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Rotational Spectroscopy and Interstellar Molecules

The fact that life exists on Earth is no secret. However, understanding the origin of life, its evolution, and the future of life on Earth remain interesting issues to be addressed. That the regions between stars contain by far the largest reservoir of chemically-bonded matter in nature obviously demonstrates the importance of chemistry in the interstellar space. The unique detection of over 200 different interstellar molecules largely via their rotational spectra has laid to rest the popular perception that the vastness of space is an empty vacuum dotted with stars, planets, black holes, and other celestial formations. Astrochemistry comprises observations, theory and experiments aimed at understanding the formation of molecules and matter in the Universe i.e. the formation of Universe. Molecules with a well-understood chemistry in the interstellar medium can be used as probes of astrophysical phenomena. Astrophysics covers a wide range of issues ranging from the study of our solar system to the study of the interstellar medium (ISM). The interstellar molecules serve as the most powerful tool for probing deep into the interior of molecular clouds. Interstellar clouds are significant because it is from them that new stars, and consequently new planets, are formed. Understanding how the simple molecules present on the early earth may have given rise to the complex systems and processes of the present-day biology is widely regarded as one of the chemistry's great unsolved questions. The biologically important molecules so far detected in the ISM serve as significant tools towards addressing the chemical origin of life.

The ISM is simply all the stuff between stars. It is the matter that exists in the space between the stars. This matter includes gas in ionic, atomic and molecular form, dust and cosmic rays. It fills the interstellar space and blends smoothly into the surrounding intergalactic space.

The ISM is composed of 99% gas and 1% dust. Of the gas in the ISM, 89% of atoms are H and 9% are He, with 2% of atoms being elements heavier than H and He, which are called 'metals' in astronomical parlance. Dust consists preferentially of particles of heavy elements. The ISM plays a crucial role in astrophysics precisely because of its intermediate role between stellar and galactic scales. It is important observationally, as it enables us, for example to observe the dynamics of the gas, such as rotation curves, because spectroscopic emission lines from the gas are prominent.

The basic approach in probing molecules in the ISM is to use spectroscopy to create a database of "fingerprints" from known molecules in the laboratory and then compare the stored readings to those captured with a spectrometer

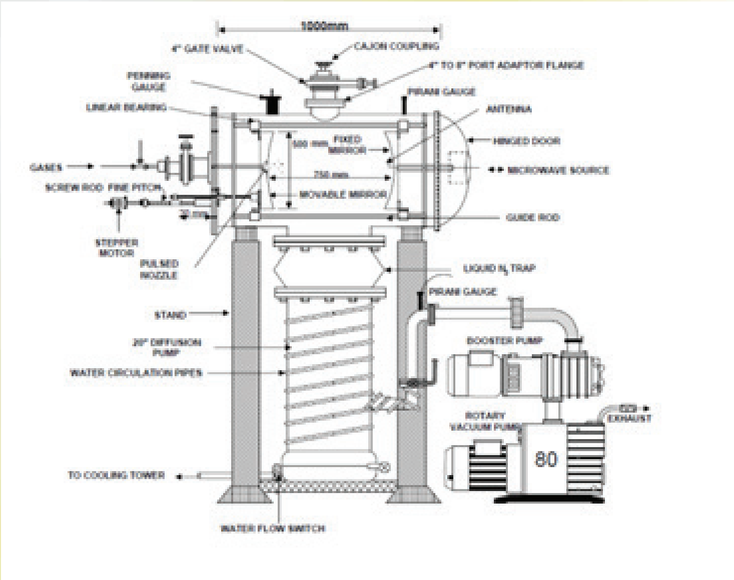

Figure 1: Mechanical design of the PN-FTMW spectrometer (Reproduced with permission from Reference 1).

connected to a telescope. From Boltzmann distribution and the low temperature of a molecular cloud, it follows that majority of the molecules in the clouds are in their vibrational and electronic ground states and not "excited states".However, rotationally excited states are populated at 10–100 K and decay by spontaneous emission. Therefore, the spectrum of the cloud in the radiofrequency and microwave regions consists of sharp lines corresponding to rotational transitions; this makes rotational spectroscopy an indispensible tool in the chemical examination of the interstellar space. Infrared emissions can be observed if molecules are occasionally excited by high energy photons emitted by hot stars in the vicinity of the cloud. This is a rare event.

Rotational Spectroscopy:

Of all the tools that may be at the disposal of an astronomer, spectroscopy which is simply the study of the interaction between matter and light (electromagnetic radiation from radiofrequency to gamma rays), has become an indispensable partner. This is because with spectroscopy, astronomers can study the universe, determine the chemical compositions, physical properties, and radial velocities of astronomical sources. The dark matter content of galaxies, the masses of two stars in orbit about each other, the mass of a cluster of galaxies, the rate of expansion of the Universe have all been measured with the help of spectroscopy. Also, it makes it possible for the astronomer to determine the physical conditions in distant stars and nebulae, including the chemical composition and temperatures, by quantitative analysis of the strengths of spectral features, thus constraining models of chemical enrichment in galaxies and the evolution of the universe.

That each molecule has a different rotational spectrum which is its distinct "fingerprint" or "signature" is the

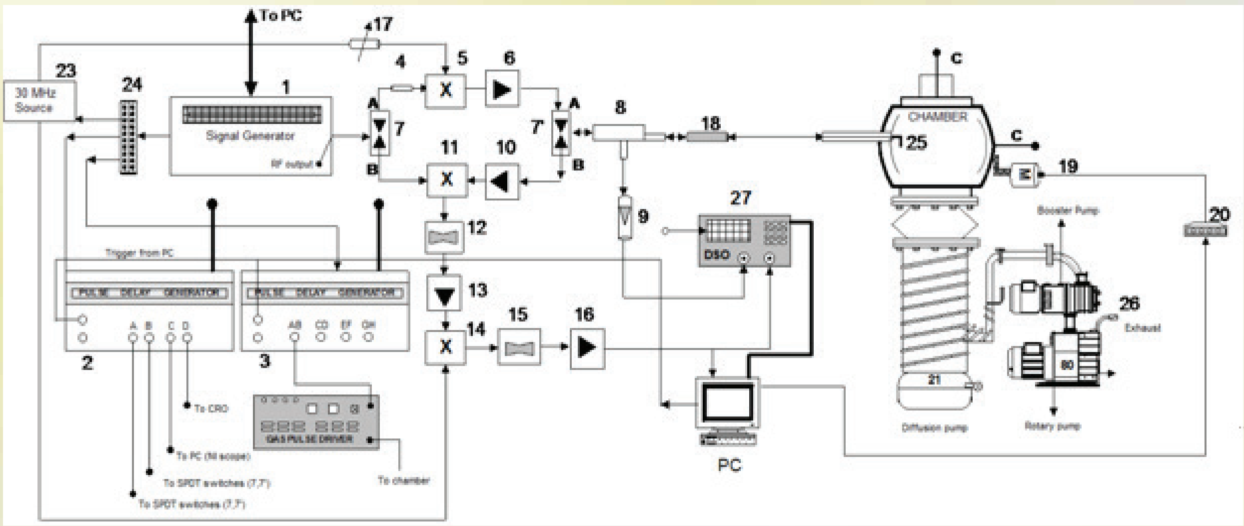

Figure 2: Electrical design of the PN-FTMW spectrometer (Reproduced with permission from Reference 1).1, Signal generator (Agilent, MXG signal generator, N5183A); 2, Delay generator (BNC-555); 3,Delay generator (SRS DG645); 4, Microwave attenuator (HP, 8493C, 3dB); 5, SSB mixer (Miteq,SMO-226LC1A); 6, Medium power amplifier (Miteq, JS3-02002600-5-7A); 7, MW SPDTswitch (Sierra Microwave, 0.5-26.5 SFD0526-000); 8, Direction coupler (Narda, 1.7-26.5–4227–16);9, Diode detector (Narda, 0.01-26.5–4507); 10, Low noise amplifier (Miteq, JS4-02002600-3-5P);11, Image rejection mixer (Miteq, IRO-0226LC1A); 12, Band pass filter (Mini Circuits, BBP-30); 13,RF amplifier (Mini Circuits, ZFL-500LN); 14, RF mixer (Mini Circuits, ZAD-1); 15, Low pass filter(Mini Circuits, BLP-5); 16, RF amplifier (HD communication corp., HD 17153BB); 17, Attenuator (Mini Circuits, ZAFT-51020); 18, Blocking capacitor (HP, 11742A); 19, Stepper motor; 20, Motordriver; 21, Diffusion pump and 22, Rotary pump; 23, 30MHz function generator (Stanford ResearchSystem, DS345); 24, Distribution amplifier (Stanford Research System, FS710); 25, Antenna; 26,Exhaust; 27, Digital storage oscilloscope (Tektronix TDS 2022).

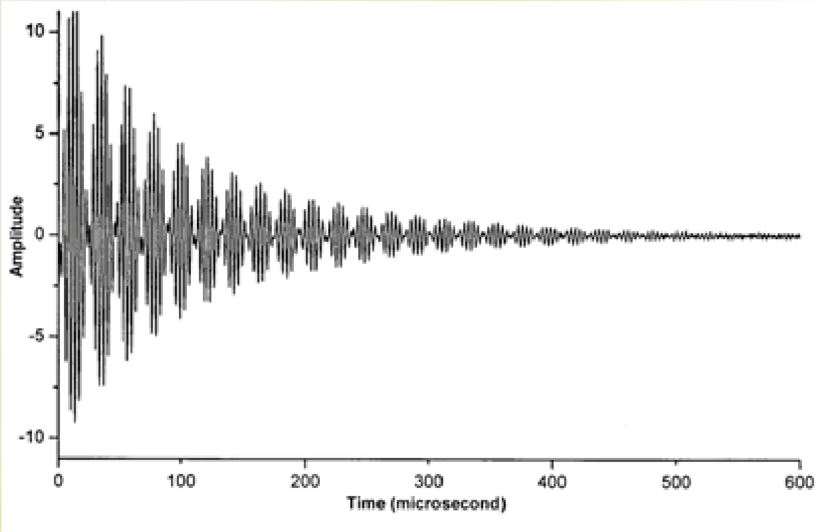

Figure 3: FID from the OCS polarized at 12162.7 MHz with a microwave pulse of 0.5μs. Backing pressure was 1 atm. 3% OCS in Argon was used (Reproduced with permission from Reference 1).

unique characteristic which makes it possible for molecules to be studied by spectroscopy. This characteristic has been found to be very useful in identification of specific molecules not only in the laboratory sample, but also in ISM. Hence, rotational spectroscopy plays a fundamental role in investigations of interstellar molecules and the study of how stars and the planetary systems are born. Precise transition frequencies for different molecular species are provided by laboratory rotational spectroscopy. These are then used by astrophysicists for the identification of these species in ISM and in derivation of their abundances from the spectrum detected by radio astronomy.

Rotational spectroscopy involves the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. These transitions arise from the rotation of the permanent dipole moment that can interact with an electromagnetic field in the microwave region of the spectrum. It is a high resolution technique with precision only limited by the Doppler width. It is also an excellent source of reference data for new high-resolution telescope facilities operating in the THz frequency region. An important application of rotational spectroscopy has been in the chemical analysis of the interstellar medium using radio telescopes.

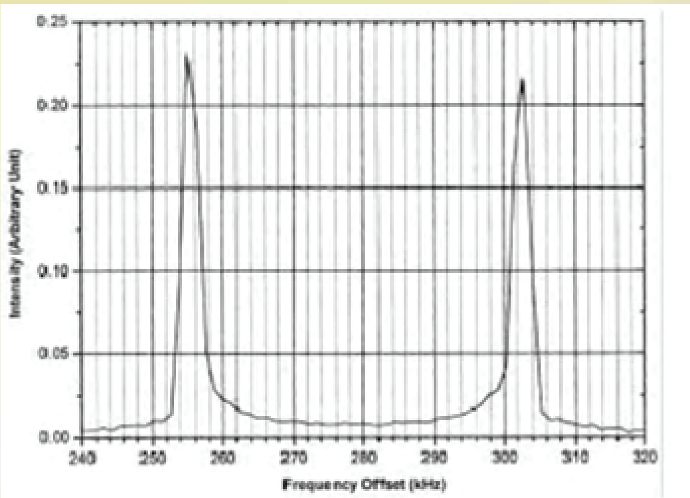

Figure 4: The frequency domain spectrum of Figure 3 showing the Doublets of the J=0→1 transition of OCS at 12162.9789 MHz(Reproduced with permission from Reference 1).

Rotational spectroscopy has been very useful in determining the structure of molecules and molecular clusters via Fourier transform microwave (FTMW) spectrometer. However, only stable molecules in gas phase could be studied using FTMW while the weakly bound complexes could only be studied using Molecular Beam Electric Resonance (MBER) spectrometers which were not very sensitive.

In the early 1980s, Balle and Flygare developed the pulsed nozzle Fourier transform microwave spectrometer(PN-FTMW) to study the conformers of organic molecules, weakly bound complexes, free radicals and reaction intermediates with great resolution and high sensitivity. In our group, we have built the PN-FTMW spectrometer based on the Balle-Flygare design with some key differences made possible due to the advances in RF and microwave technology in the intervening period [1]. Fig. 1 and 2 respectively show the mechanical and electrical designs of the PN-FTMW currently used in our lab (Figures taken from Ref. 1 with permission). Briefly, the microwave pulse (duration in microseconds) is generated by a digital source, such as a synthesizer or arbitrary waveform generator. The frequency of this pulse is tuned to be resonant with a Fabry-Perot cavity housed in a high-vacuum chamber, 10^{-6} mbar. It produces a standing wave within the cavity of frequency width of about a MHz. If the molecule/complex in the cavity has a rotational transition within this bandwidth, this pulse causes populations in the two different rotational levels (say 1 and 2) to mix, creating a macroscopic polarization. This macroscopic polarization begins to lose coherence and emits a free induction decay (FID). The FID is then converted from the time domain to the frequency domain by Fourier transform as shown in Fig. 3 and 4. Details of the working principle of this instrument can be found in our review on its advances and application [2].

On the successful completion of the PN-FTMW spectrometer in our lab, in order to test its performance and resolution, strong signals from the standard OCS (a well known interstellar molecule observed in the Sgr B2 complex since 1971) were obtained in the frequency range

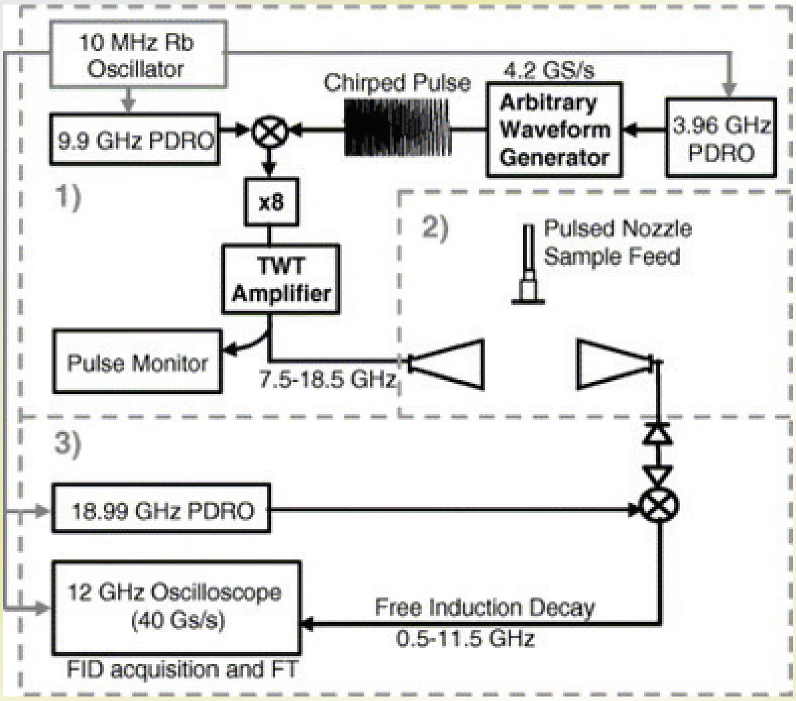

Figure 5: Schematic diagram of CP-FTMW spectrometer (Reproduced with permission from Reference 7)

of 2 to 26.5 GHz. Fig. 3 shows the time domain signal obtained from the standard OCS while Fig. 4 depicts the frequency domain spectrum of the same sample. The high resolution of our spectrometer became very obvious with the line centre that could be determined to 0.1 kHz and the doubling of the signal (as shown in Fig. 4) is due to Doppler effect. The Doppler effect or shift, which has to do with a change in frequency of a periodic event for an observer relative to its source, has been of immense use in astronomy in measuring the speed at which stars and galaxies are approaching or receding from us.

Our PNFTMW spectrometer has been in active use for studying the rotational spectra of molecules of astrophysical interest and weakly bound complexes formed in supersonic expansion. Among the molecules that were investigated in the recent years are phenylacetylene [3,4] and propargyl alcohol [5,6]. Phenylacetylene is an intermediate in the formation of soot particles observed in interstellar space. With the well established concept of isomerism existing among interstellar molecules with about 40% of all the known interstellar molecules having isomeric counterparts, we have studied the rotational spectra of propargyl alcohol and its weakly bound complexes. Propargyl alcohol is a potential candidate for astronomical observation as its isomer; propenal has been astronomically observed about a decade ago. The first branched chain molecule; isopropyl cyanide has recently

Table 1: Interstellar molecules between 2 and 7 atoms

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms
H_2, CO, CSi, CP	H_2O, H_2S, HCN, TiO_2	NH_3, H_2CO	CH_4, SiH_4	CH_3OH, CH_3SH	CH_2CHOH
CS, NO, NS, SO	HNC, CO_2, SO_2	H_2CS, C_2H_2	CH_2NH, NH_2CN	C_2H_4, HC_4H	c-C_2H_4O
HCl, NaCl, KCl	MgCN, MgNC, NaCN	HNCO, HNCS	CH_2CO, HCOOH	CH_3CN, CH_3NC	HC(O)CH_3
AlCl, AlF, PN	N_2O, NH_2, OCS	H_3O^+, SiC_3	HCCCN, HCCNC	$HCONH_2$,	H_3CCCH
SiN, SiO, SiS	CH_2, HCO, C_3	C_3S, H_2CN	c-C_3H_2, l-C_3H_2	HC_2C(O)H	CH_3NH_2
NH, OH, C_2	C_2H, C_2O, C_2S	c-C_3H, l-C_3H	CH_2CN, H_2COH^+	HC_3NH^+	CH_2CHCN
CN, HF, FeO	AlNC, HNO	HCCN, CH_3	C_4Si	HC_4N	HC_4CN
LiH, CH, CH^+	SiCN, N_2H^+	C_2CN, C_3O	C_5	C_5N, C_5H	C_6H
CO^+, SO^+, SH, NO^+	SiNC, c-SiC_2	$HCNH^+$, $HOCO^+$	HNCCC	H_2C_4, H_2CCNH	
O_2, N_2, CF^+	HCO+, HOC^+	C_3N^-, HNCO	C4H	C_5N^-	
PO, HD	HCS^+, H_3^+	HSCN	C_4H^-	c-H_2C_3O	
SiH, AlO,	OCN^-, HCP, CCP	HMgNC	HC(O)CN	E-HNCHCN	
ArH^+		H_2O_2			

Rotational (mm/sub-mm); both rotational (mm/sub-mm) and uv-vs (electronic); uv-vs (electronic); infrared (vibrational) (See further reading 9-11).

Table 2: Interstellar molecules with 8 atoms and above

8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
CH_3COOH	$(CH_3)_2O$	$(CH_3)CO$	HC_9N	C_6H_6	$HC_{11}N$
$HCOOCH_3$	CH_3CH_2CN	HOC_2H_4OH	CH_3C_6H	C_3H_7CN	C_{60}
$HOCH_2CHO$	CH_3CH_2OH	H_3CCH_2COH	$HCOOC_2H_5$	$C_2H_5OCH_3$	C_{60}^+
H_3C_3CN, C_7H, $(NH_2)_2CO$	CH_3CH_2SH	CH_3C_4CN	CH_3OCOCH_3	branched- C_3H_7CN	C_{70}
H_2C_6	CH_3C_4H				
$H(CC)_3H$	HC_7N				
$H_2CCHCHO$	C_8H				
CH_2CCHCN	CH_3CONH_2				
H_2NCH_2CN,	C_8H^-				
CH_3CHNH	CH_3CHCH_2				

Rotational (mm/sub-mm); infrared (vibrational) (See further reading 9-11)

been observed in ISM and studies have shown the possibility of more branched chain molecules in ISM. In line with this, we are planning to study the rotational spectra of isoprene and its weakly bound complexes.

Chirped-Pulse Fourier Transform Microwave (CP-FTMW) Spectroscopy:

The recent advances in the technology of microwave equipments have brought great innovations into the field of microwave spectroscopy with great impact in astronomy, astrophysics and astrochemistry. One of such innovations is the development of a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer capable of measuring 11 GHz of bandwidth in less than 10 μs [7]. The PNFTMW spectrometer had very high resolution and sensitivity, but the bandwidth was limited to about 1 MHz. It was often compared to looking through a key-hole to find out what is in a room. The CPFTMW spectrometer has opened the door and it has indeed revolutionized the field of microwave spectroscopy! Several laboratories have already built a chirped pulse version and it is only a matter of time before every microwave laboratory has one.This development has brought others to the field as well.

The schematic diagram of a CP-FTMW spectrometer is shown in Fig. 5. In catching up with these advances and the advantages offered by CP-FTMW spectroscopy, our laboratory is planning to build a CP-FTMW spectrometer as well.

The CP-FTMW spectrometer has three main components; (1) chirp microwave pulse generation, (2) microwave excitation pulse and molecular beam sample interaction region and (3) FID detection which are clearly depicted in Fig. 5. Details about the CP-FTMW spectrometer and its applications can be found in Reference 7.

Impact of Rotational Spectroscopy in Astrophysics:

The impact of rotational spectroscopy in astrophysics and by extension, astronomy, astrochemistry and astrobiology is something that cannot be overstressed. The seeds constantly sown by many spectroscopy groups around the world are unremittingly yielding fruits. The Thaddeus group at the Harvard-Smithsonian Center for Astrophysics carried out a comprehensive rotational spectroscopy study of 77 reactive organic molecules of astrophysical interest. Even before the publication of their results [8], 6 of the molecules were already detected in ISM based on their data.The ISM has been shown to consist of a bizarre mixture of both familiar molecules such as water, ammonia etc, and a large number of exotic ones such as radicals, acetylenic carbon chains, carbenes, highly reactive ions and high molecular isomers that are so unfamiliar in the terrestrial laboratory that chemists and astronomers have dubbed them "non-terrestrial". The development of radio-astronomical techniques, advancements in spectroscopic tools and the close collaboration between laboratory spectroscopists and astrophysicists have resulted in the detection of over 200 different molecular species in the interstellar space largely via their rotational emission spectra during the last four decades (Tables 1 and 2).

In 2004, our review on the advances and applications of pulsed nozzle furrier transform microwave spectrometer was published [2]. This review highlighted the impact of this indispensable tool in astronomy and astrophysics.

Tables 1 and 2 list the different interstellar molecules so far detected from different molecular clouds, grouped according to the number of atoms. From the tables, it is evident that more than 80% of all the known interstellar molecules have been observed via their rotational spectra (all the molecules indicated in black) while the other spectroscopic methods; vibrational spectroscopy (indicated in green) and uv-visible (electronic spectroscopy; indicated in blue) have also been useful for the astronomical observations of a few molecules especially the ones that are not microwave active (no permanent electric dipole moment).

The different interstellar molecules are important in diverse fields; atmospheric chemistry, astrobiology, astrochemistry, cosmology, astrophysics, prebiotic chemistry, astronomy etc, and in our understanding of our solar system. The symmetric rotors like CH_3CN and CH_3CCH are being used as interstellar thermometers. Metal-bearing molecules like SiO, AlNC, FeO, etc, give useful information about the depletion of these molecules into the molecular dust grains. The hydrides; CH, LiH, SiH etc. are believed to play an important role in cooling the highest density regions of interstellar clouds.The observations of interstellar ions; CH^+, HC_3NH^+, HOC^+,C_3N^-,C_4H^- etc, have sparked off studies on ion-molecule chemistry as the basis for the formation of interstellar molecules in the gas phase.The observation of interstellar cyclic molecules; c-C_2H_4O, c-C_3H, etc, is always a welcome development as very few of them have been observed so far.The complex molecules (molecules with six or more atoms by interstellar standards) so far observed include molecules of biological importance which are good tools in addressing the chemical origin of life which remains an open question in Chemistry. In the $C_2H_4O_2$ family of isomers, acetic acid is considered as a precursor for glycine; the simplest biologically important amino acid.This is due to the fact that in the laboratory, a biomolecular synthesis of glycine occurs when acetic acid combines with amidogen cation. Glycolaldehyde is an important biomarker being structurally the simplest member of the monosaccharide sugars. In general, each interstellar molecule tells its own story about the chemistry and physics where it was found.

Conclusion:

The widespread of molecules throughout the Universe and the astronomical observations of some of these molecules have led to the realization that the Universe is substantially molecular. To the astronomers, interstellar molecules are useful as probes of physical conditions while to the chemists, they are exciting clues to the molecular origin of life. More and larger molecules are expected to be observed in the interstellar space in the near future. With the rapid advances in technology of astronomical and spectroscopic tools, coupled with the curiosity in understanding the world around us and the solar system, the young interdisciplinary science of astrochemistry lying at the interface of astronomy, astrophysics, physics and chemistry will remain a fascinating field of study with the reach and ever expanding chemistry of the interstellar medium.

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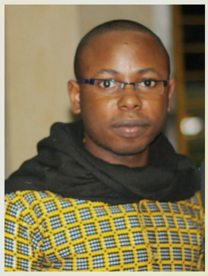

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