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The structure and bonding of mixed component radical cation clusters

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ABSTRACT

Basin hopping in conjunction with second order Møller–Plesset perturbation theory is used to characterise the lowest energy isomers of mixed component radical cation clusters of the form $[H_2O\text{-}X]^{\cdot+}$, $[(H_2O)_2\text{-}X]^{\cdot+}$ and $[H_2O\text{-}X_2]^{\cdot+}$, where X = PH_3, H_2S and HCl, with the relative energies refined using coupled cluster theory calculations. For the dimers where X = H_2S or HCl, a proton transfer based structure comprising H_3O^+ and $SH^{\cdot}$ or $Cl^{\cdot}$ radicals has the lowest energy structure whereas for X = PH_3 a hemibonded structure is most stable. For the trimers, a much wider range of possible isomers based upon both proton transfer and hemibonded structural motifs is observed.

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1. Introduction

The properties of radical cation clusters have been the subject of many experimental and theoretical studies [1–24]. In these clusters it has been established that there is competition between two distinct structural types to form the most stable structural isomer [1]. The first of these involves proton transfer to give an ion and a radical. The resulting ion–radical pair can be directly bonded to each other, or in larger clusters it may be favourable for the ion and radical to be separated [15]. The second structural type arises from an unusual type of bonding, often referred to as hemibonding. This bonding can be considered as a 2-center 3-electron interaction with a formal bond order of 1/2 and occurs when the bonding σ molecular orbital between two atoms in a molecular complex is doubly occupied while the complementary antibonding σ^* orbital is singly occupied [1,2]. Another intriguing aspect of these clusters is that they represent a case where Kohn–Sham density functional theory (DFT) with common exchange–correlation functionals can fail, and DFT often predicts the incorrect structural type to have the lowest energy [20].

Many computational studies on these clusters have focused on dimers. In particular, Gill and Radom studied eight dimer cations using second and fourth-order Møller–Plesset perturbation theory (MP2 and MP4) and showed that the first row hydride dimer cations favour proton transfer structures, while the second row hydride dimers are hemibonded [1]. Determining the lowest energy isomer for larger clusters represents a challenge since it requires an extensive search through configuration space, and there have been relatively few studies that go beyond dimers to consider larger clusters [18,15,22–24]. Cationic clusters of water are the most widely studied system, and both DFT and coupled cluster theory calculations for the water trimer cation have been reported [18]. In addition, significantly larger cationic clusters of water have been studied using DFT [15,22,23].

Recently the structure and bonding in the radical cationic clusters $(NH_3)_n^{\cdot+}$, $(H_2O)_n^{\cdot+}$, $(HF)_n^{\cdot+}$, $(PH_3)_n^{\cdot+}$, $(H_2S)_n^{\cdot+}$ and $(HCl)_n^{\cdot+}$, where $n = 2\text{–}4$ have been studied with the basin hopping (BH) search method [25] in conjunction with MP2, with the relative energies of the clusters determined using coupled cluster theory calculations [24]. The trend of the first row hydride cationic clusters favouring proton transfer based structures and the second row hydride cationic clusters adopting hemibonded structures was also found for the larger clusters. However, the clear preference of first row hydride cationic clusters for proton transfer structures and second row hydrides for hemibonded clusters raises the question of what structures will be adopted in mixed component clusters comprising both first and second row hydride molecules. Some studies of mixed component clusters of this type have been reported [4–6,9,13,21]. Bertran et al. have studied the $[NH_3\text{-}H_2O]^{\cdot+}$, $[HF\text{-}H_2O]^{\cdot+}$, $[PH_3\text{-}H_2S]^{\cdot+}$, $[HCl\text{-}H_2S]^{\cdot+}$ dimers [4,5]. It was found that for $[NH_3\text{-}H_2O]^{\cdot+}$ the energies of the non-proton transfer structure and the proton transfer structure $NH_4^{+}\text{-}OH$ were very similar, for $[HF\text{-}H_2O]^{\cdot+}$ the non-proton transfer structure was lower in energy, and for the second-row hydrides the hemibonded structure was the most stable. The $[H_2O\text{-}H_2S]^{\cdot+}$ dimer has been also been studied previously [9], and represents an example of a cluster containing a first row hydride molecule and a second row hydride molecule. Three distinct structures can exist, two proton-transfer structures with either H_2O or H_2S as the proton donor and the hemibonded structure. It was found that the proton-transfer structure with H_2S as a proton donor was the lowest energy isomer. Maity studied two-centre three-electron bonds (hemibonds) in a range of weakly bound radical cation dimers including mixed

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component clusters containing first and second row hydride molecules with both MP2 and DFT methods [6]. This study highlighted the difficultly in definitively determining the presence of hemibonding. It was found that characterisation of a hemibond based upon bond distance and binding energy was not correct in many cases. For most complexes the bond order between the two heteroatoms was close to 0.5, however, the most definitive indicator involved an analysis of the highest doubly occupied localized molecular orbital.

In this Letter, we report a systematic study of the lowest energy isomers formed by dimer and trimer cationic clusters comprising H_2O and PH_3, H_2S or HCl, characterising the bonding in the clusters. The low energy isomers are identified using BH in conjunction with MP2/6-31+G* with the energies of the structures refined using coupled cluster theory calculations.

2. Computational details

The BH algorithm approach [25] is a well established method for optimising the structure of molecular clusters and combines the Metropolis Monte Carlo sampling technique and a gradient-based local search method. This has the effect of sampling the energy basins instead of sampling configuration space. BH is one example of a technique that can be used to search configuration space and optimise the structure of molecular clusters, for a more thorough overview the reader is referred to a recent review [26]. For the calculations presented here, the BH search is performed using MP2 with an unrestricted Hartree–Fock (UHF) wavefunction with the 6-31+G* basis set. The use of quantum chemical methods, such as MP2, as opposed to empirical methods is particularly amenable for studying mixed component clusters since it is not limited by the availability of force fields. The BH method with jumping [27] implemented in a development version of Q-Chem [28,29] is used. The jumping algorithm allows the Monte Carlo search to escape from a local minimum, if the Monte Carlo moves are rejected a number of times then the temperature is raised to infinity to ensure a subsequent series of moves are accepted before returning the temperature to its normal value. For each cluster ten separate runs, consisting of 1000 Monte Carlo steps starting from different randomly generated configurations of the constituent molecules are performed. During the BH search many structures are found. In this study, the primary interest is in the lowest energy structures that have distinctly different bonding which are determined through a visual analysis of the structures identified in the BH search. Subsequently, the relative energies of the low lying clusters are determined using coupled cluster theory with single and double excitations and a perturbative treatment of triple excitations (CCSD(T)) with the aug-cc-pVTZ basis set using the MOLPRO software package [30]. For the dimers, additional geometry optimisations have been performed at the CCSD(T)/aug-cc-pVDZ level to ensure consistency with the MP2 structures. Zero point energies were evaluated from harmonic frequencies calculated at the MP2/6-31+G* level. Natural bonding orbital analysis [31] was performed using orbitals from both UHF and unrestricted B3LYP [32,33] (UB3LYP) calculations. Calculations were performed for clusters of the form $[H_2O\text{-}X]^{\cdot+}$, $[(H_2O)_2\text{-}X]^{\cdot+}$ and $[H_2O\text{-}X_2]^{\cdot+}$, where X = PH_3, H_2S and HCl.

3. Results and discussion

3.1. Dimers: $[H_2O\text{-}X]^{\cdot+}$

Figure 1 shows the optimised structures of the low energy isomers of the distinct structural types identified in the BH search for the dimers. The associated energies from the CCSD(T)/aug-cc-pVTZ calculations together with relative energies with respect to the lowest energy proton transfer isomer are given in Table 1. For all of the clusters, relative energies without and including zero point energies are given in addition to the estimated free energies at 298 K. The vibrational frequencies are computed within the harmonic approximation and this will introduce some inaccuracy since the true vibrational frequencies are anharmonic. In our discussion we focus on the relative energies that include the zero point energy (ΔE_0). For the clusters studied, there are no cases where the zero point energy correction changes the nature of the lowest energy cluster. However, there are some examples where there is a change in the relative ordering in energy for the higher energy isomers.

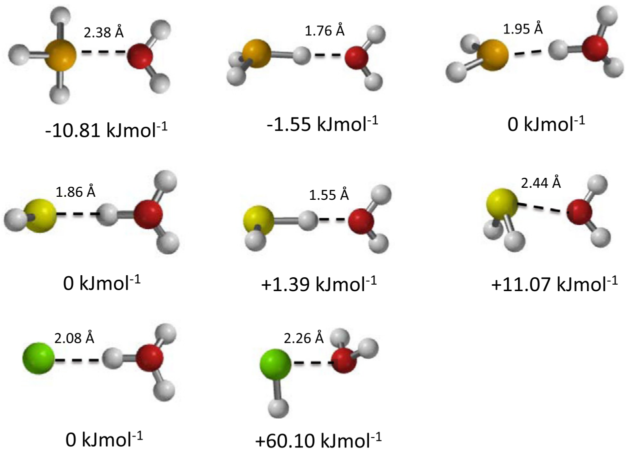

Figure 1. Low energy isomers of the $[H_2O\text{-}X]^{\cdot+}$ clusters with relative energies (ΔE_0) with respect to the lowest energy proton transfer isomer.

Table 1
Computed CCSD(T)/aug-cc-pVTZ energies of the $[H_2O\text{-}X]^{\cdot+}$ dimers, ΔE_e denotes the energies relative to the lowest energy proton transfer isomer in kJ mol^{-1}. ΔE_0 and ΔE (298 K) denote the relative energies including zero point energies and the relative free energies at 298 K in kJ mol^{-1}, respectively. HB: hemibond, PT: proton-transfer, HYB: hydrogen bonded.

Cluster	Bonding	E_e/ a.u.	ΔE_e	ΔE_0	ΔE (298 K)
$[H_2O\text{-}PH_3]^{\cdot+}$	HB	−418.757612	−12.21	−10.81	−11.76
	HYB	−418.752011	+2.49	−1.55	+1.02
	PT	−418.752960	0	0	0
$[H_2O\text{-}H_2S]^{\cdot+}$	PT	−474.978727	0	0	0
	HYB	−474.975834	+7.60	+1.39	+3.48
	HB	−474.973811	+12.91	+11.07	+13.54
$[H_2O\text{-}HCl]^{\cdot+}$	PT	−536.342864	0	0	0
	HB	−536.317080	+67.70	+60.10	+59.02

For $[H_2O\text{-}HCl]^{\cdot+}$ both the proton transfer and hemibonded isomers are found. The proton transfer form with HCl acting as the proton donor leading to $H_3O^+\text{-}Cl^{\cdot}$ is predicted to be about 60 kJ mol^{-1} more stable than the hemibonded isomer. This can be compared with $(H_2O)_2^{\cdot+}$ which favours the proton-transfer form and $(HCl)_2^{\cdot+}$ which strongly favours the hemibonded form [1]. The structure of the hemibonded isomer has a similar form to $(HCl)_2^{\cdot+}$ with H_2O replacing one of the HCl molecules and with a shorter bond distance between the heteroatoms. The lowest energy isomer for $[H_2O\text{-}H_2S]^{\cdot+}$ is a proton transfer structure with H_2S acting as the proton donor leading to $H_3O^+\text{-}SH^{\cdot}$. Another isomer with a relative energy 11 kJ mol^{-1} higher has the two heteroatoms orientated towards each other which is indicative of hemibonding, and the structure corresponds very closely to that reported in earlier work [6]. A further isomer of intermediate stability is also shown. In this structure the unpaired electron and positive charge is localised on the hydrogen sulphide fragment, and the bonding is best described as hydrogen bonding between H_2O and $H_2S^{\cdot+}$. In contrast, the proton transfer based isomer does not have the lowest energy for $[H_2O\text{-}PH_3]^{\cdot+}$. For this dimer the proton transfer isomer is over 10 kJ mol^{-1} higher in energy than the lowest energy structure found. At slightly lower energy is a hydrogen bonding type structure with the unpaired electron and positive charge localised on PH_3. The lowest energy structure conforms to a hemibonded structure with the two heteroatoms orientated towards each other. Proton transfer structure with water acting as the proton donor is not observed.

One approximation in the procedure used in this work is that the structures are derived from MP2/6-31+G* calculations. Ideally the full BH search would have been performed using CCSD(T). However, the computational cost of this makes it not a practical solution, particularly since analytical gradients for CCSD(T) are not readily available. The efficacy of the approach used relies on the MP2 calculations providing a sufficiently accurate description of the shape of the true potential energy surface. Figure 2 shows the structures and associated relative energies for the hemibonded and proton transfer isomers following optimisation using CCSD(T)/aug-cc-pVDZ. Overall, these results are consistent with those derived using the MP2 optimised structures. The largest notable difference is for the proton transfer $[H_2O\text{-}HCl]^{\cdot+}$ isomer. In the CCSD(T) structure the distance between the radical and ion is reduced by 0.08 Å, with the relative energy between the proton transfer and hemibonded isomers increasing by about 9 kJ mol^{-1} from 60 to 69 kJ mol^{-1}. The similarity between the results for the dimers suggests that using MP2 derived geometries and evaluating single point energies with CCSD(T) provides a reasonable compromise between accuracy and computational cost.

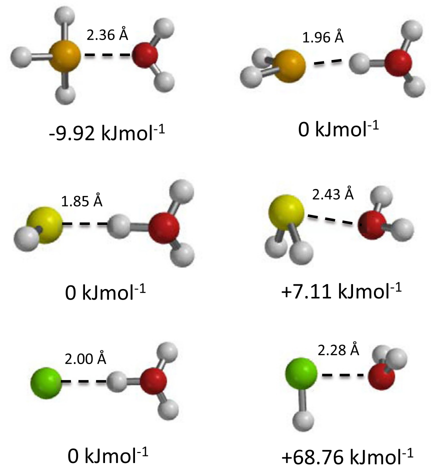

Figure 2. Lowest energy proton transfer and hemibonded isomers of the $[H_2O\text{-}X]^{\cdot+}$ clusters with relative energies (ΔE_0) with respect to the lowest energy proton transfer isomer following geometry optimisation at the CCSD(T)/aug-cc-pVDZ level.

In the previous section, some of the structures identified have been described as hemibonded structures. However, assigning a structure definitively as containing a two-centre three-electron bond is problematic, and different methods to confirm the presence of hemibonding based on techniques such NBO analysis and analysis of the localised molecular orbitals have been used [6]. We will now examine the electronic structure of the hemibonded dimers in more detail. One approach proposed to charactize hemibonding is based upon analysis of the highest doubly occupied molecular orbital, whereby hemibonding is indicated by head-on mixing of p orbitals of the heteroatoms. Figure 3 shows the relevant β spin molecular orbitals for the clusters from both UHF and UB3LYP calculations. Initially we will consider the UHF orbitals. The $[H_2O\text{-}HCl]^{\cdot+}$ dimer forms the clearest case for the presence of hemibonding. The lowest unoccupied β molecular orbital (LUMO) can be identified as the σ^* orbital formed from the end on combination of p orbitals on oxygen and chlorine, while the highest occupied molecular orbital (HOMO) is the in-phase combination with significant bonding overlap between the heavy atoms. NBO analysis is also consistent with this, giving a single electron in a two-centre bonding orbital between oxygen and chlorine.

For $[H_2O\text{-}H_2S]^{\cdot+}$, the LUMO can also be described as a σ^* orbital formed from the p orbitals on oxygen and chlorine, but the HOMO shows no σ bonding between the heteroatoms. However, an orbital slightly lower in energy does resemble the bonding σ orbital observed for $[H_2O\text{-}HCl]^{\cdot+}$, and there does not seem any reason to limit the search for the bonding orbital of this type to the highest doubly occupied orbital as indicated in previous work [6]. This would lead to a conclusion that there is hemibonding in this structure, although this is contradicted by the NBO analysis which assigns this orbital as a lone pair on oxygen. The precariousness of these analyses is illustrated if the orbitals from a UB3LYP calculation on the same structure are considered. The resulting NBO analysis does find a single electron in a two-centre bonding orbital between oxygen and chlorine. The important factor appears to be the B3LYP orbital having a component below the sulphur atom which is

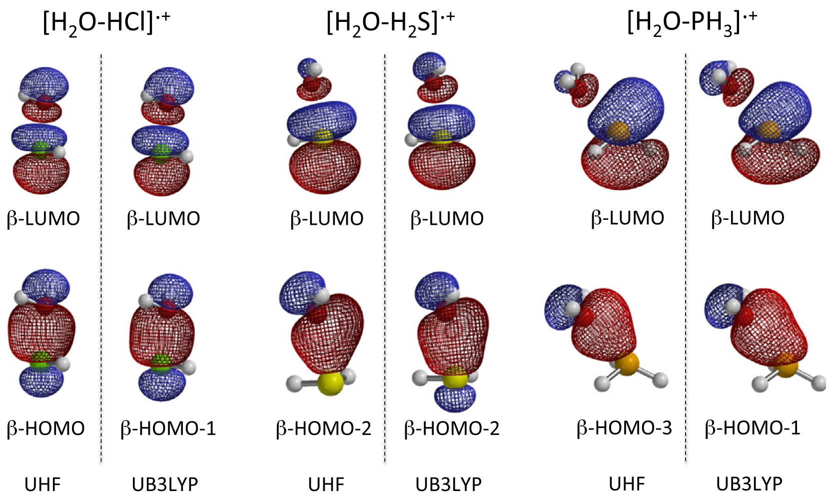

Figure 3. Localized molecular orbitals according to the Boys' procedure [34] for the σ and σ^* orbitals involved in hemibonding.

sufficient to make this orbital a two-centre bonding orbital rather than a lone pair orbital in the NBO analysis. For the $[H_2O\text{-}PH_3]^{\cdot +}$ dimer occupied β orbitals with a significant component between the two heteroatoms can be identified, and in this case there is little to visually distinguish the UHF and UB3LYP orbitals. However, the NBO analysis for the two calculations leads to different conclusions with hemibonding being present for UB3LYP and not for UHF. Overall, the different methods are consistent in predicting hemibonding in the $[H_2O\text{-}HCl]^{\cdot +}$ dimer, while there is some ambiguity for the other two dimers. In this work, we will consider hemibonding to be present in these dimers since their structural form with the heteroatoms pointing towards each other is characteristic of hemibonding, although the presence of hemibonding clearly depends on the precise nature of the definition for hemibonding to exist.

Table 2
Computed CCSD(T)/aug-cc-pVTZ energies of the $[(H_2O)_2\text{-}X]^{\cdot +}$ trimers, ΔE_e denotes the energies relative to the lowest energy proton transfer isomer in kJ mol^{-1}. ΔE_0 and ΔE (298 K) denote the relative energies including zero point energies and the relative free energies at 298 K in kJ mol^{-1}, respectively. HB: hemibond, PT: proton-transfer, HYB: hydrogen bonded.

Cluster	Bonding	E_e/ a.u.	ΔE_e	ΔE_0	ΔE (298 K)
$[(H_2O)_2\text{-}PH_3]^{\cdot +}$	PT	−495.136980	0	0	0
	HB	−495.130193	+17.82	+20.49	+16.29
	HB	−495.121144	+41.58	+39.06	+41.61
	HYB	−495.116050	+54.95	+46.79	+53.20
$[(H_2O)_2\text{-}H_2S]^{\cdot +}$	PT	−551.362003	0	0	0
	HYB	−551.345408	+43.57	+34.30	+38.91
	HB	−551.346161	+41.59	+40.90	+39.49
$[(H_2O)_2\text{-}HCl]^{\cdot +}$	PT	−612.731845	0	0	0
	PT	−612.693600	+100.41	+83.75	+87.85
	HB	−612.694368	+98.40	+86.73	+89.73
	HB	−612.680875	+133.82	+129.42	+128.14

3.2. Trimers: $[(H_2O)_2\text{-}X]^{\cdot +}$

For clusters of the form $[(H_2O)_2\text{-}X]^{\cdot +}$ the number of distinct structural isomers increases significantly, and BH becomes a useful technique to sample the configuration space. If just proton transfer and hemibonding based isomers are considered, then for the case of $[(H_2O)_2\text{-}HCl]^{\cdot +}$, clusters of the following basic structural motifs can be formed

$$OH^{\cdot}\text{-}H_3^+O\text{-}HCl \tag{1}$$

$$H_2O\text{-}H_2Cl^+\text{-}OH^{\cdot} \tag{2}$$

$$H_2O\text{-}H_3^+O\text{-}Cl^{\cdot} \tag{3}$$

$$(H_2O\therefore H_2O)^{\cdot +}\text{-}HCl \tag{4}$$

$$(H_2O\therefore ClH)^{\cdot +}\text{-}H_2O \tag{5}$$

where $\therefore$ denotes a hemibond. The first two structures follow proton transfer from water to either the other water molecule or HCl, and the third structure arises from proton transfer from HCl to water. While for the hemibonded structures, hemibonding may occur between two water molecules or water and HCl. In addition many alternative structures can be conceived. Figure 4 shows the distinct low energy isomers identified in the BH search with the computed energies given in Table 2. For $[(H_2O)_2\text{-}HCl]^{\cdot +}$ four of the structural motifs identified above are illustrated nicely. The structure that is not observed follows proton transfer from HCl to water which will clearly be of very high relative energy. The lowest energy structure has proton transfer with HCl acting as the proton donor which is consistent with the lowest energy dimer structure found. At significantly higher energy (+84 kJ mol^{-1}) the structure with proton transfer between the two water molecules is found. The two hemibonded forms of the cluster are also found in the search, although we note that the $[(H_2O\therefore H_2O)^{\cdot +}\text{-}HCl]$ cluster corresponds to a transition state with one imaginary frequency. The relative energy between the lowest proton transfer and hemibonded isomers is larger than for the dimers owing to a more favourable interaction of H_2O with H_3^+O than with $(H_2O\therefore ClH)^{\cdot +}$.

The three isomers identified for $[(H_2O)_2\text{-}H_2S]^{\cdot +}$ can be derived from binding of the additional water molecule to the dimer isomers shown earlier (Figure 1). For the cluster that is based upon hydrogen bonding, the calculations indicate that it is more favourable for the water molecule to bind to $H_2S^{\cdot +}$ than the other water molecule. Similarly to the dimer, the proton transfer structure with H_2S acting as the proton donor is found to be the lowest energy structure. Structures wherein a water molecule acts as a proton donor or where there is hemibonding between two water molecules are not observed. These structures are likely to have significantly higher energy and may correspond to transition states, and so always rearrange to give one of the structures shown during the BH search.

For the $[(H_2O)_2\text{-}PH_3]^{\cdot +}$ cluster a different picture emerges compared to the associated dimer. The hemibonded (or hemibonding-like) dimer has lower energy than the proton transfer dimer,

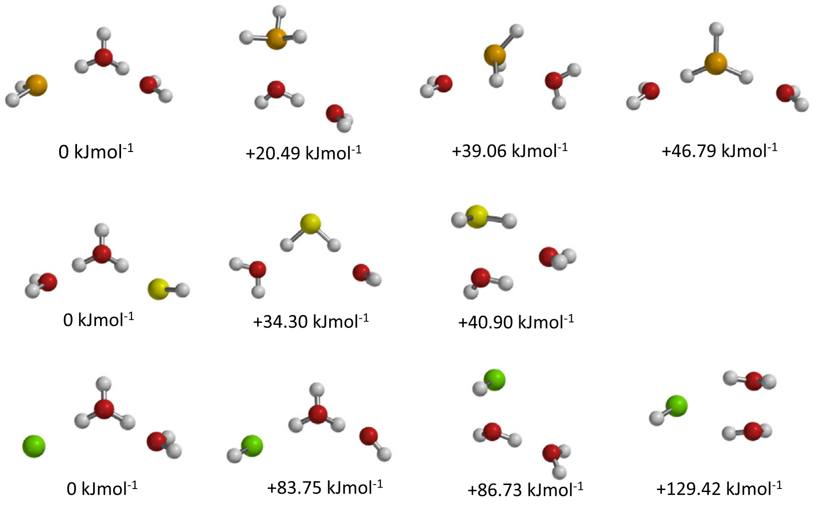

Figure 4. Low energy isomers of the $[(H_2O)_2\text{-}X]^{\cdot +}$ clusters with relative energies (ΔE_0) with respect to the lowest energy proton transfer isomer.

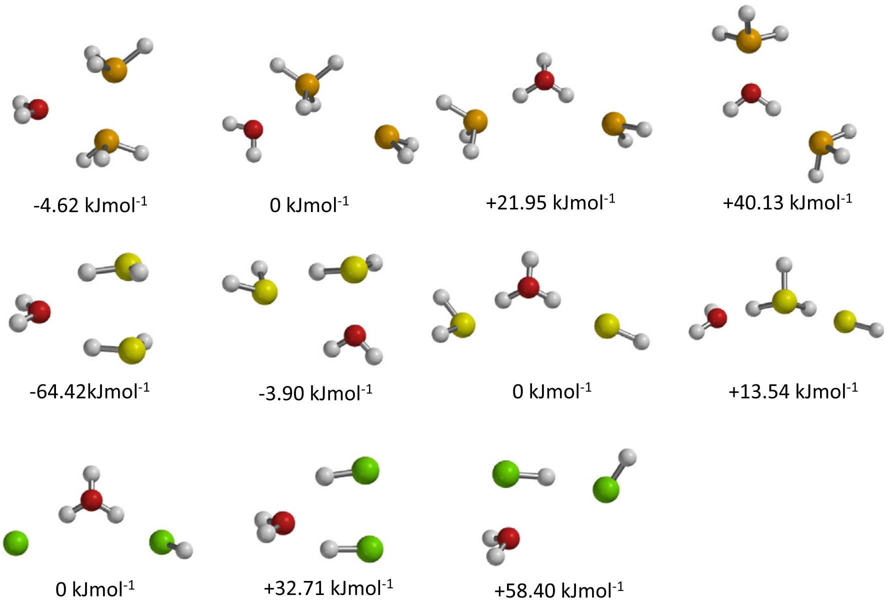

Figure 5. Low energy isomers of the $[H_2O\text{-}X_2]^{\cdot+}$ clusters with relative energies (ΔE_0) with respect to the lowest energy proton transfer isomer.

although by a relatively small amount (≈11 kJ mol^{-1}). Addition of a water molecule reverses this trend, and the proton transfer structure is found to have a lower energy by 20.5 kJ mol^{-1}. The change arises from the extra stability gained from the water molecule binding to H_3O^+ compared to a hemibonded water molecule. Further structures comprising the two water molecules bonded to a central $PH_3^{\cdot+}$ at higher energy are also shown. Like $[(H_2O)_2\text{-}H_2S]^{\cdot+}$, structures with water acting as a proton donor are not found.

3.3. Trimers: $[H_2O\text{-}X_2]^{\cdot+}$

The structures identified for clusters of the form $[H_2O\text{-}X_2]^{\cdot+}$ are shown in Figure 5 with the associated energies given in Table 3. If the example of $[H_2O\text{-}(HCl)_2]^{\cdot+}$ is considered, then proton transfer and hemibonded clusters of the following form would be expected

$$OH^{\cdot}\text{-}H_2Cl^{+}\text{-}HCl \tag{1}$$

$$H_2O\text{-}H_2Cl^{+}\text{-}Cl^{\cdot} \tag{2}$$

$$HCl\text{-}H_3^{+}O\text{-}Cl^{\cdot} \tag{3}$$

$$(H_2O\therefore ClH)^{\cdot+}\text{-}HCl \tag{4}$$

$$(HCl\therefore ClH)^{\cdot+}\text{-}H_2O \tag{5}$$

The first two structures form H_2Cl^+ following proton transfer from water or HCl. This is clearly an energetically unfavourable process and these clusters are not observed. The lowest energy isomer arises from proton transfer with HCl as the proton donor and water as the proton acceptor. The two hemibonded structures are also identified, the lowest energy of which has a water molecule binding to the hemibonded $(HCl\therefore ClH)^{\cdot+}$ core. This isomer lies 33 kJ mol^{-1} higher in energy than the proton transfer isomer, and the hemibonded isomer with HCl bonded to $(H_2O\therefore ClH)^{\cdot+}$ lies a further 25 kJ mol^{-1} higher in energy.

For $[H_2O\text{-}(H_2S)_2]^{\cdot+}$ the two lowest energy isomers show hemibonding. The most stable is the $(H_2S\therefore SH_2)^{\cdot+}\text{-}H_2O$ isomer which has a similar structure to the lowest energy $(H_2O)_3^{\cdot+}$ and $(H_2S)_3^{\cdot+}$ hemibonded isomers [24]. This isomer is significantly lower in energy than the next lowest energy isomer which has the $(H_2S\therefore OH_2)^{\cdot+}$ hemibonded unit. Two proton transfer based structures are also found at higher energy, with the lower energy structure arising when H_2S acts as the proton donor and H_2O as the proton acceptor. The isomer corresponding to proton transfer from H_2O to H_2S is not observed. A slightly smaller range in relative energies is found for the $[H_2O\text{-}(PH_3)_2]^{\cdot+}$ clusters. The lowest energy structure has a hemibonded like $(PH_3\therefore PH_3)^{\cdot+}$ core, although the structure with proton transfer between PH_3 molecules is less than 5 kJ mol^{-1} higher in energy. The next cluster shows proton transfer structure with PH_3 as a proton donor and H_2O as a proton acceptor, followed by hemibonding between H_2O and PH_3. The isomer associated with proton transfer from H_2O to PH_3 is not found.

Table 3
Computed CCSD(T)/aug-cc-pVTZ energies of the $[H_2O\text{-}X_2]^{\cdot+}$ trimers, ΔE_e denotes the energies relative to the lowest energy proton transfer isomer in kJ mol^{-1}. ΔE_0 and ΔE (298 K) denote the relative energies including zero point energies and the relative free energies at 298 K in kJ mol^{-1}, respectively. HB: hemibond, PT: proton-transfer.

Cluster	Bonding	E_e/ a.u.	ΔE_e	ΔE_0	ΔE (298 K)
$[H_2O\text{-}(PH_3)_2]^{\cdot+}$	HB	−761.540118	−5.27	−4.62	−11.29
	PT	−761.538111	0	0	0
	PT	−761.529699	+22.09	+21.95	+15.01
	HB	−761.523887	+37.39	+40.13	+31.62
$[H_2O\text{-}(H_2S)_2]^{\cdot+}$	HB	−873.997136	−62.93	−64.42	−61.81
	HB	−873.972856	+0.82	−3.90	+5.02
	PT	−873.973168	0	0	0
	PT	−873.966781	+16.77	+13.54	+17.09
$[H_2O\text{-}(HCl)_2]^{\cdot+}$	PT	−996.742733	0	0	0
	HB	−996.724431	+48.05	+32.71	+33.54
	HB	−996.714106	+75.16	+58.40	+62.11

4. Conclusions

The low energy isomers for mixed component radical cation clusters of the form $[H_2O\text{-}X]^{\cdot+}$, $[(H_2O)_2\text{-}X]^{\cdot+}$ and $[H_2O\text{-}X_2]^{\cdot+}$, where X = PH_3, H_2S and HCl, have been identified using BH in conjunction with MP2/6-31+G*. The relative energies of the clusters are refined at the CCSD(T)/aug-cc-pVTZ level. One of the limitations of performing the BH search with quantum chemical methods as opposed to empirical or semi-empirical methods is the increased cost of the calculations limits the extent of the BH search that is practically possible. In this work, each cluster was studied using ten separate runs consisting of 1000 Monte Carlo steps. The lowest energy proton transfer and hemibonded isomers were found in nearly all of the BH runs. Out of the 90 BH runs (ten each for nine clusters) there were only eight runs that failed to find either lowest energy proton transfer or hemibonded forms. The most difficult isomer to find was the $[(H_2S)(H_2O)]^{\cdot +}$ proton transfer isomer, which was found in six of the ten BH runs. For this cluster an additional four basin hopping runs were performed, but no lower energy isomers were identified.

The dimers with $X = H_2S$ and HCl give a proton transfer based structure to form H_3O^+ and $SH^{\cdot}$ or $Cl^{\cdot}$ radicals as the lowest energy structure. However, for $X = PH_3$ a hemibonded structure is the most stable. Although we highlight the difficulty in rigorously assigning these structures to contain a two-centre three electron hemibond. Additional structures that comprise H_2O hydrogen bonded to $H_2S^{\cdot +}$ and PH_3^{+} are also identified. For the trimers, there exists a much wider range of possible isomers based upon both proton transfer and hemibonded structural motifs. For $[(H_2O)_2\text{-}X]^{\cdot +}$ the lowest energy isomers arise from proton transfer from X to H_2O, and the relative stability of this isomer compared to the next lowest energy isomer increases in the order $X = PH_3$, H_2S and HCl. For PH_3 there is a change in the nature of the lowest energy isomer with respect to the dimer. This can be associated with a more favourable binding of the additional H_2O molecule to H_3O^+ compared to $[H_2O\therefore PH_3]^{\cdot +}$. For $[H_2O\text{-}(HCl)_2]^{\cdot +}$ proton transfer once again forms the lowest energy isomer, but for $[H_2O\text{-}(PH_3)_2]^{\cdot +}$ and $[H_2O\text{-}(H_2S)_2]^{\cdot +}$ hemibonding based structures emerge as the most stable. In the case of H_2S, the hemibonded isomer is significantly lower in energy that the lowest proton transfer based isomer, whereas for PH_3 the hemibonded isomer is less than 5 kJ mol^{-1} lower in energy.

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