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# Investigation of the Effect of Functional Group Substitutions on the Gas-Phase Electron Affinities and Ionization Energies of Room-Temperature Ionic Liquids Ions using Density Functional Theory

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## Abstract

The cathodic and anodic stabilities of room-temperature ionic liquids (ILs) are important factors in their applications in electrochemical devices. In this work, we investigated the electron affinities of cations and ionization energies of anions for ionic liquids by *ab initio* molecular orbital calculations at the B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d) level. Over 200 unique cations and anions, formed from a set of six base cation structures, three base anion structures, and seven functional groups, were investigated. We find the trends in calculated EAs of alkylated cations and IEs of alkylated anions to be in good agreement with observed experimental trends in relative cathodic and anodic stabilities of various ILs. In addition, we also investigated the effect that functional group substitution at distinct positions in the ions have on the EA of the 1,2,3-trimethylimidazolium cation and the IE of the PF<sub>5</sub>CF<sub>3</sub> anion. The overall impact on the EA or IE can be explained by the

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known electron-donating and electron-withdrawing inductive and resonance effects of the attached functional group, and the relative strength of the effect depends on the substitution position.

*Keywords:* electrochemical stability, ionic liquids, density functional theory, electron affinities, ionization energies

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## 1. Introduction

In recent years, there has been a steadily growing interest in using room-temperature ionic liquids (ILs) as electrolytes in electrochemical applications such as supercapacitors[1, 2, 3] and rechargeable lithium batteries.[4, 5, 6, 7] ILs have several advantages over traditional organic electrolytes such as ethylene carbonate (EC) or dimethylcarbonate (DMC). They generally exhibit low volatility, low flammability and high thermal stability, which provides significant safety advantages over flammable organic compounds. This is particularly important in the application of Li-batteries beyond small-scale portable electronics to large-scale applications such as hybrid electric vehicles (HEVs) and electric vehicles. Many ILs also exhibit wide electrochemical windows of approximately 5-6V or more[8], which are considerably larger than the 4.3-4.4V electrochemical windows of current organic electrolytes in use. A more electrochemically stable electrolyte could unlock the potential of high-voltage cathodes with higher power density. For example, LiNiPO<sub>4</sub>, which is predicted to have a potential near 5V[9], would have 50% higher energy density than the Fe-based LiFePO<sub>4</sub> system currently under development for HEVs.

In electrochemical applications, the stability of the IL electrolyte against

reduction (cathodic limit) and oxidation (anodic limit) is a key property of interest. In certain applications (e.g. supercapacitors), it is the electrochemical window, i.e. the difference between anodic and cathodic limits, that is of interest. In others, the electrolyte's stability relative to a particular electrode could be a limiting factor. For example, lithium at the graphitic node in rechargeable lithium batteries will reduce most organic solvents. Current organic electrolytes (e.g. EC/DMC with LiPF<sub>6</sub> added for Li<sup>+</sup> conductivity) work because of the formation of a passivating solid-electrolyte interphase (SEI) layer which prevents further electrolyte decomposition.[10]

Typically, the electrochemical window is determined experimentally by performing a linear sweep voltammetry using inert electrodes (e.g. Pt or Au) and measuring the cathodic and/or anodic currents, which are indicative of electrolyte reduction or oxidation. However, measured electrochemical windows depend heavily on the measurement conditions (e.g. type of electrode)[11] and also on the arbitrary current cut-off used to determine the onset of redox processes (typically between 0.1 and 1.0 mA cm<sup>-2</sup>). Comparison of data from various experimental sources is made more difficult by the different references used, some of which may not be strictly electrochemically defined. In the case of ILs, this is further compounded by their sensitivity to water, air and other impurities.[12, 13, 14] For example, Randstrom et al.[13] have recently shown that while the innate cathodic stability of *pure and dry* ILs are generally set by the reduction potential of the cation, anion reduction[15] may occur at a higher potential than cation reduction in the presence of water and oxygen.

Koch et al.[16] demonstrated earlier that the experimentally measured

electrochemical anodic stability of several ILs comprising 1,2-dimethyl-3-propylimidazolium cations paired with the PF<sub>6</sub>, AsF<sub>6</sub>, bis(trifluoromethylsulfonyl)imide (TFSI) and tris(trifluoromethylsulfonyl)methide anions correlates strongly with the highest occupied molecular orbital (HOMO) energies calculated using *ab initio* methods. In addition, there is also a significant body of work in the application of computational chemistry techniques to study redox potentials of conventional organic electrolytes[17, 18, 19] or the anions of lithium battery salts dissolved in these electrolytes.[20, 21]. In particular, Ue et al.[20] examined the anodic stability of several anions used in Li-salt additives for Li-battery electrolytes, and found that experimental oxidation potentials are highly correlated with the HOMO energies and the ionization potentials calculated using density functional theory (DFT) and molecular orbital theories.

In this work, we investigate the trends in gas-phase electron affinities (EAs) of IL cations and ionization energies (IEs) of IL anions using computational chemistry methods. The advent of efficient computational chemistry codes and inexpensive computing resources has made it possible to probe the large chemical space of IL ion structures in a systematic fashion to study how increasing “alkylation” and the substitution of electron-donating and electron-withdrawing functional groups affect the EA and IE of an ion. We will show that the qualitative trends obtained agree well with previous experimental and theoretical results, and suggest potential directions for IL design for electrochemical applications.

## 2. Methodology

### 2.1. Investigative Methodology

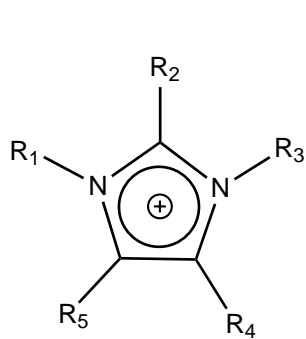
Our investigative approach is to systematically traverse the IL ion chemical space to establish trends in the EAs and IEs. To this end, we have developed a simple substitution code to replace symmetrically-distinct terminal atoms in an IL ion structure (H for cations, and F for anions) with various functional groups (see Table 3) using optimized structure templates. This process can be repeated with new structures generated and in this manner, we can span the entire chemical space for a given set of basic ion structures and functional groups. In this work, we investigated how the calculated *gas-phase* EAs and IPs of common IL ions are affected by alkylation (in this paper, the term “alkylation” is used loosely to refer to both alkyl group ( $C_nH_{2n+1}$ ) substitutions on cations and fluoroalkyl group ( $C_nF_{2n+1}$ ) substitutions on anions) and other functional group substitutions, as follows:

- To systematically probe the chemical space of alkylated ion structures, we started with an basic ion structure (e.g. simple ammonium cation,  $NH_4^+$ ). Based on the point group symmetry of the ion ( $T_d$  in the case of  $NH_4^+$ ), we substituted *symmetrically distinct* terminal atoms with methyl groups (trifluoromethyl, or  $CF_3$  groups in the case of anions) to obtain a new set ion structures. Recursive substitutions result in increasing alkylation, allowing us to sample the complete space of alkylated ions. However, given that substitution tends to break symmetry, the number of structures rapidly become unmanageable. Hence, only the cation with the lowest computed EA or the anion with the highest computed IE was retained for the next stage of substitution, i.e. a

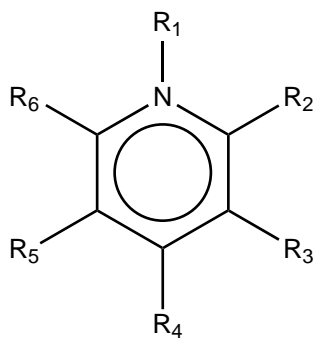
“best-first” search algorithm with minimization of the EA or maximization of the IE as the objective function. While this could theoretically mean that we may miss possible cation structures with lower EAs or anion structures with higher IEs, in practice, there is usually more than one search path to the same structure and hence, we would expect most of the likely optimal structures to be found by our sampling method.

- A similar approach was used to investigate the effect of the different functional groups such as amine ( $\text{NH}_2$ ), hydroxyl ( $\text{OH}$ ), cyanide ( $\text{CN}$ ), fluorine ( $\text{F}$ ) and carboxyl ( $\text{COOH}$ ) on a cation structure. Non-alkyl group investigations have been limited to single substitutions, and we have not explored recursive substitutions to obtain more complex ion structures.

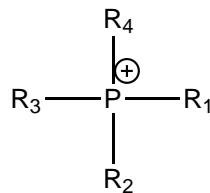
We have focused on six cation and three anion structures commonly found in ILs (see Tables 1 and 2), and a mix of seven functional groups with known electron-donating and/or electron-withdrawing effects (see Table 3). Electron donating groups tend to stabilize cations and destabilize anions while electron withdrawing groups tend to stabilize anions and destabilize cations. Functional groups donate and withdraw electron density from a system through either inductive or resonance effects.[22] The inductive effect is related to the differences in electronegativity between elements, and transfer of electron density takes place primarily through  $\sigma$  bonds. Resonance effects refer to the movement of electron density through delocalization effects, e.g. interaction between lone pairs and the  $\pi$ -bonding system in aromatic compounds.



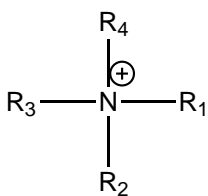
Imidazolium



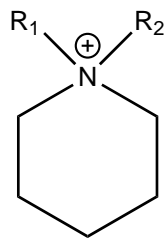
Pyridinium



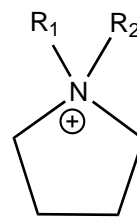
Phosphonium



Ammonium

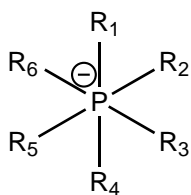


Piperidinium

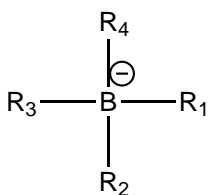


Pyrrolidinium

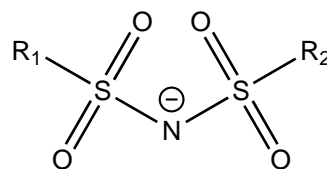
Table 1: Cations Investigated



Phosphate



Borate



Sulfonylimide

Table 2: Anions Investigated



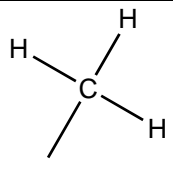
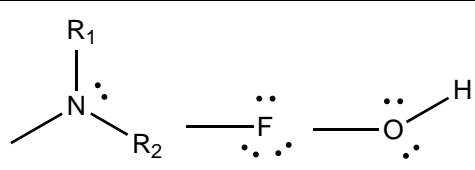
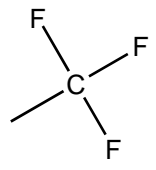
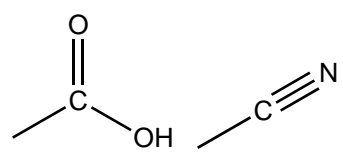
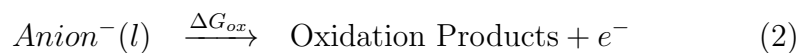
ED by Inductive Effect	EW through inductive effect ED through resonance effect
	
EW by Inductive Effect	EW by Resonance Effect
	

Table 3: Functional Groups Investigated and their known Electron-Donating (ED) and Electron-Withdrawing (EW) effects[22]

## 2.2. Computational Methodology

In pure ILs, the cathodic and anodic limits are typically set by the reduction potential of the cation, and the oxidation potential of the anion.[23, 8] In principle, the reduction potential of the cation,  $V_{red}$ , and oxidation potential of the anion,  $V_{ox}$ , in the liquid can be calculated from the free energy changes of the redox reactions,  $\Delta G_{red}$  and  $\Delta G_{ox}$ , as follows:



$$V_{red} = -\frac{\Delta G_{red}}{e} \quad (3)$$

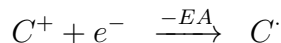
$$V_{ox} = \frac{\Delta G_{ox}}{e} \quad (4)$$

where all voltages are measured in volts and free energy changes are in electron-volts per ion. The resulting potential is with respect to the ref-

erence reaction that absorbs or donates the electron.

However, the redox decomposition products are in general not *a priori* known. While an exhaustive computational search can be done to find the most likely redox products[24], such an approach is too expensive to be scaled to modeling hundreds of possible ion structures. Koch et al.[16] and Ue et al.[20] demonstrated the correlation between experimentally measured oxidation potentials and calculated HOMO energies of anions. We therefore have reason to postulate that the reduction and oxidation potentials of a pure IL to be correlated to the electron affinity (EA) of its cation and ionization energy (IE) of its anion respectively. The lower (higher) the EA (IE) of a cation (anion), the greater its intrinsic stability against reduction (oxidation).

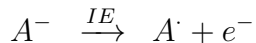
The EA of a singly-charged cation, C, is defined as the energy released when an electron is added to a cation to form a neutral radical, i.e.



It is well-established that calculated lowest unoccupied molecular orbital (LUMO) energies by time-independent quantum chemical methods are generally poor indicators of experimental EAs due to the poor description of virtual orbitals.[25] Hence, we have calculated the EA by explicitly taking the difference in energies between the cation and neutral radical. We calculated both the *vertical* EA, which is the energy difference between the cation and radical at the cation geometry, and the *adiabatic* EA, where both the cation and radical geometries were optimized.

Similarly, the ionization energy (IE) of a singly-charged anion, A, is defined as the energy needed to remove an electron from the anion to form a

neutral radical, i.e.



The anion IEs were calculated in a similar fashion to the cation EAs.

The gas-phase EA or IE is an intrinsic property of the isolated ion. It should be noted that this does not take into account possible chemical reactivity with electrode materials, and hence, trends in the calculated EAs and IEs should be compared with redox potentials measured using inert electrodes only. Possible chemical reactions with electrodes found in real-world electrochemical systems may lower the accessible electrochemical window significantly. Furthermore, gas-phase calculations do not take into account the effect that the local environment in the electrolyte has on the redox stability of the ion in the liquid state. While methods such as continuum solvation models and cluster approaches[26] can take into account local environment effects to varying degrees of approximation, these approaches either require additional input parameters such as the dielectric constant which are not available for all the ILs being explored, and/or are too computationally expensive for a high-throughput investigation involving hundreds of different IL structures.

All calculations in this paper were performed using the Gaussian 03 quantum chemistry package.[27] Geometry optimizations were carried out at the B3LYP/6-31+G(d) level and were followed by single-point energy calculations at the B3LYP/6-311+G(2d,p) level. The hybrid B3LYP density functional based on Becke’s three-parameter exchange functional[28] and the correlation functional of Lee, Yang and Parr[29] was chosen as it has been shown to provide good accuracy for EAs and IEs at a reasonable computation cost.

The inclusion of diffuse functions in the basis sets was also deliberate to ensure an adequate description of the diffuse electron cloud of anions, as well as the radicals formed from cation reduction. Close-shell restricted wave function calculations were used in the treatment of the cations and anions, while unrestricted open-shell wavefunctions were used for the radicals which have singly occupied orbitals. Frequency analysis was performed to ensure that structures obtained were minimum energy structures rather than transition structures, and also to obtain the thermochemical corrections for the Gibbs Free Energy, which are then scaled using the factor of 0.9806 determined earlier by Scott et al[30] for the B3LYP/6-31G(d) model chemistry.

### 3. Results

#### *3.1. Geometry Relaxation of Cations and Anions upon Reduction and Oxidation*

For alkylated IL ion structures, we investigated approximately 170 unique cation and 30 unique anion structures.

Figure 1 shows a composite plot of the calculated vertical EAs against adiabatic EAs of alkylated IL cations, and the calculated vertical IEs against adiabatic IEs of alkylated IL anions. The relaxation from geometry optimization means that adiabatic EAs  $>$  vertical EAs and adiabatic IEs  $<$  vertical IEs. In general, we find that the vertical and adiabatic EAs are fairly similar for most of the cations. However, we may observe that imidazolium cations appear to undergo a greater degree of geometrical relaxation upon reduction than other ions, as well as some of the smaller phosphonium, pyrrolidinium and piperidinium cations. For the anions, most appear to undergo significant

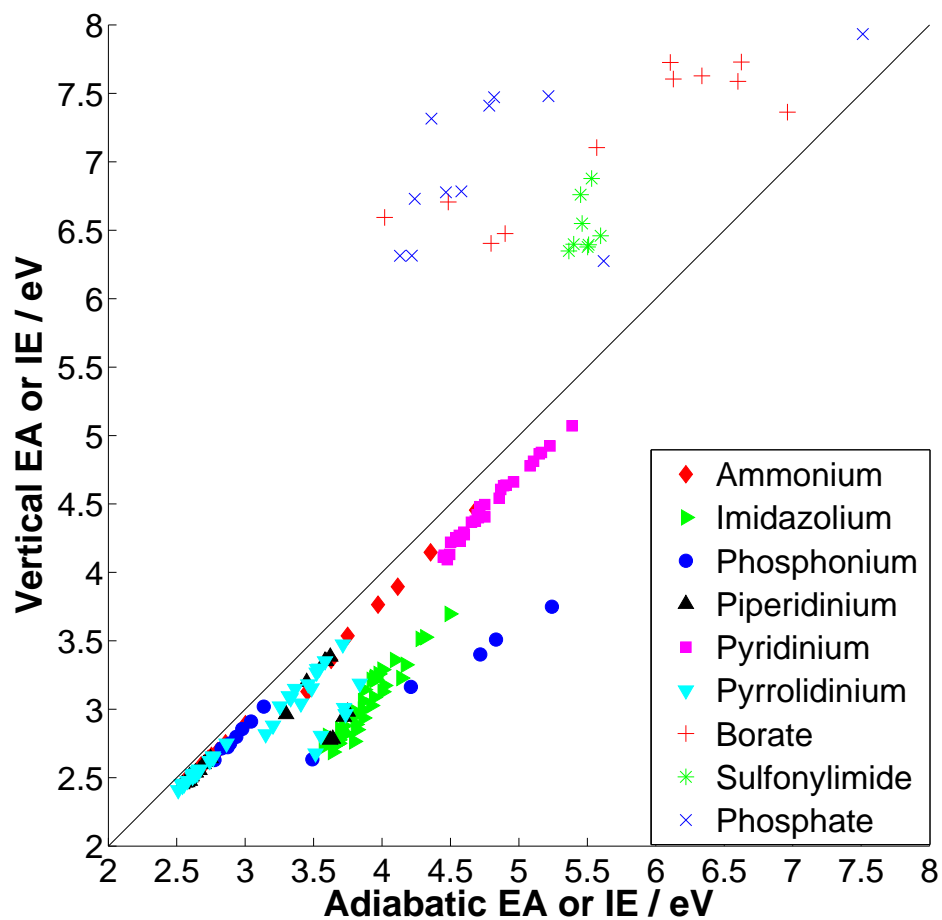


Figure 1: Plot of the calculated vertical EAs against calculated adiabatic EAs for alkylated IL cations, and calculated vertical IEs against calculated adiabatic IEs for alkylated IL anions. Six cation structures and one anion structure for which an optimized radical structure could not be found are excluded, but these do not materially affect the trends obtained.

geometry relaxation upon oxidation.

The neutral geometry-optimized radical is typically a reaction intermediate, and not the final product of the redox reaction. For instance, Kroon et al.[24] had investigated various reduction reaction paths for the 1,1-butylmethylpyrrolidinium and 1-butyl-3-methylimidazolium cations where radicals undergo decomposition into neutral fragments and smaller more stable radicals, react to form neutral molecules, or combine with one of the electrons of the  $\pi$ -bond to form a larger radical. They then verified that the predicted reduction products are indeed found experimentally. For the purposes of our work, though we would expect the adiabatic EA (IE) to be closer to the true reduction (oxidation) potential of the cation (anion), there is no way to *a priori* determine how far the neutral radical is to the final redox products energetically, which renders a comparison of the adiabatic EAs or IEs unreliable. Furthermore, there is also the practical issue that for some ions, a neutral geometry-optimized radical simply could not be obtained by adding or subtracting an electron to the ion. We have therefore chosen to look at the trends in the vertical EAs and IEs, which is indicative of how susceptible a cation (anion) is to accepting (donating) an electron, absent of geometrical relaxation effects.

### 3.2. Effect of Alkylation on EAs of Cations

In Figure 2, the calculated vertical EAs of alkylated cations are plotted against the molecular weight of the ion. Increasing molecular weight represents increasing alkylation. From the figure, we may make the following observations:

- In general, the EAs of alkylated ammonium, pyrrolidinium and phosphonium cations are lower than those of imidazolium and pyridinium

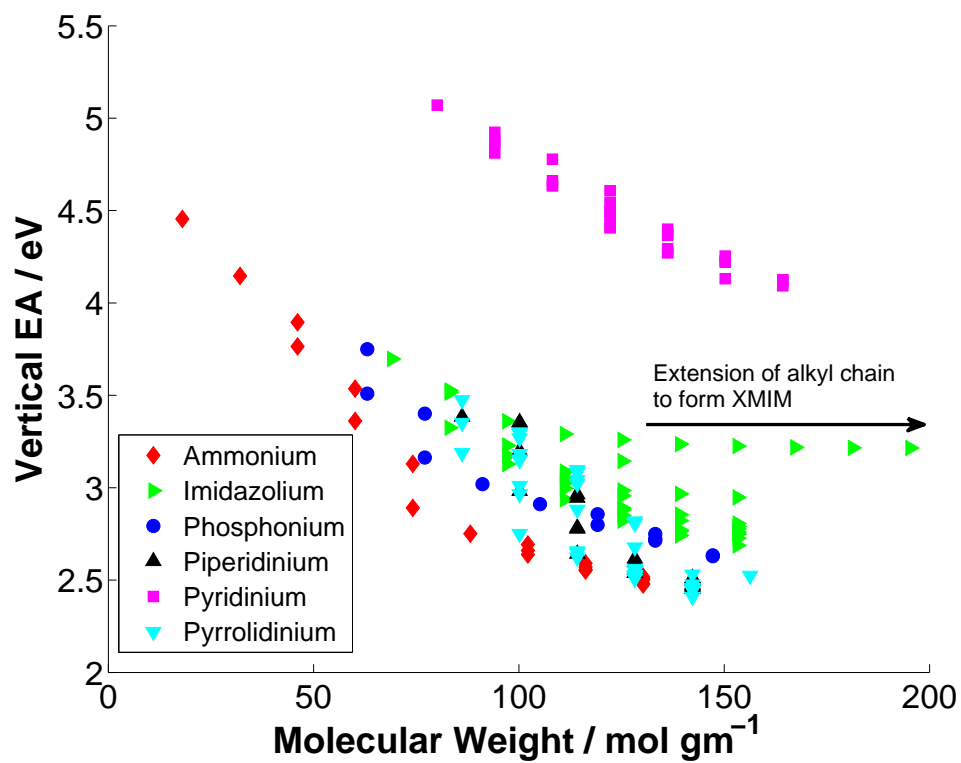


Figure 2: Effect of Increasing Alkylation on Vertical EA of IL Cations. XMIM refers to the 1-alkyl-3-methylimidazolium cation, where X ranges from ethyl (2 carbon atoms) to octyl (8 carbon atoms).

ions. This is consistent with experimental evidence that ILs containing these aliphatic cations are in general more stable against reduction as compared to ILs containing the aromatic cations.[31, 32] Our results also predict imidazolium-based cations to have better cathodic stability than pyridinium-base cations, which is consistent with a comparison of experimentally measured cathodic and anodic stabilities of several IL systems (corrected to a common ferrocene reference) compiled by Matsumoto[33].

- Increasing alkylation leads to a lowering of the EA and greater stability against reduction. This is consistent with the fact that alkyl groups are electron-donating in nature and hence would tend to stabilize a cation against reduction. Fitchett et al.[12] had earlier investigated the effect of increasing alkyl side chain lengths on the electrochemical windows of 1-alkyl-3-methylimidazolium bis(perfluoroalkylsulfonyl)imide ILs and observed a widening of the electrochemical window with increasing alkyl-chain length. More recently, Appetecchi et al.[34] has shown that the cathodic limit potential of N-alkyl-N-methylpyrrolidinium TFSI ILs steadily increases from -3.73 to -3.89V in going from a propyl to a heptyl side chain. Though Appetecchi et al. had attributed the increase in cathodic potential to the increasing shielding effect of the positively charged nitrogen in the pyrrolidinium ring with the length of the side chain, our calculations show that there is an intrinsic stabilization effect arising from an increase in the strength of the electron-donating effect from longer alkyl chains.



- The initial effect of alkylation on the EA is greater than subsequent alkylation. This may be explained by the fact that the initial alkylation typically takes place at hydrogens connected to the aromatic ring structure (in the case of imidazolium or pyridinium based ions) or the atom of formal positive charge (e.g. N atom in ammonium-based cations), and hence result in a greater decrease in the EA. The effect is especially pronounced when comparing the EAs of the XMIM cations against another imidazolium cation alkylated at the ring with the same molecular weight, i.e. the minimum EA structures at each molecular weight. Extending the alkyl side chain results in a very small decrease in the EA, while alkylation at the ring results in a much greater decrease.

We have also looked at how the EA of the 1-ethyl-3-methylimidazolium (EMI) cation is modified by alkylation at the various positions (see Figure 3). Bonhote et al.[35] had earlier demonstrated that the 1-ethyl-2,3-dimethylimidazolium TFSI IL exhibits a much wider electrochemical windows than EMI TFSI. The results from our calculations show that the greatest decrease in the EA of the EMI cation does indeed come from alkylation at the C(2) position. Again, we observe that substitution at the ring positions (Imi21100, Imi20110 and Imi20101 in Figure 3) results in a greater lowering of the EA than an extension of an existing alkyl chain (Imi20200 and Imi30100).

### *3.3. Effect of Alkylation on IEs of Anions*

Figure 4 shows a similar plot of the calculated vertical IEs of alkylated anions against the molecular weight of the ion. From the figure, we may make the following observations:

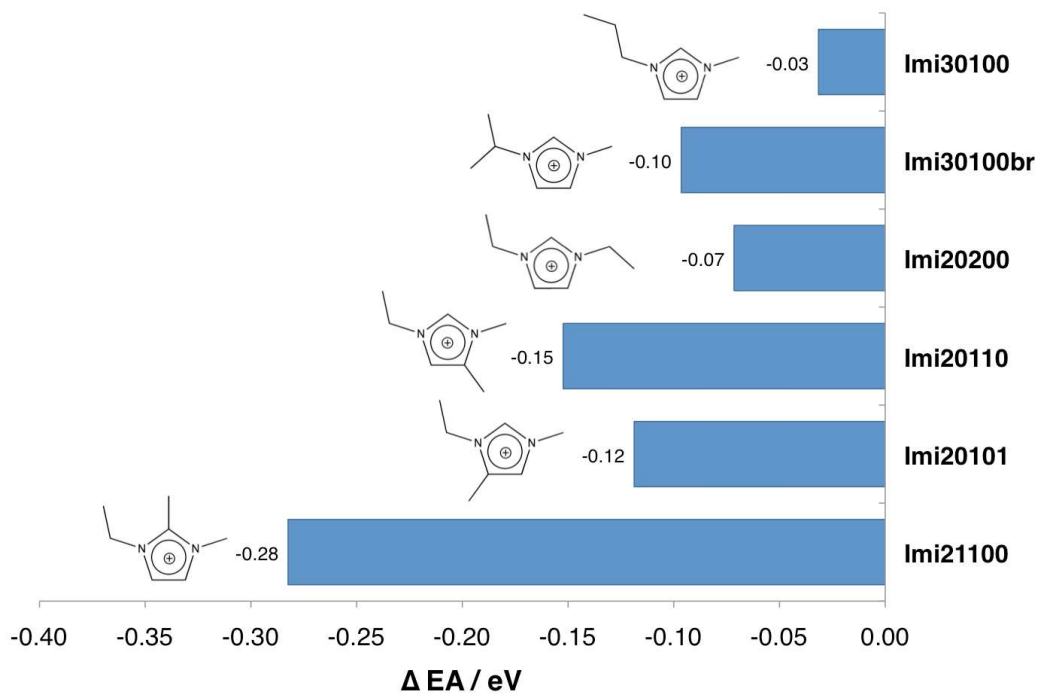


Figure 3: Effect of Alkylation on the EA of 1-ethyl-3-methylimidazolium (EMI) cation. The naming convention is based on the length of the alkyl chain attached to each ring atom, starting from the leftmost N atom and going around in a clockwise direction. Hence, Imi20100  $\equiv$  EMI cation, Imi21100  $\equiv$  1-ethyl-2,3-dimethylimidazolium, etc. Imi30100 refers to the cation having an n-propyl group attached to the leftmost N atom, while Imi30100br refers to having an isopropyl group attached at the leftmost N atom.

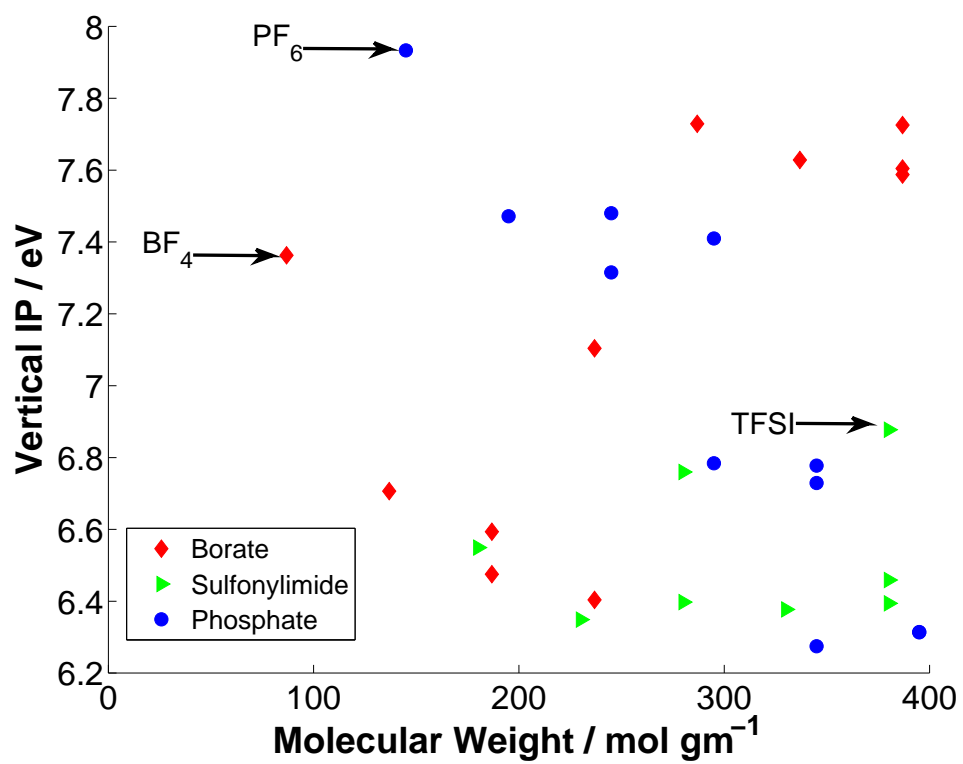


Figure 4: Effect of Increasing Alkylation on Vertical IP of IL Anions.

- Our results predict the relative stabilities of the common IL anions,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$  and bis(trifluoromethylsulfonyl)imide (TFSI) to be  $\text{PF}_6^- > \text{BF}_4^- > \text{TFSI}^-$ . This is consistent with the *ab initio* calculations and experimental measurements by Ue et al.[20], though it is inconsistent with earlier results of Koch et al.[16]
- Unlike the monotonically decreasing trend of EAs with increasing alkylation for cations, no monotonic increasing trend in IE with increasing molecular weight is observed in the case of anions for the range of molecular weights considered. This could be explained by the fact that current IL anions are already based on fluorinated organic and inorganic ions. Fluorine is the most electronegative element and hence, would already have a great inductive stabilization effect on the anions. Initial substitution of fluorine with  $\text{CF}_3$  groups therefore do not result in significantly increased stabilization. However, subsequent alkylation does appear to yield some additional stability in some instances, e.g. in the case of  $\text{BF}_4^-$  and fluorosulfonylimide anions, within the range of molecular weights explored. The decreasing trend of IE with increasing alkylation for  $\text{PF}_6^-$  could possibly be due to steric hindrance effects.

#### 3.4. Effect of Functional Groups Substitutions

We have investigated the effect of functional group substitutions on a few cation and anion structures. Figures 5 and 6 are representative plots showing the effect of different functional group substitutions on the EA of the 1,2,3-trimethylimidazolium (TMI) cation and the IE of the  $\text{PF}_5\text{CF}_3^-$  anion respectively. We have selected these ions as there are several distinct kinds

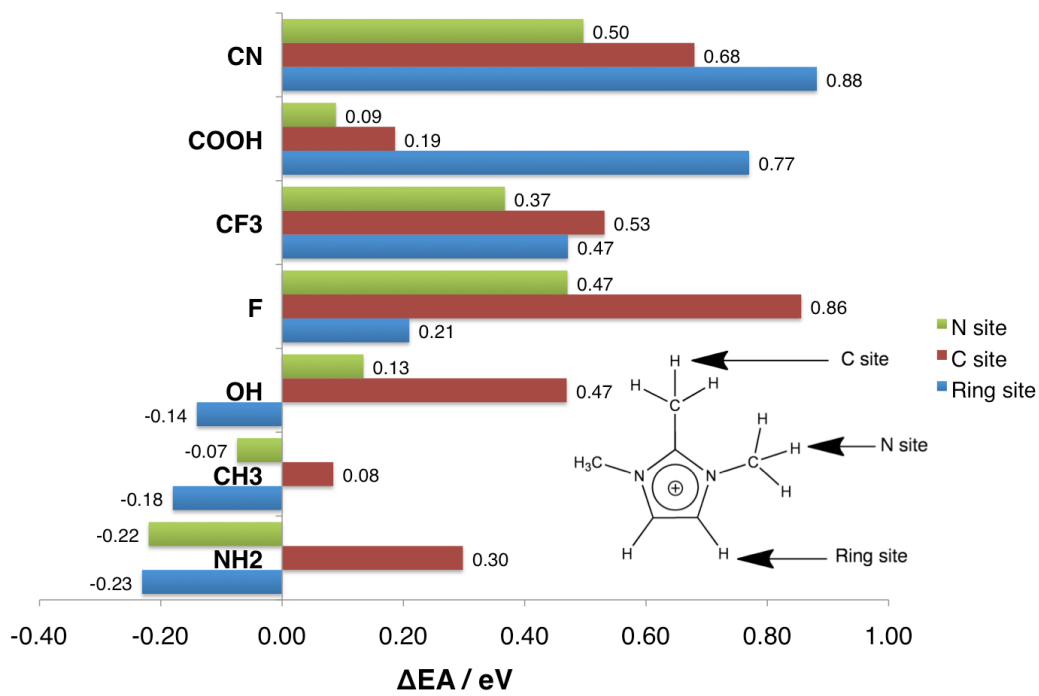


Figure 5: Effect of Functional Groups Substitutions on EA of 1,2,3-trimethylimidazolium (TMI). The change in EA from the TMI cation is plotted, i.e. difference in EA between the functionalized cation and the non-functionalized cation.

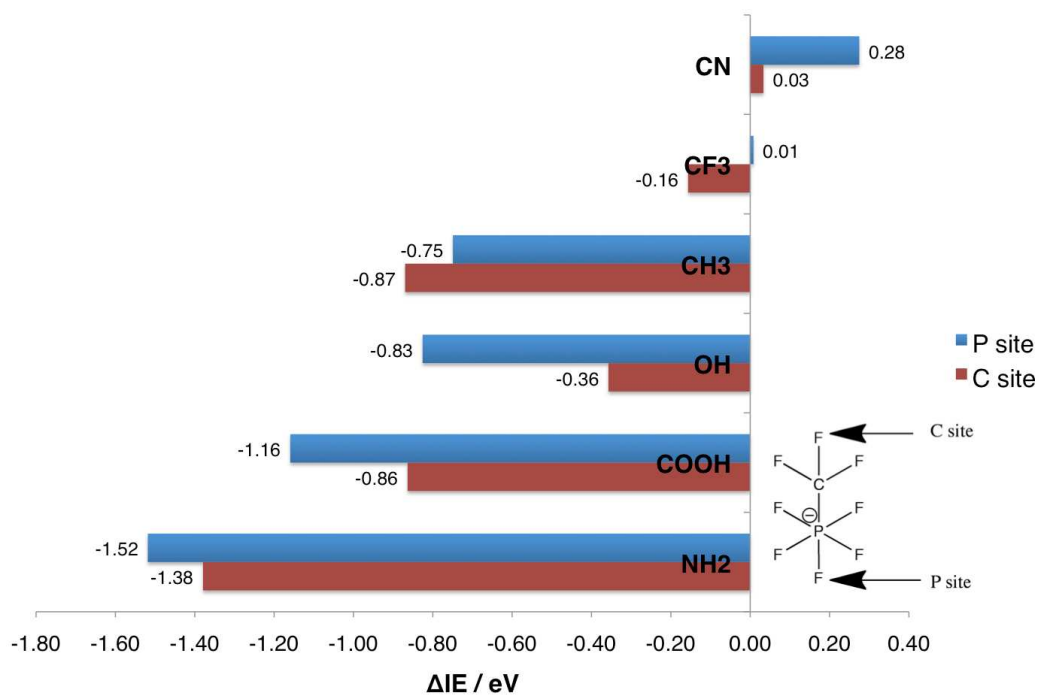


Figure 6: Effect of Functional Groups Substitutions on IE of  $\text{PF}_5\text{CF}_3$ . The change in IE from the  $\text{PF}_5\text{CF}_3$  anion is plotted, i.e. difference in IE between the functionalized anion and the non-functionalized anion.

of sites where substitution can be performed, which would provide additional insight on how the position of substitution affects the type and strength of the effect observed. For the TMI cation, three distinct sites can be identified, namely a hydrogen attached to the imidazolium ring (“Ring site”), a hydrogen on the methyl group attached to a nitrogen atom (“N site”), or a hydrogen on the methyl group attached to the carbon atom between the two nitrogen atoms (“C site”). For the  $\text{PF}_5\text{CF}_3$  anion, there are two distinct sites, namely a F atom directly attached to the P atom (“P site”), or an F atom attached to the existing  $\text{CF}_3$  group (“C site”).

From the figures, we may make the following observations:

- As expected, electron-donating (ED) groups such as alkyl,  $\text{NH}_2$  and OH groups generally stabilize the cation (leads to lower EAs) and destabilize the anion (lower IEs) while electron-withdrawing (EW) groups such as halogen, cyanide and trifluoromethane groups destabilizes the cation (increases EA) and stabilizes the anion (increases IE).
- Functional groups donate or withdraw electrons through inductive and resonance effects. For some functional groups, these two effects are in competition. For instance,  $\text{NH}_2$  and OH groups withdraw electrons inductively but donate electrons through resonance. The overall effect on the EA or IE thus depends on which effect is stronger. For these two groups, we may note that the decrease in EA of the TMI cation follows the trend : Ring site > N site > C site. Substitution at a ring site results in a decrease in the EA, while substitution at the C site results in an increase in an EA. This could be explained by the fact that substitution at the ring site results in a direct electron donation from

the lone pairs on these functional groups to the delocalized  $\pi$  orbitals in the imidazolium ring, and thus the ED resonance effect dominates over the EW inductive effect. When attached to the C site, the opposite is true and the inductive effect dominates. The same observation can be made for the functional groups which are EW by resonance such as CN and COOH. For these groups, the greatest increase in EA occurs when substitution occurs at the ring site.

- Similarly for the  $\text{PF}_5\text{CF}_3$  anion, we may observe that the greatest increase in IE comes when a group with a strong EW resonance effect (e.g. CN) is attached directly to the P site, which is the site of formal negative charge, while the greatest decrease in IE comes when a group with a strong ED resonance effect (e.g.  $\text{NH}_2$  or OH) is attached directly to the P site. Substitutions at the C site result in a significantly weaker effect.

#### 4. Discussion

Our results have shown that trends in the vertical EAs and IEs calculated using DFT methods are in qualitative agreement with relative experimental redox stabilities of ILs formed from various cations and anions, and with the general observed trend of increased cathodic stability resulting from alkylation of cations. Attaching electron-donating (ED) functional groups such as alkyl and amine groups generally decreases the EA of the cation and IE of the anion, and hence increases the stability of the cation against reduction but decreases the stability of the anion against oxidation. The reverse is true for electron-withdrawing (EW) functional groups. A monotonic decreasing



trend of cation EA with increasing alkylation was observed, while no apparent trend was observed for increasing alkylation of anions within the range of molecular weights explored. We have also demonstrated that the position of substitution is important in determining the strength of the ED or EW effects. Resonance effects are especially pronounced when the functional group is attached to an aromatic ring or the atom of formal positive/negative charge (e.g. N atom in  $\text{NH}_4^+$  or P atom in  $\text{PF}_6^-$ ).

Given that we find reasonable trends, computational chemistry techniques can contribute to a more focussed development of ILs for electrochemical applications. ILs are highly customizable solvents, and current research into ILs has barely scratched the surface of the massive chemical space for IL structures. For instance, most current research on ILs for Li-battery electrolytes has been limited to traditional ILs formed from alkylated imidazolium and ammonium-based cations with the  $\text{BF}_4$ ,  $\text{PF}_6$  and TFSI anions. One possible strategy for future IL Li-battery electrolyte development would be to functionalize existing cations with other ED groups to achieve better cathodic stability. On the anodic side, the potential for increasing the oxidation limit of anions appear to be more limited as current anions are already based on fluorinated organic and inorganic anions for which there is a strong inductive stabilization effect. Even so, our results suggest that the cyanide group could be an excellent candidate to functionalize anions. It should also be noted that the base ions and functional groups explored in this work are by no means a comprehensive list, and there could be other ions and functional groups that provide better electrochemical stability.

In real-world electrochemical applications, the electrochemical stability

is but one factor to be optimized in IL electrolytes. There are other important properties affecting electrochemical performance, most notably the ionic conductivity of the IL. Nonetheless, the insights gained from our high-throughput exercise will enable the more targeted design of ILs to satisfy the various requirements of a particular application. For instance, there is evidence that reducing the symmetry of the constituent ions generally leads to a lowering of the viscosity and increase in ionic conductivity of an IL. [36] A common approach to reduce the symmetry is to attach functional groups of different kinds or sizes to the ion. Hence, the trends obtained in our work could provide insights on which functional groups can be attached such that the electrochemical stability is improved as well, or at the very least, minimize any adverse impact on the electrochemical stability.

We should also point that out while the qualitative trends are consistent with experimental observations, gas-phase EA and IE calculations are insufficient to produce **quantitative predictions** of redox stability in real-world applications. By their very nature, gas-phase calculations ignore local environment effects present in the liquid, such as dielectric screening, the effect of the counter-ion and packing in the liquid state. Also, EAs and IEs are only approximate proxies for the redox stability, and possible chemical reactivity with real-world electrodes may significantly shrink the electrochemical window.

## 5. Conclusion

In this work, we have investigated the electron affinities and ionization energies of a large spectrum of cations and anions for ionic liquids using *ab initio*

molecular orbital theory at the B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d) level. We found that the trends in calculated EAs and IEs of alkylated IL cations and anions compare well with observed experimental trends in relative cathodic and anodic stabilities of various ILs. We also investigated the effect of functional group substitutions on the EA of the 1,2,3-trimethylimidazolium cation and IE of the  $\text{PF}_5\text{CF}_3$  anion, and explained the effects in terms of the known electron-donating and electron-withdrawing inductive and resonance effects of the functional groups. It is our belief that the insights obtained from these trends could provide the basis for a more focussed approach to IL design and customization for electrochemical applications.

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