Structure and Stability of Interstellar Molecule C_3S

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The singlet and triplet potential energy surfaces of interstellar molecule C_3S are predicted at the UB3LYP/6-311(d) and UCCSD(T)/6-311+G(2df) (single-point) levels. The linear singlet isomer CCCS with $^1\sum^+$ electronic state is found to be thermodynamically and kinetically the most stable species on the singlet surface followed by other four singlet isomers, which are unstable on the basis of calculated results. On the triplet surface, the lowest-lying species, which lies 248.79 kJ/mol above linear singlet species CCCS, is chain CCCS connectivity with $^3A'$ electronic state. Other four triplet isomers can be considered as unstable species by means of transition state and potential energy surface scan technologies. The structures, vibrational frequencies, dipole moments and rotational constants of all optimized species are also calculated.

Keywords potential energy surface, C_3S molecule, isomerization, stability

Introduction

Small clusters containing carbon and sulfur, such as CS, C_2S and C_3S, which possess large permanent dipole moments and have been identified in the carbon star IRC +10°216 and in the Taurus cold molecular dense cloud TMC-1,[1-7] have attracted much attention because of their important roles in the areas of interstellar chemistry and material science, *i.e.*, the abundance of carbon sulfur clusters near interstellar objects is thought to be only slightly less than the corresponding pure carbon clusters[2] and many semiconductor films containing C_mS_n clusters exhibit unusual electrical properties.[8] Many theoretical[9-14] and experimental[15-21] studies have been carried out on their spectra, structures, bonding and stability, *etc*. But the SC_nS clusters, having no or near-zero permanent dipole moments, have to date gone undetected because they are silent in radio astronomy observation. In this study, we choose C_3S molecule as our goal, not only because it is a very typical carbon-sulfur cluster with possible carbon-sulfur multiple bond but also because no more information about the structure and stability of its possible isomers is available. Many theoretical and experimental studies[10,13,14,19] identified that C_3S has a linear CCCS form with $^1\sum^+$ electronic state and several possible nonlinear species. But their relative stability are not discussed. And then, a detailed knowledge about structure, stability, bonding and isomerization properties of various C_3S isomers is very desirable and helpful for understanding the available experiments and for addressing the chemistry of these interesting species containing carbon-sulfur multiple bond. Quantum chemistry computation is a powerful tool to predict accurately the structure and stability of small molecules based on previous studies.[22-27] Therefore, in this paper, we report a detailed *ab initio* computational study on the C_3S system with an attempt to investigate the possible isomer forms and predict the potential isomers that are kinetically stable.

Computational methods

All computations are carried out with *Gaussian* 98 program package.[28] The isomers, transition states and

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their vibrational frequencies are obtained at the UB3LYP/6-311G(d) level.[29-32] The UB3LYP/6-311G(d) geometries are further employed to calculate single-point energies using UCCSD(T) method[33-35] with 6-311 + G(2df) basis set. Furthermore, intrinsic reaction coordinate (IRC) calculations[36,37] are carried out at the UB3LYP/6-311G(d) level to identify whether the transition states connect the correct reactants and products.

Results and discussion

Isomers

We have performed geometrical surveys on nearly all possible isomers including linear, chainlike, cyclic and stereo structures followed by vibrational analysis to confirm whether the obtained structures are local minimums or not. On the singlet and triplet potential energy surfaces of C_3S, five singlet species and five triplet isomers were found, and their total and relative energies are given in Table 1, while the detailed geometries are summarized in Fig. 1. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments and rotational constants of the C_3S species are listed in Table 2, and the predicted data of $\mathbf{1}^s$ are in good agreement with experimental results.[10,13,14,19] From Table 1, the energetic ordering of the optimized C_3S local energy minimums can be obtained. Generally, the species with lower total energy has higher thermodynamical stability. At the single-point UCCSD(T)/6-311 + G(2df) level with zero-point energies included, for singlet species, the thermodynamical stability order is then $\mathbf{1}^s$ (0.00) > $\mathbf{2}^s$ (226.10) > $\mathbf{3}^s$ (281.44) > $\mathbf{4}^s$ (318.60) > $\mathbf{5}^s$ (448.51), and for triplet isomers, $\mathbf{1}^t$ (248.79) > $\mathbf{2}^t$ (265.39) > $\mathbf{3}^t$ (358.14) > $\mathbf{4}^t$ (391.58) > $\mathbf{5}^t$ (436.27). The values in parentheses are relative energies in kJ/mol with reference to $\mathbf{1}^s$.

Table 1 Predicted total energies (a.u.), zero-point energies (ΔZPVE, kJ/mol) and relative energies (kJ/mol) for isomers and transition states of C_3S system

Species	UB3LYP/6-311G(d)	UCCSD(T)/6-311 + G(2df)	ΔZPVE	Relative energies
Chain-CCCS $\mathbf{1}^s$ ($^1\Sigma^+$)	−512.402605	−511.663902	34.27	0.00
Cyclic-SCCC $\mathbf{2}^s$ ($^1A_1$)	−512.298266	−511.574836	26.73	226.10
C-cyclic-CCS $\mathbf{3}^s$ ($^1A'$)	−512.281866	−511.553852	27.05	281.44
Cyclic-SCCC $\mathbf{4}^s$ ($^1A'$)	−512.262056	−511.538956	25.11	318.60
Chain-CSCC $\mathbf{5}^s$ ($^1A'$)	−512.210871	−511.489075	24.20	448.51
Chain-CCCS $\mathbf{1}^t$ ($^3A'$)	−512.312329	−511.566178	26.73	248.79
S-cyclic-CCC $\mathbf{2}^t$ ($^3B_2$)	−512.299776	−511.560035	27.19	265.35
Cyclic-SCCC $\mathbf{3}^t$ ($^3A''$)	−512.254804	−511.524418	26.54	358.14
SC(C)C $\mathbf{4}^t$ ($^3B_2$)	−512.240356	−511.511310	25.60	391.58
Cyclic-SCCC $\mathbf{5}^t$ ($^3B_1$)	−512.222898	−511.494240	25.51	436.27
TS1^s/$\mathbf{2}^s$ ($^1A'$)	−512.298106	−511.574310	26.09	226.85
TS1^s/$\mathbf{3}^s$ ($^1A'$)	−512.274915	−511.549098	25.45	291.05
TS3^s/$\mathbf{4}^s$ (^1A)	−512.261752	−511.537676	24.34	321.19
TS1^s/$\mathbf{3}^{s*}$ ($^1A'$)	−512.250152	−511.523694	24.35	357.85
TS1^s/$\mathbf{5}^s$ ($^1A'$)	−512.210017	−511.487232	22.69	451.82
TS1^t/$\mathbf{2}^t$ ($^3A'$)	−512.265903	−511.524837	24.88	355.38
TS3^t/$\mathbf{5}^t$ ($^3A'$)	−512.201086	−511.468643	27.08	504.99
TS1^t/$\mathbf{3}^t$ ($^3A'$)	−512.252847	−511.520481	25.60	367.55

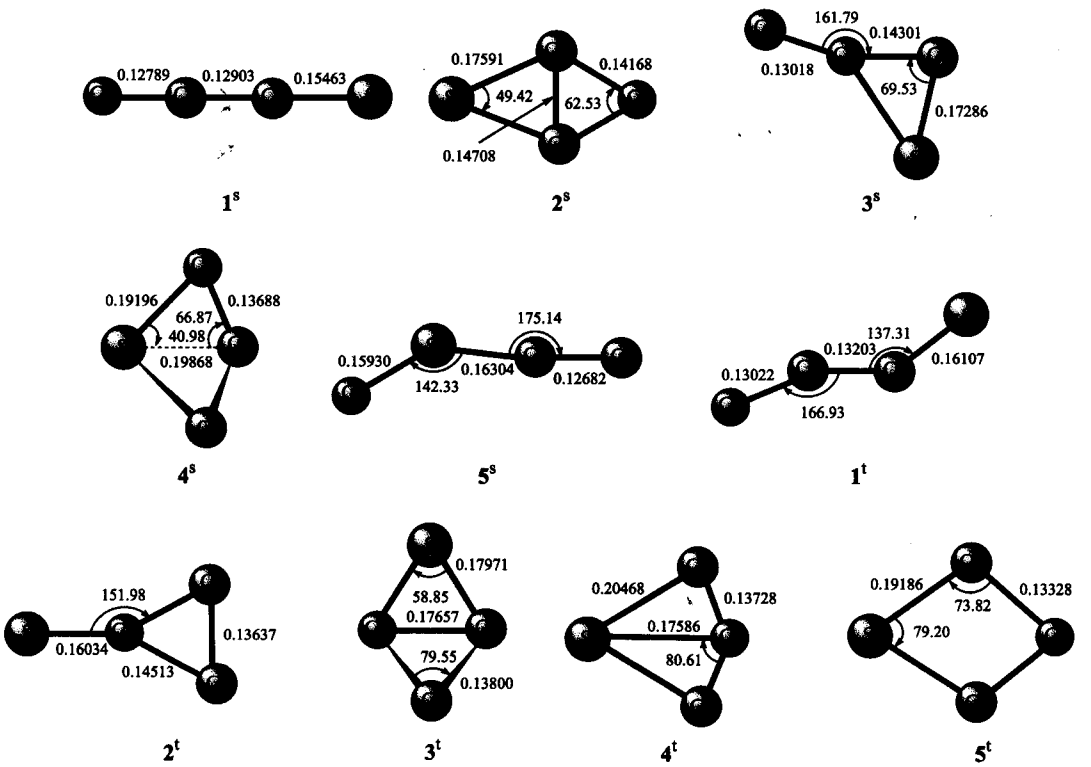

Fig. 1 Optimized geometries for isomers of C_3S system (bond lengths are in nanometer, and bond angles in degree).

Table 2 Predicted vibrational frequencies (cm^{-1}), dipole moments (Debye), and rotational constants (GHz) for isomers and transition states of C_3S system (vibrational intensities (km/mol) are placed in the parentheses)

Species	Frequencies (infrared intensity)	Dipole moments	Rotational constants
1^s	159 (3×2), 480 (0×2), 738 (13), 1566 (65), 2144 (1527)	3.4975	2.879829
2^s	132 (38), 423 (0), 691 (12), 768 (15), 997 (2), 1455 (7)	3.1006	38.938543, 6.350542, 5.460054
3^s	174 (7), 318 (1), 601 (2), 666 (142), 1006 (13), 1757 (365)	2.4886	21.019583, 6.063393, 4.765922
4^s	239 (0), 289 (29), 493 (11), 653 (0), 1218 (29), 1304 (78)	1.2473	14.781543, 9.755674, 6.358317
5^s	89 (8), 123 (0), 163 (11), 678 (19), 1097 (47), 1895 (350)	2.8863	99.180224, 3.778668, 3.639988
1^t	135 (8), 242 (8), 383 (49), 790 (2), 1266 (5), 1653 (118)	2.7710	142.55660, 3.042849, 2.979210
2^t	157 (140), 677 (8), 408 (6), 1184 (1), 571 (81), 1549 (204)	0.3625	45.291239, 4.379575, 3.993419
3^t	314 (26), 486 (9), 501 (2), 748 (33), 1140 (1), 1249 (152)	1.2895	24.647491, 7.424543, 5.947369
4^t	286 (2), 327 (0), 370 (17), 848 (14), 1041 (21), 1407 (0)	1.5304	11.479321, 11.420562, 5.724933
5^t	149 (78), 314 (1), 537 (0), 672 (6), 1246 (1), 1346 (1)	0.0462	14.078609, 10.393683, 5.979358
$TS1^s/2^s$	194i (35), 427 (0), 694 (13), 734 (14), 1034 (11), 1472 (3)		
$TS1^s/3^s$	255i (0), 278 (0), 530 (90), 637 (44), 1067 (77), 1745 (112)		
$TS3^s/4^s$	228i (3), 332 (23), 460 (15), 658 (1), 1185 (33), 1434 (117)		
$TS4^s/5^s$	182i (27), 115 (0), 132 (0), 658 (4), 1004 (62), 1885 (66)		
$TS1^t/2^t$	462i (1), 93 (1), 322 (1), 872.63 (0), 1245 (10), 1621 (40)		
$TS3^t/5^t$	1292i (56), 460 (42), 639 (3), 756 (153), 1019 (10), 1652 (2)		
$TS1^t/3^t$	275i (9), 443 (0), 477 (7), 833 (22), 1218 (4), 1308 (80)		

It is clear that isomer $\mathbf{1}^s$ is the thermodynamically most stable species. The lowest-lying species $\mathbf{1}^s$ on the singlet surface has a linear CCCS form with $^1\Sigma^+$ electronic state. In isomer $\mathbf{1}^s$, the lengths of terminal C—C bond, medial C—C bond and C—S bond are 0.12789, 0.12903 and 0.15463 nm, respectively, and it can be described as C = C = C = S structure. Isomer $\mathbf{2}^s$, which is higher in energy than $\mathbf{1}^s$ by 226.10 kJ/mol, has C_{2v} symmetry and a CCCS four-membered ring with C—C cross bonding, and isomer $\mathbf{3}^s$ is an isomer containing CCS three-membered ring with exocyclic C—C bonding. Species $\mathbf{4}^s$ has a typical butterfly structure with three longer S—C single bonds. The remaining singlet species $\mathbf{5}^s$ is a chain CSCC structure with 0.15930 nm terminal C—S bond length, which is a double bond. And, the middle C—S bond (0.16304 nm) is also a double bond with some single bond characters. The C—C bond distance is 0.12682 nm in $\mathbf{5}^s$, indicating obviously that it is a double bond with some contribution of triple bond.

For triplet species, $\mathbf{1}^t$, a chain CCCS structural form with C_s symmetry, is found to be lowest-lying isomer on the triplet surface, and can also be considered as C = C = C = S structure based on its bond distances. Species $\mathbf{2}^t$ has C_{2v} symmetry and CCC three-membered ring with exocyclic CS bonding, and C—S bond length (0.16034 nm) indicates that it is a typical single bond. Isomers $\mathbf{3}^t$ and $\mathbf{5}^t$ have SCCC four-membered ring, but $\mathbf{3}^t$ has a C—C cross bonding. The last species $\mathbf{4}^t$ has a C_{2v} structure with a single S—C bond.

Kinetic stability

Eight singlet and triplet interconversion transition states of C_3S system are obtained at UB3LYP/6-311G(d) level of theory. Their structures are shown in Fig. 2, while the total energies, zero-point energies, and relative energies are listed in Table 1. Furthermore, the frequencies and intensities of all transition states are given in Table 2. Their connections are checked by IRC calculations at UB3LYP/6-311G(d) level. **TS*m*/*n*** denotes the transition state connecting the species ***m*** and ***n***. By means of the isomers and transition states, a schematic singlet and triplet potential energy surfaces are plotted in Fig. 3. For simplicity, the details of the obtained eight transition states are omitted. Practically, we can briefly discuss the kinetic stability of the obtained isomers in terms of the smallest isomerization. First, from Fig. 3, it can be seen that isomer $\mathbf{1}^s$ can isomerize into $\mathbf{2}^s$, which is the lowest isomerization in energy from $\mathbf{1}^s$ to other isomers, via transition state $\mathbf{TS1}^s/\mathbf{2}^s$ by a 226.85 kJ/mol reaction barrier height. And thus, the lowest-lying isomer $\mathbf{1}^s$, linear singlet CCCS form, is kinetically stable species, and can be experimentally observed in normal conditions. This is in agreement with previous experiments. The remaining singlet isomers **2**, **3**, **4** and **5** may be considered to be kinetically unstable species based on corresponding lowest conversion barriers, *i.e.*, 0.75 (**2**→**1**), 9.61 (**3**→**1**), 2.59 (**4**→**3**) and 3.31 (**5**→**1**) kJ/mol. Second, we will discuss the isomerizations on the triplet surface. From Fig. 3, it can be easily known that the chain species $\mathbf{1}^t$, which is higher in energy than singlet isomers $\mathbf{1}^s$ by 248.79 kJ/mol, is lowest-lying isomer on the triplet potential energy surface, and can be considered as kinetically stable species on the surface because of the lowest isomerization barrier 106.59 kJ/mol for $\mathbf{1}^t \rightarrow \mathbf{2}^t$ via transition state $\mathbf{TS1}^t/\mathbf{2}^t$. And the reverse barrier, from $\mathbf{2}^t$ to $\mathbf{1}^t$ via transition state $\mathbf{TS1}^t/\mathbf{2}^t$, is about 89.99 kJ/mol, which indicates that $\mathbf{2}^t$ is an unstable species. It should be noted that isomer $\mathbf{4}^t$ do not appear in the Fig. 3 because the transition state was not located from isomer $\mathbf{4}^t$ to other triplet species despite the expected existence of a CCS three-membered transition state connecting $\mathbf{4}^t$ and $\mathbf{1}^t$. Therefore, for exploring its stability, a potential energy surface scan from $\mathbf{4}^t$ to $\mathbf{2}^t$ and $\mathbf{5}^t$ has been made. The lowest energy pathway is plotted in the Fig. 4. From Fig. 4, it is very easy to know that isomer $\mathbf{4}^t$ can change to $\mathbf{5}^t$ along with the decrease of angle SC_1C_2 as shown in Fig. 1. In the process, the stationary point with highest relative energy on the channel is higher in energy than $\mathbf{4}^t$ by 45.48 kJ/mol, which makes $\mathbf{4}^t$ change to $\mathbf{5}^t$ easily, and the process is followed by the isomerizations from $\mathbf{5}^t$ to $\mathbf{3}^t$ and to $\mathbf{1}^t$ via transition states $\mathbf{TS3}^t/\mathbf{5}^t$ and $\mathbf{TS1}^t/\mathbf{3}^t$ with 68.72 and 9.41 kJ/mol reaction barrier heights, respectively. Therefore, isomers $\mathbf{4}^t$, $\mathbf{5}^t$ and $\mathbf{3}^t$ are unstable species.

It should be pointed out that all discussion above is based on respective surface, which lead $\mathbf{1}^s$ and $\mathbf{1}^t$ to kinetically stable species on singlet and triplet surface, respectively. But it should be noted that the surface crossing was not taken into account, and therefore, we do not say more about the stability of species $\mathbf{1}^t$. In view of the

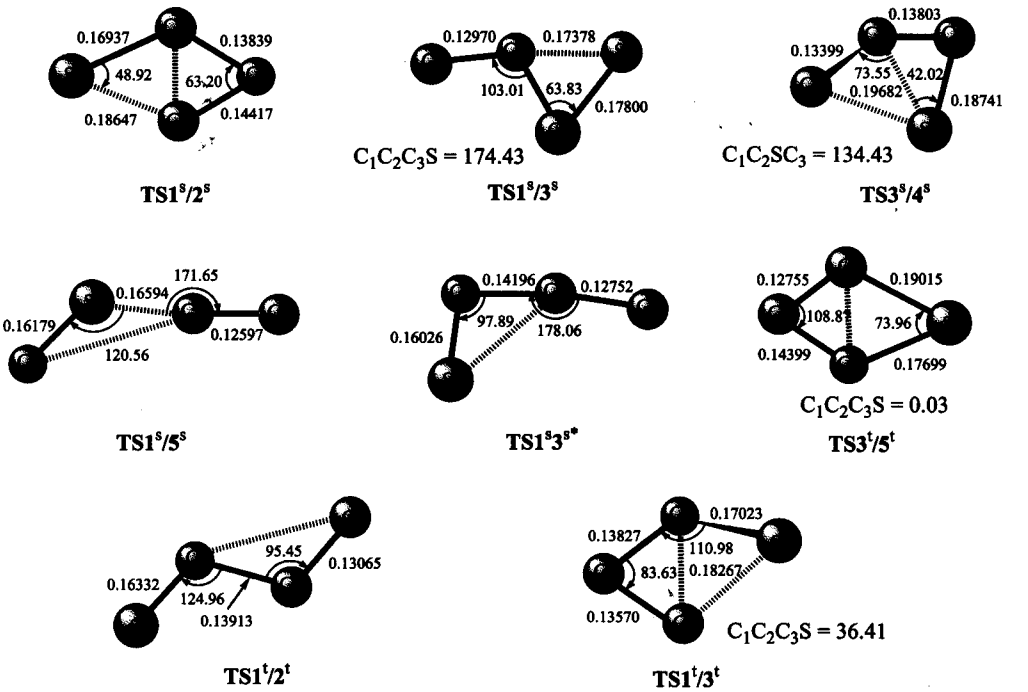

Fig. 2 Optimized structures for transition states of C_3S system (bond lengths are in nanometers, and bond angles in degrees).

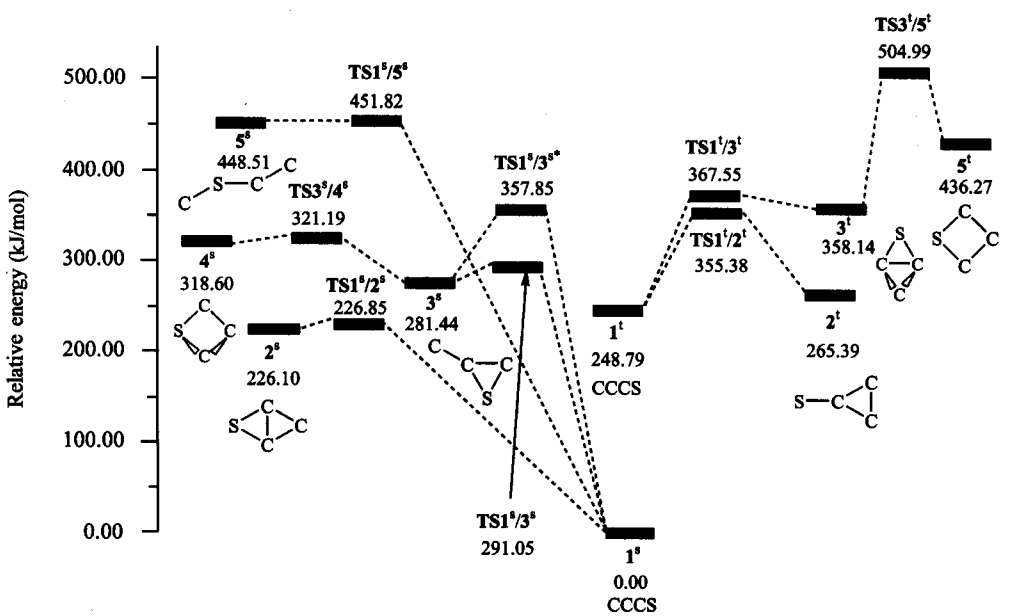

Fig. 3 Schematic potential energy surface for C_3S system at UCCSD(T)/6-311 + G(2df)// UB3LYP/6-311G(d) level of theory with zero-point vibrational energy included.

existence of 1^s identified by experiment, we hope that the calculated energy and relative stability of 1^t on triplet surface may be helpful for its experimental characterization or the nature of excited state of species 1^s.

Conclusions

UB3LYP/6-311G(d) and UCCSD(T)/6-311 + G(2df) (single-point) methods are employed to study the

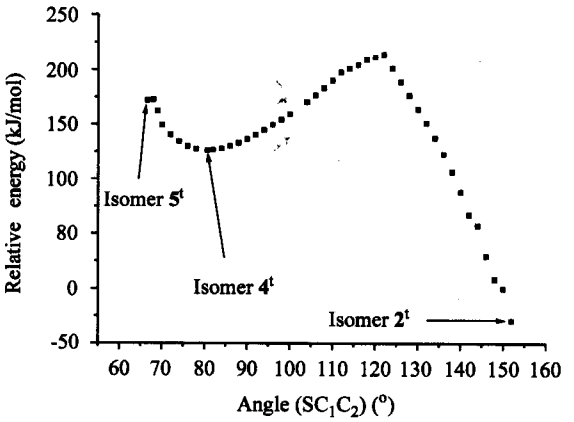

Fig. 4 Computed isomerization pathways from isomer 4^t to 5^t and 2^t by means of potential energy surface scan technology.

potential energy surfaces of the well-known interstellar molecule C_3S. Ten species are located on the surfaces, and their detailed structures are investigated. Only singlet linear CCCS species can be considered as stable isomer, and can be experimentally observed. This is in good agreement with previous experimental results. Only a triplet isomer, chain CCCS, is kinetically stable on triplet surface if surface crossing is not taken into account.

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