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SUPPLEMENTARY MATERIAL

Evidence For a Water-Stabilised Ion Radical Complex: Photoelectron Spectroscopy and *Ab Initio* Calculations

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The supporting information presented here comprises results of *ab initio* calculations performed on the $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex. Included are the structure, energies, vibrational data, and cartesian coordinates predicted at the MP2 and CCSD(T) levels of theory, with aug-cc-pVDZ, TZ, and QZ basis sets. The aug-cc-pVXZ PP basis sets were used for iodine. Collectively, these basis sets will be referred to as AVXZ.

1 Structure and Energetics

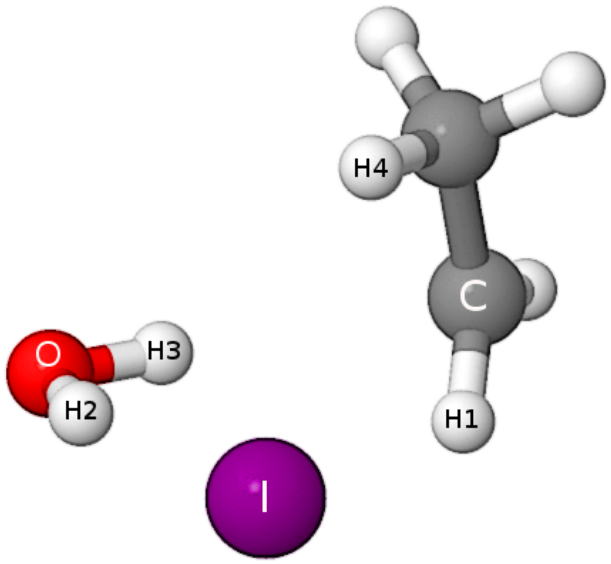

Figure S1: Schematic of the C_1 $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex at the MP2/AVQZ level of theory.

Table S1: Structural parameters of the C_1 $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex predicted from MP2/AVQZ calculations.

r(I···H1) [Å]	∠(I···H1−C) [°]	r(I···H4) [Å]	r(I···H2) [Å]	∠(I···H2−O) [°]	r(I···C) [Å]	r(C···H3) [Å]	∠(C···H3−O) [°]	r(O−H2) [Å]	r(O−H3) [Å]	∠(H2−O−H3) [°]	r(C−H1) [Å]
3.198	125.1	3.042	2.579	161.7	3.919	2.510	152.9	0.976	0.961	100.9	1.079

Table S2: Energies of the bare iodide anion and iodine radical determined from CCSD(T) calculations.

		$E_{(CCSD(T))}$ $[E_h]$	VDE [eV]	Experimental SO* [eV]	Split [eV]	Literature $^2P_{3/2}$ VDE † [eV]	Shift ‡ [eV]
I^- | I	AVDZ	-294.8832577 | -294.7690618	3.107		2.793 | 3.735		+0.266
	AVTZ	-294.9822875 | -294.8654128	3.180		2.866 | 3.808		+0.193
	AVQZ	-295.0612422 | -294.9399753	3.300		2.986 | 3.928		+0.073
	CBS	-295.1101156 | -294.9859544	3.379	-0.314 | +0.628	3.065 | 4.007	3.059	-0.006

* Values from http://www.nist.gov/pml/data/handbook/index.cfm

† Values from http://webbook.nist.gov

‡ Shift refers to the difference between the predicted and literature Electron Detachment Energy

Table S3: Energies of the C_1 $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex and neutral triplet counterpart predicted from CCSD(T) calculations.

		$Anion_{(CCSD(T))}$ $[E_h]$	$Triplet_{(CCSD(T))}$ $[E_h]$	zpe [kJ mol^{-1}]	VDE† [eV]
$I^-\cdots H_2O\cdots CH_3CH_2$	AVDZ	-450.1147176	-449.9792055		
	AVTZ	-450.3608651	-450.2225428		
	AVQZ	-450.4802765	-450.3378633	223.0*	
	CBS	-450.5522276	-450.4073746		3.59 | 4.53

* MP2/AVQZ value

† Determined using CCSD(T)/CBS energies and MP2/AVQZ zpe

2 Vibrational Data

Table S4: Vibrational frequencies for the C_1 $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex from MP2/AVQZ calculations. Frequencies in cm^{-1}, zero point energies (zpe) in kJ mol^{-1}. All mode symmetries are a.

	$I^-\cdots H_2O\cdots CH_3CH_2$
ω_1	3855
ω_2	3572
ω_3	3302
ω_4	3181
ω_5	3150
ω_6	3090
ω_7	3014
ω_8	1664
ω_9	1502
ω_{10}	1491
ω_{11}	1473
ω_{12}	1403
ω_{13}	1208
ω_{14}	1089
ω_{15}	994
ω_{16}	824
ω_{17}	602
ω_{18}	516
ω_{19}	331
ω_{20}	268
ω_{21}	233
ω_{22}	139
ω_{23}	98
ω_{24}	87
ω_{25}	85
ω_{26}	67
ω_{27}	39
zpe	223.0

3 Cartesian Coordinates

Table S5: Cartesian coordinates of the geometry of the $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex optimised at MP2/AVQZ, in Å.

		$I^-\cdots H_2O\cdots CH_3CH_2$		
		x	y	z
	C	-2.645564	-1.025988	-0.641130
	C	-2.699495	-0.634855	0.788895
	H	-1.668661	-0.781082	-1.053586
	H	-3.422253	-0.534866	-1.228752
	H	-2.790976	-2.104988	-0.764038
C_1 Anion	H	-1.777283	-0.515802	1.335625
	H	-3.636352	-0.608740	1.323610
	O	-1.367616	2.347509	-0.135700
	H	-0.546415	1.820972	-0.170869
	H	-1.979436	1.705146	0.235072
	I	1.110050	-0.147088	0.009848