Clusters of atmospheric relevance: H₂O/HCl/HNO₃. Prediction of IR & MW spectra†

Pedro C. Gómez,^{*a} Oscar Gálvez,^b Rafael G. Mosteo,^c Cristina Puzzarini^d and R. Escribano^{*b}

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Theoretical calculations at the B3LYP/aug-cc-pVQZ level are performed on ternary clusters of water, hydrogen chloride and nitric acid to predict their IR and MW spectra. The main IR spectral features and their changes in a set of 15 selected clusters are analyzed in terms of the different hydrogen bonding characteristics of the aggregates. The formation of these clusters in laboratory experiments and their possible identification based on their infrared and microwave spectral properties are discussed. Based on a calculation of the Gibbs free-energy of formation of the clusters from their monomers, the population distribution of the molecules at atmospherically relevant temperatures is evaluated, and the IR spectra of the composed mixture are predicted. The variations of specific spectral features with temperature are assessed, and the possible observation of these features is proposed as a means to detect the existence of these clusters, as well as an indication of the temperature of the corresponding atmospheric sample.

1. Introduction

Water, hydrogen chloride and nitric acid are present in our atmosphere in varying amounts and physical conditions, but all three are key species for many of the physical and chemical processes that take place in it. These molecules can interact in a large variety of ways, forming bonds in which each one of them could act as donor or acceptor for H atoms, thus allowing clusters to be formed of all three species together. In previous work (ref. 1, hereafter referred to as GGE), a comprehensive theoretical study was presented of the possible associations of these molecules to yield 3-membered clusters. It was concluded that, of the whole list of ~60 possible aggregates, only 15 of them were predicted to be true minima in their energy surface, some of them also being stable, in terms of the Gibbs free energy of formation at stratospheric temperatures. The reader is referred to the GGE¹ manuscript for a full description of these calculations.

However, considering stratospheric phenomena, these ternary species will not certainly be the final step in the aggregation process of the available molecules, nor are they the only type of clusters likely to be involved. Thus, the

characterization of all possible atmospheric constituents is a task of obvious importance. In particular, establishing a relationship between the structure and shape of these aggregates and their corresponding vibrational spectra provides an appropriate way to analyze the evolution of the aggregation as a function of time or varying atmospheric conditions (temperature, composition and also the fate of the involved species). IR spectra of naturally occurring aggregates recorded *in situ*,^{2–4} and of species produced under more controlled conditions in the laboratory^{5–10} are useful and commonly used tools for this purpose. Moreover, vibrational spectra can furnish information pertaining to the potential energy surface, in particular on the interaction between monomeric components, and can provide valuable information to be used in molecular dynamics simulations of condensed phases.^{11–13} Whereas theoretical work on aggregates formed by either nitric acid or hydrochloric acid and a growing number of water molecules have been studied in the past,^{14–20} we are not aware of similar publications concerning the ternary systems which make up the body of this investigation.

Unfortunately, the above mentioned wealth of structures existing simultaneously in different conditions makes the analysis of the spectra of the bulk samples an uncertain and difficult task, of which the first step is a good knowledge of the individual spectra of each cluster. On the other hand, it was found in GGE¹ that some of the most stable aggregates formed by water, hydrogen chloride and nitric acid possess fairly large dipole moments, being the obvious candidates for identification by means of microwave spectra techniques.

This study presents predicted IR spectra of these 15 stable aggregates. Hydrogen bonding is the dominating interaction in the stabilization of these clusters, and its effects are traceable in their vibrational spectra. Furthermore, based on the calculated rotational and centrifugal distortion constants,

^a Unidad Asociada Química-Física UCM-IEM/CSIC, Dept. Química Física I, Universidad Complutense de Madrid, Avda Complutense s/n, 28040 Madrid, Spain. E-mail: pgomez@quim.ucm.es

^b Unidad Asociada Química-Física UCM-IEM/CSIC, Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain. E-mail: rescribano@iem.cfmac.csic.es

^c Escuela Universitaria Politécnica, Universidad de Zaragoza, Ciudad Escolar s/n, 44071 Teruel, Spain

^d Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F. Selmi 2, I-40126, Bologna, Italy

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predicted rotational spectra, in the centimetre-wave region, of three of the most stable species having large dipole moments are presented. From the thermodynamic properties of the aggregates, a thermally averaged model of a realistic atmospheric mixture can be constructed and the corresponding spectra can be predicted.

After a short description of the methodology employed, the study presents the predicted spectra in three sub-sections. The first one deals with the most characteristic IR spectral features. We discuss first the assignment of the spectrum of the most stable cluster, then highlighting the striking variations that can appear among the spectra of different families. Based on that analysis, we propose in the next sub-section the best candidates for an eventual detection of some of these species under special laboratory experimental conditions, with a similar proposal for use of microwave techniques combined with jet expansions. In the third sub-section, spectra of possible atmospheric mixtures are considered in detail, and clues for their detection are offered from their variations with temperature. The Conclusions section summarizes the main findings of this investigation.

2. Methodology

The nomenclature employed to label each cluster is the same as in GGE,¹ and is only described in brief. The first letter indicates which molecule (N, W or C for nitric acid, water or hydrogen chloride, respectively) acts as proton acceptor, followed by 1A or 2A to indicate how many protons this central molecule accepts from either of its neighbours, which is then specified by its initial. Finally, a hyphen separates this root from a number identifying possible conformers, when necessary. Thus, the lowest-energy structure, labelled N1AC-5, refers to one of the five possible conformers in which the nitric acid accepts one proton from the hydrochloric acid. In this case, the nitric acid in turn donates its own proton to the water molecule.

Table 1 collects the list of 15 stable clusters arranged by increasing energy, as calculated in GGE.¹ The calculations were carried out employing a combination of a DFT method and extended basis set, B3LYP/aug-cc-pVQZ, with the Gaussian 03 suite of programs.²¹ This choice of method and basis set was found to provide good results in the often laborious geometry convergence process (GGE¹), which frequently required tight optimization criteria. The first six aggregates in the Table lie within ~ 1.5 kcal mol⁻¹, consisting of all five N1AC conformers plus N1AW-5, which, like N1AC-5, has a closed 8-membered ring structure. The next one, W2A, is unique in its class, with an open structure but with two strong hydrogen bonds (HBs) to the water unit. Next, N1AW-4 is also special, having a 6-membered ring configuration. These two clusters lie halfway between the most stable members of the set and the remaining ones, more than 7 kcal mol⁻¹ higher in energy, which consequently are expected to be less favourable. Table 1 also presents the predicted dipole moment and rotational constants of the clusters and the corresponding calculated values of the monomers.

Fig. 1 shows schematically four clusters representing members of each family. It provides an easy picture to

Fig. 1 Schematic view of four species representative of families of aggregates. Stronger hydrogen bonds are indicated by thicker dotted lines.

visualize the kinds of HBs that are formed among these molecules. Bond properties of all HBs formed in the whole series of clusters, namely bond lengths and bond densities at the bond critical point (ρ_{bcp})^{22,23} were collected in Table 4 of GGE.¹ We have depicted stronger HBs in Fig. 1 by thick dot lines and weaker bonds by thinner dash lines, with the defining principle based on $\rho_{\text{bcp}} > 0.05$ and $r < 2.1$ Å for labelling a HB as strong.

Three hydrogen bonds are formed in each of the top two clusters, making up fairly stable cyclic structures, wherein HNO₃ and H₂O are always bound by strong HBs regardless of the donor/acceptor role played by either molecule. The two other clusters shown in Fig. 1 favour the formation of only two HBs in each and yield less stable open non-cyclic structures. Both HBs in W2A are strong, with the O atom of H₂O acting as a double proton acceptor, whereas in N2A-1C3W, two different oxygen atoms of HNO₃ accept proton transfer from H₂O and HCl through weak HBs. As we shall see below, the strength of these bonds is reflected in the IR spectral features of the aggregates.

3. Results

3.1 IR spectra of individual aggregates

All of the equilibrium geometries calculated for these clusters (see GGE¹) correspond to real minima in their potential energy surface, and enable the evaluation of the vibrational modes and the prediction of their infrared spectra. In general terms, the main features in the spectra of these clusters should correspond to the strongest vibrations in the individual molecules that they are formed of, but in many cases significant alterations appear as a consequence of the creation of fairly strong intermonomeric HBs. Table 2 collects the

Table 1 Energies and molecular parameters (dipole moment and rotational constants) of the species studied in this work, at the B3LYP/aug-cc-pVQZ level of theory

Species	$\Delta E + \text{ZPE} + \text{CC})^a/$ kcal mol ⁻¹	μ/D	A/GHz	B/GHz	C/GHz
N1AC-5	0.00	3.64	3.579	1.075	0.834
N1AC-1	1.01	5.30	3.099	0.902	0.700
N1AC-3	1.14	6.10	4.927	0.764	0.662
N1AC-2	1.17	6.26	7.442	0.683	0.626
N1AW-5	1.37	2.72	3.418	1.176	0.877
N1AC-4	1.51	4.75	2.646	0.993	0.730
W2A	1.94	3.39	5.972	0.608	0.599
N1AW-4	3.30	3.00	3.321	1.024	0.789
N1AW-1'	7.01	1.92	2.176	1.104	0.733
N1AW-2	7.06	3.00	6.261	0.690	0.621
N1AW-2'	7.17	4.59	5.780	0.707	0.630
N1AC-oop-ring	7.23	2.51	3.366	1.172	1.004
N1AW-1	7.50	4.89	2.882	0.835	0.647
N2A-1W3C	8.58	2.51	3.944	0.643	0.553
N2A-1C3W	8.58	2.15	4.106	0.644	0.557
<i>Monomers</i>					
HNO ₃		2.27	13.102	12.100	6.291
H ₂ O		1.85	828.090	431.021	283.473
HCl		1.10	0.0	313.976	313.976

^a Energies are relative to the lowest-lying structure N1AC-5, for which $E = -818.36990182 E_h$ ($1E_h = 627.50955 \text{ kcal mol}^{-1}$). The quoted values include both zero-point-energy (ZPE) and counterpoise corrections (CC).

predicted wavenumbers of the most relevant vibrations of all 15 species under study, also including the calculated and experimental values of the vibrations of the individual parent molecules for reference. Table 2b, in the ESI,[†] contains the full list of vibrational wavenumbers and intensities for the normal modes of the set of 15 clusters. We first discuss in detail the assignment of the IR spectrum of N1AC-5, and then we comment on the large variations that are predicted for the spectra of other families. Some of these remarkably different values are indicated using italic characters in Table 2.

3.1 (a) N1AC-5

The predicted IR spectrum of the lowest-energy cluster N1AC-5, used as a representative of the spectra of these molecules, is displayed in Fig. 2. The stretching modes of the bonds containing the H atom lie in the high frequency region, 4000–2500 cm⁻¹, being in decreasing frequency order: asymmetric and symmetric O–H in H₂O, O–H in HNO₃ (the strongest band in the spectrum), and Cl–H. Atypically, the symmetric OH (H₂O) stretch is stronger than the anti-symmetric counterpart in this cluster, the only one where the HCl molecule is relatively close to the water unit. The charge

Table 2 Predicted harmonic wavenumbers for the main vibrations^a of the ternary clusters studied in this work, including those of the parent monomers at the B3LYP/aug-cc-pVQZ level of theory. For N1AC-3, the anharmonicity-corrected wavenumbers are also included, as calculated at the same level of theory

Modes	H ₂ O			HCl	HNO ₃					
	Asym str	Sym str	Bend		OH str	NO ₂ asym str	NOH bend	NO ₂ sym str	NO str	NOH tors
Free mols. (calc. ^b)	3907	3805	1629	2933	3719	1750	1322	1347	902	493
Free mols. (exp. ^c)	3756	3652	1595	2886	3550	1710	1303	1326	879	458
N1AC-5	3864	3700	1635	2795	3146	1723	1462	1333	966	878
N1AC-1	3886	3785	1620	2800	3167	1733	1476	1326	965	879
N1AC-3	3886	3784	1618	2814	3169	1730	1471	1343	962	879
N1AC-3-anh	3716	3627	1575	2822	2817	1689	1387	1310	945	743
N1AC-2	3886	3783	1618	2810	3170	1727	1471	1345	965	879
N1AW-5	3863	3737	1625	2272	3423	1724	1379	1335	947	660
N1AC-4	3886	3784	1619	2850	3162	1743	1477	1332	930	873
W2A	3853	3728	1620	2769	3357	1741	1454	1325	939	811
N1AW-4	3872	3760	1627	2455	3553	1742	1332	1339	904	617
N1AW-1'	3875	3757	1645	2890	3502	1729	1387	1328	940	628
N1AW-2	3889	3780	1642	2890	3539	1727	1378	1345	935	606
N1AW-2'	3890	3782	1641	2896	3538	1725	1378	1342	937	607
N1AC-oop-ring	3882	3773	1641	2796	3713	1731	1339	1358	931	467
N1AW-1	3887	3774	1643	2916	3568	1733	1368	1336	930	602
N2A-1W3C	3893	3789	1637	2872	3705	1734	1334	1348	928	493
N2A-1C3W	3894	3790	1638	2864	3707	1733	1330	1350	931	491

^a Strikingly different values compared to other frequencies along the series are shown in italic. ^b Calculated, this work. ^c Experimental: H₂O and HCl from ref. 28; HNO₃ from ref. 29–34.

Fig. 2 Predicted IR spectrum of the lowest-energy cluster, N1AC-5. Vibrations of the parent molecules are shown by broken lines with colours matching those of the main atom of each molecule in the attached figure.

displacement associated with the O–H stretching in water couples with the electronic polarizability of the Cl atom resulting in a fairly large overall dipole moment variation for this vibration.

The region between 1800 and 1250 cm^{-1} presents four bands, corresponding, in decreasing frequency order, to the NO_2 asymmetric stretch, the HOH bend, the NOH bend and the NO_2 symmetric stretch, all of them presenting varying contributions of these molecular modes.

The next two bands in decreasing frequency are assigned to the stretch of a single N–O bond and to the out-of-plane NOH torsion, *circa* 900–800 cm^{-1} . Finally, a set of weaker bands span the low frequency region, below 500 cm^{-1} ; the most intense of which corresponds to another out-of-plane vibration involving the H atoms in water and HCl. Other vibrations can be assigned to intermolecular coupling modes.

The calculated vibrations of the free monomers are indicated by coloured broken lines for comparison (red, blue and green for H_2O , HNO_3 and HCl, respectively). It is interesting to note the large red-shift in the O–H (HNO_3) stretching for the N1AC-5 cluster, $\sim 570 \text{ cm}^{-1}$, caused by the strong HB with the oxygen atom of water, which also greatly enhances the intensity of this vibration. It should be kept in mind that the simulations displayed in Fig. 2 and 3 (see below) are performed by means of Lorentzian functions of 25 cm^{-1} half-width at half-maximum (HWHM) for all vibrational modes. Actual HB modes should have a much larger width, spanning even hundreds of wavenumbers in some condensed phases.^{24–26} The corresponding shift in the Cl–H vibration is $\sim 140 \text{ cm}^{-1}$, and the stretching vibrations of H_2O , as most of the other modes, are very little changed.

3.1 (b) Other representative clusters

The main vibrations described above suffer important changes in frequency and intensity along the series of clusters. We summarize in the following paragraphs the most significant of these variations in terms of partial proton transfer among the monomeric units, implying modifications in bond strength and induced dipole moment. A more comprehensive description is

presented with the ESI of this publication,[†] together with a table containing the full list of calculated frequencies and intensities for the whole set of aggregates (Table 2b).

Fig. 3 is a composite of spectra of some of these species, arranged in such a way to facilitate the observation of spectral changes, some of them highlighted by broken lines. The spectrum of N1AC-3, at the top, similar to that of N1AC-5, can be used as reference. In the three spectra shown on the left half of the figure, the O–H (HNO_3) stretch and the Cl–H stretch are shifted in opposite senses. The H atom of HNO_3 is less involved in HBs along this set of clusters and the corresponding OH bond resembles more that of the free molecule, yielding less intense and blue-shifted bands. On the contrary, there is a growing $\text{HCl} \rightarrow \text{H}_2\text{O}$ proton transfer, resulting in a lower frequency and stronger Cl–H vibration. In the mid-frequency region, the NOH bend is red-shifted and overlaps with the NO_2 symmetric stretch, giving one single stronger band.

The spectra displayed on the right part of Fig. 3 exhibit a similar trend concerning the O–H (HNO_3) vibration, with the two bottom spectra reflecting a practically undisturbed OH (HNO_3) bond. The Cl–H stretch also recovers its value as in the free monomer, as the $\text{HCl} \rightarrow \text{HNO}_3$ proton transfer is very limited. It is interesting to note that the cluster shown last is the only one with a clearly non-planar structure, and yet its spectrum is not too different than that of N2A-1W3C, except for the far-infrared region. This illustrates the importance of this spectral region in structural investigations.²⁷

Although not shown in this figure, the spectrum of N1AW-5 contains the lowest-frequency Cl–H stretching vibration, at 2272 cm^{-1} . The displacement from the monomer is quite large, and can be compared to that calculated by Packer and Clary³⁵ for the $(\text{H}_2\text{O})_3\text{HCl}$ cluster, an 8-membered ring structure like N1AW-5. These authors predict an increasingly stronger and red-shifted Cl–H vibration in the series with a growing number of water molecules, correlated with a larger $\text{HCl} \rightarrow \text{H}_2\text{O}$ proton transfer. There is also a similar agreement between the present results for N1AW-4 and $(\text{H}_2\text{O})_2\text{HCl}$ of Packer and Clary.³⁵

All of the above discussed calculations have been carried out within the harmonic approximation. To estimate the effect of anharmonicity on the vibrational wavenumbers we have performed a fully anharmonic calculation at the same level of theory for one of the clusters, N1AC-3. This calculation was so demanding in terms of computer use that we could not attempt to extend it to the whole list. As expected, the results predict the largest shift for the vibrations involving the H atom. The O–H stretch of the HNO_3 unit is decreased by $\sim 350 \text{ cm}^{-1}$, and values of $\sim 170 \text{ cm}^{-1}$ are estimated for the same vibrations of the water unit. Bending or torsion modes are also strongly red-shifted in HNO_3 , with a more moderate displacement for H_2O . Interestingly, the Cl–H stretch is practically unaltered in the anharmonic calculation. Similar displacements can be expected for the rest of the clusters.

A final point can be raised concerning the unchanged wavenumber of the NO_2 asymmetric stretch and HOH bending vibrations, which suffer only minor changes in intensity along the whole set of spectra. This is an indication of the local character of these modes, which are not affected by the different bonds formed in these clusters.

Fig. 3 Predicted IR spectra of some representatives of the families of clusters. The variation of three of the main vibrational bands in the series is indicated by broken lines.

3.2 Prediction of laboratory spectra

In the laboratory, jet expansion techniques could enable the observation of individual members of these families. The best candidates, working in the infrared region, would be species with high absorption cross section IR bands, and preferably with comparatively large rotational constants, which would favour a less crowded rotational structure. From the spectra shown above and data from Table 1, it seems that the W2A cluster could be a good option, having fairly strong O–H (HNO_3) and Cl–H stretching bands. This cluster has a relatively large value of A , and happens to be a practically perfect accidental prolate symmetric top, with $B = 0.608$ GHz and $C = 0.599$ GHz, yielding an asymmetry parameter $\kappa = -0.997$. Moreover, the fundamental stretching bands of W2A are quite separate from the corresponding modes of the free monomers. The monomers, and possibly some dimers which could be formed in the expansion, would be the main contributors to the spectra of the jet. Therefore, the identification of any cluster would be easier when its predicted spectrum contains lines distant from those of the parent compounds. In this respect, a comparison with predicted spectra of $\text{HCl}(\text{H}_2\text{O})_n$, $n = 1, 3$,³⁶ and of $\text{HNO}_3(\text{H}_2\text{O})_n$, $n = 1-3$,³⁷ shows that very limited overlap is expected from these species, within the accuracy limit of our respective calculations. The main conflicts may appear in the region of the O–H (H_2O) symmetric stretch of $\text{HCl}(\text{H}_2\text{O})_2$ and $\text{HCl}(\text{H}_2\text{O})_3$,³⁶ predicted close to the O–H (H_2O) asymmetric stretch of the clusters considered in this investigation, and on the NOH bend and NO_2 symmetric stretch of the $\text{HNO}_3(\text{H}_2\text{O})_n$, $n = 1-3$ compounds,³⁷ but these bands being of moderate intensity, would not be specifically selected for identification purposes of our aggregates. Other possible candidates for individual detection could be N1AC-5 or N1AC-3, which have the strongest O–H (HNO_3) stretching band in the whole series of predicted spectra.

Similarly, the rotational spectra of these clusters could in principle be recorded by means of Fourier transform microwave (FTMW) spectrometers, in whose vacuum chambers the

complexes could be produced in supersonic jet expansions, where the temperature is of the order of a few Kelvin.³⁷ Making use of the rotational parameters and dipole moments from Tables 1 and 3, we have evaluated the rotational spectra for three representative species with large permanent dipole moments (N1AC-5, N1AC-3 and W2A). A graphical depiction is provided by Fig. 4, while the most intense predicted transition frequencies in the 5–35 GHz frequency range can be found in the ESI (Table 3†). The predicted microwave spectra displayed in Fig. 4 are quite crowded because of the small rotational constants of these large clusters. Insets to each full spectrum show small selected regions, where the density of lines is smaller. Colours are used to indicate the dominant dipole moment component. It can be seen that the leading MW spectra are of b -type for W2A ($\mu_b = 3.06$ D), a -type for N1AC-3 ($\mu_a = 5.76$ D), and a - and b -types for N1AC-5 ($\mu_a = 2.35$ D, $\mu_b = 2.64$ D).

3.3 Prediction of atmospheric spectra

According to the calculations performed in GGE,¹ several of these species can be present in the atmosphere, making it worthwhile to predict the spectra that could be expected from their occurrence. These clusters would exist with a varying concentration that will depend on temperature, pressure and mixing ratios of the monomers. Their relative abundance can

Table 3 Calculated ground vibrational state rotational and centrifugal distortion constants (Watson's A reduction) and asymmetry parameter for the clusters selected for Fig. 4

Rotational constant (g.s.)	N1AC-5	N1AC-3	W2A
A/MHz	3578.98	4927.75	5971.97
B/MHz	1074.63	763.34	607.51
C/MHz	833.54	661.90	598.70
$\Delta J/\text{kHz}$	1.19	0.97	1.35
$\Delta JK/\text{kHz}$	−5.82	−19.26	−50.91
$\Delta K/\text{kHz}$	23.92	206.64	653.24
$\delta J/\text{kHz}$	−0.20	0.23	0.11
$\delta K/\text{kHz}$	−1.51	3.05	9.27
κ	−0.821	−0.952	−0.997

Fig. 4 Prediction of microwave spectra of three representative clusters with large permanent dipole moment, at 10 K. Insets: blown-up frequency regions displaying predominant types of rotational transitions.

be estimated based on thermodynamic considerations. The fraction of the i th cluster relative to the total number of species N is given by

$$f_i = \frac{n_i}{N} = \frac{e^{-\Delta G_i / K_B T}}{Z} \quad (1)$$

Table 4 Population fraction of each aggregate calculated using eqn (1) for the specified temperatures, with appropriate values for Gibbs free energy of formation, relative to ΔG_f (N1AC-5) = $-5.03325 \text{ kcal mol}^{-1}$. Population values smaller than 0.005 are not listed

Species	298 K		200 K	
	ΔG	Population	ΔG	Population
N1AC-5	0	0.269	-1.203	0.550
N1AC-1	0.100	0.227	-0.725	0.165
N1AC-3	0.449	0.126	-0.445	0.082
N1AC-2	0.442	0.127	-0.457	0.084
N1AW-5	1.760	0.014	0.352	0.011
N1AC-4	0.100	0.227	-0.526	0.100
W2A	1.569	0.019	0.471	0.008

where K_B and T are the Boltzmann constant and the temperature, respectively, and the partition function Z can be calculated as the sum over all species:

$$Z = \sum_i e^{-\Delta G_i / K_B T} \quad (2)$$

In these equations ΔG_i is the Gibbs free energy, a measure of the expected viability of formation of the clusters with respect to the monomers. Assuming that all of these species are present in the atmosphere, the infrared absorption of the composite can be evaluated as the fractional sum of their individual spectra at a given temperature. We present in Table 4 the estimated Gibbs free energy values and the corresponding relative concentrations of these clusters at atmospherically relevant temperatures. At 100 K, a similar evaluation yields a distribution where more than 94% of the population is concentrated in the lowest species, N1AC-5. Fig. 5 displays composite spectra using the distributions shown in Table 4, which would be realistic for atmospheric purposes.

The spectra displayed in Fig. 5 are calculated at two temperatures: ambient temperature and that of the coldest region in the troposphere, at $\sim 10 \text{ km}$ of altitude, near the tropopause. At higher altitudes the possibility of existence of these ternary clusters in the gas phase is much smaller, although they could remain adsorbed at the surface of ice particles, similar to the polar stratospheric clouds. A global

Fig. 5 Composite atmospheric spectra; populations evaluated using Gibbs free energy values. 200 K values are offset 30 absorbance units for clarity.

Fig. 6 Composite atmospheric spectra as in Fig. 5. Three spectral regions are expanded to better appreciate some changes with temperature.

view of the spectra shows that they are dominated by the N1AC family of clusters. The presence of other species, like N1AW-5 or W2A, is barely noticeable by the weak features at 3423 and 3357 cm^{-1} , corresponding to the O–H (HNO_3) stretch of these two clusters, respectively, and by the band at 2272 cm^{-1} for the Cl–H stretching of the former.

To better appreciate the spectral variations with the temperature, three regions are expanded in Fig. 6. The symmetric O–H stretch in water is stronger than the anti-symmetric component at 200 K, and the opposite happens at 298 K (see right-hand panel of Fig. 6). The former vibration is quite intense in N1AC-5, as indicated above, and at 200 K this species prevails. On the other hand, at the warmer temperature, the N1AC-1 and N1AC-4 contributions to the mixtures are very important, and the antisymmetric stretchings, falling at exactly the same frequency for these two clusters, add up to surpass the intensity of the symmetric component of N1AC-5.

Something similar takes place for the strongest band of the spectrum, the O–H (HNO_3) stretch, near 3150 cm^{-1} , predicted as a doublet (see central panel of Fig. 6) with an intensity ratio that changes with temperature for the same reason as explained above. In atmospheric spectra, the presence of two components for this band should be direct evidence of the existence of several clusters of this type, and an estimation of the temperature could be obtained from their relative intensity. Finally, in the low-frequency region where atmospheric spectra are comparatively less accessible (left-hand panel), a peak at 310 cm^{-1} has increasing intensity at higher temperatures and becomes clearly predominant at 298 K. This band corresponds to an out-of-plane rocking of the water molecule, which is rather strong in the whole N1AC series except in the more abundant species, N1AC-5, where it is much weaker and shifted to 316 cm^{-1} . Again, the occurrence and intensity alteration of a peak at 310 cm^{-1} would be indicative of the presence of clusters of the N1AC family in the atmosphere.

4. Conclusions

Water, nitric acid and hydrogen chloride are three of the key species present in our atmosphere. Their high reactivity and involvement in both gas phase and heterogeneous atmospheric processes may lead to the formation of the clusters considered in this investigation, through thermodynamically favourable reactions. High level theoretical calculations are a useful tool to predict the spectroscopic properties of these aggregates and their variation with temperature. Such predictions can provide the means to detect these species in the atmosphere, as well as in the laboratory. The main conclusions of this work are summarized below.

From all possible forms of aggregation of the above-mentioned monomers, DFT theoretical calculations at the B3LYP/aug-cc-pVQZ level concluded (GGE¹) that 15 of them could form stable structures. This work presents an analysis of the vibrational properties of these clusters. The infrared spectrum of the most stable member of the set, N1AC-5, is a good example to discuss the most salient features. The O–H (HNO_3) stretching mode gives the strongest IR band for this cluster and for the lowest energy family, N1AC. The spectra of other species undergo important modifications when compared to those of the N1AC set. The above-mentioned band is displaced to higher wavenumbers and loses part of its intensity, whereas the Cl–H stretching mode becomes stronger and is red-shifted for some clusters. The displacements can be as high as several hundreds of wavenumbers. The calculated frequency shifts can be understood in terms of the varying hydrogen bonds that are formed in the clusters. The calculations confirm the general rule that, the less involved the H atom is in intermonomeric bonding, the closer the frequency is predicted to that in the free molecule, and the less intense the band appears in the spectrum.

Some IR bands are not displaced in the whole series of spectra, and only their relative intensity suffers some minor changes. The most outstanding example is the NO_2

asymmetric stretch, always predicted in the 1725–1742 cm^{-1} range with a nearly constant intensity. On the other hand, the spectra show strikingly different features in the low-frequency zone. Bands in this far-infrared region are weak and traditionally difficult to observe, but they could provide very valuable information for the identification of these species.

These clusters could be formed in jet expansions in laboratory experiments, and be detected by sensitive IR or microwave techniques. In either case, contamination by the spectra of the parent molecules can be expected. This work provides some hints to select the spectral regions more favourable to look for these clusters, where such contamination would be lowest.

In the atmosphere, mixtures of these aggregates could be formed. We have estimated their fractional abundance based on their Gibbs free energy of formation, and using their calculated population fraction, we predict the IR spectra of the mixture at two relevant atmospheric temperatures. Some bands show reversal of intensity patterns in the temperature range considered, 200–298 K, and thus, observation of the predicted peaks and of their relative intensity could yield the clues for the identification of these clusters from *in situ* samples.

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