Electronic Supplementary Information for PCCP

Deciphering the Infrared Spectrum of the Protonated Water Pentamer and the Hybrid Eigen-Zundel Cation

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(Dated: September 23, 2013)

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This PDF file includes:

Figs. S1 to S18

Tables S1 to S6

References

Other Electronic Supplementary Material for this manuscript includes the following:

Movies E1_50K, E1_150K, and EZ_50K

E1

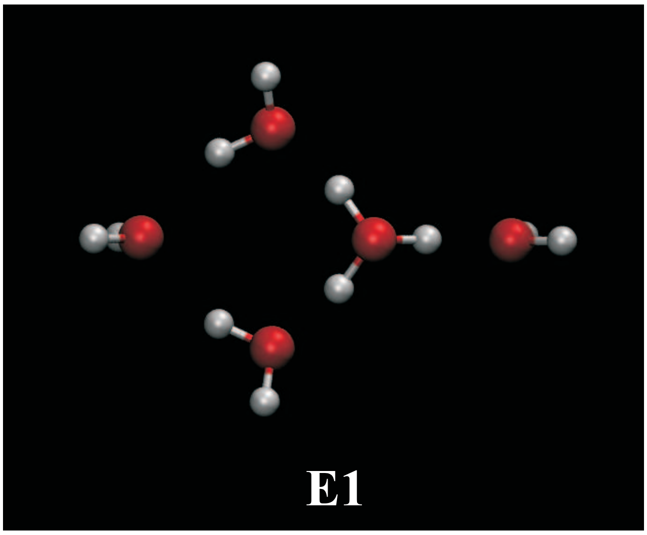

FIG. S1: Optimized structure of the E1 isomer of $H_{11}O_5^+$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S1 below.

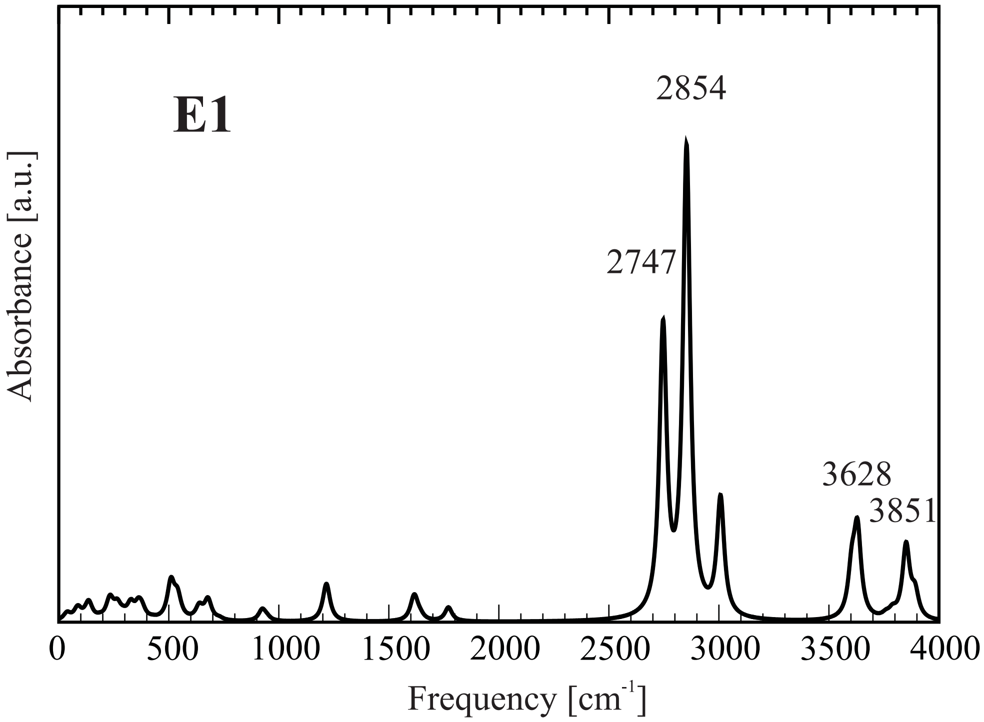

FIG. S2: Static IR spectrum of the E1 isomer of $H_{11}O_5^+$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

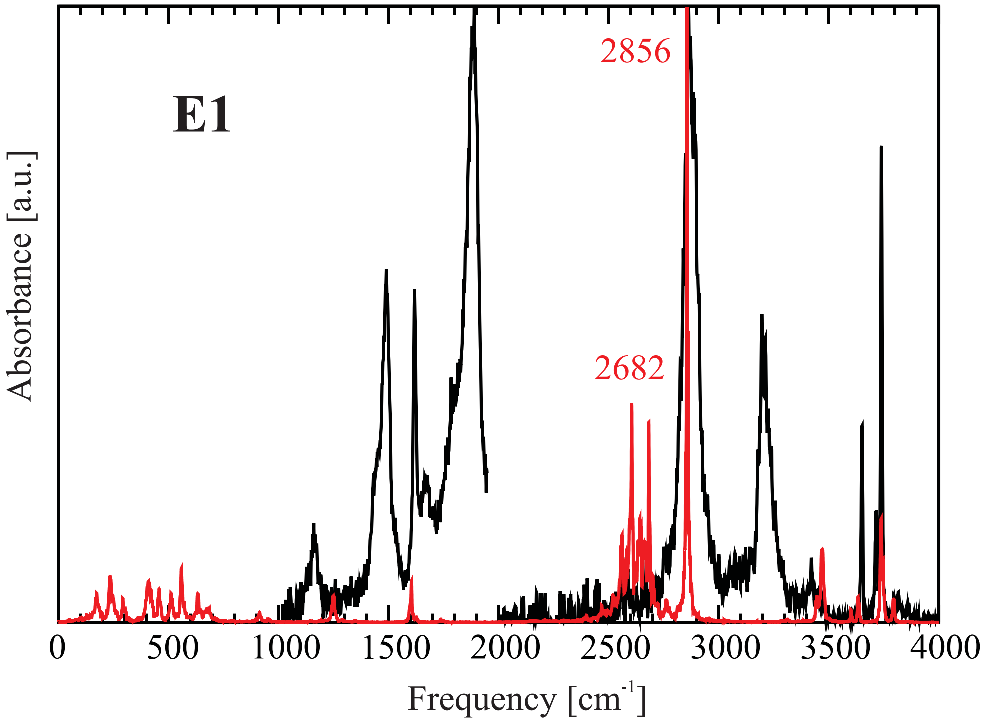

FIG. S3: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the E1 isomer of the $H_{11}O_5^+$ cation. Theoretical spectrum was calculated from a 28 ps CP2K AIMD simulation at 50 K.

E2

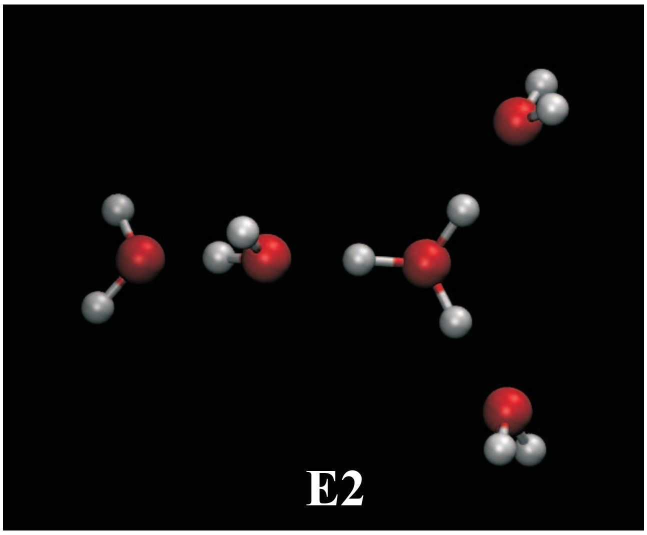

FIG. S4: Optimized structure of the E2 isomer of $H_{11}O_5^+$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S2 below.

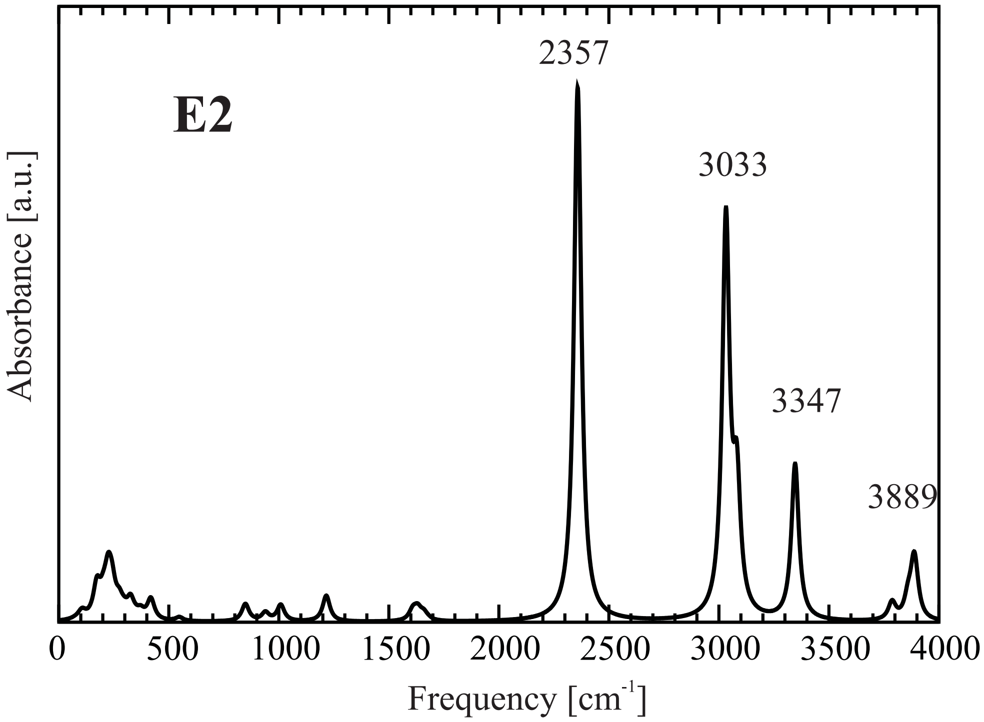

FIG. S5: Static IR spectrum of the E2 isomer of $H_{11}O_5^+$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

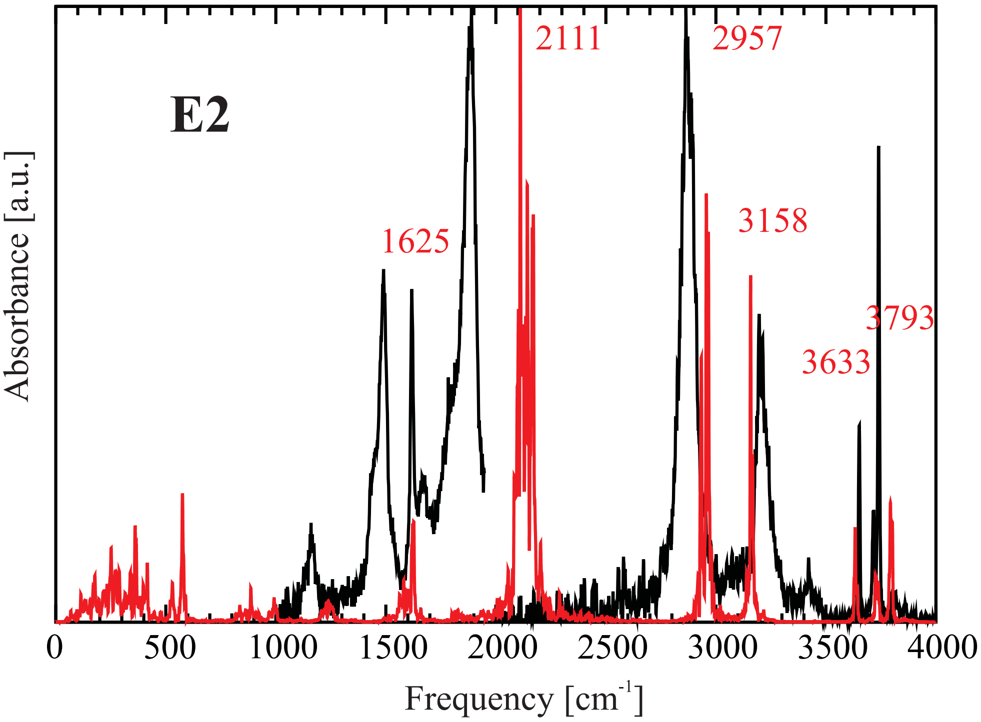

FIG. S6: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the E2 isomer of the $H_{11}O_5^+$ cation. Theoretical spectrum was calculated from a 10 ps CP2K AIMD simulation at 50 K.

E-Z

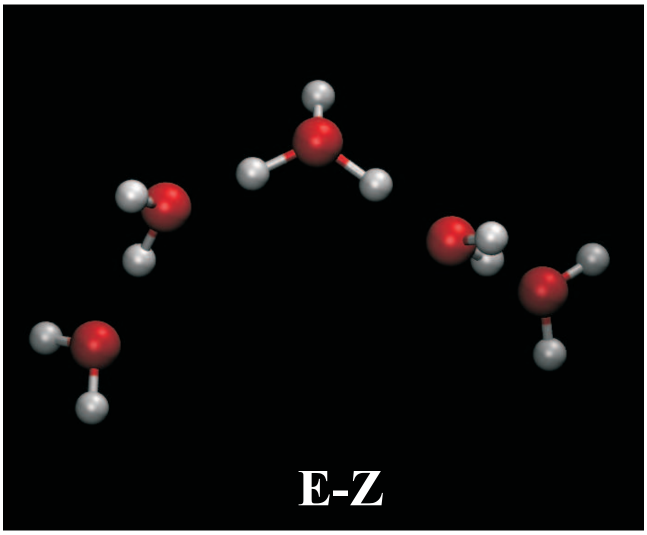

FIG. S7: Optimized structure of the E-Z isomer of $H_{11}O_5^+$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S3 below.

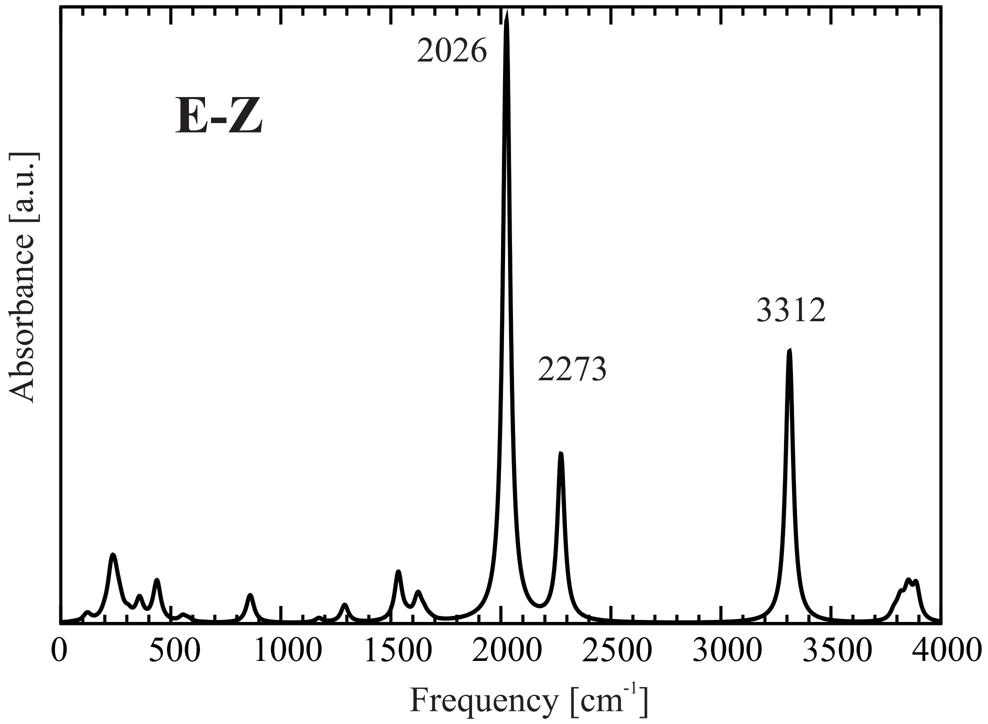

FIG. S8: Static IR spectrum of the E-Z isomer of $H_{11}O_5^+$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

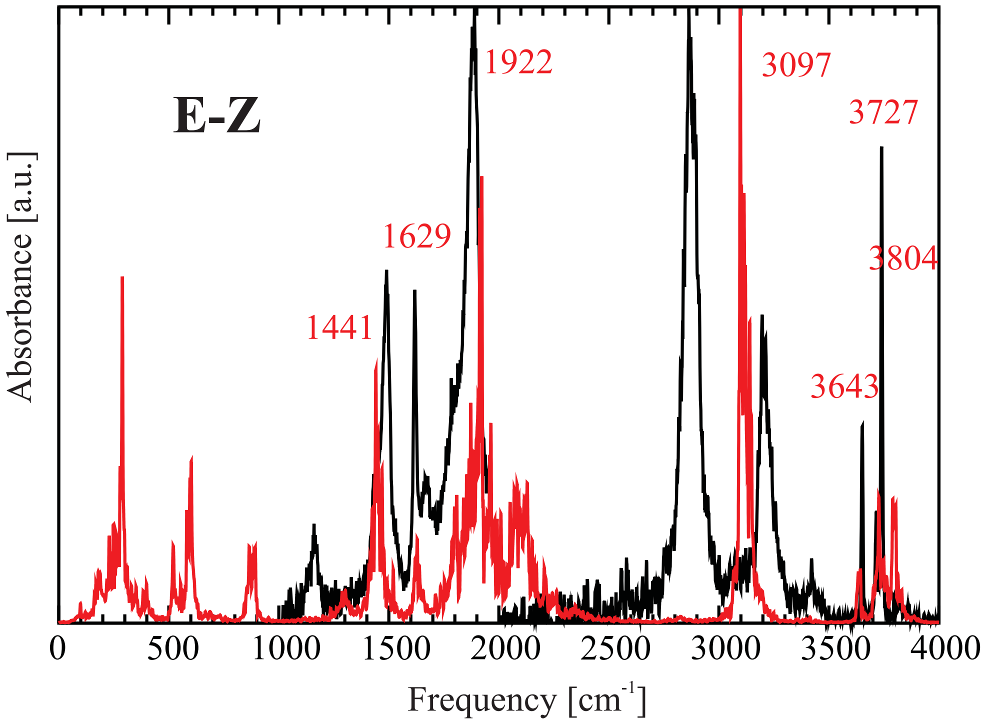

FIG. S9: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the E-Z isomer of the $H_{11}O_5^+$ cation. Theoretical spectrum was calculated from a 28 ps CP2K AIMD simulation at 50 K.

E-Z · 1Ar

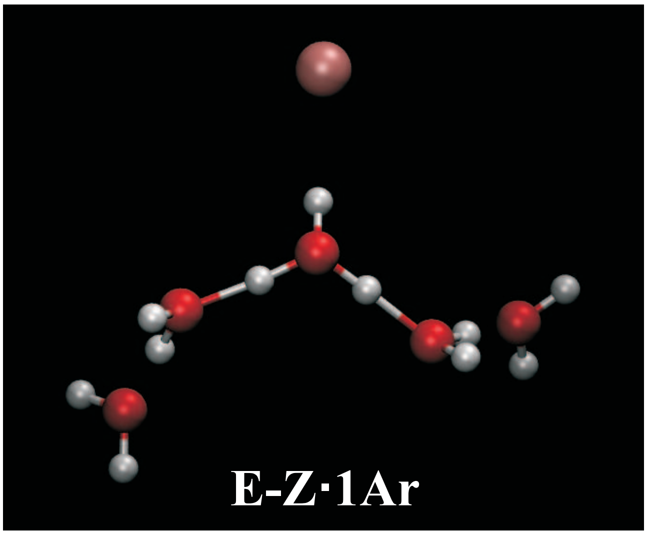

FIG. S10: Optimized structure of the E-Z · 1Ar isomer of $H_{11}O_5^+ \cdot 1Ar$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S4 below.

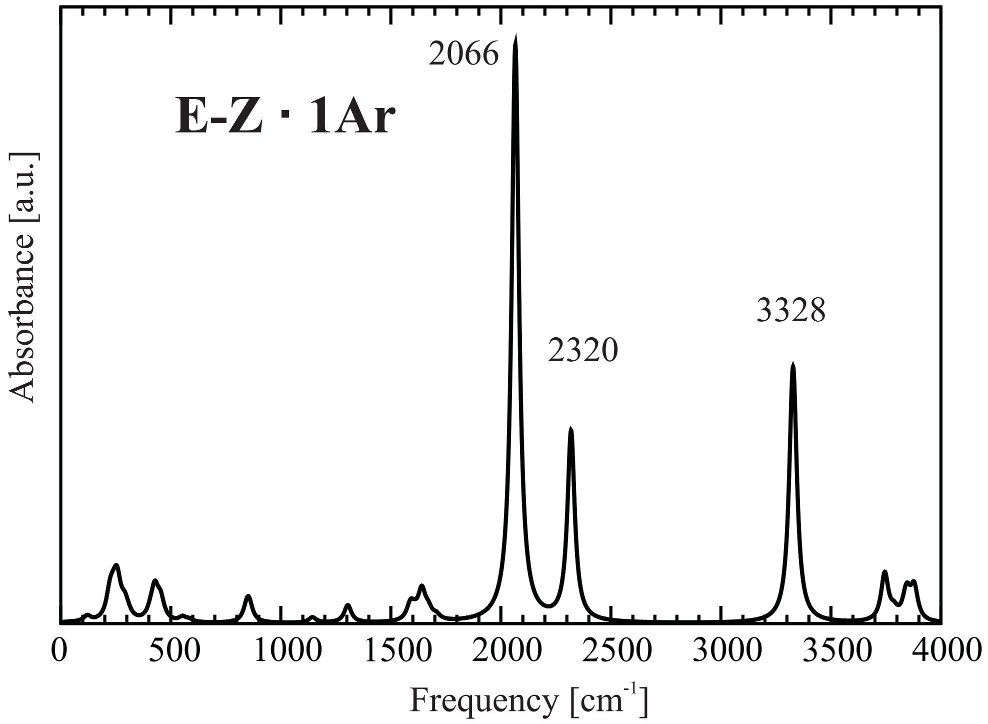

FIG. S11: Static IR spectrum of the E-Z · 1Ar isomer of $H_{11}O_5^+ \cdot 1Ar$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

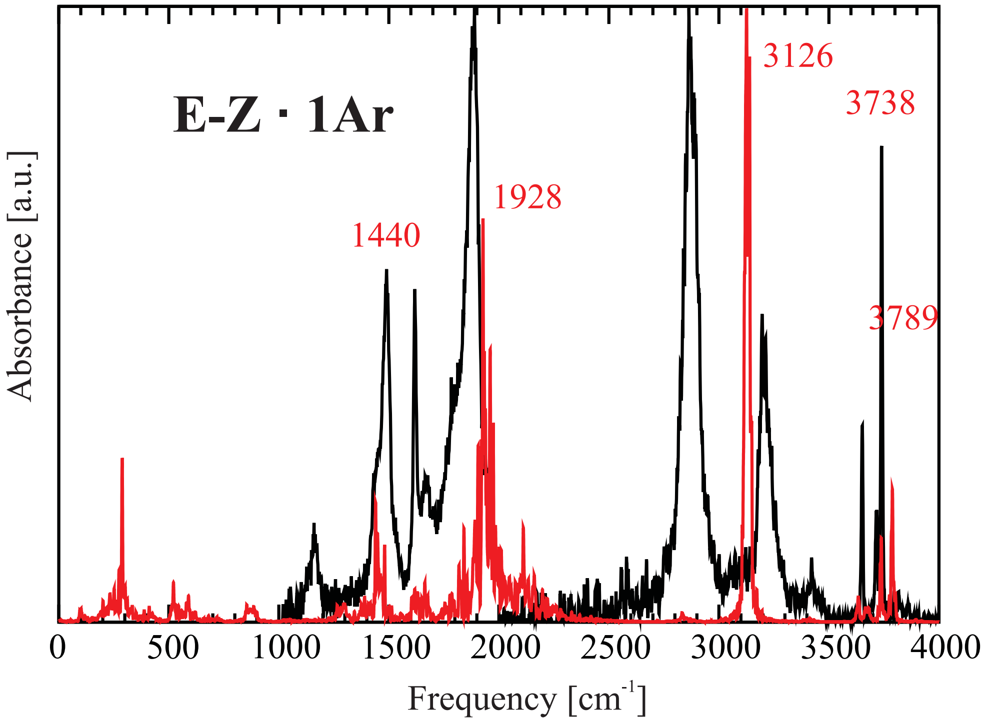

FIG. S12: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the E-Z · 1Ar isomer of the $H_{11}O_5^+ \cdot 1Ar$ cation. Theoretical spectrum was calculated from a 10 ps CP2K AIMD simulation at 50 K.

Z1

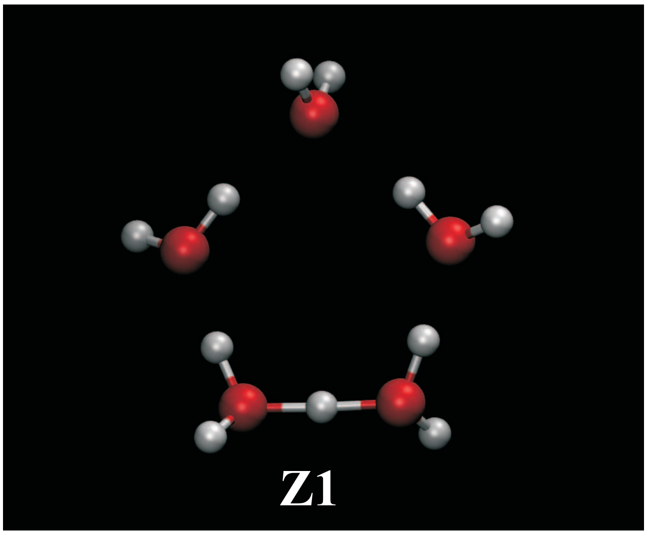

FIG. S13: Optimized structure of the Z1 isomer of $H_{11}O_5^+$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S5 below.

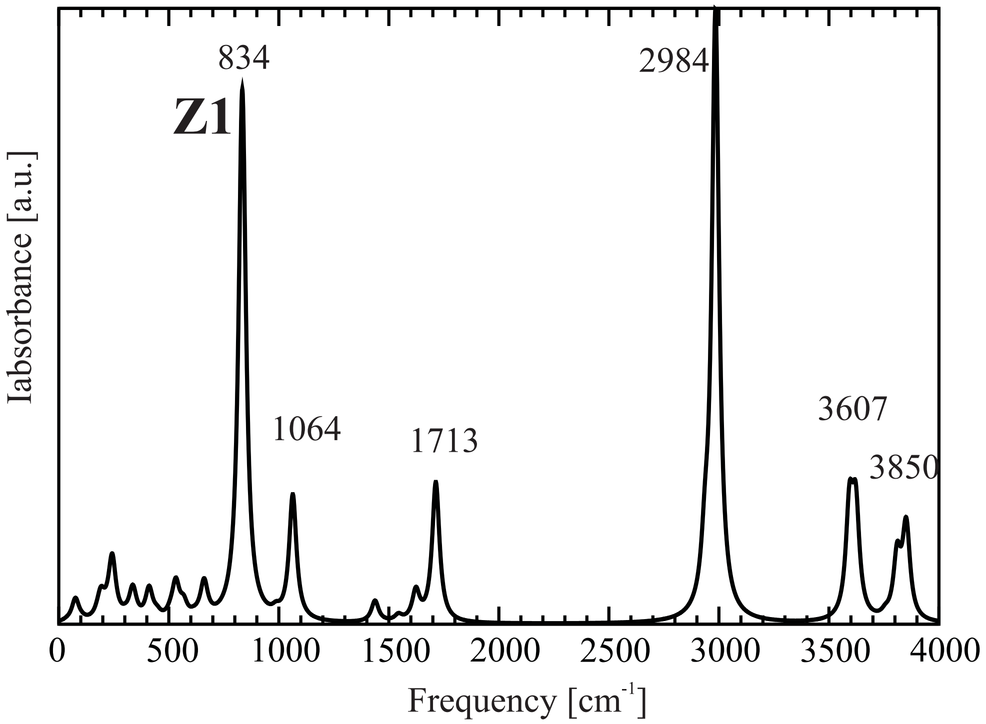

FIG. S14: Static IR spectrum of the Z1 isomer of $H_{11}O_5^+$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

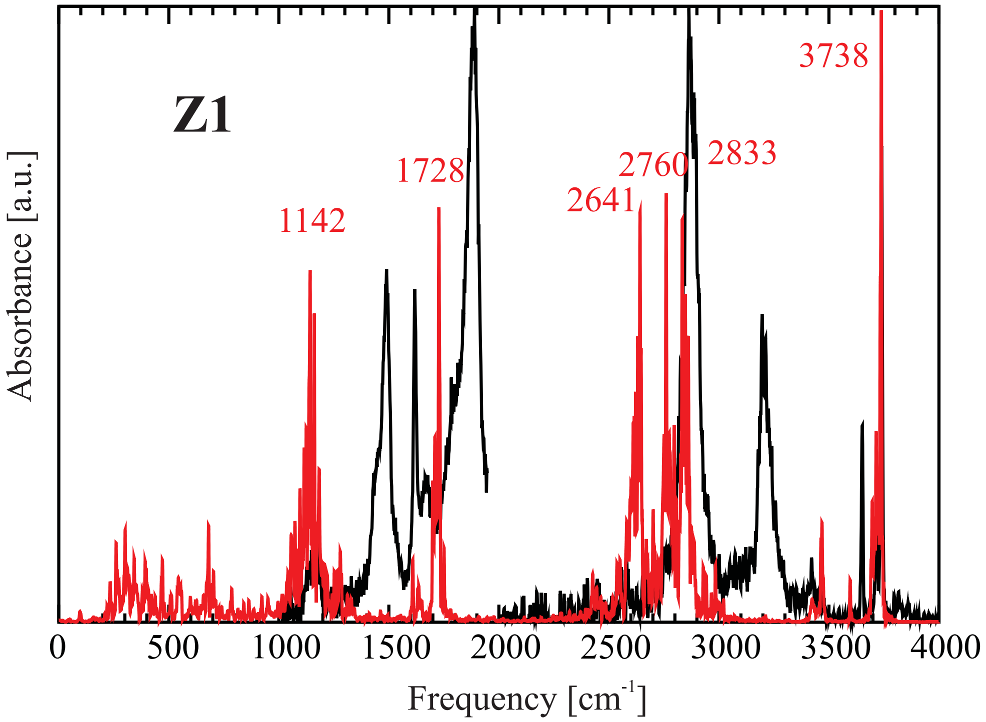

FIG. S15: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the Z1 isomer of the $H_{11}O_5^+$ cation. Theoretical spectrum was calculated from a 10 ps CP2K AIMD simulation at 50 K.

Z1 · 2Ar

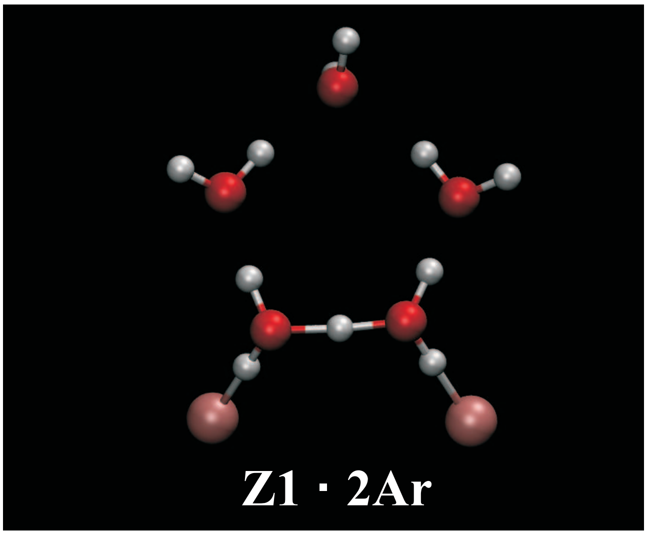

FIG. S16: Optimized structure of the Z1 · 2Ar isomer of $H_{11}O_5^+ \cdot 2Ar$ cation calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09. Atomic coordinates are given in Table S6 below.

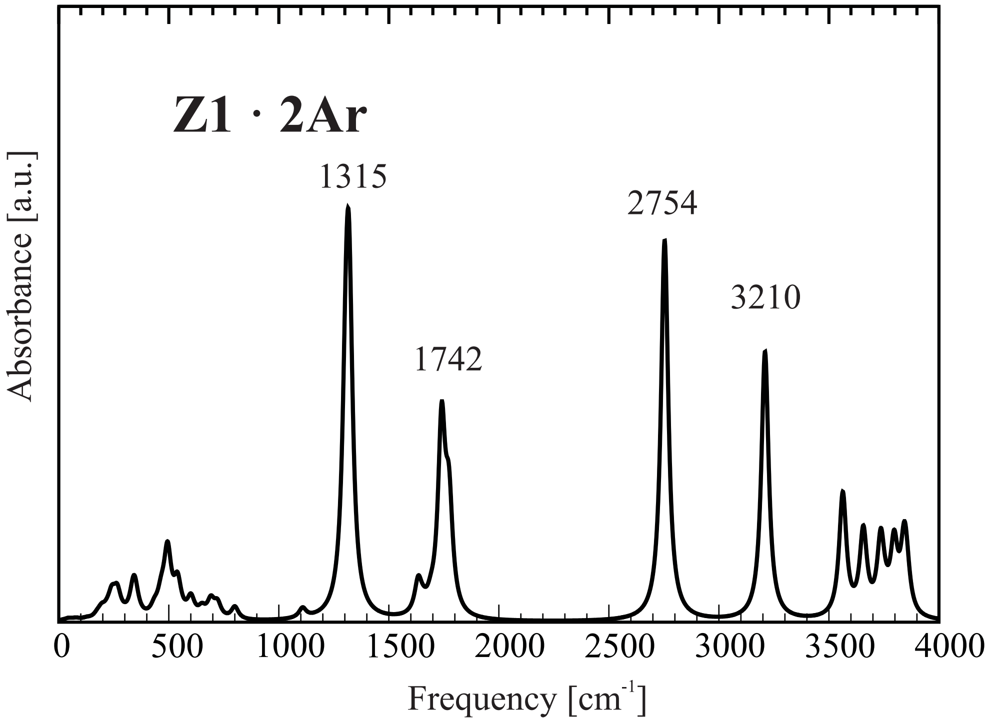

FIG. S17: Static IR spectrum of the Z1 · 2Ar isomer of $H_{11}O_5^+ \cdot 2Ar$ cation calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

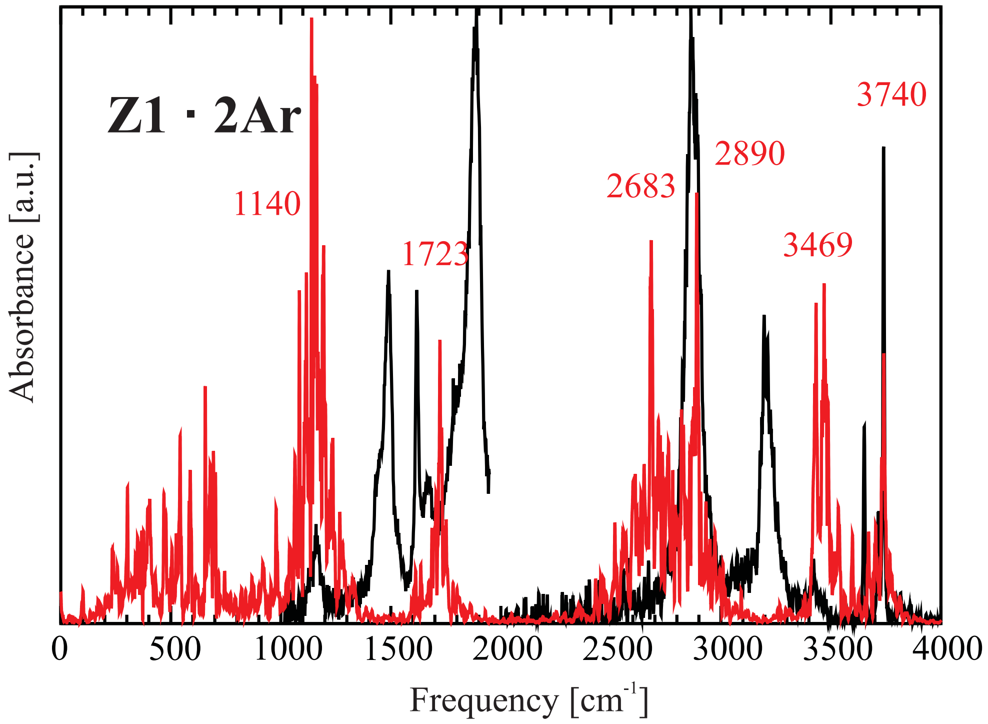

FIG. S18: Comparison between the (dynamic) theoretical (red) and experimental[1] (black) IR spectra of the Z1 · 2Ar isomer of the $H_{11}O_5^+ \cdot 2Ar$ cation. Theoretical spectrum was calculated from a 10 ps CP2K AIMD simulation at 50 K.

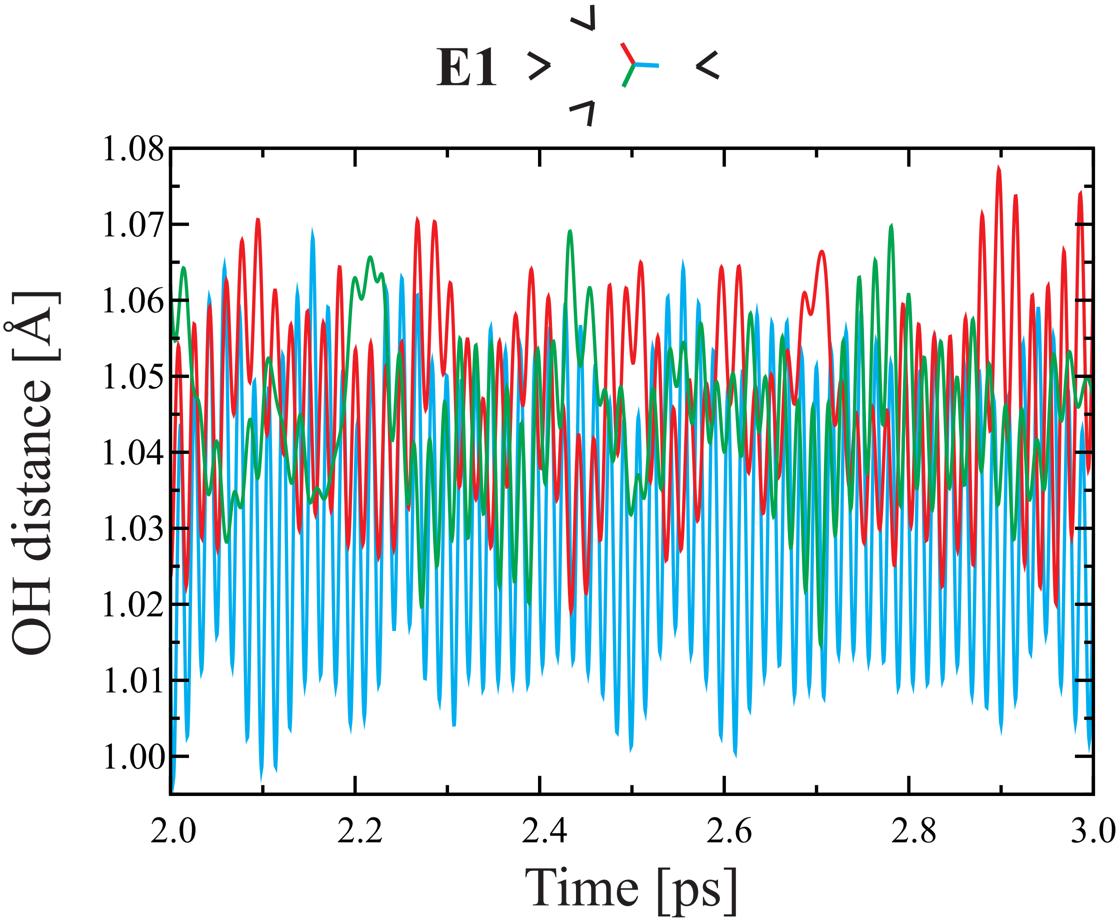

FIG. S19: OH distances of the hydronium core from a 1 ps segment of our CP2K trajectory of the E1 isomer at 50 K. The dynamics of these three OH distances of the H_3O^+ core are similar to those of the bare hydronium, indicating an E-like character of this isomer. Note that these OH distances are slightly longer than in bare hydronium, due to the presence of the hydrogen bonds.

TABLE S1: Cartesian coordinates of the local minimum of the E1 of $H_{11}O_5^+$ shown in Fig. S1, calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

16

E1 isomer, E = -240110.088 kcal/mol

O	0.685240	1.824101	-0.096417
H	1.559200	1.411664	0.039634
H	0.822156	2.693634	-0.492626
O	0.648722	-1.815520	-0.095391
H	1.531694	-1.422036	0.039291
H	0.765467	-2.690152	-0.486716
O	-3.302621	0.014673	0.449492
H	-4.133177	0.031634	-0.043041
H	-3.523698	0.077819	1.387097
O	2.834521	-0.021980	0.378637
H	3.622759	-0.031751	-0.183223
H	3.174967	-0.027739	1.285110
O	-1.005247	0.019847	-0.707049
H	-0.422971	0.832742	-0.499208
H	-0.437809	-0.803974	-0.498630
H	-1.886691	0.026672	-0.211362

TABLE S2: Cartesian coordinates of the local minimum of the E2 isomer of $H_{11}O_5^+$ shown in Fig. S4, calculated at B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

16

E2 isomer, E = -240110.045 kcal/mol

O	-2.083482	2.235848	-0.053275
H	-2.236682	2.809243	-0.815574
H	-2.166950	2.790431	0.732996
O	-2.248477	-2.109136	-0.121417
H	-2.422568	-2.660076	-0.895663
H	-2.945582	-2.300925	0.518857
O	-0.775258	0.014398	-0.288520
H	-1.261541	0.886249	-0.158499
H	-1.375872	-0.787531	-0.195219
O	3.702193	-0.064742	-0.472039
H	4.148192	-0.811710	-0.890165
H	4.351640	0.648066	-0.425693
O	1.406024	-0.076262	0.887978
H	1.549219	-0.475952	1.753647
H	2.263175	-0.098027	0.392580
H	0.133552	-0.056416	0.230914

TABLE S3: Cartesian coordinates of the local minimum of the E-Z isomer of the $H_{11}O_5^+$ cation shown in Fig. S7, calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

16

E-Z isomer, E = -240106.969 kcal/mol

O	0.000818	-1.613090	-0.399777
H	-0.830664	-1.142143	0.072809
H	-0.144425	-1.767786	-1.343329
H	0.977012	-1.228835	-0.202704
O	2.286301	-0.829836	0.021730
O	-1.893371	-0.563861	0.766443
H	2.902754	-1.399092	0.497232
H	2.628278	0.101276	0.034737
H	-2.356076	-1.079817	1.438014
H	-2.535113	0.079355	0.368032
O	3.171440	1.675050	-0.026572
O	-3.547230	1.204043	-0.337844
H	3.787609	1.986021	-0.702245
H	3.300396	2.248357	0.739676
H	-3.656598	2.099953	0.005799
H	-4.355437	1.003430	-0.826914

TABLE S4: Cartesian coordinates of the local minimum of the E-Z · 1Ar isomer of the $H_{11}O_5^+ \cdot 1Ar$ cation shown in Fig. S10, calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

17

E-Z · 1Ar isomer, E = -571147.993 kcal/mol

O	0.002357	-1.564603	-0.381926
O	2.305985	-0.862442	0.117417
O	-1.878789	-0.496166	0.805217
O	3.313027	1.600765	0.053083
O	-3.609319	1.132777	-0.406334
H	-0.813857	-1.091154	0.103900
H	-0.135210	-1.642870	-1.338757
H	0.978534	-1.218012	-0.152203
H	2.902967	-1.461788	0.580177
H	2.693192	0.049760	0.123744
H	-2.318744	-0.993765	1.505314
H	-2.549723	0.094346	0.376331
H	3.960552	1.877006	-0.608079
H	3.441074	2.181277	0.813998
H	-3.730698	2.051962	-0.135955
H	-4.432092	0.870315	-0.838434
Ar	-0.594466	-1.773200	-3.742681

TABLE S5: Cartesian coordinates of the local minimum of Z1 isomer of the $H_{11}O_5^+$ cation shown in Fig. S13, calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

16

Z1 isomer, E = -240106.982 kcal/mol

O	2.301249	-4.270640	-4.940629
O	4.000372	-5.587913	-3.524721
O	6.166513	-4.561205	-3.716656
O	5.927515	-2.270279	-4.866719
O	3.315236	-1.782898	-5.960568
H	3.343034	-1.660595	-6.920811
H	3.296238	-5.105484	-4.069351
H	1.579981	-4.668145	-5.443564
H	6.441000	-1.485389	-4.639827
H	5.072922	-1.974455	-5.233556
H	6.847349	-5.101180	-4.142347
H	6.123587	-3.652555	-4.161093
H	2.547407	-3.433918	-5.378497
H	2.814520	-1.024466	-5.626119
H	3.680895	-5.719944	-2.620949
H	5.091820	-5.090731	-3.609282

TABLE S6: Cartesian coordinates of the local minimum of the Z1 · 2Ar isomer of the $H_9O_4^+ \cdot 2Ar$ cation shown in Fig. S16, calculated at the B3LYP/aug-cc-pVTZ level of theory using Gaussian 09.

18

Z1 · 2Ar isomer, E = -902274.398 kcal/mol

O	2.479048	-4.404289	-4.956741
O	3.976082	-4.893742	-2.850595
O	6.229569	-4.323375	-3.522556
O	6.004760	-2.251866	-4.983090
O	3.364246	-1.803147	-5.953546
H	3.347328	-1.735958	-6.916881
H	3.313283	-4.799524	-3.587254
H	1.583800	-4.693686	-5.158681
H	6.516555	-1.453340	-4.817701
H	5.124279	-1.987936	-5.310340
H	6.743196	-5.011294	-3.971011
H	6.174221	-3.482385	-4.103588
H	2.591322	-3.515372	-5.330628
H	2.883394	-1.029552	-5.633053
H	3.764087	-5.653595	-2.295423
H	5.211631	-4.661634	-3.206554
Ar	3.258079	-7.577592	-0.708784
Ar	8.181844	-6.752319	-4.955831

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[1] J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765–1769.