

VIBRATIONAL DYNAMICS OF S_xSe_y RING CLUSTERS ON AB INITIO CALCULATION

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The molecular complexity of sulfur, sulfur-selenium and selenium mixtures with crystalline, glassy system has been investigated by ab initio theory calculation. The structure geometries and vibration frequencies of S_xSe_y four-, six-, eight-ring clusters have been performed on Firefly (PC Gamess) software at the DFT/B3LYP level with 3-21G basis set. We found all vibrational modes of those ring clusters can mainly be divided into S-S, S-Se and Se-Se stretching vibration area at $400\sim 500\text{cm}^{-1}$, $300\sim 400\text{cm}^{-1}$ and $\sim 250\text{cm}^{-1}$. In addition, the lower shift of peaks around 250cm^{-1} and 350cm^{-1} with adding Se atoms in Raman scattering of S-Se system can be predicted to Se content increase of local environment around S_xSe_y ring clusters.

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1. Introduction

In recent years the research on chalcogenide glasses formed by combinations of elements Se and S has increased because the study of elemental sulfur and selenium in its liquid and solid state offers an attractive challenge due to the unique diversity of stable molecules, which lead to wide applications such as optoelectronic and memory switching device [1-3]. Sulfur and its compounds are of widespread importance in chemistry and biology[4]. Amorphous selenium has been widely used as a photoconductive plate or roll of the static electricity duplicator due to its excellent light-electricity and semiconducting properties[5]. Moreover, chalcogenide alloys formed by Se and S atoms are considered to be an important type of semiconductors with excellent property of electronic p-type conductivity [6]. In order to investigate the relation between performance and structure, the noncrystalline solid have been the subject of a vast number of experimental and theoretical investigations. For example, structural, dynamical information have been measured by inelastic neutron scattering [7], X-ray absorption fine structure[8], infrared [9] and Raman spectra [10]. Among them, Raman measurement is considered to be a useful tool that contain sharp, molecularlike features, which can be associated with structural elements of the materials[11]. On the other hand, the molecular nature of the Raman spectra based on atomic clusters calculated by ab initio method also can interpret the spectral features. Up to now, concerning structural properties, relatively few investigations have been studied on amorphous S-Se system, despite the great number of investigations on Se glassy and S crystalline system. According to the literature in the past, ring clusters are supposed to one significant type of local structure in S-Se amorphous system [12-13].

In this paper, the structure geometries and vibrational modes of S_xSe_y ($x+y=4, 6, 8$) ring clusters in S-Se glassy system are calculated by ab initio method to interpret the structure information by means of comparing with unknown peaks in Raman spectra of S-Se glassy system.

2. Theoretical and calculation details

It is well known that selenium sulfide heterocycles can be formed in the molten mixtures of sulfur and selenium [14]. And different S-Se ring clusters can form solid solutions of complex molecular composition, the structures of which reported are considered to be disordered with

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sulfur and selenium randomly distributed around the atomic sites. In the solid state, pure-selenium exist in one of four major allotropes: amorphous, trigonal(hexagonal), α - and β -monoclinic allotropes[15]. On the other hand, the elemental sulfur is composed of orthorhombic sulfur (α -S) and monoclinic sulfur (β -S)[16].According to the crystal structure of S and Se, the molecular lattice mainly consist of crown-shaped eight-membered rings like S_8 and Se_8 [17], which can possibly extend to eight-membered selenium sulfide heterocycles S_nSe_{8-n} in S-Se glassy system.

With respect to the S-Se mixed molecular system, several researches have been made by scholars such as the force field calculation method for molecular vibration of Se_3S_5 , Se_4S_4 and Se_7S three ring clusters [18], because the vibration mode analysis can be very convenient to identify the specific types of molecules. From Raman data of S-Se amorphous system, the vibrational modes related to S-S bond, S-Se bond and Se-Se bond all exist, even with very little content of Se atoms in S-Se amorphous system. Though the eight-membered ring structure of the molecules was confirmed, there is considerable disorder clusters in the atomic sites. According to De Haan and Visser, the general formula of sulfur-selenium system is S_nSe_{8-n} and n can assume any value below eight [19]. In addition, the molecules of S_n and Se_n (n=4,6) also be investigated in literature in the past[20-21].

In this work, we calculate the vibrational frequencies of four-, six- and eight-membered selenium sulfide rings in order to establish the structure models under different ratio of S/Se and obtain the vibration information related to unknown peaks Raman spectra of S-Se system. All ab initio calculations on S_xSe_y ring clusters are performed on Firefly (PC Gamess) software at the DFT/B3LYP level with 3-21G basis set. B3LYP uses the non-local correlation provided by the LYP expression. In addition, LYP means the correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms [22].

3. Result and discussion

Fig. 1 shows the structure diagram of S_nSe_{4-n} (n=0, 1, 2, 3, 4) mixed four-ring molecules with the point group of D_{4h} . the structure information related to average bond length and bond number of S_nSe_{4-n} (n=0, 1, 2, 3, 4) mixed four-ring molecules are displayed in Table 1.

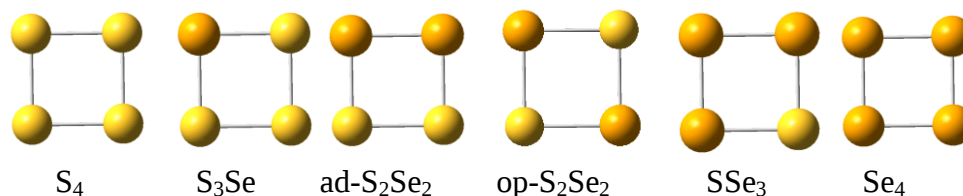


Fig. 1. The structure diagram of possible S_nSe_{4-n} (n=0, 1, 2, 3, 4) mixed four-ring molecules.

Table 1. The bond length and bond number of S_nSe_{4-n} (n=0, 1, 2, 3, 4) mixed four-ring molecules.

Clusters	Average bond length			Bond number		
	S-S	S-Se	Se-Se	S-S	S-Se	Se-Se
S_4	2.366	--	--	4	0	0
S_3Se	2.363	2.465	--	2	2	0
ad- S_2Se_2	2.360	2.463	2.578	1	2	1
op- S_2Se_2	0	2.462	0	0	4	0
SSe_3	--	2.459	2.575	0	2	2
Se_4	--	--	2.572	0	0	4

The optimization of S_nSe_{4-n} ring clusters is the process of finding an arrangement in space of a collection of atoms. With respect to the chemical bonding in clusters, the inter-atomic force of each atom is close to zero and the position on the potential energy surface is a stationary point.

Then the vibrational frequencies are calculated under the stable structure at the stationary point. According to the data above, it can be seen the bond length of S-S and Se-Se bond decrease with the increase of content of Se atoms in S_nSe_{6-n} ring clusters. On the other hand, for the clusters of S_2Se_2 , it can be seen that there are two isomers with different atom arrangement. The ad- S_2Se_2 is short for adjacent- S_2Se_2 , which means the same atoms(S or Se) are adjacent to each other. However, the op- S_2Se_2 is short for opposite- S_2Se_2 , which means the same atom(S or Se) are located at opposite side.

Fig. 2 displays the structure diagram of S_nSe_{6-n} ($n=0, 2, 3, 4, 5, 6$) mixed six-ring molecules with the point group of C_{2v} , the structure information related to average bond length and bond number of S_nSe_{6-n} ($n=0,1,2,3,4,5,6$) mixed four-ring molecules are displayed in Table 1.

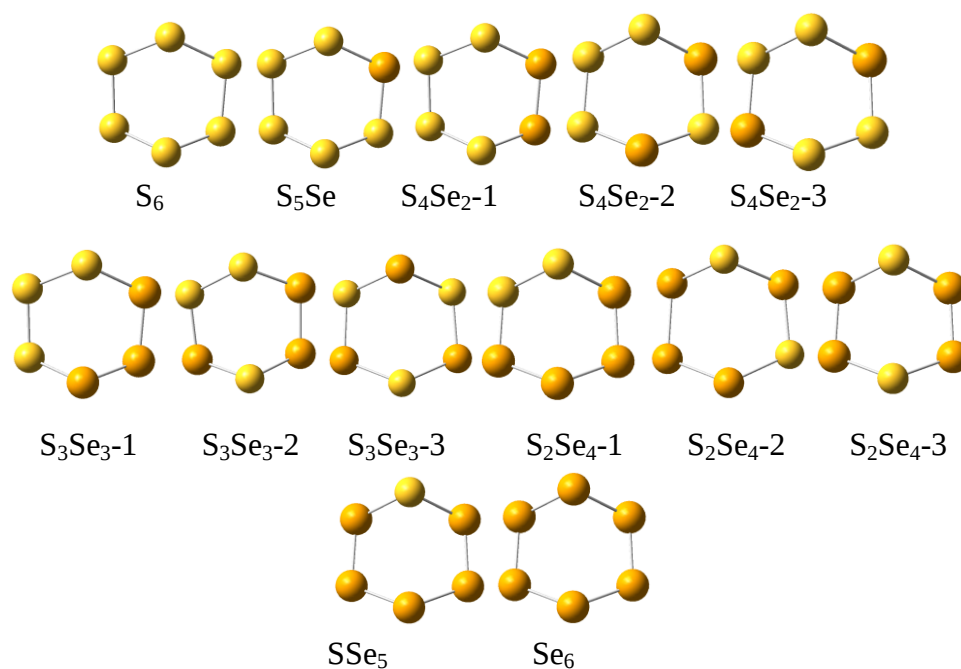


Fig. 2. The structure diagram of possible S_nSe_{6-n} ($n=0, 1, 2, 3, 4, 5, 6$) mixed six-ring molecules.

Table 2. The bond length and bond number of S_nSe_{6-n} ($n=0, 1, 2, 3, 4, 5, 6$) mixed six-ring molecules.

Clusters	Bond length			Bond number		
	S-S	S-Se	Se-Se	S-S	S-Se	Se-Se
S_6	2.248	--	--	6	0	0
S_5Se	2.258	2.343	--	4	2	0
S_4Se_2-1	2.253	2.351	2.622	3	2	1
S_4Se_2-2	2.252	2.352	--	2	4	0
S_4Se_2-3	2.268	2.512	--	2	4	0
S_3Se_3-1	2.338	2.348	2.539	2	2	2
S_3Se_3-2	2.263	2.345	2.621	1	4	1
S_3Se_3-3	--	2.346	--	0	6	0
S_2Se_4-1	2.264	2.428	2.513	1	2	3
S_2Se_4-2	--	2.406	2.535	0	4	2
S_2Se_4-3	--	2.356	2.619	0	4	2
SSe_5	--	2.357	2.540	0	2	4
Se_6	--	--	2.514	0	0	6

Compared to the S_nSe_{4-n} ring clusters, the S_nSe_{6-n} ring clusters have more isomers. For example, there are three isomers in S_4Se_2 、 S_3Se_3 and S_2Se_4 .

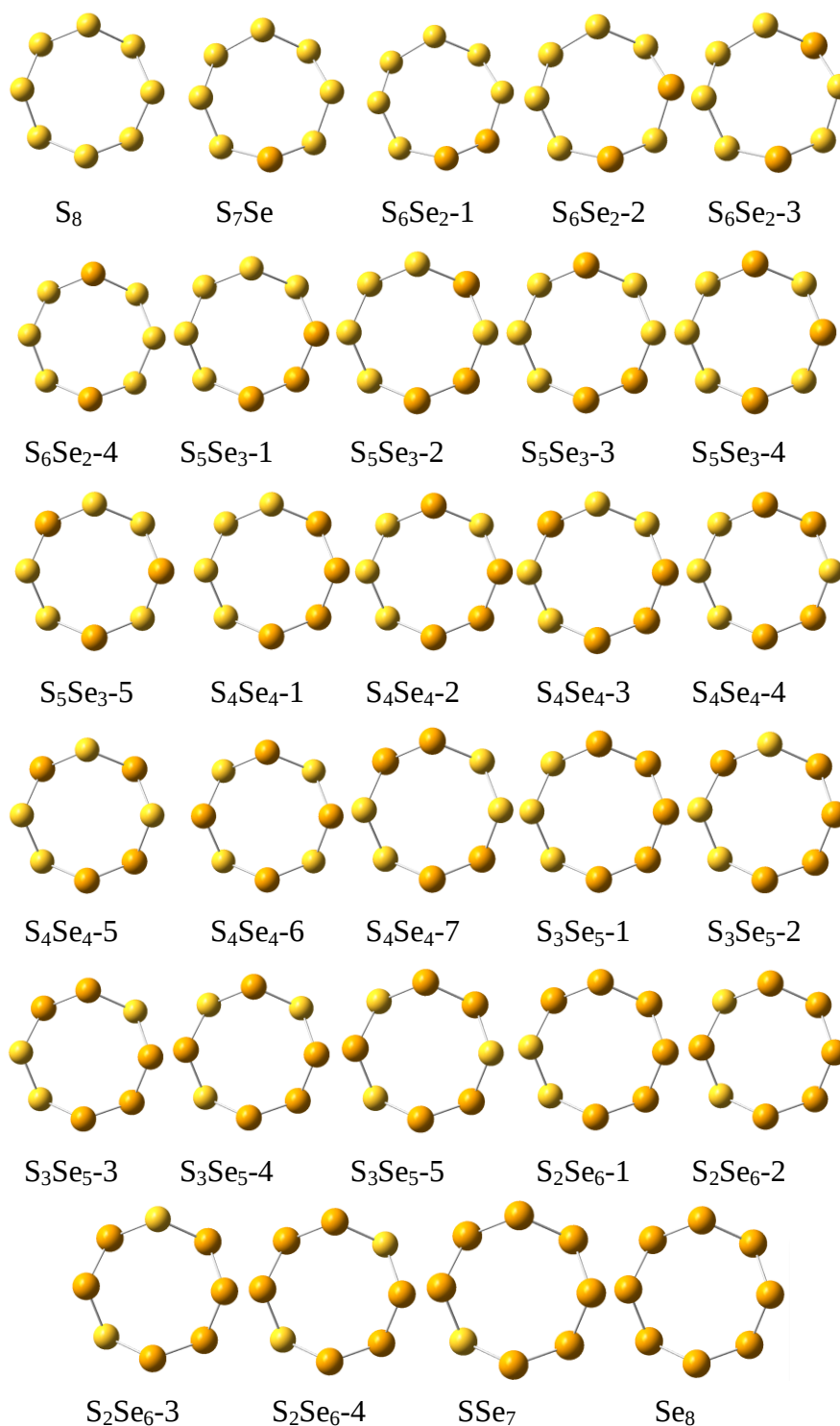


Fig. 3. The structure diagram of possible S_nSe_{8-n} ($n=0, 1, 2, 3, 4, 5, 6$) mixed eight-ring molecules.

Table 3. The bond length and bond number of S_nSe_{8-n} mixed eight-ring molecules.

Type	Bond length			Bond number		
	S-S	S-Se	Se-Se	S-S	S-Se	Se-Se
S_8	2.287	--	--	8	0	0
S_7Se	2.244	2.351	--	6	2	0
S_6Se_2 -1	2.242	2.358	2.462	5	2	1
S_6Se_2 -2	2.239	2.349	--	4	4	0
S_6Se_2 -3	2.246	2.351	--	4	4	0
S_6Se_2 -4	2.237	2.351	--	4	4	0
S_5Se_3 -1	2.244	2.356	2.469	4	2	2
S_5Se_3 -2	2.238	2.349	2.461	3	4	1
S_5Se_3 -3	2.242	2.358	2.463	3	4	1
S_5Se_3 -4	2.244	2.350	--	2	6	0
S_5Se_3 -5	2.251	2.349	--	2	6	0
S_4Se_4 -1	2.245	2.357	2.474	3	2	3
S_4Se_4 -2	2.242	2.357	2.470	2	4	2
S_4Se_4 -3	2.249	2.354	2.470	2	4	2
S_4Se_4 -4	2.242	2.360	2.462	2	4	2
S_4Se_4 -5	2.249	2.348	2.462	1	6	1
S_4Se_4 -6	2.247	2.356	2.465	2	4	2
S_4Se_4 -7	--	2.353	--	0	8	0
S_3Se_5 -1	2.243	2.358	2.473	2	2	4
S_3Se_5 -2	2.251	2.349	2.476	1	4	3
S_3Se_5 -3	2.247	2.358	2.463	1	4	3
S_3Se_5 -4	--	2.355	2.467	0	6	2
S_3Se_5 -5		2.351	2.460	0	6	2
S_2Se_6 -1	2.249	2.356	2.471	1	2	5
S_2Se_6 -2	--	2.351	2.473	0	4	4
S_2Se_6 -3	--	2.358	2.460	0	4	4
S_2Se_6 -4	--	2.358	2.469	0	4	4
SSe_7	--	2.360	2.467	0	2	6
Se_8			2.473	0	0	8

All the Se_nS_{8-n} clusters are stable with respect to the free atoms, the bond length and bond number of S_nSe_{8-n} mixed eight-ring molecules is shown in table 1 as well as the structure diagram shown in Fig. 1. According to the different ratio of S/Se atoms in S_nSe_{8-n} clusters, there are some characteristic related to vibrational performance. Compared to the S_nSe_{4-n} and S_nSe_{6-n} ring clusters, the S_nSe_{8-n} ring clusters have the most isomers. For example, the S_6Se_2 and S_2Se_6 clusters have four isomers, respectively. The S_5Se_3 and S_3Se_5 clusters have five isomers, respectively. Finally, the S_4Se_4 clusters have seven isomers.

Fig. 4 shows the calculated Raman spectra of S_nSe_{4-n} and S_nSe_{6-n} mixed ring molecules with different ratio of S/Se. Among them, for the left graph, there are two isomers for S_2Se_2 cluster such as adjacent- S_2Se_2 (ad- S_2Se_2), which the same atoms (S or Se atom) are adjacent to each other, and opposite- S_2Se_2 (op- S_2Se_2), which the same atoms (S or Se atom) are located to opposite side.

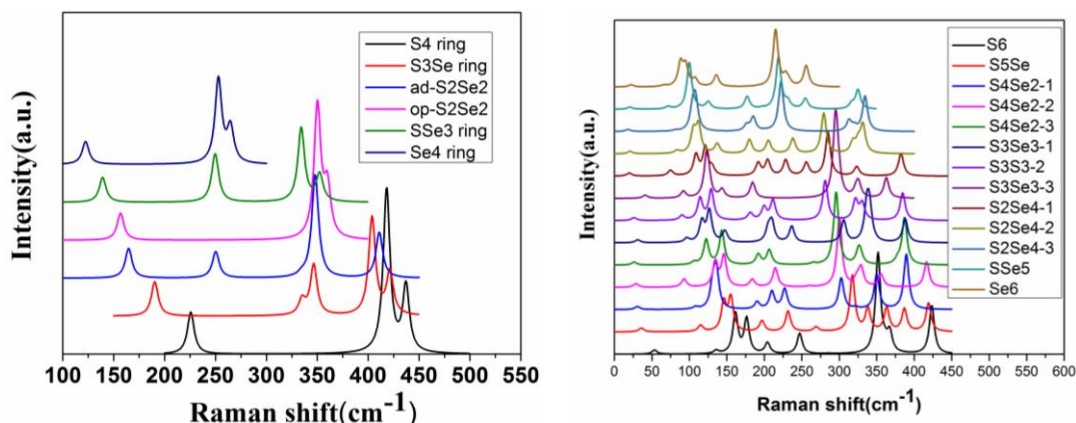


Fig.4. The calculated Raman spectra of S_nSe_{4-n} and S_nSe_{6-n} mixed ring molecules.

From figure 4 above, all vibration modes of S_nSe_{4-n} clusters can be divided into four frequency areas. Based on the molecular vibration theory, the peaks range of $400\sim 500\text{cm}^{-1}$ are related to S-S stretching vibrational modes. However, the peaks between $300\sim 400\text{cm}^{-1}$ are attributed to S-Se stretching vibrational modes. In addition, the peaks of 250cm^{-1} are assigned to Se-Se stretching vibrational modes. Finally, the rest of peaks lower than 200cm^{-1} are related to non-stretching vibration area.

For the right graph, the calculated Raman spectra of S_nSe_{6-n} ring clusters are similar to those of S_nSe_{4-n} ring clusters. For example, all the vibrational modes of S_nSe_{6-n} clusters are also can be classified by four frequency areas. The peaks at $400\sim 500\text{cm}^{-1}$, $300\sim 400\text{cm}^{-1}$ are attributed to S-S and S-Se stretching vibrational mode. And the Se-Se stretching vibrational mode are located around 250cm^{-1} . The rest of peaks lower than 200cm^{-1} are related to non-stretching vibration area.

Fig. 5 showed the calculated Raman spectra of S_nSe_{8-n} . According to the different types of replacement, all S_nSe_{8-n} clusters above can be divided into pure ring clusters (S_8, Se_8), single atom replacement (SSe_7, S_7Se), two atoms replacement (S_2Se_6, S_6Se_2), three atoms replacement (S_3Se_5, Se_5S_3) and four atoms replacement (S_4Se_4, S_4Se_4). In addition, we can find that the isomers increase with the increasement of atom replacement. For example, there are one isomer in pure ring clusters and single atom replaced ring clusters, four isomers in two atom replaced ring clusters, five isomers in three atom replaced clusters and seven isomers in four atom replaced clusters. In addition, all the frequencies of vibrational modes above 200cm^{-1} can be divided into three main region: $200\sim 300\text{cm}^{-1}$, which is related to Se-Se stretching vibration modes, $300\sim 400\text{cm}^{-1}$ that is associated with S-Se stretching vibration modes and $400\sim 500\text{cm}^{-1}$.

More specifically, the peak around 473cm^{-1} are clearly attributed to the sulfur symmetry breathing stretching modes, which is accordance with the Raman spectra of Sulfur crystalline system^[23]. This indicates that single S_8 ring clusters are the basic units of sulfur crystalline system, which are composed of S_8 ring clusters interconnection with van der Waals forces. On the other hand, the calculated data around 250cm^{-1} of Se_8 ring clusters are assigned to the selenium symmetry breathing stretching modes, which is consistent with the Raman spectra of Selenium amorphous system^[24]. This phenomenon is similar to that of S system, which also indicates the Se_8 ring clusters is basic units of Se amorphous system.

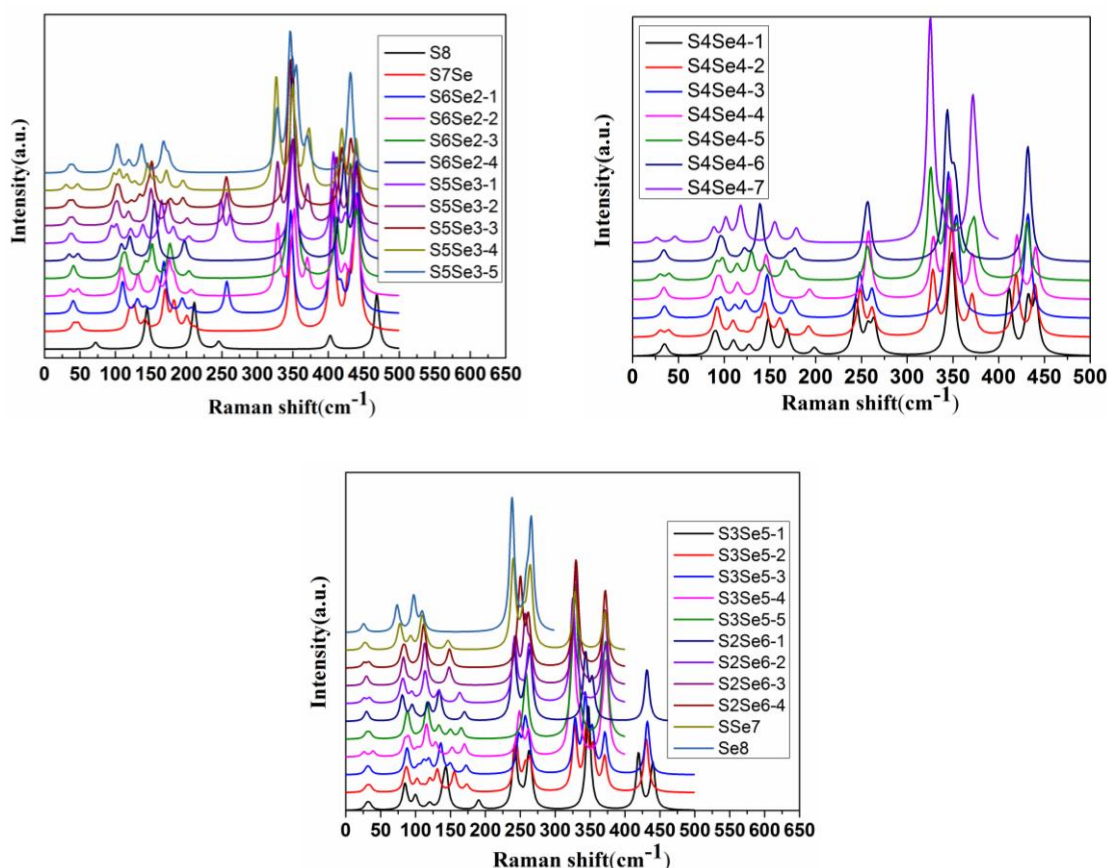


Fig. 5. The calculated Raman spectra of S_nSe_{8-n} mixed eight-ring molecules.

Raman scattering of S-Se system measured by K.D. Machado et al^[6] in the regions $240\text{-}270\text{cm}^{-1}$, $320\text{-}400\text{cm}^{-1}$ and $430\text{-}480\text{cm}^{-1}$ also correspond to the stretching vibraional modes of Se-Se, Se-S and S-S, respectively, which is accordance with the calculated Raman spectra of S_xSe_y ring clusters above. More specifically, the peak around 240cm^{-1} can be assigned to Se-chain stretching vibration mode^[24]. However, the shoulder at $\sim 260\text{cm}^{-1}$ is attributed to the stretching vibration mode of Se_8 ring clusters, and the strongest peak at $\sim 250\text{cm}^{-1}$ maybe belong to the stretching vibration mode both Se-chain and Se-ring^[25]. With the content of S atom increasing, it can be found that there is a faint higher shift at the peak of 250cm^{-1} as well as the peak around 250cm^{-1} . On the other hand, there is a series of obvious peaks around 350cm^{-1} in Raman scattering of S-Se system by K.D. Machado, which is agreement with the calculated data of S-Se stretching vibration mode above. Generally speaking, there is a rediction based on the Raman spectra analysis that when the peak position in S-Se system Raman spectra has a large shift with different ratio of S/Se, we can assume that a new vibration mode occur, otherwise, when the peak position has a small shift with different ratio of S/Se, we may consider the original vibrational mode did not change, but due to the variation of local chemical structure around the clusters. Therefore, the lower shift of peaks around 250cm^{-1} and 350cm^{-1} with adding Se atoms in Raman scattering of S-Se system by K.D. Machado can be predicted to Se content increase of local environment around S_xSe_y ring clusters.

5. Conclusions

In summary, we obtain the vibrational mode of basic ring clusters such as S_nSe_{4-n} , S_nSe_{6-n} and S_nSe_{8-n} by ab initio calculation. The alternation of S/Se ratio in ring clusters result in a change of point group, which induces an increase of number of basic vibrational modes. Based on the ab initio calculation, all vibrational modes of those ring clusters can mainly be divided into S-S, S-Se

and Se-Se stretching vibration area at $400\sim 500\text{cm}^{-1}$, $300\sim 400\text{cm}^{-1}$ and $\sim 250\text{cm}^{-1}$. In addition, the lower shift of peaks around 250cm^{-1} and 350cm^{-1} with adding Se atoms in Raman scattering of S-Se system can be predicted to Se content increase of local environment around S_xSe_y ring clusters.

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