Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Publication:

Orbital-Dependent Photodynamics of Strongly Correlated Nickel Oxide Clusters

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Neutral nickel oxide clusters are produced using a laser vaporization source and their excited states are subsequently measured through the pump-probe technique, where ionization enables detection using a home-built Wiley-McLaren[19] type time-of-flight mass spectrometer (TOFMS) discussed the main text (Fig S1). The instrument consists of a laser vaporization source for cluster production and a mass spectrometer that is maintained at high vacuum conditions (~7.5 x 10^{-8} Torr). Neutral clusters were ionized by a sequence of sub-35 fs laser pulses from a Ti:Sapphire laser.

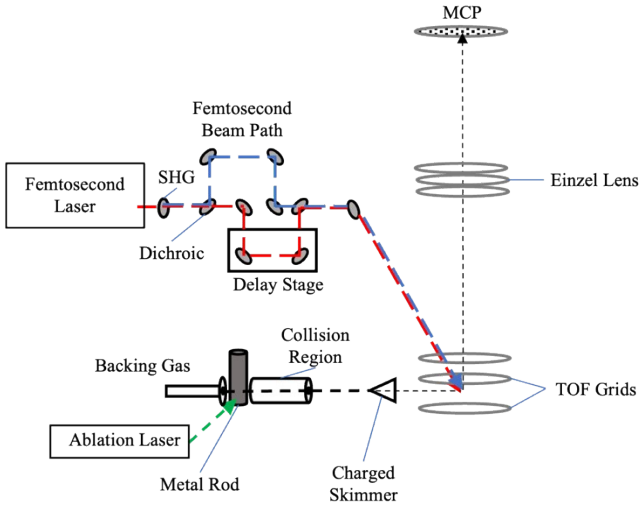

Fig. S1. Schematic of the gas phase cluster instrument and mass spectrometer. The femtosecond laser path is shown.

Figures S2-S4 show the overall change in electron density over the summation of the various atomic orbitals. It should be noted that the maximum total electron density transferred from a photoexcitation is 1, but the linear combination of several occupied-virtual pairs that contribute to the photoexcitation can reduce this value. Thus, values less than 1 indicate conflict between orbital pairs (the individual excitations cancel one another for no net change between atomic orbitals), or excitation within the d-d orbitals occurs. The Ni-f, O-s, and O-d orbitals are

involved in the calculation but do not compose a significant percentage of the charge transfer and so are not shown. Ni_6O_4 is unique in that it contains a signficant population of O-s orbitals.

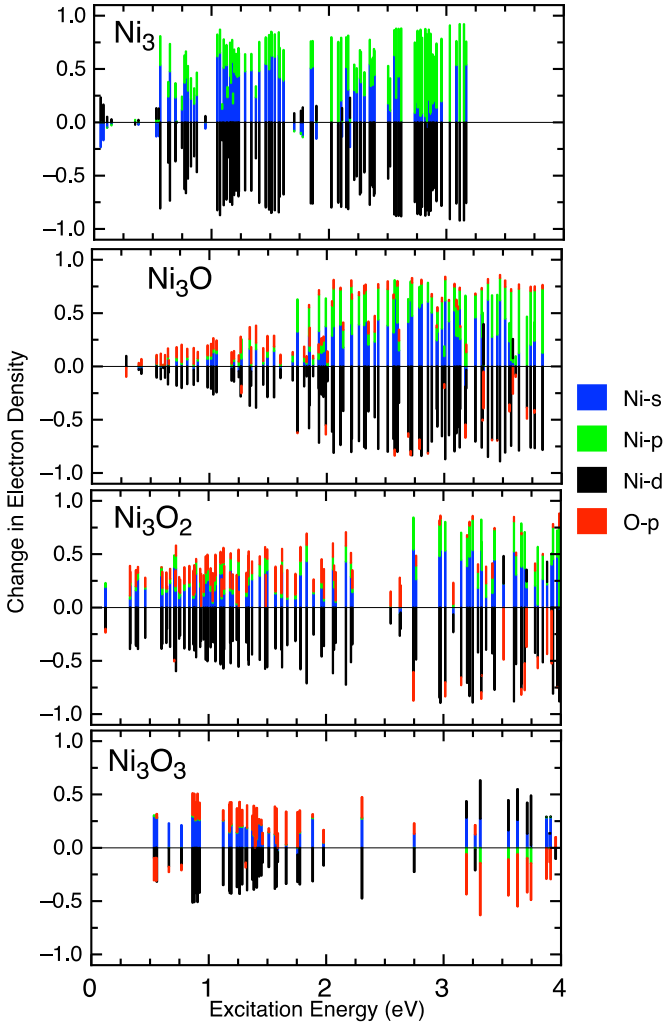

Fig. S2. C-squared population analysis of the TD-DFT excited states showing the density of states and change in electron density for the Ni-s, Ni-p, Ni-d, and Ni-p orbitals for each of the Ni_3O_x ($x < 4$) clusters.

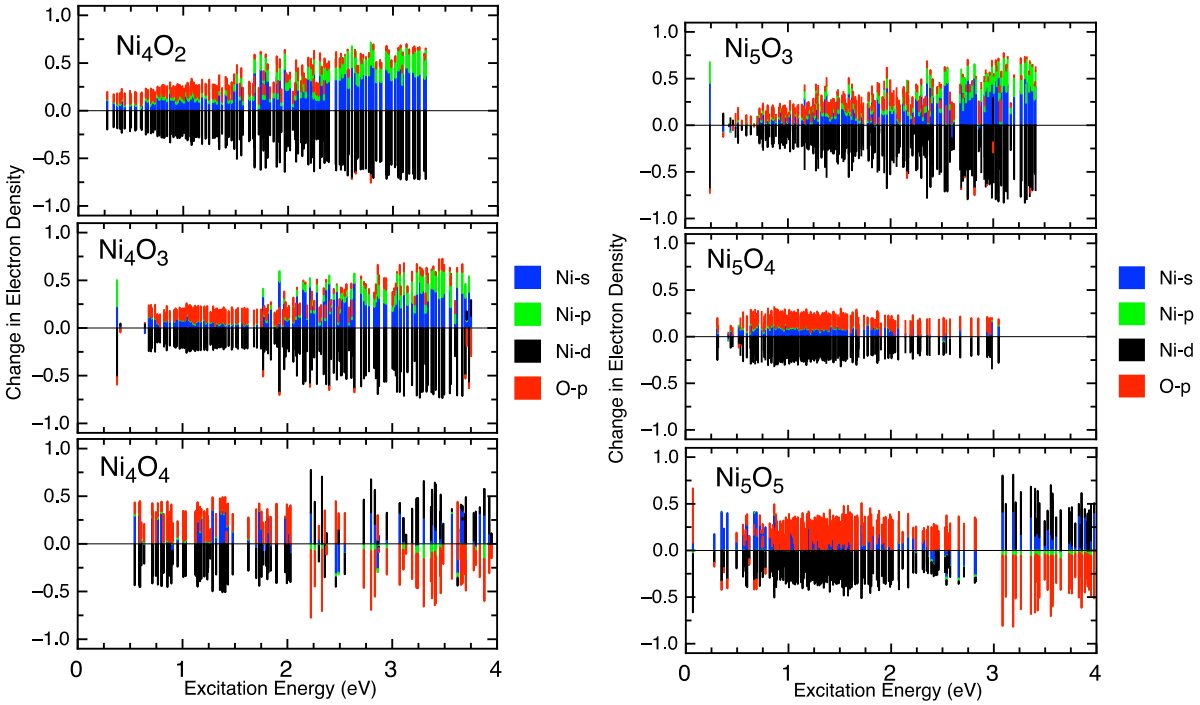

Fig. S3. C-squared population analysis of the TD-DFT excited states showing the density of states and change in electron density for the Ni-s, Ni-p, Ni-d, and Ni-p orbitals for each of the Ni_4O_x (x=2,3,4) and Ni_5O_x (x 3,4,5) clusters.

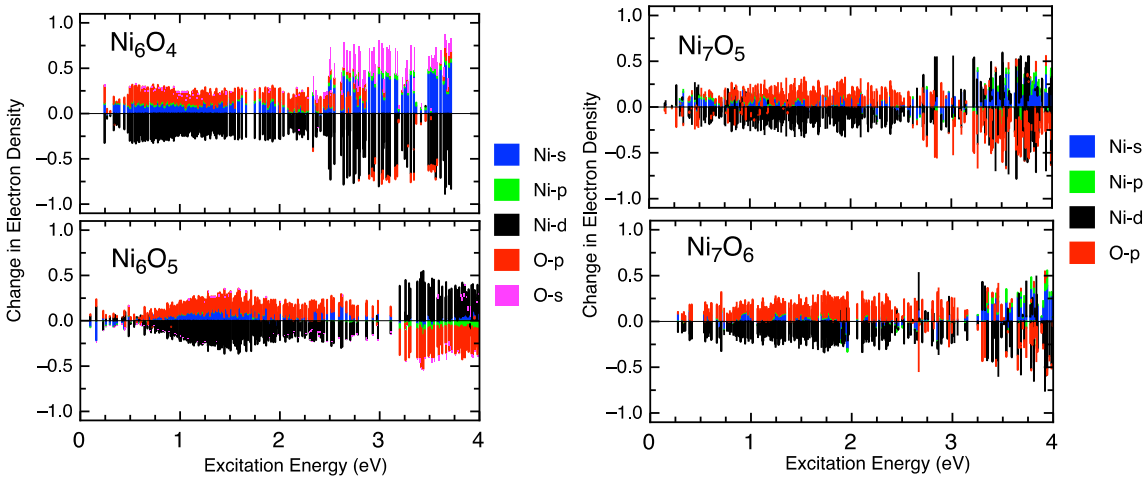

Fig. S4. C-squared population analysis of the TD-DFT excited states showing the density of states and change in electron density for the Ni-s, Ni-p, Ni-d, and Ni-p orbitals for each of the Ni_6O_x (x=4,5) and Ni_7O_x (x=5,6) clusters.

The excited state transients for larger clusters are shown in Fig. S5. Optimized structures lowest energy spin configurations for all clusters are shown in Fig. S6.

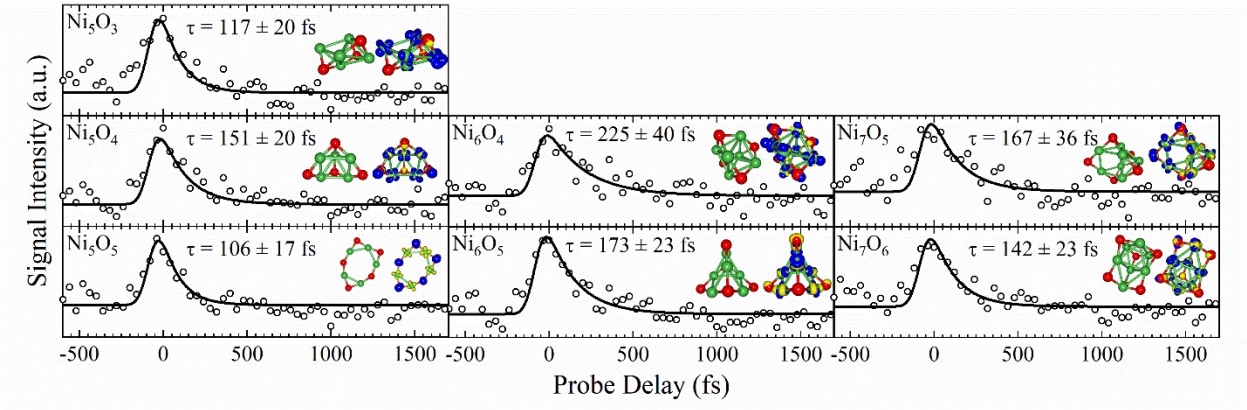

Fig. S5. The transients of the Ni_5O_x, Ni_6O_x and Ni_7O_x series showing the change in excitation lifetime as a result of oxidation. Total fit as a solid black line and lifetime (τ) above each transient.

TD-DFT BPW91 transition densities are presented at an isodensity of 0.005/Å^3. Electron densities are yellow, holes are blue, Ni atoms are green, and oxygen atoms are red.

Cluster Structures and Spin Configuration

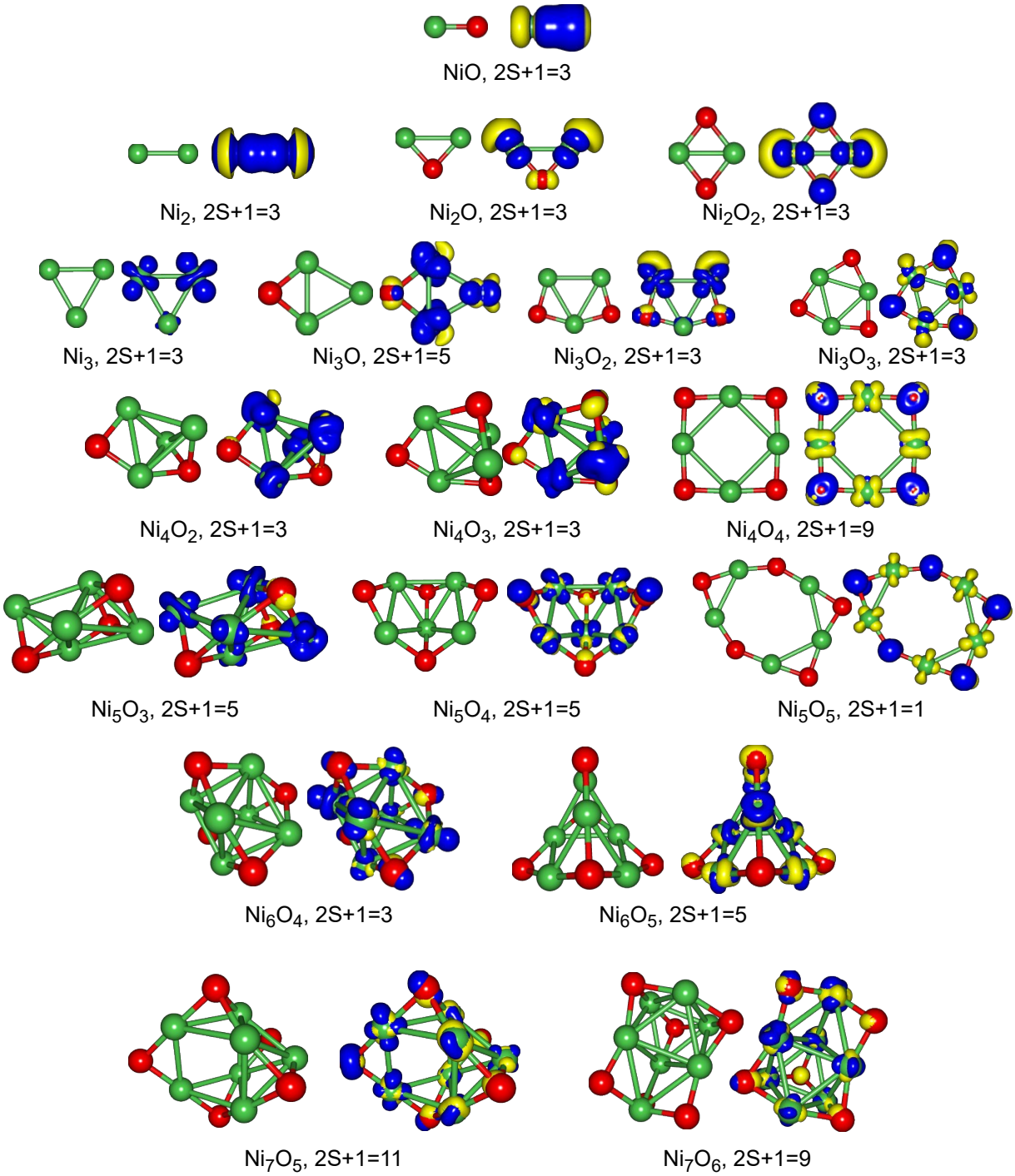

Fig. S6 TD-DFT BPW91 ground state structures and transition densities are presented at an isodensity of 0.005/Å^3. Electron densities are yellow, holes are blue, Ni atoms are green, and oxygen atoms are red. Note: Ni_2 is shown at an isodensity of 0.002/Å^3 to show the diffuse electron

XYZ Coordinates

Optimized xyz coordinates (and spin configurations) of nickel oxide clusters obtained at the ground state geometries using BPW91 and standard 6-311G+(d) basis set.

NiO (2S+1 = 3)

Ni	0.000000	0.000000	0.364260
O	0.000000	0.000000	-1.274911

$(NiO)_2$ (2S+1 = 3)

Ni	0.000000	1.085678	-0.000030
Ni	-0.000000	-1.085678	-0.000030
O	-1.404125	0.000000	0.000105
O	1.404125	-0.000000	0.000105

$(NiO)_3$ (2S+1 = 3)

Ni	1.328043	-0.315392	0.007794
Ni	-0.939246	-0.991770	0.000321
Ni	-0.391373	1.309927	-0.000470
O	-1.916220	0.456836	-0.004997
O	1.351628	1.431724	0.005717
O	0.561963	-1.885771	0.006944

$(NiO)_4$ (2S+1 = 9)

Ni	0.070829	1.828745	0.000000
Ni	1.828745	-0.070829	0.000000
Ni	-0.070829	-1.828745	0.000000
Ni	-1.828745	0.070829	0.000000
O	-1.692371	1.828745	0.000000
O	1.828745	1.692371	0.000000
O	1.692371	-1.828745	0.000000
O	-1.828745	-1.692371	0.000000

$(NiO)_5$ (2S+1 = 1)

Ni	-1.689008	-1.316697	0.000000
Ni	0.000000	2.141276	0.000000
O	-0.226516	-2.169247	0.000000
O	3.100084	-1.513929	0.000000
O	-3.117102	-0.380766	0.000000
O	-1.616188	2.691967	0.000000
O	1.571773	1.512588	0.000000
Ni	2.509022	0.103910	0.000000
Ni	1.460650	-2.042097	0.000000

Ni	-2.198393	1.073433	0.000000

$(Ni)_2$ (2S+1 = 3)

Ni	0.000000	0.000000	1.069862
Ni	0.000000	0.000000	-1.069862

(Ni_2O) (2S+1 = 3)

Ni	0.000000	1.163547	-0.159996
Ni	-0.000000	-1.163547	-0.159996
O	0.000000	-0.000000	1.119974

$(Ni)_3$ (2S+1 = 3)

Ni	0.000000	1.286404	0.000000
Ni	1.119340	-0.633987	0.000000
Ni	-1.119340	-0.652416	0.000000

(Ni_3O) (2S+1 = 5)

Ni	0.494537	-1.142170	-0.093452
Ni	0.494392	1.142205	-0.093455
Ni	-1.495323	-0.000064	0.073094
O	1.772377	0.000103	0.398343

(Ni_3O_2) (2S+1 = 3)

Ni	1.216779	-0.854176	0.000000
Ni	-1.216805	-0.854714	-0.000000
O	1.679226	0.797553	0.000000
O	-1.679134	0.797039	-0.000000
Ni	0.000000	1.253291	0.000000

(Ni_4O_2) (2S+1 = 3)

Ni	-0.827327	-0.748011	-1.068498
Ni	-0.915978	0.075278	1.243093
Ni	1.112711	-0.945770	0.346563
Ni	0.450366	1.256149	-0.362709
O	-1.374122	0.818017	-0.362586
O	2.004921	0.450223	-0.191987

(Ni_4O_3) (2S+1 = 3)

Ni	-0.999957	0.249472	1.158076
Ni	-0.985685	-0.444071	-1.112557
Ni	0.750493	1.218705	-0.222483
Ni	1.099198	-1.058078	0.163461
O	-0.670724	-1.462590	0.448069
O	2.231266	0.284988	0.010914

O	-1.084718	1.296500	-0.411722

(Ni_5O_3) (2S+1 = 5)

Ni	-0.305533	1.168431	-0.665141
Ni	-0.307554	-1.184050	-0.635149
Ni	0.428512	0.017715	1.400640
Ni	-2.038145	0.007998	0.473687
O	-1.609560	-0.015224	-1.320454
Ni	2.014405	-0.006530	-0.398175
O	1.187284	1.459059	0.375388
O	1.184819	-1.450562	0.412472

(Ni_5O_4) (2S+1 = 5)

Ni	0.006762	0.017516	-1.339334
Ni	-1.373192	1.261698	0.215626
Ni	1.417188	1.206952	0.230885
Ni	1.211528	-1.257850	0.325735
Ni	-1.266030	-1.209339	0.311517
O	0.039204	1.816149	-0.833176
O	2.207819	-0.065789	1.120634
O	-2.223210	0.021086	1.095954
O	-0.031058	-1.791036	-0.909245

(Ni_6O_4) (2S+1 = 3)

Ni	-0.005864	1.268372	-1.201304
Ni	-0.003204	1.217069	1.251257
Ni	0.012111	-1.267296	1.202325
Ni	0.009301	-1.216475	-1.252241
Ni	-1.815499	-0.011485	0.001597
Ni	1.782067	0.009701	-0.001641
O	-1.236479	-0.042329	1.733593
O	-1.239924	0.029036	-1.731309
O	1.284766	-1.767349	-0.037217
O	1.265443	1.781041	0.034956

(Ni_6O_5) (2S+1 = 5)

Ni	1.75401900	0.61705900	-0.81145800
Ni	-0.55793700	0.41788500	-1.52753800
O	0.91721500	0.96393500	-2.29230300
Ni	-1.76618600	0.80089400	0.57056800
Ni	0.51343300	0.96477700	1.30351600
Ni	1.17083400	-1.32890700	0.59707400
O	2.14221800	0.19121000	0.94212200
O	0.06514300	-2.67278900	0.45206600

O	-0.94476600	1.80317600	1.76500800
Ni	-1.11196900	-1.49233200	-0.11936000
O	-2.18748900	-0.21334800	-0.91170300

(Ni_7O_5) (2S+1 = 11)

Ni	2.18367800	-0.05438700	-0.00117000
Ni	0.43376100	1.23390900	1.18050400
Ni	-1.75498000	1.23160800	0.00045900
Ni	0.36380700	-1.24032500	-1.17963200
Ni	0.42552800	1.21082600	-1.19704200
Ni	0.35790400	-1.21789700	1.19642800
Ni	-1.83170400	-1.16950200	0.00351500
O	-0.48413200	-2.41086200	0.01690000
O	-3.08002100	0.07363700	-0.00994800
O	1.65609500	-0.02571100	1.81512100
O	1.65505600	-0.05168200	-1.81642600
O	-0.36997600	2.43480500	-0.01636100

(Ni_7O_6) (2S+1 = 9)

Ni	1.53661500	-1.44236500	-0.06564000
Ni	1.53483400	0.66487600	1.28303400
Ni	-0.45699400	1.54340600	0.06995100
Ni	-0.45654200	-0.71176700	-1.37066500
Ni	1.53736100	0.77856800	-1.21662300
Ni	-0.45677600	-0.83311900	1.30126200
Ni	-2.50261500	0.00026900	-0.00089500
O	-2.18716200	-0.80174900	-1.54739200
O	-2.18740100	1.74065100	0.07912100
O	1.32882500	-1.11635800	1.74456000
O	1.32896800	-0.95244800	-1.83895400
O	1.32864800	2.06872100	0.09403900
O	-2.18746700	-0.93835800	1.46714400