

***Ab Initio* studies of the excited state polarizabilities of Ozone and Thiozone**

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Abstract

We report an Ab Initio CIS(D) study of the electric dipole polarizability and first hyperpolarizability for the ground and five lowest electronic excited singlet states of ozone and thiozone. Optimized molecular geometries and the electric dipole moment are also given for each state. Ground state properties were also calculated using the B3LYP model. We give results for the less stable D_{3h} ring structures. Energy gaps between the C_{2v} and D_{3h} structures were also estimated by the HF, CISD, G3, B3LYP and G3B3 models. The D_{3h} structure is less polarizable than the C_{2v} ground state for both species. Our results reveal substantial differences between the electronic properties from excited state to excited state.

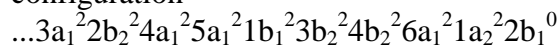
Keywords: Ab Initio, ozone, thiozone, excited states, electric dipole, dipole polarizability, dipole hyperpolarizability. Ring ozone, ring thiozone.

Introduction

Ozone is a species of great importance in environmental science and other related chemical fields. The ability of ozone molecules in the earth's atmosphere to absorb UV radiation is vital for all life on our planet.

Any respectable single-determinant HF (HF = Hartree Fock; all such quantum chemical acronyms have their usual meaning.) calculation gives the electronic

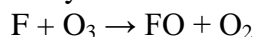
configuration



The b_1 and a_2 orbitals are the π orbitals. The LUMO ($2b_1$) has a negative orbital energy and it has long been argued that the ground state is therefore multireference in character and that electron correlation has to be taken into account [1]. HF calculations using primitive basis sets such as STO-3G even suggest that the ground state of ozone is a triplet spin state but this is simply a basis set error. Density functional methods have become the workhorse of modern computational quantum chemistry, and Murray, Handy and Amos [2] established that such methods can predict molecular properties reasonably accurately for systems such as ozone that have multireference character.

Naturally, higher levels of theory have to be used for more accurate predictions. The Multireference Coupled Cluster (MRCC) model has been widely used in recent years [3] to treat cases such as ozone where the single-reference method might fail. Definitive calculations have been reported for ozone by Vaval and Pal [4 and references therein]

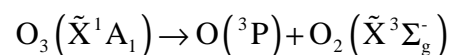
Ozone serves as a model system for experimentalists and theoreticians, and it regularly features in the literature. Thus for example, Hendrickx and Vinckier [5] report *Ab Initio* studies of the 1,3-cycloaddition of ozone to ethene, benzene and phenol. They used the B3LYP level of theory for the geometry optimizations and the CCSD(T) model for the energetics. Peiró-García and Nebot-Gil [6] report an *Ab Initio* study of the mechanism of the



reaction. They used MP2, QCISD, QCISD(T), CASSCF and CASPT2 with a variety of basis sets.

In the early days of chemistry, once it was established that ozone contained three oxygen atoms, it was automatically assumed that the structure was cyclic. In its electronic ground state, the molecule has C_{2v} symmetry with a bond length of 127.8 pm and bond angle 116.75° [7]. The electronic ground state is without question 1A_1 [8], and this structure has long been the subject of spectroscopic studies. For example, Mack and Muentner [9] report the Stark and Zeeman properties of ozone from molecular beam spectroscopy.

For many years, there has been speculation about the existence of a stable D_{3h} singlet structure, with energy higher than the C_{2v} one. There has also been speculation about the energy difference between the two structures. A key point in the argument is whether this energy difference is higher than the spectroscopic dissociation limit of the C_{2v} form of ozone



Once again, there have been a number of *Ab Initio* studies. For example, Lee's CCSD and CCSD(T) results give an O-O distance for the cyclic structure of 144.4 pm [10], and this author concludes that the energy difference is higher than the dissociation energy. Plass et. al. have recently [11] presented direct experimental evidence for the existence of the D_{3h} structure, which they found in three air-stable

surface reconstructions of MgO(1 1 1) annealed at a temperature greater than 1450 °C.

Thiozone in its C_{2v} structure has been observed experimentally, but the exact geometry is not known. Both the C_{2v} and D_{3h} ground state structures have been well studied by *Ab Initio* techniques. Any respectable HF calculation gives a ground state configuration

$$\dots 8a_1^2 6b_2^2 9a_1^2 10a_1^2 3b_1^2 7b_2^2 2a_2^2 11a_1^2 8b_2^2 4b_1^0 12a_1^0$$

for the C_{2v} structure. The LUMO has a negative orbital energy. Morin, Foti and Salahub's [12] DFT calculation suggests that the C_{2v} structure is more stable by some 59 kJ mol⁻¹. Flemmig, Wolczanski and Hoffmann [13] report an interesting attempt to 'trap' cyclic ozone and thiozone in transition metal complexes. They proposed molecular candidates first using the 18-electron rule as a guide and then optimizing their proposed structures with the B3LYP model. On this basis, they suggest the existence of complexes such as $[S_3W(NO)_3]^{3+}$ and $[O_3M(NO)_3]^{3+}$ (where M = Cr, Mo, W, Fe, Ru and Os).

A great deal of effort has therefore been expended on the electronic ground state and reactivity of these molecules and a great deal of data is available. By comparison, almost nothing is known experimentally about their excited state properties.

Studies of the ozone electronic absorption bands began with the 1880 work of Chappuis [14] who reported a broad band with a peak in the visible region (700 – 420 nm). The visible spectrum is useful for monitoring atmospheric ozone and it has been recorded many times [15].

The photochemistry of ozone in the ultraviolet region is thought to be important for stratospheric shielding and considerable progress has been made in understanding the Hartley strong absorption (300 – 214 nm) and also the Huggins band (354 – 300 nm). There is in addition a weak absorption in the near infrared, known as the Wulf band (1048 – 700 nm) [16]. It is interesting to note that present experimental knowledge about the excited states of ozone is still largely derived from these few prominent spectral bands. The Hartley and Huggins bands are thought to be combinations of the allowed transitions $\tilde{A}^1B_2 \leftarrow \tilde{X}^1A_1$ and $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ but there is still discussion in the literature about the origin of the Chappuis and Wulf bands. The difficulties in interpreting such seemingly simple data are to do with predissociation features, the diffuse character of the absorptions and the diverse nature of the possible dissociation products. On a similar line of argument, Minaev and Ågren claim that the Wulf band is a spin-forbidden singlet- triplet transition $^3A_2 \leftarrow \tilde{X}^1A_1$ rather than the symmetry-forbidden $^1A_2 \leftarrow \tilde{X}^1A_1$ transition previously assumed [17].

There have been a number of good *Ab Initio* calculations on the lower excited states of ozone, and mention should be made of the early double zeta GVB-CI work of Hay, Dunning and Goddard [18] and the more recent MCSCF calculations of Xantheas et. al. [19]. The definitive study in this field seems to be that of Palmer and Nelson [20] whose MCSCF-CI calculations give a number of valence and Rydberg, singlet and triplet excited states in the 1-12 eV energy range. These authors also give a careful comparison with VUV + EELS spectral data. We should also mention the

MRCC work of Vaval and Pal [4].

The electric dipole moment \mathbf{p}_e of a molecule is a quantity of fundamental importance in structural chemistry. This quantity is expected to have different values in different excited electronic states, due to possible changes in nuclear arrangements and redistribution of electron charge density. Even for a molecule as simple as ozone, very little experimental data is available. The experimental dipole moment for the electronic ground state (ie, the C_{2v} structure) is 0.532 D (1debye D = 3.336×10^{-30} C m) [21]

When a molecule is subject to an external electric field \mathbf{E} , the molecular charge density may rearrange and hence the dipole moment may also change [20]. This change can be described by the tensor equation (1)

$$\mathbf{p}_e = \mathbf{p}_{e,0} + \alpha : \mathbf{E} + \frac{1}{2} \beta : \mathbf{E}\mathbf{E} + \dots \quad (1)$$

Here α is a second rank tensor property called the dipole polarizability, and β is the first of an infinite series of dipole hyperpolarizabilities. $\mathbf{p}_{e,0}$, the permanent electric dipole moment, is the electric dipole moment in the absence of a field. Because the electric dipole moment may change when an external field is applied, the molecular potential energy U may also change according to equation (2)

$$U = U_0 - \mathbf{p}_e \cdot \mathbf{E} - \frac{1}{2} \alpha : \mathbf{E}\mathbf{E} - \frac{1}{6} \beta : \mathbf{E}\mathbf{E}\mathbf{E} - \dots \quad (2)$$

Hyperpolarizabilities are known to be small in magnitude, and their effect is minimal for weak electric fields, but they are quantities of fundamental importance in the new field of nonlinear optics [23,24].

There have been a number of Stark effect studies on the excited state polarizabilities (and related properties) of a number of small molecules such as SO_2 and NO_2 [25,26]. Such studies demonstrate very large changes in property from state to state. As far as we are aware, there have been no experimental studies to date on ozone or thiozone. In a recent short note, we reported the electric dipole moments, polarizabilities and hyperpolarizabilities of SO_2 in a number of electronic excited states [27] The aim of this paper is to compare corresponding results for ozone and thiozone. All calculations were done using Gaussian 03W [28], with standard basis sets, integration points, cut-offs etc. Polarizabilities were calculated numerically, by the standard Finite Field technique.

Ground State Properties

As discussed above, HF calculations of the ground state properties of O_3 and S_3 (and presumably SO_2) are likely to be in error because of the multireference nature of the state. DFT models have been shown to be acceptable. Polarizability calculations are notoriously sensitive to the choice of atomic orbital basis set, as illustrated in Table 1 where various quantities are calculated for the C_{2v} electronic ground state. Geometries were optimized in every case. The atom charge q_O refers to the central O atom and it was calculated according to the standard Mulliken population analysis scheme [29].

Molecular principal axes will be referred to in later sections and they are shown in

Figure 1. The polarizability anisotropy $\Delta\alpha$ is defined here as $\frac{1}{2}(\alpha_{aa} + \alpha_{bb}) - \alpha_{cc}$.

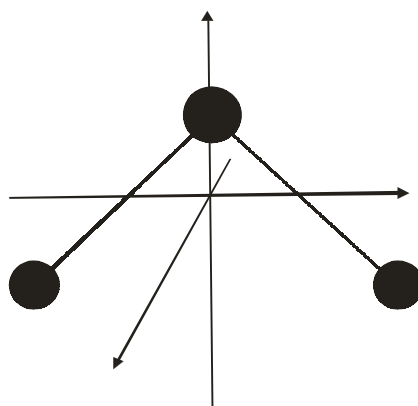


Figure 1: Principal axes

Table 1: B3LYP properties of the C_{2v} ground state of ozone.

Basis set	ϵ/E_h	p_e/D	q_o	$\langle\alpha\rangle/au.$	$\Delta\alpha/au$	R_{OO}/pm	$OOO/^\circ$
6-311G(1d)	-225.470791	0.6180	0.2028	12.74	11.28	125.79	118.20
6-311G(3d)	-225.483208	0.5766	0.2335	15.30	9.39	125.46	117.95
6-311++G(3d)	-225.491917	0.6547	0.3407	17.70	10.20	125.36	118.22
cc-pvqz	-225.519577	0.6436	0.2617	15.93	10.89	125.34	118.24
aug-cc-pvqz	-225.522271	0.6615	0.2952	18.82	10.60	125.25	118.34

The atomic unit of energy $E_h = 4.3598 \times 10^{-18} \text{ J}$ ($2625.5 \text{ kJ mol}^{-1}$), the atomic unit of polarizability $e^2 a_0^2 E_h^{-1} = 1.6488 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ and the atomic unit of β , $e^3 a_0^3 E_h^{-2} = 3.2064 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$. Here, a_0 is the first bohr radius 52.918 pm.

There are many different choices for the correlation and the exchange functionals in DFT, but the B3LYP combination seems to be the most widely used at present [30]. The main points revealed by Table 1 are that

- all basis sets give a bond angle of about 118° (compared to the experimental value of 116.75°)
- all basis sets give a short O-O bond (experimental 127.8 pm)
- Mulliken (and most other) population analysis indices are almost meaningless in isolation. They should only be used across a series of molecules at a constant level of theory.
- the mean value $\langle\alpha\rangle$ increases with the degree of sophistication of the model used, but the anisotropy is reasonably constant.
- diffuse functions (++ / aug) are essential for polarizability calculations. They

are also thought to be essential for studies of anions and excited states [30]. For the remaining calculations in this paper, we have standardized on the 6-311++G(3d,2p) basis set.

Table 2 shows some ground state calculations for the C_{2v} and D_{3h} structures of ozone and thiozone. The D_{3h} structures have bond lengths of 143.00 pm and 211.01 pm, whilst S the C_{2v}

Table 2: Some ground state properties. B3LYP unless otherwise noted

	O ₃ (C _{2v})	O ₃ (D _{3h})	S ₃ (C _{2v})	S ₃ (D _{3h})
ϵ (HF) /E _h	-224.344756	-224.319798	-1192.573380	-1192.578157
ϵ /E _h	-225.491917	-225.439754	-1194.646743	-1194.628734
$\langle\alpha\rangle$ /au.	18.03	15.40	67.49	57.70
$\Delta\alpha$ /au	10.70	6.63	38.79	17.76
β_{bcc} /au	-2.14	0	-15.47	0
β_{aab} /au	5.26	-8.42	5.94	-51.74
β_{bbb} /au	-12.06	7.66	-48.88	51.54

The energy differences between the C_{2v} and D_{3h} forms of ozone are 65.53 and 136.96 kJ mol⁻¹ at the HF and B3LYP levels. The B3LYP value is entirely consistent with Lee's CCSD/CCSD(T) estimate of 120.1 kJ mol⁻¹, and demonstrates that cyclic ozone lies above the dissociation energy of the C_{2v} form. Corresponding values for thiozone are -12.54 and 47.28 kJ mol⁻¹. The poor showing of the HF calculation is usually explained as follows. The ground state wavefunctions are poorly represented at single determinant HF level, and so their energies are poorer (higher) than would otherwise be the case. The cyclic structures by comparison are better represented, so giving too low an energy difference.

We give a number of estimates of the energy differences in Table 3, using the HF, CISD, G3, B3LYP and G3B3 models. The G3 and G3B3 results are expected to be the most accurate, and they are remarkably similar.

Table 3: Various energies

Model	O ₃ (C _{2v})	Diff / kJ mol ⁻¹	S ₃ (C _{2v})	Diff / kJ mol ⁻¹
HF	-224.344756	65.53	-1192.573380	-12.54
CISD	-224.938123	104.45	-1192.976772	13.92
G3	-225.315311	135.09	-1194.136136	27.63
B3LYP	-225.491917	136.96	-1194.646743	47.28
G3B3	-225.320209	134.19	-1194.139394	28.22

The CISD model gives a wavefunction

$$\Psi^{\text{CISD}} = \Psi^{\text{HF}} + \sum_{ij} T_{ia} \Psi(i \rightarrow a) + \sum_{ijab} T_{ijab} \Psi(ij \rightarrow ab)$$

where $i \rightarrow a$ represents a single excitation from HF orbital ψ_i to virtual orbital ψ_a and $ij \rightarrow ab$ represents a double excitation from HF orbitals ψ_i, ψ_j to virtual orbitals ψ_a, ψ_b . It is often argued that the normalizing coefficient N gives a measure of the correlation correction to the HF wavefunction (and hence the multireference nature of the state). Table 4 shows our values for N .

Table 4: CISD normalizing coefficient

O ₃ (C _{2v})	O ₃ (D _{3h})	SO ₂	S ₃ (C _{2v})	S ₃ (D _{3h})
1.0684	1.0656	1.0675	1.0887	1.0847

These values suggest that all the species considered should be perhaps treated on the same footing for electron correlation, even SO₂.

The C_{2v} Structure Excited States

In the pioneer days of the mid 1960's, the best available model for treating the electronic structure of conjugated molecules was the so-called PPP π electron treatment [30]. In order to study the electronic spectrum of a molecule like benzene, one considered a small number of singly excited states formed by excitations amongst the π electron molecular orbitals and solved the relevant Configuration Interaction (CI) eigenvalue problem, within the PPP integral approximation methodology.

The CIS model [31] can be envisaged as the logical extension of this procedure. In CIS, we consider every possible single excitation that can be formed by excitation from the electronic ground state of (doubly) occupied orbitals to the virtual orbitals. Inner shells are usually frozen for this procedure. Excited state wavefunctions for the lowest excited states can then be found by appropriate numerical procedures for finding a few lowest eigenvalues and eigenvectors of such very large matrices. The problem is simplified a little by Brillouin's theorem [32] which states that singly excited states do not interact with the ground state under such circumstances. Again, in the early days, Brillouin's theorem was often quoted as a 'justification' for the reliability of one-electron properties such as the electric dipole moment, calculated from HF wavefunctions. The CIS level of accuracy is usually thought of as an 'adequate zero-order treatment for many of the excited states of molecules', and CIS calculations give a rough and ready description of molecular excited states. They are not to be thought of as giving definitive excitation energies.

The CIS(D) model [33] was proposed in 1994 as a correction to CIS. It is a perturbation treatment based on CIS and the idea is to introduce the effect of double substitutions into the CIS wavefunction. One performs a CIS calculation and then adds a CIS(D) correction to the excitation energies. Both the CIS and the CIS(D) procedures are computationally friendly, for CIS scales as the fourth power of

molecular size whilst CIS(D) scales as the fifth power. These powers are theoretical upper limits, and do not take into account integral cut-offs and the like.

Excitation energies

Table 5 records various data for the first five singlet excited states of the C_{2v} structure. The oscillator strengths refer to transitions between each state and the ground state. The CIS(D) procedure makes significant changes to the absolute excitation energies.

Table 5: Excited state properties for C_{2v} ozone

State	Contribution	Oscillator strength	CIS energy / eV	CIS(D) energy / eV	Palmer and Nelson / eV
1^1B_1	$6a_1 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0	2.694	2.983	2.152
1^1A_2	$4b_2 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0	3.542	3.142	2.268
1^1B_2	$1a_2 \rightarrow 2b_1 (\pi \rightarrow \pi^*)$	0.3146	6.1769	6.513	4.846
2^1A_2	$3b_2 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0	10.618	11.068	
2^1B_1	$5a_1 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0.0029	11.133	11.006	

Major one-electron excitations are shown in the second column. We also compare the CIS(D) excitation energies with those given by Palmer and Nelson [20]. The poor quantitative agreement with more rigorous calculations is common in CIS(D) studies; we should also note that the CIS(D) model uses the ground state HF geometry for the excited states and the CIS(D) energies are therefore vertical excitation energies. Excited state geometries of small molecules are often quite different to those in the ground state.

Table 6: Excited state properties for C_{2v} thiozone

State	Contribution	Oscillator strength	CIS energy / eV	CIS(D) energy / eV
1^1B_1	$11a_1 \rightarrow 4b_1 (\sigma \rightarrow \pi^*)$	0	2.064	2.076
1^1A_2	$2a_2 \rightarrow 2b_1 (\pi \rightarrow \pi^*)$	0	2.142	1.982
1^1B_2	$8b_2 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0.2463	3.604	3.721
2^1A_2	$8b_2 \rightarrow 2b_1 (\sigma \rightarrow \pi^*)$	0	5.905	5.873
2^1B_2	$2a_2 \rightarrow 2b_1 (\pi \rightarrow \pi^*)$	0.0217	6.187	5.680

In order to understand the experimental ozone electronic spectrum, it is necessary to consider triplet states for the lowest three experimental excited states are 3B_2 , 3B_1 and 3A_2 . The CIS(D) procedure does indeed give these three states as the lowest states, but in an incorrect order. We also experienced insuperable convergence problems in the polarizability calculations and so did not pursue the triplet states further.

Corresponding results for thiozone are shown in Table 6. Analysis of the excited state wavefunctions is also given. We are not aware of any experimental results to afford comparison with the excitation energies.

Geometries etc.

Table 7 records various molecular parameters for the first five CIS singlet states of ozone. The 'O' symbol in isolation refers to the central oxygen atom.

Table 7: Various molecular parameters for ground (X) and excited C_{2v} ozone (HF and CIS)

State	p_e/D	q_o	R_{OO} / pm	$OOO / ^\circ$
X	.8311	.5110	119.31	119.20
1^1B_1	.4308	.4460	122.84	131.62
1^1A_2	.7239	.2402	125.36	99.86
1^1B_2	.7149	.3279	128.15	109.67
2^1A_2	.0782	.1074	142.64	148.35
2^1B_1	.7151	.3280	128.14	109.68

We note the large changes in all the properties reported, and predict that the 2^1A_2 state will have a negligible dipole moment. Similar quantities are recorded for thiozone in Table 7.

Table 7: Various molecular parameters for ground (X) and excited C_{2v} thiozone (HF and CIS)

State	p_e/D	q_o	R_{OO} / pm	$OOO / ^\circ$
X	0.5619	0.2909	188.58	117.8
1^1B_1	0.1007	0.2281	193.30	126.0
1^1A_2	0.8063	0.1229	195.48	94.9
1^1B_2	0.5575	0.2122	197.50	109.1
2^1A_2	0.0173	0.1576	207.76	141.9
2^1B_2	-0.0100	-0.3079	196.70	173.5

Once again the prediction is that the 2^1A_2 state will have a negligible dipole moment, and in addition we find that the polarity is reversed for the 2^1B_2 state.

We noted similar behaviour for SO_2 [27], and were able to demonstrate a good accord with experiment. We are not aware of any excited state values for the two molecules studied here.

Polarizability and hyperpolarizability

Table 8 records various ozone polarizability values for the first five excited states, together with the HF ground state values. All polarizabilities were calculated numerically using the finite field approach [28].

Table 8: Non-zero polarizability and hyperpolarizability data (HF and CIS) for ozone

State	$\langle\alpha\rangle/\text{au}$	$\Delta\alpha/\text{au}$	$\beta_{\text{bcc}}/\text{au}$	$\beta_{\text{aab}}/\text{au}$	$\beta_{\text{bbb}}/\text{au}$
X	17.86	11.68	-0.74	23.85	-8.09
1^1B_1	23.41	19.97	-1.18	60.20	-4.71
1^1A_2	24.58	21.75	-1.91	35.78	-4.11
1^1B_2	18.74	10.47	-14.40	71.13	-5.65
2^1A_2	25.89	20.99	-21.05	109.08	-6.40
2^1B_1	18.73	10.46	-14.44	71.01	-5.75

Table 9 records various thiozone polarizability values for the first five excited states, together with the HF ground state values.

Table 9: Non-zero polarizability and hyperpolarizability data (HF and CIS) for thiozone.

State	$\langle\alpha\rangle/\text{au}$	$\Delta\alpha/\text{au}$	$\beta_{\text{bcc}}/\text{au}$	$\beta_{\text{aab}}/\text{au}$	$\beta_{\text{bbb}}/\text{au}$
X	67.36	39.79	-6.99	89.86	-9.05
1^1B_1	103.55	91.68	-12.39	-276.8	0.00
1^1A_2	75.46	49.35	-19.92	160.1	-12.42
1^1B_2	66.67	32.47	-79.44	145.2	-18.50
2^1A_2	83.65	63.19	-27.40	98.33	-9.22
2^1B_2	79.23	54.61	0	22.03	124.00

Although not shown in the Tables, α_{cc} is constant to within 10% across the ground and excited states studied for both molecules (10.95 and 42.53 au). We noted the same behaviour for SO_2 [27]. In the case of ozone, the 1^1B_1 , 1^1A_2 and 2^1A_2 states demonstrate an appreciable enhancement in the mean polarizability. For thiozone, all the excited states studied with the exception of 1^1B_2 show considerable enhancement in $\langle\alpha\rangle$.

Conclusions

- The C_{2v} structure of ozone is more stable than the D_{3h} structure by 135 kJ mol^{-1} (on the basis of G3 and G3B3 calculations).
- The C_{2v} structure of thiozone is more stable than the D_{3h} structure by 28 kJ mol^{-1} (on the basis of G3 and G3B3 calculations).
- CIS(D) excitation energies for the two molecules studied give modest agreement with experiment and more sophisticated quantum models.
- The 2^1A_2 states of ozone and thiozone are predicted to have very small dipole

moments. The 2^1B_2 state of thiozone is predicted to have a dipole with the opposite polarity as the ground state.

- The D_{3h} structures are less polarizable than the corresponding C_{2v} structures.
- α_{cc} is roughly constant for each C_{2v} structure across the electronic states studied.
- There are substantial differences in $\langle\alpha\rangle$ and $\Delta\alpha$ between electronic states.
- There are substantial differences in hyperpolarizability tensor component between electronic states.

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