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

Supporting Information

Free electron laser infrared action spectroscopy of nitrous oxide binding to platinum clusters, $Pt_n(N_2O)^+$

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A Coordinates and Geometries of Calculated Structures

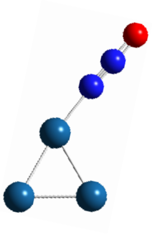
Given below are the coordinates of main reaction products observed in the Pt_n^+ + N_2O reaction for n=3-6 calculated using Gaussian[1] suite of programs at the def2TZVP[2]/TPSSh[3, 4] level. Also implemented were the GD3-BJ[5] dispersion term, which accounts for weak intramolecular interactions and the quasirelativistic Wood-Boring effective core potential (WB-ECP)[6] that freezes 60 inner electrons and introduces relativistic corrections for Pt atoms.

For n=3-5, N_2O is observed molecularly-bound to the metal cluster via the N atom. For n=6, the cluster reacts with N_2O to generate the Pt_6O^+ product.

Also, given below are the geometries for 2S +1 = 6 IRC pathway for Pt_5^+ + N_2O reaction outcome.

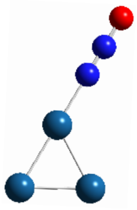
I. $Pt_3(N_2O)^+$

a) (2S +1 = 2)



Pt	-0.93779200	-0.63074800	0.00417600
Pt	1.55547200	-0.76759000	-0.00321100
Pt	0.52438600	1.38280400	0.00059700
O	-5.11894800	0.32170800	-0.01540000
N	-3.98427400	0.04334900	-0.00571300
N	-2.89138000	-0.23791600	0.00590000

b) (2S +1 = 4)

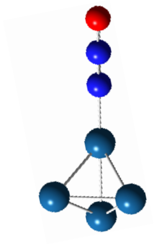


Pt	0.62076600	-1.38245200	0.00000000
Pt	1.53599900	0.87415300	0.00128500
Pt	-0.97916400	0.50092600	-0.00197700
O	-5.26453800	-0.13575100	0.00682800
N	-4.11091500	0.03556000	0.00248400
N	-2.99431300	0.20173700	-0.00258100

Figure S1. a) Lowest energy doublet and b) low-lying (+0.11 eV) quartet structures of molecularly-bound $Pt_3(N_2O)^+$ – the main reaction product observed experimentally.

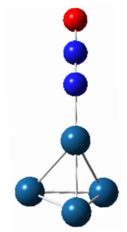
II. $Pt_4(N_2O)^+$

a) (2*S* +1 = 4)



Pt	0.53137100	0.88276400	1.27656800
Pt	0.53138600	0.88240500	-1.27681100
Pt	1.32125100	-1.17013300	0.00017800
Pt	-1.16655100	-0.60650600	0.00006000
O	-5.39729200	0.26259400	-0.00001100
N	-4.25188700	0.02750600	0.00002900
N	-3.14573200	-0.19979900	0.00004000

b) (2*S* +1 = 2)

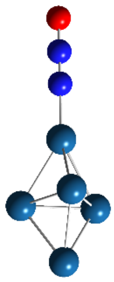


Pt	0.57927000	0.00748300	1.54431000
Pt	0.46313600	-1.47263300	-0.55045900
Pt	-1.15946900	0.54783000	-0.34298700
Pt	1.32243000	0.92713800	-0.67647700
O	-5.34891700	-0.23509200	0.23938300
N	-4.20887400	-0.02316700	0.08209000
N	-3.10930400	0.18245500	-0.07027600

Figure S2. a) Lowest energy quartet and b) low-lying (+0.24 eV) doublet structures of molecularly-bound $Pt_4(N_2O)^+$ – the main reaction product observed experimentally.

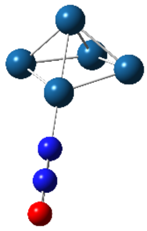
III. $Pt_5(N_2O)^+$

a) (2*S* +1 = 4)



Pt	-0.29114500	-0.12343700	-1.47921800
Pt	-0.29185100	1.34283600	0.63276900
Pt	-2.42459900	-0.00025200	-0.00040500
Pt	1.88059800	0.00035000	0.00043100
Pt	-0.29153900	-1.21934800	0.84659600
O	6.13486100	-0.00050500	-0.00097200
N	4.96295300	-0.00095900	-0.00073000
N	3.83231700	-0.00012000	-0.00009600

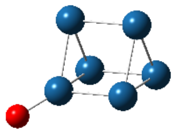
b) (2*S* +1 = 6)



Pt	0.13734500	1.94241500	-0.16681200
Pt	0.14090600	-1.94234400	-0.16739000
Pt	1.47113100	0.00138600	-1.17385500
Pt	-1.45239600	-0.00147500	0.39621900
Pt	0.94607500	0.00056500	1.33715500
O	-5.42461200	-0.00097800	-1.22729700
N	-4.34555300	-0.00185900	-0.77419500
N	-3.30613400	-0.00310800	-0.33384300

Figure S3. a) Lowest energy quartet and b) low-lying (+0.20 eV) sextet structures of molecularly-bound $Pt_5(N_2O)^+$ – the main reaction product observed experimentally.

IV. $Pt_6(O)^+$



Pt	1.54595500	1.06468100	0.00009700
Pt	-1.48627700	-0.42631500	-1.27330500
Pt	-0.85298100	1.69697200	0.00140500
Pt	-1.48394600	-0.42811900	1.27461100
Pt	0.98840800	-1.06065300	1.27764000
Pt	0.98633100	-1.05845200	-1.28051400
O	2.94945900	2.06589500	0.00065700

Figure S4. Lowest energy ($2S + 1 = 6$) calculated Pt_6O^+ structure – the dominant reaction product observed following the $Pt_6^+ + N_2O$ reaction.

V. IRC for the $Pt_5^+ + N_2O$ Reaction Showing Sextet Structures

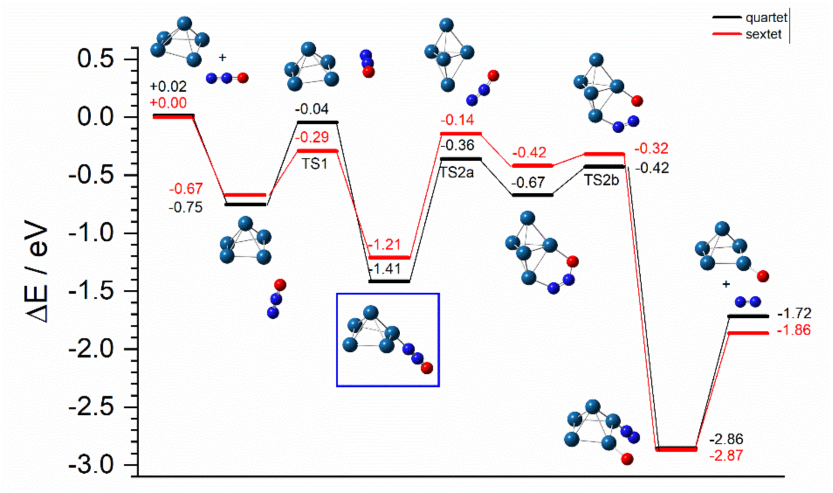


Figure S5. IRC pathway for the $Pt_5^+ + N_2O$ reaction; as Figure 3b) in the main manuscript but with calculated sextet structures shown.

B. N_2O Binding Energies and Bond Lengths

Given below are the calculated binding energies of N_2O to Pt_n^+ (n=1-5) along with Pt-N, N=N, and N=O bond lengths for the lowest energy molecularly-bound structures.

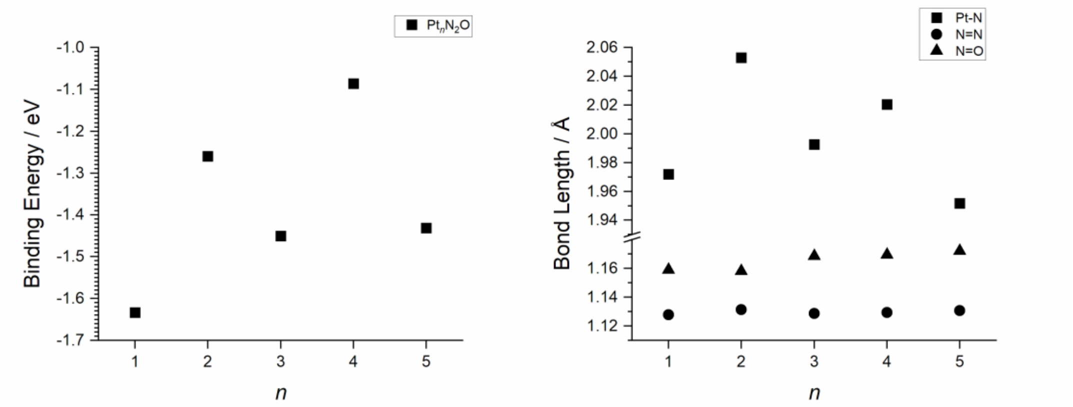


Figure S6. Calculated N_2O binding energies and bond lengths of lowest-energy N-bound $Pt_nN_2O^+$ structures.

References

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