Physical and spectral characterization of CH_3SH based on external electric field modulation

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Abstract. CH_3SH is a very important chemical substance with a wide range of applications in chemical synthesis, biomedicine and analytical monitoring. In this paper, for the first time, the molecular bond lengths, energies, dipole moments, energy level distributions, energy gaps, and Raman spectra of CH_3SH molecules under an external electric field have been investigated by using the quantum mechanical density-functional theory (DFT) of BPV86 at the level of the 6-31G basis group. It was found that the dissociation energy of a substance decreases with increasing electric field in the presence of an external electric field. This paper provides a reference for further studies of the CH_3SH molecule and the characterization of its mixtures under external electric fields.

Keywords: CH_3SH, External Electric Field, Physical Properties.

1. Introduction

Methyl mercaptan (CH_3SH) is a compound of great importance. In the field of chemical synthesis, as a key raw material for the synthesis of sulfur-containing organic compounds, it can participate in a variety of reactions, opening up unique pathways for the synthesis of new substances [1]. In the field of analytical testing, it can be used to detect the content of sulfur-containing compounds in the environment, which has an important application value. In the biomedical field, they play a role in specific physiological processes and show potential applications in drug discovery and development [2]. In the field of materials science, sulfur-containing compounds occupy a place in the preparation of specialty materials [3]. In the industrial field, it is an important intermediate in the production of certain chemical products or chemical reactions [4]. In the field of environmental protection, its in-depth study helps to clarify the sources of air and water pollution and methods of treatment [5]. In conclusion, CH3SH has attracted much attention in physical property research, chemical analysis, industrial production and other aspects, and its unique properties have brought new development opportunities and challenges for related fields.

The study of the properties of the molecules of matter in the external electric field is an important way to understand the properties of matter, in which the study of the structural properties of the molecules of matter is crucial, as it largely determines the properties of the material. Currently, the characterization in the external electric field is mainly focused on molecules such as LiF, TiO [6-12], however, the external field effect of CH_3SH molecules is relatively less studied. In this thesis, the density-functional theory (DFT) method of quantum mechanics is applied to optimize the stable configuration of the CH_3SH molecule at the level of the BPV86 basis group, and the appropriate calculation method is selected by comparing with the experimental values, which in turn calculates its molecular energy, bond length, dipole moment, orbital energy level, energy gap, and the law of the change of Raman spectra with the applied electric field. At the same time, focusing on the study of physical properties of substances to understand their intrinsic properties is essential for degrading or treating substances in the context of increasing environmental problems [13]. The study of the CH_3SH molecule is no exception, and an in-depth understanding of its behavior in the presence of an external electric field can help to grasp its physical properties and provide a basis for dealing with environmental problems that may be caused by CH_3SH. Currently, CH_3SH is widely present as a malodorous pollutant in landfills and chemical plants, and its high stability leads to less than 30% conventional photocatalytic degradation efficiency. In response to the urgent need for environmental treatment of CH_3SH molecules, this study reveals for the first time the key influence mechanism of external electric field modulation on their environmental behavior, which provides a direction for breaking through the bottleneck of traditional pollution treatment technology. For example, the stability and reactivity of CH_3SH in the environment can be inferred from the study of its molecular structural parameters, which can be used as a reference for the development of rational pollution control programs. Compared with the traditional chemical additive method, the external electric field modulation has the advantages of non-invasive and reversibility, which can reduce the CH_3SH dissociation energy and increase the degradation efficiency through the external electric field, while avoiding the secondary pollution. In summary, the combination of the study of the properties of the CH_3SH molecule in the external electric field and the study of its physical properties around the environmental problems enables a more comprehensive understanding of the substance. This will contribute to the solution of environmental problems in the future, not from a chemical point of view, but from a physical point of view.

2. Theoretical calculations and methods

In this study, in order to get the optimal method and basis group, I used different methods and basis groups in Gaussian16W quantum chemical calculation software to perform theoretical calculations and get the optimal results, specifically, I used the BPV86 method in density-functional theory (DFT) and combined with the 6-31G basis group to optimize the structure of CH_3SH molecule. The coordinate configuration of each atom during the optimization process is shown in Figure 1. In addition, I applied a series of external electric fields of different intensities (ranging from 0.000 a.u. to 0.041 a.u.) in the direction of the red arrows (parallel to the $C-S$ linkage) in the figure, and calculated the properties of the geometrical configuration, energies, bond lengths, dipole moments, orbital energy level distributions, and Raman spectral intensities of the CH_3SH molecule.

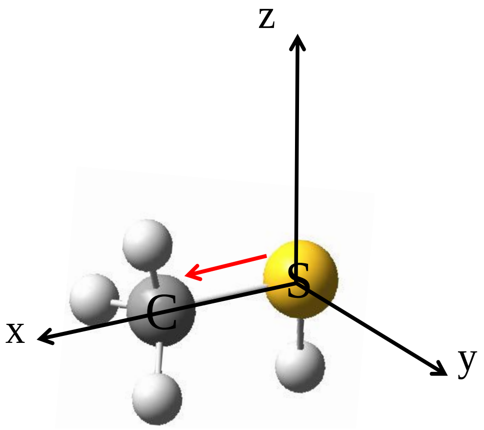

Figure 1. Stabilized conformations of CH_3SH without external electric fields

Based on these optimization results, the changing patterns of the geometrical configurations, energies, bond lengths, dipole moments, orbital energy level distributions, and Raman spectral intensities of the CH_3SH molecule with the strength of the applied electric field were further calculated and analyzed.

3. Discussion and results

3.1. Geometrical configuration of CH_3SH in the absence of an external electric field

Figure 1 illustrates the stabilized conformation of the CH_3SH molecule in the absence of an external electric field. In this structure one carbon atom forms a methyl group ($-CH_3$) with three hydrogen atoms, and the methyl group is connected to a sulfur atom through a single bond, which is connected to a hydrogen atom to form a sulfur-hydrogen bond (-SH).

The calculated results are obtained and the optimized $C-S$ molecular bond lengths Re and molecular energies are listed in Table.1 and compared with the experimental values. It can be seen that the $C-S$ molecular bond lengths obtained from the BPV86/6-31G+(d) method calculations are closest to the experimental values. Therefore, the optimization of the molecular structure of CH_3SH under the action of external electric field in this paper are all calculated at the level of the 6-31G+(d) basis group using the density generalization BPV86 method, which further yields the variation of physical properties such as molecular energy, bond length, dipole moment, orbital energy level distribution, and Raman spectra with the external electric field.

Table 1. Structural optimization of CH_3SH molecules by different methods

	BPV86/6-31G	BPV86/6-31G+	BPV86/6-31G+(d)	BPV86/6-31G++	Experimental value
Re/Å	1.9033	1.9037	1.8405	1.9035	1.8177
E/hartree	-438.6936	-438.6964	-438.7301	-438.6967	

3.2. Effect of different external electric fields on the physical properties of CH_3SH

3.2.1. Effects of external electric fields on molecular energy, bond length and dipole moment

Structural optimization of the molecules was carried out using the BPV86/6-31G+(d) base group with different electric fields (0.000a.u.-0.041a.u.) in the x-axis ($C-S$ continuum) direction to obtain stable molecular structures. Data on molecular energy, bond lengths and dipole moments were calculated for different electric field strengths.

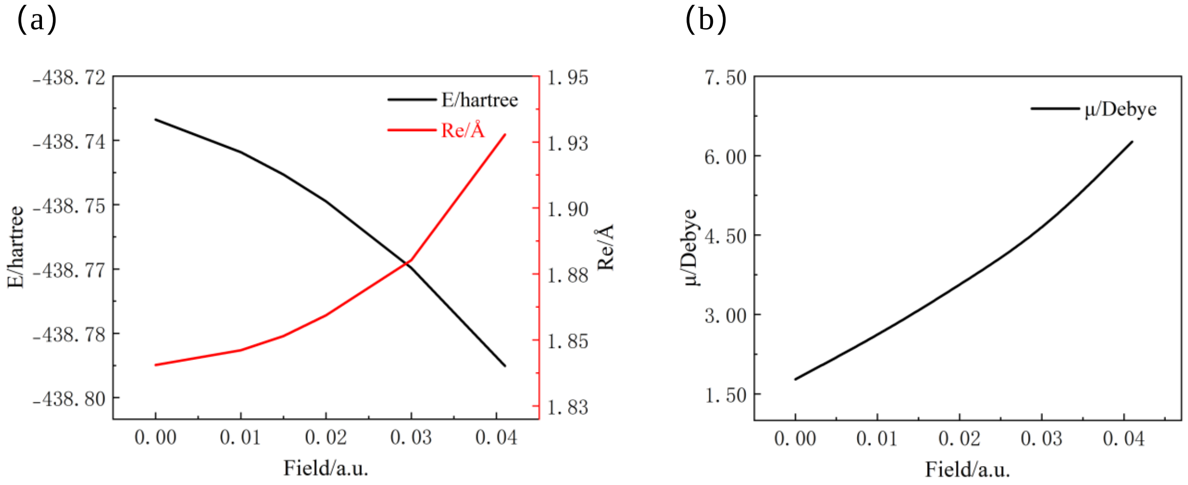

Figure 2. Effect of different external electric fields on the total molecular energy, bond length and dipole moment of CH3SH

It can be seen that the molecular energy with the increase of electric field F and gradually reduce, and the approximate linear decrease, the rule of change in Figure 2(a); molecular bond length and dipole moment are with the increase of external electric field F and increase, which dipole moment is approximately linear increase, the rule of change in Figure 2(a)(b).

3.2.2. Effect of external electric field on the orbital energy level distribution of CH_3SH

By applying the same method, the data of the lowest vacant orbital (LUMO) energy E_L, the highest occupied orbital (HOMO) energy E_H and the energy gap E_G of the CH_3SH molecules can be obtained for different strength electric fields and recorded in Table 2. The energy gap E_G in the table is calculated as in Eq. (1):

$$E_G = (E_L - E_H) \times 27.2eV \tag{1}$$

Table 2. E_L, E_H and E_G of CH_3SH molecules under different external electric fields

F/a.u.	E_L/a.u.	E_H/a.u.	E_G/a.u.
0.0000	-0.0269	-0.2077	0.1808
0.0100	-0.0286	-0.2135	0.1849
0.0150	-0.0468	-0.2168	0.1701
0.0200	-0.0685	-0.2204	0.1519
0.0300	-0.1192	-0.2285	0.1094
0.0410	-0.1830	-0.2476	0.0646

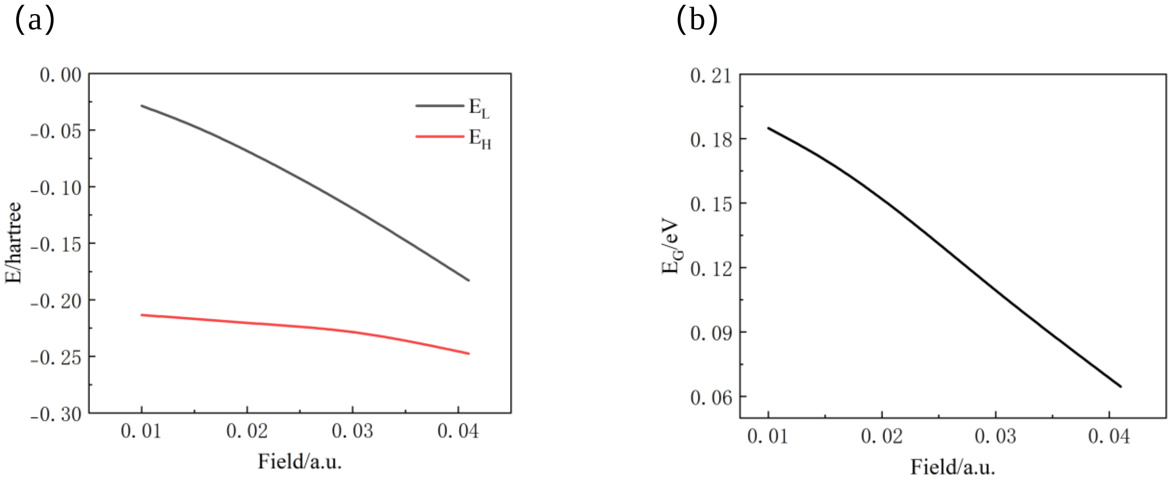

Figure 3. CH3SH molecular energy level distribution and E_G variation with external electric field

From Figure 3(a), it can be seen that both E_L and E_H of CH_3SH molecules gradually decrease with the increase of external electric field, and E_L is more affected by external electric field than E_H, and the trend of E_L is more obvious than E_H, thus leading to the gradual decrease of E_G with the increase of external electric field, as shown in Figure 3(b), which indicates that the electrons of CH_3SH molecules are more and more likely to be excited by the increasingly stronger electric field in the $C-S$ direction.

3.2.3. Effect of external electric field on Raman spectra and dissociation energies of CH_3SH

The vibrational frequencies of the Raman spectra of CH_3SH molecules and their intensities can be obtained by applying different external electric fields to the CH_3SH molecules on the BPV86/6-31G basis set, as shown in Figure 4. It was found that nine vibrational peaks appeared in the Raman spectrum of CH_3SH molecule when there was no applied field, and we found the following nine vibrational modes, and the vibrational peaks were labeled 1-9. Taking peak 7 as an example, its intensity shows a tendency to decrease and then increase, indicating that the vibration becomes unstable, so the applied electric field favors the degradation of the molecule.

Energy scan calculations for CH_3SH molecules in the absence of an applied field and at different external fields give a comparison of the potential energy curves for the single-point energy scan values in different cases, as shown in Figure 5. It can be seen that the potential energy curves of CH_3SH molecules under different electric field strengths have similar trends, but the energy values decrease with the increase of the electric field strength, and the stability of the molecules decreases, which leads to the decrease of their dissociation energies, suggesting that the electric field has an effect on the stability of the molecules.

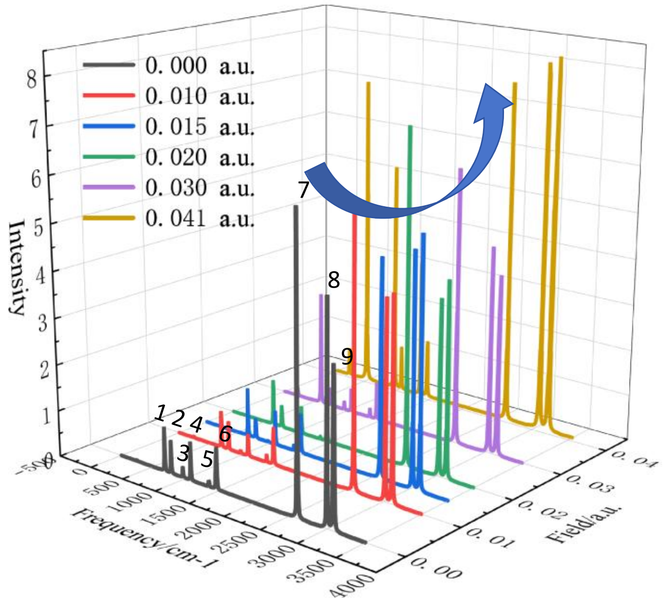

Figure 4. Raman spectra of CH3SH under different external electric fields

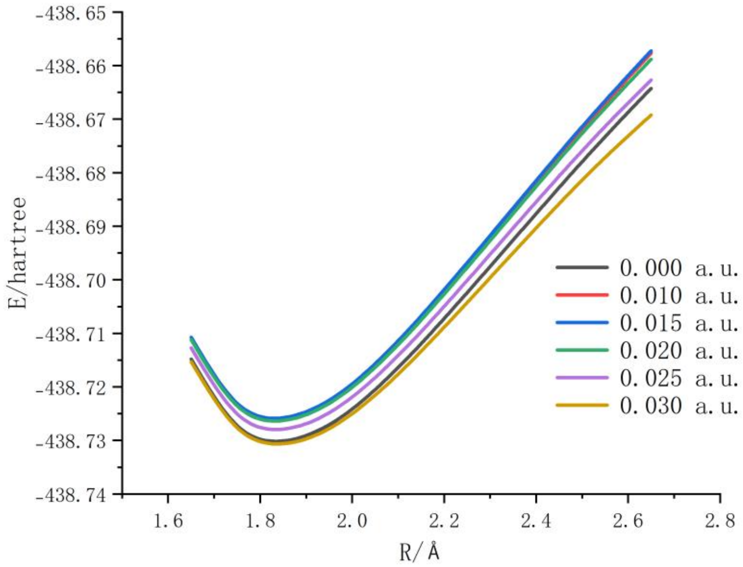

Figure 5. Comparison of potential energy curves of CH3SH for single point energy scan values in the absence of external electric field and at different external electric fields

4. Conclusion

In this paper, the stable structure of the CH_3SH molecule was first determined, and then the stable configurations of the CH_3SH molecule under the action of different external electric fields were calculated using BPV86/6-31G+(d) as the basis group. Calculations show that CH_3SH molecules exhibit significantly different properties in the presence of an external electric field compared to the case without an external electric field. When a series of electric fields (from 0.010 a.u. to 0.041 a.u.) are applied along the x-axis ($C-S$) direction, the molecular bond lengths increase with the electric field strength, the dipole moments increase with the electric field strength, and the molecular energy decreases with the electric field strength. In addition, the E_L and E_H of the CH_3SH molecule decrease with increasing external electric field, and the E_G (along the direction of the $C-S$ bond) also decreases with increasing electric field strength. Meanwhile, the external electric field also affects the Raman spectrum of CH_3SH molecule, and its intensity shows a tendency of decreasing and then increasing in peak 7, for example. The potential energy curves for the single point energy scans of CH_3SH molecules show that the molecular energy values decrease with increasing electric field strength, resulting in a decrease in their dissociation energy. In this paper, the physical and spectral properties of the CH_3SH molecule is studied in depth for the first time from the physical level, which enables a more comprehensive understanding of the substance. Meanwhile, for environmental management, chemical substances have been used to react to treat sulfur-containing pollutants, and this study contributes to the solution of environmental problems in the future, not from the chemical point of view, but from the physical point of view. In addition to this, it also provides a reference for the characterization of its mixtures under external electric field.

References

[1] YAN Junkai, LIU Xupeng, MAO Jing, et al. Progress in the catalytic reaction mechanism of methanethiol to olefin [J]. Molecular Catalysis, 2021, 35 (4): 353 - 364.

[2] Park S, Lee E S, Kim A, et al. Development of a novel tongue biofilm index using bacterial biofluorescence [J]. Scientific Reports, 2024, 14 (1): 1 - 8.

[3] Lv Y, Cui H, Meng N, et al. Recent advances in the application of sulfinic acids for the construction of sulfur-containing compounds [J]. Chinese Chemical Letters, 2022, 33 (1): 97 - 114.

[4] Akbari-Saatlu M, Schalk M, Pokhrel S, et al. Ultra-sensitive H 2 S and CH 3 SH Sensors Based on SnO 2 Porous Structures Utilizing Combination of Flame and Ultrasonic Spray Pyrolysis Methods [J]. IEEE Sensors Journal, 2024.

[5] Ruamdee K, Singhanatkaisi N, Tantirungrotechai Y. Theoretical study of hydrogen/methyl chalcogenides (H2X and CH3XH, X= S, Se) adsorption on pristine/doped graphene quantum dots [J]. Chemical Papers, 2024: 1 - 24.

[6] XU Mei, LINGHU Rongfeng, **Yingfa, et al. Physical properties of LiF molecules in an external electric field [J]. Physics Letters, 2012, 61 (9): 102 - 107.

[7] XU Guoliang, XIA Yaoqiang, LIU Xuefeng, et al. Characterization of TiO photoexcitation under external electric field [J]. Physics Letters, 2010 (11): 7762 - 7768.

[8] Stuyver T, Danovich D, Joy J, et al. External electric field effects on chemical structure and reactivity [J]. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2020, 10 (2): e1438.

[9] Hu Y, Pan Y, Wang Z, et al. Lattice distortion induced internal electric field in TiO2 photoelectrode for efficient charge separation and transfer[J]. Nature Communications, 2020, 11 (1): 2129.

[10] GAO Haozhe, **Bo Yuan, LIU Yuzhu. Properties of NO+ ions in an external electric field and their degradation [J]. Journal of Atomic & Molecular Physics (1000-0364), 2023, 40 (4).

[11] Acharya N, Sagar R. Structure and electrical properties characterization of NiMn2O4 NTC ceramics [J]. Inorganic Chemistry Communications, 2021, 132: 108856.

[12] Dege N, Gökce H, Doğan O E, et al. Quantum computational, spectroscopic investigations on N-(2-((2-chloro-4, 5-dicyanophenyl) amino) ethyl)-4-methylbenzenesulfonamide by DFT/TD-DFT with different solvents, molecular docking and drug-likeness researches [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022, 638: 128311.

[13] Ruamdee K, Singhanatkaisi N, Tantirungrotechai Y. Theoretical study of hydrogen/methyl chalcogenides (H2X and CH3XH, X= S, Se) adsorption on pristine/doped graphene quantum dots [J]. Chemical Papers, 2024: 1 - 24.