

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Periodic Trends among Interstellar Molecular Species: The Case of Oxygen- and Sulfur-Containing Species

Etim Emmanuel, Lawal Usman, Khanal Govinda and
Mbakara Idaresit

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.80884>

Abstract

Out of the 19 known S-containing interstellar molecules, 16 have the corresponding O-compound analogues marks out of the interstellar chemistry of sulfur and oxygen as a unique one among other observed interstellar periodic trends. However, the rule that the ratio of an interstellar sulfur molecule to its oxygen analogue is close to the cosmic S/O ratio is far from reality in many cases even when both species are observed from the same source. In this chapter, the effect of interstellar hydrogen bonding on the variation of the S/O abundance ratio with respect to the cosmic S/O ratio is investigated using high-level quantum chemical simulations. The detectability of the yet to be observed analogues of both S and O molecules is also examined. From the results, the deviation from the cosmic S/O ratio is largely due to hydrogen bonding on the surface of the dust grains. As the ratio of the binding energy of S- and O-species (binding energy of S/O) with water approaches unity, the S/O abundance ratio approaches cosmic S/O ratio. The more this ratio deviates from unity, the more the S/O abundance deviates from the cosmic S/O ratio. Regarding the detectability of the unknown analogues, it suffices to say that every known O-species is an indication of the presence and detectability of the S-analogue, while for every known S-species, the O-analogue is not only present in detectable abundance, it can be said to have even been overdue for astronomical detection.

Keywords: astrochemistry, interstellar medium, hydrogen bonding, abundance ratio, spectroscopy

1. Introduction

Astrophysicists and astronomers are largely concerned with discovering new molecules in the Interstellar medium (ISM) and not so much with the understanding of the chemistry and

physics of these molecules just like the early chemists were interested in discovering new chemical substances without much concern about their chemical behavior, thus leading to the emergence of the field of chemical kinetics. Understanding the chemistry of these molecules discovered by astrophysicists and astronomers has given birth to astrochemistry, a young interdisciplinary field that blends chemistry into astronomy and astrophysics. Inasmuch, we are still trying to understand the chemistry and physics of these molecules, and some of the features are very glaring to be observed by all and sundry. The dominance of organic molecules, isomerism, successive hydrogen addition, periodic trends, etc., are some of the notable features among these interstellar and circumstellar molecules. The dominance of organic molecules these molecular species is very obvious with a greater percentage of these molecules found to contain the four most important biogenic elements; C, H, N, and O. Slightly above 200 different molecular species have been detected from different astronomical sources [1]. About 132 of these species contain at least an atom of H, same number also contain at least an atom of C, 64 of these molecular species contain at least an atom of N, while not fewer than 59 contain an atom of O. The high abundances of these elements among the interstellar and circumstellar species can be seen as a direct reflection of their cosmic abundances. With the exceptions of the noble gases and the unusual abundance of Fe, these four elements (H, O, C, and N) have the highest cosmic abundances.

Isomerism among these molecular species has emerged as one of the important tools in exploring the basic chemistry of these species. This can be understood from the fact that about 40% of all interstellar and circumstellar species have isomeric counterparts, and these isomers are believed to have a common precursor for their formation routes; thus, the detection of one isomer gives an insight about the presence and the detectability of others. That most of these isomers are easily observed from the same astronomical sources strongly supports the fact that they have a common precursor for their formation process. In the C_2H_3N isomeric group, methyl cyanide, methyl isocyanide, and ketenimine have all been observed from the same astronomical source [2–4]. In the $C_2H_4O_2$ isomeric group, acetic acid, methyl formate, and glycolaldehyde have also been observed from the same molecular cloud [5–7]. This trend is common among isomers: HCN and HNC, MgCN and MgNC, SiCN, SiNC, etc. [8–13]. Successive hydrogen addition is considered as a possible route for the formation of alcohol from their corresponding aldehydes; methanol from formaldehyde, ethanol from acetaldehyde, and ethylene glycol from glycolaldehyde. Also, these molecules are commonly detected from the same spectral region. Laboratory experiments under interstellar medium conditions have demonstrated how small molecules grow into larger ones via successive hydrogen addition [14].

Periodic trends are another observable features of interstellar and circumstellar molecules. Elements from the same group are found to have corresponding molecules as known interstellar and circumstellar molecules as seen in the cases of C and Si, N and P, O and S, F and Cl, among others. Among these trends, those of O and S are very conspicuous. Of the 19 known S-containing molecules, 16 have the corresponding O-analogues as known interstellar and circumstellar molecules. Interestingly, 12 of the S- and their corresponding O-analogues were

first detected from the same astronomical sources, suggesting a common link in their formation processes [95–97]. The abundance ratio of these molecules with respect to their cosmic or elemental abundance is also an interesting feature. According to Linke [15], “*Methyl mercaptan is apparently a fairly good example of the rule that the ratio of an interstellar sulfur molecule to its oxygen analogue is close to the cosmic S/O ratio.*” This “rule” of course is far from being true in many cases even for molecules observed from the same source. It thus requires an in-depth investigation. Reactions that occur on the surfaces of the interstellar dust grains are the dominant processes for the formation of interstellar molecules. The composition of the interstellar dust grains, which create the surface for these reactions also serve as a platform for hydrogen bonding between the water molecule (the most abundant component of the interstellar dust grains) and the molecules that are formed on these surfaces. This interstellar hydrogen bonding, thus, reduces the abundance of molecules that are formed on the surface of the dust grains since a greater portion of these molecules are attached to surface of the interstellar dust grains [16]. This poses a serious exception to interstellar formation processes that have been shown to be largely thermodynamically controlled [17–19].

In the present work, the effect interstellar hydrogen bonding on the variation of the S/O abundance ratio with respect to the cosmic S/O ratio is examined using high-level quantum chemical simulations. The binding energy between water molecule on the surface of the dust grains and the O- or S-containing molecule gives inside about the level to which the interstellar abundance of such molecule is affected. There are 59 O-containing and 19 S-containing interstellar species; for 16 that are S and O analogues, there is no order regarding their astronomical observations, i.e., in some cases, the O-containing species was observed before the S-containing and vice versa. Thus, the observation of one always gives information about the presence and the possible detectability of the other. In the light of this, the known molecules from this S/O group whose corresponding analogues are not yet observed are examined for their possible detectability. These species are subjected to the effect of interstellar hydrogen bonding. Their binding energies with water on the surface of the interstellar dust grains are determined. From the ratio of the binding energies of these systems, the S/O abundance ratio is predicted for the unknown systems. For the O-containing molecules where two or more isomers are observed, standard enthalpies of formation are computed for both the O and corresponding S-analogues to guide the preference for astronomical searches for the S-analogues since the most stable isomer is more probably the most abundant in the interstellar medium except where the effect of hydrogen is well pronounced as in the case of methyl formate and acetic acid. After describing the methodology employed in this work, the results obtained are presented and discussed before the concluding remarks.

2. Computational details

The quantum chemical calculations reported in this work are carried out using the Gaussian 09 suite of programs [20]. The binding energy (B. E.) between the water molecule on the

surface of the interstellar dust grains and molecule of interest (O- or S-containing) is determined using the method as described in our recent paper [94], which is expressed as Eq. (1):

$$\text{B. E. (complex)} = E(\text{complex}) - [E(\text{water molecule}) + E(\text{heterocycle molecule})] \quad (1)$$

To obtain high accurate values for the binding energy, the MP2(full) with the 6-311++G** basis set is used in examining the effect of interstellar hydrogen bonding. By definition, the standard enthalpy of formation ($\Delta_f H^0$) of any molecule is the enthalpy change of the reaction by which it is formed from its constituent's elements. Among the different composite quantum chemical methods that are now used to accurately predict thermochemistry data, the G4 method has been found to be very effective in predicting enthalpy of formation values to chemical accuracy in many molecules as reported in literatures [17–19, 21–24]. Details regarding the steps in calculating zero-point-corrected standard enthalpy of formation have been well described in our previous studies [17–19]. The values reported in this work are calculated from the optimized geometries of the systems at the levels of theory mentioned above. The structures are found to be stationary with no imaginary frequency through harmonic vibrational frequency calculations.

3. Results and discussion

The known S-containing molecules and their corresponding O-analogues are discussed with respect to the observed S/O abundance ratio followed by the detectability of the unknown analogues of these species. **Table 1** shows all the known S-containing interstellar species in a chronological order with their corresponding O-analogues (where available); the binding energies (B. E.) of these species with water on the surface of the interstellar dust grains computed at the MP2(full)/6-311++G** level discussed above are presented in columns 2 and 4, respectively; for S- and O-species, the S/O ratio is from the observed abundances of these species taken from the references in the column 6. The magnitude of the binding energy shows the extent to which the molecule (S- or O-containing) is bonded to the surface of the interstellar dust grains. The higher the magnitude of the B. E., the more strongly bonded is the molecule and vice versa. This also implies that as molecule is strongly bonded to the surface of the interstellar dust grains, a greater portion of it is attached to the surface of the dust grains, thus reducing its overall abundance. When the S-containing species is more strongly bonded as compared to the O-analogue, the S/O abundance ratio becomes much more smaller than the S/O cosmic ratio of 0.024 (1/42) [15, 25] and the reverse becomes the case when O-analogue is more strongly bonded as compared to the S-analogue. When the ratio of the binding energy of an S-containing species and their O-analogue approach unity, the observed S/O ratio also approaches the cosmic S/O ratio. Because in this case, there is little or no much pronounced effect of interstellar hydrogen bonding, which affects the interstellar abundance of these species. The major exception to this trend is observed with the components of the interstellar ices: H₂O, CH₃OH, and H₂CO.

which are thus more abundant than their corresponding S-analogues irrespective of the effect of interstellar hydrogen bonding. **Figure 1** and **Table 2** summarize the observed trends

S-containing molecule	B. E (kcal/mol) with water	O-analogue	B. E (kcal/mol) with water	S/O ratio	References
CS (1971)	-1.967	CO (1970)	-0.913	0.013	[39, 52]
OCS (1971)	-1.521	CO ₂ (1989)	-2.898	0.032	[50, 51]
H ₂ S (1972)	-2.292	H ₂ O (1969)	-4.672	<<0.001	[48, 49]
H ₂ CS (1973)	-2.614	H ₂ CO (1969)	-4.104	≈0.025	[47]
SO (1973)	-3.063	O ₂ (2011)	-0.324	0.015	[45, 46]
SO₂ (1975)	-2.123	O₃ (not observed)	-0.512	NA	
SiS (1975)	-3.688	SiO (1971)	-6.785	≈1	[43, 44]
NS (1975)	0.272	NO (1978)	-0.097	0.005	[41, 42]
CH ₃ SH (1979)	-2.048	CH ₃ OH (1970)	-4.417	≈0.023	[15, 40]
HNCS (1979)	-7.532	HNCO (1972)	-9.146	0.025	[25, 31]
HCS ⁺ (1981)	-12.490	HCO ⁺ (1970)	-39.779	≈0.191	[38, 39]
C ₂ S (1987)	-2.602	C ₂ O (1991)	-2.493	0.01	[26, 27]
C ₃ S (1987)	-2.584	C ₃ O (1985)	-2.584	0.028	[28, 29]
SO⁺ (1992)	-18.589	O₂⁺ (not observed)	-50.272	NA	
HSCN (2009)	-98.722	HOCN (2009)	-37.227	4.5E-3	[30, 31]
SH ⁺ (2011)	-73.314	OH ⁺ (2010)	-69.343	0.029	[32, 33]
SH (2012)	-1.394	OH (1963)	-2.927	0.023	[34, 35]
CH ₃ CH ₂ SH (2014)	-1.678	CH ₃ CH ₂ OH (1975)	-4.343	0.286	[36, 37]
C₅S (2014)	-1.908	C₅O (not observed)	-2.969	NA	

Ref. [15, 25–52].

Table 1. S- and O-containing species, their B. E with water, and S/O ratio.

in **Table 1**. With the few exceptions observed above, S/O abundance ratio of all the known S-containing species and their corresponding O-analogues follows the same trend as displayed in **Table 2**. As the B. E. S/O ratio approaches unity, the observed S/O ratio approaches the cosmic S/O ratio as in the cases of HNCS/HNCO and C₃S/C₃O. When this ratio is above unity, the observed S/O ratio becomes much less than the cosmic S/O ratio, e.g., CS/CO, SO/O₂, NS/NO, C₂S/C₂O, and HSCN/HOCN and the reverse is observed when the ratio is less than unity, e.g., OCS/CO₂, SiS/SiO, HCS⁺/HCO⁺, CH₃CH₂SH/CH₃CH₂OH. In summary, the B. E. O/S ratio is inversely proportional to the observed variation of S/O abundance ratio with the cosmic S/O ratio.

Known O-containing species and detectable S-analogues: as previously mentioned, there are at least 59 known O-containing interstellar and circumstellar molecules of which 16 have the corresponding S-analogues as known astromolecules leaving us with over 40 O-containing species without the corresponding S-analogues. In assessing the detectability of these S-analogues of known O-containing molecules, the binding energies of these species (both S- and O-containing

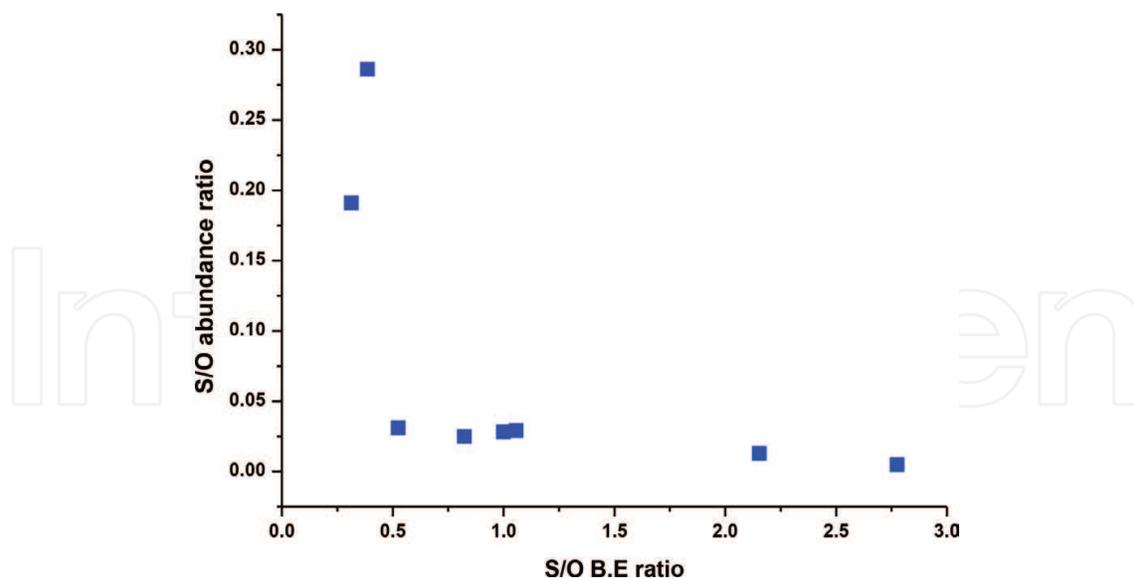


Figure 1. Correlation between B. E. and S/O abundance ratio.

S/O B. E.	S/O B. E.	S/O B. E.
>1	≈1	<1
S/O ratio	S/O ratio	S/O ratio
<Cosmic S/O ratio	≈Cosmic S/O ratio	>Cosmic S/O ratio

Table 2. Deviation from cosmic S/O ratio as a function of binding energy (B. E.).

species) with water on the surface of the interstellar dust grains have been computed. These values are presented in **Table 3**. The reported column densities for the known O-containing molecules are shown in the column 2 with the source of the data in the column 3 of the same table (refs). The column 7 shows the ratio of the binding energy of the S- and O-containing species, from this ratio, the S/O abundance ratio is predicted (column 8) following the observations made in the preceding section (see **Table 2**). That the S-containing molecular species are less bonded to the surface of the interstellar dust grains compared to their respective O-analogues as it is observed in over 80% of the systems here (**Table 3**) is a good omen with respect to the detectability of these species because their overall interstellar abundance will be less affected by the effect of interstellar hydrogen bond unlike their O-analogues. However, with respect to the role that the ratio of an interstellar sulfur molecule to its oxygen analogue is close to the cosmic S/O ratio, there will be much deviation from this role since the degree to which the S-containing species is affected by the effect of hydrogen bonding on the surface of the dust grains is much different from those of the corresponding O-analogues. As a result of this, S/O abundance ratio would be expected to be much higher than the cosmic S/O ratio as shown in the column 8 of **Table 1** for majority of the cases and in very few cases the ratio will tend toward the cosmic S/O ratio except where other processes play a role.

Interstellar formation processes have been shown to be largely thermodynamically controlled in many cases. Except with a pronounced effect of interstellar hydrogen bonding, the most

O-containing molecule	Column density (cm ⁻²)	Refs.	B. E. (kcal/mol) with water	S-analogue	B. E. (kcal/mol) with water	B. E. S/O ratio	Estimated S/O abundance ratio
CO ⁺	≈E12	[53]	-58.540	CS ⁺	-13.562	0.232	>S/O*
FeO	9E11	[54]	10.299	FeS	-3.637	0.353	>S/O*
PO	≈2.8E15	[55]	-10.236	PS	-1.228	0.120	>S/O*
OH ⁺	2.4E15	[56]	-69.343	SH ⁺	-73.314	1.057	≈S/O*
TiO	6.99E14	[57]	-3.874	TiS	-2.413	0.623	>S/O*
NO ⁺	2.2E12	[58]	-20.719	NS ⁺	-21.547	1.040	≈S/O*
AlO	≈2E15	[59]	-0.027	AlS	-15.032	556.741	<S/O*
N ₂ O	≈E15	[60]	-2.225	N ₂ S	-1.862	0.837	≈S/O*
HCO	≈E11	[61]	-27.168	HCS	-7.477	0.275	>S/O*
HNO	6E11–3.2E14	[62]	-72.436	HNS	-35.794	0.494	>S/O*
HOC ⁺	≈3E12	[63]	-72.861	HSC ⁺	-127.024	1.743	<S/O*
OCN ⁻	—	[64]	-11.887	SCN ⁻	-9.036	0.760	>S/O*
H ₂ O ⁺	7.2E12, 2.3E13, 1.1E15	[65]	-45.608	H ₂ S ⁺	-19.086	0.418	>S/O*
TiO ₂	7.5E14	[57]	-32.491	TiOS	-15.607	0.480	>S/O*
HO ₂	2.8E12	[66]	-2.066	HSO	-2.675	1.295	≈S/O*
AlOH	≈E17	[67]	-4.043	AlSH	-21.869	5.409	<S/O*
H ₃ O ⁺	3E14	[68]	-30.591	H ₃ S ⁺	-17.753	0.580	>S/O*
HOCO ⁺	—	[69]	-33.959	HOCS ⁺	-45.806	1.349	≈S/O*
HCNO	≈8.9E12	[56]	-1.948	HCNS	-1.148	0.589	>S/O*
HOOH	8E12	[70]	-5.894	HOSH	-2.747	0.466	>S/O*
HCOOH	≈5E13	[71]	-4.353	HSCHO	-0.436	0.100	>S/O*
H ₂ C ₂ O	≈E14	[72]	-2.191	H ₂ C ₂ S	-0.486	0.222	>S/O*
H ₂ COH ⁺	E12-E14	[73]	-25.388	H ₂ CSH ⁺	-15.103	0.595	>S/O*
CNCHO	1-17E14	[74]	-4.743	CNCHS	-4.201	0.887	≈S/O*
CH ₃ O	7E11	[75]	-3.180	CH ₃ S	-2.175	0.684	>S/O*
H ₂ NCO ⁺	6-14E11	[76]	-21.372	H ₂ NCS ⁺	-17.922	0.838	≈S/O*
H ₂ NCHO	2.2E16	[77]	-5.457	H ₂ NCHS	-4.171	0.764	>S/O*
HC ₂ CHO	1.5E12	[78]	-4.079	HC ₂ CHS	-2.908	0.713	>S/O*
c-H ₂ C ₃ O	≈E13	[79]	-6.081	c-H ₂ C ₃ S	-5.628	0.925	≈S/O*
CH ₃ CHO	≈1.5E14	[80]	-4.675	CH ₃ CHS	-2.544	0.544	>S/O*
c-C ₂ H ₄ O	3.3E14	[81]	-4.457	c-C ₂ H ₄ S	-2.892	0.689	>S/O*

O-containing molecule	Column density (cm ⁻²)	Refs.	B. E. (kcal/mol) with water	S-analogue	B. E. (kcal/mol) with water	B. E. S/O ratio	Estimated S/O abundance ratio
CH ₂ CHOH	2.4E13	[82]	-6.103	CH ₂ CHSH	-2.585	0.423	
CH ₃ COOH	7.3E15	[6]	-7.863	CH ₃ CSOH	-7.001	0.890	≈S/O*
HCOOCH ₃	≈1.9E17	[7]	-4.975	HCSOCH ₃	-2.418	0.486	>S/O*
HOCH ₂ CHO	2.8E16	[7]	-5.414	HSCH ₂ CHO	-4.337	0.801	>S/O*
CH ₂ CHCHO	—	[83]	-5.215	CH ₂ CHCHS	-2.843	0.545	>S/O*
(NH ₂) ₂ CO	≈E15	[84]	-7.422	(NH ₂) ₂ CS	-6.676	0.899	≈S/O*
CH ₃ OCH ₃	<18E14	[85]	-4.411	CH ₃ SCH ₃	-2.548	0.578	>S/O*
CH ₃ CONH ₂	1.8E14	[86]	-5.922	CH ₃ CSNH ₂	-3.914	0.661	>S/O*
(CH ₃) ₂ CO	2.9E16	[87]	-5.051	(CH ₃) ₂ CS	-6.711	1.329	≈S/O*
HOCH ₂ CH ₂ OH	3.2E14	[14]	-4.064	HOCH ₂ CH ₂ SH	-2.073	0.510	>S/O*
CH ₃ CH ₂ CHO	—	[83]	-4.560	CH ₃ CH ₂ CHS	-3.296	0.723	>S/O*
C ₂ H ₅ OCHO	5.4E16	[88]	-4.896	C ₂ H ₅ OCHO	-14.803	3.023	<S/O*
CH ₃ COOCH ₃	4.2E15	[88]	-4.815	CH ₃ COOCH ₃	-4.006	0.831	>S/O*
C ₂ H ₅ OCH ₃	2E14	[89]	-4.250	C ₂ H ₅ OCH ₃	-2.519	0.593	>S/O*

Where S/O* is the cosmic abundance ratio.

Refs. [7, 17, 53–89].

Table 3. Parameters for known O- and detectable S-containing molecules.

stable isomer has always been observed to be the most abundant isomer in the interstellar space. Thus, the most stable isomer is easily observed as compared to other isomers of the group. **Figure 2** pictures this concept. It shows how the interstellar abundance (column density) of two isomers each from the CHNO and CHNS groups varies with the stability (enthalpy of formation) where the most stable isomer (with lower enthalpy of formation) is found to be the most abundant in both cases. Searching for the most stable isomer is, thus, a step toward successful observation, and the successful detection of an isomer reaffirms the presences of other isomers since they are believed to have a common precursor for their formation routes. In view of this, for known O-containing molecules with at least two isomers, the standard enthalpies of formation for these isomers and their S-analogues have been determined as a guide for preference in the astronomical searches for these isomers. **Table 4** presents the enthalpy of formation for O-containing isomers and their detectable S-analogues. As would be expected, the trend of the stability for O and S-species is the same. From the parameters presented in **Table 2** coupled with the advancements in astronomical and spectroscopic equipment, that all the S-analogues of known O-containing interstellar molecular species would not be considered as exaggeration. They are detectable.

Known S-species and overdue detectable O-analogue: without any exception, an interstellar O-containing molecular species is more abundant than its S-analogue (**Table 1**). So for every

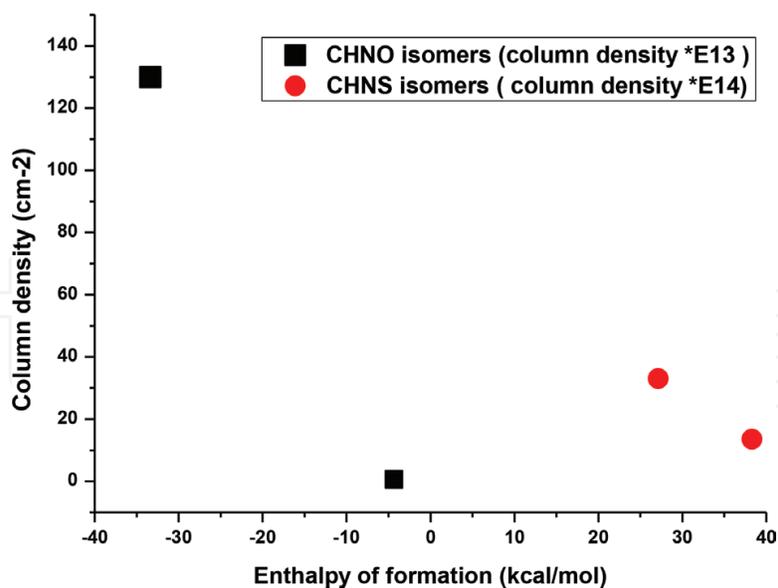


Figure 2. Dependence of column density on enthalpy of formation for CHNO and CHNS systems.

Molecule	Enthalpy of formation (kcal/mol)	
	X = O	X = S
3-atoms		
HXC ⁺	234.419	340.747
HCX ⁺	198.564	246.625
4-atoms		
HCNX	34.084	61.162
HXCN	-4.387	38.312
HNCX	-33.357	27.126
7-atoms		
c-H ₂ CH ₂ CX	-14.596	19.146
H ₂ CCHXH (anti)	-28.519	19.386
H ₂ CCHXH (syn)	-30.236	19.439
H ₃ CCHX	-42.405	16.453
8-atoms		
HXH ₂ CCHX	-70.542	31.962
H ₃ CXCHX	-89.381	20.743
H ₃ C(X)XH	-103.746	18.612
9-atoms		
(CH ₃) ₂ X	-48.956	-10.697
C ₂ H ₅ XH	-56.718	-11.943
11 atoms		

Molecule	Enthalpy of formation (kcal/mol)	
	X = O	X = S
H ₃ COC(O)CH ₃	-95.098	12.071
H ₃ CH ₂ CXCHX	-97.515	12.489

Table 4. Enthalpy of formation for O-containing isomers and their detectable S-analogues.

S-containing molecule	Column density (cm ⁻²)	References	B. E. (kcal/mol) with water	O-analogue	B. E. (kcal/mol) with water	B. E. S/O ratio	Estimated S/O abundance ratio
SO ₂	<3.5E16	93	-2.123	O ₃	-0.512	4.146	<S/O*
SO ⁺	5E12	94	-18.589	O ₂ ⁺	-50.272	0.370	>S/O*
C ₃ S	2-14E12	95	-1.908	C ₃ O	-2.969	0.643	>S/O*

Where S/O* is the cosmic abundance ratio.

Refs. [90–93].

Table 5. Parameters for known S- and detectable O-containing molecules.

known S-species, the O-analogue is not only present in detectable abundance, it can be said to have even been overdue for astronomical detection because for sure the O-species are more abundant than their S-analogue and as such could be detected with less difficulty as compared to its S-analogue. **Table 5** lists the parameters for known S-containing interstellar species and their detectable O-analogues. The high abundances reported for these S-containing species (column 2) strongly support the detectability of their O-analogues.

4. Basic inorganic chemistry of oxygen, sulfur, and hydrogen

4.1. Hydrogen

The first element in the periodic table is hydrogen. Although hydrogen is very abundant in nature, the air contains almost no free hydrogen. On the other hand, hydrogen is found in water, which is about 70% of the earth. Additionally, hydrogen compounds combined with carbon are found in space and it plays important roles in such as the nuclear fission reaction in the sun. Molecules of associated hydrogen element are the basis of astrochemical space research.

Physical properties of hydrogen

Relative atomic mass	1.008
Electron structure	1s ¹
Ionization energy	1312 KJmol ⁻¹
Electron affinity	-72 KJmol ⁻¹

Molecular formula	H ₂
Melting point	14 K
Boiling point	20 K
Density at s.t.p	0.09 KJmol ⁻¹
Bond energy, H-H	436 KJmol ⁻¹
Bond length, H-H	74 pm
Colorless, odorless, and tasteless gas.	

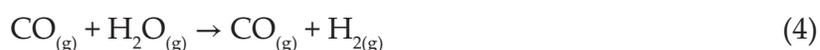
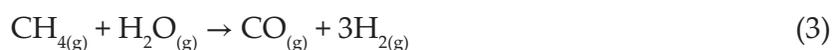
¹H, Protium (H), ²H, deuterium (D), and ³H, tritium (T) are the three known isotopes of hydrogen. The naturally occurring isotope is deuterium, while tritium is made during nuclear reaction.



Tritium is radioactive, decaying by beta emission.

4.2. Large-scale production of hydrogen

Natural gas (methane) is an important source of hydrogen. Methane is reacted with steam at high pressure of about 35 atmosphere pressure and 800°C in the presence of a nickel catalyst. The result is a mixture of carbon dioxide, carbon monoxide, and hydrogen.



In the refining industry, hydrogen is obtained in many reactions that involve cracking long-chain hydrocarbons into smaller molecules.



Bosch reaction is another method of making hydrogen; here, steam is passed over white hot coke.

Uses of hydrogen:

Majority of hydrogen produced are used in making ammonia in the Haber process. Production of margarine from vegetable oils, welding, and fuel cells are some of its other uses.

Chemical properties of oxygen:

Hydrogen gas is made up of hydrogen molecule, H₂. Hydrogen atoms are too reactive to exist on their own. The explosive mixture of hydrogen and oxygen is its commonest reaction. The possibility of explosion exists in the laboratory when hydrogen is made in large scale, and the experiment mostly goes on with caution. The normal method is to react dilute sulfuric acid with zinc.



Hydrogen forms hydride with many elements. Hydrides of metals are ionic, example NaH and CaH₂. Hydrides of nonmetals are covalent in nature, example CH₄ and NH₃. Hydrogen forms hydrogen bonding with highly electronegative atoms, for example HF and H₂O. Hydrogen gas explodes with oxygen when ignited.



As a reducing agent, hydrogen will remove oxygen from many oxides.



Hydrogen is liberated from acids by metals.



Hydrogen is prepared in the laboratory this way.

Hydrogen can exist both as H⁺_(aq) and H₃O_(aq) in water. Hydrogen ions form the active ions in aqueous acids.

4.3. Unusual hydrides of hydrogen

Chemical bonding theories were unable to explain chemical bonding in boron hydrides when they were first examined. They are several boron hydrides some of which are shown below.

Name	Formula	Comment
Diborane	B ₂ H ₆	Highly flammable and hydrolyzed easily
Tetraborane	B ₄ H ₁₀	Less reactive than diborane
Hexaborane-10	B ₆ H ₁₀	Same reactivity like tetraborane
Decaborane	B ₁₀ H ₁₄	Does not easily reacts with air or water
Icosaborane-10	B ₂₀ H ₁₆	Does not easily reacts with air or water

The simplest member of the group is diborane. The six hydrogen atoms provide six electrons for bonding, and there are three valence electrons in the shell of each work, with 12 electrons in all. However, X-ray structure of diborane reveals that each boron atom has two hydrogen atoms attached to it and another two hydrogen atoms shared between the two boron atoms. Expectedly, there will be sixteen (16) electrons participating in eight (8) bonds. Conversely, this is not the case as there appear to be too few electrons accounting for the number of bonds. Such molecules are now known as the electron-deficient molecules or compounds.

Furthermore, molecular orbital theory clarifies situations like this. Here, bridging hydrogen atoms are believed to be bonded to the boron atoms by a bond stretching across all three atoms. This type of bond is called a three center bond. Each one contains two electrons, which together with the four pairs of electrons in the bonds to the four terminal hydrogen atoms, bringing the total to the twelve (12) electrons observed. The bonding in other members of the borane group is explained in similar fashion, although bigger members show more complexity in their bonding.

Lithium tetrahydridoaluminate (III), LiAlH_4 (lithium aluminum hydride), is another hydride rather being unusual.

4.4. Oxygen

A diatomic molecule, O_2 , oxygen alone constitutes about 20.8% of air. Three isotopes of oxygen are known; ^{16}O is the main isotope with an abundance of 99.8%. The others are ^{17}O and ^{18}O with the abundance of 0.04 and 0.2%, respectively. Oxygen is very important to life of animals and plants including human being on earth. Oxygen is slightly soluble in water, which is essential for fish and other aquatic life survival.

Moreover, oxygen is an essential component of combustion reaction, especially of organic materials such as wood, oil, and coal. Our modern age is characterized by combustion of these fuels for our electricity, transportation, and heating needs.

Oxygen is located at upper layer of atmosphere where it absorbs harmful ultraviolet light from the sun. Ozone is an allotrope of oxygen, O_3 . The importance of oxygen to plant and animal life cannot be overemphasized.

Oxygen compounds of all elements are known except for those of He, Ne, and Ar. Molecular oxygen O_2 (dioxygen) react with all elements in periodic table with the exception of the halogens, some noble metals, and the rare gases.

The chemistry of oxygen is representative of having the neon stable configuration in the following ways. Gaining of electron as in the case of H_2O and sharing of electrons like in the case of OH^- , and finally formation three covalent bonds like in H_3O^+ , R_3O^+ , etc.

4.5. Oxides

The varieties of physical and chemical properties showed by oxides are functions of the bond types from primarily electrovalent to covalent. Formation of oxide ion is an energy consuming process.

In ionic metal oxide formation, energy is also expended in vaporizing and ionization of metal atom. Many ionic oxides are possible as a result of the high lattice energy of oxides that have the lesser double bond charged O^{2-} ion. Where this lattice energy is not sufficient to give the needed energy for ionization, oxides with significant covalent attributes are formed. The following are some examples BeO , SiO_2 , etc.

4.6. Sources of oxygen

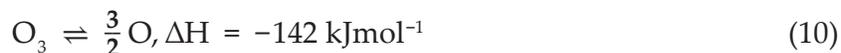
Fractional distillation of air is the main source of obtaining oxygen. Air is forced under pressure through nozzles. The compressed air is allowed to expand into a region of lower pressure, which cools the air. The air is cooled further in expansion tubes until it condenses into liquid. The liquid air is a mixture of nitrogen, oxygen, and rare gases and is separated by allowing an increase in temperature of the medium. The other gases boil more easily than oxygen, so they evaporate leaving oxygen. Liquid oxygen, which is pale blue in color and strongly paramagnetic, is stored under pressure or in insulated containers.

Oxygen extracted this way is used to aid respiration medically, for breathing by divers and astronauts, in oxy-acetylene welding and rocket fuels, etc.

4.7. Ozone

An allotrope of oxygen after dioxygen (O_2). Ozone (O_3) is formed by the action of electric current on oxygen, concentration of about 10% realized this way. Ozone is blue in color like oxygen but diamagnetic. Pure ozone is a deep blue explosive liquid, which is obtained by fractional liquefaction of O_2 - O_3 mixture. In the atmosphere, ozone comes about by the action of ultraviolet light radiation on oxygen. Ozone located at about the altitude of 25 km is responsible for preventing excess ultraviolet light from reaching on the earth.

Ozone is chemically found to be very endothermic and decomposes only slowly at 250°C in the presence of catalyst or ultraviolet (UV) light.



Ozone is triangular in shape with equal bond length of about 128 nm. The degree of single and double bonds formed by ozone is same. Each oxygen atom of the ozone has six valence electrons. Describing this with valence bond theory, each bond will involve a set of resonance hybrid in which one of the bonds is a double bond and the other is a coordinate bond. Moreover, the real structure does not swap between the resonance frames; rather, each bond partly shows a nature of a double bond and partly that of a single bond.

In the laboratory, ozone is made by passing oxygen through an electric field. An equilibrium is set up.



The metastable nature of ozone makes it transient, having the tendency of always converting to oxygen. It is a vigorous oxidizing agent, always reacting to give up oxygen gas



At an altitude of about 25 km above the earth surface, dioxygen can be split apart by ultraviolet light radiation coming from the sun. Some of these atoms react with other oxygen molecules forming the ozone layer



This reaction is of extreme importance to the maintenance of balance here on earth. This is because the ozone has the ability to absorb dangerous ultraviolet radiation from the sun, thus preventing it from reaching the earth surface. This radiation is of high energy, therefore, of short wavelength. If too much of this radiation reaches the earth, the energy balance will be upset leading to increase greenhouse effect and global atmospheric temperature.

Secondly, exposure to increase ultraviolet radiation will lead to cell mutation of living tissues. The consequences of this will increase in skin cancer incidence in particular.

4.8. Chemical properties of oxygen

4.8.1. Oxides

The ability of oxygen molecule to combine with both metals and nonmetals to form oxides is its most outstanding property. Oxides are of four different types: neutral, basic, acidic, and amphoteric. Oxides that show both basic and acidic behavior are called amphoteric oxides. Few oxides are neutral: nitrous oxide and carbon monoxide are examples. Group I and II oxides are examples of basic oxides. Oxides of nonmetals are mainly acidic in nature. Aluminum oxide is an example of amphoteric oxide.

It shows basic properties by reacting with hydrogen ions



Additionally, it shows acidic property when dissolved in alkali



Formulae of some oxides in the periodic table:

Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII
Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₅	O ₂	F ₂ O
Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₂	Cl ₂ O
K ₂ O	CaO	Ga ₂ O ₃	GeO ₂	As ₂ O ₃	SeO ₂	BrO
Rb ₂ O	SrO	In ₂ O ₃	SnO	Sb ₂ O ₃	TeO ₂	I ₂ O ₅
Cs ₂ O	BaO	Tl ₂ O	PbO	Bi ₂ O ₂	PoO ₂	

Not all the oxides are shown.

4.8.2. Peroxides

The most important peroxide of oxygen is hydrogen peroxide, H₂O₂. Hydrogen peroxide is a colorless liquid with a boiling point of 152.1 °C. It is similar to water in many of its properties

and forms hydrogen bonding too, and it is 40% denser than water. It has high dielectric constant and so used as ionizing solvent, but its utility in this capacity is limited by its strong oxidizing nature, which makes it readily decompose in the presence of many heavy-metal ions as given in the equation below.



4.9. Sulfur

Sulfur is the second member of the oxygen group in the periodic table. Sulfur has more allotropic forms than any other elements. These different forms of allotropes are to the extent to which sulfur is polymerized and the crystal structure adopted. The α or rhombic and β or monoclinic sulfur are the two most common ones. Sulfur is not a gas unlike oxygen and has a significantly lower electronegativity. They only react with group one element to form ionic compounds. In many sulfur compounds, the d-orbital is used in bonding and these bonds appear shorter than expected, which suggest a double bond character. Sulfur can make up to six covalent bonds making use of its s-, p-, and d-orbitals. Sulfates and hexafluorides are examples of this instance.

Physical property of sulfur:

Symbol	Sulfur
Electron structure	(Ne) $3s^2 3p^4$
Electronegativity	2.5
I.E. (KJmol^{-1})	1000
Melting point ($^{\circ}\text{C}$)	114.5
Boiling point ($^{\circ}\text{C}$)	444.5
Atomic radius (pm)	104
Principal oxidation number	-2, +4, +6

Uses of sulfur:

Sulfur has several purposes of uses; it is mainly used as sulfuric acid. It is also used in fertilizer, explosives, dyes, detergents, polymers, and in processing of many other chemicals.

Extraction of sulfur:

Sulfur is found in many minerals, mostly in combination with copper, mercury, lead metals. Sulfur is obtained as the byproduct of the extraction of their ore. Sulfur is also directly extracted from the ground using a method called the *Frasch* process. Sulfur in the form of hydrogen sulfide is also obtained from oil and natural gas refineries.

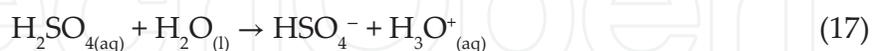
Sulfuric acid:

This is used in the manufacturing of superphosphate fertilizer, ammonium sulfate fertilizer, detergents, paper, rayon, polymer, and processing of metal ores. It is also used in the

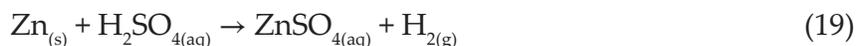
manufacture of paints and pigments, electrolytes for heavy duty batteries, and laboratory reagents. Sulfuric acid has a dynamic chemistry. In dilute solution, it behaves as a typically strong acid. When concentrated, it behaves both like an oxidizing and a dehydrating agent. It is also a sulfonating agent in organic chemistry.

Sulfuric acid as a strong acid:

In water, sulfuric acid behaves as a strong acid. It dissociates in to two stages

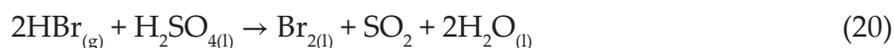


Only the first dissociation is complete; the second is partial. When it is diluted, it shows properties of an acid. It will evolve hydrogen when it reacts with metals



Sulfuric acid as oxidizing agent:

The acid shows oxidizing property in concentrated form. For example, sulfuric acid cannot be used to prepare hydrogen bromide from sodium bromide. This is because it can oxidize the hydrogen bromide produced.



This oxidizing property is a feature of sulfate ion. Since the ion has a high oxidation state of +6, it makes it to take electrons to revert to a lower oxidation state.

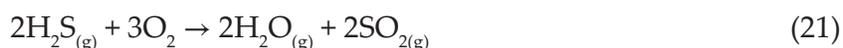
Sulfuric acid as a dehydrating agent:

Concentrated sulfuric acid will remove water from various organic compounds as can be noted when few drops of it are added to sugar (glucose). The sugar suddenly becomes very hot and frothy, leaving a black mass of carbon.

Sulfur hydrides:

Hydrogen sulfide is an important hydride of sulfur. It is a very poisonous gas, and when inhaled for some time, it can be fatal. The gas is made by mixing hydrochloric acid with a metal sulfide, often iron (II) sulfide.

Unlike water, hydrogen sulfide will burn in air with a pale blue flame.



A useful property of hydrogen sulfide is that it releases sulfide ions when dissolved in water.

5. Summary

The first part (Sections 1 to 4) of this chapter, which is based on research, discusses the nonterrestrial chemistry of oxygen, sulfur, and their compounds in the interstellar medium, while the second part of the chapter (Section 5) discusses about the basic inorganic chemistry of oxygen, sulfur, and oxygen. Both parts of this chapter point out the importance of these elements and their compounds in both terrestrial and nonterrestrial environments. Also, the importance of chemistry in these environments cannot be overemphasized.

6. Conclusions

The deviation of the observed S/O abundance from the rule that the ratio of an interstellar sulfur molecule to its oxygen analogue is close to the cosmic S/O ratio and the possibility of detecting other analogues of the known S- and O-containing species have been examined in this study. The effect of hydrogen bonding on the surface of the interstellar dust grains where these molecules are believed to be formed plays a vital role in the observed S/O abundance ratio. From the binding energy of these species with the water molecule on the surface of the dust grains, the more the molecules are strongly bonded to the surface of the dust grains, the more their abundances are reduced. As the ratio of the binding energy of S- and O-species (B. E. of S/O) with water approaches unity, the S/O abundance ratio approaches cosmic S/O ratio. When this ratio is less than one, the observed S/O abundance ratio becomes much higher than the cosmic S/O ratio and vice versa except for the species that are major components of the interstellar ice. With respect to the detectability of the unknown analogues of these species, every known O-species is an indication of the presence and detectability of the S-analogue. This has been shown to be true in many cases where the S-analogues of known O-species are successfully observed, following the detection of the O-analogues. That these S-containing species are less bonded to the surface of the interstellar dust grains as compared to their O-analogues firmly support the high abundances and the detectability of these species. For the known S-species whose O-analogues are yet to be observed, the O-analogues are not only present in detectable abundance, it can be said to have even been overdue for astronomical detection since the O-species without any exception are more abundant than their S-analogues and as such they could be detected with less difficulty as compared to their S-analogues that are already known. The second part of this chapter discusses the basic inorganic chemistry of hydrogen, oxygen, and sulfur.

Author details

Etim Emmanuel^{1*}, Lawal Usman¹, Khanal Govinda² and Mbakara Idaresit³

*Address all correspondence to: emmaetim@gmail.com

1 Department of Chemical Sciences, Federal University Wukari, Taraba State, Nigeria

2 Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

3 Department of Chemistry, University of Ibadan, Oyo State, Nigeria

References

- [1] Etim EE, Arunan E. Rotational spectroscopy and interstellar molecules. *Planex Newsletter*. 2015;5(2):16-21
- [2] Solomon PM, Jefferts KB, Penzias AA, Wilson RW. Carbon monoxide in the interstellar spectrum of zeta Ophiuchi. *The Astrophysical Journal*. 1971;168:L107
- [3] Cernicharo J, Kahane C, Guélin M, Gomez-Gonzalez J. The IRAM-30 m line survey of the horsehead PDR. III. High abundance of complex (iso-)nitrile molecules in UV-illuminated gas. *Astronomy & Astrophysics*. 1988;189:L1
- [4] Lovas FJ, Hollis JM, Remijan AJ, Jewell PR. Detection of Ketenimine (CH₂CNH) in Sagittarius B2(N) hot cores. *The Astrophysical Journal*. 2006;645:L137
- [5] Brown RD, Crofts JG, Godfrey PD, et al. Discovery of interstellar methyl formate. *The Astrophysical Journal*. 1975;197:L29
- [6] Mehringer DM, Snyder LE, Miao Y, Lovas F. Detection and confirmation of interstellar acetic acid. *The Astrophysical Journal*. 1997;480:L71
- [7] Hollis JM, Lovas FJ, Jewell PR. Interstellar Glycolaldehyde: The first sugar. *The Astrophysical Journal*. 2000;540:L107
- [8] Snyder LE, Buhl D. Observations of radio emission from interstellar hydrogen cyanide. *The Astrophysical Journal*. 1971;163:L47-L52
- [9] Zuckerman B, Morris M, Palmer P, Turner BE. Observations of CS, HCN, U99.2, and U99.7 in NGC 2264. *The Astrophysical Journal*. 1972;173:L125. *The Microwave Spectrum of HNC: Identification of U99.7*
- [10] Guélin M, Cernicharo J, Kahane C, Gomez-Gonzales J. A new free radical in IRC +10216. *Astronomy & Astrophysics*. 1986;157:17
- [11] Guélin M, Muller S, Cernicharo J, et al. Astronomical detection of the free radical SiCN. *Astronomy & Astrophysics*. 2000;369:9
- [12] Guélin M, Muller S, Cernicharo J, McCarthy MC, Thaddeus P. Detection of the SiNC radical in IRC +10216. *Astronomy & Astrophysics*. 2004;426:49
- [13] Ziurys LM, Apponi AJ. Detection of MgCN in IRC +10216: A new metal-bearing free radical. *The Astrophysical Journal*. 1995;455:L73
- [14] Hollis JM, Lovas FJ, Jewell PR, Coudert LH. Interstellar antifreeze: Ethylene glycol. *The Astrophysical Journal*. 2002;571:L59
- [15] Linke RA, Frerking MA, Thaddeus P. Interstellar methyl mercaptan. *The Astrophysical Journal*. 1979;234:L139
- [16] Etim EE, Gorai P, Das A, Arunan E. Interstellar protonated molecular species. *Advances in Space Science*. 2017;60:709-721. DOI: 10.1016/j.asr.2017.04.003

- [17] Etim EE, Inyang EJ, Ushie OA, Mbakara IE, Andrew C, Lawal U. Is ESA relationship the tool for searching for interstellar heterocycles? *FUW Trends in Science and Technology Journal*. 2017;**2**(2):665-678
- [18] Etim EE, Gorai P, Das A, Arunan E. Theoretical investigation of interstellar C–C–O and C–O–C bonding backbone molecules. *Astrophysics and Space Science*. 2018;**363**:6. DOI: 10.1007/s10509-017-3226-5
- [19] Etim EE, Mbakara IE, Inyang EJ, Ushie OA, Lawal U, Andrew C. Spectroscopy of linear interstellar carbon chain isotopologues: Meeting experimental accuracy. *Tropical Journal of Applied Natural Sciences*. 2017;**2**(1):11-16
- [20] Frisch MJ, Trucks GW, Schlegel HB, et al. G09:RevC.01. Wallingford CT: Gaussian, Inc.; 2009
- [21] Møller C, Plesset MS. Note on an approximation treatment for many-electron systems. *Physics Review*. 1934;**46**(7):618-622
- [22] Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA. Gaussian-3 (G3) theory for molecules containing first and second-row atoms. *The Journal of Chemical Physics, The Journal of Chemical Physics*. 1998;**109**:7764
- [23] Curtiss LA, Redfern PC, Raghavachari K. Gaussian-4 theory. *The Journal of Chemical Physics, The Journal of Chemical Physics*. 2007;**126**:084108
- [24] Curtiss LA, Redfern PC, Raghavachari K. Gaussian-4 theory using reduced order perturbation theory. *The Journal of Chemical Physics*. 2007;**127**:124105
- [25] Frerking MA, Linke RA, Thaddeus P. Interstellar isothiocyanic acid. *The Astrophysical Journal*. 1979;**234**:L143-L145
- [26] Ohishi M, Suzuki H, Ishikawa SI, et al. Detection of a new carbon-chain molecule, CCO. *The Astrophysical Journal*. 1991;**380**:L39-L42
- [27] Saito S, Kawaguchi K, Yamamoto S, et al. Laboratory detection and astronomical identification of a new free radical, CCS 3Sigma-. *The Astrophysical Journal*. 1987;**317**:L115
- [28] Yamamoto S, Saito S, Kawaguchi K, Kaifu N, Suzuki H. Laboratory detection of a new carbon-chain molecule C3S and its astronomical identification. *The Astrophysical Journal*. 1987;**317**:L119
- [29] Brown RD, Godfrey PD, Cragg DM, et al. Tricarbon monoxide in TMC-1. *The Astrophysical Journal*. 1985;**297**:302
- [30] Brünken S, Belloche A, Martín S, Verheyen L, Menten KL. Interstellar HOCN in the galactic center region. *Astronomy & Astrophysics*. 2010;**516**:A109
- [31] Halfen DT, Ziurys LM, Brünken S, et al. Detection of a new interstellar molecule: Thiocyanic acid HSCN. *The Astrophysical Journal*. 2009;**702**:L124
- [32] Wyrowski F, Menten KM, Güsten R, Belloche A. First interstellar detection of OH+. *Astronomy & Astrophysics*. 2010;**518**:A26

- [33] Menten KM, Wyrowski F, Belloche A, et al. Submillimeter absorption from SH⁺, a new widespread interstellar radical, ¹³CH⁺ and HCl. *Astronomy & Astrophysics*. 2011;**525**:A77
- [34] Neufeld DA, Falgarone E, Gerin M, et al. Discovery of interstellar mercapto radicals (SH) with the GREAT instrument on SOFIA. *Astronomy & Astrophysics*. 2012;**542**:L6
- [35] Weinreb S, Barrett AH, Meeks ML, Henry JC. Radio observations of OH in the interstellar medium. *Nature*. 1963;**200**:829
- [36] Kolesníková L, Tercero B, Cernicharo J, et al. Spectroscopic characterization and detection of ethyl mercaptan in orion. *The Astrophysical Journal*. 2014;**784**:L7
- [37] Pearson JC, Sastry KVLN, Herbst E, De Lucia FC. Gauche ethyl alcohol: Laboratory assignments and interstellar identification. *The Astrophysical Journal*. 1997;**480**
- [38] Thaddeus P, Guélin M, Linke RA. Three new “nonterrestrial” molecules. *The Astrophysical Journal*. 1981;**246**:L41
- [39] Penzias AA, Solomon PM, Wilson RW, Jefferts KB. Interstellar carbon monosulfide. *The Astrophysical Journal*. 1971;**168**:L53
- [40] Gottlieb CA, Ball JA, Gottlieb EW, Dickinson DF. Interstellar methyl alcohol. *The Astrophysical Journal*. 1979;**227**:422
- [41] Gottlieb CA, Ball JA, Gottlieb EW, Lada CJ, Penfield H. Detection of interstellar nitrogen sulfide. *The Astrophysical Journal*. 1975;**200**:L147
- [42] Liszt HS, Turner BE. Microwave detection of interstellar NO. *The Astrophysical Journal*. 1978;**224**:L73
- [43] Morris M, Gilmore W, Palmer P, Turner BE, Zuckerman B. Detection of interstellar SiS and a study of the IRC +10216 molecular envelope. *The Astrophysical Journal*. 1975;**199**:L47
- [44] Wilson RW, Penzias AA, Jefferts KB, Kutner N, Thaddeus P. Discovery of interstellar silicon monoxide. *The Astrophysical Journal*. 1971;**167**:L97
- [45] Gottlieb CA, Ball J. Interstellar sulfur monoxide. *The Astrophysical Journal*. 1973;**184**:L59
- [46] Goldsmith PF, Liseau R, Bell TA, et al. Herschel measurements of molecular oxygen in orion. *The Astrophysical Journal*. 2011;**737**:96
- [47] Sinclair MW, Fourikis N, Ribes JC, et al. Detection of interstellar thioformaldehyde. *Australian Journal of Physics*. 1973;**26**:85
- [48] Thaddeus P, Kutner ML, Penzias AA, Wilson WR, Jefferts KB. Interstellar hydrogen sulfide. *The Astrophysical Journal*. 1972;**176**:L73
- [49] Coutens A, Vastel C, Caux E, et al. A study of deuterated water in the low-mass protostar IRAS 16293-2422. *Astronomy & Astrophysics*. 2012;**539**:132
- [50] D’Hendecourt LB, de Muizon MJ. The discovery of interstellar carbon dioxide. *Astronomy & Astrophysics*. 1989;**223**:L5

- [51] Jefferts KB, Penzias AA, Wilson RW, Solomon PM. Detection of interstellar carbonyl sulfide. *The Astrophysical Journal*. 1971;**168**:L111
- [52] Smith AM, Stecher TP. Carbon monoxide in the interstellar spectrum of zeta Ophiuchi. *The Astrophysical Journal*. 1971;**164**:L43
- [53] Latter WB, Walker CK, Maloney PR. Detection of the carbon monoxide ion (CO⁺) in the interstellar medium and a planetary nebula. *The Astrophysical Journal*. 1993;**419**:L97
- [54] Walmsley CM, Bachiller R, Pineau des Forêts G, Schilke P. Detection of FeO toward Sagittarius B2. *The Astrophysical Journal*. 2002;**566**:L109
- [55] Tenenbaum ED, Woolf NJ, Ziurys LM. Identification of phosphorus monoxide (X 2Pi_r) in VY Canis Majoris: Detection of the first P-O bond in space. *The Astrophysical Journal*. 2007;**666**:L29
- [56] Marcelino N, Cernicharo J, Tercero B, Roueff E. Discovery of fulminic acid, HCNO, in dark clouds. *The Astrophysical Journal*. 2009;**690**:L27
- [57] Kamiński T, Gottlieb CA, Menten KM, et al. Pure rotational spectra of TiO and TiO₂ in VY Canis Majoris. *Astronomy & Astrophysics*. 2013;**551**:A113
- [58] Cernicharo J, Bailleux S, Alekseev E, et al. Tentative detection of the nitrosylium ion in space. *The Astrophysical Journal*. 2014;**795**:40
- [59] Tenenbaum ED, Ziurys LM. Millimeter detection of AlO (X 2Sigma⁺): Metal oxide chemistry in the envelope of VY Canis Majoris. *The Astrophysical Journal*. 2009;**693**:L59
- [60] Ziurys LM, Apponi AJ, Hollis JM, Snyder LE. Detection of interstellar N₂O: A new molecule containing an N-O bond. *The Astrophysical Journal*. 1994;**436**:L181
- [61] Snyder LE, Hollis JM, Ulich BL. Radio detection of the interstellar formyl radical. *The Astrophysical Journal*. 1976;**208**:L91
- [62] Snyder LE, Kuan Y-J, Ziurys LM, Hollis JM. New 3 millimeter observations of interstellar HNO—Reinstating a discredited identification. *The Astrophysical Journal*. 1993;**403**:L17
- [63] Ziurys LM, Apponi AJ, Guélin M, Cernicharo J. Detection of MgCN in IRC +10216: A new metal-bearing free radical. *The Astrophysical Journal*. 1995;**445**:47
- [64] Soifer BT, Puetter RC, Russell RW. The 4-8 micron spectrum of the infrared source W33A. *The Astrophysical Journal*. 1979;**232**:L53
- [65] Ossenkopf V, Müller HSP, Lis DC, et al. Detection of interstellar oxidaniumyl: Abundant H₂O⁺ towards the star-forming regions DR21, Sgr B2, and NGC6334. *Astronomy & Astrophysics*. 2010;**518**:L111
- [66] Parise B, Bergman P, Du F. Detection of the hydroperoxyl radical HO₂ toward ρ Ophiuchi a. additional constraints on the water chemical network. *Astronomy & Astrophysics*. 2012;**541**:L11
- [67] Tenenbaum ED, Ziurys LM. Exotic metal molecules in oxygen-rich envelopes: Detection of AlOH (X1Sigma⁺) in VY Canis Majoris. *The Astrophysical Journal*. 2010;**712**:L93

- [68] Wootten A, Boulanger F, Bogey M, et al. A search for interstellar H_3O^+ . *Astronomy & Astrophysics*. 1986;**166**:L15
- [69] Bogey M, Demuyne C, Destombes JL. Laboratory detection of the protonated carbon dioxide by submillimeter wave spectroscopy. *Astronomy & Astrophysics*. 1984;**138**:L11
- [70] Bergman P, Parise B, Liseau R, et al. Detection of interstellar hydrogen peroxide. *Astronomy & Astrophysics*. 2011;**531**:L8
- [71] Winnewisser G, Churchwell E. Detection of formic acid in Sagittarius B2 by its 2(11)-2(12) transition. *The Astrophysical Journal*. 1975;**200**:L33
- [72] Turner BE. Microwave detection of interstellar ketene. *The Astrophysical Journal*. 1977;**213**:L75
- [73] Ohishi M, Ishikawa S, Amano T, Oka H, Irvine WM, Dickens JE, et al. Detection of a new interstellar molecular ion, H_2COH^+ (protonated formaldehyde). *The Astrophysical Journal*. 1996;**471**:L61
- [74] Remijan AJ, Hollis JM, Lovas FJ, et al. Detection of interstellar cyanoformaldehyde (CNCHO). *The Astrophysical Journal*. 2008;**675**:L85
- [75] Cernicharo J, Marcelino N, Roueff E, et al. Discovery of the Methoxy radical, CH_3O , toward B1: Dust grain and gas-phase chemistry in cold dark clouds. *The Astrophysical Journal*. 2012;**759**:L43
- [76] Gupta H, Gottlieb CA, Lattanzi V, Pearson JC, McCarthy MC. Laboratory measurements and tentative astronomical identification of H_2NCO^+ . *The Astrophysical Journal*. 2013;**778**:L1
- [77] Rubin RH, Swenson GW Jr, Solomon RC, Flygare HL. Microwave detection of interstellar formamide. *The Astrophysical Journal*. 1971;**169**:L39
- [78] Irvine WM, Brown RD, Craig DM, et al. A new interstellar polyatomic molecule: Detection of propynal in the cold cloud TMC-1. *The Astrophysical Journal*. 1988;**335**:L89
- [79] Hollis JM, Remijan AJ, Jewell PR, Lovas FJ. Cyclopropenone ($c\text{-H}_2\text{C}_3\text{O}$): A new interstellar ring molecule. *The Astrophysical Journal*. 2006;**642**:933
- [80] Gilmore W, Morris M, Palmer P, et al. Observation of the 6(16)-5(15) transitions of acetaldehyde in Sagittarius B2. *The Astrophysical Journal*. 1976;**204**:43
- [81] Dickens JE, Irvine WM, Ohishi M, et al. Detection of interstellar ethylene oxide ($c\text{-C}_2\text{H}_4\text{O}$). *The Astrophysical Journal*. 1997;**489**:753
- [82] Turner BE, Apponi AJ. Microwave detection of interstellar vinyl alcohol. CH_2CHOH . *The Astrophysical Journal*. 2001;**561**:L207
- [83] Hollis JM, Jewell PR, Lovas FJ, Remijan A, Møllendal H. Green bank telescope detection of new interstellar aldehydes: Propenal and propanal. *The Astrophysical Journal*. 2004;**610**:L21
- [84] Remijan AJ, Snyder LE, McGuire BA, et al. *The Astrophysical Journal*. 2014;**783**:77

- [85] Snyder LE, Buhl D, Schwartz PR, et al. Radio detection of interstellar dimethyl ether. *The Astrophysical Journal*. 1974;**191**:L79
- [86] Hollis JM, Lovas FJ, Remijan AJ, et al. Detection of acetamide (CH₃CONH₂): The largest interstellar molecule with a peptide bond. *The Astrophysical Journal*. 2006;**643**:L25
- [87] Snyder LE, Lovas FJ, Mehringer DM, et al. Confirmation of interstellar acetone. *The Astrophysical Journal*. 2002;**578**:245
- [88] Belloche A, Garrod RT, Müller HSP, et al. Increased complexity in interstellar chemistry: Detection and chemical modeling of ethyl formate and n-propyl cyanide in Sagittarius B2(N). *Astronomy & Astrophysics*. 2009;**499**:215
- [89] Tercero B, Kleiner I, Cernicharo J, et al. Discovery of methyl acetate and gauche ethyl formate in orion*. *The Astrophysical Journal*. 2013;**770**:L13
- [90] Fuchs GW, Fuchs U, Giesen TF, Wyrowski F. Trans-ethyl methyl ether in space a new look at a complex molecule in selected hot core regions. *Astronomy & Astrophysics*. 2005;**444**:521
- [91] Snyder LE, Hollis JM, Ulich BL, et al. Radio detection of interstellar sulfur dioxide. *The Astrophysical Journal*. 1975;**198**:L81
- [92] Turner BE. Detection of interstellar SO(+)—A diagnostic of dissociative shock chemistry. *The Astrophysical Journal*. 1992;**396**:L107
- [93] Agúndez M, Cernicharo J, Guélin M. New molecules in IRC +10216: Confirmation of C₅S and tentative identification of MgCCH, NCCP, and SiH₃CN**. *Astronomy & Astrophysics*. 2014;**570**:A45
- [94] Etim EE, Gorai P, Das A, Chakrabarti SK, Arunan E. Interstellar hydrogen bonding. *Advances in Space Research*. 2018;61(11):2870-2880. DOI: 10.1016/j.asr.2018.03.003
- [95] Vidal THG, Wakelam V. A new look at Sulphur chemistry in hot cores and corinos. *Monthly Notices of the Royal Astronomical Society*. 2018;**474**:5575
- [96] Fuente A, Goicoechea J-R, Pety J, et al. First detection of interstellar S₂H. *The Astrophysical Journal*. 2017;**851**:L49
- [97] Vidal THG, Loison J-C, Jaziri AY, et al. On the reservoir of Sulphur in dark clouds: Chemistry and elemental abundance reconciled. *Monthly Notices of the Royal Astronomical Society*. 2017;**469**:435