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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 environments 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  $\text{cm}^{-1}$  using Fourier transform infrared spectroscopy. With the help of theoretical results we have identified several vibrational transitions for AN-H<sub>2</sub>O and AN-(H<sub>2</sub>O)<sub>2</sub> complexes. For the AN-H<sub>2</sub>O 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<sub>2</sub>O complex and two isomers for the AN-(H<sub>2</sub>O)<sub>2</sub> 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.

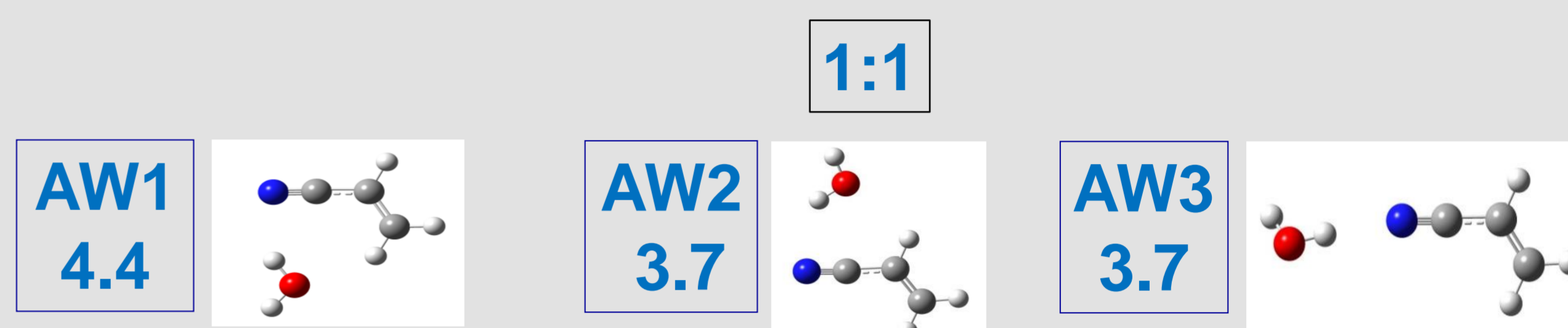


## Advantages of our matrix isolation apparatus coupled with FTIR

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

## MP2/AVTZ calculations for energy, geometry and frequencies

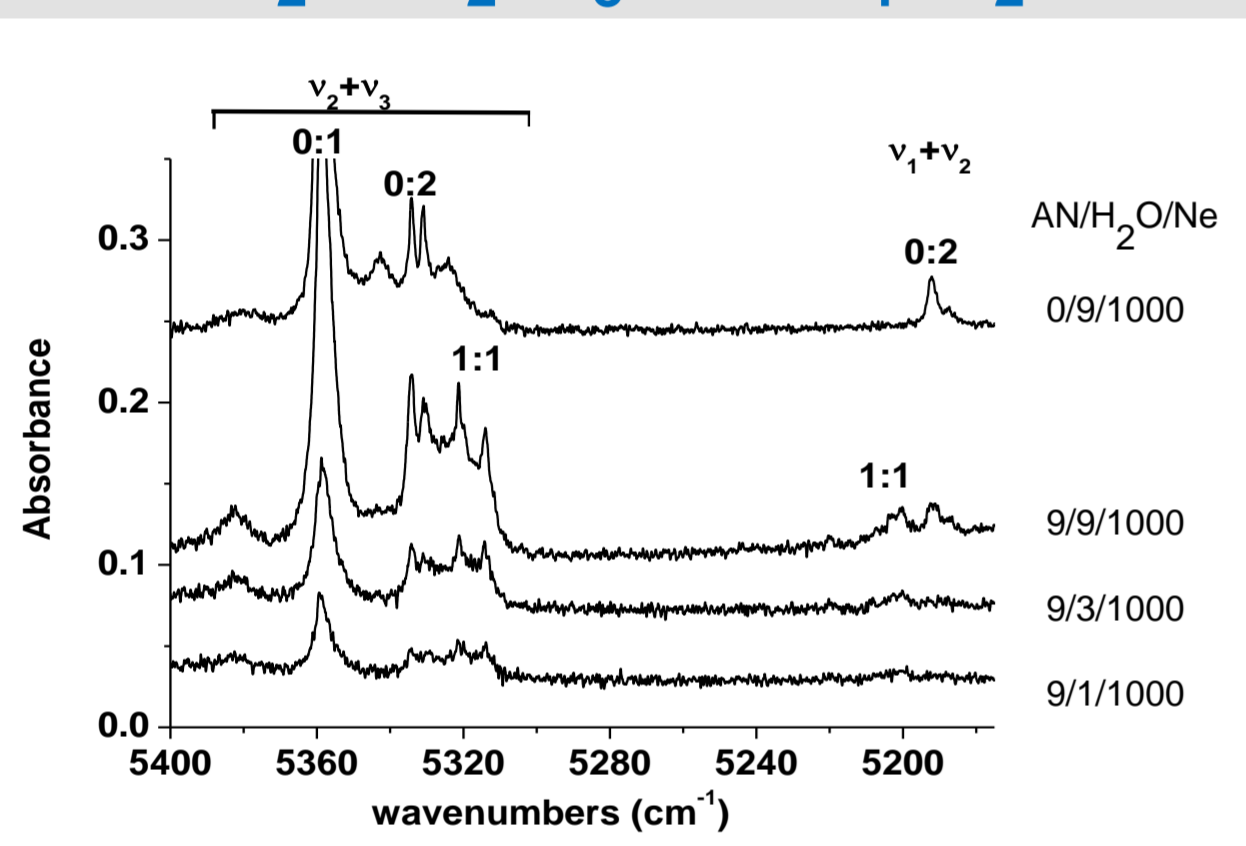
### complexes structures with $D_0(\text{kcal/mol})$



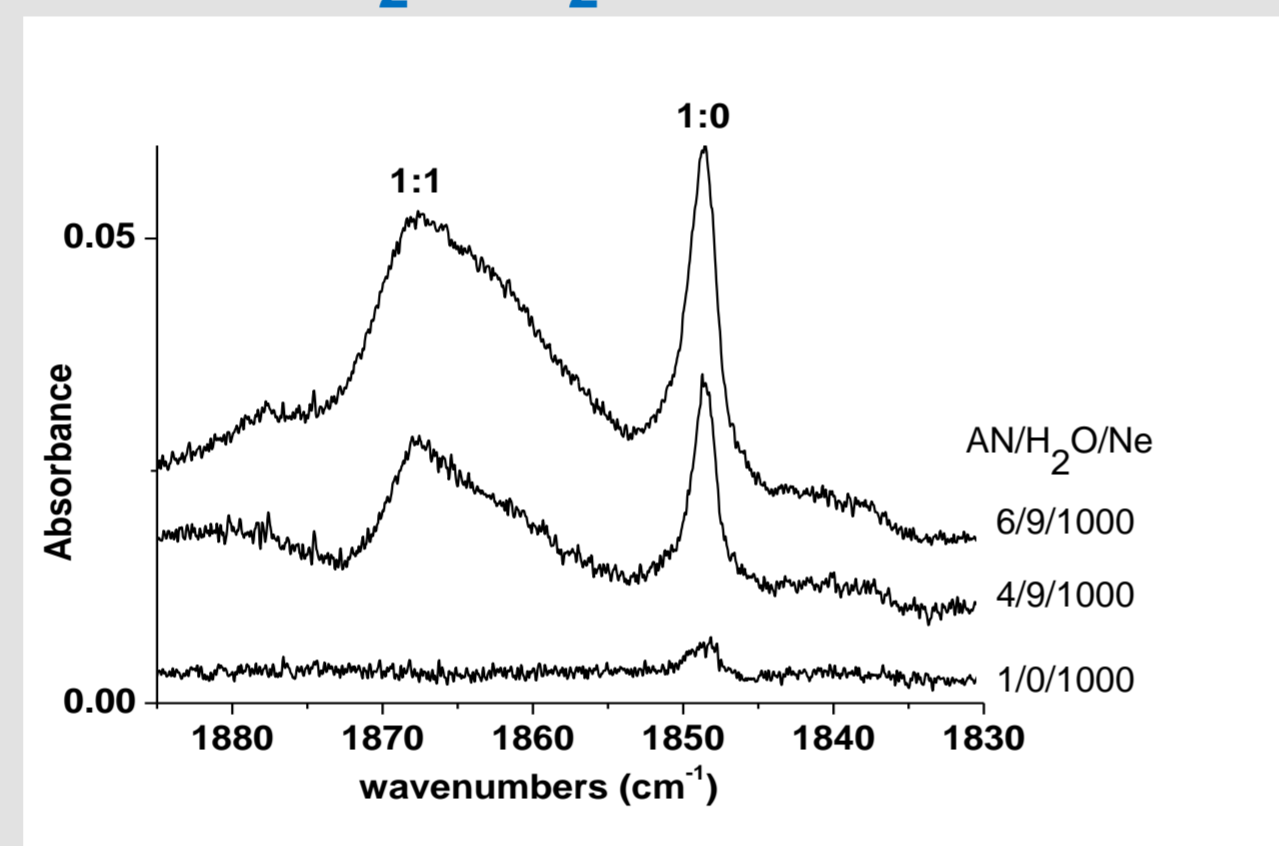
AW1 is the isomer observed in gas phase by millimeter spectroscopy<sup>1</sup>

## Infrared spectra in the acrylonitrile and water regions

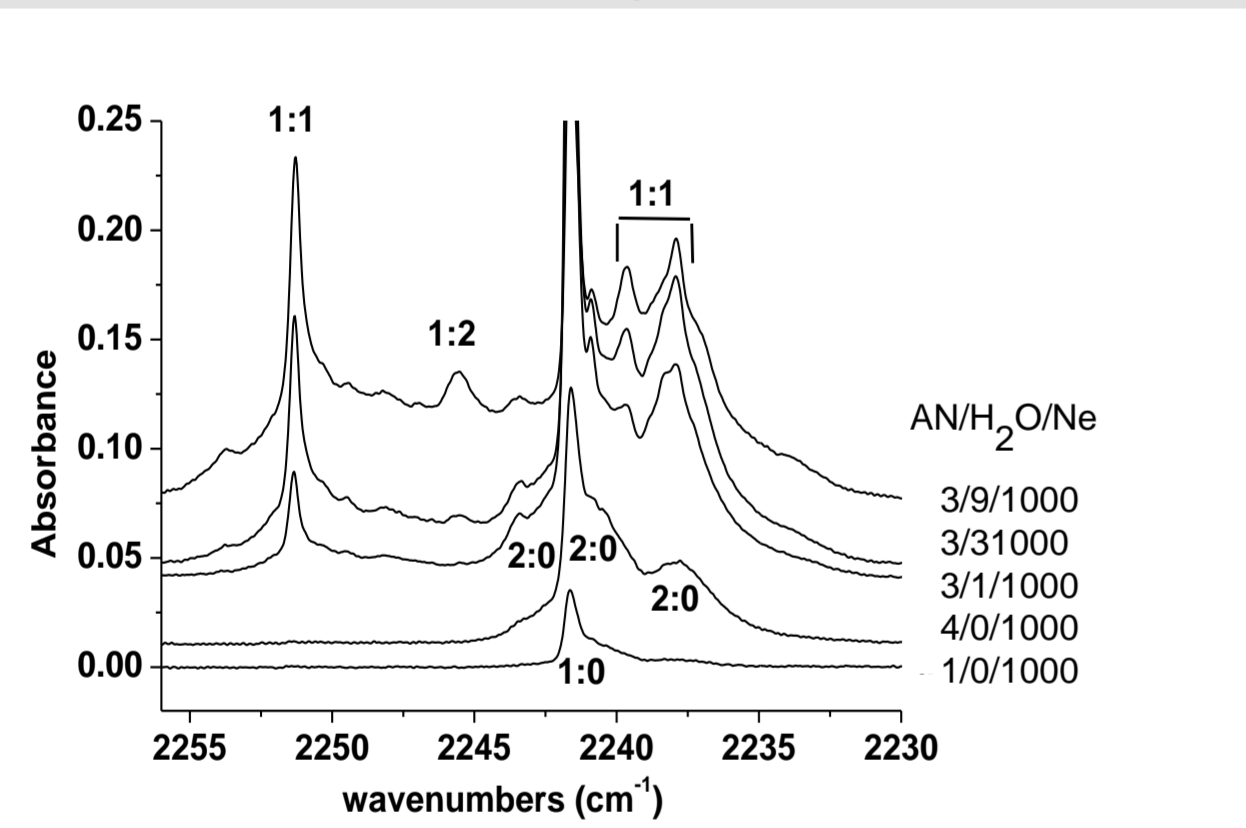
### H<sub>2</sub>O $\nu_2+\nu_3$ and $\nu_1+\nu_2$



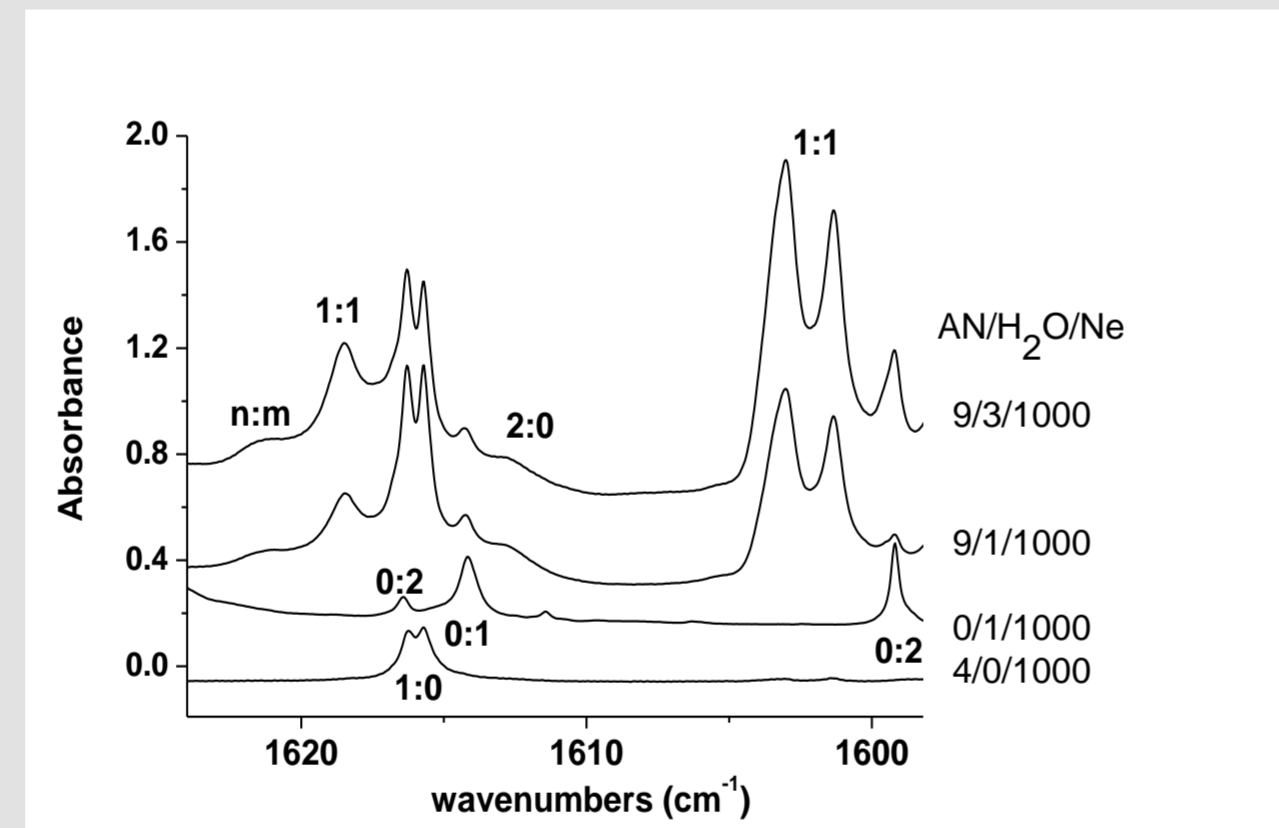
### H<sub>2</sub>O $\nu_2 + 254 \text{ cm}^{-1}$



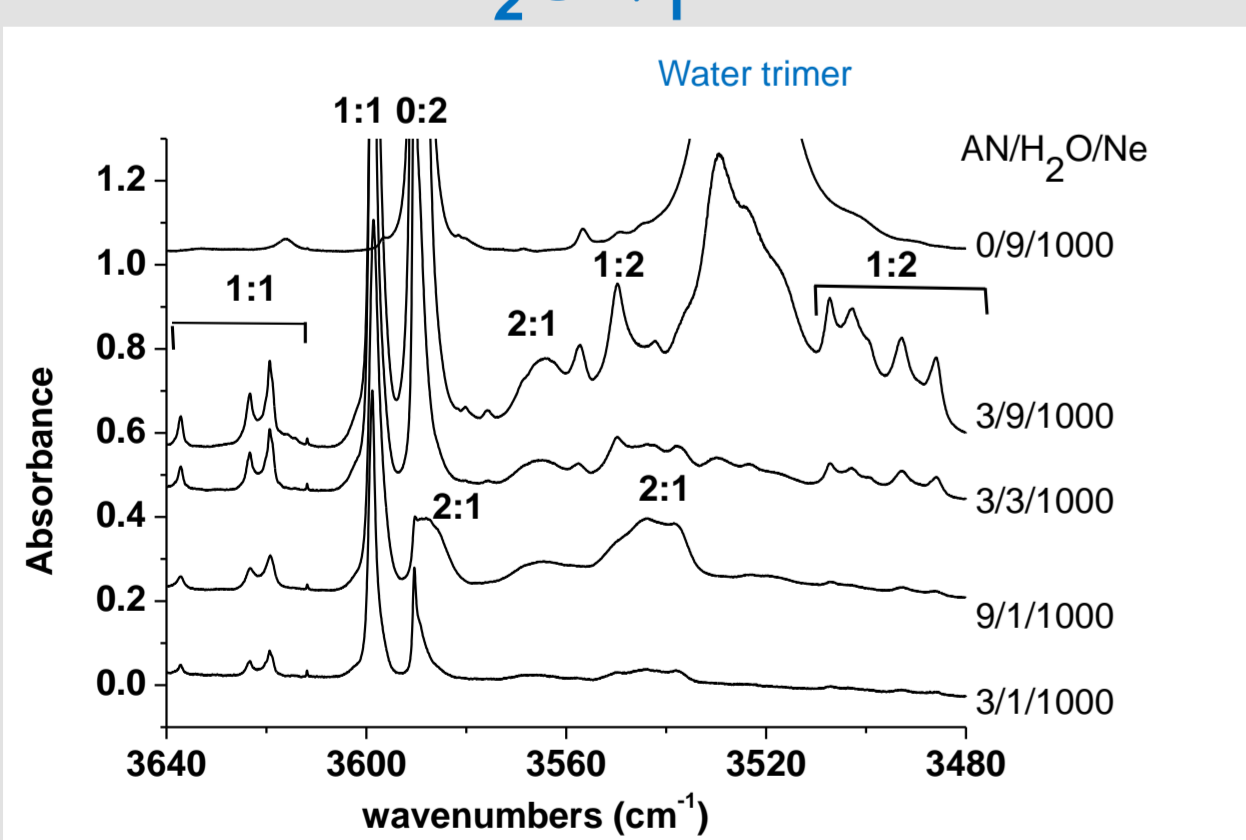
### $\nu_{\text{CN}}$



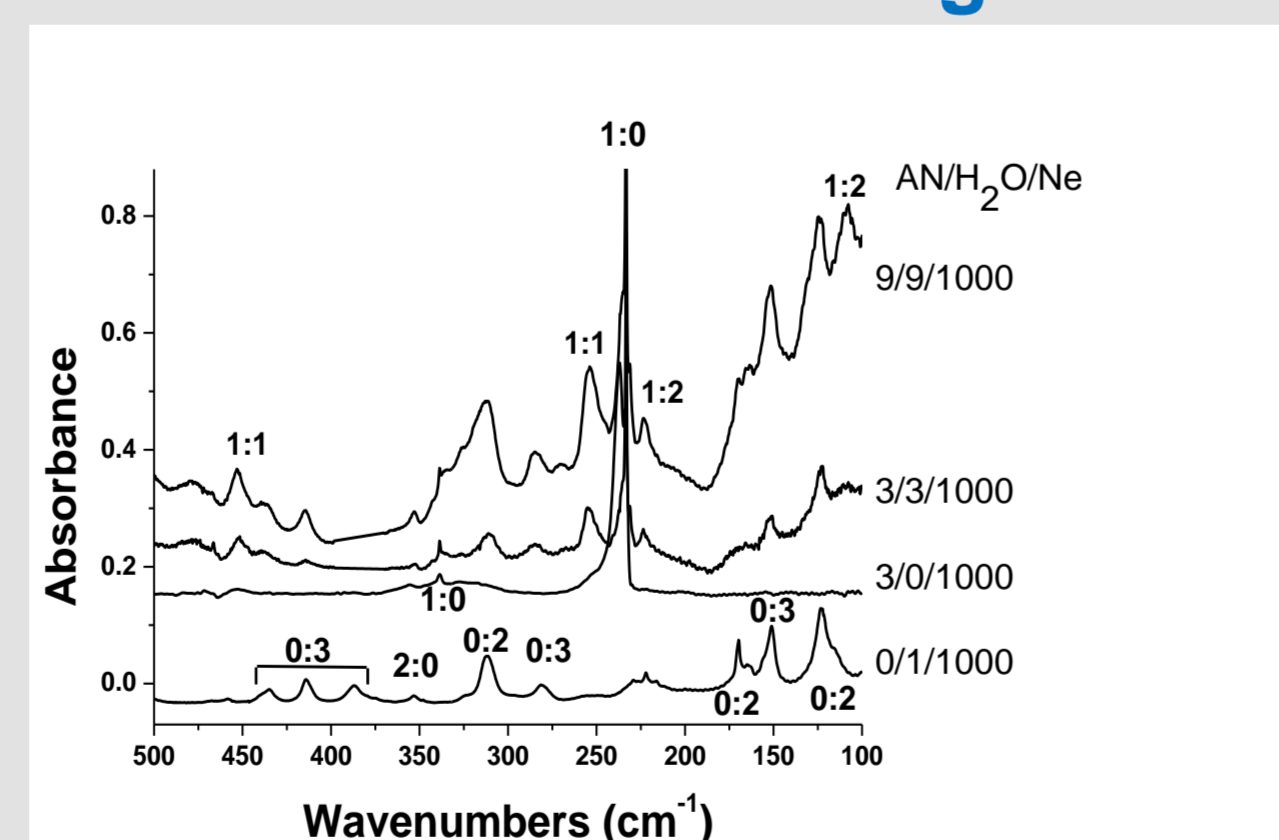
### H<sub>2</sub>O $\nu_2$



### H<sub>2</sub>O $\nu_1$



### Intermolecular region



## Comparison with other nitrile-water complexes

	HCN	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CN	CH <sub>2</sub> =CHCN	C <sub>6</sub> H <sub>5</sub> CN	CH <sub>3</sub> CN
H <sub>2</sub> O $\nu_1$ red-shift	44	57	67	66	99
D <sub>0</sub> (kcal/mol)	3.0	4.2	3.7	4.4	4.5
	Solid Ar	gas	Solid Ne	Solid Ar	Solid Ar
$\nu_{\text{CN}}$ blue-shift	19	-	10	10	8
Ref	2,3	4	This work	5	6

## References

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## Comparison of frequencies ( $\text{cm}^{-1}$ ) and shifts ( $\Delta v = v_{\text{mono}} - v_{\text{complex}}$ ) for the 1:1 complex

	Calculated				Exp		Isomer
	AW1		AW2		AW3		
	$\omega$	$\Delta$	$\omega$	$\Delta$	$\omega$	$\Delta$	
<b>H<sub>2</sub>O</b>							
$\nu_3$	3918	30	3925	23	3917	31	3740 20 AW2 3736 24 AW2 3731 29 AW1
$\nu_1$	3771	51	3791	31	3743	89	3599 67 AW3 3621 43 AW1 3637 28 AW2
$\nu_2$	1632	-8	1629	-5	1652	-28	1601 -6 AW1 or 2 1603 -8 AW1 or 2 1618 -23 AW3
<b>Acrylonitrile</b>							
$\nu_4$	2177	2	2176	3	2194	-15	2251 -10 AW3 2240 2 AW1 or 2 2238 4 AW1 or 2
$\nu_8$	1111	-5	1108	-2	1108	-2	1095 -2 AW2 or 3 1099 -6 AW1
$\nu_{13}$	990	-17	975	-2	980	-7	960 -6 AW3 969 -15 AW1
$\nu_{14}$	574	-16	561	-3	563	-5	691 -6 AW3
$\nu_{11}$	235	-9	226	0	228	-2	231 2 AW2
Inter	367	303	514	453	254	AW3	
	291	262	302	254			AW1-2-3

Identification of **three isomers for 1:1 complex**: observation of **three bands for the  $\nu_1$  water mode** separated by 12-25  $\text{cm}^{-1}$

## Comparison of frequencies and shifts for the 1:2 complex

Modes	Calculated				Exp		Isomer
	ADW1		ADW2				
	$\omega$	$\Delta$	$\omega$	$\Delta$	$\nu$	$\Delta$	
<b>H<sub>2</sub>O</b>							
$\nu_1$ PA	3679	135	3696	118	3507	154	ADW1 3550 111 ADW2
$\nu_1$ PD	3598	121	3609	110	3486	105	ADW1 3493 98 ADW2
<b>Acrylonitrile</b>							
$\nu_4$	2189	-10	2183	-4	2246	-4	ADW2
$\nu_{12}$	1064	-29	1026	-21	998	-27	ADW1
$\nu_{14}$	581	-23	575	-17	694	-11	ADW2
Inter	118	108	108	108	108		ADW1 or 2 138 135 ADW1 or 2 215 210 ADW1 or 2

PA: proton acceptor and PD: proton donor for H<sub>2</sub>O dimer

Identification of **two isomers for 1:2 complex**: observation of **two bands for the  $\nu_1$  water mode**