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Solvation effects on the N–O and O–H stretching modes in hydrated $NO_3^-(H_2O)_n$ clusters

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 $NO_3^{-}(H_2O)_n$ clusters are a molecular model used to understand the solvation interaction between water and nitrate, an important anion in nature, industrial processes and biology. We demonstrate by *ab initio* molecular dynamics simulations that among the many isomeric structures at each cluster size with n = 1-6, thermal stability is an important consideration. The vibrational profile at a particular size, probed previously by infrared multiple photon dissociation (IRMPD) spectroscopy, can be accounted for by the isomers, which are both energetically and dynamically stable. Conversion and broadening due to the fluctuation of hydrogen bonds are important not only for the O–H stretching modes but also for the N–O stretching modes. Distinct patterns for the O–H stretching modes are predicted for the various solvation motifs. We also predict a surface structure for $NO_3^{-}(H_2O)_n$ as *n* increases beyond 6, which can be verified by an early onset of strong libration bands for H₂O in the IRMPD spectra and a flattening of the vertical detachment energy in the photoelectron spectra.

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1. Introduction

Hydrated nitrate clusters, $NO_3^{-}(H_2O)_n$, are a molecular model used to understand the interaction between nitrate and water molecules. As one of the most abundant naturally occurring anions, nitrate plays an important role in biological^{1,2} and atmospheric cycles.^{3–5} Its salts are used extensively in modern agriculture as fertilizers and produced industrially as explosives, raising significant environmental concerns about possible contamination of natural water sources.^{6–8} The interaction between nitrate ion and solvent water is of fundamental importance in understanding these processes, and the study on $NO_3^{-}(H_2O)_n$ provides micro-solvation details for such interactions.

Experimentally, the hydration energy for NO₃⁻ has been measured by mass spectrometry from the equilibrium distribution of NO₃⁻(H₂O)_n with *n* up to 3.⁹⁻¹¹ Direct probing of size-selected NO₃⁻(H₂O)_n was first reported by a photoelectron spectroscopy (PES) study, with *n* up to 6, and in the case of *n* = 3, vibrational fine splitting due to the N–O stretching mode (ν (N–O)) was resolved, indicating a symmetric structure.¹² More systematic measurements on the vibrational modes were obtained by infrared multiple photon dissociation (IRMPD) spectroscopy. The IRMPD spectra of NO₃⁻(H₂O)_n (*n* = 1–6) in the 600–1800 cm⁻¹ region show

^c CUHK Shenzhen Research Institute, No. 10, 2nd Yuexing Road, Nanshan District, Shenzhen, China. E-mail: zfliu@cuhk.edu.hk considerable size-dependent variation for the ν (N–O) features.¹³ A detailed IRMPD study on NO₃⁻(H₂O), NO₃⁻(HDO), and NO₃⁻(D₂O) clusters in the O–H stretching region revealed more complexity than expected from harmonic analysis, due to the coupling between the rocking of the water molecule and its O–H stretching.¹⁴

Early theoretical studies were focused on obtaining the optimized structures and the hydration energy, with *n* up to 3.^{15–17} Above n = 3, it is more of a challenge to identify the isomer with the lowest energy.¹⁸ As demonstrated recently in an extensive structural search, the number of isomers is already 16 at n = 3, and 35 at n = 6.¹⁹ These isomers, however, do not contribute equally in spectroscopic experiments, since many of them are unstable at finite temperature and could be easily transformed into other structures, as observed in the *ab initio* molecular dynamics (AIMD) simulations on $H_2PO_4^{-}(H_2O)_n$ and $HCO_3^{-}(H_2O)_n$.^{20–22} For hydrated nitrate clusters, such dynamic effects have also been shown to be very important for the simplest case of n = 1.¹⁴

In this work, we report an AIMD study on $NO_3^{-}(H_2O)_n$, with n = 1-6, identifying the dominant structures and their dynamic signatures in the ν (N–O) region observed in the IRMPD experiment. Distinctive ν (O–H) vibrational features are predicted for future experimental verification. The evolution of $NO_3^{-}(H_2O)_n$ towards a surface cluster and the flattening of the vertical detachment energy in photoelectron spectra are also predicted.

2. Computational methods

The optimization of 0 K structures and harmonic analysis were performed by using the GAUSSIAN 09 package²³ at the B3LYP/ 6-311+G(d,p) level. A scaling factor of 0.970 was used for the low

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frequency region below 2000 cm^{-1} and 0.932 was used for the high frequency region above 3000 cm^{-1} .²⁴

Ab initio molecular dynamic (AIMD) simulations at finite temperatures were performed using the CP2K package.²⁵ A cluster under simulation was put at the center of a periodic cubic box with a length of more than twice the largest interatomic distance in the cluster and with the effect of the periodical charge density images being eliminated by the decoupling technique developed by Martyna and Tuckerman.²⁶ At every time step, the potential energy and atomic forces are calculated within the framework for density functional theory (DFT). The wave functions are represented by double-zeta Gaussians and the electron density is represented by using a mixed basis set of Gaussians and auxiliary plane waves with a cut-off of 320 Rydberg.²⁷ The Geodecker–Teter–Hutter (GTH)-type pseudopotentials are employed for the atomic cores.^{28–30} For the exchange and correlation energy, BLYP functionals are employed with dispersion corrected by Grimme's D3 scheme.³¹

The atomic motion is treated by Newtonian mechanics, with the temperature controlled by a Nose–Hoover thermostat and with a time step of 0.5 fs. The temperature is first scaled at the desired value for 3 ps, followed by a data collection run in the NVE ensemble for 15 ps. The value of dipole moment is calculated and collected at each time step, so that a vibrational spectrum can be directly simulated by the Fourier transform of the dipole time-correlation function (DTCF),³²

$$\alpha(\omega) = \frac{2\pi\beta\omega^2}{3n(\omega)cV} \int_{-\infty}^{+\infty} dt \left\langle \vec{M}(t) \cdot \vec{M}(0) \right\rangle \exp(i\omega t)$$

where $\beta = 1/kT$, $n(\omega)$ is the refractive index, *c* is the speed of light in a vacuum, and *V* is the volume. \vec{M} is the total dipole moment of the system, calculated by the polarization including both ionic and electronic contributions. Dynamic and anharmonic effects are automatically taken into account in such a scheme, although quantum effects at low temperature are not included.

3. Results and discussion

3.1. *n* = 1

The most stable isomer for $NO_3^{-}(H_2O)$ has the water molecule forming two donor (DD) HBs with the nitrate anion, shown as **1-1** in Fig. 1, which is in agreement with previous studies.¹²⁻¹⁷ Similar motifs of DD water, which shall be named as W_1 in the



Fig. 1 Optimized structures of $NO_3^{-}(H_2O)_n$ (n = 1-6). Relative energy in parentheses is in kJ mol⁻¹.

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Fig. 2 Left panel: Radial distribution function (RDF) of H atoms from the two O atoms in NO_3^- and coordination number (CN) of H atoms integrated from the RDF obtained from AIMD simulations at 100 K for isomer **1-1**. Right panel: Fluctuation in the HB distances during AIMD simulations at 100 K for isomer **1-1**.

current study, have been observed before in the hydrated clusters of other polyatomic anions, such as sulfate,³³⁻³⁵ bisulfate,³⁶ dihydrogen phosphate,^{20,21} and bicarbonate.^{22,37} Previous AIMD simulations have also shown that W1 is intrinsically unstable, because of the geometric constraint that makes it impossible to have both HBs with an O···H–O angle of 180° .^{12,22} As a result, the H₂O rocks to one side and strengthens one HB at the expense of weakening the other HB, and it then rocks to the other side, back and forth. Such a rocking motion is also observed in the case of $NO_3^{-}(H_2O)$, as shown in Fig. 2. The distance of the two HBs fluctuates from 1.7 to 2.7 Å in the 100 K AIMD trajectory, while W₁ is maintained most of the time during the 15 ps simulation. In fact, in the radial distribution function (RDF) of H atoms around each of the solvated nitrate O atoms, the first peak is at 1.85 Å, considerably shorter than the equilibrium HB distance of 2.06 Å, due to H₂O rocking.

When one of the HBs is broken in $NO_3^-(H_2O)$, the structure is transformed to 1-2, with the remaining HB shortened to an equilibrium distance of 1.82 Å, which is shorter than the B3LYP/ aug-cc-pVTZ calculated value of 2.31 Å reported before.¹² A similar geometry has been observed in HCO₃⁻⁻(H₂O) and H₂PO₄⁻⁻(H₂O) as well, but only as a transition structure.^{20,22} However, 1-2 is unstable at 20 K and 100 K, transforming into 1-1 right away during AIMD simulations. At 200 K, the extent of HB fluctuation becomes larger so that one of the HBs can be broken and 1-1 can be transformed into 1-2, albeit for only short intervals.

An unsolvated NO₃⁻ has D_{3h} symmetry, and its three N–O stretching modes are split into two degenerate antisymmetric modes $\nu_{AS}(N-O)$ and one symmetric mode $\nu_S(N-O)$ with no IR intensity. The solvation of NO₃⁻ breaks down this symmetry and splits $\nu_{AS}(N-O)$ into two peaks,¹³ as shown in Fig. 3, while $\nu_S(N-O)$ still has little IR intensity. Both 1-1 and 1-2 produce two $\nu_{AS}(N-O)$ peaks, although the calculated frequency gap of around 60 cm⁻¹ is larger than the experimental value of 34 cm⁻¹. Obviously, it is impossible to tell 1-1 and 1-2 apart



Fig. 3 Harmonic, DTCF and experimental IRMPD spectra for $NO_3^{-}(H_2O)$. Scaling factors of 0.970 and 0.932 were used in the harmonic spectra for regions below 2000 cm⁻¹ and above 3000 cm⁻¹, respectively. No scaling factor was applied to the DTCF spectrum. The experimental spectra were digitized from the literature.^{13,14}

based on ν_{AS} (N–O). More pronounced differences between 1-1 and 1-2 are observed in the ν (O–H) region, shown in Fig. 3. For 1-2, the ν (O–H) peak for the hydrogen bonded O5–H6 is red-shifted to ~3200 cm⁻¹, due to the stronger HB, O5–H6···O2. In contrast, the two ν (O–H) peaks for W₁ in 1-1 are in the region of 3400–3500 cm⁻¹.

At low temperature, **1-1** is the dominant structure, but significant broadening of its ν (O–H) mode is observed even at 20 K. At 100 K, the DTCF spectrum is similar to the experimental n = 1 IRMPD spectrum in broad outline,¹⁴ spanning the

region from 3300 cm⁻¹ to 3600 cm⁻¹, with hints of further couplings. Based on an effective Hamiltonian, these spectral features were reproduced by vibrational configuration interaction calculations and attributed to the coupling between O–H stretching and water rocking.¹⁴ By 200 K, ν (O–H) is further broadened, with an appreciable intensity around 3200 cm⁻¹, obviously due to the presence of **1-2**. As the *n* = 1 IRMPD spectrum does not show any features in this region, the presence of **1-2** can be ruled out in the experimental measurement.

3.2. n = 2

The three lowest-energy isomers of n = 2 are shown in Fig. 1. The most stable isomer, 2-1, consists of two W₁. Isomer 2-3 contains one W₁ and one dangling H₂O solvating NO₃⁻ by just one HB. A new type of solvation motif is seen at n = 2 in 2-2, which is named as W₂. It has the first H₂O (H10–O8–H9) forming two donor HBs, one with NO₃⁻ and another with the other H₂O, and the second H₂O (H6–O5–H7) forming a donor HB with NO₃⁻ and an acceptor HB with the first H₂O. In addition, there is one HB-free H atom in the second H₂O.

In AIMD simulations, the dangling water in 2-3 is unstable and the structure is transformed into 2-1 even at 20 K. The W_2 motif is quite stable, even up to 200 K, although the inter-water HB and the free OH could flip back and forth. 2-1 is also stable up to 100 K, but at 200 K, it is transformed into 2-2, or even 2-3, during part of the simulation. In relative energy, 2-1 is more stable than 2-2 by 7.40 kJ mol⁻¹.

Both 2-1 and 2-2 produce two $\nu_{AS}(N-O)$ peaks, as shown in Fig. 4, in both the harmonic and the 100 K DTCF spectra. The gap is larger for 2-2 (94 cm⁻¹, harmonic value) than for 2-1 (55 cm⁻¹, harmonic value), due to the presence of an unsolvated N–O in 2-2. Again, the calculated gaps are larger than the experimental value of 38 cm⁻¹. Interestingly, the two $\nu_{AS}(N-O)$ peaks for 2-3 are almost merged into one, despite the asymmetry of the overall structure, as each N–O is solvated by one HB. The contribution of 2-3 could probably be dismissed, due to its thermal instability, even at 20 K. It is more difficult to evaluate the relative importance of 2-1 and 2-2, since 2-1 is favored by potential energy, while 2-2 is dynamically more robust. The n = 2 IRMPD spectrum is likely due to mixed contributions from both 2-1 and 2-2, as the broadened shape of the left $\nu_{AS}(N-O)$ feature (1329 cm⁻¹) seems to contain more than one peak.

As shown in Fig. 1, there is a very strong HB in the W₂ of 2-2, with an equilibrium distance of 1.74 Å (O5H7···O2), producing a strong peak at 3100 cm⁻¹ in its harmonic spectrum (Fig. 4). On the other hand, the ν (O–H) band in the harmonic spectrum of 2-1 is around 3500 cm⁻¹. In the 100 K DTCF spectra, ν (O–H) for 2-2 is broadened with appreciable intensity below 3200 cm⁻¹. While ν (O–H) for 2-1 is also broadened, it falls off below 3300 cm⁻¹. To the best of our knowledge, there is no report of the experimental IRMPD spectrum in the ν (O–H) region for $n \ge 2$. Such a spectrum would be very helpful to indicate the relative importance of 2-1 and 2-2, because the difference between 2-1 and 2-2 is more pronounced in the ν (O–H) region. It is possible to tell the two isomers apart despite the extensive broadening of their ν (O–H) features.



Fig. 4 Harmonic, DTCF and experimental IRMPD spectra for $NO_3^{-}(H_2O)_2$. Scaling factors of 0.970 and 0.932 were used in the harmonic spectra for regions below 2000 cm⁻¹ and above 3000 cm⁻¹, respectively. No scaling factor was applied to the DTCF spectrum. The experimental spectrum was digitized from the literature.¹³

3.3. n = 3

The ν (N–O) frequency for NO₃⁻(H₂O)₃ was first observed in a PES experiment as a resolved vibrational splitting,¹² which suggested a high symmetry structure of **3-1** in Fig. 1. The high symmetry of NO₃⁻(H₂O)₃ was supported by its IRMPD spectrum, which showed a well-resolved single peak.¹³ However, the same study also identified a new symmetric structure,¹³ shown as **3-4** in Fig. 1, which also produced a single ν (N–O) peak. In **3-1**, there are 3 W₁ motifs, symmetrically distributed around the anion. In **3-4**, three water molecules form a ring, referred to as W₃ in the following discussion, with 3 axial OH solvating each of the O atoms in NO₃⁻ and with 3 equatorial OH connected to each other by HBs in a ring. Contributions from other structures (Fig. 1) could be ruled out as either being unstable during finite temperature AIMD simulations or producing a doublet ν_{AS} (N–O) or both.

Between 3-1 and 3-4, 3-1 is lower in energy by 13.40 kJ mol⁻¹ at the B3LYP/6-311+G(d,p) level in the present calculation. Previously,¹³ this energy gap was found to be 10.1 kJ mol⁻¹ at the B3LYP/aug-cc-pVTZ level, but it reduced to only 2.0 kJ mol⁻¹ at the MP2/aug-cc-pVDZ level. In AIMD simulations, 3-4 is more stable, with the W₃ ring maintained even at 200 K. 3-1 is stable at 100 K, but it transformed into 3-4 and other structures when the simulation temperature was raised to 200 K. In the harmonic and the 100 K DTCF spectra (Fig. 5), there is only one ν_{AS} (N–O) peak for both isomers, in agreement with experiment. At 200 K, two ν_{AS} (N–O) peaks are produced for 3-1 due to its structural fluctuation while a single ν_{AS} (N–O) peak is maintained for 3-4 as the W₃ ring is preserved.

Again, the ν (O-H) region would be helpful to evaluate the relative importance of **3-1** and **3-4**. Using the 100 K DTCF spectra in Fig. 5 as a guide, we predict very different patterns

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Fig. 5 Harmonic, DTCF and experimental IRMPD spectra for $NO_3^{-}(H_2O)_3$. Scaling factors of 0.970 and 0.932 were used in the harmonic spectra for regions below 2000 cm⁻¹ and above 3000 cm⁻¹, respectively. No scaling factor was applied to the DTCF spectrum. By 200 K, **3-1** is transformed to other structures, and the single peak at about 1300 cm⁻¹ is split into two features. The experimental spectrum was digitized from the literature.¹³

in the ν (O–H) region for 3-1 and 3-4. With 3 W₁, 3-1 should be broadened in the region of 3250–3650 cm⁻¹. The coupling between water rocking and O–H stretching could produce more features, similar to those observed in the n = 1 IRMPD spectrum,¹⁴ although with the presence of 3 rocking H₂O, such features are expected to be more congested for 3-1. In 3-4, there are two distinct types of HBs in the W₃ motif, the axial HB with a distance of around 1.99 Å and the equatorial HB with a distance in W₃ is considerably less than that in W₁. We therefore expect two features in the ν (O–H) region for 3-4, separated by ~100 cm⁻¹, and being somewhat broadened albeit considerably narrower than the ν (O–H) band for 3-1.

3.4. n = 4

For NO₃⁻(H₂O)₄, a ring of four water molecules named W₄, is now possible, and the corresponding isomer, labeled as **4-1** in Fig. 1, has been found to be the most stable in relative energy.^{13,19} W₄ is also remarkably stable in our AIMD simulations, even at 200 K. These results point to the conclusion that **4-1** is the dominant isomer. However, there is one problem in the comparison between the harmonic spectra and experiment (Fig. 7): the ν_{AS} (N–O) modes of **4-1** produce two peaks in the harmonic spectrum, while there is only one broadened feature

Fig. 6 Fluctuation in the HB distances during AIMD simulations at 100 K for isomers **3-1** and **3-4**.

in the IRMPD spectrum. It was suggested before that the calculated gap of 30 cm⁻¹ between these two peaks was too narrow to be resolved by the IRMPD experiment,¹³ which is not entirely convincing. In the same study,¹³ the n = 6 IRMPD spectrum indicated two ν_{AS} (N–O) peaks clearly, with a frequency gap of 29 cm⁻¹.

When the dynamic effects are taken into consideration in the DTCF spectra (Fig. 7), 4-1 stands out as the only one that would produce one peak. Actually, there are still two $\nu_{AS}(N-O)$ peaks for 4-1 in its 20 K spectrum, in agreement with its harmonic spectrum. But when the simulation temperature is raised to 100 K and 200 K, there is only one peak left for ν (N–O). Such changes are due to the dynamic nature of 4-1. NO_3^- is indeed not evenly solvated by a W4 ring. With four axial OH, one of the N-O bonds must take two donor HBs, while the other two take one each. However, during AIMD simulations at 100 K and 200 K, the mismatched NO_3^- and W_4 would rotate back and forth, so that each of the N-O bonds takes turns to become doubly solvated, making the three N-O bonds dynamically equivalent. Shown in Fig. 8 are the snapshots for such rotations during an AIMD trajectory for 4-1 at 100 K. As a result, the two ν_{AS} (N–O) modes merge into one peak. In other words, 4-1 with its two harmonic $\nu_{AS}(N-O)$ peaks separated by 30 cm⁻¹ is indeed the dominant isomer, but these two peaks are broadened into one, not due to a lack of resolution in the IRMPD experiment, but due to the internal rotation of NO₃⁻ versus W₄.

With a rotating yet stable W_4 , the ν (O–H) region could provide further evidence for the dominance of **4-1**. The axial



Fig. 7 Comparison between harmonic/DTCF and experimental IRMPD spectra in the N–O stretching region for $NO_3^-(H_2O)_4$. A scaling factor of 0.970 was used in the harmonic spectra. No scaling factor was applied to the DTCF spectrum. The experimental spectrum was digitized from the literature.¹³



Fig. 8 Snapshots from an AIMD trajectory on **4-1** at 100 K, showing the constant rotation of NO_3^- relative to the W₄ ring.

HBs of the W₄ ring are around 2.05 Å, and the equatorial HBs are around 1.93 Å, reversing the ordering of HB distance in W₃ (1.99 Å for the axial, 2.05 Å for the equatorial). These two groups of HBs would each produce a broadened but well-shaped feature in the ν (O–H) region, as shown in Fig. 9.





Fig. 9 The predicted O–H stretching region of the harmonic and DTCF spectra for **4-1**. A scaling factor of 0.932 was used in the harmonic spectra. No scaling factor was applied to the DTCF spectrum.

3.5. n = 5

The W₄ ring is also found to be important at n = 5, primarily through the structure **5-1**, shown in Fig. 1. In agreement with previous reports,^{13,19} **5-1** is the most stable structure, among the four isomers shown. In AIMD simulations, **5-1** is stable even at 200 K, while the other three structures are all transformed into **5-1** at 100 K. **5-1** can be characterized as a double layer structure. One layer is composed of a W₁ and NO₃⁻, and the other layer is a W₄ ring. There are four O atoms in the W₁ + NO₃⁻ layer, each accepting a HB from one of the four W₄ axial OH. To accommodate the W₄ ring, W₁ is veered to one side, with one HB distance (H18···O2) at 1.86 Å and the other (H19···O3) at 2.53 Å.

With the numbers of HB acceptors and donators between the two layers exactly matched, there is no rotation of the W₄ ring *versus* NO₃⁻ during AIMD simulations, in contrast to the trajectories for **4-1**. The two ν_{AS} (N–O) modes are split into two peaks, as indeed observed in the n = 5 IRMPD spectrum and in the harmonic and DTCF spectra (Fig. 10). In the ν (O–H) region, **5-1** should be similar to **4-1**, dominated by the axial and equatorial ν (O–H) features of W₄ (Fig. 10), although the equatorial ν (O–H) is further broadened.

3.6. n = 6

By n = 6, there are numerous possible isomers, as water molecules could be put in the second solvation shell with many variations in the inter-water HB network, shown in Fig. 1. Unlike n = 4 or 5, which is dominated by **4-1** or **5-1**, respectively, we do not find any isomer at n = 6 to be more stable than the others during AIMD simulations. We also tried to build structures with



Fig. 10 Harmonic, DTCF and experimental IRMPD spectra for $NO_3^{-}(H_2O)_5$. Scaling factors of 0.970 and 0.932 were used in the harmonic spectra for regions below 2000 cm⁻¹ and above 3000 cm⁻¹, respectively. No scaling factor was applied to the DTCF spectrum. The experimental spectrum was digitized from the literature.¹³



Fig. 11 The N–O stretching region of the harmonic and IRMPD spectra for $NO_3^{-}(H_2O)_6$. A scaling factor of 0.932 was used in the harmonic spectra. The experimental spectrum was digitized from the literature.¹³

 NO_3^- sandwiched between water molecules, such as **6-5** and **6-6** in Fig. 1. While such structures can be obtained by optimization, they are unstable during AIMD simulation. The water molecules would always aggregate to one side of NO_3^- . In other words, NO_3^- would stay on the cluster surface. The harmonic spectra for the four surface clusters in the $\nu_{AS}(N-O)$ region are shown in Fig. 11,

together with the IRMPD spectrum. The observed shape of the experimental ν_{AS} (N–O) feature indicates that it is likely due to a mixture of isomers (Fig. 11).

It has been observed before for $HCO_3^{-}(H_2O)_n$ that as *n* grows, the planar HCO_3^{-} would stay on the cluster surface,²² which accounts for two experimental observations. First, as water molecules aggregate on one side of the planar HCO₃⁻, the inter-water network is formed at a fairly modest size of n = 6, indicated by the appearance of pronounced water libration bands in the region of 700–1000 cm $^{-1}$.^{22,37} Second, in the PES measurement, the vertical detachment energy becomes a constant for $n \ge 9$,^{38,39} as additional water molecules are added to higher solvation shells, with little impact on the orbital energy of the negative charge on HCO₃⁻. There are indeed pronounced bands in the region of 700–1000 cm⁻¹ in the n = 6 IRMPD spectrum for hydrated nitrate clusters as well (Fig. 11).¹³ The photoelectron spectrum for $NO_3^{-}(H_2O)_n$ has only been measured up to n = 6. Whether the planar NO_3^- would stay on the cluster surface as *n* grows beyond 6 is an interesting subject for future investigation by both IRMPD and PES measurements.

4. Conclusions

Unlike $HCO_3^{-}(H_2O)_n$ or $H_2PO_4^{-}(H_2O)_n$, solvation in $NO_3^{-}(H_2O)_n$ involves the anion as a HB acceptor only and not as a HB donor. Within n = 1-6, there are a number of solvation motifs consisting of 1-4 water molecules solvating the O atoms in NO₃⁻. These motifs are energetically and dynamically favorable, and largely responsible for the experimentally observed IRMPD spectra. The stability of 3 and 4 water rings (W₃ and W₄) is especially noteworthy. Based on our previous experiences with $HCO_3^{-}(H_2O)_n$ and $H_2PO_4^{-}(H_2O)_n$ the N-O stretching mode would not be expected to be very sensitive to the fluctuation of HBs as it involves the heavier N and O atoms, not a H atom. However, the rotation of the W4 ring due to the incompatibility between NO₃⁻ and W₄ produces an interesting example of dynamic broadening for N-O stretching. O-H stretching regions should be much more sensitive to the HB fluctuation and provide characteristic shapes and broadenings due to the significant variation in the stability of these motifs. As n grows beyond 6, $NO_3^{-}(H_2O)_n$ is expected to take a surface structure, similar to the hydrated clusters of the planar bicarbonate anion, which can be verified by future IRMPD and PES experiments.

Conflicts of interest

There are no conflicts to declare.

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