

Structure and Stability of Magnesium Dication Solvated by Dimethyl sulfide

Ahmed H. Mangood,* Safinaz H. El-Demerdash, El-Sayed E. El-Shereafy

Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt
[*mangood_3000@yahoo.com](mailto:mangood_3000@yahoo.com)

Abstract: Stability of $Mg^{2+}CH_3SCH_3$ complex has been studied using density functional theory at BMK/6-311+G (2d, 2p)//BMK/6-31+G (d). The results indicated that the $Mg^{2+}CH_3SCH_3$ complexes are thermodynamically unstable toward loss of $CH_3XCH_3^+$, CH_3^+ and MgH^+ fragments. However, the presence of higher energy barriers of 44-67 kcal/mol hinders these exothermic processes. The dissociation of the complexes to CH_3 , CH_4 , H_2^+ , H^+ , CH_4^+ , H and H_2 are endothermic. The last four channels acquire further kinetic stability due to the presence of sizable energy barriers. This indicates that $Mg^{2+}CH_3SCH_3$ complexes can form metastable species and are likely observed under appropriate experimental conditions.

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1. Introduction

The difficulty in generating multiply charged metal-ligand complexes in the gas phase results from the huge difference between the second ionization energy (IE2) of a metal and the first IE (IE1) of a ligand. The first ionization energy (IE) of most common solvents lie in the range 9–13 eV, while the second IE of metal atoms are, with few exceptions, above 12 eV. Hence, electron transfer from a neutral ligand to a multiply ionized metal atom is exothermic and occurs spontaneously up contact followed by dissociation due to Coulomb repulsion [1]. This hinders sequential ligation of metal dications in a manner similar to that which occurs with singly charged ions [2]. This is called kinetically stable ligated metal dications. Three experimental methodologies have been used to generate ligated metal polycations, namely pickup [3], electrospray ionization (ESI) [1], and charge stripping (CS) [4] techniques. Experimentally, complexes of metal dications solvated by a finite number of a variety of ligands have been generated in the gas phase. These ligands included both protic (water, alcohols) and aprotic (ethers, acetone, acetonitrile, ketones, dimethyl sulfoxide (DMSO), benzene, and pyridine) solvents. [5-12].

Quantum chemical calculations have also contributed to the progress of microsolvated multicharged ion chemistry. Previously, investigation of the existence of a variety of metal di and trications solvated by a variety of neutral polar ligands such as water [13-16], ammonia [13, 14], acetone [17], acetonitrile [18], DMSO and $Mg^{2+}XH_3OH$ [15,19,20] has been reported. These studies proved the possibility of detecting most of the studied monosolvated metal dications in the gas phase and

the quantum chemical results were supported by experimental findings using CS and ESI techniques [1, 4]. Dimethyl sulfide (DMS), makes up between 50 and 90% of the total biogenic sulfur released to the atmosphere [21], is an important reduced sulfur compounds in the atmosphere. Computational chemistry is a very helpful tool for studying multiply charged systems. Experimental and theoretical investigations on the existence of aprotic solvent such as dimethyl sulfide (DMS) in the gas phase are still limited compared to other protic solvent. Therefore, we are heading toward studying DMS with magnesium dication. An important feature of the present study is going to perform a computational study (at BMK (Boese-Martin for kinetics) density functional theory (DFT) [22] on the structure and stability of $Mg^{2+}DMS$ complex to gives the evidence for detecting it in gas phase.

2. Computational methods

All electronic structure calculations were performed using the Gaussian 03W program [22]. Geometry optimizations for CH_3SCH_3 , $Mg^{2+}CH_3SCH_3$, complex and its reaction products have been performed using DFT at the BMK introduced by Boese and Martin [23] level with 6-31 + G(d) basis sets. For each stationary point, we carried out vibrational frequency calculation to characterize their nature as minima or transition states and to correct energies for zero-point energy and thermal contribution. The transition states for some unimolecular dissociation channels have been located using several techniques, including and the synchronous transit-guided quasi-Newton (TS and QST3) the eigenvalue-following (EF) optimization procedures as implemented in the

Gaussian programs. The vibrational modes were examined by using the ChemCraft program [24]. Partial charge distributions were calculated using the natural population analysis (NPA) method [25]. Energies were calculated at the BMK/6-311+G (2d, 2p)//BMK/6-31+G (d) level. Using 6-311+G (2d, 2p) basis set is expected to reduce basis set superposition error.

3- Results and Discussion

3.1 structures

3.1.1. CH₃SCH₃ and CH₃SCH₃⁺

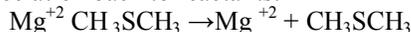
The optimized structures of CH₃SCH₃ molecules, Mg²⁺CH₃SCH₃ complexes, and transition states for dissociation channels are displayed in Figure 1. NPA atomic charges for various species are listed in Table 1. Energy barriers calculated at BMK level is displayed in Figure 2 and 3.

For DMS, it has C₁ symmetry structure as the lowest energy minimum but the out-of-plane and in-plane C–H bond distances are comparable in length for (1.096 vs. 1.097 Å) our computed geometrical parameters for DMS our calculated C-H in and out of plan bond lengths (1.096 Å and 1.097 Å) are in good agreement with the values obtained at the MP2/6-311 + G(2d,p) levels of theory (1.093 and 1.094 Å) [26]. Two S-C bond length is increased by 0.04 Å on the other hand the value for C2S1C6 bond angle (98.73°) are longer than the latter level (98.3°) and SCH bond angle is greater than the latter level (107.6°). Up ionizing the CH₃SCH₃ molecule, the two S–C shortens by 0.019 Å, and the out-of-plane C–H is decreased by 0.002 Å the corresponding C2S1C6 and two S1C2H4 and S1C6H8 angles shorten by 1.4° and .46° respectively.

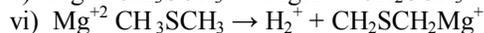
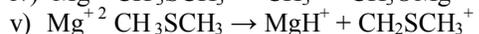
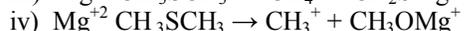
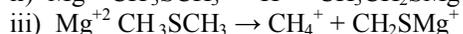
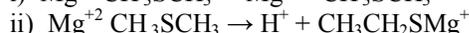
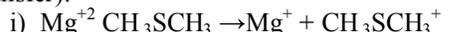
3.1.2. Interaction of Mg dication with CH₃SCH₃ molecule

Reaction of Mg ion with single CH₃SCH₃ molecules gives Mg²⁺CH₃SCH₃ dication complex. In the following sections, we are going to discuss geometrical changes in the ligands upon complexes formation. Once the dication complex is formed, it can undergo a variety of dissociation channels which can be summarized as follows:

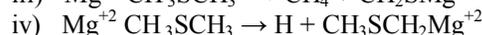
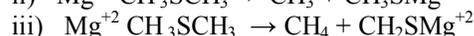
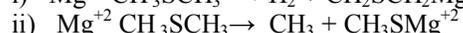
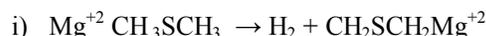
a) Dissociation back to reactants:



b) Dissociation to monovalent fragments (charge transfer):



c) Dissociation to neutral and charged dications.



Dissociation to monovalent fragments represents charge separation (electron transfer), whereas processes (a) and (c) show a loss of neutral species. Transition states for the exothermic channels and slightly endothermic ones were located and their geometrical differences compared to the dication complex will be discussed later. Frequency analysis confirmed that these transition states have only one imaginary frequency which corresponds to the stretching mode of the cleaved bond between the separated fragments.

For DMS, addition of Mg²⁺ to a single CH₃SCH₃ ligand forms the Mg²⁺CH₃SCH₃ dication, in which the two S-C bond distances are increased by 0.030 Å decrease in C2-H7 bond lengths by 0.003 Å, and a contraction in the C-S-C bond angle by 4.51° and increased in H3-C2-S1 and H3C2H4 and H9C6H7 bond angle by 0.48°, 1.03° and 1.03° respectively compared to the free CH₃SCH₃ molecule. Moreover, the charge on sulfur atom increases by 0.394 e. This indicates that the CH₃SCH₃ molecule is polarized by Mg²⁺ dictations. The charge distribution over CH₃SCH₃ in the complex of 0.3 e reveals a small but definite transfer of negative charge from CH₃SCH₃ to Mg²⁺ dictations which results in a slight reduction of the dipositive charge on Mg atom to +1.7.

The transition states located for the dissociation of Mg²⁺CH₃SCH₃ dication to Mg⁺, CH₃, H⁺, CH₄⁺, H₂ and MgH⁺ are designated as TS₁S-TS₆S. The Mg-S bond in TS₁S is significantly elongated in the transition state compared to the Mg²⁺CH₃SCH₃ dication complex (4.972 Å versus 2.382 Å) and the positive charge are transfers from Mg²⁺ to DMS in the transition state (1.2 and 0.8 e over Mg and DMS respectively). This should be compared with +0.3 and +1.7e over DMS and Mg in the Mg²⁺DMS complex. In the TS₂S the C6-S1 bond is significantly elongated (4.136 Å versus 1.870 Å). The sum of NPA charges over CH₃ is 0.9 e indicates the separation of methyl cation. But in TS₃S C2-H6 bond is significantly elongated (4.287 Å versus 1.099 Å) the NPA charge over the H fragment (+0.4 e) indicates release of hydrogen atom. The formation of methane cations (TS₄S) was confirmed from charges distribution over the relevant transition states with the expected structural changes on going from the reacting complex to transition

states. The loss of hydrogen molecules from Mg^{+2}DMS pass through TS_5S . The NPA charges over the separated H_2 molecules in the transition states (TS_5S) of +0.4 indicate release

of neutral hydrogen molecules. The formation of MgH^+ with a charge of +1.0 e over TS_6S shows that MgH^+ cation.

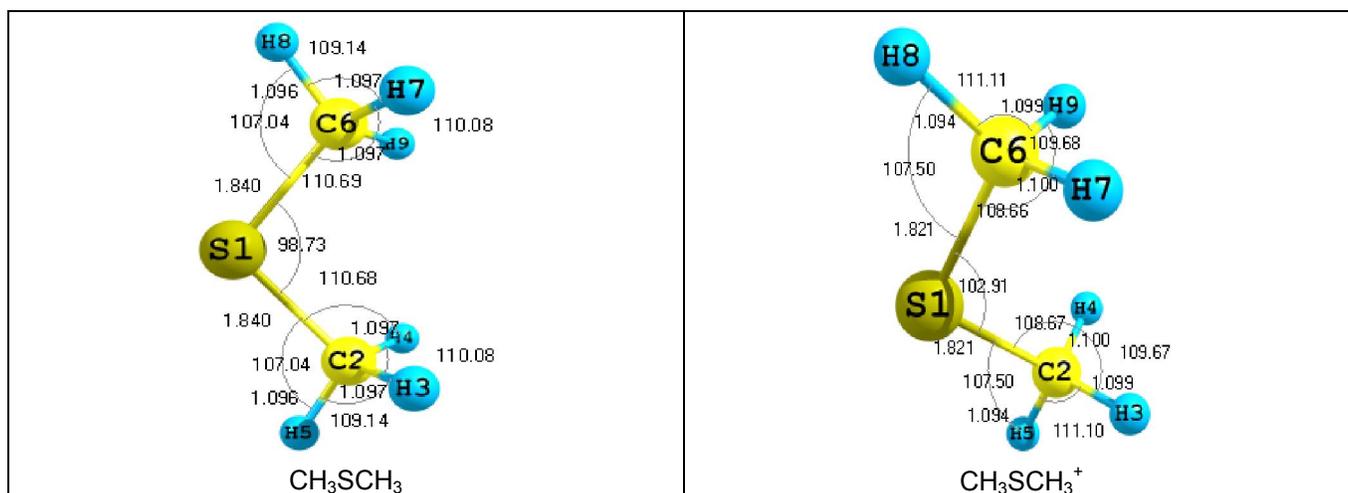
Table 1: NPA atomic charges for CH_3SCH_3 , $\text{CH}_3\text{SCH}_3^+$, $\text{Mg}^{+2}\text{CH}_3\text{SCH}_3$ and transition states at BMK/6-31+G (d)

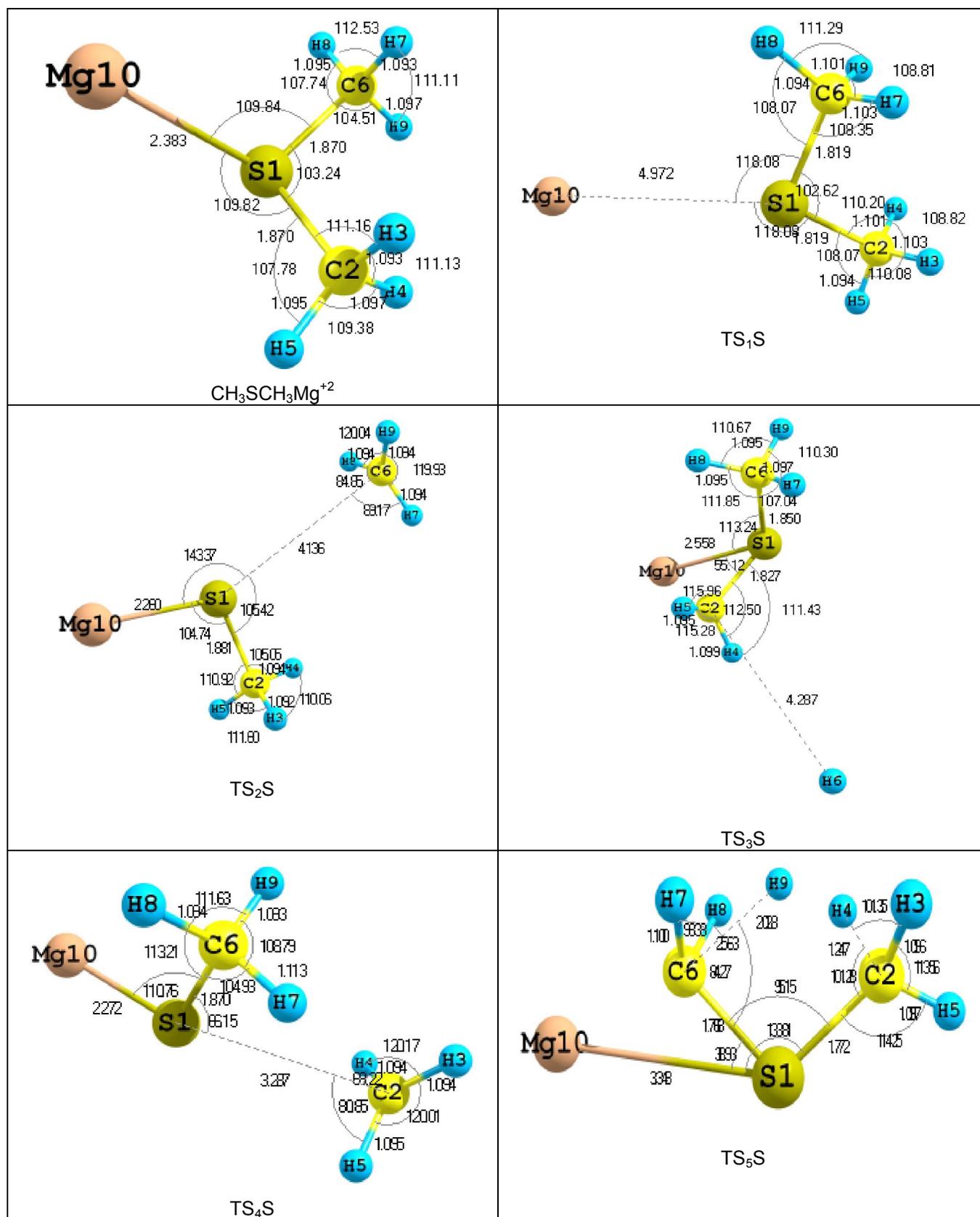
Atom	CH_3SCH_3	$\text{CH}_3\text{SCH}_3^+$	$\text{Mg}^{+2}\text{CH}_3\text{SCH}_3$
Mg			1.729
C2	-0.855	-0.914	-0.812
C6	-0.855	-0.914	-0.812
S1	0.157	0.889	0.014
H3	0.253	0.323	0.311
H4	0.253	0.321	0.328
H5	0.270	0.326	-0.301
H7	0.270	0.326	0.312
H8	0.253	0.323	0.301
H9	0.253	0.321	0.328

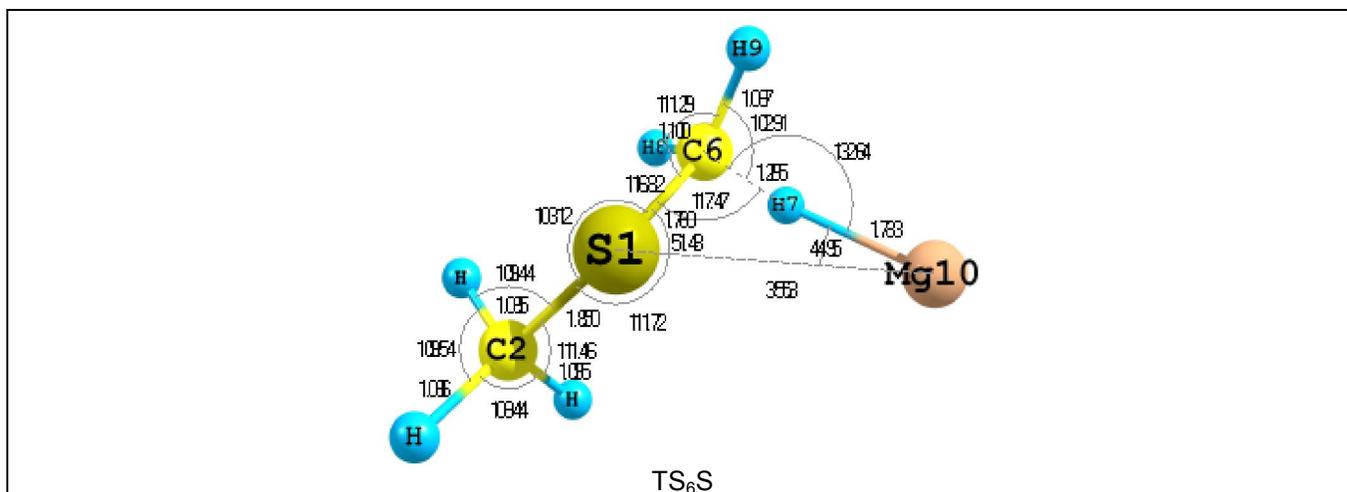
Table 1: continued

Atom	TS_1S	TS_2S	TS_3S	TS_4S	TS_5S	TS_6S
S1	0.681	-0.622	0.285	-0.624	0.567	0.376
C2	-0.901	-0.817	-1.161	0.080	-0.733	-0.846
H3	0.316	0.292	0.422	0.273	0.330	0.207
H4	0.319	0.284	0.311	0.274	0.179	0.280
H5	0.332	0.283	0.313	0.275	0.361	0.328
C6	-0.901	0.150	-0.840	-0.801	-1.247	-0.806
H7	0.316	0.259	0.327	0.297	0.320	-0.177
H8	0.319	0.260	0.316	0.226	0.163	0.334
H9	0.332	0.259	0.269	0.310	0.258	0.361
Mg	1.188	1.652	1.738	1.691	1.802	1.844
CH3		0.928				
H			0.422			
CH4				0.902		
H2					0.437	
MgH						1.567

Figure 1: Optimized structures of DMS, DMS^+ , Mg^{+2}DMS , and their transition states at BMK/6-31+G (d).







3.2 Energies

Relative energies, with respect to $\text{Mg}^{2+}\text{CH}_3\text{SCH}_3$ complex, are depicted in Figs. 2. All energies were corrected for ZPEs. The energy difference between the transition state and the corresponding $\text{Mg}^{2+}\text{CH}_3\text{SCH}_3$ complex defines the energy barrier of the respective dissociation process. For all processes, the dissociation energy is defined as the difference between the zero points corrected total energies of the dissociation products and the magnesium dication complex.

Because of the big difference between IE2 of Mg and IE1 of ligands, and in the absence of other stabilizing effect, it is expected that charge transfer occur immediately when these ligands become close to magnesium dication. Mg^{+2}DMS is thermodynamically unstable with respect to dissociation to Mg^+ , CH_3^+ and MgH^+ cations. Based on this thermodynamic behavior, one can not expect observation of $\text{Mg}^{+2}\text{CH}_3\text{SCH}_3$ in the gas phase as they will dissociate spontaneously to monovalent fragments mentioned earlier. Nevertheless, for these channels we were able to locate transition states with sizable heights that hinder such molecular dissociation and the $\text{Mg}^{+2}\text{CH}_3\text{SCH}_3$ complex can be observed experimentally.

Mg^{+2}DMS complex is thermodynamically stable toward dissociation to CH_4 , CH_3 , H_2^+ and H^+ . Loss of CH_4^+ , H , and H_2 are thermodynamically and kinetically stable. The latter was predicted based on the presence of high energy barriers, Fig 1 and 2. Loss of Mg^+ and MgH^+ from Mg^{+2}DME and Mg^{+2}DMS with barriers of 44-68 kcal/mol implies that such dissociations can not occur and these channels we were able to find with sizable barrier heights that hinder such molecular dissociation. Loss of either CH_3 cation or hydrogen atom from Mg^{+2}DMS encounters barriers of 48-142 kcal/mol

which indicates that such decompositions can not occur unless high temperature is provided to investigate the complexes. The production of methane cation and hydrogen molecule requires high energies (48 - 87 kcal/mol, respectively). Previous experimental studies using pick-up technique reported that least two methanol molecules are needed to stabilize the magnesium dication center [3, 27]. On the other hand, theoretical calculation proved that one molecule of methanol is needed to stabilize the dication centre [20]. However, the pick-up method failed to observe water monoligated copper dication in the gas phase [28], while ESI and CS experimental methods detected such complex [5, 29]. In addition, pick-up method [27] also failed to find a stable complex between Mg^{2+} ion and DMSO although ESI was able to do this job [11]. There are no ESI and CS investigations for the interaction of Mg^{2+} with dimethyl ether and dimethyl sulfide

Conclusions:

In this paper we have studied thermodynamic and kinetic stability of Mg^{+2}DMS complex to give evidence for the possibility of detecting it in the gas phase. This work has been done at the BMK/6-311+(2d, 2p)//BMK/6-31+G (d) level of theory. The results obtained can be summarized as follows:

The presence of high energy barrier confining DMS monoligated magnesium dication suggests that the $\text{Mg}^{+2}\text{CH}_3\text{SCH}_3$ represent a thermodynamically and kinetically stable species and can be observed experimentally in high abundance. Since large activation barriers control these fragmentation channels, these dissociation products are unlikely occurred through these reaction channels except at very high temperatures. We can, therefore, characterize this complex as a metastable complex.

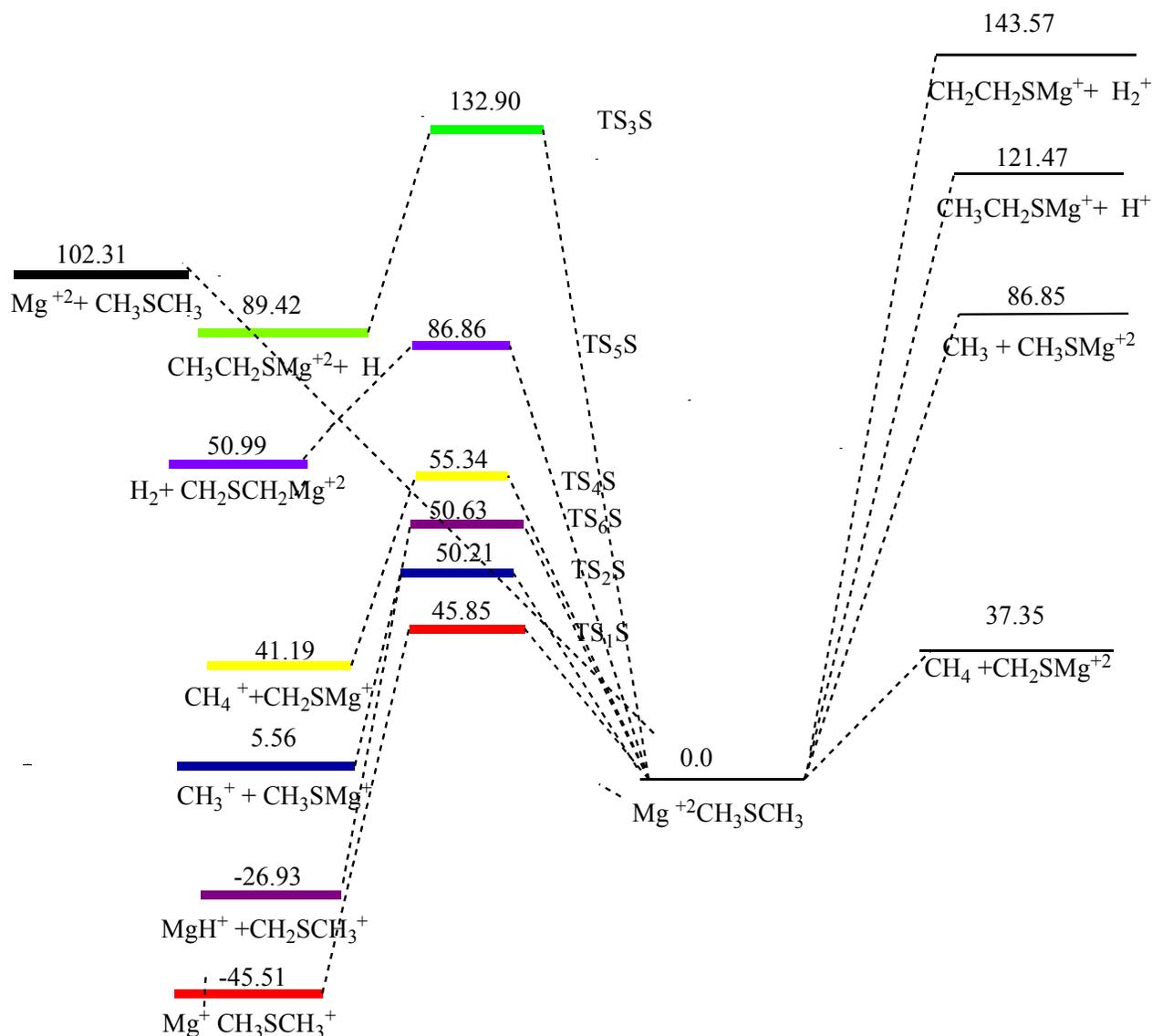


Figure 2: Potential energy diagram for unimolecular decomposition of Mg^{2+}DMS (kcal/mol) at BMK/6-31G+(d)//BMK/6-311+G(2d,2p) for clarification, products and relevant transition states have the same color.

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Corresponding author

Ahmed H. Mangood
Chemistry Department, Faculty of Science,
El-Menoufia University, Shebin El-Kom, Egypt
*mangood_3000@yahoo.com

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