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P Soulard, B Tremblay. Vibrational study of acrylonitrile dimer and acrylonitrile-water hydrogen-bonded complexes in solid neon supported by ab initio calculations. *Journal of Molecular Structure*, 2022, 10.1016/j.molstruc.2022.133503 . hal-03796456

HAL Id: hal-03796456

<https://cnrs.hal.science/hal-03796456>

Submitted on 4 Oct 2022

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Vibrational study of acrylonitrile dimer and acrylonitrile-water hydrogen-bonded complexes in solid neon supported by ab initio calculations.

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Abstract

For the first time the experimental study of the complexation of acrylonitrile molecule ($\text{CH}_3=\text{CHCN}$, noted AN) with water has been undertaken from a vibrational point of view as well as the homodimer $(\text{AN})_2$ in solid neon from 80 to 6000 cm^{-1} using Fourier transform infrared spectroscopy. From concentration effects and with the help of theoretical results we have identified several vibrational transitions for AN homodimer, AN- H_2O , AN- $(\text{H}_2\text{O})_2$, and $(\text{AN})_2\text{-H}_2\text{O}$ 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 and two isomers for the AN- H_2O and AN- $(\text{H}_2\text{O})_2$ complexes, respectively. Theoretical calculations at the second-order Møller-Plesset 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 AN- H_2O and AN- $(\text{H}_2\text{O})_2$, complexes.

KEYWORDS: Acrylonitrile dimer, Acrylonitrile-water complexes, Hydrogen Bond, Infrared Spectroscopy, Neon Matrix Isolation, ab initio calculations.

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1. Introduction

The nitrile molecules have been detected in a variety of interstellar environments and the reactions of these molecules are of interest in astrochemistry [1-3]. These molecules can have H-bonded interactions with a variety of donors [4-7] and in particular with water, it can form an AN-H₂O complex. The binding energy and the structures for three AN-H₂O complex isomers are calculated in only one work and the rotational spectrum of the most stable structure was reported [8]. The complex is formed by two interactions: one between O-H and N and another one between C-H and O. The observation of the ν_4 C \equiv N stretching mode for AN at 20 K in a pure solid AN and in N₂ and H₂O ices reported at 2229, 2232, and 2239 cm⁻¹ [2], respectively is useful for the interpretation of the detections of nitriles in Titan's atmosphere and the interstellar medium.

The AN homodimer has been studied in only three theoretical works [9-11] and infrared data of neutral and cationic AN dimers and trimers were obtained in supersonic jet using infrared dissociation with vacuum-ultraviolet photoionization and time-of-flight detection on the C-H stretching mode [11]. In solid argon and krypton the ν_{12} and ν_{13} out of plane C-H deformation were observed for the AN monomer and polymer without a specific assignment to a precise polymer [12]. Many bands were observed with blue-shifts between 2 and 17 cm⁻¹.

Therefore we have undertaken to study in solid neon the hydration of AN by infrared spectroscopy to obtain vibrational data over a wide spectral range in order to observe the isomers susceptible to exist in solid phase. So we have recorded spectra from 80 to 6000 cm⁻¹ of (AN)_n-(H₂O)_m complexes, noted n:m (n and m equal to 1 or 2) isolated in solid neon at 3 K. Harmonic ab initio calculations are also undertaken to support our observations. We have shown in the past that it is possible to obtain new vibrational data in solid neon for hydrogen bonding complexes as H₂S-H₂O, methylamine-H₂O, and methyl formate-H₂O [13-15], the works in which we prove the existence of some complexes and give the geometries of their isomers.

After a brief description of the experimental conditions and computational details, experimental spectra and theoretical results will be presented. We will report our calculations performed at the same level, MP2 aug-cc-pVTZ, for all the observed monomers, dimers, and 1:1, 2:1 and 1:2 complexes to make possible comparison between data. An assignment of the different observed bands to isomers of the 1:1, 1:2, and 2:1 complexes will be proposed with the theoretical support.

2. Experimental and theoretical details

2.1. Experimental apparatus

Samples were prepared by co-condensing AN-Ne and H₂O-Ne mixtures at a rate of 2-15 mmol/h onto one of six highly polished, rhodium-plated copper mirrors maintained at 3 K using a closed-cycle helium cryostat (Cryomech PT-405). The temperature was measured using silicon diodes. The AN/neon and the water/neon molar ratios vary between 100 and 2000 and each mixture was deposited separately by two injection systems. We use a Baratron gauge to measure the gas pressures. In the experiments with water it is important to saturate the stainless steel vacuum line to measure accurate pressures in order to avoid the adsorption of the water on the metal walls over time. Absorption spectra were recorded between 80 and 6000 cm⁻¹ on the same sample using a Bruker 120 FTIR spectrometer equipped with suitable combinations of light sources (globar, W filament), beamsplitters (Si/mylar, KBr/Ge, Si/CaF₂) and detectors (liquid N₂-cooled InSb, liquid N₂-cooled HgCdTe photoconductor, liquid He-cooled Si-B bolometer). All the spectra have been recorded at 3 K by co-adding 100 scans at 0.1 or 0.5 cm⁻¹ resolution. Natural water and AN (Sigma-Aldrich, 98.0 % purity) was degassed under vacuum before use. Ne (Air Liquide, 99.995 % purity) was used without purification.

2.2. Computational details

To compare all the vibrational data for the 1:0, 0:1, 0:2, 2:0, 1:1, 1:2 and 2:1 complexes with each other we have performed all calculations at the second order Møller-Plesset calculations (MP2) used with the Gaussian09 package [16] and the augmented correlation-consistent basis set aug-cc-pVTZ (AVTZ) of Dunning and co-workers [17,18] has been chosen. So energy calculations have been carried out at MP2/AVTZ optimized structures to compute equilibrium geometries, ground state (D_0) binding energies with BSSE and zero point energy (ZPE) corrections, and harmonic vibrational frequencies as well as infrared intensities.

3. Experimental results

Experiments were performed using different concentration ratios of AN/H₂O/Ne gas mixtures to identify the transitions of the n:m complexes: low concentration, typically AN/H₂O/Ne=1-4/1/1000 for the 1:1 complex and AN/H₂O/Ne=3/1-9/1000 for 1:2 complex. In the experiments with only AN deposition, traces of water vapor in the sample at a H₂O/Ne concentration ratio typically less than 0.05/1000 are present despite the low pressure of the experiment chamber (10^{-7} mbar).

Figures 1-8 illustrate the IR spectra for different frequencies ranges. In Tables 1-3 our measured vibrational frequencies of 1:0, 2:0, 1:1, 2:1, and 1:2 complexes for the AN and H₂O spectral regions are given. It is important to note here that the observation of several signatures for a mode may indicate the presence of different isomers.

3.1. Monomers and dimers

In a first step we study the spectra of each partner before studying complexes formed with AN and H₂O. The infrared absorptions of the H₂O monomer, dimer and trimer trapped in solid neon are well known for the fundamental modes and for many overtones and combinations [19,20]. The infrared spectra of AN have been studied in the gas phase [21-24] and in solid Ar and Kr [12]. These studies use different schemes for mode numbering and we adopt here the notation of the reference 24.

The spectra of only AN/Ne deposition in all the infrared ranges are presented in the Fig. 1-4 (spectrum a) and Fig. 8 (spectrum b). We have observed all the vibrational modes and some overtones and combinations. AN in solid neon has tendency to form dimers and their signatures appear near the AN's fundamentals and were identified through their intensities evolutions that must grow with the square of the AN concentration. The observed bands for the AN monomer and dimer are reported in Table 1 and they match well with previous gas phase studies [21-24, 11].

3.2. $(AN)_n-(H_2O)_m$ complexes

When water and AN are codeposited in neon matrix, new bands appear near the intramolecular fundamental modes in the mid-infrared, and in the far-infrared region corresponding to the intermolecular modes.

Table 1

AN and $(AN)_2$ experimental fundamental modes (cm^{-1}) in solid Ne and in gas phase.

	Assignment ^a	AN		$(AN)_2$	
		Gas ^a	Solid Ne	Gas ^b	Solid Ne
ν_{11}	$\gamma_{\text{C-C}\equiv\text{N}}$	229.4	233.3		235.9, 237.6
ν_{15}	$\gamma_{\text{C-C}\equiv\text{N}}$	333.3	338.6		355.6
ν_{14}	$\tau_{\text{C=C}}$	682	683.8		685.5, 691.3
ν_{10}	$\delta_{\text{C=C-N}}$	788	795.1		800, 805
ν_9	$\nu_{\text{C-C}}$	869	869.9		868, 871
ν_{13}	$\gamma_{\text{C-H}}$	954	954.0		959.9
ν_{12}	$\gamma_{\text{C-H}}$	971	971.4		981, 984.5, 987.3
ν_8	ρ_{CH_2}	1096	1093.5		1090.7, 1097.4
ν_7	$\delta_{\text{C-H}}$	1281	1285.5		1287.6
ν_6	δ_{CH_2}	1415	1414.3		1408.0, 1418.9
ν_5	$\nu_{\text{C=C}}$	1615	1615.7		1612.8
ν_4	$\nu_{\text{C}\equiv\text{N}}$	2240	2241.7		2237.9, 2240.3
ν_3	$\nu_{\text{C-H}}$	3042	3044.6	3041	3040, 3046

ν_2	ν_{C-H}	-	3108.9	3076	3076, 3083, 3104
ν_1	ν_{C-H}	3123	3122.0	3123	3120, 3125

^aAn assignments according to reference 24. ν : stretching, δ : in plane bending, ρ : rocking, γ : out of plane bending, τ : torsion.

^bRef 11.

3.2.1. AN spectral regions

We observe seven fundamental modes of AN perturbed by one or two water molecules. The regions of some AN modes are showed in Fig. 1-4 and 8 and signatures attributed to the 1:1 or 1:2 complexes appear near the AN's fundamentals. The observed bands are reported in Table 2.

In the region of the ν_{14} mode, two bands at 689.6 and 691.9 cm^{-1} grow near AN and $(\text{AN})_2$ signatures when H_2O is added to AN (Fig. 1) following linearly the concentration of AN, H_2O kept constant so they belong to the 1:1 complex. We observe a broad band at 694.3 cm^{-1} that appears when the H_2O concentration becomes high and we conclude that it belongs to 1:2, since it follows the evolution of the H_2O dimer. For the ν_9 mode, two bands at 872.5 and 872.9 cm^{-1} are assigned to the 1:1 complex (Fig. 1). In the region of the ν_{12} and ν_{13} modes (Fig. 2) we observe two doublets at 960.6, 959.7 and 969.1, 969.6 cm^{-1} , and a triplet at 979.2, 979.7, and 980.8 cm^{-1} , assigned to the 1:1 complex and a band at 998.4 cm^{-1} attributed to the 1:2 complex. In the region of the ν_8 mode (Fig. 3) we observe two bands for the 1:1 complex at 1095.4 and 1098.5 cm^{-1} and a weak band assigned to the 1:2 complex at 1100.8 cm^{-1} . In the region of ν_4 mode (Fig. 4) three bands are the signatures of the 1:1 complex at 2237.9, 2239.6, and 2251.3 cm^{-1} and a band is assigned to the 1:2 complex at 2245.6 cm^{-1} .

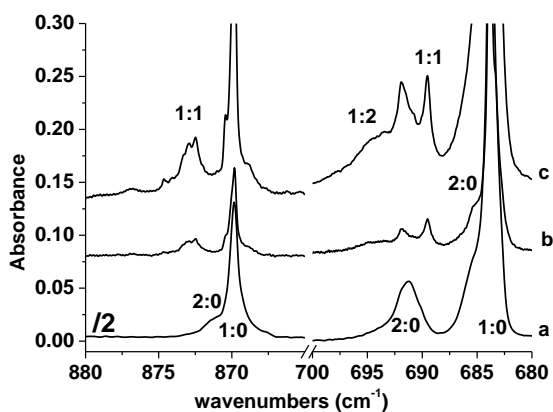


Fig. 1 Spectra in the AN ν_{14} region at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 3/0/1000 with the absorbance scale divided by 2, (b) 1/9/1000, (c) 3/9/1000.

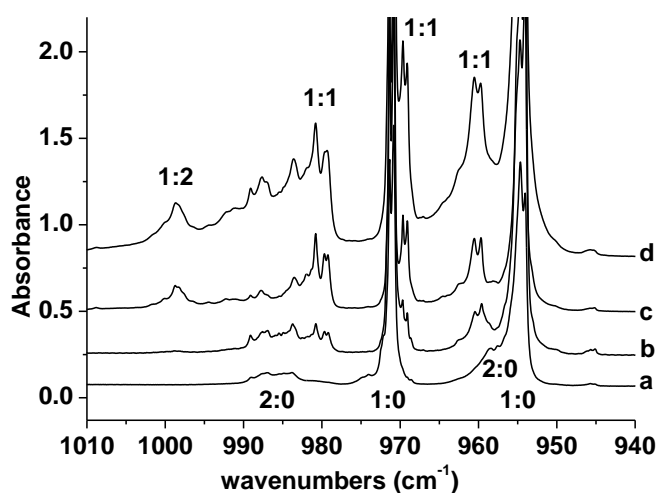


Fig. 2. Spectra in the AN ν_{12} and ν_{13} regions at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 4/0/1000, (b) 3/1/1000, (c) 3/9/1000, (d) 9/9/1000.

Table 2

Observed frequencies and assignment in AN regions for 1:1, 1:2, and 2:1 complexes isolated in solid neon.

n:m	Assignment	Frequencies (cm ⁻¹)
1:1	ν_{11}	231.0
1:1	ν_{14}	689.6, 691.9
1:2	ν_{14}	694.3
1:1	ν_9	872.5, 872.9
1:1	ν_{13}	959.7, 960.6, 969.1, 969.6
1:1	ν_{12}	979.2, 979.7, 980.8
1:2	ν_{12}	998.4

1:1	ν_8	1095.4, 1098.5
1:2	ν_4	2245.6
1:1	ν_4	2237.9, 2239.6, 2251.3

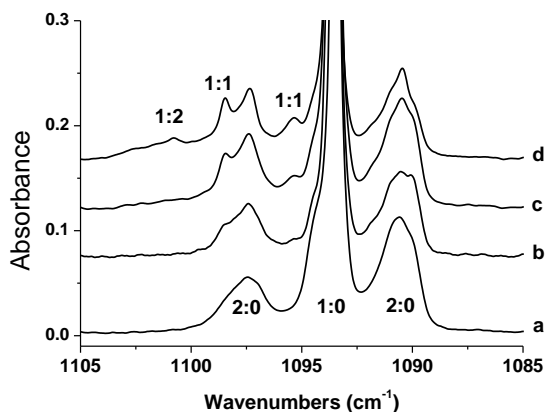


Fig. 3. Spectra in the AN ν_8 region at 3 K deposition, with different An/H₂O/Ne concentration ratios. (a) 3/0/1000, (b) 3/1/1000, (c) 3/3/1000, (d) 3/9/1000.

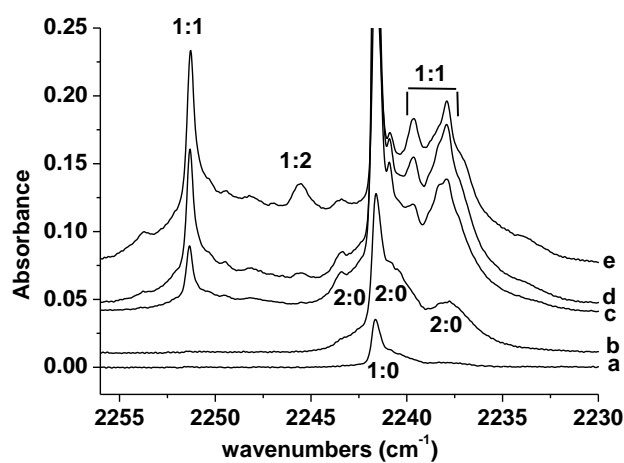


Fig. 4. Spectra in the AN ν_4 region at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 1/0/1000, (b) 4/0/1000, (c) 3/1/1000, (d) 3/3/1000, (e) 3/9/1000.

3.2.2. H₂O spectral regions

The regions of water and AN ν_5 C=C stretching modes are showed in Fig. 5-7, signatures attributed to the 1:1, 2:1, or 1:2 complexes appear near the water's fundamentals modes. The observed bands are reported in

Table 3. In the H₂O bending ν_2 region (Fig. 5) three new bands appear at 1601.4, 1603.1, and 1618.4 cm⁻¹ when AN is added to H₂O and are assigned to the 1:1 complex. As discussed later, these three bands correspond to three isomers of 1:1 complex. A broad weak band appears at 1621 cm⁻¹ and becomes important when concentrations as well for AN and H₂O are higher. It cannot belong to 1:2 or 2:1 because it doesn't follow one of the dimers concentrations, so they can be attributed to larger (AN)_n-(H₂O)_m complexes with n and m >2. We observe in the same region the ν_5 C=C stretching mode for the AN monomer at 1615.7 cm⁻¹.

In the H₂O ν_1 region (Fig. 6) the spectra are complex since they are many signatures of different complexes (0:2, 0:3, 1:1, and 1:2) between 3640 and 3480 cm⁻¹. Three groups of signatures, a doublet at 3619.4, 3623.3, and two bands at 3598.6 and 3637.1 cm⁻¹ follow linearly the concentration of H₂O or AN and are attributed to 1:1 complex. As already mentioned for ν_2 , these bands correspond to the three isomers of 1:1 complex. At higher AN concentration, a band at 3586.4 cm⁻¹ grows like the AN dimer bands so is attributed to 2:1 complex. In this region in which signatures of H₂O dimer and trimer are present [19-20], three bands at 3538.3, 3543.8, and 3565.1 cm⁻¹ appear and become important when concentrations for AN and H₂O are higher and so they can be attributed to n:m complexes with n and m >2. (Fig. 6b). At higher water concentration several bands at 3486.0, 3493.0, 3502.9, 3507.4, and 3549.8 cm⁻¹ grow like the H₂O dimer bands and are attributed to 1:2 complex. As discussed later, these bands correspond to two isomers of 1:2 complex. In the H₂O ν_3 region (Fig. 7), around the H₂O dimer signature at 3733.7 cm⁻¹, three bands at 3730.9, 3735.9, and 3739.9 cm⁻¹ are attributed to the 1:1 complex. A band at 3733.6 cm⁻¹ appears at higher AN concentration and is attributed to 2:1 complex and another one at 3722.5 cm⁻¹ is attributed to n:m complex.

In the near infrared we can attribute to the 1:1 complex, in comparison with the water dimer data, two bands at 5200.8 and 5203.3 cm⁻¹ and two others at 5314.1 and 5321.5 cm⁻¹ to the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ combinations, respectively (Table 3 and Fig. S1 in the supplementary material). At 1867.6 cm⁻¹ we observe a broad 1:1 band which is the combination of the H₂O ν_2 bending mode with the intermolecular vibration observed at 253.4 cm⁻¹ (Table 3 and Fig. S2 in the supplementary material). The bandwidth of 10

cm^{-1} of this combination band is comparable with the observed $\nu_2 + \text{intermolecular}$ mode for the water dimer and trimer [19,20].

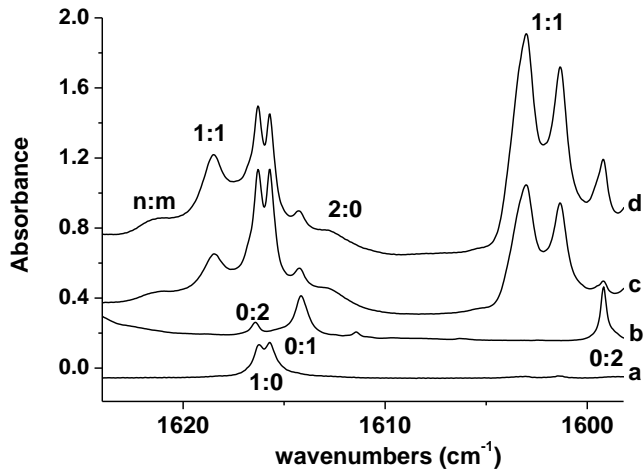


Fig. 5. Spectra in the water ν_2 region at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 4/0/1000, (b) 0/1/1000, (c) 9/1/1000, (d) 9/3/1000.

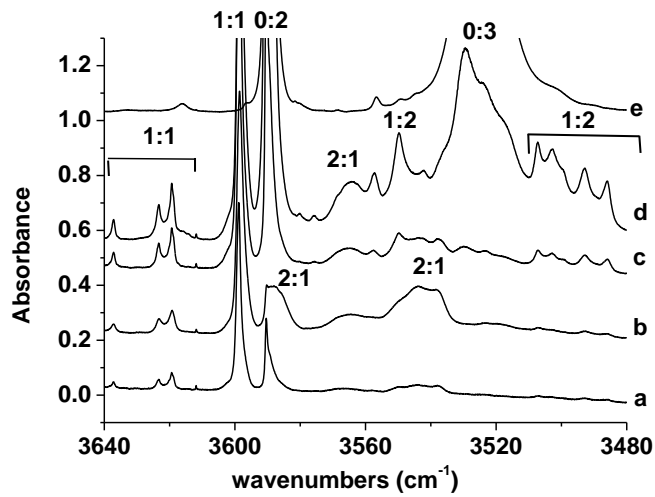


Fig. 6. Spectra in the H₂O ν_1 region at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 3/1/1000, (b) 9/1/1000, (c) 3/3/1000, (d) 3/9/1000, (e) 0/9/1000.

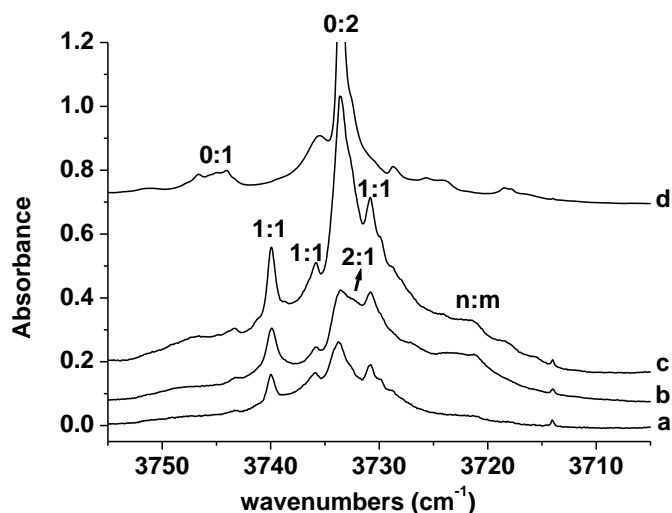


Fig. 7. Spectra in the H_2O ν_3 region at 3 K deposition, with different AN/ H_2O /Ne concentration ratios. (a) 3/1/1000, (b) 9/1/1000, (c) 3/3/1000, (d) 0/3/1000

Table 3

Observed frequencies and assignment in the far-infrared (FIR) and water regions for 1:1, 1:2, and 2:1 complexes isolated in solid neon.

n:m	Assignment	Frequencies (cm^{-1})
1:1	vinter	253.5, 452.6
1:2	vinter	108.3, 223.1
1:1	ν_2	1601.4, 1603.1, 1618.4
n:m ^a	ν_2	1621
0:1 ^b	ν_2	1595.6
0:2	ν_2 PA ^c , PD ^c	1599.2, 1616.5
1:1	$\nu_2 + 253$	1867.6
1:2	ν_1	3486.0, 3493.0, 3502.9, 3507.4, 3549.8
2:1	ν_1	3586.4
0:3	ν_1	3529.4, 3516
n:m	ν_1	3538.3, 3543.8, 3565.1
0:2	ν_1 PD, PA	3590.5, 3660.6
1:1	ν_1	3598.6, 3619.4, 3623.3, 3637.1
0:1 ^b	ν_1	3665.4
1:1	ν_3	3730.9, 3735.9, 3739.9
n:m	ν_3	3722.5
2:1	ν_3	3733.6
0:1 ^b	ν_3	3759.5
0:2	ν_3 PD, PA	3733.7, 3763.5
0:2	$\nu_1 + \nu_2$ PD	5191.2
1:1	$\nu_1 + \nu_2$	5200.8, 5203.3
0:2	$\nu_2 + \nu_3$ PD	5332.6
1:1	$\nu_2 + \nu_3$	5314.1, 5321.5

^a n:m: $(\text{AN})_n - (\text{H}_2\text{O})_m$ complexes with n and m > 2.

^b nrm (no rotating monomer) value

^c PA: proton acceptor and PD: proton donor for H₂O dimer.

3.3. Intermolecular spectral region

The FIR is the region of the intermolecular modes and so we observe (Fig. 8) many water dimer (92.6, 122, 170, and 310 cm⁻¹) and trimer bands (150, 279.5, 386.5, 414 and 434 cm⁻¹) and also two fundamentals for the AN monomer [19,20,22]. When AN and water molecules are deposited together, two bands at 253.5 and 452.6 cm⁻¹ appear and belong to the 1:1 complex because follow linearly monomers concentration, two another bands at 108.3 and 223.1 cm⁻¹ are attributed to the 1:2 complex (Table 3).

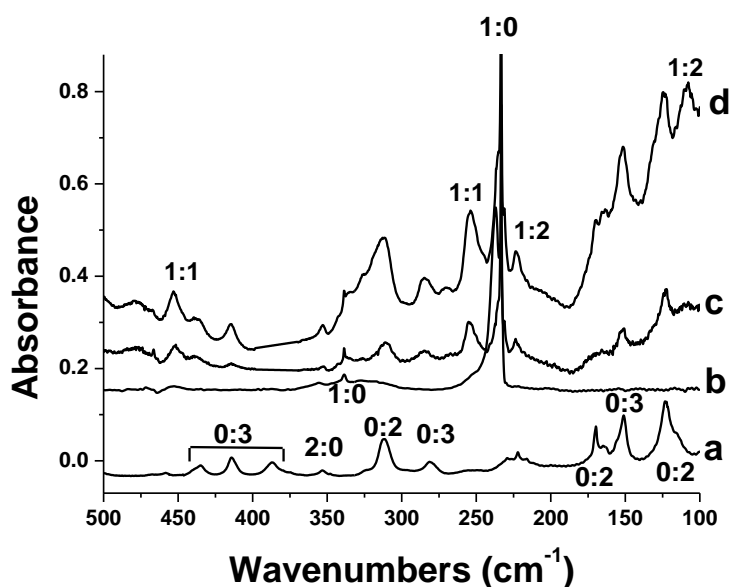
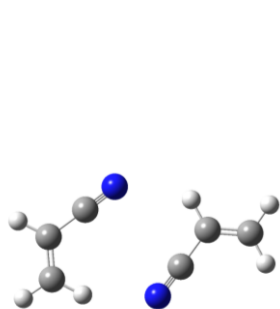


Fig. 8. Spectra in the 80-500 cm⁻¹ region at 3 K deposition, with different AN/H₂O/Ne concentration ratios. (a) 0/1/1000, (b) 3/0/1000, (c) 3/3/1000, (d) 9/9/1000.

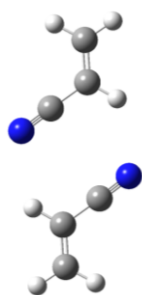
4. Theoretical results

For all the complexes, the most stable calculated geometries and the associated D₀ are reported in Fig. 9 and all the frequencies and intensities are given in the supplementary material (Table S1 for H₂O

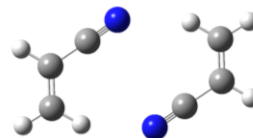
monomer and dimer, Tables S2 and S3 for AN and (AN)₂, and Tables S4, S5, and S6 for 1:1, 1:2, and 2:1 complexes).



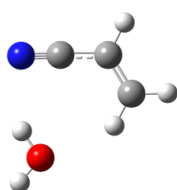
2:0 D1 (6.5)



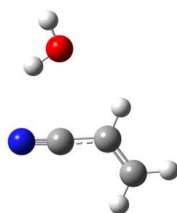
2:0 D2 (6.5)



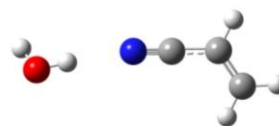
2:0 D3 (6.3)



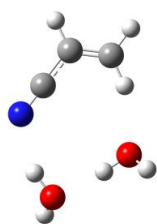
1:1 AW1 (4.4)



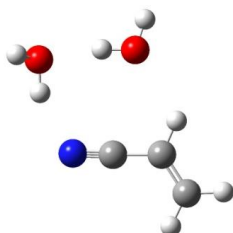
1:1 AW2 (3.7)



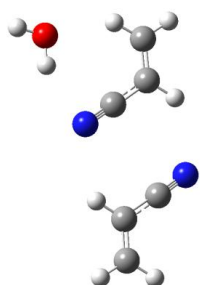
1:1 AW3 (3.7)



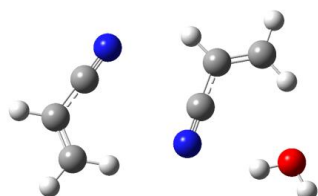
1:2 ADW1 (8.3)



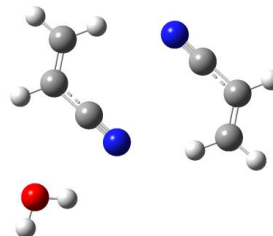
1:2 ADW2 (8.2)



2:1 DAW1 (4.1)



2:1 DAW2 (4.1)



2:1 DAW3 (3.4)

Fig. 9. MP2/AVTZ geometry of the most stable 2:0, 1:1, 1:2 and 2:1 complexes. D_0 values are indicated in parenthesis (in kcal/mol).

Three 2:0 stable structures noted D1, D2, and D3 (Fig. 9) have been calculated and have very close binding energy, 6.5 kcal/mol for D1 and D2 and 6.3 kcal/mol D3. In literature, reference 11 reports the three structures we calculate, with similar difference than our data in the binding energies to each other, and a fourth one is reported with higher energy than the other three of 2.8 kcal/mol at the B3LYP/6-311++G(d,p) level. Only the C-H stretching modes around 3000 cm^{-1} have been calculated. The reference 9 gives only one structure corresponding to D2 at the B3LYP/6-311++G** level with all the vibrational modes and reference 10 finds two structures corresponding to D2 and D3 at the the B3LYP/6-311++G(d,p) level. In this work, the authors have only reported the values of the $\text{C}\equiv\text{N}$ vibration.

For the 1:1 complex, three stable structures AW1, AW2, and AW3 are calculated with D_0 equal to 4.4, 3.7, and 3.7 kcal/mol, respectively (Fig. 9). The three complexes are formed by a bond between the terminal nitrogen and a hydrogen of water and the difference for each isomer is the position of the oxygen atom since it can pointed to a hydrogen of AN (AW1 and AW2) or not (AW3). This particularity for the AW3 isomer generates a strong shift for the ν_1 and ν_2 water modes and for the ν_4 AN mode (Table 4). For the 1:2 complex, there is no theoretical study and our results give two stable structures ADW1 and ADW2, similar to AW1 and AW2 where the water molecule is replaced by the water dimer, with calculated D_0 equal to 8.3 and 8.2 kcal/mol, respectively (Fig. 9). For the 2:1 complex, no theoretical study exists and our results give three stable DAW1, DAW2, and DAW3 isomers with structures of acrylonitrile dimer D3, D2 and D1, respectively, with calculated D_0 equal to 4.1, 4.1, and 3.4 kcal/mol, respectively (Table S6). In the two most stable structures DAW1 and DAW2 a water molecule is bind to the AN dimer as the most stable AW1 1:1.

5. Vibrational assignments and discussion

5.1. AN dimer

Three isomers, D1, D2, and D3, are found for AN dimer with very close binding energies. The geometries of 2:0 are represented in Fig. 9. We report in Table 1 the AN and (AN)₂ frequencies in solid neon and in gas phase [11]. We observe all the 15 modes attributed to the AN dimer. For many modes we observe two bands and even three and the observation of these bands cannot be only different trapping sites because of the large frequency shifts between the bands. The most likely hypothesis is that they are the signatures of different isomer since the three isomers have very close binding energy so all can be observed in the matrix. However it is impossible to associate the observed frequencies to a specific isomer because they have very similar calculated frequencies (see Table S3). The comparison of our experimental results with those obtained in the gas phase (Table 1) for the C-H stretching bands ν_1 , ν_2 , and ν_3 shows that the Ne matrix induced very small perturbations on these modes.

5.2. AN-H₂O complex

Our calculations give three stable complexes with close binding energy, in agreement with the results of references 8. In this paragraph we discuss the assignment of observed bands to the 1:1 complex and we report in Table 4 the calculated harmonic and experimental frequencies and the corresponding shifts $\Delta\omega$ or $\Delta\nu$ where $\Delta\nu = \nu(\text{monomer}) - \nu(1:1)$ values. All the calculated modes for the three 1:1 isomers are given in the Table S4 of the supplementary material.

We observe the three water modes perturbed by the complexation and for each one we observe three signatures that we can attribute, with the help of calculations, to the isomers AW1, AW2 or AW3 (Table 4). The agreement between observed and calculated shifts is very good. For the ν_2 modes, the band at 1618 cm^{-1} is clearly attributed to the isomer AW3 and the two other belong to the isomer AW1 or AW2. For the ν_1 mode, the attribution to a specific isomer is straightforward since the frequencies shifts are very different. We can also note the strong intensity of the ν_1 mode (Table 4), especially for the AW3 isomer, which indicates the hydrogen bonding between CN and H₂O. In this complex the O-H bond is quasi collinear with the C \equiv N and this structure is very similar to that of the water dimer [20] for which the ν_1 observed red-shift mode of the proton donor is 75 cm^{-1} (Table 3) and 67 cm^{-1} for AW3 (Table 4). The calculated intensity for

this mode is 297 and 364 km/mol for water dimer and AW3, respectively (Table S1 and S4). Moreover, the observed red-shift for the ν_1 water mode in the benzonitrile-water complex isolated in solid Ar [25] is 66 cm^{-1} , very similar to the AW3 one (Table 4). Also, the IR-dip spectra of jet-cooled 4-aminobenzonitrile-water 1:1 complex was obtained [26] and the observed red-shift for the ν_1 and ν_3 water modes are 65 and 27 cm^{-1} , respectively, for a similar structure complex to our AW3 isomer.

For the ν_3 bands, it is difficult to attribute them only from the frequencies shifts. However, the observation of two bands at 5314.1 and 5321.5 cm^{-1} in the $\nu_2+\nu_3$ combination region can allow us to assign the ν_2 and ν_3 bands. Indeed in the 1:1 complex the water molecule is the proton donor as a water molecule in the water dimer and in this case the X_{23} anharmonicity coefficient for the $\nu_2+\nu_3$ combination is -17.6 cm^{-1} [20]. Remark is supported by the comparison with results for other hydrogen bonding complex [13-15,27] for which the X_{23} coefficient values are similar to that of the water dimer within a few cm^{-1} . Taking into account the water dimer X_{23} coefficient value and calculated shift values, we can exclude the AW3 isomer because the combination value will be too high. The most relevant combinations are for the other ν_2 and ν_3 values: $3740+1601(1603)+X_{23}=5323(5325)$ cm^{-1} near the 5321.5 cm^{-1} combination band and $3731+1601(1603)+X_{23}=5314(5316)$ cm^{-1} near the other one at 5321.5 cm^{-1} . They match well but it is difficult to attribute without ambiguity ν_2 to AW1 or AW2. The ν_3 band at 3736 cm^{-1} , five time less intense than the one at 3740 cm^{-1} , while the calculated ones are close, can be a site of the later.

For the AN modes perturbed by the presence of water, we can also associate many signatures to a specific isomer except for ν_4 , ν_8 , ν_9 , and ν_{12} for which the calculated frequencies are too close to distinguish between them. The ν_4 mode ($\nu_{\text{C}\equiv\text{N}}$) has the particularity to have a blue or a red-shift, depending on the isomer (Table 4). A blue shift of 10 cm^{-1} is observed for the AW3 isomer where only one hydrogen atom is involved in a bond with the AN molecule. The same blue-shift was also observed on the $\nu_{\text{C}\equiv\text{N}}$ mode for the benzonitrile-water complex in solid Ar [25] and the calculated structure is a complex where the nitrogen atom of benzonitrile interacts with one hydrogen of water and the other O-H bond in free, like AW3 isomer. Two bands slightly red-shifted (2 and 4 cm^{-1}) can be attributed to AW1 or AW2 as shown by the calculated shifts but we cannot exclude that they are two sites of the same mode.

For the intermolecular bands, we attribute signatures at 253.5 and 452.6 cm^{-1} to the 1:1 complex. For the last one, the attribution to isomer AW3 is straightforward since the calculated frequencies are very different between them but for the band at 253.5 cm^{-1} the three calculated values are relatively near.

Table 4

Comparison of frequencies^a (cm^{-1}) and shifts^a ($\Delta\nu = \nu_{\text{mono}} - \nu_{\text{complex}}$) between observed and calculated data for the AW1, AW2, and AW3 isomers of the 1:1 complex. The intensities are in parenthesis.^b

Modes	Calculated						Experimental		Isomer
	AW1		AW2		AW3		ν	$\Delta\nu$	
	ω	$\Delta\omega$	ω	$\Delta\omega$	ω	$\Delta\omega$			
H₂O									
ν_3	3918	+30	3925	+23	3917	+31	3740 (5)	+20	AW2
							3736 (1)	+24	AW2
							3731 (5)	+29	AW1
ν_1	3771	+51	3791	+31	3743	+89	3599 (100)	+67	AW3
							3621 ^c (12)	+43	AW1
							3637 (2)	+28	AW2
ν_2	1632	-8	1629	-5	1652	-28	1601 (24)	-6	AW1 or 2
							1603 (34)	-8	AW1 or 2
							1618 (7)	-23	AW3
AN									
ν_4	2177	+2	2176	+3	2194	-15	2251 (10)	-10	AW3
							2240 (2)	+2	AW1 or 2
							2238 (2)	+4	AW1 or 2
ν_8	1111	-5	1108	-2	1108	-2	1095 (4)	-2	AW2 or 3
							1099 (1)	-6	AW1
ν_{12}	1016	-11	1015	-10	998	-7	980 ^c (13)	-9	AW1 or 2 or 3
ν_{13}	990	-17	975	-2	980	-7	960 ^c (27)	-6	AW3
							969 ^c (5)	-15	AW1
ν_9	889	-5	883	+1	888	-4	873 ^c (0.5)	-3	AW1 or 3
ν_{14}	574	-16	561	-3	563	-5	691 ^c (1)	-6	AW3
ν_{11}	235	-9	226	0	228	-2	231 (4)	+2	AW2
Inter ^d	367		303		514		453 (7)		AW3
	291		262		302		254 (16)		AW1 or 2 or 3

^aRounded calculated and experimental values.

^bExperimental intensities normalized on the most intense ν_1 water mode ($I=100$).

^cMean frequency of a doublet or multiplet assigned to 1:1 complex trapped in different matrix sites (see Table 1).

5.3. AN-(H₂O)₂ complex

Our work is the first report on experimental and calculated vibrational data on the 1:2 complex. Two stable structures noted ADW1 and ADW2 with very close binding energies are found (Fig. 9). With a high water/Ne concentration, typically 9/1000, we observe bands attributed to the 1:2 complex: five signatures

for the ν_1 H₂O mode, four for the AN molecule and two for the intermolecular modes (Table 2-3). All the calculated modes for the two 1:2 isomers are given in the Table S5.

We report in Table 5 the calculated harmonic and experimental frequencies and the corresponding shifts $\Delta\omega$ or $\Delta\nu$ where $\Delta\nu = \nu(\text{monomer}) - \nu(1:2)$ values. The water vibrations are compared with those of the water dimer and the AN ones with those of the AN monomer.

By comparing calculated and experimental shifts we can tentatively attribute three frequencies to the ν_1 PA and two ones to the ν_1 PD of H₂O dimer perturbed by the AN molecule. The two bands at 3503 and 3507 cm⁻¹ can be two sites of the same mode. For AN modes we can conclude more easily in view of the calculated shifts for each observed band. Two intermolecular modes are observable for 1:2 complex without a specific assignment to a precise isomer. However we can conclude that we observe the presence of the two isomers ADW1 and ADW2 of 1:2 complex in the neon matrix since these 2 isomers being isoenergetic (Fig. 9).

Table 5

Comparison of frequencies^a (cm⁻¹) and shifts^a ($\Delta\nu = \nu_{\text{mono}} - \nu_{\text{complex}}$)^b between observed and calculated data for the A and B isomers of the 1:2 complex.

Modes	Calculated				Experimental		Isomer
	ADW1		ADW2		ν	$\Delta\nu$	
	ω	$\Delta\omega$	ω	$\Delta\omega$			
H₂O							
ν_1 PA ^c	3679	+135	3696	+118	3503	+158	ADW1
					3507	+154	ADW1
					3550	+111	ADW2
ν_1 PD ^c	3598	+121	3609	+110	3486	+105	ADW1
					3493	+98	ADW2
AN							
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

^aRounded calculated and experimental values.

^bThe shifts for the water vibrations in the complex are compared with those of the water dimer.

^cPA: proton acceptor and PD, proton donor for H₂O dimer.

5.4. (AN)₂-H₂O complex

We also report the first experimental and calculated vibrational data on the 2:1 complex. We find three stable structures noted DAW1, DAW2, and DAW3 with close binding energies (Figure 9). With a high AN/Ne concentration, typically 9/1000, we observe bands attributed to the 2:1 complex only in the ν_1 and ν_3 water modes regions (Table 3). All the calculated modes for the 2:1 isomers are given in the Table S6. For ν_1 region one band is observed and the comparison between the experimental and calculated shift $\Delta\nu = \nu_{\text{H}_2\text{O}} - \nu_{2:1}$ allows us to eliminate the isomer DAW3, the least stable of the 3 isomers, but does not allow us to distinguish between the other two since $\Delta\nu_{\text{exp}} = 79 \text{ cm}^{-1}$ and $\Delta\nu_{\text{cal}} = 49, 51, \text{ and } 32 \text{ cm}^{-1}$ for DAW1, DAW2, and DAW3, respectively. For ν_3 region the observed band can be the signature of one of the three isomers since $\Delta\nu_{\text{exp}} = 26 \text{ cm}^{-1}$ and $\Delta\nu_{\text{cal}} = 29, 29, \text{ and } 23 \text{ cm}^{-1}$ for DAW1, DAW2, and DAW3, respectively. Perhaps the presence of DAW1 and DAW2 is more probable in view of the binding energy.

6. Conclusion

For the first time an experimental vibrational analysis of the AN dimer and the AN-H₂O, AN-(H₂O)₂ and (AN)₂-H₂O complexes has been carried out in solid neon from the near to the far infrared as well as a theoretical study at the same level of MP2/AVTZ calculations. We observe all the 15 modes attributed to the AN dimer but it is not possible to associate the observed frequencies to one of the three isomers because they have very similar calculated frequencies. For the 1:1 complex we observe nine signatures for the H₂O modes, eleven for the AN modes and two for the intermolecular modes. From the comparison between theoretical and experimental vibrational shifts we clearly observe three isomers especially by the observation of three bands for the ν_1 water mode. These bands are separated by 15-25 cm⁻¹ and they cannot be different trapping sites. We can also note the strong intensity of this mode, especially for the AW3 isomer, which indicates the hydrogen bonding H₃C₂C≡N···H-O-H. For the 1:2 complex we observe five

signatures for the H₂O modes, three for the AN modes and two for the intermolecular modes and we clearly observe the two isoenergetic isomers. The PA and PD ν_1 bands are red-shifted by 150 and 100 cm⁻¹, respectively, indicating a high perturbation of the water dimer under the complexation. With the help of calculations we are able to prove for 1:1 and 1:2 complexes that different isomers are formed in the matrix and we can distinguish between them showing the importance of the complementarity between theory and experience.

Declaration of competing interest

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Pascale Soulard carried out the experiments, contributed to the data analysis and manuscript drafting and performed the ab initio calculations; **Benoit Tremblay** carried out the experiments, performed the IR analysis and drafted the manuscript.

Acknowledgments

We express our sincere thanks to Professor Yongjun Hu, Director of Guangzhou Key Lab of Spectral Analysis and Functional Probes & Deputy Director of M. O. E Key Lab of Laser Life Sciences College of Biophotonics, South China Normal University, Guangzhou 510631, China, for sharing some theoretical data on acrylonitrile.

Supplementary materials

Two figures are given: figure S1 shows the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ combinations of water modes and figure S2 shows the combination of water ν_2 bending mode with the intermolecular vibration at 253.4 cm⁻¹ of the 1:1 complex. Binding energies, harmonic frequencies and intensities performed at harmonic MP2 aug-cc-pVTZ level for monomers, dimers, and the most stable 1:1, 1:2 and 2:1 complexes are given in Tables S1-S6.

References

[1] M. P. Bernstein, S. A. Sandford, L. J. Allamandola, The infrared spectra of nitriles and related

- compounds frozen in Ar and H₂O, *Astrophys. J.* 476 (1997) 932-942, doi:10.1086/303651
- [2] R. L. Hudson, M. H. Moore, Reactions of nitriles in ices relevant to Titan, comets, and the interstellar medium: formation of cyanate ion, ketenimines, and isonitriles, *Icarus* 172 (2004) 466-478, doi: 10.1016/j.icarus.2004.06.011
- [3] J. C. Loison, E. Hébrard, M. Dobrijevic, K. M. Hickson, F. Caralp, V. Hue, G. Gronoff, O. Venot, Y. Bénilan, The neutral photochemistry of nitriles, amines and imines in the atmosphere of Titan, *Icarus* 247 (2015) 218-247, doi: 10.1016/j.icarus.2014.09.039
- [4] A. T. Fafarman, P.A. Sigala, D. Herschlag, and S. G. Boxer, Decomposition of Vibrational Shifts of Nitriles into Electrostatic and Hydrogen-Bonding Effects, *J. Am. Chem. Soc.* 132 (2010) 12811-12813, doi : 10.1021/ja104573b.
- [5] P. Deb, T. Haldar, S. M Kashid, S. Banerjee, S. Chakrabarty, and S. Bagchi, Correlating Nitrile IR Frequencies to Local Electrostatics Quantifies Noncovalent Interactions of Peptides and Proteins, *J. Phys. Chem. B*, 120 (2016) 4034-4046, doi : 10.1021/acs.jpcc.6b02732.
- [6] J.T. First, J. D. Slocum, and L. J. Webb, Quantifying the Effects of Hydrogen Bonding on Nitrile Frequencies in GFP: Beyond Solvent Exposure, J. T. First, J. D. Slocum, and L. J. Webb, *J. Phys. Chem. B* 122 (2018) 6733-6743, doi :10.1021/acs.jpcc.8b03907.
- [7] C. R. Baiz, B. Błasiak, J. Bredenbeck, M. Cho, J.-H. Choi, S. A. Corcelli, A. G. Dijkstra, C.-J. Feng, S. Garrett-Roe, N.-H. Ge, M. W. D. Hanson-Heine, J. D. Hirst, T. L. C. Jansen, K. Kwac, K. J. Kubarych, C. H. Londergan, H. Maekawa, M. Reppert, S. Saito, S. Roy, J. L. Skinner, G. Stock, J. E. Straub, M. C. Thielges, K. Tominaga, A. Tokmakoff, H. Torii, L. Wang, L. J. Webb, and M. T. Zanni, Vibrational Spectroscopic Map, Vibrational Spectroscopy, and Intermolecular Interaction, *Chem. Rev.* 120 (2020) 7152-7218, doi:10.1021/acs.chemrev.9b00813.
- [8] C. Calabrese, A. Vigorito, A. Maris, S. Mariotti, P. Fathi, W. D. Geppert, S. Melandri, Millimeter Wave Spectrum of the Weakly Bound Complex CH₂=CHCN·H₂O: Structure, Dynamics, and Implications for Astronomical Search, *J. Phys. Chem. A* 119 (2015) 11674-11682, doi:10.1021/acs.jpca.5b08426.

- [9] J. M. Alía, H. G. M. Edwards, W. R. Fawcett, T.G. Smagala, An experimental Raman and theoretical DFT study on the self-association of acrylonitrile, *J. Phys. Chem. A* 111 (2007) 793-804, doi:10.1021/jp0663210.
- [10] D. K. Singh, S. K. Srivastava, B. P. Asthana, Cluster of acrylonitrile in methanol/ethanol: a structure-spectra correlation by quantum chemical and polarized Raman study, *Chem. Phys.* 380 (2011) 24-33, doi: 10.1016/j.chemphys.2010.11.012.
- [11] Y. Li, W. Song, N. Jiang, Z. Zhang, M. Xie, Y. Hu, Structural rearrangement of the acrylonitrile (AN) cluster in the gas phase under VUV one-photon radiation explored by mass-selected infrared spectroscopy, *Spectroc. Acta A*, 226 (2020) 117620, doi: 10.1016/j.saa.2019.117620
- [12] W. O. George, E. N. Lewis, D. A. Williams, W. F. Maddams, Matrix-Isolation of monomeric and polymeric forms of acrylonitrile, *Appl. Spectrosc.* 36 (1982) 592-596, doi: 10.1366/0003702824639321
- [13] P. Soulard, B. Tremblay, Vibrational study in neon matrix of $\text{H}_2\text{SH}_2\text{O}$, $\text{H}_2\text{S}-(\text{H}_2\text{O})_2$, and $(\text{H}_2\text{S})_2-\text{H}_2\text{O}$ complexes. Identification of the two isomers: $\text{HOH}-\text{SH}_2$ (H_2O proton donor) and $\text{HSH}-\text{OH}_2$ (H_2S proton donor), *J. Chem. Phys.* 151 (2019) 124308-124317, doi : 10.1063/1.5120572.
- [14] P. Soulard, B. Tremblay, Vibrational study of methylamine dimer and hydrated methylamine complexes in solid neon supported by ab initio calculations, *J. Mol. Struct.* 1236 (2021) 130308, doi:10.1016/j.molstruc.2021.130800
- [15] P. Soulard, B. Tremblay, Vibrational study of hydrated methyl formate complexes in solid neon: Observation for the first time of three isomers for methyl formate-water complex, *J. Mol. Struct.* 1257 (2022) 132604, doi:10.1016/j.molstruc.2022.132604
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel et al. Gaussian 09, Revision D.01, (2009), Gaussian Inc.: Wallingford, CT.
- [17] R.A. Kendall, T.H. Dunning, R.J. Harrison, Electron affinities of the first- row atoms revisited. Systematic basis sets and wave functions, *J. Chem. Phys.* 96 (1992) 6796-6806, doi : 10.1063/1.462569.

- [18] T.H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* 90 (1989) 1007-1023, doi : 10.1063/1.456153.
- [19] B. Tremblay, B. Madebène, M.E. Alikhani, J.P. Perchard, The vibrational spectrum of the water trimer: Comparison between anharmonic ab initio calculations and neon matrix infrared data between 11,000 and 90 cm^{-1} , *Chem. Phys.* 378 (2010) 27-36, doi : 10.1021/jp052096v.
- [20] Y. Bouteiller, B. Tremblay, J.-P. Perchard, The vibrational spectrum of the water dimer: Comparison between anharmonic ab initio calculations and neon matrix infrared data between 14,000 and 90 cm^{-1} , *Chem. Phys.* 386 (2011) 29-40, doi : 10.1016/j.chemphys.2011.05.014.
- [21] F. Halverson, R. F. Stamm, J. J. Whalen, The Vibrational Spectrum and Thermodynamic Functions of Acrylonitrile, *J. Chem. Phys.* 16 (1948) 808-816, doi: 10.1063/1.1747000.
- [22] A. R. H. Cole, A. A. Green, *J. Mol. Spectrosc.* 48 (1973) 246–253, doi: 10.1016/0022-2852(73)90189-6.
- [23] F. Cerceau, F. Raulin, R. Courtin, D. Gauthier, Infrared spectra of gaseous mononitriles: application to the atmosphere of Titan, *Icarus* 62 (1985) 207-220, doi: 10.1016/0019-1035(85)90118-6
- [24] M. Khlifi, M. Nollet, P. Paillous, P. Bruston, F. Raulin, Y. Bénilan, R. K. Khanna, Absolute Intensities of the Infrared Bands of Gaseous Acrylonitrile, *J. Mol. Spectrosc.* 194 (1999) 206-210, doi: 10.1006/jmsp.1998.7795.
- [25] R. Gopi, N. Ramanathan, K. Sundararajan, The structure of benzonitrile-water complex as unveiled by matrix isolation infrared spectroscopy: Is it linear or cyclic at low temperatures?; *J. Mol. Struct.* 1219 (2020) 128636, doi: 10.1016/j.molstruc.2020.128636
- [26] K. Sakota, N. Yamamoto, K. Ohashi, M. Saeki, S.-I. Ishiuchi, M. Sakai, M. Fujii, H. Sekiya, IR-dip and IR-UV hole-burning spectra of jet-cooled 4-aminobenzonitrile-(H_2O)₁. Observation of π -type and σ -type hydrogen-bonded conformers in the CN site, *Chem. Phys.* 283 (2002) 209-219, doi: 10.1016/S0301-0104(02)00501-3
- [27] D. Dargent, B. Madebène, P. Soulard, B. Tremblay, E. L. Zins, M. E. Alikhani, P. Asselin, Conformational landscape of the 1/1 diacetyl/water complex investigated by Infrared Spectroscopy and ab initio Calculations, *J. Phys. Chem. A* 121, (2017), 88, doi : 10.1021/acs.jpca.6b10492.