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REVIEW ON C$_{60}$S SPECTRA

We present the review on infrared and Raman spectra of $C_{60}S$ which have been calculated by Mohd Yunus & Rashid Nizam through the Hartree–Fock method. They found four isomers: closed [6,6]$C_{60}S$, open [6,6]$C_{60}S$, closed [5,6]$C_{60}S$, and open [5,6]$C_{60}S$. The simulated spectra were calculated in [13, 14] for closed [5,6]$C_{60}S$ and closed [6,6]$C_{60}S$ isomers, but Hartree–Fock method did not converge for open [5,6]$C_{60}S$ and open [6,6]$C_{60}S$ isomers. The computed spectrum is divided into four ranges of frequencies for $C_{60}S$; these are as follows: 0–600 cm^{-1}, 600–800 cm^{-1}, 800–1200 cm^{-1}, and 1200–1650 cm^{-1}. The results are analyzed in each range separately. The strong intense lines are revealed in closed [6,6]$C_{60}S$, rather than in the closed [5,6]$C_{60}S$ isomer for both Raman and IR spectra. The energy barriers equal to 233.2 $kJ \cdot mol^{-1}$ and 1.2 $kJ \cdot mol^{-1}$ are obtained in [13, 14] for the conversion of closed [6,6]$C_{60}S$ isomer to open [5,6]$C_{60}S$ isomer. The values of 82.0 $kJ \cdot mol^{-1}$ and 150.5 $kJ \cdot mol^{-1}$ are given in [13, 14] for the inverse conversion from open [5,6]$C_{60}S$ to closed [6,6]$C_{60}S$ isomer.

K e y w o r d s: Hartree–Fock method, infrared spectra, Raman spectra, C$_{60}$S.

1. Introduction

There are many derivates of fullerene having a high amount of sulphur in their structure [1–4]. However, the simplest derivative C$_{60}$S is not synthesized yet. Fullerene derivatives have many potential applications. Z. Slanina *et al.* [5] found out three stable isomers of C$_{60}$S, namely, closed [6,6]C$_{60}$S, closed [5,6]C$_{60}$S, and open [5,6]C$_{60}$S isomers. One more isomer [6,6]C$_{60}$S is found by X. Xu *et al.* M. Yunus *et al.* also found four isomers closed [6,6]C$_{60}$S, open [6,6]C$_{60}$S, closed [5,6]C$_{60}$S, and open [5,6]C$_{60}$S. Z. Slanina and X. Xu *et al.* used AM1 and MNDO methods which are not very accurate. M. Yunus *et al.* used the Hartree–Fock method, which converges only for closed [6,6]C$_{60}$S and closed [5,6]C$_{60}$S.

2. Computational Details
2.1. Structure of C$_{60}$S Isomers

C$_{60}$S consists of one molecule of fullerene and one atom of sulphur. Fullerene has sixty carbon atoms.

Sulphur has two valances, so it is connected with two carbon atoms of fullerene. C$_{60}$S has four isomers: open [5,6]C$_{60}$S, open [6,6]C$_{60}$, closed [5,6]C$_{60}$S, and closed [6,6]C$_{60}$S. Closed isomers are shown in Fig. 1, *a* and Fig. 1, *b*. In Fig. 1, *a*, one bond of sulphur is shared with one pentagon carbon atom, and the other bond shared with one hexagon carbon atom of C$_{60}$ cage; this is closed [5,6]C$_{60}$S isomer. In Fig. 1, *b*, both atoms of the sulphur atom are connected with two hexagons of C$_{60}$ cage; this is [6,6]C$_{60}$S isomer. The distances between carbon and sulphur atoms are 2.13 Å and 2.14 Å.

Mohd Yunus *et al.* determined the equilibrium structural geometry of [5,6]C$_{60}$S and [6,6]C$_{60}$S through the full optimization of geometrical parameters using the Hartree–Fock method without any constraint [13, 14]. Tables 1 and 2 show the optimized structural parameters of [5,6]C$_{60}$S and [6,6]C$_{60}$S, respectively, calculated by M. Yunus *et at.* [13, 14].

The tables show the results given by M. Yunus *et al.* [13, 14], Z. Slanina *et al.* [5], and X. Xu *et al.*
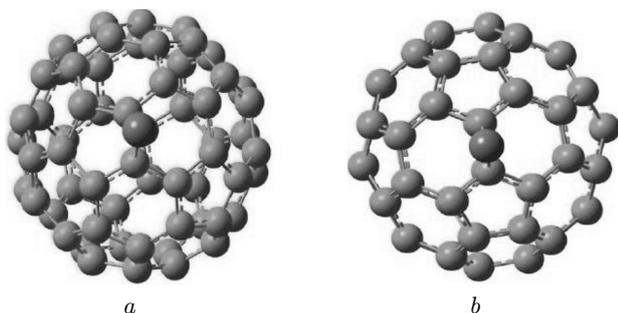
Fig. 1. (*a*) $C_{60}S$ configurations corresponding to (*a*) closed [5,6]$C_{60}S$ and (*b*) closed [6,6]$C_{60}S$. Sulphur atoms are shown in purple, and green color is used for carbon atoms

[6] in column 1, 2, and 3, respectively, and give the optimized parameters of $C_{60}S$.

Similarly in Table 2, the optimized structure of [6,6]$C_{60}S$ isomer is presented in the same manner.

Here, C^* represents the carbon atom which is attached by the sulphur atom and other carbon atoms represented by C only. C^*–S–C^* shows the angle between the sulphur atom and its attached carbon atoms. C^*–C–C^* shows the angle between the carbon atom (attached by sulphur) and other two connected carbon atoms (which are not attached by sulphur). M. Yunus *et al.* also calculated the angle between C–C^*–C^* (pentagon), C–C^*–C (hexagon) and C^*–C^*–C (hexagon) for [5,6]$C_{60}S$ isomer [13, 14] which was not given in works [5, 6]. The angle for C^*–S–C^* in [13, 14] is quite different from that in [6]. The additional geometrical information is also provided by M. Yunus *et al.*

In Table 2, we present the optimized geometrical parameters for [6,6]$C_{60}S$ given by M. Yunus *et al.* and the results of calculations by Z. Slanina and X. Xu *et al.* We note that the results given in [5, 6, 13, 14] are comparable. The angles for C–C^*–C (pentagon) and C^*–C^*–C (hexagon) for [6,6]$C_{60}S$ isomer are also given in [13, 14]. The angle C^*–S–C^*, bond length of C–C hexagon, and bond length of C–C pentagon are different.

3. Methodology

All similar calculations of the Raman and IR spectra in [13, 14] have been done according to [7].

The Raman and IR spectra for the two isomers [5,6]$C_{60}S$ and [6,6]$C_{60}S$ are given in Figs. 2, *a, b* and Figs. 3, *a, b*, respectively.

The variables used in the calculations in [13, 14] of [5,6]$C_{60}S$ and [6,6]$C_{60}S$ for Raman and IR spectra are

the same except for the nuclear repulsion energy. Rotational constants equal to 0.09, 0.08, and 0.08 GHz are used for x, y, and z directions in the fullerene derivatives. Each atom of a fullerene derivative has 309 symmetry-adapted basis functions, 927 primitive Gaussians, 309 Cartesian basis functions, 188 alpha electrons, and 188 beta electrons. The variables of the nuclear repulsion energy used in [13, 14] for the calculations of [5,6]$C_{60}S$ and [6,6]$C_{60}S$ are 9421.47 and 9418.98 Hartree, respectively.

The Raman spectrum changes significantly, when we introduce a sulphur atom in fullerene because of the redistribution of the Raman intensities among the normal as given in Tables 1 and 2.

$C_{60}S$ has 182 total degrees of freedom for each isolated atoms, in which we have three are translational and three rotational. So, 177 remaining ones are vibrational degrees of freedom. $C_{60}S$ isomers also have the same number of 177 degrees of freedom, but their spectra are different. The numerical results converge after 29 cycles and 21 cycles with the density matrices equal to 0.1950D-08 and 0.6887D-08 for $C_{60}S$ [5,6] and [6,6], respectively.

4. Results for the Raman Spectra of [5,6]$C_{60}S$ and [6,6]$C_{60}S$

1) The calculations done by M. Yunus *et al.* [13, 14] using the *ab initio* method [8–10] overestimate the Raman and IR intensities. To remove the disagreement with the experimental data, the results were scaled down in the frequency for $C_{60}S$ by a factor of 0.855 uniformly throughout the range.

2) Hartree–Fock method is the best so far for the calculation of Raman and IR spectra for $C_{60}S$ isomers. However it does not converge for open isomers of $C_{60}S$.

3) Range of frequencies is used from 0 to 1650 cm−1 in [13, 14] for the Raman and IR spectra of $C_{60}S$.

The frequency range was divided into four parts.

For the Raman spectrum of closed $C_{60}S$, they are: 0–400 cm^{-1}, 400–800 cm^{-1}, 800–1200 cm^{-1}, and 1200–1650 cm^{-1}. For the IR spectrum of closed $C_{60}S$: 0–600 cm^{-1}, 600–800 cm^{-1}, 800–1200 cm^{-1}, and 1200–1650 cm^{-1}. The results were analyzed by M. Yunus *et al.*

4) In the Raman spectra, they got the lower intensities for [6,6]$C_{60}S$ as compared with [5,6]$C_{60}S$ throughout the frequency range in [13, 14]. Five ma-

Table 1. **Results of calculations of [5,6]C_{60}O**

Molecules	Results of calculation [13, 14] [5,6]C_{60}S	Results of calculation [5] C_{60}S	Results of calculation [6] [5,6]C_{60}S
C–C hexagon	1.365–1.441 Å	–	1.493 Å
C–C pentagon	1.375–1.464 Å	–	1.493 Å
C–C*	1.463–1.515 Å	–	–
C*–C*	1.3494 Å	2.296 Å	1.639 Å
C*–S	2.145 Å	1.695 Å	2.826–1.747 Å
Angle (C*–S–C*)	36.7°	–	55.9°
Angle (C–C*–C*) pentagon	108.0°	–	–
Angle (C–C*–C) hexagon	116.8°	–	–
Angle (C*–C*–C) hexagon	120.0°	–	–
Angle (C–C–C) pentagon	107.7–108.9°	–	–
Angle (C–C–C) hexagon	118.4–121.4°	–	–
Dipole moment	1.9205 D	–	–
Basis Set	STO-3G	3-21G	B3LYP/6-31G

Table 2. **Results of calculation of [6,6]C_{60}O**

Molecules	Results of calculation [13, 14] [6,6]C_{60}S	Results of calculation [5] C_{60}S	Results of calculation [6] [6,6]C_{60}S
C–C hexagon	1.366–1.379 Å	–	1.497 Å
C–C pentagon	1.375–1.464 Å	–	1.497 Å
C–C*	1.463–1.515 Å	–	–
C*–C*	1.3475 Å	1.594 Å	1.497 Å
C*–S	2.147 Å	1.729 Å	1.747 Å
Angle (C*–S–C*)	36.72°	–	52.7°
Angle (C–C*–C) pentagon	108.0°	–	–
Angle(C*–C*–C) hexagon	120.0°	–	–
Angle (C–C–C) pentagon	107.4–108.9°	–	–
Angle (C–C–C) hexagon	120.0–121.7°	–	–
Dipole moment	1.1231 D	–	–
Basis Set	STO-3G	3-21G	B3LYP/6-31G

jor peaks for [5,6]C_{60}S and eight ones for [6,6]C_{60}S can be seen in the interval 0–400 cm^{-1}, as shown in Fig. 2. Six major peaks are present in both [5,6]C_{60}S and [6,6]C_{60}S in 400–800 cm^{-1}. Three major peaks are seen in both [5,6]C_{60}S and [6,6]C_{60}S in 800–1200 cm^{-1}. Similarly in both [5,6]C_{60}S and [6,6]C_{60}S, seven peaks are in the interval 1200–1650 cm^{-1}.

In the IR spectra, they got few numbers of peaks in 0–600 cm^{-1}, as shown in Fig. 3. All lowest peaks can be seen in 600–800 cm^{-1}. No peaks have been calculated in the 800–1200 cm^{-1} interval. The numbers of highest peaks can be seen in 1200–1650 cm^{-1}. In the first interval, it appears that carbon atoms of fullerene show only the movement keeping the sulphur atom stationary. The cage movement includes the radial breathing mode, twisted mode, zig-zag modes for carbon atoms *etc.*

6) The figures show that several intense peaks are observed in closed [5,6]C_{60}S isomer that is more than in closed [6,6]C_{60}S in Raman and IR spectra.

7) According to Z. Slanina *et al.* [5] and X. Xu *et al.* [6], we accept that closed [6,6]C_{60}S is the most stable isomer among all C_{60}S isomers. Calculations done by M. Yunus *et al.* [13, 14] also agree with this asser-
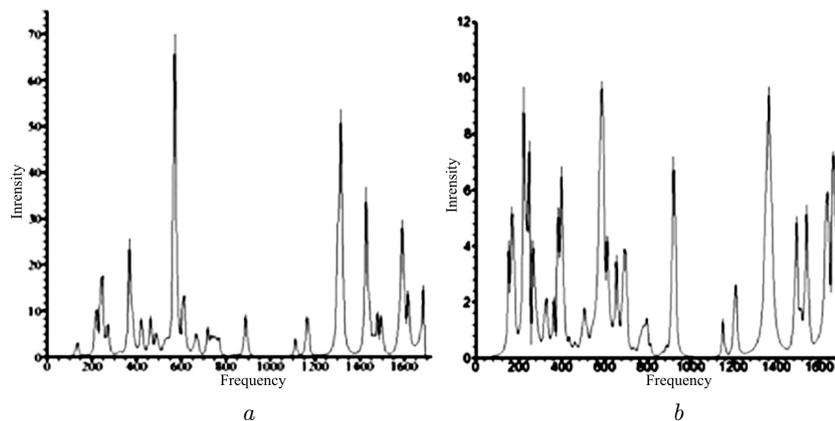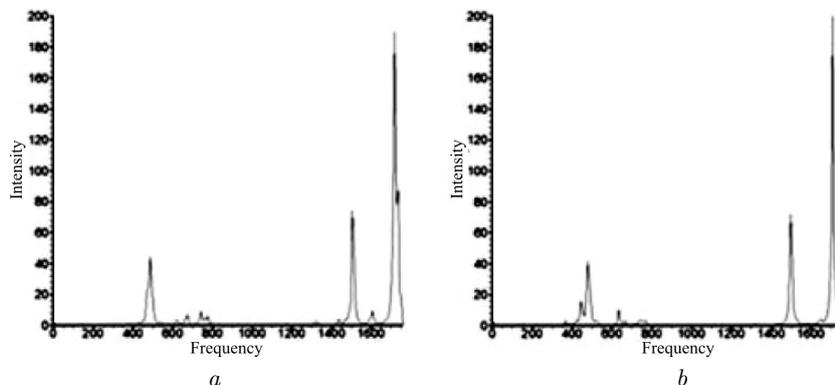
Fig. 2. Raman spectra of [5,6]C_{60}S and [6,6]C_{60}S

Fig. 3. Infrared spectra of [5,6]C_{60}S and [6,6]C_{60}S

tion. Therefore, it is possible to calculate the Raman and IR spectra of [6,6]C_{60}S. But lower Raman intensities are calculated in this case.

8) Raman spectra of C_{60}S could not be matched with the present Raman spectra of [6,6]C_{60}S, as Rthe aman spectrum of C_{60}S may not be available through semiempirical studies [5]. This suggests that C_{60}S isomers may have overestimated IR spectra. Therefore, the IR spectrum of [6,6]C_{60}S does not agree with the result given in [13, 14] for the IR spectrum of [6,6]C_{60}S. Then Z. Slanina *et al.* [5] calculated the IR spectrum for open [5,6]C_{60}S isomer, and M. Yunus *et al.* fetermined it for closed [5,6]C_{60}S isomer. No calculations were done for the IR spectrum of open [5,6]C_{60}S isomer in [13, 14], since the Hatree–Fock method shows no convergence for open [5,6]C_{60}S isomer.

9) The higher numbers of peaks and strong intense lines are observed for closed [5,6]C_{60}S as compared with closed [6,6]C_{60}S isomer. But the Raman number and Raman intense peaks will fade faster for closed [5,6]C_{60}S than for closed [6,6]C_{60}S. This indicates that the closed [5,6]C_{60}S is less stable than closed [6,6]C_{60}S isomer.

10) It has been observed [5–6] and calculated in [13, 14] that an increase in the temperature induces abrupt substantial changes in the shapes of Raman and IR spectral bands. This can occur due to two barriers for the interconversion between the closed [6,6]C_{60}S and open [5,6]C_{60}S isomers. The energy barriers calculated by M. Yunus *et al.* in [13, 14] for the conversion of closed [6,6]C_{60}S isomer to open [5,6]C_{60}S isomer are 233.2 kJ·mol^{-1} and 1.2 kJ·mol^{-1}. The inverse (reaction) conversion's barriers from open [5,6]C_{60}S to closed [6,6]C_{60}S isomer are 82.0 kJ·mol^{-1} and 150.5 kJ·mol^{-1}.

11) The results in [13, 14] show that the Raman and IR spectra of closed [5,6]C_{60}S, as given in the figures,

are not observed experimentally at room temperature due to their instability. Moreover, the Raman spectrum of [5,6]C$_{60}$S is not available.

12) We note that Z. Slanina *et al.* [5] did not compute the Raman spectrum for [6,6]C$_{60}$S. The IR spectrum for C$_{60}$S in [13, 14] does not match that in [5], because Z. Slanina calculated open C$_{60}$S, whereas M. Yunus *et al.* calculated closed C$_{60}$S. The reason is in that the parameters used by Z. Slanina *et al.* [5] for the construction of fullerene are very different from those used by M. Yunus *et al.* The carbon – carbon distance in the present studies are 1.375– 1.464 Å, whereas Z. Slanina *et al.* [5] took 1.594– 2.296 Å, which is a wrong distance for carbon – carbon. According to M D. Newton *et al.* [12] for the C$_{60}$ cage, the carbon- carbon distances equal approximately 1.40 Å.

13) Moreover, no attempt was made by Z. Slanina *et al.* [5] to scale the computed frequencies, although they were accepted to be overestimated in the calculations of the IR spectra. M. Yunus *et al.* computed the Raman frequencies that are different from those in [5], where the IR spectrum for C$_{60}$S was calculated. The MNDO energy parametrizations corresponds to room temperature, rather than to absolute zero. Therefore, there may be a chance of changing the frequencies of C$_{60}$S in the calculated IR spectra.

14) The study of IR spectra by M. Yunus *et al.* for [6,6]C$_{60}$S gave better results than those obtained by Z. Slanina *et al.* [5]. The computed Raman spectra for closed [5,6]C$_{60}$S and closed [6,6]C$_{60}$S have high accuracy. Thus, we have a good tool for computing the Raman and IR spectra at room temperature [13, 14].

5. Conclusions

The number of Raman and IR spectral peaks observed for closed [5,6]C$_{60}$S isomer is greater than for closed [6,6]C$_{60}$S. Moreover, the strong intense lines in Raman and IR spectra are found in closed [5,6]C$_{60}$S isomer, whose number is greater, as compared with [6,6]C$_{60}$S.

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ОГЛЯД СПЕКТРІВ C$_{60}$S

Зроблено огляд результатів наших розрахунків інфрачервоних та раманівських спектрів для C$_{60}$S, виконаних з використанням методу Хартрі–Фока. Розглянуто чотири ізомери: закритий [6,6]C$_{60}$S, відкритий [6,6]C$_{60}$S, закритий [5,6]C$_{60}$S та відкритий [5,6]C$_{60}$S. Спектри було розраховано в [13, 14] для закритих ізомерів [5,6]C$_{60}$S та [6,6]C$_{60}$S. Зауважимо, що метод Хартрі–Фока не є збіжним для відкритих ізомерів [5,6]C$_{60}$S та [6,6]C$_{60}$S. В кожному розрахованому спектрі розглянуто чотири області частот: 0–600 см$^{-1}$, 600–800 см$^{-1}$, 800–1200 см$^{-1}$ та 1200–1650 см$^{-1}$, які проаналізовано окремо. Виявлено інтенсивні лінії для закритого ізомера [6,6]C$_{60}$S, а не для закритого ізомера [5,6]C$_{60}$S, як в раманівських, так і в інфрачервоних спектрах. В [13, 14] розраховано енергетичні бар'єри, що дорівнюють 233,2 кДж · моль$^{-1}$ та 1,2 кДж · моль$^{-1}$ для переходу закритого [6,6]C$_{60}$S у відкритий [5,6]C$_{60}$S ізомер. Значення 82,0 кДж · моль$^{-1}$ і 150,5 кДж · моль$^{-1}$ отримані для зворотного переходу відкритого ізомера [5,6]C$_{60}$S в закритий [6,6]C$_{60}$S.

К л ю ч о в і   с л о в а: метод Хартрі–Фока, інфрачервоні спектри, раманівські спектри, C$_{60}$S.