Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Unravelling the Microhydration Frameworks of Prototype PAH by Infrared Spectroscopy: Naphthalene-(Water)$_{1-3}$

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Table S1 Comparison of calculated (MP2/6-311++G(d,p)) and experimental geometrical parameters (in Å and degrees) for neutral naphthalene.

	Np (calculated)	Np (experiment) [a]	Np(experiment) [b]
C9-C10	1.4356	1.412 (8)	1.421
C9-C1	1.4221	1.422 (3)	1.424
C1-C2	1.3834	1.381 (2)	1.377
C2-C3	1.4180	1.417 (4)	1.411
C1-H	1.0884	1.092 (1)	1.095
C2-H	1.0870	1.092 (1)	1.098
C1C9C10	118.9	119.5 (3)	119.0
C9C1C2	120.7		120.2
C1C2C3	120.3		120.5
HC1C9	118.8		117.0
HC2C1	119.9		119.9

[a] Experimental geometrical parameters from gas-phase electron diffraction measurements (S. N. Ketkar, M. Fink, *J. Mol. Struct.*, 1981, **77**, 139-147).

[b] Experimental geometrical parameters from condensed-phase X-ray diffraction (V. I. Ponomarev, O. S. Filipenko, L. O. Atovmyan, *Kristallografiya*, 1976, **21**, 392-394).

Table S2 Selected vibrational parameters of D_2O monomer, Np-$D_2O(\pi)$, Np-D_2O(18), Np-D_2O(12), and Np-D_2O(23) isomers computed at the MP2/6-311++G(d,p)

	D_2O	Np-$D_2O(\pi)$	Np-D_2O(18)	Np-D_2O(23)	Np-D_2O(12)
ν_1 (cm^{-1}) [a]	2668.1 (9)	2651.2 (17)	2655.5 (11)	2659.1 (12)	2658.5 (11)
ν_3 (cm^{-1}) [a]	2791.5 (38)	2762.9 (13)	2779.6 (44)	2782.6 (43)	2782.3 (43)

[a] Values in parentheses are IR intensities in km/mol

1. Pickup Curves

The cluster composition of $(Np)_m$-$(D_2O)_n$ and $(Np)_m$-$(CH_3OD)_n$ complexes inside helium droplets at the observed experimental vibrational resonances is evaluated by varying the partial pressure of a particular dopant molecule, while keeping the partial pressure of the other dopant fixed at a constant partial pressure. This results in pressure-dependent IR intensity variation, typically known as pickup curves, which follows Poisson statistics.[a] From this statistics, the probability (P_k) of capturing k dopant molecule(s) is as follows:

$$P_k = \frac{(\sigma\rho l)^k}{k!}\exp(-\sigma\rho l) \quad (1),$$

where σ is the pickup cross-section of the droplets, ρ is the number density of the dopant molecules, and l is the length of the pickup region.

We record the pickup curves of D_2O by fixing the laser frequency at the observed bands (Table 1), and the Np partial pressure (p_{Np}) is fixed at 3.0×10^{-6} mbar (Figure S1). The D_2O pressure-dependent IR intensity, recorded at m/z 128, exhibits a rising edge at a partial pressure of $\sim3.5\times10^{-6}$ mbar. The reference D_2O pickup curve at 2762.3 cm^{-1} is best fitted to a Poisson distribution for k=1 (equation 1, Figure S1). The pickup curve recorded at 2655.2 cm^{-1} shows similar pressure dependency for D_2O, suggesting D_2O monomer contribution, while the pickup curves acquired at 2755.1, 2750, 2643.7, and 2590.4 cm^{-1} follow a Poisson statistics of k=2 and thus corresponds to D_2O dimer contribution. The remaining transitions at 2747.3, 2745.4, 2704.3, and 2592.2 cm^{-1} are in agreement with a Poisson distribution of k=2 leading to D_2O trimer contribution. Interestingly, for the band at 2750 cm^{-1} lying on the blue wing of the band at 2747.3 cm^{-1}, the D_2O pickup curve follows k=3 distribution instead of k=2 at higher pressure range (>12×10^{-6} mbar), which is justified by the contribution of D_2O trimer clusters associated with the latter vibrational transition.

In the same way, while recording the Np pickup curves (at m/z 128), D_2O partial pressure ($p_{\mathrm{D_2O}}$) is kept constant. The reference Np pickup curve acquired at 2762.3 cm^{-1} follows k=1 Poisson distribution and exhibits a rising edge at $\sim3.0\times10^{-6}$ mbar (Figure S2), while the D_2O partial pressure is fixed at $\sim3.5\times10^{-6}$ mbar (monomer). The Np pickup curve recorded at 2655.2 cm^{-1} exhibits similar pressure dependency. The Np pickup curves at 2755.1, 2750, 2643.7, and 2590.4 cm^{-1} follow a k=1 Poisson distribution, while fixing the $p_{\mathrm{D_2O}}$ at $\sim7\times10^{-6}$ mbar. A similar k=1 Poisson distribution is observed for Np pickup curves recorded at the transitions at 2747.3, 2745.4, 2704.3, and 2592.2 cm^{-1} (constant $p_{\mathrm{D_2O}}$ $\sim10.5\times10^{-6}$ mbar). Thus, $(Np)_m$-$(D_2O)_n$ clusters containing a single Np moiety, i.e., m=1 only contributes at each of the experimental bands.

[a] M. Lewerenz, B. Schilling, J. P. Toennies, *J. Chem. Phys.*, **1995**, 102, 8191-8207.

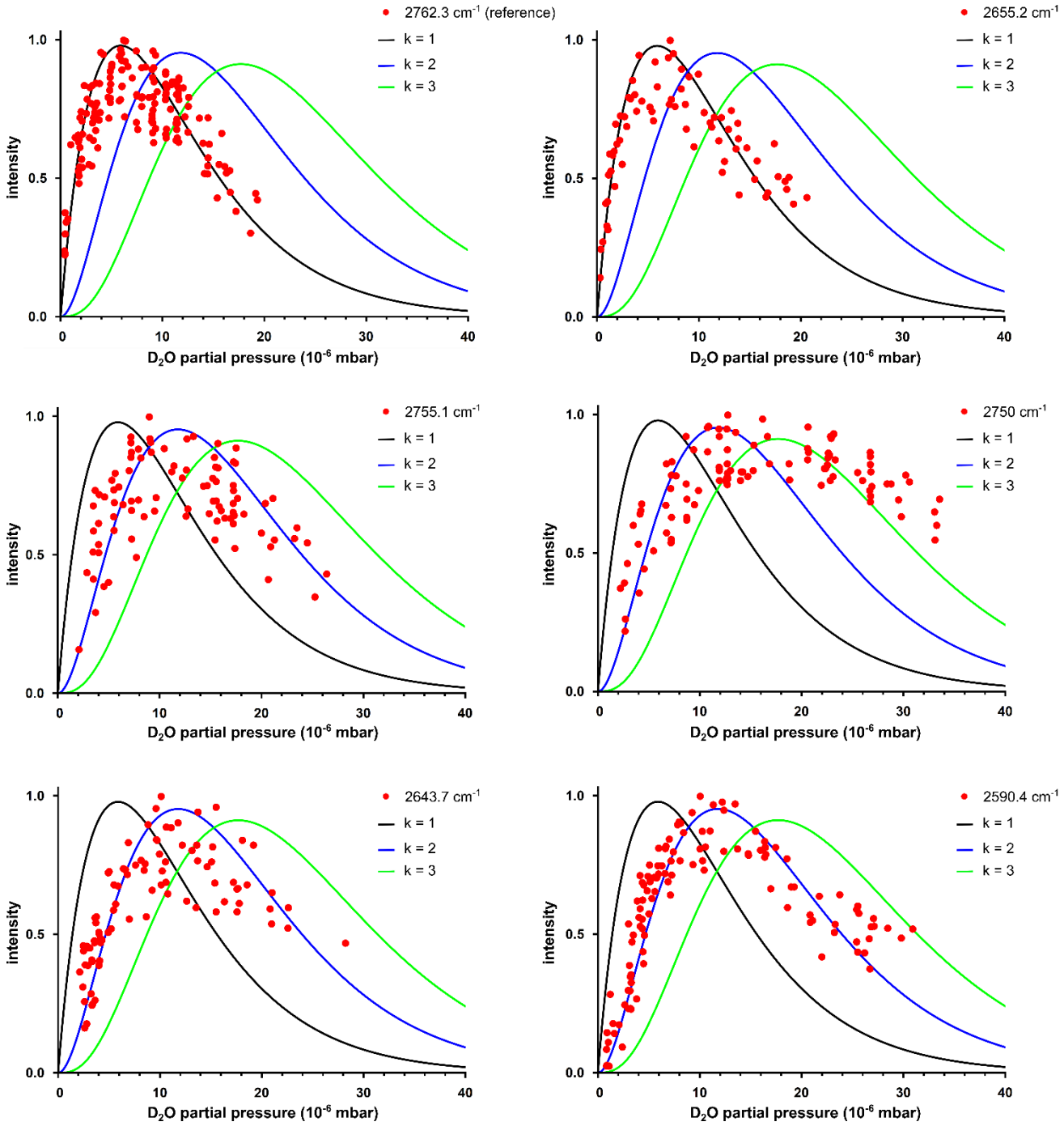

Figure S1 D_2O pick curves (at m/z 128) recorded at 2762.3, 2655.2, 2755.1, 2750, 2643.7, and 2590.4 cm^{-1}. The reference pickup curve at 2762.3 cm^{-1} is fitted with k=1 Poisson distribution (black solid line), and the predicted distributions for k=2 and k=3 are shown in blue and green solid lines, respectively. The top row demonstrates D_2O monomer contribution, and two bottom rows shows D_2O dimer contribution.

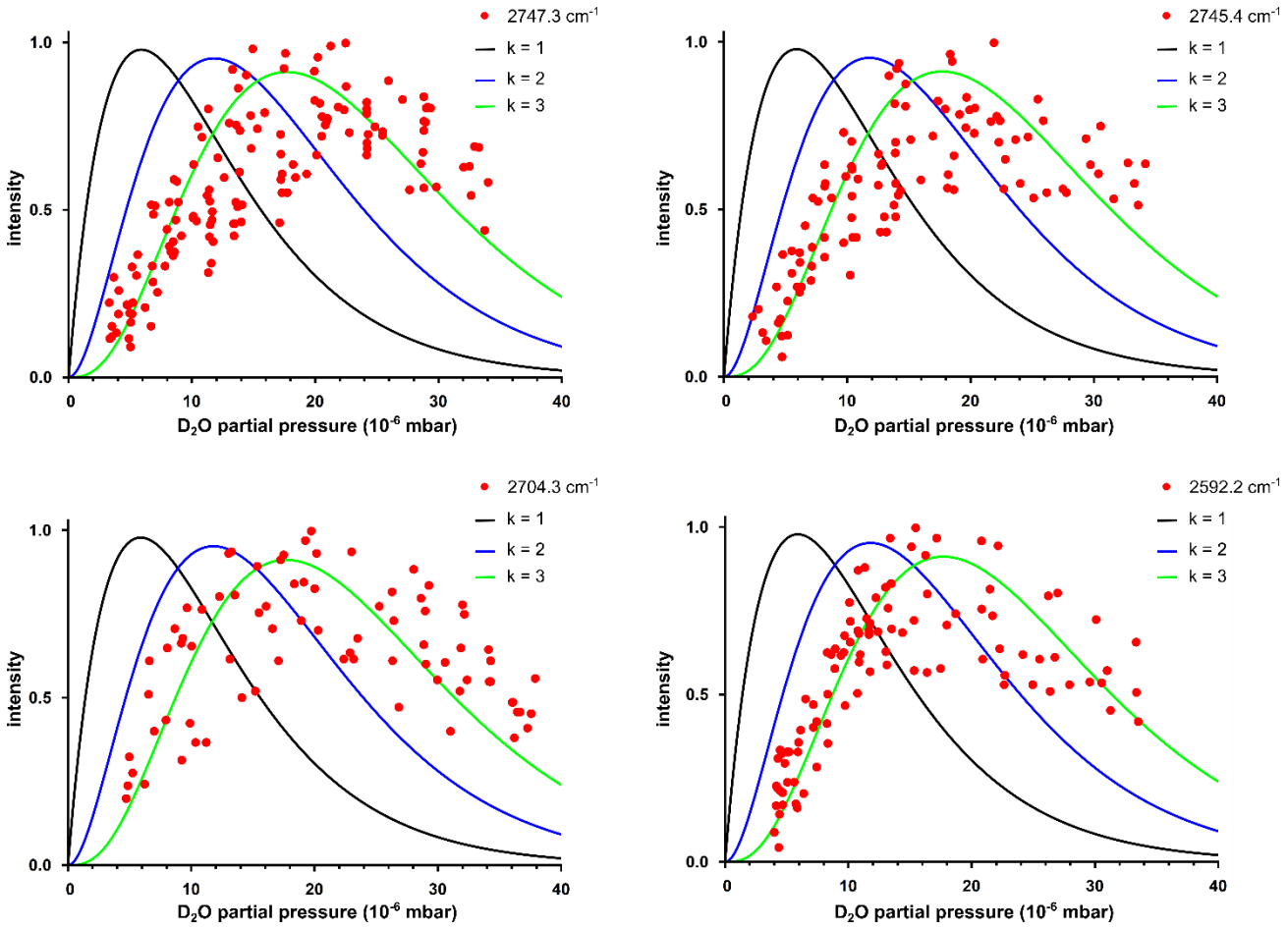

Figure S1(continued) D_2O pick curves (at m/z 128) recorded at 2747.3, 2745.4, 2704.3, and 2592.2 cm^{-1}. The reference D_2O pickup curve at 2762.3 cm^{-1} is fitted with k=1 Poisson distribution (black solid line), and the predicted distributions for k=2 and k=3 are shown in blue and green solid lines, respectively. The four pickup curves show D_2O trimer contribution.

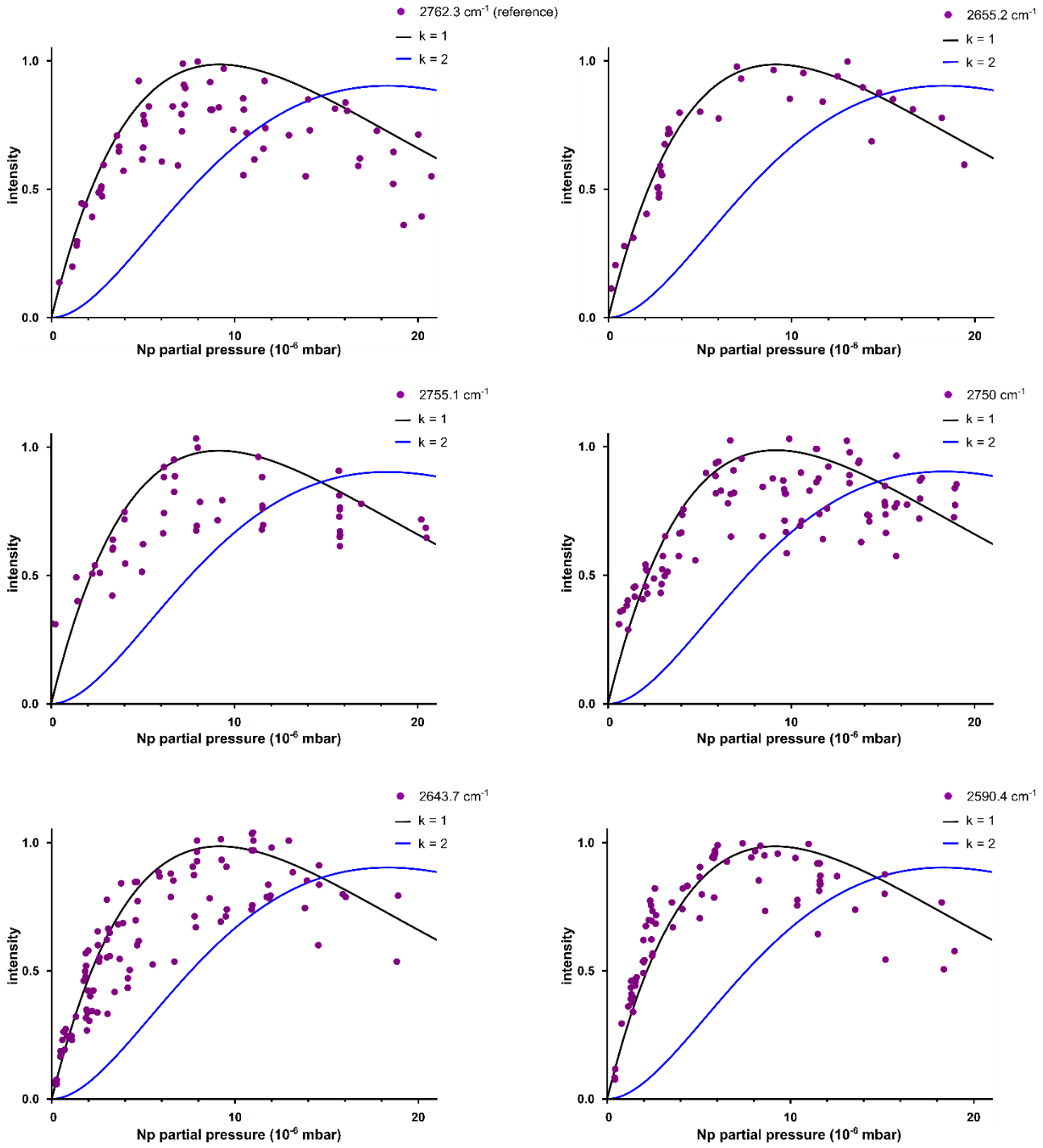

Figure S2 Np pick curves (at m/z 128) recorded at 2762.3, 2655.2, 2755.1, 2750, 2643.7, and 2590.4 cm^{-1}. The reference pickup curve at 2762.3 cm^{-1} is fitted with k=1 Poisson distribution (black solid line), and the predicted distribution for k=2 is shown in blue solid line. All these pickup curves demonstrate Np monomer contribution.

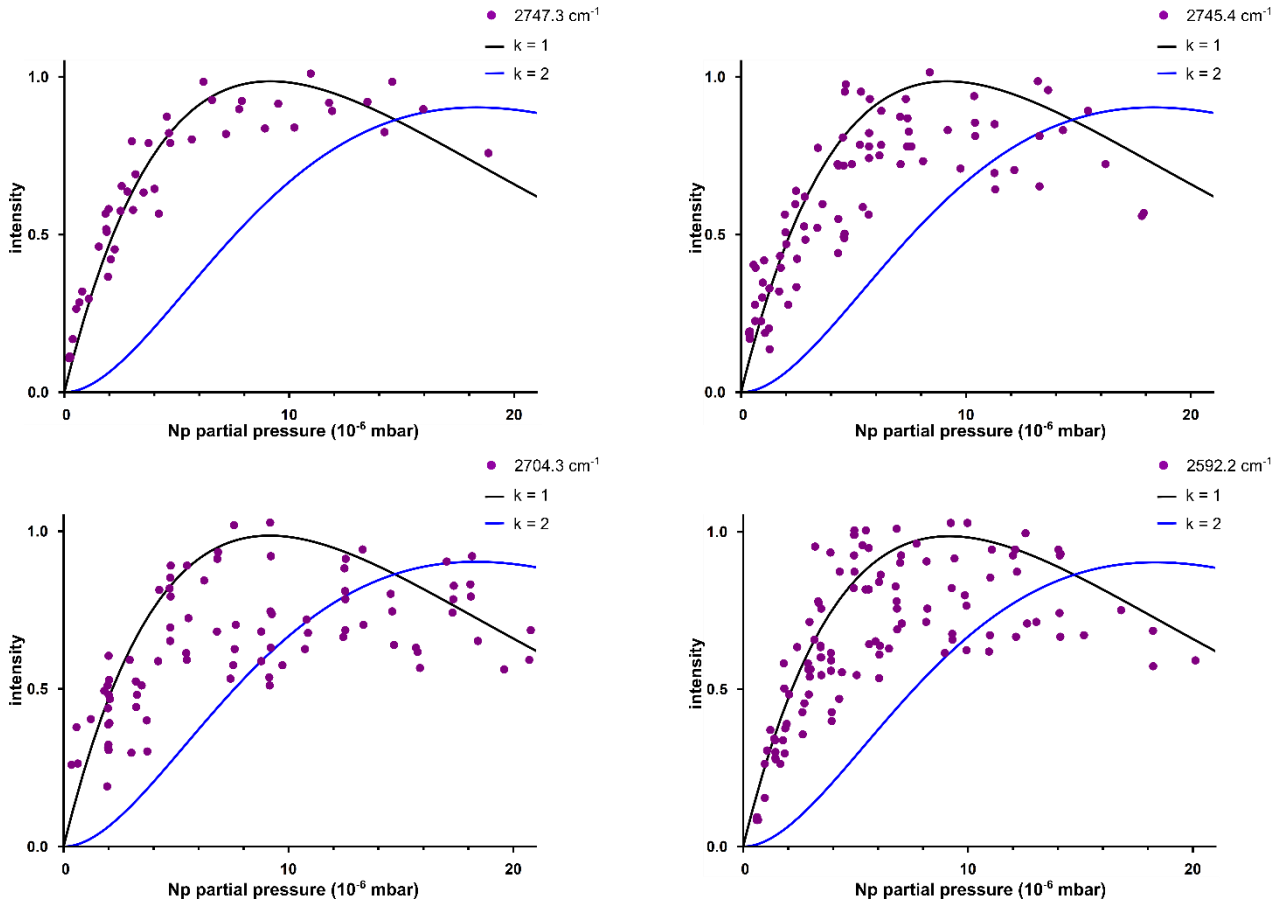

Figure S2(continued) Np pick curves (at m/z 128) recorded at 2747.3, 2745.4, 2704.3, and 2592.2 cm^{-1}. The reference Np pickup curve at 2762.3 cm^{-1} is fitted with k=1 Poisson distribution (black solid line), and the predicted distribution for k=2 is shown in blue solid line. All these pickup curves demonstrate Np monomer contribution.

Mass Spectra

Mass spectrum of pure helium droplets followed by electron impact ionization is shown in Figure S1a. Peaks at multiples of 4 (He_n^+, $n \geq 1$) confirm the formation of helium droplets and the peak at m/z 18 indicates the presence of residual water. After introducing Np vapor at a partial pressure of 3.0×10^{-6} mbar from the first pickup chamber to the helium droplets, the resulting mass spectrum features characteristics peaks of Np mass spectrum at m/z 128 (Np^+), 129, 127, and 102. In addition to these peaks, introduction of D_2O at a partial pressure of 3.5×10^{-6} mbar to the Np-doped helium clusters leads to the enhancement of signals at m/z 18 and 22 which correspond to D_2O^+ and D_3O^+ fragments.

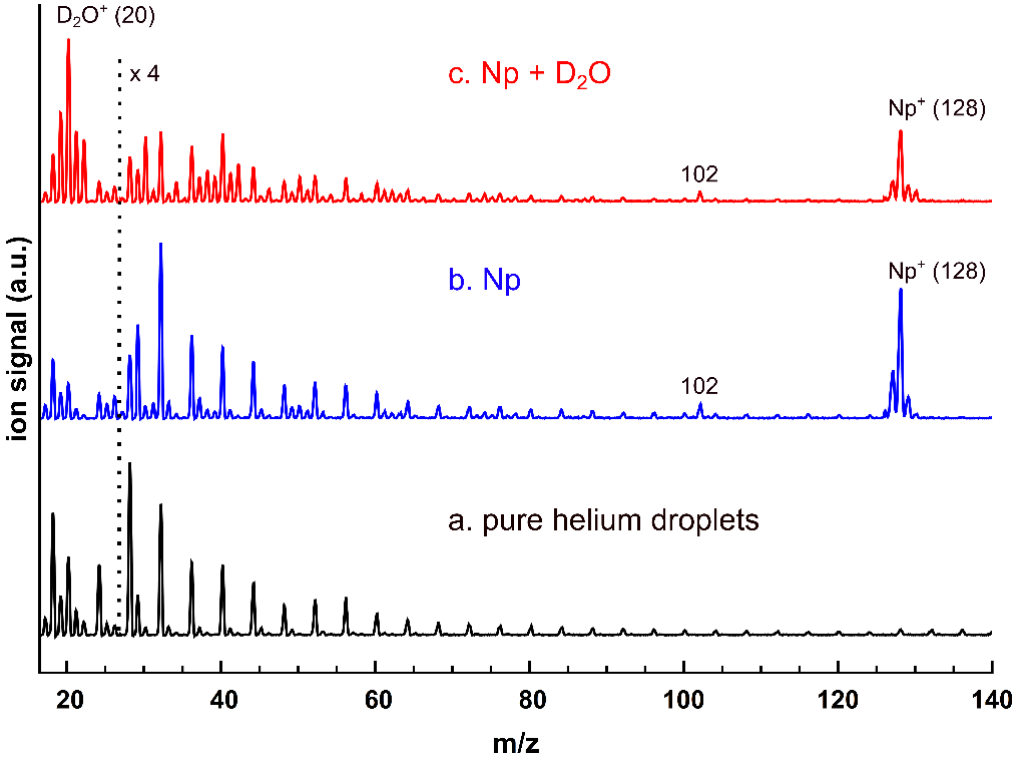

Figure S3 Mass spectra of (a) pure helium droplets, (b) Np-doped helium droplets, and (c) Np+D_2O-doped helium droplets recorded in local helium nanodroplet setup. The mass range above m/z 26 is multiplied by a factor of 4 for better visualization.

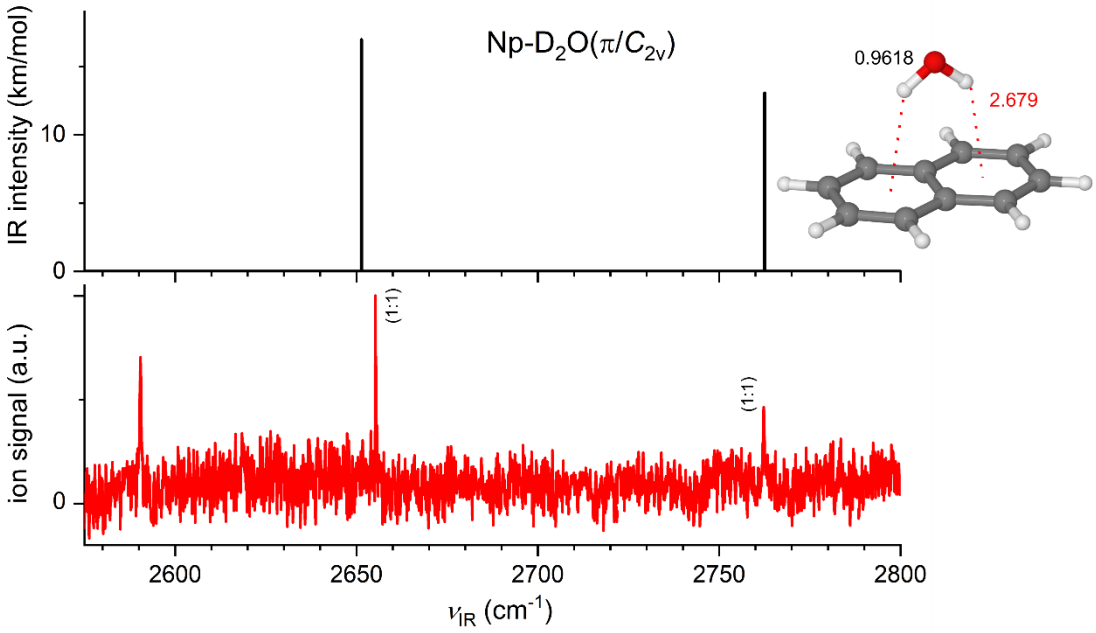

Figure S4 Comparison of experimental IR spectrum in the O-D stretch range recorded at Np monomer and D_2O monomer partial pressures with the predicted linear IR absorption spectrum of symmetric Np-D_2O(π/C_{2v}) isomer, which is computed as a transition state at the MP2/6-311++G(d,p) level. The observed vibrational transitions originating from the 1:1 cluster are marked in the bottom experimental spectrum. Bond lengths are provided in Å.

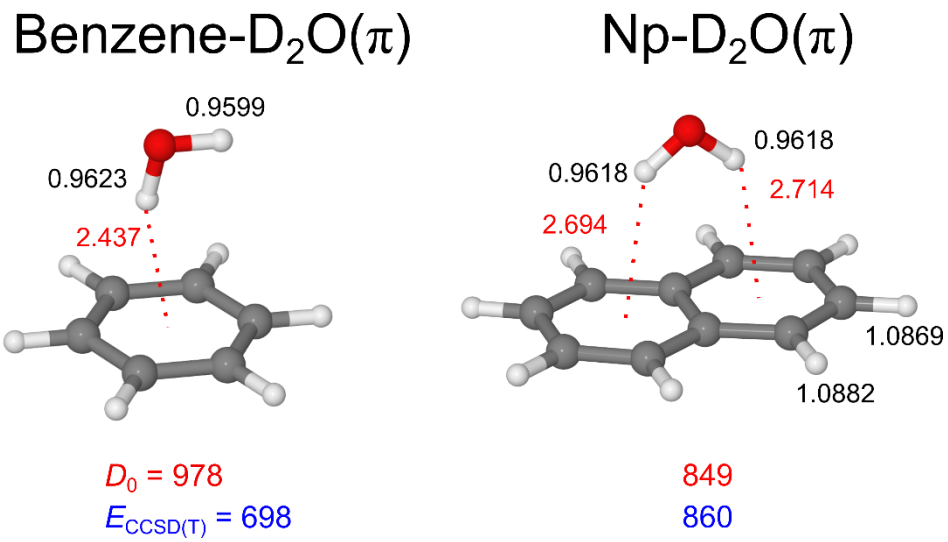

Figure S5 Optimized structures of benzene-$D_2O(\pi)$ and Np-$D_2O(\pi)$ isomers calculated at the MP2/6-311++G(d,p) level. Binding energies (D_0) and bond lengths are provided in cm^{-1} and Å, respectively. The interaction energies (in blue) computed at the CCSD(T)/6-311++G(d,p) level are corrected for BSSE only and provided in cm^{-1}.

Optimized Cartesian Coordinates

D_2O

O	0.00000000	0.00000000	0.11884700
H(Iso=2)	0.00000000	0.75335000	-0.47538600
H(Iso=2)	0.00000000	-0.75335000	-0.47538600

Np

C	-0.01734200	-0.70877800	2.43851300
C	-0.05782900	-1.40493100	1.24370700
C	0.00000000	-0.71777100	0.00000000
C	0.00008000	0.71778200	0.00000000
C	0.05785600	1.40495100	1.24372900
C	0.01729200	0.70876700	2.43850900
H	-0.08441000	-2.49297400	-1.24176300
H	-0.05073500	-1.24746900	3.38200500
H	-0.08441000	-2.49297400	1.24176300
C	-0.05782900	-1.40493100	-1.24370700
C	0.05785600	1.40495100	-1.24372900
H	0.08444500	2.49298900	1.24180600
H	0.05060600	1.24745700	3.38200700
C	0.01729200	0.70876700	-2.43850900
C	-0.01734200	-0.70877800	-2.43851300
H	0.08444500	2.49298900	-1.24180600
H	0.05060600	1.24745700	-3.38200700
H	-0.05073500	-1.24746900	-3.38200500

Np-$D_2O(\pi)$

C	-2.43122000	0.78655800	-0.24527800
C	-1.23670800	1.47483400	-0.12526400
C	0.00697500	0.79420600	-0.23676600
C	0.00707100	-0.60132800	-0.57683000
C	-1.23606400	-1.28373200	-0.68469400
C	-2.43107600	-0.60029400	-0.54407000
H	1.24848000	2.53524800	0.12023000
H	-3.37495800	1.31523200	-0.13970100
H	-1.23475500	2.53802800	0.10668500
C	1.25078400	1.47208300	-0.11173400

C	1.24984700	-1.28711900	-0.66741300
H	-1.23323500	-2.34770300	-0.91297300
H	-3.37440100	-1.13235200	-0.63564900
C	2.44482300	-0.60644200	-0.51270200
C	2.44488800	0.78077100	-0.21594600
H	1.24736500	-2.35124300	-0.89511300
H	3.38781800	-1.14116300	-0.59144300
H	3.38862100	1.30720600	-0.09992700
O	-0.04811800	-0.65193000	2.77590700
H(Iso=2)	0.70494500	-0.58065000	2.18191800
H(Iso=2)	-0.79086500	-0.50437900	2.18290200

Np-D_2O(18)

C	0.00273100	-1.32266400	2.43825800
C	0.02772300	-2.02187900	1.24442500
C	-0.01448800	-1.33456200	0.00000000
C	0.02003200	0.10047700	0.00000000
C	-0.02034200	0.79442800	1.24153700
C	0.00273100	0.09563700	2.43579200
H	0.02800300	-3.11069100	-1.24432500
H	0.02363800	-1.86119300	3.38246800
H	0.02800300	-3.11069100	1.24432500
C	0.02772300	-2.02187900	-1.24442500
C	-0.02034200	0.79442800	-1.24153700
H	-0.02286800	1.88175100	1.22614400
H	-0.01848300	0.63511200	3.37955900
C	0.00273100	0.09563700	-2.43579200
C	0.00273100	-1.32266400	-2.43825800
H	-0.02286800	1.88175100	-1.22614400
H	-0.01848300	0.63511200	-3.37955900
H	0.02363800	-1.86119300	-3.38246800
O	-0.02071500	4.05801300	0.00000000
H(Iso=2)	0.73416900	4.65261200	0.00000000
H(Iso=2)	-0.77641200	4.65157800	0.00000000

Np-D_2O(12)

C	-0.97643100	2.12017700	0.00078700
C	0.40506800	2.03832900	-0.00233000

C	1.05677800	0.77469400	0.02884900
C	0.25981800	-0.41789500	-0.03657500
C	-1.15719500	-0.30200500	-0.01704900
C	-1.76399000	0.94140900	-0.02718200
H	3.07692100	1.56237200	0.02932600
H	-1.46086500	3.09356100	-0.01170900
H	1.01104400	2.94233200	0.02023200
C	2.47388500	0.65642000	0.00612600
C	0.91237900	-1.68133700	-0.00419600
H	-1.77329500	-1.19742200	-0.03919800
H	-2.84838800	0.99871400	-0.02260700
C	2.29332400	-1.76589600	-0.00907100
C	3.08077500	-0.58686200	0.02082700
H	0.30536900	-2.58453500	-0.02683100
H	2.77817500	-2.73879600	0.00474300
H	4.16524800	-0.66175300	0.01454800
O	-4.37178600	-1.15106000	0.01974900
H(Iso=2)	-4.93541800	-1.45330000	-0.69699900
H(Iso=2)	-4.85097500	-1.41489400	0.80939500

Np-D_2O(23)

C	0.01053100	0.70896900	1.69299700
C	0.00000000	1.40619300	0.49798000
C	0.02947000	0.71738000	-0.74620100
C	-0.02947000	-0.71738000	-0.74620100
C	0.00000000	-1.40619300	0.49798000
C	-0.01053100	-0.70896900	1.69299700
H	0.01777700	2.49407000	-1.98825000
H	0.00086100	1.23192400	2.64451400
H	0.01806700	2.49474200	0.49472900
C	-0.00028800	1.40574000	-1.99018100
C	0.00028800	-1.40574000	-1.99018100
H	-0.01806700	-2.49474200	0.49472900
H	-0.00086100	-1.23192400	2.64451400
C	-0.01181200	-0.70874400	-3.18551000
C	0.01181200	0.70874400	-3.18551000
H	-0.01777700	-2.49407000	-1.98825000
H	-0.00009800	-1.24892000	-4.12881900
H	0.00009800	1.24892000	-4.12881900

O	0.00000000	0.00000000	4.95375300
H(Iso=2)	-0.75442700	0.00283200	5.54830600
H(Iso=2)	0.75442700	-0.00283200	5.54830600

Np-$(D_2O)_2$(H1)

C	-2.43659300	1.25813800	0.07079200
C	-1.24173700	1.86490700	0.41887200
C	0.00195800	1.27277700	0.06289800
C	-0.00002900	0.08829900	-0.75047700
C	-1.24204300	-0.52166700	-1.07898800
C	-2.43591700	0.06670300	-0.70001700
H	1.24889600	2.77622400	1.00821400
H	-3.38024600	1.71342700	0.36086700
H	-1.23982600	2.78002000	1.00851800
C	1.24767400	1.86110900	0.41857100
C	1.23989100	-0.52558600	-1.07926800
H	-1.23403900	-1.45073200	-1.64304800
H	-3.37922400	-0.40666800	-0.96002300
C	2.43572600	0.05904400	-0.70075400
C	2.44044600	1.25052700	0.07000000
H	1.22869100	-1.45473600	-1.64316300
H	3.37742500	-0.41731000	-0.96114500
H	3.38566400	1.70282500	0.35965700
O	-0.00075700	-1.30168800	2.11126700
H(Iso=2)	0.75198900	-0.73086000	1.92145200
H(Iso=2)	-0.75107500	-0.72753300	1.92188600
O	-0.00585200	-3.31579000	0.01840500
H(Iso=2)	-0.00427200	-2.70662700	0.77229600
H(Iso=2)	-0.00737000	-4.18370700	0.42734200

Np-$(D_2O)_2$(H2)

O	-1.65523900	2.60094300	0.29525800
H(Iso=2)	-0.71639600	2.58283500	0.06327400
O	1.21554500	2.54880000	-0.21507800
H(Iso=2)	1.70141400	2.89081600	0.54014200
H(Iso=2)	1.59737400	1.67432500	-0.35313000
H(Iso=2)	-1.89875000	1.67189200	0.28291100
C	-2.42197600	-0.87312500	0.58024700

C	-1.25936900	-0.85470800	1.33153100
C	0.00848300	-0.72616300	0.70105100
C	0.07126400	-0.70739800	-0.73363500
C	-1.14000200	-0.70130300	-1.47775900
C	-2.36088900	-0.81111200	-0.83588000
H	1.17236200	-0.80304200	2.52882300
H	-3.38570100	-0.96247800	1.07482900
H	-1.30554600	-0.89959400	2.41773200
C	1.22190100	-0.75546800	1.44265200
C	1.34240300	-0.60990500	-1.36528600
H	-1.09089600	-0.65407700	-2.56362100
H	-3.28001200	-0.81986300	-1.41563000
C	2.50795300	-0.62105000	-0.61600800
C	2.44622900	-0.67868100	0.80121600
H	1.38856700	-0.57149100	-2.45196800
H	3.47325800	-0.57254700	-1.11387900
H	3.36588900	-0.70124100	1.38029900

Np-$(D_2O)_2$(π/π)

C	2.46548400	-0.00473500	-0.71032500
C	1.27100900	-0.03712500	-1.40913700
C	0.02723000	0.00313600	-0.72038500
C	0.02668000	-0.00235000	0.71679800
C	1.26988200	0.04377900	1.40622200
C	2.46507800	0.01720800	0.70827900
H	-1.21299100	-0.07536200	-2.49751400
H	3.40909400	-0.02556600	-1.24910500
H	1.26896900	-0.05935100	-2.49698300
C	-1.21579500	-0.05258700	-1.40969600
C	-1.21717700	0.04602200	1.40521200
H	1.26717200	0.06549900	2.49406600
H	3.40836600	0.04261200	1.24745100
C	-2.41174700	0.01278500	0.70654800
C	-2.41103600	-0.02577700	-0.71205900
H	-1.21533300	0.06709600	2.49312200
H	-3.35553800	0.03596400	1.24501600
H	-3.35439700	-0.05443100	-1.25098000
O	-0.08326900	-3.25719800	0.05062800
H(Iso=2)	-0.79156800	-2.65290600	-0.19104100

H(Iso=2)	0.63790500	-2.65609200	0.25933100
O	-0.10371200	3.25726200	-0.03943600
H(Iso=2)	0.61469900	2.65935400	-0.26563900
H(Iso=2)	-0.79817200	2.65054300	0.23399700

Np-$(D_2O)_3$(c1)

O	-1.55258800	1.70914500	-1.39128900
H(Iso=2)	-0.64334400	1.60958800	-1.72119100
O	1.25032000	1.86287000	-1.45030300
H(Iso=2)	1.09292900	2.28239400	-0.59041700
H(Iso=2)	1.78981000	1.09646600	-1.23158800
H(Iso=2)	-1.86733700	0.80337900	-1.30797000
C	-2.38062800	-0.75949600	0.89331200
C	-1.22255400	-0.27214700	1.47298800
C	0.04380100	-0.50537600	0.87060000
C	0.11480000	-1.33002000	-0.30275400
C	-1.09367100	-1.79081400	-0.89461700
C	-2.31596100	-1.53054600	-0.29648900
H	1.19345700	0.54625000	2.37513000
H	-3.34371000	-0.56861000	1.35962300
H	-1.26834700	0.33329100	2.37523600
C	1.25184900	-0.06448000	1.47726200
C	1.38611800	-1.59686100	-0.88200000
H	-1.04138800	-2.39345400	-1.79957000
H	-3.23088200	-1.91090100	-0.74436800
C	2.54658200	-1.14716600	-0.27398000
C	2.47765400	-0.36561900	0.90934500
H	1.43747500	-2.20132200	-1.78573000
H	3.51417800	-1.38179300	-0.71098000
H	3.39422600	-0.02138700	1.38162600
O	-0.25124400	2.88392200	0.77342900
H(Iso=2)	-0.93260300	2.54101000	0.16608900
H(Iso=2)	-0.51431700	3.79274600	0.93740400

Np-$(D_2O)_3$(c2)

O	-2.40870600	0.93885800	-1.26569100
H(Iso=2)	-1.52285100	1.13941900	-1.61816900
O	0.13955200	1.98357300	-1.52566300

H(Iso=2)	-0.04036000	2.34103700	-0.64283700
H(Iso=2)	0.94420500	1.46859600	-1.40184600
O	-1.41482000	2.50903500	0.84043100
H(Iso=2)	-2.02072100	1.97844200	0.29586400
H(Iso=2)	-2.99979700	1.05591500	-2.01255500
H(Iso=2)	-1.92565200	3.28825200	1.07238100
C	-1.73507300	-1.69170700	0.96577200
C	-0.90784300	-0.70933300	1.47835700
C	0.35410900	-0.44399500	0.88170100
C	0.72364500	-1.15299300	-0.31079500
C	-0.14105100	-2.16752100	-0.80448400
C	-1.35764000	-2.41322400	-0.19411500
H	0.92347600	1.11884300	2.26879500
H	-2.69561700	-1.89003400	1.43429900
H	-1.19868700	-0.14319800	2.36017000
C	1.22629500	0.55950200	1.38663800
C	1.99519900	-0.89639500	-0.89558600
H	0.15066500	-2.71974300	-1.69602300
H	-2.01656700	-3.18255800	-0.58875100
C	2.83336300	0.07535500	-0.37231100
C	2.45339200	0.79552900	0.79066000
H	2.28921900	-1.45548100	-1.78236000
H	3.80069900	0.26240900	-0.83219000
H	3.11741200	1.55506400	1.19558400

Np-$(D_2O)_3$(l)

C	-1.93511200	-2.43960200	0.15941400
C	-2.52673100	-1.24663000	0.53772500
C	-1.95300600	-0.00116000	0.15867100
C	-0.80448800	0.00010700	-0.70447800
C	-0.20780700	-1.24022000	-1.06516100
C	-0.77750300	-2.43545800	-0.66153300
H	-3.41655800	1.24210100	1.16872700
H	-2.37591900	-3.38458500	0.46716300
H	-3.41394900	-1.24757100	1.16850000
C	-2.52930400	1.24307600	0.53800800
C	-0.21015300	1.24172800	-1.06472200
H	0.70074200	-1.22544600	-1.66143500
H	-0.31562600	-3.37769300	-0.94559200

C	-0.78231400	2.43568400	-0.66081300
C	-1.94004000	2.43731300	0.16001400
H	0.69844400	1.22890100	-1.66100000
H	-0.32229900	3.37892500	-0.94457400
H	-2.38276200	3.38136300	0.46786900
O	0.99550900	0.00068500	1.92098100
H(Iso=2)	0.42266400	0.75119000	1.72943100
H(Iso=2)	0.42253200	-0.74986100	1.72999000
O	2.70324100	0.00186700	-0.51964200
H(Iso=2)	2.27676900	0.00114100	0.34747200
H(Iso=2)	3.64627100	0.00258900	-0.31619800
O	5.57510800	0.00126600	0.19169200
H(Iso=2)	5.93344400	-0.75746300	0.65904800
H(Iso=2)	5.93412600	0.75684300	0.66360700