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Abstract

For the first time the investigation of water molecule complexed with methylamine (CH_3NH_2) in solid neon was performed from 80 to 6000 cm^{-1} using Fourier transform infrared spectroscopy. From concentration effects and with the help of theoretical results we have identify several vibrational transitions for CH_3NH_2 dimer, CH_3NH_2-H_2O, and CH_3NH_2-$(H_2O)_2$ complexes. For the CH_3NH_2-H_2O complex, where the two submolecules interacting through hydrogen bonding, the infrared (IR) spectral changes (frequencies as well as intensities) indicate that the water playing the role of the proton donor, in agreement with the previous theoretical works. 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 observed complexes.

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

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1. Introduction

The hydrogen bonding interaction plays a key role in many chemical processes and structures of hydrogen-bonded complexes are of great theoretical and experimental interest [1]. The high concentration of water in Earth's atmosphere makes its interactions with trace molecules important in atmosphere chemistry [2]. The polar NH_2 functional group in amines can form a strong hydrogen bond with water and alcohols and these complexes have given rise to many theoretical studies [3-17].

For the methylamine water complex (MA-H_2O), the binding energy and the structures are calculated in literature [9-17] where water is always the proton donor, but the vibrational data are often limited to the N-H and O-H stretching vibrations [11,13,14] since only one study gives all the vibrations of this complex [15]. For the experimental data only one study exists in solid neon in the far-infrared to observe the librational bands [18]. For the MA-$(H_2O)_2$ complex, there is no experimental data and this species has been the subject of five theoretical studies [12-15,17]. There is no data for the $(MA)_2$-H_2O complex, but the MA dimer has been well studied in theoretical works [19-23] and infrared data were obtained by infrared photodissociation spectra on the C-N stretching mode [24] and by a infrared-vacuum ultraviolet spectroscopic study on the N-H and C-H stretching modes [22].

Since no complete infrared study has been published, we have undertaken to study the $(MA)_n$-$(H_2O)_m$ complexes, noted n:m, and more specifically the 1:1, 1:2, and 2:0 complexes in neon matrix to obtain vibrational data. We have shown in the past that it is possible to obtain new vibrational data in solid neon for several hydrated complexes as CO_2-H_2O, N_2O-H_2O, OCS-H_2O, and H_2S-H_2O [25-28], works in which we were able to give the geometries of some complexes and to prove the existence of isomers. We performed ab initio calculations at the second-order Møller-Plesset (MP2) level with the aim of obtaining homogeneous results (same method and basis set) to be compared with the experimental data in order to determine the structures of the observed complexes and their potential isomers.

The Fourier transform infrared spectrometer permits to obtain vibrational data from the far infrared (intermolecular vibrations region) to the near infrared (overtone and combination bands region). The advantage of neon matrix cage is its weak interaction with the involved molecules or complexes and so observed vibrational data are close to the gas phase values.

After a brief description of the experimental conditions, the spectra will be presented. An assignment of the different observed bands to 2:0, 1:1, and 1:2 complexes will be given and then structures for these complexes will be proposed with the support of our calculations.

2. Experimental and theoretical details

2.1 Experimental apparatus

Samples were prepared by co-condensing MA-Ne and H_2O-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 neon/MA and the neon/water molar ratios vary between 100 and 2000 and each mixture was deposed separately by two injection systems. We use a Baratron gauge to measure the gas pressures. In the experiments with only MA deposition, traces of water vapor in the sample at a H_2O/Ne concentration ratio typically less than 0.05/1000 are present despite the low pressure of the experiment chamber (10^{-7} mbar).

In the experiments with water it is important to saturate the stainless steel vacuum line to measure accurate pressures. 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/CaF$_2$) and detectors (liquid N2-cooled InSb, liquid N_2-cooled HgCdTe photoconductor, liquid He-cooled Si-B bolometer). All the spectra have been recorded at 3 K and by co-adding 200 scans at 0.1cm^{-1} resolution. Natural water, D_2O (Euriso-top 99.90%) and MA (Fluka, 99 % 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 [29] and the augmented correlation-consistent basis set aug-cc-pVTZ (AVTZ) of Dunning and co-workers [30,31] has been chosen. So energy calculations have been carried out at MP2/AVTZ optimized structures to compute equilibrium geometries, equilibrium (D_e), ground state (D_0)

binding energies with BSSE and zero point energy (ZPE) corrections, and harmonic vibrational frequencies as well as infrared intensities.

3. Spectral data and assignments

Our experiments were performed using different concentration ratios of MA/H_2O/Ne gas mixture to identify the transitions of the n:m complexes: low concentration, typically MA/H_2O/Ne=1-4/0.5/1000 for the 1:1 complex and MA/H_2O/Ne=4/1-16/1000 for 1:2 complex. Fig. 1-6 illustrate the IR spectra for different frequencies ranges. In Tables 1-3 our measured vibrational frequencies of n:m complexes for the MA and H_2O spectral regions are given. Some experiments were also done with D_2O instead of H_2O to confirm attributions.

3.1 Monomers and dimers

In a first step we study the spectra of each partner before studying complexes formed with MA and H_2O. The infrared absorptions of the H_2O monomer, dimer and trimer trapped in solid neon are well known for the fundamental modes and for many overtones and combinations [32,33].

The infrared spectra of MA have been studied in the gas phase [34-36] and there is only a FIR study in solid neon [18]. So the first step is to obtain the spectrum of only MA/Ne deposition in all the infrared range. Our results are presented in the Fig. 1-6 (spectrum a). We have observed 14 of the 15 MA vibrational modes (intensity of ν_{14} is too weak to be observable) and some overtones and combinations. MA in solid neon has tendency to form very easily dimers and higher aggregates and their signatures appear near the MA's fundamentals. Moreover they are many trapping sites due to the cage effect of the matrix which makes the analysis complex. The observed bands for the MA monomer and dimer are reported in Table 1 and they match well with previous gas phase studies [34-36].

Table 1

MA and (MA)$_2$ experimental frequencies in solid Ne, in gas phase, the calculated harmonic ones, and $\Delta v = v(MA) - v((MA)_2)$. Intensities are in parenthesis.[a]

		MA			MA$_2$				
	Assignments[b]	Solid Ne[c]	Cal[d]	Gas[e]	Solid Ne[c]	Δv	Cal[d]	Δv	Gas
v_4+v_{10}		5049.7			4992.6	57			
v_{10}	NH$_2$ a-stretch	3428.0	3628	3424	3403.4(19)	+25	3621(7)	+7	3393[f], 3403[f]
					3398.0(49)	+30	3598(30)	+30	
v_1	NH$_2$ s-stretch	3365.0	3534	3360	3294.2(211)	+70	3473(109)	+61	3319[f],3299[f]
$2v_4$					3190.7				
v_{11}	CH$_3$ d-stretch	2983.8	3158	2985	2978.0(82)	+6	3156(29)	+2	
v_2	CH$_3$ d-stretch	2957.5, 2964.8, 2970.6, 2976.1	3129	2962	2951.6(63)	+15	3116(57)	+13	
v_5+v_6		2898.9			2876.0				
v_3	CH$_3$ s-stretch	2876.0	3041	2820	2884.4(23)	-8	3049(30)	-8	
					2866.4(43)	+10	3031(74)	+10	
$2v_6$		2776.3, 2796.8, 2818.2, 2820.8							
v_4	NH$_2$ scis	1630.1	1659						
v_{12}	CH$_3$ d-deform	1482.5	1542	1485	1481(11)	+2	1538(5)	+4	
v_5	CH$_3$ d-deform	1466.8	1522	1474	1463(11)	+4	1518(9)	+4	
v_6	CH$_3$ s-deform	1429.1	1467	1430	1426(2)	+3	1462(1)	+5	
v_{13}	NH$_2$ twist	1302.5							
v_7	CH$_3$ rock	1131.8	1181	1130	1142(6)	-10	1188(7)	-7	
v_8	CN stretch	1044.5	1077	1044	1039(18)	+6	1069(10)	+8	1038[g]
					1049(30)	-4	1080(10)	-3	1048[g]
v_9	NH$_2$ wag	785.5	840	780	837(122)	-51	900(122)	-60	
					819(145)	-33	867(119)	-37	
v_{15}	Torsion	270.0, 272.0	297	264	371(110)	-100	423(48)	-126	
					297(35)	-26	323(46)	-26	

[a]Intensity given in km/mol for calculated ones and relative values for experimental ones normalized on the most intense calculated one to 122. [b]MA assignments according to reference 36.
[c]Experimental values, this work. [d]Calculated values, this work.[e] Ref 34-36. [f]Ref 22. [g]Ref 24.

3.2 (MA)$_n$-(H$_2$O)$_m$ complexes

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

3.2.1 MA spectral regions

In the region of the ν_9 NH$_2$ wagging mode, a band at 866 cm^{-1}, already presents in Fig. 1a due to the trace of water and to its high intensity, grows near MA and (MA)$_2$ signatures when H$_2$O is added to MA (Fig. 1b,c) following linearly the concentration of H$_2$O, MA one kept constant. So it belongs to the 1:1 complex. We observe a band at 912 cm^{-1} that appears when the H$_2$O concentration becomes high and we conclude that it belongs to 1:2, since it follows the evolution of the H$_2$O dimer.

In the Fig. 1 we have also identified the ν_8 CN stretch mode of the 1:1 and 1:2 complexes at 1034.5 and 1039.9 cm^{-1} respectively, and the ν_7 CH$_3$ rock mode from 1:1 and 1:2 to 1150.4 and 1161.0 cm^{-1} respectively, the signatures of the 1:2 complexes being very weak.
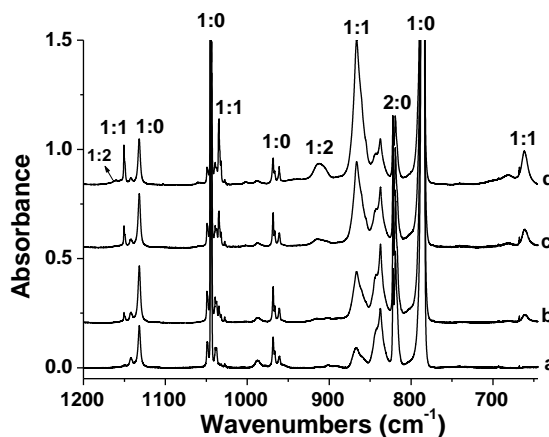

Fig. 1. Spectra in MA ν_7, ν_8, and ν_9 region at 3 K deposition, with different MA/H$_2$O/Ne concentration ratios. (a) 4/traces/1000, (b) 4/1/1000, (c) 4/3/1000, and (d) 4/9/1000.

In the region of the ν_4 NH$_2$ scissor (Fig. 2) we observe a broad band at 1586.6 cm^{-1} that belongs to the 1:1 complex because it appears when the two partners are present and follows linearly the effects of concentration. We can notice that the bandwidth of this band is comparable to the one allocated to the monomer at 1631.5 cm^{-1} (Fig. 2a). In the other MA regions (not shown), we observe the signature of 1:1

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complex for the ν_3 and ν_5 modes at 1467.4 and 2890.2 cm^{-1}, respectively, thanks to the concentration effects. We observe the combinations $\nu_5+\nu_6$ and $\nu_4+\nu_{10}$ of the 1:1 complex at 2906.6 and 5010.9 cm^{-1}, respectively (Fig. S1 in the supplementary materials). All these bands are reported in Table 2.
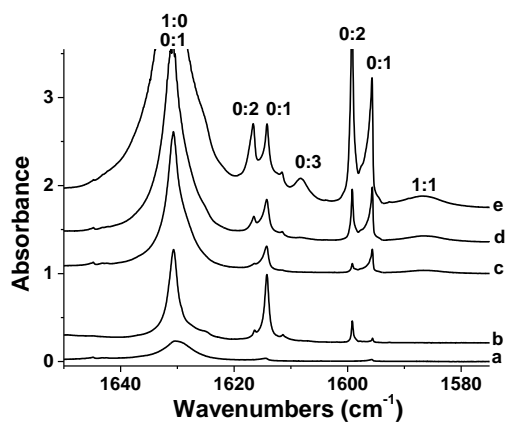

Fig. 2. Spectra in the MA ν_4 and the H$_2$O ν_2 region at 3 K deposition, with different MA/H$_2$O/Ne concentration ratios. (a) 8/traces/1000, (b) 0/1/1000, (c) 8/0.5/1000, (d) 4/1/1000, and (e) 4/3/1000.

Table 2

Observed frequencies (cm^{-1}) and assignment in different MA regions of 1:1 and 1:2 complexes isolated in solid neon.

n:m	Assignment[a]	Solid neon
1:1	ν_9 NH$_2$wag	866.0
1:2		912.0
1:1	ν_8 CN stretch	1034.5
1:2		1039.9
1:1	ν_7 CH$_3$ rock	1150.4
1:2		1161.0
1:1	ν_5 CH$_3$ d-deform	1467.4
1:1	ν_4 NH$_2$ scissor	1586.6
1:1	$2\nu_6$	2826.7, 2829.5
1:1	ν_3 CH$_3$ s-stretch	2890.2
1:1	$\nu_5+\nu_6$	2906.6
1:2		2924.9, 2927.0
1:1	$\nu_4+\nu_{10}$	5010.9

[a]MA assignments according to reference 36 and not repeated when it is the same for several below complexes.

3.2.2 H$_2$O spectral regions

In the ν_3 asymmetric O-H stretching region (Fig. 3) the 1:1 complex is characterized by a band at 3722.8 cm^{-1}. In the ν_1 proton donor O-H stretch region near the H$_2$O trimer [33] and tetramer [37] observed at 3529.4 and 3382.0 cm^{-1}, respectively, (Fig. 4) one intense band at 3379.7 cm^{-1} appears and grows linearly with the water concentration and so belongs to the 1:1 complex. Also near the $2\nu_2$ overtone of PD water dimer at 3193.7 cm^{-1}, we observe a narrow band at 3209.0 cm^{-1} attributed at $2\nu_2$ for the 1:1 complex, and a broad band at 3138.1 cm^{-1} attributed at ν_1 for the 1:2 complexe (Fig. 4 and Table 3). These assignements will be discussed in the next section. We observe signatures at 3411.0 and 3494.8 cm^{-1} that follow the intensity evolution of the MA dimer and water dimer bands, respectively (Fig. 4e). So, these bands are attributed for the first one to the 2:1 and second one to 1:2 complexes.
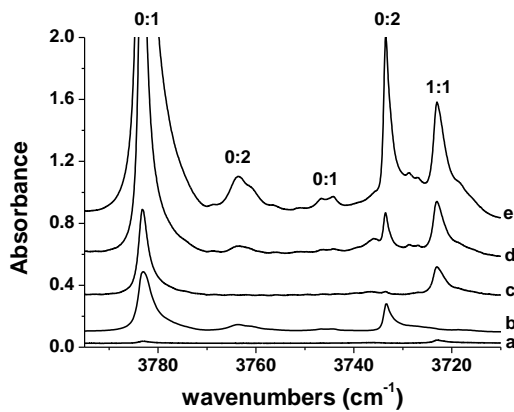

Fig. 3. Spectra in the H$_2$O stretching ν_3 region at 3 K deposition, with different MA/H$_2$O/Ne concentration ratios. (a) 8/traces/1000, (b) 0/6/1000, (c) 8/0.5/1000, (d) 4/3/1000, and (e) 4/9/1000.

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Fig. 4. Spectra in the bonded OH and the NH_2 stretching region at 3 K deposition, with different MA /H_2O/Ne concentration ratios. (a) 8/traces/1000, (b) 0/6/1000, (c) 8/0.5/1000, (d) 4/3/1000, and (e) 4/9/1000.
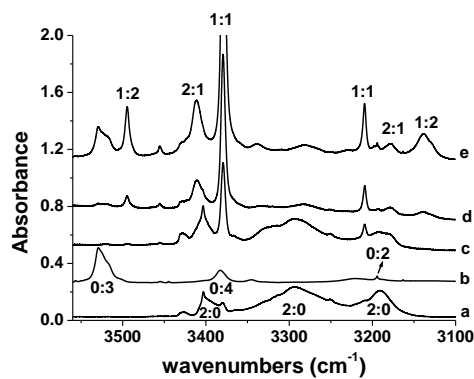
We don't observe the direct signature of ν_2 for the 1:1 complex near the ν_2 of water monomer because this region is congested from 1640 to 1620 cm^{-1} by the strong rotation line R(0) of the water monomer at 1630 cm^{-1} and the ν_4 of MA monomer (Fig. 2) but we observe combination bands and overtones which allow us to estimate the value of ν_2. In the region of the signature of the $\nu_2+\nu_3$ combination of the water dimer around 5330 cm^{-1} (Fig. 5) we observe a band at 5336.2 cm^{-1} that we can attribute to the same combination for the 1:1 complex due to the concentration effect. Using the water dimer anharmonicity values (X_{23}= -16.9 cm^{-1}) [32] of the proton donor (PD) of this combination we are able to deduce an estimated ν_2 value of 1631 cm^{-1}. We also observe two signatures of 1:1 complex at 2497.8 and 2034.5 cm^{-1} (Table 3) which can be attribute without ambiguity in view of the previous analysis at two combinations of the water mode ν_2 with MA mode ν_9 at 866 cm^{-1} and with an intermolecular mode at 419 cm^{-1} (see the next section).

Isotopic substitutions were performed using HDO and D_2O to support attributions, and the results are reported in Table 3. For the MA modes of the 1:1 complex, the ν_4 NH_2 scissor and the ν_9 NH_2 wagging modes are slightly red shifted by 1.5 and 3.5 cm^{-1}, respectively. H/D isotopic substitutions in H_2O monomer have no influence on the vibrational mode frequencies of the 1:1 complex in the other spectral regions of MA. For the H_2O modes, the observed shifts for the 1:1 and 2:1 complexes are in agreement with those observed for the NH_3-D_2O complex [38] that supports our attributions (see details later).
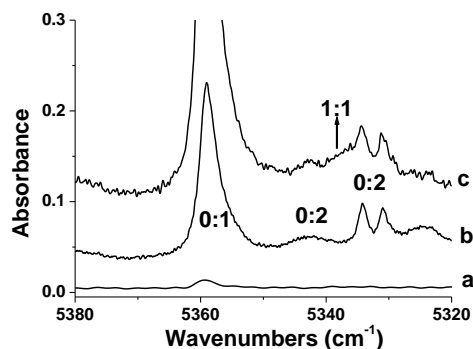
Fig. 5. Spectra in the H_2O $\nu_2 + \nu_3$ combination regions at 3 K deposition, with different $MA/H_2O/Ne$ concentration ratios. (a) 8/traces/1000, (b) 0/9/1000, and (c) 4/9/1000.

3.3. Intermolecular spectral region

A very recent study [18] limited to the observation of H_2O libration motion in the FIR has been published about microsolvation of organic molecules in Ne matrix and in particular of MA-H_2O in a brief paragraph. The authors observed two bands at 419.8 and 658.9 cm^{-1} attributed to a signature of 1:1 complex only in the 400-680 cm^{-1} range because they said that the spectrum below 400 cm^{-1} is complicated. We observe, in addition to the water dimer bands (92.6, 122, 170, and 310 cm^{-1}) and trimer bands (150, 279.5, 386.5, 414 and 434 cm^{-1}), four new bands at 100, 197.9, 419.0 (Fig. 6) and 661.0 cm^{-1} (Fig. 1 and Table 3). Due to their concentration evolution all these bands are the signatures of 1:1 complex, the higher ones match well with the results of reference 18.
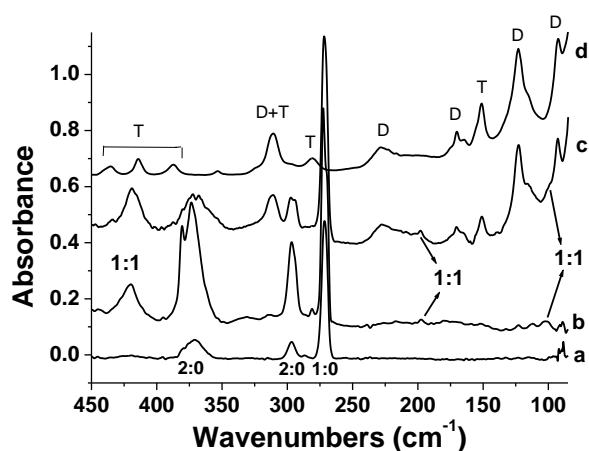
Fig. 6. Spectra in the 80-450 cm^{-1} region at 3 K deposition, with different MA/H$_2$O/Ne concentration ratios. (a) 4/traces/1000, (b) 8/0.5/1000, (c) 4/9/1000, and (d) 0/6/1000. D, T for H$_2$O dimer and trimer, respectively.

Table 3

Observed frequencies (cm^{-1}) and assignment in the far-IR and in H$_2$O regions of 1:1, 2:1 and 1:2 complexes isolated in solid neon.

n:m	Assignment[a]	H$_2$O	D$_2$O	HDO
1:1	ν_{inter}	100.0		
1:1		197.9	195.7	
1:1		419.0	259.1	
1:1		661.0	506.9	
1:2	ν_2	1588[b]	1176[b]	1395.3
2:1		1609[b]		
1:1		1631[c]		
1:1	$\nu_2 +419$	2034.5		
1:1	$\nu_2 +866$[d]	2497.8		
1:2	$2\nu_2$	3138.1	2332.7	2776.6
2:1		3177.8	2359.4	
1:1		3209.0	2372.5	
1:1	ν_1	3379.7	2496.7	
2:1		3411.0	2520.6	
1:2	PD	3494.8	2575.9, 2564.8	
1:n[e]	PD	3519.0		
1:1	ν_3	3722.8	2748.5	
1:1	$\nu_2 + \nu_3$	5336.2	3941.3	

[a]The assignment is not repeated when it is the same for several below complexes. PD: proton donor and PA: proton acceptor for H$_2$O dimer. [b]This value is deduced from the observation of the $2\nu_2$ overtone (see text). [c]This value is deduced from the observation of the combination at 5336.2 cm^{-1} (see text). [d]This combination mode is ν_2 (H$_2$O) $+ \nu_9$ (MA): $1631 + 866 = 2497$ cm^{-1} (see text). [e]-n>2

4. Discussion: Comparison between experimental and theoretical data

For such hydrogen bonding complexes, thanks to the comparison of the vibrational shifts between the monomer and complexes ($\Delta\nu=\nu_{mono}-\nu_{complex}$) of the experimental and calculated data, it is possible to match the observed bands to modes of the different complexes. We can also determine their structures that appear in the matrix. So for 0:1, 1:0, 0:2, 2:0, 1:1, 1:2 and 2:1 complexes we have performed calculations at MP2 PVTZ level to determine the most stable structures, the dissociation energies D$_0$, the harmonic frequencies and intensities (Table S1-S6 in the supplementary material). For all these complexes if we discuss in terms

of compared stabilities we can notice that those involving three molecules are more stable than the others (Table S6). It is undoubtedly because they form a pseudo-cycle strengthening the energy of the complex as mentioned in reference 12 comparing $MA-H_2O$ and $MA-(H_2O)_2$ and in reference 39 comparing Trimethylamine-H_2O and the (Trimethylamine)$_2$-H_2O.

4.1. MA dimer

Two isomers are found for 2:0 noted 2:0-a, the most stable, and 2:0-b with a difference of the binding energy of 0.9 kcal/mol. The geometry of 2:0-a is represented in Fig. 7. We report in Table 1 in addition of the MA and (MA)$_2$ frequencies in solid neon and in gas phase [22] the calculated frequencies at the MP2 level and the shifts $\Delta v=v(MA)-v((MA)_2)$. Only the frequencies of 2:0-a are reported. (see the supplementary material for geometry and frequencies for 2:0-b in Fig. S2 and Table S2 and S3). The spectra of the MA dimer are complicated because each monomer's mode is split in two modes since one matches with the proton donor and the other one with the proton acceptor. In fact, we have observed only one band for the majority of the modes and, for this reason we indicate only the calculated values comparable to the experimental results (Table 1).

The MA dimer attributions are supported by the gas phase observation and also by calculations. We first discuss the red-shifted NH_2 stretching modes v_{10} and v_1 and the blue-shifted NH_2 wag and torsion modes v_9 and v_{15} (Table 1). Thanks to the observation of the movements of the calculated modes and with the Δv values we can attribute the observed bands at 3403.4 and 3398.0 cm^{-1} to v_{10} vibrations of the proton acceptor and proton donor, respectively, and the one at 3294.2 cm^{-1} is the signature of the v_1 mode of the proton donor (Table 1). We attribute without ambiguity the bands at 837 and 819 cm^{-1} and at 371 and 297 cm^{-1} to the v_9 and v_{15} modes, respectively, thanks to the comparison between the calculated and observed shifts that are in very good agreement. The blue shifts for these modes have been observed for solid MA [40] and it can be interpreted as the consequence of electronic change around the N atom following the hydrogen bond formation [41].The experimental and theoretical values, Δv and intensities, match well also for v_8, v_9 and v_{15} and for all MA dimer modes. Finally, the comparison of our experimental results with

those obtained in the gas phase shows that the Ne matrix induced very small perturbations for the intramolecular vibrations.

4.2. MA-H$_2$O complex

The MP2 calculations for the 1:1 complex give only one stable complex according to data of references 12-14 where the water is the proton donor and the hydrogen bond is formed between one H atom of water and the N atom of MA (Fig. 7) with a D$_0$ value of -5.37 kcal/mol. 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 intensities and corresponding Δv=v(monomer)-v(1:1) values. All the vibrations are given in Table S4 in the supplementary material.
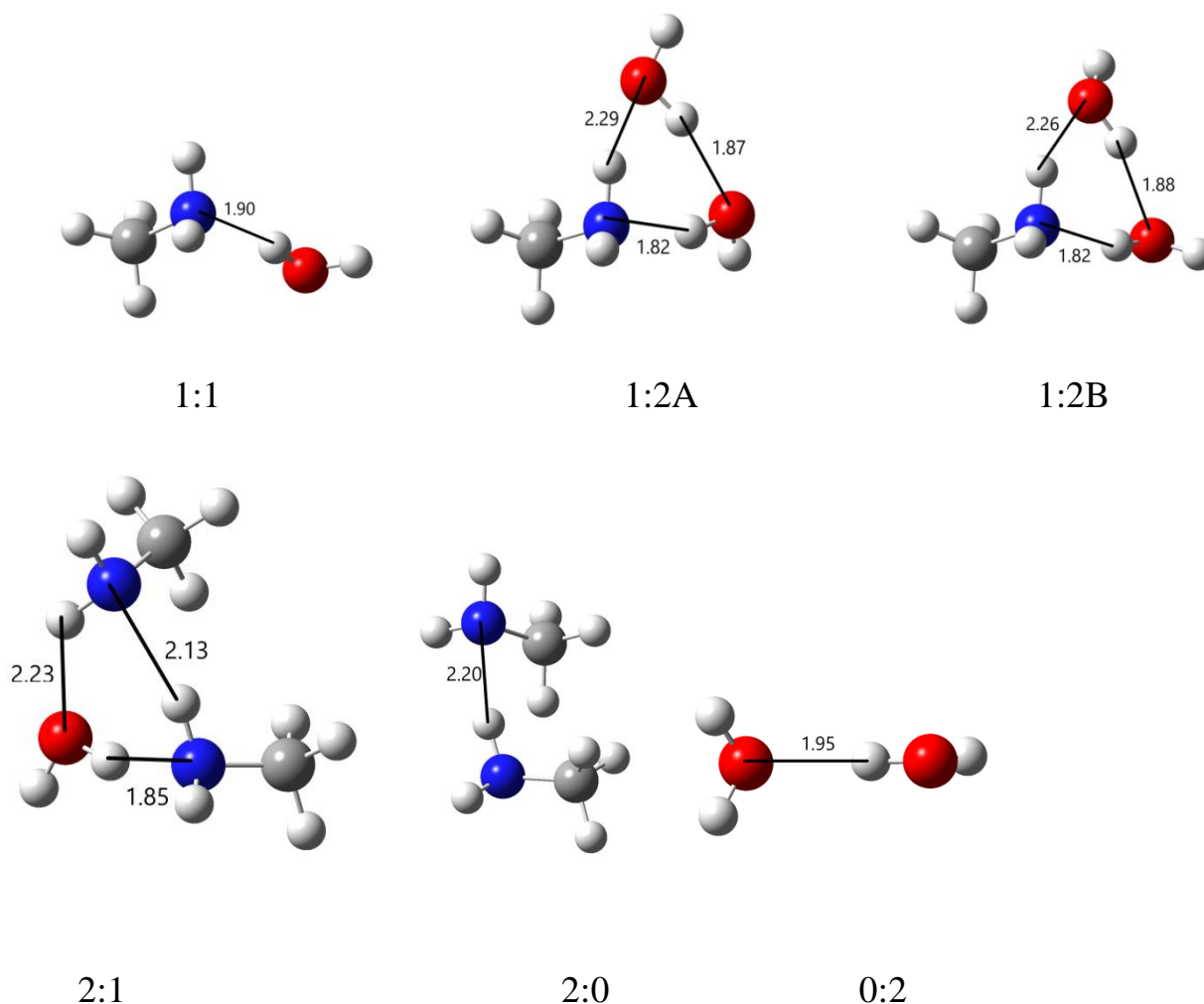

Fig. 7. MP2/AVTZ geometry of the most stable n:m complexes. All the distances between the molecules are in Å.

The experimental and theoretical values, frequency shifts and intensities match very well for the three water modes and for five of six MA observed modes (except ν_4). This confirms that the calculated structure of the 1:1 complex is the only one observed in the Ne matrix.

For the MA modes, ν_9 (NH$_2$ wagging) is the most perturbed with a blue shift of 80.5 cm^{-1}, which can be explained by the fact that the N atom is directly involved in the bond between water and MA. For ν_4 (NH$_2$ scissor) the observed blue shift of 43.5 cm^{-1} does not agree with the calculated one of 6 cm^{-1} (Table 4), but this calculated value is in agreement with data of the references 11 and 15 (6 and 4 cm^{-1}, respectively). For the MA-HBr complex, a blue shift of 40 cm^{-1} was also observed in solid argon [42] but there are no calculations in the literature for this complex. Maybe the N$\cdots$H length or the N$\cdots$H–O angle is not correctly calculated and so this mode would be particularly perturbed. However the attribution of the observed band at 1586.6 cm^{-1} to the ν_4 mode is experimentally confirmed since we observe the combination mode $\nu_4+\nu_{10}$ for MA and for the 1:1 complex (Table 1 and 2). In addition we observe a very small frequency shift of 1.5 cm^{-1} for this band when D$_2$O was injected instead of H$_2$O, which confirms it is a MA mode and not a H$_2$O one. The other observed MA modes are less involved in the complexation which explains their low shifts.

For H$_2$O modes we can attribute the strong observed band at 3379.9 cm^{-1} to the signature of the O-H hydrogen bond ν_1 with a red shift of 286 cm^{-1}. In a very recent work in gas phase, this band was observed at 3397 and 3377 cm^{-1} for the dimethylamine and trimethylamine water complexes, respectively [43]. The complexation lightly disturbs the ν_3 and ν_2 H$_2$O modes, the first one is red shifted by 36.7 cm^{-1}, and the second one blue shifted of the same value 36 cm^{-1}. By comparison with the NH$_3$-H$_2$O complex isolated in solid neon [38], these modes are red and blue shifted by 34 and 29.4 cm^{-1}, respectively, and ν_1 is red shifted by 209 cm^{-1}. Also, the H$_2$O/D$_2$O shifts for the ν_3 and ν_1 modes, 974 and 883 cm^{-1}, respectively, are similar with those of the NH$_3$-H$_2$O complex, 971 and 883 cm^{-1}, respectively.

Table 4

Comparison of vibrational data (cm^{-1}) between observed and MP2 harmonic calculated values for the 1:1 complex. The intensities are in parenthesis.[a]

		Calculated	Δv^{b}	Experimental	Δv^{b}
H$_2$O	v_3	3904(78)	+44	3722.8(98)	+37
modes	v_1	3508(630)	+314	3379.7 (630)	+286
	v_2	1671(72)	-43	1631^{c}	-36
MA	v_3	3061(53)	-20	2890.2(10)	-11
modes	v_4	1653(36)	+6	1586.6 (35)	+44
	v_5	1522(5)	+0	1467.4(6)	-1
	v_7	1193(8)	-12	1150.4(14)	-19
	v_8	1065(12)	+12	1034.5(16)	+10
	v_9	894(133)	-54	866(420)	-81
	v_{inter}	758(68)		661.0(60)	
	v_{inter}	455(99)		419.0(113)	
	v_{inter}	217(9)		197.9(6)	
	v_{inter}	112(73)		100(12)	

[a]Intensity in km/mol for calculated ones and relative values for experimental ones normalized on the most intense calculated one to 630. [b]For the rounded calculated and experimental values, $\Delta v = v$(Monomer)-v(1:1). [c]Deduced value from the combination modes observed at 5336.2 cm^{-1} (see text).

For the intermolecular bands, we attribute signatures at 100, 197.9, 419.0 and 661.0 cm^{-1} to the 1:1 complex. For the last two ones, the similar modes were observed in the NH$_3$-H$_2$O complex at 661.9 and 429.5 cm^{-1}, with very similar H$_2$O/D$_2$O shifts [38], and they are assigned to the out-of-plane and the in-plane H$_2$O librational modes, respectively.

Finally, we can note the observation of the strong intensity of the $2v_2$ overtones (Fig. 4) of the 1:1, complex. If we compare with the intensity of the v_1 band for these complexes, the intensity ratio $2v_2/v_1$ is around 20 %, while this ratio is 2% for the PD in the water dimer [32]. This strong intensity is due to a Fermi resonance between the $2v_2$ and v_1 H$_2$O bands [39] in these complexes since these two bands are separate of approximately 200 cm^{-1}, while they are separate of 400 cm^{-1} in the water dimer.

4.3. MA-(H₂O)₂ complex

Our work is the first report on experimental vibrational data on the 1:2 complex since in literature there is only theoretical studies [12-14]. We have performed calculations at MP2 pVTZ level and find two stable structures labeled A and B, their vibrational data are given in Table S5.

The Fig. 7 presents the A and B structures formed by a slightly distorted water dimer where MA is added through a hydrogen bond between one H atom of MA and O atom of water, and one H atom of water and N atom of MA. Calculated bond dissociation energies D_0 are found at -9.68 and -9.57 kcal/mol for A and B isomers, so quasi isoenergetic complexes. The water vibrations of 1:2 complex are compared with those of the water dimer and the MA vibrations with those of the MA monomer (Table 5).

We attribute without ambiguity the bands at 3494.8 and 3138.5 cm^{-1} to the ν_1 (H₂O)₂ PD and ν_1 (H₂O)₂ PA vibrations thanks to the comparison between the calculated and observed shifts that are in very good agreement. For the MA vibrations the attributions can be made with any ambiguity with the help of calculations and experimental and theoretical $\Delta\nu$ match well. Since the vibrational data are very similar for the two A and B structures, it was impossible to attribute the bands to a specific structure.

Concerning the (MA)₂-H₂O complex, we observed only one band at 3411.0 cm^{-1} attributed to ν_1 O-H hydrogen bond between H₂O and the MA dimer. The H₂O/D₂O shift for this band, 882 cm^{-1}, is the same as the 1:1 complex, 883 cm^{-1}.

Table 5

Experimental and calculated (MP2/AVTZ) frequencies and shifts (cm^{-1}) for 1:0, 0:2, and 1:2 complexes. Intensities are in parenthesis[a]

H$_2$O modes	Calculated			Experimental		
	0:2	1:2	Δv [b]	0:2 [c]	1:2	Δv [b]
v_1	3719 PD	3612(267) A	+107	3590.5	3494.8(267)	+98
		3614(266) B	+105			
	3814 PA	3300(863) A	+514	3660.6	3138.5	+522
		3306(857) B	+508			
MA modes	1:0	1:2	Δv [e]	1:0	1:2	Δv [e]
v_7	1181	1201(14) A	-20	1131.8	1161.0(5)	-29
		1202(13) B	-21			
v_8	1077	1071(14) A	+6	1044.5	1039.9(9)	+5
		1069(12) B	+8			
v_9	840	954(71) A	-90	785.5	912.0(142)	-127
		950(165) B	-94			

[a]Intensity in km/mol for calculated ones and relative values normalized on the most intense calculated one to 267. [b]rounded $\Delta v = v(H_2O)_2 - v(1:2)$. [c]ref 32. [d]Deduced value from the overtone mode observed at 3138.1 cm^{-1}. [e]rounded $\Delta v = v(MA) - v(1:2)$

5. Conclusion

For the first time the investigation of water molecules complexed with methylamine in solid neon was performed from the far infrared to the near infrared using Fourier transform infrared spectroscopy. From concentration effects and with the help of theoretical results we have identify many vibrational transitions for the MA$_2$, MA-H$_2$O, and MA-(H$_2$O)$_2$ complexes. A vibrational analysis of the MA dimer was performed and the comparison of our experimental results with those obtained in the gas phase shows the very small perturbations induced by the Ne matrix. For the MA-H$_2$O complex, the IR data indicate that the two molecules interact through hydrogen bonding and the water molecule plays the role of the proton donor. The first overtone of the H$_2$O bending mode appears very intense due to a strong Fermi resonance with the O-H bound stretching mode. MP2/aug-cc-pVTZ harmonic level calculations have been performed

to obtain the equilibrium geometries and vibrational spectra of the $(MA)_n$-$(H_2O)_m$ complexes, useful tool to support frequencies attribution and to specify which structures are observable in the Ne matrix.

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.

Supplementary materials

Spectra in the $\nu_4 + \nu_{10}$ combination MA regions, Spectra of the $2\nu_2$ H_2O region, Geometry of 1:2 complex, Harmonic frequencies and Intensities calculated for monomers, dimers, and the most stable 1:1 and 1:2 complexes, and binding energies.

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