Electronic Supporting Information

Table S1. Augmented correlation consistent valence basis set L2a_3 contraction scheme as compared to the aug-cc-pVTZ basis.

Basis	C, N, O, atoms contraction scheme	H atom contraction scheme
L2a_3	{5s,4p,3d,2f}/{17s,11p,6d,4f}	{4s,3p,2d}/{11s,6p,4d}
aug-cc-pVTZ	{5s,4p,3d,2f}/{11s,6p,3d,2f}	{4s,3p,2d}/{6s,3p,2d}

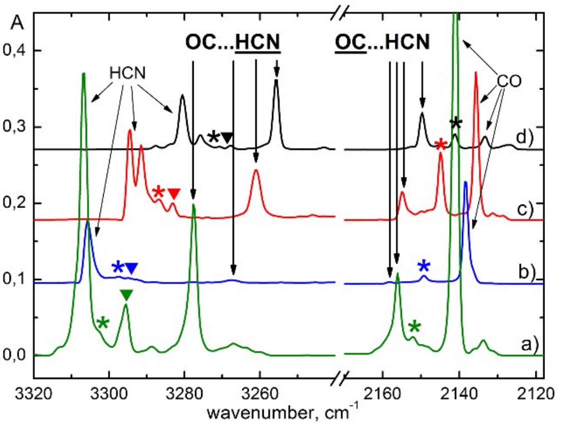

Figure S1. Fragments of the IR spectra of deposited (a) HCN/CO/Ne, (b) HCN/CO/Ar, (c) HCN/CO/Kr, and (d) HCN/CO/Xe at 5 K. The component ratio was 1/1/1000 in all the cases. The bands of CO...H_2O and HCN...H_2O complexes are marked with asterisks; bands of $(HCN)_n$ associates are marked with triangles.

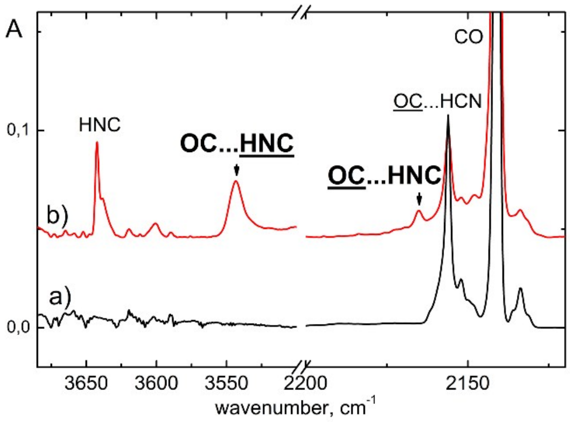

Figure S2. Fragments of the IR spectra of (a) deposited and (b) irradiated HCN/CO/Ne matrix.

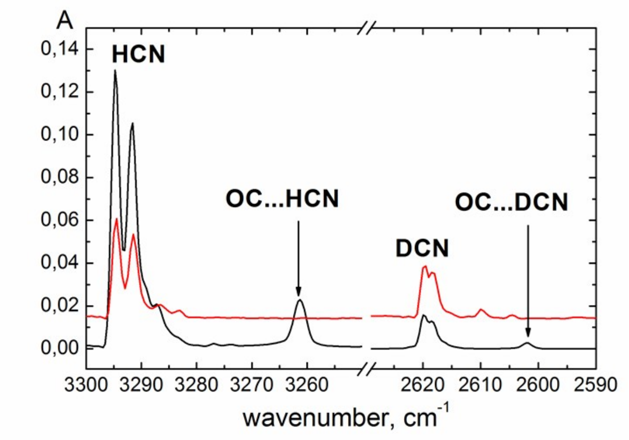

Figure S3a. Fragments of the IR spectra of deposited HCN+DCN/Kr (1/1000) (upper trace) and HCN+DCN/CO/Kr (1/1/1000) (lower trace).

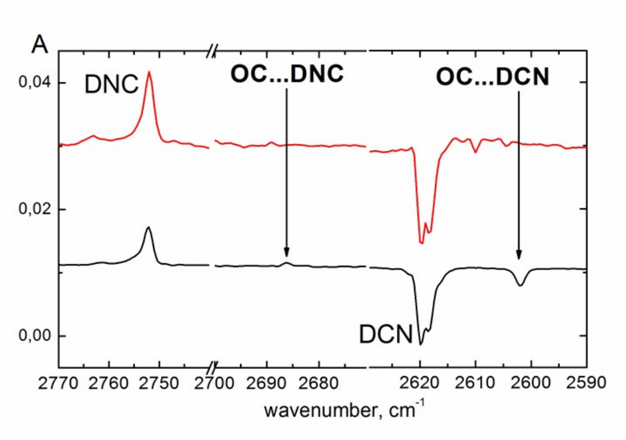

Figure S3b. Fragment of difference IR spectra (irradiated – deposited) for DCN/HCN/CO/Kr 1/1/1000 (lower trace) and DCN/HCN/Kr 1/1000 (upper trace) samples.

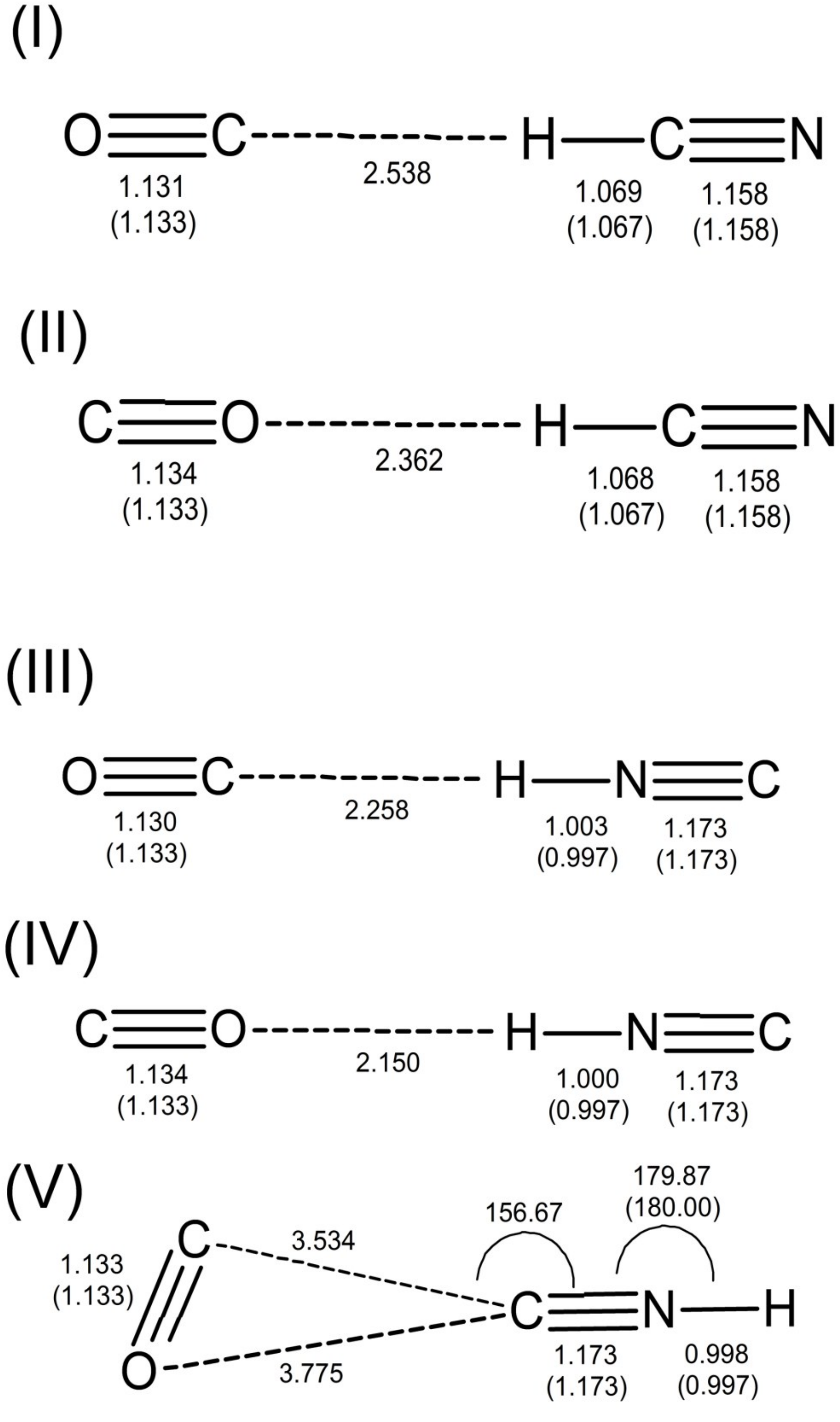

Figure S4. Calculated structures of HCN…CO and HNC..CO complexes

Table S2. Interaction energies of complexes, kcal/mol

Structure	Interaction energies of complexes, kcal/mol			
		BSSE corrected	ZPVE corrected	ZPVE+BSSE corrected
I	1.96	1.69	1.28	1.01
II	1.42	1.02	0.92	0.52
III	3.26	2.90	2.23	1.87
IV	2.08	1.57	1.39	0.88
V	0.75	0.63	0.51	0.39

Table S3. Comparison between computational and experimental shifts (complex vs. monomer), cm^{-1}

Mode type	OC...HCN (I)	OC...HCN (II)	Ne	Ar	Kr	Xe
H-C-N bending	+42.1	+25.1	+29	+32	+31,4	+29,9
C-O stretching	+17.6	-8.1	+15	+20	+19,5	+16,7
H-C stretching	-33.3	-10.2	-29,5	-38,3	-33,8	-24,3

Table S4. Comparison between computational and experimental shifts, cm^{-1}

Mode type	OC...HNC (III)	CO...HNC (IV)	Ne	Ar	Kr	Xe
H-N-C bending	+137.2	+73.31	+95,7		+102	
C-N stretching	+1.3	+4.2	+1,6	+3.5	+3	
C-O stretching	+26.5	-10.0	+24	+29	+27,5	+25
H-N stretching	-107.6	-35.0	-100	-118	-100	-77

Calculated harmonic vibrational frequencies (cm^{-1}), reduced masses, IR intensities (km/mol), molecular geometries and energies for HCN, HNC, CO, HCN…CO and HNC…CO complexes

Abbreviations used:

E –energy ,a.u.

ZPVE –zero point vibration energy, a.u.

E0 –ZPVE corrected energy, a.u.

Mode – Mode number

Freq. – Harmonic Frequencies (cm^{-1}),

Mass.- Reduced Masses (a.m.u.),

IR Int. - IR Intensities (km/mol),

HCN

Mode	Freq.	Mass.	IR Int.
1	720.81	1.34	35.574
2	720.81	1.34	35.574
3	2116.51	5.33	0.108
4	3444.62	1.18	62.864

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
   7    -1.12736089   0.00000011   0.00000000
   6     0.03034614  -0.00000024   0.00000000
   1     1.09701474   0.00000012   0.00000000
$end
```

E = -93.294272; E0 = -93.278319; ZPVE = 0.015953 a.u.

CO

Mode	Freq.	Mass.	IR Int.
1	2154.13	13.44	63.439

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
   8     0.56646569   0.00000000   0.00000000
   6    -0.56646569   0.00000000   0.00000000
$end
```

E = -113.179620; E0 = -113.174712; ZPVE = 0.004907 a.u.

HNC

Mode	Freq.	Mass.	IR Int.
1	461.25	1.29	128.488
2	461.25	1.29	128.488
3	2044.23	7.06	57.677
4	3809.12	1.12	239.371

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
   7    -0.05863794  -0.00000001   0.00000000
   6     1.11471726   0.00000001   0.00000000
   1    -1.05607933   0.00000001   0.00000000
$end
```

E = -93.270376; E0 = -93.254940; ZPVE = 0.015437 a.u.

Structure I

Mode	Freq.	Mass.	IR Int.
1	44.42	5.42	14.912
2	44.42	5.42	14.912
3	80.95	10.93	0.465
4	118.94	5.87	10.624
5	118.94	5.87	10.625
6	762.94	1.29	29.264
7	762.94	1.29	29.264
8	2114.47	5.24	6.356
9	2171.72	13.40	59.066
10	3411.29	1.18	172.715

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
  7    0.00000021  -0.00000072  -2.80928401
  6   -0.00000009   0.00000015  -1.65133156
  1   -0.00000033   0.00000094  -0.58221040
  6    0.00000038   0.00000006   1.95594183
  8   -0.00000017  -0.00000043   3.08688414
$end
```

E = -206.477018; E0 = -206.455077; ZPVE = 0.021941 a.u.

Structure II

Mode	Freq.	Mass.	IR Int.
1	33.70	6.84	11.354
2	33.70	6.84	11.354
3	77.70	10.95	0.454
4	85.04	4.64	16.359
5	85.04	4.64	16.360
6	745.96	1.31	31.622
7	745.96	1.31	31.622
8	2116.59	5.31	4.074
9	2146.02	13.43	91.461
10	3434.41	1.18	143.344

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
  7    0.00000025   0.00000039  -2.73830543
  6   -0.00000005  -0.00000007  -1.58046997
  1   -0.00000034  -0.00000046  -0.51295496
  8   -0.00000006  -0.00000023   1.84880594
  6    0.00000019   0.00000038   2.98292445
$end
```

E = -206.476152; E0 = -206.454500; ZPVE = 0.021652 a.u

Structure III

Mode	Freq.	Mass.	IR Int.
1	59.09	6.44	13.504
2	59.14	6.44	13.502
3	108.33	10.90	1.350
4	148.68	9.49	2.511
5	148.68	9.49	2.511
6	598.41	1.15	104.983
7	598.42	1.15	104.984
8	2045.49	6.88	30.028
9	2180.63	13.43	57.541
10	3701.54	1.12	693.036

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
  6    -0.00000000  -0.00000000  -2.66943781
  7    -0.00000000  -0.00000000  -1.49637757
  1    -0.00000000  -0.00000000  -0.49320704
  6     0.00000000   0.00000000   1.76452810
  8     0.00000000   0.00000000   2.89449433
$end
```

E = -206.455196; E0 = -206.433215; ZPVE = 0.021981 a.u.

Structure IV

Mode	Freq.	Mass.	IR Int.
1	41.52	7.85	10.131
2	41.52	7.85	10.131
3	96.39	10.94	1.156
4	100.26	6.31	11.221
5	100.26	6.31	11.221
6	534.56	1.20	117.234
7	534.56	1.20	117.234
8	2048.38	7.03	40.495
9	2144.08	13.43	105.010
10	3774.12	1.12	532.606

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
   6    0.00000019  -0.00000007  -2.62507435
   7   -0.00000007   0.00000003  -1.45210057
   1   -0.00000022   0.00000004  -0.45256008
   8   -0.00000001   0.00000011   1.69763678
   6    0.00000011  -0.00000011   2.83209823
$end
```

E = -206.453313; E0 = -206.431862; ZPVE = 0.021450 a.u.

Structure V

Mode	Freq.	Mass.	IR Int.
1	11.45	4.65	28.078
2	23.54	4.44	31.498
3	46.76	11.49	0.133
4	80.84	10.18	4.814
5	462.87	1.29	126.125
6	464.21	1.29	126.367
7	2046.82	7.06	62.738
8	2154.00	13.44	59.784
9	3807.99	1.12	254.525

Atomic Coordinates:

```
$molecule
 cartesian
 set=L2a_3
   6    0.23219830   0.78029973  -0.00000191
   7    0.03849724   1.93719486   0.00000193
   1   -0.12851993   2.92064101  -0.00000039
   6   -0.61216441  -2.65125081  -0.00000014
   8    0.46998881  -2.98688469   0.00000050
$end
```

E = -206.451196; E0 = -206.430468; ZPVE = 0.020728 a.u.

Calculated harmonic vibrational frequencies (cm^{-1}), reduced masses, IR intensities (km/mol) for DCN, DNC, DCN…CO and DNC…CO complexes. The structures numbers for the deuterated complexes correspond to those for HCN…CO and HNC…CO

DCN

Mode	Freq.	Mass.	IR Int.
1	574.67	3.13	10.648
2	574.67	3.13	10.648
3	1942.40	3.91	3.428
4	2704.06	3.47	32.273

DNC

Mode	Freq.	Mass.	IR Int.
1	362.53	2.98	55.122
2	362.53	2.98	55.122
3	1952.70	5.68	28.085
4	2872.85	2.72	189.281

Structure I (OC...DCN)

Mode	Freq.	Mass.	IR Int.
1	42.00	42.00	13.823
2	42.00	42.00	13.823
3	80.21	11.22	0.458
4	114.08	7.28	7.562
5	114.08	7.28	7.562
6	601.13	2.99	8.762
7	601.13	2.99	8.762
8	1934.94	3.82	21.105
9	21.105	13.43	59.680
10	2685.56	3.54	74.126

Structure II (CO...DCN)

Mode	Freq.	Mass.	IR Int.
1	32.45	7.32	11.081
2	32.45	7.32	11.081
3	77.00	11.23	0.447
4	79.70	6.02	11.832
5	79.70	6.02	11.832
6	590.42	3.04	9.473
7	590.42	3.04	9.473
8	1940.99	3.88	15.366
9	2146.01	13.44	92.017
10	2697.72	3.49	63.121

Structure III (OC...DNC)

Mode	Freq.	Mass.	IR Int.
1	56.71	7.04	12.821
2	56.76	7.04	12.819
3	107.32	11.18	1.331
4	146.59	10.05	2.136
5	146.60	10.05	2.136
6	451.85	2.55	47.683
7	451.86	2.55	47.684
8	1946.15	5.37	2.967
9	2180.63	13.43	57.702
10	2803.16	2.79	443.879

Structure IV (CO...DNC)

Mode	Freq.	Mass.	IR Int.
1	40.39	8.24	10.023
2	40.39	8.24	10.023
3	95.51	11.23	1.138
4	96.13	7.32	9.338
5	96.13	7.32	9.338
6	409.43	2.70	52.102
7	409.43	2.70	52.102
8	1954.77	5.59	9.682
9	2144.06	13.44	107.235
10	2848.90	2.74	354.696

Structure V (DNC...CO)

Mode	Freq.	Mass.	IR Int.
1	10.73	5.69	23.756
2	21.96	5.54	26.211
3	46.37	11.79	0.148
4	80.14	10.95	3.740
5	363.96	2.99	54.190
6	364.86	2.98	54.521
7	1954.94	5.67	30.517
8	2154.00	13.44	59.794
9	2872.37	2.72	202.571