Structure, spectra, and intracluster chemistry of gas-phase platinum nitrosyl ion-molecule complexes

*Philip A. J. Pearcy, Edward I. Brewer, Gabriele Meizyte, Scott Harrington, Matthew Doll, Peter D. Watson, Christian T. Haakansson, and Stuart R. Mackenzie**

Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, United Kingdom, OX1 3TA

Supporting Information

Contents

1. Time of Flight Spectra

a. Platinum ablation in pure argon

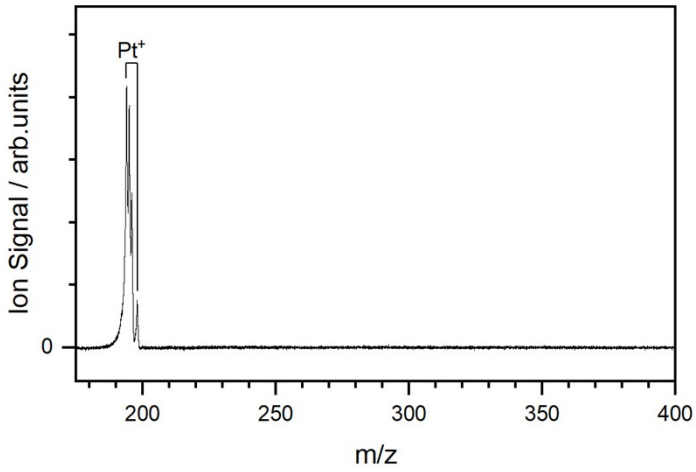


Figure S1: Time-of-flight (ToF) mass spectrum produced upon ablating a Pt target in the presence of Ar carrier gas at a backing pressure of 5 bar. The only species observed are the isotopes of Pt^+. There is no evidence of PtO_x^+ production.

2. Density Functional Theory Calculations

a. Tabulated values for relevant ligands and complexes highlighted in paper

Electronic energies and structural information of the most relevant complexes, as described in the paper. The structures were calculated using B3P86/def2TZVP level of theory. All energies are zero-point corrected (EE + ZPE). Only the frequencies and intensities associated with the stretches are presented. The modes are labelled numerically from the lowest energy vibration. Vibrations in $[PtO_x(NO)_n]^+$ complexes are scaled by 0.9347.

Ligands:

NO (neutral, doublet)

EE+ ZPE / Hartree: -130.199366

xyz coordinates:

N	0.000000	0.000000	-0.608914
O	0.000000	0.000000	0.532800

Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	Intensity / km mol^{-1}
1	2006.79	40.6601

NO_2 (neutral, doublet)

EE+ ZPE / Hartree: -205.558503

xyz coordinates:

N	0.000000	0.318412	0.000000
O	1.093884	-0.139288	0.000000
O	-1.093884	-0.139323	0.000000

Mode #	IR frequency (unscaled) / cm^{-1}	Intensity / km mol^{-1}
1	775.33	6.9702
2	1422.53	0.3281
3	1752.83	435.9361

N_2O (neutral, singlet)
EE+ ZPE / Hartree: -185.115869

xyz coordinates:

N	0.000000	0.000000	-0.071525
N	0.000000	0.000000	-1.191385
O	0.000000	0.000000	1.105046

Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	Intensity / km mol^{-1}
1	631.10	6.3036
2	631.10	6.3036
3	1362.05	64.1322
4	2384.98	394.5206

N_2O_3 (neutral, singlet)
EE+ ZPE / Hartree: -335.772885

xyz coordinates:

N	-0.000000	0.628172	0.000000
O	1.192719	0.631584	0.000000
O	-0.794365	1.517794	0.000000
N	-0.686038	-1.066555	0.000000
O	0.201930	-1.765794	0.000000

Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	Intensity / km mol^{-1}
1	141.94	0.5169
2	226.30	0.5129
3	301.14	27.2109
4	483.01	8.5986
5	689.30	24.1459
6	833.20	40.1204
7	1407.17	262.7389
8	1764.80	402.4754
9	1952.33	404.1126

Pt core:

Pt (+1, doublet)
EE + ZPE / Hartree: -119.36159

PtO (+1, quartet)
EE+ ZPE / Hartree: -194.720361

xyz coordinates:

Pt	0.000000	0.000000	0.160523
O	-0.000000	-0.000000	-1.565099

Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	Intensity / km mol^{-1}
1	842.11	1.4985

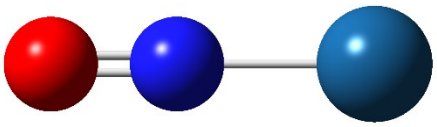
Complexes:

$[Pt(NO)]^+$

Isomer 1a (Singlet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -249.692761

xyz coordinates:



Pt	-0.000000	0.375607	-0.000000
N	0.000461	-1.362076	0.000000
O	-0.000403	-2.470356	0.000000

Vibrational frequencies

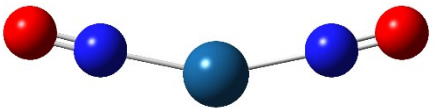
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	217.00	202.83	5.8229
2	592.37	553.69	28.3279
3	2163.45	2022.17	623.2744

$[Pt(NO)_2]^+$

Isomer 2a (Doublet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -379.965483

xyz coordinates:



Pt	0.000008	-0.141831	-0.000851
N	-1.786071	0.225647	0.011297
O	-2.872808	0.494050	-0.005710
N	1.786137	0.225187	0.011154
O	2.872673	0.494323	-0.005633

Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	37.27	34.84	4.6331
2	66.93	62.56	1.9227
3	294.74	275.49	0.0100
4	299.07	279.54	0.0266
5	366.36	342.43	1.1215
6	478.61	447.36	1.2581
7	519.08	485.19	1.4182
8	2052.76	1918.72	2047.6270
9	2127.44	1988.52	31.7927

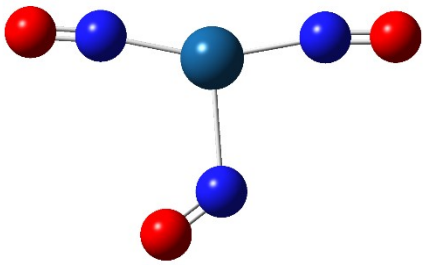
$[Pt(NO)_3]^+$

Isomer 3a (Triplet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -510.199931

xyz coordinates:

Pt	0.0614720	-0.212386	0.000084
N	-0.042798	1.9371000	-0.001803
O	-1.006404	2.515891	0.001138
N	-1.671999	-0.781382	-0.000161
O	-2.785574	-0.97701	-0.000297
N	1.9038060	-0.323825	0.000205
O	3.0272410	-0.196027	-0.000124



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	39.20	36.64	0.7956
2	63.00	58.89	1.0123
3	72.57	67.83	0.4436
4	93.78	87.65	0.0243
5	200.37	187.29	24.3438
6	232.72	217.53	0.0044
7	259.35	242.41	19.9165
8	331.36	309.73	1.3578
9	353.31	330.24	22.1014
10	478.58	447.33	8.2685
11	498.40	465.85	1.5784
12	516.47	482.74	14.7886
13	1945.38	1818.35	1028.8138
14	1980.21	1850.90	2097.0147
15	2060.92	1926.34	10.7070

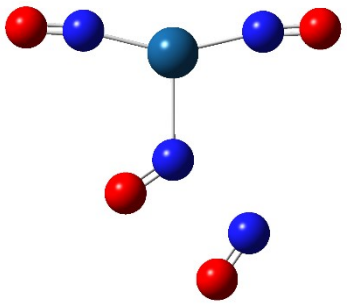
$[Pt(NO)_4]^+$

Isomer 4a (Doublet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -640.412452

xyz coordinates:

Pt	-0.591933	0.157496	-0.000284
N	3.273945	0.228704	-0.000532
O	3.883699	-0.697194	-0.000037
N	1.371192	-0.626315	0.000293
O	1.633565	-1.746784	0.000844
N	-1.659119	-1.324397	-0.000233
O	-2.136988	-2.351044	0.000971
N	-0.313168	1.969277	0.000110
O	0.052324	3.043076	0.001306



Vibrational frequencies

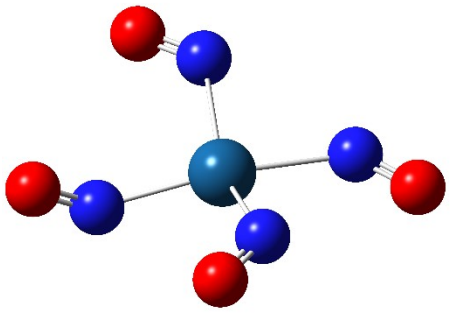
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	20.93	19.56	0.2937
2	26.37	24.65	0.6798
3	41.48	38.77	0.4818
4	60.87	56.90	3.1392
5	83.43	77.98	6.7730
6	116.43	108.83	0.0395
7	186.08	173.93	9.5478
8	236.25	220.82	0.0120
9	253.42	236.87	0.0020
10	265.30	247.98	2.2959
11	268.83	251.27	11.7151
12	380.15	355.33	2.8648
13	438.03	409.43	0.5415
14	502.69	469.86	12.9957
15	519.39	485.48	16.2755
16	563.54	526.74	27.1238
17	677.02	632.81	10.2151
18	1779.21	1663.03	203.3077
19	1965.26	1836.93	1936.2874
20	2003.31	1872.49	1536.8493
21	2087.63	1951.30	604.6984

Isomer 4c (Quartet, ΔE = 0.04 eV)

EE+ ZPE / Hartree: -640.410820

xyz coordinates:

Pt	-0.025794	-0.052637	-0.060213
N	-1.444709	-1.559144	-0.088050
O	-2.576554	-1.506772	-0.137955
N	-1.530026	1.280533	0.384325
O	-1.483539	2.414111	0.322768
N	1.330925	-1.707039	0.342762
O	2.461665	-1.662237	0.300208
N	1.372789	1.221863	-0.523669
O	2.087061	1.936424	0.001108



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	16.20	15.14	0.2301
2	27.35	25.57	0.0292
3	66.23	61.90	0.4234
4	83.41	77.96	1.5250
5	88.44	82.67	1.2605
6	97.21	90.86	2.3470
7	115.35	107.82	0.1964
8	155.21	145.08	1.7195
9	159.94	149.50	2.6515
10	201.66	188.49	9.6233
11	224.78	210.10	3.5706
12	256.00	239.28	4.5048
13	296.51	277.14	0.6860
14	336.30	314.34	3.0614
15	401.39	375.18	7.9620
16	419.29	391.91	10.3820
17	464.27	433.95	4.9845
18	1918.72	1793.43	380.9045
19	1938.82	1812.21	1004.7580
20	1957.74	1829.90	766.9464
21	2001.57	1870.87	18.4115

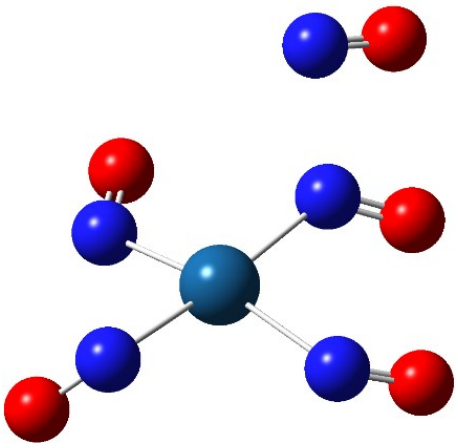
$[Pt(NO)_5]^+$

Isomer 5a (Triplet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -770.626548

xyz coordinates:

Pt	-0.450717	0.000834	-0.068950
N	-2.393202	-0.415518	-0.424654
O	-3.145102	-1.064458	0.126396
N	3.086380	-0.734032	-0.622076
O	3.917990	-0.120025	-0.218367
N	1.506408	0.377831	0.050408
O	2.044052	1.248946	0.591404
N	-0.970575	2.094131	-0.155913
O	-0.337072	2.900074	0.335888
N	-0.115080	-1.977032	0.377055
O	0.939938	-2.399878	0.515228



Vibrational frequencies

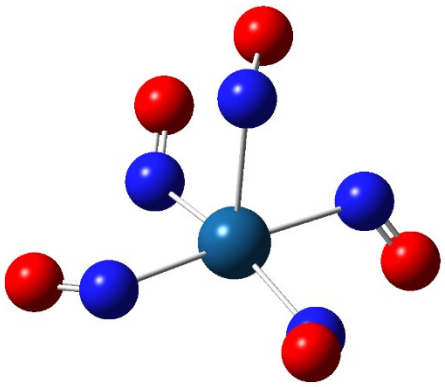
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	34.68	32.42	0.1885
2	37.11	34.69	1.0325
3	56.00	52.35	0.6266
4	63.13	59.01	0.6408
5	74.02	69.18	1.4457
6	91.31	85.34	1.5263
7	103.31	96.56	0.4995
8	123.48	115.42	3.7345
9	143.74	134.36	1.6451
10	160.31	149.84	11.9281
11	190.89	178.42	5.2058
12	209.84	196.14	3.5411
13	227.87	212.99	5.2359
14	253.86	237.28	11.7514
15	260.93	243.89	11.4649
16	315.64	295.03	5.7945
17	341.75	319.43	2.5176
18	389.40	363.97	1.7910
19	412.71	385.76	1.3794
20	487.31	455.49	7.0939
21	503.52	470.64	27.4212
22	721.30	674.20	5.7696
23	1771.22	1655.56	109.1731
24	1856.92	1735.66	773.8488
25	1922.72	1797.17	687.1685
26	1962.16	1834.04	732.7033
27	2069.80	1934.64	975.8211

Isomer 5c (Triplet, ΔE = 0.06 eV)

EE+ ZPE / Hartree: -770.624597

xyz coordinates:

Pt	0.138849	0.006982	-0.140698
N	-0.735974	-0.19096	1.926123
O	-1.845674	-0.011806	2.012391
N	1.387373	-1.744851	-0.039288
O	1.052031	-2.735513	-0.480223
N	-1.066204	1.836889	-0.298408
O	-0.729387	2.625838	-1.041680
N	1.825608	1.172864	0.070707
O	2.721467	1.01722	0.757315
N	-1.446688	-1.031571	-0.916267
O	-2.520814	-1.000885	-0.526011



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	32.21	30.10	0.0955
2	37.71	35.25	0.3069
3	48.68	45.51	0.0355
4	61.73	57.70	0.1684
5	70.80	66.18	0.0745
6	73.21	68.43	0.3564
7	90.88	84.94	0.2423
8	96.39	90.10	0.6548
9	121.93	113.97	6.2218
10	128.25	119.87	1.3546
11	136.78	127.85	6.7833
12	146.78	137.19	9.6837
13	168.63	157.62	10.2008
14	191.11	178.63	3.9834
15	204.88	191.50	1.1121
16	230.61	215.55	23.5939
17	285.88	267.21	1.9532
18	354.18	331.05	1.5542
19	413.37	386.38	1.1628
20	422.57	394.97	1.7575
21	439.93	411.20	1.0260
22	471.62	440.83	1.8237
23	1862.51	1740.89	826.3578
24	1912.09	1787.23	424.7251
25	1919.79	1794.43	1213.6233
26	1929.86	1803.84	970.1768
27	1992.58	1862.47	94.1830

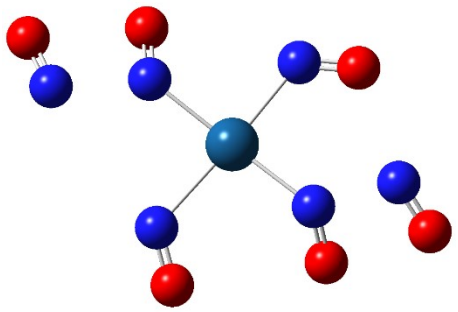
$[Pt(NO)_6]^+$

Isomer 6a (Doublet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -900.840162

xyz coordinates:

Pt	0.060284	-0.011295	-0.080888
N	3.555892	0.530059	0.875665
O	4.393094	-0.148097	0.596452
N	2.022307	-0.469141	0.012426
O	2.564129	-1.372169	-0.464451
N	-3.298845	-0.592300	1.039179
O	-4.200481	-0.025794	0.715337
N	-1.877412	0.415819	0.026961
O	-2.488739	1.231667	-0.523691
N	0.686979	2.035333	-0.118047
O	-0.023300	2.880302	-0.406394
N	-0.375215	-2.001828	-0.415005
O	-1.456966	-2.383983	-0.372132



Vibrational frequencies

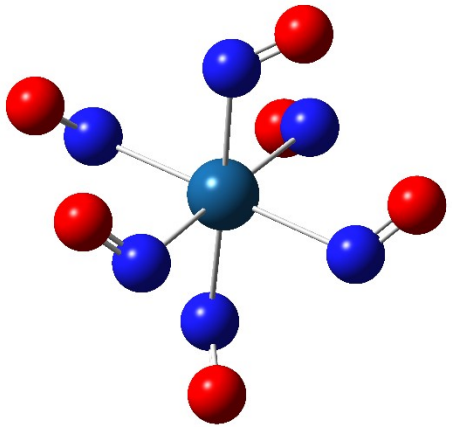
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	25.31	23.66	0.8123
2	34.40	32.15	1.3795
3	45.46	42.49	0.7049
4	53.03	49.57	1.4034
5	68.93	64.43	0.2685
6	74.45	69.59	1.2425
7	80.65	75.38	0.2996
8	99.42	92.92	1.5740
9	120.13	112.28	8.1511
10	127.39	119.07	1.8897
11	143.87	134.48	1.2236
12	166.68	155.80	10.5390
13	183.84	171.84	24.2299
14	194.56	181.85	1.2090
15	239.05	223.44	2.9524
16	251.08	234.68	9.3603
17	268.58	251.04	12.5670
18	295.19	275.91	20.5792
19	322.77	301.69	3.9083
20	358.43	335.03	23.8008
21	399.75	373.64	2.4937
22	421.06	393.56	9.5453
23	473.58	442.65	2.5586
24	521.66	487.60	25.7402
25	523.98	489.76	6.4650
26	730.74	683.02	17.5732
27	741.92	693.47	0.3264
28	1769.45	1653.90	112.4404
29	1785.31	1668.73	80.2447
30	1838.40	1718.36	1307.4707
31	1909.36	1784.67	444.9343
32	2040.10	1906.88	2441.5854
33	2065.47	1930.60	90.7390

Isomer 6c (Doublet, ΔE = 0.02 eV)

EE+ ZPE / Hartree: -900.839510

xyz coordinates:

Pt	0.000308	-0.058678	0.003153
N	-1.630465	-0.076822	-1.500954
O	-2.518094	0.617814	-1.358137
N	1.681108	-0.123179	1.451315
O	2.527631	0.627510	1.351394
N	-1.411585	0.029305	1.630981
O	-2.277183	0.767749	1.583824
N	1.480368	-0.165396	-1.605089
O	1.283806	-0.841222	-2.498013
N	-0.075460	-2.257062	0.057791
O	-0.090952	-2.793600	1.059106
N	0.020033	2.084698	-0.111631
O	1.015790	2.638758	-0.101031



Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	40.96	38.28	0.0333
2	44.50	41.59	0.0557
3	47.06	43.98	0.0489
4	53.41	49.92	0.0615
5	62.30	58.23	0.0298
6	69.98	65.41	0.0288
7	71.92	67.22	0.0918
8	76.49	71.50	0.0499
9	87.44	81.73	0.0544
10	100.41	93.85	0.0689
11	108.65	101.56	0.3312
12	112.62	105.26	0.0774
13	127.99	119.63	3.8162
14	133.81	125.07	2.8843
15	142.41	133.11	6.9300
16	151.13	141.26	3.8803
17	164.50	153.76	12.8655
18	169.97	158.87	13.4866
19	173.83	162.48	17.7584
20	192.46	179.89	7.2599
21	243.91	227.99	1.2455
22	394.93	369.14	0.0902
23	404.43	378.02	0.1709
24	421.19	393.68	0.3277
25	431.43	403.26	0.1619
26	442.46	413.56	0.0246
27	477.83	446.62	0.2023
28	1878.59	1755.92	791.6955
29	1885.74	1762.60	899.6804
30	1908.97	1784.31	594.7499
31	1918.86	1793.56	872.4148
32	1921.42	1795.96	1151.2276
33	1986.00	1856.31	0.2632

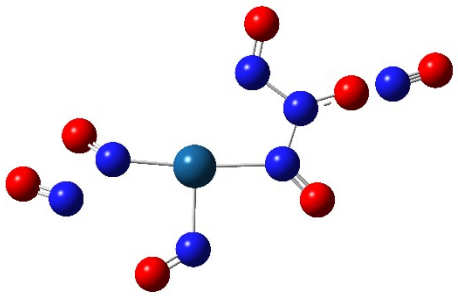
$[Pt(NO)_7]^+$

Isomer 7a (Singlet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -1031.048598

xyz coordinates:

Pt	0.553428	-0.122810	0.163620
N	-2.277157	0.235124	0.284087
O	-3.532167	0.127452	0.441087
N	-1.406788	-0.823104	0.199532
O	-1.868631	-1.914372	0.199098
N	3.710504	0.387866	-1.333869
O	4.521648	1.052631	-0.955520
N	2.300969	0.739129	0.034150
O	2.813682	1.491635	0.753478
N	-1.515224	1.431517	0.259846
O	-2.137489	2.422814	0.305796
N	1.290207	-1.928062	0.128632
O	2.403565	-2.106984	-0.079247
N	-4.465100	0.092182	-1.141117
O	-5.529259	0.006398	-0.887335



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	24.72	23.11	1.5932
2	28.48	26.62	2.1733
3	33.59	31.40	0.4451
4	49.75	46.50	0.1909
5	50.99	47.66	0.8458
6	63.89	59.72	9.5551
7	76.13	71.16	1.9363
8	102.18	95.51	3.4698
9	122.12	114.15	7.7001
10	134.31	125.54	1.5757
11	138.32	129.29	0.9408
12	164.68	153.93	1.3236
13	185.37	173.27	15.6573
14	197.09	184.22	11.0698
15	225.40	210.68	23.6698
16	265.56	248.22	7.8710
17	271.68	253.94	31.0991
18	320.55	299.62	23.6343
19	331.18	309.55	20.9866
20	349.72	326.88	13.5031
21	369.90	345.75	31.8364
22	393.96	368.23	6.7717
23	401.26	375.06	6.5453
24	502.96	470.12	12.5470
25	506.78	473.69	58.5039
26	564.42	527.57	15.0809
27	633.12	591.77	48.7935
28	673.41	629.44	146.3630
29	707.42	661.23	223.9332
30	764.95	715.00	22.9759
31	979.95	915.96	151.5904

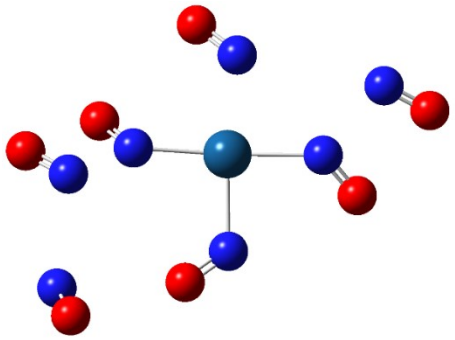
32	1045.50	977.23	82.4273
33	1330.97	1244.05	45.3635
34	1659.77	1551.39	255.8911
35	1745.53	1631.55	88.2661
36	1768.09	1652.63	301.7600
37	1835.39	1715.54	806.3859
38	2040.98	1907.70	1335.5477
39	2133.10	1993.81	1175.9275

Isomer 7c (Triplet, ΔE = 0.08 eV)

EE+ ZPE / Hartree: -1031.045734

xyz coordinates:

Pt	0.415285	0.068205	-0.143568
N	-4.150776	-1.298298	0.107495
O	-4.26937	-2.121098	0.859304
N	3.847332	-0.079454	1.097077
O	4.571680	-0.894763	0.866407
N	2.240591	-0.77038	0.093963
O	2.642949	-1.756016	-0.355809
N	-3.099434	0.70336	0.995288
O	-3.658142	1.592964	0.605712
N	-1.375421	0.946931	-0.143853
O	-1.678456	1.883968	-0.760609
N	1.436452	1.927473	0.067213
O	0.960957	2.921484	-0.234025
N	-0.286047	-1.74443	-0.805927
O	-1.404761	-2.016092	-0.816046



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	16.95	15.84	0.8423
2	26.92	25.16	0.2876
3	33.84	31.63	0.6737
4	39.52	36.94	1.0969
5	48.01	44.88	0.2329
6	54.03	50.50	0.8336
7	58.61	54.78	0.1534
8	70.53	65.93	0.3936
9	89.18	83.36	1.9829
10	90.13	84.24	0.4182
11	98.92	92.46	1.4141
12	116.17	108.59	3.5393
13	123.42	115.36	3.4711
14	134.27	125.50	4.8167
15	143.87	134.48	2.7215
16	166.27	155.42	4.2346
17	177.54	165.95	3.4435
18	192.16	179.61	21.9166
19	238.14	222.59	2.4431
20	248.05	231.86	11.7548
21	273.86	255.97	2.6865
22	297.95	278.50	3.6025
23	308.90	288.73	57.6943
24	325.83	304.55	7.2846
25	372.46	348.14	14.5308
26	409.90	383.13	6.7057
27	421.18	393.68	8.9882
28	464.51	434.18	2.6014
29	481.50	450.06	19.7037
30	528.56	494.05	7.5399

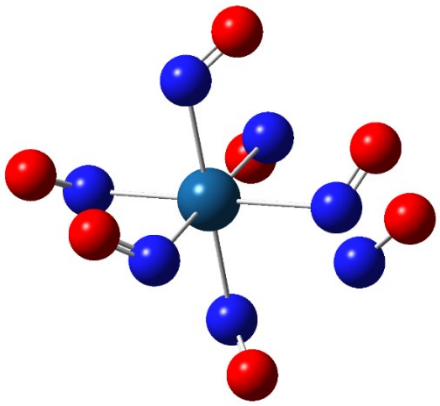
31	704.08	658.10	7.5519
32	741.39	692.98	10.8487
33	1746.67	1632.62	165.5231
34	1783.64	1667.17	41.4620
35	1819.88	1701.04	1028.6099
36	1897.40	1773.50	160.5616
37	1927.02	1801.19	1619.3131
38	2037.61	1904.56	2391.2931
39	2063.07	1928.35	208.9436

Isomer 7d (Triplet, ΔE = 0.10 eV)

EE+ ZPE / Hartree: -1031.044815

xyz coordinates:

Pt	-0.364241	-0.028665	0.052473
N	3.625703	0.79037	0.354063
O	4.374852	0.167182	-0.201558
N	-2.483876	0.524883	-0.145082
O	-2.763048	1.394273	-0.825262
N	1.770025	-0.717700	0.309959
O	2.183631	-1.502261	-0.418208
N	0.244696	2.013661	0.081857
O	-0.184030	2.737381	-0.689921
N	-0.942336	-2.13991	0.040573
O	-1.836120	-2.475839	0.659290
N	-0.574668	-0.021406	2.227297
O	0.178460	0.546787	2.863708
N	-0.196177	-0.05799	-2.081065
O	0.334652	-0.930955	-2.588811



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	24.72	23.11	1.5932
2	28.48	26.62	2.1733
3	33.59	31.40	0.4451
4	49.75	46.50	0.1909
5	50.99	47.66	0.8458
6	63.89	59.72	9.5551
7	76.13	71.16	1.9363
8	102.18	95.51	3.4698
9	122.12	114.15	7.7001
10	134.31	125.54	1.5757
11	138.32	129.29	0.9408
12	164.68	153.93	1.3236
13	185.37	173.27	15.6573
14	197.09	184.22	11.0698
15	225.40	210.68	23.6698
16	265.56	248.22	7.8710
17	271.68	253.94	31.0991
18	320.55	299.62	23.6343
19	331.18	309.55	20.9866
20	349.72	326.88	13.5031
21	369.90	345.75	31.8364
22	393.96	368.23	6.7717
23	401.26	375.06	6.5453
24	502.96	470.12	12.5470
25	506.78	473.69	58.5039
26	564.42	527.57	15.0809
27	633.12	591.77	48.7935
28	673.41	629.44	146.3630
29	707.42	661.23	223.9332
30	764.95	715.00	22.9759
31	979.95	915.96	151.5904
32	1045.50	977.23	82.4273

33	1330.97	1244.05	45.3635
34	1659.77	1551.39	255.8911
35	1745.53	1631.55	88.2661
36	1768.09	1652.63	301.7600
37	1835.39	1715.54	806.3859
38	2040.98	1907.70	1335.5477
39	2133.10	1993.81	1175.9275

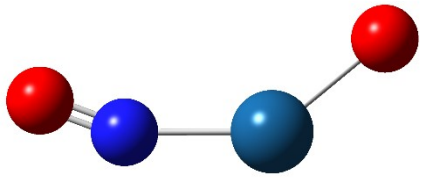
$[PtO(NO)]^+$

Isomer 1'a (Triplet, ΔE = 0.00 eV)

EE+ ZPE / Hartree: -325.010861

xyz coordinates:

Pt	0.231777	-0.138443	-0.000009
O	1.702401	0.886901	0.000026
N	-1.577176	-0.001898	0.000161
O	-2.582199	0.464575	-0.000077



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	100.09	93.56	2.2614
2	375.33	350.82	0.2432
3	465.29	434.90	4.3959
4	522.94	488.79	44.5488
5	708.71	662.44	2.8468
6	2127.29	1988.38	847.4619

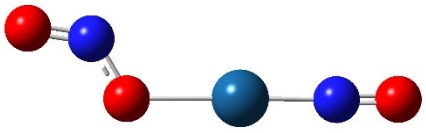
$[PtO(NO)_2]^+$

Isomer 2'a (Doublet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -455.309389

xyz coordinates:

Pt	0.288404	0.091898	-0.003560
N	1.987078	-0.223756	0.000915
O	3.076080	-0.445456	0.014801
N	-2.543863	-0.423640	-0.005107
O	-3.693690	-0.380468	0.004144
O	-1.707139	0.496393	0.019430



Vibrational frequencies

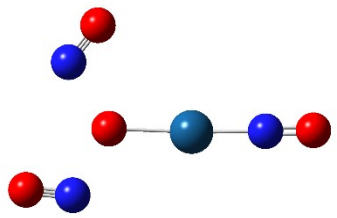
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	51.77	48.39	1.2687
2	78.23	73.12	0.0549
3	136.16	127.27	6.3071
4	154.03	143.97	0.8475
5	314.33	293.81	0.2897
6	420.34	392.89	3.7389
7	424.48	396.76	0.7218
8	635.65	594.14	42.4178
9	797.95	745.85	21.3889
10	1206.50	1127.72	91.9513
11	1803.42	1685.66	595.8625
12	2159.90	2018.86	1031.0585

$[PtO(NO)_3]^+$

Isomer 3'a (Singlet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -585.556372

xyz coordinates:



Pt	0.523050	-0.085412	-0.000291
N	2.252801	-0.068030	0.000725
O	3.372570	-0.046866	0.001314
N	-2.253350	-1.556117	-0.000026
O	-3.347337	-1.431755	0.001316
O	-1.405962	-0.008764	-0.001304
N	-2.348978	1.537996	0.000603
O	-1.663174	2.395534	0.000371

Vibrational frequencies

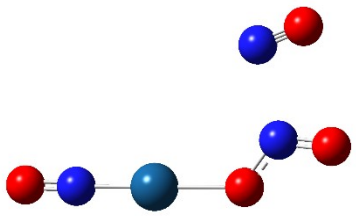
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	42.61	39.83	2.0731
2	46.71	43.66	0.0003
3	78.20	73.09	8.0834
4	105.99	99.07	0.0079
5	155.98	145.79	0.5023
6	184.35	172.31	0.4482
7	248.65	232.42	78.7936
8	346.95	324.29	1.4983
9	349.74	326.90	17.1742
10	464.07	433.77	2.4733
11	465.91	435.49	0.2224
12	556.43	520.10	10.5023
13	649.47	607.06	12.8596
14	869.75	812.96	41.6321
15	1219.36	1139.74	714.7911
16	1725.36	1612.69	405.0188
17	2129.93	1990.85	1317.5191
18	2168.58	2026.97	463.5134

Isomer 3'b (Singlet, ΔE = 0.02 eV)

EE + ZPE / Hartree: - 585.555621

xyz coordinates:

Pt	-0.729474	-0.180318	-0.000305
N	-2.272687	0.583285	0.001015
O	-3.265682	1.094588	0.001926
N	2.196308	-0.486391	0.000388
O	3.183393	-1.112469	0.003180
O	1.052715	-1.051136	-0.002217
N	2.730077	1.510916	-0.002074
O	3.819959	1.420281	0.000670



Vibrational frequencies

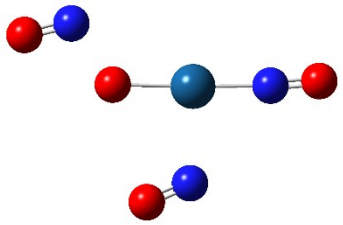
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	42.61	39.83	2.0731
2	46.71	43.66	0.0003
3	78.20	73.09	8.0834
4	105.99	99.07	0.0079
5	155.98	145.79	0.5023
6	184.35	172.31	0.4482
7	248.65	232.42	78.7936
8	346.95	324.29	1.4983
9	349.74	326.90	17.1742
10	464.07	433.77	2.4733
11	465.91	435.49	0.2224
12	556.43	520.10	10.5023
13	649.47	607.06	12.8596
14	869.75	812.96	41.6321
15	1219.36	1139.74	714.7911
16	1725.36	1612.69	405.0188
17	2129.93	1990.85	1317.5191
18	2168.58	2026.97	463.5134

Isomer 3'c (Singlet, ΔE = 0.23 eV)

EE + ZPE / Hartree: -585.547830

xyz coordinates:

Pt	0.260349	-0.185523	-0.000878
O	-1.534049	0.188039	0.005162
N	0.657621	2.024809	0.032380
O	-0.216697	2.695513	-0.023553
N	-2.747763	-0.986773	-0.005340
O	-3.735141	-0.483007	0.005637
N	1.980545	-0.609484	-0.001896
O	3.043383	-0.966680	-0.000684



Vibrational frequencies

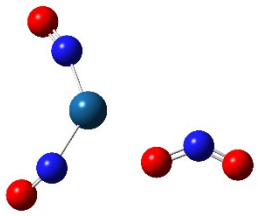
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	37.03	34.61	7.4063
2	55.23	51.63	1.0337
3	57.02	53.30	2.3756
4	76.59	71.59	0.0151
5	91.29	85.33	0.2135
6	123.29	115.24	3.2775
7	150.79	140.94	35.8970
8	209.96	196.25	54.1913
9	315.30	294.71	158.1496
10	487.75	455.90	35.8084
11	543.84	508.33	191.8162
12	572.00	534.65	2.7945
13	593.36	554.62	430.6907
14	618.59	578.19	104.3561
15	799.22	747.03	229.9846
16	2039.24	1906.08	1985.0654
17	2059.58	1925.09	1088.9174
18	2113.21	1975.22	270.6464

Isomer 3'd (Triplet, ΔE = 0.46 eV)

EE + ZPE / Hartree: -585.539266

xyz coordinates:

Pt	-0.315968	-0.053465	-0.081022
N	-1.600365	-1.290960	0.035324
O	-2.569194	-1.793088	0.312101
N	2.724966	-0.642945	0.049077
O	3.880209	-0.701585	0.134907
O	1.944416	0.294402	0.093942
N	-0.397609	1.887500	-0.219595
O	-0.810859	2.762157	0.367309



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	31.45	29.40	1.0876
2	37.03	34.61	1.0993
3	54.35	50.80	0.0532
4	72.92	68.16	0.2791
5	111.89	104.58	3.4718
6	140.97	131.77	1.7150
7	184.34	172.30	3.0747
8	197.52	184.62	13.3892
9	275.76	257.75	2.1189
10	351.26	328.33	2.9453
11	414.04	387.00	4.1477
12	473.93	442.99	1.4085
13	551.53	515.51	8.3333
14	785.04	733.78	5.0500
15	1326.44	1239.82	215.9055
16	1774.93	1659.03	544.6979
17	1961.52	1833.43	1111.3922
18	2050.90	1916.97	633.4422

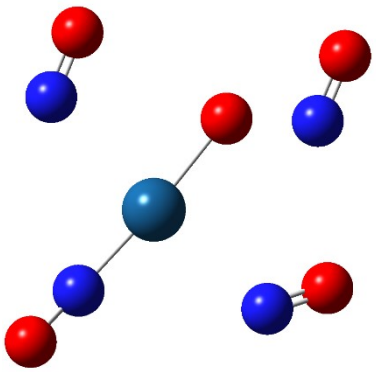
$[PtO(NO)_4]^+$

Isomer 4'a (Doublet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -715.771536

xyz coordinates:

Pt	-0.348700	-0.021788	-0.004070
O	1.400392	0.595061	-0.153976
N	-2.044720	-0.476337	0.173758
O	-3.118717	-0.759441	0.330949
N	2.653622	-0.176540	0.420742
O	3.570209	0.471096	0.344016
N	0.346195	-2.324861	-0.034093
N	-0.792679	2.367857	-0.146213
O	1.304190	-2.576325	-0.553548
O	0.101634	3.015686	-0.290179



Vibrational frequencies

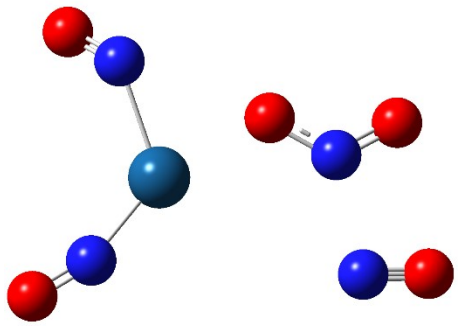
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	33.42	31.24	0.1981
2	42.36	39.60	4.2164
3	65.03	60.78	0.7693
4	68.37	63.91	1.2322
5	78.16	73.05	0.2199
6	83.40	77.95	0.4436
7	95.25	89.03	0.6232
8	112.38	105.04	3.4799
9	125.38	117.20	0.5796
10	130.36	121.85	1.6908
11	142.18	132.90	1.5221
12	184.72	172.66	46.0170
13	330.24	308.68	167.8554
14	381.15	356.26	12.4967
15	397.86	371.88	1.4636
16	524.49	490.24	237.7618
17	555.17	518.92	7.2675
18	582.87	544.81	525.4666
19	601.16	561.91	1.3597
20	818.18	764.75	44.8554
21	1945.49	1818.45	852.1635
22	1987.68	1857.89	2100.9918
23	2031.42	1898.77	936.5782
24	2098.23	1961.21	516.4987

Isomer 4'f (Doublet, ΔE = 0.04 eV)

EE + ZPE / Hartree: -715.769998

xyz coordinates:

Pt	0.586511	-0.084391	-0.057644
O	-1.161426	1.127339	0.030046
N	1.567499	-1.572565	0.044351
O	2.458812	-2.249152	0.220485
N	-2.943550	-1.28738	-0.015126
O	-4.031765	-1.140036	0.031556
N	-2.321887	0.647072	0.057801
O	-3.288331	1.309724	0.126450
N	1.459681	1.720707	-0.296139
O	2.262705	2.205584	0.336462



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	17.41	16.27	3.8613
2	33.48	31.30	0.4037
3	45.75	42.76	1.6399
4	52.64	49.20	0.2654
5	81.49	76.17	4.6100
6	100.96	94.37	1.2988
7	135.32	126.49	4.3578
8	166.50	155.63	1.7170
9	176.86	165.31	22.4135
10	242.55	226.71	36.6147
11	266.79	249.37	11.4176
12	305.55	285.60	20.6009
13	355.93	332.69	3.7227
14	378.04	353.35	2.3869
15	418.50	391.18	2.3307
16	463.85	433.56	11.8450
17	554.79	518.56	12.3089
18	583.67	545.56	7.0714
19	860.80	804.59	30.4740
20	1278.69	1195.19	599.0217
21	1707.55	1596.04	354.8414
22	1945.99	1818.91	967.6018
23	2017.38	1885.64	644.6705
24	2132.34	1993.10	626.3539

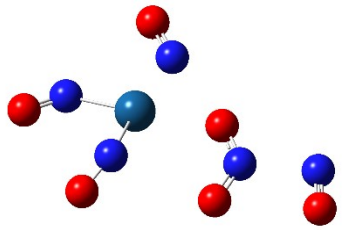
$[PtO(NO)_5]^+$

Isomer 5'a (Triplet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -845.999188

xyz coordinates:

Pt	-0.648207	0.059082	0.043101
N	-2.527745	-0.247687	-0.262178
O	-3.112934	-1.227546	-0.212079
N	-0.967310	2.14024	-0.118226
O	-1.936958	2.709272	0.046759
N	-0.083309	-1.792461	0.485681
O	-0.284492	-2.795948	-0.019429
N	2.453907	0.124295	-0.076736
O	2.482325	-1.03463	-0.324660
O	1.445922	0.819784	0.067907
N	4.303294	0.869643	0.100587
O	4.944670	-0.004253	-0.091724



Vibrational frequencies

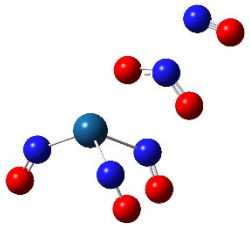
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	28.03	26.20	0.5203
2	35.40	33.09	1.0276
3	43.96	41.09	1.3812
4	52.70	49.25	1.7100
5	79.25	74.08	0.7115
6	91.08	85.13	1.8005
7	104.35	97.53	0.0629
8	116.84	109.21	0.1118
9	121.22	113.30	3.6319
10	128.41	120.03	0.0302
11	147.44	137.81	0.2847
12	168.35	157.36	0.2810
13	196.40	183.58	10.8425
14	218.40	204.14	25.6750
15	233.71	218.45	13.8206
16	272.12	254.35	114.8914
17	285.64	266.99	5.7470
18	349.50	326.68	34.3135
19	355.12	331.93	1.4247
20	426.16	398.33	3.0893
21	431.81	403.62	2.7764
22	544.51	508.96	15.5351
23	590.74	552.17	23.0983
24	853.49	797.75	16.3868
25	1345.13	1257.29	377.3382
26	1665.26	1556.52	167.0070
27	1874.15	1751.77	578.8732
28	1916.45	1791.30	1105.6983
29	1963.65	1835.43	349.1172
30	2112.64	1974.69	1052.1253

Isomer 5'b (Singlet, ΔE = 0.11 eV)

EE + ZPE / Hartree: -845.995270

xyz coordinates:

Pt	-0.702278	-0.384931	0.000530
N	-2.463349	-0.963033	-0.000768
O	-3.540176	-0.591507	-0.001896
N	-0.371525	1.094637	1.420325
O	-0.732106	2.157383	1.250199
N	-0.373249	1.094802	-1.420898
O	-0.733915	2.157322	-1.249952
N	2.429361	-0.254960	-0.000335
O	2.358565	0.931698	-0.000379
O	1.486780	-1.042060	-0.000080
N	4.324312	-0.877457	-0.000801
O	4.905702	0.058002	-0.000895



Vibrational frequencies

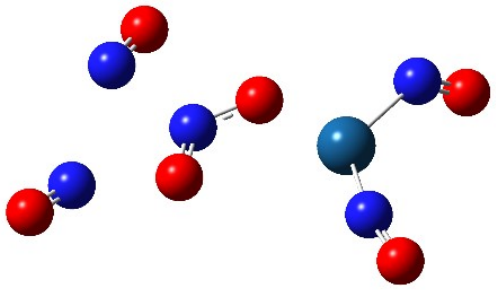
Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	22.08	20.64	0.2264
2	39.58	37.00	1.4594
3	40.75	38.09	2.2240
4	47.31	44.22	0.5439
5	57.78	54.01	0.0892
6	81.61	76.28	0.1477
7	101.75	95.10	0.5870
8	119.46	111.66	1.1286
9	145.69	136.18	2.6984
10	154.91	144.79	0.0236
11	182.31	170.40	0.0608
12	204.40	191.05	21.6109
13	210.94	197.17	15.5399
14	214.69	200.67	0.1450
15	286.39	267.69	158.6247
16	304.59	284.70	29.7587
17	338.86	316.73	0.0389
18	422.51	394.92	8.3062
19	429.84	401.77	1.2289
20	475.24	444.21	0.1578
21	521.76	487.69	6.4562
22	587.23	548.89	7.8950
23	593.72	554.95	32.3501
24	853.28	797.56	18.4186
25	1364.69	1275.58	352.0496
26	1656.72	1548.54	194.6985
27	1831.06	1711.49	810.7599
28	1898.55	1774.57	1531.1835
29	1966.54	1838.13	564.9832
30	2109.97	1972.19	975.9676

Isomer 5'c (Triplet, ΔE = 0.21 eV)

EE + ZPE / Hartree: -845.991459

xyz coordinates:

Pt	1.136558	-0.030192	0.113049
O	-0.900544	0.741030	0.188289
N	2.194083	-1.475540	0.061542
O	3.017876	-2.185664	-0.256843
N	-1.796986	-0.129122	0.321083
O	-1.554681	-1.292794	0.351359
N	-3.679372	0.782954	0.693199
O	-3.581995	1.859440	0.445290
N	-4.485922	-0.584626	-1.012066
O	-4.749198	-1.593275	-0.628764
N	1.638709	1.821896	-0.197206
O	2.050406	2.402018	-1.084788



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	17.60	16.45	0.1518
2	22.96	21.46	0.6037
3	33.11	30.95	1.3374
4	35.22	32.92	1.5568
5	46.66	43.61	0.9812
6	53.37	49.88	0.4962
7	73.81	68.99	1.2014
8	79.16	73.99	0.3194
9	104.71	97.87	2.3396
10	121.70	113.76	1.9440
11	140.93	131.73	23.7811
12	167.66	156.71	0.6579
13	184.69	172.63	3.6539
14	202.67	189.43	76.8942
15	261.54	244.46	31.3273
16	293.33	274.18	13.9100
17	362.46	338.80	10.0435
18	388.69	363.30	1.9909
19	426.72	398.86	3.2311
20	446.55	417.39	19.1209
21	477.69	446.50	10.4889
22	502.69	469.86	75.4997
23	547.56	511.81	2.6238
24	866.06	809.50	24.7697
25	1246.35	1164.96	406.3543
26	1626.98	1520.74	99.6070
27	1920.95	1795.51	853.9539
28	1967.40	1838.93	1725.5996
29	2005.90	1874.91	1055.6719
30	2115.53	1977.39	570.4615

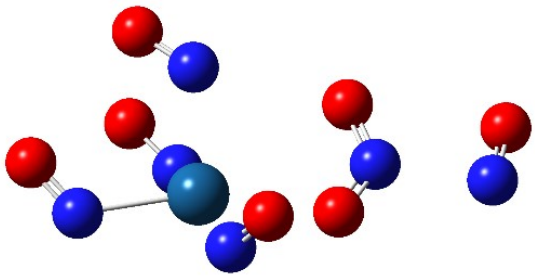
$[PtO(NO)_6]^+$

Isomer 6'a (Doublet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -976.212226

xyz coordinates:

Pt	0.588434	0.217668	-0.255194
N	0.807633	2.325002	-0.104841
O	0.507570	2.964478	0.787459
N	2.559817	-0.010570	-0.608859
O	3.131289	-0.860911	-0.095331
N	0.718568	-0.385142	1.764296
O	1.411495	-1.250599	2.002621
N	0.159449	-1.717048	-0.863439
O	0.715175	-2.632663	-0.464161
N	-2.554415	-0.019918	-0.025166
O	-2.376682	-1.052499	0.535603
O	-1.693804	0.746395	-0.442874
N	-4.493795	0.355841	-0.238100
O	-4.979871	-0.516103	0.231423



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	25.05	23.42	0.7330
2	32.98	30.83	0.7069
3	35.15	32.85	0.4393
4	46.65	43.60	0.4970
5	56.19	52.52	0.6014
6	69.52	64.98	1.3147
7	78.26	73.15	0.2968
8	95.48	89.24	0.0948
9	98.93	92.47	1.2216
10	110.22	103.02	0.5913
11	114.91	107.40	2.7379
12	138.19	129.16	0.7513
13	154.84	144.73	0.4116
14	159.91	149.47	3.6978
15	184.33	172.30	2.3121
16	189.86	177.46	10.5715
17	199.07	186.07	9.8259
18	211.30	197.50	2.6577
19	237.35	221.85	10.5690
20	251.45	235.03	105.3518
21	280.86	262.52	105.1632
22	323.94	302.79	3.9823
23	369.03	344.93	0.3217
24	431.22	403.06	1.3798
25	446.20	417.06	2.1328
26	498.04	465.52	3.5945
27	598.54	559.46	24.4555
28	608.65	568.91	25.9129

29	851.09	795.51	19.9530
30	1369.15	1279.74	374.8747
31	1661.78	1553.27	178.3492
32	1814.08	1695.62	949.1417
33	1852.89	1731.89	830.0134
34	1912.78	1787.87	1156.1885
35	1961.33	1833.26	257.5190
36	2098.66	1961.62	1045.9376

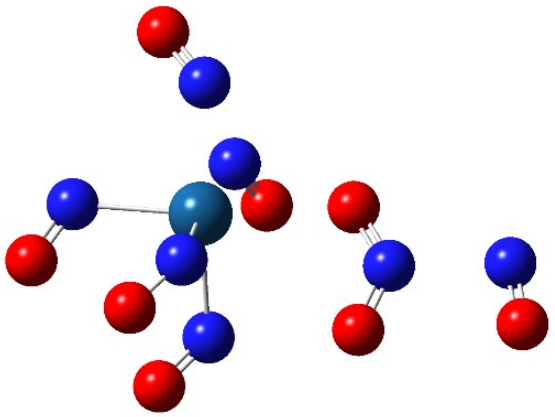
$[PtO(NO)_7]^+$

Isomer 7'a (Triplet, ΔE = 0.00 eV)

EE + ZPE / Hartree: -1106.423855

xyz coordinates:

Pt	0.566071	0.135955	-0.034867
N	0.783056	1.784202	1.417397
O	0.346097	1.702328	2.463138
N	2.600442	-0.275677	-0.014068
O	2.910907	-1.374209	0.060706
N	0.154429	-1.188583	1.548551
O	0.612429	-2.236023	1.549981
N	0.147816	-1.359567	-1.455765
O	0.669461	-2.373192	-1.389355
N	-2.675081	0.093241	-0.096530
O	-2.574607	-1.090480	-0.024900
O	-1.772192	0.912899	-0.105762
N	-4.564555	0.635699	-0.216286
O	-5.11708	-0.321951	-0.188944
N	0.841358	1.646276	-1.609529
O	1.779257	2.286424	-1.651961



Vibrational frequencies

Mode #	IR frequency (unscaled) / cm^{-1}	IR frequency (scaled) / cm^{-1}	Intensity / km mol^{-1}
1	25.33	23.68	0.6717
2	31.94	29.85	0.5947
3	35.09	32.80	0.8910
4	39.84	37.24	0.1505
5	50.83	47.51	0.2216
6	66.65	62.30	0.1760
7	73.49	68.69	0.3471
8	82.35	76.97	0.3530
9	85.58	79.99	0.6372
10	89.87	84.00	1.8679
11	90.95	85.01	4.1825
12	101.89	95.24	3.3777
13	105.75	98.85	2.9681
14	118.03	110.32	0.6950
15	129.46	121.00	3.2567
16	137.15	128.19	3.4321
17	153.05	143.05	0.3190

18	159.94	149.49	5.0121
19	164.01	153.30	6.2272
20	171.07	159.90	7.5428
21	185.37	173.27	3.6551
22	199.84	186.79	10.3493
23	221.61	207.14	10.8556
24	241.58	225.81	96.9457
25	266.83	249.41	92.1374
26	293.90	274.71	4.4589
27	379.35	354.58	0.4035
28	395.82	369.97	0.5150
29	433.29	404.99	1.4754
30	459.09	429.11	0.3186
31	488.00	456.13	1.3168
32	579.47	541.63	14.5074
33	609.31	569.52	30.4077
34	847.94	792.57	21.2128
35	1383.68	1293.33	350.7810
36	1665.41	1556.66	157.7548
37	1817.57	1698.88	923.3535
38	1844.55	1724.10	846.8527
39	1898.05	1774.11	1543.4122
40	1925.33	1799.61	598.0597
41	1968.23	1839.70	192.8286
42	2081.66	1945.72	1027.6712

3. Energies from single point calculations for BDE calculation following loss of NO from N_2O_3

These structures were generated by performing an energy calculation on the optimised structure following the removal of the NO in the N_2O_3 moiety.

Daughter from Isomer 4'f: EE + ZPE / Hartree: -585.53226

Daughter from Isomer 5'a: EE + ZPE / Hartree: -715.760038

Daughter from Isomer 6'a: EE + ZPE / Hartree: -845.974954

Daughter from Isomer 7'a: EE + ZPE / Hartree: -976.190783

4. Calculating energy of formation for $[Pt(NO)_n]^+ \rightarrow [Pt(NO_2)(NO)_{n-3}]^+ + N_2O$

Energies of lowest energy structures relevant to the formation of $[PtNO_2(NO)_{n-3}]^+$ formation.

Calculated EE+ZPE for N_2O (neutral, singlet, B3P86/def2TZVP level of theory): 185.115869 Hartree

Isomer energies calculated using zero-point corrected electronic energy (EE + ZPE).

ΔH_f is calculated as: $E([Pt(NO_2)(NO)_{n-3}]^+) + E(N_2O) - E([Pt(NO)_n]^+)$

n	$[Pt(NO)_n]^+$ isomer	$E[Pt(NO)_n]^+$ / Hartree	$[Pt(NO_2)(NO)_{n-3}]^+$ isomer	$E[Pt(NO_2)(NO)_{n-3}]^+$ / Hartree	ΔH_f / Hartree	ΔH_f / eV
2	2a	-379.965483	PtO^+	-194.720362	0.129252	3.517
3	3a	-510.199931	1'a	-325.010861	0.073201	1.992
4	4c	-640.41082	2'a	-455.309389	-0.014438	-0.393
5	5c	-770.624597	3'b	-585.5529	-0.046893	-1.276
5	5c	-770.624597	3'c	-585.547831	-0.039102	-1.064
6	6c	-900.83951	4'a	-715.771536	-0.047895	-1.303
6	6c	-900.83951	4'f	-715.769998	-0.046357	-1.261
7	7c	-1031.045734	5'a	-845.999188	-0.069323	-1.886
7	7c	-1031.045734	5'b	-845.99527	-0.065405	-1.780
7	7d	-1031.044815	5'a	-845.999188	-0.070242	-1.911
7	7d	-1031.044815	5'b	-845.99527	-0.066324	-1.805

5. Gaussian deconvolution of IRPD spectra

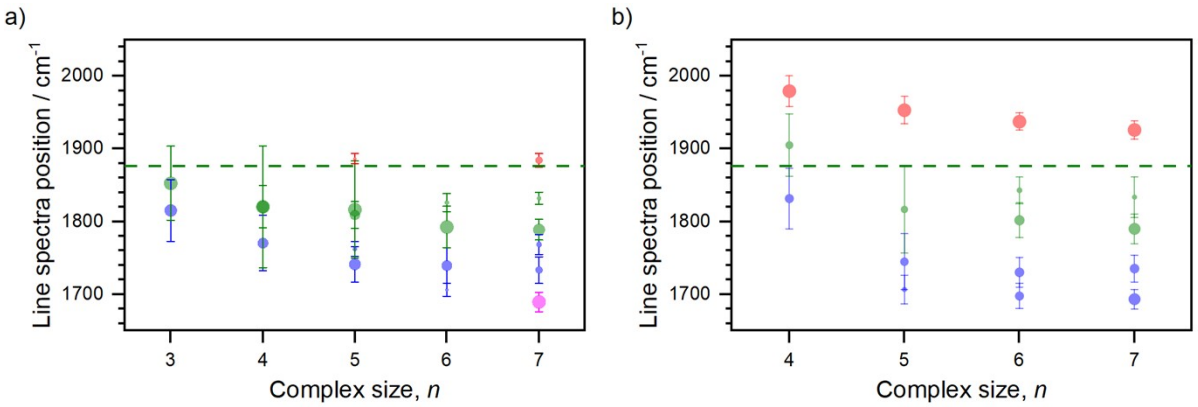


Figure S2: Line spectra peak positions plotted as a function of cluster size, *n*, for **a)** $[Pt(NO)_n]^+$ and **b)** $[PtO(NO)_n]^+$. The uncertainties in peak positions correspond to the FWHM of the Gaussian curves used for peak deconvolution. The area of the spots for each complex size is scaled internally to the normalised amplitude of the largest Gaussian used in the deconvolution. The green dashed line indicates the position of the free NO vibrational frequency at 1875.84 cm^{-1}.[1] In panel **a)**, for $n = 7$, the peak arising from the localised stretch of the $(NO)_2$ dimer moiety is highlighted in magenta, with the symmetric in-phase "breathing" motion for $[Pt(NO)_5]^+$ and $[Pt(NO)_7]^+$ highlighted in pink.

6. Comparison of IRPD and simulated spectra

The five lowest energy structures calculated using DFT for the different complexes are provided here, along with the IRPD spectra for them. Other figures within Section 6 also illustrate the vibrational modes of the complexes that best describe the experimental data.

a. $[Pt(NO)_{3,4}]^+$

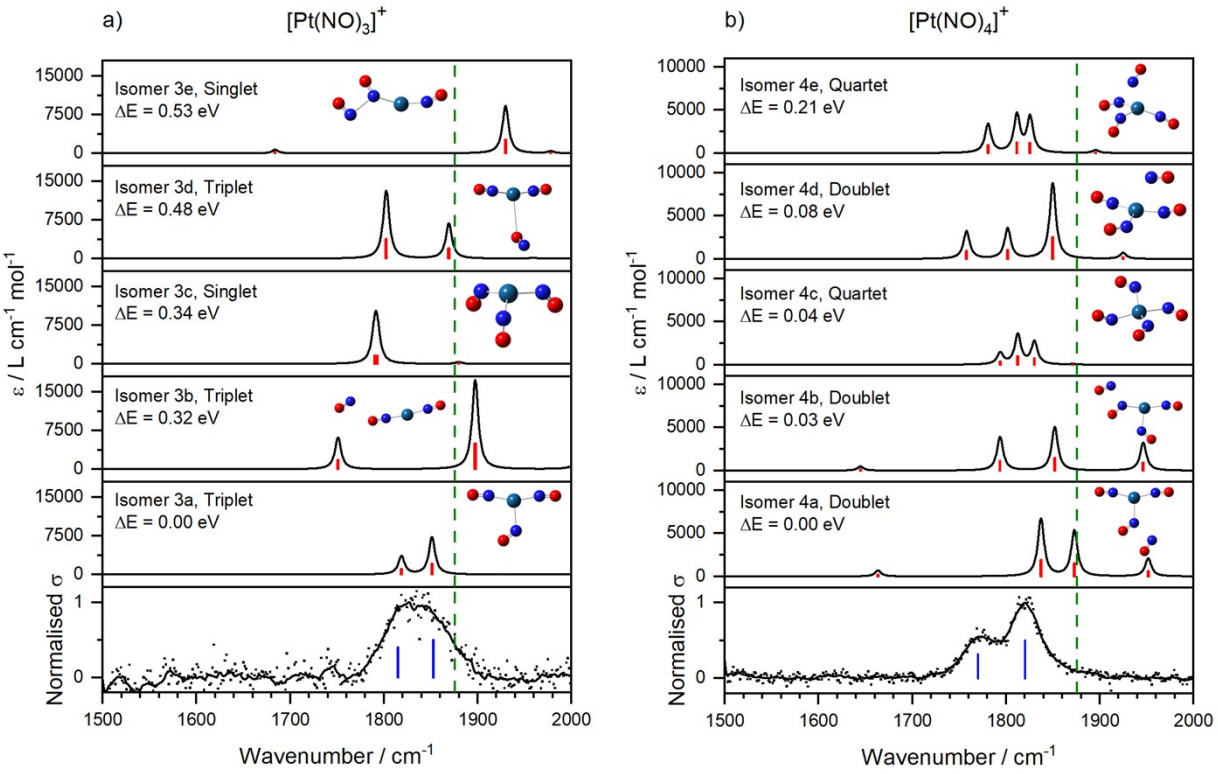


Figure S3: Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures for the five lowest-lying isomers for **a)** $[Pt(NO)_3]^+$, and **b)** $[Pt(NO)_4]^+$. The green dashed line indicates the free NO stretch at 1875.84 cm^{-1}.[1]

b. $[Pt(NO)_{5\text{-}7}]^+$

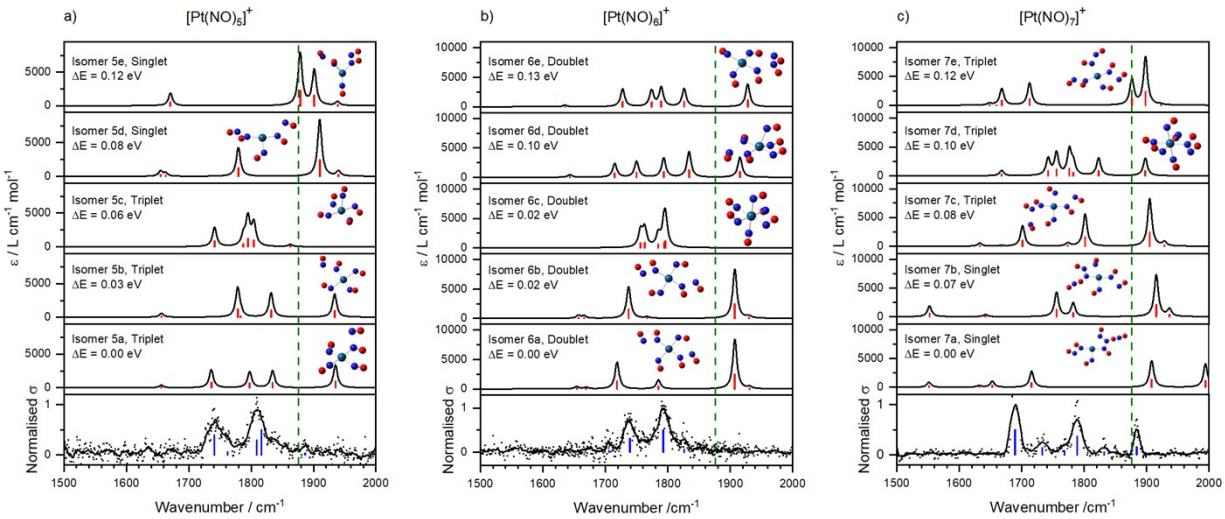


Figure S4: Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures (top panels) for the five lowest-lying isomers for **a)** $[Pt(NO)_5]^+$, **b)** $[Pt(NO)_6]^+$, and **c)** $[Pt(NO)_7]^+$. The green dashed line indicates the free NO stretch at 1875.84 cm^{-1}.[1]

c. Calculated $[Pt(NO)_{5-7}]^+$ complexes: square-pyramid/octahedral with $(NO)_2$ dimer.

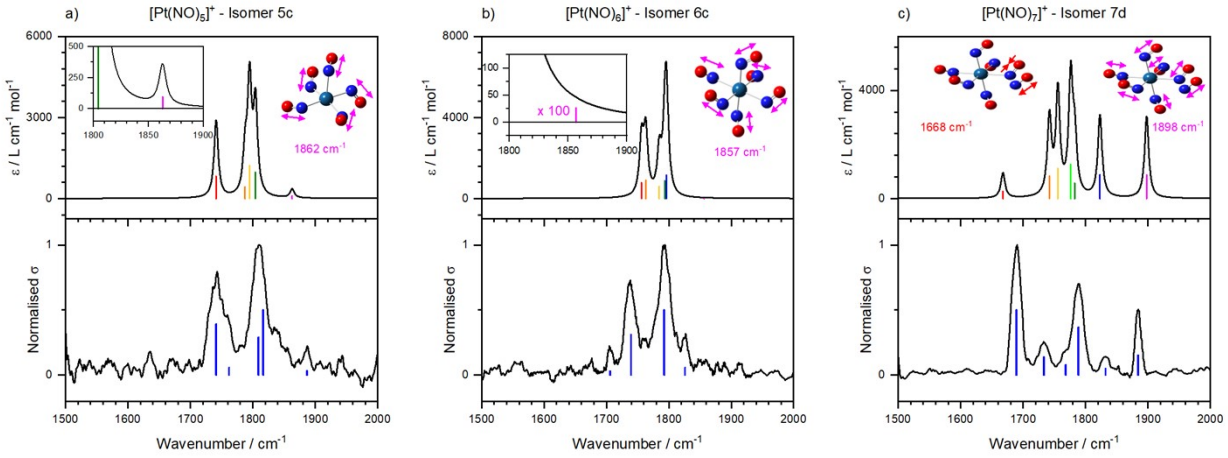


Figure S5: Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures (top panel), for the lowest-lying isomers for **a)** Isomer 5c, **b)** Isomer 6c, and **c)** Isomer 7d for $[Pt(NO)_5]^+$, $[Pt(NO)_6]^+$, and $[Pt(NO)_7]^+$, respectively. Within **a)** and **b)**, there is an inset for the range 1800-1900 cm^{-1} to highlight the symmetric in-phase "breathing" motion. The colour-coded mode vectors on top of the structures highlight the key motions for these $[Pt(NO)_n]^+$ complexes.

d. $[PtO(NO)_{4,5}]^+$

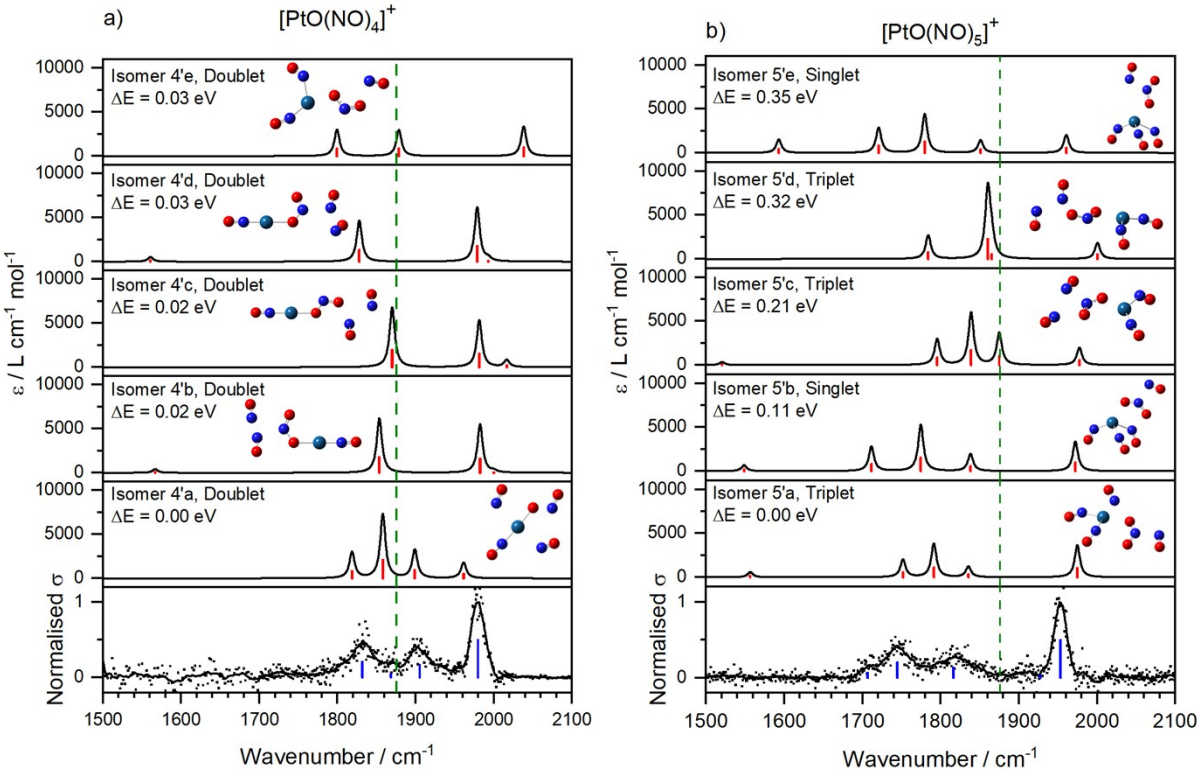


Figure S6: Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures for the five lowest-lying isomers for **a)** $[PtO(NO)_4]^+$, and **b)** $[Pt(NO)_5]^+$. The green dashed line indicates the free NO stretch at 1875.84 cm^{-1}.[1]

e. $[PtO(NO)_4]^+$ vibrational modes.

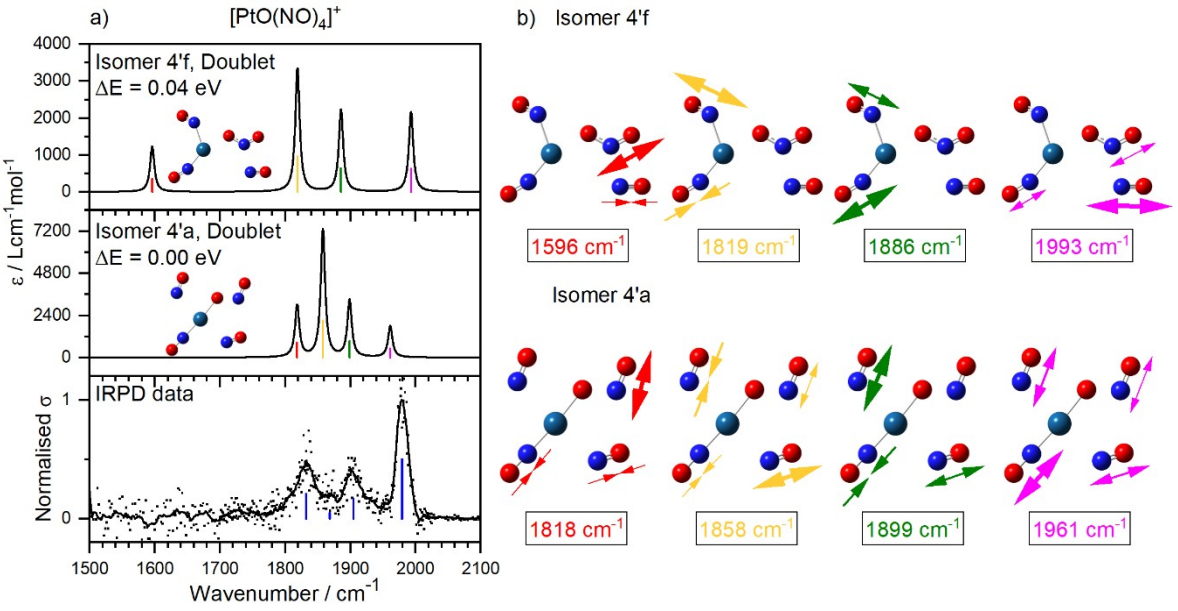


Figure S7: **a)** Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures (top panels) for the two low-lying isomers that best fit the experimental spectrum of $[PtO(NO)_4]^+$. **b)** The vibrational modes for Isomers 4'a and 4'f illustrated using arrows. The colours match the line spectra that appear in **a)**. The thickness of the arrow indicates the relative amplitude of the vibration for the molecule within the specific normal mode.

f. $[PtO(NO)_{6\text{-}7}]^+$

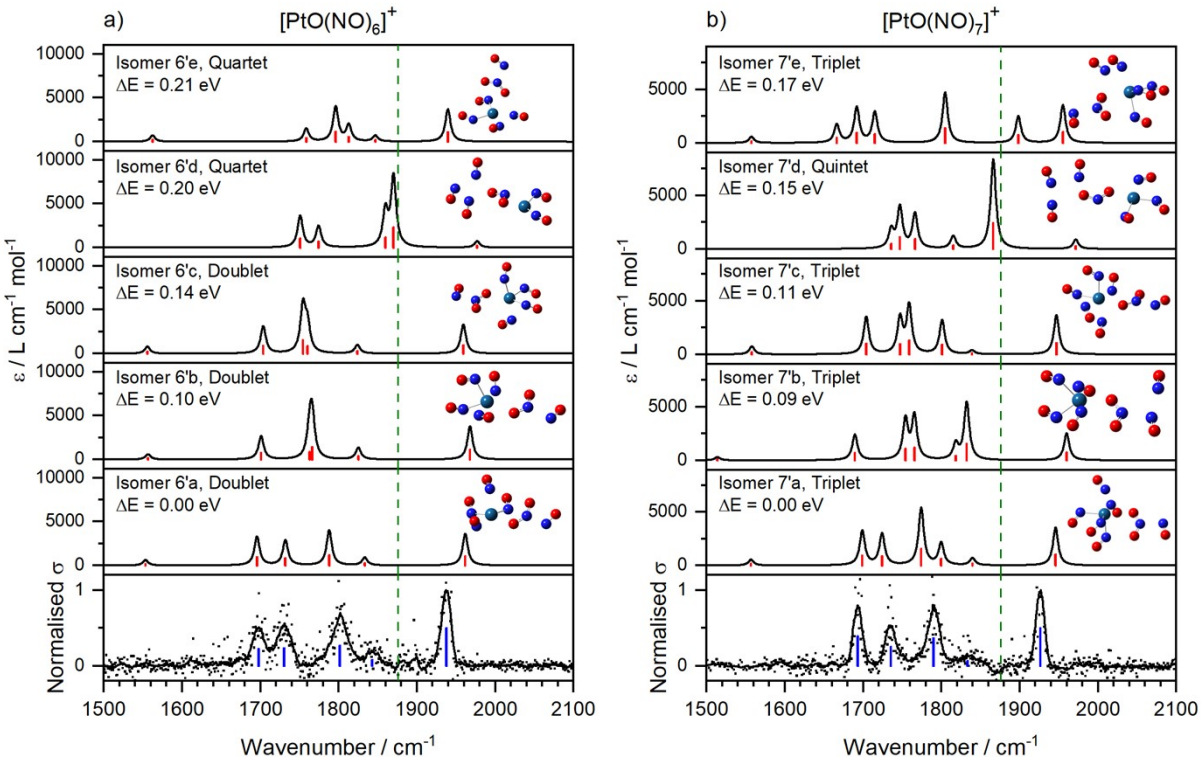


Figure S8: Experimental IRPD spectra (bottom panel), along with the simulated IR spectra and structures (top panels) for the five lowest-lying isomers for **a)** $[PtO(NO)_6]^+$, and **b)** $[PtO(NO)_7]^+$. The green dashed line indicates the free NO stretch at 1875.84 cm^{-1}.[1]

7. Structural properties of $[Pt(NO)_n]^+$ complexes

In order to show the $[Pt(NO)_n]^+$ complex can accommodate up to six ligands in the primary coordination shell and adopts a near-perfect octahedral structure, it was helpful to show how the NO bond length and Pt-N=O angle changes as a function of complex size, *n*. For *n* = 6, the distribution of NO bond lengths and Pt-N=O is at its narrowest. For *n* = 7, the structure adopts an octahedral structure, with the seventh NO adding into the second coordination.

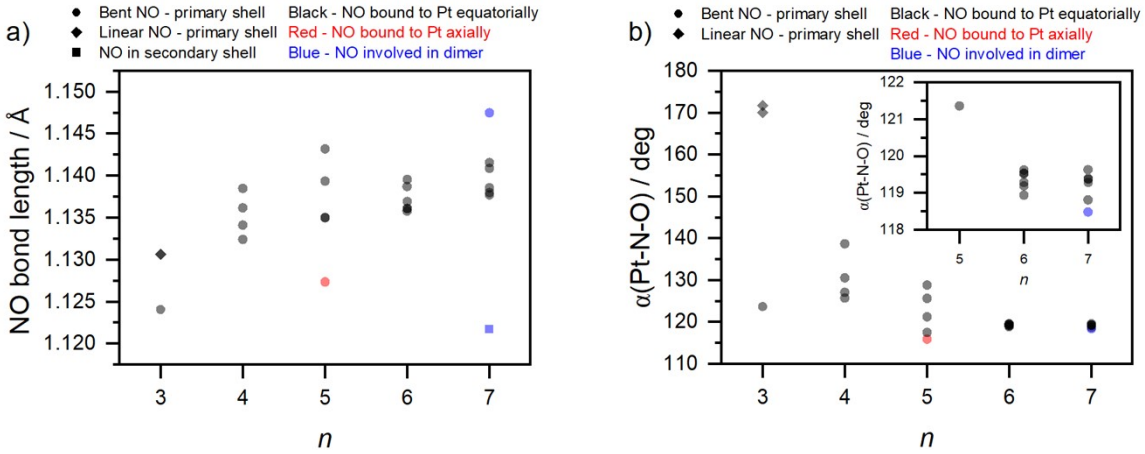


Figure S9: a) NO bond length vs cluster size, *n*, for the calculated structures which best fit the experiment IRPD spectra for $[Pt(NO)_n]^+$. **b)** Pt-N-O bond angle, α, versus cluster size, *n*, for the calculated structures which best fit the experiment IRPD spectra for $[Pt(NO)_n]^+$. The different types of NO molecule are highlighted using the different symbols and colours. The symbols illustrate whether the NO is in the primary or secondary shell, and whether it is bound in a linear or bent fashion, and the colours illustrate where the NO is in the complex. For *n* = 7, the data is from Isomer 7d (octahedral core).

8. Structures of N_2O_3 moiety within $[PtO(NO)_n]^+$ complex

The IRPD spectra and quantum chemical calculations for the $[PtO(NO)n]^+$ identified the emergence of a N2O3 moiety, previously invoked in mass spectrometric studies,2 with the complexes taking the structural form $[Pt(NO)_n(N_2O_3)]^+$. The N_2O_3 unit is comprised of an NO molecule and an NO_2 molecule that interact through the nitrogen atoms to form a planar structure. Bond length and angle contractions can be explained through the removal of antibonding population when the two radicals are paired, forming a singlet species, and the delocalisation of the electrons across the π system that forms between the two molecules, with some charge transfer from the NO to the NO_2.[3] The bond lengths and angles for the isolated N_2O_3, calculated using DFT, where ascertained, as well as for the moiety within the $[Pt(NO)_n(N_2O_3)]^+$ complexes.

a. Calculated structure of isolated N_2O_3

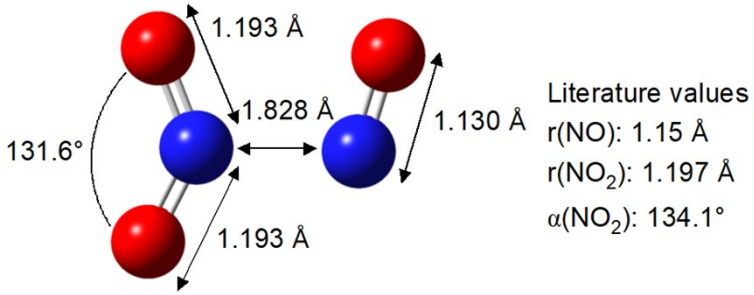


Figure S10: Lowest energy structure for neutral N_2O_3 (2S+1 = 1). The bond lengths and angles within the N_2O_3 moiety are shown. These are compared to the literature values for the free NO bond length, and the free NO_2 bond lengths and angle.

b. Structure of N_2O_3 within $[PtO(NO)_7]^+$

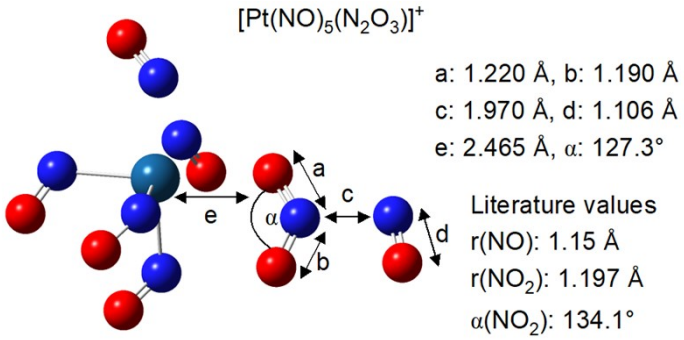


Figure S11: The structure of Isomer 7'a for $[PtO(NO)_7]^+$, which adopts the form $[Pt(NO)_5(N_2O_3)]^+$. The bond lengths and angles within the N_2O_3 moiety are illustrated and labelled, with literature values for the bond length of the free NO, and also for the bond length and angle for the free NO_2 being provided. The N_2O_3 moiety is planar, and is rotated approximately 44° out of the equatorial plane formed by the NO directly opposite it, two other NO molecules and the Pt^+ core.

c. Properties of N_2O_3 moiety as a function of complex size, n.

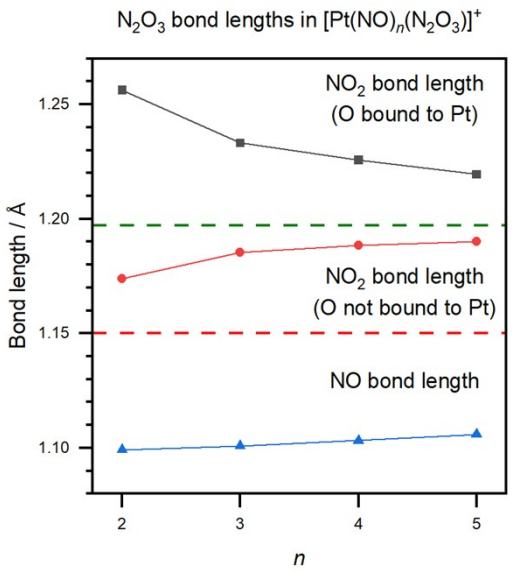


Figure S12: The change in the NO and NO_2 lengths within the N_2O_3 moiety in the structures $[Pt(NO)_n(N_2O_3)]^+$ as a function of *n*. The NO_2 bond lengths are separated to distinguish which oxygen atom is binding to the Pt^+ core in the calculated structure (in each case, the lowest energy calculated structure containing the N_2O_3 moiety). The red dashed lined illustrates the free NO bond length (1.15 Å), and the green dashed line illustrates the free NO_2 bond length (1.197 Å). As the complex size increases, the calculated bond lengths are tending towards the known values for the free molecules, as well as towards the values calculated for the isolated N_2O_3, as shown in **Figure S10**.

9. Binding energies

Bond dissociation energies (BDE) for the reaction: $[PtO_x(NO)_n]^+ \rightarrow [PtO_x(NO)_{n-1}]^+ + NO$

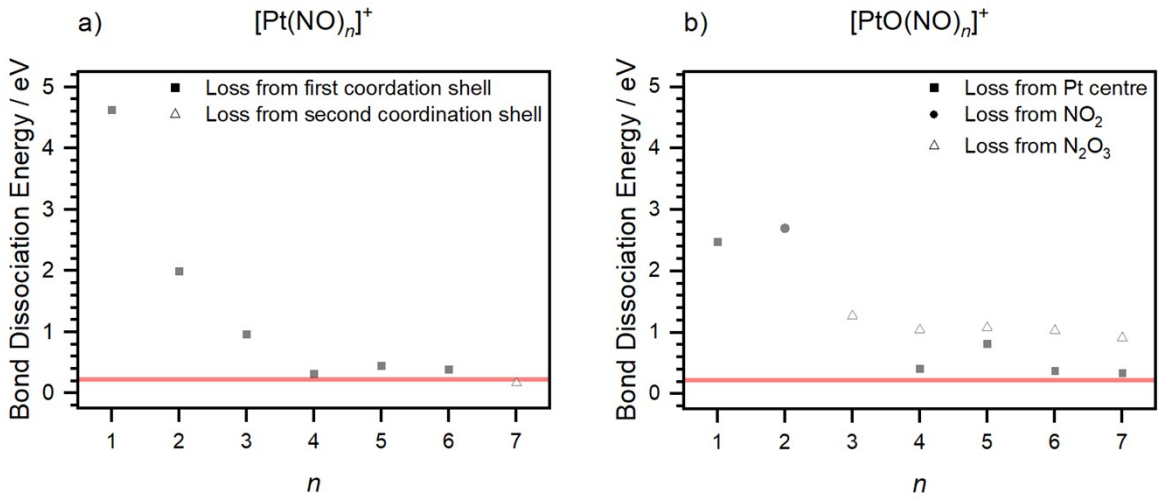


Figure S13: Bond dissociation energy (BDE) for the reaction $[PtO_x(NO)_n]^+ \rightarrow [PtO_x(NO)_{n-1}]^+ + NO$, for increasing cluster size, n, for **a)** $x = 0$, and **b)** $x = 1$. For $n = 1, 2$ for both Pt and PtO, the BDE is calculated using the lowest energy computed structures. In **a)**, for n = 3-6, the BDE has been calculated using the computed structures that best fit with the experimental data. For $n = 7$, the BDE is calculated by removing the NO in the second coordination shell from Isomer 7'd. In **b)**, for n = 1-2, the BDE is calculated using the lowest energy structures. For $n = 3$, the BDE is calculated for the lowest energy structure with an N_2O_3 moiety. For n = 4-7, the BDE are calculated by removing an NO from either the Pt centre (black squares) or the N_2O_3 unit (white triangle) from the computed structures that best fit with the experimental data (energies from Section 3). The red shaded region indicates the range of IR photon energies across the OPO/OPA scan range used to record the $[PtO_x(NO)_n]^+$ IRPD spectra (1500-2100 cm^{-1}).

10. Population analysis

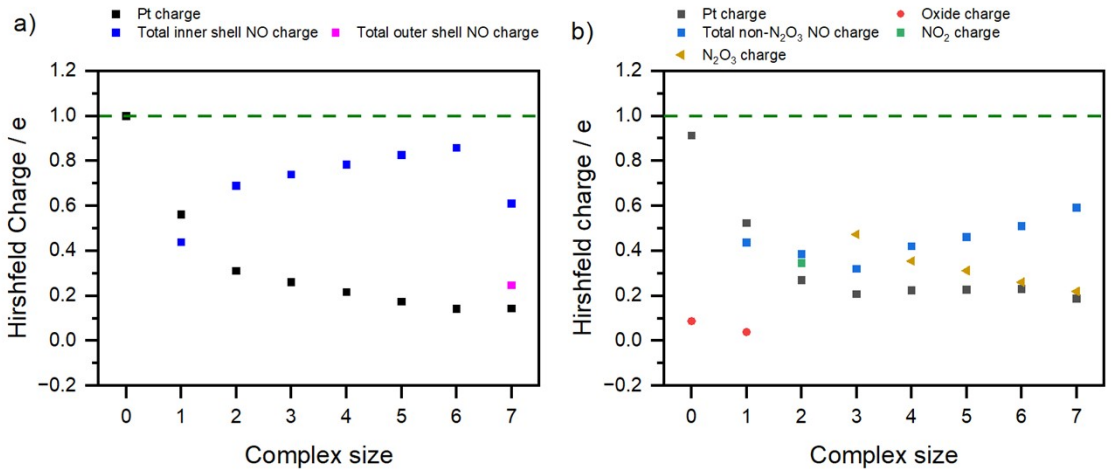


Figure S14: Hirshfeld charges for the different components of **a)** $[Pt(NO)_n]^+$ and **b)** $[PtO(NO)_n]^+$ as a function of *n* using the complexes that best fit the experimental IRPD data. The different colours representing the distinct moieties and metal cores are shown at the top of each panel. The green dashed line is used to illustrate the overall charge of the complexes (+1).

(1) Herzberg, G. *Molecular Spectra and Molecular Structure, Volume I. Spectra of Diatomic Molecules*; Krieger Publishing Company, 1989.

(2) Martin, M. Z.; Desai, S. R.; Feigerle, C. S.; Miller, J. C. Chemistry in Clusters: Synthesis of $NO^+(N_2O_3)_n$ and $NO_2^+(N_2O_3)_n$ Species. *The Journal of Physical Chemistry* **1996**, *100* (20), 8170–8174. DOI: 10.1021/jp953337+.

(3) Harcourt, R. D.; Wolynec, P. P. A Parametrized Valence-Bond Study of the Origin of the Long, Weak N−N Bond of asym-N2O3. *The Journal of Physical Chemistry A* **2000**, *104* (10), 2138–2143. DOI: 10.1021/jp9938314.