



Photoionization of zwitterionic liquids

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ARTICLE INFO

Article history:

Received 4 July 2021

Revised 26 August 2021

Accepted 28 August 2021

Available online 02 September 2021

Keywords:

Zwitterionic liquids
Photoelectron spectra
Electronic structure

ABSTRACT

The electronic structures of three zwitterionic liquids (Zw-IL) have been studied using high-level ab initio method: equation-of-motion coupled-cluster (IP-EOM-CCSD) method. This method was found to match experimental UV photoelectron spectrum (UPS) of related N-methylimidazole better than Outer-valence Green's Function (OVGF) method or Symmetry Adapted Cluster-Configuration Interaction (SAC-CI) method. Zw-IL gas phase photoelectron spectra have been simulated in the valence ionization regions based on the vertical ionization energies calculated. Valence ionizations have been attributed to specific molecular orbitals to specific functional groups. The calculated electronic structures and valence ionization energies of Zw-ILs can be related to their polarizability which in turn influences the AC conductivity. AC conductivity is one of the principal properties of Zw-ILs which makes them very useful as electrolyte materials in lithium ion batteries or electric capacitors.

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1. Introduction

Zwitterionic liquids (Zw-IL) are similar to the well-known aprotic ionic liquids (IL), but with cation and anion tethered within the same molecule. Zw-ILs have many potential applications due to their low vapor pressure, high AC bulk ionic conductivity and easily modified physical properties [1–3]. The structure of Zw-ILs is such that the ions cannot migrate along the electric field like in conventional ionic liquids. Therefore Zw-ILs have low DC, but high AC bulk ionic conductivity. Zw-ILs are good at suppressing long range ion migration in DC devices which use ILs as electrolytes. The Zw-IL applications include their use as environmentally benign solvents or as electrolytes for lithium ion batteries, fuel cells, solar cells or capacitors.

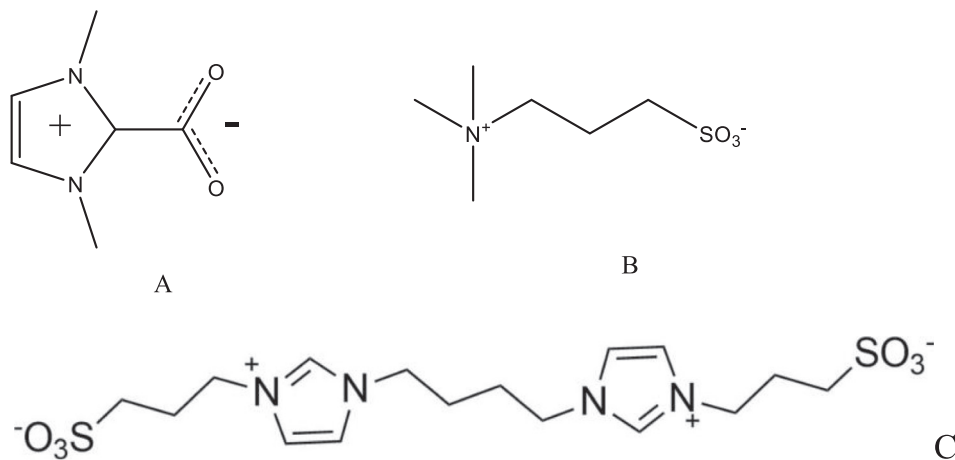
The electronic structure of Zw-ILs is of interest because of their unusual structure and properties. The method of gas-phase photoelectron spectroscopy (UPS) is one of the best available to study electronic structure of molecules and ions [4]. However, in many cases it is not possible to measure UPS spectra because the desired species cannot be obtained in the gas phase as free molecules since the substance studied is involatile or may undergo thermal decomposition at temperatures which are required for sample vaporization. A possible alternative is computational simulation of the spectra using high-level quantum chemical methods. This computational approach has been recently applied successfully to the zwitterion of amino-acid betaine [5]. In this work we report simulated, gas-phase photoelectron spectra of three Zw-ILs (Scheme 1).

2. Theoretical methodology

The molecular geometries of three Zw-ILs were fully optimized at ω B97XD/6-311G(d,p) level using Gaussian G16 software [6]. No imaginary frequencies were found indicating that optimized geometries were true minima on potential energy surfaces. The UV photoelectron spectra (UPS) were then simulated using high-level equation-of-motion coupled-cluster (IP-EOM-CCSD) method [7] and optimized geometries. This method was tested on a set of 155 molecules and shown to be a method of choice for calculating vertical ionization energies. Furthermore, the comparison of three methods: SAC-CI [8], OVGF [9] and IP-EOM-CCSD vs. experimental UPS spectrum of N-methylimidazole has shown (Fig. S1 in Supplementary materials) that spectra simulated by IP-EOM-CCSD method match experimental spectrum [10] best. Nevertheless, OVGF results have been included as well in the Table S1 (Supplementary materials). SAC-CI simulated spectrum showed poor match with the experimental N-methylimidazole spectrum therefore SAC-CI method was not used in the simulation of UPS of Zw-ILs.

The IP-EOM-CCSD method is implemented in ORCA 5 ab initio software package [11]. The basis sets used were of aug-cc-pVDZ quality and were shown to be satisfactory for the level of computational methods used [7,9]. The optimized geometries, vertical valence ionization energies and molecular orbital shapes (MOs) are given in Supplementary material. The bands in the spectra were simulated using Gaussian band shapes [5,12] and the superimposed profiles drawn using Mathematica software resulting in spectra in Figs. 2–4.

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Scheme 1. Structures of three zwitterionic liquids A-C studied in this work.

The molecular structures of A-C in the solid state have been reported [13–15] and these geometries have been used as starting points during full geometry optimization. An interesting observation regarding C in the solid state is shown in Fig. 1. The molecular structure of C in the solid state is considerably different from the structure of the free molecule. In the free molecule the two oppositely charged moieties (sulfonate and imidazolium) are closer to each other than in the solid state. The presence of attractive electrostatic interactions in the free molecule predominates while in the solid state the crystal packing forces govern the observed molecular structure.

This observation can be related to the reported difference in intermediate range ordering in Zw-ILs compared to ILs [1]. The former substances were shown to be subject to nano-domain aggregation while the latter form hydrogen-bonding networks [1].

3. Results and discussion

The simulated spectra of A-C are shown in Figs. 2–4 and calculated vertical, valence ionization energies are given in Table S1 of the [Supplementary material](#).

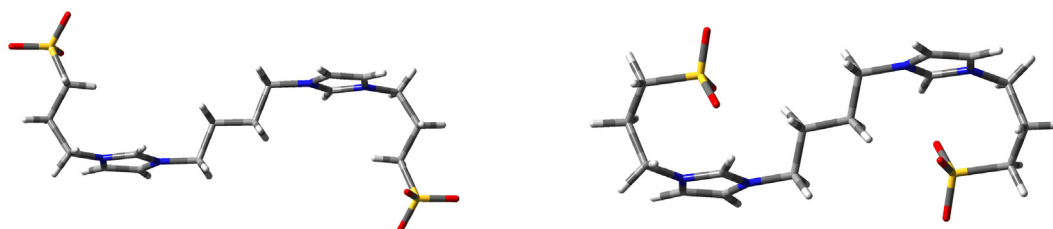


Fig. 1. Geometries of Zw-IL C in the solid state (left) and in the gas-phase (right).

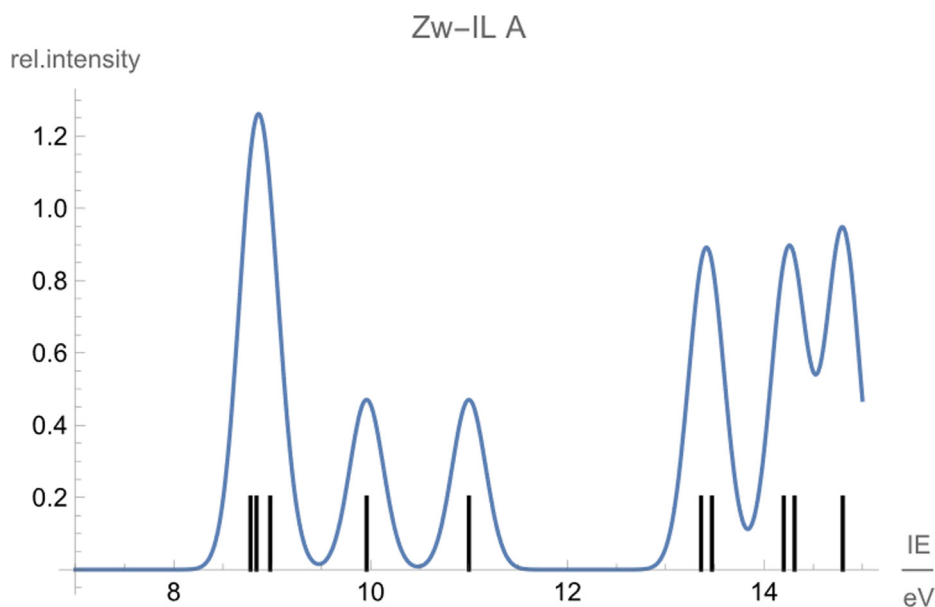


Fig. 2. Simulated UV photoelectron spectrum of A in the region 8–15 eV.

The UPS of A shows four bands at approximately 9, 10, 11 and 13.5 eV (Fig. 2). The first band has three times the intensity of other bands and corresponds to ionization of three σ -orbitals which can be described as linear combinations of oxygen lone pairs on negatively charged carboxylate moiety. The second and third bands correspond to ionizations of π -orbitals localized on positively charged imidazolium moiety. The fourth band corresponds to ionization from orbital of π -symmetry localized on the carboxylate group. The two π -orbitals in N-methylimidazole which can be considered as neutral analogue of positively charged imidazolium moiety in A, have ionization energies of 8.69 and 9.75 eV [10]. In A the corresponding π -ionization energies are much higher at 9.96 and 11.00 eV which is due to the positive charge of imidazolium moiety.

The UPS of B shows several bands with low ionization energies in the region 7–10 eV. Figures of MO shapes given in [Supplementary material](#) indicate that they correspond to various linear com-

binations of oxygen localized, lone pair orbitals on sulfonate group (SO_3). The bands with ionization energies above 12 eV correspond to σ -orbitals of alkyl groups.

The UPS of C can be understood by noting that C has two composite molecular blocks, each part comprising positively charged imidazolium and negatively charged sulfonate moieties.

The bands in the 8–12 eV region in spectrum of C correspond to ionization of orbitals localized on sulfonate groups with exception of the shoulder at around 10 eV. The shoulder band corresponds to ionizations of electrons from π -orbitals localized on imidazolium ring as shown in [Supplementary material](#). The ionization energies of these π -orbitals (two per each imidazolium moiety) are at 10.13 & 10.18 and 10.93 & 11.07 eV, respectively which is again higher than in neutral imidazole analogue. This can again be attributed to positive charge on the imidazolium moiety.

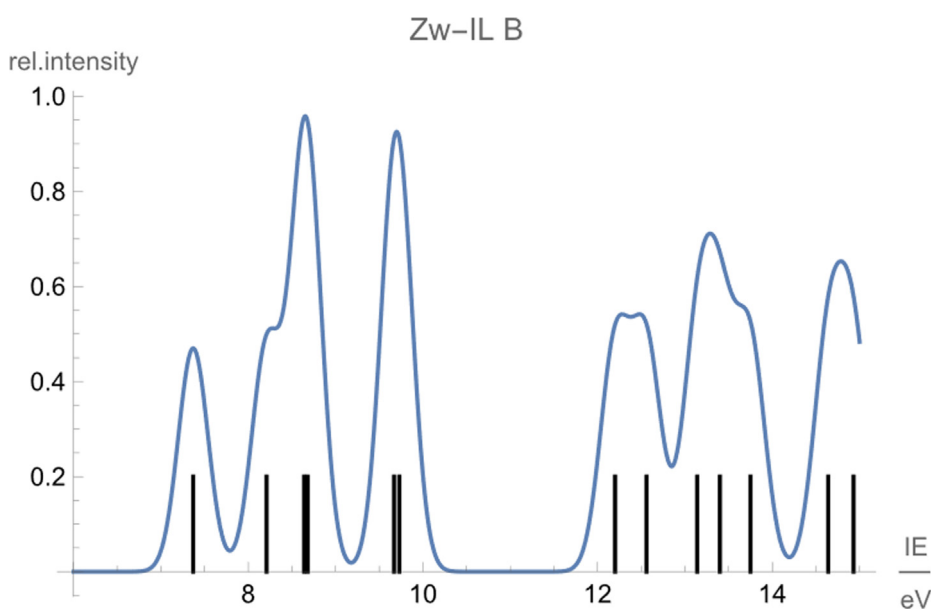


Fig. 3. Simulated UV photoelectron spectrum of B in the region 6–15 eV.

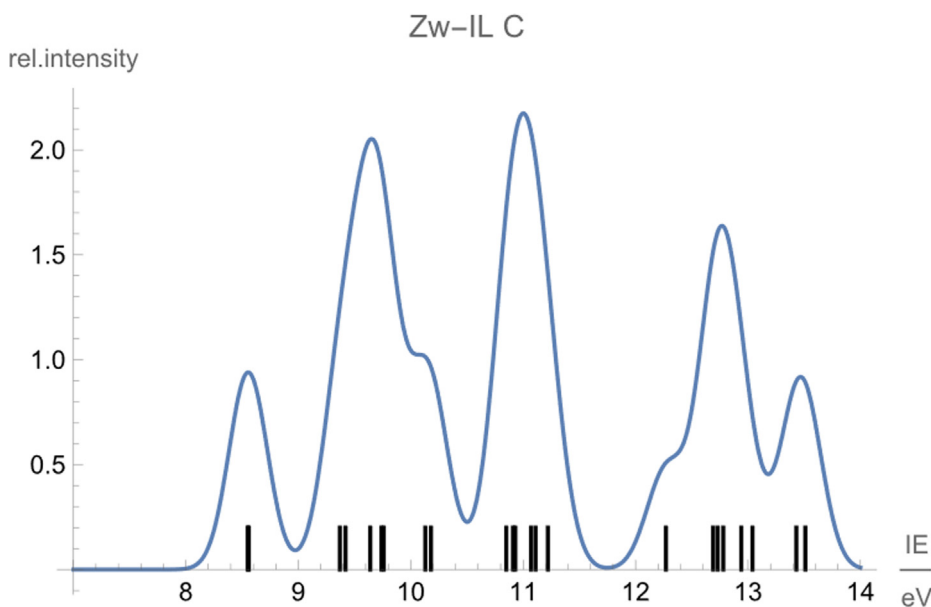
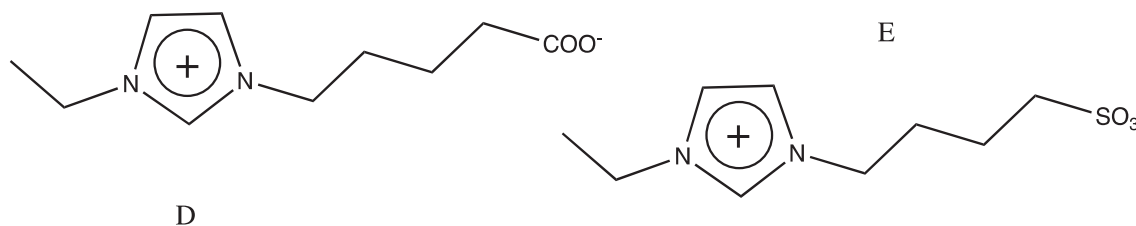


Fig. 4. Simulated UV photoelectron spectrum of C in the region 7–14 eV.



Scheme 2. Zw-ILs with measured AC conductivities.

What is a possible use of this knowledge of the electronic structure Zw-ILs? It is known that the AC ionic conductivity can be related to polarizability of ionic liquids [16]. The higher the polarizability of charged moieties in Zw-IL the larger its AC conductivity shall be. Furthermore, there exists an inverse relationship between local ionization energy and polarizability [17] i.e. the higher the ionization energy the lower the polarizability. Our results show that ionization energy of negatively charged carboxylate moiety is larger than for negatively charged sulfonate moiety. We suggest therefore that the Zw-IL with the highest potential AC conductivity amongst the three Zw-ILs studied here is substance B. An example which supports the relationship between ionic conductivity and polarizability concerns two Zw-ILs (in Scheme 2) whose measured ionic conductivities are $1.8 \cdot 10^{-5}$ and $6.1 \cdot 10^{-5}$ S/cm, for D and E, respectively [2]. The sulfonate Zw-IL can be expected (on the basis of our results) to have lower ionization energy and therefore higher AC conductivity.

The reason why polarizability is one of the factors influencing AC ionic conductivity can be attributed to the importance of ion-dipole interactions between alkali metal salts and zwitterionic liquids in materials which are used as electrolytes in various applications.

4. Conclusions

In this work we have described the electronic structures of three, free zwitterions which comprise components of zwitterion liquids. The electronic structures we studied based on calculated valence vertical ionization energies which were then represented as corresponding UV photoelectron spectra.

Natural bond orbital (NBO) analysis carried out for Zw-IL A-C (Scheme S1, Supplementary materials) shows transferability of atomic charges on heteroatoms e.g. in A and C atomic partial charges on nitrogen are almost the same. The same applies to nearly equal charges attributed to sulfur and oxygen atoms of B and C. The molecular structure of A in the gas phase was found to be planar unlike in the solid where carboxylate group is distorted by 29° from the ring plane [13]. The consequence of the distortion is that ionization energies of bands associated with orbitals of COO^- group are higher in A (8.74, 8.84, 8.98 eV) than in betaine zwitterion (8.21, 8.38, 8.57 eV) [5]. This is due to the increased conjugative/resonance interaction between COO^- group and imidazolium ring.

The calculated electronic structures and valence ionization energies of Zw-ILs can be related to their polarizability which in turn influences the AC conductivity. AC conductivity is one of the principal properties of Zw-ILs which makes them very useful as electrolyte materials in lithium ion batteries or electric capacitors [18].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Author thanks Charles Sturt University for research grant (CSU ref.no. OPA 4068).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.117432>.

References

- [1] B. Wu, K. Kuroda, K. Takahashi, E.W. Castner Jr., Structural analysis of zwitterionic liquids vs. homologous ionic liquids, *J. Chem. Phys.* 148 (2018) 193807.
- [2] M. Yoshizawa, A. Narita, H. Ohno, Design of ionic liquids for electrochemical applications, *Aust. J. Chem.* 57 (2004) 139–144.
- [3] H. Ohno, M. Yoshizawa-Fujita, Y. Kohno, Design and properties of functional zwitterions derived from ionic liquids, *Phys. Chem. Chem. Phys.* 20 (2018) 10987–10991.
- [4] J.H.D. Eland, *Photoelectron Spectroscopy: An Introduction to Ultraviolet Photoelectron Spectroscopy in the Gas Phase*, 2nd ed., Butterworths-Heinemann, London, 2013.
- [5] I. Novak, Photoionization of glycine-betaine: A permanent zwitterion, *J. Mol. Liquids* 335 (2021) 116558, <https://doi.org/10.1016/j.molliq.2021.116558>.
- [6] M.J. Frisch, et al., Gaussian16, rev.C. Gaussian, Inc.: Wallingford, CT, 2016.
- [7] D.S. Ransinghe, J.T. Margraf, A. Perera, R.J. Bartlett, Vertical valence ionization potential benchmarks from equation-of-motion coupled cluster theory and QTP functionals, *J. Chem. Phys.* 150 (2019) 074108.
- [8] R. Fukuda, M. Ehara, Efficiency of perturbation-selection and its orbital dependence in the SAC-CI calculations for valence excitations of medium-size molecules, *J. Comput. Chem.* 35 (2014) 2163–2176.
- [9] D. Danovich, Green's function methods for calculating ionization potentials, electron affinities, and excitation energies, *WIREs Comput. Mol. Sci.* 1 (3) (2011) 377–387.
- [10] L. Klasinc, B. Rušćić, F. Kajfež, V. Šunjić, Photoelectron spectroscopy of the heterocycles, imidazole and methylimidazoles, *Int. J. Quantum Chem. Quantum Biol. Symp.* 5 (1978) 367–371.
- [11] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, The ORCA quantum chemistry program package, *J. Chem. Phys.* 152 (2020) 224108.
- [12] D.L. Lichtenberger, A.S. Copenhaver, Ionization band profile analysis in valence photoelectron spectroscopy, *J. Electron Spectrosc. Rel. Phenom.* 50 (2) (1990) 335–352.
- [13] J.D. Holbrey, W.M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, 1,3-Dimethylimidazolium-2-carboxylate: the unexpected synthesis of an ionic liquid precursor and carbene- CO_2 adduct, *Chem. Commun.* 28–29 (2003).
- [14] T. Yokoyama, G. Murakami, H. Akashi, M. Zenki, Crystal structure of zwitterionic trimethylammonio propane sulfonate, *Anal. Sci.* 19 (2003) 805–806.
- [15] A. Udvardy, S. De, T.G. Gal, G. Papp, C.E. Czegeni, F. Joo, Crystal structure of zwitterionic 3,3'-[1,1'-(butane-1,4-diyl)bis(1H-imidazol-3-ium-3,1-diyl)]bis(propane-1-sulfonate) dihydrate, *Acta Cryst. E* 76 (2020) 1353–1356.
- [16] Z. Osman, M.I. Mohd Ghazali, L. Othman, K.B. Md Isa, AC ionic conductivity and DC polarization method of lithium ion transport in PMMA-LiBF₄ gel polymer electrolytes, *Results Phys.* 2 (2012) 1–4.
- [17] P. Jin, J.S. Murray, P. Politzer, Local ionization energy and local polarizability, *Int. J. Quantum Chem.* 96 (2003) 394–401.
- [18] C. Tiyapiboonchaiya, J.M. Pringle, J.-Z. Sun, N. Byrne, P.C. Howlett, D.R. MacFarlane, M. Forsyth, The zwitterion effect in high-conductivity polyelectrolyte materials, *Nat. Mater.* 3 (2004) 29–32.