

Reactivity of the $\text{O}_2^+(\text{H}_2\text{O})_n$ and $\text{NO}^+(\text{H}_2\text{O})_n$ Cluster Ions in the D-region of the Ionosphere

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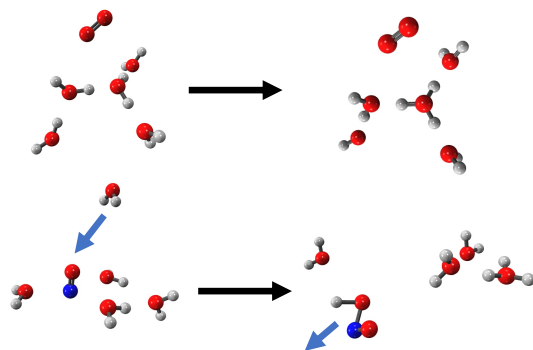
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Abstract

The protonated water clusters present in the D-region of the ionosphere have been postulated to be formed from cluster ions such as $\text{O}_2^+(\text{H}_2\text{O})_n$ and $\text{NO}^+(\text{H}_2\text{O})_n$, although the detailed mechanism of the underlying reactions is not understood. Second order Møller-Plesset perturbation theory based Born-Oppenheimer ab initio molecular dynamics (AIMD) simulations of the reactions of the $\text{O}_2^+(\text{H}_2\text{O})_n$ and $\text{NO}^+(\text{H}_2\text{O})_n$ cluster ions to form protonated water clusters reveal different mechanisms for the O_2^+ and NO^+ based ions. AIMD simulations of $\text{O}_2^+(\text{H}_2\text{O})_{n=2-5}$ with initial velocities of the atoms sampled from the Maxwell-Boltzmann distribution at 220 K show that following charge transfer, a reaction to form a protonated water cluster and OH occurs rapidly where the neutral O_2 molecule is just a spectator. In contrast, the reaction of $\text{NO}^+(\text{H}_2\text{O})_{n=4,5}$ has been hypothesised to involve an intracuster reaction, but no reaction is observed in AIMD simulations using thermal initial velocities. However, it is shown that reactions to form protonated water clusters do occur in simulations when a water molecule collides with a $\text{NO}^+(\text{H}_2\text{O})_4$ cluster.

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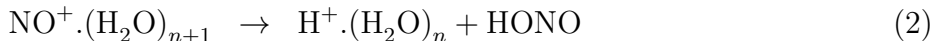
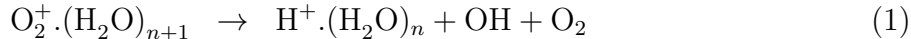


Ab initio molecular dynamics simulations reveal different reactivities of $\text{NO}^+(\text{H}_2\text{O})_n$ and $\text{O}_2^+(\text{H}_2\text{O})_n$ cluster ions in the D-region of the ionosphere.

Introduction

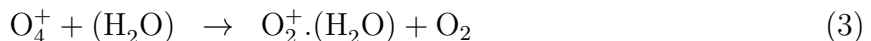
The Earth’s ionosphere is a region of the upper atmosphere that contains many ions, and is often considered to comprise several regions/layers. The most complicated chemistry occurs in the D-region, which lies from about 50 km to 90 km in altitude and is notable for the existence of cluster ions and its rich ion chemistry.¹ The composition of the D-layer has important consequences for the attenuation of radio signals. Neutral species can be readily ionised by solar radiation and the major positive ions in the atmosphere are predicted to be NO^+ , O_2^+ and N_2^+ in order of decreasing abundance in line with their ionization energies.² Once these ions have been formed they can be involved in complicated reactions, and characterizing the mechanisms of these reactions is important for our understanding of the chemical composition of the ionosphere. The nature of these reactions can be studied with quantum chemical calculations. However, some caution is required when applying quantum chemical methods to study these reactions since the ionic species involved can lead to unusual bonding, such as three-electron two-centre bonds,³ and weak interactions that can be a challenge for methods such as density functional theory (DFT) to model accurately.^{4–6}

Measurements have shown O_2^+ and NO^+ to have a high abundance in the upper E- and F-layers of the ionosphere.⁷ However, at lower levels in the D-layer protonated water clusters are the major positively charged ions.^{8–10} $\text{X}^+(\text{H}_2\text{O})_n$ clusters can be formed in a step-wise solvation process, and the resulting clusters can then undergo intracuster reactions to form protonated water clusters

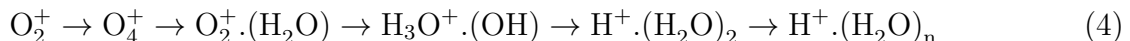


where in reaction (2) nitrous acid (HONO) is formed.

A number of studies have attempted to rationalize the formation of protonated water clusters from O_2^+ . Fehsenfeld and Ferguson¹¹ studied the ions produced following the addition of water vapour to flowing streams of O_2^+ and proposed that protonated water clusters could form from $O_2^+.(H_2O)$ ions. In this scheme H_3O^+ was hypothesised to form from a collision of $O_2^+.(H_2O)$ with a second water molecule. It was also suggested that $O_2^+.(H_2O)$ could be formed from O_4^+



where O_4^+ is produced from a 3-body reaction involving O_2^+ and O_2 . Good et al.¹² proposed the following reaction mechanism for the formation of protonated water clusters under ionospheric conditions



which supported the ion-molecule scheme of Fehsenfeld and Ferguson.

$O_2^+.(H_2O)_2$ and $O_2^+.(H_2O)_3$ ions have been observed in laboratory based experiments.^{12–15} The formation of $O_2^+.(H_2O)_2$ was attributed to a direct 3-body addition of water to $O_2^+.(H_2O)$.¹² However, a different study proposed that it was formed via a $H_3O^+.(OH)$ intermediate.¹³ The formation of protonated water clusters from O_2^+ was also studied using ion-drift mass spectrometry.¹⁴ The $O_2^+.(H_2O)_2$ ion was observed and it was suggested that this cluster has two different stable structures, with the ion structure $O_2^+.(H_2O)_2$ expected to produce $(H_3O)^+.(H_2O)$ ions less readily than $(H_3O)^+.(OH).O_2$. Experimental studies have also shown $O_2^+.(H_2O)$ to exist¹⁶ and has a binding energy of about 77.2 kJ mol^{-1} .¹⁷

The fragmentation patterns of $O_2^+.(H_2O)_n$ have also been studied by Angel and Stace.^{18,19} For $n \geq 2$ it was noted that charge transfer could initially occur from O_2^+ to the water

molecules, leading to a cluster that adopts the structure $\text{O}_2 \cdot (\text{H}_2\text{O})_{n-2} \cdot \text{H}_3\text{O}^+ \cdot \text{OH}$. This can then lead to the formation of protonated water clusters with OH and O_2 leaving the cluster. However, the dominant reaction product was $(\text{H}_2\text{O})_n^+$, and since there is no evidence of the unprotonated ions in the ionosphere there would then need to be an effective process to form protonated water clusters from $(\text{H}_2\text{O})_n^+$. It was thus postulated that reactions of $(\text{H}_2\text{O})_n^+$ with additional water molecules would lead to the formation of protonated water clusters with the loss of OH. The study also determined the critical hydration size for the formation of proton hydrates to be $\text{O}_2^+ \cdot (\text{H}_2\text{O})_2$.

The infrared (IR) spectrum of the $\text{O}_2^+ \cdot (\text{H}_2\text{O})$ cation has been measured.²⁰ Absorptions corresponding to the OH asymmetric stretch (3430.7 cm^{-1}), the OH symmetric stretch (3341.7 cm^{-1}) and the O-O stretch (1601.1 cm^{-1}) were observed, with a further mode assigned to a H_2O - O_2 stretch at 731.0 cm^{-1} . Quantum chemical calculations of the structure and harmonic vibrational frequencies were performed using DFT and CCSD(T) methods. The calculated frequencies showed a surprising level of discrepancy with the experimental data. For example, the CCSD(T) frequencies are over 200 cm^{-1} too high after the application of a suitable scaling factor and the H_2O - O_2 stretching frequency is too low. This poor agreement was associated by the authors with the large spin contamination ($\langle S^2 \rangle = 1.68$ for a doublet state) present in the calculations. There does not appear to be much computational work reported on the structures of large $\text{O}_2^+ \cdot (\text{H}_2\text{O})_n$ clusters, although the structures of neutral $\text{O}_2 \cdot (\text{H}_2\text{O})_{n=1-6}$ clusters have been studied.²¹

$\text{NO}^+ \cdot (\text{H}_2\text{O})_n$ has been studied extensively by both experiment and theory.^{6,10,22-33} One key feature of the reaction involving NO^+ is the formation of nitrous acid. Experimental work based upon infrared spectroscopy has shown that the formation of HONO is dependent on the size and structure of the water cluster, in particular HONO formation occurs when $n=4$ and becomes dominant at $n=5$ (reaction (2)).²⁸ Temperature can also play a role

since at increased temperatures higher energy isomers become more populated.^{29,30} Computational studies, including both wavefunction-based (coupled cluster theory and Møller-Plesset perturbation theory) methods and DFT, have characterized the low energy structures of $\text{NO}^+(\text{H}_2\text{O})_n$ and it has been shown that the energy difference between the lowest energy clusters that contain NO^+ and HONO decreases as n increases.^{6,32} Some caution is required when studying these systems with DFT. Recent work has shown that the predicted low energy structures of $\text{NO}^+(\text{H}_2\text{O})_n$ depend significantly on the exchange-correlation functional used in DFT calculations.⁶ Functionals with a low fraction of Hartree-Fock (HF) exchange overestimate the binding energy between NO^+ and H_2O and incorrectly predict the structure of $\text{NO}^+(\text{H}_2\text{O})_2$. This was associated with an artefact of the calculations whereby a delocalisation of the charge from NO^+ to H_2O occurs. Through molecular dynamics simulations the reactivity and the reaction mechanisms can be studied in detail. Ab initio molecular dynamics (AIMD) simulations using DFT with the BLYP+D functional showed reactions for the $n=4$ and $n=5$ clusters and identified critical structures in the reaction mechanism.³³ However, more recent work simulated the reactivity of the $n=5$ clusters using AIMD simulations with MP2 and found the clusters did not react to form HONO.⁶ In the present paper the reaction of O_2^+ and NO^+ ions with water are studied with AIMD simulations based upon second order Møller-Plesset perturbation theory, and it is shown that there are significant differences between the reactivity of the two ions.

Computational Details

The lowest energy structures of $\text{O}_2^+(\text{H}_2\text{O})_{n=1-5}$ were calculated using a hierarchical procedure where a lower level of theory is used to search the conformational space and identify low energy isomers that are then re-optimized at a higher level of theory. This approach has been used successfully in the study of related systems.^{4-6,34,35} In this work the conformational search is performed using unrestricted HF with the 6-31+G* basis set with a random search

approach. In this approach after an initial geometry optimization the oxygen and water molecules are subjected to 20 random moves that include translations and rotations and the resulting structure is re-optimized. The structural moves are subject to the constraints that the molecules are kept separated by a least 0.2 bohr at the point of closest contact and the molecules are kept within a box of length 10 bohr. This procedure was repeated 100 times to give a total of 101 (including the initial) structures. The structural searches were performed for both doublet and quartet spin states. The distinct low energy structures were then re-optimized at the unrestricted MP2/6-311++G** level and harmonic frequencies computed. The computed harmonic frequencies were scaled by 0.95 and in the simulated spectra the vibrational bands are represented by Lorentzian functions with full-width at half-maximum of 10 cm^{-1} . The computed spectra have been normalized so that the intensity of the most intense band is equal to one. Binding energies are computed subject to the counterpoise correction³⁶ (performed with the individual moieties frozen at their optimized geometries in the complex) and atomic charges and spin were calculated from a natural bonding orbital analysis.

Born-Oppenheimer AIMD simulations were performed at the MP2/6-31+G* level of theory at a temperature of 220 K, which is representative of the temperature of the ionosphere, with initial velocities sampled from a Maxwell-Boltzmann distribution. For $\text{O}_2^+(\text{H}_2\text{O})_{n=2-5}$ clusters, a time step of 0.484 fs was used with a total simulation time of 4.84 ps, and the dynamics were run for the quartet state. The initial structures consisted of O_2^+ with n undissociated water molecules in a configuration where the position of the oxygen atoms correspond to the lowest energy structures obtained from the random search procedure since for $n \geq 2$ the lowest energy structures have the form $\text{O}_2.\text{H}_3\text{O}^+.\text{OH}.\text{(H}_2\text{O)}_{n-2}$ (see below). Born-Oppenheimer AIMD simulations were also performed for the $\text{NO}^+(\text{H}_2\text{O})_{n=4,5}$ clusters but with a significantly longer total simulation length of 9.676 ps and initial structures of the lowest energy structure of the clusters.⁶ For these clusters simulations were performed

using MP2 and a range of basis sets. All calculations were performed with the Q-Chem software package,³⁷ except the multi-reference configuration interaction calculations where the MOLPRO package was used.^{38,39}

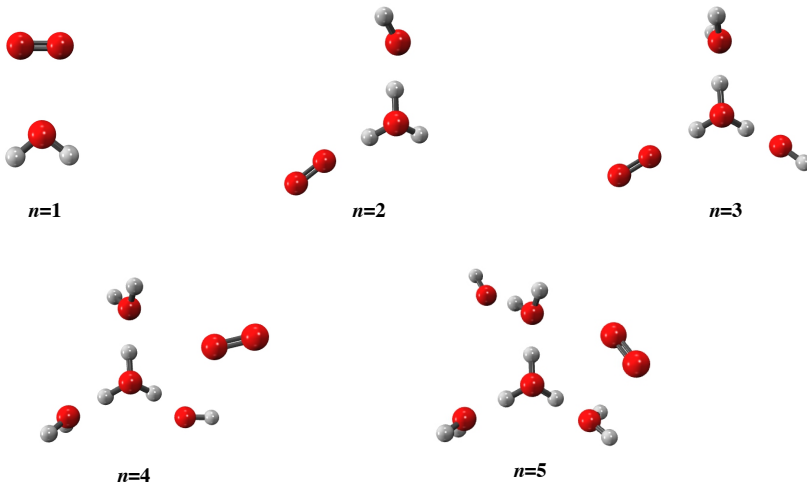


Figure 1: Minimum energy structures of $\text{O}_2^+(\text{H}_2\text{O})_{n=1-5}$.

Results and Discussion

$\text{O}_2^+(\text{H}_2\text{O})_n$

Figure 1 shows the lowest energy structures for the $\text{O}_2^+(\text{H}_2\text{O})_{n=1-5}$ complexes. The lowest energy cluster for $n=1$ corresponds to a complex of a water and oxygen diatomic cation and has a doublet state. In the structure shown, the hydrogen atoms of the water lie in the same plane as the oxygen ion, although the corresponding structure with the hydrogen atoms lying approximately perpendicular to the oxygen ion has a very similar energy. The atomic charges and spin are shown in Figure 2 and confirm that the positive charge and spin are localized on the oxygen molecule. Previously calculations on $\text{O}_2^+(\text{H}_2\text{O})$ found a high degree of spin contamination,²⁰ however, $\langle S^2 \rangle = 0.76$ for the calculation reported here, and the structure of the cluster found in the current study is also significantly different with the oxygen atom of water much closer to one of the oxygen atoms of the diatomic cation.

The lowest energy quartet spin state structure (shown in the SI) lies 147 kJ mol^{-1} higher in energy but also consists of a water and oxygen molecule. However, the structure of the complex is different with the water molecule binding to oxygen through a hydrogen atom rather than the oxygen atom. The binding energies for the doublet state of $\text{O}_2^+(\text{H}_2\text{O})$ for a range of different methods including DFT are given in Table 1. The DFT calculations show a large variation in the values for the binding energy from 90 kJ mol^{-1} to 185 kJ mol^{-1} . The magnitude of the error increases as the fraction of Hartree-Fock exchange in the functional decreases and the source of the error can be attributed to an artificial delocalization of charge from O_2^+ to the water molecule. The artificial delocalization of charge associated with the use of approximate exchange in DFT studies of related systems is well documented.⁴⁰⁻⁴² The HF value is in closer agreement with the coupled cluster values than DFT with any of the exchange-correlation functionals considered. The values show that the binding energies computed with MP2 are in close agreement with coupled cluster values. A limitation of coupled cluster theory calculations is that they are based upon a single HF reference determinant. We have also calculated the binding energy using multi-reference configuration interaction (MRCI+Q) calculations. The calculations used an active space that includes the highest five occupied orbitals and six lowest virtual orbitals with the core 1s orbitals of the three heavy atoms frozen. The MP2 optimized structure and 6-311++G** basis set were used. The binding energy is evaluated as the difference in the MRCI+Q energy for the complex and the energy of the system when the water molecule is moved 100 \AA away from O_2^+ using the same active space. This gives a value of the binding energy, that is not corrected for basis set superposition error, of 81.1 kJ mol^{-1} , which is consistent with the MP2 and coupled cluster values. The MRCI wavefunction also shows the positive charge to be localised on O_2 , and there is no delocalization of charge onto the water molecule. We note that the basis set used is also an important factor and the binding energy for MP2/aug-cc-pVTZ is 78.2 kJ mol^{-1} , which is about 5 kJ mol^{-1} higher than the MP2/6-311++G** value. Both of these values are consistent with the experimental value of 77.2 kJ mol^{-1} .¹⁷ Similar to the

$\text{NO}^+(\text{H}_2\text{O})$ complex, DFT gives a wide range of values for the binding energy depending on the exchange-correlation function used. In general, the binding energy is overestimated and the extent of this over-estimation increases as the fraction to HF exchange in the functional decreases.

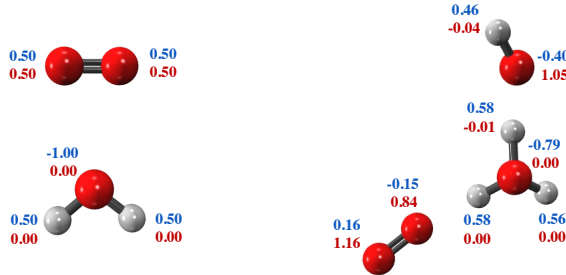


Figure 2: Atomic charges (upper value in blue) and spin densities (lower value in red) for $\text{O}_2^+(\text{H}_2\text{O})$ and $\text{O}_2^+(\text{H}_2\text{O})_2$.

Table 1: Computed binding energies with the 6-311++G** basis set and difference with respect to CCSD(T) ($\Delta\text{CCSD(T)}$) for $\text{O}_2^+.\text{H}_2\text{O}$ in kJ mol^{-1} . ^aCCSD structure used. The experimental value for the binding energy is 77.2 kJ mol^{-1} .¹⁷

Method/Functional	Binding Energy	$\Delta\text{CCSD(T)}$
CCSD(T) ^a	72.8	+0.0
CCSD	72.8	+0.0
MP2	73.1	+0.3
HF	74.8	+2.0
M06-HF	90.0	+17.2
PBE50	107.1	+34.3
$\omega\text{B97X-D}$	114.2	+41.5
M06-2X	142.4	+69.7
M06	172.4	+99.7
PBE0	174.2	+101.4
B3LYP	174.4	+101.6
B3LYP-D	185.5	+112.8

For the larger clusters there is a fundamental change in the nature of the lowest energy structures. The lowest energy structures correspond to quartet states, these states have $\langle S^2 \rangle = 3.79$ and are not spin contaminated. For these clusters, the unrestricted HF calculations for the doublet states have a high degree of spin contamination and it is difficult to

converge the self-consistent field calculation. In the lowest energy clusters the charge has transferred from oxygen to water, and there has been a subsequent reorganization of the water molecules to form H_3O^+ and OH. The atomic charge and spin values (Figure 2) for $\text{O}_2^+(\text{H}_2\text{O})_2$ are consistent with this, showing the positive charge to be localised on H_3O^+ and two unpaired electrons on O_2 and a single unpaired electron on OH. This behaviour is consistent with the ionization energies. The ionization energy of neutral O_2 is less than the ionisation energy of an H_2O molecule but greater than the ionisation energy of $(\text{H}_2\text{O})_2$.

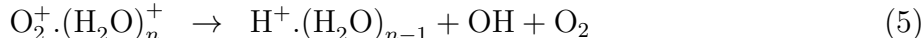
Several studies have considered the structure of ionised water clusters,^{4,43} and the structure of the $\text{O}_2^+(\text{H}_2\text{O})_{n=2-5}$ clusters shown have the form of O_2 interacting with the lowest energy structure for $(\text{H}_2\text{O})_{n=2-5}^+$. In particular, the $n=5$ structure has the separated ion-radical pair structure where the OH radical is not directly interacting with H_3O^+ which has been shown to be the most stable structure for $(\text{H}_2\text{O})_5^+$. These calculations are consistent with the observation from the experiments of Angel and Stace that H_3O^+ is formed for $n \geq 2$.^{18,19}

The computed IR spectra for the lowest energy structures are shown in Figure 3. The spectra focus on the O-H stretching region since this is the region of the spectrum that is typically measured in the reported spectra. For $n=1$ the symmetric and antisymmetric stretching modes of water are observed. In the cluster the frequency of the antisymmetric mode is shifted to lower frequency by about 30 cm^{-1} and there is an increase in the relative intensity of the symmetric stretching mode compared with an isolated water molecule. The calculated frequencies of the asymmetric stretch, symmetric stretch and O-O stretch are 3772 cm^{-1} , 3698 cm^{-1} and 1456 cm^{-1} , respectively. The closest mode to the reported $\text{H}_2\text{O}-\text{O}_2$ stretch lies at 650 cm^{-1} and corresponds to a rocking of the water molecule relative to O_2 .

The computational method used here predicts the vibrational frequencies of gas-phase

water⁴⁴ to within 50 cm⁻¹, and the frequencies are consistent with the CCSD(T) frequencies reported in the experimental paper.²⁰ However, the calculated frequencies for the O₂⁺.(H₂O) complex are considerably higher than the reported experimental spectrum.²⁰ One potential reason for this discrepancy could be the effects of anharmonicity. Exploratory anharmonic frequency calculations based upon transition-optimized shifted Hermite theory⁴⁵ at the HF/6-311++G** level show that the anharmonic frequency correction for the O-H stretching modes in the O₂⁺.(H₂O) complex are about 100 cm⁻¹ larger than for the isolated water molecule. This suggests that the scaling factor of 0.95 is underestimating the anharmonic effects in the complex. This would bring the calculated frequencies in closer agreement with the experimental values. Although we note that none of the calculated frequencies upon which the assignment of the measured spectrum to the O₂⁺.(H₂O) complex is based are in very good agreement with the experimental values suggesting that further experimental work should be undertaken to confirm those values, or otherwise. For the clusters $n=2-5$, the calculations show new intense bands at lower frequencies. These bands are associated with the O-H stretching modes of H₃O⁺ moiety. There is a significant shift in the frequency of these bands between $n=3$ and $n=4$ which is a consequence of O₂ no longer being directly hydrogen bonded to H₃O⁺.

AIMD simulations allow the reaction to form OH from the O₂⁺.(H₂O) _{n} clusters to be studied.



An example AIMD simulation for $n=5$ cluster is included in the SI with the initial and final structures for $n=2-5$ simulations illustrated in Figure 4. All of the simulations start with a structure where O₂ is bound to a cluster of water molecules. The calculations show that for these structures the positive charge is localized on a water molecule. This is consistent

with the highest occupied molecular orbital for the neutral clusters corresponding to a lone pair on a water molecule. With the positive charge on a water molecule, as the simulation progresses with thermal initial velocities there is a rearrangement of the water molecules to form H_3O^+ and OH, and during this process the O_2 molecule is largely just a spectator. For all of the simulations the formation of OH occurs on a fast timescale and within the simulation length of 4.84 ps. We note that for analogous simulations for the $n=1$ cluster no reactions to form OH occur. For clusters with $n \geq 2$ the process of charge transfer to the solvent followed by formation of H_3O^+ and OH has been suggested in previous work.¹⁸ However, in the experiments this reaction channel was smaller than the reaction channel where OH is not formed. In our calculations for $n \geq 2$ we have not considered the doublet state in detail owing to the large spin contamination and erratic convergence associated with the reference HF calculation. Consequently an accurate description of this state is challenging for single reference methods and multireference methods are likely to be required. Our calculations for the doublet state indicate that it is higher in energy than the corresponding quartet state and it corresponds to $\text{O}_2^+(\text{H}_2\text{O})_n$ where OH has not been formed. This can be rationalized by considering the spin of the system. For charge transfer to occur in the doublet state to form O_2 and $(\text{H}_2\text{O})_n^+$, the resulting O_2 must be in an excited (singlet) state which will be energetically less favourable process than the corresponding process for the quartet state where O_2 is in its ground (triplet) state. Consequently, charge transfer and reaction to form OH is less likely in the doublet state.

$\text{NO}^+(\text{H}_2\text{O})_n$

The low energy isomers of $\text{NO}^+(\text{H}_2\text{O})_n$ and their IR spectra have been discussed in detail in previous studies.^{6,26,27,32} It has been established that the lowest energy structures do not conform to structures where a rearrangement to form protonated water clusters and HONO has occurred. The lowest energy structures with HONO have been estimated to be 7.5 kJ

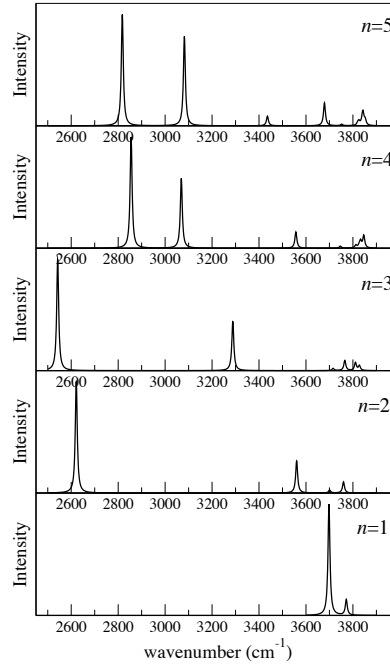


Figure 3: Computed infrared spectra for the lowest energy conformers of $\text{O}_2^+(\text{H}_2\text{O})_{n=1-5}$.

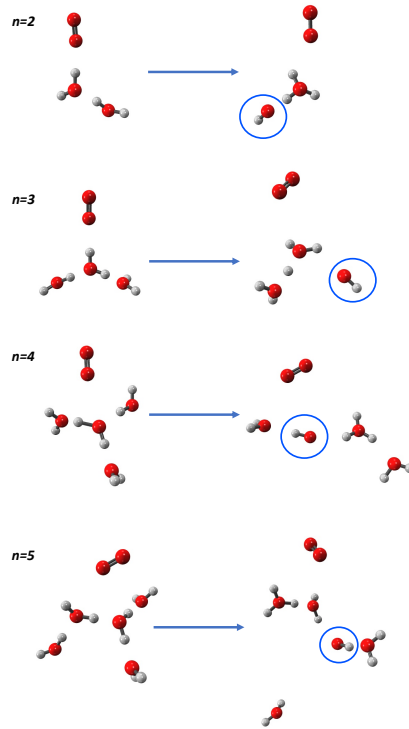
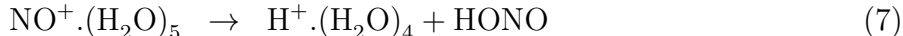
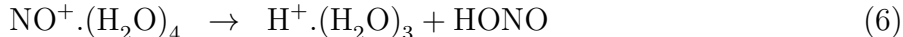


Figure 4: Initial and final structures from the AIMD of $\text{O}_2^+(\text{H}_2\text{O})_n$ with the OH fragment formed circled.

mol⁻¹ and 6.3 kJ mol⁻¹ higher in energy than the global minimum energy structure for $n=4$ and 5, respectively.⁶ We have explored the reactivity of the lowest energy NO⁺.(H₂O)₄ and NO⁺.(H₂O)₅ clusters with respect to the formation of HONO based upon AIMD simulations with initial velocities sampled from the Maxwell-Boltzmann distribution at 220 K.



These simulations have been performed using MP2 with the 6-31G, 6-31+G* and 6-311++G** basis sets and for both $n=4$ and 5 no reaction was observed within the 4.84 ps simulation. In contrast to the simulations with O₂⁺.(H₂O) _{$n=2-4$} , the ionization energy of NO is less than than water so there is no charge transfer to the water molecules. The initial and final structures for the MP2/6-311++G** simulations are shown in the SI. During the simulations the molecules move around their initial positions and there is no large change in the structure of the cluster and no indication that a reaction will occur. This is consistent with previous simulations using in MP2⁶ and in contrast to the observations for equivalent simulations using DFT where reaction to form HONO occurs on a fast timescale.^{6,33} In making these observations it is important to note some of the limitations of the simulations. The simulations are adiabatic, and as a result are confined to a single potential energy surface and consequently changing electronic state is not possible. Another factor is that the simulations do not account for zero-point energy, which could potentially promote reactivity. However, we note that simulations run at significantly higher temperatures also do not show reactivity and hence it appears unlikely that zero-point vibrational energy effects will significantly alter the picture deduced herein.

The results of the MP2 based simulations appear to be inconsistent with the presence

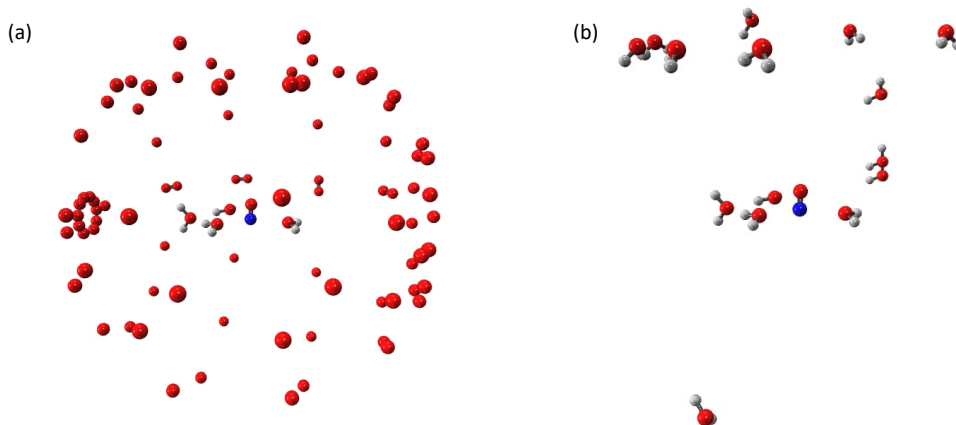


Figure 5: (a) Composite diagram showing the initial positions of the water molecules in the collision-based AIMD simulations, the hydrogen atoms of the colliding water molecules have been omitted for clarity. (b) Composite diagram showing the initial locations of the water molecules that led to the formation of protonated water clusters.

of HONO and protonated water clusters in the upper atmosphere. In order to explain the reactivity of these clusters we consider the initial conditions of the cluster. In the upper atmosphere a $\text{NO}^+(\text{H}_2\text{O})_n$ cluster and water molecule can combine to form a $\text{NO}^+(\text{H}_2\text{O})_{n+1}$ cluster. The water molecule joining the cluster will impart additional energy to the cluster owing to its kinetic energy and the favourable binding energy. As a consequence the resulting energy of the cluster will not conform to equilibrium conditions at 220 K. We have simulated the collision of a water molecule with most stable $\text{NO}^+(\text{H}_2\text{O})_4$ cluster. AIMD simulations were performed where an additional water molecule was started at a location away from the $\text{NO}^+(\text{H}_2\text{O})_4$ cluster and provided with a kinetic energy of approximately 100 kJ mol^{-1} and a velocity directed towards the NO^+ ion. The initial velocities of atoms of the $\text{NO}^+(\text{H}_2\text{O})_4$ cluster were sampled from the Maxwell-Boltzmann distribution and the simulations were performed using MP2/6-311++G**. The initial starting locations of the water molecules are illustrated in Figure 5. It is not practicable to sample all possible initial conditions, such as initial position, velocity and orientation of the colliding water molecule since a AIMD simulation is necessary for each choice. Consequently, the aim of the simulations is to illustrate that protonated water cluster are formed under some of the test conditions.

A key observation of the simulations is that some collisions with the $\text{NO}^+(\text{H}_2\text{O})_4$ cluster do indeed lead to the formation of protonated water clusters. These collisions lead to various other fragments being formed including dissociated nitrous acid i.e. NO and OH. The initial positions of the water molecules that resulted in the formation of protonated water clusters are also shown in Figure 5. The majority of the successful reactions arise when the colliding water molecule makes contact with the oxygen atom of NO^+ first. Collisions with the water molecules surrounding NO^+ do not appear to lead to reactions to form protonated water clusters. A sample movie of a reactive collision is included in the SI and illustrates how a reaction can occur. The initial orientation of the water molecule does not appear to be important because once the water molecule feels the NO^+ potential it re-orientates to collide oxygen-atom first. The colliding water molecule loses a proton which becomes associated with the surrounding water molecules and the HONO fragment leaves the cluster. In all of the examples studied where HONO is formed, the fragment is too energetic and dissociates to give OH and NO. For the reaction shown, reducing the initial velocity of the water molecule by 10% does not lead to the formation of protonated water clusters but to the ejection of NO^+ from the cluster. This indicates that both the impact direction and velocity of the colliding water molecule are important factors.

Conclusions

Quantum chemical MP2 calculations have been performed to study the formation of protonated water clusters from $\text{O}_2^+(\text{H}_2\text{O})_n$ and $\text{NO}^+(\text{H}_2\text{O})_n$ cluster ions. For the 1:1 $\text{O}_2^+(\text{H}_2\text{O})$ cluster the most stable cluster corresponds to a doublet state with O_2^+ and H_2O fragments. The binding energy computed with MP2 is in good agreement with experimental measurements while the binding energy computed with DFT is highly dependent on the exchange-

correlation functional used. For the large clusters, $n=2-5$, the lowest energy cluster corresponds to a quartet state and contains the H_3O^+ and OH moieties. AIMD simulations show that the charge is transferred from oxygen to water and there is a reorganization of the water molecules to form H_3O^+ and OH. For the $\text{NO}^+(\text{H}_2\text{O})_n$ clusters, different behaviour is observed. The reactions of $\text{NO}^+(\text{H}_2\text{O})_n$ involve an intracluster bimolecular reaction to form protonated water clusters and HONO. MP2 based AIMD simulations with initial velocities sampled from the Maxwell-Boltzmann distribution at 220 K show no reaction, which is in contrast to simulations based upon DFT.^{6,20} This inconsistency with atmospheric and experimental observations can be resolved by considering a collision of a water molecule with a $\text{NO}^+(\text{H}_2\text{O})_n$ cluster. AIMD simulations replicating these conditions in which a water molecule collides with the $\text{NO}^+(\text{H}_2\text{O})_4$ cluster do indeed show that reactions to form protonated water clusters can occur under the conditions of a collision. Overall, the results demonstrate that the underlying mechanisms that lead to the formation of protonated water clusters from the two ions O_2^+ and NO^+ in the D-region of the ionosphere differ significantly.

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