Supplementary Material

The Structures, Molecular Orbital Properties and Vibrational Spectra of the Homo- and Heterodimers of Sulphur Dioxide and Ozone. An *ab initio* Study

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Table S1. Properties of the valence molecular orbitals of sulphur dioxide dimer 5.

No.	Symmetry	Energy/*H*	Approximate description [a,b,c]
1-14			core
15	a′	-1.49308	σ(OSO) (EA)
16	a′	-1.48726	σ(OSO) (ED)
17	a″	-1.39319	σ(OSO) (EA)
18	a′	-1.38860	σ(OSO) (ED)
19	a′	-0.88456	lp(S) (EA)
20	a′	-0.87809	lp(S) (ED)
21	a″	-0.70026	lp(O) (EA)
22	a′	-0.69666	σ(S1…O5,O6)
23	a′	-0.69512	σ(S4…O2)
24	a′	-0.68779	lp(O) (ED)
25	a′	-0.65532	π(OSO) (EA)
26	a″	-0.65442	π(OSO) (ED)
27	a″	-0.54556	π(nb)(OSO) (EA)
28	a′	-0.54157	lp(O) (ED)
29	a″	-0.52401	lp(O) (EA)
30	a″	-0.51163	π(nb)(OSO) (ED)
31	a′	-0.50408	n(O) (EA)
32 (HOMO)	a′	-0.49575	lp(O) (ED)
33 (LUMO)	a′	-0.00765	π*(OSO) (EA)
34	a″	-0.00230	π*(OSO) (ED)
35	a′	0.05754	σ*(OSO) (EA)
36	a′	0.06414	σ*(OSO) (ED)
37	a″	0.06859	σ*(OSO) (EA)
38	a′	0.07064	σ*(OSO) (ED)

[a] See Figure 1 for numbering of atoms.

[b] EA – electron acceptor; ED – electron donor.

[c] lp – lone pair; nb – non-bonding.

Table S2. Properties of the valence molecular orbitals of sulphur dioxide dimer 2.

No.	Symmetry	Energy/*H*	Approximate description [a,b]
1-14			core
15	a_g	-1.48846	σ(O3S1O5) + σ(O4S2O6)
16	a_u	-1.48535	σ(O3S1O5) - σ(O4S2O6)
17	a_g	-1.38795	σ(O3S1O5) + σ(O4S2O6)
18	a_u	-1.38760	σ(O3S1O5) - σ(O4S2O6)
19	a_u	-0.88028	lp(S1) – lp(S2)
20	a_g	-0.87636	lp(S1) + lp(S2)
21	a_u	-0.69560	lp(O3S1O5) - lp(O4S2O6)
22	a_g	-0.69536	lp(O3S1O5) + lp(O4S2O6)
23	a_u	-0.68715	lp(O3S1O5) - lp(O4S2O6)
24	a_g	-0.68435	lp(O3S1O5) + lp(O4S2O6)
25	a_g	-0.66656	π(O3S1O5) + π(O4S2O6)
26	a_u	-0.64081	π(O3S1O5) - π(O4S2O6)
27	a_g	-0.54082	π(nb)(O3S1O5) + π(nb)(O4S2O6)
28	a_u	-0.53946	π(nb)(O3S1O5) - π(nb)(O4S2O6)
29	a_g	-0.51556	σ(S1…O4) + σ(S2…O3)
30	a_u	-0.51463	σ(S1…O4) - σ(S2…O3)
31	a_g	-0.49962	lp(O3S1O5) + lp(O4S2O6)
32 (HOMO)	a_u	-0.49343	lp(O3S1O5) - lpO4S2O6)
33 (LUMO)	a_u	-0.00908	π*(O3S1O5) – π*(O4S2O6)
34	a_g	0.00368	π*(O3S1O5) + π*(O4S2O6)
35	a_u	0.05745	σ*(O3S1O5) – σ*(O4S2O6)
36	a_g	0.06510	σ*(O3S1O5) + σ*(O4S2O6)
37	a_u	0.06995	σ*(O3S1O5) – σ*(O4S2O6)
38	a_u	0.07260	σ*(O3S1O5) + σ*(O4S2O6)

[a] See Figure 1 for numbering of atoms.

[b] lp – lone pair; nb – non-bonding.

Table S3. Properties of the valence molecular orbitals of ozone dimer 2.

No.	Symmetry	Energy/*H*	Approximate description [a,b]
1-6			core
7	a_g	-1.73863	σ(O3O1O5) + σ(O4O2O6)
8	a_u	-1.73579	σ(O3O1O5) - σ(O4O2O6)
9	a_u	-1.42452	σ(O3O1O5) - σ(O4O2O6)
10	a_g	-1.42125	σ(O3O1O5) + σ(O4O2O6)
11	a_g	-1.10253	σ(O1…O4) + σ(O2…O3)
12	a_u	-1.09149	lp(O3O1O5) - lp(O4O2O6)
13	a_g	-0.82521	lp(O3O1O5) + lp(O4O2O6)
14	a_u	-0.82494	lp(O3O1O5) - lp(O4O2O6)
15	a_u	-0.80047	lp(O3O1O5) - lp(O4O2O6)
16	a_g	-0.79187	lp(O3O1O5) + lp(O4O2O6)
17	a_g	-0.77739	π(O3O1O5) - π(O4O2O6)
18	a_u	-0.76467	π(O3O1O5) + π(O4O2O6)
19	a_g	-0.56449	π(nb)(O3O1O5) - π(nb)(O4O2O6)
20	a_u	-0.56138	π(nb)(O3O1O5) + π(nb)(O4O2O6)
21	a_g	-0.55901	lp(O3O1O5) + lp(O4O2O6)
22	a_u	-0.54704	lp(O3O1O5) - lp(O4O2O6)
23	a_u	-0.49258	σ(O1…O4) - σ(O2…O3)
24 (HOMO)	a_g	-0.47566	lp(O3O1O5) + lp(O4O2O6)
25 (LUMO)	a_g	-0.05937	π*(O3O1O5) – π*(O4O2O6)
26	a_u	-0.03645	π*(O3O1O5) + π*(O4O2O6)
27	a_u	0.09591	σ*(O3O1O5) – σ*(O4O2O6)
28	a_u	0.09690	σ*(O3O1O5) - σ*(O4O2O6)
29	a_g	0.10330	σ*(O3O1O5) + σ*(O4O2O6)
30	a_g	0.11570	σ*(O3O1O5) + σ*(O4O2O6)

[a] See Figure 3 for numbering of atoms.

[b] lp – lone pair; nb – non-bonding.

Table S4. Properties of the valence molecular orbitals of sulphur dioxide-ozone complex 2a. All orbitals are of *a* symmetry

No.	Energy/*H*	Approximate description [a,b]
1-10		core
11	-1.74704	σ(O4O2O6)
12	-1.48367	σ(O3S1O5)
13	-1.43319	σ(O4O2O6)
14	-1.38485	σ(O3S1O5)
15	-1.11011	lp(O4O2O6)
16	-0,87619	lp(O3S1O5)
17	-0.83491	lp(O4O2O6)
18	-0.80607	lp(O4O2O6)
19	-0.78562	π(O4O2O6)
20	-0.69138	π(nb)(O3S1O5)
21	-0.68221	lp(O3S1O5)
22	-0.65120	π(O3S1O5)
23	-0.57690	π(nb)(O4O2O6)
24	-0.56423	lp(O4O2O6)
25	-0.53722	lp(O3S1O5)
26	-0.51410	lp(O3S1O5)
27	-0.49526	σ(S1…O4) + σ(O2…O3)
28 (HOMO)	-0.49118	σ(S1…O4) - σ(O2…O3)
29 (LUMO)	-0.06202	π*(O4O2O6)
30	0.00537	π*(O3S1O5)
31	0.06597	σ*(O3S1O5)
32	0.07245	σ*(O4O2O6)
33	0.07292	σ*(O3S1O5)
34	0.08376	σ*(O4O2O6)

[a] See Figure 5 for numbering of atoms.

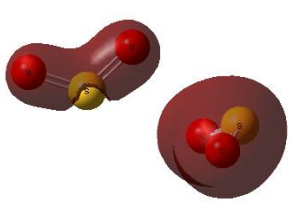
[b] lp – lone pair; nb – non-bonding.

Table S5. Properties of the valence molecular orbitals of sulphur dioxide-ozone complex 5b.

No.	Symmetry	Energy/*H*	Approximate description [a,b]
1-10			core
11	a′	-1.74803	σ(O2O1O3)
12	a′	-1.48894	σ(O5S4O6)
13	a′	-1.43315	σ(O2O1O3)
14	a″	-1.38968	σ(O5S4O6)
15	a′	-1.10438	lp(O2O1O3)
16	a′	-0.87975	lp(O5S4O6)
17	a′	-0.83584	lp(O2O1O3)
18	a′	-0.80403	lp(O2O1O3)
19	a″	-0.78086	π(O2O1O3)
20	a″	-0.69598	lp(O5S4O6)
21	a′	-0.68758	lp(O5S4O6)
22	a′	-0.65703	π(O5S4O6)
23	a′	-0.57122	σ(O2…S4)
24	a′	-0.56105	lp(O2O1O3)
25	a″	-0.54172	lp(O5S4O6)
26	a″	-0.51781	π(nb)(O5S4O6)
27	a′	-0.49842	lp(O5S4O6)
28 (HOMO)	a″	-0.49343	π(nb)(O2O1O3)
29 (LUMO)	a″	-0.05678	π*(O2O1O3)
30	a′	-0.00367	π*(O5S4O6)
31	a′	0.06210	σ*(O5S4O6)
32	a″	0.07117	σ*(O2O1O3)
33	a′	0.07118	σ*(O5S4O6)
34	a′	0.08294	σ*(O2O1O3)

[a] See Figure 5 for numbering of atoms.

[b] lp – lone pair; nb – non-bonding.



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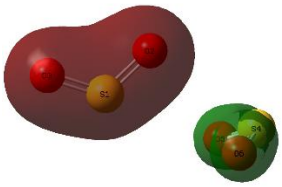

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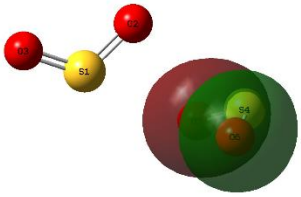

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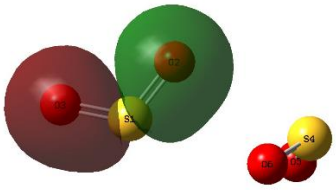

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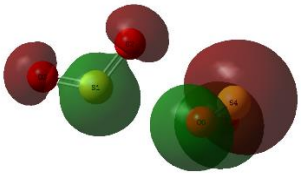

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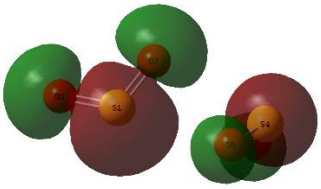

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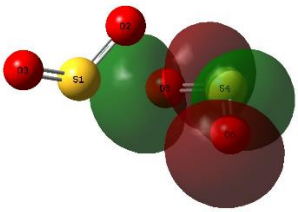

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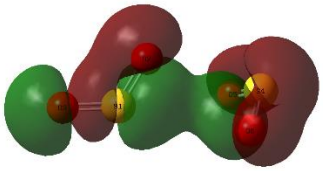

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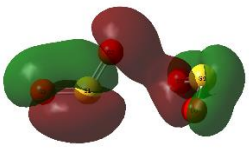

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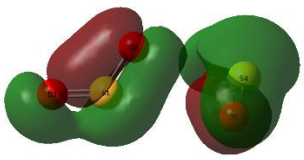

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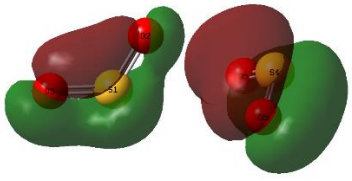

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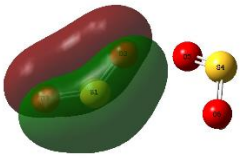

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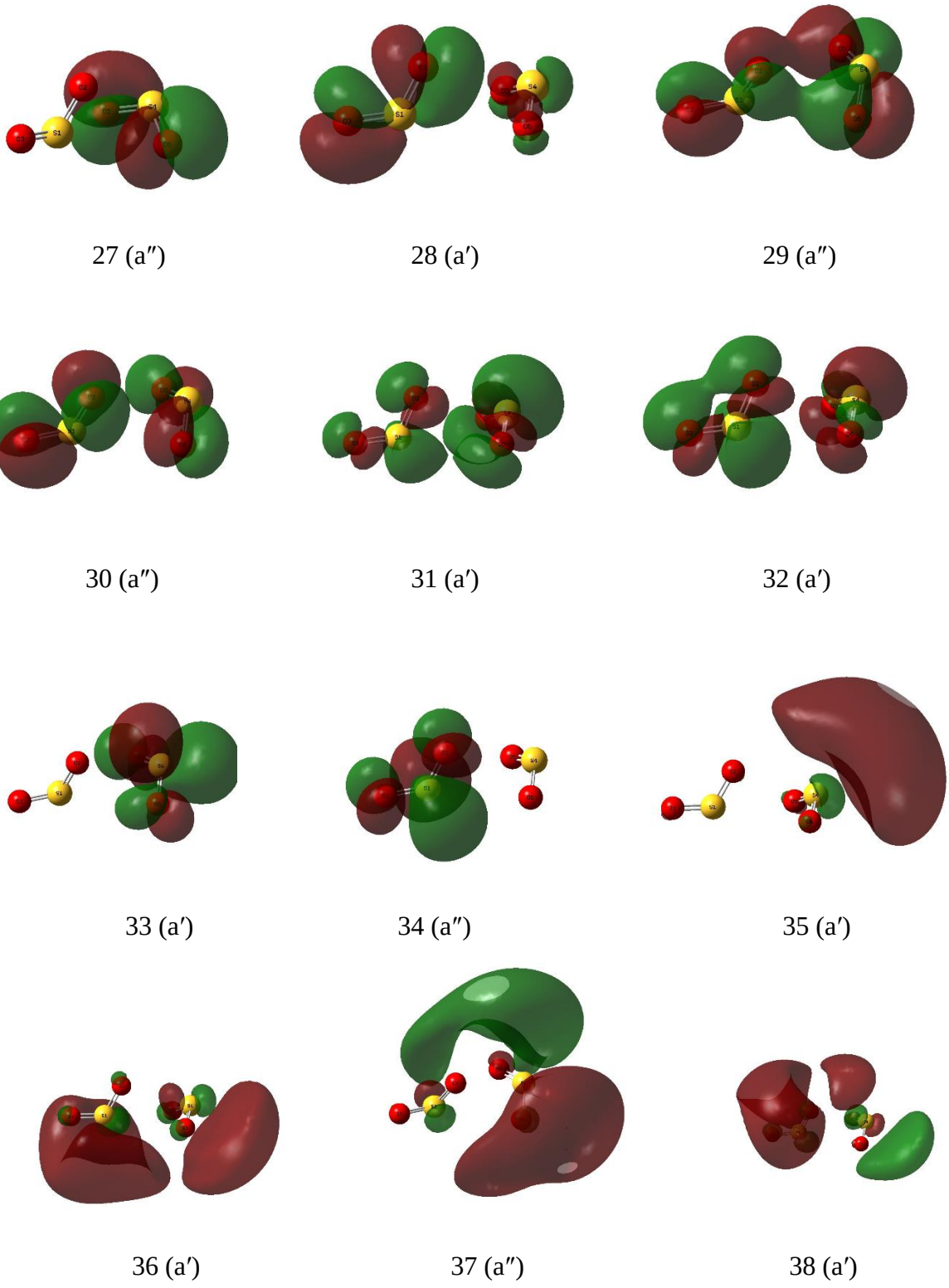
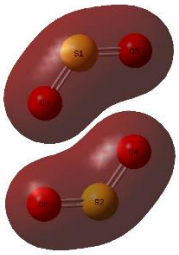


Figure S1. Valence molecular orbitals of sulphur dioxide dimer 5.



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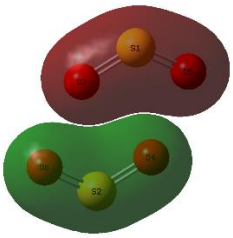

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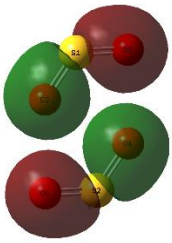

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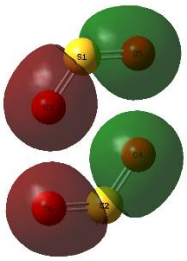

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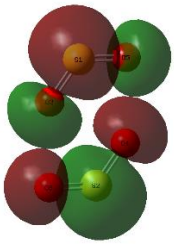

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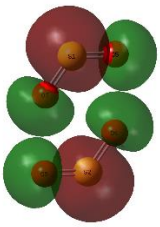

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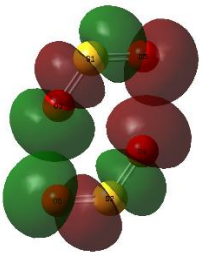

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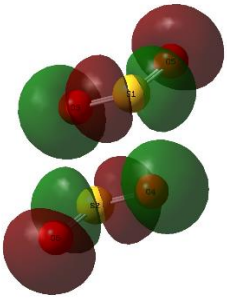

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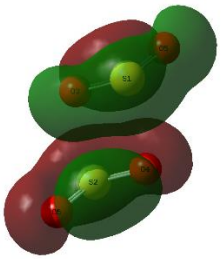

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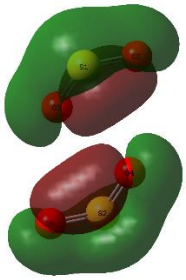

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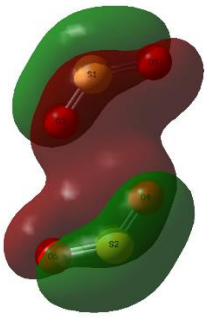

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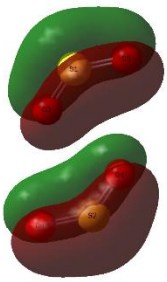

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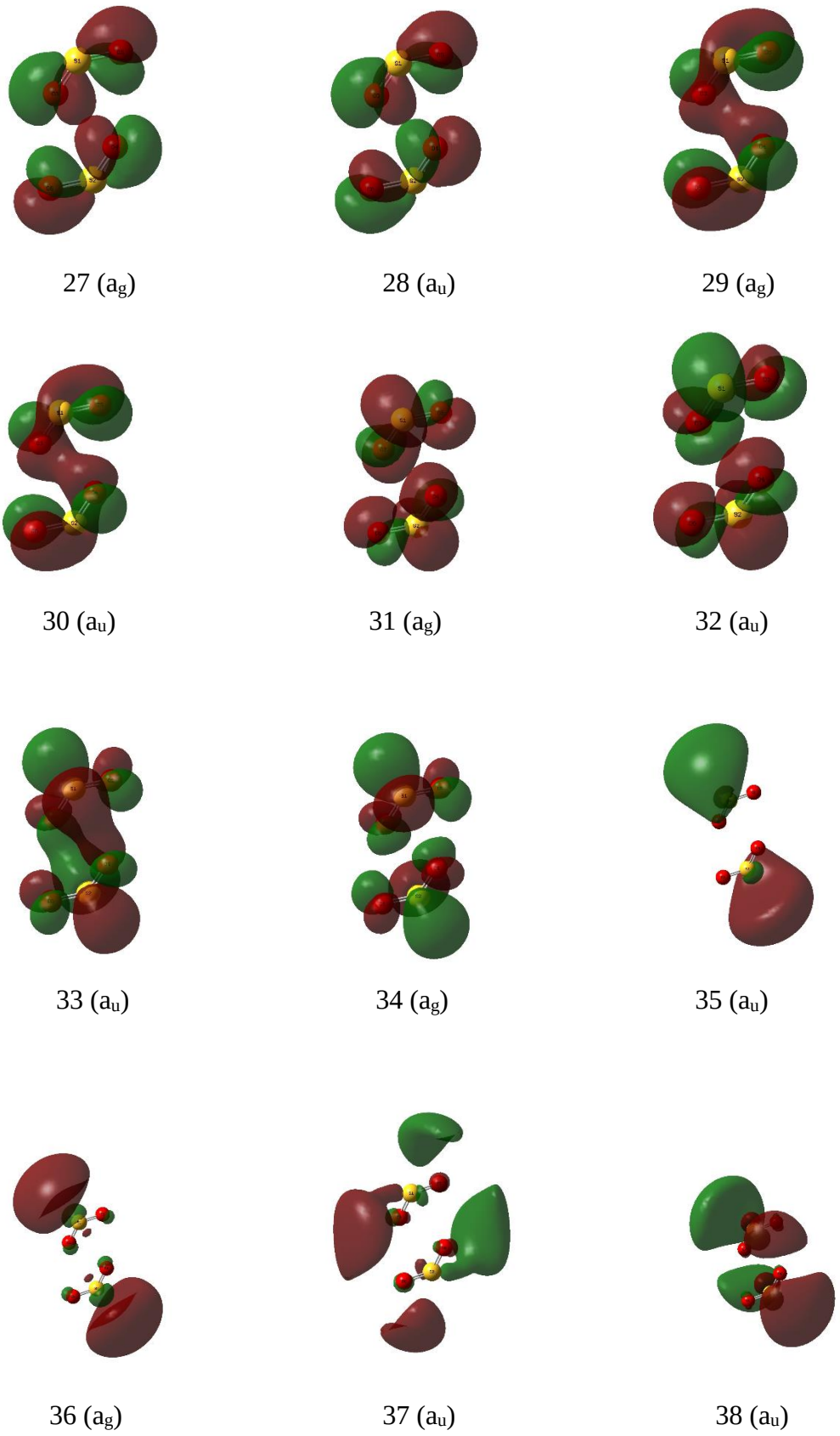
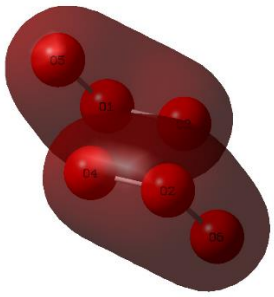


Figure S2. Valence molecular orbitals of sulphur dioxide dimer 2.



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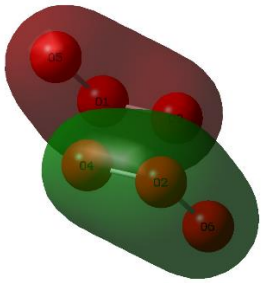

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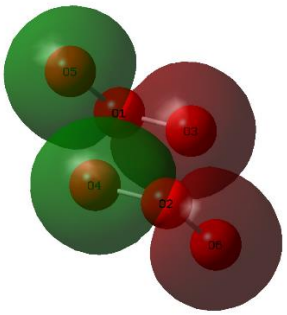

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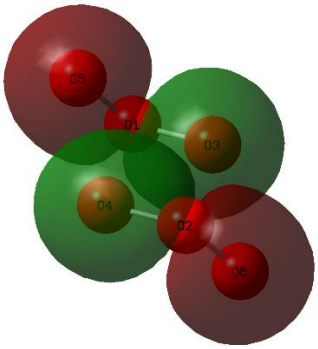

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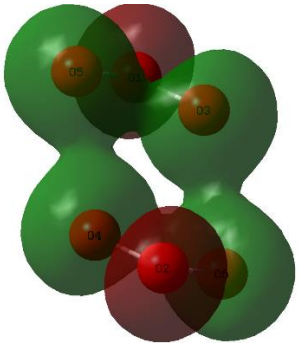

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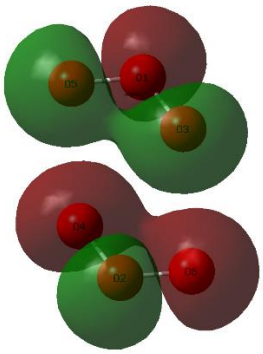

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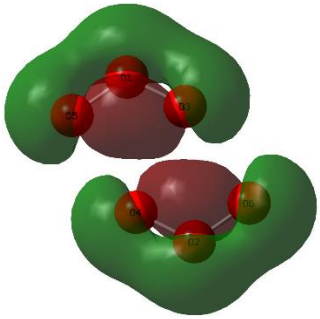

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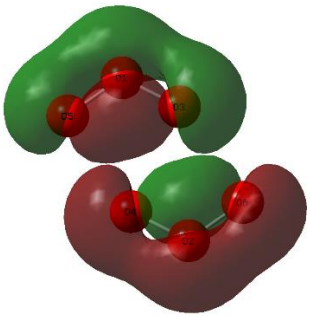

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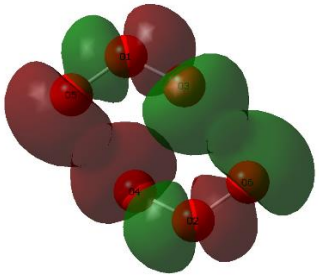

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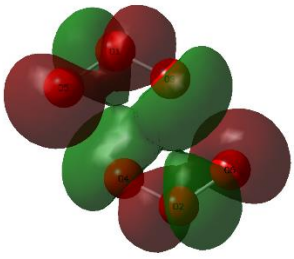

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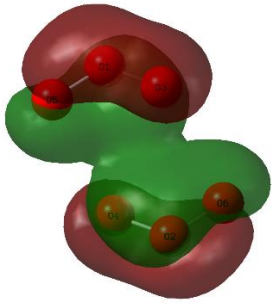

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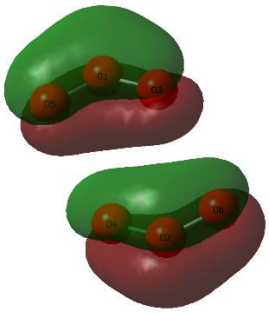

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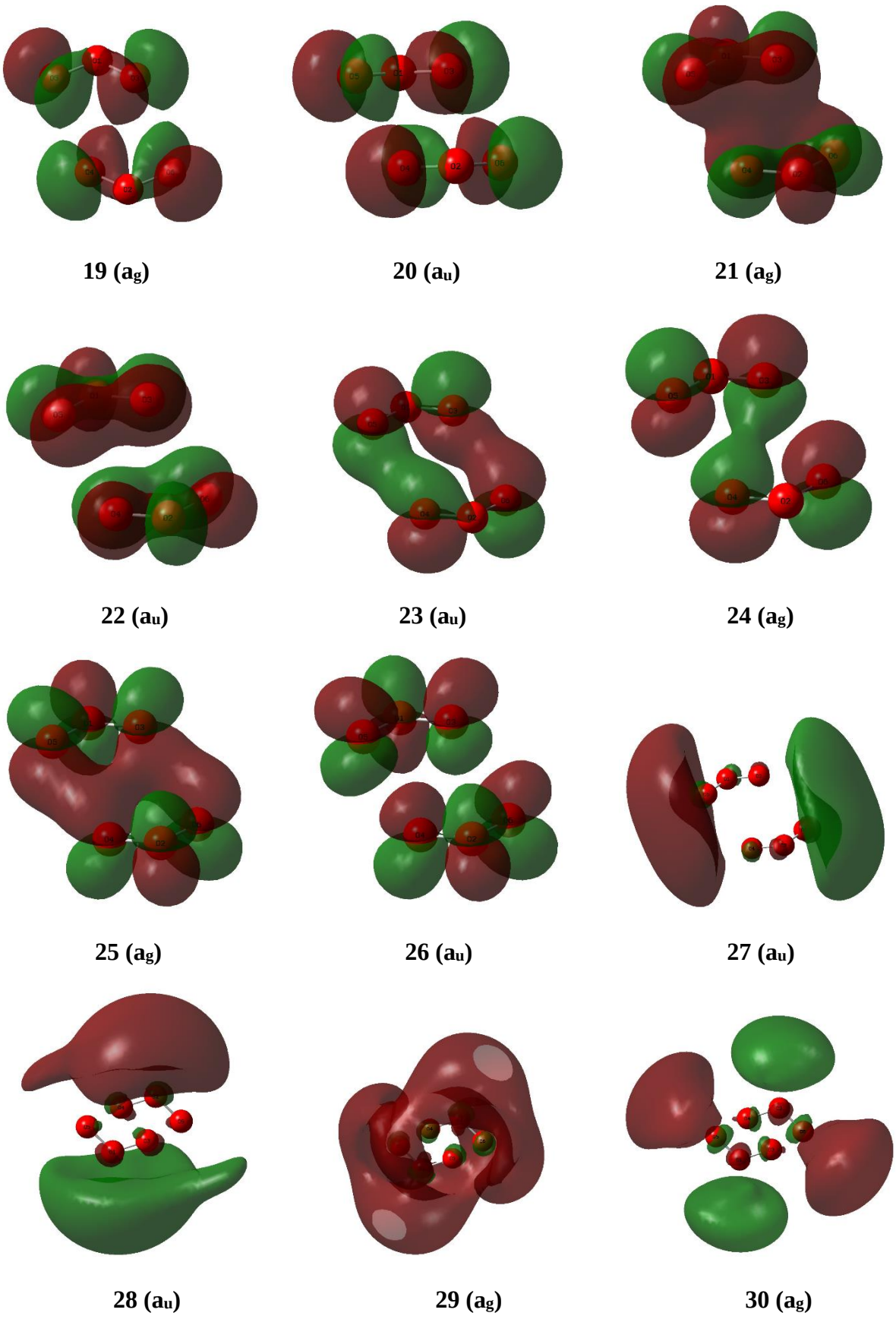
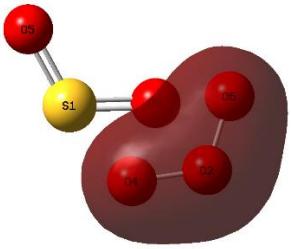


Figure S3. Valence molecular orbitals of ozone dimer 2.



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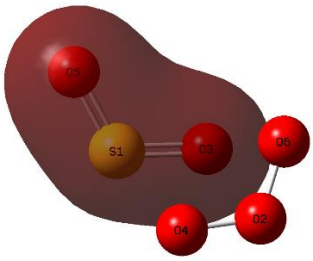

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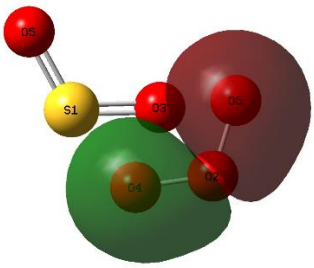

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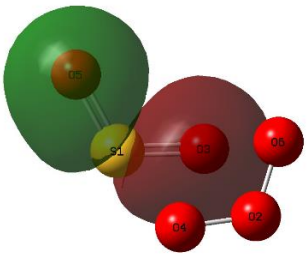

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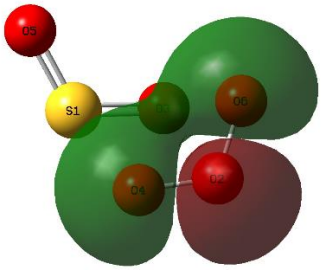

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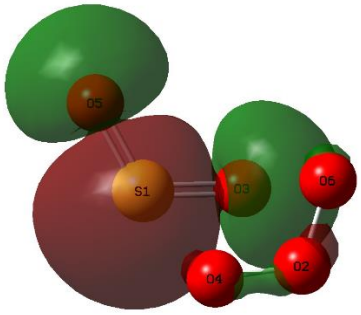

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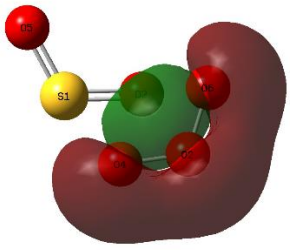

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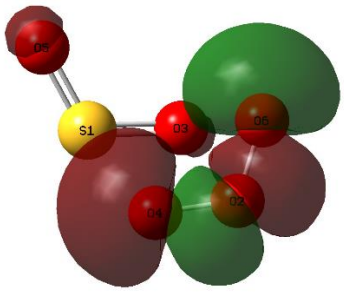

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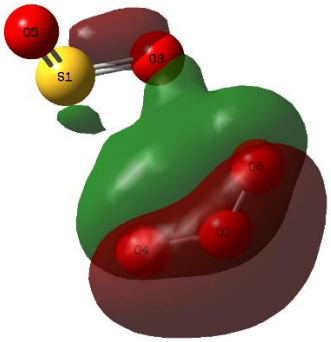

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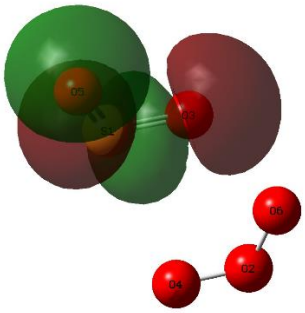

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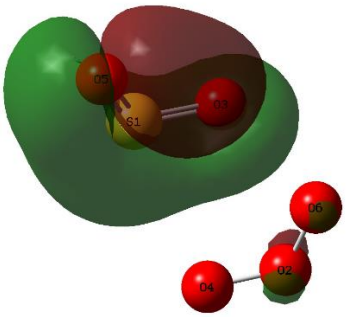

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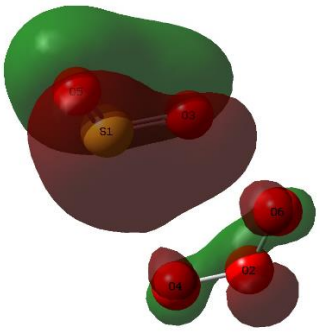

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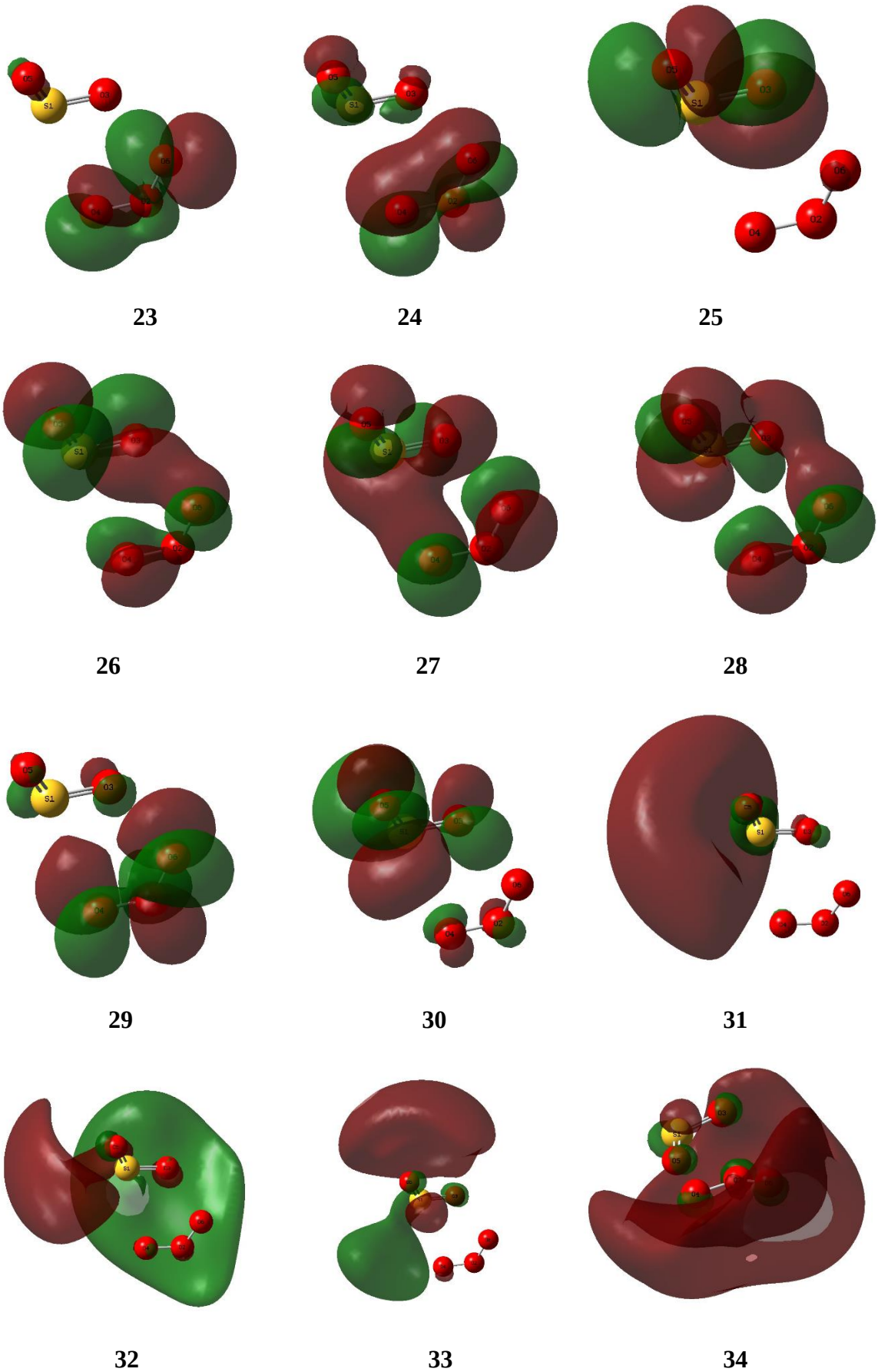
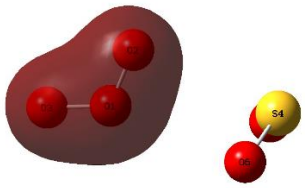


Figure S4. Valence molecular orbitals of sulphur dioxide-ozone complex 2a.



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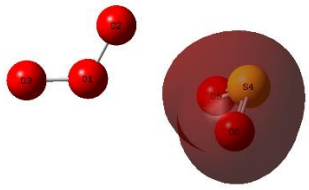

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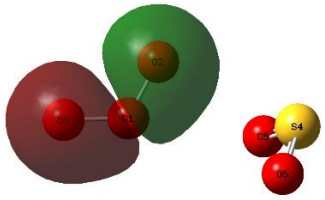

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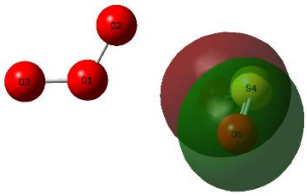

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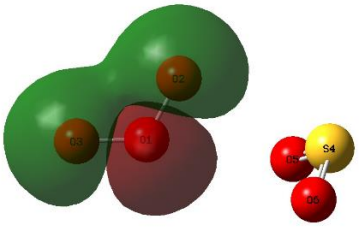

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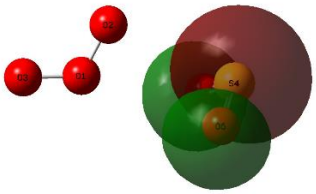

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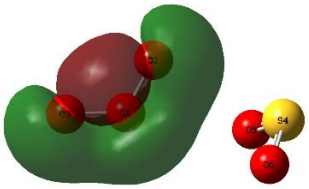

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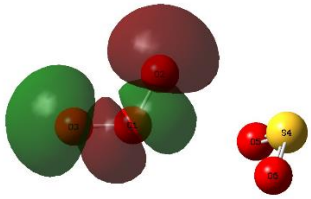

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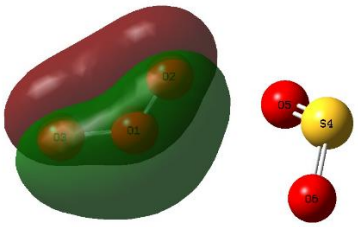

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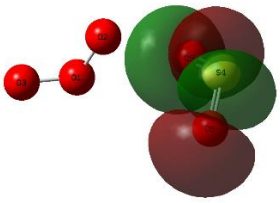

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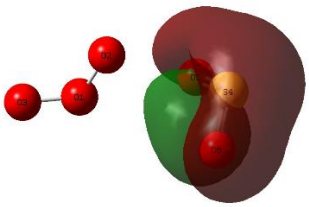

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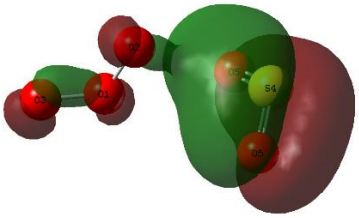

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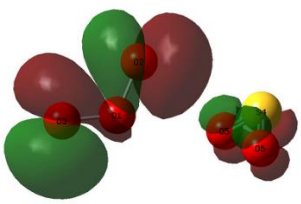

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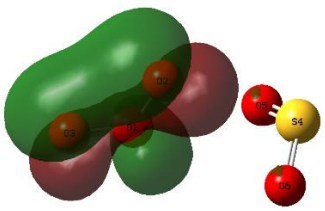

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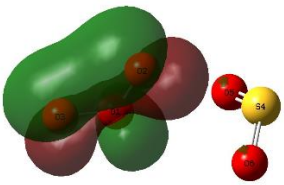

25 (a″)

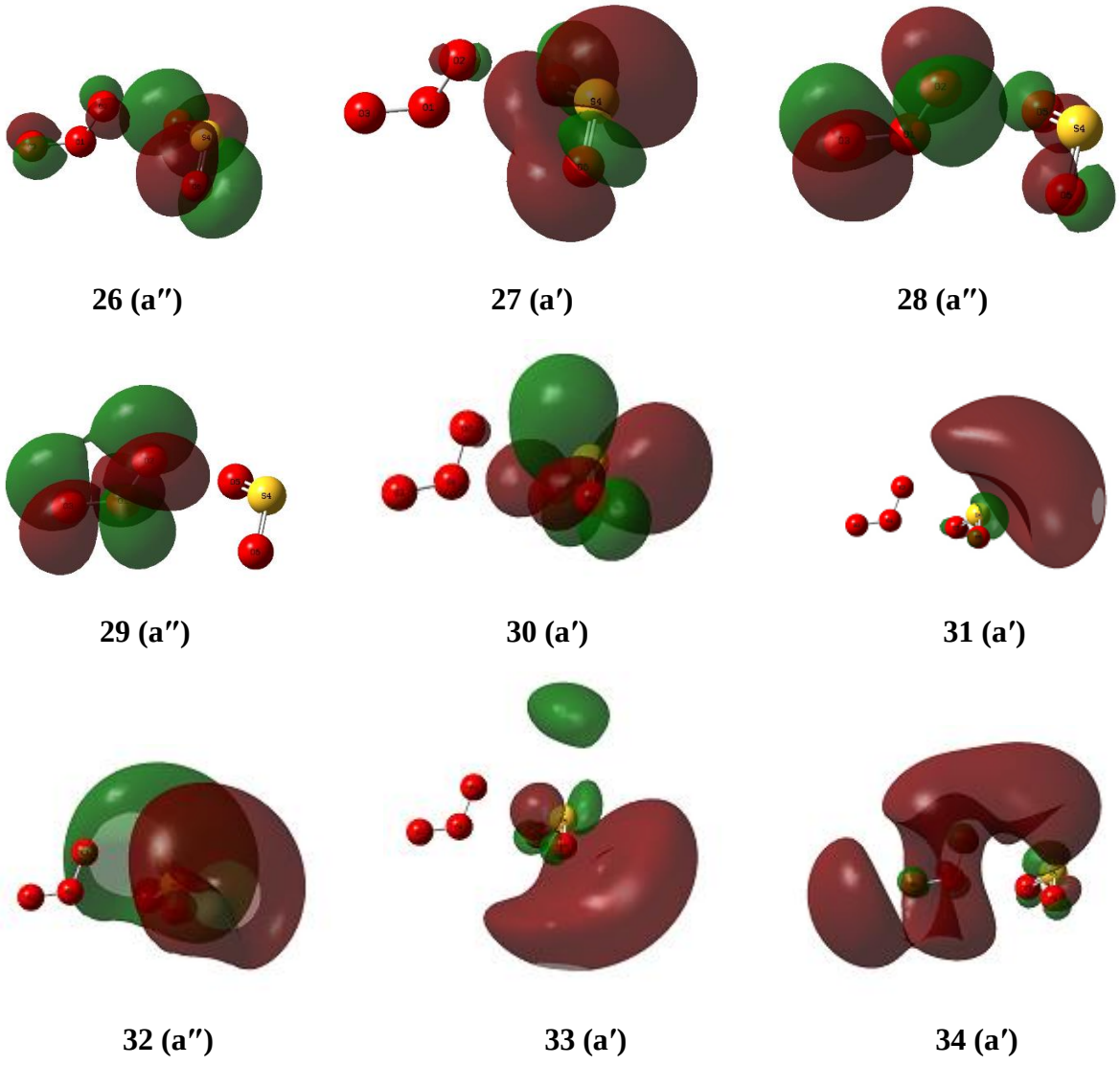

Figure S5. Valence molecular orbitals of sulphur dioxide-ozone complex 5b.