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ORIGINAL PAPER

A Gaussian-3 theoretical study of the alkylthio radicals and their anions: structures, thermochemistry, and electron affinities

Aifang Gao · Xuli Liang · Luhua Li · Jinghua Cui

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Abstract The optimized geometries, electron affinities, and dissociation energies of the alkylthio radicals have been determined with the higher level of the Gaussian-3(G3) theory. The geometries are fully optimized and discussed. The reliable adiabatic electron affinities with ZPVE correction have been predicted to be 1.860 eV for the methylthio radical, 1.960 eV for the ethylthio radical, 1.980 and 2.074 eV for the two isomers (n-C_3H_7S and i-C_3H_7S) of the propylthio radical, 1.991, 2.133 and 2.013 eV for the three isomers (n-C_4H_9S, t-C_4H_9S, and i-C_4H_9S) of the butylthio radical, and 1.999, 2.147, 2.164, and 2.059 eV for the four isomers (n-$C_5H_{11}S$, b-$C_5H_{11}S$, c-$C_5H_{11}S$, and d-$C_5H_{11}S$) of the pentylthio radical, respectively. These corrected EA_{ad} values for the alkylthio radicals are in good agreement with available experiments, and the average absolute error of the G3 method is 0.041 eV. The dissociation energies of S atom from neutral $C_nH_{2n+1}S$ (n=1–5) and S^- from corresponding anions $C_nH_{2n+1}S^-$ species have also been estimated respectively to examine their relative stabilities.

Keywords Alkylthio radicals · Dissociation energies · Electron affinities · Geometries · G3 theory

Introduction

The alkylthio radicals are important intermediates in atmospheric chemistry, combustion chemistry, and environmental chemistry, especially at atmospheric oxidation processes [1, 2] of reduced sulfur compounds. The formation and transformation of some radicals play an important role in atmospheric acid–base chemistry and in the formation and growth of aerosol particles. There have been several studies mainly on the methylthio and the ethylthio radical. On the experimental aspect, there are some investigations on electronic state, spectroscopy, dynamics, and energy of the two ethylthio radicals [3–15]. People carried out studies of the methylthio radical and ethylthio radical adopting electron photodetachment, photoelectron spectroscopy, and laser-excited fluorescence methods, and so on. For example, Schwartz *et al.* [3] reported a 364-nm negative-ion photoelectron spectrum of CH_3S^- *via* photoelectron spectroscopy technique. Bahou and Lee [4] obtained the infrared absorption IR spectrum of the methylthio radical in p-H_2. Black and Jusinski [13, 15] observed the ethylthio radical's dispersed fluorescence and fluorescence excitation spectra. Hung *et al.* [12] reported vibronic analysis of the ethylthio radical by laser-induced fluorescence method. On the theoretical aspect, Marenich and Boggs [6] reported *ab initio* study of spin-vibronic dynamics in the ground and excited electronic states of CH_3S radical. The other related investigation [16] on C_2H_5S is combined experimental and theoretical work on photoionization and photodissociation of the $C_2H_5S/C_2H_5S^+$ system. Theoretical calculations [12] were performed for equilibrium geometry and vibrational frequencies of ethylthio radical; predictions of vibrational

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A. Gao (✉) · X. Liang · L. Li
Shijiazhuang University of Economics, Shijiazhuang 050031, People's Republic of China
e-mail: llhx2006@126.com

A. Gao
Hebei Province Key Laboratory of Sustained Utilization and Development of Water Resources, Shijiazhuang 050031, People's Republic of China

J. Cui
Hebei Chemical Pharmaceutical College, Shijiazhuang 050026, People's Republic of China

wave numbers agree with experimental results. Xu *et al.* [17] employed the structures and electronic properties of some alkylthio radicals with density functional theory in conjunction with DZP++ basis sets. The other members of the alkylthio series, propylthio, butylthio and pentylthio radicals, received less attention on the vibronic structure and spectroscopic properties theoretically.

The electron affinity (EA) is both a key spectroscopic value and vitally important for use in the chemical cycle in order to determine bond dissociation energy. Over the past decades, there are many experimental studies for EA of the alkylthio radicals [18–25]. However, there only has been a theoretical report on the electron affinities of the alkylthio radicals [17]. The thermochemical properties and the ground or electronic states of the neutral and anion species are indispensable tools for understanding chemical reactivity and predicting the reaction mechanism. With this motivation, we have carried out a detailed study of structures, thermochemistry, and electron affinities of the alkylthio radicals and their anions using the higher level of the Gaussian-3(G3) techniques [26, 27]. The Gaussian-3 theory is a composite technique in which a sequence of well-defined *ab initio* molecular orbital calculations is performed to arrive at a total energy of given molecular species.

In this paper, we have carried out a detailed study of the alkylthio radicals $C_nH_{2n+1}S$ (n=1–5) and the corresponding anions by means of the higher level of the G3 theory [26, 27], intending to provide the theoretical description of the structures, electron affinities (EAs), and dissociation energies (De) as a reference for further experimental studies. We would like to establish reliable theoretical predictions for the simplest $C_nH_{2n+1}S/C_nH_{2n+1}S^-$ (n=1–5) species in the absence of experimental results and in some cases to challenge existing experiments.

Theoretical methods

The geometries, electron affinities, and dissociation energies of the alkylthio radicals have been performed through the Gaussian-3 (G3) method using the Gaussian 09 package [28]. Yang *et al.* [29, 30] checked the reliability of the higher level of the G3 theory by predicting the electron affinities and dissociation energies of small silicon-lithium clusters and arsenic clusters, and illustrated [30] the rationality of HF for vibrational frequencies. All species stationary point geometries were interrogated by the evaluation of their harmonic vibrational frequencies at the higher level of Gaussian-3 schemes. Zero-point vibrational energies (ZPVEs) are evaluated at the G3 level. These differences may be used as corrections to the adiabatic electron affinities.

The adiabatic electron affinities (EA_{ad}) are evaluated as the difference of total energy between the ground state geometry of the alkylthio radical and the ground state geometry of anion. The De for $C_nH_{2n+1}S/C_nH_{2n+1}S^-$ (n=1–5) are determined from differences in total energies in the following manner: the De for the radicals refer to the reaction:

$$C_nH_{2n+1}S \rightarrow C_nH_{2n+1} + S \quad (1)$$

the De for the anions refer to the reaction,

$$C_nH_{2n+1}S^- \rightarrow C_nH_{2n+1} + S^-. \quad (2)$$

Results and discussion

The geometries optimized with MP2(full)/6-31G(d) level for the simplest alkylthio radicals and their anions are displayed in Figs. 1, 2, 3 and 4 and Tables 1–11 of the Supporting information. Frequencies are calculated to verify that the structures are local minima on the potential energy surface and not transition states at MP2(full)/6-31G(d) level. Xu *et al.* [17] reported the structures and electron affinities of some alkylthio radical with density functional theory in conjunction with DZP++ basis sets.

The methylthio radical and the methylthio anion

Marenich and Boggs [6] reported *ab initio* study of spin-vibronic dynamics in the ground and excited electronic states of CH_3S radical. Xu *et al.* [17] employed the structures and electronic properties of the methylthio radical with density functional theory. The results of G3 calculation show that the geometry of the ground state structure of CH_3S displays C_s symmetry (Fig. 1 and Table 1 of the Supporting information). The C-S bond length is calculated to be 1.799 Å for $^2A'$ electronic state. For negatively charged ion CH_3S^-, the ground state structure possesses C_s symmetry with $^1A'$ state. The C-S bond length is calculated to be 1.825 Å, which is lengthier than that of neutral by 0.026 Å at MP2(full)/6-31G(d) level. The A (2,1,4) and A(3,1,4) angles increase by about 0.9° and 5.6° from the radical to the corresponding anion.

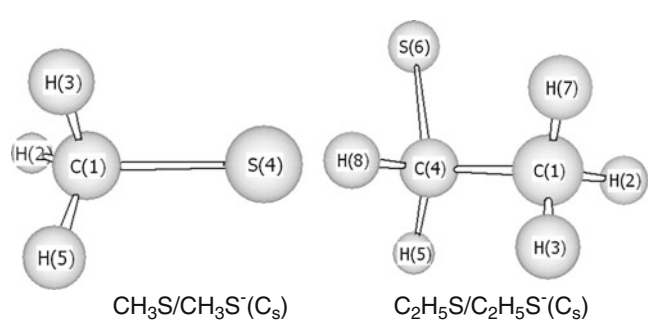

Fig. 1 Optimized geometries for the methylthio and ethylthio radicals and corresponding anions

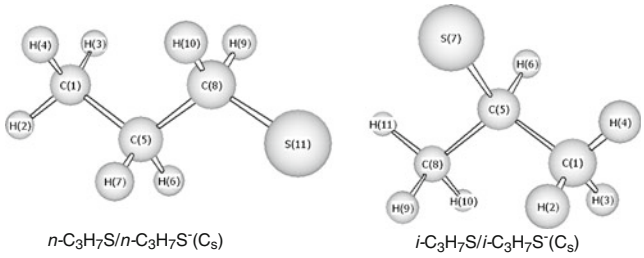

Fig. 2 Optimized geometries for the propylthio radical and corresponding anion

The ethylthio radical and the ethylthio anion

Our optimized geometries for both the ethylthio radical (C_2H_5S) and the anion are displayed in Fig. 1 and Table 2 of the Supporting information. The equilibrium geometry of the ethylthio radical in its $^2A''$ ground state has C_s symmetry geometry, while the ethylthio anion has a $^1A'$ ground state with C_s symmetry geometry at MP2(full)/6-31G(d) level. The ethylthio radical and anion have all real harmonic vibrational frequencies with the MP2(full)/6-31G(d) method. There are no experimental geometries available for comparison.

The equilibrium geometry and vibrational frequencies of the ground state of C_2H_5S are predicted with the UHF/cc-pVTZ, B3LYP/cc-pVTZ, and MP2/cc-pVTZ by Hung *et al.* [12] in 1996. Xu *et al.* [17] reported the structure of the ethylthio radical with density functional theory in conjunction with DZP++ basis sets. In the present paper, the geometries of C_2H_5S and $C_2H_5S^-$ are similar, with the biggest difference being a change in the A (6,4,8) angle by about 4.4°. From the radical to the anion, the C-S bond distance increases by about 0.017 Å, and the C-C bond distance increases by about 0.007 Å. Other bond distances and bond angles do not reveal significant differences when comparing the geometries of C_2H_5S and $C_2H_5S^-$.

The propylthio radical and the propylthio anion

There are two isomers for the propylthio (C_3H_7S) radical: *n*-C_3H_7S and *i*-C_3H_7S. Our optimized geometries of the ground states for the two isomers of the propylthio radical and their anions are shown in Fig. 2 and Tables 3–4 of the Supporting information. They are with C_s symmetry of the $^2A''$ ground state of for the *n*-C_3H_7S radical and with C_s symmetry structure of the $^2A'$ ground state of the *i*-C_3H_7S radical and with C_s symmetry geometry for the $^1A'$ ground state of two anions. The *i*-C_3H_7S radical is predicted to lie 0.060 eV lower in energy than the *n*-C_3H_7S radical at the G3 level of theory. The two corresponding anionic isomers, *n*-$C_3H_7S^-$ and *i*-$C_3H_7S^-$, the result is the same and the G3 energy for *i*-$C_3H_7S^-$ is 0.154 eV lower than that for *n*-$C_3H_7S^-$.

From the *n*-C_3H_7S radical to corresponding anion, we find that the C-S, C(5)-C(8), and C(1)-C(5) bond distances increase by about 0.017, 0.005, and 0.004 Å, respectively. A(5,8,11) angle decreases by about 1.6°, while A(1,5,8) angle increases by about 2.0°. The other bond distances and bond angles change only slightly. As for *i*-C_3H_7S radical and corresponding anion, the C-S bond distance changes by about 0.009 Å. A(1,5,8) angle decreases by about 2.7°, while A(6,5,7) angle increases by about 6.5°.

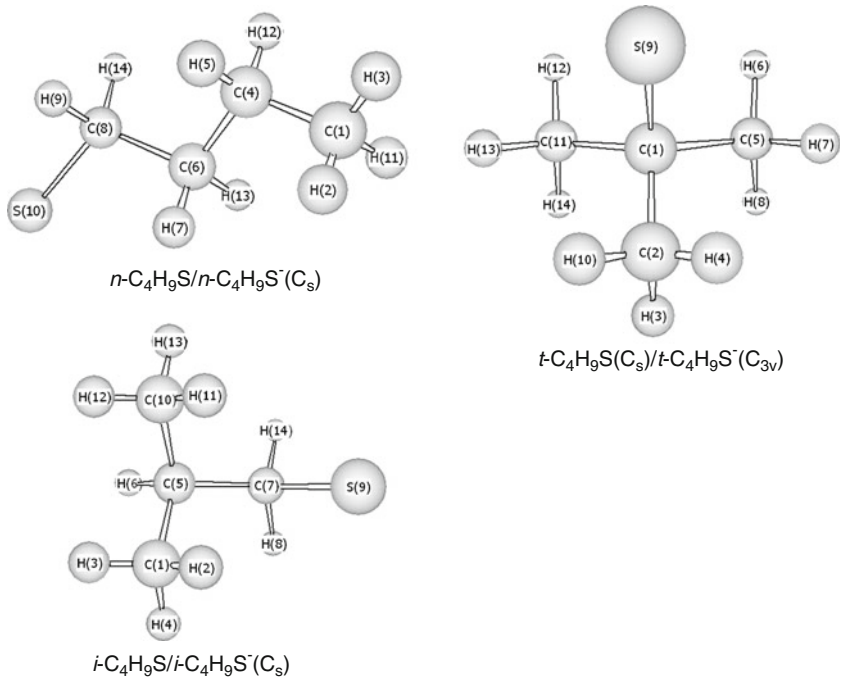

Fig. 3 Optimized geometries for the butylthio radical and corresponding anion

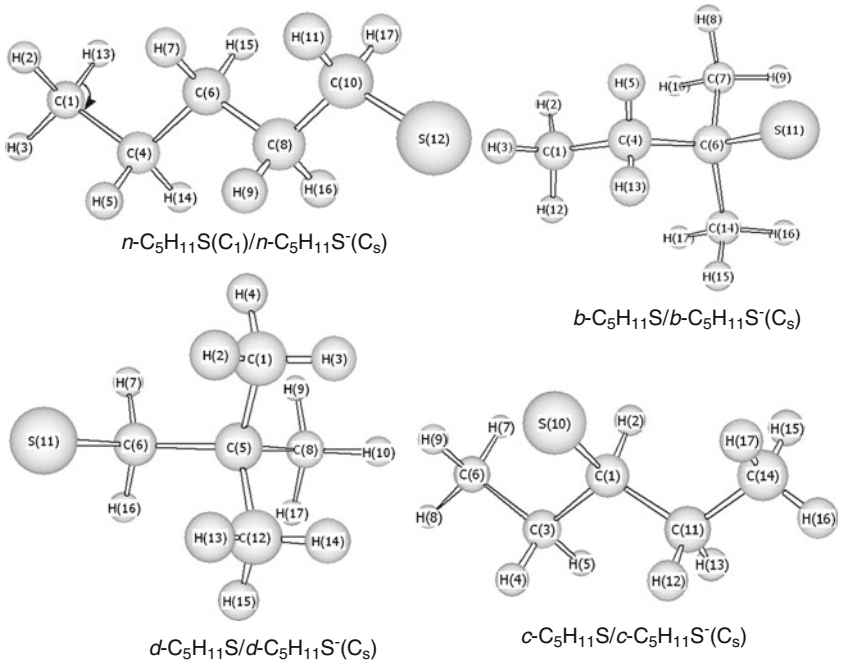

Fig. 4 Optimized geometries for the pentylthio radical and corresponding anion

There are very small differences in other bond lengths and bond angles. There are still no experimental data available for comparison.

The butylthio radical and the butylthio anion

We have obtained three isomers (n-C_4H_9S, t-C_4H_9S, and i-C_4H_9S) for the butylthio radical. The equilibrium geometries of the t-C_4H_9S radical and the C_s symmetry geometry of the $^2A''$ ground state of the n-C_4H_9S and i-C_4H_9S radicals and the C_s symmetry structure of the $^1A'$ ground state of the n-$C_4H_9S^-$ and i-$C_4H_9S^-$ are given in Fig. 3 and Tables 5–7 of the Supporting information. The t-C_4H_9S radical is with C_s symmetry structure for the $^2A'$ ground state and the t-$C_4H_9S^-$ is with C_{3v} symmetry geometry for the $^1A_1$ ground state. It is known to us there are no experimental and theoretical geometries available for comparison. The t-C_4H_9S radical is predicted to lie 0.202 and 0.109 eV lower in energy than the n-C_4H_9S and i-C_4H_9S radical (at the G3 level), respectively. The three corresponding anionic isomers, n-$C_4H_9S^-$, t-$C_4H_9S^-$, and i-$C_4H_9S^-$, the result is the same and the G3 energy for t-$C_4H_9S^-$ is 0.344 and 0.228 eV lower than that for n-$C_4H_9S^-$ and i-$C_4H_9S^-$, respectively. A vibrational analysis is carried out for each radical and anion, and all are found to be genuine minima.

Three radicals and corresponding anions' geometries are quite similar. With the MP2(full)/6-31G(d) scheme, the C-S bond lengths for the n-butylthio, t-butylthio, and i-butylthio radical are predicted to be 1.804 Å, 1.823 Å, and 1.805 Å, and those for the anionic species are 1.822, 1.829 Å, and 1.824 Å, respectively. From the n-C_4H_9S radical to corresponding anion, the C(6)-C(8) bond distance changes by about 0.006 Å and A(6,8,10) bond angle decreases by about 1.7°. The other bond distances and bond angles change only slightly. As for i-C_4H_9S radical and corresponding anion, the C(5)-C(7) bond distance changes by about 0.012 Å. A (1,5,10) and A (5,7,9) angles decrease by about 0.8° and 0.6°, respectively. For the t-C_4H_9S radical and corresponding anion, A (5,1,11) angle decreases by about 2.1°, while A (2,1,9) angle increases by about 4.6°. Other bond lengths

Table 1 Adiabatic electron affinities for the alkylthio radicals

Radicals	EA_{ad}	Corrected EA_{ad}	Expt.
CH_3S	1.867	1.860	1.8670±0.0040[b]
			1.871±0.012[c]
			1.8610±0.0040[d]
C_2H_5S	1.959	1.960	1.9530±0.0040[e]
			1.947±0.013[c]
n-C_3H_7S	1.974	1.980	2.000±0.020[e]
i-C_3H_7S	2.065	2.074	2.020±0.020[e]
n-C_4H_9S	1.983	1.991	2.030±0.020[e]
t-C_4H_9S	2.117	2.133	2.070±0.020[e]
i-C_4H_9S	2.002	2.013	2.06±0.14[f]
n-$C_5H_{11}S$	1.991	1.999	2.090±0.020[e]
b-$C_5H_{11}S$	2.128	2.147	
c-$C_5H_{11}S$	2.150	2.164	
d-$C_5H_{11}S$	2.046	2.059	2.12±0.14[f]

Presented in eV with the G3 schemes. [b] Ref. [3], [c] Ref. [22], [d] Ref. [19], [e] Ref. [20], [f] Ref. [24]

Table 2 Dissociation energies (De) of the alkylthio radicals and anions

Radicals	De	Corrected De	Anions	De	Corrected De
$CH_3S \rightarrow CH_3 + S$	4.375	4.191	$CH_3S^- \rightarrow CH_3 + S^-$	3.070	2.809
$C_2H_5S \rightarrow C_2H_5 + S$	4.380	4.223	$C_2H_5S^- \rightarrow C_2H_5 + S^-$	3.414	2.941
$n\text{-}C_3H_7S \rightarrow n\text{-}C_3H_7 + S$	4.421	4.276	$n\text{-}C_3H_7S^- \rightarrow n\text{-}C_3H_7 + S^-$	3.259	3.014
$i\text{-}C_3H_7S \rightarrow i\text{-}C_3H_7 + S$	4.344	4.205	$i\text{-}C_3H_7S^- \rightarrow i\text{-}C_3H_7 + S^-$	3.167	3.037
$n\text{-}C_4H_9S \rightarrow n\text{-}C_4H_9 + S$	4.416	4.272	$n\text{-}C_4H_9S^- \rightarrow n\text{-}C_4H_9 + S^-$	3.157	3.020
$t\text{-}C_4H_9S \rightarrow t\text{-}C_4H_9 + S$	4.326	4.201	$t\text{-}C_4H_9S^- \rightarrow t\text{-}C_4H_9 + S^-$	3.200	3.092
$i\text{-}C_4H_9S \rightarrow i\text{-}C_4H_9 + S$	4.440	4.289	$i\text{-}C_4H_9S^- \rightarrow i\text{-}C_4H_9 + S^-$	3.200	3.061
$n\text{-}C_5H_{11}S \rightarrow n\text{-}C_5H_{11} + S$	4.419	4.276	$n\text{-}C_5H_{11}S^- \rightarrow n\text{-}C_5H_{11} + S^-$	3.168	3.033
$b\text{-}C_5H_{11}S \rightarrow b\text{-}C_5H_{11} + S$	4.311	4.191	$b\text{-}C_5H_{11}S^- \rightarrow b\text{-}C_5H_{11} + S^-$	3.197	3.096
$c\text{-}C_5H_{11}S \rightarrow c\text{-}C_5H_{11} + S$	4.388	4.258	$c\text{-}C_5H_{11}S^- \rightarrow c\text{-}C_5H_{11} + S^-$	3.296	3.181
$d\text{-}C_5H_{11}S \rightarrow d\text{-}C_5H_{11} + S$	4.482	4.336	$d\text{-}C_5H_{11}S^- \rightarrow d\text{-}C_5H_{11} + S^-$	3.286	3.153

The values are in eV

and bond angles have small differences in geometry between t-C_4H_9S radical and corresponding anion.

The pentylthio radical and the pentylthio anion

We have examined four isomers for the $C_5H_{11}S$ radical: n-$C_5H_{11}S$, b-$C_5H_{11}S$, c-$C_5H_{11}S$ and d-$C_5H_{11}S$ (Fig. 4 and Tables 8–11 of the Supporting information). The b-$C_5H_{11}S$ and c-$C_5H_{11}S$ radicals display C_s symmetry in their $^2A'$ ground states. The n-$C_5H_{11}S$ radical and d-$C_5H_{11}S$ radical have $^2A''$ ground states with C_s symmetry structure. Their anionic counterparts all are with C_s symmetry geometry of the $^1A'$ ground states. The d-$C_5H_{11}S$ radical structure is the global minimum, while the n-$C_5H_{11}S$ lies 0.163 eV above it (at the G3 level), the b-$C_5H_{11}S$ radical lies 0.078 eV above it and c-$C_5H_{11}S$ lies higher, 0.159 eV above the global minimum. For the anionic counterparts, the structure b-$C_5H_{11}S^-$ is the global minimum, the n-$C_5H_{11}S^-$ lies 0.311 eV above it with the G3 method, the d-$C_5H_{11}S^-$ lies 0.010 eV above it and the relative energy of the c-$C_5H_{11}S^-$ is 0.063 eV. Vibrational analyses show that all these structures are genuine minima.

The predicted change for the C-S bond is 0.017 Å, and the changes of A(12,10,17) and A(8,10,12) angles are 2.9 and 1.7 Å from the n-$C_5H_{11}S$ radical to the n-$C_5H_{11}S^-$. As for the b-$C_5H_{11}S$ and the b-$C_5H_{11}S^-$, the change for the C-S bond is 0.005 Å and for the C(4)-C(6) bond is 0.003 Å with the G3 functional. The changes of A(4,6,11) and A(7,6,14) angles are 4.2° and 2.0°, respectively. From the c-$C_5H_{11}S$ radical to corresponding anion, the C-S bond increases by about 0.011 Å, while the other bonds almost have no change. A(2,1,10) angle increases by about 6.3°, while A(3,1,11) angle decreases by about 3.3°. From the d-$C_5H_{11}S$ radical to corresponding anion, the C-S bond increases by about 0.018 Å. A(11,6,16) and A(6,5,8) angles increase by about 4.2° and 1.8°, while A(5,6,16) and A(5,6,11) angles decrease by about 3.8° and 0.7°, respectively. For all pentylthio radicals and anions, other bond lengths and bond angles have very small changes.

Electron affinities

The theoretical EA_{ad} and the experimental electron affinity data are listed in Table 1. There are several experimental studies of the electron affinity for the methylthio radical. In 1980, Janousek and Brauman [19] reported the experimental adiabatic electron affinity of the methylthio radical to be 1.8610±0.0040 eV *via* laser photodetachment method. In 1988, Moran and Ellison [22] obtained the EA of CH_3S to be 1.871±0.012 eV with laser photoelectron spectroscopy (LPES). Later (2000), Schwartz *et al.* [3] reported the more accurate electron affinities to date for phenylnitrene, 1.8670±0.0040 eV using LPES. The ZPVE corrected electron affinities (1.860 eV) of the methylthio radical is closely matched by the more recent (and more reliable) experimental value (only deviating about 0.007 eV) at the G3 level. The result is in good accord with the experimental value and convincing. There have been four experimental values reported [20–23] for the ethylthio radical. The more reliable experimental EA_{ad} [20] was obtained to be 1.9530±0.0040 eV by Janousek *et al.* in 1980. Moran and Ellison [22] estimated the electron affinities to be 1.947±0.013 eV by laser photoelectron spectroscopy. The EA_{ad} (with ZPVE correction) is predicted to be 1.960 eV with the G3 method, and our value is reasonable compared with two more reliable experiment results, deviating 0.007 and 0.013 eV, respectively. For the isomer of the C_3H_7S radical, in 1979, experimental electron affinities of 2.02±0.13 eV and 2.05±0.13 eV were reported by Bartmess *et al.* [21] with D-EA method. After 1 year, Janousek *et al.* [20] presented the experimental adiabatic electron affinity of the propylthio radical (n-C_3H_7S) to be 2.000±0.020 eV and the i-C_3H_7S radical to be 2.020±0.020 eV *via* laser photodetachment spectroscopy. Compared with the more reliable experimental values [20], our G3 results with ZPVE correction (1.980 and 2.074 eV) are very reliable and satisfying, with the absolute errors of 0.020 and 0.054 eV, respectively. Compared with the most reliable experimental value of the n-C_4H_9S radical (2.030±0.020 eV) [20], the EA_{ad}

value (1.991 eV) predicted by the G3 method is close to the experimental value, with the absolute error being 0.039 eV. There have experimentally been two studies [20, 21] of the electron affinity for the *t*-C_4H_9S radical. In 1980, Janousek, Reed and Brauman [20] estimated the most accurate electron affinity (2.070±0.020 eV) to date of the value for the radical *via* photoelectron spectroscopy. Compared with the most reliable experimental value, the G3 value (2.133 eV) is considered to be reasonable and satisfactory, deviating about 0.043 eV. For *i*-C_4H_9S radical, Taft [24] obtained the electron affinity using the D-EA method in 1987. The EA_{ad} value (2.013 eV) with ZPVE correction predicted by the G3 method is in agreement with the experimental value [24], only deviating 0.047 eV. There has been one experimental value of the linear chain pentylthio radical reported [20] using electron photodetachment method. Compared with the reliable experimental value (2.090±0.020 eV), our G3 calculated result (1.999 eV) is reasonable and the absolute error is 0.091 eV. Compared with the experimental value (2.12±0.14 eV) [24] for the *d*-$C_5H_{11}S$ radical, the predicted value with ZPVE correction (2.059 eV) is in agreement with the experimental result, which deviates 0.061 eV. In addition, at the G3 level, the theoretical predicted values for the *b*-$C_5H_{11}S$ and *c*-$C_5H_{11}S$ radicals are 2.147 and 2.164 eV, respectively. Xu *et al.* [17] reported the adiabatic electron affinities of seven alkylthio radicals, obtained by B3LYP method, are 1.838 eV (CH_3S), 1.925 eV (C_2H_5S), 1.939 eV (*n*-C_3H_7S), 1.961 eV (*n*-C_4H_9S), 1.969 eV (*n*-$C_5H_{11}S$), 2.023 eV (*i*-C_3H_7S), and 2.055 eV (*t*-C_4H_9S), respectively. The average absolute error of the B3LYP method remained 0.047 eV. In this paper, at the G3 level, our theoretical EA values for the alkylthio radicals are in good agreement with the available experimental results, with average absolute error of only 0.041 eV. In addition, the experimental electron affinities for the alkoxy radicals are reported to be 1.5690±0.0019 eV [31] for CH_3O, 1.7120±0.0040 eV [32] for C_2H_5O, 1.789±0.033 eV [33] for *n*-C_3H_7O, 1.8740±0.0040 eV [32] for *i*-C_3H_7O, 1.80±0.13 eV [34] for *n*-C_4H_9O, 1.9090±0.0040 eV [32] for *t*-C_4H_9O, 1.88±0.11 eV [35] for *i*-C_4H_9O, 1.89±0.13 eV [36] for *n*-$C_5H_{11}O$, 1.94±0.15 eV [34] for *b*-$C_5H_{11}O$, 1.94±0.12 eV [37] for *c*-$C_5H_{11}O$, and 1.95±0.13 eV [35] for *d*-$C_5H_{11}O$, respectively. Compared with the electron affinities of the alkoxy radicals, we find that the electron affinities of the linear chain the alkylthio radicals and the alkoxy radicals are both larger with the number of carbon atoms increased and the change trend are in accord with each other.

Dissociation energies

The dissociation energies for $C_nH_{2n+1}S/C_nH_{2n+1}S^-$($n$=1–5) systems are given in Table 2. The dissociation energy (De) (defined as the energy required in the reaction $C_nH_{2n+1}S \rightarrow C_nH_{2n+1} + S$) of the alkylthio radicals are evaluated with the G3 scheme to be 4.191(4.375) eV for CH_3S, 4.223 (4.380) eV for C_2H_5S, 4.276 (4.421) and 4.205 (4.344) eV for the two isomers of C_3H_7S, 4.272 (4.416), 4.201 (4.326) and 4.289 (4.440) eV for the three isomers of C_4H_9S, and 4.276 (4.419), 4.191 (4.311), 4.258 (4.388), and 4.336 (4.482) eV for the four isomers of $C_5H_{11}S$ (presented in parentheses without ZPVE correction). From the De, the stability of bonding an S atom to alkyl radical can be found. The higher the values of these dissociation energies, the more stable the alkyl radicals bonding of an S atom. Table 2 shows that the dissociation energies for the linear chain $C_nH_{2n+1}S \rightarrow C_nH_{2n+1} + S$ become larger when *n* is incremental (excepting *n*-C_3H_7S radical). For the anions, $C_nH_{2n+1}S^-$, dissociation to a neutral C_nH_{2n+1} plus anionic S^- is calculated at the G3 level. The theoretical results are listed in Table 2. Our predicted values De($C_nH_{2n+1} - S^-$) are 2.809 (3.070) eV for CH_3S^-, 2.941 (3.414) eV for $C_2H_5S^-$, 3.014 (3.259) and 3.037 (3.167) eV for the two isomers of $C_3H_7S^-$, 3.020 (3.157), 3.092 (3.200) and 3.061 (3.200) eV for the three isomers of $C_4H_9S^-$, and 3.033 (3.168), 3.096 (3.197), 3.181 (3.296), and 3.153 (3.286) eV for the four isomers of $C_5H_{11}S^-$. The general trend for these linear chain anions *n*-$C_nH_{2n+1}S^-$ dissociation energies to *n*-$C_nH_{2n+1} + S^-$ is upward with *n* increased. It shows that when the size of the species increases, dissociation becomes less preferable. There are no experimental values for comparison.

Conclusions

The equilibrium geometries and electron affinities of the simplest 11 alkylthio radicals and their anions have been systematically investigated by means of the higher level of the G3 scheme. The reliable adiabatic electron affinities are predicted to be 1.860(1.867) eV for CH_3S, 1.960 (1.959) eV for C_2H_5S, 1.980 (1.974) and 2.074 (2.065) eV for the two isomers of C_3H_7S, 1.991 (1.983), 2.133 (2.117) and 2.013 (2.002) eV for the three isomers of C_4H_9S, and 1.999 (1.991), 2.147 (2.128), 2.164 (2.150), and 2.059 (2.046) eV for the four isomers of $C_5H_{11}S$ (presented in parentheses without ZPVE correction), respectively. Our theoretical EA values of the G3 level are in good accord with the available experimental results and the average absolute deviation from experiment for the simplest 11 alkylthio radicals is only 0.041 eV. The dissociation energies of S from the alkylthio radicals have been calculated and used to reveal relative stability. The dissociation energies are predicted to be 4.191(4.375) eV for CH_3S, 4.223 (4.380) eV for C_2H_5S, 4.276 (4.421) and 4.205 (4.344) eV for the two isomers of C_3H_7S, 4.272 (4.416), 4.201 (4.326) and 4.289 (4.440) eV for the three isomers of C_4H_9S, and 4.276 (4.419), 4.191 (4.311), 4.258 (4.388), and 4.336 (4.482) eV for the four isomers of $C_5H_{11}S$ to loss of an S atom (presented in

parentheses without ZPVE correction). The dissociation energies ($C_nH_{2n+1}S^- \rightarrow C_nH_{2n+1} + S^-$, n=1–5) are estimated to be 2.809 (3.070) eV for CH_3S^-, 2.941 (3.414) eV for $C_2H_5S^-$, 3.014 (3.259) and 3.037 (3.167) eV for the two isomers of $C_3H_7S^-$, 3.020 (3.157), 3.092 (3.200) and 3.061 (3.200) eV for the three isomers of $C_4H_9S^-$, and 3.033 (3.168), 3.096 (3.197), 3.181 (3.296), and 3.153 (3.286) eV for the four isomers of $C_5H_{11}S^-$ (presented in parentheses without ZPVE correction), respectively. To the best of our knowledge, there are no experimental data regarding the dissociation energy for the alkylthio radicals systems. Our results may thus provide a reference for further investigations.

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