

Chapter 1

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 perturbation 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 screening effect of the core electron level excites electrons in valence level to unbound states. The difference between the photon energy of the incident x-ray($h\nu$), 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

$$E_{kin} = h\nu - E_{bind} - \theta_f \quad (1.1)$$

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

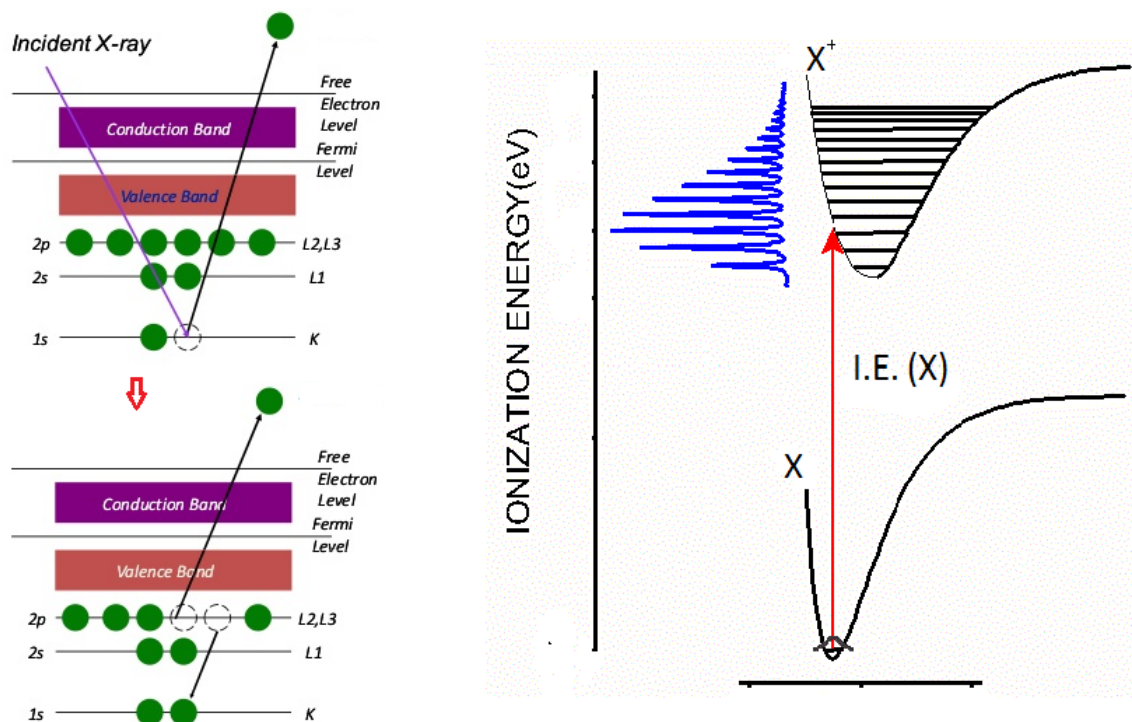


Figure 1.1

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

$$I_j = -\epsilon_j, \quad E_{B,K} = -\epsilon_{B,K} \quad (1.2)$$

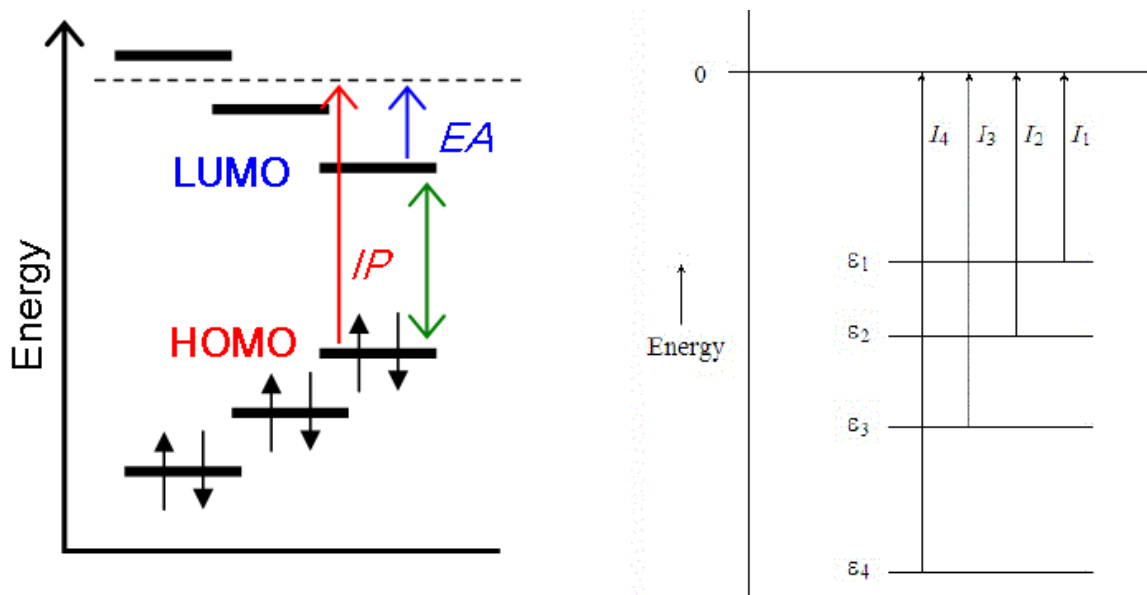


Figure 1.2

1.1 XPS studies on complex systems

Intensity of the ionic Cl intensity depletes at the uppermost surface compared to the deeper region, followed by a slower intensity decay with depth than HCl, which is an indication that HCl is only formed at the surface, while ionic Cl resides deeper in the ice surface region. The presence of ionic Cl induces significant changes to the hydrogen bonding network of water ice by binding the molecules into solvation (perturbation of the hydrogen bonding network by ionic Cl). The water molecules within the interfacial region are mobile or flexible enough to accommodate the need of ionic Cl. HCl leads to an extended disordered layer on the ice. Significant fraction of water molecules are engaged in solvating the ionic Cl and is similar to those in aqueous solution. Chemical shift in binding energy of 2.2 eV between covalent and ionic Cl was observed for both Cl 1s singlets and Cl 2p doublets and were determined by the flexibility in the hydrogen bonding network. Full dissociation of HCl on ice surface was observed at few nanometers. The coexistence of both molecular HCl and ionic Cl exhibited Janus type behavior of the acid which is different from liquid bulk phase and the dissociation occurs only at some distinct location deeper within the air-ice interface. The increasing presence of HCl leads to the line shape of the NEXAFS to

transits from solid ice towards that of liquid water between the main-edge peak and the post-edge peak. HCl partially dissociates upon adsorption at a fraction of a Langmuir monolayer at 253K. A sharp decrease of the apparent HCl/Cl^- intensity ratio in individual XPS spectra with increasing probing depth, indicating that the presence of molecular HCl relative to Cl^- is strongly favored at the outermost surface of ice. Their model indicates that the presence of molecular HCl is limited to a surface layer less than observation of molecular HCl at warm ice surface. HCl adsorption on ice at 253 K deviates from the Langmuir kinetics (Kong et al., 2017)

HCl dissociate into ionic Cl^- and H^+ by making 3 hydrogen bonds by direct reaction with water ice and by self-solvation at low temperatures. Chemical shift in binding energy of 2.6 eV and 1.3 eV were observed between covalent Cl and ionic Cl 1s singlet and 2P doublet respectively. The disappearance of $\sigma(\text{H-Cl})$ resonance (transition from HOMO to LUMO) and the similarity of the XPS spectrum to that of atomic chlorine indicated the dissociation of H-Cl upon adsorption on ice. The formation of the Cl^- anion pulling the ionization potential (IP) downward led to the 4s Rydberg transition is also shifted from 203.3 eV to 200.0 eV. HCl is fully ionized by making three hydrogen bonds with water (contact ion pair $\text{H}_3\text{O}^+:\text{Cl}^-$) or HCl is fully ionized by making three hydrogen bonds, two with water and one with a solvating HCl (that is not dissociated). HCl is adsorbed molecular, singly ($\text{HCl}[1]$) or doubly ($\text{HCl}[2]$) hydrogen bonded with water (Parent et al., 2011).

The C 1s spectra of acetone adsorption on ice showed a chemical shift binding energy of 3.0 eV which were assigned to methyl and carbonyl group. The O K-edge showed transition of O 1s core level into unoccupied π^* orbital. The carbonyl oxygen formed a strong hydrogen bond with a hydrogen atom of a dangling OH on the ice, while one or two weak bonds are involve in the hydrogen atoms of methyl groups and oxygen atoms on the ice surface. Acetone does not induce premelting transition at the ice surface at temperatures up to 245 K. Acetone adsorbs with its molecular plane almost parallel to the ice surface. There is a weak interaction between acetone and ice (Starr et al., 2011).

The C 1s XPS spectra of 2-propanol adsorption on ice surface at 227 K revealed a chemical

shift of binding energy of 1.5 eV, which were assigned to alcohol group and 2 methyl group. 2-propanol does not interact with ice surface strongly. There is minimal lateral interactions between adsorbed 2-propanol molecules and strong hydrogen bonding of the alcohol OH group with ice surface. Ice–OH interaction dominates the overall adsorption energetics which is consistent with a Langmuirian mechanism where lateral interactions are negligible (Newberg and Bluhm, 2015).

The C 1s XPS spectra displayed two features with a chemical shift of binding energy of 3.8 eV, which were assigned to protonated and deprotonated acetic acid. The acetic acid resides within the topmost bilayers of the ice surface. The O-edge spectra indicated only minor perturbations of the hydrogen bonding network and that acetic acid does not lead to extended disordered layer on the ice surface between 230 K and 240 K. The O K-edge NEXAFS are sensitive to the local hydrogen-bonding structure and can help assess whether acid adsorption has an effect on the extent of the QLL or surface premelting. The degree of protonation of acetic acid at the ice surface, about 60%, which is higher than that of an aqueous solution (Krepelova et al., 2013).

1.2 Gas phase studies with XPS and theoretical calculations

Photoelectron spectroscopy and density functional theory were used to study Uranium pentahalides, of particular interest is Uranium pentachloride complexes. The PES spectra revealed that the ionic pentachloride complex is electronically stable at an adiabatic binding energy of 4.76 eV at 157 nm, which is also an electron affinity of neutral pentachloride. Dissociation of the pentachloride anion was observed by the PES at 245 nm. The DFT approach and CC methods calculations (in particular the WFT approach and the EOM-CCSD(T) on the uranium pentachloride complexes provided reliable ground- and excitation-state energies. The chemical bonding of the U-X interactions were dominated in the pentachloride anion were dominated by ionic bonding. Kohn-Sham orbitals and their orbital energies are significant in the interpretation of electron detachments and spectroscopy properties. The photoelectron spectroscopy and the electronic structure calculations provided detailed information in the valence region of the molecular orbitals of the pentachloride complexes. The U-X bond strength decreases from F to I, as a result of the reduced electrostatic interactions,

amid the increase of the relatively weak covalent interactions. The theoretical investigations revealed that the ground-state of the pentachloride anion is a triplet (Su et al., 2013)

The PES spectra of the two hydrated species were similar to that of the solute $UO_2F_4^{2-}$ dianion, except a systematic shift of the electron binding energies due to the solvation effects. The binding energy of the solute $UO_2F_4^{2-}$ dianion and the hydrated $UO_2F_4^{2-}$ dianion were 2.0 eV and 1.7 eV respectively. The adiabatic detachment energy (ADE) and vertical detachment energy (VDE) calculated with the scalar relativistic (SR) CCSD(T) yields accurate results, which is in agreement with experiment. The use of spin-orbit (SO) corrections from the PBE calculations and the SR CCSD(T) gives ADE and VDE of $UO_2F_4^{2-}$ to be around 1.20 and 1.72 eV respectively, which are comparable to the experiment but a little too high. The partial inclusion of multi-reference treatment for excited states in the CCSD(T) yields accurate energies. Both DFT and CCSD(T) calculations proved capable by complementing each other in the accurate description of coulomb repulsion in the dianions and the U-O chemical bonding. DFT and CCSD(T) yielded accurate ground state transitions that are consistent with experimental results (Dau et al., 2012).

1.3 DFT

Kohn-Sham DFT-based molecular dynamics provide accurate description of strong acids interaction with water molecules. The DFT-calculations indicate that Cl^- is solvated with approximately six water molecules in symmetric hydration shell; whereas the molecular HCl only donate one strong hydrogen bond and does not accept any. The free-energy separating the undissociated form of the acids from the ionic form depend on the identity of the acid (Baer et al., 2014).

DFT provide accurate description of hydrogen bonding between hydrogen halides and water molecules comparable to ab initio with less computational cost. Hydrogen halides dissociation is governed by dipole interactions as the dipoles in the water molecules stabilize the ion-pair formed upon dissociation (Cabaleiro-Lago et al., 2002).

DFT and coupled-cluster theory with singles and doubles excitation gives accurate binding energies and electronic properties of hydrogen halides interaction with water molecules comparable

to ab initio method (Odde et al., 2004)

DFT with GGA provides accurate description of the nature of bond with less computational hydrogen halides interaction with water molecules. The chemical shift in binding energies at the core-level indicates the existence of molecular and ionic Cl. The study proved to be accurate in describing the bond breaking and dynamics of the system in self-consistent manner (Calatayud et al., 2003).

Studies on the structure and binding energies of ion- π complexes using DFT/CSSD and ab initio determined that DFT describes ion- π interaction accurately comparable to ab initio method at less computational cost. DFT neglects dispersion effects and overestimate ion- π interactions making it essential in the study of complex systems (Quiñonero et al., 2005)

1.4 QM/MM approaches

Recent studies based QM/MM indicate that classical force based on parametrization of potential energy surface applied on chemical reactions which are strongly influenced by the environment such as the dissociation of HCl at ice surfaces are prone to problems of potential transferability and provide poor description of intermolecular interactions and hydrogen bonding. It underestimates the proton affinity of the chloride anion and overestimate the proton transfer barrier. semi-empirical approaches need reoptimization of the core-core functions and reparameterization of the electronic terms in order to provide accurate description of interaction energies. Chemical shift in the binding energies between the ionic and the covalent was not resolved (Arillo-Flores et al., 2007).

Model parameterized to ab initio calculations determined the binding energies of hydrogen halides in solvent. The study indicates that semi-empirical approach need parameterization of electronic functions to provide accurate description of intermolecular interactions since it was difficult to sample transitions from the molecular form to the contact ion pair form, thereby leading to neglect of the molecular form of the hydrogen halides in the potential of mean force (Wick, 2017).

Chapter 2

DFT and MBPT

The study of electron affinity of water determined that density functional calculations and G0W0 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. However, the G0W0 calculations yielded a mean absolute error (MAE) with respect to measured spectra of 0.18 eV for trajectories including nuclear quantum effects(NQE) and 0.38 eV for classical trajectories. The electron affinity computed with coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] method indicate that the CCSD(T) agrees with, G0W0 for quasiparticle energies agree within 0.05 eV (Gaiduk et al., 2018).

The Green function (GF) method like GW approximation and CC approach are the most suitable approach up to now for studying the excited-state properties of molecular systems. The GW approximation on the other hand is considered to be the most fruitful approximation for self-energy calculations. However, despite the success of the GW approximation in self-energy calculations, it lacks the ability to account for the presence of spin-dependence in the coulombic interactions, not self-consistent and computationally costly and inaccurate in its application to large and complex systems (Aryasetiawan and Gunnarsson, 1998).

Chapter 3

Relativistic coupled-cluster

Chapter 4

Density functional theory

Chapter 5

Frozen density embedding

For FDE to be able account for polarization of the solvent, there is the need to relax the solvent density with respect to the solute in freeze-and-thaw cycles. FDE presents an exact framework that can predict accurately the ground state properties (dipole and quadrupole moments) of short range effects such as direct hydrogen bonding between solute and solvent as well as Pauli repulsion of the solvent on diffuse excited states. FDE provides accurately excitation energies comparable to supermolecular calculations of solvents (Jacob et al., 2006).

FDE presents an exact framework that allows DFT to be substituted with WFT (WFT-in-DFT). This WFT-in-DFT approach allows the incorporation of coupled-cluster density that makes it possible to calculate the embedding potential for the ground state as well as the excited states via the calculation of the kernel contributions to the CC Jacobian matrix. WFT-in-DFT provides accurate variation in electronic spectra induced by solvent molecules. This approach allows the efficient calculation of excitation energies of solvents without compromising the accuracy (Höfener et al., 2013).

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