PCCP



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Supporting Information:

Quantum Molecular Motion in the Mixed Ion-Radical Complex, $[(H_2O)(H_2S)]^+$

S. D. Floris,^{a,b} J. J. Talbot,^b M. J. Wilkinson,^b J.D. Herr,^b and R. P. Steele^b



Fig. S1. Comparison of harmonic spectra (left) and bond distributions (right) from the CCSD and MPW1K methods for the PT_0 isomer. Colors are consistent in the two plots



Fig. S2. Potential energy scan along the proton-stretch normal mode of the PTO isomer, using CCSD and MPW1K. For the latter, two basis sets were considered, the results of which nearly overlap in the plot.

2.2 2.4 2.6

^{a.} Current: Dept of Chemistry, University of Washington, Seattle, WA, USA. ^{b.} Department of Chemistry and Henry Eyring Center for Theoretical Chemistry,

University of Utah, Salt Lake City, UT, USA.

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Fig. S3. Histogrammed distribution of the *S*-*O*-*H*⁺ H-bond angle from PIMD (300K) simulations with MPW1K/6-31++G(d,p). Analogous results for the water dimer cation are also shown.

Method	Basis -	ΔE_e , relative to PT ₀	
		PTs	HB
BLYP	6-31G**	36.52	-1.70
	6-31++G**	36.60	-2.02
	cc-pVDZ	35.08	-1.49
	cc-pVTZ	36.26	-2.38
	cc-pVQZ	36.02	-2.69
	aug-cc-pVDZ	36.74	-1.72
	aug-cc-pVTZ	36.00	-2.58
	aug-cc-pVQZ	35.88	-2.77
B3LYP	6-31G**	36.42	1.60
	6-31++G**	36.03	0.92
	cc-pVDZ	34.84	1.69
	cc-pVTZ	35.80	0.71
	cc-pVQZ	35.43	0.27
	aug-cc-pVDZ	36.24	1.23
	aug-cc-pVTZ	35.50	0.45
	aug-cc-pVQZ	35.30	0.19
B97M-V	6-31G**	34.07	-0.47
	6-31++G**	33.45	-0.94
	cc-pVDZ	31.86	-0.82
	cc-pVTZ	33.49	-0.44
	cc-pVQZ	32.63	-1.20
	aug-cc-pVDZ	32.72	-0.91
	aug-cc-pVTZ	33.18	-0.69
	aug-cc-pVQZ	32.48	-1.30

Table S1. Additional density functional theory relative energies for the three stable isomers of $(H_2 O)(H_2 S)^+$. Note that the HB relative energy is severely underestimated in each method, with both BLYP and B97M-V incorrectly predicting the sign of the energy of the HB isomer.