Theoretical Study on the Structures and Vibrational Spectra of $(H_2O\text{-}Ar_n)^+$, n=1,2: Formation of Hemi-bond of Water Radical Cation

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Contents:

Table S1. Relative stability of H_2O^+-Ar_n (in kcal/mol)

	Ia	Ib	IIa	IIb	IIc
MP2/aVDZ[a]	0.0	2.45	0.0	1.92	3.93
CCSD/aVDZ[b]	0.0	1.20	0.0	1.17	2.37
CCSD/VDZ[c]	0.0	1.77	0.0	1.61	2.90
MP2/CCSD/aVDZ[d]	0.0	1.06			
MP2/aVTZ[e]	0.0	3.06	0.0	2.44	5.03
MP2/VTZ[f]	0.0	3.46			
CCSD/aVTZ[g]	0.0	1.78	0.0	1.71	3.42
CCSD/VTZ[h]	0.0	2.27			
MP2/CCSD/aVTZ[i]	0.0	1.62			
CCSD(T)/aVTZ[j]	0.0	1.53	0.0	1.22	2.92
CCSD(T)/aVnZ[k]	0.0	0.92	0.0	1.28	2.54
VPT2, CCSD(T)/VnZ[l]	0.0	0.56	0.0	0.84	2.40

[a] optimized at MP2/aVDZ level

[b] optimized at CCSD/aVDZ level

[c] optimized at CCSD/VDZ level

[d] full anharmonic correction using our anharmonic algorithm with CCSD/1-,2-body/MP2/6-body/aVDZ level.

[e] optimized at MP2/aVTZ level

[f] optimized at MP2/VTZ level

[g] optimized at CCSD/aVTZ level

[h] optimized at CCSD/VTZ level

[i] full anharmonic correction with CCSD/1-,2-body/MP2/6-body/aVTZ level.

[j] optimized at CCSD(T)/aVTZ level

[k] optimized at CCSD(T)/aVTZ level; electron part calculated at CCSD(T)/aV5Z

[l] simulated by Duncan with VPT2, CCSD(T)/VTZ for H_2O^+-Ar_1 and VPT2, CCSD(T)/VDZ for H_2O^+-Ar_2

Table S2. vibrational transitions of H_2O^+-Ar_2 in MIR and NIR window with assignments for isomer one (IIb and IIc).

	Fre.(cm^{-1})	Assignments	Experiment[2]	VPT2[2]
IIb	2797.5	$2\nu_2$		
	2886.7	ν_1	2700	2867
	3347.9	ν_3	3324	3301
	4745.5	$\nu_2+\nu_3$		
	5390.2	$2\nu_1$		
	5499.2	$2\nu_1+\nu_s^{H\text{-}Ar}$		
	6548.8	$2\nu_3$		
IIc	3259.5	ν_1		3263
	3322.3	ν_3		3345
	4711.2	$\nu_2+\nu_3$		
	6418.0	$2\nu_1$		
	6429.1	$\nu_1+\nu_3$		
	6599.5	$2\nu_3$		

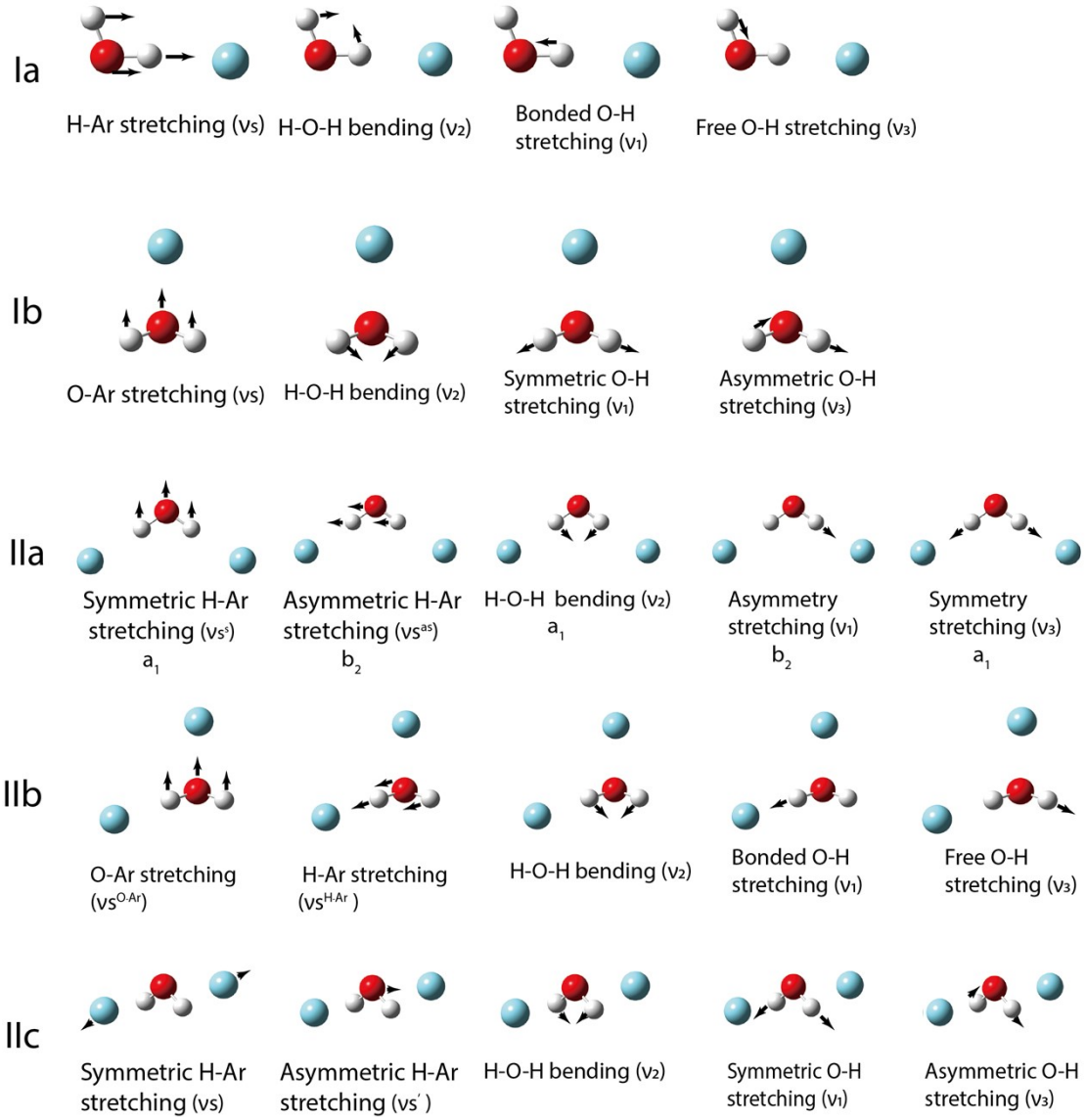

Figure S1. The four/five normal modes for conformers of H_2O^+-Ar_n (n=1,2) complex whose notations are in parenthesis, respectively. The major displacement vectors are indicated. Conformer IIa belongs to C_{2v} symmetry, the corresponding irreducible representation are given in the picture.

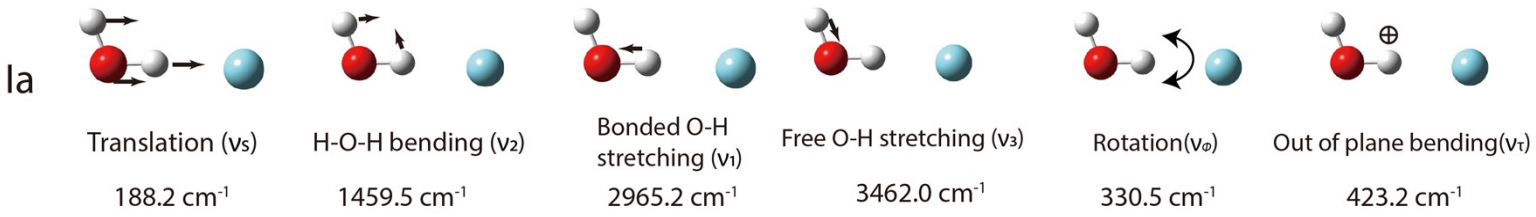

Figure S2. Normal modes of conformer Ia of H_2O^+-Ar.

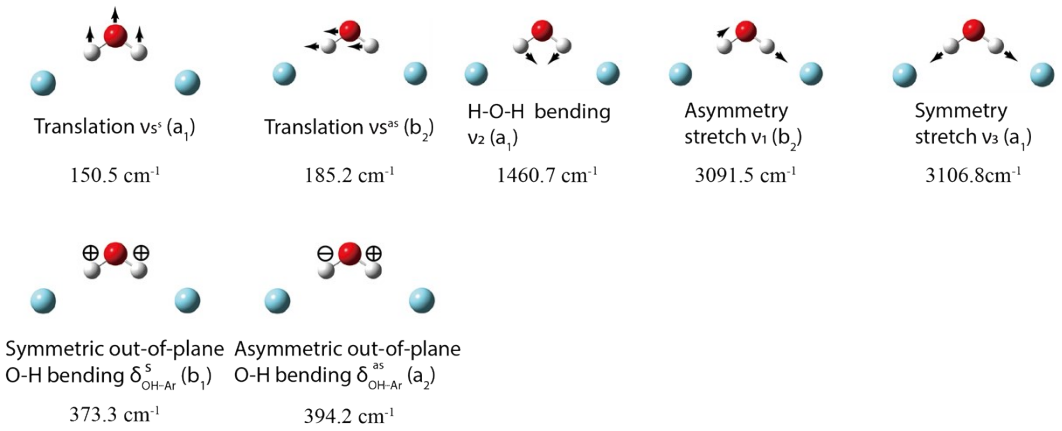

Figure S3. Normal modes of conformer IIa of H_2O^+-Ar_2 which has C_{2v} symmetry. The corresponding irreducible representation of each mode are presented in parentheses.

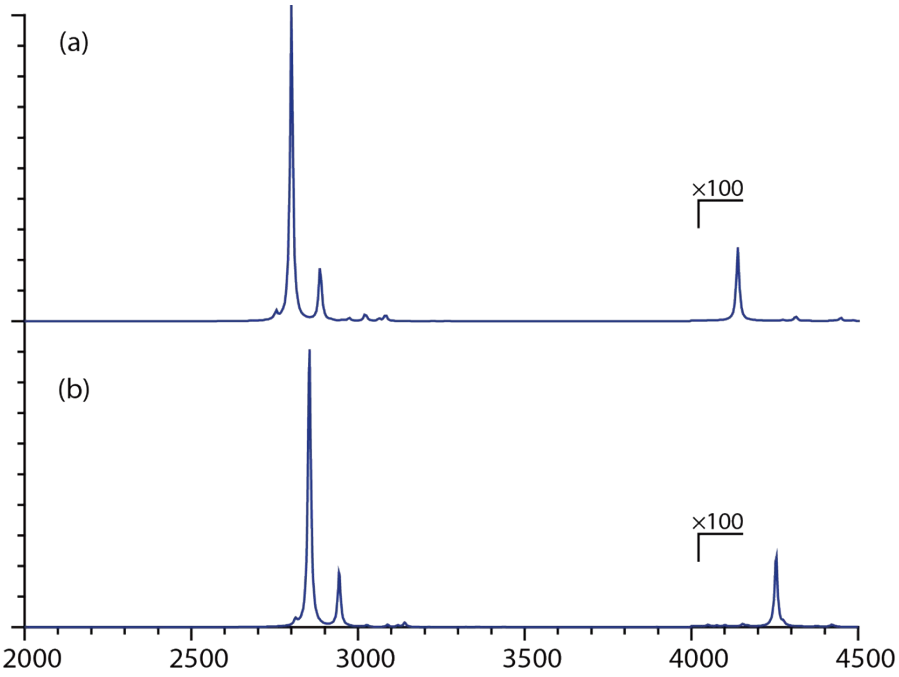

Figure S4. Vibrational spectra of IIa conformer of the H_2O^+-Ar_2 complex:(a) simulated basing on 5-dimensional Hamiltonian. (b) simulated basing on 7-dimensional Hamiltonian (including two out-plane bending modes)

References

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2. Dopfer, O.; Roth, D.; Maier, J. P., Microsolvation of the Water Cation in Argon: II. Infrared Photodissociation Spectra of $H2O+{-}Ar_n$ (n = 1−14). The Journal of Physical Chemistry A 2000, 104 (50), 11702-11713.