First-Principles study of the role of interconversion between NO_2, N_2O_4, *cis*-ONO-NO_2 and *trans*-ONO-NO_2 in chemical processes.

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Supporting Information:

This material contains the scan of N-N distance of this van der Waals complex, atomic coordinates of all intermediates and TS shown in this study. Methods include RCCSD(T), RCCSD, UCCSD(T), UCCSD, RMP2, UMP2 and GVB-RCI at cc-pVDZ basis, and B3LYP/6311G*+ . Tables of CBS calculation contain energetics for different methods at different basis as well as E_∞, A and γ in the formula $E(n) = E_\infty + An^{-\gamma}$. For MP2, CCSD and CCSD(T), the correlation energy is reported.

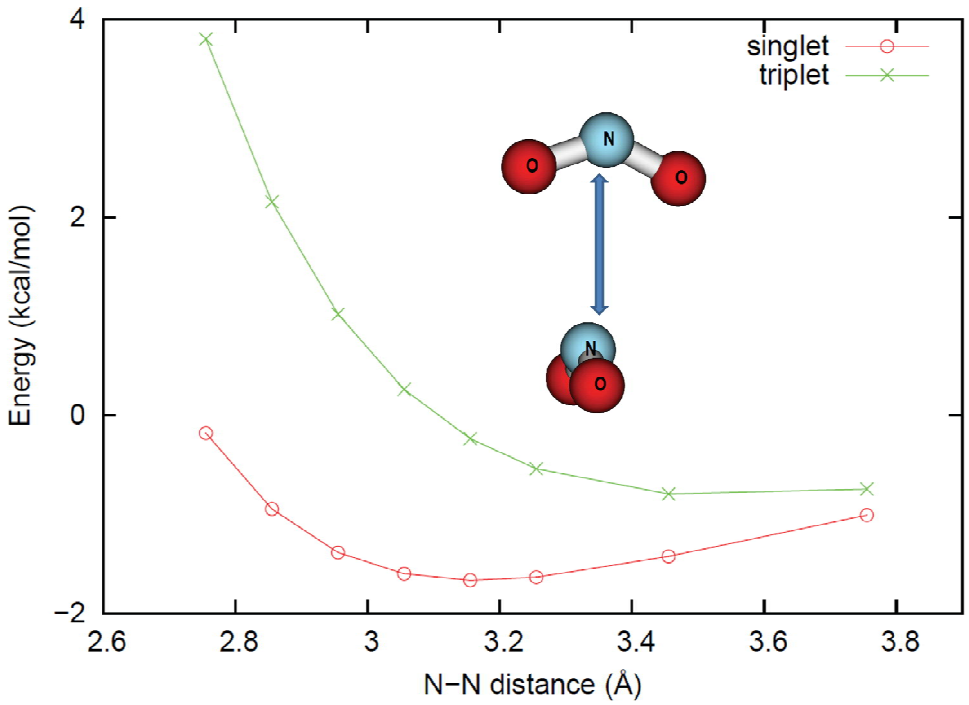

Figure S1: The rigid scan of N-N distance of the C_{2v} van der Waals complex at UCCSD(T)/cc-pVTZ level. Part of the triplet PES is lower than 0, indicating that some binding energy comes from the electrostatic interaction (dipole alignment).

NO_2
optimized by B3LYP/6311G*+

N	0.0000000000	0.0000000000	-0.0000001115
O	0.0000000000	1.1001914234	0.4625045930
O	0.0000000000	-1.1001912788	0.4625046487

B3LYP/6311G*+ -205.140677
UMP2/cc-pVDZ -204.586177
UCCSD(T)/cc-pVDZ -204.603747
UCCSD(T)/cc-pVTZ -204.800161

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-204.03973934	-0.54959692	-0.53999230	-0.56507962
cc-pVTZ	-204.10104975	-0.67929086	-0.66272726	-0.70011066
cc-pVQZ	-204.11683320	-0.72834231	-0.70594792	-0.74677924
E_∞	-204.12927800	-0.80146800	-0.76214300	-0.80542400

A	0.64422100	0.86753500	0.87820400	0.98500400
γ	2.84697000	1.78424000	1.98301000	2.03502000

optimized by UMP2/cc-pVDZ
N 0.0000000000 0.0000000000 0.3265173135
O 0.0000000000 -1.1127837084 -0.1448336567
O 0.0000000000 1.1127837084 -0.1448336567
B3LYP/6311G*+ -205.139994
UMP2/cc-pVDZ -204.589136
UCCSD(T)/cc-pVDZ -204.604503
UCCSD(T)/cc-pVTZ -204.800016

$2NO_2$ with N-N distance 4A D_{2h}(reference for GVB-RCI)
N -0.00000 -0.00000 2.00009
O 0.00000 1.10021 2.46228
O -0.00000 -1.10021 2.46228
N 0.00000 -0.00000 -2.00009
O -0.00000 1.10021 -2.46228
O 0.00000 -1.10021 -2.46228
B3LYP/6311G*+ -410.281270
UMP2/cc-pVDZ -409.170312
UCCSD(T)/cc-pVDZ -409.207397
GVB-RCI/cc-pVDZ -408.223726

$2NO_2$ C_{2v} van der Waals complex
N 0.0000000000 0.0000000000 1.8538138362
O 1.0947153766 0.0000000000 1.3775296057
O -1.0947153766 0.0000000000 1.3775296057
N 0.0000000000 0.0000000000 -1.2014642381
O 0.0000000000 1.0990340585 -1.6630859815
O 0.0000000000 -1.0990340585 -1.6630859815
B3LYP/6311G*+ -410.283205
UCCSD(T)/cc-pVDZ -409.210970
UCCSD(T)/cc-pVTZ -409.602871

N_2O_4
optimized by B3LYP/6311G*+
N 0.0000000000 0.0000000000 0.9041012746
O 0.0000000000 1.0963153103 1.3606900008
O 0.0000000000 -1.0963153103 1.3606900008

N	0.0000000000	0.0000000000	-0.9041012746
O	0.0000000000	1.0963153103	-1.3606900008
O	0.0000000000	-1.0963153103	-1.3606900008

B3LYP/6311G*+ -410.302850
UMP2/cc-pVDZ -409.138032
UCCSD(T)/cc-pVDZ -409.221577
GVB-RCI/cc-pVDZ -408.233424

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.06165840	-1.14900920	-1.10998785	-1.16558039
cc-pVTZ	-408.18626392	-1.41186104	-1.35684151	-1.43799089
cc-pVQZ	-408.21767050	-1.51187600	-1.44460439	-1.53293098
E_∞	-408.24171200	-1.66279400	-1.56074600	-1.65405700
A	1.34848000	1.74913000	1.74944000	1.96993000
γ	2.90484000	1.76740000	1.95646000	2.01178000

cis-ONO-NO_2
optimized by B3LYP/6311G*+

N	2.2674038965	-3.6266697487	1.3456289202
O	2.0768216408	-2.5618687272	1.0542555631
O	3.0058260758	-3.8678620294	2.8717595524
N	3.4221674930	-2.7372426704	3.5801455768
O	3.7936425369	-1.7887467184	2.9201656546
O	3.3704590802	-2.8519279936	4.7757176999

B3LYP/6311G*+ -410.280380
UMP2/cc-pVDZ -409.135508
UCCSD(T)/cc-pVDZ -409.207603
GVB-RCI/cc-pVDZ -408.233424

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.06831398	-1.11010641	-1.09231480	-1.14244668
cc-pVTZ	-408.19180615	-1.37483056	-1.34033574	-1.41611937
cc-pVQZ	-408.22330801	-1.47475671	-1.42802597	-1.51102805
E_∞	-408.24782900	-1.62314700	-1.54288600	-1.63103100

A	1.31419000	1.77377000	1.76750000	1.98924000
γ	2.87200000	1.78967000	1.97188000	2.02554000

trans-ONO-NO_2
optimized by B3LYP/6311G*+

N	1.9701272066	-2.8148502189	2.6359630817
O	3.2122489254	-1.7468281800	2.7186522799
O	1.9653211133	-3.2496574068	1.5929485314
N	3.3594764501	-1.2029205750	4.0234540744
O	4.0219286722	-0.2025537496	4.0353791298
O	2.8365641315	-1.7960322860	4.9324507037

B3LYP/6311G*+ -410.284020
UMP2/cc-pVDZ -409.152907
UCCSD(T)/cc-pVDZ -409.212647
GVB-RCI/cc-pVDZ -408.232695

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.07447295	-1.10639129	-1.09141675	-1.14022317
cc-pVTZ	-408.19849237	-1.37115282	-1.33949888	-1.41392289
cc-pVQZ	-408.22981701	-1.47089589	-1.42706239	-1.50867440
E_∞	-408.25386600	-1.61843300	-1.54139900	-1.62809900
A	1.33819000	1.77709000	1.77095000	1.99308000
γ	2.89909000	1.79518000	1.97659000	2.03042000

TS1
optimized by B3LYP/6311G*+

N	2.4312357132	-3.6087058724	1.6917618433
O	1.8492691295	-2.5600397800	1.6728744219
O	3.3034400201	-3.8746058909	2.5185774478
N	3.4474406994	-2.2248979689	3.6889500964
O	4.3091630783	-1.5136507056	3.3124988145
O	2.7872795783	-2.3359334915	4.6594053132

B3LYP/6311G*+ -410.277663
UMP2/cc-pVDZ -409.096053
UCCSD(T)/cc-pVDZ -409.175143
GVB-RCI/cc-pVDZ -408.210914

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.00436011	-1.15395507	-1.11860793	-1.17959580
cc-pVTZ	-408.12735480	-1.41884709	-1.36447775	-1.45116358
cc-pVQZ	-408.15945179	-1.51864753	-1.45135073	-1.54519483
E_∞	-408.18525100	-1.66629400	-1.56500300	-1.66375200
A	1.26831000	1.77784000	1.75332000	1.97717000
γ	2.80971000	1.79495000	1.97369000	2.02989000

TS2
optimized by B3LYP/6311G*+

N	2.4312357132	-3.6087058724	1.6917618433
O	1.8492691295	-2.5600397800	1.6728744219
O	3.3034400201	-3.8746058909	2.5185774478
N	3.4474406994	-2.2248979689	3.6889500964
O	4.3091630783	-1.5136507056	3.3124988145
O	2.7872795783	-2.3359334915	4.6594053132

B3LYP/6311G*+ -410.277663
UMP2/cc-pVDZ -409.121621
UCCSD(T)/cc-pVDZ -409.195012
GVB-RCI/cc-pVDZ -408.224797

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.01485341	-1.16663194	-1.12494563	-1.18981334
cc-pVTZ	-408.13621162	-1.43141364	-1.37079324	-1.46157362
cc-pVQZ	-408.16777254	-1.53135604	-1.45789262	-1.55593914
E_∞	-408.19301700	-1.67975500	-1.57241000	-1.67553000
A	1.25739000	1.77424000	1.74842000	1.97273000
γ	2.81915000	1.78983000	1.96621000	2.02200000

TS3
optimized by B3LYP/6311G*+

N	2.0478105694	0.6929775924	2.1025573234
O	1.1742599556	0.1980750995	2.7447702862
O	2.6300090413	-0.0159396741	1.2040392642
N	3.5303868994	1.8601340696	1.1651581198
O	4.5136211145	1.7800091267	1.7864948980
O	3.0356889798	2.4589812747	0.2957636888

B3LYP/6311G*+ -410.2353795

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-407.96813410	-1.16456799	-1.12052942	-1.18401730
cc-pVTZ	-408.09372451	-1.42875216	-1.36715201	-1.45645229
cc-pVQZ	-408.12620278	-1.52873566	-1.45451604	-1.55106285
E_∞	-408.15198000	-1.67798900	-1.56935700	-1.67098900
A	1.31139000	1.76613000	1.75413000	1.97739000
γ	2.83457000	1.78238000	1.96652000	2.02169000

TS4

optimized by RMP2/cc-pVDZ

N	-0.6759616587	-1.2642660385	-0.8610066046
O	0.4604672738	0.1053330192	-0.8653233790
O	-1.7388231320	-0.9298949262	-0.6183291937
N	0.6041918200	0.5471496170	0.4353559445
O	1.3547466539	1.4967260161	0.5491904421
O	-0.0153579371	-0.0460563676	1.3101693307

B3LYP/6311G*+ -410.2742610

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.05864187	-1.11819502	-1.09922351	-1.14990236
cc-pVTZ	-408.18132617	-1.38248694	-1.34633112	-1.42298018
cc-pVQZ	-408.21265224	-1.48227279	-1.43370627	-1.51766274
E_∞	-408.23707000	-1.63052300	-1.54817200	-1.63733400
A	1.30384000	1.77052000	1.76083000	1.98535000
γ	2.86935000	1.78904000	1.97163000	2.02612000

TS5
optimized by RMP2/cc-pVDZ

N	2.0733569052	-2.9147085235	3.0871411753
O	3.3996970987	-1.5069641640	2.5947251565
O	1.0585605423	-2.7273658015	2.6031966490
N	3.3900749136	-1.1194607202	3.8205238365
O	4.2162471517	-0.3406720551	4.2633051894
O	2.4492533884	-1.6087087356	4.5478579934

B3LYP/6311G*+ -410.2782800

	RHF	MP2	CCSD	CCSD(T)
cc-pVDZ	-408.05077528	-1.12626055	-1.10111257	-1.15561528
cc-pVTZ	-408.17303687	-1.39057767	-1.34808740	-1.42857107
cc-pVQZ	-408.20466631	-1.49061410	-1.43575956	-1.52350310
E_∞	-408.22977900	-1.63995400	-1.55145400	-1.64416100
A	1.27596000	1.76698000	1.75296000	1.97813000
γ	2.83352000	1.78231000	1.96070000	2.01757000