Infrared Spectra and Theoretical Calculations of BS$_2$ and BS$_2^-$: Strong Pseudo Jahn-Teller Effect

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(Dated: Received on November 2, 2017; Accepted on November 22, 2017)

Laser ablated boron atoms have been reacted with hydrogen sulfide and the reaction products condensed with argon at 4 K, which gave BS$_2$, BS$_2^-$, HSBS, and HBS molecules. Reagent isotopic substitution (H$_2$S, H$_2$SO$_4$, D$_2$S, $^{10}$B, $^{11}$B) and variation of boron and hydrogen sulfide concentrations have been used to identify the major products. Both BS$_2^-$ and BS$_2$ were identified as linear molecules with no significant difference in the structure parameters, but the B–S anti-symmetric stretching vibration of BS$_2$ is significantly lower than that of BS$_2^-$, which is ascribed to pseudo Jahn-Teller effect. Theoretical calculation was employed to have an insight into the interaction nature of the bonds in the corresponding products.

Key words: Matrix isolation, Pseudo Jahn-Teller effect, Multicenter bond

I. INTRODUCTION

BO$_2$ molecule and its anion, BO$_2^-$, have been produced in the reaction of boron with water in solid argon and the observed anti-symmetric B–O stretching vibration of BO$_2^-$ at 1931.0 cm$^{-1}$ is significantly higher than the same B–O stretching mode at 1274.6 cm$^{-1}$ of BO$_2$ molecule [1]. Moreover, for the first excited state (A$^2$I$_u$) of BO$_2$ molecule the B–O antisymmetric stretch mode at 2357 cm$^{-1}$ in the gas phase also shows significant frequency upshift compared with the ground state (X$^2$I$_g$) [2]. The Remer-Teller molecules such as BO$_2$ are of fundamental interest [3–7]. The BS$_2$ molecule is isoelectronic to BO$_2$ in the valence shell, which is expected to have high electron affinities and anomalously low anti-symmetric B–S stretching frequency. The absorption of BS$_2^-$ was measured in neon matrix from the reaction of vaporizing zinc sulfide with boron [8]; however, there has been no experimental measurement on the BS$_2^-$ in the literature based on our knowledge.

In this work, we report the infrared spectra of BS$_2$, BS$_2^-$, HSBS and HBS, which were produced from the reaction of laser ablated boron atoms with hydrogen sulfide in solid argon. Matrix isolation technique combined with in situ infrared spectroscopy was employed to study the reaction intermediates and products that could be isolated in our experiment. Quantum chemical frequency calculations were used to reproduce infrared spectra of the reaction products and explore the electronic structures of the chemical bonding.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

Our experimental method has been described in detail previously [9, 10]. Briefly, the 1064 nm laser beam (Nd: YAG laser fundamental, 10 Hz repetition rate and 8 ns pulse width) is focused onto rotating boron targets. The laser-ablated natural boron ($^8$B (Aldrich, 80.4% $^{11}$B, 19.6% $^{10}$B), enriched $^{10}$B (Eagle Pitcher, 93.8% $^{10}$B, 6.2% $^{11}$B), or enriched $^{11}$B (Eagle Pitcher, 97.5% $^{11}$B, 2.5% $^{10}$B) was co-deposited with H$_2$S/Ar mixture onto a 4 K CsI window, which is mounted onto cold tip closed-cycle helium refrigerator (Sumitomo Heavy Industrious, Model RDK408D) for 1 h at a rate of 2–4 mmol/h. The H$_2$S/Ar mixtures were prepared in a stainless steel vacuum line using standard manometric technique. The H$_2$S, H$_2$SO$_4$ and D$_2$S samples were prepared by the previously described method [11, 12]. After deposition, infrared spectra were recorded on a Bruker 80 V spectrometer at 0.5 cm$^{-1}$ resolution between 4000 and 400 cm$^{-1}$ using a liquid nitrogen cooled broad band MCT detector. The samples were annealed at different temperatures and cooled back to 4 K quickly after reaching the desired temperature, and more spectra were taken. Selected samples were also subjected to photolysis using a mercury lamp (175 W, without globe) as light source, with the aid of band filters to permit selected wavelength to pass through.

All structures have been fully optimized at the B3LYP level in conjunction with the def2-TZVPP basis sets [13]. Subsequent optimizations at the CCSD(t) level were carried out for all the molecules and con-
FIG. 1 IR spectra in selected regions from co-deposition of laser evaporated boron atoms with hydrogen sulfide in excess argon: (a) $^{10}$B+0.4% H$_2$S in argon co-deposited for 1 h, (b) after 20 K annealing, (c) after >300 nm irradiation, (d) after full-arc mercury lamp irradiation.

FIG. 2 IR spectra in selected regions from co-deposition of laser evaporated boron atoms with hydrogen sulfide in excess argon: (a) $^{8}$B+0.4% H$_2$S in argon co-deposited for 1 h, (b) after 20 K annealing, (c) after >300 nm irradiation, (d) after full-arc mercury lamp irradiation.

firmed as minimum by frequency analysis. DFT calculations were performed with ORCA soft package [14], the coupled cluster theoretical calculations were performed with CFOUR [15], and MCQDPT calculations performed with GAMESS [16]. The Multiwf code [17] was used for the topological analysis of the electronic structure.

III. RESULTS

Infrared spectra for the reactions of laser-ablated (typically 20 mJ/pulse) $^{10}$B and $^{8}$B (natural boron: 80.4% $^{11}$B+19.6% $^{10}$B) with 0.4% H$_2$S in solid argon in selected regions are shown in FIG. 1 and FIG. 2, respectively. Based on the behavior of absorptions on the stepwise annealing and photolysis process, four groups of new absorptions were identified in the reaction of $^{10}$B+H$_2$S in argon matrix. The first weak band (labeled A) at 1057.8 cm$^{-1}$ (site at 1059.2 cm$^{-1}$) appeared on deposition, increased slightly on annealing to 20 K, and enhanced markedly on full-arc irradiation. Another weak absorption at 1352.8 cm$^{-1}$ (labeled B) increased following annealing to 20 K and the relative intensity of this absorption increased with higher laser energy and tighter focusing. This absorption displayed nearly no change on annealing and >300 nm irradiation but disappeared upon full-arc mercury lamp irradiation. Another absorption at 1410.9 cm$^{-1}$ (labeled C) appeared as weak absorption after co-deposition, showed nearly no change on the annealing process, but sharply increased upon full-arc mercury lamp irradiation. The last group of absorptions at 2738.9 and 1202.2 cm$^{-1}$ (labeled D in figures) appeared after co-deposition, slightly increased following annealing to 20 K and increased by 20% on full-arc mercury lamp irradiation.

The experiments were performed using different H$_2$S concentrations ranging from 0.1% to 1.5% in argon with different laser energies. All absorptions were observed even in the lowest H$_2$S concentration of 0.1% in argon matrix. With the increase of H$_2$S concentration, the relative intensities of all product absorptions increased correspondingly, suggesting these species are produced by the reaction of boron atom with two or more H$_2$S molecules.

The experiments were repeated using the combination of $^{10}$B, $^{11}$B with H$_3^{32}$S, H$_3^{34}$S and the mixtures as reagent. The infrared spectra from co-depositions of laser-ablated $^{8}$B with H$_3^{34}$S and $^{11}$B with mixtures of H$_2$S and H$_2$^{34}S are presented in FIG. 3 and FIG. 4.

DOI:10.1063/1674-0068/30/1711201 ©2017 Chinese Physical Society
FIG. 3 IR spectra in selected regions from co-deposition of laser evaporated boron atoms with hydrogen sulfide in excess argon: (a) $^{10}$B + 0.4% H$_2$S in argon co-deposited for 1 h, (b) after 20 K annealing, (c) after >300 nm irradiation, (d) after full-arc mercury lamp irradiation.

FIG. 4 IR spectra in selected regions from co-deposition of laser evaporated boron atoms with hydrogen sulfide in excess argon: (a) $^{11}$B+0.2% H$_2$S+0.2% H$_2^{34}$S in argon co-deposited for 1 h, (b) after 20 K annealing, (c) after >300 nm irradiation, (d) after full-arc mercury lamp irradiation.

FIG. 5 presents the spectra from reactions with different combinations of $^{10}$B, $^{11}$B, $^{9}$B with H$_2$S and H$_2^{34}$S as reagents. The absorptions of the observed new products are summarized in Table I. In addition experiments deuterium substitution experiments were performed using D$_2$S to confirm our assignments. Quantum chemical calculations were performed to prove the spectral assignments and to have an insight into the electronic structures of the experimentally observed species. The calculated frequencies and absorbance intensities are listed in Table I. The optimized structure parameters are shown in FIG. 6.

IV. DISCUSSION

A. BS$_2$(A) and BS$_2^-$ (B)

After co-deposition of $^{10}$B with H$_2$S in solid argon, a weak band at 1057.8 (site at 1059.2) cm$^{-1}$ (labeled A) appeared (FIG. 1) and increased on annealing to 20 K and enhanced greatly on full-arc mercury lamp irradiation. In the reaction of $^{11}$B+H$_2$S, this band shifted to 1015.6 (site at 1016.8) cm$^{-1}$, giving $^{10}$B/$^{11}$B isotopic ratio of 1.0416. In the reaction of $^{11}$B+0.2% H$_2$S+0.2% H$_2^{34}$S (FIG. 4), the absorption splits into triplet absorptions at 1015.6, 1013.4, 1011.2 cm$^{-1}$ (relative intensity ratio=1:2:1), suggesting two sulfur atoms in the symmetric sites are involved in this molecule. In addition for this band no deuterium shift was observed for all boron reaction with D$_2$S. This set of absorptions are nearly identical to the B-S anti-symmetric vibration of BS$_2$ observed at 1014.6 cm$^{-1}$ in neon matrix [8]. Notice the slightly blue shift of the absorptions in argon matrix suggests a little influence of matrix on the BS$_2$ molecule.

Another absorption at 1352.8 cm$^{-1}$ (labeled B) appeared after co-deposition in the $^{10}$B+H$_2$S reaction in argon matrix (FIG. 1). This absorption shifted to 1299.5 cm$^{-1}$ in the reaction of $^{11}$B+H$_2$S ($^{10}$B/$^{11}$B=1.0410) and shifted to 1347.5 cm$^{-1}$ in the $^{10}$B+H$_2^{34}$S ($^{32}$S/$^{34}$S=1.0039) reaction. Furthermore, in the reaction of $^{11}$B+0.2% H$_2$S+0.2%H$_2^{34}$S, the 1299.5 cm$^{-1}$ band split into triplet at 1299.5, 1296.9, and 1294.6 cm$^{-1}$ (relative intensity ratio=1:2:1), suggesting two sulfur atoms in the symmetric site were in-

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FIG. 5 IR spectra in 1000–1450 cm$^{-1}$ region from co-deposition of laser evaporated boron atoms with hydrogen sulfide in excess argon: (a) $^{10}$B+0.4% H$_2$S in argon co-deposited for 1 h following annealing to 20 K, (b) after full-arc mercury lamp irradiation, (c) $^{10}$B+0.4% H$_2$S in argon co-deposited for 1 h following annealing to 20 K, (d) after full-arc mercury lamp irradiation, (e) $^{10}$B+0.4% H$_2$S in argon co-deposited for 1 h following annealing to 20 K, (f) after full-arc mercury lamp irradiation.

FIG. 6 Structure parameters optimized at CCSD(t)/def2-TZVPP level.

infrared active. The bending modes were calculated below 400 cm$^{-1}$ for both molecules (Table I), which are out of the measurement limit of our equipment. Based on the isotopic labeled experiments ($^{10}$B, $^{11}$B, $^{32}$S, $^{34}$S) and theoretical frequency calculations, we confirmed the assignments of the 1057.8 and 1352.8 cm$^{-1}$ absorptions to BS$_2$ and BS$_2^-$, respectively.

B. HSBS(C)

As shown in FIG. 1, the reaction of $^{10}$B+H$_2$S gave absorption at 1410.9 cm$^{-1}$ that appeared as a weak absorption after co-deposition and sharply increased upon full arc photolysis. This band shifted to 1356.2 cm$^{-1}$ in the reaction of $^{11}$B+H$_2$S ($^{10}$B/$^{11}$B=1.0403) and to 1404.6 cm$^{-1}$ in the reaction of $^{10}$B+H$_2$S$^{34}$S ($^{32}$S/$^{34}$S=1.0045), which is appropriate to the B–S stretching vibration. In the reaction of $^{11}$B+H$_2$S (FIG. 2), this band split into doublet at 1410.9 and 1356.2 cm$^{-1}$, suggesting only one boron atom is involved in the molecule. In addition there is no deuterium shift observed for this band. Moreover, this absorption split into quadruplet (1356.2, 1355.0, 1350.7 and 1349.7 cm$^{-1}$ with nearly the same intensities) in the reaction of $^{11}$B+0.2% H$_2$S+0.2% H$_2$S$^{34}$S in argon matrix (FIG. 4), indicating two sulfur atoms in asymmetric site were involved in the molecule. This absorption is appropriate to the HSBS molecule.

Quantum-chemical calculations support the assign-
ment. The anharmonic corrected frequencies calculated at CCSD(t)/def2-TZVPP theoretical level are summarized in Table I. The calculated asymmetric B–S stretching vibration of HS\(^{10}\)BS at 1423.2 cm\(^{-1}\) is in good consistence with the experimental value of 1410.9 cm\(^{-1}\). Importantly, the predicted \(^{10}\)B/\(^{11}\)B and \(^{32}\)S/\(^{34}\)S isotopic shifts also match the experimental values very well, which give evidence for our reasonable assignment. Notice the calculated S–H stretching and B–S bending modes are very weak, which were not observed in our experiments.

Table I Observed and calculated fundamental frequencies (cm\(^{-1}\)) at CCSD(t)/def2-TZVPP level. Values in parenthesis are calculated intensities in km/mol.

<table>
<thead>
<tr>
<th>CCSD(t)</th>
<th>Obsd.</th>
<th>CCSD(t)</th>
<th>Obsd.</th>
<th>CCSD(t)</th>
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<th>CCSD(t)</th>
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<th>CCSD(t)</th>
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<th>CCSD(t)</th>
<th>Obsd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^{11})BS</td>
<td>2740.9(21)</td>
<td>2732.2</td>
<td>2756.3(23)</td>
<td>2738.9</td>
<td>2740.9(21)</td>
<td>2732.2</td>
<td>2756.3(23)</td>
<td>2738.9</td>
<td>2108.5(29)</td>
<td>2095.0</td>
<td></td>
</tr>
<tr>
<td>1172.8(38)</td>
<td>1167.4</td>
<td>1207.3(41)</td>
<td>1202.2</td>
<td>1163.6(38)</td>
<td>1158.3</td>
<td>1198.7(40)</td>
<td>1193.2</td>
<td>1115.4(32)</td>
<td>1090.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>682.2(0x2)</td>
<td>689.8(0x2)</td>
<td>681.9(0x2)</td>
<td>689.5(0x2)</td>
<td>559.5(0x2)</td>
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\(^{11}\)BS\(^{2}\) | 1049.2(336) | 1016.8 | 1097(365) | 1059.2 | 1044.4(333) | 1012.5 | 1092.4(362) | 1054.9 | 1059.2 |
| 532.4(0) | 533.1(0) | 517.7(0) | 533.7(0) |
| 321.6(0) | 335(0) | 320.2(0) | 333.7(0) |
| 259.3(2) | 270.1(2) | 258.2(2) | 269.1(2) |

\(^{10}\)BS\(^{2}\) | 1311.9(1202) | 1299.5 | 1365.7(1304) | 1352.8 | 1306.4(1192) | 1294.6 | 1360.4(1294) | 1347.5 | 1352.8 |
| 543.2(0) | 543.2(0) | 527.3(0) | 527.3(0) |
| 356.7(77x2) | 380.8(84x2) | 364.1(76x2) | 379.3(83x2) |

H\(^{11}\)BS | 2600.6(8) | 2600.6(8) | 2598.4(8) | 2598.4(8) | 2598.4(8) | 2598.4(8) | 2188.9(4) | 2188.9(4) |
| 1368.1(285) | 1356.2 | 1423.2(309) | 1410.9 | 1361.6(283) | 1349.7 | 1417.0(307) | 1404.6 | 1423.1(309) | 1410.9 |
| 804.9(7) | 809.4(7) | 803.5(7) | 807.9(7) | 630.6(4) |
| 506.1(1) | 499.2(1) | 484.5(1) | 486.3(1) | 475.3(2) |
| 330.4(0) | 343.7(0) | 329(0) | 342.0(0) | 334.2(0) |
| 285(3) | 294.8(3) | 283.9(2) | 293.8(3) | 272.2(2) |

C. HBS(D)

After co-deposition of \(^{10}\)B with H\(_2\)S in solid argon, two bands at 2738.9 and 1202.2 cm\(^{-1}\) (labeled D) appeared as very weak absorptions, which increased upon full arc mercury lamp irradiation. The 2738.9 cm\(^{-1}\) band showed no \(^{34}\)S/\(^{32}\)S isotopic shift, but shifted to 2723.2 cm\(^{-1}\) in the \(^{11}\)B+H\(_2\)S reaction and to 2095.0 cm\(^{-1}\) in the \(^{10}\)B+D\(_2\)S reaction. The band position, \(^{10}\)B/\(^{11}\)B isotopic ratio (1.0058) and H/D isotopic ratio (1.0074) are appropriate to the terminal B(III)-H stretching vibration [18]. Another band at 1202.2 cm\(^{-1}\) shifts to 1167.4 cm\(^{-1}\) in the reaction of \(^{11}\)B+H\(_2\)S \(^{10}\)B/\(^{11}\)B=1.0298, shifts to 1158.3 cm\(^{-1}\) in the reaction of \(^{11}\)B+H\(_2\)S \(^{32}\)S/\(^{34}\)S=1.0079 and split into doublet at 1167.4 and 1158.3 cm\(^{-1}\) in the reaction of \(^{11}\)B+0.2% H\(_2\)S+0.2% H\(_2\)\(^{34}\)S, suggesting this absorption is the B–S stretching vibration with only one sulfur atom involved in the molecule. These two bands were assigned to HBS molecule, by comparison to literature infrared spectra of this species (2739.9 for B–H stretching vibration, closed to 1200 cm\(^{-1}\) for B–S stretching vibration in gas phase for H\(^{11}\)BS) [18–20].

The HBS molecule was predicted to have linear structure with \(^1\Sigma^+\) ground state. The B–H and B–S stretching vibrations of HBS molecule were calculated at 2756.3 and 1207.3 cm\(^{-1}\) by anharmonic corrected frequencies calculated at CCSD(t) level, which are in very good agreement with our experimental value of 2738.9 and 1202.2 cm\(^{-1}\).

V. ELECTRONIC STRUCTURE

Both BS\(_2\) and BS\(_2\)^+ have highly symmetry D\(_{\infty h}\) stable structures in the \(^2\)I\(_g\) and \(^1\Sigma^+\) ground states, respectively. As shown in FIG. 6, the calculated B–S bond length for both molecules shows no significant difference. Based on NBO\(^{21}\) analysis, dual 3 center 4 electron hyper bonds (3c-4e) are found in BS\(_2\)^– as shown in FIG. 7. Similarly one 3c-4e and one 3c-3e bonds are formed for BS\(_2\) molecule. Such multiple center bond can be described as a strong resonance hybrid of two localized Lewis structure representations described as S2-B1-S3+->S2-B1:S3. In addition the calculated Wiberg bond index for B–S bond of BS\(_2\) is 1.87, which is basically the same as the corresponding B–S bond index of 2.

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FIG. 7 The diagrams of the valence molecular orbitals of the ground state structure of BS$_2$, BS$_2^-$, and HSBS.

1.86 for BS$_2^-$ anion. Almost identical B–S bond length and Wiberg bond index for both BS$_2$ and BS$_2^-$ suggest similar B–S bond strength and vibrational stretching frequencies. Indeed the B–S symmetric stretching vibration of BS$_2$ shows no significant difference from BS$_2^-$ based on our frequency calculations (Table I). Unfortunately we cannot measure this mode in our experiment because the mode is infrared inactive. However, the B–S antisymmetric stretching mode is located at 1050.2 cm$^{-1}$ in our experiment, which is about 300 cm$^{-1}$ lower than the same mode for BS$_2^-$ . Our calculated frequencies match experimental values very well (Table I). Extensive theoretical and experimental work suggests this frequency upshift is due to pseudo Jahn-Teller effect [20]. FIG. 8 displays the adiabatic energy curves of the ground state and first excited state as a function of the anti-symmetric stretching coordinate for both BS$_2$ and BS$_2^-$ molecules. For BS$_2$ due to the mixing and vibronic coupling of the ground $^2\Pi_g$ and first excited state $^2\Pi_u$ states, the ground state is softened and excited state is steepened, expressed experimentally by the frequency red-shift, resulting in the anomalously low B–S anti-symmetric stretching vibration of BS$_2$. However, for BS$_2^-$ the large energy gap between the first excited state ($^4\Pi_u$) and the ground state ($^1\Sigma_g^-$) makes it difficult for the vibronic coupling of the two states to take place, indicating the negligible influence on the B–S antisymmetric vibration of the ground state BS$_2^-$ anion. Similar anomalously low B–O asymmetric stretching vibration was observed and calculated for ground state BO$_2$ molecule [22].

For comparison the HSBS molecule is calculated to have $C_s$ symmetry with bond angle S–B–S of 177.8º in $^1\text{A}^\prime$ ground state. No multi-center bond was identified in HSBS molecule from NBO analysis; however, there is a triple bond (Wiberg bond index=2.36) formed between boron and the terminal sulfur atom and a single $\sigma$ bond is found between boron and another sulfur atom. In the ELF [23] picture (FIG. 9), 3.11 electrons are localized in the bi-synaptic basin in the interac-

FIG. 8 Adiabatic energy curves of the ground state and first excited state calculated at MCQDPT level as a function of the anti-symmetric stretching coordinate for BS$_2$ and BS$_2^-$ molecule.

FIG. 9 The ELF isosurface (isovalue=0.85) for corresponding products. Wave functions were generated by using the B3LYP/def2-TZVPP calculations.
tion region of boron and terminal sulfur atom and 2.12 electrons localized in the interaction region of boron and another sulfur atom, corresponding to the covalent bond formed between boron atom and two sulfur atoms in HSBS molecule. However, 2.64 and 2.53 electrons are found in the B–S interaction region for BS2 and BS2−, respectively, suggesting a weaker B–S bond for later two molecules. The linear structure HBS molecule has 1Σg ground state, triple bond was formed between boron and sulfur atoms (Wiberg bond index=2.47) in HBS molecule. The bi-synaptic basin in the interaction region between boron and sulfur is occupied by 3.23 electrons, suggesting the strongest covalent interaction in all boron sulfides observed in these experiments.

VI. CONCLUSION

BS2 radical and BS2− anion produced by the reaction of boron atom/anion with hydrogen sulfide molecules were identified in low temperature argon matrix through infrared spectra of 10B, 11B, and 34S substitution and from theoretical frequency calculations. Multiple center bond (S–B–S) was identified in BS2 and BS2− from theoretical calculation analysis. The anomalously low anti-symmetric stretching frequency of BS2 molecule was due to the vibronic coupling between the ground 2Πg state with the first excited state 2Πu (pseudo Jahn-Teller effect). In addition HSBS and HBS molecules were also identified and multiple B–S bond was found.

VII. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.21373152).

J. Almbl and P. R. Taylor, the Integral Packages MOLECULE.
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