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PAPER

Proton transfer and autoionization in $\text{HNO}_3\cdot\text{HCl}\cdot(\text{H}_2\text{O})_n$ particles†F. Mine Balci,^{*a} Nevin Uras-Aytemiz,^a Pedro C. Gómez^b and Rafael Escribano^c

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The structure and spectroscopic properties of clusters of $\text{HNO}_3\cdot\text{HCl}\cdot(\text{H}_2\text{O})_n$, with $n = 1$ to 6, have been calculated at the MP2/aug-cc-pVDZ level of theory. Altogether 22 different clusters have been found as stable structures, with minima in their potential energy surfaces. The clusters can be grouped in families with the same number of water molecules, and with close aggregation energies within each family. The addition of each new water molecule increments the aggregation energy of the clusters by a nearly constant value of 76.2 ± 0.1 Hartree. The proton transfer parameter and the coordination number of HNO_3 and HCl in each cluster have been evaluated, and the wavenumber shifts for the X^-H^+ vibration from the corresponding mode in the isolated molecules have also been predicted. These values allow classification of the acidic species in the clusters into three types, characterized by the strength of the hydrogen bond and the degree of ionization. A correspondence is found between the coordination number of HNO_3 and the magnitude of the X^-H^+ vibrational shift.

1. Introduction

Proton transfer lies at the very heart of acid–base chemistry and also of many important biological processes. A good example of this is the auto-ionization of water, which is also at the origin of the proton conducting properties of the liquid through the so-called water wire¹ from which many of its physiological properties stem.

From a purely chemical point of view, HNO_3 , HCl and H_2O can form stable species, where hydrogen bonding is the main type of interaction among the molecular units. H-bonds can be stretched to the limit of proton transfer between donor and acceptor, yielding two charged species stable in condensed phases^{2–4} when the number of water molecules reaches a certain value in the cluster. An interesting review of this has appeared recently.⁵ The origin of this fact is due to the effect that an increasing number of water molecules has on the electronic structure of the aggregate and in particular on the HX bond. However, direct experimental observation of these effects is difficult because of the short time scale at which they happen, and electron structure methods, whether wavefunction or density functional theory (DFT), are appealing tools to try to understand these phenomena.

From a different point of view, nitric acid and hydrogen chloride are well known to play relevant roles in atmospheric processes. Just as an example, HNO_3 is formed by oxidation of NO_2 and may reach the Earth's surface in the form of wet deposition, usually called acid rain, which may also contain chlorhydric acid, sulphuric acid and other acidic species (see ref. 6 and references therein). Also nitric acid is a key constituent of polar stratospheric clouds (PSC) where ozone depletion processes are initiated.^{7–10} HCl also takes part in these processes by sequestering active chlorine atoms into the more stable chloride molecule.^{11–13} These two acids can also be found in some relevant atmospheric aerosols, which can contain different species, for instance inorganic salts, and a variable number of water molecules depending on the relative humidity of the environment, among other factors.^{14,15}

The number of water molecules required for proton transfer to occur is an open topic of research, where many interesting contributions have appeared in the literature.^{16,17} For HCl -water clusters,¹⁸ an acid to water ratio smaller than 1 : 3 has been found necessary to stabilize the ionic forms. In this line of work, there have been several species studied as aggregates with an increasing number of water molecules, e.g. $\text{HCl}\cdot(\text{H}_2\text{O})_n$,¹⁹ $\text{HNO}_3\cdot(\text{H}_2\text{O})_n$,^{16,20} and $\text{HOCl}\cdot(\text{H}_2\text{O})_n$.²¹

In spite of the wealth of information on clusters containing one single acid molecule plus water the effect of a second competing acid within the cluster has gone relatively unnoticed so far. We are not aware of any investigations based on ternary or higher order systems apart from three recent papers by Gómez *et al.*,^{22,23} focused on $\text{HNO}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$, and by Balci and Uras-Aytemiz.²⁴ Yet, this is an important point since more often than not two or more acids are present in many systems of chemical interest. The role played by the second

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acid (HCl or HNO₃) within the aggregate, and the number of water molecules required for acidic dissociation, are obvious questions but certainly not the only ones.

The aim of this work is to investigate nitric acid-hydrogen chloride-water systems with up to 6 water molecules. We study the variation of structural and spectroscopic properties of the aggregates with a growing number of water molecules. In particular, the existence of proton transfer in some special cases and the conditions for proton transfer to take place are discussed in detail.

2. Methodology

2.1 Computational details

Geometry optimizations and vibrational normal mode calculations have been performed at second-order Møller–Plesset perturbation (MP2) level with the aug-cc-pVDZ basis set in the frozen core approximation. Considering the large size of many of the clusters studied here, even modest DZ basis sets (383 basis functions for the largest cluster, with six water molecules plus the two acids) seem a reasonable choice to perform an affordable and systematic study of the aggregates. Nevertheless in some selected cases we have used aug-cc-pVTZ for comparison purposes. The calculated differences, although noticeable in terms of geometric parameters (bond distances and angles), do not induce a change in the proton transfer picture stemming from the DZ results. In an ongoing study, DFT calculations with various functionals have been tested in order to simulate an ice slab with HCl and HNO₃ (to be published separately). For the present work, we are including our MP2 results only. All calculations have been carried out using the Gaussian03 suite of program.²⁵

All the refined structures have been checked to correspond to true minima on the intermolecular potential energy surface (IPES), yielding real harmonic vibrational frequencies.

Table 1 contains the structural parameters of the monomers, HNO₃, HCl and H₂O, calculated at the MP2 level with the aug-cc-pVDZ basis sets, compared with the corresponding experimental values. The MP2 results agree reasonably well with the experimental values.

Table 1 Structural properties of HNO₃, HCl and H₂O molecules. Distances (*r*) are given in Angstroms and angles (*∠*) in degrees

Structural parameters	MP2/aug-cc-pVDZ	Experiment
HNO₃		
<i>r</i> (O–H)	0.98	0.96 ^a
<i>r</i> (N–O)	1.42	1.41
<i>r</i> (N–O2)	1.22	1.21
<i>r</i> (N–O3)	1.21	1.19
HCl		
<i>r</i> (H–Cl)	1.29	1.27 ^b
H₂O		
<i>r</i> (O–H)	0.96	0.96 ^c
<i>∠</i> (HOH)	103.8	104.5

^a Ref. 26. ^b Ref. 27. ^c Ref. 28.

2.2 Proton transfer parameters and coordination number

Since one of the main purposes of this study is to explore the extent of acid ionization, a proton transfer parameter (ρ_{PT}) (ref. 29–31 and references therein) can be used to represent numerically the degree of HNO₃ and HCl ionization within the clusters. As we shall show, this parameter can change substantially depending on the number of water molecules and on the different configurations found for our clusters.

The proton transfer parameter, ρ_{PT} , can be calculated using the following equations:

$$\rho_{PT}(\text{HNO}_3) = (r_{OH} - r_{OH}^o) - (r_{H...O} - r_{H...O}^o) \quad (1)$$

$$\rho_{PT}(\text{HCl}) = (r_{HCl} - r_{HCl}^o) - (r_{H...O} - r_{H...O}^o) \quad (2)$$

In eqn (1), r_{OH} and $r_{H...O}$ indicate the interatomic distances between the shared H atom and the appropriate O atoms of the donor (HNO₃) and acceptor (H₂O or HCl) species, that is to say, O₂NO–H, and H...OH₂ or H...Cl/H, respectively, and, similarly, for HCl in eqn (2), Cl–H and H...OH₂ (or H...ONO₂H in some cases). The ^o superscripts refer to the corresponding geometric parameters in the individual isolated monomers. A graphical example is illustrated in Fig. 1.

Inspection of eqn (1) and (2) reveals that the proton transfer parameter ρ_{PT} would be >0 for an ion pair and negative for molecular (nonionic) complexes, whereas a near zero value of ρ_{PT} indicates proton sharing between both participating molecules.

The protonated species of the monomers, *i.e.* H₃O⁺, H₂NO₃⁺ and H₂Cl⁺, were also optimized at the MP2 level with the aug-cc-pVDZ basis set to provide the necessary parameters for eqn (1) and (2). Table 2 contains the relevant bond distances of these protonated species. H₂Cl⁺ and H₂NO₃⁺ were already studied^{32–34} in the previous literature, albeit with a different level of theory and basis sets. The optimized structures of H₂NO₃⁺ and H₂Cl⁺ are shown on the left panel of Fig. 2, where two different configurations of the protonated nitric acid are displayed. They correspond to clusters in which HCl donates a proton to a non-acidic oxygen atom of HNO₃, as in NC1W-1, NC2W-2 or NC3W-2 (see below for nomenclature). Besides, a protonated nitric acid structure (not shown here) in which the acidic oxygen accepts

Fig. 1 An example of the calculation of proton transfer parameters of HNO₃ (top) and HCl (bottom) for a given cluster.

Table 2 Bond distances (Å) optimized at the MP2 level with aug-cc-pVDZ for the neutral and ionic species used in the calculation of proton transfer parameters^a

Species	MP2
OH of HNO ₃	0.98
OH of H ₂ NO ₃ ⁺	
(a)	0.99
(b)	0.98
H–Cl	1.29
H ₂ Cl ⁺	1.32
H ₃ O ⁺	0.98
H ₂ O	0.96

^a (a) and (b) correspond to the structures depicted in Fig. 2, left panel.

a proton was also found in our calculations, similar to a NO₂⁺·H₂O species optimized by D'Auria *et al.*³² at B3LYP level with the 6-311++G(d,p) basis set.

We have made use of another parameter, the coordination number, defined as the number of H-bonds formed in a particular molecule, either of the proton donor or the proton acceptor type. As an example, in the nitric acid case (Fig. 2, right panel) there are six sites that can act as proton acceptors plus the acidic H that could be donated, giving a maximum coordination number of seven. However, as will be shown in the species studied here, the maximum coordination number found is three.

2.3 Description of the systems

Following the nomenclature employed in ref. 22, the systems under study are designated NC_nW-*m*, where N, C and W represent nitric acid, hydrogen chloride and water molecules, *n* indicates how many water molecules participate in the cluster, and *m* is just a running index for several species within a given NC_nW set. Thus, for instance, NC3W-4 specifies the fourth aggregate (in increasing energy order) of the HNO₃·HCl·(H₂O)₃ family, which happens to be a very special structure that we will discuss later. Fig. 3–8 collect the schematic representation of the clusters found in this work for 1 to 6 water molecules consecutively. Table 3 displays the energies of the whole set of species under consideration, all of which have stable equilibrium geometries in our calculations.

Fig. 3 NC1W family.

The NC1W family has already been investigated.^{22–24} Gómez *et al.*²² reported fifteen structures characterized by true minima located on the IPES, the NC1W-1 aggregate being the most stable one among them. These structures are especially suitable for studying proton transfer parameter variations in the smallest clusters. In the NC1W family, both HNO₃ and HCl molecules have coordination number two.

The aggregates in the NC2W-*m* set are basically planar, forming rings with 4 H-containing bonds, of which clusters with *m* = 1, 3 and 6 are characterized by 8-membered rings and the other three by 10-membered rings. In all NC2W-*m* cases, as in the NC1W family, the coordination number for both HNO₃ and HCl is equal to two.

In NC3W-2 the water molecules and the O–H atoms of HNO₃ form one ring, with the hydrogen chloride attached to a different O atom of nitric acid. Thus, two rings are created, implying coordination number of 3 for nitric acid, the same as

Fig. 2 Left: Schematic representation of protonated HNO₃ (H₂NO₃⁺) (a–b) and protonated HCl (H₂Cl⁺) (c). Right: sites where proton transfer can take place by accepting a proton on the O atoms of HNO₃.

Fig. 4 NC2W family.

Fig. 5 NC3W family.

Fig. 6 NC4W family.

Fig. 7 NC5W family.

Fig. 8 NC6W cluster.

Table 3 Full list of stable aggregates $\text{HNO}_3 \cdot \text{HCl} \cdot (\text{H}_2\text{O})_n$, with $n = 1-6$. In the first column the energy of the most stable species of each family (E) is given in Hartree (E_h), and below is the energy difference to that one for the other clusters of the same family (ΔE), in Kcal mol^{-1} . All calculations were performed at the MP2/aug-cc-pVDZ level. Binding energies, zero-th order corrections and corrected energies are also listed in consecutive columns, all of them in Kcal mol^{-1}

	$E/E_h; \Delta E/\text{Kcal mol}^{-1}$	E_{bind}	ΔZPEC	$(E_{\text{bind}} + \text{ZPEC})$
NC1W-1	-816.823478	-16.23	3.44	-12.79
NC1W-2	0.90	-15.22	3.33	-11.89
NC1W-3	1.18	-15.01	3.40	-11.61
NC1W-4	2.57	-13.44	3.22	-10.22
NC2W-1	-893.101690	-27.08	5.87	-21.21
NC2W-2	0.03	-26.99	5.81	-21.18
NC2W-3	0.21	-26.70	5.70	-21.00
NC2W-4	0.22	-26.83	5.84	-20.99
NC2W-5	1.62	-25.33	5.74	-19.59
NC2W-6	1.84	-25.07	5.70	-19.37
NC3W-1	-969.377963	-36.72	8.07	-28.65
NC3W-2	0.19	-36.33	7.87	-28.46
NC3W-3	0.21	-35.87	7.43	-28.44
NC3W-4	0.76	-37.06	9.17	-27.89
NC4W-1	-1045.656147	-47.56	10.19	-37.37
NC4W-2	0.15	-46.63	9.41	-37.22
NC4W-3	0.43	-47.76	10.82	-36.94
NC4W-4	0.93	-47.14	10.70	-36.44
NC4W-5	1.27	-46.02	9.92	-36.10
NC5W-1	-1121.939684	-61.76	14.71	-47.05
NC5W-2	2.2	-59.48	14.63	-44.85
NC6W	-1198.218706	-73.13	16.95	-56.18

in all other structures of this set but the first one, NC3W-1. NC3W-4 is the first example in which the Cl atom is fully ionized, having lost its H to one of the water molecules, and being characterized by a positive ρ_{PT} parameter. This species is the least favourable of this family in terms of energy, and its structure could be described as a cage. It was found in previous works^{18,35} that HCl is ionized when linked to 4 water molecules. In this investigation, we show that when HNO_3 replaces one H_2O , HCl becomes ionized with 3 water molecules.

The NC4W- m set has several interesting elements. In the $m = 3$ and 4 structures the nitric acid is ionized, donating the H atom to water molecules. This effect is reflected in the corresponding ρ_{PT} values, as collected in Table 2. Of these, NC4W-4 was initially built from ionic nitric acid, H_2NO_3^+ , reaching the quoted structure after geometry optimization.

In the two clusters of the NC5W set the Cl atom is ionized, and in NC5W-2 the nitric acid is also ionized, this being the only structure of the whole set in which NO_3^- , Cl^- and two H_3O^+ species coexist.

Finally, in NC6W, which was derived from NC5W-2 by adding one more water molecule, both nitric acid and hydrogen chloride are ionized.

In the last three families of clusters, the coordination number is always 3 for nitric acid, involved in two rings with the other species. The coordination number for hydrogen chloride is normally 2, except when it is almost completely ionized, as in NC5W and in NC6W, or in the special case NC4W-3 mentioned above.

3. Results and discussion

3.1 Energy

Table 3 shows that each family contains more than one member (except NC6W), and in fact the existence of other possible stable structures cannot be totally discarded. In our search for structures, we rejected those for which a stable minimum in the potential energy surface could not be reached. Most members within each family lie in a close energy gap, in spite of some fairly different structures that are sometimes found, and of the different types of bonding among the individual molecular species.

The aggregation energy, understood as the energy involved in the process of addition of one water molecule to the previous structure, has a nearly constant value of the order of 76 Hartree (see Fig. 9), to be compared with the narrow margin of less than 2.5 Kcal mol^{-1} , in which all the members of a family lie. Again, this linear behaviour could be considered as somewhat surprising, taking into account the differences in size and number of bonds between the smaller and larger sets of clusters. It reveals that aggregation is produced on some particular sites of the cluster with no co-operative effects, that is to say with small or no perturbation of the electronic structure.

3.2 Proton transfer

Proton transfer parameters, as calculated using eqn (1) and (2), have been evaluated for all the clusters. The results are

Fig. 9 Energy level diagram and aggregation energy for the clusters under study. On the left hand side, the energy of the lowest structure within each family (in Hartree) and the energy spread (in Kcal mol^{-1}) are shown.

shown in Table 4. A discussion is presented below, but it is worth noting at this point that the H atom in HNO_3 is always fixed to its molecular unit (ρ_{PT} negative) except in four cases, where the acid is completely ionized: NC4W-3, NC4W-4, NC5W-2 and NC6W. For HCl, the acid is only ionized in the NC3W-4, NC5W-1, NC5W-2 and NC6W structures. Therefore NC5W-2 and NC6W are the only species where both acids are ionized.

According to the results summarized in Table 4 there are three major effects that seem to determine whether proton transfer will occur or not. In the first place, the obvious factor is the number of water molecules in the cluster (hereafter hydration number). It is known that increasing hydration number enhances proton transfer in anionic systems,^{36,37} as well as in neutral aggregates of water and one acid (HCl, HBr or HNO_3)^{38–40} where at least four water molecules seemed to be required to stabilize the ionic pair formed. We find here a similar effect, albeit with a smaller hydration number, for HCl. We conclude that at least three water molecules are necessary to promote ionization of HCl (when nitric acid is present) and more than three for the same effect on HNO_3 (when HCl is present in the aggregate).

The second effect is whether the proton acceptor of nitric acid is water or hydrogen chloride. Our results show water to be a much better proton acceptor than HCl, in terms of both better promotion of proton transfer and larger stabilization energy. This explains the striking difference in ρ_{PT} values between NC5W-1 and NC5W-2, and the relative ρ_{PT} values within all the families. This fact was also found in previous papers studying ternary clusters.^{22,23}

Finally, the third factor involved in proton transfer in HNO_3 is related to the existence of a proton donor acting

over the acidic oxygen atom, and also to which molecule that donor may be. For instance, proton transfer does not occur when the proton donor is water, as in NC4W-5 or NC4W-1, whereas in NC4W-4 a HCl donor on the acidic oxygen has a marked effect, making ρ_{PT} become positive. The same effect is present on NC4W-2 although not strong enough to induce proton transfer.

In NC5W-2 and NC6W a chain proton transference seems to occur. HNO_3 accepts partial proton transfer from two H_2O molecules, and at the same time yields its proton to a third water molecule, which, in turn, seems to foster H^+ transference from the hydrogen chloride to a fourth close-by water molecule. In the same clusters, the Cl^- ion is in contact with two H_3O^+ ions, and therefore we calculated two ρ_{PT} values for HCl, labeled (1) and (2) in Table 4 as well as in Fig. 7 and 8. However, inspection of these figures shows that proton transfer from HCl takes place only to the molecule labeled (2), the other H_3O^+ ion arising from proton transfer from the nitric acid.

In all these calculations, a maximum value for ρ_{PT} of 0.6 has been obtained. This magnitude could be taken as an indication of the maximum relative displacement of the proton between the acid and the accepting water molecule for these clusters.

In previous reports on nitric acid hydrates, the proton transfer parameter for $\text{HNO}_3(\text{H}_2\text{O})_2$ has been calculated as $-0.64 \text{ \AA}$ by using experimental bond distances.^{29–31} The structure of this cluster contains an 8-membered ring in which the nitric acid molecule donates and accepts a proton from its H_2O neighbors. In the NC1W family of our investigation, in which one HCl takes the place of one water molecule as compared to the dihydrate, NC1W-1 forms an 8-membered ring as well. We calculate a proton transfer parameter of

Table 4 Wavenumber shifts of the O–H (in NO_3H) and Cl–H modes with respect to the frequencies of the monomers (3704 cm^{-1} and 2920 cm^{-1} , respectively), calculated at MP2/aug-cc-pVDZ level. The proton transfer parameter, the cluster type and the total coordination number are also listed. Units are: $\Delta\nu$ in cm^{-1} , ρ_{PT} in $\text{\AA}^a$

Cluster	ρ_{PT}	$\Delta\nu$ to isolated HNO_3	HNO_3 Type	Coord. HNO_3	ρ_{PT}	$\Delta\nu$ to isolated HNO_3	HCl Type	Coord. HCl
NC1W-1	–0.66	509	1	2	–0.94	55	2	2
NC1W-2	–0.65	565	1	2	—	41	2	2
NC1W-3	–0.90	231	2	2	–0.65	485	1	2
NC1W-4	–1.04	142	2	2	–0.73	350	1	2
NC2W-1	–0.58	752	1	2	–0.63	553	1	2
NC2W-2	–0.56	794	1	2	–0.86	132	2	2
NC2W-3	–0.54	852	1	2	—	195	2	2
NC2W-4	–0.60	658	1	2	–0.64	513	1	2
NC2W-5	–0.83	326	2	2	–0.52	798	1	2
NC2W-6	–0.85	295	2	2	–0.52	795	1	2
NC3W-1	–0.58	726	1	2	–0.52	795	1	2
NC3W-2	–0.47	1106	1	3	–0.98	20	2	2
NC3W-3	–0.41	1337	1	3	—	166	2	2
NC3W-4	–0.51	1122	1	3	0.36	978	3	2
NC4W-1	–0.48	1042	1	3	–0.44	1244	1	2
NC4W-2	–0.27	1830	1	3	—	138	2	2
NC4W-3	0.60	—	3	3	–0.40	1073	1	3
NC4W-4	0.30	1509	3	3	–0.75	410	1	2
NC4W-5	–0.42	1247	1	3	–0.95	70	2	2
					0.60		3	3
NC5W-1	–0.57	847	1	3	(1) 0.60	168	3	3
NC5W-2	0.44	1385	3	3	(2) 0.62	75	3	3
NC6W	0.37	1559	3	3	(1) 0.60	4	3	3
					(2) 0.61		3	3

^a (1) and (2) in NC5W-2 and NC6W refer to proton transfer from HCl to the corresponding water molecules as indicated in Fig. 7 and 8.

HNO_3 to water of $-0.66 \text{ \AA}$, in very close agreement to the value for $\text{HNO}_3(\text{H}_2\text{O})_2$.

On the other hand, in the NC1W-3 cluster, in which an 8-membered ring is also formed, the nitric acid molecule donates its proton to HCl. The ρ_{PT} value in this case ($-0.90 \text{ \AA}$) is smaller than that for NC1W-1. Furthermore, to highlight the differences in these structures, it is also noteworthy to remark that the interaction energy of the $\text{HNO}_3 \dots \text{H}_2\text{O}$ dimer is approximately twice that of the $\text{HNO}_3 \dots \text{HCl}$ dimer.²⁴

Sedo *et al.* have calculated the ρ_{PT} value for the 10-membered ring $\text{HNO}_3(\text{H}_2\text{O})_3$ cluster as $-0.54 \text{ \AA}$ at MP2/6-311++G(2df,2pd) level.³¹ Nitric acid trihydrate could be compared to our NC2W-*m* series. The ρ_{PT} values of HNO_3 in the NC2W-2,-4,-5 clusters, all of which contain 10-member rings, are calculated as $-0.56 \text{ \AA}$, $-0.60 \text{ \AA}$, $-0.83 \text{ \AA}$, respectively. Only in NC2W-5 does the HNO_3 molecule donate its proton to HCl, yielding consequently a much more negative value of ρ_{PT} , whereas for the other two clusters the agreement with ref. 31 is very good.

In view of the previous discussion a preliminary conclusion is that proton transfer in HNO_3 is not clearly fostered by the substitution of a water molecule by HCl, at least in the clusters with a small number of water molecules studied here.

3.3 Frequency shifts and bonding types

The predicted IR spectra of these species can also shed light on their proton transfer and hydrogen bond characteristics. We have calculated the vibrational spectra of all these clusters, and also those of the monomers. Fig. 10 displays the predicted spectra of a few selected clusters, taken as paradigms for the following discussion, while the whole set of spectra is shown in the Supporting Information.† Table 4 lists frequency shifts with respect to the vibrations of the monomers, ρ_{PT} values, and an approximate classification of the clusters according to their bonding properties, as discussed below.

Fig. 10 The predicted IR spectra of a few selected clusters. Bands are represented by Lorentzian curves with a HWHM of 10 cm^{-1} .

Consideration of the ensemble of predicted spectra of these species leads to the observation of common patterns that are followed in different sets of spectra. In general, the O–H vibration of the nitric acid and the Cl–H vibration of HCl are predicted as the strongest spectral features, and whereas for the low water-content clusters these bands stand out clearly, when there are 3 or more H_2O molecules, the spectra become much more complex, and it is not always evident how to assign the acidic vibrations by simple inspection.

With respect to the characteristics of the X–H acidic mode, three more or less clear patterns can be discerned. We have labeled them as follows:

Type 1: The acid species (HNO_3 or HCl) is involved in a strong hydrogen bond with water. The X...H vibration is strongly red-shifted with respect to the corresponding mode in the isolated molecule, and appears as a strong band in the spectrum. The proton transfer parameter for these bonds is $-0.5 > \rho_{\text{PT}} > -0.7$.

Type 2: It is the opposite case. There exists a weak H-bonding between one of the acids and the other one, which acts as proton acceptor (*i.e.* $\text{NO}_3\text{H} \dots \text{ClH}$ or $\text{ClH} \dots \text{ONO}_2\text{H}$). The corresponding bands have weak or medium intensity and a small redshift with respect to the isolated species' vibrations. In this case, the proton transfer parameter is more negative, $-0.8 > \rho_{\text{PT}} > -1.0$.

Type 3: The acid is almost, or totally, ionized. The vibrational mode between the almost ionic X^- species and the proton appears at low frequency and may be inconspicuous in the midst of water O–H modes, or it may even be missing, as in NC4W-3, where it has been replaced by some H_3O^+ mode. The proton transfer parameter is positive in these cases, $0.3 < \rho_{\text{PT}} < 0.6$.

It seems surprising that most of the clusters under consideration follow remarkably well either of these simple patterns. The corresponding type number is listed on the 4th and 8th columns of Table 4.

We have collected in Fig. 10 spectra of leading representatives of these kinds of behavior. The spectra of NC1W-1 and NC1W-3 are characteristic of well isolated vibrations, with the O–H (NO_3H) and Cl–H modes standing out as the strongest peaks. For NC1W-1, the O–H is the strongest band, largely red-shifted from the HNO_3 monomer wavenumber (typical type 1), and the Cl–H has a moderate intensity and small shift from free HCl (type 2). These roles are fully reversed for NC1W-3. The spectrum of NC4W-3 presents several vibrations of similar intensity. Only when the atomic displacements per normal mode are scrutinized is it possible to assign the vibrations. The strongest features above 1500 cm^{-1} are: Cl–H stretching, 1850 cm^{-1} ; O–H in H_3O^+ , 2300 cm^{-1} ; O–H asymmetric and symmetric modes, 2950 and 3050 cm^{-1} , respectively, with other O–H (H_2O) modes above 3300 cm^{-1} . In this species, the nitric acid is completely ionized and the O–H in NO_3H mode is missing. Finally, the spectrum of NC5W-2 is special, inasmuch as the O–H (HNO_3) and Cl–H vibrations clearly protrude from the rest of the bands, fairly uncontaminated by other vibrations, and appear in the reverse of the expected order, *i.e.* $\nu(\text{ClH}) > \nu(\text{HNO}_3)$. Both acids are almost completely ionized in this case, and the shifts from the corresponding monomers are almost the highest and the

smallest in the whole series for nitric acid and hydrogen chloride, respectively. The spectrum of NC6W, shown in the Supporting Information,[†] is fairly similar, but with heavier mixing with water vibrations.

From the results summarized in Table 4 it can be inferred that proton transfer is not always indicative of strong hydrogen bond. Strong hydrogen bonds, characterized by large red shifts in IR spectra, often imply proton transfer, reflected by positive values of ρ_{PT} , as for instance in NC4W-3,4,5, NC5W-2 and NC6W for HNO₃, and NC3W-4 for HCl. But in some other cases strong hydrogen bond characteristics leading to noticeable red shifts do not involve proton transfer, as in NC3W-2,3,4, NC4W-5 and NC5W-1 for HNO₃, or NC4W-1 and NC4W-3 for HCl. Finally there are some curious cases like NC5W-1,2 and NC6W, in which there is proton transfer in HCl but due to the hydrogen chloride being surrounded by H₃O⁺ ions, and so is unable to polarize the H-bond, the spectra display very small red shifts.

On the other hand, the coordination number for nitric acid gives a clear indication of the expected wavenumber shift with respect to the corresponding vibration in the monomer. When the acid accepts partial proton transfer on any of the non-acidic oxygen atoms, the O–H bond is weakened, and the corresponding vibration is shifted to lower wavenumber. For all cases where the coordination number is 3, the shift is near to, and often quite higher than, 1000 cm^{−1}.

4. Conclusions

Nitric acid and hydrogen chloride can form stable species with water molecules by creating a variety of hydrogen bonds among them. This theoretical work predicts the structure and spectroscopic properties of clusters of the acids and up to six water molecules, calculated at the MP2/aug-cc-pVDZ level of theory. The proton transfer parameter and the coordination number associated with the acid molecules in each cluster provide an appropriate means to study the nature and characteristics of the hydrogen bonds formed, and to interpret the predicted wavenumber shifts for the X[−]–H⁺ vibration from the corresponding values in the isolated species.

Addition of each water molecule increments the aggregation energy of the clusters by a nearly constant value of −76 Hartree, regardless of the large structural differences existing among some of the species. Families of clusters with the same number of water molecules are bundled in very close energy gaps of 2.56 Kcal mol^{−1} at the most.

In view of the predicted X[−]–H⁺ wavenumber shifts and proton transfer parameters, three types of behaviour of the acidic species can be devised, which are in most cases distinctly followed. These types correspond to a strong hydrogen bond, with wavenumber shifts above 500 cm^{−1}; a weak hydrogen bond, with shifts of around 300 cm^{−1} or less; and an almost completely ionized acid species, in which the meaning of the X[−]–H⁺ mode is not always clear, and for which the proton transfer parameter is positive, with a value of ∼0.5 Å.

The coordination number for nitric acid is clearly linked to the predicted magnitude of the X[−]–H⁺ wavenumber shift from the corresponding value for the individual molecule. A coordination number of 3, the highest value found in these

complexes, is associated with a shift of ∼1000 cm^{−1} or higher. However, a similar rule is not followed by HCl.

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