Research Article
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Mutual Transformations of Polysulfide Chromophore Species in Sodalite-Group Minerals: A DFT Study on S_6 Decomposition

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It is known that various polysulfide species determine the color of sodalite-group minerals (haüyne, lazurite, and slyudyankaite), and that heating induces their transformations and color change, but the mechanisms of the transitions are unknown. A prominent example is the decay of cyclic S_6 molecule. Using density-functional simulations, we explore its main decay pathways into the most probable final reaction products (the pairs of radical anions $S_3^{\bullet-}+S_3^{\bullet-}$ and $S_2^{\bullet-}+S_4^{\bullet-}$). It was found that the most favorable reaction path involves initial capture of one electron by the S_6 molecule, which greatly facilitates its decay of S_6 and leads to the opening of the S_6 cycle, and subsequent decomposition of the thus formed chain radical anion, with a limiting energy barrier of ~0.4 eV. Neutral polysulfide molecules capture one electron with a significant energy reduction. The radical anions $S_n^{\bullet-}$ ($n=2-6$) are the most stable ones among corresponding species with the same n values and different charges. The capture of the second electron by $S_6^{\bullet-}$ occurs with a huge energy barrier (~2 eV). The results of the DFT calculations are in agreement with experimental data on the products of thermal conversions of extra-framework S-bearing groups in sodalite-group minerals.

Introduction

Various polysulfide molecules, anions and radical anions have been identified as extra-framework components within structural cavities of sodalite group minerals.[1,2] The sodalite-related minerals haüyne, lazurite, and recently discovered mineral species slyudyankaite are components of the rock lapis lazuli - which is widely used as a beautiful ornamental gemstone. Sodalite-group minerals and their synthetic analogues used as pigments are characterized by a wide variation in S-bearing extra-framework components including various polysulfide groups ($S_2^{\bullet-}$, $S_3^{\bullet-}$, $S_4^{\bullet-}$ radical anions, and neutral S_4 and S_6 particles) which are chromophores[3–5] determining different colors of these materials (blue, green, yellow or lilac: see color space chromaticity diagram for sodalite-group minerals.[6]

For example, deep blue color of the mineral lazurite is due to the presence of the $S_3^{\bullet-}$ chromophore ions.[7–10] The S_4 molecules are responsible for the red color (with purple or lilac hue if additionally trace amounts of $S_3^{\bullet-}$ are present).[4,11] Green color of sluydankaite[7] is caused by the simultaneous presence of $S_2^{\bullet-}$ and S_6 particles (yellow chromophores) and minor amounts of $S_3^{\bullet-}$ radical anions (a strong blue chromophore). Yellow color of the sodalite-group mineral bolotinaite, ideally $Na_6K(Al_6Si_6O_{24})F\cdot 4H_2O$, is caused by the admixture of $S_2^{\bullet-}$ and the absence of other chromophore centers.[12,13] Thus, understanding the role of sulfur-bearing species as chromophores helps in explaining the coloration mechanisms of various minerals.[10,14]

The occurrence of various S-bearing groups in these minerals along with specific features of their crystal structures sheds light on the conditions under which these minerals were formed, providing a deeper understanding of the geological history of host rocks.[15,16]

Negatively charged polysulfide groups are also present in some minerals belonging to other structure types. For example, the S_5^{2-} ions occur in structural cavities of the members of the bystrite–sulfhydrylbystrite solid-solution series, $(K,Na)_2Na_5Ca(Al_6Si_6O_{24})S_5^{2-}(Cl^-,HS^-)$.[17–19]

In this study, we conducted comprehensive theoretical analysis of the formation of chromophore polysulfide species as a result of thermal transformations of S_6 molecules. This involves consideration of all the main decomposition pathways of the S_6 particles, including possible capture of one or two electrons.

According to the experimental data,[1,12] the scheme of transformations of extra-framework components in SO_4^{2-}-bearing members of the sodalite group during their heating at 700 °C under reducing conditions may include the elementary processes $3SO_4^{2-}\rightarrow S_3^{\bullet-}+5e+6O_2(gas)$ and $6SO_4^{2-}\rightarrow S_2^{\bullet-}+S_4^{\bullet-}+10e+12O_2(gas)$ and $2CO_2+2e\rightarrow C_2O_4^{2-}$ ($e=$electron). Subsequent annealing in air at 800 °C results in the partial reverse

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transformations as well as the reactions $S_4^{\bullet-}+S_2^{\bullet-}\rightarrow 2S_3^{\bullet-}$, $S_3^{\bullet-}+5e+6O_2(gas)\rightarrow 3SO_4^{2-}$, and $C_2O_4^{2-}\rightarrow 2CO_2(gas)+2e$. The reduction of extra-framework water molecules in accordance with the scheme $3H_2O\rightarrow 2H_3O+{}^1\!/_2O_2+2e$ could be an alternative source of electrons.

Based on the experimental data,[20–22] it was concluded that the $S_3^{\bullet-}$ radical anion is the most stable polysulfide group. Heating of the S_6-bearing triclinic lazurite-related mineral slyudyankaite, ideally $Na_{28}Ca_4(Si_{24}Al_{24}O_{96})(SO_4)_6(S_6)_{1/3}(CO_2)\cdot 2H_2O$,[7] above 500 °C results in its irreversible transformation to a sodalite-type compound with a cubic structure.[23] After heating slyudyankaite at 700 °C under reducing conditions, the S_6 and SO_4^{2-} groups transform to the extra-framewotk species HS^-, $S_2^{\bullet-}$, and $S_4^{\bullet-}$. Further annealing of preheated slyudyankaite at 800 °C in air results in the disappearance of HS^-, $S_2^{\bullet-}$, and $S_4^{\bullet-}$ and formation of the $S_3^{\bullet-}$ groups.[1] The $S_3^{\bullet-}$ radical anion is the only polysulfide species among products of annealing of S_4-bearing haüyne at 800 °C.[12]

In this work, the energy barriers of the elementary stages in different channels of the S_6 thermal transformations were determined. Based on these data, the most likely pathways for chromophore formation were identified. Additionally, we found which particles tend to form more frequently in the minerals mentioned above. This study enhances the knowledge of coloration mechanisms in sodalite-group minerals and the role of polysulfide groups as possible markers of the conditions of geological processes during which these minerals were formed.

Computational Methodology

In this study, the energies and geometries of the particles were calculated using the Gaussian 16 software.[24] The initial atomic structures of the cyclic S_5 ("boat" conformation) and S_6 ("armchair" conformation) molecules were taken from our previous study.[25] We utilized Gaussian's Transition State (TS) calculations to determine the intermediate states along the reaction pathways.[26] To validate found TS, we conducted Intrinsic Reaction Coordinate (IRC) calculations.[27] Based on this approach, the progression of reactions in both forward and backward directions from the obtained transition state could be thoroughly examined. We verified that in all local minima there are no imaginary frequencies, while in each TS only one imaginary frequency was found. We also calculated the vibrational spectra of particles in all states. In all calculations we used the hybrid B3LYP functional,[28] along with the 6-311+G(d,p) basis set.[29] Previous studies showed that results of B3LYP/6-311G* calculations of the geometry and energetics of neutral and charged sulfur molecules are consistent with those obtained at the MP2 level of theory[30] and experimental data[26,31] (see SI Section S1 for more details). All the reaction pathways were constructed using total energy differences. The main pathway of S_6 decomposition was additionally verified using the NEB[32] method in the ORCA[33] program. Additionally, for this pathway, thermal corrections at finite temperature were calculated, and the reaction profile of Gibbs free energies was constructed.

Results and Discussion

DFT calculations have shown that the studied reaction of decomposition of the S_6 molecule can proceed *via* three possible scenarios: (1) decomposition of the uncharged S_6 molecule followed by the capture of electron; (2) capture of one electron with the opening of the six-membered cycle followed by decomposition with subsequent product charging; (3) charging the S_6 molecule to form first $S_6^{\bullet-}$ and thereafter S_6^{2-} and subsequent breaking of the structure into various products. The final products of the considered reaction pathways are the pairs of chromophores $S_3^{\bullet-}+S_3^{\bullet-}$ and $S_4^{\bullet-}+S_2^{\bullet-}$. The overall scheme showing all meaningful decomposition pathways is shown in Figure 1.

In each of these pathways the starting point is the molecule S_6 in the chair conformation. The bond lengths in this molecule are 2.12 Å, and the angles are 103.1°. The final particles are chromophore ions $S_2^{\bullet-}$, $S_3^{\bullet-}$ and $S_4^{\bullet-}$. The bond lengths are 2.05 Å; 2.04 Å, 2.00 Å, 2.28 Å and the bond angles in $S_3^{\bullet-}$ and $S_4^{\bullet-}$are 115.9° and 109.5° respectively, which is consistent with previous computational and experimental studies.[25,30,31] Some intermediate geometries are consistent with the data from Ref.[31] The geometries of all stable particles are given in SI Section S3. Below, each of the scenarios is considered in more detail.

The first pathway of the scenario (1) involves the decomposition of the uncharged S_6 molecule followed by the capture of electrons. There are several possibilities for the implementation of this scenario. Let us start by considering the simplest one. In this path, initially, the uncharged S_6 molecule transforms into a chain (see Figure 2a). The barrier of this reaction stage is 1.74 eV. Next, with smaller barriers, the chain can decompose into different products both before and after capture of one electron. For example, the uncharged S_6 chain can decompose into S_4 and S_2 molecules, as demonstrated in Figure 2a. We considered it meaningless to further explore this pathway due

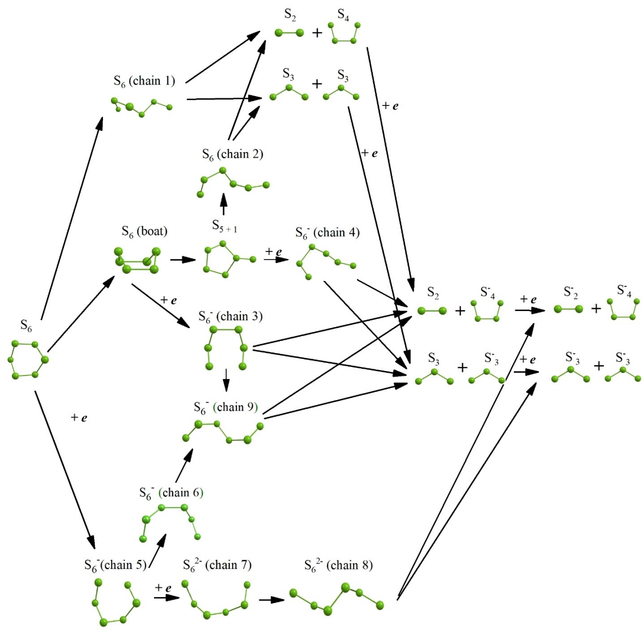

Figure 1. Overall scheme showing main decomposition pathways of the S_6 molecule. The numbering of the S_6 structures in the chain form is the same as in the figures below.

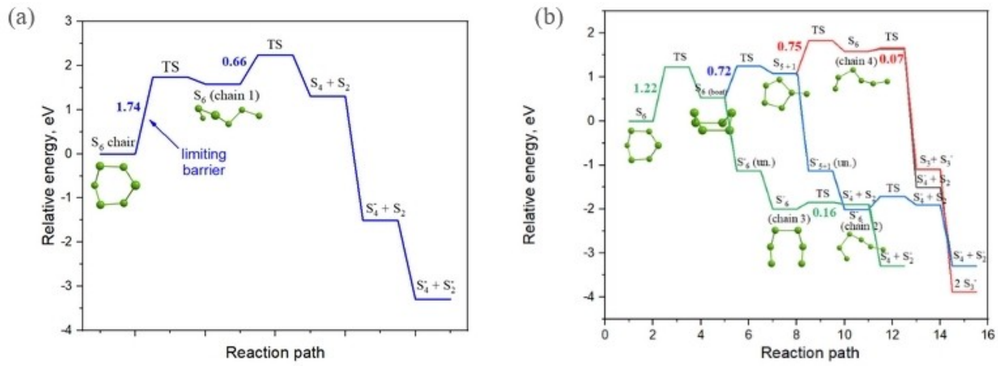

Figure 2. Decomposition of the uncharged S_6 molecule without (a) and through (b) initial conformational change from chair to boat. The numbers near to the lines on these and subsequent graphs correspond to the values of energy barriers in eV. The energy level of an unrelaxed particle at the initial moment after electron capture is marked by $S_x^{\bullet-}$(un) where x is the number of atoms in the particle. In the fork points of the reaction pathway, one of the branches is drawn in a new color.

to the very high first energy barrier, which makes the reaction unlikely.

In the second pathway of the scenario (1), the S_6 molecule in the armchair conformation undergoes a transformation to the less stable boat conformation (see Figure 2b). According to our calculations, the energy difference between these two conformations is 0.53 eV. The energy barrier for this transformation is 1.22 eV. This high barrier explains the experimental fact that in the structural cavities of the sodalite-type framework the S_6 molecules predominantly occur in the armchair conformation.[7] Let us, however, continue for a moment the discussion of the decay of the S_6 molecule in the boat conformation. The S_6-boat can transform into an unusual strained five-membered ring with an attached S atom (we refer to this configuration as S_{5+1}) with the energy barrier of 0.72 eV. Thereafter S_{5+1} can further transform into a chain with an energy barrier ~0.75 eV and then with a very low barrier (0.07 eV) break down into two neutral molecules. There are two possible products of this reaction: S_4+S_2 or $2S_3$. Subsequently, each of the particles can capture an electron without a barrier and with an energetic advantage, indicating greater stability of the charged particles.

Both for the S_6 boat conformation and for the S_{5+1} ring, the uptake of one electron is also energetically very favorable. In Figure 2b, we show the energy levels of these molecules immediately after electron capture (unrelaxed products) and after relaxation. In the next elementary stage, one bond breaks and ring configuration transforms into a chain form. The charged particles can decompose into S_2 and $S_4^{\bullet-}$ with a very low barrier (0.16 and 0.29 eV, respectively) or into S_3 and $S_3^{\bullet-}$ particles with significantly higher barriers (this is why it is not shown in the graph).

The S_6 molecule in the initial (armchair) configuration can also accept one electron. This is the next fundamental pathway (scenario 2, see Figure 3). On the graph, we showed the energy level corresponding to the energy of the molecule at the initial moment of electron capture (unrelaxed) and the energy of the optimized charged particle. During the optimization stage, one bond breaks and the molecule transforms into a charged chain isomer (chain 5). The overall energy decrease upon electron capture is more than 2 eV.

The subsequent most favorable pathway involves the sequential inversion of the chain 5, progressing through an intermediate local minimum (chain 6), and leading into chain 9, with the corresponding energy barriers of 0.23 and 0.13 eV. Furthermore, the system can decompose into $S_4^{\bullet-}+S_2$ or $S_3^{\bullet-}+S_3$ reaction products with energy barriers of ~0.5 eV. Additionally, for this pathway, considered to be the most probable (since it has the lowest activation barrier), a reaction profile using free energy (ΔG) at 300 K was determined and included in the SI Section 2.

The third scenario involves the sequential capture of two electrons by the S_6 molecule with its further breakdown (Figure 4a). One should note that the capture of the second electron is extremely unfavorable, by nearly 2 eV. This value was determined as the difference between the energies of the molecule at the initial moment of the second electron capture and of the optimized particle with the charge of -1. The instability of S_6^{2-} makes this process unlikely. However, based on the Raman spectroscopy data, the presence of trace amounts of the S_6^{2-} anions in sodalite cages of the mineral slyudyankaite cannot be excluded.[7] For this reason, the following decomposition of S_6^{2-} has been studied.

During the optimization of the S_6^{2-} anion, the chain changes its shape with energy decrease of 1.22 eV. Further transition to the chain of another conformation (with the barrier of 0.17 eV) and its subsequent decay into $S_4^{\bullet-}+S_2^{\bullet-}$ (barrier 1.06 eV) or $S_3^{\bullet-}+S_3^{\bullet-}$ (barrier 0.45 eV) is the most favorable path. It can be noted that the energy of $S_3^{\bullet-}+S_3^{\bullet-}$ is lower than the energy of $S_4^{\bullet-}+S_2^{\bullet-}$(by 0.59 eV).

Additionally, we studied the process of electron capture by S_5 molecules, since, as noted above, the S_5^{2-} ions occur in structural cavities of some minerals belonging to the cancrinite group which is related to the sodalite group[18,19] (see Figure 4b). The charging process is similar to those for S_6 molecules. At the first moment after the electron capture, the energy decrease is 1.15 eV. During the optimization process, the $S_5^{\bullet-}$ radical anion transforms into a chain with further energy reduction of

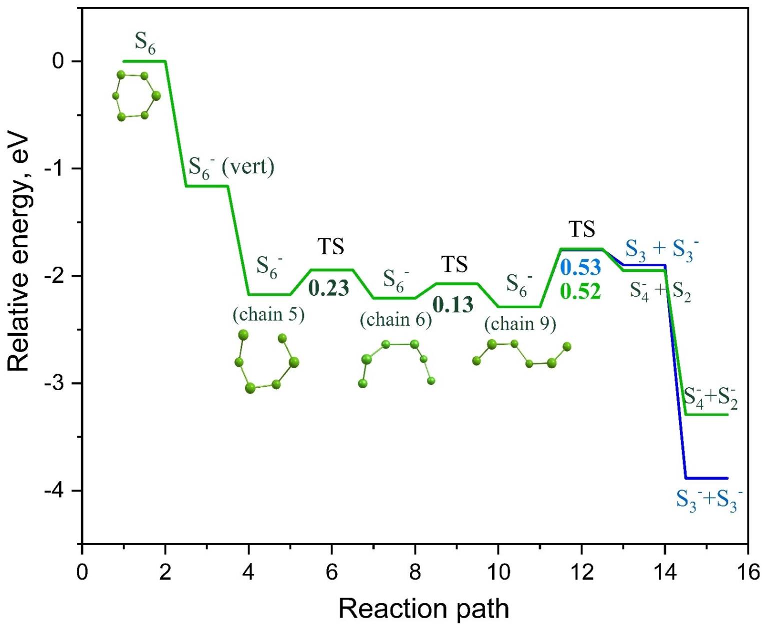

Figure 3. Reaction pathway involving capture of 1 electron by armchair S_6 molecule followed by its decomposition. The energy level corresponding to the energy of the unrelaxed $S_6^{\bullet-}$ radical anion at the initial moment of electron capture is marked by $S_6^{\bullet-}$ (un). In the fork point of the reaction pathway, one of the branches is drawn in a new color.

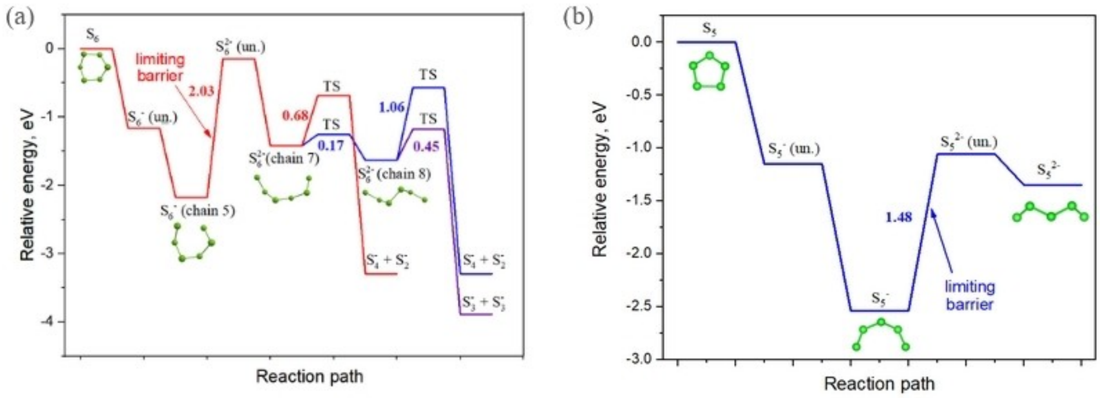

Figure 4. (a) Reaction pathway involving sequential capture of two electrons by the S_6 molecule with further breakdown, (b) Reaction pathway involving sequential capture of two electrons by the S_5 molecule. The energy levels corresponding to the energies of unrelaxed particles at the initial moment of electron capture are marked by $S_x^{\bullet-}$ (un) or S_x^{2-} (un), where x is the number of atoms in a particle. In the fork points of the reaction pathway, one of the branches is drawn in a new color.

1.39 eV. The capture of a second electron occurs with the energy barrier of 1.48 eV, which is lower than the corresponding barrier for the S_6 molecule.

Conclusions

A systematic study of mutual transformations of chromophore polysulfide species (neutral molecules, radical anions and anions) has been carried out starting from the S_6 molecule. These particles are crucial components determining the colors of sodalite group minerals such as haüyne, lazurite, and slyudyankaite, as well as important markers of the conditions under which their host rocks were formed. This involves determination of various decomposition pathways of the S_6 molecule. At any stage of these paths the system can get additional electrons from external sources. We found that getting one electron is favorable, but getting two electrons is not (explaining why S_6^{2-} anions in sodalite-group minerals have not been found in any significant quantities). As all bonding molecular orbitals in cyclic S_n molecules are fully occupied, the extra electron goes into an antibonding orbital and induces a barrierless opening of the S_n ring. Electrons thus act as "scissors", cutting covalent S–S bonds. The final products of decay of S_6^- are the pairs of radical anions, $S_3^{\bullet-}+S_3^{\bullet-}$ or $S_2^{\bullet-}+S_4^{\bullet-}$, and in both cases the limiting energy barrier is ~0.4 eV. These pairs of radical anions are thermodynamically more stable than the original S_6 molecule (with $S_3^{\bullet-}+S_3^{\bullet-}$ being the most stable), but the decay of S_6 requires an electron source (to reduce the barriers and stabilize decomposition products) and temperature (to overcome the activation barrier of 0.4 eV). Our findings confirm that electron capture is a spontaneous process followed by a significant energy reduction. In addition, the radical anions $S_n^{\bullet-}$ ($n = 2-6$) are the most stable ones among corresponding particles with different charges.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Chromophore species · DFT · Reaction barriers · Sodalite-group minerals · Sulfur molecules

[1] N. V. Chukanov, R. Y. Shendrik, M. F. Vigasina, I. V. Pekov, A. N. Sapozhnikov, V. D. Shcherbakov, D. A. Varlamov, *Minerals (Basel)* **2022**, *12*, 887.
[2] R. Steudel, T. Chivers, *Chem. Soc. Rev.* **2019**, *48*, 3279–3319.
[3] I. Gayday, A. Teplukhin, D. Babikov, *Mol. Phys.* **2019**, *117*, 2546–2558.
[4] P. Rejmak, *Phys. Chem. Chem. Phys.* **2020**, *22*, 22684–22698.
[5] B. Eckert, R. Steudel, in *Topics in Current Chemistry*, Springer Berlin Heidelberg, Berlin, Heidelberg **2012**, 31–98.
[6] N. V. Chukanov, R. Y. Shendrik, M. F. Vigasina, I. V. Pekov, A. N. Sapozhnikov, V. D. Shcherbakov, D. A. Varlamov, *Minerals (Basel)* **2022**, *12*, 887.
[7] A. N. Sapozhnikov, N. B. Bolotina, N. V. Chukanov, R. Y. Shendrik, E. V. Kaneva, M. F. Vigasina, L. A. Ivanova, V. L. Tauson, S. V. Lipko, *Am. Mineral.* **2023**, *108*, 1805–1817.
[8] A. N. Sapozhnikov, V. L. Tauson, S. V. Lipko, R. Y. Shendrik, V. I. Levitskii, L. F. Suvorova, N. V. Chukanov, M. F. Vigasina, *Am. Mineral.* **2021**, *106*, 226–234.
[9] N. V. Chukanov, R. Y. Shendrik, M. F. Vigasina, I. V. Pekov, A. N. Sapozhnikov, V. D. Shcherbakov, D. A. Varlamov, *Minerals (Basel)* **2022**, *12*, 887.
[10] T. Chivers, P. J. W. Elder, *Chem. Soc. Rev.* **2013**, *42*, 5996–6005.
[11] A. N. Sapozhnikov, V. L. Tauson, S. V. Lipko, R. Y. Shendrik, V. I. Levitskii, L. F. Suvorova, N. V. Chukanov, M. F. Vigasina, *Am. Mineral.* **2021**, *106*, 226–234.
[12] N. V. Chukanov, N. V. Shchipalkina, R. Y. Shendrik, M. F. Vigasina, V. L. Tauson, S. V. Lipko, D. A. Varlamov, V. D. Shcherbakov, A. N. Sapozhnikov, A. V. Kasatkin, N. V. Zubkova, I. V. Pekov, *Minerals (Basel)* **2022**, *12*, 1456.
[13] N. V. Chukanov, N. V. Zubkova, C. Schäfer, I. V. Pekov, R. Y. Shendrik, M. F. Vigasina, D. I. Belakovskiy, S. N. Britvin, V. O. Yapaskurt, D. Y. Pushcharovsky, *Mineral. Mag.* **2022**, *86*, 920–928.
[14] N. V. Chukanov, R. Y. Shendrik, M. F. Vigasina, I. V. Pekov, A. N. Sapozhnikov, V. D. Shcherbakov, D. A. Varlamov, *Minerals (Basel)* **2022**, *12*, 887.
[15] Y. Li, Y. Li, Y. Liu, Y. Wu, J. Wu, B. Wang, H. Ye, H. Jia, X. Wang, L. Li, M. Zhu, *Sci. Adv.* **2020**, *6*(47), eabc3687.
[16] Y. Li, H. Ye, R. Yin, Z. Hu, J. Zhu, Y. Du, H. Ding, Y. Lai, C. Wang, A. Lu, Y. Li, *Geochim. Cosmochim. Acta* **2023**, *348*, 355–368.
[17] N. V. Chukanov, R. Y. Shendrik, M. F. Vigasina, I. V. Pekov, A. N. Sapozhnikov, V. D. Shcherbakov, D. A. Varlamov, *Minerals (Basel)* **2022**, *12*, 887.
[18] A. N. Sapozhnikov, E. V. Kaneva, L. F. Suvorova, V. I. Levitsky, L. A. Ivanova, *Mineral. Mag.* **2017**, *81*, 383–402.
[19] N. V. Chukanov, A. N. Sapozhnikov, E. V. Kaneva, D. A. Varlamov, M. F. Vigasina, *Mineral. Mag.* **2023**, *87*, 455–464.
[20] G. S. Pokrovski, L. S. Dubrovinsky, *Science* **2011**, *331*, 1052–1054.
[21] G. S. Pokrovski, J. Dubessy, *Earth Planet. Sci. Lett.* **2015**, *411*, 298–309.
[22] R. Steudel, T. Chivers, *Chem. Soc. Rev.* **2019**, *48*, 3279–3319.
[23] V. G. Ivanov, A. N. Sapozhnikov Lazurites of the USSR. Nauka, Novosibirsk, **1985**, 173 (in Russian).
[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Peters-son, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Ren-dell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Revision C.01, Gaussian Inc., Wallingford CT, **2016**.
[25] M. Fedyaeva, S. Lepeshkin, A. R. Oganov, *Phys. Chem. Chem. Phys.* **2023**, *25*, 9294–9299.
[26] J. L. Durant, *Chem. Phys. Lett.* **1996**, *256*, 595–602.
[27] K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363–368.
[28] M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.
[29] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.
[30] J. Cioslowski, A. Szarecka, D. Moncrieff, *J. Phys. Chem. A* **2001**, *105*, 501–505.
[31] Y. Jin, G. Maroulis, X. Kuang, L. Ding, C. Lu, J. Wang, J. Lv, C. Zhang, M. Ju, *Phys. Chem. Chem. Phys.* **2015**, *17*, 13590–13597.
[32] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9901–9904.
[33] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78.

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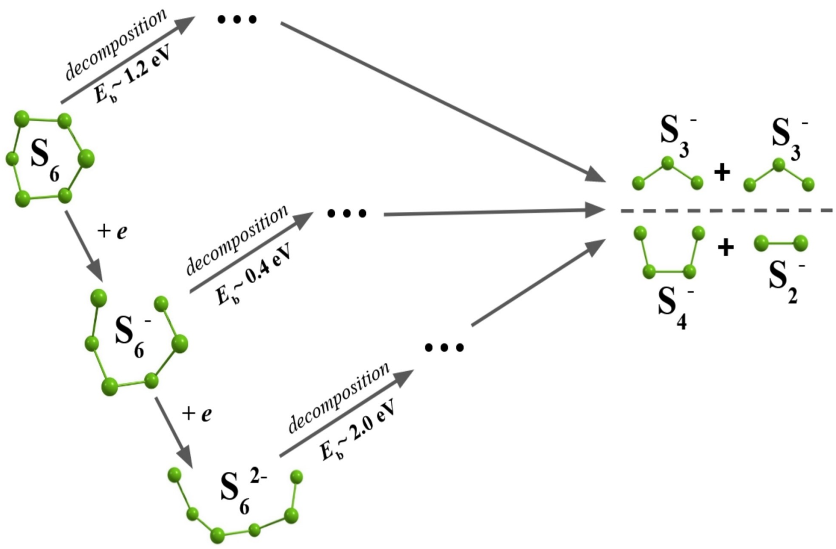
RESEARCH ARTICLE

Decomposition scheme of S_6 molecule



It is known that various polysulfide species determine the color of sodalite-group minerals. Using DFT simulations, we explore thermal conversions of extra-framework S-bearing group (S_6) into particles-chromophores in sodalite-group minerals.

M. Fedyaeva, S. Lepeshkin, N. V. Chukanov, A. R. Oganov*

1 – 6

Mutual Transformations of Polysulfide Chromophore Species in Sodalite-Group Minerals: A DFT Study on S_6 Decomposition