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

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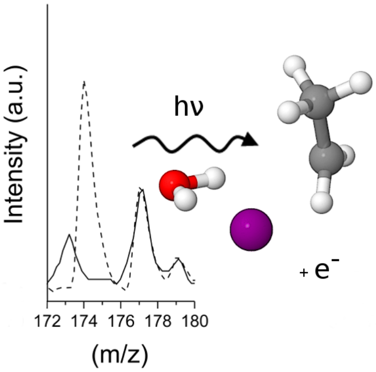
TOC Graphic



Abstract

A photoelectron spectrum corresponding to an unknown 174 m/z anion complex has been recorded. Initially believed to be $I^- \cdots CH_3CH_2OH$ (173 m/z), the spectrum has been assigned as belonging to that of an $I^- \cdots H_2O \cdots CH_3CH_2$ radical anion complex. The major peaks in the photoelectron spectrum occur at 3.54 eV and 4.48 eV as the $^2P_{3/2}$ and $^2P_{1/2}$ spin-orbit states of iodine respectively. *Ab initio* calculations were performed in order to rationalise the existence of the complex, with all structures converging to a 'ring-like' geometry, with the iodide anion bound to both the water molecule as well as a hydrogen of the ethyl radical, with the other hydrogen of water bound to the unpaired electron site of the ethyl. Simulated vertical detachment energies of 3.59 eV and 4.53 eV were found to be in agreement with the experimental results.

Introduction

Complexes formed between radicals and water are key to understanding a number of atmospheric processes, with the nature of this complexation either hindering or aiding reactions within an atmospheric context, especially when considering the strong likelihood of a water complex playing the role of a pre-reaction adduct, or as a catalysing agent in reducing heights of transition state barriers.[1,2] Radical-water complexes, such as RO_2-H_2O,[3,4] methyl-H_2O,[5,6] and pertinent to this work, ethyl-H_2O,[7] have all been investigated along this line of motivation, among others.[8] Being both a hydrogen bond donor and acceptor results in water forming an array of such radical complexes, with stabilities comparable to water-molecule systems. There is also a suggestion that water complexation leads to the stabilisation of metastable molecules such as HO_3.[9]

An important example to highlight is the $HO_2 \cdots H_2O$ radical complex, where computational studies have shown that up to 30% of the total HO_2 concentration under atmospheric conditions can exist as the water-bound form,[10] with further indications that the $HO_2 + HO_2$ self reaction is faster in the presence of water.[11–13] Additionally, it has been noted that large errors are introduced into atmospheric models when the effects of H_2O on HO_2 are not considered.[14] In a general sense, however, there is much to learn about the true role of radical-water complexes in the atmosphere, and so a need exists to characterise these complexes via more spectroscopic means.[1]

Anion photoelectron spectroscopy (PES) is one such technique that can be used to derive fundamental information about the neutral forms of molecules, with recent examples provided here.[15–17] Anion PES can extend to ion-molecule complexes, with notable work conducted in the Johnson lab in studying halide-radical gas phase anion complexes, including the $I^- \cdots CH_3$ and $Cl^- \cdots CCl_3 \cdots nH_2O$ systems, albeit with infrared predissociation spectroscopy for the latter.[18,19] The main caveat of anion PES is the determination of the electron binding energy (eBE) of the complex or species, with higher resolutions allowing for the elucidation of vibrational states of the subsequent neutral.[20]

For ion-molecule and ion-radical complexes, the increase in eBE as compared to that of the bare ion yields structural information in the form of potential bonding motifs, perhaps being that of ion-dipole or ion-induced dipole in nature, for example. With reference to the bare iodide photoelectron spectrum, which features a $^2P_{3/2}$ electron detachment peak of 3.06 eV,[21] the dipole-bound $I^-\cdots H_2O$ complex has a subsequent photoelectron peak occurring at 3.51 eV,[22] while the $I^-\cdots N_2$ $^2P_{3/2}$ peak occurs at 3.07 eV[23]. Thus the stronger ion-dipole interactions lead to a larger stabilisation of the associated negative charge.

In this paper, from serendipitous circumstances, we present the photoelectron spectrum assigned to a gas phase complex formed between an iodide anion, an ethyl radical and a water molecule. The geometry of this $I^-\cdots H_2O\cdots CH_3CH_2$ radical anion complex has been optimised using *ab initio* methods, with simulated CCSD(T) electron detachment energies compared directly to that obtained via experiment.

Surprisingly, ethyl-water radical gas phase complexes have faced little scrutiny within the literature, although the disproportionation and combination reactions of ethyl radicals in the presence of water has been studied,[24] while Hammerum also demonstrated the ability of charged hydrogen bond donors to form moderately strong bonds with various alkyl radical species.[25] There has been, however, an encompassing computational study on the existence of the ethyl-water radical complex, showing that the unpaired electron site of the ethyl radical is bound to a hydrogen of water by 4.81 kJ mol^{-1} (CCSD(T)/CBS), and at a distance of 2.31Å at the CCSD(T)/6-311++G(2df,2p) level of theory.[7] The interaction between the radical site of C_2H_5 and the hydrogen of water also leads to a predicted red shift of the O−H stretches of water, increasing the intensity by up to 25 times that of the unperturbed molecule, suggesting this would be a good 'fingerprint' identification of the complex. Additionally, the stabilising of the ground state leads to a shift in the predicted UV absorption bands to higher energies.

Although the resolution required to discern the experimental existence of the ethyl-water radical complex by its vibrational perturbation is not inherent in this work, a combination of photoelectron spectroscopy, mass spectrometry, and *ab initio* calculations will demonstrate how this system can also undergo complexation with an iodide anion. The fundamental characterisation through these experimental and theoretical means will lead to the assignment of an unidentified 174 m/z peak as belonging to the gas phase $I^- \cdots H_2O \cdots CH_3CH_2$ radical anion complex.

Methods

The mass and photoelectron spectra of this paper were recorded using a Wiley-McLaren style mass spectrometer[26] coupled to a photoelectron spectrometer, whose magnetic-bottleneck design is owed to Cheshnovsky.[27] The apparatus is best described in higher detail in other works.[28] The gas mixture which led to the unidentified 174 m/z peak consisted of small amounts of 99% CH_3CH_2OH and CH_3I, via their vapour pressures, brought up to 400 kPa with Ar. A piezoelectric nozzle was used to pulse the gas mixture into the mass spectrometer, with anions and anion complexes formed after a process of dissociative electron attachment, with electrons provided by a hot rhenium filament. As a side note, the 174 m/z peak was found to grow in after a period of approximately two weeks settling for the gas mixture, with intensity later found to be correlated positively with increased voltage supplied to the nozzle, which affects the dynamics of the supersonic gas expansion.

Mass separation occurs as a result of the respective time-of-flights of individual anions and anion complexes. The pulsing of a 4.661 eV laser at 10 Hz, with this threshold of photodetachment produced via the fourth harmonic of a 1064 nm Nd:YAG laser (Spectra Physics Quanta Ray Pro), is timed to coincide with the arrival of a particular anion complex. In cases where there are several mass peaks within a small vicinity, a mass gate is used prior to photodetachment in order to scatter any unwanted ions or ion complexes. Ejected photoelectrons are collected using the previously mentioned magnetic-bottleneck approach, with a characteristic kinetic energy indicative of the complex eBE as displayed in Equation 1;

$$eBE = h\nu - eKE \tag{1}$$

where eKE is the kinetic energy of the photoelectron, obtained from its flight time through a 1.8 m long tube upon reaching a microchannel plate detector, and $h\nu$ is the energy of the input photon. The photoelectron counts were initially recorded as individual events within particular time bins, with subsequent conversion to eKE and then eBE. A Jacobi transform was applied to the raw photoelectron spectral results, meaning the intensities of the photoelectron peaks are consistent with energy-dependent intervals instead of time-dependent intervals, and additionally, the $^2P_{3/2}$ and $^2P_{1/2}$ photoelectron peaks of bare iodide were used in order to calibrate the electron binding energies of the unknown species.

Computational Methods

The calculations featured in this work were conducted using the Gaussian 09 program.[29] The geometry of the iodide-water-ethyl radical anion complex was optimised at the MP2 level of theory, with aug-cc-pVQZ basis sets for first row atoms,[30] and aug-cc-pVQZ PP for iodide, and will be collectively referred to henceforth as AVQZ.[31,32] Frequency analyses were performed using the same parameters to ensure the stationary point is a true minimum on the potential energy surface. Tighter converge criteria (1 x 10^{-8} E_h $a_0{}^{-1}$) were used in the geometry optimisations given the looser nature of the van der Waals interactions. Subsequent CCSD(T) energies were computed in order to perform a complete basis set extrapolation in accordance with W1w protocol,[33] where the SCF is extrapolated from AVTZ/AVQZ, the CCSD component from AVTZ/AVQZ, and the (T) inclusion from AVDZ/AVTZ. Vertical detachment energies (VDE) were computed at the same geometry as the anion complex, varying only the charge and multiplicity to simulate the detachment of an electron. Both detachment pathways, that to respective singlet and triplet states, were calculated initially.

Lastly, computational VDEs were split into the $^2P_{3/2}$ and $^2P_{1/2}$ spin-orbit states based on the experimental coupling constant of bare iodine, with a shift of -0.006 eV applied, being the difference between the experimental detachment energy of iodide and the CCSD(T)/CBS result.

Results and Discussion

Mass Spectrometry

The initial impetus behind the work presented here was the aim of characterising the $I^-\cdots CH_3CH_2OH$ gas phase anion complex with mass spectrometry and photoelectron spectroscopy. A mass peak at first believed to be corresponding to that of m/z =173 (i.e. $I^-\cdots CH_3CH_2OH$) was irradiated with a 4.661 eV photon and the subsequent photoelectron spectrum recorded. Calibration of the appropriate mass spectrum determined the mass peak to occur at m/z = 174, the increase in just one mass unit bearing heavy implications for analysis.

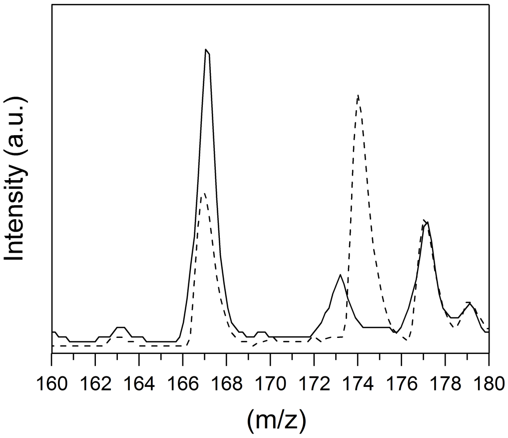


Figure 1: Two mass spectra recorded with the same gas mixture. The first (solid line) has a peak at 173 m/z that is replaced by a 174 m/z peak in the spectrum recorded several weeks later (dotted line). See main text for the assignment of peaks.

Figure 1 shows two mass spectra overlayed on top of one another, using the exact same gas mixture consisting of CH_3I, CH_3CH_2OH, and Ar, albeit recorded two weeks apart. In the earlier spectrum, shown with a solid line, peaks are present at m/z values of 167, 173, 177 and 179. The first corresponds to $I^-\cdots Ar$, the second $I^-\cdots CH_3CH_2OH$, and the remaining two $^{35}Cl^-\cdots CH_3I$ and $^{37}Cl^-\cdots CH_3I$, as evidenced by the apparent isotopic splitting, with the chloride anions produced from CCl_4 which was a remnant from a previous experiment. The complexes present at 167 m/z and 173/174 m/z have no such isotopic splitting apparent, and are thus are either I^- based complexes, or perhaps, although unlikely, molecular anions.

The dotted line shows the mass spectrum recorded two weeks after the first. It is more than apparent that the originally appearing peaks at m/z ratios of 167, 177, and 179 are still present, although with slightly different intensities. However, the mass peak at 173 m/z appears to have been replaced by a more intense peak occurring at 174 m/z instead. This 174 m/z peak was found to grow in with increasing voltage applied to the nozzle, and reducing the voltage saw a small return of the 173 m/z complex.

Ubiquitous to all of our conventional experiments are mass peaks that allude to halide complexes with H_2O, N_2, and Ar, and these iodide-based clusters can be seen at m/z ratios 145, 155, and 167 in Figure 2. Additionally, the previous gas mixture included CH_2O vapour, and residual $I^- \cdots CH_2O$ is also observed. However, these traditional complexes give little insight as to the identity of the 174 m/z peak.

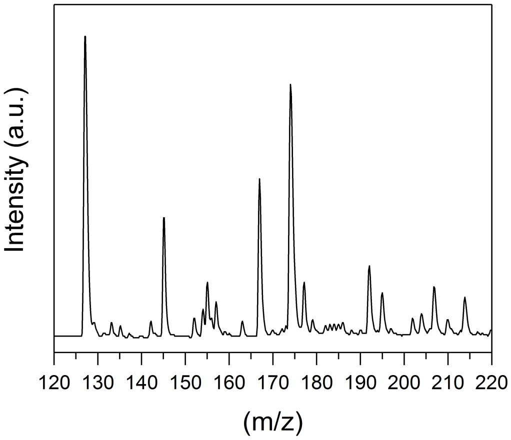


Figure 2: A full mass spectrum of a gas mixture containing CH_3I, CH_3CH_2OH, and Ar. The major peaks to note are that of I^- at 127 m/z, the assigned $I^- \cdots H_2O \cdots CH_3CH_2$ radical complex at 174 m/z, as well as $I^- \cdots (H_2O)_2 \cdots CH_3CH_2$ at 192 m/z.

Photoelectron Spectroscopy

The photoelectron spectrum of the 174 m/z species is shown in Figure 3, the two peaks occurring at 3.54 eV and 4.48 eV respectively. The sputtering in between these peaks was found to be consistent across multiple spectra and is believed to be a result of vibrational transitions. Given the resolution of the 3.54 eV photoelectron peak at 0.12 eV, based on a beam energy of 1500 eV as well as the mass of the ion complex,[27] this assumption cannot be appropriated fully. In these types of experiments involving van der Waals systems, the photoelectron spectrum can be thought of as a perturbation to that of the original or bare anion, rather than as a combined molecular system.[34]

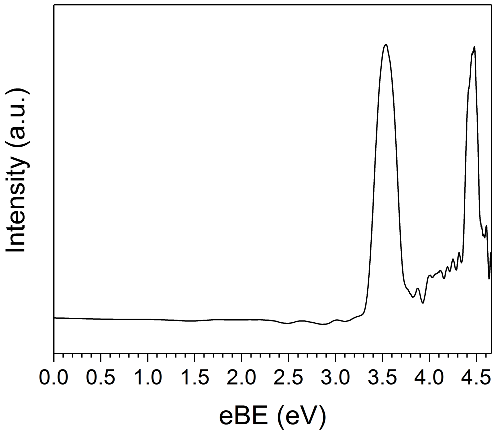


Figure 3: Photoelectron spectrum of the unidentified 174 m/z anion complex. The two large peaks correspond to *eBE* values of 3.54 eV and 4.48 eV respectively.

The distance between the peaks in Figure 3 is indicative of the spin-orbit splitting of the $^2P_{3/2}$ and $^2P_{1/2}$ atomic states of bare iodine at 0.94 eV, albeit shifted to higher *eBE*. This infers that the unidentified system is an anionic iodide complexing with some feature(s) that correspond to a m/z contribution of 47. However, there is precedent for the splitting of the degenerate components of the $^2P_{3/2}$ and $^2P_{1/2}$ states following the complexation of a halide with a neutral molecule, which may alter the magnitude of the original splitting, although any indications of this feature are not resolved in this work.[35] The originally sought ethanol complex would of course have been 46 mass units. Now begins the deductive work, assisted by *ab initio* calculations and based on reasonable assumptions of the elements composing the experimental gas mixture.

The photoelectron spectrum can also be seen to have a large shift in electron binding energy relative to bare iodide. The assigned $^2P_{3/2}$ and $^2P_{1/2}$ peaks are found at energies of 3.54 eV and 4.48 eV respectively for the unidentified complex, compared to 3.06 eV and 4.00 eV for the electron binding energies of bare iodide.[21] This large electron stabilisation energy (E_{stab}) of 0.48 eV is indicative of a strong bonding motif of the anion complex, likely ion-dipole in nature.

Returning to the previously stated example, the dipole-bound $I^{-}\cdots H_2O$ complex has a $^2P_{3/2}$ photoelectron peak occurring at 3.51 eV[22] and an E_{stab} of 0.45 eV, while the $I^{-}\cdots N_2$ $^2P_{3/2}$ peak is at 3.07 eV[23] with an assigned E_{stab} of 0.02 eV. That the unidentified complex is characterised by an electron stabilisation larger than that experienced by the $I^{-}\cdots H_2O$ complex is certainly suggestive of a tightly bound anion structure.

These points were considered in an attempt to make up the missing 47 mass units and elucidate the identity of the anion complex. The evidence so far was suggestive of an iodide-centred, tightly bound anion complex, based on the photoelectron peak splitting, as well as the lack of isotopic splitting in the mass spectrum. It is perhaps prudent to demonstrate now, before continuing any further, that the photoelectron spectrum of $I^{-}\cdots CH_3CH_2OH$ has since been recorded. With a $^2P_{3/2}$ binding energy of 3.64 eV, as opposed to 3.54 eV for the unidentified complex, the unlikely interference of this system can be definitively ruled out. These results will form the basis of future publications.

The working theory, however, was that the 47 mass units were attributable in some form to the ethanol in the gas mixture, given the mass increase of only one in addition to the coinciding of the appearance of the mass peak when ethanol experiments began. A protonated ethanol would not be observed, and a deuterated ethanol would be an unlikely cause due to the low abundance of naturally occurring deuterated ethanol. Additionally, this reasoning would hold true to rule out the presence of 13C. The first serious consideration came in the form of a combination of an ethyl radical and water molecule, with a full discussion related to the assignment of the photoelectron spectrum featuring in a later section.

Computational Geometry and Detachment Energies

Any and all attempts to locate a stable minimum for a hypothetical iodide-water-ethyl radical anion complex returned the structure in Figure 4. The geometry shown was optimised at the MP2/AVQZ level of theory, with all vibrational modes found to be real, indicating it is a minimum on the global potential energy surface. Full cartesian coordinates, structural information, and frequency calculation data can be found in the Supplementary Material. Several different arrangements were considered, including a linear geometry, as well as one with the ethyl radical rotated 180 degrees.

However, only a single minimum was located at the chosen level of theory. The optimised complex geometry is of C_1 symmetry and is best thought of as a form of loose ring structure between the water, iodide anion, and C−H group of the ethyl radical. The iodide anion is bound to a hydrogen of water at a a distance of 2.595 Å and a hydrogen of the ethyl radical by 3.198 Å. The other hydrogen of water is bound to the radical carbon of ethyl, approximately 2.510 Å apart. The ethyl-water radical complex proposed by Lin et al.,[7] has a corresponding distance of 2.31 Å. Their structure, of C_s symmetry, was used as an initial guess for these calculations, although it is apparent that while the bonding structure between H_2O and the C_2H_5 radical remains similar, the mirror plane is lost swiftly when moving to a three-membered system, with the water molecule in this work twisting out of plane to form the aforementioned ring structure.

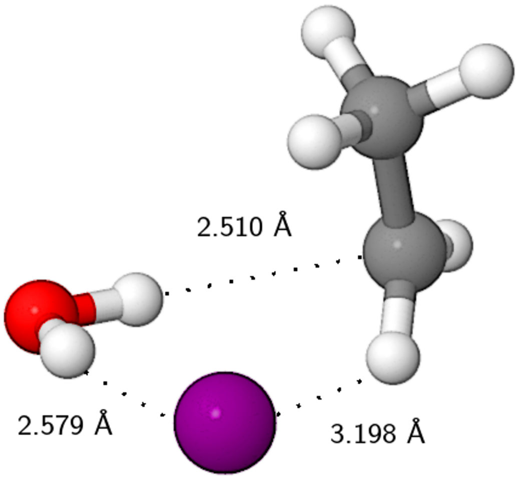


Figure 4: Optimised geometry of the $I^-\cdots H_2O\cdots CH_3CH_2$ radical anion complex at the MP2/aug-cc-pVQZ level (aug-cc-pVQZ PP for iodide).

Computational vertical detachment energies (VDE) have been shown to have excellent agreement with the experimentally observed electron binding energies, especially at the CCSD(T) level of theory.[23,36,37] Considering two electron detachment pathways: that to a singlet and a triplet state, VDE simulations were conducted of the computed $I^-\cdots H_2O\cdots CH_3CH_2$ radical anion complex. The findings of these results are summarised in Table 1, in addition to the experimentally determined binding energies.

Detachment to the singlet state was ruled out early, with MP2 energies being too large to be experimentally determined, with a predicted $^2P_{3/2}$ photoelectron peak occurring just on the threshold of laser detachment at 4.661 eV. This of course makes sense as according to Hund's rule, with the most stable state having the largest number of unpaired electrons. The CCSD(T)/CBS energies are shown to have decent agreement with those found experimentally, falling within 0.05 eV at most. There is an argument to be made that VDE simulations of iodide-core systems using MP2/AVQZ optimised geometries and W1w energies can slightly overestimate experimental spectra, with the application of this method to the $I^- \cdots CH_3COCH_3$ anion complex predicting detachment energies 0.04 eV above the associated experimental value.[38] Combined with the empirical evidence presented within this paper, these theoretical results position us to assign the photoelectron spectrum of Figure 3 as being that of a gas phase iodide-water-ethyl radical anion complex.

Table 1: Summary of experimental and computational detachment energies for the iodide-water-ethyl radical anion complex, with detachment occurring from the doublet anion state to a triplet neutral state. CBS refers to the complete basis set limit.

	$^2P_{3/2}$ (eV)	$^2P_{1/2}$ (eV)
Experimental	3.54	4.48
CCSD(T)/CBS	3.59	4.53

Assignment of the $I^- \cdots H_2O \cdots CH_3CH_2$ Radical Anion Complex

The items below present a summary of the experimental and theoretical evidence discussed previously in this paper that suggests the existence of the iodide-water-ethyl radical anion complex:

- The distinct increase of one mass unit from 173 m/z to 174 m/z, as well as a lack of isotopic splitting, in the mass spectrum.

- The resultant photoelectron spectrum with major peaks at 3.54 eV and 4.48 eV indicative of an iodide-centred anion complex, with a missing 47 mass units.

- An E_{stab} of 0.48 eV, suggesting a bonding motif on par with the stability of ion-dipole interactions.

- Computational data in good agreement with experimental values.

Further empirical evidence can be gathered through returning to the full mass spectrum of Figure 2; first of all, as to whether an $I^{-}\cdots CH_3CH_2$ radical anion complex is observed, as may be expected if $I^{-}\cdots H_2O\cdots CH_3CH_2$ is indeed the system at hand. There is a small shoulder of the $I^{-}\cdots N_2$ mass peak that could correspond to a complex m/z of 156, although definitive conclusions are tentative based on the obscurity of this shoulder relative to the neighbouring $I^{-}\cdots N_2$ and $I^{-}\cdots CH_2O$ mass peaks, occurring at 155 m/z and 157 m/z respectively.

One would also postulate that if the 47 missing mass units were attributable to an ethyl-water radical complex that additional water molecules may feature in subsequent complexations, i.e., in the same way that $I^{-}\cdots H_2O$ (145 m/z) and $I^{-}\cdots(H_2O)_2$ (163 m/z) are observed in Figure 2, $I^{-}\cdots(H_2O)_2\cdots CH_3CH_2$ and $I^{-}\cdots(H_2O)_3\cdots CH_3CH_2$ (192 m/z and 210 m/z respectively) may also make an appearance. Looking to Figure 2, these mass peaks are certainly present; the most notable being the 192 m/z peak given its large intensity.

Next, some mechanism of formation will be suggested, given the odd nature of the proposed complex. As just discussed, water molecules are ubiquitous within the gas mixture, and multiply solvated complexes are found throughout the mass spectrum. Thus it is highly probable that the H_2O of $I^{-}\cdots H_2O\cdots CH_3CH_2$ was not produced by any external mechanism or reaction, but was present to begin with, with the water molecule contributing to the stability of the complex. Thus the existence of water in the complex is thought to be unrelated to the formation of the ethyl radicals.

As for the radicals themselves, the sensible route of formation is from the ethanol within the gas mixture, given that no 174 m/z iodide based complex was observed prior to the experiments detailed here. C_2H_5 radicals can be produced from ethanol via a decomposition mechanism,[39,40] although this is not a primary pathway, and the conditions of our experiment make this unlikely. A process of dissociative electron attachment to ethanol is a more reasonable explanation, with the major anions produced being OH^{-} and O^{-}, leading of course to the formation of C_2H_5 radicals.[41–43]

Additionally, it has been observed that low energy anion collisions with ethanol results in mass spectra consistent with that proceeding dissociative electron attachment.[44] It was previously noted that an increase in applied nozzle voltage resulted in the 174 m/z peak growing in as the

173 m/z peak descreased drastically in intensity. It is possible that this affected the dynamics of the supersonic expansion to an extent to produce the ethyl radicals via these two mechanisms. For example, the increase is gas pressure would result in a far greater cross section of anion collision with gas phase ethanol molecules. As a result, the proposed route of ethyl radical formation is either through dissociative electron attachment to ethanol or as a result of anion collisions to form OH^-, both of which are plausible within our experimental apparatus.

One dissenting factor is that OH^- peaks were not observed in our mass spectra, however this is likely attributed to the time-of-flights of each species with respect to the pulsing of the experiment i.e. a m/z of 17 is unlikely to be seen while the region of optimised interest is of 127 m/z and above. In previous experiments, altering the conditions of pulsing for the time-of-flight mass separation has allowed for certain complexes of lower m/z ratios to be detected. In this case, no OH^- anions would be observed while the current settings were in place.

Comparison With Other Iodide Complexes

Lastly, in Table 2 we present a comparison of the $^2P_{3/2}$ photoelectron detachment energies of various I^- based complexes, making a note of the electron stabilisation energies for each. Going down the table sees an increase in E_{stab} values as clear patterns begin to emerge, with the nature of the van der Waals interaction between the solvating molecule and the anion giving a strong indication of the strength of the electron stabilisation energy. The weak ion-induced dipole motif of the $I^- \cdots N_2$ and $I^- \cdots Ar$ complexes leads to only a small shift in photoelectron peak signal, whereas the ion-dipole interactions of $I^- \cdots H_2O$ and $I^- \cdots CH_3CN$ incurs shifts of more than an order of magnitude larger.

The $I^- \cdots H_2O \cdots CH_3CH_2$ radical anion complex of this work has an E_{stab} on the order of that of $I^- \cdots CH_3CN$, suggesting a strong interaction. Interesting to note as well, is that when the subsitution or solvation of the anion increases, moving from one H_2O molecule to two, there is again a marked increase in the E_{stab} value. This is a universal trait amongst multiply solvated species, as the negative charge is further stabilised, justifying the experimental E_{stab} of $I^- \cdots H_2O \cdots CH_3CH_2$ lying slightly above that of $I^- \cdots H_2O$, with minimal charge stabilisation contributions from complexation with an ethyl radical.

Table 2: ${}^2P_{3/2}$ detachment energies and E_{stab} values of various iodide-centred gas phase anion complexes.

Species	${}^2P_{3/2}$ (eV)	E_{stab} (eV)
I^-	3.06[21]	
$I^- \cdots N_2$	3.07[23]	0.02
$I^- \cdots Ar$	3.10[45]	0.04
$I^- \cdots H_2O$	3.51[22]	0.45
$I^- \cdots CH_3CN$	3.54[46]	0.48
$I^- \cdots H_2O \cdots CH_3CH_2$	3.54	0.48
CCSD(T)/CBS	*3.56*	
$I^- \cdots (H_2O)_2$	3.92[22]	0.86

Conclusion

In summary, a photoelectron spectrum of a gas phase anion complex was recorded, originally believed to be that of $I^- \cdots CH_3CH_2OH$, with two major detachment peaks occurring at 3.54 eV and 4.48 eV. Inspection of the mass spectrum revealed a distinct increase in one mass unit, from 173 m/z to 174 m/z (Figure 2), resulting in the unidentified complex requiring investigation. The photoelectron peak splitting, as well as the lack of isotopic splitting in the mass spectrum suggested an iodide complex with a species of 47 unaccounted for mass units. The large E_{stab} value of 0.48 eV observed in the photoelectron spectrum, relative to that of bare iodide, was also a factor. *Ab initio* calculations were then performed on a supposed system. The theoretical binding energies, coupled with the empirical results, were highly indicative that the complex in question consists of an iodide anion, and ethyl radical, and a water molecule.

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Supplementary Material

- Detailed structure and energetics of the $I^{-}\cdots H_2O\cdots CH_3CH_2$ radical anion complex, as well as vibrational modes and cartesian coordinates.

The authors declare no conflicts of interest.

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SUPPLEMENTARY MATERIAL

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

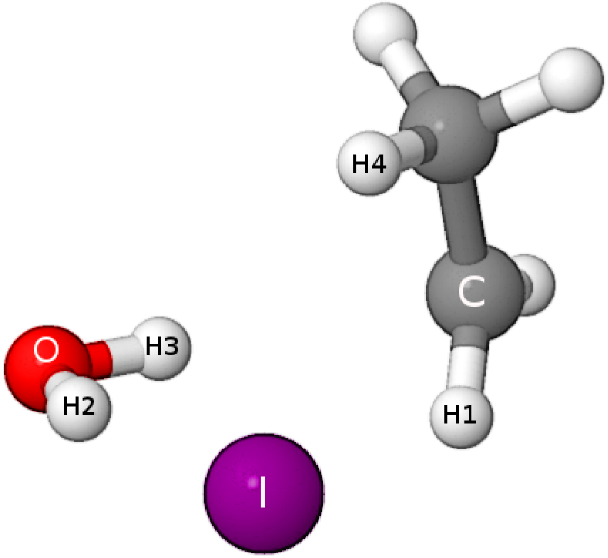

Figure 1: Schematic of the C_1 $I^-\cdots H_2O\cdots CH_3CH_2$ gas phase anion radical complex at the MP2/AVQZ level of theory.

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.

$r(\mathrm{I\cdots H1})$ [Å]	$\angle(\mathrm{I\cdots H1-C})$ [°]	$r(\mathrm{I\cdots H4})$ [Å]	$r(\mathrm{I\cdots H2})$ [Å]	$\angle(\mathrm{I\cdots H2-O})$ [°]	$r(\mathrm{I\cdots C})$ [Å]	$r(\mathrm{C\cdots H3})$ [Å]	$\angle(\mathrm{C\cdots H3-O})$ [°]	$r(\mathrm{O-H2})$ [Å]	$r(\mathrm{O-H3})$ [Å]	$\angle(\mathrm{H2-O-H3})$ [°]	$r(\mathrm{C-H1})$ [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.

		$E_{(\text{CCSD(T)})}$ $[E_h]$	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.

		$\text{Anion}_{(\text{CCSD(T)})}$ $[E_h]$	$\text{Triplet}_{(\text{CCSD(T)})}$ $[E_h]$	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_1 Anion	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
	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