Infrared Action Spectroscopy of Nitrous Oxide on Cationic Gold and Cobalt Clusters

Supporting Information

Ethan M. Cunningham[1], Alice E. Green[1], Gabriele Meizyte[1], Alexander S. Gentleman[1], Peter W. Beardsmore[1], Sascha Schaller[2], Kai M. Pollow[3], Karim Saroukh[3], Marko Förstel[3], Otto Dopfer[3]*, Wieland Schöllkopf[3], André Fielicke[2,3]* & Stuart R. Mackenzie[1]*

1. Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom
2. Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany
3. Institut für Optik und Atomare Physik, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Contents

Time-of-Flight Mass Spectra

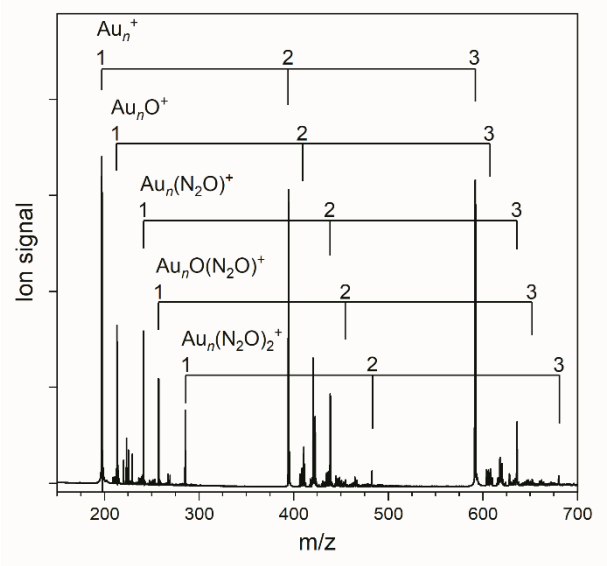

Figure S1. Time-of-flight mass spectrum illustrating the production of Au_n^+ and Au_nO^+ (n = 1-3) clusters with attached nitrous oxide obtained following laser ablation of a gold rod in the presence of a helium carrier gas (10 bar backing pressure) and reaction gas of N_2O delivered downstream *via* the reaction channel.

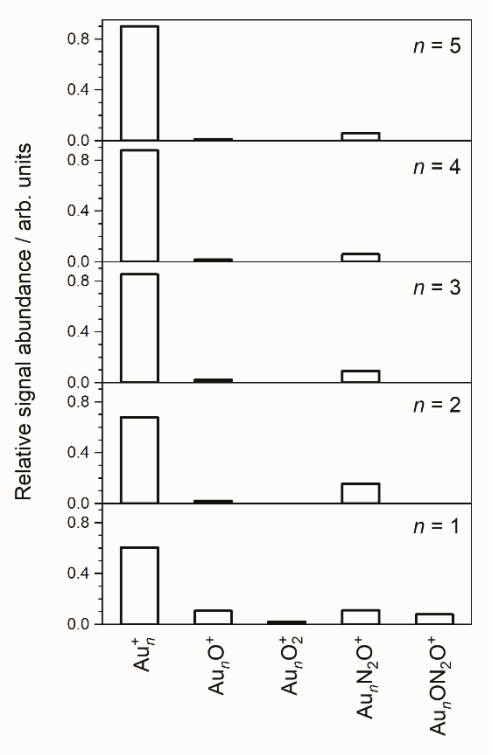

Figure S2. Bar graph illustrating the relative abundances of each of the ion signals (from the time-of-flight mass spectrum) Au_n^+, Au_nO^+, $Au_nO_2^+$, $Au_nN_2O^+$, and $Au_nON_2O^+$ (n = 1-5).

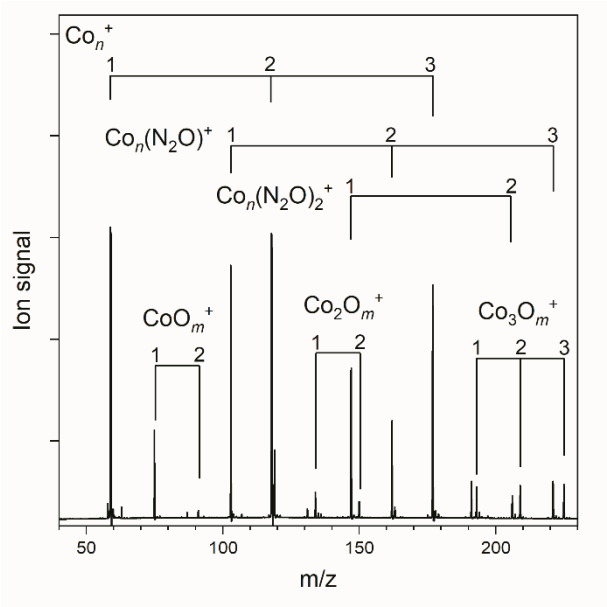

Figure S3. Time-of-flight mass spectrum illustrating the production of Co_n^+ (*n* = 1-3) with attached nitrous oxide and $Co_nO_m^+$ (*n* = 1-3; *m* = 1-3) obtained following laser ablation of a cobalt rod in the presence of a helium carrier gas (10 bar backing pressure) and reaction gas of N_2O delivered downstream *via* the reaction channel.

Simulated Infrared Spectra

Simulated spectra are illustrated together with the experimental IR-MPD spectra, and are scaled by a factor of 0.955, derived from the stretching frequencies of isolated nitrous oxide.[1]

$Au(N_2O)^+$

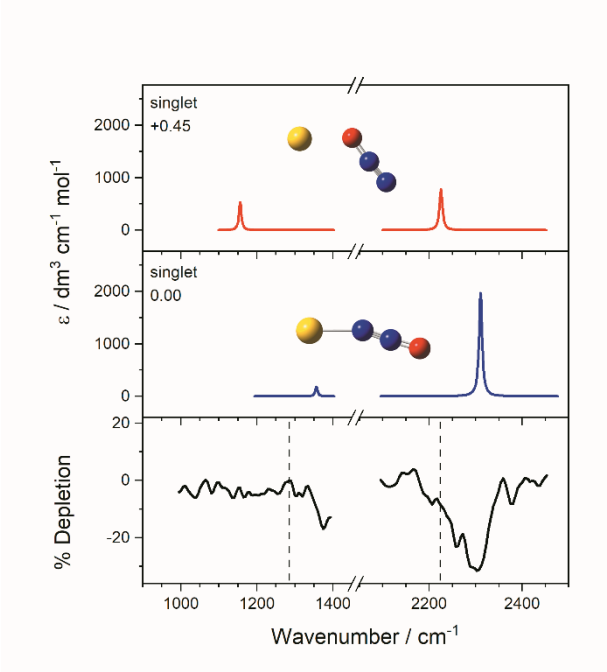

Figure S4. IR-MPD depletion spectrum of $Au(N_2O)^+$, along with simulated IR spectra of singlet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines at 1285 and 2224 cm^{-1} indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O, respectively.[1]

$Au_2(N_2O)^+$

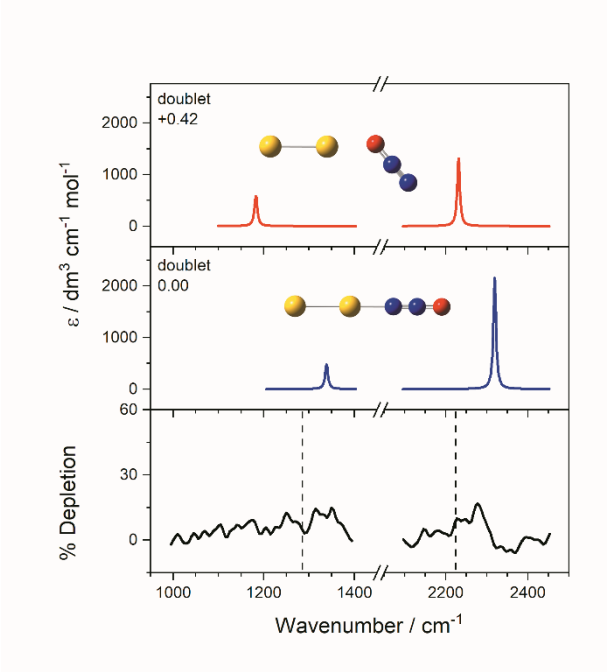

Figure S5. IR-MPD depletion spectrum of $Au_2(N_2O)^+$, along with simulated IR spectra of doublet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines at 1285 and 2224 cm^{-1} indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O, respectively.[1]

$Au_5(N_2O)^+$

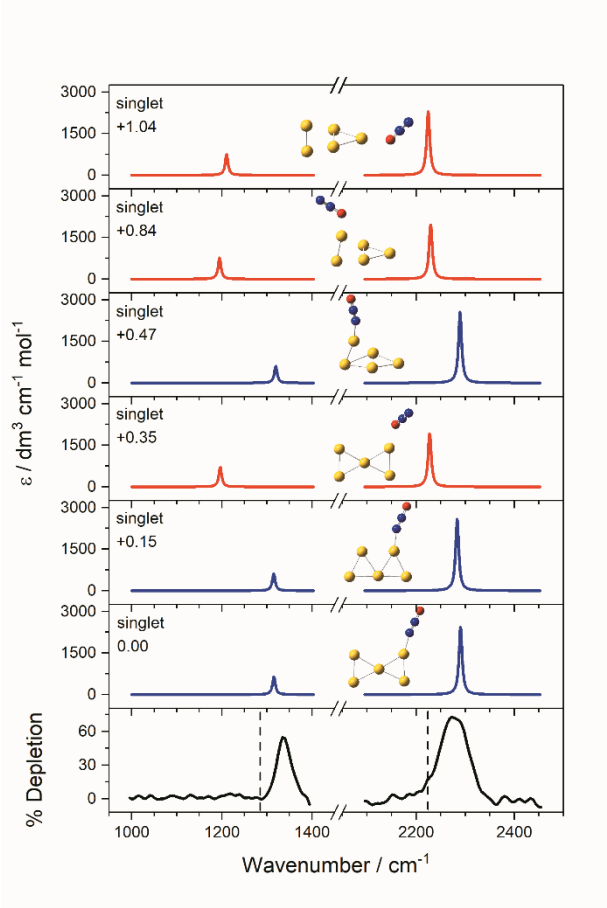

Figure S6. IR-MPD depletion spectrum of $Au_5(N_2O)^+$, along with simulated IR spectra of singlet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines at 1285 and 2224 cm^{-1} indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O, respectively.[1]

$Co_4(N_2O)^+$

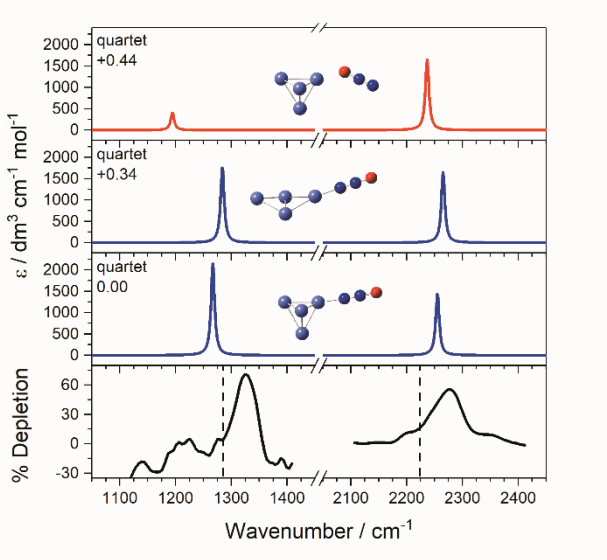

Figure S7. IR-MPD depletion spectrum of $Co_4(N_2O)^+$, along with simulated IR spectra of quartet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines at 1285 and 2224 cm^{-1} indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O, respectively.[1]

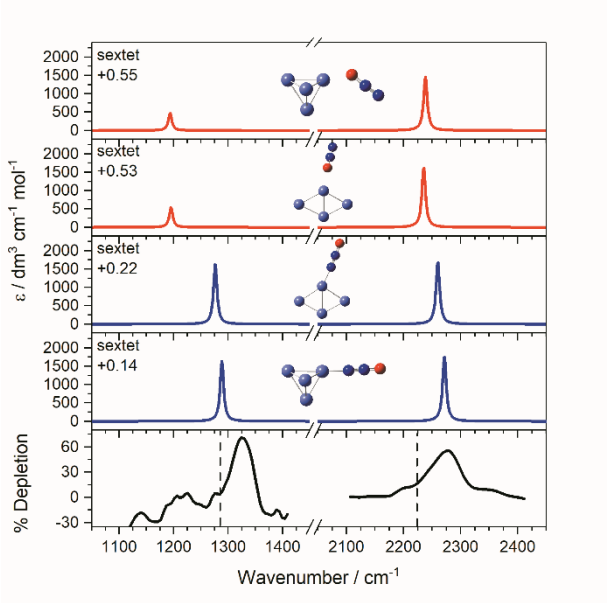

Figure S8. IR-MPD depletion spectrum of $Co_4(N_2O)^+$, along with simulated IR spectra of sextet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O.[1]

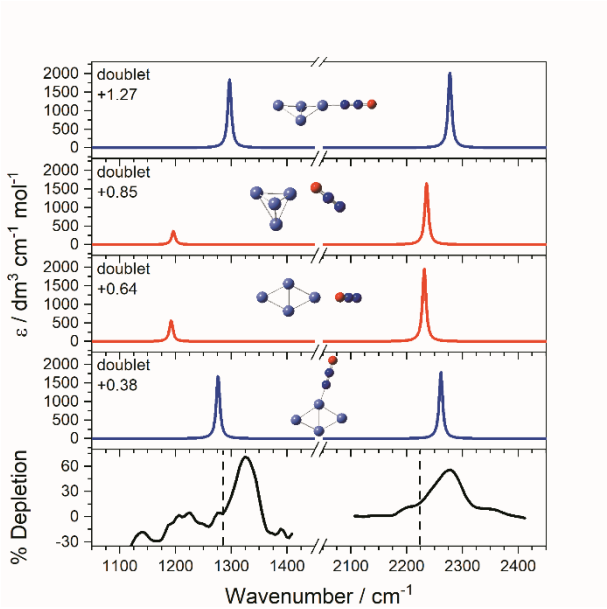

Figure S9. IR-MPD depletion spectrum of $Co_4(N_2O)^+$, along with simulated IR spectra of doublet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O.[1]

$Co_5(N_2O)^+$

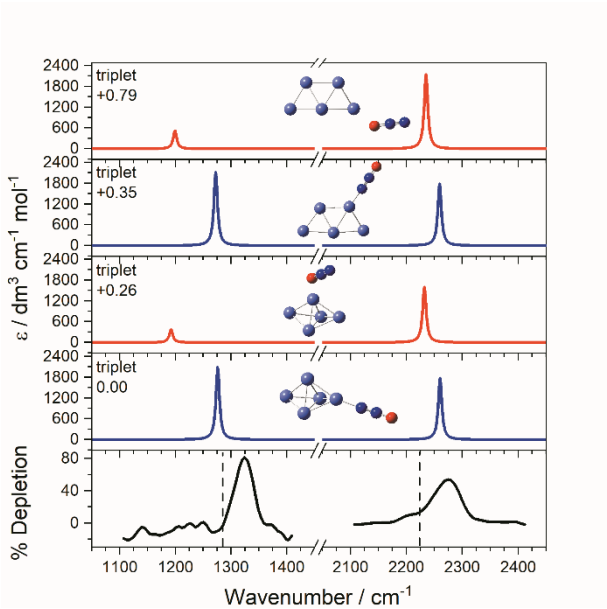

Figure S10. IR-MPD depletion spectrum of $Co_5(N_2O)^+$, along with simulated IR spectra of triplet-state isomers in the region of the N_2O symmetric (N=O) and asymmetric (N=N) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of different isomers are given in eV. The vertical dashed lines at 1285 and 2224 cm^{-1} indicate the wavenumber of the ν_1(N=O) and ν_3(N=N) modes in isolated N_2O, respectively.[1]

Calculated Structures

Density functional theory calculations were performed employing the TPSSh functional and Def2TZVP basis set using the Gaussian09 package.[2] The quadratically convergent SCF procedure was used along with 1.00D-06 hartree convergence criterion along with the Gaussian 09 "Very tight" geometry optimisation convergence. For each cluster, starting structures were generated from existing calculations of cationic gold[3] and cobalt clusters.[4] To accurately determine the multiplicity of each cluster structure, together with the relative energy, for each calculated structure the DFT wavefunction was stabilised and tested. For each structure, cartesian coordinates (Å) along with relative energies (eV) are given.

The adsorption of N_2O has minimal effect on the relative ordering of different isomers and/or spin states of Au_n^+ and Co_n^+ clusters. Likewise, the geometrical structure of the metal cluster substrate does not change significantly upon N_2O binding.

$Au_n(N_2O)^+$

$Au_2(N_2O)^+$

2*S*+1 = 2;
Lowest energy structure: N-bound
Au 0.874428 1.676623 -0.062429
Au 0.254200 -0.844890 0.030750
N -0.506522 -3.932270 0.144275
N -0.237823 -2.838562 0.105644
O -0.784222 -5.060540 0.184882

2*S*+1 = 4;
N-bound, E_{rel}= 3.07 eV
Au 1.523270 -0.326430 0.000000
Au -1.138327 0.024615 0.000000
N 1.817842 -3.471001 0.000000
N 1.127845 -2.564748 0.000000
O 2.498833 -4.412690 0.000000

O-bound, E_{rel} = 0.42 eV
Au 2.114280 0.064210 0.053901
Au -0.481459 -0.038961 0.193372
N 5.139367 0.017670 0.694152
N 5.931002 -0.115804 1.470788
O 4.324730 0.171398 -0.187455

O-bound, E_{rel} = 3.19 eV
Au 1.695813 0.013021 -0.852664
Au -0.489515 0.181837 0.701870
N 3.715904 2.285711 0.232003
N 4.712455 2.740247 0.004289
O 2.637685 1.807120 0.491356

$Au_3(N_2O)^+$

$2S+1$ = 1;

Lowest energy structure: N-bound

Au 0.978731 0.054944 0.142263

Au -1.655903 -0.127305 -0.094605

Au -0.235497 -2.288859 -0.107521

N 3.650581 1.804344 0.486500

N 2.711437 1.192416 0.361983

O 4.619853 2.436322 0.614426

O-bound, E_{rel} = 0.38 eV

Au 1.893078 0.607970 0.550879

Au -0.724286 0.537189 0.215993

Au 0.721316 -1.496076 -0.530981

N 4.456670 2.373236 0.721902

N 5.147030 3.072596 0.189650

O 3.738466 1.621754 1.337590

$2S+1$ = 3;

N-bound, E_{rel} = 2.16 eV

Au 1.311711 -0.510826 0.151055

Au -1.191494 0.363475 -0.038705

Au -0.504386 -2.224837 -0.133089

N 3.469053 1.812347 0.473159

N 2.836602 0.883765 0.367010

O 4.147715 2.747937 0.583616

O-bound, E_{rel} = 2.53 eV

Au 1.373311 -0.508117 0.216635

Au -1.091723 0.439026 0.265988

Au -0.461690 -2.042506 -0.549300

N 3.428216 1.765406 0.467945

N 3.804084 2.736610 0.065771

O 3.063006 0.713409 0.946067

$Au_4(N_2O)^+$

$2S+1 = 2$;

Lowest energy structure: N-bound

Au 1.160947 -0.935873 1.896374
Au -0.261433 0.717857 0.263284
Au 0.800216 -1.558901 -0.642098
Au -0.551801 -0.052241 -2.333246
N -1.296651 3.579156 1.338104
N -1.071355 2.530186 0.987736
O -1.546279 4.657134 1.703273

N-bound, E_{rel} = 0.11 eV

Au 1.227001 -0.002017 0.001885
Au -1.429466 -0.055851 0.000220
Au -0.001582 -2.361277 -0.012172
Au -0.217327 2.287859 0.014589
N -0.187998 5.506802 0.039503
N 0.054920 4.403562 0.027996
O -0.415995 6.649200 0.051118

N-bound, E_{rel} = 0.14 eV

Au 0.768360 0.009021 2.733285
Au -0.317841 -0.005789 0.348866
Au 1.133122 0.011860 -1.888760
Au -1.489556 -0.019491 -1.992387
N 3.947385 0.027081 -3.431635
N 3.019700 0.032216 -2.789661
O 4.914225 0.023231 -4.082886

N-bound, E_{rel} = 0.15 eV

Au 0.869300 -0.920374 3.332136
Au 0.250161 -0.171749 0.903263
Au 1.088323 -0.790473 -1.487806
Au -0.803108 0.977435 -1.330567
N -3.104574 3.135832 -1.952502
N -2.282368 2.391944 -1.747881
O -3.952533 3.906767 -2.166458

N-bound, E_{rel} = 0.34 eV

Au 0.040943 -0.092977 3.041909
Au -0.627831 -0.168547 0.549350
Au 1.290214 0.350431 -1.183129
Au -1.062661 -0.149165 -2.149076
N 0.239831 -0.230453 6.227411
N 0.374086 -0.102852 5.114173
O 0.124024 -0.354859 7.381654

O-bound, E_{rel}= 0.34 eV

Au -0.069191 -0.007568 0.444222
Au -0.734784 0.284083 -2.135662
Au -0.970581 -2.098570 -1.003225
Au 0.181854 2.376419 -0.795111
N -0.099595 -0.148954 3.620143
N -0.712612 -0.041700 4.549580
O 0.590296 -0.272742 2.639349

O-bound, E_{rel} = 0.39 eV

Au 1.238642 -0.153588 0.301172
Au -1.363303 -0.007318 -0.290254
Au -0.178301 -2.397293 -0.064948
Au 0.046621 2.217734 0.103489
N 0.343891 5.319027 -0.579053
N 0.562626 6.071082 -1.377948
O 0.104649 4.531879 0.301553

O-bound, E_{rel} = 0.52 eV

Au -1.088406 0.227356 3.230095
Au -0.056739 0.076611 0.831774
Au 1.377898 0.041338 -1.453942
Au -1.194307 -0.279630 -1.505711
N 4.357075 -0.529086 -2.222568
N 5.128442 -1.314205 -2.420169
O 3.555193 0.348349 -2.017505

O-bound, E_{rel} = 0.66 eV

Au -0.077982 0.237899 2.833624
Au -0.536120 0.079542 0.287347
Au 1.369038 -0.324689 -1.498333
Au -1.071948 -0.062781 -2.353787
N -0.553034 0.602491 5.979132
N -1.307392 0.806348 6.780331
O 0.281643 0.381244 5.141229

$Au_5(N_2O)^+$

2*S*+1 = 1;

Lowest energy structure: N-bound

Au 0.452100 -1.896035 -0.187487
Au -1.765437 -0.316820 -0.043206
Au -1.903526 -2.919289 -0.366365
Au -1.425072 2.314007 0.279075
Au -3.831830 1.386486 0.131834
N 3.654180 -1.690310 -0.090950
N 2.527655 -1.636347 -0.107922
O 4.820345 -1.731443 -0.071347

N-bound E_{rel} = 0.15 eV

Au -0.556657 -2.156457 -0.250405
Au -2.965701 -0.922389 -0.258584
Au -2.722507 -3.546098 -0.648802
Au -0.883051 0.774738 0.178535
Au -3.364731 1.623065 0.106026
N 2.099235 1.798290 0.583818
N 1.143443 1.220541 0.416471
O 3.099694 2.372655 0.754304

O-bound, E_{rel} = 0.35 eV

Au 0.172853 -2.153535 -0.215258
Au -1.831813 -0.352375 -0.067300
Au -2.262769 -2.919103 -0.540184
Au -1.287384 2.230181 0.354000
Au -3.755791 1.502289 0.119645
N 3.124329 -2.623075 0.744948
N 3.775406 -3.125024 1.503636
O 2.455495 -2.068736 -0.090191

N-bound E_{rel} = 0.47 eV

Au -0.280043 0.029119 -2.817395
Au -0.313926 1.313937 -0.480129
Au -0.318968 -1.305447 -0.508221
Au -1.105182 -0.020022 1.888657
Au 1.428726 -0.020416 1.422691
N 4.582746 -0.044714 1.925480
N 3.514967 -0.027777 1.560685
O 5.692712 -0.061151 2.281457

O-bound, E_{rel} = 0.83 eV

Au -0.438671 0.352680 -2.845909
Au -0.121622 1.385771 -0.408808
Au -0.511408 -1.193096 -0.675314
Au -1.114137 -0.034452 1.855197
Au 1.386654 -0.354948 1.338618
N 4.332166 -0.883056 2.240001
N 5.006054 -1.070068 3.112549
O 3.639011 -0.683828 1.273395

O-bound, E_{rel} = 1.04 eV

Au -0.078986 0.035986 -2.687095
Au -0.055243 1.301394 -0.337580
Au 0.058431 -1.296484 -0.378782
Au -1.235845 -0.088089 1.924418
Au 1.332198 0.024655 1.874744
N 0.620586 0.122325 -5.897559
N 1.438944 0.174631 -6.660746
O -0.269135 0.065908 -5.093617

$Co_n(N_2O)^+$

$Co_2(N_2O)^+$

2*S*+1 = 6;

Lowest energy structure: N-bound

Co -2.373164 0.046364 0.044090
Co -0.119900 0.002296 0.002276
N 2.997270 -0.058498 -0.055739
N 1.867351 -0.036505 -0.034668
O 4.157547 -0.081099 -0.077377

O-bound, E_{rel} = 0.24 eV

Co 2.244857 0.271635 0.000044
Co 0.090882 -0.346913 -0.000098
N -2.925322 0.154474 0.000050
N -3.821670 0.819435 -0.000063
O -1.979498 -0.598107 0.000195

2*S*+1 = 4;

N-bound, E_{rel} = 0.70 eV

Co -0.060379 -0.099999 0.564067
Co 0.379553 1.222030 -1.394993
N -1.002824 -2.946469 0.312544
N -0.648386 -1.876661 0.415363
O -1.368221 -4.049643 0.203203

O-bound, E_{rel}= 1.11 eV

Co 0.102087 -1.631681 0.698892
Co -0.042557 0.673725 0.322116
N -0.197784 3.434783 -0.889853
N -0.226035 4.150371 -1.747209
O -0.170665 2.702171 0.070055

2*S*+1 = 2;

N-bound, E_{rel} = 0.05 eV

Co 0.099783 0.100210 -0.000065
Co 2.392819 -0.064494 0.000002
N -2.996311 -0.040372 0.000376
N -1.866900 0.013459 0.000256
O -4.157223 -0.096995 -0.000339

O-bound, E_{rel} = 0.24 eV

Co -0.067501 0.254974 1.102051
Co 0.190821 -0.423694 -1.103573
N 0.204537 1.018960 -3.827746
N 0.538341 1.838644 -4.507653
O -0.178455 0.117904 -3.117447

$Co_3(N_2O)^+$

2*S*+1 = 3;

Lowest energy structure, N-bound

Co 1.575679 0.069304 0.049642
Co -0.504369 1.371541 0.055138
Co -0.533627 -1.020656 -0.064426
N 4.440020 -0.936850 0.082329
N 3.366950 -0.575866 0.072843
O 5.546951 -1.314326 0.088899

O-bound, E_{rel} = 0.44 eV

Co 1.395776 0.232667 -0.264279
Co -0.716613 1.216524 0.429564
Co -0.468535 -1.140799 0.073444
N 4.239433 -0.693564 -0.666564
N 5.067611 -1.429481 -0.517134
O 3.371411 0.122174 -0.852217

2*S*+1 = 5;

N-bound, E_{rel} = 0.68 eV

Co 0.491853 -1.583491 0.123532
Co 0.587800 0.704444 -0.114093
Co -1.529211 -0.404188 0.059973
N 3.220528 2.143493 -0.320428
N 2.228856 1.601445 -0.242708
O 4.246604 2.701496 -0.398550

O-bound, E_{rel} = 1.02 eV

Co 1.207019 -0.719418 -0.341658
Co 0.253780 1.347207 -0.055626
Co -1.024546 -0.546351 0.380388
N 4.214543 -0.821420 0.105887
N 5.165874 -0.373105 0.482897
O 3.204319 -1.334368 -0.308797

$Co_4(N_2O)^+$

2*S*+1 = 4;

Lowest energy structure: N-bound

Co 0.659469 -0.711715 -0.092536
Co 0.041795 1.449723 -0.790058
Co -0.657733 0.661856 1.310686
Co -1.726272 -0.347852 -0.637039
N 1.772315 -3.142761 1.327923
N 1.313635 -2.232299 0.833155
O 2.237782 -4.083601 1.850117

N-bound, E_{rel} = 0.34 eV

Co -0.138825 1.010750 1.242706
Co -2.190656 -0.168503 1.346392
Co 1.375502 0.189512 -0.541535
Co -0.200003 -1.259612 0.725401
N 3.456071 0.620564 -2.722104
N 2.672721 0.468830 -1.918638
O 4.265596 0.779379 -3.553225

O-bound, E_{rel}= 0.44 eV

Co 1.713639 -0.048260 0.077123
Co -0.097484 0.753393 -1.183208
Co -0.390153 0.548777 1.250411
Co -0.179406 -1.387500 -0.261015
N 4.252188 -0.755491 -1.260397
N 4.787273 -1.194294 -2.138333
O 3.711737 -0.273060 -0.296470

2*S*+1 = 6;

N-bound, E_{rel} = 0.14 eV

Co 0.886392 0.315886 -0.235432
Co -0.954737 0.335488 1.202932
Co -1.392732 0.244693 -1.162406
Co -0.346472 -1.665675 -0.054997
N 3.872362 0.352021 0.334781
N 2.758347 0.326416 0.137781
O 5.023023 0.374209 0.541324

N-bound, E_{rel} = 0.22 eV

Co -0.286694 1.057427 -0.096919
Co 0.145856 0.428220 2.105015
Co 0.179082 -0.374338 -1.922370
Co 0.043686 -1.346945 0.373700
N 0.098040 -4.320932 -0.221808
N 0.077565 -3.198739 -0.068205
O 0.119520 -5.480248 -0.391073

O-bound, E_{rel} = 0.53eV

Co -0.061210 1.120300 0.003539
Co 0.162894 0.003070 2.164542
Co -0.032974 0.052655 -2.106057
Co 0.011221 -1.184815 -0.012966
N 0.885336 -4.032645 -0.675545
N 1.672955 -4.774688 -0.956256
O 0.010889 -3.259330 -0.373690

O-bound, E_{rel} = 0.55 eV

Co 0.745241 -0.726895 -1.400429
Co 0.141400 1.389147 -0.346635
Co 0.684361 -0.496863 0.908671
Co -1.416698 -0.495586 -0.357560
N 3.050994 0.040844 2.630509
N 3.956513 0.651137 2.867104
O 2.082032 -0.643146 2.409343

2*S*+1 = 2;

N-bound, E_{rel} = 0.38eV

Co -0.769319 1.013692 0.121068
Co -1.377360 -0.150355 2.118710
Co 1.343416 0.262341 -0.471845
Co -0.245693 -1.233546 0.313041
N 3.613726 0.617095 -2.470971
N 2.779456 0.489191 -1.718230
O 4.473756 0.748992 -3.249518

O-bound, E_{rel} = 0.64 eV

Co 1.241366 -0.413188 -0.912526
Co -0.285204 1.352501 -0.254034
Co 0.583083 -0.221854 1.401669
Co -1.111305 -0.890074 -0.557760
N 4.198365 -0.723217 -1.022689
N 5.192015 -0.764522 -0.511458
O 3.147625 -0.679815 -1.611920

O-bound, E_{rel} = 0.85 eV

Co -0.357347 1.089751 0.041376
Co 0.378549 -0.001022 2.136201
Co -0.126183 0.051004 -2.189016
Co 0.007817 -1.142557 -0.022312
N 0.662213 0.297132 -5.125101
N 1.424524 0.486428 -5.920970
O -0.183640 0.088297 -4.291891

N-bound, E_{rel} = 1.27 eV

Co -1.456703 0.546271 0.127336
Co 0.167337 0.219229 1.888429
Co -0.746945 0.679769 -2.111731
Co 0.806484 -0.260490 -0.388452
N 3.536198 -1.547799 -0.095576
N 2.514205 -1.062194 -0.145533
O 4.593215 -2.049193 -0.032401

$Co_5(N_2O)^+$

2*S*+1 = 3;

Lowest energy structure: N-bound

Co -0.058773 -0.078146 1.313855
Co -2.042833 0.196078 -0.087908
Co -0.065504 -1.104534 -0.870827
Co 2.005239 -0.221671 0.115387
Co 0.130993 1.319055 -0.633960
N -4.944333 -0.362595 0.677220
N -3.862510 -0.171386 0.404071
O -6.062176 -0.563838 0.965021

O-bound, E_{rel} = 0.26 eV

Co -0.297084 -0.536656 1.229458
Co -1.810636 -0.138113 -0.711750
Co 0.460908 -0.829759 -0.997394
Co 1.971585 0.210980 0.616850
Co 0.014299 1.360329 -0.249591
N 0.004797 -3.113387 -2.807190
N -0.691366 -3.832576 -3.306090
O 0.789614 -2.359785 -2.288853

N-bound, E_{rel} = 0.35 eV

Co -3.180375 1.540343 -0.638097
Co -4.701338 0.129470 0.468335
Co -2.334262 -0.407642 0.230471
Co -0.754163 1.525739 0.113141
Co 0.046488 -0.683045 -0.280133
N 1.226366 3.783749 0.554686
N 0.506571 2.925490 0.388344
O 1.976204 4.668659 0.726329

O-bound, E_{rel} = 0.79 eV

Co -3.314043 1.698354 -0.298918
Co -4.603816 -0.214716 0.400611
Co -2.175230 -0.393674 -0.188810
Co -0.887674 1.574211 0.298871
Co 0.210384 -0.528306 -0.268406
N -7.433291 -1.193805 1.077186
N -8.531145 -1.011017 1.188808
O -6.255445 -1.418035 0.962673

2*S*+1 = 5;

N-bound, E_{rel} = 0.48 eV

Co 0.098564 -0.135294 1.333523
Co -2.024912 0.401497 0.326531
Co -0.404217 -1.110035 -0.803032
Co 1.819556 -0.470314 -0.256301
Co 0.076194 1.319703 -0.598533
N -0.121118 -3.654708 -2.350952
N -0.187639 -2.686192 -1.766298
O -0.043110 -4.657097 -2.958552

O-bound, E_{rel} = 0.72 eV

Co -0.493648 0.353257 1.182289
Co -1.981608 -0.540909 -0.435112
Co 0.269846 -1.479111 -0.368230
Co 1.723183 0.444323 0.285079
Co -0.200318 0.893256 -1.066929
N -4.670614 0.672016 -0.478346
N -5.311751 1.576355 -0.331092
O -4.009980 -0.321603 -0.645936

N-bound, E_{rel} = 0.93 eV

Co -3.835393 1.476621 -0.180192
Co -4.657221 -0.805467 0.223744
Co -2.380363 -0.409189 0.024968
Co -1.432505 1.801042 0.218938
Co -0.001582 0.004521 -0.183319
N -4.458703 4.368424 -0.788760
N -4.144794 3.305325 -0.550887
O -4.771437 5.471822 -1.033861

O-bound, E_{rel} = 1.31 eV

Co -3.248768 1.642834 -0.625844
Co -4.762602 -0.156876 -0.366009
Co -2.360929 -0.390553 -0.034243
Co -1.039273 1.467393 0.588442
Co 0.080962 -0.588175 0.229190
N -7.227377 -1.154942 1.155458
N -7.774965 -1.297777 2.120074
O -6.657307 -1.008893 0.104947

Bond Lengths

(N_2O)

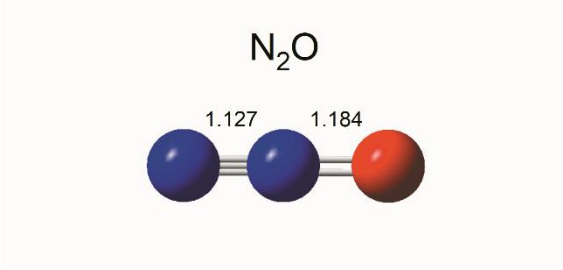

Figure S11. Bond lengths (Å) of N_2O calculated at the TPSSh/Def2TZVP level of theory.

The experimental bond lengths[1] of nitrous oxide are presented also for comparison:

r(N=N): 1.128 Å

r(N=O): 1.184 Å

$Au_n(N_2O)^+$

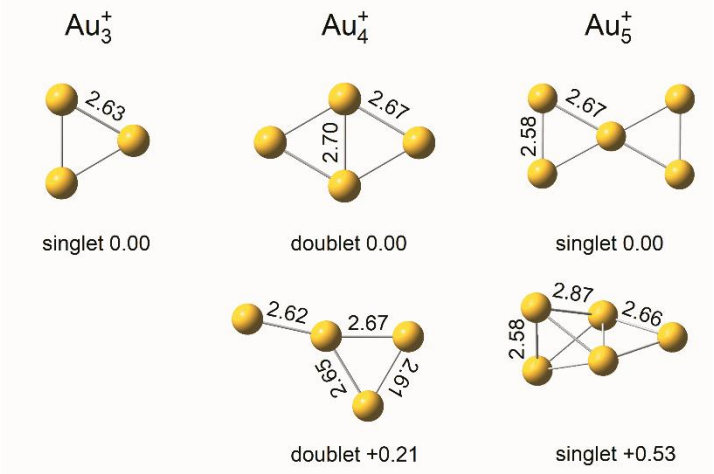

Figure S12. Low-lying isomers of Au_n^+ (n = 3-5) clusters calculated at the TPSSh/Def2TZVP level of theory. Energies are given in eV and distances in angstroms.

Table S1. Bond lengths (Å) of the calculated $Au_n(N_2O)^+$ structures, employing TPSSh functional and Def2TZVP basis set. In this case, N1 represents the terminal N atom and Au represents the gold atom bound to the N_2O molecule (either N- or O-bound).

Isomer	Au-N1	Au-O	N=N	N=O
$^1AuNNO^+$	2.034	---	1.130	1.157
$^1AuONN^+$	---	2.187	1.115	1.218
$^2Au_2NNO^+$	2.055	---	1.127	1.163
$^2Au_2ONN^+$	---	2.226	1.117	1.210
$^1Au_3NNO^+$	2.084	---	1.128	1.164
$^1Au_3ONN^+$	---	2.248	1.118	1.208
$^2Au_4NNO^+$	2.113	---	1.129	1.165
$^2Au_4ONN^+$	---	2.307	1.119	1.206
$^1Au_5NNO^+$	2.093	---	1.128	1.167
$^1Au_5ONN^+$	---	2.287	1.119	1.205

$Co_n(N_2O)^+$

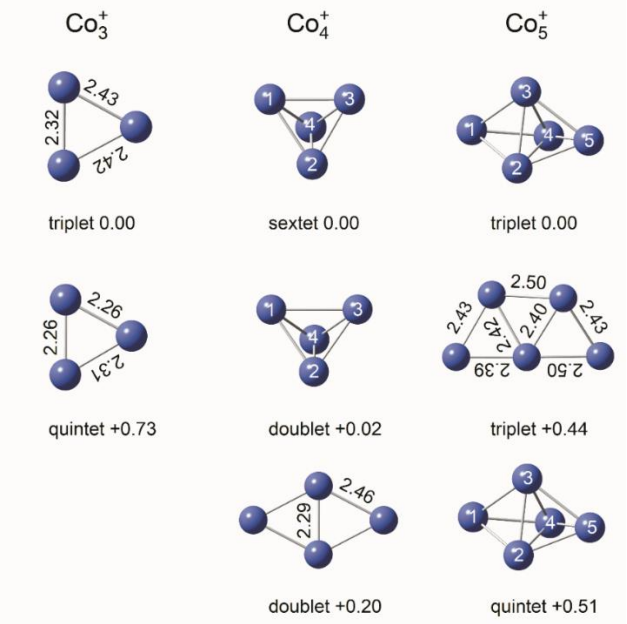

Figure S13. Low-lying isomers of Co_n^+ (*n* = 3-5) clusters calculated at the TPSSh/Def2TZVP level of theory. Energies are given in eV and distances in angstroms.

Table S2. Bond lengths (Å) of calculated non-planar $^{6/2}Co_4^+$ clusters, whereby title integers represent atom labels presented in Figure S13.

Cobalt Cluster	1-2	1-3	1-4	2-3	2-4	3-4
$^6Co_4^+$	2.41	2.45	2.45	2.45	2.38	2.29
$^2Co_4^+$	2.43	2.73	2.41	2.45	2.41	2.41

Table S3. Bond lengths (Å) of calculated non-planar $^{3/5}Co_5^+$ clusters, whereby title integers represent atom labels presented in Figure S13.

Cobalt Cluster	1-2	1-3	1-4	2-3	2-4	3-4	2-5	3-5	4-5
$^3Co_5^+$	2.40	2.48	2.49	2.41	2.40	2.50	2.39	2.46	2.56
$^5Co_5^+$	2.40	2.53	2.38	2.43	2.43	2.56	2.40	2.53	2.38

Table S4. Bond lengths (Å) of the calculated $Co_n(N_2O)^+$ structures, employing TPSSh functional and Def2TZVP basis set. In this case, N1 represents the terminal N atom and Co represents the cobalt atom bound to the N_2O molecule (either N- or O-bound).

Isomer	Co-N1	Co-O	N=N	N=O
$^3CoNNO^+$	1.879	---	1.131	1.162
$^3CoONN^+$	---	1.993	1.116	1.212
$^6Co_2NNO^+$	1.988	---	1.130	1.161
$^6Co_2ONN^+$	---	2.086	1.116	1.209
$^3Co_3NNO^+$	1.904	---	1.132	1.170
$^3Co_3ONN^+$	---	2.068	1.117	1.207
$^4Co_4NNO^+$	1.914	---	1.132	1.171
$^4Co_4ONN^+$	---	2.045	1.118	1.206
$^3Co_5NNO^+$	1.941	---	1.131	1.171
$^3Co_5ONN^+$	---	2.082	1.118	1.204

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