Supplementary Materials

Infrared and microwave spectra of the acetylene-ammonia and carbonyl sulfide-ammonia complexes: a comparative study of a weak C-H···N hydrogen bond and an S···N bond

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Supplementary Materials include:

1. *Ab initio* harmonic and anharmonic frequency calculations
2. Calculation of electrostatic interactions
3. The experimental infrared and microwave transitions are listed in Table 2 and Table 3

1 *Ab initio* harmonic and anharmonic frequency calculations

Harmonic and anharmonic vibrational frequencies and zero-point energies of the complexes and the monomer subunits at the MP2/aug-cc-pVTZ level of theory.

HCCH-NH_3:

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3496.371	3384.925	0.180750	-0.001946	-0.001946
2(1)	3494.521	3361.181	0.161732	-0.001980	-0.001980
3(1)	3335.407	3259.993	0.189251	-0.000978	-0.000978
4(1)	1949.820	1924.933	0.193146	-0.002007	-0.002007
5(1)	1076.846	1014.298	0.147592	-0.002292	-0.002292
6(1)	130.982	136.235	0.193765	-0.003977	-0.003977
7(1)	3639.281	3471.484	0.183533	-0.002027	-0.002027
8(1)	3639.281	3471.639	0.183533	-0.002027	-0.002027
9(1)	1669.153	1626.978	0.136596	-0.001978	-0.002004
10(1)	1669.153	1627.728	0.136596	-0.002004	-0.001978
11(1)	868.800	773.318	0.197668	-0.003414	-0.003388
12(1)	868.800	774.761	0.197668	-0.003388	-0.003414
13(1)	640.486	644.191	0.194749	-0.002215	-0.002246

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14(1)              640.486      646.389    0.194750   -0.002246   -0.002215
15(1)              213.692      223.212    0.540488   -0.002460   -0.002516
16(1)              213.692      217.098    0.540487   -0.002516   -0.002460
17(1)               90.760      151.613    0.150804   -0.001465   -0.001682
18(1)               90.760      156.274    0.150804   -0.001682   -0.001465
ZPE(harm) = 0.16585D+03 kJ/mol         ZPE(anh)= 0.16338D+03 kJ/mol
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OCS-NH_3:

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Mode(Quanta)      E(harm)      E(anharm)    Aa(z)        Ba(x)        Ca(y)
Fundamental Bands (DE w.r.t. Ground State)
 1(1)            3496.905     3352.323    0.310162   -0.000321   -0.000321
 2(1)            2069.121     2044.655    0.352849   -0.000399   -0.000399
 3(1)            1061.474      986.344    0.300634   -0.000466   -0.000466
 4(1)             878.034      865.696    0.352474   -0.000318   -0.000318
 5(1)              86.661       69.156    0.352690   -0.001312   -0.001312
 6(1)            3642.217     3474.483    0.344760   -0.000326   -0.000326
 7(1)            3642.217     3474.412    0.344760   -0.000326   -0.000326
 8(1)            1668.642     1621.773    0.295348   -0.000351   -0.000347
 9(1)            1668.642     1622.226    0.295348   -0.000347   -0.000351
10(1)             534.858      542.887    0.353333   -0.000430   -0.000439
11(1)             534.858      537.535    0.353333   -0.000439   -0.000430
12(1)             123.310      111.301    0.842806   -0.000338   -0.000353
13(1)             123.310      114.526    0.842811   -0.000353   -0.000338
14(1)              33.234       41.209    0.328577   -0.000293   -0.000388
15(1)              33.234       51.612    0.328575   -0.000388   -0.000293
ZPE(harm) = 0.11721D+03 kJ/mol         ZPE(anh)= 0.11519D+03 kJ/mol
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NH_3:

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Mode(Quanta)      E(harm)      E(anharm)    Aa(z)        Ba(x)        Ca(y)
Fundamental Bands (DE w.r.t. Ground State)
 1(1)            3503.370     3360.670   -0.217151   -0.217197   -0.154949
 2(1)            1039.089      961.134   -0.149187   -0.149168   -0.174113
 3(1)            3650.040     3484.095   -0.241515   -0.240649   -0.120067
 4(1)            3650.040     3484.114   -0.240613   -0.241551   -0.120067
 5(1)            1668.900     1621.450    0.300007    0.016024   -0.172464
 6(1)            1668.900     1621.453    0.016029    0.300003   -0.172464
ZPE(harm) = 0.90799D+02 kJ/mol         ZPE(anh)= 0.89335D+02 kJ/mol
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HCCH:

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Frequencies --   601.3897              601.3897              753.9250
Frequencies --   753.9250             1967.8846             3431.6016
Frequencies --  3533.6350
Zero-point correction=                          0.026526 (Hartree/Particle)
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OCS:

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Frequencies --   522.6526                522.6526                888.0232
Frequencies --  2083.7994
Zero-point correction=                                0.009152 (Hartree/Particle)
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2 Calculations of electrostatic interactions

Potential energies for the dipole-dipole interaction in the C_{3V} symmetric conformer of the complexes is:[1]

$$E_{d-d} = -2\,\frac{\mu^A\,\mu^B}{4\pi\varepsilon_0 r^3} \tag{1}$$

dipole-quadrupole interaction (C_{3V} symmetric conformation, with the dipole moment pointing to or away from the quadrupole):

$$E_{d-q} = \pm 3\,\frac{\mu^A\,Q^B_{ZZ}}{4\pi\varepsilon_0 r^4} \tag{2}$$

dipole-quadrupole interaction (T-shaped conformation, with the dipole moment of NH_3 pointing to HCCH in HCCH-NH_3 or pointing away from OCS in OCS-NH_3):

$$E_{d-q} = \mp 1.5\,\frac{\mu^A\,Q^B_{ZZ}}{4\pi\varepsilon_0 r^4} \tag{3}$$

quadrupole-quadrupole interaction (C_{3V} symmetric conformer):

$$E_{q-q} = 6\,\frac{Q^A_{ZZ}\,Q^B_{ZZ}}{4\pi\varepsilon_0 r^5} \tag{4}$$

quadrupole-quadrupole interaction (T-shaped conformer):

$$E_{q-q} = -3\,\frac{Q^A_{ZZ}\,Q^B_{ZZ}}{4\pi\varepsilon_0 r^5} \tag{5}$$

By taking the experimental values for the dipole moments of ammonia (1.472 Debye)[2] and OCS (0.715 Debye)[3], quadrupole moment of acetylene (6.335 DebyeÅ)[4], ammonia (-2.320 DebyeÅ)[5], and OCS (-0.584 DebyeÅ)[6], and the distance between the subunits determined from this work, the electrostatic interaction energies were estimated and listed in Table 1 (negative means attractive).

Table 1 Electrostatic interaction energies of HCCH-NH_3 and OCS-NH_3 (in kJ/mol)

	C_{3V}-HCCH-NH_3	T-shaped HCCH-NH_3	C_{3V}-OCS-NH_3	T-shaped OCS-NH_3
dipole-dipole			-1.5	
quadrupole-dipole	-6.2	-3.1	0.4	-0.2
dipole-quadrupole			-0.8	
quadrupole-quadrupole	-4.8	2.4	0.3	-0.2
sum	-11.0	-0.7	-1.6	-0.4

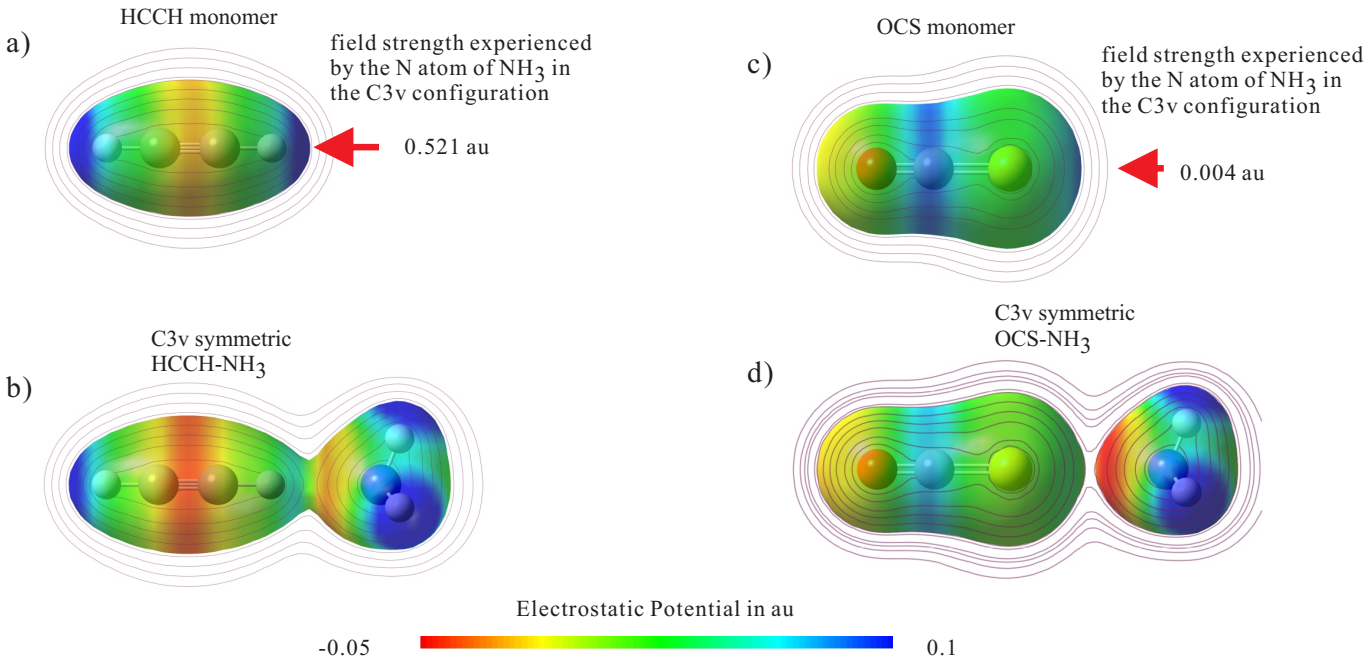

Fig. 1 Electrostatic potential (from -0.05 au to 0.1 au) mapped on the electron density isosurface of 0.01 for a) HCCH, b)HCCH-NH_3, c) OCS, and d) OCS-NH_3. The blue part of the surface shows a positive electrostatic potential and hence attracts the electronegative N atom of ammonia. In a) and c), the arrows indicate the attractive field strength experienced by the N atom of ammonia if a ammonia molecule is placed at the position as in the corresponding complexes observed.

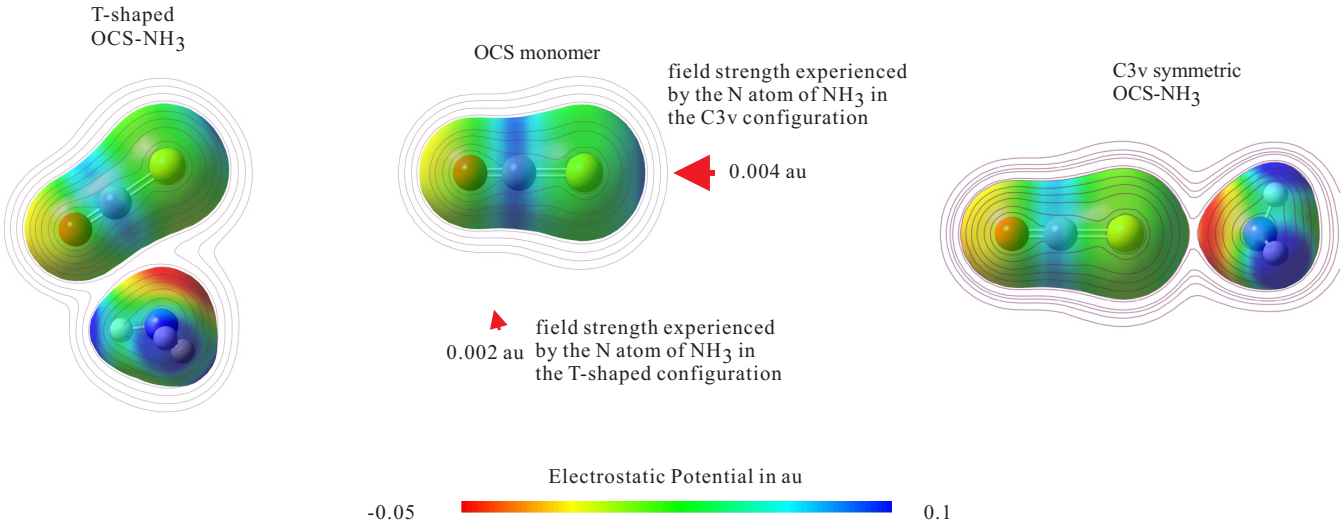

Fig. 2 Electrostatic potential (from -0.05 au to 0.1 au) mapped on the electron density isosurface of 0.01 for OCS, C_{3V} and T-shaped OCS-NH_3. The blue part of the surface shows a positive electrostatic potential and hence attracts the electronegative N atom of ammonia. For the two possible binding sites of ammonia, the attractive field strengths experienced by the N atom of ammonia are different, showing a subtle preference for the linear configuration.

3 The experimental infrared and microwave transitions

The observed infrared and microwave transitions are listed in Table 2 and Table 3.

Table 2 Observed infrared transitions of HCCH-NH_3 $K = 1 \leftarrow 0$ subband and OCS-NH_3 $K = 2 \leftarrow 1$ subband (in cm^{-1})

$J' \leftarrow J''$	HCCH-NH_3	$\Delta\nu$	OCS-NH_3	$\Delta\nu$
11←12	1652.5440	-0.0001		
10←11	1652.7250	-0.0003		
9←10	1652.9082	-0.0001		
8←9	1653.0911	-0.0002	1636.6666	-0.0004
7←8			1636.7667	-0.0006
6←7	1653.4573	0.0005	1636.865	-0.0024
5←6	1653.6400	0.0006	1636.967	-0.0008
4←5	1653.8219	-0.0000	1637.0681	0.0000
3←4	1654.0038	-0.0004	1637.269	0.0046
2←3	1654.1857	0.0005	1637.1728	0.0002
1←2			1637.3692	0.0006
1←0			1637.6693	0.0007
2←1	1655.0943	-0.0010	1637.7684	-0.0001
3←2	1655.2756	-0.0002	1637.8685	0.0000
4←3	1655.4566	-0.0004	1637.9674	-0.0008
5←4	1655.6377	-0.0001	1638.0679	-0.0001
6←5	1655.8187	0.0002	1638.1682	0.0005
7←6	1655.9995	0.0004	1638.2673	-0.0002
8←7	1656.1786	-0.0004	1638.3674	0.0003
9←8	1656.3595	0.0003	1638.4670	0.0003
10←9	1656.5388	0.0001	1638.5658	-0.0003
11←10	1656.7183	0.0002	1638.667	0.0010
12←11	1656.8969	-0.0004	1638.7647	-0.0003
13←12	1657.0767	0.0006		
14←13	1657.2529	-0.0006		

Table 3 Observed microwave transitions of HCCH-NH_3 and OCS-NH_3 (in MHz)

$J'K'$	F'	$J''K''$	F''	HCCH-NH_3	$\Delta\nu^b$	OCS-NH_3	$\Delta\nu^b$
1 0	1	0 0	1			5448.3207	0.6
	2		1			5449.2573	2.0
	0		1			5450.6695	1.4
2 0	2	1 0	2	5996.4415	3.2	10897.1010	0.1
	1		0	5996.5962	2.7	10897.2572	0.3
	2		1	5997.3359	1.2	10898.0414	1.2
	3		2	5997.4092	8.3	10898.1065	0.8
	1		1	5998.8251	0.4		
2 1	2	1 1	1	5994.8918	0.1	10893.6791	0.7
	2		2	5995.3354	2.5		
	1		1	5995.6453	9.6	10894.4634	0.9
	3		2	5995.8145	1.5	10894.6523	0.1
	1		0	5996.7507	0.4	10895.6364	0.1
3 0	3	2 0	3	8994.9376	0.4	16345.6342	1.7
	2		1	8995.7436	0.9	16346.4841	1.9
	3		2	8995.8890	4.3	16346.6342	4.5
	4		3	8995.9320	3.2	16346.6768	0.7
	2		2	8997.2346	2.4	16348.0478	0.2
3 1	3	2 1	3	8992.6776	1.0	16340.5782	2.8
	3		2	8993.1555	0.9	16341.0885	4.4
	4		3	8993.4175	2.8	16341.3620	1.7
	2		2	8994.1584	0.4	16342.1410	0.2
3 2	3	2 2	2			16324.4750	0.4
	2		1			16326.0382	1.7
	4		3			16325.4821	1.3
4 0	4	3 0	4	11993.3234	1.2		
	3		2	11994.2455	5.6		
	4		3	11994.3152	0.3		
	5		4	11994.3392	1.8		
	3		3	11995.5906	0.6		
4 1	4	3 1	4	11990.0958	2.7		
	4		3	11990.8376	0.7		
	3		2	11990.9114	5.1		
	5		4	11990.9550	0.2		
	3		3	11991.9177	3.0		
5 0	4	4 0	3	14992.5149	6.4		
	5		4	14992.5613	4.6		
	6		5	14992.5749	2.6		
5 1	5	4 1	4	14988.2605	4.4		
	4		3	14988.2971	0.3		
	6		5	14988.3304	0.8		
6 0	5	5 0	4	17990.5478	3.6		
	7		6	17990.5876	2.1		
6 1	6	5 1	5	17985.4453	1.9		
	7		6	17985.4940	6.7		

[a] $\mathbf{F} = \mathbf{I_N} + \mathbf{J}$

[b] $\Delta\nu = \nu_{experimental} - \nu_{calculated}$ (in kHz)

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