Chapter 1

Summary

The interaction of trace gases, in particular strong acids with ice surface at the air/liquid interface presents many proceses that are essential to the heterogenous chemistry of the atmosphere. A lot of studies have been conducted to derive information about such interaction experimentally and theoretically. Spectroscopic techniques have been employed to probe the electronic structure at the core and valence region of trace gases adsorption on ice surface at low temperatures (Parent et al., 2011). These studies determined that strong acids dissociate on ice surface. 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 Cl for both Cl 1s singlets and Cl 2p doublets. 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), however, detailed information on how such process occurs is not indicated. This implies that molecular dynamics simulation is important to study type of bonding at the core and valence region of strong acids interaction with ice surface. Theoretical studies based on semi-empirical method employed to investigate the nature of bonding of HCl on ice surface determined no chemical shift in the binding energies between ionic and covalent chlorine (HCl does not dissociate on ice surface). These observations were due to the fact that semi-empirical methods overestimate the proton transfer barrier and underestimate the proton affinity of halide anions (Arillo-Flores et al., 2007). Recent studies probing the ground-state properties of hydrogen halides in solvent

have also determined 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 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 electronic interactions are not optimized or parameterized. The electronic structure calculations to give predictive quantitative description of the electronic properties of solute-solvent systems such as hydrogen halides interaction with water molecules is full quantum mechanics based on the combination of first principle molecular dynamics DFT and many-body perturbation theory (MBPT) in the GW approximation. Study of electron affinity of water determined that density functional calculations followed by the G_0W_0 approximation in the many-body perturbation theory (MBPT) is the most accurate method for computing the interatomic interactions and binding energies of electrons in water in gaseous and condensed phases (Gaiduk et al., 2018; **?**). GW approximation is accurate in self-energy calculations, however, it lacks the ability to account for the presence of spin-dependence in the coulombic interactions, inaccurate in its application to large and complex systems, not self-consistent (Aryasetiawan and Gunnarsson, 1998) and computationally costly (**?**) in its coupling with DFT. Currently, the most widely used electronic structure calculations to yield accurate ground-state photoelectron spectra, including excitation energies is the frozen density embedding (FDE) approach in DFT. This complicated approach give reliable ground-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. The use of FDE is able to predict accurately the ground state properties (dipole and quadrupole moments) of short range effects such direct hydrogen bonding between solute and solvent as well Pauli repulsion of the solvent on diffuse diffuse excited states. Studies involving the use of FDE have shown that it provide accurate excitation energies comparable to supermolecular calculations of solvents (Jacob et al., 2006). Although, the use of this embedding scheme in the treatment subsystems is fruitful in eradicating unwanted

charge-transfer excitation in solute-solvent systems, however, it is not without downsides. The DFT-in-DFT for instance is deficient in intermolecular charge-transfer, spin-orbit (SO) coupling inclusion in the excitation of heavy open-shell systems and in cases of adiabatic approximation (**?**). 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) (**?**Höfener et al., 2013) or for all the subsystem under consideration (WFT-in-WFT) (**?**) 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. This approach is capable to account for the failures in the DFT-in-DFT scheme. Studies on the structure and binding energies of hydrated hydrogen halides (Odde et al., 2004) and ion-π complexes (Quiñonero et al., 2005) using DFT and coupled-cluster theory with singles and doubles (CSSD) excitation have shown yield results that are agrees with the ab initio calculations at less computational cost. DFT neglects dispersion effects and overestimate ion-π interactions making it possible to probe the valence region complex systems together with CCSD.

Chapter 2

CORE SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) is one of the most well-established methods to provide detailed information about the chemical state and electronic properties of molecules given its surface sensitivity. XPS is based on the interaction of X-ray with molecules to cause excitation of the core electrons out of their bound orbits. The kinetic energies and angular distributions from the excitation of the core electrons obtained gives an insight into the structure of the molecules. The X-ray induces peturbation in the core electrons leading to transition in which electrons from a bonding orbital can be moved to anti-bonding orbital with core ionization. Following the photoelectron emission, unpaired electrons may couple with other unpaired electrons, resulting in ion with several possible final states with different energies (multiplet splitting). That is, the energy generated as a results of the relaxation of the final state configuration due to loss of sreening effect of the core electron level exites electrons in valence level to unbound states. The difference between the photon energy of the incident x-ray(hv), the element and chemical state binding energy (E_{bind}) of the core electron, and a workfunction dependent (θ_f) gives the kinetic energy (E_{kin}) of the photoelectron, which is expressed as

$$E_{kin} = hv - E_{bind} - \theta_f \tag{2.1}$$

The E_{bind} of the core electron is proportional to the E_{kin} for the detected electron.
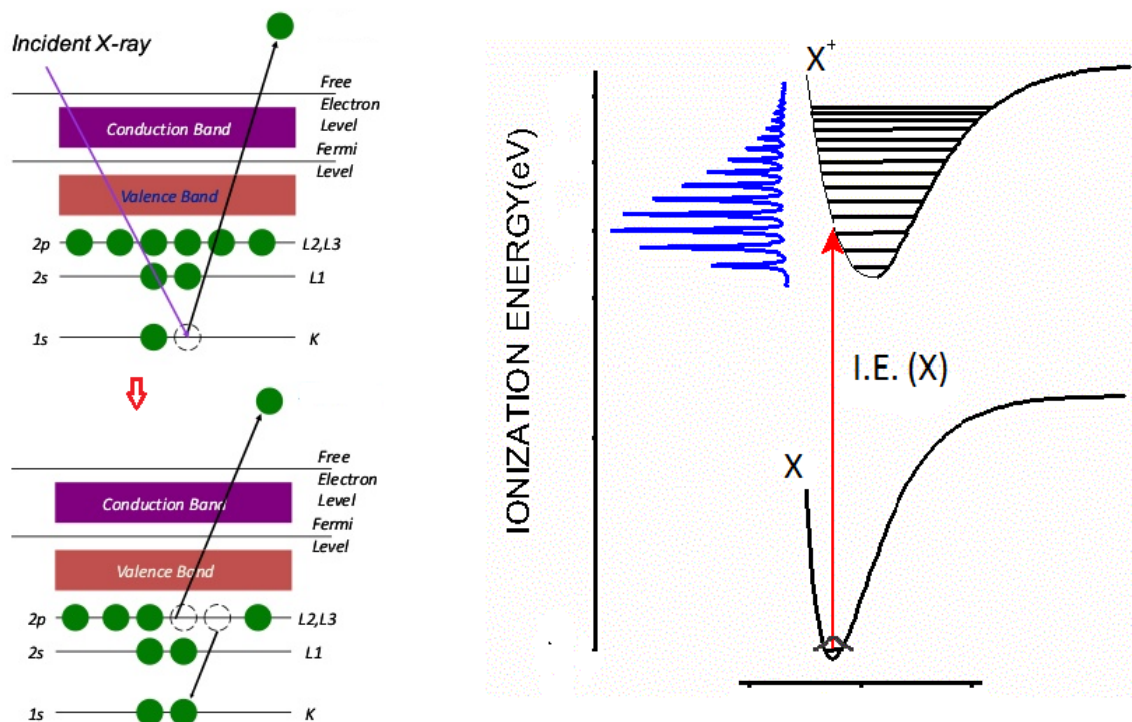
Figure 2.1

The XPS gives the negative Hartree-Fock orbital energy (eigenvalues) based on the assumption that the occupied orbitals from the Hartree-Fock calculations (initial state) is equal to the ionization energy to the ion state (final state) formed by the removal of electron from the orbital provided the distributions of the remaining electrons do not change (frozen). The energies of the orbital give the amount of energy capable to remove (ionize) the electron out of the molecular orbital, which corresponds to a negative ionization potential. In this respect, the ionization energies are directly related to the energies of molecular orbitals and the Koopman's binding energy is given as

$$I_j = -\epsilon_j, \qquad E_{B,K} = -\epsilon_{B,K} \tag{2.2}$$
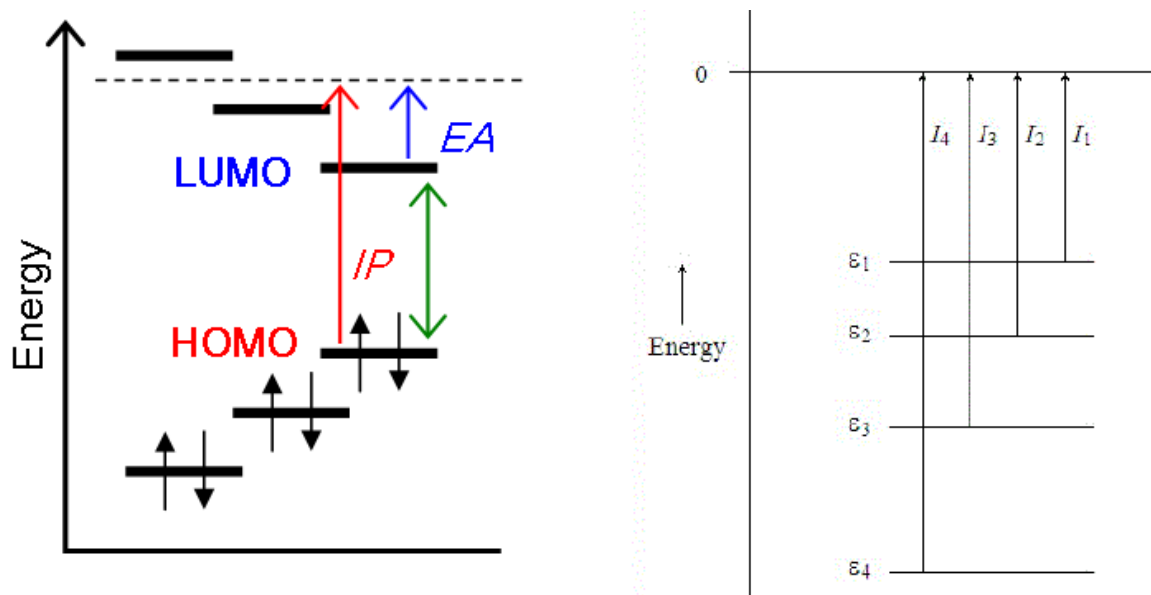
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Figure 2.2

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