Ion Vibrational Spectroscopy of the Microhydrated Iodate Anion: Unveiling the Onset of Heterogeneous Ion Solvation

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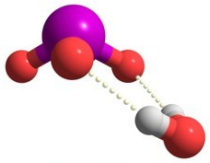
Table of Content:

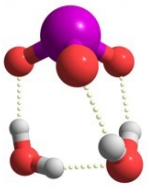
Figure S1a. Structures and their zero-point energy corrected relative electronic energies (ΔE_0 in kJ/mol) of each $IO_3^-(H_2O)_n$ (n = 1-5) clusters obtained with MP2/def2TZVP and B3LYP/def2TZVP methods. Relative energies obtained at DFT level are in *italic* in the parenthesis.

***n* = 1**

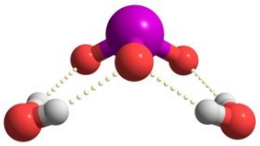


1.2.0
(0.0, *0.0*)

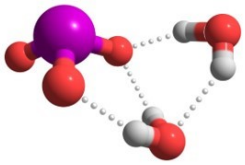
***n* = 2**



2.3.1
(0.0, *0.0*)

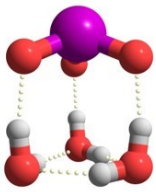


2.4.0
(0.5, *1.0*)

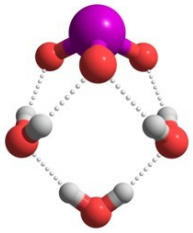


2.3.1
(4.5, *3.6*)

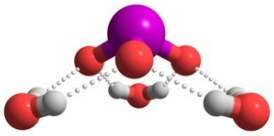
***n* = 3**



3.3.3
(0.0, *0.0*)

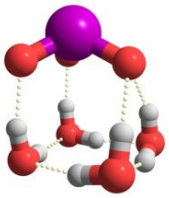


3.4.2
(9.5, *10.5*)

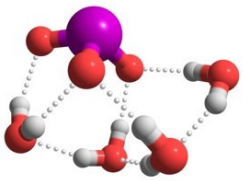


3.6.0
(10.4, *14.8*)

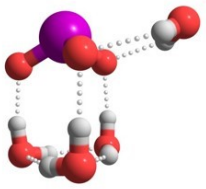
***n* = 4**



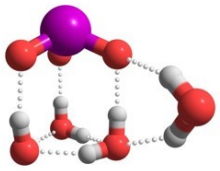
4.4.4
(0.0, *0.0*)



4.5.3a
(6.0, *9.2*)

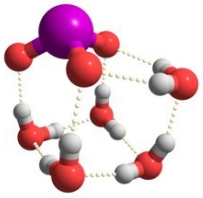


4.5.3b
(9.5, *11.4*)

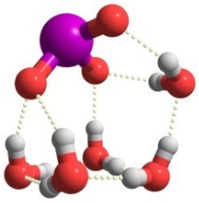


4.4.4a
(11.1, *11.1*)

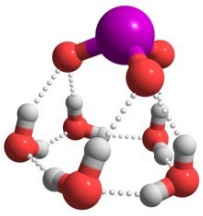
***n* = 5**



5.5.5a
(0.0, *0.0*)



5.5.5b
(6.0, *5.6*)



5.5.5c
(6.2, -.-)

Figure S1b. Structures and their zero-point energy corrected relative electronic energies (ΔE_0 in kJ/mol) of each $IO_3^-(H_2O)_n$ (n = 6-8,11) clusters obtained with MP2/def2TZVP and B3LYP/def2TZVP methods. Relative energies obtained at DFT level are in *italic* in the parenthesis.

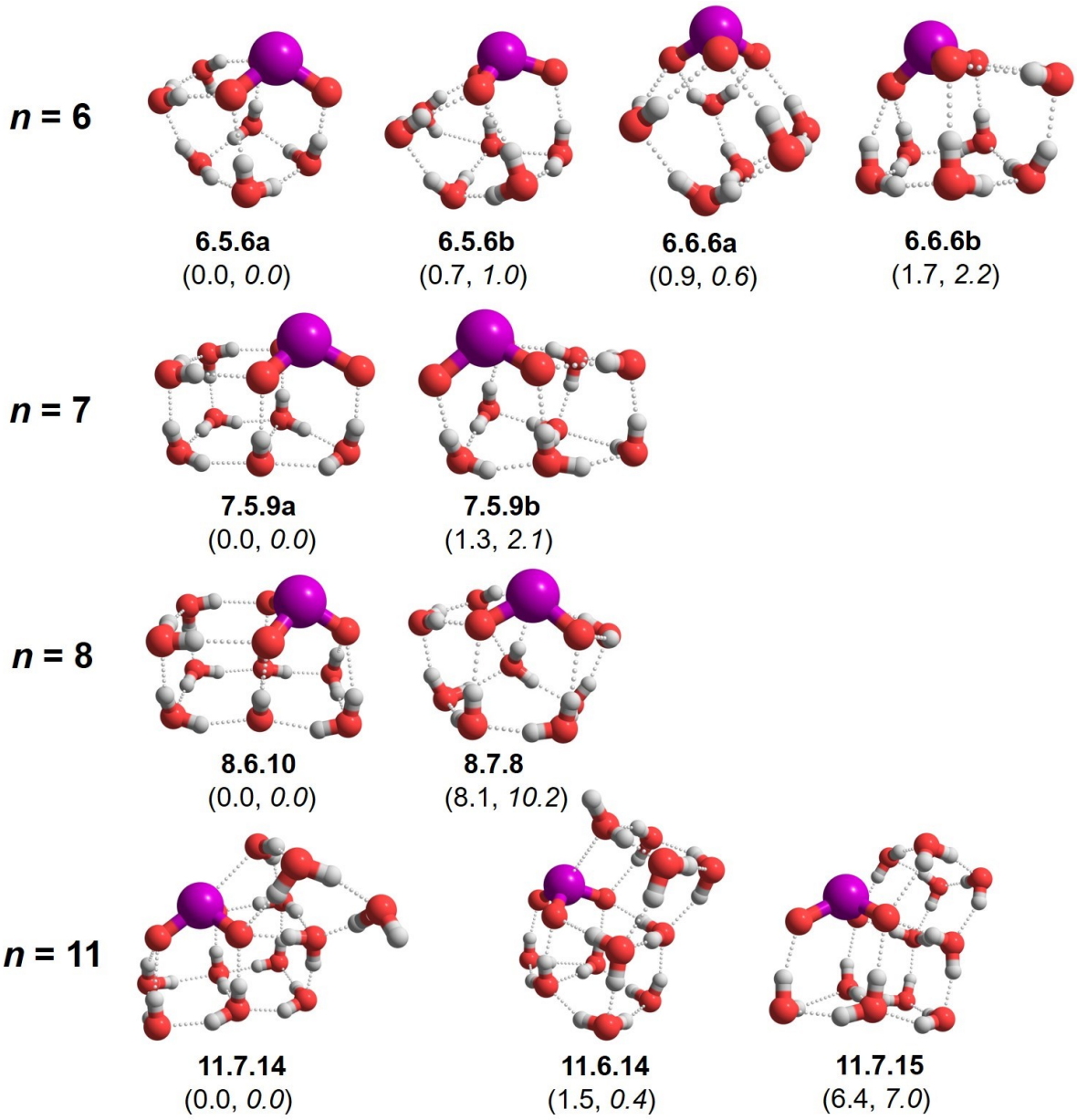


Figure S1c. Structures and their zero-point energy corrected relative electronic energies (ΔE_0 in kJ/mol) of $IO_3^-(H_2O)_{10}$ clusters obtained with MP2/def2TZVP and B3LYP/def2TZVP methods. Relative energies obtained at DFT level are in *italic* in the parenthesis.

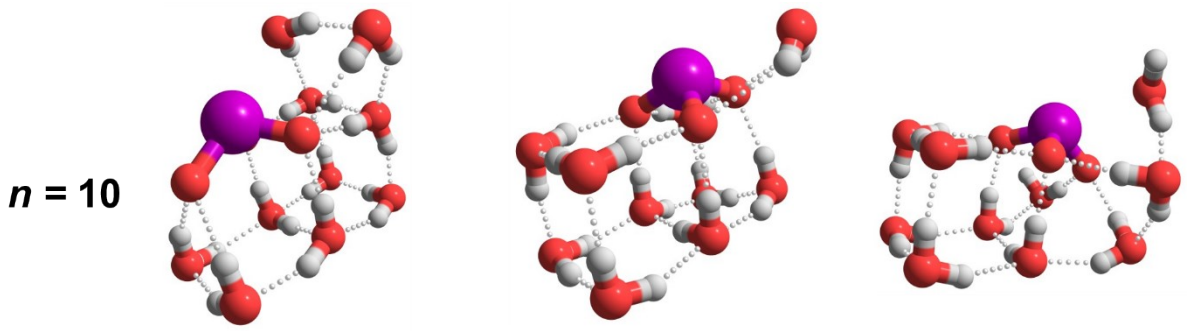


Table S1a. Relative electronic energies without (ΔE in kJ/mol) and with zero-point energy (ΔE_0 in kJ/mol) correction of lowest minimum of each $IO_3^-(H_2O)_n$ (n = 1-8) clusters calculated at DFT and MP2.

Species	Isomers	DFT		MP2	
		ΔE	ΔE_0	ΔE	ΔE_0
n = 1	**1.2.0**	0.0	0.0	0.0	0.0
2	**2.3.1**	0.0	0.0	0.0	0.0
	2.4.0	3.7	1.0	3.2	0.5
	2.3.1	4.7	3.6	5.4	4.5
3	**3.3.3**	0.0	0.0	0.0	0.0
	3.4.2	14.8	10.5	12.9	9.0
	3.6.0	23.9	14.8	19.2	10.4
4	**4.4.4**	0.0	0.0	0.0	0.0
	4.5.3a	12.5	9.2	9.4	6.0
	4.5.3b	15.0	11.4	13.5	9.5
	4.4.4a	16.8	11.0	18.5	13.8
5	**5.5.5a**	0.0	0.0	0.0	0.0
	5.5.5b	7.3	5.6	7.2	6.0
	5.5.5c	7.7	6.2	7.6	6.5
6	**6.5.6a**	0.0	0.0	0.0	0.0
	6.5.6b	1.8	0.6	2.4	0.9
	6.6.6a	1.6	1.0	1.1	0.7
	6.6.6b	3.1	2.2	2.9	1.7
7	**7.5.9a**	0.0	0.0	0.0	0.0
	7.5.9b	3.7	2.1	2.2	1.3
	7.5.7	8.8	5.3		
8	**8.6.10**	0.0	0.0	0.0	0.0
	8.7.8	13.9	10.2	11.6	8.1

Table S1b. Relative electronic energies without (ΔE in kJ/mol) and with zero-point energy (ΔE_0 in kJ/mol) correction of lowest minimum of each $IO_3^-(H_2O)_n$ (n = 10-12) clusters calculated with DFT.

Species	Isomers	DFT		MP2	
		ΔE	ΔE_0	ΔE	ΔE_0
n = 10	**10.7.13**	0.0	0.0	0.0	0.0
	10.9.11	12.8	8.4	16.4	12.3
	10.7.11	17.5	12.6	19.5	14.6
11	**11.7.14**	0.0	0.0	0.0	0.0
	11.6.14	0.6	0.4	2.2	1.5
	11.7.15	5.5	4.8	6.5	6.4
	11.7.13	15.6	12.3	14.5	11.8
	11.7.14	26.9	21.9	27.9	23.3
	11.9.12	29.9	23.5	28.6	22.3
12	**12.7.16**	0.0	0.0	0.0	0.0
	12.8.16	11.1	10.8	11.5	10.3
	12.7.15	22.4	16.3	23.9	18.0
	12.7.15	29.3	24.2	21.7	16.5
	12.8.15	34.8	28.1	33.3	27.3
	12.9.14	43.9	36.7	36.0	27.4

Table S2. Relative MP2 electronic energies after entropic energy (ΔE_0 in kJ/mol) correction for the lowest lying structures of $[IO_3^-(H_2O)_n]$ at cluster size n = 2 and 11.

Cluster Size	**Isomers**	**ΔE**		
		0 K	**100 K**	**200 K**
n = 2	2.3.1	0.0	0.5	1.8
	2.4.0	0.5	0.0	0.0
n = 11	11.7.14	0.0	0.0	0.0
	11.6.14	1.5	2.7	3.2

Figure S2a. Comparison of IRPD spectrum (trace a) of D_2-tagged $IO_3^-(H_2O)$ with scaled MP2/def2TZVP and unscaled VPT2/MP2/def2TZVP derived harmonic (trace b) and anharmonic (trace c) IR spectra of the lowest energy isomer **1.2.0**, respectively. The effect of messenger (D_2) tagging has been computed in trace d.

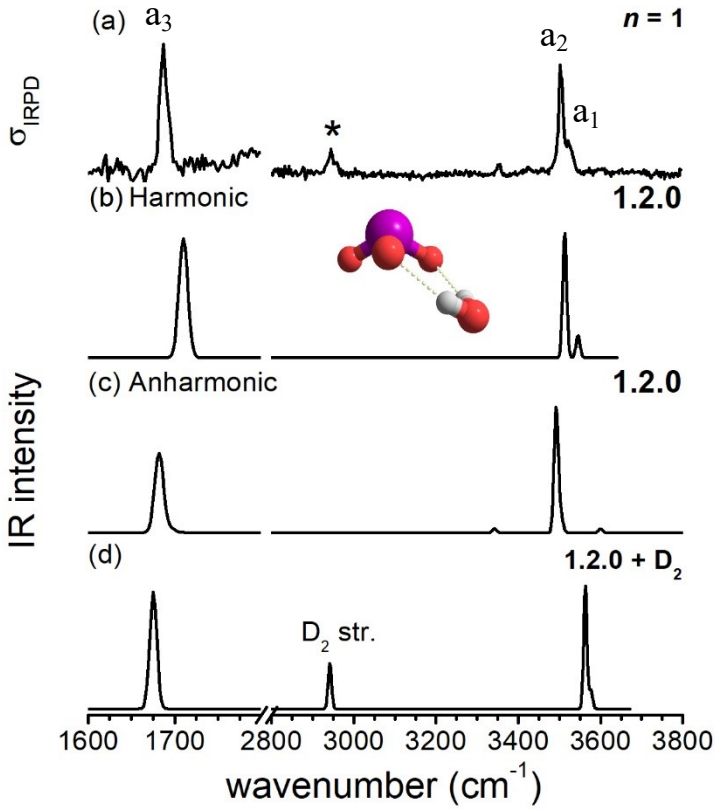
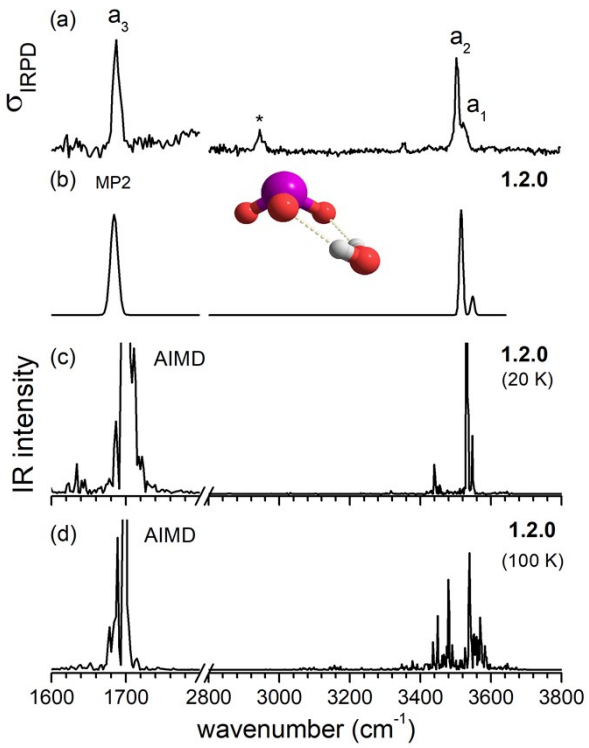


Figure S2b. Comparison of IRPD spectrum (trace a) of D_2-tagged $IO_3^-(H_2O)$ with scaled MP2/def2TZVP (trace b) and unscaled AIMD simulated IR spectra of the lowest energy isomer **1.2.0** at temperature 20 K (trace c) and 100 K (trace d).



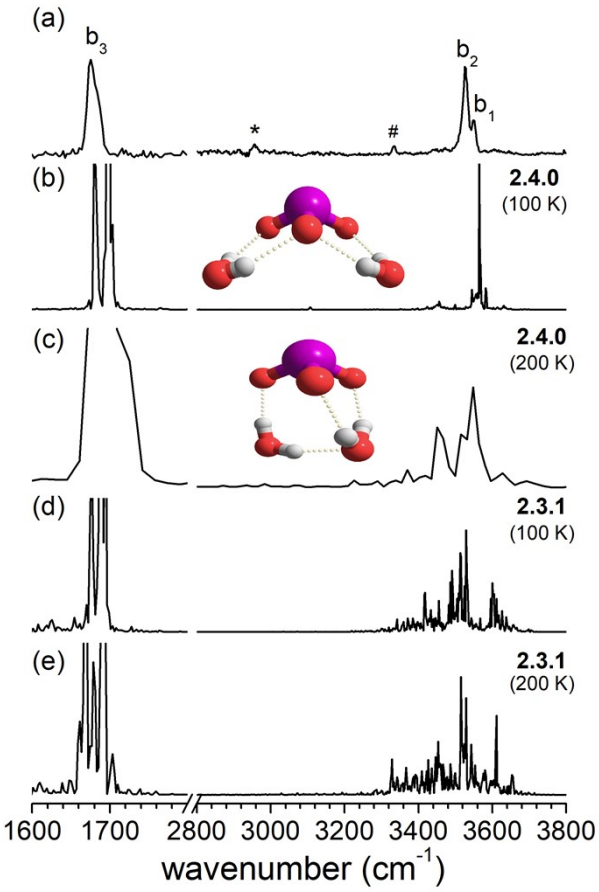
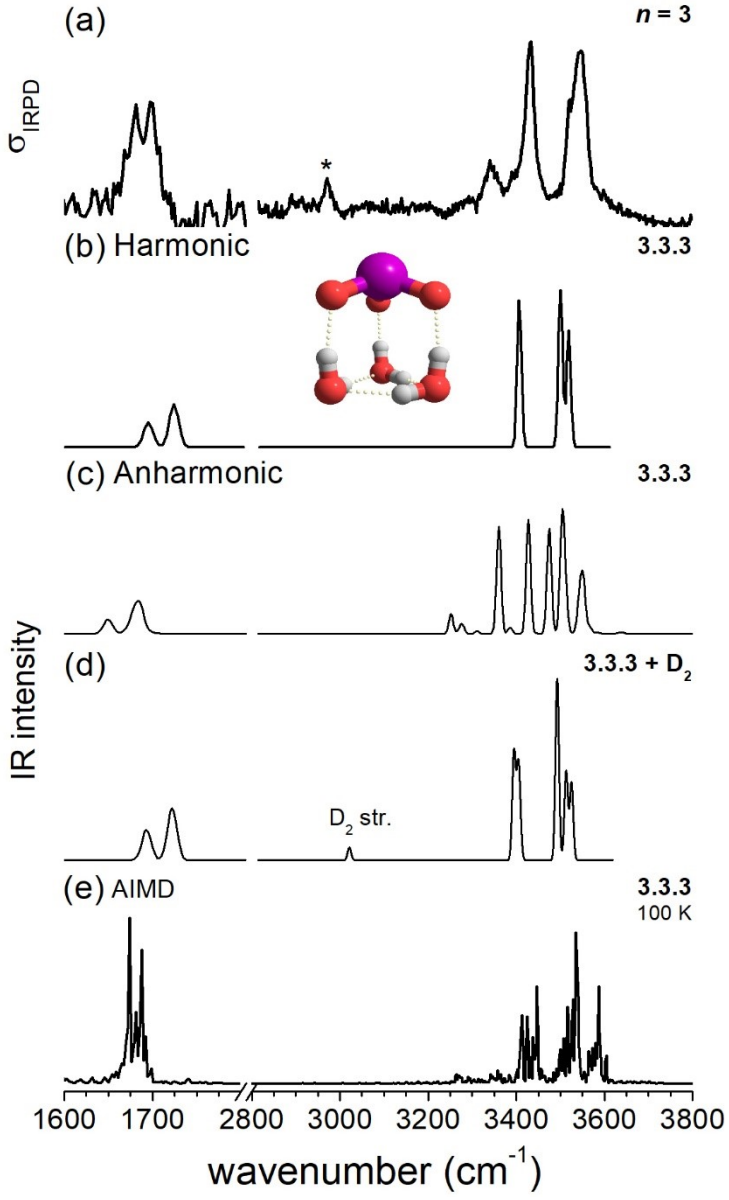


Figure S3. Comparison of IRPD spectrum (trace a) of D_2-tagged $[IO_3^-(H_2O)_2]$ with the AIMD derived spectra from the two lowest energy isomer **2.4.0** (trace b and c) and **2.3.1** (trace d and e) at 100 K and 200 K. The band due to D_2 stretching oscillator and the feature arises from overtone of scissoring bend mode of H_2O are denoted by asterisk (*) and hash (#), respectively.

Figure S4. Comparison of IRPD spectrum (trace a) of D_2-tagged $IO_3^-(H_2O)_3$ with scaled MP2/def2TZVP (trace b) and unscaled VPT2/MP2/def2TZVP derived anharmonic (trace c) IR spectra of the lowest energy isomer **3.3.3**, respectively. The effect of messenger (D_2) tagging and MD simulated spectra obtained at 100 K from starting structure **3.3.3** have been shown in



trace d and e, respectively.

Figure S5. (a) Structure of the most stable isomer **3.3.3** of $[IO_3^-(H_2O)_3]$, (b) a snapshot from AIMD simulation at 20 K exhibiting the deformation of the structure, notably, with elongation of a hydrogen bond to 302 pm from 192 pm.

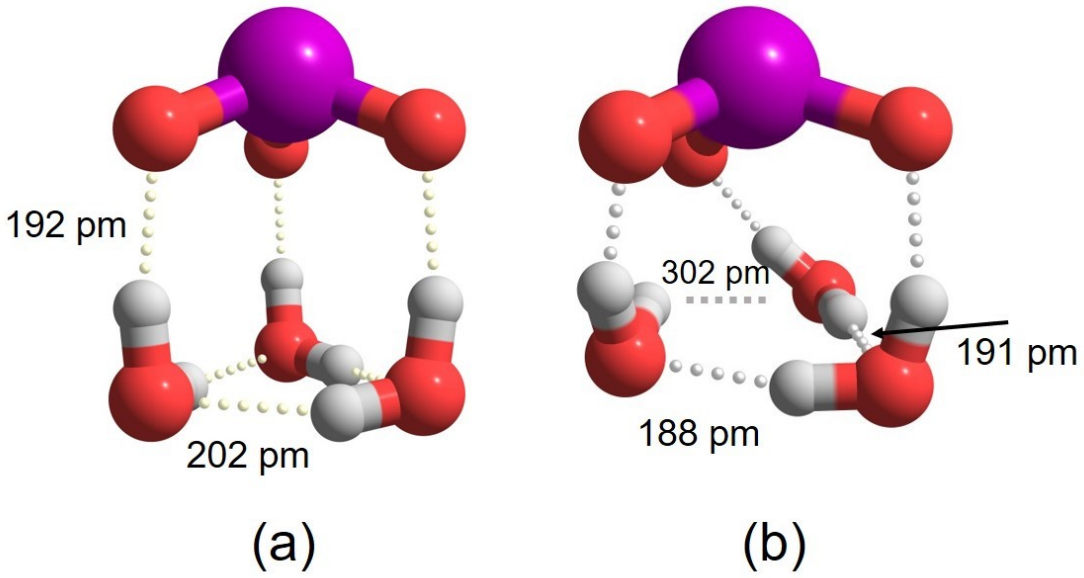


Figure S6. Comparison of IRPD spectrum (trace a) of D_2-tagged $IO_3^-(H_2O)_6$ with scaled MP2/def2TZVP derived harmonic IR spectra of the lowest energy isomers **6.5.6a** (trace b), **6.5.6b** (trace c), **6.6.6a** (trace d) and **6.6.6b** (trace e). The band due to D_2 stretching oscillation is marked with * in trace a.

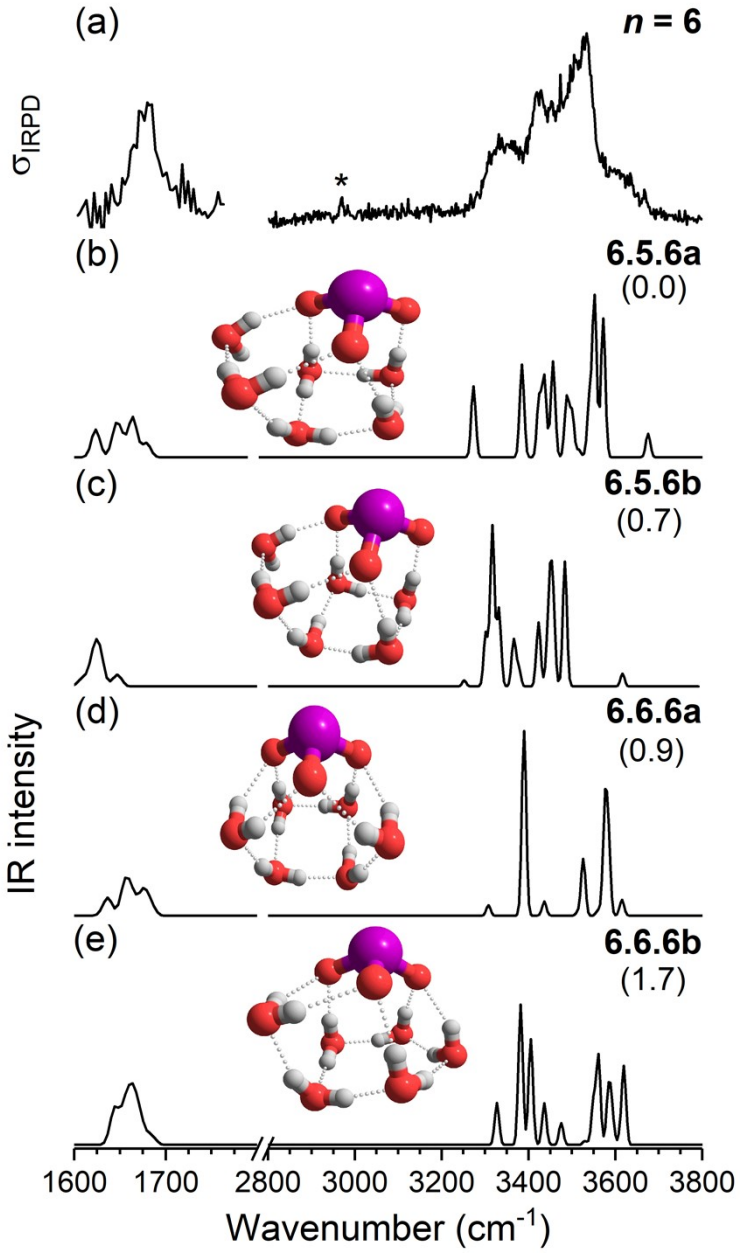


Figure S7. Comparison of IRPD spectrum of D_2-tagged $IO_3^-(H_2O)_7$ (trace a) with scaled MP2/def2TZVP derived harmonic IR spectra of the lowest energy isomer **7.5.9a** (trace b) and **7.5.9b** (trace c). The band due to D_2 stretching mode is marked with * in trace a.

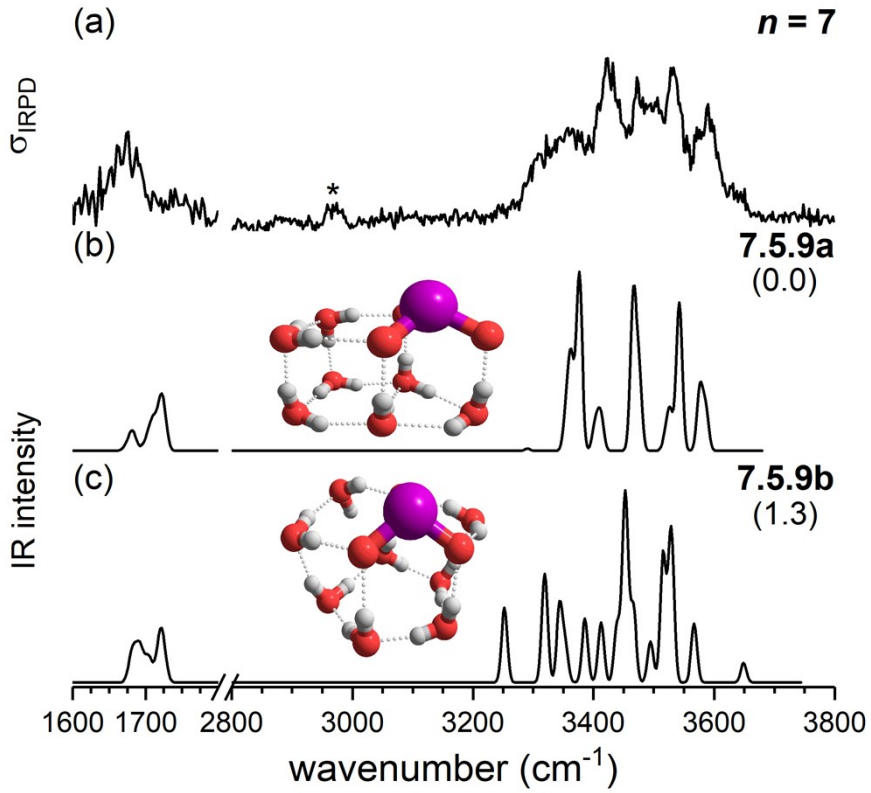
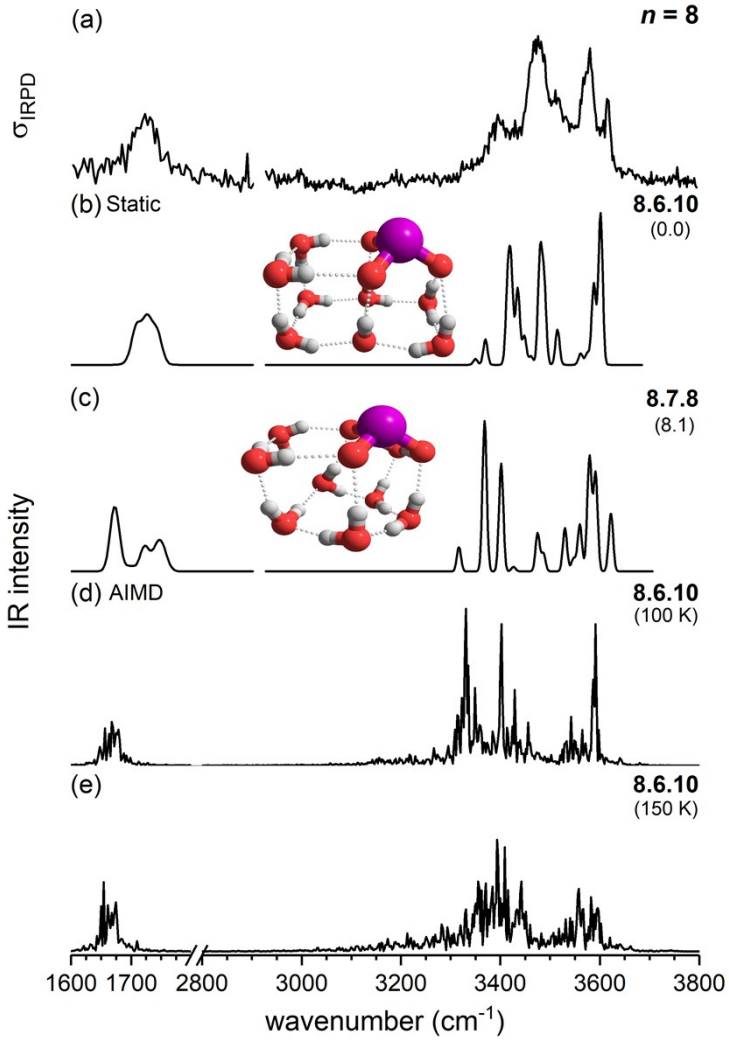


Figure S8. Comparison of IRPD spectrum of D_2-tagged $IO_3^-(H_2O)_8$ (trace a) with scaled MP2/def2TZVP derived harmonic IR spectra of the lowest energy isomer **8.6.10** (trace b) and **8.7.8** (trace c). The unscaled AIMD spectra derived at 100 K and 150 K from **8.6.10** are plotted



in trace d and e, respectability.

Fig S9. Mass spectrum of iodate-water clusters, $IO_3^-(H_2O)_n$, in the m/z range up to 900 amu, obtained by spraying 10 mM solution of KIO_3 in 1:1 water/acetonitrile mixture. The progression with an origin 175 amu and a spacing of 18 amu is assigned to n = 0 to 40 clusters size.

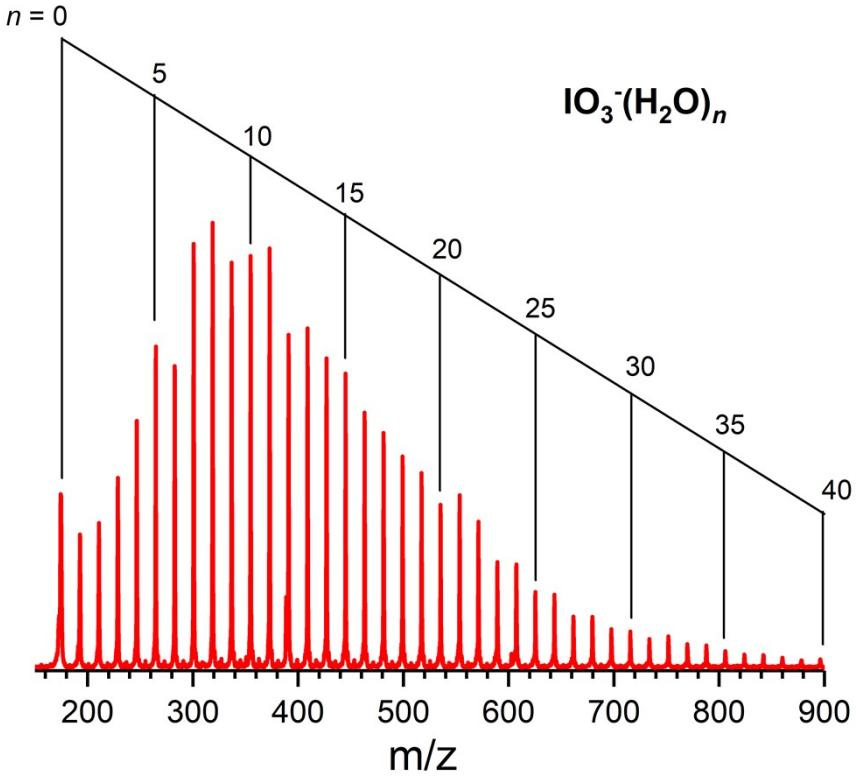


Figure S10. Comparison of IRPD spectrum (trace a) with IRMPD (trace b) one for the iodate-water complex $[IO_3^-(H_2O)_n]$ at n = 11 in OH stretching region. IRPD and IRMPD traces are recorded monitoring the D_2 and H_2O dissociation channels, respectively. Bands i_3 and i_4 are IRMPD transparent.