INTERSTELLAR C₃S: DIFFERENT DIPOLE MOMENT, DIFFERENT COLUMN DENSITY, SAME ASTRONOMICAL SOURCE

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Abstract: Investigation of the physical and chemical conditions of the different molecular clouds requires accurate knowledge of the abundances and distributions of the various molecules. Abundances of interstellar and circumstellar species are vital parameters for astronomical and astrophysical models. These abundances rely on the dipole moments of the molecules. The more accurate the dipole moments are, the more reliable the estimated abundances resulting in highly plausible models. The linear carbon chain molecule, C₃S with singlet ground state has been astronomically observed by three different sets of researchers with each of them using a different dipole moment to calculate the column density, thus resulting in different column density for the same molecule even from the same astronomical source, thereby posing a constraint on the use of these values for astronomical and astrophysical models. This article reports theoretically calculated dipole moment for this molecule with excellent agreement with the experimentally measured value which could be used in estimating accurate column abundance for this molecule. Recalculation of the abundance of this molecule is necessary due to the difference in the values of the dipole moments previously used in estimating the abundance of C₃S.

Keywords: Astrochemistry, column density, dipole moment, interstellar molecule, periodic trends

Introduction

The early astronomical observations witnessed the detection of molecules composed of only four elements; H, C, N and O from the first two rows of the periodic table leading to the earlier conclusion that interstellar molecules are only composed of these four elements. The subsequent astronomical observations of sulphur compounds (from the 1970s) in interstellar medium (ISM) and circumstellar envelopes (CEs) serve as the main exception to this earlier conclusion. The unique astronomical detections of 19 different interstellar sulphur containing molecules, conspicuously established the prevalence of S-compound in interstellar medium and circumstellar envelopes.

Table 1 gives a chronological list of the known S-containing molecules and their corresponding O-analogues (where available). The year 2014 was astronomically very successful with nine new interstellar molecules detected as compared to the yearly average of four molecules, (Kolesnikova *et al.,* 2014; Belloche *et al.,* 2014; Anderson & Ziurys 2014; Remijan *et al.,* 2014; Cernicharo *et al.,* 2014; Agundez *et al.,* 2014). Of the nine molecules observed in 2014, two are S-containing molecules; ethyl mercaptan (CH₃CH₂SH) and C₅S.

Table 1: Chronological listing of interstellar S-containing molecules and their O-analogues

S-containing molecule	O-analogue
CS (1971)	CO (1970)
OCS (1971)	CO₂ (1989)
H₂S (1972)	H₂O (1969)
H₂CS (1973)	H₂CO (1969)
SO (1973)	O₂ (2011)
SO₂ (1975)	*O₃ not observed*
SiS (1975)	SiO (1971)
NS (1975)	NO (1978)
CH₃SH (1979)	CH₃OH (1970)
HNCS (1979)	HNCO (1972)
HCS⁺ (1981)	HCO⁺ (1970)
C₂S (1987)	C₂O (1991)
C₃S (1987)	C₃O (1985)
SO⁺ (1992)	*O₂⁺ not observed*
HSCN (2009)	HOCN (2009)
SH⁺ (2011)	OH⁺ (2010)
SH (2012)	OH (1963)
CH₃CH₂SH (2014)	CH₃CH₂OH (1975)
C₅S (2014)	*C₅O not observed*

The close relationship of the chemistry of S and O-containing molecules in ISM can easily be comprehended by the fact that of the 19 S-containing molecules observed in ISM, 16 have the corresponding O-containing molecules uniquely detected in ISM. Notwithstanding the differences which may exist in the interstellar space between the chemistries of sulphur and oxygen, a simple guideline has proven effective in searching for new sulphur containing molecules in ISM, i.e. the abundance of S-compound relative to its O-analogue is approximately equal to the cosmic S/O ratio, 1/42 as seen in methyl mercaptan, thioisocyanic acid, etc., except where other factors dominate (Linke *et al.,* 1979; Frerking *et al.,* 1979).

Astrophysical and astronomical models give insight into the heart of what is going on, unfolding the existence of phenomena and effects that would otherwise not have been known. With respect to interstellar molecules, these models help in elucidating some of the properties of the known molecules, give insight about the unknown and the ones that are highly plausible for astronomical observations. These models rely greatly on the estimated column densities (or abundances) of the known interstellar and circumstellar molecules (Muller and Woon 2013). Accurate column density depends on accurate dipole moment. Dipole moment contributes to the intensities of rotational transitions and also affects the reactivity of the molecule. The intensities of rotational transitions scale with the square of the dipole moment, the higher the dipole moment, the higher the intensity of the lines. Dipole moment determination depends on Stark effect measurement. About 80% of all the known interstellar and circumstellar molecules have been detected via their rotational transition spectra (Etim and Arunan, 2015; Etim *et al.,* 2016a,b; Etim *et al.,* 2017a,b,c). The Fourier transform microwave spectroscopy used in determining the rotational spectra of these molecules is not commonly used in measuring Stark effect due to the unstable nature of some of the molecules generated by discharge. For charged molecules, the electric field causes a frequency shift due to acceleration or deceleration of the ion thereby making Stark effect measurement a nearly impossible task. Theoretically calculated dipole moments are well embraced in estimating

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574

the abundances of interstellar and circumstellar molecules due to the difficulty in applying external field to the discharge plasma for Stark effect measurement in the laboratory. This has been shown to be very successful with good agreement between high-level theory and experimental values (where available) indicating that the predictions for other species are likely to be very reliable (Lovas *et al.,* 1992; Muller and Woon 2013).

C_3S, the sulphur analogue of C_3O has been experimentally and theoretically shown to be a linear molecule with a singlet ground state, (Saito *et al.,* 1987; Yamamoto *et al.,* 1987). C_3S has been detected in the interstellar space by three different sets of researchers (Cernicharo *et al.,* 1987; Bell *et al.,* 1993; Yamamoto *et al.,* 1987), two of these astronomical observation were made from the same source (IRC+10216) while the other was made from a different source (TMC). Surprisingly, all of these groups used different values of dipole moment in estimating the column abundance of this molecule, thus resulting in different estimates for the column abundance of C_3S even from the same astronomical source in which the values are expected to be approximately same as seen in case of its oxygen analogue, C_3O, where the abundance from the same astronomical source (TMC-1) estimated by different sets of researchers is approximately same ($\approx 1*10^{12}$ cm^{-2}), (Brown *et al.,* 1985; Mathews *et al.,* 1984). The inconsistent abundance estimated for interstellar C_3S has placed a constraint on the accurate estimate of C_3S abundance in ISM and CEs for application in astronomical and astrophysical models of interstellar and circumstellar molecules. This article reports accurate theoretically calculated dipole moment for C_3S with excellent agreement with the experimentally measured value ($<\pm0.1D$) that can be used in estimating consistent interstellar abundance for C_3S.

Computational details

All the calculations reported here are done using Gaussian 09 suite of programs (Frisch *et al.,* 2009). Different levels of theory ranging from the less expensive to the high level quantum chemical calculation methods are employed in order to estimate accurate dipole moment, these include; the Hartree-Fock (HF), reduced Hartree-Fock (RHF) (Pople&Nesbet, 1954), the Becke (1996), three-parameter correlation functional of Lee, Yang, and Parr, (B3LYP) (Lee *et al.,* 1988), the second (MP2) and third (MP3) orders order Møller–Plesset perturbation methods (Head-Gordon *et al.,* 1988; Pople *et al.,* 1977), coupled cluster using single and double substitutions (CCSD) (Čížek 1966), Weizmann theory (W1U and W2U) (Martin & de Oliveira 1999; Parthiban & Martin 2001), Gaussian methods (G2, G3, G4 and G4MP2) (Curtiss *et al.,* 1998, 2007a,b), complete basis set (CBS) and the configuration integration (CI) method with single (CIS) and double (CISD) substitutions (Foresman *et al.,* 1992; Etim *et al.,* 2016a,b; Etim *et al.,* 2017a,b,c). Taking into cognizance the importance of appropriate choice of basis set, we employed the augmented Dunning's correlation consistent basis sets (pvdz, pvtz, pvqz) and the commonly used 6-31G*, 6-311G* basis sets (Dunning Jr., 1989). The stationary point geometries were fully optimized and confirmed by harmonic vibrational frequency calculations where equilibrium species possess no imaginary frequency.

Results and Discussion

Table 2 shows the theoretically calculated dipole moment for C_3S. The values reported in Table 2 are in excellent agreement with the experimentally measured value (3.704D; Suenram&Lovas, 1994) with the difference between the theoretically calculated and the experimentally measured values of less than ±0.01D. Other values outside this excellent

agreement from other levels of theory and basis sets are reported in the appendix.

Table 2: Dipole moment of C₃S from different levels of theory and basis sets

Method	Dipole moment (in Debye)	Calc.- expt (3.704)
B3LYP/aug-cc-pvdz	3.614	-0.090
B3LYP/aug-cc-pvtz	3.733	0.029
B3LYP/aug-cc-pvqz	3.773	0.069
W1U	3.625	0.079
W2U	3.781	0.077
CI/aug-cc-pvdz	3.737	0.033

The different theoretically calculated values of different moment reported for C_3S (indicated with green) in literature, the value for from the present work (indicated with red) and the experimentally measured value (indicated with red) are depicted in Fig. 1. From the plot, it is crystal clear that the result from the present work is in excellent agreement with the experimentally measured value as compared with other reported values in literature.
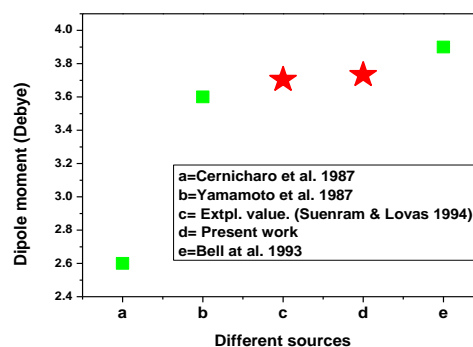

Fig. 1: Plot of the experimental dipole moment of C_3S in comparison with theoretically calculated values.

The different values of dipole moment reported in literature for C_3S have been used in estimating the column density (abundance) of this molecule from the same and different molecular clouds/astronomical sources. The reported abundances for interstellar C_3S are tabulated in Table 3. It is normal to expect the interstellar abundance of a molecule from the same source estimated by different groups/scientists to be same or approximately same as seen in the case of the oxygen analogue of C_3S (Brown *et al*., 1985; Mathews *et al*., 1984) but this is not observed in the reported values for the interstellar abundance of C_3S. The reason beside this is quite simple, the different groups used different values of dipole moment in estimating the column abundance of C_3S thereby resulting in different values even for the same astronomical source (IRC+10216). The values of dipole moment used in estimating the reported column density of C_3S differs from the experimental value in the range of -1.104 to 0.196D.

Table 3 depicts the direct link between the dipole moment of a molecule and its column density. The higher the dipole moment of a molecule, the lower its estimated column density and vice versa. Equation 1 below shows the relation used in estimating the column density of the upper state for an optically thin transition (e.g C_3S).

$$N_u = \frac{8\pi k v^2}{hc^3 A_{ul}\eta_{mb}} \int T_A dv$$

Where: A_{ul} = Einstein coefficient for spontaneous emission; η_{mb}= main beam efficiency of the; telescope; T_A= Antenna temperature; k= Boltzmann constant; h= Planck constant; c= Speed of light and v= frequency of the transition.

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575

Table 3: Column density of C3S estimated with different dipole moment values

Dipole moment (cal.)	Calc.-expt	Column density (cm⁻²)	Astronomical source
2.6D	*-1.104*	*1.1 *10¹⁴*	*IRC+10216[a]*
3.9±0.1D	*0.196*	*6.7*10¹²*	*IRC+10216[b]*
3.6D	-0.104	1.3±0.6*10¹³	TMC[c]

[a]Cernicharo *et al.,* 1987; [b]Bell *et al.,* 1993; [c]Yamamoto *et al.,* 1987

The quantity, A_{ul}, depends on the *dipole moment*, angular momentum of the upper state and the frequency of the transition. Hence, inaccurate value of dipole moment has a direct effect on the final value of the column density of the molecule as seen in the case of C_3S, where three different values of dipole moment have resulted in three different values of column density for the same molecule, the astronomical source notwithstanding. The reported column abundances for C_3S place a serious constraint on the use of these values for astronomical and astrophysical models of interstellar/circumstellar molecules, because different experts could choose to use different reported column density for C_3S since there is no consensus value even for the observation from the same astronomical source, thus leading to likely misleading and non-plausible models.
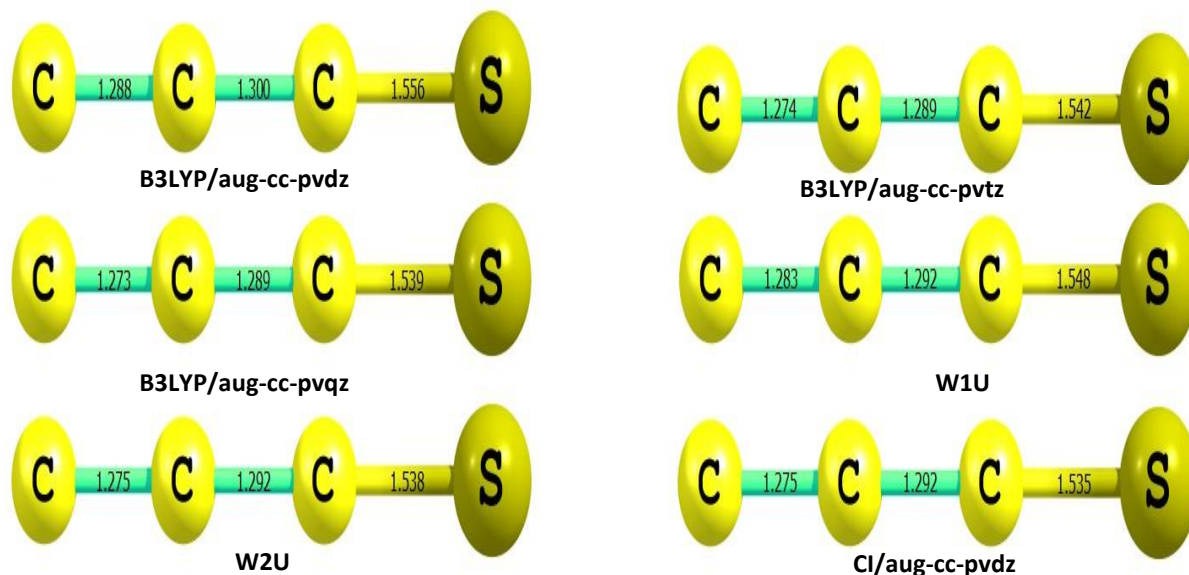

Fig. 2: Optimized geometry of C_3S from different levels of theory and basis sets

Figure 2 shows the optimized geometry of C_3S with the bond length from the different methods and basis sets that predict the dipole moment in excellent agreement with the experimental value (Table 1). C_3S has been shown to be linear from both experimental measurements and theoretical calculations (Peeso*et al.,* 1990; Saito *et al.,* 1987; Yamamoto *et al.,* 1987); the methods adopted here for the accurate dipole moment determination of C_3S are in excellent agreement with this fact as all the methods also predict linear structure for C_3S. The bond lengths between the carbon atoms (the first and second carbons; the second and the third carbons) are close to each other in all the cases suggesting a cumulated bond among the carbon atoms rather than an alternating single and triple bonds (Peeso *et al.,* 1990).

Conclusion

Accurate dipole moment of C_3S has been theoretically calculated with excellent agreement with the experimental value. The different values of dipole moment used in calculating the interstellar abundance of C_3S has been shown to be responsible for the different values obtained for the same molecule even in the same molecular cloud thereby placing a constraint on the use of these values in astrophysical and astronomical models. A recalculation of the column density of C_3S using accurate dipole moment reported in this study is necessary in order to provide accurate and reliable column density for this molecule for the same and different molecular clouds.

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576

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Appendix: The dipole moments calculated for C₃S from all the methods employed in this study are shown below (Table 2). The values that are in excellent agreement with the experimental value are indicated with red; these values are presented and discussed in Table 1.

Table 4: Dipole moments calculated for C₃S from all the methods employed in this study

Method	Dipole moment	Calc.- expt (3.704)
HF/6-31G*	2.645	-1.059
HF/6-311G*	3.128	-0.576
HF/aug-cc-pvdz	3.189	-0.515
HF/aug-cc-pvtz	3.356	-0.348
HF/aug-cc-pvqz	2.818	-0.886
RHF/6-31G*	2.645	-1.059
RHF/6-311G*	3.128	-0.576
B3LYP/6-31G*	3.042	-0.662
B3LYP/6-311G*	3.497	-0.207
B3LYP/aug-cc-pvdz	*3.614*	*-0.090*
B3LYP/aug-cc-pvtz	*3.733*	*0.029*
B3LYP/aug-cc-pvqz	*3.773*	*0.069*
MP2/6-31G*	2.451	-1.253
MP2/6-311G*	2.911	-0.793
MP2/aug-cc-pvdz	2.888	-0.816
MP2/aug-cc-pvtz	3.089	-0.624
MP3/6-31G*	2.611	-1.093
MP3/6-311G*	3.092	-0.612
MP3/aug-cc-pvdz	3.970	0.266
CCSD/6-31G*	3.530	-0.174
CCSD/6-311G*	4.046	0.342
CCSD/aug-cc-pvdz	3.907	0.203
W1U	3.625	0.079
W2U	3.781	0.077
G2	2.412	-1.292
G3	2.412	-1.292
G4MP2	3.214	-0.490
G4	3.214	-0.490
CBS-QB3	3.551	-0.153
CI/6-31G*	3.299	-0.405
CI/6-311G*	3.317	-0.387
CI/aug-cc-pvdz	*3.737*	*0.033*
CIS/6-31G*	1.814	-1.89
CIS/aug-cc-pvdz	2.267	-1.437
CISD/6-31G*	3.314	-0.39
CISD/6-311G*	3.831	0.127

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577