effects predicted $^1\Sigma$ state as the ground state with a low-lying $^3\Delta$ as the first excited state. The observation of $A^1\Pi$-$X^1\Sigma^+$ band along with $d^3\Phi$-$a^3\Delta$, by Ram and Bernath [27] supported the predicted $^1\Sigma^+$ ground state symmetry of LaH [26]. However, their result is not a direct confirmation of ground state symmetry since they observed these bands in discharge source. In order to confirm the identity of the ground state and to get information on excited electronic states of LaH, we carried out LIF spectroscopic
investigations in the energy range 13300-22500 cm$^{-1}$. The LaH molecules are produced in jet-cooled molecular beam by reaction of laser produced lanthanum metal plasma with 2% ammonia seeded in helium. A number of new excited electronic states are observed. The combination difference (CD) method confirmed that the lower state involved in these transition is the same as observed earlier by Ram and Bernath [27]. Since our spectra are obtained in a jet-cooled molecular beam where the major population exists in the ground state, we are entitled to conclude that the $X^1\Sigma^+$ state is indeed the ground state of the LaH molecule. In addition, the first intercombination transition in LaH is observed at 15623 cm$^{-1}$ and assigned as $0^+\left(^3\Sigma^->X^1\Sigma^+\right)$ and is discussed in detail in this chapter. The presence of $P$, $Q$, and $R$ branch structure in bands with origin at 17398 and 17549 cm$^{-1}$ indicated that the observed transitions are type $\Delta \Omega = \pm 1$ and thus the upper states are assigned as $D1$ and $E1$. Short radiative lifetimes and strong intensities associated with these electronic states indicated that the transitions occur within the same multiplicity and thus the parent term assignment of the $D1$ and $E1$ states is $^1\Pi$. Three more electronic states with term energy at 20042, 21970 and 22100 cm$^{-1}$ indicated the triplet character as evident from the dispersed fluorescence spectrum. However, the short radiative lifetimes of ~40 ns associated with these states contradict their triplet character. The state at 20042 cm$^{-1}$ is assigned as $\Omega = 1$ and those at 21970 and 22100 cm$^{-1}$ are assigned as $\Omega = 0^+$ in Hund’s case(c), which is usual in heavy molecules. The molecular constants for all the newly observed excited electronic states are determined by fitting the observed set of transition wavenumbers of the excitation bands to the rotational energy level expression. The experimental results are compared with the available ab initio calculation. This chapter thus provides an experimental confirmation of ground state symmetry and molecular constants for several new excited electronic states of LaH molecule.
Chapter 4 presents the Dispersed Fluorescence (DF) study of LaH molecules. The principal motivation behind this study is to establish the missing energy linkage between singlet and triplet manifolds and also to determine the vibrational constants of the ground state of LaH molecule. In the absence of observation of inter-combination transition, the singlet and triplet stack of electronic states observed by earlier workers [25, 27] were not placed energetically with respect to each other. This chapter provides the DF study of LaH by exciting single isolated rotational levels of excited electronic states reported in chapter 3. The DF spectrum with a moderate resolution (FWHM~50 cm\(^{-1}\)) gave information about the energies of the low-lying electronic states and their vibrations. The coarse spectra are then examined under relatively higher resolution (FWHM~15 cm\(^{-1}\)) to resolve the rotational structure, wherever possible, to confirm the identity of the lower states. The DF spectrum from \(0^+ (^3\Sigma^-)\) state revealed the presence of the first low-lying excited electronic state \((a^3\Delta_1)\) of LaH molecule. This observation was important for establishing the missing energy link between the singlet ground state and \(a^3\Delta\) state. The DF spectrum from \(0^+ (^3\Sigma^-)\) state also provided the vibrational constants of the ground state from the observed vibrational levels \(v = 0-2\). The DF spectra from the \(D1\) and \(E1\) electronic states revealed the presence of low-lying electronic states \(a^3\Delta_2\), \(b^3\Pi_0^\pm,1\) and \(B^1\Delta_2\), predicted by earlier \textit{ab initio} studies [26]. However, \(b^3\Pi_2\) low-energy electronic state was observed from the DF spectrum of \([20, 0]|\Omega = 1\) excited state. All the low-lying states below 11000 cm\(^{-1}\) predicted by \textit{ab initio} calculations are observed and characterized in this chapter. Although \textit{ab initio} studies predicted vibrations quite accurately, the term energies and spin-orbit separations are largely overestimated. In contrary to the \textit{ab initio} prediction [26], the spin-orbit splitting of the \(^3\Pi\) state is observed to be regular. These discrepancies between the present observations and earlier theoretical results may stimulate more refined \textit{ab initio} studies leading to a better understanding of
the electronic structure of LaH. The current information on the electronic structure of LaH is compared with those of isovalent ScH and YH molecules.

Chapter 5 deals with the study of excited electronic states of zirconium nitride (ZrN) molecules. Transition metal atoms have relatively high abundances in many stars [28] and several transition metal hydrides and oxides have been detected. Transition-metal nitrides (TMNs) are also possible to be present in the stellar atmosphere. However, TMNs have not been observed in the stellar atmosphere partly due to the lack of precise spectroscopic data required for their meaningful search in the complex stellar spectra. The motivation for this work is to extend the $B^3\Sigma^+-X^2\Sigma^+$ and $A^2\Pi-X^2\Sigma^+$ systems to the higher vibrational levels to improve the molecular constants at equilibrium. Bates and Dunn [29] first recorded the spectra of ZrN molecule. They observed (0,0) band of $B^3\Sigma^+-X^2\Sigma^+$ system and (0,0), (1,1), and (2,2) bands of $A^2\Pi-X^2\Sigma^+$ system using conventional emission spectroscopy. Bates and Gruen [30] confirmed the $X^2\Sigma^+$ as the ground state of ZrN. Later, Cheung and co-workers revisited the $B^3\Sigma^+-X^2\Sigma^+$ and $A^2\Pi-X^2\Sigma^+$ systems of ZrN [31-37] using laser-induced fluorescence (LIF) spectroscopy. They studied the previously observed (0,0), (1,1), and (2,2) bands [31,33,35] of $A^2\Pi-X^2\Sigma^+$ system for the various isotopomer of ZrN. Cheung and co-workers did not observe the (1,0) band in $B^3\Sigma^+-X^2\Sigma^+$ system, and attributed their lack of success to a very unfavorable Franck-Condon factor. However, we observed (1,0), (1,1), (2,0), (2,1), (2,3) bands with considerable intensity and a weak (3,4) band. We have also observed (3,3) band of $A^2\Pi-X^2\Sigma^+$ system along with the previously reported (0,0), (1,1), and (2,2) bands. Perturbations are observed in all the bands of the $B-X$ system. The perturbed lines are removed from the fit while determining the molecular constants. The rotational perturbations are identified at several places in the (0,0), (1,1) and (2,2) sub-bands of $A^2\Pi_{3/2}-X^2\Sigma^+$ system in the previous works [31,33,35]. However, (3,3) band of the $A^2\Pi_{3/2}-X^2\Sigma^+$ system is found to be unperturbed in the present
work and the rotational constants and the term energies of both states are determined. The e-parity levels of (3,3) band in the $A^2\Pi_{1/2} - X^2\Sigma^+$ system are found to be free from perturbation and the rotational constants are determined by fitting only the e levels. However, rotational perturbations are observed in the f-parity levels of (3,3) band in the $A^2\Pi_{1/2} - X^2\Sigma^+$ system. The DF spectra from various newly observed bands of the $B-X$ system provided the vibrational energies of the ground state up to $v = 5$.

Chapter 6 describes the radiative lifetime measurements of neutral Lanthanum (La I) atom using time-resolved laser-induced fluorescence spectroscopy in supersonic free-jet. Measurement of laboratory radiative data of atoms like, transition probabilities, radiative lifetimes and branching fractions is of great interest. This is useful in analyzing the available stellar spectra for the quantitative determination of their abundance in the Sun and peculiar stars [38]. In addition, radiative data on rare earth elements is of commercial importance due to their usage as additives in metal halide high-intensity discharge (MH-HID) lamps which provide a pleasing white light with higher luminous efficacy as compared to conventional incandescent light sources [39]. There is a need for measurement of radiative lifetime data for many levels, particularly below 18000 cm$^{-1}$ in La I. In the present work, the technique of laser vaporization in conjunction with supersonic expansion is used for generating a supersonic free-jet of lanthanum atoms. In supersonic free-jet, the excitation of atoms takes place in collision-free environment at a low atom number density and thus measured radiative lifetimes are free from collisional and radiation trapping effects. This study provided-radiative lifetime data, accurate within ±10%, for 63 odd-parity levels belonging to the odd 5d6s6p, 4f6s$^2$, 6s$^2$6p, 5d$^2$6p, 4f5d6s electronic configurations in La I in the energy range 13260 – 30965 cm$^{-1}$. Care was taken to minimize the influence on the lifetime measurements due to various effects like flight-out-of view, radiation trapping, saturation, and collisional depopulation. The measured
lifetime values fall in the range 9.5 to 313 ns. For levels that have lifetimes longer than 80 ns, lifetimes are evaluated by fitting the observed fluorescence decay curve to a single exponential decay function. However, for the short-lived excited states, lifetimes are evaluated by fitting the observed fluorescence decay curve with a convolution between a Gaussian function which represented the excitation laser pulse and an exponential function with adjustable parameters. Lifetimes for the 45 levels among the obtained results are reported for the first time.

References:


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