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Supporting Information

Theory Meets Experiment for Noncovalent Complexes: The Puzzling Case of Pnicogen Interactions

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Supporting information

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S1. Table of the experimental transition frequencies (*v*/MHz: 198 *a*-type, 208 *b*-type, and 127 *c*-type transitions, respectively) together with the corresponding observed – calculated differences (Δ*v*/kHz) for (^{14}N)nitroethane - (^{14}N)trimethylamine.

J'	K_a'	K_c'	F_1'	F'	←	J''	K_a''	K_c''	F_1''	F''	ν/MHz	Δν/kHz
4	0	4	3	3		3	0	3	2	2	7626.3847	0.3
4	0	4	3	4		3	0	3	2	3	7626.3847	2.0
4	0	4	5	5		3	0	3	4	4	7626.5038	-1.7
4	0	4	4	4		3	0	3	3	3	7626.4906	-6.3
4	0	4	4	5		3	0	3	3	4	7626.4906	1.7
4	0	4	4	3		3	0	3	3	2	7626.5152	4.4
4	0	4	5	6		3	0	3	4	5	7626.5280	-1.6
4	0	4	5	4		3	0	3	4	3	7626.5457	0.4
4	1	4	4	3		3	1	3	3	2	7462.7819	2.2
4	1	4	4	5		3	1	3	3	4	7462.7819	0.9
4	1	4	4	4		3	1	3	3	3	7462.8141	-2.5
4	1	4	3	4		3	1	3	2	3	7462.8971	-2.3
4	1	4	5	4		3	1	3	4	3	7462.9681	1.3
4	1	4	5	6		3	1	3	4	5	7462.9681	0.3
4	1	4	5	5		3	1	3	4	4	7462.9936	-4.3
4	1	3	4	5		3	1	2	3	4	7986.7853	0.6
4	1	3	4	3		3	1	2	3	2	7986.8055	5.9
4	1	3	4	4		3	1	2	3	3	7986.8650	2.0
4	1	3	3	4		3	1	2	2	3	7986.9009	-1.2
4	1	3	3	3		3	1	2	2	2	7986.9721	3.6
4	1	3	5	6		3	1	2	4	5	7986.9721	0.3
4	1	3	5	4		3	1	2	4	3	7986.9721	-2.5
4	1	3	5	5		3	1	2	4	4	7987.0076	-1.7
5	0	5	4	4		4	0	4	3	3	9456.9988	1.3
5	0	5	4	5		4	0	4	3	4	9457.0146	-2.1
5	0	5	4	3		4	0	4	3	2	9457.0443	0.2
5	0	5	6	6		4	0	4	5	5	9457.0725	0.6
5	0	5	5	5		4	0	4	4	4	9457.0546	-3.2
5	0	5	5	6		4	0	4	4	5	9457.0725	-0.5
5	0	5	6	7		4	0	4	5	6	9457.1021	0.0
5	0	5	5	4		4	0	4	4	3	9457.0836	-5.6
5	0	5	6	5		4	0	4	5	4	9457.1175	3.1
5	1	5	5	6		4	1	4	4	5	9308.8150	0.6
5	1	5	5	4		4	1	4	4	3	9308.8150	-2.5

5	1	5	5	5		4	1	4	4	4	9308.8348	4.4
5	1	5	4	5		4	1	4	3	4	9308.8598	-0.8
5	1	5	4	3		4	1	4	3	2	9308.8763	8.2
5	1	5	4	4		4	1	4	3	3	9308.8763	0.4
5	1	5	6	7		4	1	4	5	6	9308.9173	-0.1
5	1	5	6	5		4	1	4	5	4	9308.9173	-2.5
5	1	5	6	6		4	1	4	5	5	9308.9331	4.6
5	1	4	5	6		4	1	3	4	5	9952.8740	1.3
5	1	4	5	4		4	1	3	4	3	9952.8877	-0.6
5	1	4	5	5		4	1	3	4	4	9952.9074	0.6
5	1	4	4	5		4	1	3	3	4	9952.9199	2.9
5	1	4	4	4		4	1	3	3	3	9952.9412	-1.5
5	1	4	4	3		4	1	3	3	2	9952.9412	-6.6
5	1	4	6	7		4	1	3	5	6	9952.9736	-0.8
5	1	4	6	6		4	1	3	5	5	9952.9851	0.0
5	1	4	6	5		4	1	3	5	4	9952.9851	3.2
6	0	6	5	5		5	0	5	4	4	11262.7504	4.0
6	0	6	5	6		5	0	5	4	5	11262.7642	-5.2
6	0	6	5	4		5	0	5	4	3	11262.7784	-7.5
6	0	6	7	7		5	0	5	6	6	11262.8038	7.2
6	0	6	6	6		5	0	5	5	5	11262.7784	-1.6
6	0	6	6	7		5	0	5	5	6	11262.8038	2.9
6	0	6	7	8		5	0	5	6	7	11262.8214	-3.5
6	0	6	6	5		5	0	5	5	4	11262.8038	-8.1
6	0	6	7	6		5	0	5	6	5	11262.8335	-0.2
6	1	6	6	6		5	1	5	5	5	11145.3093	-0.3
6	1	6	6	7		5	1	5	5	6	11145.3093	5.2
6	1	6	6	5		5	1	5	5	4	11145.3093	1.4
6	1	6	5	5		5	1	5	4	4	11145.3243	-5.2
6	1	6	5	6		5	1	5	4	5	11145.3243	-0.4
6	1	6	5	4		5	1	5	4	3	11145.3314	0.2
6	1	6	7	7		5	1	5	6	6	11145.3695	-1.0
6	1	6	7	8		5	1	5	6	7	11145.3695	1.1
6	1	6	7	6		5	1	5	6	5	11145.3695	-1.8
6	1	5	5	5		5	1	4	4	4	11894.2182	4.0
6	1	5	6	6		5	1	4	5	5	11894.1941	-7.8
6	1	5	6	7		5	1	4	5	6	11894.1941	0.6
6	1	5	5	6		5	1	4	4	5	11894.2156	4.4
6	1	5	6	5		5	1	4	5	4	11894.2156	8.3
6	1	5	5	4		5	1	4	4	3	11894.2334	-0.5

6	1	5	7	7		5	1	4	6	6	11894.2488	-0.3
6	1	5	7	8		5	1	4	6	7	11894.2569	1.7
6	1	5	7	6		5	1	4	6	5	11894.2668	3.4
7	0	7	6	6		6	0	6	5	5	13056.7857	0.8
7	0	7	6	7		6	0	6	5	6	13056.8050	0.1
7	0	7	6	5		6	0	6	5	4	13056.8050	-10.0
7	0	7	7	7		6	0	6	6	6	13056.8050	1.7
7	0	7	8	8		6	0	6	7	7	13056.8218	0.9
7	0	7	7	8		6	0	6	6	7	13056.8218	-0.1
7	0	7	7	6		6	0	6	6	5	13056.8218	-7.5
7	0	7	8	9		6	0	6	7	8	13056.8427	-0.9
7	0	7	8	7		6	0	6	7	6	13056.8510	1.2
7	1	7	7	7		6	1	6	6	6	12973.1821	-1.4
7	1	7	6	6		6	1	6	5	5	12973.2000	7.0
7	1	7	7	8		6	1	6	6	7	12973.1821	-1.3
7	1	7	7	6		6	1	6	6	5	12973.1821	-4.7
7	1	7	6	7		6	1	6	5	6	12973.2000	6.5
7	1	7	6	5		6	1	6	5	4	12973.2000	1.4
7	1	7	8	8		6	1	6	7	7	12973.2265	1.5
7	1	7	8	9		6	1	6	7	8	12973.2265	-0.6
7	1	7	8	7		6	1	6	7	6	12973.2265	-3.4
7	1	6	6	6		6	1	5	5	5	13803.0082	-2.8
7	1	6	7	7		6	1	5	6	6	13803.0082	-0.5
7	1	6	7	8		6	1	5	6	7	13803.0135	-3.8
7	1	6	8	9		6	1	5	7	8	13803.0560	-1.2
8	0	8	8	9		7	0	7	7	8	14848.8943	2.6
8	0	8	9	9		7	0	7	8	8	14848.8943	-0.4
8	0	8	8	7		7	0	7	7	6	14848.8943	-2.3
8	1	8	8	8		7	1	7	7	7	14793.9483	2.5
8	1	8	8	9		7	1	7	7	8	14793.9483	-0.1
8	1	8	7	7		7	1	7	6	6	14793.9483	-2.3
8	1	8	8	7		7	1	7	7	6	14793.9483	-3.0
8	1	7	7	7		7	1	6	6	6	15673.4018	5.8
8	1	7	8	8		7	1	6	7	7	15673.4018	4.1
8	1	7	8	9		7	1	6	7	8	15673.4105	-7.6
8	1	7	9	9		7	1	6	8	8	15673.4105	-8.1
8	1	7	7	8		7	1	6	6	7	15673.4105	-8.6
8	1	7	8	7		7	1	6	7	6	15673.4284	0.0
8	1	7	7	6		7	1	6	6	5	15673.4284	-4.5
8	1	7	9	10		7	1	6	8	9	15673.4525	6.9

8	1	7	9	8		7	1	6	8	7	15673.4525	-0.5
9	0	9	9	9		8	0	8	8	8	16643.3336	-8.8
9	0	9	8	9		8	0	8	7	8	16643.3556	6.5
9	0	9	10	10		8	0	8	9	9	16643.3556	-3.4
9	0	9	9	10		8	0	8	8	9	16643.3556	2.3
9	0	9	10	11		8	0	8	9	10	16643.3750	3.6
9	0	9	10	9		8	0	8	9	8	16643.3750	0.7
9	1	9	9	9		8	1	8	8	8	16609.2781	4.8
9	1	9	8	8		8	1	8	7	7	16609.2781	2.2
9	1	9	9	10		8	1	8	8	9	16609.2781	1.0
9	1	9	9	8		8	1	8	8	7	16609.2781	-1.3
9	1	9	8	9		8	1	8	7	8	16609.2781	-2.0
9	1	9	10	10		8	1	8	9	9	16609.3050	8.6
9	1	9	10	11		8	1	8	9	10	16609.3050	3.6
9	1	9	10	9		8	1	8	9	8	16609.3050	1.6
9	1	8	10	10		8	1	7	9	9	17505.0809	-1.5
9	1	8	10	11		8	1	7	9	10	17505.1196	5.4
4	2	3	4	5		3	2	2	3	4	7740.6999	0.2
4	2	3	4	4		3	2	2	3	3	7740.8115	-1.1
4	2	3	5	4		3	2	2	4	3	7741.3012	-0.7
4	2	3	5	6		3	2	2	4	5	7741.3250	-1.4
4	2	3	5	5		3	2	2	4	4	7741.4581	-0.2
4	2	3	3	4		3	2	2	2	3	7741.4986	1.8
4	2	3	4	3		3	2	2	3	2	7740.6705	1.5
4	2	3	3	3		3	2	2	3	3	7741.6115	-5.0
4	2	3	3	2		3	2	2	2	1	7741.4581	4.7
4	2	2	4	3		3	2	1	3	2	7865.6764	-2.6
4	2	2	4	5		3	2	1	3	4	7865.7109	-1.9
4	2	2	4	4		3	2	1	3	3	7865.8445	1.3
4	2	2	5	4		3	2	1	4	3	7866.3133	-6.4
4	2	2	5	6		3	2	1	4	5	7866.3366	-1.7
4	2	2	5	5		3	2	1	4	4	7866.5044	-2.2
4	2	2	3	4		3	2	1	2	3	7866.5201	3.2
4	2	2	3	3		3	2	1	2	2	7866.6649	2.3
5	2	4	5	4		4	2	3	4	3	9659.6483	-1.2
5	2	4	5	6		4	2	3	4	5	9659.6603	3.7
5	2	4	5	5		4	2	3	4	4	9659.7255	2.7
5	2	4	6	5		4	2	3	5	4	9659.9781	-1.6
5	2	4	6	7		4	2	3	5	6	9659.9899	3.5
5	2	4	4	5		4	2	3	3	4	9660.0247	5.0

5	2	4	6	6		4	2	3	5	5	9660.0518	-0.2
5	2	3	5	6		4	2	2	4	5	9891.5750	-0.1
5	2	3	5	5		4	2	2	4	4	9891.6810	-0.5
5	2	3	6	5		4	2	2	5	4	9891.9006	7.8
5	2	3	6	7		4	2	2	5	6	9891.9006	-2.8
5	2	3	4	5		4	2	2	3	4	9891.9367	0.5
5	2	3	6	6		4	2	2	5	5	9892.0093	1.1
5	2	3	4	4		4	2	2	3	3	9892.0485	5.9
6	2	5	6	7		5	2	4	5	6	11567.7255	2.2
6	2	5	6	5		5	2	4	5	4	11567.7255	1.8
6	2	5	6	6		5	2	4	5	5	11567.7631	2.5
6	2	5	5	6		5	2	4	4	5	11567.9211	3.7
6	2	5	7	6		5	2	4	6	5	11567.9211	2.3
6	2	5	7	8		5	2	4	6	7	11567.9211	1.7
6	2	5	5	4		5	2	4	4	3	11567.9211	0.9
6	2	5	7	7		5	2	4	6	6	11567.9577	4.3
6	2	5	5	5		5	2	4	4	4	11567.9577	3.9
6	2	4	6	5		5	2	3	5	4	11930.4366	-1.6
6	2	4	6	7		5	2	3	5	6	11930.4366	-2.8
6	2	4	6	6		5	2	3	5	5	11930.5104	-2.0
6	2	4	5	6		5	2	3	4	5	11930.6297	1.9
6	2	4	7	6		5	2	3	6	5	11930.6297	1.4
6	2	4	5	4		5	2	3	4	3	11930.6297	-0.2
6	2	4	7	8		5	2	3	6	7	11930.6297	-1.4
6	2	4	5	5		5	2	3	4	4	11930.6970	-2.0
6	2	4	7	7		5	2	3	6	6	11930.6970	-1.9
8	2	7	8	9		7	2	6	7	8	15345.5067	8.7
8	2	7	8	7		7	2	6	7	6	15345.5067	5.3
8	2	7	8	8		7	2	6	7	7	15345.5067	0.0
8	2	7	7	8		7	2	6	6	7	15345.5741	3.0
8	2	7	7	6		7	2	6	6	5	15345.5741	-2.0
8	2	7	7	7		7	2	6	6	6	15345.5741	-4.7
8	2	7	9	10		7	2	6	8	9	15345.5938	8.9
8	2	7	9	8		7	2	6	8	7	15345.5938	6.4
8	2	7	9	9		7	2	6	8	8	15345.5938	2.7
8	2	6	8	9		7	2	5	7	8	15985.1519	-0.9
8	2	6	8	7		7	2	5	7	6	15985.1583	0.8
8	2	6	8	8		7	2	5	7	7	15985.1838	3.2
8	2	6	7	8		7	2	5	6	7	15985.2151	0.2
8	2	6	7	6		7	2	5	6	5	15985.2151	-7.1

8	2	6	9	10		7	2	5	8	9	15985.2378	7.2
8	2	6	9	8		7	2	5	8	7	15985.2378	4.6
8	2	6	7	7		7	2	5	6	6	15985.2378	-2.7
8	2	6	9	9		7	2	5	8	8	15985.2545	1.0
4	1	4	3	4		3	0	3	2	3	8111.2046	0.6
4	1	4	3	2		3	0	3	2	1	8111.2923	0.6
4	1	4	3	3		3	0	3	2	2	8111.0967	0.6
4	1	4	5	5		3	0	3	4	4	8111.2559	0.3
4	1	4	5	6		3	0	3	4	5	8111.4034	2.4
4	1	4	5	4		3	0	3	4	3	8111.4330	-5.8
4	1	4	4	4		3	0	3	3	3	8111.4253	0.1
4	1	4	4	5		3	0	3	3	4	8111.5186	-2.1
4	1	4	4	3		3	0	3	3	2	8111.5702	-0.7
5	1	5	4	4		4	0	4	3	3	9793.5879	0.3
5	1	5	4	5		4	0	4	3	4	9793.6801	-1.8
5	1	5	6	6		4	0	4	5	5	9793.6801	1.5
5	1	5	4	3		4	0	4	3	2	9793.7237	-5.5
5	1	5	6	7		4	0	4	5	6	9793.7892	0.5
5	1	5	6	5		4	0	4	5	4	9793.8151	1.6
5	1	5	5	5		4	0	4	4	4	9793.7583	-0.2
5	1	5	5	6		4	0	4	4	5	9793.8456	-0.5
5	1	5	5	4		4	0	4	4	3	9793.8806	2.9
6	1	6	5	5		5	0	5	4	4	11481.9179	-1.7
6	1	6	7	7		5	0	5	6	6	11481.9760	-1.2
6	1	6	5	6		5	0	5	4	5	11481.9912	1.2
6	1	6	5	4		5	0	5	4	3	11482.0081	-8.2
6	1	6	6	6		5	0	5	5	5	11482.0183	7.9
6	1	6	7	8		5	0	5	6	7	11482.0580	3.0
6	1	6	7	6		5	0	5	6	5	11482.0687	-1.7
6	1	6	6	7		5	0	5	5	6	11482.0802	3.0
6	1	6	6	5		5	0	5	5	4	11482.0950	-1.3
7	1	7	6	6		6	0	6	5	5	13192.3664	0.1
7	1	7	8	8		6	0	6	7	7	13192.4042	-1.4
7	1	7	6	7		6	0	6	5	6	13192.4146	0.5
7	1	7	6	5		6	0	6	5	4	13192.4317	2.6
7	1	7	7	7		6	0	6	6	6	13192.4146	0.7
7	1	7	8	9		6	0	6	7	8	13192.4593	2.2
7	1	7	8	7		6	0	6	7	6	13192.4593	-7.3
7	1	7	7	8		6	0	6	6	7	13192.4593	-0.4
7	1	7	7	6		6	0	6	6	5	13192.4748	3.6

8	1	8	7	7		7	0	7	6	6	14929.5325	0.5
8	1	8	9	9		7	0	7	8	8	14929.5660	5.2
8	1	8	7	8		7	0	7	6	7	14929.5660	3.0
8	1	8	7	6		7	0	7	6	5	14929.5660	-5.7
8	1	8	8	8		7	0	7	7	7	14929.5549	-1.4
8	1	8	9	10		7	0	7	8	9	14929.5950	1.4
8	1	8	9	8		7	0	7	8	7	14929.5950	-4.4
8	1	8	8	9		7	0	7	7	8	14929.5846	-1.7
8	1	8	8	7		7	0	7	7	6	14929.5950	1.8
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7	2	6	8	8		6	1	6	7	7	17883.3471	6.7
2	2	1	1	2		1	1	1	1	2	6903.7246	7.3
2	2	1	3	3		1	1	1	2	2	6905.1150	0.3
2	2	1	3	4		1	1	1	2	3	6905.1845	0.4
2	2	1	3	2		1	1	1	2	1	6905.2260	3.0
2	2	1	1	2		1	1	1	0	1	6905.3353	-1.6
2	2	1	2	2		1	1	1	1	1	6905.6804	0.7
2	2	1	2	1		1	1	1	1	1	6905.9283	-1.1
2	2	1	2	1		1	1	1	1	0	6906.4025	2.0.
2	2	1	2	3		1	1	1	1	2	6906.0624	1.6
2	2	1	2	3		1	1	1	2	3	6906.6420	0.1
2	2	1	2	2		1	1	1	2	2	6906.7330	1.3
3	3	0	2	3		2	2	0	2	3	10745.9622	-0.1
3	3	0	2	2		2	2	0	1	2	10747.9739	3.5
3	3	0	4	4		2	2	0	3	3	10748.0195	2.0
3	3	0	4	5		2	2	0	3	4	10748.1381	1.1
3	3	0	4	3		2	2	0	3	2	10748.1433	-3.0
3	3	0	3	3		2	2	0	2	2	10748.4157	-3.1
3	3	0	3	4		2	2	0	2	3	10748.5827	-3.4
3	3	1	4	4		2	2	1	3	3	10760.4328	-1.3
3	3	1	4	5		2	2	1	3	4	10760.5362	0.6
3	3	1	4	3		2	2	1	3	2	10760.5362	-4.9
3	3	1	2	2		2	2	1	1	1	10760.5362	-1.3

3	3	1	2	3		2	2	1	1	2	10760.6980	-6.6
3	3	1	3	3		2	2	1	2	2	10760.8239	-0.7
3	3	1	3	4		2	2	1	2	3	10760.9828	-2.4
4	3	1	3	3		3	2	1	2	2	12662.6592	-1.8
4	3	1	5	5		3	2	1	4	4	12662.7998	-0.3
4	3	1	3	4		3	2	1	2	3	12662.7998	-4.5
4	3	1	5	6		3	2	1	4	5	12662.9533	0.3
4	3	1	5	4		3	2	1	4	3	12662.9900	-0.4
4	3	1	4	4		3	2	1	3	3	12663.3642	0.5
4	3	1	4	5		3	2	1	3	4	12663.5030	-0.1
4	3	1	4	3		3	2	1	3	2	12663.5446	0.0
4	3	2	3	3		3	2	2	2	2	12722.2181	-1.5
4	3	2	3	4		3	2	2	2	3	12722.3139	-0.6
4	3	2	5	5		3	2	2	4	4	12722.3592	1.0
4	3	2	5	6		3	2	2	4	5	12722.4622	-0.9
4	3	2	5	4		3	2	2	4	3	12722.4796	-3.2
4	3	2	4	4		3	2	2	3	3	12722.9217	0.4
4	3	2	4	5		3	2	2	3	4	12723.0119	0.3
4	3	2	4	3		3	2	2	3	2	12723.0320	-3.9

S2. Table of the Experimental transition frequencies (ν/MHz: 48 *a*-type, 57 *b*-type, and 12 *c*-type transitions, respectively) together with the corresponding observed – calculated differences ($\Delta\nu$/kHz) for (^{14}N)nitroethane - (^{15}N)trimethylamine.

J'	K_a'	K_c'	F'	←	J''	K_a''	K_c''	F''	ν/MHz	$\Delta\nu$/kHz
4	1	4	3		3	1	3	2	7431.5250	-1.7
4	1	4	4		3	1	3	3	7431.5542	1.0
4	1	4	5		3	1	3	4	7431.5250	0.7
4	0	4	4		3	0	3	3	7594.8237	1.6
4	0	4	5		3	0	3	4	7594.8540	1.3
4	0	4	3		3	0	3	2	7594.8853	-2.4
4	1	3	5		3	1	2	4	7951.1407	1.7
4	1	3	4		3	1	2	3	7951.1678	-3.3
4	1	3	3		3	1	2	2	7951.1678	0.1
5	0	5	5		4	0	4	4	9418.6590	0.1
5	0	5	6		4	0	4	5	9418.6935	0.7
5	0	5	4		4	0	4	3	9418.7082	-5.5
5	1	5	5		4	1	4	4	9270.0285	0.8
5	1	5	4		4	1	4	3	9270.0285	5.3
5	1	5	6		4	1	4	5	9270.0166	-1.3
5	1	4	5		4	1	3	4	9908.9582	-0.2
5	1	4	6		4	1	3	5	9908.9498	-1.5
5	1	4	4		4	1	3	3	9908.9735	0.5
6	1	6	6		5	1	5	5	11099.1333	1.4
6	1	6	5		5	1	5	4	11099.1333	-2.2
6	1	6	7		5	1	5	6	11099.1333	2.6
6	0	6	6		5	0	5	5	11217.6188	-2.9
6	0	6	7		5	0	5	6	11217.6574	4.9
6	0	6	5		5	0	5	4	11217.6574	-8.1
6	1	5	6		5	1	4	5	11842.6315	-1.1
6	1	5	7		5	1	4	6	11842.6410	0.0
6	1	5	5		5	1	4	4	11842.6561	-1.4
7	1	7	7		6	1	6	6	12919.7267	0.7
7	1	7	6		6	1	6	5	12919.7331	0.1
7	1	7	8		6	1	6	7	12919.7267	-2.1
7	0	7	7		6	0	6	6	13004.5973	2.6
7	0	7	8		6	0	6	7	13004.6200	1.0
7	0	7	6		6	0	6	5	13004.6307	3.3
7	1	6	7		6	1	5	6	13744.5901	-0.5

7	1	6	8		6	1	5	7	13744.6072	-3.0
7	1	6	6		6	1	5	5	13744.6246	0.9
8	1	7	8		7	1	6	7	15608.8781	1.5
8	1	7	9		7	1	6	8	15608.9034	-1.1
8	1	7	7		7	1	6	6	15608.9195	3.9
9	0	9	9		8	0	8	8	16576.3262	-2.6
9	0	9	10		8	0	8	9	16576.3451	3.2
9	0	9	8		8	0	8	7	16576.3451	-0.3
9	1	9	9		8	1	8	8	16541.3358	-1.8
9	1	9	8		8	1	8	7	16541.3459	0.3
9	1	9	10		8	1	8	9	16541.3459	2.8
9	1	8	9		8	1	7	8	17434.8451	0.3
9	1	8	10		8	1	7	9	17434.8736	-3.8
9	1	8	8		8	1	7	7	17434.8889	2.4
4	1	4	4		3	0	3	3	8086.3523	0.0
4	1	4	5		3	0	3	4	8086.5114	1.6
4	1	4	3		3	0	3	2	8086.5763	-1.2
5	1	5	5		4	0	4	4	9761.5550	-2.8
5	1	5	6		4	0	4	5	9761.6767	1.6
5	1	5	4		4	0	4	3	9761.7113	-1.6
6	1	6	6		5	0	5	5	11442.0326	1.7
6	1	6	7		5	0	5	6	11442.1141	1.1
6	1	6	5		5	0	5	4	11442.1364	1.6
7	1	7	7		6	0	6	6	13144.1350	-0.1
7	1	7	8		6	0	6	7	13144.1890	-0.3
7	1	7	6		6	0	6	5	13144.2045	2.4
8	1	8	8		7	0	7	7	14872.7891	-0.3
8	1	8	9		7	0	7	8	14872.8223	-1.8
8	1	8	7		7	0	7	6	14872.8328	1.1
9	1	9	9		8	0	8	8	16624.7894	2.3
9	1	9	10		8	0	8	9	16624.8119	2.7
9	1	9	8		8	0	8	7	16624.8119	-1.9
10	1	10	10		9	0	9	9	18393.9775	-0.8
10	1	10	11		9	0	9	10	18393.9927	0.0
10	1	10	9		9	0	9	8	18393.9927	-3.1
4	0	4	3		3	1	3	2	6939.8350	-1.9
4	0	4	5		3	1	3	4	6939.8680	0.9
4	0	4	4		3	1	3	3	6940.0239	1.0
5	0	5	4		4	1	4	3	8927.0209	-3.0
5	0	5	6		4	1	4	5	8927.0350	-0.6

5	0	5	5		4	1	4	4	8927.1289	0.3
6	0	6	6		5	1	5	5	10874.7236	0.9
6	0	6	7		5	1	5	6	10874.6715	1.3
6	0	6	5		5	1	5	4	10874.6643	-2.0
7	0	7	7		6	1	6	6	12780.1862	0.7
7	0	7	8		6	1	6	7	12780.1597	1.2
7	0	7	6		6	1	6	5	12780.1597	1.4
9	0	9	9		8	1	8	8	16492.8805	1.1
9	0	9	10		8	1	8	9	16492.8805	4.8
9	0	9	8		8	1	8	7	16492.8805	3.2
10	0	10	10		9	1	9	9	18318.0063	-1.6
10	0	10	11		9	1	9	10	18318.0063	-2.1
10	0	10	9		9	1	9	8	18318.0063	-3.6
3	2	2	3		2	1	1	2	8567.3751	1.7
3	2	2	4		2	1	1	3	8567.6751	-5.5
3	2	2	2		2	1	1	1	8567.8529	1.5
3	2	1	2		2	1	2	1	9024.8860	2.2
3	2	1	4		2	1	2	3	9024.8860	-1.6
3	2	1	3		2	1	2	2	9024.9133	-0.6
4	2	3	4		3	1	2	3	10298.4596	-1.3
4	2	3	5		3	1	2	4	10298.7208	-1.6
4	2	3	3		3	1	2	2	10298.8265	-0.1
5	2	4	5		4	1	3	4	11965.1929	-0.7
5	2	4	6		4	1	3	5	11965.4187	-2.9
5	2	4	4		4	1	3	3	11965.4944	3.3
3	3	0	3		2	2	1	2	10756.9216	1.1
3	3	0	2		2	2	1	1	10756.9768	1.4
3	3	0	4		2	2	1	3	10757.0098	-2.0
3	3	1	3		2	2	0	2	10743.1407	-4.7
3	3	1	2		2	2	0	1	10743.2358	1.8
3	3	1	4		2	2	0	3	10743.2614	2.8
4	1	3	3		3	0	3	2	9391.8972	-2.0
4	1	3	5		3	0	3	4	9391.9082	1.0
4	1	3	4		3	0	3	3	9392.0455	1.7
5	1	4	4		4	0	4	3	11705.9881	3.6
5	1	4	6		4	0	4	5	11706.0057	-0.2
5	1	4	5		4	0	4	4	11706.1788	-1.3
3	2	1	3		2	1	1	2	8631.3631	3.2
3	2	1	4		2	1	1	3	8631.6164	1.4
3	2	1	2		2	1	1	1	8631.7670	-0.4

4	2	2	4		3	1	2	3	10485.0009	0.5
4	2	2	5		3	1	2	4	10485.1679	-3.4
4	2	2	3		3	1	2	2	10485.2540	1.7

S3. Computational details: calculation of energetics and spectroscopic parameters.

A preliminary scan of the trimethylamine(TMA)···nitroethane(NE) potential energy surface was carried out by using the hydrid B3LYP functional[1] in conjunction with the polarized double-ζ SNSD basis set[2]. This led to the identification of three minima labeled from M1 to M3 (with a fourth stationary point M3' being equivalent to M3), as reported in Figure 1 of the manuscript, and the transition states ruling their interconversion. Successively, calculations were refined by employing the double-hybrid B2PLYP functional[3] in conjunction with the maug-cc-pVTZ basis set[4] in which *d* functions on hydrogen atoms were removed (namely, the maug-cc-pVTZ-*d*H basis set[5]). All density functional theory (DFT) calculations were corrected for dispersion effects according to Grimme's DFT-D3[6] scheme employing the Becke-Johnson damping function[7]. Harmonic frequency calculations were carried out at both B3LYP-D3 and B2PLYP-D3 levels of theory in order to check the nature of the stationary points; these calculations also provided zero-point vibrational energy (ZPE) contributions within the harmonic approximation. For all the stationary points, accurate electronic energies were computed by adopting the so-called "cheap" composite scheme introduced in reference [8]. This considers the coupled-cluster singles and doubles approximation augmented by a perturbative treatment of triple excitations, CCSD(T)[9], as starting point. Indeed, the frozen-core CCSD(T)/cc-pVTZ electronic energies were corrected according to the scheme:

$$E_{elec}^{best} = E(CCSD(T)/cc-pVTZ) + \Delta E_{corr}^{MP2/\infty} + \Delta E_{CV}^{MP2/pCVTZ} \qquad (1)$$

where $\Delta E_{corr}^{MP2/\infty}$ accounts for the extrapolation to the complete basis set (CBS) limit and is obtained by extrapolating to the CBS limit the Hartree-Fock electronic energy ($E^{HF-SCF/\infty}$) according to the three point extrapolation formula[10] adopting the cc-pVnZ n = T, Q, 5[11] sets and the MP2[12] correlation energy by using the n^{-3} formula[13] in conjunction with the cc-pVTZ and cc-pVQZ basis sets. $\Delta E_{CV}^{MP2/CVTZ}$ represents the core-valence correlation correction and it is obtained as difference of the MP2 energies evaluated correlating all electrons and within the frozen-core approximation, in conjunction with the cc-pCVTZ basis set[14]. For all stationary points, computed electronic energies were then employed to derive the complex interaction energy, which was in all cases corrected for harmonic ZPE contributions at the B2PLYP-D3 level as well as for the basis set superposition error (BSSE), thus resorting to the counterpoise procedure proposed by Boys and Bernardi[15]. All results, along with the binding energies, are reported in Table S3.1.

Table S3.1. Relative (E_{rel}) and binding energies (ΔE) for the stationary points on the PES of the TMA···NE complex (kJ·mol^{-1}).

	E_{rel} best [a]	ΔE_{el} best[a]	E_{rel} B2PLYP-D3[b]	ΔE B2PLYP-D3[b]	E_{rel}^0 [c]	ΔE_0 [c]
M1	0.0	-27.1	0.0	-24.4	0.0	-24.0
M2	0.9	-26.2	0.8	-23.7	0.5	-23.4
M3 = M3'	2.7	-24.4	2.4	-22.1	2.7	-21.3
TS12	1.3	-	1.1	-	0.8	-
TS13	3.2	-	2.7	-	2.7	-
TS23'	3.3	-	2.9	-	2.9	-
TS33'	3.3	-	2.7	-	2.9	-

[a] Electronic energy from the "cheap" composite scheme corrected for BSSE.

[b] B2PLYP-D3/maug-cc-pVTZ-*d*H electronic energy corrected for BSSE.

[c] Electronic energy (BSSE corrected) from the "cheap" composite scheme corrected for the ZPE at the B2PLYP-D3/maug-cc-pVTZ-*d*H level.

For the three minima configurations, equilibrium rotational constants, B_x^e (x = *a*, *b* or *c*), were straightforwardly derived from the B2PLYP-D3/maug-cc-pVTZ-*d*H optimized geometries, while the rotational constants of the vibrational ground-state, B_x^0, were obtained by correcting the equilibrium values according to the following equation

$$B_x^0 = B_x^e - \frac{1}{2}\sum_{k=1}^{3N-6} \alpha_k^x \qquad (2)$$

where the sum runs over all vibrational normal modes. The vibration-rotation interaction constants (α_k^x) were obtained within the vibrational perturbation theory to second order (VPT2) applied to the B3LYP/SNSD cubic force field[16]. The reliability of vibrational corrections to rotational constants evaluated at this level of theory has been widely demonstrated in the framework of accurate equilibrium structure determinations by means of the semi-experimental approach[17]. In passing, it should be noted that for the present case, the presence of large amplitude motions, basically corresponding to inter-monomers vibrations, can slightly degrade their accuracy. To complete the rotational spectroscopic characterization, equilibrium dipole moments and nitrogen nuclear quadrupolar coupling constants were calculated at the B2PLYP-D3/maug-cc-pVTZ-*d*H level. This level of theory was also employed to determine the quartic centrifugal distortion constants. Anharmonic calculations were carried out by using the generalized perturbative machinery[18] implemented in the Gaussian16 software[19], which was employed for all quantum chemical calculations, but the energy evaluation at the CCSD(T)/cc-pVTZ level, for which the CFOUR quantum-package code was used[20]. All results for the isomers of the (^{14}N)TMA···(^{14}N)NE complex are reported in Table S3.2, where they are compared to the available experimental data. In Table S3.3 the equilibrium and vibrationally corrected rotational constants are listed for the same isomers of the (^{15}N)TMA···(^{14}N)NE complex along with the experimental ground state rotational constants.

Table S3.2. Theoretical equilibrium, rotational constants, vibrational corrections and ground state rotational parameters computed for all the minima and the averaged M1/M2 structure of the (^{14}N)TMA···(^{14}N)NE complex. Comparison to experimental results is also provided.

		M1	M2	M3	Avg12 [a]	Exp
A_e[b] [MHz]		1952.96	1951.59	2262.48	1929.75	-
B_e[b] [MHz]		1053.78	1030.22	888.61	1039.95	-
C_e[b] [MHz]		917.46	893.42	829.18	903.38	-
ΔA^{vib} [c] [MHz]		-17.90	-22.90	-34.45	-20.40	-
ΔB^{vib} [c] [MHz]		-24.37	-26.50	-9.50	-25.44	-
ΔC^{vib} [c] [MHz]		-20.18	-20.90	-10.07	-20.54	-
A_0[d] [MHz]		1935.06	1928.69	2228.03	1909.35	1956.7717(1)
B_0[d] [MHz]		1029.41	1003.72	879.11	1014.51	1035.08972(6)
C_0[d] [MHz]		897.28	872.52	819.11	882.85	902.83562(4)
D_J[e] [kHz]		0.48	0.86	0.40		0.5608(4)
D_K[e] [kHz]		-1.58	-2.06	0.24		-1.77(1)
D_{JK}[e] [kHz]		1.28	1.69	0.59		1.385(5)
d_1[e] [kHz]		-0.07	-0.11	-0.03		-0.0772(2)
d_2[e] [kHz]		0.00	0.00	0.01		-
^{14}N(TMA) [MHz][f]	χ_{aa}	-4.81	-4.71	-5.27		-4.632(1)
	χ_{bb}- χ_{cc}	-0.49	0.32	-0.15		-0.407(2)
	χ_{ab}	2.18	-1.16	1.22		-
	χ_{ac}	0.76	2.17	-0.94		-
	χ_{bc}	-0.27	0.33	0.09		-
^{14}N(NE) [MHz][f]	χ_{aa}	1.04	1.05	1.01		1.039(3)
	χ_{bb}- χ_{cc}	-0.88	-0.69	-1.92		-0.866(3)
	χ_{ab}	0.16	-0.19	0.34		-
	χ_{ac}	-0.03	0.12	-0.05		-
	χ_{bc}	-0.86	0.89	0.02		-
μ_a[g] [D]		0.70	-0.64	0.12		Observed[h]
μ_b[g] [D]		2.90	2.93	3.38		Observed[h]
μ_c[g] [D]		1.48	-1.48	-0.04		Observed[h]

[a] Effective structure obtained as the average between M1 and M2.

[b] Equilibrium rotational constants at the B2PLYP-D3/maug-cc-pVTZ-*d*H level.

[c] Vibrational corrections to rotational constants at the B3LYP-D3/SNSD level.

[d] Vibrational ground-state rotational constants obtained by combining [b] and [c] according to Eq. (2).

[e] Quartic centrifugal distorsion constants (Watson S-reduction).

[f] Equilibrium quadrupole coupling constants at the B2PLYP/maug-cc-pVTZ-*d*H level.

[g] Equilibrium dipole moment components (B2PLYP/maug-cc-pVTZ-*d*H) along the principal axes of inertia.

[h] To indicate the type of transitions assigned (μ_a-, μ_b- and μ_c-type rotational transitions.

Table S3.3. Theoretical equilibrium rotational constants, vibrational corrections and ground state rotational constants computed for all the minima of the (^{15}N)TMA···(^{14}N)NE complex. Comparison to experimental results.

	M1	M2	M3	Avg12 [a]	Exp
A_e[b] [MHz]	1952.91	1951.54	2262.01	1929.72	-
B_e[b] [MHz]	1048.73	1025.17	884.35	1034.96	-
C_e[b] [MHz]	913.62	889.62	825.41	899.61	-
ΔA^{vib} [c] [MHz]	-17.90	-22.84	-32.71	-20.37	-
ΔB^{vib} [c] [MHz]	-24.22	-26.26	-9.53	-25.24	-
ΔC^{vib} [c] [MHz]	-20.06	-20.69	-9.77	-20.37	-
A_0[d] [MHz]	1935.01	1928.70	2229.30	1909.35	1956.7625(5)
B_0[d] [MHz]	1024.51	998.91	874.82	1009.72	1030.25149(8)
C_0[d] [MHz]	893.56	868.93	815.64	879.24	899.13798(5)

[a] Effective structure obtained as the average between M1 and M2.

[b] Equilibrium rotational constants at the B2PLYP-D3/maug-cc-pVTZ-*d*H level.

[c] Vibrational corrections to rotational constants at the B3LYP-D3/SNSD level.

[d] Vibrational ground-state rotational constants obtained by combining [b] and [c] according to Eq. (2).

S4. Cartesian coordinates of the structures of M1, M2 and M3 isomers optimized at the B2PLYP-D3/m-aug-cc-pVTZ-*d*H level.

Table S4.1. M1-isomer: Cartesian coordinates together with the corresponding molecular representation.

	X	*Y*	*Z*
N	1.528065	0.075238	-0.004861
C	1.952511	-0.528525	1.248677
H	1.855408	0.194096	2.058660
H	1.321951	-1.386479	1.472697
H	3.000960	-0.864142	1.218478
C	2.306518	1.267245	-0.296974
H	1.955780	1.719195	-1.223631
H	2.189743	1.993477	0.506656
H	3.380944	1.051812	-0.408798
C	1.620097	-0.884447	-1.096244
H	1.002529	-1.752045	-0.874756
H	1.253356	-0.431846	-2.015293
H	2.654103	-1.224282	-1.262721
O	-1.240467	-1.558758	0.622768
O	-1.614202	-0.454960	-1.212649
N	-1.456200	-0.524707	-0.001337
C	-1.572243	0.735709	0.816980
H	-2.523653	0.631774	1.336066
H	-0.770110	0.662284	1.541674
C	-1.499829	1.987728	-0.021022
H	-1.579861	2.851812	0.637237
H	-0.551365	2.037229	-0.547204
H	-2.305741	2.029011	-0.747411

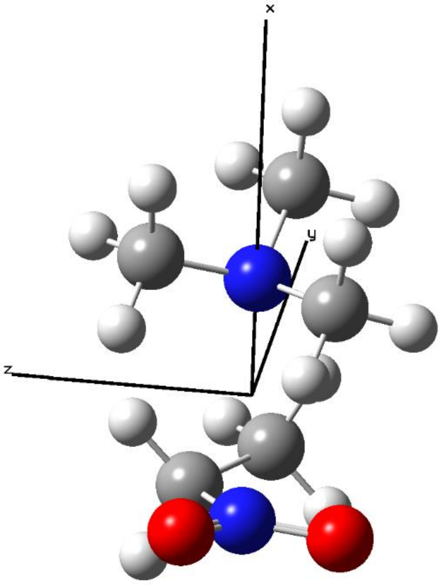


Table S4.2. M2-isomer: Cartesian coordinates together with the corresponding molecular representation

	X	*Y*	*Z*
N	-1.561220	0.071127	-0.049169
C	-2.413833	0.546098	-1.126478
H	-2.245671	1.609857	-1.290909
H	-2.177590	0.012699	-2.046117
H	-3.484517	0.399405	-0.913089
C	-1.827618	0.797001	1.182970
H	-1.136140	0.469372	1.956684
H	-1.686189	1.865013	1.021663
H	-2.856059	0.641969	1.545428
C	-1.733546	-1.360871	0.154453
H	-1.489661	-1.895599	-0.761056
H	-1.059791	-1.703635	0.936581
H	-2.764872	-1.615719	0.444257
O	1.426636	-0.435586	1.225607
O	1.395626	-1.611521	-0.602910
N	1.456227	-0.550127	0.006694
C	1.585595	0.691232	-0.839388
H	2.478658	0.521706	-1.436034
H	0.717163	0.654875	-1.488315
C	1.649614	1.958363	-0.024124
H	1.742042	2.803804	-0.704619
H	0.747927	2.084229	0.566577
H	2.504358	1.959826	0.646465

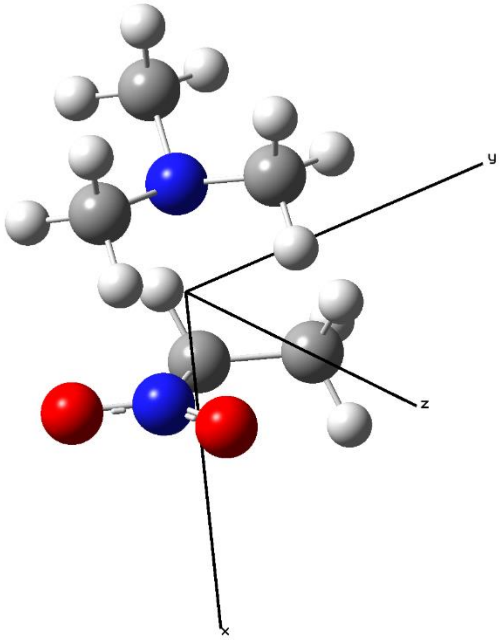
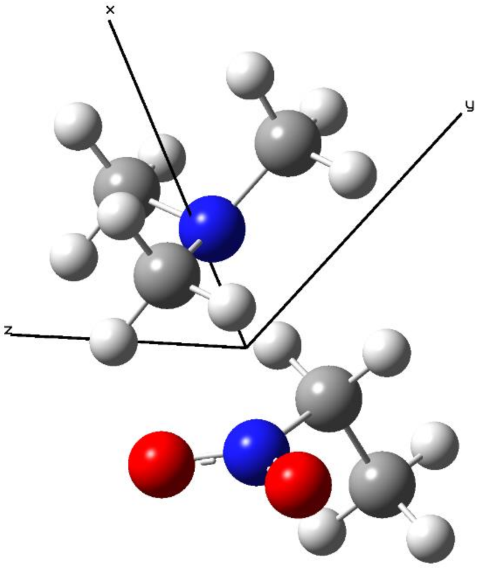


Table S4.3. M3-isomer: Cartesian coordinates together with the corresponding molecular representation.

	X	*Y*	*Z*
N	1.663340	0.215524	-0.034600
C	1.993890	0.467788	1.358273
H	1.738626	1.494640	1.618911
H	1.421465	-0.202877	1.996095
H	3.064782	0.320492	1.569794
C	2.352881	1.143778	-0.913915
H	2.057994	0.960760	-1.946050
H	2.085767	2.167831	-0.654935
H	3.448855	1.051783	-0.850080
C	1.958875	-1.163082	-0.395442
H	1.393574	-1.837778	0.244040
H	1.662065	-1.344465	-1.426339
H	3.029615	-1.398785	-0.292960
O	-1.085448	-1.056435	1.104133
O	-1.228820	-1.120256	-1.067308
N	-1.219150	-0.527000	0.005167
C	-1.457095	0.951986	-0.026312
H	-0.975304	1.349774	0.858469
H	-0.963974	1.310993	-0.921520
C	-2.953548	1.214164	-0.042098
H	-3.128033	2.287868	-0.066583
H	-3.413841	0.770886	-0.921904
H	-3.427684	0.810297	0.849684



S5. “Natural Orbital for Chemical Valence/Charge-Displacement” (NOCV/CD) scheme detailed description and results completion.

S5.1. Brief outline of the method

Given an adduct AB formed by fragments A and B, the electron charge rearrangement taking place after formation of the A−B bond can be formulated as the difference $\Delta\rho(x, y, z)$ between the total electron density of the adduct and those of the unbound fragments A and B taken at their in-adduct geometries. A quantitative analysis of the charge-rearrangement profile along a given directional axis z (typically chosen as a suitably defined “interaction axis”) can be performed by means of the following spatial integral:

$$\Delta q(z) = \int_{-\infty}^{z} dz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta\rho(x, y, z') dx dy \qquad (1)$$

thus giving the exact amount of electron charge that, upon bond formation, has flown from right to left across a plane orthogonal to the z axis through that point. Insight on the contributions in terms of molecular orbitals of the fragments to the overall charge rearrangement can be gained by adopting a slightly different reference density for the unbound fragments A and B. Rather than summing the respective densities, such a new reference density is constructed from the occupied molecular orbitals of the fragments (as above, taken at their in-adduct geometries) previously made orthonormal to each other. We shall refer to the slightly different charge-rearrangement resulting from this choice as to $\Delta\rho'$. If all densities are worked out from single-determinant wavefunctions (as in HF or DFT calculations), by diagonalizing the so-called “valence operator” and finding its eigenvalues w_k and eigenfunctions φ_k termed as “natural orbitals for chemical valence” (NOCVs), $\Delta\rho'$ can be decomposed into weighted contributions ascribable to pairs of NOCVs coupled by the eigenvalue w_k:

$$\Delta\rho' = \sum_{k} w_k \left(|\varphi_k|^2 - |\varphi_{-k}|^2\right) = \sum_{k} w_k \Delta\rho_k \qquad (2)$$

where the spatial dependence of densities and orbitals has been dropped for clarity. In other words, the total electron charge rearrangement $\Delta\rho'$ taking place after bond formation is decomposed into additive charge flows of w_k electrons flowing from orbital φ_{-k} to orbital φ_k, with k ranging from one to the number of occupied molecular orbitals of the adduct. Only a few NOCV components in Equation (2) have a significant weight and thus contribute non-negligibly to the overall charge rearrangement. The chemical character of these contributions can be recognized by a visual inspection in the 3D space of the related electron-density differences. The interested reader is referred to References [21–29] for further details.

S5.2. Computational details

Bond analysis was performed on electron densities calculated at the B2PLYP-D3/maug-cc-pVTZ-*d*H level of theory by interfacing Gaussian16 with an ad hoc written program.[30] Numerical analysis on discretized electron densities in the form of Gaussian cube files was conducted using the CUBES program suite.[31]

S5.3. Results

A volume rendering representation of the overall charge rearrangement $\Delta\rho(x,y,z)$ occurring upon bonding of TMA to NE is given in Figure S5.1 for the M1, TS12 and M2 stationary points of the resulting complex.

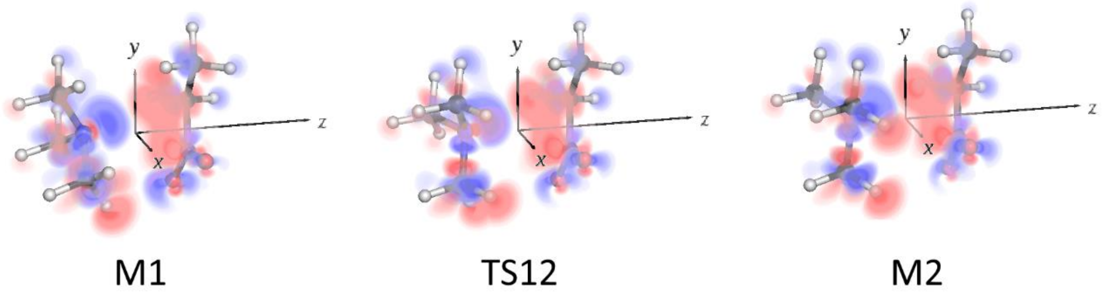


Figure S5.1. Volume rendering representation (isosurface layers between ±0.002 $(e/bohr^3)^{1/2}$) of $\Delta\rho(x,y,z)$ for the M1, TS12 and M2 stationary points of the TMA-NE complex. Red volume indicates electron depletion, blue volume indicates electron accumulation.

For all of them, the lone-pair region of the nitrogen atom of TMA results enriched in electron charge while electron depletion is observed from the p orbital hosting the lone pair of the nitrogen atom of NE. On the other hand, a charge flow in the opposite direction is observed between the hydrogen atoms of TMA and the neighboring oxygen atoms of NE. As mentioned above, a quantitative picture of the charge-rearrangement profile along a directional axis can be obtained via integration of Equation (1). To the purpose of analyzing the interaction between TMA and NE, a natural choice for the reference frame (x,y,z) to be used for that integration, is that of the principal axes of inertia of the resulting complex (precisely those shown in Figure S5.1), naturally accounting for the overall 3D shape of the complex. As the reader can intuitively get by inspecting Figure S5.1, one of these axes (hereinafter referenced as z) joins the fragments through the center of mass of the adduct, while the remaining two identify a plane xy naturally adapting between the planar orientations of the two fragments. The charge-rearrangement profile $\Delta q(z)$ along the interaction axis z upon bonding of TMA and NE is shown in Figure S5.2 for M1 (red line), TS12 (black line) and M2 (blue line).

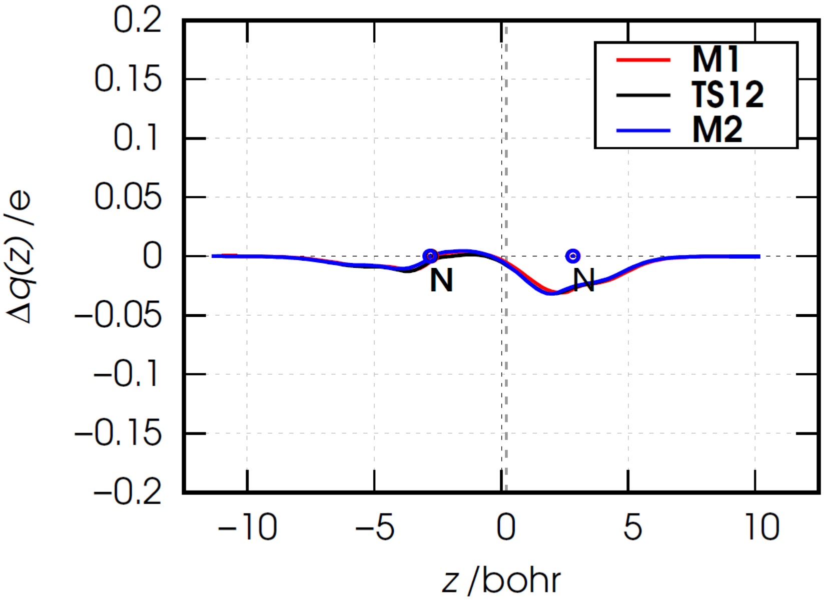


Figure S5.2. Charge-rearrangement profile along the interaction axis *z* upon bonding of TMA to NE.

As a result of the two opposite-direction charge flows highlighted above, the overall charge-rearrangement profile along the interaction axis results quite flat, with oscillations between approximately 10 me and −35 me (we recall here that, by definition, positive values of $\Delta q(z)$ quantify a charge flow from right to left for a given *z*, while negative values quantify a charge flow in the opposite direction). By fixing a plausible dividing plane between the fragments (our standard choice is the *z* point where equal-valued isodensity surfaces of the isolated fragments become tangent, see the dashed vertical line in Figure S5.2), a net charge transfer of 10 me from TMA to NE is found for all isomers. As mentioned above, an insight on the contribution in terms of the molecular orbitals of the fragments to the overall charge rearrangement can be gained through decomposition in NOCV pairs (Equation 2). The weights of the first six ($k \leq 6$) contributions to the charge rearrangement following bond formation between TMA and NE are reported in Table S5.3.

Table S5.1. Weights (NOCV eigenvalues w_k) of the first six charge-rearrangement components upon bonding of TMA to NE.

	M1	TS12	M2
k	w_k	w_k	w_k
1	0.090	0.081	0.078
2	0.034	0.030	0.031
3	0.026	0.026	0.027
4	0.023	0.022	0.023
5	0.019	0.018	0.020
6	0.018	0.017	0.017

For the first four of them, a graphical representation through isodensity-surface plots of the related NOCV orbitals and associated charge rearrangement is given in Figures S5.3, S5.4 and S5.5. A visual inspection of these plots reveals that for all conformers the most important contribution ($k = 1$, $w_k = 0.090$, 0.081 and 0.078 for M1, TS12 and M2, respectively) involves a charge flow between the two nitrogen atoms of the complex. The next two contributions describe mainly a charge flow between the hydrogen atoms of TMA and the neighboring oxygen atoms of NE (this is better seen through the related orbital plots, column 1 and 2, rather than through the density-difference plots, column 3, which are barely informative due to their associated lower weights). The fourth contribution, which is even less important, describes the charge flow between orbitals from the nitrogen atom of TMA and a hydrogen atom of NE.

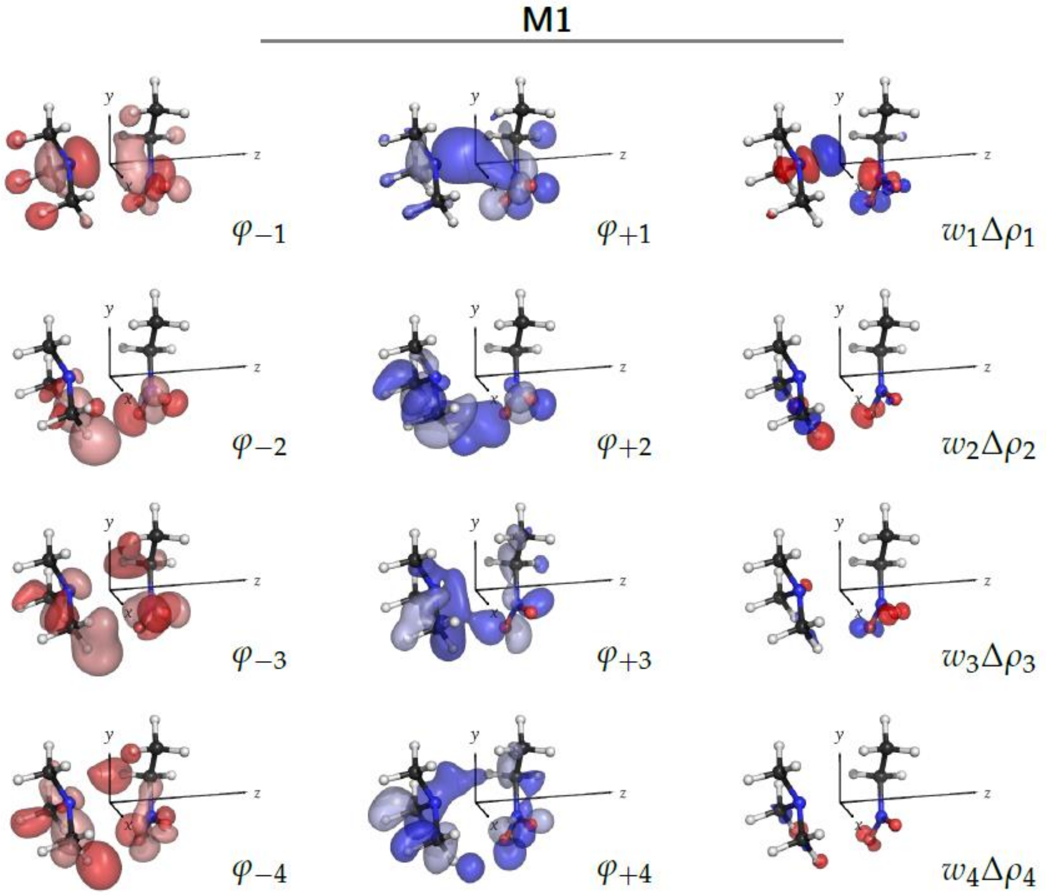


Figure S5.3. First four NOCV pairs (φ_{-k} and φ_k, isodensity surfaces at ±0.05 (e/bohr^3)$^{1/2}$) and associated charge rearrangement ($w_k\Delta\rho_k$, isodensity surfaces at ± 0.0005 e/bohr^3) for the M1 isomer. Density-difference plots: red isosurfaces indicate regions of electron depletion, blue isosurfaces indicate regions of electron accumulation.

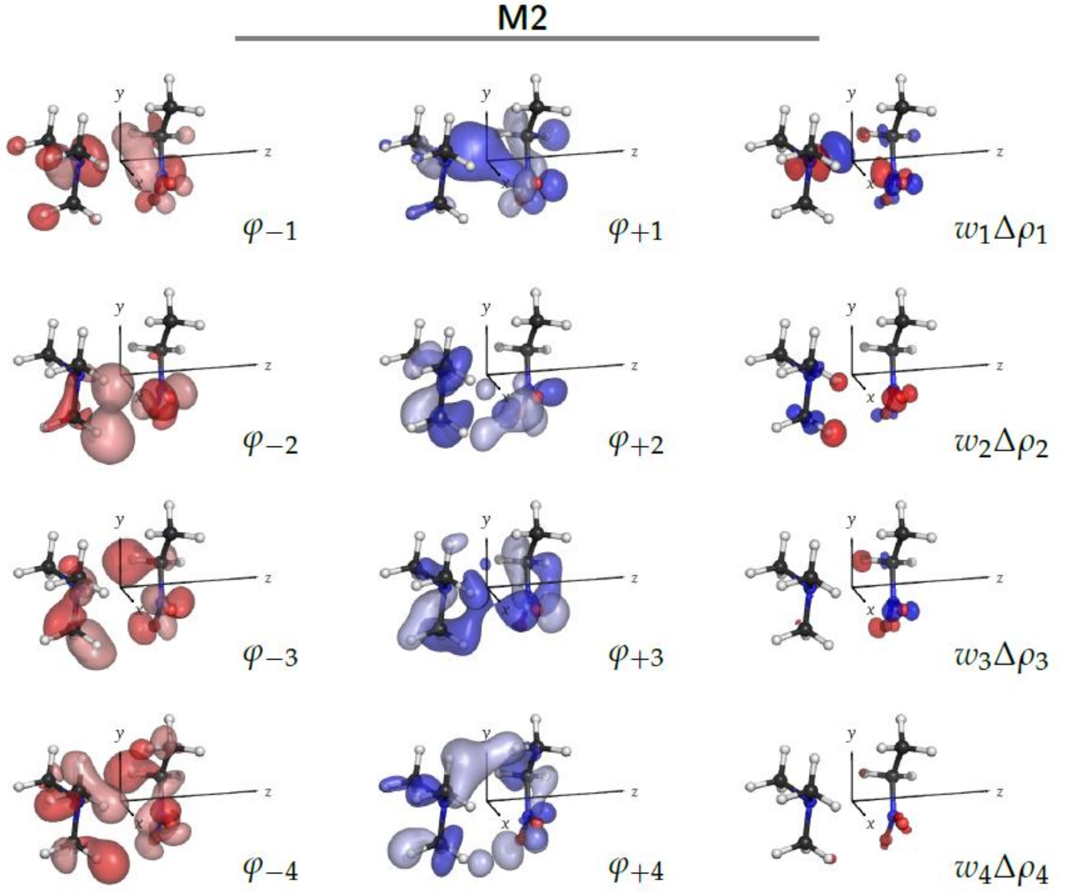


Figure S5.4. First four NOCV pairs (φ_{-k} and φ_k, isodensity surfaces at ±0.05 (e/bohr^3)$^{1/2}$) and associated charge rearrangement ($w_k\Delta\rho_k$, isodensity surfaces at ± 0.0005 e/bohr^3) for the M2 isomer. Density-difference plots: red isosurfaces indicate regions of electron depletion, blue isosurfaces indicate regions of electron accumulation.

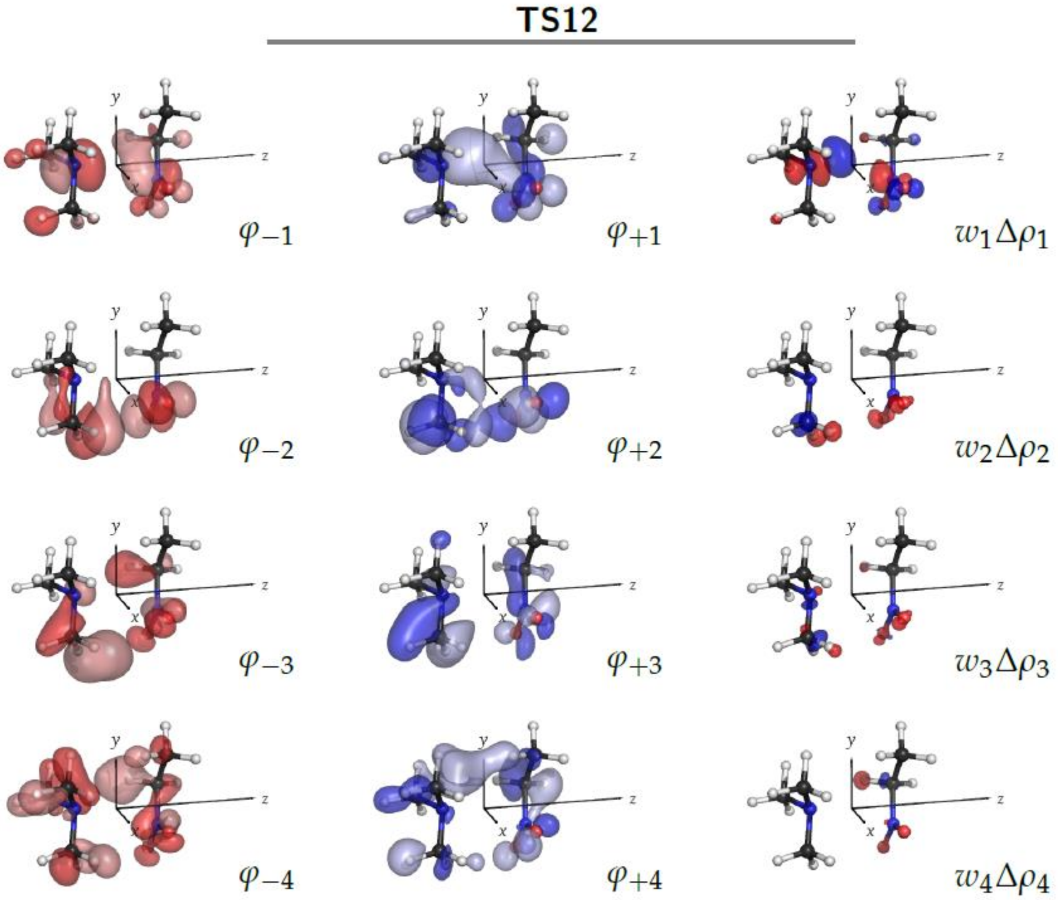


Figure S5.5. First four NOCV pairs (φ_{-k} and φ_k, isodensity surfaces at ±0.05 $(e/bohr^3)^{1/2}$) and associated charge rearrangement ($w_k\Delta\rho_k$, isodensity surfaces at ± 0.0005 $e/bohr^3$) for the M1-M2 (TS12) transition state. Density-difference plots: red isosurfaces indicate regions of electron depletion, blue isosurfaces indicate regions of electron accumulation.

S6. Energy decomposition analysis using the Symmetry-Adapted Perturbation Theory (SAPT) for M1, M2 and TS12 structures.

The nature of the interactions occurring in the formation of the 1:1 TMA-NE complex can be evaluated using the Symmetry-Adapted Perturbation Theory (SAPT)[32], which allows the decomposition of the binding energy into different contributions, namely electrostatics, induction, dispersion and exchange-repulsion terms. The results obtained at the SAPT2+3/aug-cc-pVDZ-RI level using the PSI4 package[33] are summarized in Table S6.1.

Table S6.1. Results of the SAPT analysis for the M1, M2 and TS12 structures. All the values are in kJ/mol.

Complex	Electrostatics	Induction	Dispersion	Exchange	Total
M1	-29.40	-7.31	-31.07	39.84	-27.94
M2	-27.81	-6.62	-29.10	36.57	-26.96
TS12	-28.04	-6.66	-29.19	37.19	-26.70

S7. Results of the NBO analysis for M1, M2 and TS12 structures.

From the Natural Bond Orbital (NBO)[34] analysis at the B3LYP-D3/maug-cc-pVTZ-*d*H level the 2nd order perturbative stabilization energies are derived for the M1, M2 and TS12 stationary points (see Tables S7.1, S7.2 and S7.3). The corresponding NBO atomic charges (Table S7.4) have also been obtained. Calculations have been performed with the Gaussian16 package[19].

Table S7.1. Stabilization energy contributions (≥ 0.1 kcal/mol) for the M1 isomer.

Donor NBO	Acceptor NBO	E(2) [kcal/mol]
FROM TMA TO NE		
BD (1) C2 - H4	LP (3) O14	0.10
BD (1) C6 - H7	BD*(1) C20 - H22	0.11
LP (1) N1	RY*(1) H19	0.11
LP (1) N1	**BD*(2) O15 - N16**	**0.75**
LP (1) N1	BD*(1) N16 - C17	0.10
LP (1) N1	BD*(1) C17 - H18	0.29
FROM NE TO TMA		
BD (2) O15 - N16	BD*(1) C10 - H13	0.14
BD (1) C17 - H19	BD*(1) C2 - H5	0.10
BD (1) C17 - C20	RY*(1) N1	0.11
BD (1) C20 - H22	BD*(1) C6 - H9	0.11
LP (3) O14	BD*(1) C2 - H4	0.13
LP (3) O14	BD*(1) C10 - H11	0.10

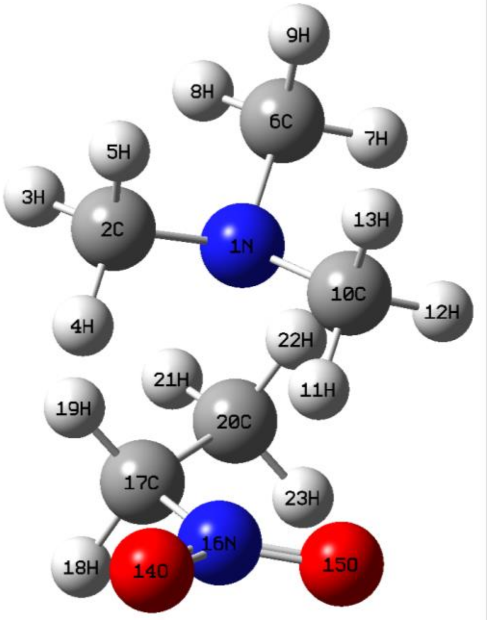


Table S7.2. Stabilization energy contributions (≥ 0.1 kcal/mol) for the M2 isomer.

Donor NBO	Acceptor NBO	E(2) [kcal/mol]
FROM TMA TO NE		
BD (1) C6 - H8	BD*(1) C20 - H22	0.19
LP (1) N1	RY*(1) H19	0.19
LP (1) N1	**BD*(2) O14 - N16**	**0.46**
LP (1) N1	BD*(1) N16 - C17	0.11
LP (1) N1	BD*(1) C17 - H18	0.26
FROM NE TO TMA		
BD (1) C20 - H22	BD*(1) C6 - H9	0.11
LP (3) O15	BD*(1) C10 - H13	0.17

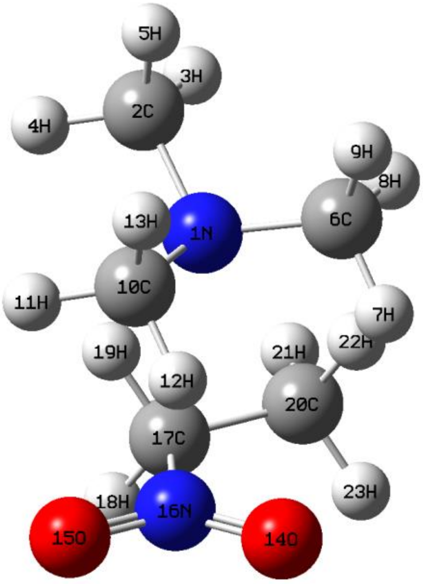


Table S7.3. Stabilization energy contributions (≥ 0.1 kcal/mol) for TS12.

Donor NBO	Acceptor NBO	E(2) [kcal/mol]
FROM TMA TO NE		
BD (1) C10 - H11	LP (3) O15	0.13
LP (1) N1	RY*(1) H19	0.13
LP (1) N1	**BD*(2) O14 - N16**	**0.58**
LP (1) N1	BD*(1) N16 - C17	0.10
LP (1) N1	BD*(1) C17 - H18	0.26
FROM NE TO TMA		
BD (1) C20 - H22	BD*(1) C6 - H9	0.13
LP (3) O15	BD*(1) C10 - H13	0.11

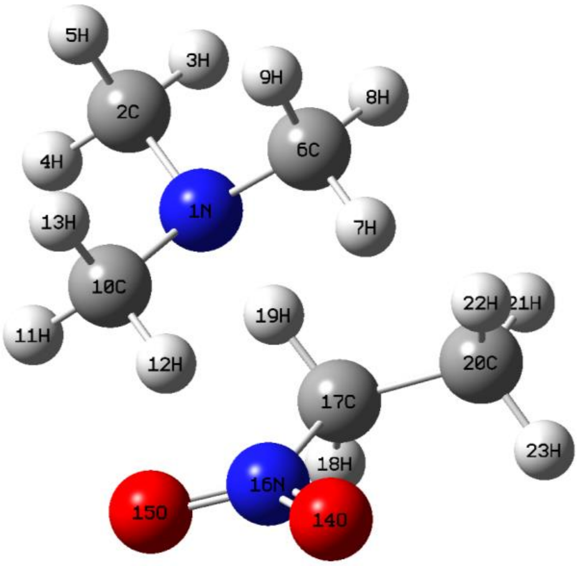


Table S7.4. NBO charges for the M1, M2 isomers, the TS12 transition state, TMA and NE.

	M1	M2	TS12	TMA	NE
N	**-0.535**	**-0.535**	**-0.534**	**-0.512**	
C	-0.379	-0.372	-0.374	-0.370	
H	0.186	0.189	0.187	0.191	
H	0.207	0.192	0.196	0.191	
H	0.165	0.165	0.166	0.158	
C	-0.372	-0.376	-0.375	-0.370	
H	0.192	0.206	0.199	0.191	
H	0.189	0.186	0.187	0.191	
H	0.166	0.164	0.165	0.158	
C	-0.379	-0.378	-0.381	-0.370	
H	0.207	0.198	0.204	0.191	
H	0.198	0.205	0.204	0.191	
H	0.162	0.162	0.162	0.158	
O	-0.388	-0.380	-0.378		-0.372
O	-0.375	-0.380	-0.383		-0.379
N	**0.516**	**0.516**	**0.517**		**0.507**
C	-0.245	-0.248	-0.248		-0.243
H	0.215	0.215	0.215		0.216
H	0.225	0.230	0.229		0.214
C	-0.605	-0.605	-0.605		-0.593
H	0.210	0.210	0.210		0.216
H	0.221	0.220	0.220		0.213
H	0.218	0.216	0.217		0.220

S8. Experimental vs Simulated spectra comparison using VMS-ROT.

The VMS-ROT[35] program can deal with the Doppler splitting due to the instrumental setup (see the *Experimental Section* in the manuscript) by means of a tool that averages frequency and intensity of the peak pairs arising from the Doppler effect.

In Figure S8.1, the $5_{05} \leftarrow 4_{14}$ rotational transition is shown: in the top panel the simulated stick spectrum with the corresponding quadrupolar hyperfine components is drawn, while in the bottom panel the experimental spectrum (in blue), showing the Doppler splitting, and the averaged experimental spectrum (stick spectrum in red), with the Doppler splitting averaged, are reported. It is noted that the simulated spectrum well matches the averaged experimental one.

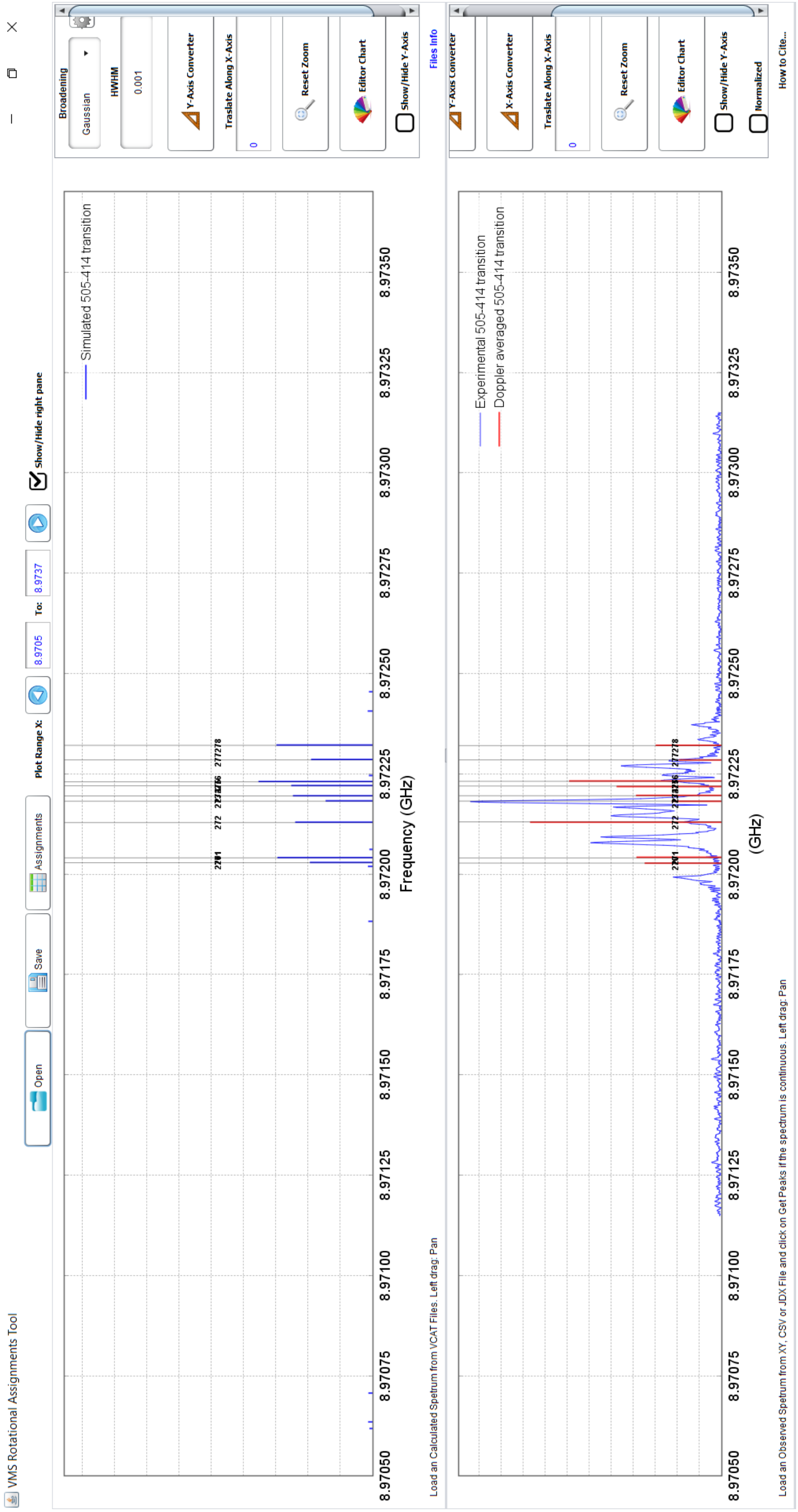


Figure S8.1. Demonstration of the assignment of the 5_{05}←4_{14} rotational transition using the VMS-ROT program.

S9. References

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