Matrix isolation FTIR and theoretical study of weakly bound complexes of isocyanic acid with nitrogen

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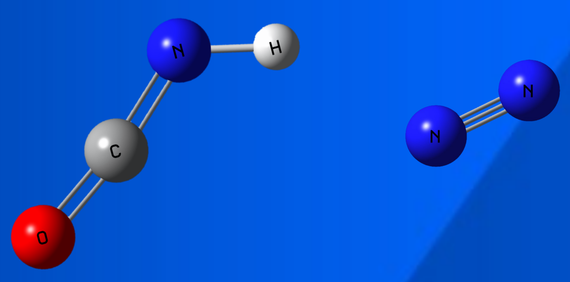


Objectives

Non-covalent interactions are often involved in a variety of processes in biology and chemistry such as protein folding, DNA structure or molecular crystals formation. Weak molecular interactions have also an important contribution to chemical and physical processes taking place in the Earth's atmosphere.

Isocyanic acid HNCO is an atmospheric pollutant that is emitted into the air from primary and secondary processes. The preliminary sources of this toxic compound are various combustion processes such as fossil fuel combustion and biomass burning.

Nitrogen, being the most abundant component of the Earth's atmosphere is considered to be chemically inert. However, it has an electric quadrupole moment and was found to interact strongly with various molecules.

The infrared spectroscopy is the most commonly used to study various types of interactions, including van der Waals and hydrogen bonding. Among the most often studied weakly bound aggregates are those containing N_2 molecules. Therefore, our research is focused on complexes formed between isocyanic acid and N_2 molecules (**ON**).

Experimental Details

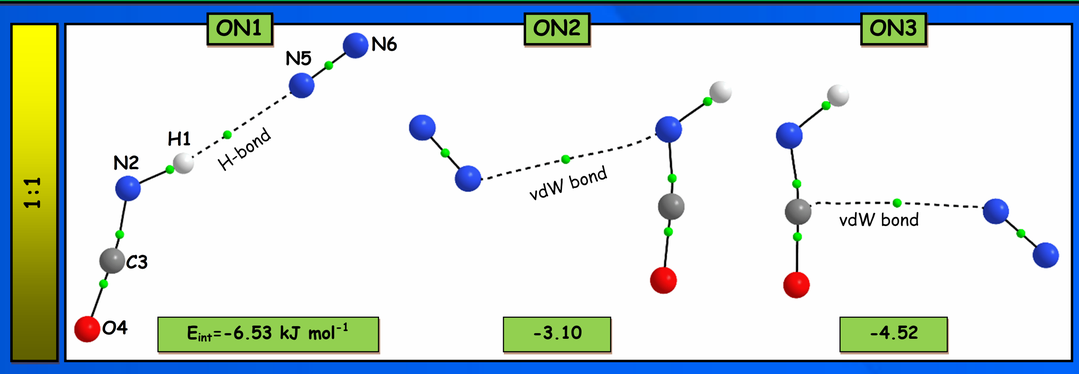
Quantum-chemical calculations

- All calculations performed with the Gaussian 16 program package. Methods: MP2 and DFT [B3LYPD3, B2PLYPD3] with the 6-311++G(3df,3pd) basis set.
- Topological analysis of the electron density (AIM) calculated at MP2/6-311++G(3df,3pd) level.

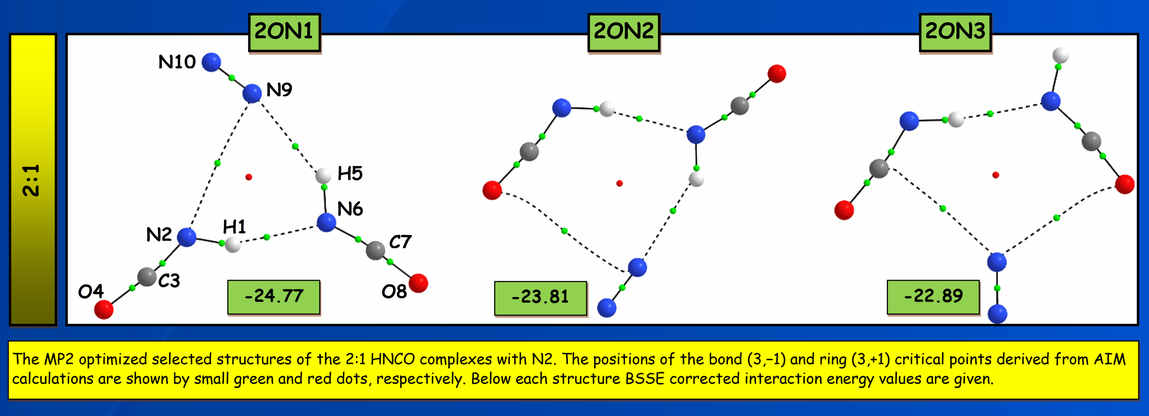
FTIR matrix isolation studies

- HNCO synthesis: $(HNCO)_3$ heated up to ca. 450°C in the oven.
- The gaseous mixtures were prepared by mixing HNCO and N_2 with argon in the same bulb in a vacuum system.
- FTIR spectrometer Bruker IFS 66 equipped with a liquid N_2 cooled MCT detector with 0.5 cm^{-1} resolution.

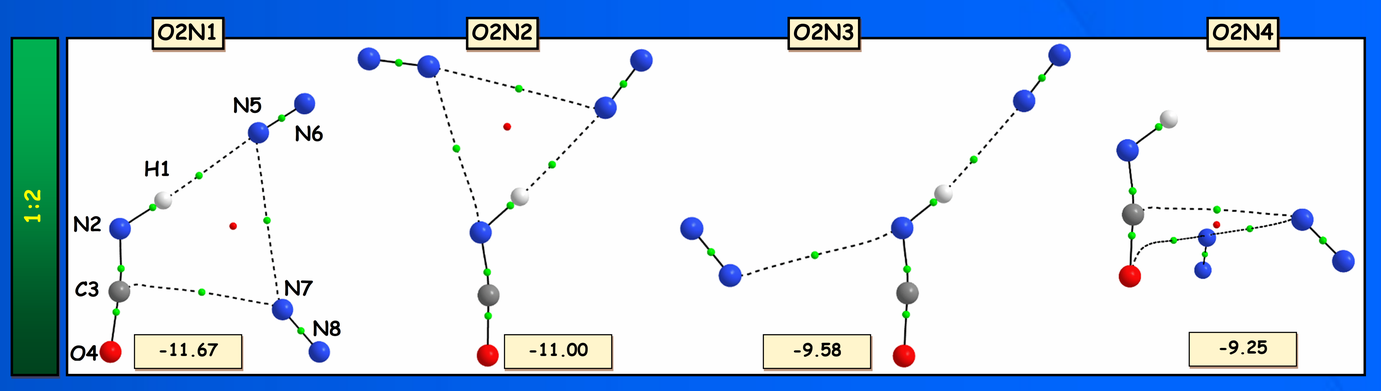
Calculated HNCO···N_2 complexes (MP2)



The MP2 optimized structures of the 1:1 HNCO···N_2 complexes. The positions of the bond (3,–1) critical points derived from AIM calculations are shown by small green dots. Below each structure BSSE corrected interaction energy values are given.

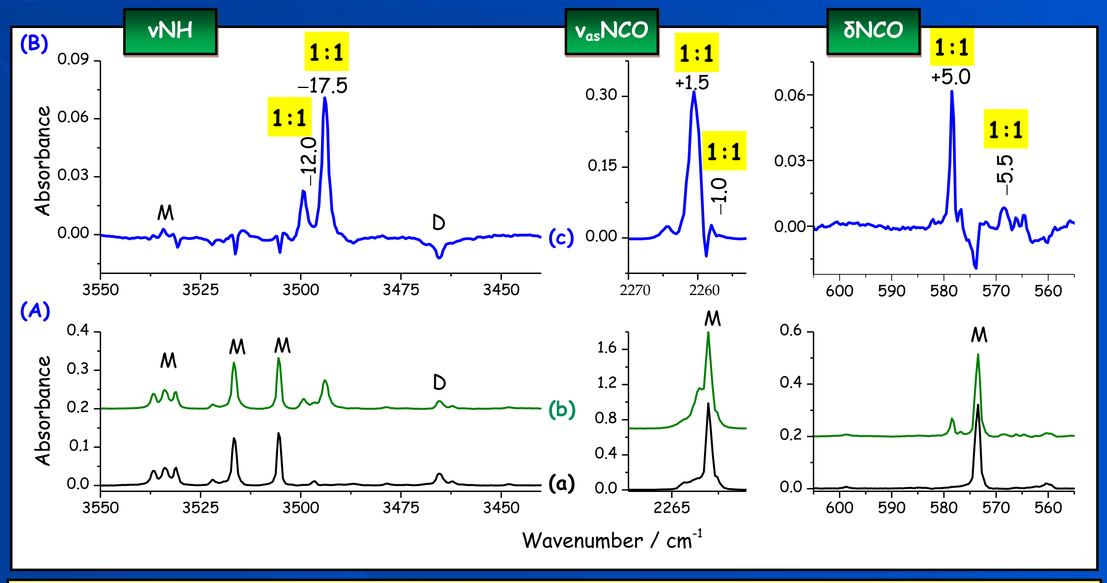


The MP2 optimized selected structures of the 2:1 HNCO complexes with N2. The positions of the bond (3,–1) and ring (3,+1) critical points derived from AIM calculations are shown by small green and red dots, respectively. Below each structure BSSE corrected interaction energy values are given.



The MP2 optimized structures of the 1:2 HNCO complexes with N2. The positions of the bond (3,–1) and ring (3,+1) critical points derived from AIM calculations are shown by small green and red dots, respectively. Below each structure BSSE corrected interaction energy values are given.

Infrared spectra of HNCO···N_2 in Ar matrix



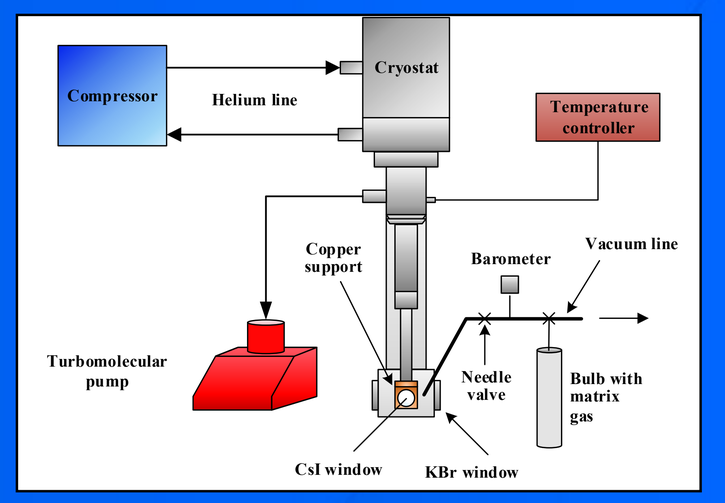
(A) The vNH, ν_{as}NCO and δNCO regions in the spectra of matrices: HNCO/Ar = 1/6000 (a), HNCO/N2/Ar = 1/4/5600 (b); (B) the difference spectrum (c) obtained by subtracting the spectrum (a) from the spectrum (b) (blue trace). Letters M and D denote the HNCO monomer and dimer bands, respectively.

Calculated harmonic (unscaled) wavenumber shifts Δν (cm^{-1}) and intensities I (km mol^{-1}) of the HNCO complexes with N_2 of the 1:1, 1:2 and 2:1 stoichiometry.

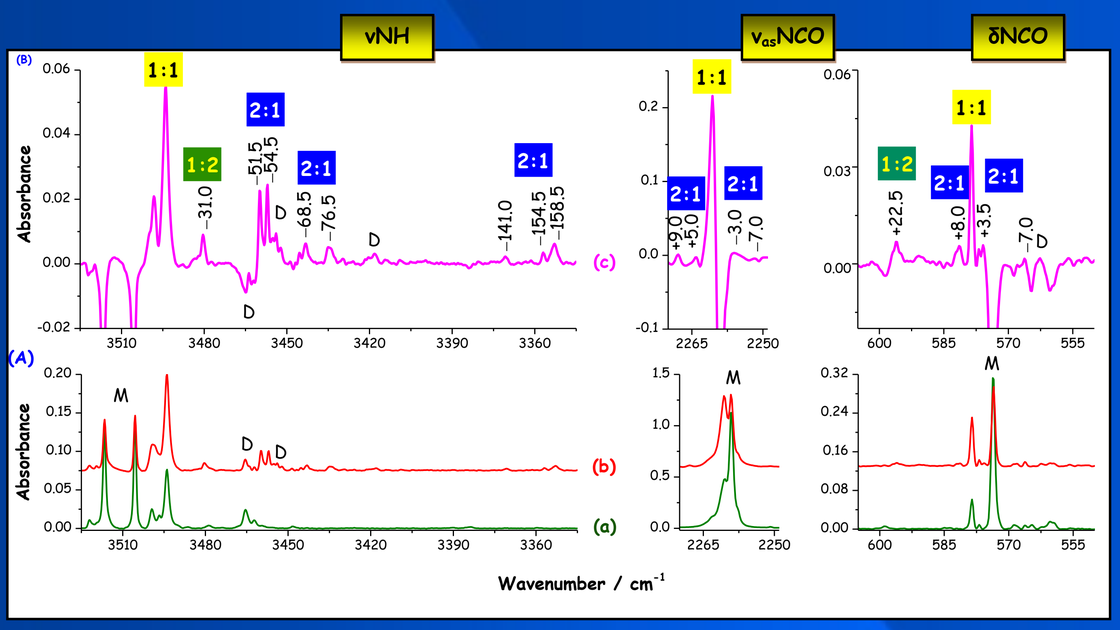
1:1	νNH		ν_{as}NCO		δNCO	
	Δν	I	Δν	I	Δν	I
MP2						
ON1	–25	405	+2	706	+21	76
ON2	–6	169	–2	631	–3	83
ON3	–9	163	–2	636	–6	97
B3LYPD3						
ON1	–23	392	+2	798	+20	67
ON2	–4	155	0	712	–3	75
1:2	**νNH**		**ν_{as}NCO**		**δNCO**	
	Δν	I	Δν	I	Δν	I
MP2						
O2N1	–35	380	0	662	+16	73
O2N2	–33	398	0	740	+22	81
O2N3	–31	397	0	661	+19	69
O2N4	–11	159	–1	604	–6	96
B3LYPD3						
O2N1	–29	364	0	748	+16	66
O2N2	–23	345	0	837	+16	78
O2N3	–26	386	+1	751	+17	62

2:1	νNH				ν_{as}NCO				δNCO			
	Δν	I	Δν	I	Δν	I	Δν	I	Δν	I	Δν	I
MP2												
2ON1	–64	361	–145	769	+5	486	–6	1090	+66	0	+4	187
2ON2	–61	340	–150	770	+5	21	–7	1553	+63	37	+11	26
2ON3	–39	177	–153	784	+5	697	–9	650	+61	22	–5	72
B3LYPD3												
2ON1	–60	344	–170	830	+9	635	–7	1145	+64	2	+10	137
2ON2	–53	315	–174	810	+8	43	–8	1738	+65	3	+14	22
2ON3	–34	163	–171	808	+9	799	–9	734	+61	4	–1	60

Calculated wavenumbers (intensities) of the HNCO monomer are equal to: 3681 (159), 2330 (757), 576 (83) at B3LYPD3 and 3729 (175), 2337 (675), 571 (94) at MP2.



Scheme of matrix isolation setup.



(A) The vNH, ν_{as}NCO and δNCO regions in the spectra of matrices: HNCO/N2/Ar = 1/4/5600 (a), and matrix (a) after 10 min at 33 K/10 K (b); (B) the difference spectrum (c) obtained by subtracting the spectrum (a) from the spectrum (b) (pink trace). Letters M and D denote the HNCO monomer and dimer bands, respectively.

Concluding Remarks

- For the first time, theoretical and FTIR matrix isolation studies of weakly bound complexes formed between isocyanic acid and nitrogen (ON) were performed.
- The calculations revealed three different HNCO···N_2 structures of the 1:1 stoichiometry. One of them involves a weak N–H···N hydrogen bond whereas two other geometries are stabilized by van der Waals interactions of N···N or C···N types.
- Four structures of 1:2 and ten of 2:1 complexes were optimized. Similarly as for 1:1 species, for 1:2 and 2:1 stoichiometry the N–H···N(O) hydrogen bond and different types of vdW interaction are responsible for the stability of these aggregates.
- Analysis of the HNCO/N_2/Ar spectra indicates that the three 1:1 structure are present after deposition of the matrices.
- Annealing at 33 K leads to the formation of higher aggregates HNCO with nitrogen of the 1:2 and 2:1 stoichiometry.
- Both experimental and computational studies indicate that HNCO and nitrogen molecules can engage into specific intermolecular interactions, leading to notable vibrational spectral changes.

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