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**THEORETICAL STUDIES ON THE SPECTROSCOPIC PROPERTIES
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The properties of the ground and low-lying excited states of methyl mercaptan (CH₃SH) are studied by using quantum chemistry methods. The geometric parameters and energies of the ground state and the triplet excited state are calculated in this work. It is shown that the calculated geometries of the ground and triplet state are stable and the triplet state potential energy surface has the repulsive feature. The calculated vertical excitation energies and vertical ionization potentials of methyl mercaptan are in best agreement with the experimental values. In addition, the vertical electron affinity and the adiabatic electron affinity of the CH₃SH molecule are also calculated.

Keywords: methyl mercaptan (CH₃SH), ground state, triplet state, excitation energy, ionization energy, electron affinity.

INTRODUCTION

Methyl mercaptan (CH₃SH) is a very important sulfur compound both in atmosphere and industry [1]. The ultraviolet (UV) photodissociation studies of methyl mercaptan (CH₃SH) have received a great deal of attention in recent years [2–4]. The near UV electronic spectrum [5] of CH₃SH shows two absorption bands. The former has a broad band centered around 235 nm and the latter exhibits a very pronounced peak centered around 204 nm. Both bands correlate with the excitation from the ground state to the first two excited singlet states, which are the 1, 2 ¹A' states.

Despite some theoretical and experimental efforts on the spectroscopic studies of CH₃SH [6, 7], the investigations of the properties of the ground and low-lying excited states of methyl mercaptan (CH₃SH) are still needed. In this work, the geometric parameters, energies, and the harmonic vibrational frequencies of the ground state and the triplet state are obtained by quantum chemistry methods. The vertical excitation energies of the singlet excited states of CH₃SH are also calculated and the theoretical results are compared with available experimental results. In addition, the vertical ionization energy, adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity of the methyl mercaptan are calculated, as well. These results could serve as a guide for the experimental and theoretical studies in the future.

THEORY AND CALCULATION DETAILS

It is found that the MP2/aug-cc-pVTZ level of theory could produce the best results for the methyl mercaptan molecule after comparing various theoretical results with experimental results, therefore, the MP2/aug-cc-pVTZ level of theory is chosen in the present study in order to calculate the

geometric parameters, energies, frequencies of the ground state and the triplet excited state of methyl mercaptan (CH_3SH). The vertical excitation energies of the singlet excited states of CH_3SH are also calculated using the TD-DFT [8] (b3p86/6-311++G**) method. The reliability of the method is validated since the theoretical results are in best agreement with the experimental results. In addition, the ionization energies and the electron affinities of methyl mercaptan (CH_3SH) are also calculated.

According to the Koopmans theorem, the vertical ionization potentials can be considered as the negative values of the corresponding occupied molecular orbital energies. The optimized geometry of the ground state of CH_3SH is used to calculate the vertical ionization energies. On the other hand, the adiabatic ionization energy is obtained from the energy difference between the positive molecular ion and the neutral CH_3SH molecule at their respective optimized geometries. Accordingly, the vertical electron affinity is obtained from the energy difference between the negative molecular ion and the neutral CH_3SH molecule at the optimized geometry of the ground state of CH_3SH . What is more, the adiabatic electron affinity is obtained from the energy difference between the negative molecular ion and the neutral CH_3SH molecule at their respective optimized geometries. All the calculations are performed using the Gauss09 software [9].

RESULTS AND DISCUSSION

Optimized geometries of the ground state and the triplet state of methyl mercaptan. Table 1 presents the geometric parameters and experimental results of methyl mercaptan calculated at various methods and basis sets. The experimental results [10, 11], which use microwave spectroscopy to determine the molecular geometry, is a closer approximation to the equilibrium geometry and can be directly compared with the theoretical values. It can be found that the geometry optimized at the MP2/aug-cc-pVTZ level of theory is in the best agreement with the experimental results. Therefore, the MP2/aug-cc-pVTZ level of theory is chosen in order to calculate other properties of the methyl mercaptan molecule. For the ground state of methyl mercaptan, the C—S bond length of 1.8165 Å is 0.0025 Å shorter than the experimental value of 1.819 Å. The H—S bond length of 1.3365 Å is 0.0035 Å shorter than the experimental value of 1.34 Å. The $\angle\text{CSH}$ bond angle is 96.74° and the experimental value is 96.5°. The dihedral angle $D(\text{H,C,S,H})$ is 180.0329° and the experimental value is 177.8°. The theoretical geometric parameters agree very well with the experimental counterparts.

Fig. 1 plots the ground state geometry of methyl mercaptan optimized at the MP2/aug-cc-pVTZ level of theory. Fig. 2 plots the triplet state geometry of methyl mercaptan optimized at the MP2/aug-

Table 1

Geometric parameters of methyl mercaptan (CH_3SH) calculated by various methods and basis sets along with experimental results; bond lengths are in angstroms (Å) and angles are in degrees (deg.)

Level	$r(\text{C—S})$	$r(\text{S—H})$	$r(\text{C—H})$	$\angle\text{HSC}$	$\angle\text{HCH}$	$D(\text{H,C,S,H})$
Observed [10, 11]	1.819	1.34	1.09	96.5	109.8	–177.8
CCSD/6-311++G**	1.820	1.338	1.092	96.3233	108.5006	180.0359
CCSD(full)/6-311++G**	1.8179	1.3374	1.0914	96.2846	108.4598	180.0875
CCSD/aug-cc-pVDZ	1.839	1.3535	1.0998	96.72	110.4743	179.9939
MP2/6-311++G(<i>d,p</i>)	1.839	1.3535	1.100	96.72	108.9005	179.9939
MP2(full)/6-311++G(<i>d,p</i>)	1.8109	1.3338	1.0897	96.2224	108.345	180.007
MP2/6-311++G(2 <i>d,2p</i>)	1.8239	1.3306	1.0828	96.5577	108.7222	180.0393
MP2(full)/6-311++G(2 <i>d,2p</i>)	1.8217	1.33	1.0816	96.5588	108.6792	180.0506
MP2/aug-cc-pVDZ	1.833	1.3496	1.0979	96.6553	108.8622	–180.0605
MP2/aug-cc-pVTZ	1.8165	1.3365	1.0858	96.7394	108.9694	180.0329
B3LYP/6-311++G**	1.8355	1.3485	1.0894	96.944	108.8078	–180.005
B3LYP/6-31++G(<i>d</i>)	1.8368	1.3509	1.0929	96.9344	110.126	–180.0166

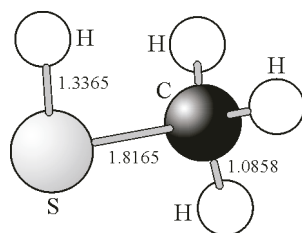


Fig. 1. The ground state geometry of methyl mercaptan

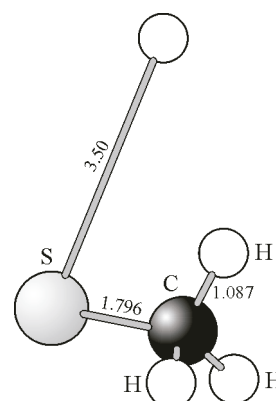


Fig. 2. The triplet state geometry of methyl mercaptan

Table 2

Geometric parameters and energies of the ground state (1^1A) and the triplet state (1^3A) of methyl mercaptan; bond lengths are in angstroms (Å) and angles are in degrees (deg.)

State	$r(\text{C}-\text{S})$	$r(\text{C}-\text{H})$	$r(\text{S}-\text{H})$	$\angle\text{HCH}$	$\angle\text{HSC}$	$D(\text{H,C,S,H})$	Energy
Observed [10, 11]	1.819	1.09	1.34	109.8	96.5	-177.8	
Ground state	1.8165	1.0858	1.3365	108.9694	96.7394	180.0329	-438.128
Triplet state	1.796	1.087	3.50	108.77	78.94	-170.9	-437.985

cc-pVTZ level of theory. The calculated results illustrate that the ground state of methyl mercaptan molecule (1^1A) has the C_s symmetry while the triplet state has the C_1 symmetry.

Table 2 presents the geometric parameters and energies of the ground state (1^1A) and the triplet state (1^3A) of methyl mercaptan optimized at the MP2/aug-cc-pVTZ level of theory. The geometric parameters of the ground state are in good accordance with the experimental values. The triplet state geometry and energy are different from the counterpart of the ground state. At the MP2/aug-cc-pVTZ level of theory, the ground state energy of methyl mercaptan is -438.128 hartree and the lowest triplet state energy of methyl mercaptan is -437.985 hartree. When the molecule is excited to the triplet state (1^3A), the S—H bond length is lengthened to 3.50 Å and the C—S bond length is shortened to 1.796 Å. The substantial increase in the S—H bond length strongly indicates that the triplet state potential energy surface has the repulsive nature. The corresponding products of the channel are the hydrogen atom and CH_3S radical.

Calculated results of the excitation energies. The vertical excitation energies of the singlet excited states of CH_3SH are calculated using different methods (time-dependent density functional theory (TD-DFT) and singlet configuration interaction (CIS)) and basis sets at the MP2/aug-cc-pVTZ optimized geometry. Table 3 presents the vertical excitation energies of the singlet excited states. It can be found that the TD-DFT results are more accurate than the CIS results after the comparison with the experimental results. The theoretical results performed by different TD-DFT methods are also quite different. It is found that the theoretical results performed by the TDDFT-b3p86 method are the most adjacent to the experimental results. Moreover, the excitation energies calculated by b3p86 with different basis sets are also different. The results calculated by b3p86/6-311++G** are much better than the counterparts calculated by b3p86/aug-cc-pVDZ after comparing them with the experimental results. Overall, the theoretical results obtained by the TDDFT (b3p86/6-311++G**) method are in the best agreement with the experimental results.

Harmonic frequencies. Table 4 presents the vibrational frequencies of the ground state and the triplet state of methyl mercaptan as well as available experimental vibrational frequencies [12] of the

Table 3

Vertical excitation energies (in nm) for low-lying excited electronic states of CH₃SH based on the geometry at MP2/aug-cc-pVTZ level along with the experimental results

CH ₃ SH	X ¹ A' → 1 ¹ A''	X ¹ A' → 2 ¹ A''
Experiment [5]	235	204
TD-pbepbe/6-311++G**	258.76	226.87
TD-pw91pw91/6-311++G**	260.45	228.01
TD-b3p86/6-311++G**	232.70	205.63
TD-b3lyp/6-311++G**	245.66	216.64
TD-pbepbe/aug-cc-pVDZ	259.12	229.37
TD-pw91pw91/aug-cc-pVDZ	261.81	231.02
TD-b3p86/aug-cc-pVDZ	232.38	207.05
TD-b3lyp/aug-cc-pVDZ	245.58	218.53
RCIS/6-311++G**	210.68	184.94

Table 4

Harmonic vibrational frequencies calculated at the ground state and triplet state geometries of methyl mercaptan as well as available experimental frequencies in Parentheses [12] (in cm⁻¹)

State	Frequencies
Ground	237, 735, 811, 991, 1106, 1372, 1498, 1512, 2767, 3093, 3195, 3197 (708, 803, 976, 1074, 1335, 1430, 1475, 2597, 2931, 3000, 3000)
Triplet	31, 60, 106, 625, 748, 907, 1350, 1427, 1497, 3064, 3153, 3179

molecule in the ground state. The vibrational strength analysis of the singlet and triplet states is carried out. It is found that the vibrational strength is largest at a wave number of 3093 cm⁻¹ which corresponds to the stretching vibration mode. As for the triplet state of methyl mercaptan, the vibrational strength is the largest at a wave number of 625 cm⁻¹ which corresponds to the rocking vibration mode. The calculated geometries of the ground state and the triplet state are stable because all frequencies are real. The experimental frequencies are also listed for comparison. The frequencies in the theory and the experiment show good consistency, which means that the calculated IR spectra are close to the experimental values for the title molecule. In summary, the theoretical methods employed in the present work are reliable and feasible.

Ionization energies. Table 5 presents the vertical ionization potentials, the adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity of methyl mercaptan calculated at the MP2/aug-cc-pVTZ level.

The vertical ionization potentials of methyl mercaptan calculated at the MP2/aug-cc-pVTZ level are listed in Table 5. Previous theoretical and experimental values are also exhibited for comparison. Compared with the previous theoretical results [13], the current theoretical results are in much better agreement with experimental values [14, 15]. The theoretical results in the present work are slightly larger than the experimental values of the ionization energies which were obtained from photoelectron spectroscopy [14]. The adiabatic ionization energy of methyl mercaptan is calculated to be 9.45 eV. The calculated vertical electron affinity and the adiabatic electron affinity of the CH₃SH molecule are 0.597 eV and 0.595 eV, respectively. It can be concluded that the molecule needs more energy when

Table 5

Calculated vertical ionization potentials (VIP), adiabatic ionization potentials (AIP, eV), vertical electron association energies (VEA, eV), and adiabatic electron association energies (AEA, eV) of CH₃SH

CH ₃ SH	VIP	AIP	VEA	AEA
MP2/aug-cc-pVTZ	9.49	9.45	0.597	0.595
Calc[13]	9.66			
Exp[14]	9.438 ₆ —9.441 ₅			
Exp[15]	9.44±0.01			
Exp[16]	9.446±0.010			

losing an electron than obtaining an electron. That is to say, the ability of obtaining an electron is stronger than that of losing an electron. The calculated results could serve as the guidance for future experimental observations.

CONCLUSIONS

The properties of the ground and low-lying excited states of methyl mercaptan (CH_3SH) have been studied in this work. The geometric parameters and energies of the ground state and the triplet state are calculated at the MP2/aug-cc-pVTZ level of theory. The stable ground and triplet states are characterized by all real frequencies. Beginning with the triplet state structure, the repulsive feature of the triplet state potential energy surface is explained. The vertical excitation energies of the singlet excited states of CH_3SH are calculated. After comparing vertical excitation energies of the singlet excited states calculated by different model chemistries with the experimental results, it is found that the theoretical results obtained by TDDFT (b3p86/6-311++G**) are in best agreement with the experimental results. The vertical ionization potentials of methyl mercaptan calculated at the MP2/aug-cc-pVTZ level are in good accordance with the experimental results. The calculated vertical electron affinity and the adiabatic electron affinity of the CH_3SH molecule are 0.597 eV and 0.595 eV, respectively. The reliability of the theoretical method chosen is assessed, and the method proved to be successful in predicting the experimental observations. The calculated results could not only be used for comparison with experimental results, but also can serve as a guide for future experimental and theoretical investigations.

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