

Electronic Supplementary Information:

Evaluation of Ar tagging toward the vibrational spectra and zero point energy of X-HOH, X-DOH and X-HOD, X=F, Cl, Br

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For Ar.F-H₂O, we have compared the zero point vibration energy dependence for the full 9 dimensional calculation versus lower dimension cuts. Harmonic frequencies calculated by various quantum chemistry methods are given. For Ar.Cl-H₂O and Ar.Br-H₂O, we compare the vibrational spectra on the position of Ar tagging. In addition, the peak position and absorption intensity for F-H₂O, F-HOD, F-DOH, and Ar.X-H₂O (X=F, Cl, Br) calculated using MP2/6-311++G(3df,3pd), as well as those for Ar.X-H₂O Ar.X-HOD and Ar.X-DOH calculated using B3LYP/6-31+G(d,p) are given.

9 Dimensional calculations

We can look at the problem concerning the Ar-tagging from two points, the vibrational effect of how the addition of the Ar vibrational modes perturbs the vibrational spectra of the X·H₂O, and from the variation of the electronic state of the X·H₂O due to the existence of the Ar atom. To answer all the problems, we require a 9 dimensional (9D) calculation for all Ar·X·H₂O system studied here. However, it is beyond our capability to perform such calculations for all systems. So we have evaluated the effect of the full 9D calculation toward the zero point energy (ZPE) of Ar·F·H₂O perp conformer using MP2/6-311++G(3df,3pd).

To perform the 9D simulation, we could not use 9 grid points for all degrees of freedom ($9^9=387,420,489$ points). Thus we reduced it to 7 points for the low frequency vibrations modes involving Ar...F·H₂O VDW motions and 5 points for the 6 vibrational modes for F·H₂O, resulting in $7^35^6= 5,359,375$ points. To confirm that such a grid is valid, we have performed several 3D vibrations. We have listed the ZPE calculated by different grid points for the different frequency regimes in Table S1. Here High frequency means the H₂O bending, IHB OH stretching, free OH stretching modes, while the middle frequency means the X...H₂O VDW stretching, H₂O in-plane wagging, H₂O out-of-plane OH wagging modes, and the low frequency means the vibrational modes involving the Ar motion. One can see that for the high and middle frequency range, which corresponds to the vibrations of F·H₂O, 5 grid points can give ZPE values within 1 cm⁻¹ compared to that of 9 grid points. On the other hand, for the low frequency modes, we need 7 points to give ZPE values within 5 cm⁻¹ (~0.015 kcal mol⁻¹).

Table S1: Grid point dependence of the Zero point energy, in cm⁻¹, for the 3D vibrational calculation for Ar·F·H₂O Perp conformer obtained using MP2/6-311++G(3df,3pd)

| | 9 pt | 7pt | 5pt |
|---|--------|-------|--------|
| High (H ₂ O intramolecular) | 3684.1 | - | 3683.3 |
| Mid (F·H ₂ O intermolecular) | 1173.5 | - | 1173.2 |
| Low (Ar...F·H ₂ O VDW) | 336.2 | 331.6 | 276.6 |

Next, we compare the ZPE obtained from the 9D vibrational calculation, 4903 cm⁻¹, versus the 6D+3D harmonic oscillator model mentioned in the main text, 4932 cm⁻¹. We can see that an error of 30 cm⁻¹ (~0.08 kcal mol⁻¹) will be expected from

using the present 6D+3D harmonic oscillator model to obtain the absolute value of ZPEs.

Binding energies of Ar

Below we list the binding energies of Ar for the X⁻H₂O, X⁻HOD, and X⁻DOH systems.

Table S2: Electronic binding energy, in kcal mol⁻¹, of the Ar atom for Ar.X⁻H₂O obtained from the electronic energies calculated by MP2, CCSDS(T), and B3LYP.

| MP2/6-311++G(3df,3pd) | Perp conformer | Lin conformer | Out conformer |
|-------------------------------------|----------------|---------------|---------------|
| Ar.F ⁻ H ₂ O | 2.18 | 1.86 | |
| Ar.Cl ⁻ H ₂ O | 1.57 | 1.25 | |
| Ar.Br ⁻ H ₂ O | 1.37 | | 1.28 |
| CCSD(T)/6-311++G(3df,3pd) | Perp conformer | Lin conformer | Out conformer |
| Ar.F ⁻ H ₂ O | 2.16 | 1.92 | |
| Ar.Cl ⁻ H ₂ O | 1.51 | 1.23 | |
| Ar.Br ⁻ H ₂ O | 1.36 | | 1.23 |
| B3LYP/6-31+G(d,p) | Perp conformer | Lin conformer | Out conformer |
| Ar.F ⁻ H ₂ O | | 0.77 | |
| Ar.Cl ⁻ H ₂ O | 0.24 | 0.21 | |
| Ar.Br ⁻ H ₂ O | 0.64 | | 0.64 |

Table S3: Free energy correction, in kcal mol⁻¹, due to rotational entropy contributions for the Perp conformer of Ar.X⁻DOH and Ar.X⁻HOD

| Temp (K) | Ar.F ⁻ DOH | Ar.F ⁻ HOD | Ar.Cl ⁻ DOH | Ar.Cl ⁻ HOD | Ar.Br ⁻ DOH | Ar.Br ⁻ HOD |
|----------|-----------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| | Perp | Perp | Perp | Perp | Perp | Perp |
| 50 | -0.90 | -0.90 | -0.97 | -0.97 | -1.02 | -1.02 |
| 100 | -2.00 | -2.01 | -2.14 | -2.15 | -2.24 | -2.25 |
| 150 | -3.18 | -3.19 | -3.40 | -3.41 | -3.54 | -3.55 |

Table S4: Free energy correction, in kcal mol⁻¹, due to rotational entropy contributions for the Lin and Out conformer of Ar.X⁻DOH and Ar.X⁻HOD

| Temp (K) | Ar.F ⁻ DOH | Ar.F ⁻ HOD | Ar.Cl ⁻ DOH | Ar.Cl ⁻ HOD | Ar.Br ⁻ DOH | Ar.Br ⁻ HOD |
|----------|-----------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| | Lin | Lin | Lin | Lin | Out | Out |
| 50 | -0.76 | -0.79 | -0.84 | -0.86 | -1.02 | -1.03 |
| 100 | -1.73 | -1.79 | -1.88 | -1.93 | -2.25 | -2.25 |
| 150 | -2.77 | -2.87 | -3.00 | -3.07 | -3.55 | -3.56 |

Table S5: The anharmonic ZPE difference, in kcal mol⁻¹, between X⁻HOD and X⁻DOH for the intramolecular and intermolecular modes calculated using MP2/6-311++G(3df,3pd)

| Halide | intramolecular 3D | intermolecular 3D | 6D |
|-----------------|-------------------|-------------------|------|
| F ⁻ | -0.48 | 0.37 | 0.00 |
| Cl ⁻ | -0.09 | 0.31 | 0.18 |
| Br ⁻ | -0.07 | 0.29 | 0.17 |

Table S6: Shift of the peak position, in cm⁻¹, for the HOD vibrations for X⁻HOD and X⁻DOH in comparison to bare HOD calculated using MP2/6-311++G(3df,3pd)

| Vibrational Modes | F ⁻ HOD | Cl ⁻ HOD | Br ⁻ HOD |
|-------------------|--------------------|---------------------|---------------------|
| Bending | 162 | 116 | 91 |
| OD stretch | 111 | -7 | -9 |
| OH stretch | -2329 | -651 | -489 |
| Vibrational Modes | F ⁻ DOH | Cl ⁻ DOH | Br ⁻ DOH |
| Bending | -96 | 0 | 5 |
| OD stretch | -1660 | -452 | -346 |
| OH stretch | 3 | 5 | -27 |

Vibrational Spectra

In Tables S7 to S9, we have presented the harmonic frequencies calculated by different quantum chemistry methods. As one can see, compared to the CCSD(T) results, the difference in the harmonic frequencies by B3LYP is at most 30 cm^{-1} for the high frequency X-H₂O vibrations. Consistent with the weaker binding energy by B3LYP, the vibrations involving Ar have much smaller frequencies. On the other hand, for MP2, the Free OH stretching frequencies are off by 60 to 80 cm^{-1} . The IHB OH stretching mode for Ar.F-H₂O is off by 150 cm^{-1} . However, we should note that for the highly anharmonic IHB OH stretching mode, it is hard to evaluate the validity by harmonic frequencies. We also evaluated the overlap of the mass weighted Cartesian normal mode eigenvectors calculated using CCSD(T), and MP2. We found that all modes had overlaps greater than 98%. This signifies that the characteristics of the vibrational modes are the same for the two methods.

Looking at the harmonic frequencies for the Ar tagged versus bare clusters, we see that the differences are within 10 cm^{-1} except for the IHB OH stretching and the H₂O in plane wagging modes. Even for these two modes, the shift is at most 40 cm^{-1} .

Table S7 Comparison of harmonic frequencies, in cm^{-1} , by calculated by different quantum chemistry methods for F-H₂O and Ar.F-H₂O

| Vibrational mode | Ar perp CCSD(T) | Ar perp MP2 | Bare MP2 | Ar Lin B3LYP | Bare B3LYP |
|-----------------------------|--------------------|----------------|-------------|-----------------|---------------|
| Free OH Str | 3854 | 3938 | 3939 | 3864 | 3864 |
| IHB OH Str | 2198 | 2039 | 2052 | 2220 | 2182 |
| HOH Bend | 1727 | 1717 | 1710 | 1703 | 1700 |
| H2O Out of plane wag | 1161 | 1228 | 1231 | 1173 | 1177 |
| H2O In plane wag | 567 | 599 | 592 | 558 | 561 |
| H2O...F VDW Str | 388 | 416 | 412 | 391 | 393 |
| Ar Out of Plane wag | 97 | 101 | | 48 | |
| Ar In plane wag | 67 | 68 | | 25 | |
| Ar...H ₂ O.F Str | 12 | 46 | | 14 | |

Table S8 Comparison of harmonic frequencies, in cm^{-1} , by calculated by different quantum chemistry methods for $\text{Cl}^-\text{H}_2\text{O}$ and $\text{Ar}.\text{Cl}^-\text{H}_2\text{O}$

| Vibrational mode | Ar perp CCSD(T) | Ar perp MP2 | Bare MP2 | Ar Lin B3LYP | Bare B3LYP |
|------------------------------|----------------------------|------------------------|---------------------|-------------------------|-----------------------|
| Free OH Str | 3867 | 3936 | 3938 | 3874 | 3873 |
| IHB OH Str | 3372 | 3366 | 3387 | 3363 | 3373 |
| HOH Bend | 1690 | 1680 | 1677 | 1666 | 1664 |
| H2O Out of plane wag | 744 | 771 | 769 | 746 | 740 |
| H2O In plane wag | 372 | 387 | 374 | 348 | 340 |
| H2O...Cl VDW Str | 205 | 202 | 198 | 188 | 181 |
| Ar Out of Plane wag | 70 | 80 | | 35 | |
| Ar In plane wag | 51 | 53 | | 32 | |
| Ar...H ₂ O.Cl Str | 34 | 35 | | 7 | |

Table S9 Comparison of harmonic frequencies, in cm^{-1} , by calculated by different quantum chemistry methods for $\text{Br}^-\text{H}_2\text{O}$ and $\text{Ar}.\text{Br}^-\text{H}_2\text{O}$

| Vibrational mode | Ar perp CCSD(T) | Ar perp MP2 | Bare MP2 | Ar Lin B3LYP | Bare B3LYP |
|------------------------------|----------------------------|------------------------|---------------------|-------------------------|-----------------------|
| Free OH Str | 3867 | 3934 | 3936 | 3870 | 3872 |
| IHB OH Str | 3472 | 3492 | 3513 | 3443 | 3448 |
| HOH Bend | 1683 | 1671 | 1669 | 1658 | 1659 |
| H2O Out of plane wag | 675 | 682 | 680 | 721 | 717 |
| H2O In plane wag | 330 | 333 | 314 | 340 | 345 |
| H2O...Cl VDW Str | 164 | 160 | 156 | 147 | 151 |
| Ar Out of Plane wag | 68 | 78 | | 31 | |
| Ar In plane wag | 47 | 51 | | 14 | |
| Ar...H ₂ O.Br Str | 26 | 26 | | 10 | |

Below we list and plot the results for the vibrational spectra calculations for the $\text{Ar}.\text{X}^-\text{H}_2\text{O}$ where $\text{X}=\text{Cl}$ and Br calculated using B3LYP/6-31+G(d,p).

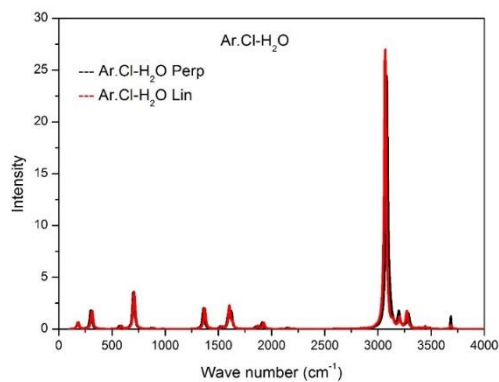


Fig S1. The calculated vibrational spectra of Ar.Cl⁻H₂O at two Ar positions. The peak positions and intensities were calculated using B3LYP/6-31+G(d,p)

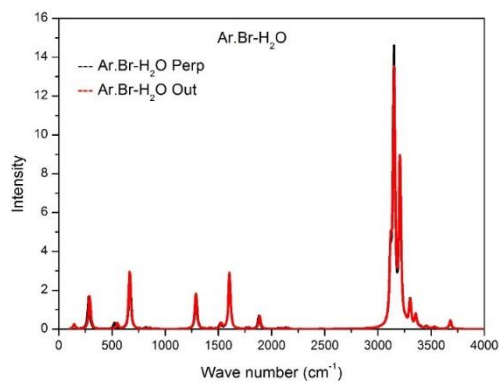


Fig S2. The calculated vibrational spectra of Ar.Br⁻H₂O at two Ar positions. The peak positions and intensities were calculated using B3LYP/6-31+G(d,p)

Table S10 The Calculated peak positions, in cm^{-1} , and absorption intensity, in km mol^{-1} , of Ar.F \cdot H $_2$ O, Ar.F \cdot HOD, Ar.F \cdot DOH obtained using B3LYP/6-31+G(d,p). Experimental peak positions of Ayotte et al.¹ are given in parenthesis “()”, while the theoretical results for F \cdot H $_2$ O are given in brackets “[]”. The quantum numbers in the Assignment correspond to (X \cdot ...H $_2$ O VDW stretching, H $_2$ O in-plane wagging, H $_2$ O out-of-plane OH wagging, H $_2$ O bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.F \cdot H $_2$ O Lin | | Ar.F \cdot HOD Lin | | Ar.F \cdot DOH Lin | |
|---------------|---------------------------|-------------|----------------------|-----------|----------------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0,0) | 423 [428] | 158 [145] | 405 | 124 | 397 | 167 |
| (0,1,0,0,0,0) | 542 [542] | 42 [41] | 429 | 58 | 494 | 50 |
| (2,0,0,0,0,0) | 822 [830] | 0 [0] | 800 | 0 | 778 | 4 |
| (0,2,0,0,0,0) | 1073 (1083) [1075] | 18 [17] | 842 | 1 | 877 | 1 |
| (0,0,1,0,0,0) | 1156 [1161] | 118 [120] | 1157 | 112 | 832 | 81 |
| (3,0,0,0,0,0) | 1205 [1213] | 6 [8] | 1235 | 4 | 1209 | 0 |
| (0,0,2,0,0,0) | 2172 [2148] | 45 [23] | 2166 | 8 | 1658 | 16 |
| (0,0,0,1,0,0) | 1595 (1650) [1630] | 553 [596] | 1624 | 282 | 1209 | 34 |
| (1,0,0,1,0,0) | 2068 [2102] | 1 [2] | 2010 | 6 | 1658 | 2 |
| (0,0,0,0,1,0) | 1651 (1523) [1558] | 1240 [1690] | 1646 | 1598 | 1269 | 1261 |
| (1,0,0,0,1,0) | 2183 [2016] | 16 [7] | 2049 | 83 | 1511 | 5 |
| (0,1,0,0,1,0) | 2210 [2311] | 11 [20] | 2305 | 29 | 1770 | 8 |
| (0,0,1,0,1,0) | 2642 [2632] | 11 [25] | 2704 | 2 | 2225 | 13 |
| (0,0,0,2,0,0) | 3257 [3120] | 23 [4] | 3246 | 17 | 2363 | 8 |
| (0,0,0,0,2,0) | 3289 [2996] | 54 [46] | 2981 | 17 | 2442 | 25 |
| (0,0,0,1,1,0) | 3257 [3018] | 23 [17] | 3109 | 1 | 2362 | 19 |
| (0,0,0,0,0,1) | 3678 (3682) [3678] | 4 [2] | 2617 | 20 | 3681 | 2 |

Table S11 The Calculated peak position, in cm^{-1} , and absorption intensity, in km mol^{-1} , of $\text{Ar.Cl}^-\text{H}_2\text{O}$, $\text{Ar.Cl}^-\text{HOD}$, $\text{Ar.Cl}^-\text{DOH}$ Perp obtained using B3LYP/6-31+G(d,p). Experimental peak positions of Horvath et al.² are given in parentheses “()”, while the theoretical results for $\text{Cl}^-\text{H}_2\text{O}$ by B3LYP are given in brackets “[]”. Results for $\text{Cl}^-\text{H}_2\text{O}$ by MP2/6-311++G(3df,3pd) are given in curly brackets “{}”. Results for $\text{Ar.Cl}^-\text{H}_2\text{O}$ by MP2/6-311++G(3df,3pd) are given in quotation marks ””. The quantum numbers in the Assignment correspond to ($\text{X}^-\dots\text{H}_2\text{O}$ VDW stretching, H_2O in-plane wagging, H_2O out-of-plane OH wagging, H_2O bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.Cl ⁻ H ₂ O Perp | | Ar.Cl ⁻ HOD Perp | | Ar.Cl ⁻ DOH Perp | |
|---------------|--|---------------------------|-----------------------------|-----------|-----------------------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0,0) | 189 [180] {194} “198” | 25 [22] {26} “27” | 180 | 27 | 179 | 22 |
| (0,1,0,0,0,0) | 338 [300] {341} “361” | 44 [63] {57} “68” | 256 | 37 | 270 | 49 |
| (2,0,0,0,0,0) | 372 [354] {381} “391” | 0 [0] {0} “0” | 354 | 0 | 353 | 0 |
| (0,2,0,0,0,0) | 550 [550] {643} “688” | 0 [10] {11} “10” | 488 | 5 | 471 | 5 |
| (0,0,1,0,0,0) | 711 (738) [704] {731} “733” | 62 [127] {88} “76” | 708 | 104 | 522 | 97 |
| (3,0,0,0,0,0) | 519 [524] {565} “579” | 0 [0] {0} “0” | 525 | 0 | 523 | 0 |
| (0,0,2,0,0,0) | 1376 (1404) {1411} [1363] “1415” | 68 [69] {74} “72” | 1360 (1369) | 85 | 1024 (1057) | 28 |
| (0,0,0,1,0,0) | 1610 (1653) [1621] {1623} “1624” | 67 [59] {81} “78” | 1472 (1507) | 58 | 1371 (1404) | 91 |
| (0,1,0,1,0,0) | 1913 [1910] {1934} “1960” | 20 [24] {28} “35” | 1701 | 18 | 1642 | 16 |
| (0,0,0,0,1,0) | 3030 (3146) [3078] {3081} “3057” | 1041 [846] {970} “933” | 3075 (3156) | 330 | 2299 (2357) | 554 |
| (1,0,0,0,1,0) | 3202 [3277] | 18 [20] {11} | 3278 | 21 | 2491 | 7 |

| | | | | | | |
|---------------|--|----------------------|-------------|----|---------------|----|
| | {3194} "3202" | "8" | | | | |
| (0,0,0,2,0,0) | 3243 (3287) [3197] {3221} "3230" | 65 [45] {11} "12" | 2916 (2990) | 74 | 2719 (2880??) | 1 |
| (0,0,0,0,0,1) | 3688 (3697) [3684] {3750} "3749" | 10 [10] {20} "18" | 2711 (2716) | 10 | 3699 (3697) | 10 |

Table S12 The Calculated peak position, in cm^{-1} , and absorption intensity, in km mol^{-1} , of Ar.Br H_2O , Ar.Br HOD , Ar.Br DOH conformer 1 obtained using B3LYP/6-31+G(d,p). Experimental peak positions of Horvath et al.² are given in parentheses “()”, while the theoretical results for Br H_2O are given in brackets “[]”. Results for Br H_2O by MP2/6-311++G(3df,3pd) are given in curly brackets “{ }”. Results for Ar.Br H_2O by MP2/6-311++G(3df,3pd) are given in quotation marks ” ”. The quantum numbers in the Assignment correspond to (X...H $_2\text{O}$ VDW stretching, H $_2\text{O}$ in-plane wagging, H $_2\text{O}$ out-of-plane OH wagging, H $_2\text{O}$ bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.Br H_2O Perp | | Ar.Br HOD Perp | | Ar.Br DOH Perp | |
|---------------|-------------------------------------|---------------------------|-------------------------|-----------|-------------------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0,0) | 146 [144] {152} “157” | 8 [9] {8} “8” | 141 | 10 | 141 | 8 |
| (0,1,0,0,0,0) | 269 [285] {271} “200” | 42 [35] {54} “59” | 239 | 37 | 250 | 45 |
| (2,0,0,0,0,0) | 288 [287] {301} “310” | 1 [24] {0} “6” | 280 | 0 | 280 | 0 |
| (0,2,0,0,0,0) | 496 [542] {507} “568” | 9 [10] {10} “10” | 458 | 5 | 468 | 7 |
| (0,0,1,0,0,0) | 624 (664) [666] {643} “646” | 61 [104] {86} “74” | 668 | 84 | 496 | 80 |
| (3,0,0,0,0,0) | 427 [430] {446} “449” | 0 [0] {0} “0” | 417 | 0 | 418 | 0 |
| (0,0,2,0,0,0) | 1212 (1262) [1286] {1249} “1255” | 52 [63] {55} “54” | 1283 (1227) | 65 | 969 (959) | 27 |
| (0,0,0,1,0,0) | 1606 (1647) [1604] {1616} “1615” | 101 [102] {110} “112” | 1448 (1484) | 60 | 1369 (1409) | 98 |
| (0,1,0,1,0,0) | 1872 [1883] {1883} “1910” | 28 [24] {25} “18” | 1704 | 6 | 1620 | 16 |
| (0,0,0,0,1,0) | 3151 (3296) [3151] {3262} “3245” | 280 [239] {572} “464” | 3184(3294) | 541 | 2361 (2445) | 498 |
| (1,0,0,0,1,0) | 3308 [3461] {3425} “3411” | 30 [49] {25} “20 “203” | 3341 | 36 | 2511 | 16 |
| (0,0,0,2,0,0) | 3213 (3238) [3206] {3184} “3185” | 417 [275] {70} “309” | 2888 (2950??) | 23 | 2717 | 2 |
| (1,0,0,2,0,0) | 3366 [3354] | 19 [23] {12} | 3108 | 20 | 2873 | 0 |

| | | | | | | |
|---------------|-------------------------------------|---------------------|----------------|---|----------------|---|
| | {3352} “3345” | “20” | | | | |
| (0,0,0,0,0,1) | 3679 (3695) [3682] {3742} “3743” | 8 [14] {15} “25” | 2708 (2720) | 8 | 3724 (3688) | 7 |

Table S13. The Calculated peak positions, in cm^{-1} , and absorption intensity, in km mol^{-1} , of F·H₂O, F·HOD, and F·DOH obtained using MP2/6-311++G(3df,3pd). The quantum numbers in the Assignment correspond to (X...H₂O VDW stretching, H₂O in-plane wagging, H₂O out-of-plane OH wagging, H₂O bending, IHB OH stretching, free OH stretching).

| Assignment | F·H ₂ O | | F·HOD | | F·DOH | |
|---------------|--------------------|-----------|---------------|-----------|---------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0) | 462 | 180 | 407 | 82 | 428 | 217 |
| (0,1,0,0,0) | 569 | 37 | 444 | 109 | 526 | 47 |
| (2,0,0,0,0) | 890 | 3 | 830 | 2 | 834 | 1 |
| (0,2,0,0,0) | 1129 | 16 | 883 | 2 | 938 | 1 |
| (0,0,1,0,0) | 1218 | 109 | 1199 | 104 | 1035 | 228 |
| (3,0,0,0,0) | 1293 | 100 | 1288 | 119 | 1227 | 53 |
| (0,0,2,0,0) | 2499 | 12 | 2480 | 10 | 2024 | 32 |
| (0,0,0,1,0) | 1614 | 73 | 1538 | 145 | 1280 | 59 |
| (0,1,0,1,0) | 2166 | 41 | 2019 | 31 | 1745 | 1 |
| (0,0,0,0,1,0) | 1423 | 2307 | 1423 | 2307 | 1103 | 1105 |
| (1,0,0,0,1,0) | 1957 | 28 | 1825 | 23 | 1532 | 1 |
| (0,1,0,0,1,0) | 2015 | 54 | 1971 | 127 | 1632 | 8 |
| (0,0,1,0,1,0) | 2592 | 40 | 2549 | 11 | 2120 | 7 |
| (0,0,0,2,0,0) | 3216 | 2 | 3072 | 6 | 2251 | 3 |
| (0,0,0,0,2,0) | 2931 | 36 | 2850 | 25 | 2058 | 60 |
| (0,0,0,1,1,0) | 2977 | 27 | 2859 | 10 | 2231 | 2 |
| (0,0,0,0,0,1) | 3754 | 1 | 2875 | 17 | 3755 | 1 |

Table S14. The Calculated peak positions, in cm^{-1} , and absorption intensity, in km mol^{-1} , of the two conformers of $\text{Ar.F}^-\text{H}_2\text{O}$ Lin obtained using MP2/6-311++G(3df,3pd). The quantum numbers in the Assignment correspond to ($X^-\dots\text{H}_2\text{O}$ VDW stretching, H_2O in-plane wagging, H_2O out-of-plane OH wagging, H_2O bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.F ⁻ H ₂ O Perp | | Ar.F ⁻ H ₂ O Lin | |
|---------------|---|-----------|--|-----------|
| | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0) | 466 | 166 | 453 | 207 |
| (0,1,0,0,0) | 576 | 44 | 569 | 40 |
| (2,0,0,0,0) | 899 | 4 | 875 | 1 |
| (0,2,0,0,0) | 1145 | 16 | 1130 | 20 |
| (0,0,1,0,0) | 1212 | 94 | 1210 | 106 |
| (3,0,0,0,0) | 1306 | 100 | 1275 | 45 |
| (0,0,2,0,0) | 2516 | 7 | 2493 | 7 |
| (0,0,0,1,0) | 1616 | 81 | 1623 | 96 |
| (0,1,0,1,0) | 2176 | 37 | 2176 | 47 |
| (0,0,0,1,0) | 1428 | 2334 | 1476 | 2732 |
| (1,0,0,1,0) | 1974 | 40 | 2022 | 23 |
| (0,1,0,1,0) | 2027 | 49 | 2042 | 27 |
| (0,0,1,1,0) | 2600 | 35 | 2602 | 29 |
| (0,0,0,2,0) | 3235 | 3 | 3201 | 3 |
| (0,0,0,2,0) | 2942 | 32 | 2970 | 43 |
| (0,0,0,1,1,0) | 2973 | 19 | 3018 | 45 |
| (0,0,0,0,1) | 3756 | 2 | 3755 | 1 |

Table S15. The Calculated peak position, in cm^{-1} , and absorption intensity, in km mol^{-1} , of $\text{Ar.Cl}^-\text{H}_2\text{O}$, $\text{Ar.Cl}^-\text{HOD}$, $\text{Ar.Cl}^-\text{DOH}$ Lin conformer obtained using B3LYP/6-31+G(d,p). The quantum numbers in the Assignment correspond to ($X \dots \text{H}_2\text{O}$ VDW stretching, H_2O in-plane wagging, H_2O out-of-plane OH wagging, H_2O bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.Cl ⁻ H ₂ O Lin | | Ar.Cl ⁻ HOD Lin | | Ar.Cl ⁻ DOH Lin | |
|---------------|---|-----------|----------------------------|-----------|----------------------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0,0) | 189 | 27 | 177 | 26 | 176 | 22 |
| (0,1,0,0,0,0) | 338 | 44 | 248 | 39 | 264 | 50 |
| (2,0,0,0,0,0) | 372 | 0 | 349 | 0 | 347 | 0 |
| (0,2,0,0,0,0) | 551 | 0 | 471 | 5 | 489 | 6 |
| (0,0,1,0,0,0) | 711 | 63 | 702 | 107 | 518 | 99 |
| (3,0,0,0,0,0) | 519 | 0 | 516 | 0 | 513 | 0 |
| (0,0,2,0,0,0) | 1375 | 70 | 1348 | 77 | 1016 | 28 |
| (0,0,0,1,0,0) | 1610 | 70 | 1467 | 64 | 1370 | 92 |
| (0,1,0,1,0,0) | 1913 | 21 | 1692 | 11 | 1636 | 16 |
| (0,0,0,0,1,0) | 3031 | 1063 | 3089 | 334 | 2309 | 545 |
| (1,0,0,0,1,0) | 3202 | 19 | 3261 | 14 | 2499 | 12 |
| (0,0,0,2,0,0) | 3244 | 65 | 2904 | 62 | 2717 | 1 |
| (0,0,0,0,0,1) | 3688 | 10 | 2710 | 9 | 3701 | 6 |

Table S16. The Calculated peak position, in cm^{-1} , and absorption intensity, in km mol^{-1} , of Ar.Br⁻H₂O, Ar.Br⁻HOD, Ar.Br⁻DOH conformer 2 obtained using B3LYP/6-31+G(d,p). The quantum numbers in the Assignment correspond to (X⁻...H₂O VDW stretching, H₂O in-plane wagging, H₂O out-of-plane OH wagging, H₂O bending, IHB OH stretching, free OH stretching).

| Assignment | Ar.Br ⁻ H ₂ O Out | | Ar.Br ⁻ HOD Out | | Ar.Br ⁻ DOH Out | |
|---------------|---|-----------|----------------------------|-----------|----------------------------|-----------|
| | Peak position | Intensity | Peak position | Intensity | Peak position | Intensity |
| (1,0,0,0,0,0) | 146 | 7 | 140 | 10 | 141 | 8 |
| (0,1,0,0,0,0) | 270 | 42 | 242 | 36 | 253 | 44 |
| (2,0,0,0,0,0) | 288 | 1 | 280 | 0 | 280 | 0 |
| (0,2,0,0,0,0) | 499 | 9 | 462 | 5 | 464 | 6 |
| (0,0,1,0,0,0) | 625 | 60 | 666 | 87 | 495 | 82 |
| (3,0,0,0,0,0) | 428 | 0 | 417 | 0 | 417 | 0 |
| (0,0,2,0,0,0) | 1214 | 50 | 1279 | 65 | 966 | 26 |
| (0,0,0,1,0,0) | 1606 | 97 | 1447 | 30 | 1369 | 99 |
| (0,1,0,1,0,0) | 1872 | 23 | 1705 | 7 | 1623 | 16 |
| (0,0,0,0,1,0) | 3150 | 354 | 3189 | 455 | 2362 | 495 |
| (1,0,0,0,1,0) | 3307 | 27 | 3341 | 34 | 2511 | 16 |
| (0,0,0,2,0,0) | 3211 | 388 | 2884 | 28 | 2717 | 2 |
| (1,0,0,2,0,0) | 3365 | 16 | 3102 | 17 | 2872 | 0 |
| (0,0,0,0,0,1) | 3679 | 8 | 2707 | 8 | 3725 | 7 |

XYZ geometries

Below are the optimized geometries for the Ar.X-H₂O (X=F, Cl, and Br) obtained at MP2/6-311+G(3df,3pd) level of theory. Unit: Angstrom.

F-H₂O

| | | | |
|---|--------|--------|-------|
| O | -1.189 | -0.107 | 0.000 |
| H | -0.123 | -0.079 | 0.000 |
| H | -1.409 | 0.825 | 0.000 |
| F | 1.227 | 0.012 | 0.000 |

F-H₂O Perp

| | | | |
|----|--------|--------|-------|
| O | -1.510 | -1.153 | 0.000 |
| H | -2.456 | -1.300 | 0.000 |
| H | -1.452 | -0.087 | 0.000 |
| F | -1.413 | 1.262 | 0.000 |
| Ar | 1.595 | -0.042 | 0.000 |

F-H₂O Lin

| | | | |
|----|--------|--------|-------|
| O | -3.303 | -0.062 | 0.000 |
| H | -3.474 | 0.880 | 0.000 |
| H | -2.242 | -0.091 | 0.000 |
| F | -0.878 | -0.067 | 0.000 |
| Ar | 2.225 | 0.017 | 0.000 |

Cl-H₂O

| | | | |
|----|--------|--------|-------|
| O | 0.031 | 1.981 | 0.000 |
| H | 0.163 | 1.003 | 0.000 |
| H | -0.926 | 2.028 | 0.000 |
| Cl | 0.031 | -1.111 | 0.000 |

Ar.Cl-H₂O Perp

| | | | |
|----|--------|--------|--------|
| O | -0.602 | 0.230 | -1.974 |
| H | 0.087 | -0.020 | -1.305 |
| H | -0.790 | 1.143 | -1.727 |
| Cl | 1.516 | -0.037 | 0.339 |
| Ar | -1.200 | -2.573 | -4.089 |

Ar.Cl-H₂O Lin

| | | | |
|---|--------|-------|-------|
| O | 0.043 | 3.881 | 0.000 |
| H | -0.116 | 2.902 | 0.000 |
| H | 1.007 | 3.920 | 0.000 |

| | | | |
|----|--------|--------|-------|
| Cl | 0.128 | 0.728 | 0.000 |
| Ar | -0.181 | -3.497 | 0.000 |

BrH₂O

| | | | |
|----|--------|--------|-------|
| O | 0.017 | 2.588 | 0.000 |
| H | 0.193 | 1.623 | 0.000 |
| H | -0.941 | 2.590 | 0.000 |
| Br | 0.017 | -0.712 | 0.000 |

Ar.BrH₂O Perp

| | | | |
|----|--------|--------|--------|
| O | -0.876 | 1.245 | -1.775 |
| H | -0.302 | 0.490 | -1.495 |
| H | -0.628 | 1.929 | -1.141 |
| Ar | -0.371 | -3.985 | -3.847 |
| Br | 1.264 | -0.931 | -0.406 |

Ar.BrH₂O Out

| | | | |
|----|--------|--------|--------|
| O | 0.182 | 1.036 | -2.418 |
| H | 0.475 | 0.430 | -1.695 |
| H | -0.519 | 1.539 | -1.986 |
| Ar | -2.795 | -3.612 | -1.406 |
| Br | 0.733 | -0.741 | 0.361 |

Reference

- 1 P. Ayotte, J. A. Kelley, S. B. Nielsen and M. A. Johnson, *Chem. Phys. Lett.*, 2000, **316**, 455–459.
- 2 S. Horvath, A. B. McCoy, B. M. Elliott, G. H. Weddle, J. R. Roscioli and M. A. Johnson, *J. Phys. Chem. A*, 2010, **114**, 1556–1568.