Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

CH stretching vibration of N-methylformamide as a sensitive probe of its complexation: infrared matrix isolation and computational study.

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Supplementary information: additional computational details

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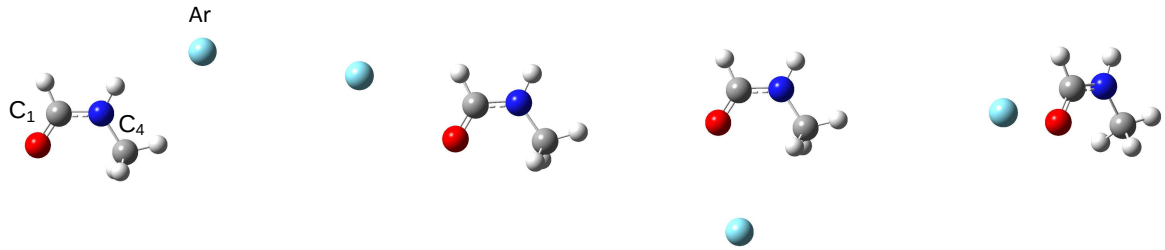
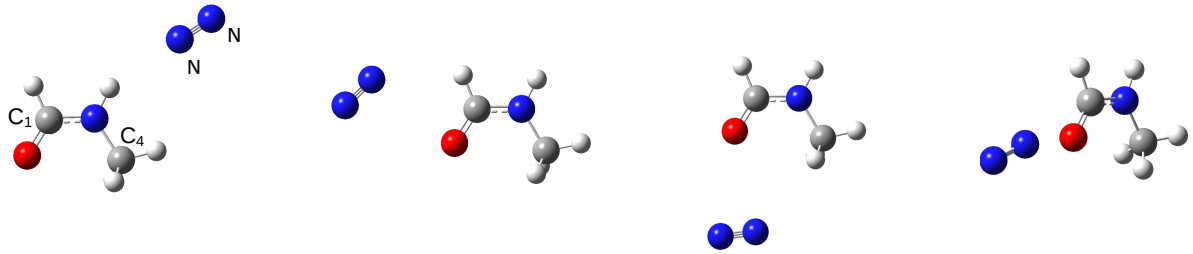
Figure S1. The optimized structures of the *t*-NMF complexes with Ar, N_2 ,CO and H_2O.

t-NMF-Ar



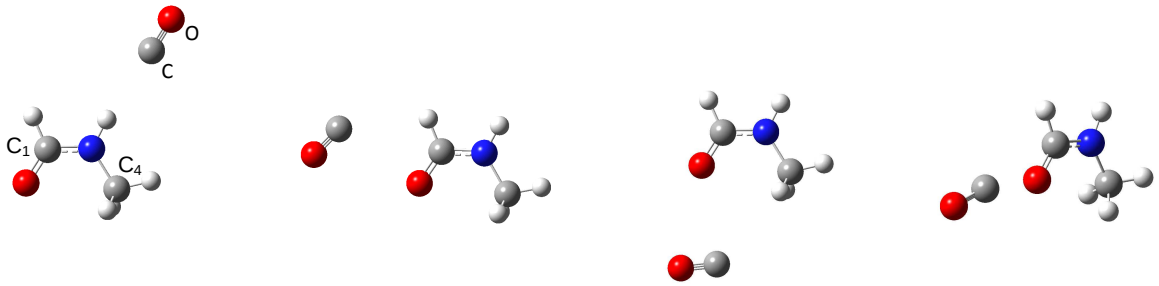
I **II** **III** **IV**

***t*-NMF – N_2**



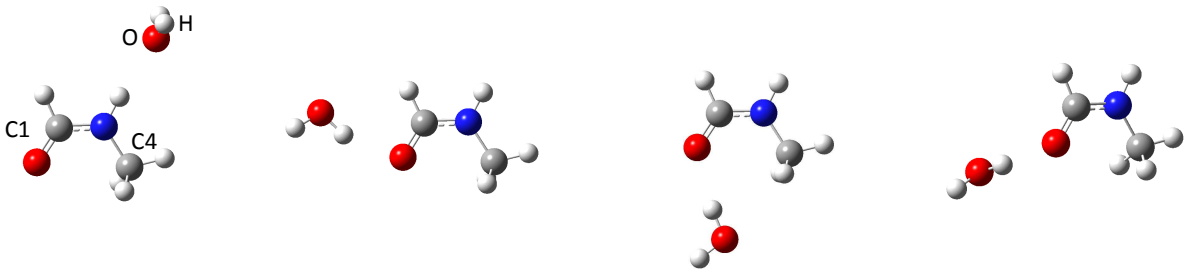
I **II** **III** **IV**

***t*-NMF - CO**



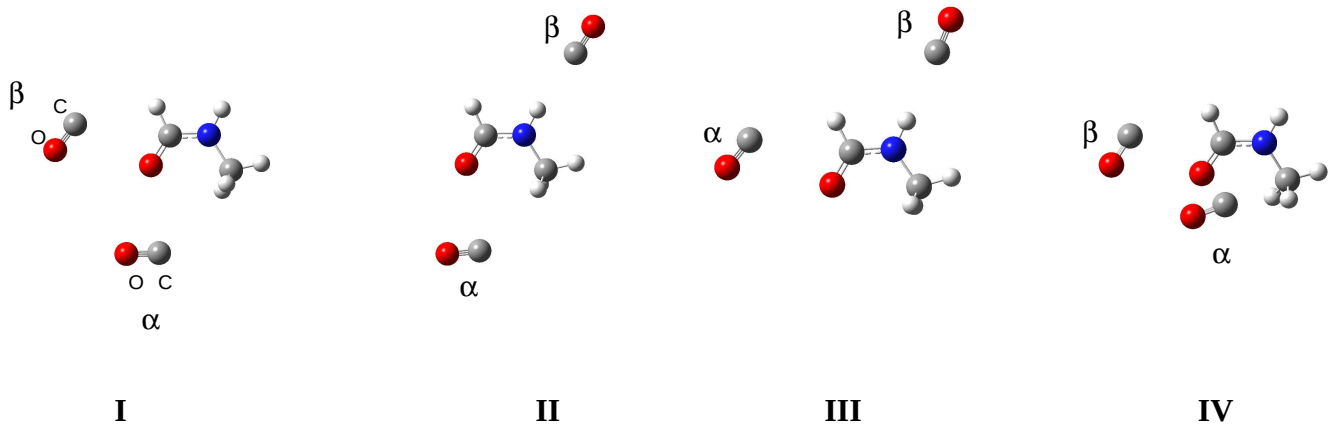
I **II** **III** **IV**

***t*-NMF – H_2O**



I **II** **III** **I**

Figure S2. The optimized structures of the $(CO)_\alpha$ -NMF- $(CO)_\beta$ complexes.



I **II** **III** **IV**

We calculated the two-body and three-body contributions to the interaction energies (kcal/mol) of the four optimized $(CO)_\alpha$ -NMF- $(CO)_\beta$ complexes; these are collected in Table below. In parantheses the BSSE corrected values are presented. As one can see the contribution of the three-body terms to an overall interaction energy is very small. The calculations were performed according the scheme proposed by K. Mierzwicki and Z. Latajka (Chem. Phys. Lett. 380, 2003, 654).

Two-body and three-body contributions (kcal/mol) to the interaction energies of the four optimized $(CO)_\alpha$ -NMF- $(CO)_\beta$ complexes.

	$\varepsilon^{(2)}$(NMF-CO1)	$\varepsilon^{(2)}$(NMF-CO2)	$\varepsilon^{(2)}$(CO1-CO2)	$\varepsilon^{(3)}$(NMF-CO1-CO2)
I	-1.95 (-1.44)	-1.84 (-1.33)	-0.21 (-0.11)	0.04 (0.01)
II	-2.35 (-1.76)	-1.86 (-1.36)	-0.01 (-0.01)	-0.03 (-0.03)
III	-2.34 (-1.75)	-1.96 (-1.45)	-0.04 (-0.02)	-0.04 (-0.03)
IV	-1.83 (-1.35)	-1.87 (-1.30)	-0.44 (-0.21)	-0.03 (-0.01)

Table S1 Comparison of the calculated vibrational wavenumbers of the *trans* and *cis* isomers of NMF[a] with the observed wavenumbers of the two NMF isomers isolated in argon and neon matrices.

trans-NMF				*cis*-NMF				
Harmonic freq/cm^{-1}	Anharmonic freq/cm^{-1}	Ar matrix freq/cm^{-1}	Ne matrix freq/cm^{-1}	Harmonic freq/cm^{-1}	Anharmonic freq/cm^{-1}	Ar matrix freq/cm^{-1}	Ne matrix freq/cm^{-1}	Assignment[c]
3695 (46)[b]	3550	3493.5	3501.5 3500.5	3650 (42)	3483	3456.0	3451.8	ν NH (100)
3204 (9)	3052			3184 (12)	3044			ν_{as} CH_3 (97)
3172 (13)	3018	2940.0		3158 (18)	3014			ν_{as} CH_3 (99)
3095 (30)	3038	2963.5		3085 (47)	2908			ν_{s} CH_3 (100)
3021 (91)	2908	2855.1	2843.5 2844.5	3003 (70)	2885	2848.0	2839.7	ν CH (99)
1748 (340)	1707	1725.3	1731.3	1763 (504)	1725		1740.8	ν CO (69), δ CH (14), ν CN (11)
1560 (83)	1487	1525.8 1517.8	(1515)	1490 (2)	1452	1497.7		δ NH (50), ν CN (26), δ_s CH_3 (10) [$\delta_{as}CH_3$ (68), ρ CH_3 (12)]
1526 (41)	1480	1464.0		1516 (6)	1497			δ_{as} CH_3 (74) δ_{as} CH_3 (85)
1509 (21)	1456	1456.4	1473 br	1562 (14)	1504			δ_{as} CH_3 (85) [δ NH (40), δ_{as} CH_3 (35)]
1478 (20)	1483	1408.6	1423 br	1496 (13)	1478			δ_{s} CH_3 (80)
1432 (7)	1413	1393.3	1412 br	1417 (17)	1401			δ CH (55), δ OCN (34)
1242 (51)	1217	1204.7	1205.0	1314 (121)	1286	1292.8	1285.2	ν CN (30), ν N-CH_3 (22), δ NH (18) [ν CN (45), δ NH (28)]
1176 (6)	1148	1146.4	1154.5	1023 (42)	1004	1000.4	1001.5	ρ CH_3 (64), δ NH (12) [ρ CH_3 (35), ν N-CH_3 (24), ν CN (15)]
1172 (0)	1169	1143.0	1149.5	1173 (1)	1142			ρ CH_3 (77)
1032 (1)	1010			1043 (4)	1020			γ CH (94)
974 (19)	961	947.5	949.7	1179 (35)	1145	1133.3	1136.0	ν N-CH_3 (65), ν CN (24) [ν N-CH_3 (49), ρ CH_3 (34)]
774 (5)	775			613 (10)	604			δ OCN (41), δ CNC (21), ρ CH_3 (15) [δ OCN (35), ν N-CH_3 (19), ν CN (15)]
481 (19)	482			596 (115)	571	601.5		γ CN (88) [γ CN (62), γ NH (23)]
270 (11)	219			345 (7)	343			δ CNC (68), δ OCN (15), δ CH (10) [δ CNC (72), δ OCN (15)]
209 (90)	339			198 (1)	185			γ NH (87) [γ NH (41), τ CH_3 (33), γ CN (16)]
41 (5)	225			92 (1)	106			τ CH_3 (21), ρ CH_3 (24) [τ CH_3 (55), γ CN (22), γ NH (14)]

[a] In all calculations the MP2/6-311++G(2d,2p) method was used. [b] The IR calculated intensities expressed in km mol^{-1}. [c] Main elements of PED (larger than 10%); the assignment obtained for *cis*-NMF is given in brackets; Abbreviations: ν – bond stretching, δ – bending, deformation in plane, ρ – rocking, γ – out of plane bending, torsion, τ – twisting.

Table S2 Selected structural parameters calculated for the NMF-Ar, NMF-N_2, NMF-CO and NMF-H_2O complexes[a]

Property	I	II	III	IV
NMF-Ar				
r((N)H···Ar) r((C_1)H···Ar) r(N···Ar)	3.025	 3.270		 3.795
r((C_4)H···Ar) r(O···Ar)	3.384	 3.723	3.490 3.650	3.253
ϕ(NH···Ar) ϕ(C_1H···Ar)	140.0	 115.9		
ϕ(C_4H···Ar) ϕ(C_1O···Ar)	125.7	 88.0	112.8 136.7	127.3 75.3
θ(C_4NH···Ar) θ(NC_1H···Ar) θ(NC_4H···Ar)	4.8	 179.7	 107.4	 1.9
θ(C_1NH···Ar) θ(OC_1H···Ar) θ(NC_1O···Ar)	179.1	 -0.8 -179.9	 -8.0	 -93.1 -78.8
NMF-N_2				
r((N)H···N(N)) r((C_1)H···N(N))	2.522	 2.860		
r((C_4)H···N(N)) r(O···N(N))		 3.621	3.101 3.267	2.921 3.320
ϕ(NH···N(N)) ϕ(C_1H···N(N))	151.1	 111.2		
ϕ(C_4H···N(N)) ϕ(C_1O···N(N))		 105.1	115.6 135.5	124.4 84.8
θ(C_4NH···N(N)) θ(NC_1H···N(N)) θ(NC_4H···N(N))	0.05	 -180.0	 -103.0	 -34.1
θ(C_1NH···N(N)) θ(OC_1H···N(N)) θ(NC_1O···N(N)) θ(C_1H···NN) θ(C_4H···NN)	-179.5	 -0.4 179.8 0.9	 -0.2 86.9	 -73.6
NMF-CO				
r((N)H···C(O)) r((C_1)H···C(O))	2.519	 2.922		
r((C_4)H···C(O)) r(O···C(O))		 3.125	3.150 3.194	3.043 3.275
ϕ(NH··· C(O)) ϕ(C_1H···C(O))	174.3	 106.1		
ϕ(C_4H···C(O)) ϕ(C_1O···C(O))		 91.9	118.1 138.6	125.5 90.5
θ(C_4NH···C(O)) θ(NC_1H···C(O))	0.0	 179.9		

θ(NC_4H···C(O))			-98.8	-38.1
θ(C_1NH···C(O)) θ(OC_1H···C(O)) θ(NC_1O···C(O)) θ(C_1H···CO) θ(C_4H···CO)	180.0	 0.2 -179.8 -0.6	 -2.1 83.0	 -75.0 -72.4
NMF-H_2O				
	C	B	A	
r((N)H···O(H_2)) r((C_1)H···O(H_2))	2.071	 2.781		
r((C_4)H···O(H_2)) r(O···H(OH))			2.801 1.944	
ϕ(NH···O(H_2)) ϕ(C_1H···O(H_2))	175.6	 101.4		
ϕ(C_4H···O(H_2)) ϕ(C_1O···H(OH))		 101.2	105.5 132.4	
θ(C_4NH···O(H_2)) θ(NC_1H···O(H_2)) θ(NC_4H···O(H_2))	0.0	 177.2	 100.7	
θ(C_1NH···O(H_2)) θ(OC_1H···O(H_2)) θ(NC_1O···H(OH)) θ(C_1O···HO(H))	180.0	 -2.9 -177.7 2.59	 0.0 0.0	

[a] In all calculations the MP2/6-311++G(2d,2p) method was used; the interacting atoms refer to the Figure 5; the bond distances are given in Å, the angles in degrees.

Table S3 Wavenumbers (in cm^{-1}) of the NMF-Ar complexes calculated by the MP2/6-311++G(2d,2p) method.

I	II	III	IV	Assignmt.[a]
3696 (60)[b]	3695 (46)	3696 (47)	3694 (46)	νNH
3204 (9)	3204 (9)	3204 (11)	3204 (88)	νCH_3
3172 (13)	3172 (13)	3172 (12)	3173 (14)	νCH_3
3095 (28)	3095 (28)	3095 (26)	3095 (28)	νCH_3
3020 (90)	3022 (89)	3022 (95)	3020 (88)	νCH
1748 (348)	1748 (332)	1747 (339)	1748 (324)	νC=O
1560 (89)	1560 (87)	1559 (86)	1561 (79)	δNH
1526 (46)	1526 (44)	1526 (43)	1527 (39)	δCH_3
1510 (22)	1509 (21)	1508 (15)	1510 (21)	δCH_3
1477 (23)	1478 (21)	1479 (20)	1476 (19)	δCH_3
1432 (8)	1433 (9)	1432 (8)	1432 (7)	δCH
1242 (50)	1242 (55)	1242 (47)	1242 (49)	νCN
1176 (4)	1176 (6)	1176 (5)	1176 (6)	ρCH_3
1172 (1)	1172 (0)	1173 (0)	1171 (1)	ρCH_3
1032 (1)	1032 (1)	1032 (1)	1032 (1)	γCH
975 (21)	975 (20)	975 (19)	975 (17)	ν N-CH_3
774 (5)	774 (5)	774 (5)	774 (4)	δOCN
485 (17)	482 (19)	478 (17)	483 (21)	γCN
271 (10)	270 (12)	268 (10)	271 (10)	δCNC
213 (83)	209 (87)	202 (87)	213 (96)	γNH
43 (4)	40 (5)	47 (3)	44 (9)	τCH_3
31 (1)	28 (0)	31 (0)	40 (1)	intermolecular
25 (6)	25 (6)	24 (6)	37 (0)	intermolecular
10 (11)	6 (0)	14 (14)	25 (9)	intermolecular

[a] Only the main components of PED calculated for *t*-NMF monomer are presented. Relatively weak intermolecular interaction has small effect on PED of amides [N.S. Myshakina, Z. Ahmed, S. A. Asher, J. Chem. Phys. B, Letters, 112, 2008, 11873.].

[b] The IR calculated intensities expressed in km mol^{-1}.

Table S4. Wavenumbers (in cm^{-1}) of the NMF-N_2 complexes calculated by the MP2/6-311++G(2d,2p) method.

I	II	III	IV	Assignmt.[a]
3696 (108)[b]	3695 (48)	3696 (48)	3690 (45)	νNH
3201 (12)	3204 (9)	3205 (11)	3205 (4)	νCH_3
3169 (13)	3172 (13)	3174 (12)	3175 (15)	νCH_3
3095 (27)	3095 (28)	3097 (24)	3095 (31)	νCH_3
3020 (91)	3027 (77)	3023 (94)	3020 (88)	νCH
1746 (356)	1746 (335)	1746 (345)	1749 (330)	νC=O
1560 (100)	1560 (89)	1558 (94)	1567 (80)	δNH
1528 (53)	1527 (45)	1524 (37)	1530 (24)	δCH_3
1507 (8)	1509 (19)	1508 (14)	1514 (30)	δCH_3
1479 (23)	1478 (22)	1480 (20)	1471 (17)	δCH_3
1431 (9)	1435 (12)	1431 (8)	1434 (8)	δCH
1247 (48)	1243 (55)	1242 (44)	1240 (58)	νCN
1176 (3)	1177 (6)	1176 (5)	1176 (2)	ρCH_3
1174 (0)	1172 (0)	1172 (0)	1170 (7)	ρCH_3
1032 (1)	1036 (1)	1033 (1)	1032 (1)	γCH
977 (19)	976 (21)	975 (18)	972 (17)	ν N-CH_3
775 (6)	774 (6)	774 (5)	773 (3)	δOCN
502 (19)	483 (19)	479 (17)	504 (30)	γCN
265 (9)	271 (12)	268 (10)	283 (11)	δCNC
230 (79)	212 (87)	206 (86)	242 (92)	γNH
72 (1)	69 (0)	68 (0)	76 (2)	intermolecular
62 (0)	50 (2)	52 (2)	64 (0)	intermolecular
55 (0)	41 (6)	47 (3)	45 (2)	τCH_3
24 (10)	37 (3)	34 (4)	33 (10)	intermolecular
15 (5)	34 (1)	21 (14)	30 (1)	intermolecular
13 (0)	14 (3)	13 (0)	20 (2)	intermolecular
2172 (0)	2171 (0)	2170 (0)	2168 (0)	νNN

[a] See footnote at Table S3. [b] The IR calculated intensities expressed in km mol^{-1}.

Table S5. Wavenumbers (in cm^{-1}) of the NMF-CO complexes calculated by the MP2/6-311++G(2d,2p) method.

I	II	III	IV	Assignmt.[a]
3677 (165)[b]	3696 (48)	3695 (48)	3690 (46)	νNH
3200 (12)	3204 (9)	3205 (10)	3204 (5)	νCH_3
3168 (14)	3172 (13)	3176 (12)	3176 (14)	νCH_3
3094 (28)	3096 (28)	3097 (24)	3096 (28)	νCH_3
3018 (93)	3033 (69)	3024 (95)	3020 (87)	νCH
1745 (366)	1743 (346)	1745 (354)	1747 (332)	νC=O
1566 (100)	1560 (91)	1558 (97)	1567 (82)	δNH
1532 (26)	1527 (46)	1524 (33)	1530 (27)	δCH_3
1507 (8)	1509 (17)	1508 (16)	1513 (25)	δCH_3
1479 (17)	1478 (23)	1480 (20)	1472 (17)	δCH_3
1430 (10)	1434 (14)	1432 (9)	1434 (9)	δCH
1252 (58)	1244 (55)	1243 (44)	1241 (54)	νCN
1180 (4)	1177 (6)	1177 (4)	1177 (3)	ρCH_3
1174 (0)	1173 (0)	1170 (0)	1179 (6)	ρCH_3
1032 (1)	1039 (1)	1033 (1)	1033 (1)	γCH
978 (17)	976 (21)	974 (18)	974 (17)	ν $N\text{-}CH_3$
775 (6)	774 (5)	774 (5)	773 (4)	δOCN
528 (23)	485 (18)	482 (18)	504 (30)	γCN
265 (10)	272 (14)	268 (10)	281 (11)	δCNC
260 (79)	215 (86)	212 (86)	246 (92)	γNH
92 (0)	107 (0)	95 (0)	92 (1)	intermolecular
82 (0)	64 (1)	60 (2)	71 (1)	intermolecular
64 (1)	50 (3)	51 (4)	29 (2)	intermolecular
39 (6)	43 (6)	39 (4)	40 (0)	τCH_3
19 (0)	33 (4)	25 (15)	31 (9)	intermolecular
12 (4)	19 (4)	14 (0)	26 (8)	intermolecular
2124 (35)	2117 (34)	2118 (32)	2117	νCO

[a] See footnote at Table S3. [b] The IR calculated intensities expressed in km mol^{-1}.

Table S6 Wavenumbers (in cm^{-1}) of the $(CO)_{\alpha}$ -NMF- $(CO)_{\beta}$ complexes calculated by the MP2/6-311++G(2d,2p) method (without CP-correction).

I	II	III	IV	Assignmt.[a]
3693 (51)[b]	3672 (201)	3672 (197)	3690 (48)	νNH
3205 (9)	3200 (15)	3200 (12)	3203 (7)	νCH_3
3175 (12)	3172 (11)	3167 (13)	3177 (12)	νCH_3
3096 (25)	3095 (25)	3093 (29)	3096 (27)	νCH_3
3036 (71)	3021 (97)	3032 (70)	3033 (65)	νCH
1739 (371)	1741 (386)	1739 (378)	1740 (338)	νC=O
1559 (103)	1568 (114)	1570 (109)	1564 (85)	δNH
1525 (30)	1528 (11)	1534 (18)	1529 (34)	δCH_3
1509 (20)	1507 (10)	1507 (8)	1511 (20)	δCH_3
1479 (21)	1481 (15)	1480 (17)	1473 (18)	δCH_3
1432 (16)	1430 (12)	1432 (19)	1434 (14)	δCH
1243 (49)	1254 (54)	1255 (67)	1244 (53)	νCN
1178 (4)	1182 (3)	1183 (4)	1178 (3)	ρCH_3
1171 (1)	1171 (0)	1174 (0)	1171 (4)	ρCH_3
1039 (1)	1033 (1)	1041 (0)	1037 (1)	γCH
976 (21)	979 (17)	981 (19)	976 (17)	ν N-CH_3
775 (6)	776 (6)	775 (8)	774 (5)	δOCN
492 (21)	564 (31)	564 (29)	502 (25)	γCN
277 (15)	267 (10)	271 (15)	280 (13)	δCNC
230 (84)	287 (60)	290 (59)	246 (93)	γNH
122 (1)	105 (0)	117 (0)	112 (0)	intermolecular
104 (0)	102 (0)	105 (2)	100 (1)	intermolecular
75 (2)	96 (1)	98 (1)	75 (3)	intermolecular
66 (4)	81 (0)	78 (0)	73 (1)	intermolecular
63 (2)	61 (1)	70 (1)	59 (0)	intermolecular
57 (3)	57 (2)	56 (2)	55 (6)	intermolecular
43 (2)	48 (4)	44 (2)	46 (4)	τCH_3
36 (8)	47 (4)	50 (5)	42 (3	intermolecular
21 (1)	24 (0)	27 (1)	35 ()	intermolecular
19 (1)	11 (0)	22 (1)	32 (4)	intermolecular
8 (1)	10 (0)	8 (0)	22 (1)	intermolecular
2115 (19)	2116 (32)	2116 (35)	2113 (48)	$\nu(CO)_{\alpha}$
2114 (43)	2125 (35)	2125 (34)	2114 (13)	$\nu(CO)_{\beta}$

[a] See footnote at Table S3. [b] The IR calculated intensities expressed in km mol^{-1}.

Table S7. Wavenumbers (in cm^{-1}) of the NMF-H_2O complexes calculated by the MP2/6-311++G(2d,2p) method.

I	II	III	Assignmt.[a]
3630 (365)[b]	3696 (48)	3693 (138)	νNH
3199 (12)	3208 (9)	3211 (8)	νCH_3
3162 (16)	3176 (11)	3187 (5)	νCH_3
3091 (31)	3100 (24)	3105 (15)	νCH_3
3017 (97)	3061 (36)	3047 (84)	νCH
1741 (368)	1735 (328)	1741 (380)	νC=O
1575 (109)	1563 (101)	1563 (109)	δNH
1535 (9)	1530 (10)	1526 (19)	δCH_3
1508 (8)	1509 (11)	1513 (12)	δCH_3
1478 (14)	1481 (24)	1486 (19)	δCH_3
1428 (13)	1439 (26)	1436 (16)	δCH
1260 (60)	1252 (42)	1252 (36)	νCN
1184 (2)	1182 (2)	1186 (2)	ρCH_3
1174 (0)	1174 (0)	1165 (0)	ρCH_3
1034 (1)	1046 (1)	1036 (1)	γCH
984 (12)	981 (14)	972 (14)	ν N-CH_3
777 (7)	779 (6)	776 (4)	δOCN
98 (9)	585 (110)	583 (72)	intermolecular
643 (67)	496 (23)	500 (43)	γCN
162 (14)	389 (145)	369 (126)	intermolecular
267 (12)	290 (43)	275 (20)	δCNC
324 (82)	246 (80)	251 (75)	γNH
67 (0)	151 (2)	161 (9)	intermolecular
124 (62)	69 (110)	131 (129)	intermolecular
119 (190)	52 (42)	89 (12)	intermolecular
41 (0)	36 93)	79 (1)	τCH_3
32 (2)	26 (2)	26 (6)	intermolecular
3975 (95)	3950 (110)	3947 (110)	ν_3 H_2O
3858 (21)	3705 (386)	3727 (353)	ν_1 H2O
1664 (68)	1689 (126)	1690 (84)	ν_2 H_2O

[a] See footnote at Table S3. [b] The IR calculated intensities expressed in km mol^{-1}.

Table S8. AIM atomic properties computed at MP2/6-311++G(2d,2p) level for NMF-Ar complexes (in atomic units)

BCP between X and Y	ρ	$\nabla^2\rho$	ε	H	$DI(X,Y)$
		NMF-Ar I			
C1 - N2	0.3236	-1.0662	0.1744	-0.4745	0.9319
C1 - O3	0.4060	-0.5432	0.1197	-0.7373	1.1428
N2 - C4	0.2579	-0.7057	0.0399	-0.3019	0.8293
N2 - H6	0.3485	-1.8519	0.0510	-0.5305	0.7218
C1 - H5	0.2865	-1.0806	0.0286	-0.3076	0.7755
C4 - H7	0.2878	-1.0750	0.0325	-0.3144	0.8255
C4 - H8	0.2897	-1.0906	0.0288	-0.3173	0.8193
C4 - H9	0.2884	-1.0805	0.0300	-0.3170	0.8336
H6 - Ar10	0.0034	0.0139	0.0203	0.0008	0.0162
H9 - Ar10	0.0021	0.0084	0.4902	0.0005	0.0113
		NMF-Ar II			
C1 - N2	0.3237	-1.0662	0.1741	-0.4748	0.9319
C1 - O3	0.4061	-0.5418	0.1189	-0.7374	1.1415
N2 - C4	0.2578	-0.7054	0.0408	-0.3018	0.8297
N2 - H6	0.3485	-1.8495	0.0512	-0.5299	0.7287
C1 - H5	0.2865	-1.0798	0.0286	-0.3074	0.7726
C4 - H7	0.2897	-1.0905	0.0290	-0.3174	0.8196
C4 - H8	0.2880	-1.0763	0.0323	-0.3146	0.8253
C4 - H9	0.2884	-1.0809	0.0300	-0.3171	0.8368
O3 - Ar10	0.0025	0.0109	0.1751	0.0007	0.0196
H5 - Ar10	0.0024	0.0103	0.2440	0.0007	0.0130
		NMF-Ar III			
C1 - N2	0.3239	-1.0673	0.1744	-0.4756	0.9319
C1 - O3	0.4060	-0.5435	0.1195	-0.7371	1.1421
N2 - C4	0.2577	-0.7052	0.0417	-0.3017	0.8291
N2 - H6	0.3485	-1.8505	0.0513	-0.5302	0.7284
C1 - H5	0.2866	-1.0811	0.0287	-0.3077	0.7756
C4 - H7	0.2894	-1.0877	0.0295	-0.3168	0.8185
C4 - H8	0.2882	-1.0778	0.0318	-0.3149	0.8225
C4 - H9	0.2884	-1.0810	0.0296	-0.3171	0.8364
O3 - Ar10	0.0028	0.0112	0.0159	0.0007	0.0215
H7 - Ar10	0.0019	0.0076	1.3292	0.0005	0.0075
		NMF-Ar IV			
C1 - N2	0.3235	-1.0654	0.1745	-0.4743	0.9293
C1 - O3	0.4061	-0.5414	0.1200	-0.7374	1.1406
N2 - C4	0.2578	-0.7057	0.0402	-0.3021	0.8290
N2 - H6	0.3484	-1.8483	0.0511	-0.5297	0.7287
C1 - H5	0.2865	-1.0806	0.0286	-0.3076	0.7749
C4 - H7	0.2898	-1.0913	0.0287	-0.3175	0.8189
C4 - H8	0.2878	-1.0745	0.0325	-0.3143	0.8223
C4 - H9	0.2883	-1.0803	0.0303	-0.3170	0.8365
N2 - Ar10	0.0029	0.0110	0.8907	0.0006	0.0166
H8 - Ar10	0.0026	0.0105	0.3023	0.0006	0.0135

Table S9. AIM atomic properties computed at MP2/6-311++G(2d,2p) level for NMF-N_2 complexes (in au)

BCP between X and Y	ρ	$\nabla^2\rho$	ε	H	$DI(X,Y)$
		NMF-N_2 I			
C1 - N2	0.3248	-1.0717	0.1755	-0.4783	0.9343
C1 - O3	0.4054	-0.5467	0.1197	-0.7358	1.1404
N2 - C4	0.2585	-0.7081	0.0423	-0.3019	0.8311
N2 - H6	0.3485	-1.8789	0.0503	-0.5364	0.7067
C1 - H5	0.2864	-1.0797	0.0288	-0.3074	0.7757
C4 - H7	0.2886	-1.0815	0.0304	-0.3156	0.8225
C4 - H8	0.2886	-1.0815	0.0304	-0.3156	0.8225
C4 - H9	0.2881	-1.0789	0.0292	-0.3167	0.8351
H6 - N10	0.0072	0.0270	0.0519	0.0013	0.0273
N10 - N11	0.6595	-2.4978	0.0004	-1.1834	2.2728
		NMF-N_2 II			
C1 - N2	0.3240	-1.0673	0.1730	-0.4762	0.9331
C1 - O3	0.4053	-0.5436	0.1165	-0.7355	1.1389
N2 - C4	0.2578	-0.7055	0.0410	-0.3018	0.8292
N2 - H6	0.3485	-1.8508	0.0511	-0.5302	0.7283
C1 - H5	0.2870	-1.0834	0.0285	-0.3081	0.7706
C4 - H7	0.2897	-1.0899	0.0291	-0.3172	0.8198
C4 - H8	0.2881	-1.0768	0.0321	-0.3147	0.8250
C4 - H9	0.2884	-1.0811	0.0299	-0.3172	0.8365
O3 - N11	0.0049	0.0183	0.3113	0.0008	0.0260
H5 - N11	0.0043	0.0169	0.4639	0.0009	0.0168
N10 - N11	0.6596	-2.5002	0.0016	-1.1837	2.2688
		NMF-N_2 III			
C1 - N2	0.3245	-1.0701	0.1753	-0.4775	0.9338
C1 - O3	0.4054	-0.5460	0.1184	-0.7357	1.1387
N2 - C4	0.2573	-0.7037	0.0414	-0.3016	0.8282
N2 - H6	0.3485	-1.8514	0.0511	-0.5303	0.7281
C1 - H5	0.2867	-1.0820	0.0287	-0.3079	0.7757
C4 - H7	0.2883	-1.0787	0.0319	-0.3150	0.8221
C4 - H8	0.2896	-1.0890	0.0298	-0.3170	0.8171
C4 - H9	0.2884	-1.0811	0.0297	-0.3172	0.8366
O3 - N10	0.0046	0.0167	0.4513	0.0007	0.0225
H8 - N10	0.0029	0.0106	0.2881	0.0006	0.0100
N10 - N11	0.6595	-2.4997	0.0021	-1.1834	2.2675
		NMF-N_2 IV			
C1 - N2	0.3230	-1.0620	0.1763	-0.4722	0.9325
C1 - O3	0.4058	-0.5431	0.1183	-0.7366	1.1387
N2 - C4	0.2577	-0.7047	0.0331	-0.3029	0.8287
N2 - H6	0.3484	-1.8452	0.0500	-0.5288	0.7294
C1 - H5	0.2866	-1.0808	0.0285	-0.3077	0.7747
C4 - H7	0.2904	-1.0961	0.0272	-0.3183	0.8153
C4 - H8	0.2877	-1.0730	0.0342	-0.3142	0.8235
C4 - H9	0.2881	-1.0778	0.0325	-0.3164	0.8362
O3 - N10	0.0042	0.0158	0.5168	0.0007	0.0205
H8 - N10	0.0039	0.0136	0.1016	0.0006	0.0162
N10 - N11	0.6593	-2.4986	0.0015	-1.1826	2.2670

Table S10. AIM atomic properties computed at MP2/6-311++G(2d,2p) level for NMF-CO complexes (in au)

BCP between X and Y	ρ	$\nabla^2\rho$	ε	H	$DI(X,Y)$
		NMF-CO I			
C1 - N2	0.3255	-1.0756	0.1768	-0.4796	0.9381
C1 - O3	0.4049	-0.5493	0.1190	-0.7343	1.1405
N2 - C4	0.2588	-0.7090	0.0424	-0.3017	0.8322
N2 - H6	0.3475	-1.8913	0.0494	-0.5387	0.6947
C1 - H5	0.2863	-1.0786	0.0289	-0.3073	0.7756
C4 - H7	0.2885	-1.0807	0.0303	-0.3154	0.8226
C4 - H8	0.2885	-1.0807	0.0303	-0.3154	0.8226
C4 - H9	0.2881	-1.0788	0.0291	-0.3167	0.8362
H6 - C10	0.0089	0.0291	0.0611	0.0014	0.0425
C10 - O11	0.4841	0.3922	0.0000	-0.9278	1.5457
		NMF-CO II			
C1 - N2	0.3244	-1.0686	0.1721	-0.4779	0.9336
C1 - O3	0.4045	-0.5461	0.1147	-0.7335	1.1344
N2 - C4	0.2578	-0.7060	0.0414	-0.3020	0.8294
N2 - H6	0.3485	-1.8524	0.0510	-0.5305	0.7279
C1 - H5	0.2875	-1.0876	0.0284	-0.3089	0.7702
C4 - H7	0.2882	-1.0775	0.0320	-0.3149	0.8247
C4 - H8	0.2896	-1.0892	0.0293	-0.3171	0.8201
C4 - H9	0.2884	-1.0812	0.0298	-0.3172	0.8366
O3 - C10	0.0069	0.0229	0.1680	0.0009	0.0370
C10 - O11	0.4826	0.3703	0.0012	-0.9246	1.5304
		NMF-CO III			
C1 - N2	0.3250	-1.0722	0.1762	-0.4786	0.9359
C1 - O3	0.4050	-0.5473	0.1179	-0.7346	1.1373
N2 - C4	0.2570	-0.7023	0.0407	-0.3016	0.8275
N2 - H6	0.3485	-1.8513	0.0509	-0.5303	0.7282
C1 - H5	0.2868	-1.0826	0.0287	-0.3080	0.7759
C4 - H7	0.2883	-1.0783	0.0322	-0.3150	0.8224
C4 - H8	0.2899	-1.0919	0.0296	-0.3176	0.8162
C4 - H9	0.2884	-1.0808	0.0300	-0.3171	0.8366
O3 - C10	0.0054	0.0190	0.4466	0.0008	0.0262
H8 - C10	0.0032	0.0106	0.1429	0.0006	0.0137
C10 - O11	0.4828	0.3736	0.0020	-0.9248	1.5329
		NMF-CO IV			
C1 - N2	0.3238	-1.0664	0.1764	-0.4743	0.9345
C1 - O3	0.4053	-0.5476	0.1171	-0.7353	1.1362
N2 - C4	0.2575	-0.7040	0.0347	-0.3026	0.8285
N2 - H6	0.3484	-1.8460	0.0499	-0.5290	0.7290
C1 - H5	0.2866	-1.0814	0.0285	-0.3078	0.7749
C4 - H7	0.2902	-1.0948	0.0276	-0.3181	0.8168
C4 - H8	0.2880	-1.0756	0.0336	-0.3146	0.8225
C4 - H9	0.2881	-1.0780	0.0322	-0.3164	0.8363
O3 - C10	0.0048	0.0167	0.2965	0.0008	0.0247
H8 - C10	0.0038	0.0119	0.0851	0.0006	0.0192
C10 - O11	0.4829	0.3752	0.0017	-0.9251	1.5353

Table S11. AIM atomic properties computed at MP2/6-311++G(2d,2p) level for NMF-H_2O complexes (in atomic units)

BCP between X and Y	ρ	$\nabla^2\rho$	ε	H	$DI(X,Y)$
		NMF-H_2O A			
C1 - N2	0.3302	-1.0955	0.1850	-0.4932	0.9543
C1 - O3	0.3997	-0.5514	0.1130	-0.7216	1.1129
N2 - C4	0.2541	-0.6909	0.0373	-0.3008	0.8218
N2 - H6	0.3487	-1.8626	0.0491	-0.5324	0.7247
C1 - H5	0.2886	-1.0972	0.0288	-0.3113	0.7763
C4 - H7	0.2900	-1.0917	0.0323	-0.3174	0.8172
C4 - H8	0.2887	-1.0836	0.0309	-0.3177	0.8370
C4 - H9	0.2900	-1.0917	0.0323	-0.3174	0.8172
C4 - O10	0.0057	0.0262	15.1871	0.0013	0.0212
O3 - H11	0.0233	0.0819	0.0267	0.0010	0.0641
O10 - H11	0.3577	-2.6930	0.0218	-0.7535	0.5014
O10 - H12	0.3717	-2.7090	0.0228	-0.7667	0.6177
		NMF-H_2O B			
C1 - N2	0.3294	-1.0918	0.1761	-0.4930	0.9467
C1 - O3	0.3994	-0.5638	0.1104	-0.7204	1.1121
N2 - C4	0.2568	-0.7034	0.0409	-0.3023	0.8262
N2 - H6	0.3487	-1.8690	0.0495	-0.5338	0.7231
C1 - H5	0.2898	-1.1070	0.0269	-0.3128	0.7709
C4 - H7	0.2893	-1.0865	0.0307	-0.3166	0.8220
C4 - H8	0.2890	-1.0846	0.0311	-0.3162	0.8227
C4 - H9	0.2889	-1.0848	0.0296	-0.3179	0.8366
O3 - H11	0.0252	0.0860	0.0330	0.0006	0.0674
O10 - H11	0.3569	-2.6800	0.0218	-0.7509	0.5034
O10 - H12	0.3718	-2.7111	0.0227	-0.7673	0.6185
		NMF-H_2O C			
C1 - N2	0.3279	-1.0874	0.1810	-0.4846	0.9475
C1 - O3	0.4031	-0.5580	0.1173	-0.7298	1.1346
N2 - C4	0.2599	-0.7118	0.0415	-0.3012	0.8350
N2 - H6	0.3447	-1.9366	0.0464	-0.5472	0.6571
C1 - H5	0.2861	-1.0772	0.0293	-0.3071	0.7757
C4 - H7	0.2881	-1.0767	0.0300	-0.3147	0.8230
C4 - H8	0.2881	-1.0767	0.0301	-0.3147	0.8230
C4 - H9	0.2883	-1.0798	0.0286	-0.3169	0.8360
H6 - O10	0.0176	0.0653	0.0470	0.0016	0.0586
O10 - H11	0.3693	-2.7423	0.0240	-0.7704	0.5887
O10 - H12	0.3693	-2.7423	0.0240	-0.7704	0.5887
		NMF-H_2O TS			
C1 - N2	0.3295	-1.0919	0.1806	-0.4925	0.9486
C1 - O3	0.4010	-0.5602	0.1077	-0.7246	1.1110
N2 - C4	0.2561	-0.6997	0.0404	-0.3018	0.8243
N2 - H6	0.3485	-1.8658	0.0491	-0.5330	0.7236
C1 - H5	0.2885	-1.0968	0.0276	-0.3110	0.7761
C4 - H7	0.2892	-1.0861	0.0309	-0.3162	0.8216
C4 - H8	0.2889	-1.0851	0.0300	-0.3179	0.8364
C4 - H9	0.2894	-1.0880	0.0308	-0.3169	0.8224
O3 - H11	0.0194	0.0752	0.0657	0.0018	0.0559
O10 - H11	0.3615	-2.7132	0.0223	-0.7598	0.5201
O10 - H12	0.3718	-2.7096	0.0233	-0.7669	0.6202

Table S12. Changes of AIM atomic properties computed at MP2/6-311++G(2d,2p) level. All data reported in atomic units.

	Complex	B	H	$\Delta q(H)^a$	$\Delta E(H)^a$	$\Delta M(H)^a$	$\Delta V(H)^a$	$\Delta r_B{}^a$	$\Delta r_H{}^a$
I	**NMF-Ar**	Ar10	H6	0.001	0.000	-0.003	1.262	0.235	0.189
		Ar10	H9	0.000	-0.001	-0.003	1.344	0.021	0.023
II	**NMF-Ar**	Ar10	H5	0.000	0.000	-0.001	1.410	0.112	0.077
III	**NMF-Ar**	Ar10	H7	-0.008	-0.004	0.001	2.132	-0.026	-0.009
IV	**NMF-Ar**	Ar10	H8	0.002	0.000	-0.003	0.985	0.127	0.112
I	**NMF-N_2**	N10	H6	0.013	0.004	-0.013	-1.478	0.580	0.507
II	**NMF-N_2**	N11	H5	0.006	0.002	-0.003	-0.104	0.370	0.332
III	**NMF-N_2**	N10	H8	0.022	0.007	-0.006	-1.557	0.168	0.203
IV	**NMF-N_2**	N10	H8	0.001	-0.001	-0.006	0.061	0.304	0.302
I	**NMF-CO**	C10	H6	0.017	0.008	-0.014	-1.425	0.770	0.570
III	**NMF-CO**	C10	H8	0.024	0.009	-0.006	-1.605	0.283	0.227
IV	**NMF-CO**	C10	H8	0.003	0.000	-0.005	0.440	0.360	0.269
I	**NMF-H_2O**	O10	H6	0.054	0.023	-0.039	-7.515	0.983	0.883
II	**NMF-H_2O**	O3	H11	0.045	0.027	-0.035	-7.714	1.158	0.953
III	**NMF-H_2O**	O3	H11	0.048	0.029	-0.038	-8.045	1.134	0.932

a

$\Delta q(H) = q(H)_{complex} - q(H)_{monomer}$; $\Delta E(H) = E(H)_{complex} - E(H)_{monomer}$; $\Delta M(H) = M(H)_{complex} - M(H)_{monomer}$
$\Delta V(H) = V(H)_{complex} - V(H)_{monomer}$; $\Delta r_H = r^H_{monomer} - r^H_{complex}$; $\Delta r_B = r^B_{monomer} - r^B_{complex}$

The above table presents the values of the four Koch' and Popelier' criteria ($\Delta q(H)$, $\Delta E(H)$, $\Delta M(H)$ $\Delta V(H)$) for the hydrogen bonding interaction:

- *loss of the hydrogen atom's charge ($\Delta q(H) = q(H)_{complex} - q(H)_{monomer}$),*

- *energetic destabilization of the hydrogen atom ($\Delta E(H) = E(H)_{complex} - E(H)_{monomer}$),*

- *decrease of the hydrogen atom's dipolar polarization ($\Delta M(H) = M(H)_{complex} - M(H)_{monomer}$),*

- *decrease of the volume of the hydrogen atom ($\Delta V(H) = V(H)_{complex} - V(H)_{monomer}$),*

- *mutual penetration of hydrogen and acceptor atom ($\Delta r_H = r^H_{monomer} - r^H_{complex}$, $\Delta r_B = r^B_{monomer} - r^B_{complex}$).*

As could be expected, all the criteria are all met for the H_2O-NMF complexes. Similarly, one can observe $\Delta q(H)>0$, $\Delta E(H)>0$, $\Delta M(H)<0$, $\Delta V(H)<0$, $\Delta r_H >0$, and $\Delta r_B >0$ for the CO, I and N_2, I complexes, though some of these values are rather small. But it can be attributed to very weak nature of the hydrogen bond present in these molecules. For the CO, IV and N_2, IV complexes two conditions are not fulfilled ($\Delta E(H)>0$, $\Delta V(H)<0$). For the CO, III and N_2, III complexes all these criteria are met, but as it was mentioned before, the $\nabla^2\rho$ values are too small. Moreover, closer inspection of the mutual penetration in this molecules, shows that Δr_H and Δr_B values are closer to those in van der Waals complexes with argon, than in hydrogen-bonded ones. And finally remains the most problematic complex with N_2 (II). Though all the conditions are met, very low values of $\nabla^2\rho$, $\Delta q(H)$, $\Delta E(H)$, $\Delta M(H)$, and specially $\Delta V(H)$, do not lead us to consider this interaction as hydrogen bond.