Eur. Phys. J. D **27**, 109–113 (2003)
DOI: 10.1140/epjd/e2003-00257-7

THE EUROPEAN
PHYSICAL JOURNAL D

Molecular properties of selected diatomic molecules of astrophysical interest

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Received 28 March 2003

Abstract. Molecular properties such as bond length, dipole moment, harmonic frequency, IR intensity, atomization energy, electron affinity and ionization potential of the selected diatomic molecules of astrophysical interest have been studied using hybrid density functional HF/DF B3LYP method. The consistency and convergence of the results have been tested with four basis sets from 6-311++G (2df, 2pd) to aug-cc-pVTZ with improved size and quality. Most of the results for dipole moment, harmonic frequency, IR intensity, electron affinity and ionization potential are new. The reported results agree well with theoretical and experimental data wherever available.

PACS. 31.15.Ew Density-functional theory – 33.15.Ry Ionization potentials, electron affinities, molecular core binding energy – 33.15.Dj Interatomic distances and angles – 33.15.Fm Bond strengths, dissociation energies

1 Introduction

Recently, in a series of papers Turner *et al.* [1–3] discussed about the physics and chemistry of small translucent molecular clouds and the formation and identification of small diatomic molecules such as CS, SiO, SO, ClO, SiS, SiN in the interstellar medium (ISM). Among silicon bearing molecules, SiO is the most widespread and shows a large variation in abundance under varying physical conditions [3]. The SO molecule plays an important role in the chemical processes which follow the photo-dissociation of SO_2 or OCS occurred in the atmospheres of Venus [4], Io [5], the Earth [6] and in interstellar clouds [7]. The formation and abundance of the cationic species CS^+, SO^+, SiO^+ and SiS^+ in the medium through different reaction processes are also described in detail [2,3]. The radical ClO is of great interest because they are central to the ClO_x cycle responsible for the depletion of ozone in the stratosphere [8]. It is also noted that SiN has been predicted abundances that might be detectable in translucent clouds, but not in cold dense clouds [3]. However, the detection of these molecules has been greatly facilitated if their molecular properties such as bond length, dipole moment, harmonic frequencies, IR intensities, atomization energies, electron affinities and ionization potentials are known accurately in their ground and excited states. Different experimental techniques have been adopted to estimate particularly the bond lengths and harmonic frequencies of these molecules in their ground state but the theoretical works in this regard are very limited. Among different experimental techniques, spectroscopic techniques of Herzberg [9], Huber and Herzberg [10], and Maki *et al.* [11], multiphoton ionization spectroscopy of Duignan and Hudgens [12], radio frequency spectroscopy of Field and Bergman [13], photoelectron spectroscopy of Gilles *et al.* [14] are important. The theoretical approaches applied so far for studying these molecules are CCSD(T) method of Martin [15] and G1 and G2 methods of Curtiss *et al.* [16].

Due to lack of theoretical and experimental data, particularly for the dipole moment, harmonic frequency, IR intensity, electron affinity, and ionization potential we studied the molecular properties of these astrophysically important molecules in their ground states with reasonable accuracy. The consistency and convergence of the results have been verified using different basis sets with improved size and quality.

2 Method

In the present article we have used hybrid HF/DF B3LYP method to study the molecular properties. The form of a variant of Becke's 3 parameters hybrid HF/DF method [17,18] can be written as

$$\begin{aligned}E = {}& AE_x^{\text{Slater}} + (1-A)E_x^{\text{HF}} \\ &+ B\Delta E_x^{\text{Becke}} + E_C^{\text{VWN}} + C\Delta E_C^{\text{nonlocal}}\end{aligned}$$

where E_x^{Slater} and E_x^{Becke} refer to Slater's local spin density approximation [19] and Becke's gradient corrected expression [20] for exchange energies, E_x^{HF} refers to an HF energy, E_C^{VWN} represents Vosko, Wilk, and Nusair's

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Table 1. Bond lengths (Å) for selected diatomic molecules of astrophysical interest.

	Basis set				Other values	
Molecule	6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Theor.	Expt.
SiN	1.569	1.566	1.573	1.574		1.571[a]
CS	1.534	1.532	1.537	1.536		1.534[a]
CS^+	1.488	1.486	1.491	1.491		1.495[a]
SiO	1.514	1.512	1.519	1.519		1.510[a]
SiO^+	1.523	1.521	1.530	1.530		
SO	1.493	1.488	1.500	1.499		1.493[b]
SO^+	1.425	1.421	1.431	1.431		1.42[a]
ClO	1.584	1.576	1.593	1.590		1.570[a]
SiS	1.941	1.938	1.945	1.945		1.929[a]
SiS^+	1.927	1.923	1.932	1.932		

[a] Reference [10]; [b] reference [9].

local correlation functional [21] and E_C^{nonlocal} is the nonlocal term. Using the gradient corrected functional of Perdew (P86) [22] for the nonlocal term in the above expression, the parameters $A = 0.20$, $B = 0.72$, and $C = 0.81$ were obtained empirically to reproduce experimental energies and molecular properties. For this study, the gradient corrected correlation functional of Perdew for the nonlocal term has been replaced by that of Lee, Yang and Parr (LYP) [23]. Bauschlicher and Patridge [24] showed that the thermochemical accuracy can be achieved by using the parameters A, B, and C fixed to B3P86 and the LYP functional as well. Moreover, the B3LYP method [17,18,25] has been applied successfully in the past to reproduce molecular properties including geometries, frequencies, electron affinities of numerous polyatomic [26,27]. All calculations have been carried out using Gaussian 98 [28] suite of quantum chemistry programs.

3 Results and discussions

In this communication we have studied bond length, dipole moment, harmonic frequency, IR intensity, electron affinity, atomization energy, and ionization potential of the selected diatomic molecule of astrophysical interest using the hybrid HF/DF B3LYP method. The consistency and convergence of the calculated results have been confirmed to check the values at four different basis sets from 6-311++G(2df, 2pd) to correlation consistent aug-cc-pVTZ of Dunning *et al.* [29–34]. In Table 1 we have summarized the calculated bond lengths of the selected diatomic molecules at different basis sets along with the experimental results of Herzberg [9] and Huber and Herzberg [10]. In general good agreement is observed between the calculated values and the experimental results. For CS^+ molecule, for example, the deviation from experimental value is about 0.004 Å at the highest basis set aug-cc-pVTZ. The improvement of the quality of the basis set increases the bond length of about 0.007 Å and it ultimately converges at the higher basis set aug-cc-pVTZ. The maximum deviation of about 0.020 Å is noticed for ClO molecule at aug-cc-pVTZ basis set but the calculated bond length at 6-311++G (3df, 3pd) basis set agrees very well with experimental value. Similar situation is observed for the SiO, SO^+ and SiS molecules; the bond lengths calculated at 6-311++G (3df, 3pd) gives much better agreement than that calculated using other basis sets. In general the bond length increases with improvement of the quality of basis set from 6-311++G (3df, 3pd) to aug-cc-pVTZ.

The calculated dipole moments of these molecules are displayed in Table 2 along with the experimental results wherever available. The dipole moments of CS and SO molecules at aug-cc-pVTZ are little bit lower than the experimental values [13,35] but the calculated value at 6-311++G (2df, 2pd) agrees very well with the experiment. But for ClO molecule, the dipole moment calculated at aug-cc-pVTZ basis set agrees much better than that estimated by using other basis sets. In general the dipole moment decreases with the improvement of the quality of basis set from 6-311++G (2df, 2pd) to aug-cc-pVTZ but for CS^+ and SiS^+, the dipole moment increases at aug-cc-pVTZ compared to that calculated at 6-311++G (3df, 3pd).

Table 3 compares the calculated and experimental harmonic frequencies. The calculated IR intensities are given in the parenthesis. The experimental results are available for most of the molecules except for the two cationic species SiO^+ and SiS^+. The theoretical coupled cluster result is available only for SO molecule. For SO, our calculated frequency at 6-311++G (3df, 3pd) agrees well with the CCSD(T) result of Martin [15] using AV5Z2d1f basis set. The experimental result of Clerbaux [36] is little higher than that of Huber and Herzberg [10]. Our calculated value at aug-cc-pVTZ agrees very well with the experimental value [10]. Excellent agreement is also obtained for SO^+, ClO and SiO with aug-cc-pVTZ basis set, the deviation between the estimated values and the experimental results varies from 1 to 5 cm^{-1}. The discrepancy

Table 2. Dipole moment (Debye) for selected diatomic molecules of astrophysical interest.

Molecule	Basis set				Other values	
	6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Theor.	Expt.
SiN	2.864	2.862	2.644	2.857		
CS	1.983	1.990	1.871	1.923		1.98[a]
						1.958[b]
CS^+	0.514	0.518	0.562	0.561		
SiO	3.216	3.209	2.987	3.200		
SiO^+	4.426	4.419	4.366	4.394		
SO	1.639	1.552	1.574	1.559		1.550[a]
SO^+	2.324	2.291	2.302	2.281		
ClO	1.411	1.329	1.340	1.311		1.262[a]
SiS	1.840	1.796	1.813	1.838		
SiS^+	3.529	3.497	3.561	3.533		

[a]Reference [35]; [b]reference [13].

Table 3. Harmonic frequency (cm^{-1}), IR intensity (km/mole) for selected diatomic molecules of astrophysical interest.

Molecule	Basis set				Other values	
	6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Theor.	Expt.
SiN	1180 (28.79)	1184 (28.42)	1178 (22.68)	1175 (28.29)		1151[a]
CS	1307 (88.35)	1313 (87.21)	1304 (88.35)	1305 (85.56)		1285[b]
CS^+	1413 (17.09)	1419 (17.23)	1409 (16.42)	1409 (16.34)		1385[a]
SiO	1253 (55.78)	1252 (55.09)	1252 (46.38)	1247 (56.68)		1242[c]
SiO^+	1142 (2.40)	1141 (2.05)	1134 (2.68)	1131 (2.65)		
SO	1152 (18.89)	1157 (20.13)	1148 (11.39)	1146 (18.04)	1158[d]	1149[a]
						1151[e]
SO^+	1366 (5.73)	1372 (5.64)	1363 (5.06)	1359 (5.05)		1360[a]
ClO	855 (3.35)	860 (2.06)	846 (5.20)	852 (2.96)		854[f,g]
SiS	744 (52.56)	746 (51.68)	742 (48.53)	741 (51.86)		749[a]
SiS^+	708 (11.61)	711 (10.81)	703 (11.36)	703 (11.27)		

[a]Reference [10]; [b]reference [13]; [c]reference [9]; [d]reference [15]; [e]reference [36]; [f]reference [12]; [g]reference [11].
Note: IR intensities are given in the parenthesis.

is relatively large for CS^+, SiN and CS molecules, the deviation is about 20 to 25 cm^{-1}.

The electron affinities of these molecules are displayed in Table 4 along with the experimental value. Excellent agreement is obtained for ClO between the estimated value using aug-cc-pVTZ basis set and the experimental result [14]. It should be noted here that the electron affinity values calculated using aug-cc-pVTZ basis set are higher than that calculated using cc-pVTZ basis set for most of the molecules studied here except for SiO where the two values are almost equal. The two other electron affinity values of SiO estimated using 6-311++G (2df, 2pd) and 6-311++G (3df, 3pd) basis sets are relatively lower than that calculated using cc-pVTZ and aug-cc-pVTZ basis sets. For all other molecules the electron affinity values obtained using 6-311++G (2df, 2pd) are nearly equal to that estimated using aug-cc-pVTZ basis set. It should be pointed out here that the electron affinity of CS calculated using cc-pVTZ basis set is much lower compared to that obtained using other three basis sets. The difference of ground state energies calculated using cc-pVTZ basis set for CS and its anion is much smaller relative to that calculated using other three basis sets.

The atomization energies for these molecules are summarized in Table 5 along with the experimental and other theoretical results. It is observed from the table that the calculated values for SO and SiS using aug-cc-pVTZ basis set agree well with experimental values and the existing theoretical values obtained by G2 method [16], the deviation compared to the experimental values is about 2 to 3 kcal/mol. Excellent agreement is noticed for ClO, the deviation between the calculated atomization

Table 4. Electron affinity (kcal/mol) for selected diatomic molecules of astrophysical interest.

Molecule	Basis set 6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Other values Theor.	Expt.
SiN	66.11	66.01	59.67	66.24		
CS	6.96	7.12	0.032	7.47		
SiO	4.06	4.08	6.42	6.13		
SO	27.19	26.79	25.75	28.32		
ClO	51.84	51.48	40.52	52.43		52.5[a]
SiS	14.06	13.94	8.75	14.85		

[a]Reference [14].

Table 5. Atomization energy (kcal/mol) for selected diatomic molecules of astrophysical interest.

Molecule	Basis set 6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Other values Theor.	Expt.
SiN	168.95	169.74	168.32	167.64		
CS	163.89	164.76	162.56	162.91	170.5[a]	169.5[b]
SiO	184.66	185.59	183.06	183.16	188.8[a]	190.5[b]
SO	123.27	124.88	121.39	121.83	120.8[a]	123.5
ClO	63.64	65.12	62.39	62.98	61.2[a]	63.3[b]
SiS	140.52	140.99	139.39	139.35	145.0[a]	147.4±3[b]

[a]Reference [16]; [b]values quoted in reference [16].

Table 6. Ionization potential (kcal/mol) for selected diatomic molecules of astrophysical interest.

Molecule	Basis set 6-311++G (2df, 2pd)	6-311++G (3df, 3pd)	cc-pVTZ	aug-cc-pVTZ	Other values Theor.	Expt.
SiN	270.69	270.60	269.74	270.45		
CS	263.76	263.66	263.62	264.24	264.51[a]	261.28[b]
SiO	264.80	264.81	263.13	264.22		
SO	243.82	243.58	222.08	244.29		
ClO	287.03	286.36	284.22	287.24		
SiS	240.47	240.52	240.45	240.64		

[a]Reference [16]; [b]values quoted in reference [16].

energy using aug-cc-pVTZ basis set and experiment is about 0.3 kcal/mol. The discrepancy is relatively large for CS and SiO, the deviation is about 7 kcal/mol. As seen from the table, the atomization energy calculated with cc-pVTZ and aug-cc-pVTZ are almost same but these values are little lower than those calculated with 6-311++G (2df, 2pd) and 6-311++G (3df, 3pd) basis sets. In general, the atomization energy decreases with the improvement of basis set.

A comparison of calculated and existing experimental and theoretical ionization potential of these diatomic molecules is shown in Table 6. The estimated ionization potential for CS using aug-cc-pVTZ agrees well with the theoretical value of Curtiss *et al.* [16] using G2 method. The deviation between the calculated value and the experiment is about 3 kcal/mole. For rest of the molecules, there are no theoretical and experimental data available for comparison.

4 Conclusion

Bond length, dipole moment, harmonic frequency, IR intensity, electron affinity, atomization energy, and ionization potential have been studied for the selected diatomic molecules and their cations of astrophysical interest using the hybrid HF/DF B3LYP method. Four basis sets have been used to check the consistency and convergence of the calculated values. The quality of the basis set has been improved from 6-311++G (2df, 2pd) to aug-cc-pVTZ. In general the bond length and electron affinity increase with improvement of the basis set whereas harmonic frequency, dipole moment and atomization energy decrease. However very small change in values is observed for the ionization potentials of these molecules at 6-311++G (2df, 2pd) and aug-cc-pVTZ basis sets. The effect of diffuse functions is very important as far as harmonic frequencies are concerned. In general good agreement between our calculated molecular properties and the existing results is observed for the aug-cc-pVTZ basis set. Most of the results for dipole moment, electron affinity, ionization potential, IR intensity are new. In view of satisfactory agreement in general between the calculated values and the available theoretical and experimental data for the properties studied here, the predicted results may serve as a reliable set of data for future references.

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