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# Microhydration of PAH<sup>+</sup> cations: evolution of hydration network in naphthalene<sup>+</sup>-(H<sub>2</sub>O)<sub>n</sub> clusters (n ≤ 5)<sup>†</sup>

Kuntal Chatterjee and Otto Dopfer \*

The interaction of polycyclic aromatic hydrocarbon molecules with water (H<sub>2</sub>O = W) is of fundamental importance in chemistry and biology. Herein, size-selected microhydrated naphthalene cation nanoclusters, Np<sup>+</sup>-W<sub>n</sub> (n ≤ 5), are characterized by infrared photodissociation (IRPD) spectroscopy in the C–H and O–H stretch range to follow the stepwise evolution of the hydration network around this prototypical PAH<sup>+</sup> cation. The IRPD spectra are highly sensitive to the hydration structure and are analyzed by dispersion-corrected density functional theory calculations (B3LYP-D3/aug-cc-pVTZ) to determine the predominant structural isomers. For n = 1, W forms a bifurcated CH...O ionic hydrogen bond (H-bond) to two acidic CH protons of the bicyclic ring. For n ≥ 2, the formation of H-bonded solvent networks dominates over interior ion solvation, because of strong cooperativity in the former case. For n ≥ 3, cyclic W<sub>n</sub> solvent structures are attached to the CH protons of Np<sup>+</sup>. However, while for n = 3 the W<sub>3</sub> ring binds in the CH...O plane to Np<sup>+</sup>, for n ≥ 4 the cyclic W<sub>n</sub> clusters are additionally stabilized by stacking interactions, leading to sandwich-type configurations. No intracluster proton transfer from Np<sup>+</sup> to the W<sub>n</sub> solvent is observed in the studied size range (n ≤ 5), because of the high proton affinity of the naphthyl radical compared to W<sub>n</sub>. This is different from microhydrated benzene<sup>+</sup> clusters, (Bz-W<sub>n</sub>)<sup>+</sup>, for which proton transfer is energetically favorable for n ≥ 4 due to the much lower proton affinity of the phenyl radical. Hence, because of the presence of polycyclic rings, the interaction of PAH<sup>+</sup> cations with W is qualitatively different from that of monocyclic Bz<sup>+</sup> with respect to interaction strength, structure of the hydration shell, and chemical reactivity. These differences are rationalized and quantified by quantum chemical analysis using the natural bond orbital (NBO) and noncovalent interaction (NCI) approaches.

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## 1. Introduction

The interactions and chemical reactions of aromatic molecules and their cations with surrounding solvent molecules are of fundamental importance for many phenomena in chemistry and biology.<sup>1–4</sup> In particular, the interaction of benzene and polycyclic aromatic hydrocarbon molecules (PAH) and their cations (PAH<sup>+</sup>) with water (H<sub>2</sub>O = W) plays a crucial role in the areas of combustion,<sup>5</sup> organic chemistry,<sup>6–14</sup> astrochemistry,<sup>15–26</sup> and biomolecular recognition.<sup>3,4,27–29</sup> For example, intermolecular interactions involving aromatic hydrocarbons and water are the driving force for many biochemical processes, such as the conformation and folding of proteins, base pair stacking in DNA, drug design, macromolecular assemblies, and biological

membranes. The relative strengths of the various interaction types (e.g., OH...π, CH...O, cation...π)<sup>4,28,30–32</sup> strongly depend on the charge state of the PAH. In the context of astrochemistry, PAH molecules, their radical cations (PAH<sup>+</sup>), and their protonated species (H<sup>+</sup>PAH) are suggested to be carriers of the unidentified infrared emission bands as well as the diffuse interstellar bands.<sup>33–38</sup> Concerning ions of the most simple PAH (naphthalene, C<sub>10</sub>H<sub>8</sub>, Np), the postulation<sup>39</sup> and tentative identification of the Np<sup>+</sup> cation as a DIB carrier<sup>40,41</sup> provided a great stimulus for the plethora of laboratory spectroscopy of both Np<sup>+</sup> (ref. 39 and 42–51) and H<sup>+</sup>Np<sup>52–58</sup> in the gas phase and isolated in rare gas matrices in both the infrared and optical range of the electromagnetic spectrum. In addition, the spectroscopy and photochemistry of Np and Np<sup>+</sup> deposited in ice or on ice grains as well as in aqueous solution have been studied.<sup>6,18,19,23,59,60</sup>

For a deeper understanding of the interaction between water and PAH molecules in various charge states at the molecular level, the accurate knowledge of the involved interaction potential is required. To this end, the combination of spectroscopy of molecular clusters isolated in the gas phase with

Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany. E-mail: dopfer@physik.tu-berlin.de; Tel: +49 30 31423018

<sup>†</sup> Electronic supplementary information (ESI) available: Detailed NBO and NCI analyses, structures and IR spectra of less stable Np<sup>+</sup>-W<sub>n</sub> isomers and W<sub>n</sub> clusters, Cartesian coordinates of all optimized structures. See DOI: 10.1039/c7sc05124g



quantum chemical calculations provides the most direct access to this potential. Herein, we combine infrared photodissociation (IRPD) spectroscopy with dispersion-corrected density functional theory (DFT) calculations to probe the initial microhydration steps in size-selected cold  $\text{Np}^+-\text{W}_n$  clusters produced in a supersonic plasma expansion using electron ionization. This approach has recently been applied in our laboratory to a variety of microhydrated aromatic ions.<sup>61–72</sup> Significantly, the employed cluster ion source generates predominantly the most stable isomer of a given cluster ion, because of the sequential cluster growth realized in the high-pressure region in the supersonic expansion.<sup>73,74</sup>

Surprisingly, despite their importance only very scarce information is available for the spectroscopy of  $\text{PAH}^{(\pm)}-\text{W}_n$  clusters, and this is even true for the most simple  $\text{Np}^{(\pm)}-\text{W}_n$  clusters. For example, no spectral data have been reported yet for neutral  $\text{Np}-\text{W}_n$  clusters, and thus all information about their structure and interaction potential has to barely rely on rather limited computational studies available only for  $n \leq 2$ .<sup>75</sup> The latter predict  $\pi$  H-bonded structures, in which the W ligands bind *via*  $\text{OH} \cdots \pi$  stacking to the aromatic  $\pi$ -electron system of Np either as single W ligands or as a H-bonded  $\text{W}_2$  dimer. The situation is more favorable for  $\text{Np}^--\text{W}_n$  anion clusters, which were characterized by photoelectron<sup>76–78</sup> and IR<sup>79</sup> spectroscopy up to the size range  $n = 6$ . While  $\text{Np}^-$  is unstable with respect to electron detachment because of the negative electron affinity of Np, microhydrated  $\text{Np}^--\text{W}_n$  clusters with  $n \geq 1$  are stable and can be produced in supersonic expansions. Computational analysis of the IR spectra of  $\text{Np}^--\text{W}_n$  reveals that also the anion clusters prefer  $\pi$  H-bonded structures, in which W ( $n = 1$ ), a H-bonded  $\text{W}_2$  dimer ( $n = 2$ ), or cyclic  $\text{W}_n$  clusters ( $n = 3$  and  $4$ ) bind to the  $\pi$  cloud of  $\text{Np}^-$  *via* (multiple)  $\text{OH} \cdots \pi$  interactions.<sup>79</sup> The first and only information about  $\text{Np}^+-\text{W}_n$  cation clusters prior to our work came from a very recent mass spectrometric study,<sup>14</sup> in which  $\text{Np}^+-\text{W}_n$  clusters up to  $n = 6$  were generated by injecting  $\text{Np}^+$  cations produced by electron ionization into a drift cell of an ion mobility mass spectrometer containing water vapor. For the  $n = 1$  dimer, the signal was strong enough to measure clustering equilibria, which yield a binding enthalpy of  $-\Delta H = 7.8 \pm 1 \text{ kcal mol}^{-1}$  ( $2730 \pm 350 \text{ cm}^{-1}$ ) for  $\text{Np}^+-\text{W}$ . Out of the four isomers calculated for  $\text{Np}^+-\text{W}$ , the three lowest-energy structures have a bifurcated  $\text{CH} \cdots \text{O}$  H-bond, while the  $\pi$ -bonded structure is least stable (Fig. 1). Although the calculated binding energy of the global minimum ( $7.7 \text{ kcal mol}^{-1}$ ) agrees with the measured enthalpy, the other two H-bonded isomers are also quite low in energy ( $6.8$  and  $6.5 \text{ kcal mol}^{-1}$ ) and thus no reliable conclusion about the cluster structures can be drawn from the mass spectra.<sup>14</sup> For  $n > 1$ , only very weak mass peaks were reported, and the most stable computed structures determined for  $n = 2$ – $6$  have a linear H-bonded  $\text{W}_n$  chain attached to  $\text{Np}^+$ .<sup>14</sup>

In a recent spectroscopic study,<sup>72</sup> we analysed the IRPD spectrum of  $\text{Np}^+-\text{W}$  recorded in the C–H and O–H stretch ( $\nu_{\text{CH/OH}}$ ) range by dispersion-corrected DFT calculations (B3LYP-D3/aug-cc-pVTZ) to obtain the first spectroscopic information about the interaction of a  $\text{PAH}^+$  cation with W. This spectral range is highly sensitive to the details of the H-bonded

structure. The analysis of the observed IR spectrum confirms that the bifurcated  $\text{CH} \cdots \text{O}$  binding motif involving two CH groups of two different rings (denoted  $\text{Np}^+-\text{W}(18)$  in Fig. 1) corresponds indeed to the global minimum of  $\text{Np}^+-\text{W}$  predicted by the calculations, and no other isomer is identified in the cold molecular beam. In addition to the reliable structure determination, frequency-dependent photofragmentation branching ratios monitored for IRPD of cold  $\text{Np}^+-\text{W}-\text{Ar}$  clusters yield a spectroscopic determination of the  $\text{Np}^+-\text{W}$  binding energy ( $D_0 = 2800 \pm 300 \text{ cm}^{-1}$ ), in excellent agreement with the calculated value ( $D_0 = 2773 \text{ cm}^{-1}$ ) and the enthalpy derived from mass spectrometry ( $-\Delta H = 2730 \pm 350 \text{ cm}^{-1}$ ).<sup>14</sup> Detailed analysis using the natural bond orbital (NBO) approach elucidates the binding mechanisms and interaction strengths of the various possible bifurcated  $\text{CH} \cdots \text{O}$  H-bonding motifs,<sup>72</sup> as well as differences in structure and binding energy between the most stable  $\text{Np}^+-\text{W}$  isomer and that of the monohydrated benzene cation ( $\text{Bz}^+-\text{W}$ ).

Herein, we extend our combined IRPD and DFT approach to larger  $\text{Np}^+-\text{W}_n$  clusters up to  $n \leq 5$  to reliably determine the structure of the microhydration network formed around this most simple  $\text{PAH}^+$  cation. Surprisingly, our results yield cyclic solvent structures, in disagreement with the recent computational study predicting linear  $\text{W}_n$  structures.<sup>14</sup> Comparison between neutral,<sup>72,75</sup> anionic,<sup>76–79</sup> and cationic<sup>14,72</sup> polyhydrated  $\text{Np}^{(\pm)}-\text{W}_n$  clusters elucidates the drastic effects of the charge state on the hydration network and the interaction strength. Comparison of  $\text{Np}^+-\text{W}_n$  with the related and well-studied ( $\text{Bz}-\text{W}_n$ )<sup>+</sup> clusters<sup>10,12,61,62,73,80–88</sup> reveals the qualitative difference in structure and chemical reactivity of both cluster systems. The  $\text{Np}^+-\text{W}$  interaction is quite different from that of  $\text{Bz}^+-\text{W}$  with respect to structure, interaction strength, and binding mechanism.<sup>14,72</sup> In addition, the proton affinity of the naphthyl radical is much larger than that of the phenyl radical. Hence, the structure of the hydration shell and also the chemical reactivity with respect to intracluster proton transfer are expected to be very different for  $(\text{Np}-\text{W}_n)^+$  and  $(\text{Bz}-\text{W}_n)^+$ .

## 2. Experimental and computational techniques

### 2.1 Experimental methods

IRPD spectra of mass-selected  $\text{Np}^+-\text{W}_n$  clusters with  $n \leq 5$  are recorded in a tandem quadrupole mass spectrometer coupled to an electron-ionization cluster ion source described in detail elsewhere.<sup>73,89</sup> Briefly,  $\text{Np}^+-\text{W}_n$  clusters are produced in a pulsed supersonic plasma expansion by electron and/or chemical ionization of Np and subsequent clustering reactions in the high-pressure regime of the expansion.<sup>72</sup> The expanding gas mixture is generated by passing Ar carrier gas (8–10 bar) through a reservoir containing solid Np (Sigma-Aldrich, >99%, heated to 70 °C). To produce hydrated clusters, 10  $\mu\text{l}$  of distilled water are added to the gas line before the sample reservoir. The desired  $\text{Np}^+-\text{W}_n$  parent clusters are mass-selected in the first quadrupole mass filter and irradiated in an adjacent octopole ion guide with a tunable IR laser pulse ( $\nu_{\text{IR}}$ ) of an optical



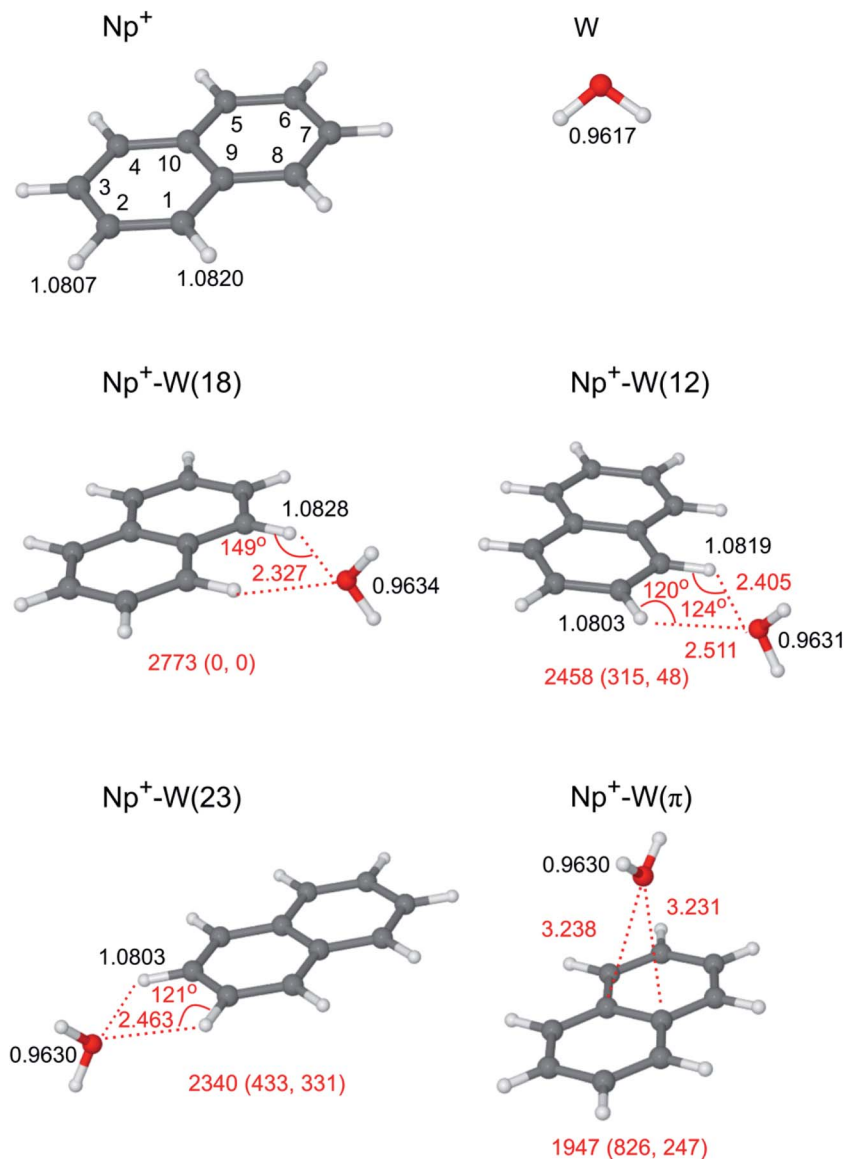
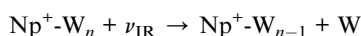


Fig. 1 Structures of W, Np<sup>+</sup> (with numbering of carbon atoms), and the (18), (12), (23), and (π) isomers of Np<sup>+</sup>-W calculated at the B3LYP-D3/aug-cc-pVTZ level. Binding energies ( $D_0$ ) and bond lengths are given in cm<sup>-1</sup> and Å, respectively. Numbers in parenthesis correspond to relative energies and free energies ( $E_0$ , G).

parametric oscillator (IR-OPO), which is pumped by a nanosecond Q-switched Nd:YAG laser. The IR-OPO laser pulses are characterized by an energy of 2–5 mJ in the C–H/O–H stretch range, a repetition rate of 10 Hz, and a bandwidth of 1 cm<sup>-1</sup>. Calibration of  $\nu_{\text{IR}}$  to better than 1 cm<sup>-1</sup> is accomplished by a wavemeter. Resonant vibrational excitation upon single-photon absorption leads to evaporation of a single W ligand corresponding to following photodissociation reaction:



No other fragmentation channel is observed under the employed experimental conditions. The generated Np<sup>+</sup>-W<sub>n-1</sub> fragment ions are mass-selected by the second quadrupole mass filter and monitored by a Daly detector as a function of  $\nu_{\text{IR}}$  to extract the IRPD spectrum of the Np<sup>+</sup>-W<sub>n</sub> parent cluster. All

IRPD spectra are linearly normalized for laser intensity variations monitored with a pyroelectric detector. Several spectra in the 2950–3800 cm<sup>-1</sup> range are composed of separate scans recorded in the O–H and C–H stretch ranges, respectively. They are connected such that the intensities of overlapping bands are adjusted. The peak width in the IRPD spectra mainly arises from unresolved rotational structure, sequence hot bands involving inter- and intramolecular modes, lifetime broadening, and possible overlap of transitions of different isomers. To separate the laser-induced Np<sup>+</sup>-W<sub>n-1</sub> fragments from those generated by metastable decay in the octopole region, the ion source is triggered at twice the laser frequency, and signals from alternating triggers are subtracted. The composition of the mass-selected Np<sup>+</sup>-W<sub>n</sub> clusters is confirmed by collision-



induced dissociation experiments, facilitated by filling the octopole ion guide with N<sub>2</sub> collision gas (10<sup>-5</sup> mbar).

## 2.2 Computational techniques

Quantum chemical calculations are carried out for Np<sup>+</sup>-W<sub>n</sub> at the B3LYP-D3 level to determine their structural, vibrational, and energetic properties.<sup>90</sup> Initial extensive manual screening of the potential energy surface is conducted using the cc-pVTZ basis set and final optimization is performed with the larger aug-cc-pVTZ basis set. The dispersion-corrected B3LYP-D3 functional describes the electrostatic, induction, and dispersion forces of aromatic clusters rather well, and reproduces their experimental IR spectra and binding energies to satisfactory accuracy using the aug-cc-pVTZ basis set.<sup>67,68,71,91</sup> This is particularly true for the properties of Np, Np<sup>+</sup>, W, and the Np<sup>+</sup>-W interaction, as was demonstrated in our recent report.<sup>72</sup> In addition, spin contamination of the radical cation clusters is negligible at this computational level.<sup>72</sup> All coordinates are relaxed in the search for stationary points, and their nature as minima or transition states is verified by harmonic frequency analysis. Harmonic intramolecular vibrational frequencies are linearly scaled by the factor 0.96266, derived from fitting calculated harmonic O-H and C-H stretch frequencies of W and Np to experimental values.<sup>72</sup> Harmonic scaled IR stick spectra are convoluted with a Gaussian line shape (fwhm = 10 cm<sup>-1</sup>) for facile comparison to the experimental IRPD spectra. All reported binding energies (*D*<sub>0</sub>), relative energies (*E*<sub>0</sub>), and relative free energies (*G*) are corrected for harmonic vibrational zero-point energies. Energies are not corrected for basis set superposition error, because it was found to be very small (<1%) for Np<sup>+</sup>-W and related microhydrated aromatic cations at this computational level.<sup>71</sup> Natural bond orbital (NBO) analysis is employed to evaluate charge distribution and charge transfer in Np<sup>+</sup>-W<sub>n</sub>, as well as second-order perturbation energies (*E*<sup>(2)</sup>) of donor-acceptor orbital interactions involved in the H-bonds.<sup>92,93</sup> Interaction types and strengths are determined using the noncovalent interaction (NCI) approach.<sup>94,95</sup> To this end, the reduced gradient of the electron density, *s*( $\rho$ ) ~ |grad( $\rho$ )|/ $\rho$ <sup>4/3</sup>, is evaluated as a function of the electron density  $\rho$  oriented by the sign of the second eigenvalue  $\lambda_2$  of the Hessian,  $\rho^* = \rho \text{sign}(\lambda_2)$ . The  $\rho^*$  values (given in a.u.) provide a measure of the strengths of the intermolecular bonds.

## 3. Results and discussion

Fig. 2 compares the IRPD spectra of Np<sup>+</sup>-W<sub>n</sub> in the 2950–3800 cm<sup>-1</sup> spectral range recorded in the Np<sup>+</sup>-W<sub>n-1</sub> fragment channel. This range covers the aromatic C-H modes of Np<sup>+</sup> ( $\nu_{\text{CH}}$ ) and the O-H stretch modes of the W ligands ( $\nu_{\text{OH}}$ ), and thus provides a sensitive probe of the evolution of the structure of the H-bonded hydration network around Np<sup>+</sup> in its <sup>2</sup>A<sub>u</sub> electronic ground state. The positions and widths of the transitions observed are listed in Table 1, along with their suggested vibrational and isomer assignments. In general, the bands labeled A–C occurring in the 3600–3800 cm<sup>-1</sup> range are attributed to free O-H stretch modes of the W ligands, whereas

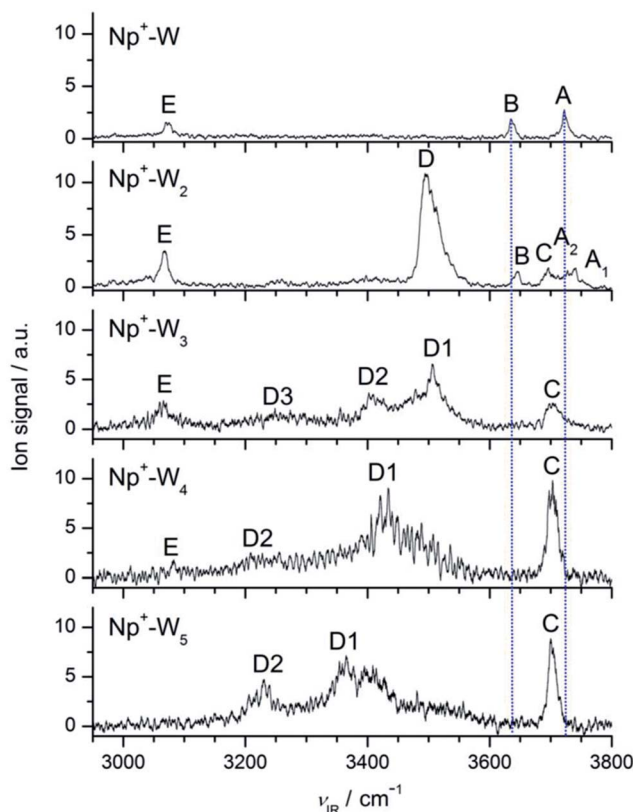


Fig. 2 IRPD spectra of Np<sup>+</sup>-W<sub>n</sub> (*n* = 1–5) recorded in the Np<sup>+</sup>-W<sub>n-1</sub> fragment channel in the O–H and C–H stretch range. The positions, widths, and vibrational and isomer assignments of the transitions observed (A–E) are listed in Table 1. The dashed lines are included to guide the eye for illustrating relative positions of the free O–H stretch bands (A–C).

transitions D in the 3200–3600 cm<sup>-1</sup> range arise from H-bonded O–H stretch vibrations of the W<sub>n</sub> hydration network. Finally, band E near 3080 cm<sup>-1</sup> is assigned to aromatic C–H stretch modes of Np<sup>+</sup>. In the following, we discuss the structural evolution of the hydration network of Np<sup>+</sup>-W<sub>n</sub> by comparing the measured IRPD spectra to computed linear IR absorption spectra of the most stable isomers as a function of the cluster size (*n*). Clearly, the IRPD spectra of Np<sup>+</sup>-W<sub>n</sub> in Fig. 2 show a large variation in appearance as the number of W molecules in the cluster increases, thereby illustrating the qualitative changes in the hydration network structure induced by sequential addition of W ligands in this size regime.

### 3.1 Np<sup>+</sup> and W monomers

The geometric, vibrational, and electronic structures of W, Np, and Np<sup>+</sup> obtained at the B3LYP-D3/aug-cc-pVTZ level were discussed in detail in our earlier report on Np<sup>+</sup>-W.<sup>72</sup> Briefly, the O–H bond parameters of W in its <sup>1</sup>A<sub>1</sub> ground state (*R*<sub>OH</sub> = 0.9617 Å,  $\nu_1$  = 3656 cm<sup>-1</sup>,  $\nu_3$  = 3755 cm<sup>-1</sup>) agree well with the experimental data (0.9578 Å, 3657 and 3756 cm<sup>-1</sup>).<sup>96,97</sup> The optimized planar structures of both Np and Np<sup>+</sup> have *D*<sub>2h</sub> symmetry. The calculated geometry and vibrational frequencies of neutral Np in its <sup>1</sup>A<sub>g</sub> electronic ground state are in excellent agreement with



**Table 1** Positions, widths (FWHM in parentheses), and suggested vibrational and isomer assignments of the transitions observed in the IRPD spectra of  $\text{Np}^+-\text{W}_n$  compared to frequencies of most stable isomers calculated at the B3LYP-D3/aug-cc-pVTZ level. For comparison, available data for  $\text{W}_n$  with  $n \leq 2$  are also listed

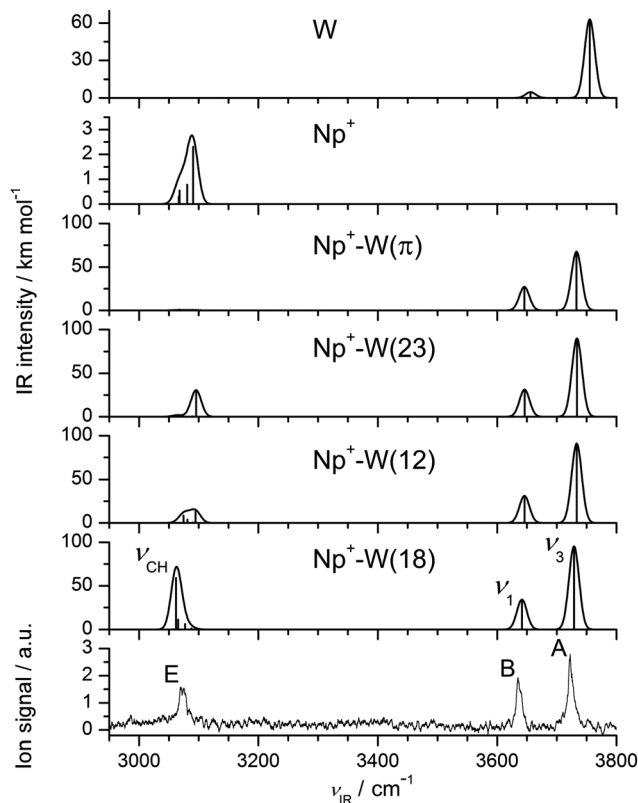
Cluster	Exp ( $\text{cm}^{-1}$ )	Vibration	Calc <sup>a</sup> ( $\text{cm}^{-1}$ )	Isomer	
W	3657 <sup>b</sup>	$\nu_1$	3656 (5, a <sub>1</sub> )		
	3756 <sup>b</sup>	$\nu_3$	3755 (63, b <sub>2</sub> )		
W <sub>2</sub>	3601 <sup>b</sup>	$\nu_b$	3540 (341, a')		
	3654 <sup>b</sup>	$\nu_1$	3650 (9, a')		
	3735 <sup>b</sup>	$\nu_f$	3727 (87, a')		
	3746 <sup>b</sup>	$\nu_3$	3745 (84, a'')		
Np <sup>+</sup> -W	E 3072 (13)	$\nu_{\text{CH}}$	3062 (59, a <sub>1</sub> )	Np <sup>+</sup> -W(18)	
	B 3635 (10)	$\nu_1$	3641 (34, a <sub>1</sub> )	Np <sup>+</sup> -W(18)	
	A 3722 (9)	$\nu_3$	3729 (95, b <sub>1</sub> )	Np <sup>+</sup> -W(18)	
Np <sup>+</sup> -W <sub>2</sub>	E 3068 (10)	$\nu_{\text{CH}}$	3051 (143, a')	Np <sup>+</sup> -W <sub>2</sub> (18)	
		$\nu_{\text{CH}}$	3063 (108, b <sub>3u</sub> )	Np <sup>+</sup> -W <sub>2</sub> (1845)	
	D 3496 (33)	$\nu_b$	3434 (696, a')	Np <sup>+</sup> -W <sub>2</sub> (18)	
	B 3646 (13)	$\nu_1$	3649 (22, a')	Np <sup>+</sup> -W <sub>2</sub> (18)	
		$\nu_1$	3642 (65, a <sub>g</sub> )	Np <sup>+</sup> -W <sub>2</sub> (1845)	
	C 3696 (14)	$\nu_f$	3708 (84, a')	Np <sup>+</sup> -W <sub>2</sub> (18)	
	A2 3728 (10)	$\nu_3$	3731 (186, b <sub>1u</sub> )	Np <sup>+</sup> -W <sub>2</sub> (1845)	
	A1 3740 (9)	$\nu_3$	3741 (99, a'')	Np <sup>+</sup> -W <sub>2</sub> (18)	
	Np <sup>+</sup> -W <sub>3</sub>	E 3065 (24)	$\nu_{\text{CH}}$	3123 (18)	Np <sup>+</sup> -W <sub>3</sub> (c1)
			$\nu_{\text{CH}}$	3079 (113)	Np <sup>+</sup> -W <sub>3</sub> (c2)
D3 3248 (broad)		$2\beta_{\text{OH}}$			
D2 3402 (broad)		$\nu_b$	3415 (162)	Np <sup>+</sup> -W <sub>3</sub> (c1)	
		$\nu_b$	3417 (85)	Np <sup>+</sup> -W <sub>3</sub> (c2)	
D1 3507 (broad)		$\nu_b$	3485 (313)	Np <sup>+</sup> -W <sub>3</sub> (c1)	
			3528 (197)		
		$\nu_b$	3472 (380)	Np <sup>+</sup> -W <sub>3</sub> (c2)	
			3502 (335)		
C 3703 (28)		$\nu_f$	3713 (79)	Np <sup>+</sup> -W <sub>3</sub> (c1)	
			3711 (137)		
			3708 (120)		
		$\nu_f$	3717 (68)	Np <sup>+</sup> -W <sub>3</sub> (c2)	
			3715 (143)		
		3714 (126)			
Np <sup>+</sup> -W <sub>4</sub>	E 3082 (4)	$\nu_{\text{CH}}$	3087 (4)	Np <sup>+</sup> -W <sub>4</sub> (c)	
	D2 3210 (broad)	$\nu_b$	3240 (56)	Np <sup>+</sup> -W <sub>4</sub> (c)	
		$2\beta_{\text{OH}}$			
	D1 3433 (broad)	$\nu_b$	3319 (752)	Np <sup>+</sup> -W <sub>4</sub> (c)	
		3332 (778)			
		3375 (170)			
C 3703 (16)	$\nu_f$	3710 (94)	Np <sup>+</sup> -W <sub>4</sub> (c)		
		3708 (122)			
		3708 (153)			
		3706 (18)			
Np <sup>+</sup> -W <sub>5</sub>	D2 3230 (49)	$\nu_b$	3180 (182)	Np <sup>+</sup> -W <sub>5</sub> (c1)	
		$2\beta_{\text{OH}}$			
	D1 3365 (broad)	$\nu_b$	3256 (1327)	Np <sup>+</sup> -W <sub>5</sub> (c1)	
			3281 (816)		
			3317 (429)		
			3356 (134)		
	C 3700 (13)	$\nu_f$	3712 (117)	Np <sup>+</sup> -W <sub>5</sub> (c1)	
			3710 (146)		
			3708 (84)		
			3707 (74)		
		3706 (29)			

<sup>a</sup> IR intensity (in  $\text{km mol}^{-1}$ ) and vibrational symmetry are listed in parentheses. For the  $\nu_{\text{CH}}$  modes, only the by far most intense calculated vibration is listed. <sup>b</sup> Ref. 97, 107, 127 and 128.

the experimental data.<sup>98–100</sup> The  $^2\text{A}_u$  ground electronic state of  $\text{Np}^+$  is derived by removal of a bonding  $\pi(\text{a}_u)$  electron from the highest occupied molecular orbital of Np, which is delocalized over the aromatic ring.<sup>48,50,51,72</sup> The NBO analysis reveals that the excess positive charge is mostly distributed over the peripheral hydrogen atoms of the bicyclic aromatic ring.<sup>72</sup> In contrast to large C–C bond length changes, ionization induces only minor contractions of the C–H bonds ( $\leq 1$  mÅ). Importantly, the IR activities of all C–H stretch fundamentals is very weak ( $< 2$   $\text{km mol}^{-1}$ ),<sup>72</sup> and hence  $\nu_{\text{CH}}$  fundamentals of  $\text{Np}^+$  have never been detected, neither in the gas phase<sup>72</sup> nor in rare gas matrices.<sup>43,101</sup>

### 3.2 Np<sup>+</sup>-W

The possible structural isomers of  $\text{Np}^+-\text{W}$  and the assignment of its IRPD spectrum have been discussed in detail in the previous communication.<sup>72</sup> They shall be briefly summarized herein for completeness, because they provide the basis for the discussion of the larger clusters. The four nonequivalent minima on the  $\text{Np}^+-\text{W}$  potential<sup>14,72</sup> are shown in Fig. 1, and their predicted IR spectra are compared in Fig. 3 to the measured IRPD spectrum. For comparison, also the spectra calculated for bare  $\text{Np}^+$  and W are shown (although at a different intensity scale). The attraction in all four  $\text{Np}^+-\text{W}$  isomers is largely given by the electrostatic charge–dipole interaction between the positive charge on



**Fig. 3** Comparison of experimental IRPD spectrum of  $\text{Np}^+-\text{W}$  to linear IR absorption spectra of all four nonequivalent isomers calculated at the B3LYP-D3/aug-cc-pVTZ level (Fig. 1, Table 1). For comparison, also the spectra calculated for  $\text{Np}^+$  and W are shown (at a different intensity scale).



$\text{Np}^+$  and the dipole moment of W. As a consequence, the dipole of W points away from the  $\text{Np}^+$  cation in all isomers. The  $\text{Np}^+\text{-W}(18)$  global minimum with  $C_{2v}$  symmetry features a symmetric bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond, in which two neighboring CH groups of the two different aromatic rings act as proton donors for two intermolecular H-bonds to the two in-plane lone pairs of W. Its calculated dissociation energy of  $D_0 = 2773 \text{ cm}^{-1}$  is in good agreement with the values extracted from IRPD spectra of  $\text{Np}^+\text{-W-Ar}$  recorded in various fragment channels ( $D_0 = 2800 \pm 300 \text{ cm}^{-1}$ ),<sup>72</sup> and mass spectrometric experiments ( $-\Delta H = 2730 \pm 350 \text{ cm}^{-1}$ ).<sup>14</sup> The other two planar  $\text{Np}^+\text{-W}(12)$  and  $\text{Np}^+\text{-W}(23)$  isomers with  $C_s$  and  $C_{2v}$  symmetry have a similar bifurcated  $\text{CH}\cdots\text{O}$  H-bond motif, with the main difference that both CH proton donor groups belong to the same aromatic ring. As a result, the  $\text{CH}\cdots\text{O}$  H-bonds deviate substantially more from linearity than those in the (18) isomer. Therefore, they are significantly weaker and longer, leading to correspondingly smaller binding energies of  $D_0 = 2458$  and  $2340 \text{ cm}^{-1}$ , respectively. This view is fully supported by the NBO analysis of the donor-acceptor energies of the orbital interactions involved in the  $\text{CH}\cdots\text{O}$  H-bond motif.<sup>72</sup> The three in-plane  $\text{Np}^+\text{-W}$  isomers are separated by calculated barriers of  $V_b = 99\text{--}485 \text{ cm}^{-1}$ . The fourth  $\text{Np}^+\text{-W}(\pi)$  isomer with a  $\pi$ -bonded structure and  $D_0 = 1947 \text{ cm}^{-1}$  is less stable than the in-plane isomers.

The consequences of the formation of the  $\text{Np}^+\text{-W}$  dimer on the appearance of its IR spectrum in the O–H and C–H stretch range are visualized in Fig. 3 for the four ligand binding sites. The large disparity in the ionization energies of Np and W ( $\text{IE} = 65\,687$  and  $101\,787 \text{ cm}^{-1}$ )<sup>51,102</sup> implies that the positive charge in  $(\text{Np-W})^+$  mainly remains on the Np moiety, justifying the notation of  $\text{Np}^+\text{-W}$ . Nonetheless, formation of the  $\text{Np}^+\text{-W}$  dimer is accompanied by modest charge transfer from  $\text{Np}^+$  to the W ligand, which scales with the interaction strength. For example,  $\Delta q = 12$ , 7, and 8 me for the (18), (12), and (23) isomers. As a result of this charge transfer, the O–H bonds of W become weaker, leading to minor red shifts in the symmetric and anti-symmetric O–H stretch modes from the frequencies of bare W,  $\nu_{1/3} = 3656/3755 \text{ cm}^{-1}$ . For the (18) global minimum, the effects are largest, with  $\Delta r_{\text{OH}} = 1.7 \text{ mÅ}$  and  $\Delta\nu_{1/3} = -15/-26 \text{ cm}^{-1}$ . In addition to the  $\Delta\nu_{1/3}$  shifts, the relative IR intensity of  $\nu_1$  is strongly enhanced compared to that of bare W, which is typical for cation-W dimers.<sup>61,73,80</sup> Concerning the aromatic C–H bonds of  $\text{Np}^+$ , the largest impact is observed for the CH proton donor groups. The elongation of the C–H bonds upon formation of the  $\text{CH}\cdots\text{O}$  ionic H-bond is rather minor, and the corresponding red shift in  $\nu_{\text{CH}}$  is small. For example, for the (18) global minimum, the values are  $\Delta r_{\text{CH}} = 0.8 \text{ mÅ}$  and  $\Delta\nu_{\text{CH}} = -5 \text{ cm}^{-1}$ . However, the IR intensity enhancement is substantial with up to two orders of magnitude. As a consequence, the nearly IR inactive  $\nu_{\text{CH}}$  modes of bare  $\text{Np}^+$  ( $I_{\text{CH}} \leq 2 \text{ km mol}^{-1}$ ) become visible in the  $\text{Np}^+\text{-W}$  spectrum of the in-plane isomers, and reach intensities comparable to the  $\nu_{\text{OH}}$  fundamentals (e.g.,  $I_{\text{CH}} = 59 \text{ km mol}^{-1}$  for (18)). Of course, for  $\text{Np}^+\text{-W}(\pi)$  there is essentially no effect on the C–H bond properties upon monohydration.

The comparison of the IRPD spectrum measured for  $\text{Np}^+\text{-W}$  with the linear IR spectra calculated for the four  $\text{Np}^+\text{-W}$  isomers

suggests an immediate assignment of the experimental spectrum to the most stable (18) isomer, because of the good agreement with respect to both the positions and relative intensities of the transitions.<sup>72</sup> The bands A, B, and E observed at  $3722$ ,  $3635$ , and  $3072 \text{ cm}^{-1}$  are attributed to  $\nu_3$ ,  $\nu_1$ , and  $\nu_{\text{CH}}$  of (18) calculated at  $3729$ ,  $3641$ , and  $3062 \text{ cm}^{-1}$ , with systematic deviations of  $7\text{--}10 \text{ cm}^{-1}$ , respectively. The single intense  $\nu_{\text{CH}}$  normal coordinate of (18) corresponds mostly to a symmetric elongation of the C1–H and C8–H bonds, which is in phase with a minor elongation of the opposite C4–H and C5–H bonds. The detection of three single narrow transitions in the IRPD spectra of  $\text{Np}^+\text{-W}$  (and also the colder  $\text{Np}^+\text{-W-Ar}$  cluster not shown here) indicates that the experimental spectrum is mainly produced by the (18) isomer.<sup>72</sup> The predicted IR spectra of the other three isomer have  $\nu_{\text{OH}}$  and  $\nu_{\text{CH}}$  frequencies, which are clearly different from those of (18) when considering the achieved spectral resolution. Thus, if any of the less stable local minima would be present in the expansion, the spectral features measured in the  $\nu_{\text{OH}}$  and  $\nu_{\text{CH}}$  range should exhibit splittings and/or shoulders, in disagreement with the experimental observation. Hence, the population of the (12), (23), and ( $\pi$ ) isomers of  $\text{Np}^+\text{-W}$  is below the detection limit. This result is in line with the relative (free) energies of the four isomers (Fig. 1).

### 3.3 $\text{Np}^+\text{-W}_2$

Fig. 4 summarizes the low-energy  $\text{Np}^+\text{-W}_2$  structures considered in this work, along with the geometry of bare  $\text{W}_2$ .  $\text{Np}^+\text{-W}_2$  clusters with  $\pi$ -bonded W ligands are no longer discussed here, because of their low binding energies. There are two principal ways to add a second W ligand to the H-bonded  $\text{Np}^+\text{-W}$  dimer to form  $\text{Np}^+\text{-W}_2$ . In the first category, which corresponds to the formation of a H-bonded solvent network, an H-bonded  $\text{W}_2$  dimer is attached to the  $\text{Np}^+$  cation *via* an in-plane bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond. Depending on the three nonequivalent binding sites, these are denoted  $\text{Np}^+\text{-W}_2(18)$ ,  $\text{Np}^+\text{-W}_2(12)$ , and  $\text{Np}^+\text{-W}_2(23)$ . Their total binding energies of  $D_0 = 5529$ ,  $5019$ , and  $4851 \text{ cm}^{-1}$  follow the same trend as found for the  $\text{Np}^+\text{-W}$  dimers (Fig. 1), and their relative free energies ( $G$ ) are similar to the relative energies ( $E_0$ ). The formation of the H-bonded solvent network is strongly cooperative because of the nonadditive induction forces, as will be illustrated in some detail quantitatively for the (18) isomers of  $n = 1$  and  $n = 2$ . Attachment of the second W ligand strongly strengthens the ionic  $\text{CH}\cdots\text{O}$  bond, which contracts from  $2.327 \text{ Å}$  ( $n = 1$ ) to  $2.242 \text{ Å}$  ( $n = 2$ ). This result is in line with the larger proton affinity of  $\text{W}_2$  as compared to W ( $\text{PA} = 808$  and  $691 \text{ kJ mol}^{-1}$ ).<sup>103,104</sup> As a consequence of the stronger  $\text{CH}\cdots\text{O}$  bond, the C–H proton donor bonds are elongated from  $1.0828$  to  $1.0836 \text{ Å}$ , and the corresponding C–H stretch frequency decreases from  $3062$  to  $3051 \text{ cm}^{-1}$  along with an enhancement of the IR intensity from  $59$  to  $143 \text{ km mol}^{-1}$ . On the other hand, the H-bond of the  $\text{W}_2$  dimer becomes much stronger by the presence of the  $\text{Np}^+$  cation. The nearby positive charge polarizes the first W ligand and the additional induced dipole strengthens the W–W H-bond. The isolated  $\text{W}_2$  dimer has a calculated dissociation energy of  $D_0 = 1108 \text{ cm}^{-1}$ , in good agreement with the



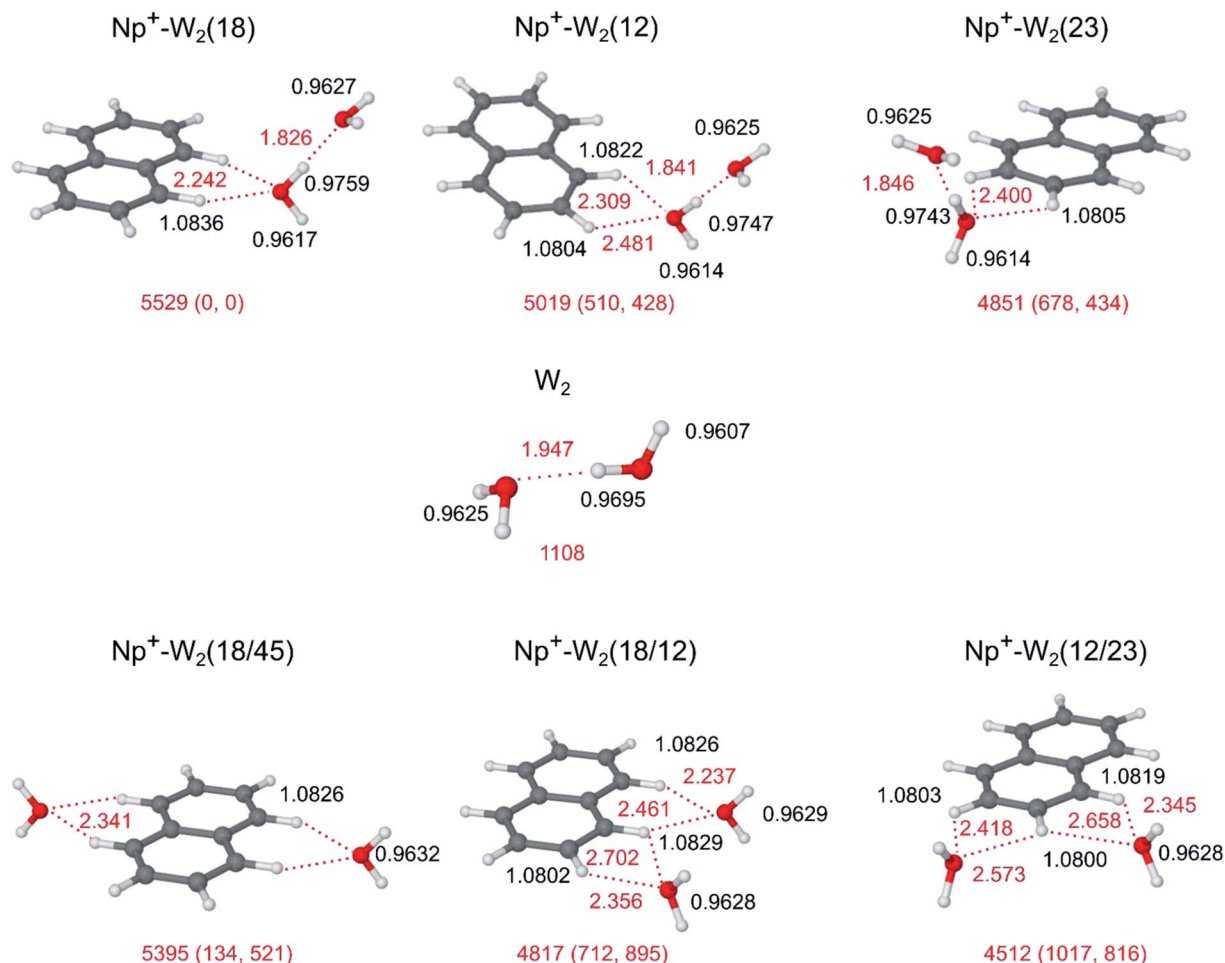


Fig. 4 Optimized structures of  $W_2$  and most stable isomers of  $Np^+-W_2$  calculated at the B3LYP-D3/aug-cc-pVTZ level. The (18), (12), and (23) isomers correspond to formation of a H-bonded solvent network, while the (18/45), (18/12), and (12/23) isomers are examples of interior ion solvation. Binding energies ( $D_0$ ) and bond lengths are given in  $cm^{-1}$  and  $\text{\AA}$ , respectively. Numbers in parenthesis correspond to relative energies and free energies ( $E_0$ ,  $G$ ).

experimental value of  $1105 \pm 10 \text{ cm}^{-1}$ ,<sup>105</sup> illustrating that the chosen B3LYP-D3/aug-cc-pVTZ level reliably describes the W–W interaction. The W–W OH $\cdots$ O H-bond contracts from 1.947  $\text{\AA}$  in free  $W_2$  to 1.826  $\text{\AA}$  in  $Np^+-W_2(18)$ . The total binding energy of  $D_0 = 5529 \text{ cm}^{-1}$  for  $Np^+-W_2(18)$  exceeds the sum of the dissociation energies of  $W_2$  (1108  $cm^{-1}$ ) and the  $Np^+-W(18)$  dimer (2773  $cm^{-1}$ ) by 42%, providing a quantitative energetic measure for the strong cooperativity. The formation of the  $W_2$  dimer in  $Np^+-W_2$  has unique signatures in the  $\nu_{OH}$  range of the IR spectrum (Fig. 5). The localized bound O–H stretch of the proton donor is largely red shifted to  $\nu_b = 3434 \text{ cm}^{-1}$  with high IR intensity (696  $km \text{ mol}^{-1}$ ), because of the elongated O–H bond (0.9759  $\text{\AA}$ ), while the uncoupled free O–H stretch of the dangling OH group (0.9617  $\text{\AA}$ ) of this W molecule occurs at  $\nu_f = 3708 \text{ cm}^{-1}$ . The  $\nu_b$  mode in  $Np^+-W_2(18)$  is shifted to lower frequency by 106  $cm^{-1}$  compared to bare  $W_2$  (3540  $cm^{-1}$ ), as a result of the stronger OH $\cdots$ O H-bond. The coupled  $\nu_1$  and  $\nu_3$  frequencies of the proton acceptor OH groups (0.9627  $\text{\AA}$ ) are predicted at 3649 and 3741  $cm^{-1}$ , *i.e.* they occur 8 and 11  $cm^{-1}$  blueshifted from those of the  $n = 1$  cluster, because the W molecule is further away from the  $Np^+$  charge and thus their

O–H bonds are shorter than in  $n = 1$  (0.9634  $\text{\AA}$ ). Further measures of the degree of noncooperativity provided by the NBO and NCI analyses are detailed in ESI (Fig. S1–S3, Table S1†). Both the NBO and NCI indicators suggest that the neutral OH $\cdots$ O H-bond in  $Np^+-W_2(18)$  is stronger than the CH $\cdots$ O ionic H-bond! Similar cooperative effects as found for the (18) structure of  $Np^+-W_2$  are also observed for the (12) and (23) isomers, although both the OH $\cdots$ O and CH $\cdots$ O H-bonds are weaker in these less stable local minima as compared to the (18) isomer.

In the second category of  $Np^+-W_2$  structures, which corresponds to interior ion solvation, both W ligands bind separately to the  $Np^+$  cation *via* two individual CH $\cdots$ O ionic H-bonds. The three most stable examples of this category are  $Np^+-W_2(18/45)$ ,  $Np^+-W_2(18/12)$ , and  $Np^+-W_2(12/23)$ , with binding energies of  $D_0 = 5395$ , 4817, and 4512  $cm^{-1}$ , respectively (Fig. 4). Other possible isomers such as (18/23), (18/34), *etc.* are less stable. In contrast to clusters with an H-bonded solvent network, the nonadditive polarization forces are slightly noncooperative for interior ion solvation, mainly because of enhanced charge delocalization. This effect shall be illustrated in some detail quantitatively for the (18) and (18/45) isomers of  $n = 1$  and  $n =$



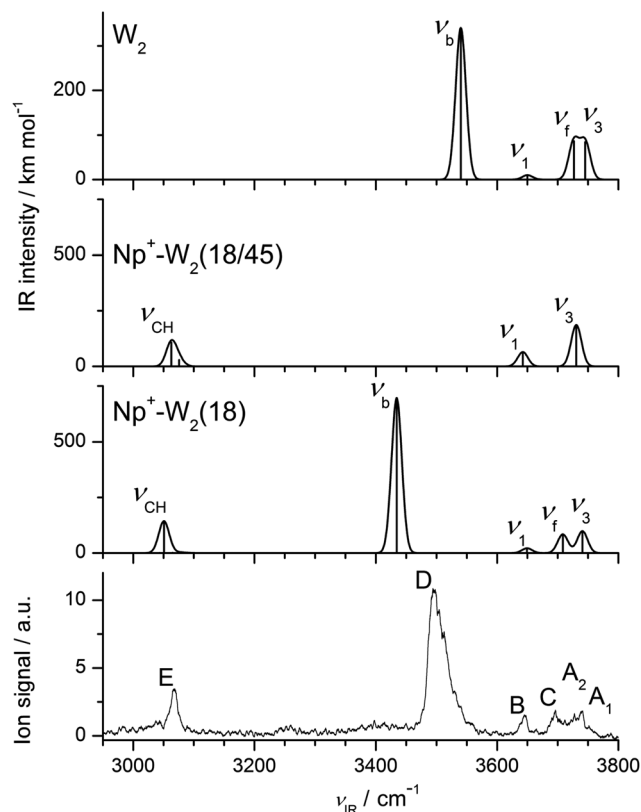


Fig. 5 Comparison of experimental IRPD spectrum of  $\text{Np}^+\text{-W}_2$  to linear IR absorption spectra of the most stable (18) and (18/45) isomers of  $\text{Np}^+\text{-W}_2$  calculated at the B3LYP-D3/aug-cc-pVTZ level (Fig. 4, Table 1). For comparison, also the spectrum calculated for bare  $\text{W}_2$  is shown (at a different intensity scale). Comparison of the IRPD spectrum to linear IR spectra of less stable isomers is available in Fig. S4 in ESI.†

2, respectively, which are both characterized by bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bonds to the  $\text{C}\alpha\text{H}$  groups of  $\text{Np}^+$ . The (18/45) isomer with  $D_{2h}$  symmetry has two equivalent  $\text{CH}\cdots\text{O}$  H-bonds with  $R = 2.341 \text{ \AA}$  and  $D_0 = 2698 \text{ cm}^{-1}$ , while the corresponding bond in the  $n = 1$  cluster ( $C_{2v}$ ) is slightly stronger ( $R = 2.327 \text{ \AA}$ ,  $D_0 = 2773 \text{ cm}^{-1}$ ). Energetically, the non-cooperativity thus is evaluated as 3%. As a consequence of the slightly weaker  $\text{CH}\cdots\text{O}$  H-bond, the C-H proton donor bonds contract from  $1.0828 \text{ \AA}$  ( $n = 1$ ) to  $1.0826 \text{ \AA}$  ( $n = 2$ ), and the corresponding (averaged) C-H stretch frequency increases from  $3064$  to  $3070 \text{ cm}^{-1}$ . In addition, the O-H bonds of the individual W ligands are less affected by the interaction with  $\text{Np}^+$  in  $n = 2$  as compared to  $n = 1$  ( $\Delta r_{\text{OH}} = 1.5$  vs.  $1.7 \text{ m\AA}$ ,  $\Delta\nu_{1/3} = -14/-24$  vs.  $-15/-26 \text{ cm}^{-1}$ ). Similar noncooperative effects are observed for other isomers with interior ion solvation.

According to the calculations, the most stable  $\text{Np}^+\text{-W}_2$  isomer is the (18) isomer with  $\text{W}_2$  attached to C1H and C8H. The next stable isomer is (18/45) with  $E_0 = 134 \text{ cm}^{-1}$  and  $G = 521 \text{ cm}^{-1}$ , *i.e.* the formation of an H-bonded network is favored over interior ion solvation (Fig. 4). The other considered isomers of both categories are substantially higher in energy, and from experience with the analysis of the  $n = 1$  spectrum, they are not expected to substantially contribute to the experimental IRPD

spectrum of  $\text{Np}^+\text{-W}_2$ . To this end, the IR spectra calculated for the (18) and (18/45) isomers are compared in Fig. 5 to the measured IRPD spectrum. The latter exhibits six transitions at  $3740$  (A1),  $3728$  (A2),  $3696$  (C),  $3646$  (B),  $3496$  (D), and  $3068$  (E)  $\text{cm}^{-1}$ . The bands D and C are newly observed in the  $n = 2$  spectrum (Fig. 2) and are a clear signature of a  $\text{Np}^+\text{-W}_2$  isomer with a H-bonded  $\text{W}_2$  dimer. They correspond to the bound and free O-H stretch modes of the proton donor W molecule ( $\nu_{b/f}$ ) in the  $\text{W}_2$  dimer. As a consequence, transitions D and C at  $3496$  and  $3696 \text{ cm}^{-1}$  are assigned to  $\nu_b$  and  $\nu_f$  of the (18) isomer, in good agreement with the calculated frequencies of  $3434$  and  $3708 \text{ cm}^{-1}$ . The remaining free O-H stretch modes of the terminal W acceptor molecule are predicted at  $\nu_1 = 3649$  and  $\nu_3 = 3741 \text{ cm}^{-1}$ , and thus are assigned to transitions B and A1 observed at  $3646$  and  $3740 \text{ cm}^{-1}$ , respectively. Transition E at  $3068 \text{ cm}^{-1}$  is then attributed to  $\nu_{\text{CH}}$  of the (18) isomer predicted at  $3051 \text{ cm}^{-1}$ . The experimental red shift of  $\nu_{\text{CH}}$  upon attachment of the second W ligand ( $-4 \text{ cm}^{-1}$ ) is somewhat smaller than the predicted shift ( $-11 \text{ cm}^{-1}$ ). In addition, the enhanced relative intensity of  $\nu_{\text{CH}}$  compared to the free  $\nu_{\text{OH}}$  bands observed experimentally is nicely reproduced by the spectrum calculated for (18). While for  $n = 1$ ,  $\nu_{\text{CH}}$  is less intense than  $\nu_{\text{OH}}$ , the opposite is true for  $n = 2$ . Overall, most of the major transitions of the IRPD spectrum of  $\text{Np}^+\text{-W}_2$  agree well with those predicted for the (18) global minimum with respect to position and relative intensity. The other less stable  $\text{Np}^+\text{-W}_2$  local minima with a  $\text{W}_2$  structure, (12) and (23), have a qualitatively similar IR spectrum (Fig. S4 in ESI†) but may be excluded for several reasons. First, the calculated relative energies are rather high ( $E_0 > 500 \text{ cm}^{-1}$ ), and thus their presence may be excluded for thermodynamic reasons. For the  $n = 1$  cluster, all local minima with  $E_0 > 300 \text{ cm}^{-1}$  are below the detection limit. In addition, since the  $\text{OH}\cdots\text{O}$  H-bonds are weaker in the (12) and (23) isomers as compared to the (18) isomer ( $R = 1.841$  and  $1.846$  vs.  $1.862 \text{ \AA}$ ), their bound O-H stretch frequencies occur at significantly higher energies ( $\nu_b = 3456$  and  $3462$  vs.  $3434 \text{ cm}^{-1}$ ). However, band D assigned to  $\nu_b$  occurs as a single peak and does not show any splitting. The asymmetric blue-shaded band contour of band D with a sharp rise on the red side and a long monotonic decreasing tail on the blue side is typical for excitation of proton donor stretch vibrations<sup>73</sup> and not an indication for the presence of further isomers. Similarly, band E assigned to  $\nu_{\text{CH}}$  does not exhibit any splitting or shoulder. While for the (12) isomer the  $\nu_{\text{CH}}$  intensity is predicted to be much weaker than for (18) ( $I_{\text{CH}} = 23$  vs.  $143 \text{ km mol}^{-1}$ ) and thus difficult to detect, the most intense  $\nu_{\text{CH}}$  fundamental of (23) is predicted to occur with substantial intensity at  $3094 \text{ cm}^{-1}$  ( $52 \text{ km mol}^{-1}$ ). This frequency is far from the measured  $\nu_{\text{CH}}$  band E at  $3068 \text{ cm}^{-1}$ , and thus the population of (23) is clearly below the detection limit.

Although at first glance the IRPD spectrum of  $\text{Np}^+\text{-W}_2$  can mostly be assigned to the dominating (18) global minimum, closer inspection reveals subtle hints for the minor presence of a second isomer, which belongs to the class of interior ion solvation. The clearest signature is transition A2 at  $3728 \text{ cm}^{-1}$ , which occurs close to band A of  $\text{Np}^+\text{-W}$  at  $3722 \text{ cm}^{-1}$ . This band thus is attributed to the free  $\nu_3$  mode of a W ligand directly



attached to  $\text{Np}^+$ . The small observed blue shift of  $6 \text{ cm}^{-1}$  from  $n = 1$  to  $n = 2$  is consistent with the noncooperative effect when attaching the second W ligand. Hence, band A2 of  $\text{Np}^+-\text{W}_2$  is assigned to  $\nu_3$  of the by far most stable (18/45) isomer with interior ion solvation predicted at  $3731 \text{ cm}^{-1}$ . The other transitions calculated for this isomer ( $\nu_3 = 3642 \text{ cm}^{-1}$ ,  $\nu_{\text{CH}} = 3063 \text{ cm}^{-1}$ ) overlap with bands B and E at  $3646$  and  $3068 \text{ cm}^{-1}$  mainly assigned to the (18) global minimum. This overlap may explain the somewhat higher relative intensity of band B in the IRPD spectrum, which cannot be explained by the calculated spectrum of (18) alone. Comparing the ratio of the integrated band intensities of bands A1 and A2 ( $>3 : 1$ ) with the IR cross sections calculated for  $\nu_3$  of the (18) and (18/45) isomers ( $1 : 2$ ), we estimate the maximum abundance of the (18/45) local minimum to be below 20%. This result is consistent with its relative (free) energy of  $E_0 = 134$  (521)  $\text{cm}^{-1}$ . An alternative explanation for band A2 may be unresolved structure of (hindered) internal rotation of the terminal W ligand of the (18) isomer of  $\text{Np}^+-\text{W}_2$ . Although we cannot exclude this interpretation, we favor currently the scenario with the coexistence of the two isomers. Other isomers with interior ion solvation may safely be excluded for thermodynamic reasons ( $E_0 > 700 \text{ cm}^{-1}$ ). In addition, their spectra predicted in the  $\nu_{\text{CH}}$  range do not match well with band E, because of their weaker  $\text{CH}\cdots\text{O}$  H-bonds (Fig. S4 in ESI†).

### 3.4 $\text{Np}^+-\text{W}_3$

Interestingly, the IRPD spectrum of  $\text{Np}^+-\text{W}_3$  in Fig. 2 is dominated in the free O–H stretch range by band C at  $\nu_f = 3703 \text{ cm}^{-1}$ . Unlike the spectra for the  $n = 1$  and  $n = 2$  clusters, the  $n = 3$  spectrum does not show anymore pronounced peaks A and B assigned to coupled  $\nu_3$  and  $\nu_1$  transitions of W ligands acting barely as proton acceptors in H-bonding. While there is definitely no signal around  $3650 \text{ cm}^{-1}$  (B,  $\nu_1$ ), some weak signal in the blue shoulder of band C near  $3730 \text{ cm}^{-1}$  may be attributed to  $\nu_3$  transitions (A). On the other hand, there are intense and broad transitions D1 and D2 peaking at  $3507$  and  $3402 \text{ cm}^{-1}$ , which clearly come from H-bonded O–H stretch modes. These observations are taken as evidence that the predominant  $\text{Np}^+-\text{W}_3$  structures contributing to the IRPD spectrum have only W ligands, which act as proton donor in H-

bonds, either as single donor or double donor. In such structures, a cyclic H-bonded  $\text{W}_3$  trimer is attached to the  $\text{Np}^+$  cation. The still high intensity of transition E at  $3065 \text{ cm}^{-1}$  indicates that at least in some of these  $\text{Np}^+-\text{W}_3$  clusters, the cyclic  $\text{W}_3$  unit is connected to the  $\text{Np}^+$  cation *via*  $\text{CH}\cdots\text{O}$  ionic H-bonding.

The calculations yield a large number of stable structures for  $\text{Np}^+-\text{W}_3$ . Similar to the case of  $\text{Np}^+-\text{W}_2$ , the possible  $\text{Np}^+-\text{W}_3$  isomers may be classified into those with interior ion solvation and those forming a single hydration network. The latter may further be divided into those having a linear, branched, or cyclic  $\text{W}_3$  unit. Several of the low-energy structures representing prototypes for these classes of  $\text{Np}^+-\text{W}_3$  clusters are shown in Fig. 6 and S5 in ESI†. Amongst all optimized structures,  $\text{Np}^+-\text{W}_3(\text{c1})$  with  $D_0 = 8355 \text{ cm}^{-1}$  is the most stable isomer ( $E_0 = 0$ ). In this structure, a cyclic neutral distorted H-bonded  $\text{W}_3$  trimer is attached to the  $\text{Np}^+$  cation *via* two nearly linear  $\text{CH}\cdots\text{O}$  ionic H-bonds involving the C1H and C8H proton donor groups. For comparison, the structure and IR spectrum calculated for bare  $\text{W}_3$  are shown in Fig. S6 and S7 in ESI†. Its dissociation energy for W loss ( $D_0 = 2809 \text{ cm}^{-1}$ ) is in good agreement with the experimental value of  $2650 \pm 150 \text{ cm}^{-1}$ .<sup>106</sup> The three intermolecular  $\text{OH}\cdots\text{O}$  bonds in  $\text{Np}^+-\text{W}_3(\text{c1})$  are rather different ( $R = 1.880, 1.904, 2.059 \text{ \AA}$ ), giving rise to three isolated bound O–H stretch oscillators ( $\nu_b = 3415, 3485, 3528 \text{ cm}^{-1}$ , Fig. 7) due to rather different O–H bond lengths ( $0.9762, 0.9733, 0.9712 \text{ \AA}$ ). In contrast, the free O–H bonds have essentially the same length ( $0.9619 \pm 0.0001 \text{ \AA}$ ), producing three free O–H stretch bands with similar frequency ( $3708\text{--}3713 \text{ cm}^{-1}$ ). A similar cyclic structure  $\text{Np}^+-\text{W}_3(\text{c2})$  shown in Fig. 6 with  $D_0 = 7846 \text{ cm}^{-1}$  is slightly higher in energy ( $E_0 = 509 \text{ cm}^{-1}$ ). In the most stable linear (18) isomer with  $D_0 = 8140 \text{ cm}^{-1}$  ( $E_0 = 215 \text{ cm}^{-1}$ ), a linear  $\text{W}_3$  chain is attached to the  $\text{Np}^+$  cation *via* a bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond between the acidic C1H and C8H protons and the first W ligand of the chain (Fig. S5 in ESI†). Such linear chains may also start between the less acidic C1H and C2H protons or the C2H and C3H protons, yielding the less stable (12) and (23) isomers with  $D_0 = 7524$  and  $7262 \text{ cm}^{-1}$  ( $E_0 = 831$  and  $1093 \text{ cm}^{-1}$ ).  $\text{Np}^+-\text{W}_3$  clusters with a branched  $\text{W}_3$  network are less stable than those with a linear  $\text{W}_3$  chain (*e.g.*,  $D_0 = 7787$  *versus*  $8140 \text{ cm}^{-1}$  for attachment of  $\text{W}_3$  at the C8H and C1H protons). Amongst all the isomers with interior ion hydration,

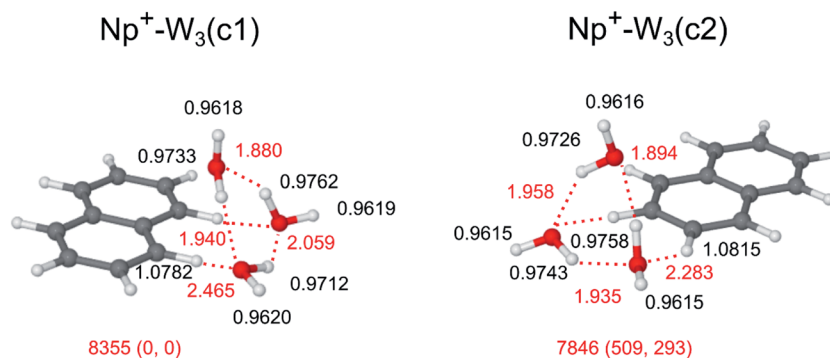


Fig. 6 Optimized structures of the two most stable cyclic  $\text{Np}^+-\text{W}_3$  isomers obtained at the B3LYP-D3/aug-cc-pVTZ level. Binding energies ( $D_0$ ) and bond lengths are given in  $\text{cm}^{-1}$  and  $\text{\AA}$ , respectively. Numbers in parenthesis correspond to relative energies and free energies ( $E_0, G$ ).



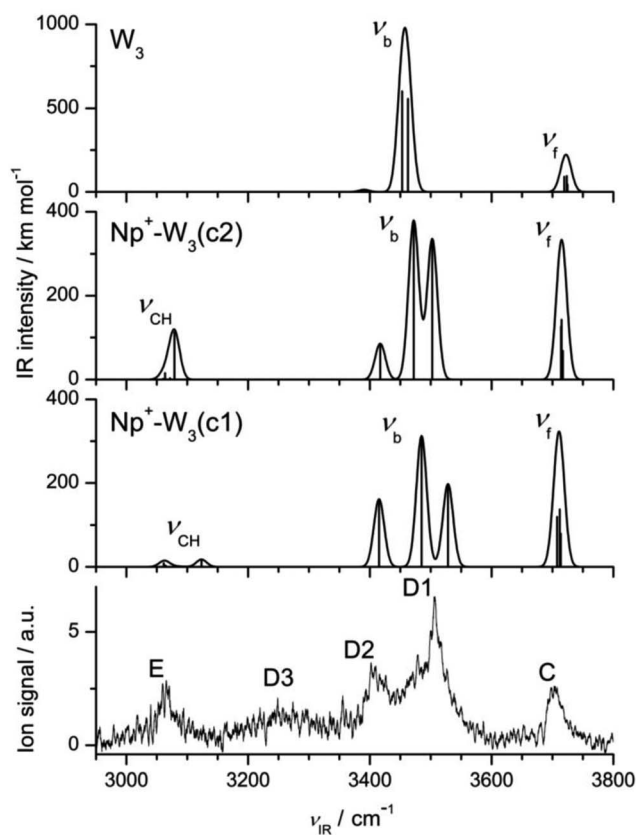


Fig. 7 Comparison of experimental IRPD spectrum of  $\text{Np}^+\text{-W}_3$  to linear IR absorption spectra of the most stable cyclic isomers of  $\text{Np}^+\text{-W}_3$  calculated at the B3LYP-D3/aug-cc-pVTZ level (Fig. 6, Table 1). For comparison, also the spectrum calculated for bare  $\text{W}_3$  is shown (at a different intensity scale).

the most stable (18/45) isomer with  $D_0 = 8059 \text{ cm}^{-1}$  ( $E_0 = 296 \text{ cm}^{-1}$ ) binds a  $\text{W}_2$  unit *via* bifurcated  $\text{CH}\cdots\text{O}$  H-bonds to C1H and C8H and a single W ligand to the C4H and C5H protons. As expected, the most stable  $\text{Np}^+\text{-W}_3$  isomer, in which all three W ligands bind separately to  $\text{Np}^+$  *via* individual ionic  $\text{CH}\cdots\text{O}$  H-bonds, is the (18/45/12) isomer with  $D_0 = 7300 \text{ cm}^{-1}$  ( $E_0 = 1055 \text{ cm}^{-1}$ ). When considering entropic effects at room temperature, the linear and branched structures as well as structures with interior ion solvation become more favorable than cyclic structures because the latter ones are more rigid (see  $G$  values in Fig. 6 and S5 in ESI†).

The IRPD spectrum of  $\text{Np}^+\text{-W}_3$  is compared in Fig. 7 to the IR spectra calculated for the two considered cyclic isomers (c1) and (c2), while comparison to IR spectra of the other isomers is available in Fig. S8 in ESI†. As mentioned above, the lack of bands A and B in the  $\text{Np}^+\text{-W}_3$  spectrum provides a strong indication that the experimental spectrum is largely dominated by cyclic isomers, and indeed it can fully be rationalized by the two lowest-energy cyclic isomers (Fig. 7). The resulting assignments are summarized in Table 1. While the (c1) global minimum can account well for free and bound O–H stretch bands (C, D1, D2), it fails to reproduce the intense  $\nu_{\text{CH}}$  band E. In contrast, the (c2) isomer can explain the latter transition and, in addition, also the O–H stretch part of its spectrum is compatible with the

experimental one. The minor signal in the blue wing of band C near  $3730 \text{ cm}^{-1}$  may provide weak evidence for the presence of the most stable linear (18) isomer (Fig. S8 in ESI†), which for energetic reasons may also have a significant population. Because its terminal W is far away from the  $\text{Np}^+$  charge, its  $\nu_{1/3}$  bands have low IR activity, and thus may not readily be detected here. The broad transition D3 near  $3250 \text{ cm}^{-1}$  cannot be rationalized by any of the calculated  $\text{Np}^+\text{-W}_3$  isomers. This band thus is tentatively attributed to the first overtone of the bending vibrations of the W ligands ( $2\nu_{\text{OH}}$ ), which is expected in this spectral range and not included in the harmonic calculations. Clearly, the IR spectrum predicted for cyclic  $\text{W}_3$  (Fig. 7) is quite different from that of  $\text{Np}^+\text{-W}_3(\text{c1})$ . The perturbation by the nearby  $\text{Np}^+$  cation arises from both charge-induced and steric effects.

### 3.5 $\text{Np}^+\text{-W}_4$

The evolution of the IRPD spectra of  $\text{Np}^+\text{-W}_n$  in Fig. 2 yields the following major conclusions for the  $n = 4$  cluster. Bands A and B assigned to  $\nu_3$  and  $\nu_1$  modes of W ligands not acting as H-bond donors, which are strong for  $n \leq 2$  and very weak and/or absent for  $n = 3$ , definitively disappear for  $n = 4$ . This result indicates that the  $n = 4$  clusters are dominated by isomers with a cyclic  $\text{W}_4$  unit. Second, compared to the spectra of the  $n = 1\text{--}3$  clusters, also the relative intensity of band E attributed to  $\nu_{\text{CH}}$  of  $\text{Np}^+$  becomes very weak relative to the  $\nu_{\text{OH}}$  transitions for  $n = 4$ . This observation indicates that the population of  $\text{Np}^+\text{-W}_4$  isomers with  $\text{CH}\cdots\text{O}$  ionic H-bonds of  $\text{Np}^+$  to the  $\text{W}_4$  unit is small, and the cyclic  $\text{W}_4$  ring may preferentially bind above or below the  $\text{Np}^+$  ring. The O–H stretch spectral range is now completely dominated by the sharp band C and a broader band D1 characteristic for  $\nu_f$  and  $\nu_b$  of single-donor W ligands.

Out of the many stable structures computed for  $\text{Np}^+\text{-W}_4$ , the cyclic  $\text{Np}^+\text{-W}_4(\text{c})$  isomer shown in Fig. 8 is the most stable one, with a total binding energy of  $D_0 = 12\,557 \text{ cm}^{-1}$ . In this structure, a distorted neutral H-bonded  $\text{W}_4$  unit is located above the aromatic  $\text{Np}^+$  ring, with a strongly nonplanar bifurcated  $\text{CH}\cdots\text{O}$  H-bond motif to one W molecule of the  $\text{W}_4$  cycle. As a result, the  $\text{C1H}\cdots\text{O}$  and  $\text{C8H}\cdots\text{O}$  H-bonds are rather weak ( $2.685$  and  $2.491 \text{ \AA}$ ) compared to the planar bifurcated  $\text{CH}\cdots\text{O}$  H-bonds found for  $n \leq 3$ . Like for  $n = 3$ , also for  $n = 4$  all free O–H bonds of the cyclic  $\text{W}_4$  ring point away from the  $\text{Np}^+$  cation to maximize the electrostatic charge–dipole attraction. For comparison, also a low-energy linear  $\text{Np}^+\text{-W}_4(\text{l})$  isomer is shown in Fig. 8 ( $D_0 = 11\,103 \text{ cm}^{-1}$ ), although its relative energy is already rather high compared to  $\text{Np}^+\text{-W}_4(\text{c})$ ,  $E_0 = 1454 \text{ cm}^{-1}$ . Note that this linear isomer differs from that reported in ref. 14 such that the W ligands are closer to the  $\text{Np}^+$  cation. The global minimum reported in ref. 14 could not be optimized at the current theoretical level.

The IRPD spectrum of  $\text{Np}^+\text{-W}_4$  is compared in Fig. 9 to the IR spectra calculated for the cyclic and linear isomers shown in Fig. 8. In general, the overall appearance of the  $\text{Np}^+\text{-W}_4(\text{c})$  spectrum agrees well with the measured spectrum, in particular in view of the fact that the computations somewhat overestimate the red shift of the bound O–H stretch bands



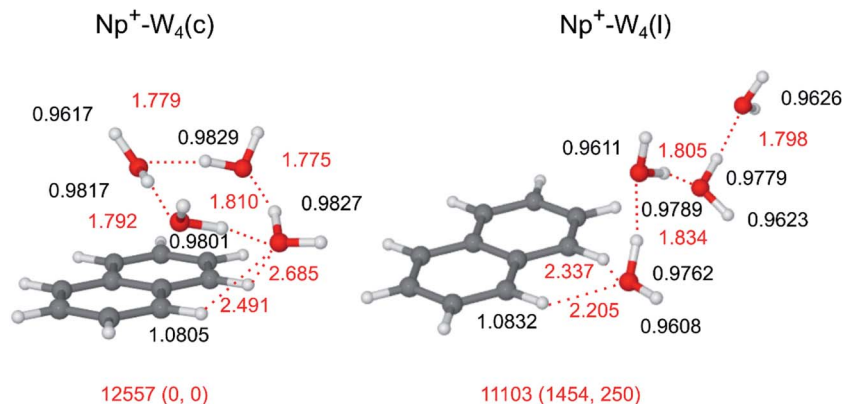


Fig. 8 Optimized structures of the most stable  $\text{Np}^+-\text{W}_4$  isomers with a cyclic (c) and linear (l)  $\text{W}_4$  solvent cluster obtained at the B3LYP-D3/aug-cc-pVTZ level. Binding energies ( $D_0$ ) and bond lengths are given in  $\text{cm}^{-1}$  and  $\text{\AA}$ , respectively. Numbers in parenthesis correspond to relative energies and free energies ( $E_0$ , G).

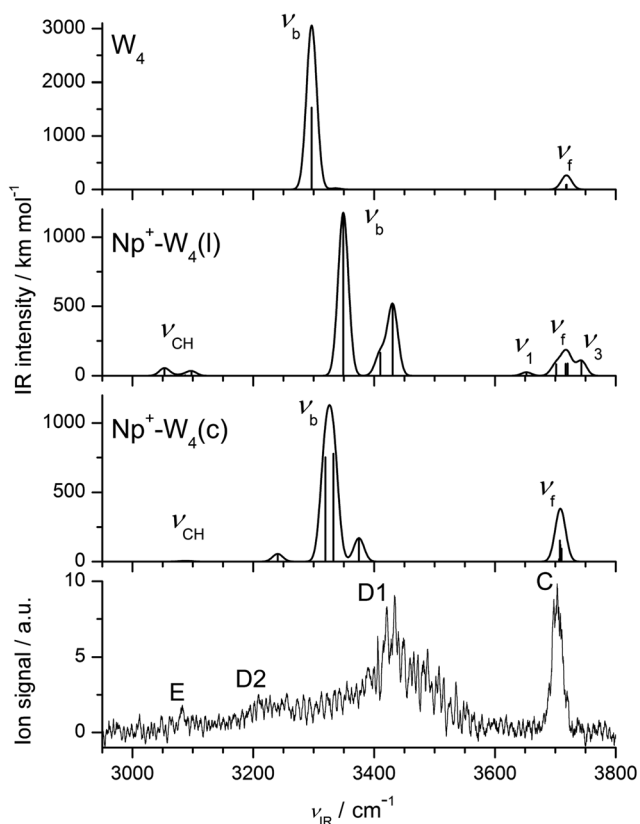


Fig. 9 Comparison of experimental IRPD spectrum of  $\text{Np}^+-\text{W}_4$  to linear IR absorption spectra of the most stable cyclic and linear isomers of  $\text{Np}^+-\text{W}_4$  calculated at the B3LYP-D3/aug-cc-pVTZ level (Fig. 8, Table 1). For comparison, also the spectrum calculated for bare  $\text{W}_4$  is shown (at a different intensity scale).

(see Fig. 5 for  $n = 2$ ). This is true for the overall appearance, the positions and relative intensities of the transitions, and the simplicity of the spectrum. Hence, bands C and D1 at 3703 and 3433  $\text{cm}^{-1}$  in the IRPD spectrum are assigned to  $\nu_f$  and  $\nu_b$  modes of  $\text{Np}^+-\text{W}_4(\text{c})$ , calculated in the narrow 3706–3710  $\text{cm}^{-1}$  range for  $\nu_f$  and more widely spread out at 3240, 3319, 3332, and

3375  $\text{cm}^{-1}$  for  $\nu_b$  (Table 1). The transition D2 at 3210  $\text{cm}^{-1}$  is again tentatively attributed to  $2\beta_{\text{OH}}$ , and may also cover the lowest-frequency  $\nu_b$  mode (3240  $\text{cm}^{-1}$ ). Consistent with the experimental spectrum, the  $\nu_{\text{CH}}$  intensity of this isomer is very small (4  $\text{km mol}^{-1}$ ). In fact, the visible band E at 3082  $\text{cm}^{-1}$  is probably not (only) produced by the  $\text{Np}^+-\text{W}_4(\text{c})$  global minimum but may be an indicator for the presence of less stable cyclic and/or linear/branched  $\text{Np}^+-\text{W}_4$  isomers with stronger  $\text{CH}\cdots\text{O}$  contacts. One such example may be the computed  $\text{Np}^+-\text{W}_4(\text{l})$  isomer. On the other hand, this isomer has the  $\nu_1$  and  $\nu_3$  transitions typical of the terminal W ligand, which are not detected in the experimental spectrum, although their IR activity is predicted to be higher than that of  $\nu_{\text{CH}}$ . Interestingly, the spectrum calculated for cyclic  $\text{W}_4$  (Fig. S6 in ESI<sup>†</sup>) is not too different from that of  $\text{Np}^+-\text{W}_4(\text{c1})$  (Fig. 9). The strongly IR active ring stretch mode of  $\text{W}_4$  is measured at  $\nu_b = 3416 \text{ cm}^{-1}$ ,<sup>107</sup> *i.e.* somewhat lower than the maximum of band D1 of  $\text{Np}^+-\text{W}_4$  at 3433  $\text{cm}^{-1}$ . In addition, it is substantially higher than the predicted frequency of  $\nu_b = 3297 \text{ cm}^{-1}$ , confirming that the DFT calculations overestimate the red shift of the bound O–H stretch frequencies.

### 3.6 $\text{Np}^+-\text{W}_5$

The following conclusions are evident from the comparison of the IRPD spectrum of  $\text{Np}^+-\text{W}_5$  with those of the smaller hydrates in Fig. 2. First, band C near 3700  $\text{cm}^{-1}$  gains further in relative intensity, because the number of single-donor W ligands in the clusters increases and their  $\nu_f$  bands occur all at the same position. In addition, its width becomes narrower, because the binding energy for W elimination becomes smaller as the cluster size increases. Second, like for the other  $n \geq 3$  clusters, bands A and B are absent, indicating that clusters with cyclic  $\text{W}_5$  units dominate the cluster population. Third, band E disappears completely for  $n = 5$ , revealing that the observed cluster structures have no (or only a weak)  $\text{CH}\cdots\text{O}$  ionic H-bond. Thus, the trend observed already for  $n = 4$  continues for  $n = 5$ , and the spectrum points toward  $\text{Np}^+-\text{W}_5$  clusters with cyclic  $\text{W}_5$  rings above the  $\text{Np}^+$  plane. Fourth, the transition D1 associated for  $\nu_b$



transitions becomes broader and shifted to lower frequency, indicating that the OH...O H-bonds of the  $W_5$  solvent network become stronger. Finally, similar to band C, the band D2 assigned to the  $2\beta_{\text{OH}}$  overtone increases in relative intensity, because the number of W ligands in the cluster becomes larger and possibly the anharmonic interaction (Fermi resonances) with the nearby  $\nu_b$  fundamentals becomes stronger. Part of the D2 intensity may also arise from  $\nu_b$  transitions.

The most stable structure out of the plethora of minima found for  $\text{Np}^+-W_5$  is the  $\text{Np}^+-W_5(\text{c1})$  isomer shown in Fig. 10, with a total binding energy of  $D_0 = 15\,927\text{ cm}^{-1}$ . In this structure, a distorted cyclic neutral  $W_5$  pentamer is connected to the most acidic C1H and C8H protons by a strongly nonplanar bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond to a single W molecule. This structure is similar to the most stable  $\text{Np}^+-W_4(\text{c})$  structure of the  $n = 4$  cluster, with the simple insertion of one W ligand into the cyclic water cluster ring. All W molecules act as single-donor single-acceptor, except for the W molecule connecting the  $W_5$  cycle to  $\text{Np}^+$ . For comparison, a related cyclic  $\text{Np}^+-W_5(\text{c2})$  isomer is also shown in Fig. 10, in which one W ligand is a double acceptor in the cyclic  $W_5$  pentamer. This less stable structure is substantially higher in energy ( $E_0 = 2718\text{ cm}^{-1}$ ), illustrating that  $W_5$  rings with only single-donor single-acceptor molecules are energetically very favorable. Other linear or branched structures or cyclic structures with smaller  $W_{n<5}$  rings (ring-tail structures) are not considered in detail because they are less stable and, similar to  $\text{Np}^+-W_4$ , do not fit the experimental spectrum in the free O-H stretch range. Similar to the  $n = 4$  cluster, the global minimum reported in ref. 14 with a linear  $W_5$  chain pointing away from  $\text{Np}^+$  could not be found at the current theoretical level.

In Fig. 11 the IRPD spectrum measured for  $\text{Np}^+-W_5$  is compared to the IR spectra calculated for the (c1) and (c2) isomers of  $\text{Np}^+-W_5$  and bare  $W_5$ . The spectrum of the most stable  $\text{Np}^+-W_5(\text{c1})$  isomer agrees well with the measured spectrum, when we recall that the calculations underestimate the frequencies of the bound O-H stretch bands ( $\nu_b$ ). The resulting assignments are listed in Table 1. All  $\nu_f$  modes of  $\text{Np}^+-W_5(\text{c1})$  are predicted in the narrow range of  $3709 \pm 3\text{ cm}^{-1}$ , in good

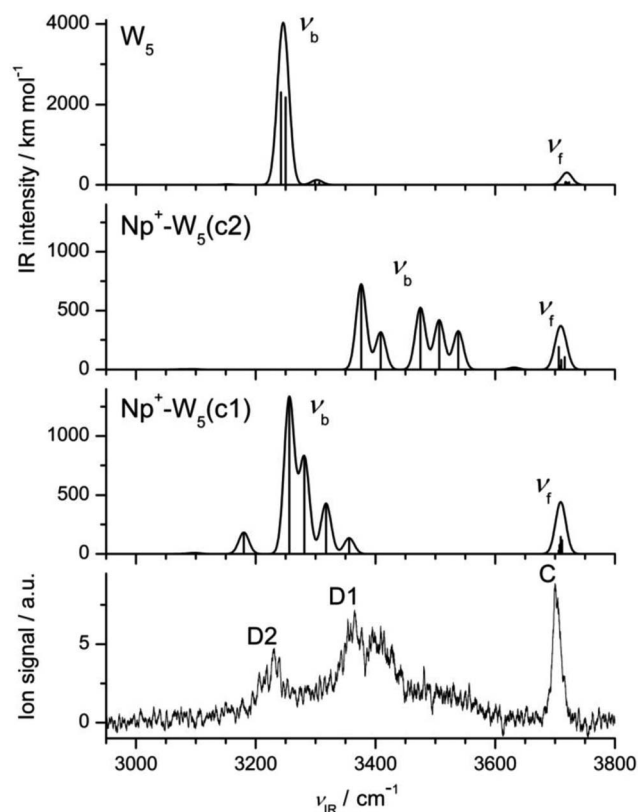


Fig. 11 Comparison of experimental IRPD spectrum of  $\text{Np}^+-W_5$  to linear IR absorption spectra of the cyclic  $\text{Np}^+-W_5$  isomers calculated at the B3LYP-D3/aug-cc-pVTZ level (Fig. 10, Table 1).

agreement with band C at  $3700\text{ cm}^{-1}$  (which has a width of  $13\text{ cm}^{-1}$ ). The highly red shifted  $\nu_b$  modes assigned to the OH...O H-bonds at  $3180, 3256, 3281, 3317,$  and  $3356\text{ cm}^{-1}$  correlate with the broad bands D2 and D1 peaking at  $3230$  and  $3365\text{ cm}^{-1}$ , respectively. As for the other cluster sizes, band D2 may also contain contributions from  $2\beta_{\text{OH}}$  overtone transitions. Although the  $\text{Np}^+-W_5(\text{c2})$  isomer is quite high in energy, clusters of this type may account for the signal observed in the

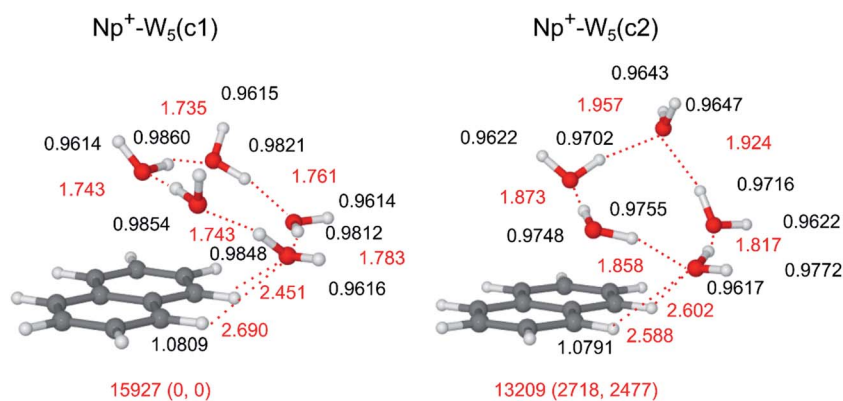


Fig. 10 Optimized structures of the two most stable cyclic  $\text{Np}^+-W_5$  isomers obtained at the B3LYP-D3/aug-cc-pVTZ level. Binding energies ( $D_0$ ) and bond lengths are given in  $\text{cm}^{-1}$  and  $\text{Å}$ , respectively. Numbers in parenthesis correspond to relative energies and free energies ( $E_0, G$ ). For comparison, also the spectrum calculated for bare  $W_5$  is shown (at a different intensity scale).



3400–3600  $\text{cm}^{-1}$  range because of their weaker  $\text{OH}\cdots\text{O}$  bonds and thus higher  $\nu_b$  frequencies. Comparison of the IR spectra calculated for  $\text{Np}^+\text{-W}_5(\text{c1})$  and bare  $\text{W}_5$  reveals that the presence of  $\text{Np}^+$  causes a smaller perturbation than for the  $n = 4$  case. Again, the strongly IR active  $\nu_b$  modes of  $\text{W}_5$  calculated at 3248  $\text{cm}^{-1}$  (averaged value) are around 100  $\text{cm}^{-1}$  lower than the measured band (3360  $\text{cm}^{-1}$ ),<sup>107</sup> confirming that the calculations overestimate the red shifts of the bound O–H stretch frequencies of the cyclic  $\text{W}_n$  ring.

## 4. Further discussion

### 4.1 Cluster growth

The analysis of the IRPD spectra utilizing the DFT calculations provides a detailed and consistent picture of the preferential sequential cluster growth in microhydrated  $\text{Np}^+\text{-W}_n$  clusters. The observed IRPD spectra can readily be explained by the most stable clusters predicted by the calculations. For the most probable cluster growth, we obtain the following scenario. As discussed in detail in our previous report,<sup>72</sup> the population of the  $\text{Np}^+\text{-W}$  dimer ( $n = 1$ ) is dominated by the  $\text{Np}^+\text{-W}(18)$  isomer, in which W binds in a planar bifurcated  $\text{CH}\cdots\text{O}$  H-bond to the most acidic C1H and C8H protons of  $\text{Np}^+$ . For  $n = 2$ , the formation of a H-bonded solvent network is more favorable than interior ion solvation, even though the cation–dipole interaction in  $\text{Np}^+\text{-W}$  ( $D_0 = 2800 \pm 300 \text{ cm}^{-1}$ )<sup>72</sup> is nearly three times stronger than the neutral W–W H-bond bond ( $D_0 = 1105 \pm 10 \text{ cm}^{-1}$ ).<sup>105</sup> This at first glance surprising result is attributed to the massive effects of the nonadditive three-body induction forces. For the formation of the H-bonded solvent network, these are highly cooperative, while for interior ion solvation they are slightly noncooperative. For  $\text{Np}^+\text{-W}_2$ , these can be quantified as +42% for the H-bonded  $\text{Np}^+\text{-W}_2(18)$  global minimum and –3% for the  $\text{Np}^+\text{-W}_2(18/45)$  local minimum, respectively. For  $\text{Np}^+\text{-W}_2$ , the cooperative effects involved in H-bonded networks eventually override the large difference between the  $\text{Np}^+\text{-W}$  and W–W binding energies. Thus, the detected  $\text{Np}^+\text{-W}_2$  clusters are mostly attributed to the  $\text{Np}^+\text{-W}_2(18)$  global minimum, in which a  $\text{W}_2$  dimer is attached to the acidic C1H and C8H protons *via* a planar bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond ( $D_0 = 5529 \text{ cm}^{-1}$ ). A minor part of the population (<20%) is tentatively assigned to the less stable  $\text{Np}^+\text{-W}_2(18/45)$  isomer, in which two individual W ligands separately bind to  $\text{Np}^+$  *via* equivalent planar bifurcated  $\text{CH}\cdots\text{O}$  H-bonds ( $D_0 = 5395 \text{ cm}^{-1}$ ). For  $n \geq 3$ , isomers with interior ion solvation are not observed anymore, and only the more stable  $\text{Np}^+\text{-W}_n$  structures with cyclic H-bonded  $\text{W}_n$  rings are detected. However, while for  $n = 3$  these rings bind in the  $\text{Np}^+$  plane to the acidic C–H protons of  $\text{Np}^+$  *via* two linear  $\text{CH}\cdots\text{O}$  H-bonds, for  $n = 4$  and 5 the cyclic  $\text{W}_n$  rings are located above the aromatic plane and are connected to  $\text{Np}^+$  *via* strongly nonplanar bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bonds. In such sandwich-type structures, the W ligands are closer to the positive charge of the  $\text{Np}^+$  cation, and thus can maximize the strong electrostatic charge–dipole and inductive charge-induced dipole interactions. The gain in electrostatic and induction energy is larger than the energy penalty arising from the deviation from linearity and planarity of the

$\text{CH}\cdots\text{O}$  ionic H-bonding. Some additional stabilization may also come from increased dispersion between the cyclic  $\text{W}_n$  ring and the  $\pi$ -electron system of the aromatic  $\text{Np}^+$  ring in the sandwich-type configuration. Thus, the  $\text{Np}^+\text{-W}_n$  structures with  $n = 4$  and 5 strongly benefit from the cooperative induction forces arising from the cyclic H-bonded ring, and the sandwich configuration maximizes both dispersion and electrostatic forces. In addition, the  $\text{W}_n$  rings in  $\text{Np}^+\text{-W}_n$  are all more or less distorted structures derived from those of isolated neutral cyclic  $\text{W}_n$  rings (Fig. S6 in ESI†). Although all of them have only single-donor single-acceptor solvent molecules in the most stable  $\text{Np}^+\text{-W}_n$  isomers, the free dangling OH groups are all pointing away from the  $\text{Np}^+$  cation to optimize the cation–dipole attraction. When considering the predicted  $\text{Np}^+\text{-W}_n$  global minima, the incremental dissociation energies,  $\Delta D_0(n) = D_0(n) - D_0(n - 1)$ , are 2773, 2756, 2826, 4202, and 3370  $\text{cm}^{-1}$  for  $n = 1$ –5, respectively. Although there is no monotonic trend in the whole considered size range,  $\Delta D_0$  increases for small  $n$  and peaks at  $n = 4$ , illustrating the strong cooperativity effects for the hydration network above the  $\text{Np}^+$  cation. The magnitude of these incremental binding energies is also in line with the experimental observation of single W loss under the single-photon IRPD conditions employed in the present work (with  $h\nu_{\text{IR}} \leq 4000 \text{ cm}^{-1}$ ). The structure of the cyclic neutral  $\text{W}_n$  clusters are distorted by the presence of the  $\text{Np}^+$  cation, and their IR spectroscopic signatures change as well, although their coarse geometries remain unaffected (Fig. S6 and S7 in ESI†). Also, their total and incremental binding energies, which vary as  $\Delta D_0(n) = 1108, 2810, 3539, \text{ and } 2521 \text{ cm}^{-1}$  for  $n = 2$ –5, respectively, are smaller than those of the corresponding  $\text{Np}^+\text{-W}_n$  clusters, illustrating the cooperative effect of the nearby positive charge on the cyclic H-bonded network. As expected, the averaged  $\text{OH}\cdots\text{O}$  bond length in bare  $\text{W}_n$  clusters decreases monotonically as  $1.947 > 1.903 > 1.764 > 1.733 \text{ \AA}$  for  $n = 2$ –5. Interestingly, the corresponding variation in  $\text{Np}^+\text{-W}_n$  is strongly nonmonotonic ( $1.826 < 1.972 > 1.789 > 1.753 \text{ \AA}$  for  $n = 2$ –5). In addition, for  $n \geq 3$  the H-bond lengths in  $\text{Np}^+\text{-W}_n$  is even larger than in bare  $\text{W}_n$  although the incremental binding energies are smaller. This effect is attributed to the steric effects of the  $\text{Np}^+$  cation on the structure of the H-bonded  $\text{W}_n$  network. Interestingly, also the interaction of the  $\text{W}_n$  cluster with the CH groups of  $\text{Np}^+$  changes nonmonotonically in the most stable  $\text{Np}^+\text{-W}_n$  clusters, with averaged  $\text{CH}\cdots\text{O}$  bond lengths of  $2.327 > 2.242 < 2.467 < 2.588 > 2.571 \text{ \AA}$ . The drop from  $n = 1$  to  $n = 2$  is due to cooperativity, while the increase for  $n \geq 3$  arises from the fact that the  $\text{CH}\cdots\text{O}$  bond becomes weaker because of the formation of the sandwich structures with the  $\text{W}_n$  rings lying above the  $\text{Np}^+$  plane. The destabilization of the  $\text{CH}\cdots\text{O}$  interaction with increasing cluster size is clearly visible in the decreasing intensity of  $\nu_{\text{CH}}$  in the IR spectra (band E in Fig. 2). Interestingly, the evolution of the microhydration network around  $\text{Np}^+$  is similar to that inferred for the heterocyclic aromatic imidazolium ion, in which the two acidic NH groups of the monocyclic five-membered ring are protected by substitution with bulky alkyl groups.<sup>108</sup> Finally, the solvation of the  $\text{Np}^+$  cation by nonpolar ligands (such as Ar) is preferentially *via*  $\pi$ -stacking,



because for these clusters dispersion and polarization forces dominate the attraction.<sup>48,49,72,109</sup>

Significantly, the cluster growth scenario derived herein from IRPD spectroscopy and DFT calculations is very different from the one reported previously from mass spectrometry and computations.<sup>14</sup> In the latter study,  $\text{Np}^+-\text{W}_n$  clusters are generated by electron ionization of Np and injecting these ions into a drift cell filled with He buffer gas and water vapor with partial cooling down to 249 K. In the resulting mass spectra,  $\text{Np}^+-\text{W}_n$  clusters can be detected up to  $n = 6$ , although for cluster sizes with  $n \geq 2$  the ion signal is barely above the noise level. This is in marked contrast to our much more efficient electron-impact supersonic plasma cluster ion source, in which *via* the same sequential cluster growth mechanism much higher yields of  $\text{Np}^+-\text{W}_n$  clusters can be generated under cold molecular beam conditions and at concentrations sufficient to record IRPD action spectra. The low  $\text{Np}^+-\text{W}_n$  yield in the previous study<sup>14</sup> allowed to perform cluster aggregation equilibria to be measured only for  $n = 1$ , and the obtained binding enthalpy of  $-\Delta H = 2730 \pm 350 \text{ cm}^{-1}$  is in good agreement with our recent spectroscopic value of  $D_0 = 2800 \pm 300 \text{ cm}^{-1}$ .<sup>72</sup> In addition to mass spectra, the previous study also reported results of DFT calculations at the B3LYP and M06-2X levels for  $\text{Np}^+-\text{W}_n$  clusters up to  $n = 6$ .<sup>14</sup> For  $n = 1$  and 2, the reported minima<sup>14</sup> are in good agreement with our structures. However, for  $n \geq 3$  there is a qualitative discrepancy between the previous study<sup>14</sup> and the most stable structures derived herein from both IR spectroscopy and DFT computations. No cyclic structures were reported (and possibly also not considered) previously,<sup>14</sup> and it was claimed that in the most stable  $\text{Np}^+-\text{W}_n$  clusters, a linear H-bonded  $\text{W}_n$  chain is attached to  $\text{Np}^+$  *via*  $\text{CH}\cdots\text{O}$  bonding. This is in contrast to our computations, which clearly show that cyclic structures are by far more stable than linear ones for  $n \geq 3$ , a conclusion strongly supported by our IRPD spectra. If linear H-bonded chains were attached to  $\text{Np}^+$  at the C1H and C8H protons, transitions A, B, and E should be detected in the  $\text{Np}^+-\text{W}_n$  spectra with substantial intensity (in disagreement with the experimental observation). Since our electron-impact cluster ion source is known to produce the most stable isomers of a given cluster size,<sup>73,74</sup> we are confident that the cyclic structures are indeed the global minima for  $\text{Np}^+-\text{W}_n$  with  $n \geq 3$ . The failure of finding the global minima in the previous study<sup>14</sup> illustrates the rather limited capabilities of mass spectrometry and incomplete structural survey by computations for finding the most stable cluster structures. At the same time, it highlights the high sensitivity of vibrational spectroscopy in the X–H stretch range for the determination of the H-bonded solvation networks in polyhydrated clusters.

The ionization energy of Np (IE = 8.144 eV)<sup>51</sup> is by far lower than that of  $\text{W}_n$  clusters (>10 eV for  $n \leq 20$ ).<sup>110,111</sup> Consequently, the excess positive charge is mostly localized on the aromatic molecule even for large  $n$ , in line with the notation  $\text{Np}^+-\text{W}_n$ . There is some partial charge transfer from  $\text{Np}^+$  to the  $\text{W}_n$  network, which for the most stable  $\text{Np}^+-\text{W}_n$  isomers amounts to  $\Delta q = 12, 14, 22, 28,$  and  $32 \text{ me}$  for  $n = 1\text{--}5$  according to the NBO analysis (Fig. S3 in ESI†). Interestingly, the magnitude of the charge transfer for the cyclic solvent structures is slightly larger

than that predicted for linear chain structures (*e.g.*,  $\Delta q = 23 \text{ me}$  for  $n = 6$ ).<sup>14</sup> Similarly, the proton affinity of the naphthyl radical (PA = 234.5 kcal mol<sup>-1</sup>)<sup>11</sup> is by far larger than those of  $\text{W}_n$  clusters in this size range (PA = 167–216 kcal mol<sup>-1</sup> for  $n = 1\text{--}6$ ).<sup>112</sup> Thus, no proton transfer to the solvent cluster occurs in  $(\text{Np}-\text{W}_n)^+$ , because  $\text{C}_{10}\text{H}_8^+-\text{W}_n$  clusters are much more stable than  $\text{C}_{10}\text{H}_7-\text{H}^+\text{W}_n$ . Test calculations for  $(\text{Np}-\text{W}_n)^+$  clusters with a protonated  $\text{H}^+\text{W}_n$  solvent cluster with  $n = 4$  and  $n = 5$  reveal that they are more than 1 eV less stable than corresponding  $\text{Np}^+-\text{W}_4$  clusters (Fig. S9 in ESI†).

It is instructive to compare the properties of  $\text{Np}^+-\text{W}_n$  clusters characterized herein with those of neutral<sup>72,75</sup> and anionic clusters<sup>76–79</sup> to extract the considerable impact of the charge on the hydration network of PAHs. So far, no experimental data are available for neutral  $\text{Np}-\text{W}_n$  clusters, and thus all information for this complex has to rely on computations carried out for  $n \leq 2$ .<sup>72,75</sup> According to the calculations, the most stable  $\text{Np}-\text{W}$  and  $\text{Np}-\text{W}_2$  clusters have  $\pi$  H-bonded structures, in which either a single W ligand or a H-bonded  $\text{W}_2$  forms two intermolecular  $\text{OH}\cdots\pi$  H-bonds with the aromatic  $\pi$  electron system of Np. In such  $\pi$  H-bonds, the OH protons can favourably interact with the negative  $\pi$  electron cloud.<sup>72,75,113</sup> Because of the lack of the positive charge, the interaction is much weaker in neutral  $\text{Np}-\text{W}_n$  than in the  $\text{Np}^+-\text{W}_n$  cation. Ionization of the  $n = 1$  and  $n = 2$  clusters thus causes a drastic change in the potential energy surface with respect to both the structure and interaction strength of the aromatic molecule with  $\text{W}_n$  from the  $\text{OH}\cdots\pi$  H-bonded neutral clusters to  $\text{CH}\cdots\text{O}$  H-bonded cation clusters. Such ionization-induced changes in the hydration motif give rise to solvent rearrangement reactions occurring on the picosecond timescale.<sup>87,114</sup> These may be probed in the future for  $\text{Np}-\text{W}_n$  clusters by time-resolved pump-probe IR spectroscopy,<sup>114,115</sup> a technique recently applied to monitor solvent rearrangement reactions in related aromatic clusters in real time.<sup>116–120</sup> Although  $\text{Np}^-$  is an unstable anion because of its negative electron affinity, stable microhydrated  $\text{Np}^--\text{W}_n$  clusters can be produced in supersonic expansions and have been characterized by photoelectron ( $n \leq 8$ )<sup>76–78</sup> and IR ( $n \leq 6$ )<sup>79</sup> spectroscopy. The computational analysis of these IR spectra<sup>79</sup> yields multiple  $\pi$  H-bonded structures for  $\text{Np}^--\text{W}_n$  for  $n \leq 4$ , in which H-bonded  $\text{W}_n$  clusters are attached to a single side of Np. For  $n = 3$  and 4, cyclic solvent structures with single-donor single-acceptor W molecules are most favourable. However, in contrast to the cation clusters, in  $\text{Np}^--\text{W}_n$  the H atoms not involved in the  $\text{OH}\cdots\text{O}$  H-bonded  $\text{W}_n$  network point toward the  $\text{Np}^-$  anion to form  $\text{OH}\cdots\pi$  H-bonds. For  $\text{Np}^+-\text{W}_n$  cations, this configuration is repulsive and the free OH groups point away from  $\text{Np}^+$ . In all three charge states, the formation of  $\text{W}_n$  networks strongly benefit from cooperativity.

## 4.2 Comparison to $(\text{Bz}-\text{W}_n)^+$ clusters

Comparison between  $\text{Np}^+-\text{W}_n$  and  $(\text{Bz}-\text{W}_n)^+$  clusters reveals the effects of the second aromatic ring present in Np on the interaction between  $\text{PAH}^+$  cations and W. The geometric and electronic structure of  $(\text{Bz}-\text{W}_n)^+$  clusters are well characterized by IR ( $n \leq 23$ )<sup>61,62,73,80–83</sup> and electronic ( $n \leq 4$ )<sup>84</sup> spectroscopy,



photoionization spectroscopy ( $n = 1$ ),<sup>85</sup> mass spectrometry ( $n \leq 40$ ),<sup>10,12,86</sup> and quantum chemistry.<sup>87,88</sup> A detailed comparison between the  $\text{Np}^+\text{-W}$  and  $\text{Bz}^+\text{-W}$  dimers ( $n = 1$ ) has been presented in our previous report.<sup>72</sup> Briefly, the structures and H-bonding motifs in  $\text{Bz}^+\text{-W}$  and  $\text{Np}^+\text{-W}$  are principally different. While in the  $\text{Np}^+\text{-W}(18)$  global minimum, the W ligands forms a bifurcated  $\text{CH}\cdots\text{O}$  H-bond to two adjacent  $\text{C}_6\text{H}$  groups of two different rings, in the most stable  $\text{Bz}^+\text{-W}(12)$  structure W is attached to two CH groups obviously from the same ring. Because in  $\text{Bz}^+$  the excess charge is delocalized over only a single ring, the electrostatic interaction in  $\text{Bz}^+\text{-W}$  is stronger than in  $\text{Np}^+\text{-W}$ . This view is consistent with the NBO<sup>72</sup> and NCI (Table S1 in ESI†) analyses of the charge distribution in both ions, which show that the CH protons in  $\text{Np}^+$  carry a lower positive partial charge. This electrostatic effect is partly compensated for by the more linear H-bonds in  $\text{Np}^+\text{-W}(18)$  enabled by simultaneous binding of W to the two fused rings. As a net result, the dissociation energy of  $\text{Bz}^+\text{-W}$  ( $D_0 = 3290 \pm 120 \text{ cm}^{-1}$ )<sup>83</sup> inferred from spectroscopic measurements is still substantially larger than that of  $\text{Np}^+\text{-W}$  ( $D_0 = 2800 \pm 300 \text{ cm}^{-1}$ ),<sup>72</sup> in good agreement with the values calculated at the B3LYP-D3/aug-cc-pVTZ level ( $D_0 = 3209$  and  $2773 \text{ cm}^{-1}$ ) and binding enthalpies extracted from mass spectrometry ( $-\Delta H = 3150 \pm 350$  and  $2730 \pm 350 \text{ cm}^{-1}$ ).<sup>12,14</sup> For both aromatic monohydrates, there is a large geometry change from the neutral cluster ( $\pi$  H-bonded)<sup>113,121–126</sup> to the cation cluster ( $\text{CH}\cdots\text{O}$  H-bonded).<sup>61,73,80,87</sup>

Similar to  $\text{Np}^+\text{-W}_2$ , also for the  $\text{Bz}^+\text{-W}_2$  trimer the isomer with a  $\text{W}_2$  dimer attached to  $\text{Bz}^+$  is found to be more stable than isomers with individual W ligands and both isomers are observed in the IR spectra.<sup>62,81</sup> Previous computations and IR spectra indicate that the low-energy isomers of  $\text{Bz}^+\text{-W}_3$  have linear and branched  $\text{W}_3$  networks attached to  $\text{Bz}^+$ , while cyclic isomers have not been identified as minima on the potential.<sup>13,62,81</sup> This is in contrast to  $\text{Np}^+\text{-W}_3$ , for which our calculations indicate that cyclic structures are not only stable but also yield the global minimum. This difference is rationalized by the stronger  $\text{Bz}^+\text{-W}$  bond with larger electrostatic interactions, which are considerably stronger than the W–W bonds and thus favor branched and linear structures *via* directional charge-dipole forces. In  $\text{Np}^+\text{-W}_n$ , the  $\text{Np}^+\text{-W}$  bond is weaker and less dominant. Therefore, in  $\text{Np}^+\text{-W}_3$  the W–W H-bond interactions become more competitive and can maximize the number of H-bonds by forming a cyclic ring.

Starting from  $n \geq 4$ , in  $(\text{Bz}-\text{W}_n)^+$  clusters one proton from  $\text{Bz}^+$  is transferred to the  $\text{W}_n$  solvent cluster, *i.e.* the ground state structure has the form  $\text{C}_6\text{H}_5\text{-H}^+\text{W}_n$ , in which a phenyl radical binds to the surface of a protonated water cluster. This intra-cluster ion–molecule reaction is inferred from IR<sup>62,81,82</sup> and electronic<sup>84</sup> spectroscopy and is consistent with mass spectrometry<sup>10,12,13</sup> and calculations.<sup>13,81,88</sup> The proton affinity of  $\text{W}_n$  clusters increases with cluster size  $n$  ( $\text{PA} = 691, 808, 862, 900, 904, 908 \text{ kJ mol}^{-1}$  for  $n = 1\text{--}6$ ),<sup>10,103,112</sup> and starting from  $n = 4$  it becomes larger than the one of the phenyl radical ( $884 \text{ kJ mol}^{-1}$ ).<sup>103</sup> Thus, for  $(\text{Bz}-\text{W}_n)^+$  with  $n \geq 4$ , the proton-transferred structure  $\text{C}_6\text{H}_5\text{-H}^+\text{W}_n$  is thermodynamically more stable than the  $\text{Bz}^+\text{-W}_n$  form. In contrast, the proton affinity of the naphthyl radical is rather high ( $981 \text{ kJ mol}^{-1}$ ),<sup>11</sup> so that

proton transfer from  $\text{Np}^+$  to  $\text{W}_n$  in  $(\text{Np}-\text{W}_n)^+$  is thermodynamically not feasible in the cluster size range studied here.

## 5. Concluding remarks

In summary, microhydrated clusters of  $\text{Np}^+$  are characterized by IR spectroscopy and dispersion-corrected DFT calculations to probe the stepwise evolution of the structure of the microhydration network around this prototypical  $\text{PAH}^+$  cation. Significantly, the presented data provide the first spectroscopic impression of the  $\text{Np}^+\text{-W}_n$  (and thus the  $\text{PAH}^+\text{-W}_n$ ) interaction and the stepwise hydration process at the molecular level. The IR spectra recorded in the C–H and O–H stretch range are highly sensitive to the solvation network and change substantially with cluster size. Hence, their computational analysis provides unprecedented insight into the preferential cluster growth. Notably, the cold  $\text{Np}^+\text{-W}_n$  clusters are produced in a supersonic plasma beam expansion. Thus, the predominant population corresponds to the global minima on the respective potential energy surfaces, which is supported by the analysis of the IR spectra. The salient results can be summarized as follows.

(1) The most stable  $\text{Np}^+\text{-W}$  dimer ( $n = 1$ ) is stabilized by a strong, planar, and symmetric bifurcated  $\text{CH}\cdots\text{O}$  ionic H-bond, in which the two lone pairs of W bind to two CH protons belonging to different rings of the bicyclic  $\text{Np}^+$  ion. The  $\text{CH}\cdots\text{O}$  H-bond in  $\text{Np}^+\text{-W}$  differs qualitatively in both structure and interaction type from the corresponding  $\text{CH}\cdots\text{O}$  H-bond in  $\text{Bz}^+\text{-W}$ . The H-bond in  $\text{Bz}^+\text{-W}$  is stronger than in  $\text{Np}^+\text{-W}$  ( $3290 \pm 120$  versus  $2800 \pm 300 \text{ cm}^{-1}$ ), because the positive charge density is more localized in the monocyclic  $\text{Bz}^+$  cation leading to larger charge–dipole attraction. However, because the bifurcated H-bonds in  $\text{Np}^+\text{-W}$  deviate much less from linearity, enabled by the simultaneous interaction with two fused aromatic rings, the molecular orbital interaction stabilizing the H-bond is stronger than in  $\text{Bz}^+\text{-W}$ . These qualitative differences in bonding between  $\text{Bz}^+\text{-W}$  and  $\text{Np}^+\text{-W}$  will also hold for larger  $\text{PAH}^+\text{-W}$  clusters, because they arise from the presence of fused rings in  $\text{Np}^+$  and other  $\text{PAH}^+$  ions. The quantum chemical NBO and NCI analyses quantitatively explain these differences.

(2) For  $\text{Np}^+\text{-W}_n$  clusters with  $n \geq 2$ , two types of clusters can compete, namely those with interior ion solvation and those with a H-bonded hydration network. The former are slightly less stabilized by small noncooperative nonadditive induction forces due to charge delocalization. In contrast, the latter strongly benefit from cooperative nonadditive polarization forces due to enhanced H-bond strengths in the multiple H-bonded network. Consequently,  $\text{Np}^+\text{-W}_2$  clusters ( $n = 2$ ) with a H-bonded  $\text{W}_2$  dimer attached to the  $\text{Np}^+$  cation *via* a bifurcated  $\text{CH}\cdots\text{O}$  H-bond dominate the population (>80%), because they are more stable than structures in which two individual W ligands bind separately to  $\text{Np}^+$ . The degree of cooperativity and noncooperativity can be quantified by considering the binding energies, the vibrational frequency shifts upon H-bonding, and the NCI and NBO analyses (charge transfer and molecular orbital interactions). Concerning the binding energy, the cooperativity is quantified as +42% for the most stable  $\text{Np}^+\text{-W}_2$



isomer with a  $W_2$  dimer, while the noncooperativity is  $-3\%$  for the most stable  $Np^+-W_2$  isomer with two single W ligands.

(3)  $Np^+-W_n$  clusters with  $n \geq 3$  prefer a cyclic  $W_n$  network anchored to the  $Np^+$  cation *via*  $CH\cdots O$  ionic H-bonds. In all these  $Np^+-W_n$  clusters, the cyclic  $W_n$  network is composed of single-donor single-acceptor W ligands. In the most stable  $Np^+-W_3$  cluster, cyclic  $W_3$  is attached to  $Np^+$  in the aromatic plane *via* two single linear  $CH\cdots O$  H-bonds, while in  $Np^+-W_n$  with  $n = 4$  and 5 the cyclic  $W_n$  clusters bind to  $Np^+$  *via* a single nonplanar bifurcated  $CH\cdots O$  H-bond to form sandwich-like structures. This subtle change in structural motifs arises from the optimization of the sum of various competing contributions, such as steric hindrance (repulsion), strengths and number of the different H-bonds ( $OH\cdots O$ ,  $CH\cdots O$ ), charge–dipole (electrostatics) and charge-induced dipole (polarization) attractions, and dispersion forces. In the larger  $n = 4$  and 5 sandwich structures, electrostatic, polarization, and dispersion forces as well as the  $OH\cdots O$  H-bonds of the  $W_n$  subclusters are enhanced, while the  $CH\cdots O$  H-bond is less favored but also less important for the total interaction energy. For the smaller  $n = 3$  cluster, the  $CH\cdots O$  H-bonds still provide an important contribution.

(4) The presence of the  $Np^+$  cation in  $Np^+-W_n$  has an important impact on the structure and IR spectrum of the  $W_n$  unit, although the coarse structure of  $W_n$  remains unaffected (*e.g.*, monocyclic for  $n = 3-5$ ). In particular, the free OH groups of the single-donor single-acceptor cyclic network in  $Np^+-W_n$  with  $n = 3-5$  all point away from the positive charge.

(5) The cyclic  $Np^+-W_n$  clusters ( $n = 3-5$ ) obtained here by IR spectroscopy and DFT calculations deviate substantially from the ones with linear  $W_n$  chains predicted recently by mass spectrometry and DFT calculations,<sup>14</sup> indicating that the former combined approach is much more sensitive in predicting reliable cluster structures.

(6) Comparison of cationic  $Np^+-W_n$  with neutral  $Np-W_n$  and anionic  $Np^-W_n$  illustrates the important impact of the charge state on the  $PAH^{(\pm)}-W_n$  interaction. While anionic and neutral  $Np^{(-)}-W_n$  clusters benefit from (multiple)  $OH\cdots\pi$  H-bonds and thus have H-bonded  $W_n$  clusters attached to the aromatic  $\pi$ -electron system, these configurations are repulsive for cationic  $Np^+-W_n$ , because the cation–dipole forces turn the free OH groups of  $W_n$  away from  $Np^+$ .

(7) Comparison of  $(Np-W_n)^+$  with  $(Bz-W_n)^+$  reveals the drastic differences in intermolecular interaction, microhydration, and chemical reactivity upon attachment of the second ring. First, for  $n \leq 2$ , the H-bonds in  $Bz^+-W_n$  are stronger than in  $Np^+-W_n$ , because the charge is more localized in the former ion, leading to increasing electrostatic and polarization forces. Second, for the same reason,  $Bz^+-W_3$  prefers a linear/branched  $W_3$  structure over a cyclic  $W_3$  ring observed in  $Np^+-W_3$ . Third,  $(Bz-W_n)^+$  clusters with  $n \geq 4$  exhibit proton transfer to solvent, because the proton affinity of  $W_{n \geq 4}$  exceeds the one of the phenyl radical. No such intracluster proton transfer is observed for  $(Np-W_n)^+$  because of the substantially higher proton affinity of the naphthyl radical. The same will be true for  $(PAH-W_n)^+$  clusters with larger PAH molecules because the proton affinity of their radicals will be even higher.

In future work, this combined spectroscopic and computational strategy may be employed to extend these cluster studies to larger degree of hydration, larger  $PAH^+$  cations, different solvents (polar/nonpolar, protic/nonprotic), and protonated PAH. Exploration of larger  $(PAH-W_n)^+$  cations eventually converges to the limit of  $PAH^+$  cations embedded in ice or located on ice surfaces, which are particularly relevant for astrochemical applications. Because the charge remains on  $Np^+$  even in large polyhydrated clusters, the highly reactive  $Np^+$  radical cation generated in ice grains or on their surfaces by radiation or particle impact is readily available for ion–molecule reactions involving other organic molecules deposited in and/or on the grains.

## Conflicts of interest

There are no conflicts to declare.

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