

Chapter 1

Summary

The interface between air and ice governs many phenomena that are essential to chemical processes in the atmosphere. Ice ever-present in the atmosphere and possess a wide range of microenvironments in which trace gases can interact, including a quasi-liquid disordered layer (Toubin et al., 2001; Bartels-Rausch et al., 2014). Studies connected to ice indicate that it can initiate and influence photochemical processes that could lead to ozone destruction (Solomon, 1999; Abbatt, 2003) in the troposphere. In view of this, chemical processes at the air/liquid interface have attracted a lot of scientific research, of particular interest is acids with liquid water or water-like layer on ice. A number of surface sensitive techniques including Infrared spectroscopy (Darvas et al., 2012) and vibrational sum frequency spectroscopy (Gordon et al., 2018) have been conducted over the years to derive information about the electronic properties of such reaction through the study of the hydrogen-bonding and proton transfer of such reaction. The reason being that the dissociation of trace gases upon interaction with liquid water or the liquid-like layer on ice surface is related to the distortion of the hydrogen-bonding network. X-ray photoelectron spectroscopy (XPS) is one of the most well-established methods to provide detailed information about the chemical composition and electronic properties of molecular systems (Hüfner, 2013) given its surface sensitivity. XPS has been applied to investigate the properties of various molecules at the core-valence region. Studies at interface between metal oxides such as Bismuth Vanadate (Starr et al., 2017), Magnesium oxide (Newberg et al., 2011), and $\alpha - Fe_2O_3$ (Yamamoto et al., 2010) and

aqueous electrolyte solution have indicated that XPS is a powerful tool to investigate the binding energies at the core-valence region. These studies revealed that XPS is able to resolve metal oxide, hydroxyl, surface molecular water and water vapor peaks arising from the core-valence region of water adsorption on metal surface based on their binding energies. Studies into the adiabatic electron binding energies of gaseous species including Uraniumpentachloride (Su et al., 2013) and Uranyl tetrafluoride (Dau et al., 2012) indicate that XPS suitable to study ionic bonding of heavier halogen complexes at the core-valence level. Studies conducted by (Olivieri et al., 2016) with XPS to investigate the ionization energies of aqueous solutions at the core level revealed huge shift in ionization energies of gas phase water in the presence of liquid water and that the ionization energy of the liquid water depends on the chemical composition of the solution. Quite recently, the use of XPS to study the surface of saturated sodium chloride (Tissot et al., 2015; Gaiduk et al., 2016) indicate that XPS is able to resolve ionic chlorine form aqueous solution of sodium chloride based on the core level shift of binding energies with respect to the bulk liquid. XPS has also been utilized to investigate the the impact of acids on liquid water or water ice at the air-liquid interface at core-valence level. Investigations into the bound state of weak acid such as 2-propanol (Newberg and Bluhm, 2015), acetone (Starr et al., 2011) and acetic acid (Krepelova et al., 2013) on ice surface indictate that such species do not produce any significant changes in the hydrogen-bonding network of water ice. It has been suggested that, strong acid on ice surface on the other hand fully dissociate leading to modification in the hydrogen-bonding network of water ice at low temperatures (Parent et al., 2011). Quite recently, experiment on the interaction of HCl at warm ice surface revealed a huge chemical shift in binding energy of 2.2 eV between covalent and ionic form of solvated HCl. The photoelectron spectroscopy experiment further revealed that the ionic form of the HCl perturbs the hydrogen bonding network of the water ice by binding them into solvation (Kong et al., 2017). In this respect, there is the need for molecular dynamics simulation in order to either provide theoretical support or give detailed information on the type of bonding at the core-valence regions to the experimental findings. Theoretical studies based on semi-empirical method aimed to provide understanding of the electronic properties of solvated

HCl determined no chemical shift in the binding energies between ionic and covalent chlorine. These observations fact that semi-empirical methods overestimate the proton transfer barrier and underestimate the proton affinity of chloride anions (Arillo-Flores et al., 2007). Recent studies probing the ground-state properties of hydrogen chloride in solvent suggest that classical molecular dynamics models coupled with ab initio calculations need parameterization of some of the core-core functions to provide accurate description of intermolecular interactions due to the difficulties to sample transitions from the molecular form to the contact ion pair form (Wick, 2017). These are indication that classical models parameterized with ab initio calculations are prone to problems of potential transferability and lead to poor description of intermolecular interactions and hydrogen bonding between solute and solvents if some of the electronic interactions are not optimized or parameterized. At the moment, the electronic structure calculations to give predictive quantitative description of the ground-state electronic properties of solute-solvent systems such as solvated hydrogen halides including excitation energies is a full quantum mechanics based on the combination of first principle molecular dynamics density functional theory (DFT) and many-body perturbation theory (MBPT) in the G_0W_0 approximation. According to studies on the ionization potential and electron affinity of solute-solvent system, density functional calculations followed by the G_0W_0 approximation (Gaiduk et al., 2018; Pham et al., 2017; Opalka et al., 2014) yield accurate results in self-energy calculations, however, it lacks the ability to account for the presence of spin-dependence in coulombic interactions, inaccurate in its application to large and complex systems, not self-consistent (Aryasetiawan and Gunnarsson, 1998) and computationally costly. An alternative approach to the G_0W_0 approximation to probe the ground-state electronic properties of solute-solvent systems to derive photoelectron spectra is the coupled-cluster method. Coupled-cluster formalism at the single and double (triple) (CCSD(T) levels (Bartlett and Musiał, 2007) on water clusters (Blase et al., 2016) and implementations based on equation-of-motion at coupled-cluster single and double levels (EOM-CCSD) (Musiał et al., 2011) on water clusters (Lange and Berkelbach, 2018) have been applied to probe the ionization potential at the ground-state level. These studies indicate that the use of DFT followed by CC approaches predicts binding

energies of solvent systems accurately with small errors compared to G_0W_0 , which underestimate the ionization potential. In addition, prediction of the ionization potential of water clusters based on approximate variant of EOM-CCSD (Dutta et al., 2017, 2018) such as P-EOM-MBPT2 yield results that can be compared to G_0W_0 (Lange and Berkelbach, 2018). Not only have the EOM-CCSD proved to be a significant tool to derive the electronic properties of water clusters but also shown to be a powerful approximation to accurately account for relativistic effects such as spin-orbit coupling in describing the electron affinity, ground- and excited-state properties of halogen species (Shee et al., 2018; Bouchafra et al., 2018). Quite recently, (Peng et al., 2015) have developed a much more elaborate method to target core excitation energies within the EOM-CCSD ansatz based on the core valence separation (CVS) approximation (Cederbaum et al., 1980). This approach is seen to provide a path that only includes excitations from the essential core orbitals when computing the core-level spectra. In this study, we present the use of a new approach in the DFT in the form the so-called frozen density embedding (FDE) method and CVS-EOM-CCSD to provide accurate ground-state photoelectron spectra, including excitation energies of the interaction hydrogen chloride on ice surface. This complicated approach give reliable ground- and excited-state properties based on its partitioning of large systems into subsystems and taking the effect of the environment on a subsystem of interest into account. Recent formulation of FDE have shown that FDE still possesses an exact framework that allows the DFT to be substituted with WFT for one subsystem (WFT-in-DFT) (Gomes et al., 2008; Höfener et al., 2013; Daday et al., 2013) or for all the subsystem under consideration (WFT-in-WFT) (Höfener and Visscher, 2012) as well as the incorporation of coupled-cluster theory, making it possible to calculate the embedding potential for the ground state as well as the excited states at high accuracy and with less computational cost.

In the evaluation of the binding energy of the interaction HCl with ice surface, the statistical averaging orbital potential (SAOP) model (Schipper et al., 2000) would be employed prior to the DFT calculation. Photoelectron spectra obtained with the SAOP model suggest that it provides balanced approach to the exchange correlation potential that predict accurately the ionization en-

ergies (Lemierre et al., 2005; Segala and Chong, 2009) and binding energies of molecules at the core level (Takahata and Chong, 2003). The reason being that, the approximation based on the SAOP model has a perfect long-range (asymptotic) behavior with the ability to reduce self interaction errors in cases where there are discontinuities in the derivative of the total energy as the number of particles varies and also to correctly depict atomic shell structure both in the inner and outer regions which are necessary in the evaluation of ionization potentials in the Kohn-Sham densities (Tecmer et al., 2011) compared to (meta)GGA's, which underestimate the ionization potential in such situation.

1.1 Potential Model

To study the adsorption of HCl on ice surface, we describe the surface interaction potential between them. To compute the intramolecular and molecule-surface interaction energy of this system, the charges, center of masses, and radii for each atom and atom pairs were taken and applied to their corresponding force fields. Based on the fact that different force fields employ different parameter sets, the interaction potential arising from the collision between the HCl and the surface of ice was considered as additive, consisting of the sum of pair potentials, V_{HCl-H_2O} over all water molecules(w), which can be expressed as

$$V_{HCl-ice} = \sum_{w,w_i,j} \frac{q_i q_j}{r_{w_i,j}} + \sum_{w,w_i,j} \frac{C_{6,i,j}}{r_{w_i,j}^6} D(r_{w_i,j}) + \sum_{w,w_i,j} a_{i,j} \exp(-b_{i,j} r_{w_i,j}) \quad (1.1)$$

where the first term on the right hand side of the above equation is the electrostatic potential from the attraction and repulsion between charges of the HCl and water molecules, the second term is the dispersion potential and the last term is the short-range repulsion potential. The q_i 's and q_j 's are the charges on the water molecules and the HCl molecule respectively and the $r_{w_i,j}$ is the distance between the charges. The $a_{i,j}$ and $b_{i,j}$ in the repulsion potential contribution are atom-atom parameters (X-Y), where X= H, O and Y= Cl, H. In the case of the dispersion potential, the coefficient C_6 is from $X - H_2O$, where i = X, (X= Cl, H) and j = H_2O based on the Slater-Kirkwood formula, the $r_{w_i,j}$ is the distance between the centers of mass of the molecules and the

$D(r_{w_i,j})$ is a damping function.

For the water molecules, point charges based on the TIP4P pair potential model (Jorgensen et al., 1983) was used to describe them. This model type consists of two positive point charges representing the hydrogen atoms (+0.52 au) and a negative point charge (-1.04 au) situated at the bisection of the hydrogen sites near the oxygen atom of the water molecule. For the HCl molecule, it was describe with a positive point charge (+0.403 au), a negative point charge (-0.909 au) representing hydrogen atom and chlorine atom respectively and a third positive point charge (+0.506 au) located in a direction opposite the hydrogen atom and 1 au away from the chlorine atom. The values of the parameters C_6 in the dispersion term, and $a_{i,j}$ and $b_{i,j}$ in repulsion term to describe the surface interaction potential between HCl on ice were taken from (Woittequand et al., 2007). The value of the $D(r_{w_i,j})$ was obtained by applying the damping function equation (Kroes and Clary, 1992).

References

- Abbatt, J. P. (2003). Interactions of atmospheric trace gases with ice surfaces: Adsorption and reaction. *Chemical reviews*, 103(12):4783–4800.
- Arillo-Flores, O., Ruiz-López, M., and Bernal-Uruchurtu, M. (2007). Can semi-empirical models describe hcl dissociation in water? *Theoretical Chemistry Accounts*, 118(2):425–435.
- Aryasetiawan, F. and Gunnarsson, O. (1998). The gw method.
- Bartels-Rausch, T., Jacobi, H.-W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P., Ammann, M., Blackford, J. R., Bluhm, H., Boxe, C., et al. (2014). A review of air–ice chemical and physical interactions (aici): liquids, quasi-liquids, and solids in snow. *Atmospheric chemistry and physics*, 14(3):1587–1633.
- Bartlett, R. J. and Musiał, M. (2007). Coupled-cluster theory in quantum chemistry. *Reviews of Modern Physics*, 79(1):291.
- Blase, X., Boulanger, P., Bruneval, F., Fernandez-Serra, M., and Duchemin, I. (2016). Erratum:“gw and bethe-salpeter study of small water clusters”[j. chem. phys. 144, 034109 (2016)]. *The Journal of chemical physics*, 145(16):169901.
- Bouchafra, Y., Shee, A., Réal, F., Vallet, V., and Gomes, A. S. P. (2018). Predictive simulations of ionization energies of solvated halide ions with relativistic embedded equation of motion coupled cluster theory. *Physical review letters*, 121(26):266001.
- Cederbaum, L. S., Domcke, W., and Schirmer, J. (1980). Many-body theory of core holes. *Physical Review A*, 22(1):206.

- Daday, C., Konig, C., Valsson, O., Neugebauer, J., and Filippi, C. (2013). State-specific embedding potentials for excitation-energy calculations. *Journal of chemical theory and computation*, 9(5):2355–2367.
- Darvas, M., Lasne, J., Laffon, C., Parent, P., Picaud, S., and Jedlovszky, P. (2012). Adsorption of acetaldehyde on ice as seen from computer simulation and infrared spectroscopy measurements. *Langmuir*, 28(9):4198–4207.
- Dau, P. D., Su, J., Liu, H.-T., Liu, J.-B., Huang, D.-L., Li, J., and Wang, L.-S. (2012). Observation and investigation of the uranyl tetrafluoride dianion ($\text{UO}_2\text{F}_4^{2-}$) and its solvation complexes with water and acetonitrile. *Chemical Science*, 3(4):1137–1146.
- Dutta, A. K., Vaval, N., and Pal, S. (2018). Lower scaling approximation to eom-ccsd: A critical assessment of the ionization problem. *International Journal of Quantum Chemistry*, 118(14):e25594.
- Dutta, A. K., Vavala, N., and Pal, S. (2017). Assessment of low scaling approximations to eom-ccsd method for ionization potential. *arXiv preprint arXiv:1708.01293*.
- Gaiduk, A. P., Govoni, M., Seidel, R., Skone, J. H., Winter, B., and Galli, G. (2016). Photoelectron spectra of aqueous solutions from first principles. *Journal of the American Chemical Society*, 138(22):6912–6915.
- Gaiduk, A. P., Pham, T. A., Govoni, M., Paesani, F., and Galli, G. (2018). Electron affinity of liquid water. *Nature communications*, 9(1):247.
- Gomes, A. S. P., Jacob, C. R., and Visscher, L. (2008). Calculation of local excitations in large systems by embedding wave-function theory in density-functional theory. *Physical Chemistry Chemical Physics*, 10(35):5353–5362.
- Gordon, B. P., Moore, F. G., Scatena, L. F., Valley, N. A., Wren, S. N., and Richmond, G. L. (2018). Model behavior: Characterization of hydroxyacetone at the air–water interface using

- experimental and computational vibrational sum frequency spectroscopy. *The Journal of Physical Chemistry A*, 122(15):3837–3849.
- Höfener, S., Gomes, A. S. P., and Visscher, L. (2013). Solvatochromic shifts from coupled-cluster theory embedded in density functional theory. *The Journal of chemical physics*, 139(10):104106.
- Höfener, S. and Visscher, L. (2012). Calculation of electronic excitations using wave-function in wave-function frozen-density embedding. *The Journal of chemical physics*, 137(20):204120.
- Hüfner, S. (2013). *Photoelectron spectroscopy: principles and applications*. Springer Science & Business Media.
- Jorgensen, W. L., Chandrasekhar, J., Madura, J. D., Impey, R. W., and Klein, M. L. (1983). Comparison of simple potential functions for simulating liquid water. *The Journal of chemical physics*, 79(2):926–935.
- Kong, X., Waldner, A., Orlando, F., Artiglia, L., Huthwelker, T., Ammann, M., and Bartels-Rausch, T. (2017). Coexistence of physisorbed and solvated hcl at warm ice surfaces. *The journal of physical chemistry letters*, 8(19):4757–4762.
- Kroes, G. J. and Clary, D. C. (1992). Sticking of hydrogen chloride and chlorine hydroxide to ice: A computational study. *The Journal of Physical Chemistry*, 96(17):7079–7088.
- Krepelova, A., Bartels-Rausch, T., Brown, M. A., Bluhm, H., and Ammann, M. (2013). Adsorption of acetic acid on ice studied by ambient-pressure xps and partial-electron-yield nexafs spectroscopy at 230–240 k. *The Journal of Physical Chemistry A*, 117(2):401–409.
- Lange, M. F. and Berkelbach, T. C. (2018). On the relation between equation-of-motion coupled-cluster theory and the gw approximation. *Journal of chemical theory and computation*, 14(8):4224–4236.
- Lemierre, V., Chrostowska, A., Dargelos, A., and Chermette, H. (2005). Calculation of ioniza-

- tion potentials of small molecules: A comparative study of different methods. *The Journal of Physical Chemistry A*, 109(37):8348–8355.
- Musiał, M., Perera, A., and Bartlett, R. J. (2011). Multireference coupled-cluster theory: The easy way. *The Journal of chemical physics*, 134(11):114108.
- Newberg, J. T. and Bluhm, H. (2015). Adsorption of 2-propanol on ice probed by ambient pressure x-ray photoelectron spectroscopy. *Physical Chemistry Chemical Physics*, 17(36):23554–23558.
- Newberg, J. T., Starr, D. E., Yamamoto, S., Kaya, S., Kendelewicz, T., Mysak, E. R., Porsgaard, S., Salmeron, M. B., Brown Jr, G. E., Nilsson, A., et al. (2011). Formation of hydroxyl and water layers on mgo films studied with ambient pressure xps. *Surface Science*, 605(1-2):89–94.
- Olivieri, G., Goel, A., Kleibert, A., Cvetko, D., and Brown, M. A. (2016). Quantitative ionization energies and work functions of aqueous solutions. *Physical Chemistry Chemical Physics*, 18(42):29506–29515.
- Opalka, D., Pham, T. A., Sprik, M., and Galli, G. (2014). The ionization potential of aqueous hydroxide computed using many-body perturbation theory. *The Journal of chemical physics*, 141(3):034501.
- Parent, P., Lasne, J., Marcotte, G., and Laffon, C. (2011). Hcl adsorption on ice at low temperature: a combined x-ray absorption, photoemission and infrared study. *Physical Chemistry Chemical Physics*, 13(15):7142–7148.
- Peng, B., Lestrang, P. J., Goings, J. J., Caricato, M., and Li, X. (2015). Energy-specific equation-of-motion coupled-cluster methods for high-energy excited states: Application to k-edge x-ray absorption spectroscopy. *Journal of chemical theory and computation*, 11(9):4146–4153.
- Pham, T. A., Govoni, M., Seidel, R., Bradforth, S. E., Schwegler, E., and Galli, G. (2017). Electronic structure of aqueous solutions: Bridging the gap between theory and experiments. *Science advances*, 3(6):e1603210.

- Schipper, P., Gritsenko, O., Van Gisbergen, S., and Baerends, E. (2000). Molecular calculations of excitation energies and (hyper) polarizabilities with a statistical average of orbital model exchange-correlation potentials. *The Journal of Chemical Physics*, 112(3):1344–1352.
- Segala, M. and Chong, D. P. (2009). An evaluation of exchange-correlation functionals for the calculations of the ionization energies for atoms and molecules. *Journal of Electron Spectroscopy and Related Phenomena*, 171(1-3):18–23.
- Shee, A., Saue, T., Visscher, L., and Severo Pereira Gomes, A. (2018). Equation-of-motion coupled-cluster theory based on the 4-component dirac-coulomb (–gaunt) hamiltonian. energies for single electron detachment, attachment, and electronically excited states. *The Journal of chemical physics*, 149(17):174113.
- Solomon, S. (1999). Stratospheric ozone depletion: A review of concepts and history. *Reviews of Geophysics*, 37(3):275–316.
- Starr, D., Pan, D., Newberg, J., Ammann, M., Wang, E., Michaelides, A., and Bluhm, H. (2011). Acetone adsorption on ice investigated by x-ray spectroscopy and density functional theory. *Physical Chemistry Chemical Physics*, 13(44):19988–19996.
- Starr, D. E., Favaro, M., Abdi, F. F., Bluhm, H., Crumlin, E. J., and van de Krol, R. (2017). Combined soft and hard x-ray ambient pressure photoelectron spectroscopy studies of semiconductor/electrolyte interfaces. *Journal of Electron Spectroscopy and Related Phenomena*, 221:106–115.
- Su, J., Dau, P. D., Xu, C.-F., Huang, D.-L., Liu, H.-T., Wei, F., Wang, L.-S., and Li, J. (2013). A joint photoelectron spectroscopy and theoretical study on the electronic structure of ucl5- and ucl5. *Chemistry–An Asian Journal*, 8(10):2489–2496.
- Takahata, Y. and Chong, D. P. (2003). Dft calculation of core-electron binding energies. *Journal of electron spectroscopy and related phenomena*, 133(1-3):69–76.

- Tecmer, P., Gomes, A. S. P., Ekström, U., and Visscher, L. (2011). Electronic spectroscopy of UO_2^{2+} , UO_2^+ and UO_2 : an evaluation of time-dependent density functional theory for actinides. *Physical Chemistry Chemical Physics*, 13(13):6249–6259.
- Tissot, H., Olivieri, G., Gallet, J.-J., Bournel, F., Silly, M. G., Sirotti, F., and Rochet, F. (2015). Cation depth-distribution at alkali halide aqueous solution surfaces. *The Journal of Physical Chemistry C*, 119(17):9253–9259.
- Toubin, C., Picaud, S., Hoang, P., Girardet, C., Demirdjian, B., Ferry, D., and Suzanne, J. (2001). Dynamics of ice layers deposited on MgO (001): Quasielastic neutron scattering experiments and molecular dynamics simulations. *The Journal of Chemical Physics*, 114(14):6371–6381.
- Wick, C. D. (2017). A comparison of sodium and hydrogen halides at the air-water interface. *The Journal of chemical physics*, 147(16):161703.
- Woittequand, S., Duflot, D., Monnerville, M., Pouilly, B., Toubin, C., Briquez, S., and Meyer, H.-D. (2007). Classical and quantum studies of the photodissociation of a HX ($\text{X} = \text{Cl}, \text{F}$) molecule adsorbed on ice. *The Journal of chemical physics*, 127(16):164717.
- Yamamoto, S., Kendelewicz, T., Newberg, J. T., Ketteler, G., Starr, D. E., Mysak, E. R., Anderson, K. J., Ogasawara, H., Bluhm, H., Salmeron, M., et al. (2010). Water adsorption on $\alpha\text{-Fe}_2\text{O}_3$ (0001) at near ambient conditions. *The Journal of Physical Chemistry C*, 114(5):2256–2266.