Electronic Supplementary Information

Intermolecular amide and aldehyde interactions: rotational spectroscopy of the complexes of formaldehyde with 2-azetidinone and formamide

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Table S1. The spectroscopic parameters, electric dipole moment components, and binding energies (E_B) of the three isomers of the 2-azetidinone-H_2CO complex calculated at the MP2/6-311++G(d,p) and B3LYP-D3(BJ)/def2-TZVP levels of theory.

Parameters	A-I		A-II		A-III	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
A/MHz	4909	5011	5251	5429	3733	3768
B/MHz	1381	1414	1513	1525	1902	1818
C/MHz	1093	1118	1223	1230	1556	1502
χ_{aa}/MHz	2.00	2.05	1.98	2.25	-3.4	-3.4
$(\chi_{bb}-\chi_{cc})$/MHz	5.76	5.84	5.37	5.66	-0.6	-0.9
$|\mu_a|$ /D	0.6	-0.7	1.6	-2.0	0.6	-0.1
$|\mu_b|$ /D	-1.4	-1.4	-1.0	-1.0	-1.9	-1.8
$|\mu_c|$ /D	0.0	0.0	-0.1	0.6	0.5	-0.6
P_{cc}/u$Å^2$	3.24	3.21	8.56	6.84	38.19	37.78
E_B /kJ mol^{-1}	24.3	25.3	20.6	21.7	17.9	16.1

Table S2. The spectroscopic parameters, electric dipole moment components, and binding energies (E_B) of the four isomers of the formamide-H_2CO complex calculated at the MP2/6-311++G(d,p) and B3LYP-D3(BJ)/def2-TZVP level of theory.

Parameters	F-I		F-II		F-III		F-IV	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
A/MHz	8790	8872	13462	13637	19315	16699	8419	8755
B/MHz	2459	2561	2081	2168	1403	1532	2660	2478
C/MHz	1921	1988	1825	1896	1380	1466	2103	2059
χ_{aa}/MHz	1.48	1.43	2.10	2.03	1.35	1.19	-3.53	-3.05
$(\chi_{bb}-\chi_{cc})$/MHz	6.02	5.92	6.18	6.20	1.99	0.77	0.43	0.55
$|\mu_a|$ /D	-0.04	0.0	-2.9	-3.3	5.07	4.9	-0.7	-0.2
$|\mu_b|$ /D	1.40	-1.5	0.5	0.6	-0.4	-0.5	-1.7	-1.8
$|\mu_c|$ /D	0.0	0.0	0.0	0.0	-1.2	-1.1	-0.7	0.7
P_{cc}/u$Å^2$	0.0	0.0	1.76	1.76	10.1	7.62	8.62	8.11
E_B /kJ mol^{-1}	19.0	26.2	10.4	16.7	10.5	15.2	6.8	12.3

Table S3. The results of NBO analysis for 2-azetidinone-H_2CO.

2-azetidinone-H_2CO					
From 2-azetidinone to H_2CO			**From H_2CO to 2-azetidinone**		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C5−C2	RY*(4) C12	0.07	BD(1)C12−H13	RY*(8) C2	0.05
BD(1)C5−C2	RY*(1) H13	0.08	BD(1)C12−H14	BD*(1) N3−H10	0.12
BD(1)C5−C2	BD*(1)C12−H13	0.09	**LP(1)O11**	**BD*(1) N3−H10**	**1.81**
BD(1)N3−H10	BD*(2)C12−O11	0.11	LP(2)O11	RY* (2) H10	0.28
LP(1) O1	RY *(4) C12	0.09	LP(2)O11	RY* (3) H10	0.14
LP(1) O1	RY *(3) H13	0.09	LP(2)O11	RY* (6) H10	0.07
LP(1) O1	**BD*(1)C12−H13**	**0.35**	**LP(2)O11**	**BD*(1) N3−H10**	**4.66**
LP(2) O1	**BD*(1)C12−H13**	**1.58**	LP(2)O11	BD*(1) N3−C4	0.13

[a]BD for 2−center bond, LP for 1−center valence lone pair the unstarred and starred labels corresponding to Lewis and non−Lewis NBOs, respectively.

[b]RY* for 1−center Rydberg, and BD* for 2−center antibond, the unstarred and starred labels corresponding to Lewis and non−Lewis NBOs, respectively.

Table S4. The results of NBO analysis for formamide-H_2CO.

formamide-H_2CO					
From formamide to H_2CO			**From H_2CO to formamide**		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(2)O3−C2	RY*(2) H10	0.05	BD(1)C8−H9	RY*(1) H6	0.05
BD(1)C2−H4	RY*(6) C8	0.06	BD(1)C8−H9	BD*(1) N1−H6	0.11
BD(1)C2−H4	RY*(7) H10	0.06	BD(1)C8−H10	BD*(2) O3−C2	0.06
BD(1)C2−H4	BD*(1)C8−H10	0.08	LP(1)O7	RY* (6) N1	0.11
BD(1)N1−H6	RY*(5) O7	0.06	**LP(1)O7**	**BD* (1) N1−H6**	**2.11**
BD(1)N1−H6	BD*(2)C8−O7	0.09	LP(2)O7	RY* (1) H6	0.27
LP(1)O3	RY*(5) H10	0.07	LP(2)O7	RY* (3) H6	0.08
LP(1)O3	**BD*(1) C8−H10**	**0.85**	LP(2)O7	RY* (4) H6	0.07
LP(2)O3	RY*(3) C8	0.08	**LP(2)O7**	**BD* (1) N1−H6**	**6.36**
LP(2)O3	BD*(1) C8−H9	0.12			
LP(2)O3	**BD*(1) C8−H10**	**1.68**			

[a]BD for 2−center bond, LP for 1−center valence lone pair the unstarred and starred labels corresponding to Lewis and non−Lewis NBOs, respectively.

[b]RY* for 1−center Rydberg, and BD* for 2−center antibond, the unstarred and starred labels corresponding to Lewis and non−Lewis NBOs, respectively.

Table S5. The results of the SAPT analysis for FM-H_2O and 2AT-H_2O[a] complex.

Complexes		E_{elec}	E_{ind}	E_{disp}	E_{exch}	E_t
FM-H_2O	a	-66.6	-21.4	-22.0	69.2	-40.9
	b	-41.9	-14.0	-14.7	41.6	-29.1
	c	-23.6	-7.9	-5.7	20.7	-16.5
2AT-H_2O	a	-59.8	-18.9	-21.7	60.1	-40.3
	b	-44.6	-15.1	-17.8	45.1	-32.3

[a] All values are given in kJ mol^{-1}.

Table S6. Experimental transition frequencies of the observed parent species of isomer **A-I** of the 2-azetidinone-H_2CO complex.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$ (MHz)
2	1	2	3	1	0	1	2	8329.3656	0.0016
2	1	2	1	1	0	1	0	8329.5567	0.0000
5	0	5	5	4	1	4	4	9668.5985	0.0031
5	0	5	6	4	1	4	5	9669.0154	0.0005
5	0	5	4	4	1	4	3	9669.1866	0.0034
3	1	3	2	2	0	2	1	10405.5802	-0.0021
3	1	3	3	2	0	2	2	10406.4432	-0.0039
4	1	4	3	3	0	3	2	12365.9950	-0.0047
4	1	4	5	3	0	3	4	12366.1169	0.0007
4	1	4	4	3	0	3	3	12366.8604	-0.0006
6	0	6	6	5	1	5	5	12429.5189	-0.0031
6	0	6	7	5	1	5	6	12429.8516	-0.0044
6	0	6	5	5	1	5	4	12429.9727	0.0030
4	2	3	4	4	1	4	4	12739.9180	-0.0002
4	2	3	5	4	1	4	5	12741.1968	0.0021
5	1	5	4	4	0	4	3	14243.8376	0.0017
5	1	5	6	4	0	4	5	14243.9225	-0.0017
5	1	5	5	4	0	4	4	14244.6108	-0.0001
7	0	7	7	6	1	6	6	15123.6681	-0.0013
7	0	7	8	6	1	6	7	15123.9081	-0.0013
7	0	7	6	6	1	6	5	15123.9842	-0.0028
2	2	1	1	1	1	0	0	16132.2168	0.0000
2	2	1	2	1	1	0	2	16132.9398	-0.0027
2	2	1	3	1	1	0	2	16133.5565	-0.0001
2	2	1	2	1	1	0	1	16134.0633	0.0001
2	2	1	1	1	1	0	1	16135.0192	0.0004
6	1	6	5	5	0	5	4	16080.6267	0.0005
6	1	6	7	5	0	5	6	16080.6945	0.0076
6	1	6	6	5	0	5	5	16081.2822	0.0011
2	2	0	2	1	1	1	1	16436.6608	-0.0001
2	2	0	2	1	1	1	2	16437.2060	-0.0021
2	2	0	1	1	1	1	1	16437.7159	-0.0046
2	2	0	3	1	1	1	2	16437.8984	0.0091
2	2	0	1	1	1	1	0	16439.0866	-0.0023
8	0	8	8	7	1	7	7	17732.4869	0.0026
8	0	8	9	7	1	7	8	17732.6362	-0.0045
8	0	8	7	7	1	7	6	17732.6918	-0.0016

7	1	7	6	6	0	6	5	17918.8949	0.0008
7	1	7	8	6	0	6	7	17918.9292	-0.0023
7	1	7	7	6	0	6	6	17919.4148	-0.0031
3	2	2	2	2	1	1	1	18346.7728	-0.0025
3	2	2	4	2	1	1	3	18347.0982	-0.0033
3	2	1	3	2	1	2	2	19290.8877	0.0000
3	2	1	4	2	1	2	3	19292.2697	0.0095
3	2	1	2	2	1	2	1	19292.9846	-0.0030
4	1	4	5	3	1	3	4	9398.6341	0.0003
4	1	4	3	3	1	3	2	9398.7321	-0.0010
4	1	4	4	3	1	3	3	9398.7627	0.0005
4	0	4	5	3	0	3	4	9843.3628	-0.0019
4	0	4	3	3	0	3	2	9843.4019	0.0014
4	0	4	4	3	0	3	3	9843.5092	-0.0083
4	1	3	3	3	1	2	2	10545.2495	0.0008
4	1	3	5	3	1	2	4	10545.3114	-0.0007
4	1	3	4	3	1	2	3	10545.4002	-0.0042
5	1	5	6	4	1	4	5	11721.1740	0.0012
5	1	5	4	4	1	4	3	11721.2401	0.0035
5	1	5	5	4	1	4	4	11721.2667	-0.0008
5	0	5	6	4	0	4	5	12191.7660	-0.0003
5	0	5	4	4	0	4	3	12191.7931	0.0106
5	0	5	5	4	0	4	4	12191.9370	-0.0018
5	2	4	4	4	2	3	3	12469.4236	-0.0023
5	2	4	6	4	2	3	5	12469.4448	0.0003
5	2	4	5	4	2	3	4	12469.6037	-0.0037
5	2	3	4	4	2	2	3	12783.7634	-0.0001
5	2	3	6	4	2	2	5	12783.7634	-0.0020
5	2	3	5	4	2	2	4	12783.7634	-0.0027
5	1	4	4	4	1	3	3	13146.5092	-0.0006
5	1	4	6	4	1	3	5	13146.5416	-0.0022
5	1	4	5	4	1	3	4	13146.6259	0.0030
6	1	6	7	5	1	5	6	14028.5292	0.0003
6	1	6	5	5	1	5	4	14028.5721	-0.0007
6	1	6	6	5	1	5	5	14028.6090	0.0000
6	0	6	7	5	0	5	6	14482.0135	-0.0005
6	0	6	5	5	0	5	4	14482.0287	0.0056
6	0	6	6	5	0	5	5	14482.1937	-0.0004
6	2	5	5	5	2	4	4	14933.1856	-0.0006
6	2	5	7	5	2	4	6	14933.1856	-0.0044
6	2	5	6	5	2	4	5	14933.3036	-0.0016

6	3	4	6	5	3	3	5	15081.9870	0.0011
6	2	4	6	5	2	3	5	15457.8327	-0.0011
6	2	4	7	5	2	3	6	15457.8887	-0.0018
6	2	4	5	5	2	3	4	15457.8974	-0.0015
6	1	5	5	5	1	4	4	15721.0570	0.0076
6	1	5	7	5	1	4	6	15721.0750	0.0027
6	1	5	6	5	1	4	5	15721.1589	0.0034
7	1	7	8	6	1	6	7	16320.2595	0.0006
7	1	7	6	6	1	6	5	16320.2962	0.0052
7	1	7	7	6	1	6	6	16320.3309	-0.0001
7	0	7	8	6	0	6	7	16722.5789	-0.0033
7	0	7	6	6	0	6	5	16722.5899	-0.0002
7	0	7	7	6	0	6	6	16722.7592	0.0028

Table S7. Experimental transition frequencies of the observed parent species of isomer **F-I** of the formamide-H_2CO complex.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	ν_{obs}/MHz	$\Delta\nu_{obs\text{-}calc}$ (MHz)
1	1	0	1	1	0	1	1	6892.4102	0.0061
1	1	0	1	1	0	1	2	6892.7992	0.0030
1	1	0	2	1	0	1	1	6893.4102	-0.0024
1	1	0	2	1	0	1	2	6893.8006	-0.0042
2	1	1	2	2	0	2	2	7480.1637	0.0041
2	1	1	2	2	0	2	3	7480.6490	-0.0021
2	1	1	3	2	0	2	2	7480.8080	-0.0120
2	1	1	2	2	0	2	1	7480.9137	-0.0105
2	1	1	1	2	0	2	1	7481.1834	-0.0037
2	1	1	3	2	0	2	2	7481.3155	0.0038
2	1	1	1	2	0	2	3	7481.9594	0.0075
3	0	3	3	2	1	2	2	7414.5199	0.0000
3	0	3	4	2	1	2	3	7414.9832	0.0017
3	0	3	2	2	1	2	1	7415.3657	0.0006
3	1	2	3	3	0	3	3	8424.6428	0.0010
3	1	2	4	3	0	3	4	8425.8126	0.0000
3	1	2	2	3	0	3	2	8426.2286	0.0060
4	1	3	4	4	0	4	4	9794.9728	0.0041
4	1	3	5	4	0	4	5	9796.2191	-0.0049
4	1	3	3	4	0	4	3	9796.5494	0.0023
1	1	1	0	0	0	0	1	10797.8607	0.0017
1	1	1	2	0	0	0	1	10798.7813	-0.0017
1	1	1	1	0	0	0	1	10799.3965	-0.0001
5	1	4	5	5	0	5	5	11665.2930	-0.0030
5	1	4	6	5	0	5	6	11666.6568	-0.0006
5	1	4	4	5	0	5	4	11666.9370	0.0022
4	0	4	4	3	1	3	3	12384.7645	0.0000
4	0	4	5	3	1	3	4	12385.2356	-0.0053
4	0	4	3	3	1	3	2	12385.4780	-0.0001
2	1	2	1	1	0	1	1	14702.9086	0.0005
2	1	2	1	1	0	1	0	14703.8839	0.0076
2	1	2	3	1	0	1	2	14703.9042	0.0011
2	1	2	2	1	0	1	1	14704.5970	0.0086
2	1	2	2	1	0	1	2	14704.9825	0.0020
5	2	3	4	5	1	4	4	17025.3241	-0.0027
5	2	3	6	5	1	4	6	17025.3777	0.0044
5	2	3	5	5	1	4	5	17025.5992	-0.0021

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4	2	2	3	4	1	3	3	17664.6516	0.0018
4	2	2	5	4	1	3	5	17664.7374	-0.0015
4	2	2	4	4	1	3	4	17665.0849	-0.0002
5	0	5	5	4	1	4	4	17359.2128	0.0019
5	0	5	6	4	1	4	5	17359.6166	0.0001
5	0	5	4	4	1	4	3	17359.7733	0.0017
3	2	1	2	3	1	2	2	18386.2821	-0.0022
3	2	1	4	3	1	2	4	18386.4175	0.0042
3	2	1	3	3	1	2	3	18386.7813	-0.0004
3	1	3	2	2	0	2	1	18345.9108	-0.0019
3	1	3	4	2	0	2	3	18346.0762	-0.0015
3	1	3	3	2	0	2	2	18346.8346	-0.0033
4	0	4	5	3	0	3	4	9843.3628	-0.0019
4	0	4	3	3	0	3	2	9843.4019	0.0014
4	0	4	4	3	0	3	3	9843.5092	-0.0083
2	2	0	3	2	1	1	3	19056.3568	0.0040
2	2	0	2	2	1	1	2	19056.5164	-0.0053
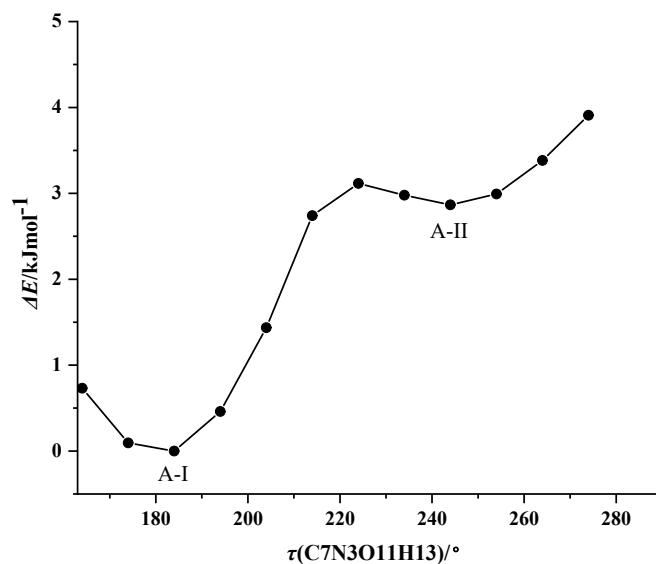
Figure S1. Potential energy curve relating to the interconversion of different conformations of 2-azetidinone-H$_2$CO calculated at the MP2/6-311++G(d,p) level.