The Conformational Landscape of the 1/1 Diacetyl/water Complex Investigated by Infrared Spectroscopy and Ab Initio Calculations

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Abstract

The complexes of diacetyl with water have been studied experimentally by Fourier transform infrared (FTIR) spectroscopy coupled to solid neon matrix and supersonic jet, and anharmonic ab initio calculations. The vibrational analysis of neon matrix spectra over the 100-7500 cm^{-1} infrared range confirms the existence of two nearly isoenergetic one-to-one (1/1) diacetyl-water S_1 and S_2 isomers already evidenced in a previous argon matrix study. A third form (S_3) predicted slightly less stable [D. Dargent et al. , J. Mol. Mod. **21**, 214 (2015)] is not observed. The correct agreement obtained between neon matrix and anharmonic calculated vibrational frequencies is exploited in several cases to derive band assignments for the vibrational modes of a specific isomer. Thereafter, theoretical x_{ij} anharmonic coupling constants are used for the attribution of combination bands and overtones relative to the 1/1 dimer. Finally, the most stable isomer of the one-to-two (1/2) diacetyl-water complex is identified in the OH stretching region of water on the grounds of comparison of experimental and calculated vibrational shifts between water dimer and the three most stable 1/2 isomers.

I - Introduction

It is now well established that non-covalent interactions such as hydrogen bonds involved in small hydrated clusters play an essential role in atmospheric chemistry, astrophysics and also in many biochemical and catalytic processes.[1] Since the pioneering spectroscopic works about the enthalpy and the hydrogen bridges in crystallographic structures such as ice and liquid water,[2,3] many advanced experimental methods were developed in the last thirty years to interpret the bulk water structure and dynamics. In this context, the spectroscopic study of small water clusters produced at very low temperature in nearly isolated conditions proved to be determinant for improving the building of reliable intermolecular potential energy surfaces based on a back and forth procedure between experiment and theory. As a first step toward this objective, we can cite the challenging studies based on jet-cooled far- and near-IR laser and microwave spectroscopy which yielded new insights into the tunneling motions of the water dimer[4-6] and allowed to determine a polarisable water pair potential.[7]

The huge capacity of water to establish hydrogen bonds with the close environment owing to its twice role of hydrogen-bond donor and acceptor would suggest to use a molecular approach based on a step by step increase of the size of hydrates for most studies related to the hydration process of organic species. It has been shown in many previous solid[8] and gas phase studies[9-11] that very different structural architectures of hydrated organic

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M/H$_2$O clusters could be obtained, depending on the nature of the organic molecule M involved.

The objective of the present work is to characterize by a combined experimental and theoretical approach the first step of hydration of an organic molecule M. In a recent paper[12], a six-step methodological approach aiming at characterizing the conformational landscape of mono-hydrated 1/1 M/H$_2$O isomers emphasized the value of topological methods to evidence the most stable isomers.

We selected the small centro-symmetric diacetyl molecule (C$_4$H$_6$O$_2$, DAC) as partner of the hydration process. This atmospheric pollutant[13,14] can be considered as the simplest analogue of a small biologic molecule with two methyl and two carbonyl groups, the latter ones being possibly involved in π-hole-like interactions. Two previous experimental studies were reported about the 1/1 DAC/H$_2$O complex: a Fourier Transform InfraRed (FTIR) study by Mucha and Mielke[15] in argon matrix evidenced two 1/1 isomeric structures from annealing effects realized about intramolecular perturbed DAC and H$_2$O vibrations. With the support of ab initio calculations at the MP2/6-311++G(2d,2p) level, they assigned them to two nearly isoenergetic forms (noted S$_1$ and S$_2$, respectively) for which the water molecule may be zusammen or entgegen with respect to the methyl group attached to the same carbonyl group to which water is linked. More recently, a rotational study of Favero and Caminati[16] by FT microwave spectroscopy nicely confirms that the most stable form is the zusammen (S$_1$) one, complemented by the determination of very weak barriers (around 4 kJ/mol) to the internal rotation of methyl groups.

In the following we reported a series of experiments mainly achieved in solid neon and at a least degree in the supersonic expansion of the Jet-AILES facility on the infrared beamline of the SOLEIL synchrotron. Previous studies realized in our group about the characterization of small hydrated complexes highlighted all the interest to combine gas and solid neon phases spectroscopic methods over the whole infrared range to gain information from intermolecular modes, overtones and combinations, while anharmonic ab initio calculations are necessary to guide the assignment of vibrational signatures related to the conformation of a complex of a given size and in counterpart to validate the choice of the selected theoretical method.[17,18]

The present paper is structured as follows: section II provides experimental details about neon matrix and Jet-AILES set-ups coupled to FTIR spectroscopy and computational details. Section III reports on ab initio, jet-cooled and neon matrix results, mainly on the 1/1 complex and few ones on the 1/2 complex. In section IV, vibrational analyses of low temperature FT spectra are finally discussed with the support of anharmonic vibrational calculations related to the most stable isomers.

II Experimental and computational details
II-1 Helium cryostat device.

Diacetyl + H$_2$O samples were prepared in a closed-cycle helium cryostat (Cryomech PT-405) by slow deposition (10 mmol/h) of about 30 up to 120 mn in double injection (diacetyl/neon and water/neon) on one side of a highly polished, Rh-plated copper mirror maintained at 3 K. The temperature was measured using silicon diodes, and thermal annealing was regulated by a Neocera LTC-II temperature controller.

Molar ratios (X/Ne, X= DAC, H_2O) between 5.10^{-3} to 5 % were prepared in a vacuum line but variable desorption of water from the stainless steel vacuum line precluded accurate concentration measurements for H_2O/Ne. Ne gas was obtained from Air Liquide with a purity of 99.995 % and DAC was obtained from Sigma Aldrich with a purity of 97 % while natural water was degassed in situ.

Absorption spectra in the mid-IR and far-IR ranges were collected on samples through ICS and polyethylene windows respectively mounted on a rotatable flange separating the interferometer vacuum (10^{-3} mbar) from the cryostatic cell vacuum (10^{-7} mbar). Bare mirror backgrounds, recorded from 50 to 8000 cm^{-1} prior to sample deposition were used as references in processing the sample spectra. Infrared absorption spectra of the resulting samples were recorded at 3 K with a Bruker IFS 120 HR spectrometer equipped with suitable combinations of infrared sources (globar, W filament), beamsplitters (composite, KBr/Ge, Si/CaF$_2$), and detectors (InSb, HgCdTe, Si-B bolometer). Matrix spectra of 50-200 coadded interferograms were recorded at a resolution of 0.5 cm^{-1}.

II-2 Jet-AILES apparatus

Jet-cooled spectra have been recorded using the Jet-AILES apparatus already described in detail in previous studies[19] and coupled to the high resolution Bruker IFS 125 FT spectrometer associated with AILES beamline at the synchrotron facility SOLEIL. Briefly, a slit nozzle of 60 mm length and 80 μm width was used to expand the sample into a expansion chamber connected to a set of roots pumps delivering a pumping capacity of about 1800 m^3 h^{-1}. The flow of H_2O vapor was regulated using a Controlled Evaporation Mixer (Bronkhorst CEM model W303A-22-K) supplied by a first flow of argon as buffer gas (Bronkhorst 2-100 l min^{-1} model F-202AV) and liquid water (Bronkhorst mini CORI-FLOW 1000 g h^{-1} model M13). In the absence of a second CEM, DAC vapor was carried from an oven and swept by argon through a second gas line independent from the first one and finally the H_2O/DAC/Ar gas mixture flows through a mildly heated gas line (310 K) upstream of the stagnation reservoir of the slit nozzle.

In our supersonic expansion conditions, backing and residual pressures were typically comprised in the 250-400 Torr and 0.3-0.5 Torr ranges, respectively. Relative concentrations of DAC in the ternary mixture were estimated from relative variations of backing pressures measured with and without DAC. FT spectra were recorded in the OH stretching range of H_2O using the configuration W filament/CaF$_2$/InSb. A band pass filter centered on the 3300-3800 cm^{-1} spectral range was used to maximize the number of photons in the investigated spectral window.

II-3 Computational details

Dunning and coworkers augmented correlation consistent basis set aug-cc-pVDZ (AVDZ) and aug-cc-pVTZ (AVTZ) have been used.[20,21] Second order Møller-Plesset (MP2) calculations have been performed using the Gaussian09 package.[22] All geometry optimizations were performed with « tight » convergence. Anharmonic frequencies have been calculated at MP2/AVTZ level of theory using vibrational perturbation theory (VPT2) approach as implemented in Gaussian09 for 1/1 DAC/H_2O isomers. Due to computational

limitations for 1/2 DAC/H_2O isomers, only MP2/AVDZ harmonic frequencies have been computed.

III Results

III-1 Theoretical results

In a recent theoretical paper about 1/1 DAC/H_2O complex[12] we have shown that the analysis of monomers realized with the combination of topological tools, mainly MESP, ELF and QTAIM allowed identifying favorable interaction sites to predict 1/1 structures. Three isomers have been characterized, namely S_1, S_2 and S_3, and their structures optimized at the MP2/AVTZ level of theory are reported in Figure 1. This topological approach allowed to identify the S_3 isomer which had not previously been reported in the literature. The striking results about the structural, energetic and topological analyses of the three isomers of complex 1/1 DAC/H_2O can be summarized as follows:

- Each 1/1 DAC/H_2O isomer has a cyclic structure involving two complementary interactions.

- In the case of S_1 and S_2, the complex is stabilized by traditional non covalent hydrogen bonds. The water molecule lies within the symmetry plane of DAC and the primary hydrogen bond is formed between one hydrogen atom of water and the oxygen atom of one of the carbonyl groups of DAC. The oxygen from water molecule interacts with the hydrogen of the closest methyl leading to one (S_1) or two (S_2) secondary hydrogen bonds.

- In the case of S_3, the water molecule is perpendicular to symmetry plane of DAC. The oxygen atom of the water molecule is involved in two non covalent bonds: one hydrogen bond with hydrogen atom of a methyl group and one non covalent bond with the oxygen atom of the carbonyl.

- The three isomers are nearly isoenergetic with ZPE-corrected binding energies D_0 at 17.5, 17.5 and 16.2 kJ/mol (MP2/AVTZ level) for S_1, S_2 and S_3, respectively. Caminati et al. observed the S_1 isomer as proved by the excellent agreement (within 0.2%) between their experimental[16] and our calculated ground state rotational constants. Equilibrium and ground state rotational constants and binding energies of the three isomers are reported in Table 1.

In the present work we complete the energetic and topological studies of the complex 1/1 DAC/H_2O by the vibrational properties of the three isomers. First, our computational approach has been validated on H_2O and DAC monomers[12]. Harmonic and anharmonic frequencies have been computed at MP2/AVTZ level of theory for both molecules and are reported in the electronic supplementary material (SM1) with experimental frequencies: from Ref 23 for water (gas phase), from Ref 24 for diacetyl IR active modes (gas phase) and from Ref 25 for IR inactive modes (liquid phase). The computed anharmonic frequencies for both water and DAC molecules are in satisfactory agreement with observed frequencies. The root mean square deviation from experimental values (RMSD) is only 20 cm^{-1} with a maximum deviation of 40 cm^{-1} for the methyl torsions in DAC, which are not supposed to be properly described by VPT2 approach.

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All harmonic and anharmonic frequencies of the three 1/1 DAC/H_2O isomers have been computed at the same level of theory and are reported in supplementary material SM2.

Only the calculated frequencies of main bands observed for 1/1 isomers and corresponding monomers are gathered in Table 2. Frequency shifts with respect to the frequency of monomers are also reported for the three isomers.

The following informations can be deduced from the analysis of Table 2:

- Either in the middle or the far infrared, each isomer has several modes with enough intense frequencies to be observed.
- As expected water vibrational modes are the most affected ones. Bonded (ν_{OHb}) and free (ν_{OHf}) O-H stretching are substantially red shifted (with respect to the H_2O monomer) for the three isomers. Experimental and theoretical frequency shifts between 1/1 and monomer bands (hereafter noted Δ_{exp} and Δ_{th}) will be used to guide our assignments.
- Few DAC vibrational modes in the complexes are slightly affected by the formation of the isomers.
- Overall, S_1 and S_2 have a quite similar vibrational spectrum, while that of S_3 reveals two major differences: the intensity of the ν_{OHb} band is weaker and intermolecular frequencies are smaller than for the other isomers. These data are consistent with the different bonding nature of S_3 compared to the more traditional hydrogen bond within the S_1 and S_2 complexes.

III-2 Jet-cooled data

The bands observed at 3601, 3532, 3397 and 3354 cm^{-1} in the pure H_2O/Ar jet-FT spectrum (Figure 2a) are unambiguously assigned to bonded OH stretching bands of $(H_2O)_{n=2-5}$ while the broad peak at about 3719 cm^{-1} corresponds to the stacking of free OH stretching bands of $(H_2O)_{n=2-5}$.[26] When adding DAC to the H_2O/Ar gas mixture, additional bands are expected to be observed. Only two jet-FT spectra with largely different DAC/H_2O molar flow ratios could be recorded. In order to enhance the formation of the 1/1 dimer, DAC and H_2O gas flows were firstly injected in nearly equimolar proportion (Figure 2b). The DAC/Ar spectrum (not shown in Figure 2) only displayed a weak peak at 3463 cm^{-1} assignable to the first overtone of the antisymmetric CO stretching ($\nu_{C=O\ as}$) mode of DAC monomer. Two new bands are observed at 3575 and 3599 cm^{-1} with respect to the pure H_2O/Ar spectrum. Additional broad and unstructured absorptions are observed when still increasing the water concentration (Figure 2c): two peaks at 3497 and 3560 cm^{-1} (30 cm^{-1} full-width-at-half-maximum) will be further discussed because they could correspond to larger 1/n hydrated heteroclusters.

Unlike in oxirane-H_2O jet-FT spectra previously recorded in the OH stretch range with Jet-AILES[18] no partially resolved rovibrational band contour was observed in the jet spectra of DAC-H_2O. The presence of low barriers to internal rotation for the two methyl groups (determined to be about 4 kJ/mol from rotational spectroscopy) could explain the broadening of bands observed even when recording jet-FT spectra at 0.1 cm^{-1} resolution. In these conditions, the sensitivity limits of the Jet-AILES set-up in its actual configuration only

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allows to provide vibrational gas phase data on small DAC/H_2O clusters in the region of intense OH stretching bands.

III-3 Neon matrix data

The high detectivity of the neon matrix isolation technique over all the infrared range is likely to reveal most of the vibrational transitions of the 1/1 dimer, such as intra- and intermolecular fundamentals. Due to the small neon matrix induced perturbations, the observed vibrational frequencies are expected to be only slightly shifted with respect to gas phase ones. When DAC and H_2O are codeposited in a neon matrix, new bands are observed near H_2O and DAC fundamentals, in the region of intermolecular modes and higher in energy due to combinations and overtones.

III-3-1 The 1/1 complex

H_2O stretching region: 3550-3850 cm^{-1}

Figure 3 displays three neon matrix spectra recorded in the OH stretching mode region, firstly with only DAC (a) and H_2O (b) diluted in Ne, and lastly with a DAC/H_2O/Ne ternary mixture (c) suitable to the formation of dimeric species, as proved by the only absorptions of water monomer and dimer observed in the pure water neon matrix spectrum (Figure 3b). Four additional absorptions at 3568.2, 3594.2, 3726.8 and 3732.7 cm^{-1} are observed in the spectrum (c) with respect to the pure water and DAC spectra. The concentration dependence of these bands varies linearly with respect to either H_2O or DAC, which gives confidence for assigning these four absorptions to a 1/1 dimer. Adsorbed residual water on gas line walls contributes to weak 1/1 absorptions (as shown in Figure 3a) while pure DAC background recordings are wanted.

H_2O bending and DAC CO stretch region: 1580-1750 cm^{-1}

Other absorptions were evidenced in the 1580-1750 cm^{-1} region : one band in the bending mode region of H_2O at 1603.2 cm^{-1} and two strong ones at 1721.6 and 1726.1 cm^{-1} and one weaker at 1734 cm^{-1} near the CO stretch band of DAC monomer at 1731 cm^{-1}. They are all correlated with the four bands observed in the OH stretching region, and consequently belong to species with the same 1/1 stoichiometry.

Intermolecular mode region: 100-600 cm^{-1}

Figure 4 illustrates the complexity to extract intermolecular neon solid data of weakly bound binary hydrated complexes owing to the competition with strong absorptions of small pure water clusters. Three DAC monomer bands (Figure 4a) and eleven bands (some of them in overlap) assigned to water dimer[27], trimer[28] and tetramer[29] (Figure 4b) are observed in the 100-600 cm^{-1} range, likely to mask weak absorptions of DAC-H_2O heteroclusters. On the grounds of concentration effects of the DAC/H_2O/Ne mixture, three intermolecular bands at 115.9, 282.1 and 322.8 cm^{-1} could be assigned to the 1:1 dimer as well as a broad band at 547 cm^{-1} (with a shoulder at 545.5 cm^{-1}) blue-shifted by 7 (5.5) cm^{-1} with respect to a strong DAC monomer band. The vibrational analysis of the intermolecular mode region will be detailed in section IV with the support of combination band analysis and ab initio calculations.

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Combinations and overtones region: 1900-7500 cm^{-1}

In the near-IR region, the same hindrances as in the far-IR one exist, due to the presence of strong water clusters bands few shifted in frequency with respect to binary water complexes. Nevertheless, 11 bands are unambiguously correlated with the 1/1 complex (Table 3). Figure 5 displays neon matrix spectra in the 3900-4200 cm^{-1} range, dense in combination bands involving one ν_{intra} intramolecular mode (OH proton donor stretching band ν_{OHb} or ν_{OHf}) and one ν_{inter} intermolecular mode. Besides the four bands ascribed to a 1/1 complex, one band at 4098 cm^{-1} is found to correlate with a larger complex.

III-3-2 The 1/2 complex

When H_2O concentration is growing, seven new bands between 3500 and 7300 cm^{-1} (3503.7, 3555.8, 4098.9, 5110, 6881, 7111 and 7232.3 cm^{-1}) and possibly one at 375 cm^{-1} are correlated to the relative intensity variations of the water dimer. Figure 6 displays a series of neon matrix spectra from (a) to (c) recorded in the OH stretching region for different relative molar ratios DAC/H_2O with respect to Ne. Two new bands at 3503.7 et 3555.8 cm^{-1} grow in the same time and on both sides of bonded OH stretchings (at 3517.5 and 3529.5 cm^{-1}) of H_2O trimer and at lower frequencies as the 1/1 bands (Figure 6c). The behavior of all these bands argues in favor of a 1/2 complex and will be discussed hereafter.

Table 3 gathers all the vibrational bands of H_2O and DAC monomers, 1/1 and 1/2 complexes observed in the present work from neon matrix experiments and compared to argon matrix data of Mucha and Mielke.[15] As a first step, neon matrix experiments realized throughout the infrared region enabled to identify almost thirty bands to the 1/1 hetero dimer and seven ones probably assignable to the 1/2 hetero trimer. For going further in the assignments, ab initio calculations should be used.

IV Discussion

We exploit now the vibrational analyses carried out for the three calculated nearly isoenergetic S_1, S_2 and S_3 isomers of 1/1 DAC-H_2O. The objective is to fully assign each band observed to the vibrational mode of a specific isomer of the 1/1 complex. In the case of larger complexes, tentative assignments will be proposed with the support of ab initio harmonic calculations realized about the three most stable isomers of the 1/2 complex.[30]

H_2O fundamentals

In the OH stretching region of H_2O, jet-cooled bands at 3575 and 3599 cm^{-1} correspond to the same bands as neon matrix ones at 3568.2 and 3594.2 cm^{-1} taking into account the small redshift (about 6 (1) cm^{-1}) due to the solid neon cage with respect to the gas phase. These bands are clearly assigned to bonded OH (ν_{OHb}) stretching modes of S_1 and S_2 with Δ_{exp} equal to -97 and -71 cm^{-1}, respectively, and Δ_{th} equal to -106 and -72 cm^{-1}. The frequency shift between ν_{OHb} bands of S_1 and S_2 is 24 cm^{-1} (gas), 26 cm^{-1} (solid neon) and 34

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cm^{-1} (MP2/AVTZ anharmonic) which fully validates the mode assignments. With the same arguments, the bands at 3726.8 and 3732.7 cm^{-1} with Δ_{exp} equal to -41 and -35 cm^{-1} are assigned to free OH ones (ν_{OHf}) of both S_1 and S_2. The corresponding Δ_{th} are equal to -35 and -31 cm^{-1}. About the S_3 isomer, the frequency calculated 5 to 9 cm^{-1} higher than for S_1 and S_2 (Table 2) suggests that this OH band could be overlapped by the proton donor ν_3 band of water dimer (Figure 3c).

In the δ bending mode region, one weak band of the 1/1 complex was observed at 1603.2 cm^{-1} surrounded by intense absorptions of H_2O monomer, dimer and trimer. Compared to the largely positive value of Δ_{exp} (+7 cm^{-1}), the Δ_{th} shifts for S_1, S_2 and S_3, respectively equal to 16, 15 and -1 cm^{-1}, do not allow to clearly assign this band to a specific isomer. On the other hand, the presence of two bands very close in frequency at 3181.1 and 3184.8 cm^{-1} well correlate with our observations in the δ fundamental mode region and to very close Δ_{th} shift values for S_1 and S_2. Consequently, these 2 bands are assigned to the (2δ) overtone of S_1 and S_2 with $x_{\delta\delta}$ = -12.7 and -10.8 cm^{-1}, respectively.

DAC fundamentals

Besides the intense antisymmetric $\nu_{C=O\ as}$ CO stretch at 1731 cm^{-1}, several slightly shifted bands were observed on both sides of three weaker intense infrared active DAC modes: the symmetric $\gamma_{CH_3\ s}$ and antisymmetric $\gamma_{CH_3\ as}$ at 950 and 1120.4 cm^{-1} and the $\delta_{CH_3\ s}$ symmetric bend CH$_3$ at 1360.5 cm^{-1}. [24,25] Comparison between values of Δ_{exp} and Δ_{th} (Table 2) generally provides no clear tendency. Theoretical shifts derived from MP2/AVTZ frequency calculations give too large uncertainties which make doubtful any assignment when Δ_{exp} is smaller than 10 cm^{-1}.

In this context, we take advantage of argon matrix spectra recorded by Mucha and Mielke[15] for which two sets of bands were evidenced using annealing effects. The global agreement observed between Δ_{exp} values both measured in neon and argon matrices leads us to assign nine bonded DAC bands observed in neon matrix (cf Table 4).

Consequently, assigning experimental bands to a specific 1/1 isomer on the grounds of comparison with anharmonic ab initio calculations is not relevant to few perturbed DAC fundamentals, even in the favorable case of bonded $\nu_{C=O\ as}$ bands, both intense (> 100 km/mol) and most shifted ones (3-10 cm^{-1}) with respect to DAC monomer. The intermolecular mode region remains to investigate to evidence other fingerprints of the 1/1 isomers.

Intermolecular modes

The bands observed at 115.9, 282.1, 322.8, 545.5 and 547 cm^{-1} and correlated to a 1/1 dimer are compared with anharmonic calculated frequencies. Accounting for the detectivity of the neon matrix set-up, only modes with intensities larger than 35 km/mol are likely to be observed, which represents 14 possible intermolecular signatures including two low frequency modes of DAC ($\delta_{C=O\ as}$ and $\delta_{C-C-C\ as}$) and three of the six intermolecular modes of 1/1 DAC/H_2O isomers ($\gamma_{H_2O\ f}$, $\gamma_{H_2O\ b}$ and δ_{H_2O}). Some of them fall in far-IR windows where absorptions of DAC and of water complexes up to the tetramer are predominant (Figure 4). Among the five bands observed, three intermolecular ones and the bonded $\delta_{C=O\ as}$ DAC one

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are calculated close to neon matrix frequencies : $\gamma_{H_2O\ f}$ (S_2 or S_3) for the 115.9 cm^{-1} band, $\gamma_{H_2O\ b}$ (S_1) and $\gamma_{H_2O\ b}$ (S_2) for the bands at 322.8 and 282.1 cm^{-1}, and $\delta_{C=O\ as}$ (S_1 or S_2) for the 545.5-547 cm^{-1} one. We have the opportunity to validate independently these intermolecular signatures in the near-IR range by the assignment of combinations of the type ($\nu_{intra} + \nu_{inter}$).

Combination modes

In the 3900-4200 cm^{-1} range, four bands respectively at 3914.4, 4013.0, 4054.7 and 4139.6 cm^{-1} are correlated with a 1/1 dimer. Taking into account the calculated x_{ij} anharmonic coupling constants for the three isomers at the MP2/AVTZ level, the numbering of all possible combinations of fundamental frequencies close to these bands provides the following ($\nu_{intra} + \nu_{inter}$) sums: $\nu_{OHb}(S_1) + 322.8$ or $\nu_{OHb}(S_2) + 322.8$ for the 3914 cm^{-1} band, $\nu_{OHf}(S_1) + 282.1$ or $\nu_{OHf}(S_2) + 282.1$ for the 4013 cm^{-1} band, $\nu_{OHf}(S_1) + 322.8$ or $\nu_{OHb}(S_1) + \delta_{H_2O}$ for the 4054.7 cm^{-1} band and $\nu_{OHb}(S_2) + 545.5(547)$ for the 4139.6 cm^{-1} band.

The 3914.4 cm^{-1} band

On the grounds of the strong coupling calculated between ν_{OHb} and γ_{H_2Ob} (x_{ij}(calc) = 32 cm^{-1} for S_1), this band is assigned to the combination mode ν_{OHb} (S_1) + $\gamma_{H_2O\ b}$ (S_1) with x_{ij}(exp) equal to 23.4 cm^{-1} rather than its analogue with S_2 which would give x_{ij} equal to -2.6 cm^{-1}, very different from the calculated one (25 cm^{-1} for S_2). Consequently the 322.8 cm^{-1} band is unambiguously attributed to $\gamma_{H_2O\ b}$ (S_1).

The 4013.0 cm^{-1} band

Using the same arguments, this band is associated to the combination mode ν_{OHf} (S_2) + $\gamma_{H_2O\ b}$ (S_2). Indeed x_{ij}(exp) = -1.8 cm^{-1} is closer to x_{ij}(calc) = 0 for S_2 while for its analogue with S_1, a larger difference is observed between x_{ij}(exp) = +4.2 cm^{-1} and x_{ij}(calc) = -2 cm^{-1}, which enables to assign the 282.1 cm^{-1} band to $\gamma_{H_2O\ b}$ (S_2).

The 4054.7 cm^{-1} band

The only possible assignment for this band is the analogue of the 4013 cm^{-1} band for S_1, namely the combination ν_{OHf} (S_1) + $\gamma_{H_2O\ b}$ (S_1) which would give x_{ij}(exp) = +5.1 cm^{-1}, reasonably close from the x_{ij}(calc) value equal to -2 cm^{-1}.

The 4139.6 cm^{-1} band

The most probable attribution is the combination band $\nu_{OHb}(S_2) + \delta_{C=O\ as}$ but error margins in x_{ij}(calc) values for S_1 and S_2 do not allow for unique assignment of the 545.5 and 547 cm^{-1} bands to the S_1 or S_2 isomer. The x_{ij}(calc) value equal to +1 cm^{-1} for S_2, slightly closer to x_{ij}(exp) = -0.1 cm^{-1} with the 545.5 cm^{-1} band than x_{ij}(exp) = -1.6 cm^{-1} with the 547 cm^{-1} one is not a decisive argument for an isomer assignment.

The assignments of other overtones and combination bands involving H_2O fundamentals is rather straightforward, excepted for the band at 1927.7 cm^{-1} which could not be assigned to the combination $\delta + \gamma_{H_2O\ b}$ of the S_1 isomer because it would imply a very difference between x_{ij}(exp) and x_{ij}(calc) (+1.7 against -14 cm^{-1}).

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In summary, the analysis of neon matrix combination bands gives confidence for assigning the 282.1 and 322.8 cm^{-1} bands to the γ_{H_2Ob} mode of S_2 and S_1 isomers and the 545.5 and 547 cm^{-1} bands to the $\delta_{C=O\,as}$ mode of S_1 or S_2. MP2/AVTZ anharmonic calculations well agree with neon matrix intermolecular frequencies (less than 5 % obs. – calc. difference). About the lowest frequency band at 115.9 cm^{-1}, anharmonic frequencies for the free OH rocking mode ($\gamma_{H_2O\,f}$) of S_2 and S_3 are very close with similar intensities but the predominance of S_1 and S_2 isomers in the whole infrared range highly supports the assignment of the 115.9 cm^{-1} band to $\gamma_{H_2O\,f}$ (S_2) . A balance sheet of our assignments clearly shows that intermolecular modes with intensities smaller than 80 km/mol could not be detected with our neon matrix set-up, excepted for the broad band observed around 547 cm^{-1} (main component) likely composed of two $\delta_{C=O\,as}$ bands very close in frequency of S_1 and S_2 (calculated at 545 and 542 cm^{-1} with intensities around 40 km/mol). However, there exists a large discrepancy between calculated and experimental intensities for this band, the most intense one observed for the 1/1 complex. Other intermolecular modes could not be detected due to the probable overlap of the $\gamma_{H_2O\,f}$ (S_1) mode by rotational bands of water monomer, and of the $\gamma_{H_2O\,f}$ (S_2) mode by the acceptor wag mode of the water dimer at 122.6 cm^{-1}.[27] Table 4 gathers the intramolecular (fundamentals, combinations and two-quanta transitions) and intermolecular modes of mainly two isomers of the 1/1 dimer derived from the assignments of neon (or argon[15]) matrix spectra and compared to anharmonic MP2/AVTZ ab initio calculations. Table 5 reports the anharmonic coupling constants derived from neon matrix experiments compared to corresponding MP2/AVTZ calculated ones.

The vibrational analysis of neon matrix spectra enabled to evidence several vibrational signatures of the S_1 and S_2 isomers of the 1/1 dimer. No evidence of the S_3 isomer could be proved in the whole infrared region. Overlapping with water clusters bands is always possible but we should expect that the less stable S_3 isomer bands are more difficult to observe experimentally than those of S_1 or S_2 isomers. Previous experimental studies have focused either on one (S_1 for the microwave study[16]) or two isomeric forms (S_1 and S_2 for the argon matrix study[15]) while three nearly isoenergetic forms were calculated.[30]

Nevertheless, our neon matrix set-up enables to probe the whole infrared region, particularly the far-infrared region where significant frequency differences are often observed between the intermolecular modes of isomeric forms. On the other hand, bonded intramolecular frequencies are either too weakly shifted with respect to the free ones, or overlapped by water clusters. Due to the comparable binding energy D_0 of water dimer[31] and trimer[32] (13 and 44 kJ/mol, respectively) with respect to those of most stable isomers of 1/1 and 1/2 (17 and 53 kJ/mol, respectively), a delicate balance should be found to maximize the absorption signals of hetero water clusters containing DAC with respect to those of pure water ones.

About the microwave study reported by Favero and Caminati[16] it would be interesting to bring a definite answer about the presence of other isomers than S_1 in the jet-cooled He seeded pulsed expansion of very diluted DAC/H$_2$O mixtures. It is difficult to anticipate a priori the stabilization of slightly less stable isomers, by considering the quick relaxation in axisymmetric supersonic expansions toward very low rotational temperatures (around 1 K). The rather weakly relaxing effect of helium with respect to argon is rather favorable to

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stabilize also less stable isomers with small differences of binding energies with respect to the most stable one, unless that these conformers are separated by low interconversion barriers.[33]

The 1/2 complex

Among the neon matrix bands assigned to the 1/2 complex, we are focusing on the bands at 3503.7 and 3555.8 cm^{-1} assigned to bonded OH stretching modes more red shifted than the 1/1 dimer, in agreement with the increase of the vibrational red shift depending on the size of pure water clusters.[17,18] The frequency positions of neon matrix bands are rather close of jet-cooled 1/n bands estimated at about 3497 and 3560 cm^{-1} in the spectrum rich in water (Figure 2c), and should correspond to OH stretching bands of the 1/2 complex. The three most stable isomers noted $\pi\_like\_(H_2O)_2\_side\_P2$, $\pi\_like\_(H_2O)_2\_side\_P1$ and $P1\_(H_2O)_2$ in a recent paper[30] will be designated hereafter by T1, T2 and T3. The bonded OH stretching ν_{OHb1} mode of the water molecule in interaction with the carbonyl group should be distinguished from the ν_{OHb2} mode in interaction with the oxygen atom of the second water molecule. We are searching now to attribute these bands to a specific isomer with the support of ab initio calculations. Experimental and harmonic MP2/AVDZ[30] calculated frequencies relative to the OH stretching modes of the most stable isomers of the 1/2 complex and water dimer are gathered in Table 6. Structure optimizations revealed that most stable 1/2 isomers are predominantly water dimers interacting with the diacetyl molecule.[30] Consequently, we compared experimental (Δ_{exp}) and theoretical (Δ_{th1}, Δ_{th2} and Δ_{th3}) frequency differences between the three 1/2 isomers and the water dimer, The Δ_{exp} values for ν_{OHb2} and ν_{OHb1}, respectively equal to -86 and -34 cm^{-1}, are largely closer to Δ_{th1} than Δ_{th3}, and at a least degree than Δ_{th2}On these grounds, we tentatively assign these two experimental bands to the T1 isomer. However, we cannot fully exclude the T2 isomer because MP2 calculations tend to overestimate vibrational shifts (by about 10 % for the 1/1 isomers). The other 1/2 bands observed at 4098.9, 5110, 6881 and 7232.3 cm^{-1} are attributed to (ν_{OHf} + 375), (ν_{OHb2} + δ), ($2\nu_{OHb2}$) and (ν_{OHb2} + ν_{OHf}) combination bands, respectively.

Conclusion

In the present work, Fourier transform spectra of diacetyl-water complexes have been recorded in neon matrix spectra over the whole infrared range, and in a supersonic jet in the OH stretching region of H_2O, to find vibrational signatures aiming to characterize the conformational landscape of binary and ternary hydrated complexes.

About the 1/1 dimer, vibrational analyses of FTIR neon matrix spectra have been realized with the support of high level anharmonic MP2/AVTZ calculations to guide our attributions:

- Several vibrational signatures of the two most stable isomers S_1 and S_2 have been unambiguously identified from the fundamentals, combinations and overtones (9 for S_1, 9 for S_2).
- No vibrational signature could be proved for the less stable S_3 isomer even in the intermolecular mode region. Two possible reasons could be explain this result : (i) the expected lower population of the less stable S_3 isomer makes more probable the overlapping of S_3 bands by small water clusters and DAC monomer bands, (ii) the

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neon matrix technique reached its limits in the case of DAC-H_2O system to properly discriminate vibrational bands of 1/1 heterodimers likely to be masked by intense bands of water and DAC monomers in the mid-IR range, or of pure water dimer and trimer in the far-IR range.

The present solid neon study coupled to FT spectroscopy also reveals the difficulty to characterize hetero hydrated clusters beyond dimer because of recurrent overlapping bands and competition with water clusters. However, in the H_2O stretching region where large red shifts enable to discriminate between water trimer and the 1/2 complex, two bonded OH bands could be tentatively assigned to the most stable isomer noted T1 on the grounds of relative vibrational shifts between water dimer and the three most stable 1/2 complexes, both characterized by the presence of a water dimer interacting with the diacetyl molecule and large cooperative effects in terms of interaction energies.[30]

As a perspective, high resolution gas phase rovibrational spectroscopy coupled to supersonic expansions recently proved its capacity to untangle the conformational landscape of weakly bound complexes or to discriminate between small sized clusters.[34,35] In a near future, the present neon matrix study could be exploited to target a spectral region favorable to the searching of hetero hydrated clusters using the tunable IR laser spectrometer coupled to a pulsed supersonic jet recently developed in our group.
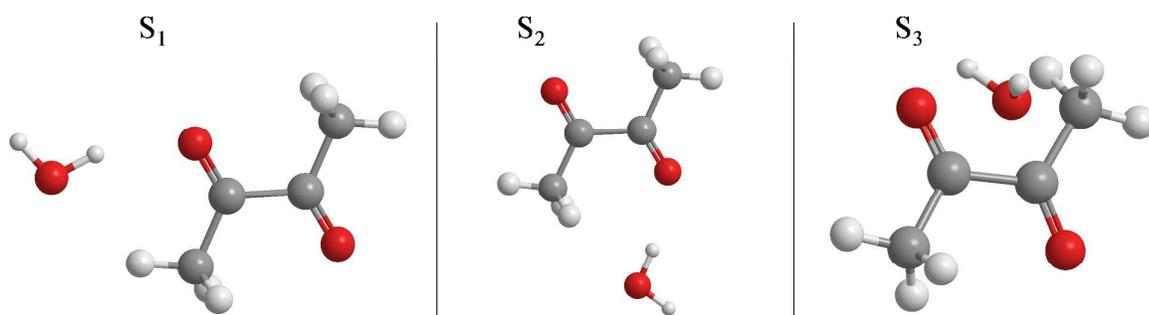
Figure 1: The three isomers for the 1/1 complex optimized at MP2/AVTZ level of theory.
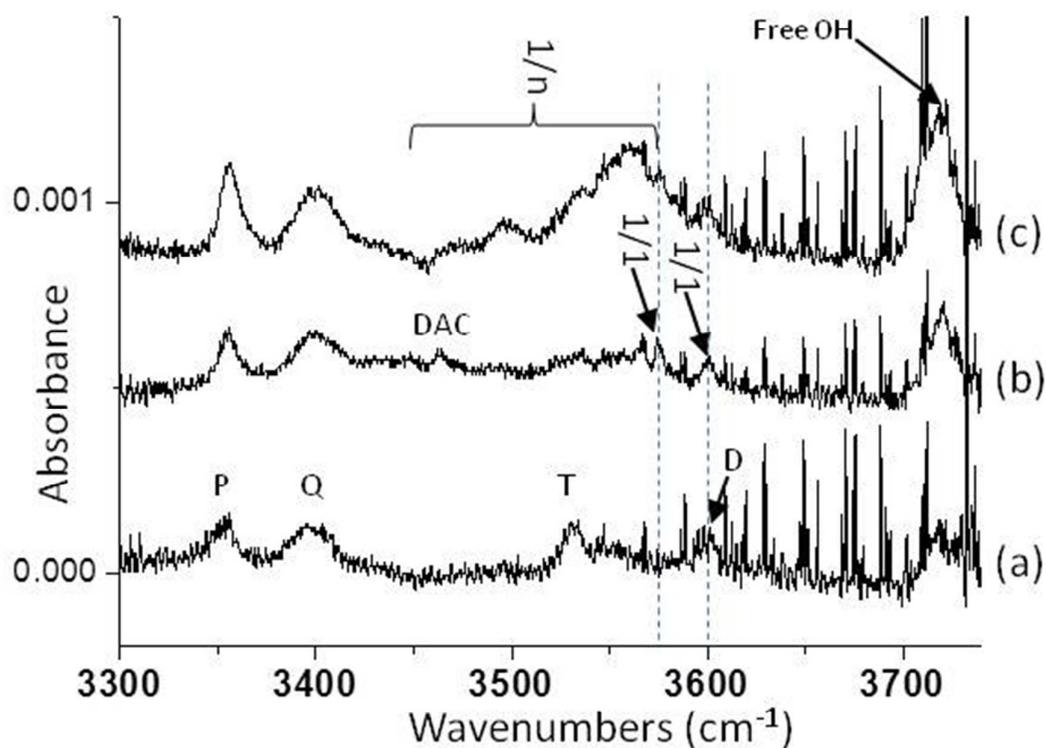
Figure 2: Jet-AILES FTIR spectrum in the OH bonded and free stretching region of water containing complexes recorded at 0.5 cm^{-1} resolution for different dilutions of the ternary mixture DAC/H$_2$O/Ar: (a) 0/8/1000, (b) 8/8/1000, (c) 8/16/1000. The notation D stands for water dimer, T for water trimer, Q for water tetramer and P for water pentamer.

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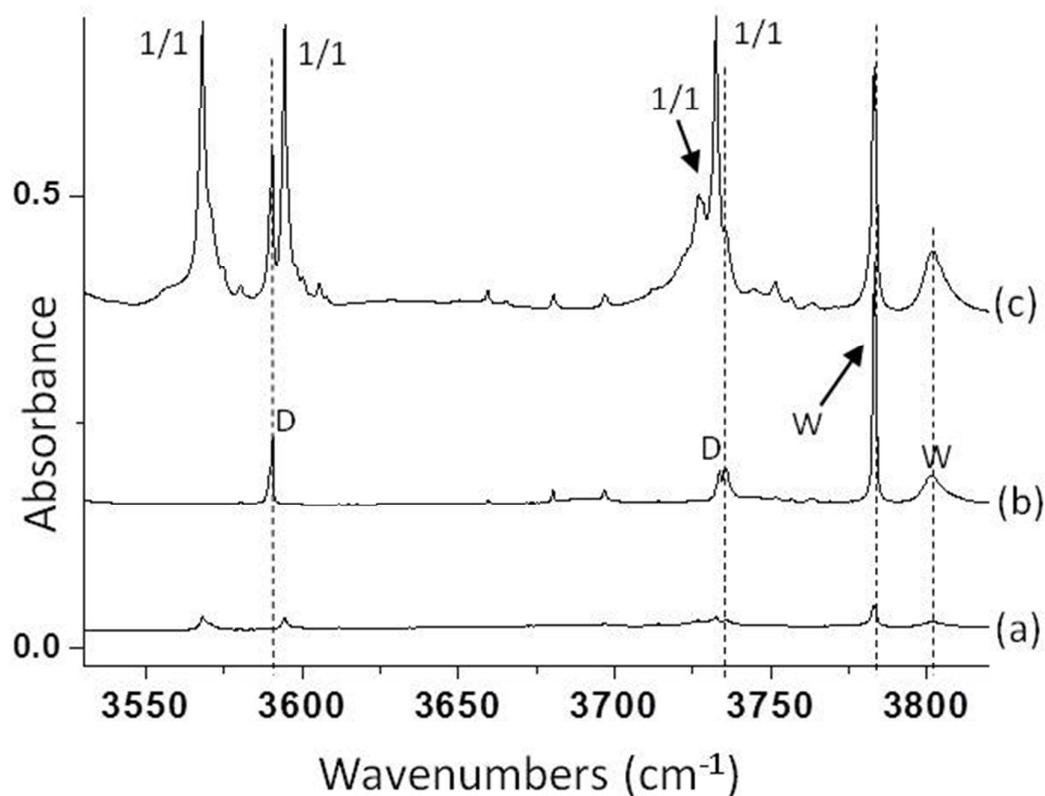
Figure 3: Neon matrix spectra after deposition at 3.5 K recorded in the OH stretching region of H$_2$O monomer, H$_2$O and 1/1 dimers for different dilutions of the ternary mixture DAC/H$_2$O/Ne: (a) 2/0/1000, (b) 0/1/16000, (c) 1/0.025/1000. The notation W stands for H$_2$O monomer and D for water dimer.
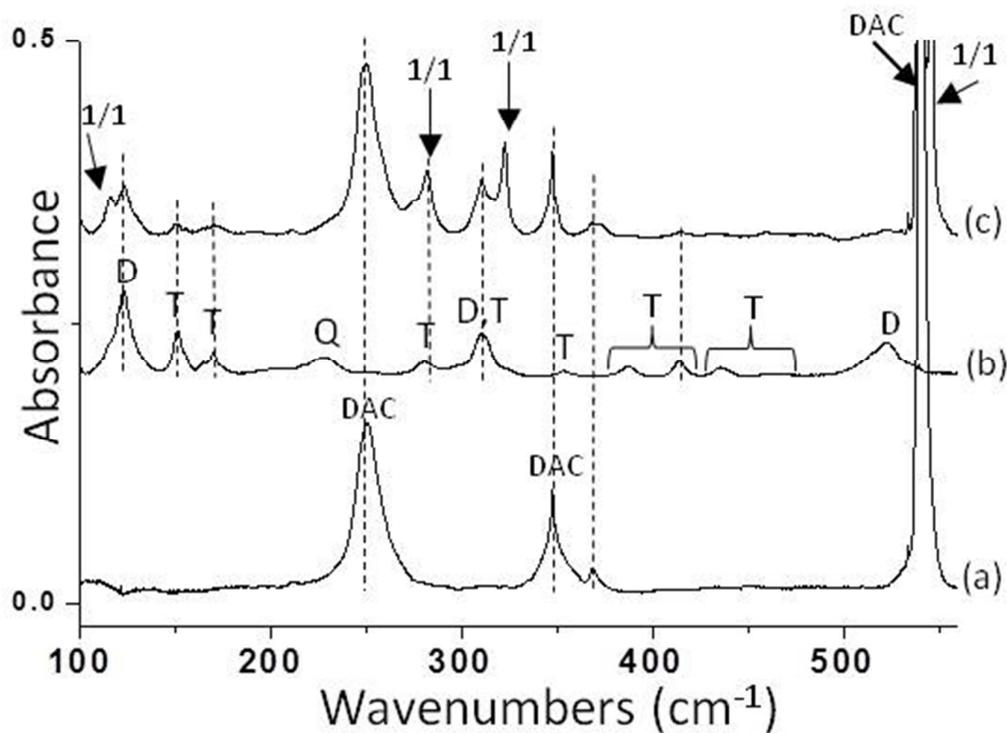
Figure 4: Neon matrix spectra after deposition at 3.5 K recorded in the intermolecular mode region of H_2O dimer and trimer and 1/1 dimers for different dilutions of the ternary mixture DAC/H_2O/Ne: (a) 6/0/1000, (b) 0/1/1000, (c) 6/1/1000. The notation D stands for H_2O dimer, T for H_2O trimer, Q for H_2O tetramer. Neon matrix assignments for water dimer and trimer in the intermolecular mode region come from Perchard et al.,[27,28] and those for water tetramer from Ceponkus et al.[29]
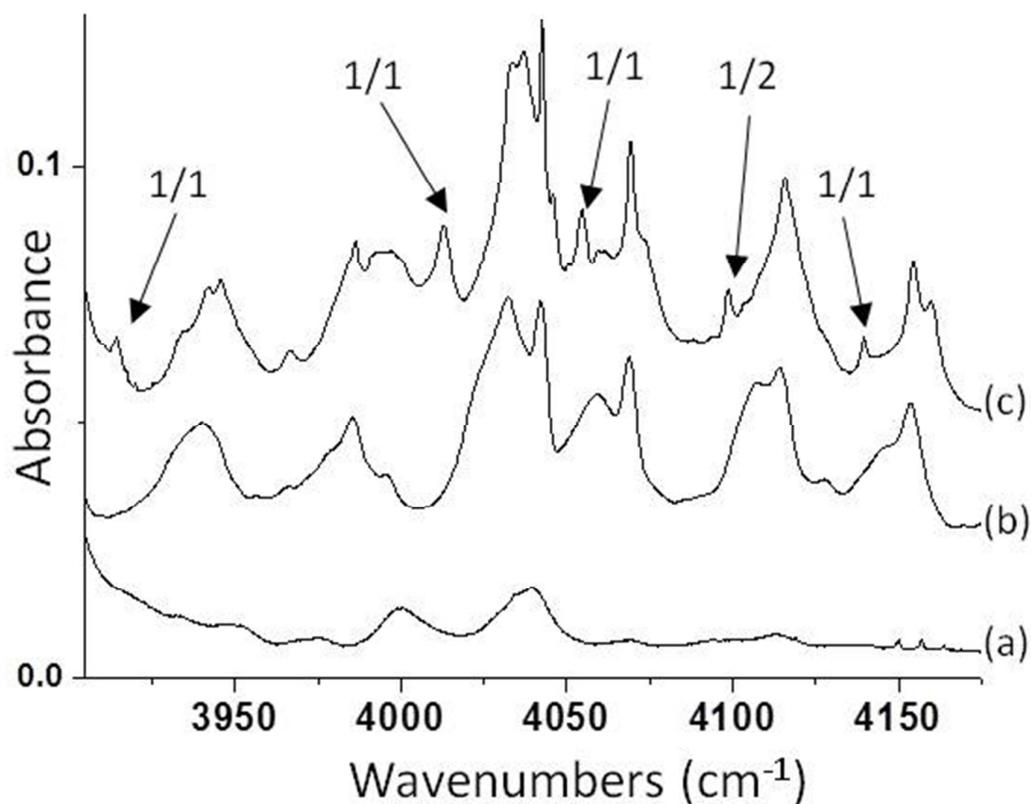
Figure 5: Neon matrix spectra after deposition at 3.5 K recorded in the 3900-4200 cm^{-1} region of $\nu(OH) + \nu_{inter}$ combinations of small H_2O and DAC-H_2O clusters for different dilutions of the ternary mixture DAC/H_2O/Ne: (a) 6/0/1000, (b) 0/2/1000, (c) 3/3/1000.
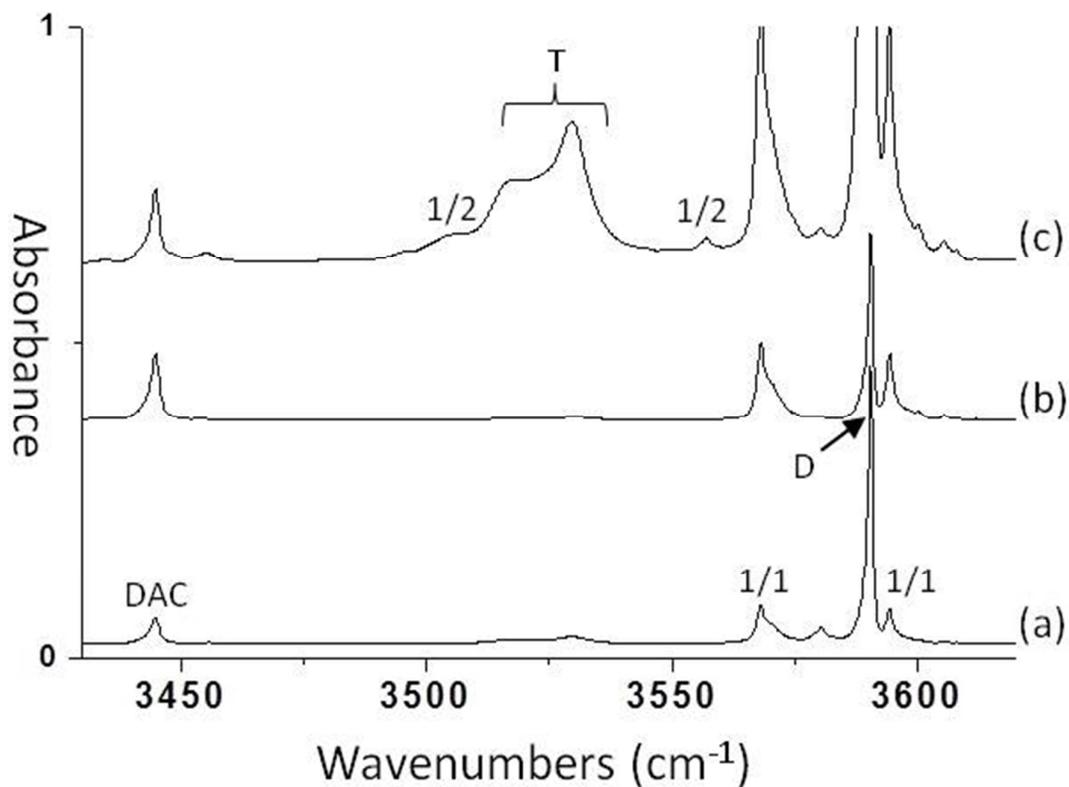
Figure 6: Neon matrix spectra after deposition at 3.5 K recorded in the OH stretching region of small H_2O cluster, 1/1 and 1/2 complexes for different dilutions of the ternary mixture $DAC/H_2O/Ne$: (a) 0.17/0.3/1000, (b) 0.5/0.3/1000, (c) 0.5/1/1000. The presence of the band at 3580 cm^{-1}, assigned to the N_2-$(H_2O)_2$ trimer, is due to small leaks of N_2 (tens of ppm) in the gas line.

	S_1	S_2	S_3
A_e	0.16093	0.11351	0.08234
A_0	0.15938 *(0.159688)*	0.11219	0.08152
B_e	0.04154	0.05226	0.07044
B_0	0.04046 *(0.040464)*	0.05067	0.07051
C_e	0.03342	0.03625	0.05473
C_0	0.03272 *(0.032735)*	0.03562	0.05526
D_e	24.7	24.8	21.8
D_0	17.5	17.5	16.2

Table 1 : Equilibrium (X_e) and ground state (X_0) rotational parameters (cm^{-1}) and binding energies ($kJ.mol^{-1}$) for 1/1 isomers. MP2/AVTZ *(Experimental)*.[16]

			ν			$\Delta\nu$		
		Monomers	S_1	S_2	S_3	S_1	S_2	S_3
H_2O	ν_{OHf}	3768	3733 (135)	3737 (152)	3742 (90)	-35	-31	-26
	ν_{OHb}	3654	3548 (334)	3582 (298)	3624 (10)	-106	-72	-30
	δ	1578	1594 (90)	1593 (62)	1577 (133)	16	15	-1
Diacetyl	$\nu_{C=O\ as}$	1703	1703 (98)	1702 (161)	1706 (151)	0	-1	3
	$\nu_{C=O\ s}$	1696	1692 (67)	1697 (40)	1699 (6)	-4	1	3
	$\delta_{CH_3\ s}$	1353	1358 (58)	1361 (60)	1350 (63)	5	8	-3
	$\gamma_{CH_3\ as}$	1116	1126 (70)	1125 (60)	1121 (63)	10	9	5
	$\gamma_{CH_3\ s}$	943	945 (5)	946 (4)	947 (8)	2	3	4
	$\delta_{C=O\ as}$	535	545 (37)	542 (39)	537 (42)	10	7	2
	$\delta_{C-C-C\ as}$	253	247 (50)	236 (15)	231 (35)	-6	-17	-22
Inter.	δ_{H_2O}		479 (60)	407 (60)	231 (46)			
	$\gamma_{H_2O\ b}$		315 (129)	297 (143)	208 (72)			
	$\gamma_{H_2O\ f}$		14 (118)	140 (110)	138 (113)			

Table 2: Calculated frequencies (cm^{-1}) of the main bands observed for the isomers of 1/1 complex and the corresponding frequencies of monomers. The shifts from monomer frequencies ($\Delta\nu$) and anharmonic MP2/AVTZ frequencies (harmonic intensities in parenthesis in $km.mol^{-1}$) are also reported.

Neon matrix	Argon matrix[a]

Monomer	1/1	1/2	Monomer	1/1
	115.9 *(100)*	375		
	282.1 *(190)*			
	322.8 *(130)*			
540	545.5, 547 *(250)*			
904.6, 907.6	-		900.5, 903.4	906.0, 910.0
950	946.4, 952		946.8	943.6, 948.8
1120.4	1123.8, 1126.7		1115	1118.7, 1122.4, 1126.0
1360.5	1361.5, 1363.3		1355.9	1356.9, 1358.5
1596	1603.2 *(30)*		1590	1606.0
1731	1721.6, 1726.1, 1734		1723.1	1715.8, 1719.8, 1728.8
	1927.7 *(1)*			
	3181.1, 3184.8 *(3)*			
3665	3568.2 *(100)* 3594.2 *(75)*	3503.7	3638.0	3553.8
		3555.8		3582.8
3759	3726.8 *(75)* 3732.7 *(55)*		3735.0	3708.3
	3914.4 *(0.03)*			
	4013.0 *(0.3)*	4098.9		
	4054.7 *(0.1)*			
	4139.6 *(0.03)*			
	5163.9 *(2)*	5110		
	5189.3 *(1.5)*			
	6957 *(0.04)* 7020.4 *(0.03)*	6881		
		7111		
		7232.3		

[a]Ref [15].

Table 3 : Observed frequencies of H_2O and DAC monomers, 1/1 and 1/2 complexes in the present neon matrix experiments compared to those obtained in the previous argon matrix study of Mucha and Mielke.[15] Experimental intensities of most 1/1 bands, referenced with respect to the intensity of the 3568.2 cm^{-1} band set to 100, are reported between parentheses.

	Neon matrix		Ab initio					
	S_1	S_2	S_1		S_2		S_3	
Fundamentals								
$\gamma_{H_2O\,f}$		115.9^b	$<102^*$	(118)	140	(110)	138	(113)
$\gamma_{H_2O\,b}$	322.8	282.1	315	(129)	297	(143)	208	(72)
$\delta_{C=O\,as}$	545.5 / 547		545	(37)	542	(39)	537	(42)
$\gamma_{CH_3\,s}$	952^a	946.4^a	945	(5)	946	(4)	947	(8)
$\gamma_{CH_3\,as}$	1126.7^a	1123.8^a	1126	(70)	1125	(60)	1121	(63)
$\delta_{CH_3\,s}$	1363.3^a	1361.5^a	1358	(58)	1361	(60)	1350	(63)
δ	1603.2	1603.2	1594	(90)	1593	(62)	1577	(133)
$\nu_{C=O\,as}$	1721.6^a	1726.1^a	1703	(98)	1702	(161)	1706	(151)
ν_{OHb}	3568.2	3594.2	3548	(334)	3582	(298)	3624	(10)
ν_{OHf}	3726.8	3732.7	3733	(135)	3737	(152)	3742	(90)
Combination modes								
$\nu_{OHb}+ \gamma_{H_2O\,b}$	3914.4							
$\nu_{OHf} + \gamma_{H_2O\,b}$	4054.7	4013.0						
$\nu_{OHb} + \delta_{C=O\,as}$	4139.6							
$\delta + \nu_{OHb}$	5163.9	5189.3						
Two quanta modes								
2δ	3181.1	3184.8						
$2\nu_{OHb}$	6956.8	7020.4						

[a] Assignments from annealing effects in argon matrix spectra[15]

[b] The assignment of the band at 115.9 cm^{-1} to the S_3 isomer is not fully discarded (cf text)

Table 4: Attribution of vibrational bands (fundamentals, combination modes and two-quanta transitions) of the S_1 and S_2 isomers of the 1/1 dimer observed in neon matrix experiments in the far- mid- and near- infrared regions, compared to the anharmonic MP2/AVTZ frequencies. All wavenumbers are expressed in cm^{-1}. Harmonic infrared intensities are reported in parentheses in km/mol. The notation * corresponds to the harmonic frequency of the γ_{H_2Of} mode for the S_1 isomer.

		δ		ν_{OHb}		ν_{OHf}
		S_1	S_2	S_1	S_2	S_2
$\gamma_{H_2O\,b}$	S_1			23.4 [32]		
	S_2					-1.8 [0]
$\delta_{C=O\,as}$	S_2				-1.6/-0.1 [1]	
δ	S_1	-12.7 [-18.3]		-7.3 [-12.0]		
	S_2		-10.8 [-17.6]		-8.2 [-13.9]	
ν_{OHb}	S_1			-89.6 [-81.5]		
	S_2				-84.1 [-72.2]	

Table 5: Anharmonic coupling constants (cm^{-1}) for the S_1 and S_2 isomers of the 1/1 dimer derived from neon matrix experiments. Calculated constants from VPT2 calculation at MP2/AVTZ level of theory are reported in square brackets.

| | (H$_2$O)$_2$ | MP2/AVDZ | | | | | | Neon matrix | | |
| | | T1 | | T2 | | T3 | | (H$_2$O)$_2$ | 1/2 | |
	ω(I_IR)	ω(I_IR)	Δ_{th1}	ω(I_IR)	Δ_{th2}	ω(I_IR)	Δ_{th3}	ν	ν	Δ_{exp}
ν_{OHb2}	3704 (280)	3616 (184)	-88	3606 (207)	-98	3599 (439)	-105	3590	3504	-86
ν_{OHb1}	-	3675 (328)	-29	3666 (345)	-38	3647 (509)	-57	-	3556	-34
D$_0$		53.4		52.9		42.6				

Table 6: Calculated harmonic MP2/AVDZ and neon matrix vibrational frequencies (cm^{-1}) of the OH stretching modes for the three most stable isomers of the 1/2 complex. Harmonic infrared intensities are reported in parentheses in km/mol. The notation Δ corresponds to the experimental or calculated vibrational shift (cm^{-1}) of the two intramolecular modes of the three isomers perturbed with respect to the pure water dimer. MP2/AVDZ binding energies D$_0$ are also reported (kJ.mol^{-1})

SM1 : Calculated and experimental vibrational properties of water and diacetyl monomer. Harmonic frequencies, [anharmonic frequencies], (harmonic IR intensities), *experimental frequencies*. Wavenumbers in cm^{-1}, intensities in km.mol^{-1}

	Vibrational mode (symmetry)	Ab initio MP2/AVTZ			Experiment IR Gaz[a]	Ne Matrix[a]	Raman Liquid[a]
H$_2$O	ν_{OH} as (b2)	3948	[3768]	(75)	3756	3759	
	ν_{OH} s (a1)	3822	[3654]	(6)	3657	3665	
	δ (a1)	1628	[1578]	(72)	1595	1596	
Diacetyl	νCH$_3$ as (b$_u$)	3209	[3065]	(7)	3024	3037	
	νCH$_3$ as (a$_g$)	3209	[3065]	(0)			3016
	νCH$_3$ as (b$_g$)	3164	[3019]	(0)			2978
	νCH$_3$ as (a$_u$)	3163	[3019]	(2)	2979	2995	
	νCH$_3$ s (b$_u$)	3083	[2969]	(1)	2945	2947	
	νCH$_3$ s (a$_g$)	3083	[2969]	(0)			2928
	νC=O as (b$_u$)	1736	[1703]	(166)	1729	1731	
	νC=O s (a$_g$)	1734	[1696]	(0)			1720
	δCH$_3$ as (b$_g$)	1485	[1431]	(0)			1431
	δCH$_3$ as (a$_u$)	1480	[1428]	(20)	1426	1433	
	δCH$_3$ as (b$_u$)	1473	[1429]	(31)	1424	1426	
	δCH$_3$ as (a$_g$)	1473	[1427]	(0)			1424
	δCH$_3$ s (a$_g$)	1408	[1365]	(0)			1364
	δCH$_3$ s (b$_u$)	1395	[1353]	(58)	1360	1358	
	νC-C (ag)	1309	[1277]	(0)			1275
	γCH$_3$ (b$_u$)	1147	[1120]	(67)	1116	1121	
	γCH$_3$ (b$_g$)	1073	[1046]	(0)			1050
	γCH$_3$ (a$_g$)	1018	[998]	(0)			1005
	γCH$_3$ (a$_u$)	968	[943]	(4)	950	950	
	νC-CH$_3$ as (b$_u$)	927	[908]	(20)	912	907	
	νC-CH$_3$ s (a$_g$)	704	[686]	(0)			685
	γC =O s (b$_g$)	619	[609]	(0)			608
	δC=O as (b$_u$)	539	[535]	(39)	540	540	
	δC=O s (a$_g$)	526	[521]	(0)			537
	δC-C-C s (a$_g$)	363	[363]	(0)			369
	γC =O as (a$_u$)	345	[348]	(6)	340	348	
	δC-C-C as (b$_u$)	239	[253]	(16)	249	251	
	τCH$_3$ s (b$_g$)	128	[121]	(0)			
	τCH$_3$ as (a$_u$)	127	[121]	(0)	112		
	τC-C (a$_u$)	55	[47]	(11)	48		

ν : stretching　δ : bending　γ : rocking　τ : torsion　s: symmetric　as: antisymmetric

Experimental data from Refs 23 and 24 (a), this work (b) and Ref 25 (c)

SM2 : Calculated vibrational properties of the three isomers of 1/1 complex at MP2/AVTZ level of theory. Harmonic frequencies, [anharmonic frequencies], (harmonic IR intensities). Wavenumbers in cm^{-1}, intensities in km.mol^{-1}

		S1			S2			S3		
H$_2$O	ν_{OH} as (b2)	3911	[3733]	(135)	3911	[3737]	(152	3924	[3742]	(90)
	ν_{OH} s (a1)	3701	[3548]	(334)	3731	[3582]	(298)	3792	[3624]	(10)
	δ (a1)	1645	[1594]	(90)	1646	[1593]	(62)	1620	[1577]	(133)
Diacetyl	νCH$_3$ as (b$_u$)	3211	[3071]	(2)	3211	[3075]	(4)	3208	[3063]	(7)
	νCH$_3$ as (a$_g$)	3209	[3066]	(4)	3209	[3071]	(3)	3207	[3064]	(0)
	νCH$_3$ as (b$_g$)	3163	[3021]	(1)	3164	[3026]	(0)	3168	[3027]	(0)
	νCH$_3$ as (a$_u$)	3160	[3018]	(0)	3160	[3021]	(0)	3166	[3022]	(1)
	νCH$_3$ s (b$_u$)	3083	[2970]	(0)	3084	[2972]	(0)	3083	[2970]	(1)
	νCH$_3$ s (a$_g$)	3081	[2970]	(1)	3083	[2969]	(2)	3083	[2973]	(2)
	νC=O as (b$_u$)	1736	[1703]	(98)	1735	[1702]	(161)	1737	[1706]	(151)
	νC=O s (a$_g$)	1730	[1692]	(67)	1732	[1697]	(40)	1735	[1699]	(6)
	δCH$_3$ as (b$_g$)	1486	[1432]	(0)	1487	[1434]	(4)	1489	[1431]	(9)
	δCH$_3$ as (a$_u$)	1481	[1430]	(19)	1480	[1430]	(17)	1482	[1431]	(6)
	δCH$_3$ as (b$_u$)	1475	[1430]	(19)	1472	[1432]	(44)	1477	[1434]	(19)
	δCH$_3$ as (a$_g$)	1474	[1432]	(6)	1470	[1431]	(4)	1472	[1428]	(15)
	δCH$_3$ s (a$_g$)	1412	[1372]	(5)	1410	[1373]	(0)	1406	[1365]	(1)
	δCH$_3$ s (b$_u$)	1398	[1358]	(58)	1396	[1361]	(60)	1391	[1350]	(63)
	νC-C (ag)	1315	[1280]	(0)	1311	[1281]	(0)	1310	[1279]	(0)
	γCH$_3$ (b$_u$)	1154	[1126]	(70)	1152	[1125]	(60)	1150	[1121]	(63)
	γCH$_3$ (b$_g$)	1075	[1047]	(0)	1071	[1047]	(0)	1074	[1046]	(0)
	γCH$_3$ (a$_g$)	1023	[1002]	(0)	1023	[1002]	(0)	1021	[999]	(0)
	γCH$_3$ (a$_u$)	971	[945]	(5)	965	[946]	(4)	970	[947]	(8)
	νC-CH$_3$ as (b$_u$)	931	[911]	(18)	933	[914]	(16)	930	[911]	(18)
	νC-CH$_3$ s (a$_g$)	709	[707]	(0)	706	[693]	(0)	706	[690]	(0)
	γC =O s (b$_g$)	620	[610]	(0)	619	[615]	(1)	617	[610]	(0)
	δC=O as (b$_u$)	548	[545]	(37)	546	[542]	(39)	541	[537]	(42)
	δC=O s (a$_g$)	532	[527]	(1)	526	[522]	(1)	529	[523]	(0)
	δC-C-C s (a$_g$)	372	[364]	(8)	369	[390]	(0)	370	[368]	(1)
	γC =O as (a$_u$)	348	[348]	(2)	347	[352]	(5)	348	[333]	(6)
	δC-C-C as (b$_u$)	255	[247]	(50)	244	[236]	(15)	246	[231]	(35)
	τCH$_3$ s (b$_g$)	130	[138]	(0)	176	[188]	(14)	145	[117]	(1)
	τCH$_3$ as (a$_u$)	123	[87]	(10)	129	[138]	(0)	122	[122]	(2)
	τC-C (a$_u$)	51	[45]	(1)	57	[68]	(3)	45	[51]	(6)
Intermolecular	δH$_2$O	542	[479]	(60)	525	[407]	(60)	309	[231]	(46)
	γH$_2$Ob	370	[315]	(129)	326	[297]	(143)	238	[208]	(72)
	νinter	138	[119]	(0)	143	[130]	(3)	139	[122]	(29)
	γH$_2$Of	102	[14]	(118)	153	[140]	(110)	159	[138]	(113)
	δDAC	81	[54]	(7)	87	[74]	(5)	85	[88]	(18)
	γDAC	30	[25]	(3)	8	[108]	(1)	26	[1]	(4)

ν: stretching δ : bending γ : rocking τ : torsion   s: symmetric   as: antisymmetric

For clarity, the nomenclature used for the water and DAC vibration modes in the complexes is that of the isolated monomers, although obviously their symmetry no longer exists in the complexes.

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