CHAPTER ~ 1

Introduction
1.1 Introduction:

1.1.1 Cosmic Molecules

The space between the stars is not void, but filled with interstellar matter, mainly composed of dust and gas, which gather in large interstellar clouds. Driven by gravitation these clouds collapse and star formation commences. The life cycle of stars is accompanied by a rich interstellar chemistry possessing an astonishingly rich population of both familiar and exotic molecules. These interstellar molecules were found to serve as extremely useful diagnostic tools of star formation and the dynamics of the interstellar medium (ISM) in general. Until now more than 170 interstellar molecules have been identified. It is expected that many more interstellar molecules will be discovered in space once their characteristic spectra are known from the laboratory. Therefore, it is necessary to have the knowledge of physical properties of these molecules, their cations, anions, electron affinity and ionization potential, dipole moment, energy of the molecule etc. These properties can be obtained using quantum chemical methods.

Molecules are identified in the interstellar regions by their spectroscopic signatures in the millimeter, infrared and optical regions of the electromagnetic spectrum.

The diatomic molecules such as CH, CHC, and CN were reported in space more than fifty years ago from visible absorption of diffuse clouds [1-3]. More than 170 different varieties of molecules have been found in the interstellar medium ranging from simple molecules such as methyledene (CH), water (H₂O), hydrogen cyanide (HCN), nitrous oxide or "laughing gas" (N₂O), to complex molecules such as ethanol (CH₃CH₂OH), anthracene (C₁₄H₁₀) to a C₆₀. Fullerene is a molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid or tube, the biggest known of which is the C₇₀. The two isomers of C₃H₂, are the cyclopropenyldiene [4] and propadienyldiene [5], which are the cyclic molecules detected
initially in interstellar space. The isomers of C$_2$H$_4$O molecule, acetaldehyde (CH$_3$CHO), ethylene oxide (c-C$_2$H$_4$O) and vinyl alcohol (CH$_2$CHOH), are formed in the interstellar and cometary ices and studied in the terrestrial laboratory [6]. The isomers which are separated by bonding energy differences are also found to be distributed in different interstellar environments [7].

Apart from the above mentioned class of molecules, some deuterated class of molecules are also detected in space such as HD, DCO and DCN. Iglesias-Groth et al. reported the evidence of the naphthalene cation in the interstellar medium using anomalous microwave emission [8]. The formation and distribution of large molecules in the gas and solid state is far from being understood. In the envelopes of carbon-rich late-type stars, carbon is mostly locked in CO and C$_2$H$_2$. C$_2$H$_2$ molecules are precursors for soot formation, where Polycyclic Aromatic Hydrocarbons (PAHs) might act as intermediates [9]. The ubiquitous presence of aromatic structures in the ISM and in external galaxies has been well documented by numerous observations with the Infrared Space Observatory, or ISO. Evidence for carbon-chains and fullerenes arises from the characterization of the Diffuse Interstellar Bands (DIBs) [10-13]. Diamonds were recently proposed to be the carriers of the 3.4 and 3.5 μm emission bands [14] observed in planetary nebulae. Hydrogenated amorphous carbon (HAC) seems to be responsible for the 2200 Å bump in the interstellar extinction curve [15]. A variety of complex aromatic networks are likely to be present on carbonaceous grains [16]. Recent laboratory studies point toward PAHs, carbon chains, and carbon rings or fullerenes as the potential carriers for some DIBs [10-11, 17-20]. From this evidence it is confirmed that more ionic forms of the molecules may also present in the interstellar medium. Table 1.1 gives the list of molecules detected so far in the interstellar medium. It is expected that many larger molecules to be present in the interstellar gas and on dust grains in such environment.
Table 1.1 List of interstellar molecules detected so far.

<table>
<thead>
<tr>
<th>List of interstellar molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diatomic</strong></td>
</tr>
<tr>
<td>H₂, SiO, CS, SO, SiS, NS, C₂, NO, HCl, NaCl, AlCl, KCl, AlF, PF, SiC, CP, NH, SiN, SO⁺, CO⁺, HF, LiF, SH, FeO, N₂, CFO₂, CH, CH⁺, CO, CN, CH⁺, and OH</td>
</tr>
<tr>
<td><strong>Triatomic</strong></td>
</tr>
<tr>
<td>H₂O, HCO⁺, HCN, OCS, H₂S, HNC, N₂H⁺, C₂P, SO₂, HDO, HCO, HNO, OCN⁻, HCS⁺, HOC⁺, c-SiC₂, MgNC, C₂S, C₃, CO₂, CH₂, C₂O, NH₂, NaCN, N₂O, MgCN, H₃⁺, SiCN, AlNC, AlOH, KCN, HCP SiNC</td>
</tr>
<tr>
<td><strong>Four atoms</strong></td>
</tr>
<tr>
<td>NH₃, H₂CO, HNCO, H₂CS, C₃N, HNCS, HSCN, HOCN, HCN, HCCN, HOCO⁺, HCNH⁺, H₃O⁺, C₂S, C₃O, c-C₃H, C₂H₂, HC₂N, H₂CN, H₂CN, SiC₃, CH₃ and HOOH</td>
</tr>
<tr>
<td><strong>Five atoms</strong></td>
</tr>
<tr>
<td>HC₃N, HCOOH, CH₂NH, NH₂CN, H₂C₂O, C₄H, SiH₄, c-C₃H₂, CH₂CN, C₅, SiC₄, l-C₃H₂, CH₄, HC₂NC, HNC₃, H₂COH⁺ and C₄H⁺</td>
</tr>
<tr>
<td><strong>Six atoms</strong></td>
</tr>
<tr>
<td>CH₃OH, CH₃CN, NH₂HCO, C₂H₄, C₅H, CH₂CHO, HC₃NH⁺, C₃N, H₂COH⁺, C₄H⁺, C₄H₂, HC₄N, c-C₂H₃O, CH₂CNH</td>
</tr>
<tr>
<td><strong>Seven atoms</strong></td>
</tr>
<tr>
<td>CH₃NH₂, CH₃CHCN, CH₃C₂H, HC₃N, CH₃CHO, C₄H, c-C₃H₄O, CH₂CHOH, and C₅H⁺</td>
</tr>
<tr>
<td><strong>Eight atoms</strong></td>
</tr>
<tr>
<td>CH₃C₃N, C₇H, CH₃COOH, CH₂OHCHO, C₆H₂, CH₂CHCHO, CH₂CCHCN and NH₂CH₂CN</td>
</tr>
<tr>
<td><strong>Nine atoms</strong></td>
</tr>
<tr>
<td>CH₃OCH₃, C₂H₂OH, CH₃CH₂CN, HC₇N, CH₃C₄H, C₈H and CH₃CONH₂, CH₃CHCH₂</td>
</tr>
<tr>
<td><strong>Ten atoms</strong></td>
</tr>
<tr>
<td>(CH₃)₂CO, NH₂CH₂COOH, CH₃CH₂CHO and CH₃C₃N</td>
</tr>
<tr>
<td><strong>11 atoms</strong></td>
</tr>
<tr>
<td>HCN, HOCHC₂H₂OH, C₂H₅COOH and CH₃C₆H</td>
</tr>
<tr>
<td><strong>12 atoms</strong></td>
</tr>
<tr>
<td>C₄H₆ and CO(CH₂OH)₂, CH₃CH₂CH₂CN</td>
</tr>
<tr>
<td><strong>13 atoms</strong></td>
</tr>
<tr>
<td>HC₁₁N</td>
</tr>
<tr>
<td><strong>60 and 70 atoms</strong></td>
</tr>
<tr>
<td>C₆₀ (Buckminsterfullerene), C₇₀(Fullerene)</td>
</tr>
<tr>
<td><strong>Deuterated molecules</strong></td>
</tr>
<tr>
<td>HD, H₂D⁺, HD₂⁺, HDO, D₂O DCN DCO DNC N₂D⁺ NH₂D, NHD₂, ND₃ HDOCO, D₂CO,CH₂DCCH, CH₃CCD</td>
</tr>
<tr>
<td><strong>Unconfirmed</strong></td>
</tr>
<tr>
<td>H₂NH₂CCOOH, CO(CH₂OH)₂, C₂H₅OCH₃, C₁₀H₈⁺, SiH, PH₃, C₂₄C₆₀⁺</td>
</tr>
</tbody>
</table>
Among the large molecules suspected in diffuse clouds are the carbon chains, diamonds, amorphous carbon (hydrogenated and bare), and complex kerogen-type aromatic networks.

The IR spectrum is where the emission and absorption lines of virtually all molecules as well as numerous atoms and ions lie. IR spectra are providing stunning information about the role of interstellar molecules in the formation of stars, planets and possibly even life. IR spectral data have shown that complex organic molecules can form rapidly in the environment around old stars and are abundant in many regions of space. These elements and molecules will likely find their way into new stars and planets as they form molecular cloud. The interstellar medium is composed of multiple phases, distinguished by whether matter is ionic, atomic, or molecular, and the temperature and density of the matter. Figure 1.1 displays the chemical structure of some carbon compounds that are likely present in space. The thermal pressures of these phases are in rough equilibrium with one another. Magnetic fields and turbulent motions also provide pressure in the ISM, and are typically more important dynamically than the thermal pressure.

Molecules are found in a wide variety of astronomical objects including interstellar clouds, planetary nebulae, circumstellar envelopes, stellar atmosphere and comets. Examples include small molecules such as HF, CH$_4$, H$_2$O as well as large molecules such as C$_{60}$, polycyclic aromatic hydrocarbons (PAHs) etc. These molecules play an active role in the energy balance of clouds. Interstellar space is a unique cosmic laboratory in which chemical processes can occur that are not normally found on terrestrial laboratory. To understand physical changes in molecular clouds, such as fragmentation and collapse leading to star formation, it is not sufficient to merely study the physical properties of a cloud; it is also necessary to understand the cloud's chemistry.
Figure 1.1 Some of the various forms of carbon that are likely present in gaseous and solid state in the ISM and in solar system material.
The ISM contains about 10% of the mass of our galaxy and consists of gas (99%) and submicromter sized grain particles (1%) with averaged number densities of 1 H atom cm$^{-3}$ and 10$^{-11}$ grains cm$^{-3}$, respectively [21-24]. These data translate to pressures of about 10$^{-18}$ mbar at 10 K, which is beyond any ultrahigh vacuum achieved in terrestrial laboratories so far. The chemical composition of the ISM is dominated by neutral hydrogen (93.38%) and helium (6.49%), whereas biogenic elements oxygen, carbon, and nitrogen contribute 0.11% (O: C: N=7:3:1) [25]. The third-row elements neon, silicon, magnesium, and sulfur are less copious (0.002%) and have relative abundances of 8:3:3:2; all remaining elements furnish only 0.02%. This elementary classification is well-reflected in the molecular composition of the ISM. Molecules, radicals, and ions are ubiquitous in extraterrestrial environments and have been detected in extraordinary diversity ranging from small molecules such as hydrogen (H$_2$) to astrobiologically important species such as the simplest sugar glycolaldehyde (HOCH$_2$CHO) and possibly the amino acid glycine (H$_2$NCH$_2$COOH).

Table 1.1 lists all species identified in the interstellar medium so far, many of them thermally unstable and extremely reactive in terrestrial laboratories [26]. The majority of these molecules were detected with radio telescopes by observing their rotational transitions in emission; to a minor extent, infrared (IR), visible (VIS), and ultraviolet (UV) astronomy fostered their identification. Diatomic molecules with second and third-row elements are particularly prevalent; in particular, carbon (C$_2$, CN, CO, CS) and silicon (SiC, SiN, SiO, SiS) bearing species have to be named. CP and PN are the only phosphorus-containing molecules identified so far; NO, NS, and SO represent the sole extraterrestrial radicals carrying atoms of the fifth and sixth period.
## 1.1.2 Phases of Interstellar medium

<table>
<thead>
<tr>
<th>ISM Component</th>
<th>Common designation</th>
<th>Temp (K)</th>
<th>Density (cm$^3$)</th>
<th>State of hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot ionized medium</td>
<td>Coronal gas</td>
<td>10$^6$</td>
<td>0.003</td>
<td>H$^+$</td>
</tr>
<tr>
<td>Warm ionized medium</td>
<td>diffuse ionized gas</td>
<td>10$^4$</td>
<td>&gt;10</td>
<td>H$^+$</td>
</tr>
<tr>
<td>Warm neutral medium</td>
<td>Inter cloud HI</td>
<td>10$^4$</td>
<td>0.1</td>
<td>H</td>
</tr>
<tr>
<td>Atomic Cold Neutral med</td>
<td>Diffuse clouds</td>
<td>100</td>
<td>10-100</td>
<td>H+H$_2$</td>
</tr>
<tr>
<td>Molecular Cold Neutral med</td>
<td>Molecular clouds</td>
<td>&lt; 50</td>
<td>10$^3$-10$^5$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>(Dense cores)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot molecular core</td>
<td>Protostellar cores</td>
<td>100-300</td>
<td>&gt;10$^6$</td>
<td>H$_2$</td>
</tr>
</tbody>
</table>
1.2 Extraterrestrial Environments

1.2.1 Diffuse clouds

Diffuse clouds typically have densities of the order of 100–500 cm$^{-3}$, and temperatures that range from 30–100 K [27]. They contain up to a few thousand solar masses. ζ Oph (Ophiuchi), and ξ Per (Persei) represent typical examples of diffuse clouds. These structures are called ‘diffuse’ because the interstellar ultraviolet radiations easily penetrate. UV photons play a significant role in the chemistry of diffuse clouds as they ensure photodissociation of molecules. Diffuse molecular clouds can be observed in sightlines with a wide range of visual extinction, or total hydrogen column density. The lower limit of $N_{\text{H}}$ where molecular hydrogen begins to shield itself from interstellar radiation is a few times $10^{20}$ cm$^{-2}$, or $A_V$~0.2. The presence of abundant H$_2$ in diffuse molecular clouds permits chemistry to begin in earnest. Molecules are observed in these clouds in absorption in the UV/visible (e.g., CO, CH, CN, C$_2$, C$_3$), in the infrared (CO, H$_2^+$), and at millimeter wavelengths (e.g., HCO$^+$, OH, C$_2$H). The triatomic species identified in the diffuse clouds are the HCN, HNC, C$_2$H, and HCO$^+$ [28]. Recently, C$_3$ has been observed towards ζ Oph (Ophiuchi), and ξ Per (Persei) [29]. Although large molecules are also thought to be present in diffuse clouds as PAH-like structures, the latter are not formed in situ but are injected into the interstellar medium from winds of dying, carbon-rich stars or indirectly via erosion of carbonaceous solid-state matter.

1.2.2 Translucent clouds

The clouds with the sufficient protection from the interstellar radiations which are suggested to form bridge between diffuse and dense structures and carbon begins to transition from ionized atomic form in to neutral atomic (C) or molecular (CO) form [30]. These clouds are defined by moderate number densities of $10^2$–$10^3$ atoms/cm$^3$ and relatively low kinetic
temperatures of 50-100 K compared to diffuse structures [31]. The clouds are called “translucent”, because they are thin enough that optical absorption line observations can be performed, provided that there is a bright background star located fortuituitously behind the cloud. These clouds are interstellar clouds with the total visual extinctions $A_V^{\text{tot}} \approx 2-5$ mag. These clouds provide the important link between the classical diffuse clouds, such as ζ Oph ($A_V^{\text{tot}} \approx 1$ mag), and the classical dense clouds, such as TMC-1 ($A_V^{\text{tot}} \geq 10$ mag). They can be either small isolated clouds by themselves, or represent the outer parts of dense, dark clouds. Due to the penetration of radiation in these clouds the photoprocesses play an important role in the chemistry.

In steady state, translucent cloud material must be surrounded by diffuse molecular cloud material, and because of the insufficient shielding of radiation it is not expected to be present for sightlines with $A_V$ less than about unity. Thus, sightlines with $A_V > 1$ are candidates for hosting translucent clouds. However, a high value of $A_V$ alone does not imply the presence of translucent material, as it could represent simply a pile-up of diffuse molecular clouds along the line of sight (e.g., Cygnus OB2 12). Once again, it is the local parameters that define this cloud type. Such high extinction sightlines are still observable with optical absorption line techniques, and can be observed at millimeter wavelengths in both absorption and emission.

In the UV increasing extinction makes observations very difficult. It has not yet been possible to observe (at UV wavelengths) sightlines that are clearly dominated by translucent clouds. The molecular composition of translucent clouds such as Cyg OB2 No.12, HD 29647, HD 147889, and Cas A is well-reflected by small diatomics $\text{H}_2$, CH, $\text{CH}^+$, CS, CN, $\text{C}_2$, OH, and CO together with larger species HCN, HNC, $\text{C}_2\text{H}$, HCO$^+$, and $\text{H}_2^-$, CO. The tricarbon molecule $\text{C}_3$ was tentatively identified toward HD 147889 [32]. The high resolution optical spectroscopy with the mm-wave observations has been used to study CH and CN in translucent clouds [33-
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35]. Further, the abundance of interstellar CH\textsubscript{2} is significantly enhanced in a cold translucent cloud compared to low-density regions. So far, no signatures of early stars, so-called pre main sequence stars, have been found in these environments.

1.2.3 Dense molecular clouds

Dense clouds are formed from low-density clouds and characterized by typical number densities of 10\textsuperscript{2}-10\textsuperscript{4} atoms cm\textsuperscript{-3}. Due to their low kinetic gas temperatures of only 10-15 K [36], these dense clouds are also referred to as cold clouds. There is very rich literature on dense cloud chemistry, both from observational and theoretical perspectives. In fact, the earliest chemical models were focused on these environments [37-39]. Most of the interstellar molecules were detected through observational microwave rotational transitions in such clouds.

In diffuse and translucent clouds the formation of molecules is dominated by photochemistry and photoionization whereas the interstellar dust particles-submicrometer-sized silicate and carbonaceous based grain nuclei inside dense clouds shield complex molecules from the destructive short wavelength radiation field. The dense clouds are also known as dark clouds because they often appear on images as black patches. The chemistry of the Taurus Molecular Cloud 1 (TMC-1) has been studied extensively. Its composition is dominated by molecular hydrogen (H\textsubscript{2}); only trace amounts of atomic energy of about 1 atom/cm\textsuperscript{3} exist. The carbon molecules C(\textsuperscript{3}\textit{P})\textsubscript{j} detected towards the molecular clouds Orion A [40], TMC-1 [41-42], L134N, and IC5146 [43] with ratios of 0.05-0.2 compared to carbon monoxide (CO). The second most abundant molecule with fractional abundances \( f \) of 8\times10\textsuperscript{-5} compared to hydrogen, followed by hydroxyl radical (OH; \( f=10\textsuperscript{-7} \)). Apart from this, dense clouds contain the further variety of hydrogen deficient carbon chains such as cyanopolyynes, cummulene carbenes, methylated molecules.
1.2.4 Star forming regions, Young stellar Objects, and Hot Molecular Cores

Dense clouds are in a precollapse phase and contain the basic ingredients to form massive and low mass stars [44]. The theory of star formation requires that the core of a quiescent molecular cloud collapse under its own gravity. These cores have masses of typically $10^4$ solar masses and are denser than the outer regions of the molecular clouds. The core collapse due to the condensation of gas phase species onto the cold mantles of grains inside dense clouds. This aggregation continues until the force of gravity overcomes the resistance provided by the gas and magnetic pressure for about $10^5$ years. Once clump has broken free from the other parts of the cloud core becomes 10-50 solar mass and has its own gravity. The infrared sources are indicative as the young stellar objects (YSOs), it might take up to $10^7$ years. The density increases from $10^4$ atoms/cm$^3$ in cold clouds up to $10^9$ atoms/cm$^3$ in the circumstellar disk still surrounding the young stellar object. After the new star has formed, its radiation heats the surrounding matter and molecules sublime from the remaining icy grain mantles back in to the gas phase. This early phase of the life of the star is called 'T Tauri' phase [45]. Tauri stars such as the Trapezium cluster in the Orion Nebula are always embedded in the clouds of gas from which they were born and can lose up to one half of its mass before becoming the main sequence star.

The energetic environment surrounding a protostar is called the hot molecular core (HMC) containing several tens of solar masses. HMCs are found in regions of massive star formation such as ρ Ophiuchi complex with 300 young stellar objects [46-47]. The molecular inventory of hot cores is dominated by saturated molecules (CH$_3$OH, C$_2$H$_5$OH, CH$_3$OCH$_3$, C$_2$H$_5$CN, CH$_3$COCH$_3$, CH$_4$, H$_2$O, and NH$_3$) [48-52] and, also contains complex molecules such as acetaldehyde (CH$_3$CHO), formic acid (HCOOH), acetic acid (CH$_3$COOH), glycolaldehyde (HOCH$_2$CHO), carbon dioxide (CO$_2$) and possibly glycine (NH$_2$CH$_2$COOH) [53-58]. The identification of gaseous hydrogen cyanide (HCN), acetylene (C$_2$H$_2$), carbon dioxide (CO$_2$), and
methane (CH₄) in the infrared regime employing the Infrared Space Observatory (ISO) [59-60] clearly demonstrates the unique power of this technique [61]. Most important, the molecular composition of ices can be unraveled once the YSO forms in the infrared regime utilizing the ISO; recall that molecules frozen on grains show no rotational spectrum and hence cannot be probed via radio telescopes. W33A and NGC7538:IRS9 denote the best studied protostellar and high-mass young stellar objects, respectively [62-65]. So far, only eight simple molecules have been identified unambiguously in ices toward protostellar and YSOs [64,65-67]. In cold outer envelopes of YSO, where typical temperatures of 10-20 K reside, ices contain a significant fraction of non polar carbon monoxide (CO) and carbon dioxide (CO₂) (apolar ices). As we move closer to the inner warm envelope, the temperature rises to 20-90 K and molecules such as methane (CH₄) and carbon monoxide (CO) are too volatile to exist in ices; therefore, polar ices of methanol and water are very abundant.

1.2.5 Circumstellar envelopes

Our sun is the best example for the main sequence stars. Once contraction of a protostar is finished the star evolves only slowly burning hydrogen into helium [68-69]. Due to this structural change of the star takes place, the radius and luminosity increases steadily. Hydrogen is now fused into helium and to meta-stable ⁸Be to ¹²C and ¹⁶O with increasing densities and temperature in the core continue until the most stable ⁵⁶Fe formed [70-71]. During the helium fusion, the star expands its shell. Under certain circumstances, a red giant is formed, where the carbon-oxygen core is surrounded by a helium-burning shell, a helium buffer layer, and a hydrogen-burning shell. These stars are becoming increasingly unstable and leave the main sequence to become an asymptotic giant branch (AGB) star [72-73]. These late-type AGB stars lose significant amounts of their mass once they left the main sequence and are surrounded by expanding matter, which is often called the circumstellar shell or the circumstellar envelope.
Circumstellar envelopes consist of gas phase molecules and submicrometer-sized grain particles.

The carbon star IRC+10216 is the brightest carbon-rich object in the infrared sky [77]. It has an extended envelope in which more than 60 species have been observed. The molecules such as carbon cluster C\textsubscript{n} (n=2, 3, 5), hydrogen deficient carbon chains C\textsubscript{n}H (n=2-8), the radicals and cummulenes C\textsubscript{n}H\textsubscript{2} have been detected so far in the circumstellar envelopes. No ion has been identified so far in any CSE.

1.2.6 Planetary nebula

Planetary nebulae (PNe) are the descendants from AGB stars [78-79]. This phase is characterized by a very efficient mass loss of the dying star. The reshaping of the circumstellar envelope which is initially formed by material expelled during the AGB phase over 10\textsuperscript{6} years is dictated by high-velocity winds from the central star. An increasing photon flux in the UV range accompanies this process as the remaining hydrogen shell burns up by nuclear fusion. While the ejecta move away from the central star, the enhanced photon emission will gradually photodissociate and ionize the circumstellar shell which at the same time is growing as more material is swept up [80-81]. These fast stellar winds and photon field sweep the circumstellar envelope into the ring-shaped, planetary-like structure we see in planetary nebulae.

Planetary nebulae disclose a unique chemistry. The molecular inventory is imposed by photodissociation and -ionization processes leading to detectable amounts of CH\textsuperscript{+}, CO, CO\textsuperscript{+}, HCO\textsuperscript{+}, CH, OH, H\textsubscript{2}, and possibly H\textsubscript{2}O as observed around NGC 7027. The temperature decreases from 3000 K in regions close to the star down to 200 K in the outer edges of the shell. A temperature of 200 K is interpreted as an averaged temperature of the shocked gas behind the shock front of the out-flowing gas [82]. The planetary nebula CRL 618 presents a particular wealth of complex hydrocarbons, as diacetylene (C\textsubscript{4}H\textsubscript{2}), triacetylene (C\textsubscript{6}H\textsubscript{2}), and benzene (C\textsubscript{6}H\textsubscript{6})
have been identified for the very first time outside our solar system [83-84]. This might be attributed to the fact that CRL 618 has higher fractional abundances of ethinyl radicals (C$_2$H) due to photodissociation of acetylene, which are thought to be key ingredients for the formation of polyacetylenes and benzene.

1.3 Molecules in Comets

Comets are difficult tools for the comprehension of the formation of the Solar system. They were formed 4.5 billion years ago, at the same time as the Sun, in the outer parts of the Primitive Solar Nebula - probably at the distance of Uranus and Neptune, and are, with the asteroids, the direct descendants of the small bodies whose agglomeration gave rise to planets. Relegated to the borders of the Solar system in a very cold environment, the cometary cores evolved very little since their formation. The study of their chemical composition thus gives us access to the chemical composition of the outer parts of the Solar Nebula such as it was 4.5 billion years ago. It is essential to establish whether this composition reflects the composition of the interstellar protosolar cloud or whether it reveals the chemistry which would have taken place in the Primitive Nebula, like that invoked in the inner parts to explain, for example, the composition of the meteorites.

The modern view of the composition of comets began with the "dirty Snowball" model [85-86]. This model proposed that cometary nuclei were predominantly made of water ice with an admixture of small rock particles. An evaluation of the most important issues in cometary astronomy during the last 4 decades is reviewed by Festou et al (1993 a,b) [87-88]. Today this model has been refined, and the nuclei of comets are thought to be composed of ice, rock, and large organic entities (commonly referred to as CHON particles), since these nuclei are composed primarily of carbon, hydrogen, oxygen, and nitrogen [89-90]. The chemical
composition of a comet nucleus has been recently constrained by Greenberg et al. [91], who proposes that 26% of the mass is incorporated in silicates, 23% in refractory material, 9% in small carbonaceous molecules, and ~30% in H$_2$O ice (with small contributions of CO, CO$_2$, CH$_3$OH, and other simple molecules). Comets, if coma composition reflects nucleus composition, are made of roughly equal masses of dust and ices (within a factor of 10, depending on the comet). The PUMA data allowed the tentative, but not unambiguous, identification of many distinct organic molecules emanating from the carbonaceous dust [82]. The organic inventory has been summarized by Kissel et al 1987; Cottin et al 1999; and Fomenkova 1999 [92, 93-94].

The majority of grains contain hetero polymers and different mixtures of carbon phases and compounds including alcohols, aldehydes, ketones, and acids. Other organic species identified include PAHs, highly branched aliphatic hydrocarbons, and unsaturated hydrocarbon chains, including alkenes, dienes, various large nitriles, and analogous species with imino and amino end-groups. Several nitrogen hetero cycles have also been identified; these include pyrrole, pyrroline, pyridine, pyrimidine, imidazole, and perhaps purine and adenine. The nitrogen bearing molecules in comets that crashed into Earth millions of years ago may have provided a sort of "pre-biotic jump start" to form the complex molecules that eventually led to life. All DNA bases and amino acids have atomic nitrogen in them. The nitrogen in its simplest form, the atomic form, is much more reactive and can more easily form complex prebiotic organics in space". These complex organics were incorporated into comets and were provided to the Earth.

1.4 Molecules in Meteorite

An object from space that hits the ground are meteorites. A meteorite is a natural object originating in outer space that survives impact with the Earth's surface. Meteorites can be big or
small. Most meteorites derive from small astronomical objects called meteoroids, but they are also sometimes produced by impacts of asteroids. When a meteoroid enters the atmosphere friction causes the body to heat up and emit light, thus forming a fireball, also known as a meteor or shooting/falling star. The term bolide refers to either an extraterrestrial body that collides with the Earth, or to an exceptionally bright, fireball-like meteor regardless of whether it ultimately impacts the surface. Meteorite falls have been observed throughout history with even ancient reports of stones falling from sky.

Through the use of laser desorption mass spectrometry (LDMS), PAHs, kerogen-like material, fullerenes, and fulleranes have been detected in meteorites [95]. The presence of carbon onions in acid residues of the Allende meteorite suggested that higher fullerenes or nanotubes may be present in meteorites. This has been recently confirmed by LDMS measurements of the higher fullerenes (C\textsubscript{100} to C\textsubscript{400}) in the Allende meteorite [96]. Many classes of organic molecules have been discovered in the Murchison carbonaceous chondrite [97]. One explanation for the origin of these compounds is that they were formed from organic matter residing on interstellar dust grains that survived entry into the region of the protosolar nebula where comets and other icy bodies formed and that ultimately became incorporated into the parent bodies of carbonaceous meteorites [98].

1.5 Interstellar ices

Icy grain mantles which cover dust particles in dense cold clouds have been revisited with the Infrared Space Observatory (ISO). ISO data were compiled to establish an inventory of interstellar ice species and measure their abundances in various interstellar environments [99]. After ISO, the Spitzer Space telescope (operating at lower resolution) and ground based observations have provided outstanding data in the main interstellar ice species. Icy grain
mantles are formed in cold, dense environments by efficient accretion of atoms and molecules from the interstellar gas. In Figure 1.2 we display the spectrum toward the massive protostar W33A [64,66].

Diffusion of small species allows reaction pathways on grain surface, leading to the formation of new molecules. H$_2$O is the major component of interstellar grains, but many features observed in the near and mid-infrared are of organic nature. ISO-SWS and ground based data show that the major organic species in the interstellar ices are CO, CO$_2$, and CH$_3$OH [64, 101-104]. The stretching mode of CO is widely observed toward high and low-mass protostars as well as in the quiescent medium [105-107]. The existence of hydrogen-rich ices (polar ices) and hydrogen-poor ices (apolar ices) has been inferred from the CO band profile with the help of laboratory spectra [108-109]. Polar ices, dominated by H$_2$O ice, in general evaporate around 90 K under astrophysical conditions and can therefore survive in higher-temperature regions close to the star [110]. Apolar ices, composed of molecules with high volatility (evaporation temperatures of <20 K) such as CO, O$_2$, and N$_2$ [111] can only be formed and survive in cold, dense regions. During their passage through different cloud environments, grain mantles may accrete layers of polar and apolar ice. Pure CO$_2$ ice layers were confirmed that indicate thermal processing actually described as “distillation” after CO has evaporated in cloud regions that exceeds 20 K. A c2d Spitzer survey of CH$_4$ ice showed that 25 out of 52 targets displayed a feature at 7.7 μm attributed to CH$_4$. Ice abundances of CH$_4$ seem to correlate with H$_2$O and CO$_2$ but not with CO and CH$_3$OH. Photodesorption of pure ices seem to be much more efficient according to laboratory results than previously assumed [112].

1.5.1 Origin of the ices

Ices are formed in translucent clouds (clouds where H$_2$ dominates over HI and carbon is converted from C II to C I to CO), in regions that are shielded from UV radiation. At extinctions...
Figure 1.2 the ISO-SWS spectrum toward the protostar W33A.
Av≥3 mag, species from the gas phase accrete onto dust grains and initiate the formation of ices [113-114]. Therefore, the chemical content of the gas phase at this extinction is crucial to determine which species accrete onto dust and what the composition of ices is. Gas phase chemistry of dense cores [115] shows that a high D/H ratio can be reached because of the inclusion of ions such as HD$_2^+$ and D$_3^+$ in gas phase chemistry, which produce deuterons upon dissociative recombination. This gas phase model is able to reproduce a high deuteration of formaldehyde in dense cores. Also, the degree of deuteration of molecular ions are sensitive to the ortho: para H$_2$ ratio and hence to the chemical and thermal history of the precursor molecular cloud [116].

So the molecules are found in different regions of the interstellar medium. They are found as neutral, ions or deuterated molecules depending upon the physical conditions of the ISM. In order to detect many more molecules in space, their thorough spectroscopic characterization is essential. Quantum chemical methods helps in this task. Following are the objectives of the present thesis.

i) To predict the IR and electronic absorption spectra of astrobiological relevant cosmic molecules using quantum chemical methods.

ii) To perform theoretical study of possible conformers/isomers of cosmic molecules in neutral, ionic and protonated forms.

iii) To study the effect of ionization on IR and electronic absorption spectra of these molecules in gas phase.

iv) To predict IR and electronic absorption spectra of these molecules in astrophysical ices.
v) To suggest lines especially good to detect these molecules in different astrophysical environment.

vi) To study the rotational and centrifugal distortion constants for these molecules, which are useful for the calculating rotational spectra.

vii) To study these molecules in excited state to get excitation energy, electronic transitions, transition symmetry and oscillator strength, which are helpful to derive cosmic abundance.
References

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2.1 Introduction

Molecular structure can be calculated using molecular mechanics or quantum mechanics. In quantum chemistry we are interested in the physical properties of many-particle systems like atoms, molecules and solids. These systems consist of electrons, protons and neutrons which are all spin-1/2 fermions. The protons and neutrons together form the nuclei of these systems. A complete (nonrelativistic) description of the physics of these many-particle systems is governed by the quantum-mechanical wave function $\Psi(x_1,x_2,\ldots,x_n,t)$, where $n$ is the number of particles in the system and the coordinates $x_i$ consist of the space-coordinate as well as the spin-coordinate. This $n$-particle wave function can be obtained by solving the Schrödinger equation $H\Psi = E\Psi$. Here $H$ is the Hamiltonian operator for a system consisting of nuclei and electrons, $\Psi$ is the wavefunction known as the eigenfunction using which we can get the probability of finding a particle and $E$ is the energy of the system known as the eigenvalue [1-11]. Its expectation value describes the total energy of a system.

The Hamiltonian operator is a sum of the kinetic and potential energy terms of the system.

$$H = T + V$$

The Hamiltonian operator for a system with $N$ electrons and $M$ nuclei is

$$H = \sum_{i=1}^{N} \frac{1}{2m_i} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A \frac{1}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

(2.1)

In the above equation, $M_A$ is the ratio of the mass of nucleus $A$ to the mass of the electron, $Z_A$ is the atomic number of nucleus $A$. The Laplacian operators involve differentiation with respect to the coordinates of the $i^{th}$ electron and the $A^{th}$ nucleus.

The first term in Eq.(2.1) is the operator for the kinetic energy of the electrons; the second term is the operator for the kinetic energy of the nuclei; the third term represents the Coulomb attraction between electrons and nuclei; the fourth and fifth terms represent the repulsion between electrons and between nuclei, respectively.