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First infrared spectra of the acrylonitrile-water hydrogen-bonded complexes isolated in solid neon

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The nitrile molecules have been detected in a variety of interstellar environnements and these molecules are interest in astrochemistry. The experimental study of the complexation of acrylonitrile molecule (AN) with water has been undertaken from a vibrational point of view in solid neon at 3 K from 80 to 6000 cm^{-1} using Fourier transform infrared spectroscopy. With the help of theoretical results we have identified several vibrational transitions for AN-H_2O and AN-$(H_2O)_2$ complexes. For the AN-H_2O complex, in which the two submolecules interacting through hydrogen bonding, the infrared spectral changes (frequencies as well as intensities) indicate that the water plays the role of the proton donor. We highlight the presence of three isomers for the AN-H_2O complex and two isomers for the AN-$(H_2O)_2$ complex. Theoretical calculations at the MP2/AVTZ level have been performed to obtain their equilibrium geometries and vibrational spectra at the harmonic level and comparison with experimental data allows us to give structures of these complexes.

Advantages of our matrix isolation apparatus coupled with FTIR

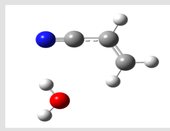
Absorption spectra collected on the same sample from the Far IR (intermolecular region) to Near IR (combinations and overtones region) from 80 to 6000 cm^{-1} with a Bruker 120 FTIR spectrometer (InSb or MCT or bolometer detectors).

MP2/AVTZ calculations for energy, geometry and frequencies

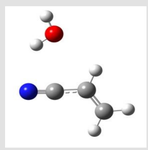
complexes structures with D_0(kcal/mol)

1:1

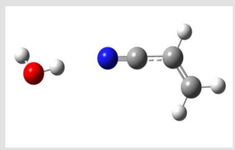
AW1 4.4



AW2 3.7



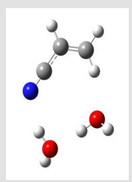
AW3 3.7



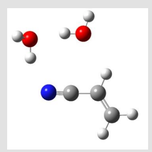
AW1 is the isomer observed in gas phase by millimeter spectroscopy[1]

1:2

ADW 8.3

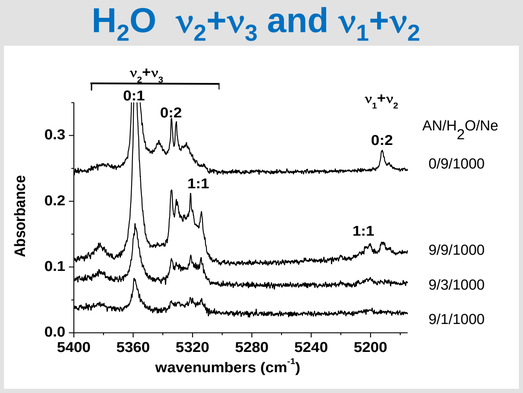


ADW2 8.2

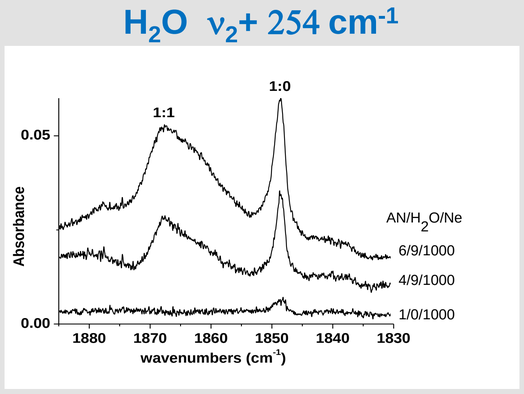


Infrared spectra in the acrylonitrile and water regions

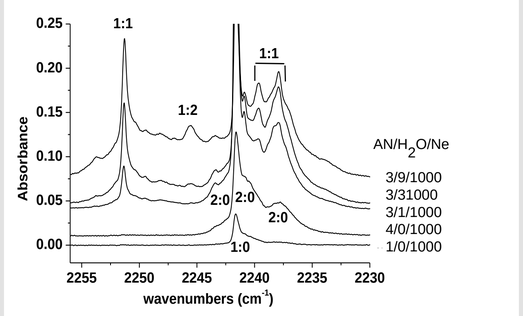
H_2O $\nu_2+\nu_3$ and $\nu_1+\nu_2$



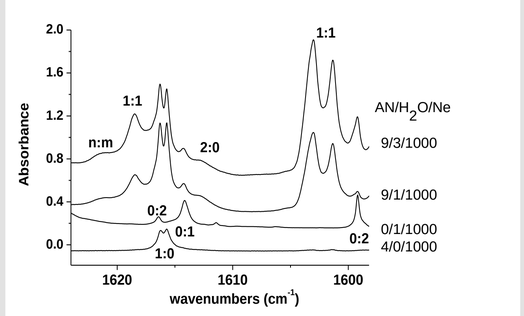
H_2O ν_2+ 254 cm^{-1}



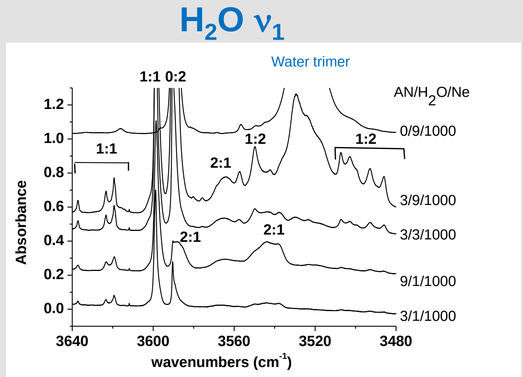
ν_{CN}



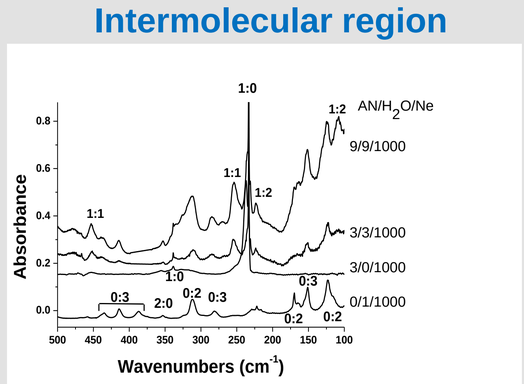
H_2O ν_2



H_2O ν_1



Intermolecular region



Comparison of frequencies (cm^{-1}) and shifts ($\Delta\nu=\nu_{mono}-\nu_{complex}$) for the 1:1 complex

	Calculated						Exp		Isomer
	AW1		AW2		AW3				
	ω	Δ	ω	Δ	ω	Δ	ν	Δ	
H_2O									
ν_3	3918	30	3925	23	3917	31	3740	20	AW2
							3736	24	AW2
							3731	29	AW1
ν_1	3771	51	3791	31	3743	89	3599	67	AW3
							3621	43	AW1
							3637	28	AW2
ν_2	1632	-8	1629	-5	1652	-28	1601	-6	AW1 or 2
							1603	-8	AW1 or 2
							1618	-23	AW3
Acrylonitrile									
ν_4	2177	2	2176	3	2194	-15	2251	-10	AW3
							2240	2	AW1 or 2
							2238	4	AW1 or 2
ν_8	1111	-5	1108	-2	1108	-2	1095	-2	AW2 or 3
							1099	-6	AW1
ν_{13}	990	-17	975	-2	980	-7	960	-6	AW3
							969	-15	AW1
ν_{14}	574	-16	561	-3	563	-5	691	-6	AW3
ν_{11}	235	-9	226	0	228	-2	231	2	AW2
Inter	367		303		514		453		AW3
	291		262		302		254		AW1-2-3

Identification of **three isomers for 1:1 complex**: observation of **three bands for the ν_1 water mode** separated by 12-25 cm^{-1}

Comparison with other nitrile-water complexes

	HCN	$C_6H_5(CH_2)_2CN$	CH_2=CHCN	C_6H_5CN	CH_3CN
H_2O ν_1 red-shift	44	57	67	66	99
D_0 (kcal/mol)	3.0	4.2	3.7	4.4	4.5
	Solid Ar	gas	Solid Ne	Solid Ar	Solid Ar
ν_{CN} blue-shift	19	-	10	10	8
Ref	2,3	4	This work	5	6

Comparison of frequencies and shifts for the 1:2 complex

	Calculated				Exp		Isomer
	ADW1		ADW2				
Modes	ω	Δ	ω	Δ	ν	Δ	
H_2O							
ν_1 PA	3679	135	3696	118	3507	154	ADW1
					3550	111	ADW2
ν_1 PD	3598	121	3609	110	3486	105	ADW1
					3493	98	ADW2
Acrylonitrile							
ν_4	2189	-10	2183	-4	2246	-4	ADW2
ν_{12}	1064	-29	1026	-21	998	-27	ADW1
ν_{14}	581	-23	575	-17	694	-11	ADW2
Inter	118		108		108		ADW1 or 2
	138		135		108		ADW1 or 2
	215		210		223		ADW1 or 2

PA: proton acceptor and PD: proton donor for H_2O dimer

Identification of **two isomers for 1:2 complex**: observation of **two bands for the ν_1 water mode**

References

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[4] P. A. Robertson, I. A. Lobo, D.J.D. Wilson, E. G. Robertson, Nitriles as directionally tolerant hydrogen bond acceptors: IR-UV ion depletion spectroscopy of benzenepropanenitrile and its hydrate clusters; Chem. Phys. Lett. 660 (2016) 221-227.

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[6] R. Gopi, N. Ramanathan, K. Sundararajan, Acetonitrile–water hydrogen-bonded interaction: Matrix-isolation infrared and ab initio computation; J. Mol. Struct. 1094 (2015) 118-129.