Matrix isolation IR spectra of 1:1 hydrogen-bonded complexes of [H,C,N] and [H,C,N,O]

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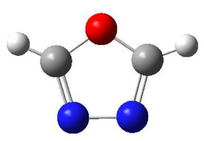
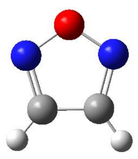
Introduction

Pseudohalogens are among the most abundant molecules in space. Several representatives of these compounds have already been identified in the interstellar medium, including HCN, HNC, HCNO, HNCO and HOCN. It is expected that their H-bonded complexes are present on the surface of interstellar grains, and the H-bonding interaction may assist the formation of larger organic molecules. The goal of the present study was to prepare and spectroscopically characterize these complexes by the help of quantum chemical computations. The complexes were prepared *in situ* in Ar matrix from 1,3,4- and 1,2,5-oxadiazoles by laser photolysis at 220 nm and, using a H-lamp, by secondary photolysis at 121.6 nm.

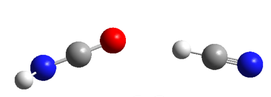


1,3,4-oxadiazole

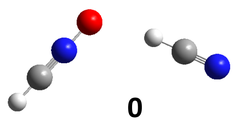


1,2,5-oxadiazole

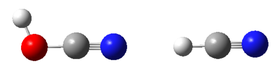
Computed structures and relative energies[a] (in kJ mol^{-1}) of [H,N,C,O]···HCN and HCN···[H,N,C,O] complexes



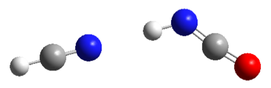
6.3
HNCO···HCN



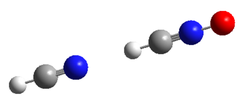
0
HCNO···HCN



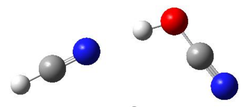
17.5
HOCN···HCN



0
HCN···HNCO



0.7
HCN···HCNO



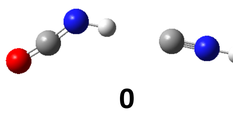
0
HCN···HOCN

[a]The lower energy complex from each pair is the reference.

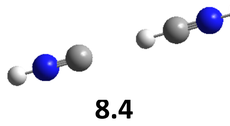
Methods

- Sample (precursors): prepared by standard organic synthesis methods; purity was checked by NMR, IR spectroscopies and MS spectrometry
- 1:1000 – 1:2000 sample: Ar premix was prepared and deposited at 12 K onto a CsI plate
- Spectra were recorded by a Bruker IFS 55 spectrometer, using an MCT detector at 1 cm^{-1} resolution
- Laser irradiation: 220 nm (also 213 and 235 nm), Spectra Physics Quanta Ray LAB150 Nd:YAG + GWU/Spectra-Physics VersaScan MB 240
- H-lamp: Hydrogen-flow MW discharge
- Computations: B3LYP-D3/cc-pVTZ
- Correction of the computed vibrational frequencies: scaling (single factor) and shifting the computed frequency of the complex by the „error" (computed – observed in Ar matrix) of the computed frequency of the corresponding vibrational mode of the monomer
- Assignments (<u>still preliminary</u>) are based on: computations, kinetic curves obtained during the photolysis, correlation of peaks upon photolysis at different wavelengths, annealing experiments

Computed structures and relative energies[a] (in kJ mol^{-1}) of [H,N,C,O]···HNC and HNC···[H,N,C,O] complexes



2.4
HNCO···HNC



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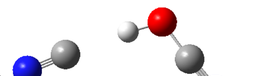
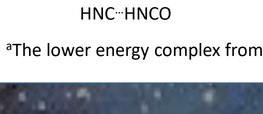
HCNO···HNC

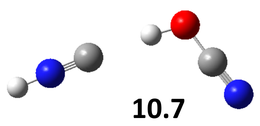


0
HOCN···HNC



0
HNC···HNCO

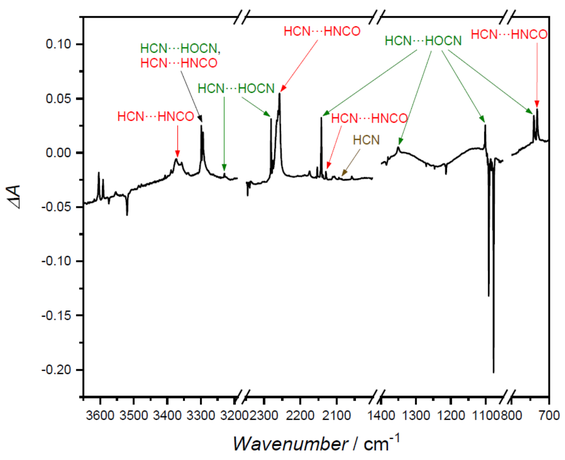
8.4
HNC···HCNO

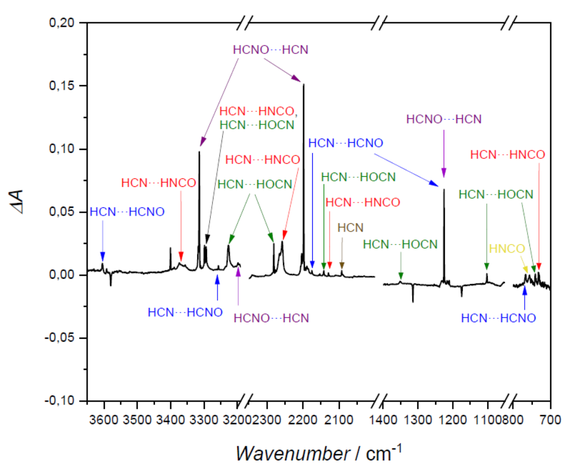


10.7
HNC···HOCN

[a]The lower energy complex from each pair is the reference.

Difference spectra of 1,3,4- and 1,2,5-oxadiazoles obtained upon 220 nm laser photolysis





Examples of tentative assignments[a]

HCN···HNCO

Computed			Experimental	
$\tilde{\nu}_{comp}$ / cm^{-1}	$\tilde{\nu}_{corr}$ / cm^{-1}	I / km · mol^{-1}	$\tilde{\nu}$ / cm^{-1}	I
631	630	20.9		
654		0.02		
771	731	34.1	732	s
844		251.8		
1339		10.3		
2219	2124	7.1	2130	w
2340	2262	737.2	2257	s
3438	3294	121.0	3294	s
3528	3362	901.2	3357	s

HCNO···HCN

Computed			Experimental	
$\tilde{\nu}_{comp}$ / cm^{-1}	$\tilde{\nu}_{corr}$ / cm^{-1}	I / km · mol^{-1}	$\tilde{\nu}$ / cm^{-1}	I
557	555	2.3		
562	561	1.9		
825	784	30.0		
848	806	53.0		
1272	1225	165.3	1225	s
2190	2096	43.7	2093	w
2328	2197	384.8	2198	s
3347	3204	362.7	3198	br
3490	3305	273.6	3314	s

HNCO···HNC

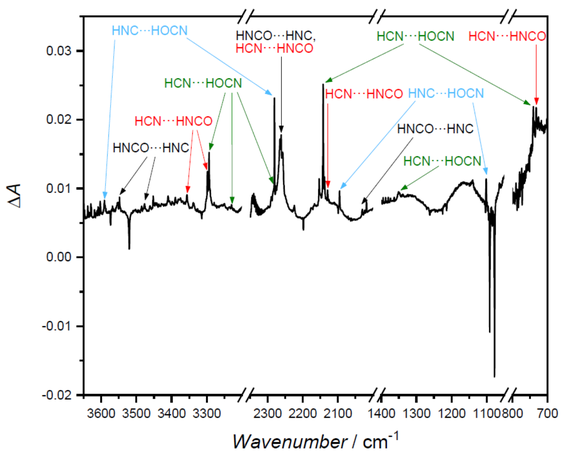
Computed			Experimental	
$\tilde{\nu}_{comp}$ / cm^{-1}	$\tilde{\nu}_{corr}$ / cm^{-1}	I / km · mol^{-1}	$\tilde{\nu}$ / cm^{-1}	I
622	621	67.8		
626	624	115.1		
644		90.1		
744		211.0		
1345		9.1		
2112	2037	18.4	2031	w
2346	2268	873.2	2258	s
3660	3492	1031.6	3470	br
3696	3527	137.2	3548	w

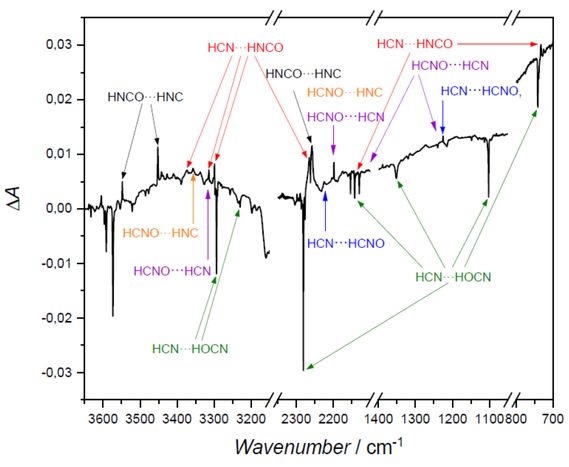
HCN···HOCN

Computed			Experimental	
$\tilde{\nu}_{comp}$ / cm^{-1}	$\tilde{\nu}_{corr}$ / cm^{-1}	I / km · mol^{-1}	$\tilde{\nu}$ / cm^{-1}	I
780	739	34.4	741	m
1122	1105	61.0	1102	m
1363	1340	77.0	1351	w
2235	2140	16.3	2142	m
2368	2276	202.6	2276	s
3373	3229	1582.8	3227	br
3438	3294	19.0	3293	s

[a]Low frequency vibrations are not shown.

Difference spectra obtained upon subsequent irradiation by H-lamp (121.6 nm)





Conclusions

- The major product of the 220 nm photolysis of 1,2,5-oxadiazole is the HCNO···HCN complex. HCN···HNCO and HCN···HOCN were observed as byproducts (likely formed upon the photoisomerization of HCNO···HCN).
- In the case of the 220 nm photolysis of 1,3,4-oxadiazole HCN···HNCO and HCN···HOCN were obtained.
- 121.6 nm photolysis resulted in the isomerisation of HCN to HNC, and HNCO···HNC, HCNO···HNC, and HNC···HOCN were formed.

Acknowledgements

Győző Lajgút (synthesis), Lendület program of the Hungarian Academy of Sciences and ELTE Excellence Program (1783-3/2018/FEKUTSTRAT) supported by the Hungarian Ministry of Human Capacities (EMMI) for financial support