Chang Q Sun

Spectrometrics

Bond-Electron-Phonon Cooperativity

In memory of and dedicated to my parents

Spectrometrics resolves atomistic, dynamic, and quantitative information on the bond-electron-phonon cooperativity in solid and aqueous substance subjecting to perturbation

O:H-O bond segmental disparity and O-O repulsivity form the soul dictating the extraordinary adaptivity, cooperativity, recoverability, and sensitivity of water and ice

— CQ Sun and Yi Sun, *The Attribute of Water*, Springer, 2016

Bond and nonbond relaxation and the associated energetics, localization, entrapment, and polarization of electrons mediate the performance of substance accordingly

— CQ Sun, *Relaxation of the Chemical Bond*, Springer, 2014

Preface

The following questions wondered me since 1993 when I attended the International Conference on Scanning Tunnelling Microscopy in Beijing:

1. Can one probe transformation of bonds and electrons at sites of point defects and monolayer skins of a substance?
2. How a chemical reaction does occur in temporal domain in a bond-by-bond order?
3. How do bond-electron-phonon cooperate when an object is subject to reaction or external perturbation?
4. Can one derive quantitative information on the evolution of bonds, electrons, and phonons simultaneously from spectroscopic studies?

This volume aims to share my personal thinking and practice, principles and strategies, in reconciling spectrometrics of electron emission, electron diffraction, and phonon absorption and reflection for various subjects. Practice has led to distillation of atomic scale, dynamic, local, quantitative information on: 1) bond dissociation and formation in oxidation reaction; 2) transformation of bond stiffness (phonon frequency shift), abundance (fraction of bonds involved in reaction), and fluctuation (linewidth); 3) electron entrapment and polarization under perturbation by mechanical compression, thermal excitation, atomic (molecular) undercoordination; and, 4) their consequence on the site-resolved atomic cohesive energy, local energy density, Debye temperature, elasticity, etc.

This volume contains four parts with focus on the photoelectron emission spectrometrics, low-energy electron diffraction spctrometrics, solid multifield phonon spectrometrics and solvation phonon spectrometrics:

Part 1 accounts wonders of observations, principles and strategies of approaches. The entire work is founded on the bond order-length-strength correlation and the nonbonding electron polarization (BOLS-NEP) theory for irregular coordinated systems, local bond average (LBA) approach for systems under perturbation of mechanical compression or tension and thermal excitation， and the bond-band-barrier correlation for electron diffraction from chemisorbed surfaces. The strategies include the differential spectrometrics for phonons and electrons that distil transformation of length, energy, and stiffness of bonds and the fraction of bonds transforming upon chemical or physical conditioning.

Part 2 features the coordination-resolved electron spectrometrics and the associated analytical strategies in extracting the atomistic, dynamic, local and quantitative information of bond relaxation in length and energy, core charge quantum entrapment and valence charge polarization, energy density and atomic cohesive energy pertaining to the irregularly (under- and hetero-) coordinated atoms and their joint effect on these entities. Complementing scanning tunnelling microscopy/spectroscopy (STM/S), photoelectron spectroscopy (PES includes XPS and UPS), Auger electron spectroscopy (AES), the BOLS-NEP notion has enabled the combination of AES and XPS as the Auger and photoelectron coincidence spectroscopy (APECS) to determine two energy levels of a specimen and resolve the screening of one level by the other and the charge sharing effect in reaction. The BOLS-NEP theory also enabled the zone-resolved photoelectron spectrometrics (ZPS) that distils information of bond relaxation and associated energetics, localization, quantum entrapment, and polarization of electrons pertaining to adatoms, point defects, terrace edges, monolayer skins, nanocrystals, impurities, and interfaces.

Practice has resulted in clarification, correlation, formulation, and quantification of the electron binding energies in various bands of the following: i) layer and registration resolved fcc(Al, Ag, Pd, Rh, Pt, Ir), bcc (W, Mo, Ta), hcp(Be, Ru, Re), and diamond (Si, Ge) skins, ii) Pt and Rh adatoms, W, Re, and Rh terrace edges, graphite monolayer skin and point defects; iii) carbon allotropes and Si clusters; iii) Au, Ag, Cu, Ni, Co, Fe, Pt, Pd, Li, Na, K, Rb, Cs atomic clusters and nanocrystals; iv) Ag/Pd, Cu/Pd, Be/W, Zn/Pd, C/Si, C/Ge, Ge/Si, Cu/Sn, and Cu/Si interfaces; and, v) the coupling of hetero- and under- coordination effect on TiO_2 skin and ZnO nanocrystals. Exercises have led to information of the local bond length, bond energy, binding energy density, atomic cohesive energy, energy levels of an isolated atom and their coordination–resolved shifts. It is clarified that: i) perturbation to the Hamiltonian by the undercoordination-induced bond contraction, the heterocoordination-induced bond nature alteration, and the polarization of the nonbonding electrons dictate intrinsically the binding energy shift; ii) the local densification and quantum entrapment results in the globally positive core level shift, of which the extent is proportional to the local bond energy; and iii) polarization of the nonbonding states by the densely-entrapped bonding electrons screens and splits the crystal potential and hence offsets the entrapped states negatively. Most strikingly, it has been uncovered that: i) Pt adatoms and Cu/Pd alloy serve as acceptor-type catalysts because of the dominance of entrapment while Rh adatoms and Ag/Pd alloy as donor-type catalysts due to the dominance of polarization; ii) graphitic Dirac-Fermi polarons result from the isolation and polarization of the dangling σ bond electrons by the densely, locally entrapped bonding electrons surrounding the defects and at the zigzag edges of graphene. Charge entrapment and polarization at extremely lower atomic coordination sites shall be related to the ending states, topological states, superfluidity, superconductivity, supersolidity, superelasticity, superlubricity, superhydrophobicity, supercatalysticity, and nanostructural size dependency.

Part 3 deals with the decoding strategies and outcomes of very-low-energy electron diffraction (VLEED) for O-Cu(001) surface in particular. Interplaying with STM/S and PES, VLEED probes the behaviour of atoms and electrons in the valence band and above, which reveals information on bond geometry, valence energy states, and potential barrier from the second atomic layer and above. VLEED determines the variation of work function, atomic muffin-tin inner potential constant, Brillouin zones, and the effective mass of electrons near the Brillouin zone boundaries. Most strikingly, the exposure-resolved VLEED spectral decomposition clarifies the four-stage bonding dynamics of transiting the pairing CuO_2 pyramids to Cu_2O_3 pairing tetrahedrons and the bond-energy relaxation dynamics. O-Cu(001) reaction takes place in four discrete stages: i) O_2 dissociates into 2O atoms that bond to one Cu atom to form a pair of off-cantered pyramids; ii) O^- seeks for the next neighbour from underneath to form the second bond associated with bond angle and bond length relaxation, and meanwhile, the Cu(001) surface misses its every fourth $(\sqrt{2}\times 2\sqrt{2})R45^\circ$ row of Cu atoms to form the missing-row vacancies iii) the sp^3 orbital hybridization takes place, and the nonbonding electron lone pairs polarize its neighbours into paired dipoles across over the missing rows; iv) further bond relaxation stabilizes the surfaces. It ascertains that an O atom tends to form tetrahedral structure in solid phase and the O can only capture one-by-one electron from its different nearest neighbours. The bonding and electronic environment is atomically anisotropic and the angle between bonds varies from 90 to 105° and the angle between lone pairs amounted at 130-150°. VLEED forms such a uniquely sophisticated means that integrates information of bond geometry, three-dimensional surface potential barrier, and electron binding energies from merely the second atomic layer and above.

Part 4 features the Raman and Infrared phonon spectrometrics for comprehensive information of bond length and bond energy varying with stimulus of pressure, temperature, coordination and chemical environment. The BOLS-derived differential phonon spectrometrics (DPS) resolves the transition of bond stiffness (frequency shift), abundance (integral of spectral peak), and the fluctuation order (linewidth) upon the normalization of the spectrum features. Exercises has quantified the local bond length and bond energy from the coordination-, pressure-, and temperature-resolved phonon relaxation of group IV, III-V, II-VI nanocrystals, layered graphene ribbons and WX_2 flakes; water and ice and hydrogen-bond network phonon relaxation dynamics of acid, base, salt, alcohol, sugar, and H_2O_2 solutions.

As a new degree of freedom, the size dependence of phonon frequency shift specifies the reference from which the phonon frequency shifts, bond nature index, as well as the number of bonds involved in the vibration. Atomic dimer vibration dictates the frequency shift of the G mode of graphene, the Eg mode of WX_2, TiO_2, and black phosphor while the collective vibration of an atom with its nearest neighbours governs the D modes of graphene, Ag mode of WX_2 and TiO_2. Reproduction of the pressure-dependent phonon frequency shift derives the biding energy density and the elasticity of a crystal. Temperature-dependent phonon relaxation gives rise to the atomic cohesive energy and the Debye temperature of a substance. The orientation and strain dependent phonon relaxation derives the force constant of single bond of graphene. Dependence of the H-O and O:H phonon frequency on molecular coordination, pressure, and temperature confirms the O:H-O bond cooperativity – O ions dislocate in the same direction along the O:H-O bond by different amount with respect to the H coordination origin. The type and concentration resolved phonon spectra of acid, base, salt, sugar, alcohol, and H_2O_2 solutions verified the essentiality of the H↔H anti-hydrogen-bond fragilization, O:⇔:O super-hydrogen-bond compression, and the ionic polarization of the O:H-O hydration shells in aqueous solutions. Therefore, DPS forms such a powerful tool that resolves solvation dynamics, solute capabilities, and solute-solvent molecular interactions, which is beyond the scope of conventional approaches.

It is a great pleasure to share these personal learnings though some formulations need further refinement and improvement. Critiques from readers are cordially welcome and much appreciated.

I hope that this volume, complementing existing spectroscopy techniques, could inspire more analytically-oriented approaches extracting bond-electron-phonon information and stimulate more interest and activities toward correlating the bond-electron-phonon cooperativity to the performance substance. Directing effort to the areas of extraordinary coordination bond engineering and materials gene engineering could be even more challenging, fascinating, promising, and rewarding.

I would like to express my sincere thanks to colleagues, friends, peers, and seniors for their encouragement, invaluable input, and support, to my students and collaborators for their contribution, and to my family, my wife Meng Chen and daughter Yi, for their assistance, patience, support, and understanding throughout this pleasant journey.

Chang Q Sun

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Author Biography

Chang Q Sun, received his BSc in 1982 from Wuhan University of Science and Technology and an MSc in 1987 from Tianjin University, China and served on its faculty until 1992. He earned his PhD in Surface Physics at Murdoch University, Australia in 1996.

Dr Sun has been working on the Coordination Bonding and Electronic Engineering since 1990 with origination of the unique Bond Relaxation and Hydrogen Bond Cooperativity Theories that have enabled: 1) invention of the Coordination-Resolved Electron and Phonon Spectrometrics; 2) reconciliation of the behaviour of bonds and electrons associated with undercoordinated atoms of defects, skins, nanostructures of various shapes and heterocoordinated atoms in chemisorption and interfaces; 3) formulation of the atomistic, multifield solid mechanics; 4) correlation of bond relaxation and polarization to detectable quantities of aqueous and solid specimens; and 5) resolution of multiple mysteries of water and ice.

His contribution has been featured in three monographs: *Spectrometrics: Bond-Electron-Phonon Cooperativity; The Attribute of Water: Single Notion, Multiple Myths; Relaxation of the Chemical Bond*, in both English and Chinese versions, and some 20 treatises published in *Chemical Reviews*, etc. He has been honoured with the First Laureate of the 25th Khwarizmi International Science Award in 2012.

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- *Features the latest progress and future trends in transiting spectroscopies to spectrometrics*
- *Reinforces principles of bond-electron-phonon cooperativity in responding to perturbations*
- *Narrates strategies extracting atomic-scale and quantitative information from spectroscopies*
- *Establishes referential database for coordination bonding and electronic energineering*

Back cover

This volume features the advancement in transiting the traditional electron-phonon spectroscopies to the bond-electron-phonon cooperativity spectrometrics. Strategies have enabled atomic scale, dynamic, and quantitative information on bond relaxation in length and energy, bonding electron quantum entrapment, nonbonding electron polarization, atonic cohesive energy, binding energy density. Exercises also led to information on transition of phonon frequency, abundance, fluctuation order pertaining to irregularly coordinated atoms and molecules under various excitations and their consequences on the performance of aqueous and solid substances.

Targeted audience includes researchers, scientists, and engineers, in chemistry, physics, surface and interface science, materials science and engineering.