

Supporting Information:

Nonorthogonal Active Space Decomposition of Wavefunctions with Multiple Correlation Mechanisms

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1 Molecular geometries

1.1 Ozone [O₃]

Table S1: Ozone cartesian coordinates

O	0.8822749	0.6839687	0.0000000
O	0.1946029	-0.3909559	0.0000000
O	-1.0768778	-0.2930128	0.0000000

1.2 Nickel-actelyene [NiC₂H₂]

Table S2: Ni-actylene cartesian coordinates

Ni	0.0000000	0.0000000	-1.5826858
C	0.6420065	0.0000000	0.1340163
H	-1.5920883	0.0000000	0.6573266
H	1.5920883	0.0000000	0.6573266
C	-0.6420065	0.0000000	0.1340163

1.3 Bis (μ -oxo) dicopper ammonia [(Cu(NH)₃)₂O₂]

Table S3: **Bis** (μ -oxo) dicopper ammonia cartesian coordinates

Cu	0.000000	1.400000	0.000000
Cu	0.000000	-1.400000	0.000000
O	0.000000	0.000000	1.150000
O	0.000000	0.000000	-1.150000
N	0.000000	3.400000	0.000000
N	0.000000	-3.400000	0.000000
H	-0.939693	3.742020	0.000000
H	0.939693	-3.742020	0.000000
H	0.469846	3.742020	0.813798
H	-0.469846	-3.742020	-0.813798
H	0.469846	3.742020	-0.813798
H	-0.469846	-3.742020	0.813798

1.4 Per (μ -oxo) dicopper ammonia [(Cu(NH)₃)₂O₂]

Table S4: **Per** (μ -oxo) dicopper ammonia cartesian coordinates

Cu	0.000000	1.800000	0.000000
Cu	0.000000	-1.800000	0.000000
O	0.000000	0.000000	0.700000
O	0.000000	0.000000	-0.700000
N	0.000000	3.800000	0.000000
N	0.000000	-3.800000	0.000000
H	-0.939693	4.142020	0.000000
H	0.939693	-4.142020	0.000000
H	0.469846	4.142020	0.813798
H	-0.469846	-4.142020	-0.813798
H	0.469846	4.142020	-0.813798
H	-0.469846	-4.142020	0.813798

2 Total energies and occupation numbers

Table S5: Ozone total energies and occupation numbers for NO-ASD, average density UNO-CAS(CI and SCF), CASSCF, and DMRG. DMRG results are directly taken from S. Keller *et al.* *J. Chem. Phys.* **2015**, 142, 244104. All calculations use the cc-PVTZ basis set.

Methods	UHF 1	UHF 2	NO-ASD 2e,2o x 2e,2o	NO-ASD 4e,4o x 2e,2o	Average Density of UHF 1 and UHF 2	UNO-CASCI 6e,4o Average	UNO-CASSCF 6e,4o Average	UNO-CASCI 8e,7o Average	UNO-CASSCF 8e,7o Average	CASSCF 12e,9o	DMRG 18e,32o
Energy (Har.)	-224.3412647	-224.4261939	-224.4339198	-224.4478995		-224.4317326	-224.4358661	-224.5104361	-224.5553859	-224.5688159	-224.820227
Orb. 4	1.99999	1.99998	2.00000	2.00000	1.99963	2.00000	2.00000	2.00000	2.00000	2.00000	1.99070
Orb. 5	1.99990	1.99979	2.00000	2.00000	1.99939	2.00000	2.00000	2.00000	2.00000	2.00000	1.98215
Orb. 6	1.99978	1.99970	2.00000	1.99998	1.99890	2.00000	2.00000	2.00000	2.00000	2.00000	1.98673
Orb. 7	1.99973	1.99935	1.99999	1.99995	1.99887	2.00000	2.00000	2.00000	2.00000	1.99208	1.97144
Orb. 8	1.99897	1.99901	1.99994	1.99973	1.99856	2.00000	2.00000	2.00000	2.00000	1.99001	1.97208
Orb. 9	1.99887	1.99787	1.99980	1.99944	1.99683	2.00000	2.00000	1.96751	1.96573	1.96341	1.94598
Orb. 10	1.99800	1.99783	1.99975	1.99925	1.97943	1.99813	1.99886	1.96653	1.95692	1.95656	1.94717
Orb. 11	1.99000	1.99727	1.99734	1.98427	1.89314	1.98491	1.99286	1.96374	1.94981	1.94789	1.94114
Orb. 12	1.78975	1.28871	1.59032	1.63147	1.63809	1.66143	1.62528	1.74171	1.77146	1.78649	1.79002
Orb. 13	0.21025	0.71129	0.41243	0.37169	0.47757	0.35553	0.38300	0.29077	0.26150	0.25096	0.24165
Orb. 14	0.01000	0.00273	0.00020	0.01311	0.00812	0.00000	0.00000	0.04266	0.05334	0.06164	0.06281
Orb. 15	0.00400	0.00217	0.00016	0.00064	0.00493	0.00000	0.00000	0.02709	0.04125	0.05096	0.05394
Orb. 16	0.00113	0.00213	0.00003	0.00024	0.00289	0.00000	0.00000	0.00000	0.00000	0.00000	0.01589
Orb. 17	0.00103	0.00099	0.00002	0.00011	0.00111	0.00000	0.00000	0.00000	0.00000	0.00000	0.01052

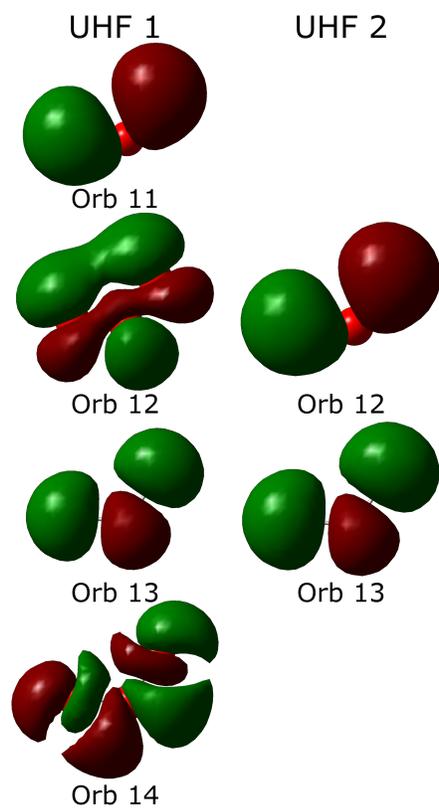


Figure S1: Pictorial Representation of the Natural Orbitals of Ozone's two UHF solutions

Table S6: Nickel-Actelyene total energies and occupation numbers for NO-ASD, average density UNO-CAS(CI and SCF), CASSCF, and DMRG. DMRG results are directly taken from S. Keller *et al. J. Chem. Phys.* **2015**, 142, 244104. All calculations use the cc-PVTZ basis set.

Methods	UHF 1	UHF 2	NO-ASD 4e,4o x 2e,2o	Average Density of UHF 1 and UHF 2	UNO-CASCI 4e,4o Average	UNO-CASSCF 4e,4o Average	UNO-CASCI 12e,14o Average	CASSCF 12e,14o	DMRG 18e,33o
Energy (Har.)	-1583.623755	-1583.625392	-1583.695693		-1583.657517	-1583.661859	-1583.803501	-1583.901295	-1583.957662
Orb. 15	1.99970	1.99970	1.99953	1.99928	2.00000	2.00000	2.00000	2.00000	1.97657
Orb. 16	1.99956	1.99970	1.99952	1.99836	2.00000	2.00000	1.97163	1.98026	1.97498
Orb. 17	1.99935	1.99949	1.99739	1.99692	2.00000	2.00000	1.96700	1.98017	1.96307
Orb. 18	1.99900	1.99926	1.99545	1.99624	2.00000	2.00000	1.96374	1.97127	1.95777
Orb. 19	1.99817	1.99658	1.99433	1.99325	2.00000	2.00000	1.95968	1.94729	1.95607
Orb. 20	1.99176	1.63678	1.98580	1.57026	1.79357	1.90443	1.91949	1.93524	1.92576
Orb. 21	1.51138	1.16270	1.80952	1.52607	1.55755	1.83540	1.84140	1.85911	1.88574
Orb. 22	0.48862	0.83730	0.13558	0.47151	0.44146	0.16661	0.17079	0.13946	0.14113
Orb. 23	0.00824	0.36322	0.06359	0.42896	0.20742	0.09356	0.06322	0.07438	0.07644
Orb. 24	0.00183	0.00342	0.00567	0.00506	0.00000	0.00000	0.03815	0.05094	0.03957
Orb. 25	0.00100	0.00074	0.00455	0.00371	0.00000	0.00000	0.03417	0.01862	0.02396
Orb. 26	0.00065	0.00051	0.00399	0.00369	0.00000	0.00000	0.03336	0.01840	0.02091
Orb. 27	0.00044	0.00030	0.00235	0.00303	0.00000	0.00000	0.02037	0.01659	0.01915
Orb. 28	0.00030	0.00030	0.00091	0.00143	0.00000	0.00000	0.01396	0.00421	0.01586
Orb. 29	0.00021	0.00025	0.00055	0.00115	0.00000	0.00000	0.00305	0.00407	0.00674

Table S7: Energy of NO-ASD(4e,4o;2e,2o) compared to averaged density UNO-CASCI with active spaces of increasing size.

Method	Energy
NO-ASD	-1583.695693
4e,4o x 2e,2o	
UNO-CASCI	
4e,4o	-1583.657517
Average	
UNO-CASCI	
6e,6o	-1583.685784
Average	
UNO-CASCI	
8e,8o	-1583.693130
Average	
UNO-CASCI	
10e,10o	-1583.721180
Average	
UNO-CASCI	
12e,12o	-1583.769435
Average	

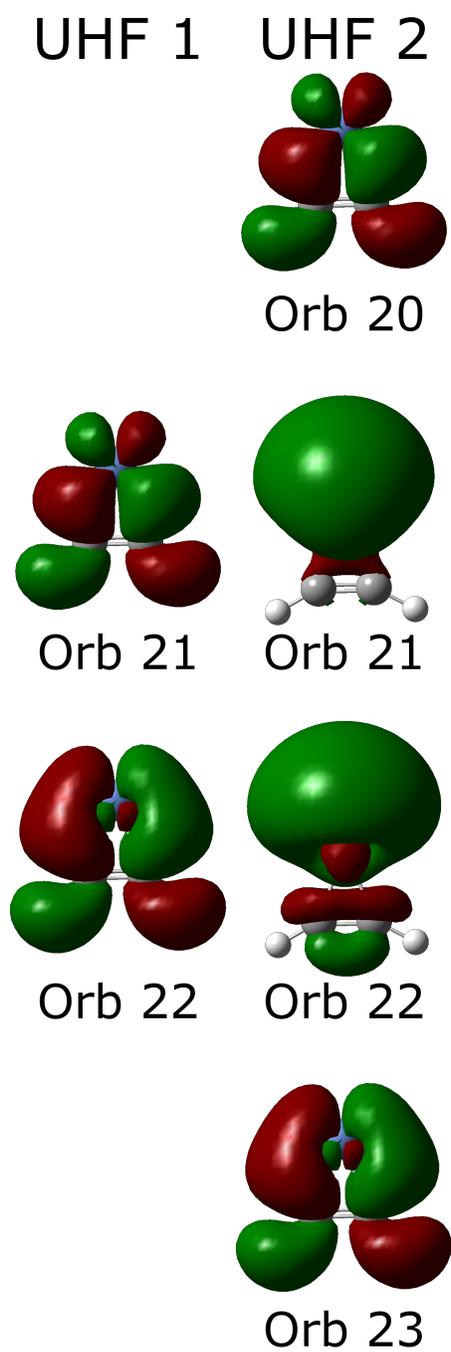


Figure S2: Pictorial Representation of the Natural Orbitals of Ni-Acetylene's two UHF solutions

Table S8: **Bis** $\mu - oxx$ dicopper ammonia total energies and occupation numbers for NO-ASD and average density UNO-CAS(CI and SCF). All calculations use the cc-PVDZ basis set.

Methods	UHF 1	UHF 2	NO-ASD 4e,4o x 4e,4o	Average Density of UHF 1 and UHF 2	UNO-CASCI 6e,5o Average	UNO-CASSCF 6e,5o Average	UNO-CASCI 8e,7o Average	UNO-CASSCF 8e,7o Average
Energy (Har.)	-3539.561699	-3539.441595	-3539.549569		-3539.538011	-3539.558614	-3539.552426	-3539.584802
Orb. 38	1.99973	1.99986	2.00000	1.99886	2.00000	2.00000	2.00000	2.00000
Orb. 39	1.99971	1.99986	2.00000	1.99662	2.00000	2.00000	2.00000	2.00000
Orb. 40	1.99947	1.99986	2.00000	1.99645	2.00000	2.00000	2.00000	2.00000
Orb. 41	1.99937	1.99948	1.99997	1.99373	2.00000	2.00000	2.00000	2.00000
Orb. 42	1.99864	1.99924	1.99994	1.99135	2.00000	2.00000	2.00000	2.00000
Orb. 43	1.99844	1.98857	1.99990	1.84150	2.00000	2.00000	1.98506	1.93111
Orb. 44	1.99832	1.98481	1.99842	1.77254	1.78410	1.99875	1.79674	1.83180
Orb. 45	1.09615	1.70607	1.52755	1.50557	1.04394	1.41574	1.03621	1.38719
Orb. 46	1.09522	1.17177	1.21582	1.23111	1.34492	1.35443	1.34672	1.68843
Orb. 47	0.90478	0.82823	0.81490	0.91937	0.95303	0.66487	0.97621	0.69147
Orb. 48	0.90385	0.29393	0.44283	0.73101	0.87400	0.56622	0.85260	0.45497
Orb. 49	0.00168	0.01519	0.00006	0.00998	0.00000	0.00000	0.00647	0.01503
Orb. 50	0.00156	0.01143	0.00001	0.00822	0.00000	0.00000	0.00000	0.00000
Orb. 51	0.00136	0.00076	0.00001	0.00102	0.00000	0.00000	0.00000	0.00000
Orb. 52	0.00063	0.00052	0.00000	0.00089	0.00000	0.00000	0.00000	0.00000

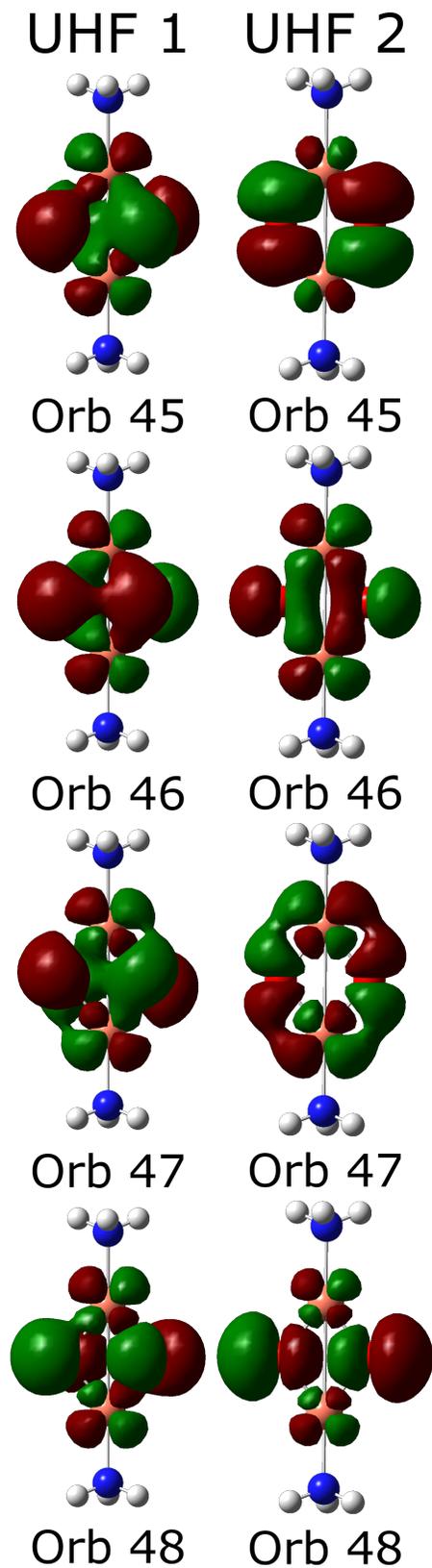


Figure S3: Pictorial Representation of the Natural Orbitals of **Bis** μ - *oxo* dicopper ammonia's two UHF solutions

Table S9: **Per** $\mu - oxo$ dicopper ammonia total energies and occupation numbers for NO-ASD and average density UNO-CAS(CI and SCF). All calculations use the cc-PVDZ basis set.

Methods	UHF 1	UHF 2	NO-ASD 4e,4o x 4e,4o	Average Density of UHF 1 and UHF 2	UNO-CASCI 6e,5o Average	UNO-CASSCF 6e,5o Average	UNO-CASCI 8e,7o Average	UNO-CASSCF 8e,7o Average
Energy (Har.)	-3539.536109	-3539.435828	-3539.544548		-3539.537789	-3539.573556	-3539.538169	-3539.597849
Orb. 38	1.99990	1.99978	2.00000	1.99969	2.00000	2.00000	2.00000	2.00000
Orb. 39	1.99985	1.99957	2.00000	1.99918	2.00000	2.00000	2.00000	2.00000
Orb. 40	1.99985	1.99947	2.00000	1.99907	2.00000	2.00000	2.00000	2.00000
Orb. 41	1.99985	1.99880	1.99999	1.99733	2.00000	2.00000	2.00000	2.00000
Orb. 42	1.99985	1.99846	1.99997	1.99673	2.00000	2.00000	2.00000	2.00000
Orb. 43	1.99976	1.99812	1.99979	1.99652	2.00000	2.00000	1.99976	1.99995
Orb. 44	1.99975	1.99680	1.99221	1.98454	1.99363	1.99722	1.99355	1.97830
Orb. 45	1.99780	1.67970	1.97638	1.83637	1.97414	1.93995	1.97427	1.94307
Orb. 46	1.07825	1.08270	1.19583	1.08489	1.15786	1.19407	1.15965	1.17716
Orb. 47	0.92175	0.91730	0.80866	0.92619	0.84394	0.80847	0.84204	0.82448
Orb. 48	0.00220	0.32030	0.02423	0.17377	0.03043	0.06029	0.03053	0.05770
Orb. 49	0.00025	0.00320	0.00287	0.00209	0.00000	0.00000	0.00020	0.01934
Orb. 50	0.00024	0.00188	0.00001	0.00118	0.00000	0.00000	0.00000	0.00000
Orb. 51	0.00015	0.00154	0.00000	0.00089	0.00000	0.00000	0.00000	0.00000
Orb. 52	0.00015	0.00120	0.00000	0.00062	0.00000	0.00000	0.00000	0.00000

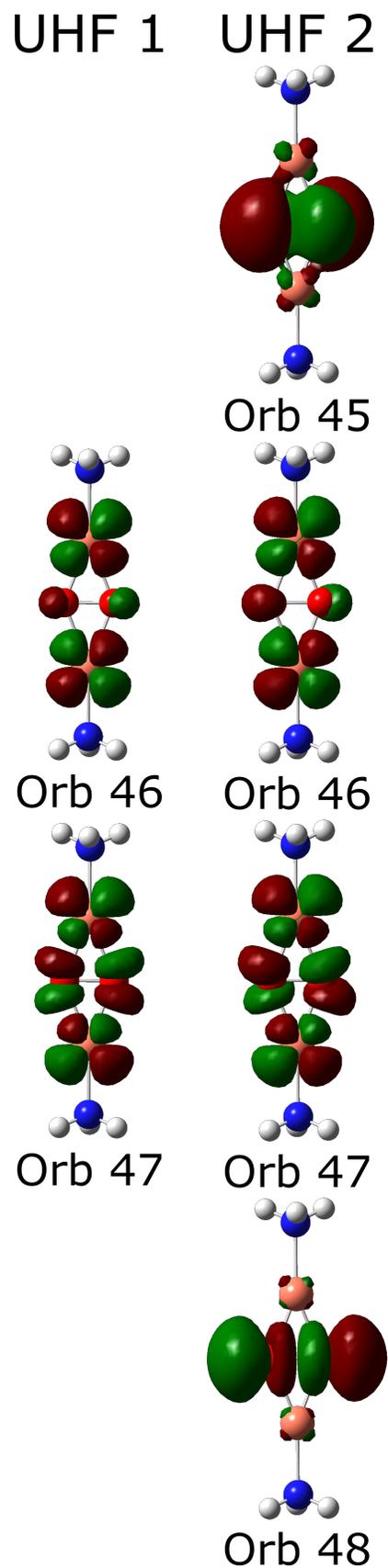


Figure S4: Pictorial Representation of the Natural Orbitals of **Per** μ -*oxo* dicopper ammonia's two UHF solutions

3 Effect of Natural Orbital Occupation Number Thresholds on Energy Discontinuities

To test the hypothesis that NO-ASD is less affected by the exact choice of threshold than averaged density UNO methods, we examined the SCF density and average density natural orbitals along the O-O-O bending coordinate for the two SCF determinants identified in this study (fig. S5). Using the 0.02-1.98 threshold, natural orbitals 12 and 13 are always included in the active space regardless of whether the density of SCF 1, SCF 2, or the averaged density is used. Natural orbital 11 is always outside the active using SCF 1 or SCF 2 densities, but inside the active space using the averaged density. Natural orbital 10 is always outside the active space using SCF 1 or SCF 2 density, but switches from being outside the active space at 105 degrees, to being inside the active space at 110 degrees. The average density show a much greater variation in occupation number of close-to-threshold natural orbitals 10 and 11 than the individual SCF densities, supporting the hypothesis that NO-ASD will suffer less from the effect of occupation number threshold crossing discontinuities.

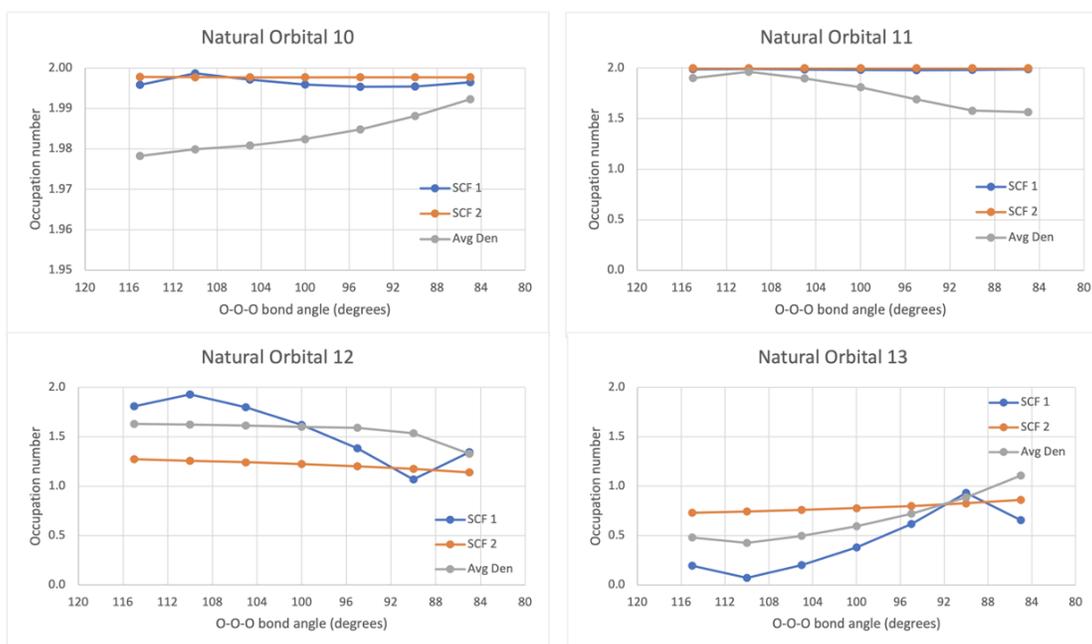


Figure S5: Selected natural orbital occupation numbers along the O-O-O bending coordinate of ozone.