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Spectroscopy of atoms, molecules and clusters in the vacuum ultraviolet (VUV) region (6-25 eV) is of vital importance for understanding of their electronic structure and various photo-induced processes, principally, photoionization and photodissociation. At the basic level these studies help to validate and improve the predictions of the *ab-initio* quantum mechanical calculations, while at the applied level they find use in the understanding of photophysics and photochemistry pertaining to atmosphere, biological processes and astrophysical objects. The first ionization potential of most molecules lies typically in ~ 9-12 eV region. Spectroscopic studies in this region are therefore important for probing the excited state structure of molecules and understanding of phenomena occurring near and above the first ionization limit. These investigations cover a wide spectrum of issues relating to structure, electron correlations, and dynamics of photo-ionization, photodissociation and photo-fragmentation etc. Spectroscopy in the VUV region requires special sources
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and equipment. Synchrotron radiation (SR) is an intense and continuous source of radiation, which is ideally suited for this purpose. Spectroscopy of atoms and molecules using SR sources has been a subject of immense interest in recent years, having implications in diverse fields such as basic atomic and molecular physics, environmental science, astrophysics, astrochemistry, combustion dynamics, etc. [1-6].

Among the various spectroscopic techniques adopted in the VUV region, high resolution gas phase photoabsorption spectroscopy is a well-established technique which is ideally suited for studies involving the electronic structure, geometry, vibrational modes and vibronic interactions of excited states; both valence and Rydberg type. The high brilliance and continuous tunability of SR sources have been exploited in gas phase VUV photoabsorption studies since the early days of storage rings and SR sources thereby providing exceedingly rich and crucial information on spectroscopy and structure of a large number of molecules. Much of this work is intimately connected with the molecules and molecular processes of importance in atmosphere and astrophysical objects. In addition to the gas phase studies, there has been a considerable interest in the spectroscopic studies of molecules trapped in inert gas matrices under cryogenic temperature. The matrix isolation spectroscopy (MIS) technique in conjunction with a SR source provides an ideal platform for studies of molecule-molecule and photon-molecule interactions in the crystalline and amorphous states of the matrix. Such studies are of significant importance in the understanding of spectroscopy and molecular processes in astrophysical ices, which is intimately connected to the emerging field of astrochemistry [7].

The present thesis deals with VUV photoabsorption spectroscopy of polyatomic molecules in gas and matrix isolated states using Indus-1 SR source, which is a 450 MeV storage ring with critical wavelength of 61 Å. Molecules investigated in this work are sulphur dioxide, acetone and
chloroform; spectroscopy of which is of significant importance in atmospheric sciences. The work reported here consists of two broad objectives: First one is concerned with the design and development of high resolution vacuum ultraviolet (HRVUV) beamline and experimental stations for photoabsorption spectroscopy in gas and matrix isolated phases. The second one is related to the detailed investigations of VUV spectroscopy of the selected polyatomic molecules and their interpretations in the light of \textit{ab initio} quantum chemical calculations. The thesis is organized in seven chapters and the details of the work included therein are as follows:

Chapter-1 presents a brief introduction to the subject of VUV spectroscopy of polyatomic molecules with a focus on the current developments in the field. Discussed here briefly are the important aspects of molecular physics including the Rydberg and valance states, molecular symmetry and group theoretical formalism, \textit{ab initio} quantum chemical calculations and the importance of VUV spectroscopy in basic and applied sciences. The contents of this chapter, thus, provide both the motivation and the basis for the work presented in subsequent chapters.

Chapter-2 is devoted to the design and development of experimental systems for VUV spectroscopy, which includes the HRVUV beamline and experimental stations for photoabsorption spectroscopy and matrix isolation spectroscopy. HRVUV beamline is designed and developed to provide high resolution (resolving power \( \geq 10^4 \)) in the VUV region 1050 – 3000 Å. The beamline consists of a pre-focusing optical system, a gas phase absorption set-up and a high resolution VUV spectrometer. The pre-focusing optical system, which consists of three cylindrical mirrors, serves the purpose of maximizing the throughput in the VUV region and matching the source aperture to the spectrometer aperture within the constraints of the SR source. The spectrometer is based on the off-plane Eagle mounting utilizing a concave spherical grating of radius of curvature 6.65 m. The central wavelength of interest is selected by appropriate rotation and translation of the grating. The spectrum
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is scanned by moving the exit slit-cum-photomultiplier (PMT) assembly vertically along the focal plane over a bandwidth of 160 mm about the central wavelength. The linear and rotational motion of the grating and the linear motion of the PMT are controlled by a 3-axis stepper motor controller and driver system. The beamline is interfaced with a PC for control and data acquisition. The beamline and spectrometer are maintained at $10^{-9}$ and $10^{-6}$ mbar vacuum respectively. The experimental station for gas phase absorption consists of an absorption cell and sample filling system. Performance of the beamline is evaluated by recording VUV photoabsorption spectra of Xe and O$_2$ and further compared with other high resolution (resolving power $\geq 10^4$) VUV beamlines (5-25eV) based on bending magnet as well as undulators installed on synchrotron sources around the world. Details of the optical and mechanical designs of various sub-systems of the beamline together with the optical alignment and performance evaluation of the beamline are discussed. In addition to the HRVUV beamline, a medium resolution (resolving power $\sim 10^3$) beamline, i.e., Photophysics beamline, on Indus-I synchrotron source is also used for the gas phase absorption studies. In order to study VUV spectroscopy of molecules trapped in inert gas matrices at cryogenic temperatures, a matrix isolation spectroscopy set-up is designed, developed and demonstrated by recording VUV absorption spectra of CO in Argon matrix. This set-up consists of a gas mixing chamber with deposition line, sample holder and an experimental chamber connected to a liquid He cryostat for matrix deposition. Design of the MIS set-up, its integration with the Photophysics beamline and its performance evaluation are reported in this chapter. The design and development of experimental systems discussed in this chapter thus form the main experimental part of the thesis, and the results obtained with them are presented in the chapters which follow.

Chapter-3 deals with the gas phase photoabsorption studies of sulphur dioxide (SO$_2$) in the VUV region using HRVUV beamline. Specific aim of these studies is to understand the nature of the
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\( \tilde{E} - \tilde{X} \) system lying in the region 7.5 – 9.0 eV (60500 – 72600 cm\(^{-1}\)). The electronic states and their symmetries involved in this system have been debated extensively in the literature. Owing to the high resolution afforded by the present experimental system, rich spectral features are obtained compared to the earlier reported studies. Vibronic analysis of the observed VUV spectra is carried out to show that most of the observed bands in the \( \tilde{E} - \tilde{X} \) system can be arranged into four series with successive band spacing of 500 – 620 cm\(^{-1}\). In addition two additional series are observed with average separation of \( \sim 1750 \) and \( \sim 1000 \) cm\(^{-1}\). These vibronic intervals are significantly different from the frequencies of the ground state vibrational modes, i.e., \( v_1 \) (symmetric stretch), \( v_2 \) (bending) and the \( v_3 \) (asymmetric stretch). In order to aid vibronic analysis, \textit{ab initio} calculations using the GAMESS (USA) suite of programs are performed. Geometry optimization and vibrational frequencies of ground state are carried out using DFT and CIS methods. Vertical excitation energies are calculated at the ground state optimized geometry using TDDFT. Equilibrium geometry, vibrational frequencies and adiabatic excitation energies are also calculated for first few excited singlet and triplet states. Based on the \textit{ab initio} calculations it is concluded that at least three dominant excitations involved in the \( \tilde{E} - \tilde{X} \) system are \( \tilde{X}^1A_1 \rightarrow 3^1A_1, \tilde{X}^1A_1 \rightarrow 2^1A_1 \) and \( \tilde{X}^1A_1 \rightarrow 2^1B_1 \). The observed vibrational features are found to be mainly due to excitation of the combination modes \((v_1 + v_2)\) and \((v_2 + v_3)\) with some contributions from \( v_1 \) and \( v_3 \). Geometry optimization calculations indicate that the molecule maintains \( C_{2v} \) symmetry in these excited states although the bond lengths and bond angle do differ from their ground state values. This work in totality provided a consolidated picture of the \( \tilde{E} - \tilde{X} \) system for the first time.

Chapter-4 presents a detailed work on VUV spectroscopy of acetone-\( h_6 \) (\( \text{CH}_3\text{COCH}_3 \)) and its deuterated counterpart acetone-\( d_6 \) (\( \text{CD}_3\text{COCD}_3 \)). The UV-VUV photoabsorption spectra of these
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molecules are recorded in the region 3.5 – 11.8 eV (28000 – 95000 cm\(^{-1}\)). The VUV spectrum of acetone shows extensive Rydberg series (ns, np and nd) converging to its first ionization potential at 9.708 eV. Vibronic assignments are carried out by taking into account the symmetry selection rules and contributions of hot bands from low lying torsional modes. These two considerations provide significantly improved vibronic assignments compared to earlier reported works [8] where these issues are not taken into account. Revised quantum defect values for some of the Rydberg transitions and a few new assignments are also proposed in this work. Several non-totally symmetric modes are observed arising due to the Herzberg-Teller effect. Some of the unresolved questions in the VUV spectrum of acetone-\(\text{h}_6\) are the existence of transitions with multiple assignments, difficulty in unambiguous location of the \(v_{00}\) origins of some of the excited states, and the observation of anomalous quantum defects in \(n_d_{xy}\) series. These issues are sorted out by the study of VUV photoabsorption spectrum of acetone-\(\text{d}_6\), which is reported for the first time. A comparative study of the Rydberg series and accompanying vibronic structure observed in acetone-\(\text{h}_6\) and acetone-\(\text{d}_6\) has clarified and consolidated many of the vibronic assignments. Attribution of the anomalous intensity pattern observed in acetone-\(\text{h}_6\) to vibronic coupling with nearby valence states of the same symmetry is confirmed on the basis of observation of the same effect in acetone-\(\text{d}_6\). The frequency of the \(v_{19'}\) mode of the \(3p_y\) state is obtained as 340 ± 5 cm\(^{-1}\) for acetone-\(\text{d}_6\) on the basis of observation of an extensive progression of this mode. This chapter describes a complete quantum defect analysis and vibronic analysis of Rydberg series observed in acetone-\(\text{h}_6\) and acetone-\(\text{d}_6\), thus providing a unified picture of the VUV spectroscopy of acetone and its deuterated derivative.

Chapter-5 presents a detailed investigation of the electronic spectra of chloroform (\(\text{CHCl}_3\)) and its deuterated counterpart (\(\text{CDCl}_3\)) in the energy region 6.2 – 11.8 eV (50,000 – 95000 cm\(^{-1}\)) using Photophysics beamline. Rydberg series converging to the first four ionization limits at 11.48, 11.91,
12.01 and 12.85 eV corresponding to excitation from the 1a₂, 4a₁, 4e, 3e orbitals of CHCl₃ respectively are identified and analyzed. Quantum defect values are observed to be consistent with excitation from the chlorine lone pair orbitals. Analysis of Rydberg series and vibronic features observed in the electronic absorption spectra is greatly aided by quantum chemical computations. The ground state geometry optimization and vibrational frequency calculations for neutral and ionized CHCl₃ and CDCl₃ are performed using DFT. The vertical excited state energies are calculated at the optimized ground state geometries using the TDDFT method. The experimental spectrum is found to be in good agreement with that predicted by TDDFT calculations. Comparison of the experimental and theoretical data is carried out by establishing a correspondence between the Rydberg series members originating from a given MO, i.e. 1a₂, 4a₁, 3e or 4e (based on quantum defect analysis) with the theoretically calculated energies for excitation from that particular MO. Vibrational progressions observed in the region of 72,500 – 76,500 cm⁻¹ have been reassigned to ν₃ (CCl₃ s-deform) mode and combination modes of ν₃ and ν₆ (CCl₃ d-deform) belonging to 1a₂→4p transition in contrast to earlier studies [8] where they were assigned to a ν₃ progression superimposed on the 3e→4p Rydberg transition. The assignments are further confirmed based on study of vibronic spectrum of CDCl₃ whose VUV photoabsorption spectrum is reported here for the first time. The frequencies of the ν₃ and ν₆ modes in the 4p Rydberg state of CHCl₃ (CDCl₃) are proposed to be ~ 450 (407) cm⁻¹ and 105 (137) cm⁻¹ respectively based on the vibronic analysis. This chapter presents a consolidated analysis of the VUV photoabsorption spectrum of chloroform.

Chapter-6 is devoted to the study of VUV spectroscopy of molecules isolated in inert gas matrices at cryogenic temperatures. These studies are a prelude to the understanding of VUV photo-induced processes in these systems and assume importance in investigation of molecule-matrix interactions. In order to understand the differences in the spectra in gas phase and matrix isolated
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phase, VUV spectra of SO2 and acetone are studied in some detail. The gas phase spectroscopy of these molecules is reported in Chapter-3 and -4 of this thesis. Experiments are performed by isolating SO2 and acetone in Argon matrices at 10 K, at different ratios ranging from 0.2:1000 to 5:1000. It is quite well established that in condensed phase, electronic states having a Rydberg character are either shifted considerably to higher energies or simply obliterated from the spectrum. In contrast valence transitions show small shifts in condensed phase compared to the gas phase [9]. Electronic transitions observed in matrix isolated acetone show blue shifts of \(\sim 3000 - 6000 \text{ cm}^{-1}\), as expected in view of the Rydberg nature of these transitions. In the case of SO2, the first three absorption bands are not shifted much in the matrix phase as compared to the gas phase, whereas the higher excited states show larger shifts. This is in line with the assignment of the first three gas phase absorption systems to valence transitions, and higher bands to transitions of valence-Rydberg mixed or Rydberg character. This chapter thus presents the investigations of VUV absorption processes in matrix isolated molecules.

Finally the important conclusions of the present study and scope for future work are discussed in Chapter-7.

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Signature of the Student:

Date: 09.11.2013

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