2.2 The Franck-Condon Principle (FCP)

2.2.1 FCP and Born-Oppenheimer Approximation

The Franck-Condon Principle originated in molecular spectroscopy in 1925 when J. Franck proposed (and later Condon provided a theoretical basis for) the idea that, when molecules absorb photons to undergo an electronic transition from the ground state (see E_0 in Figure 2-2) to an excited state (E_1), the electronic transition occurs so rapidly that heavy nuclei do not have time to rearrange to their new equilibrium positions (see q_{01}). In effect, this means that the photon-induced electronic transitions are most likely to occur from the ground vibrational level (i.e., $v'' = 0$) of the ground electronic state to an excited vibrational level (i.e., $v' = 2$) of the upper electronic state (see the vertical arrow in Figure 2-2). A year later, Born and Oppenheimer justified what later became known as the Franck-Condon principle in terms of the large mass difference between the electron and average nuclei in a molecule (Born and Oppenheimer 1927). The proton is 1,836 times as massive as the electron.

The Born-Oppenheimer approximation is also known as the "adiabatic pathway" meaning that there is a complete separation between nuclear and electronic motions within atoms. Although this approximation has been found to be generally valid in atomic and molecular spectroscopy and in chemical reactions, there are also well-established exceptions, which are referred to as "non-adiabatic pathways", "non-Born-Oppenheimer coupling" (Bowman 2008, Garand et al 2008).

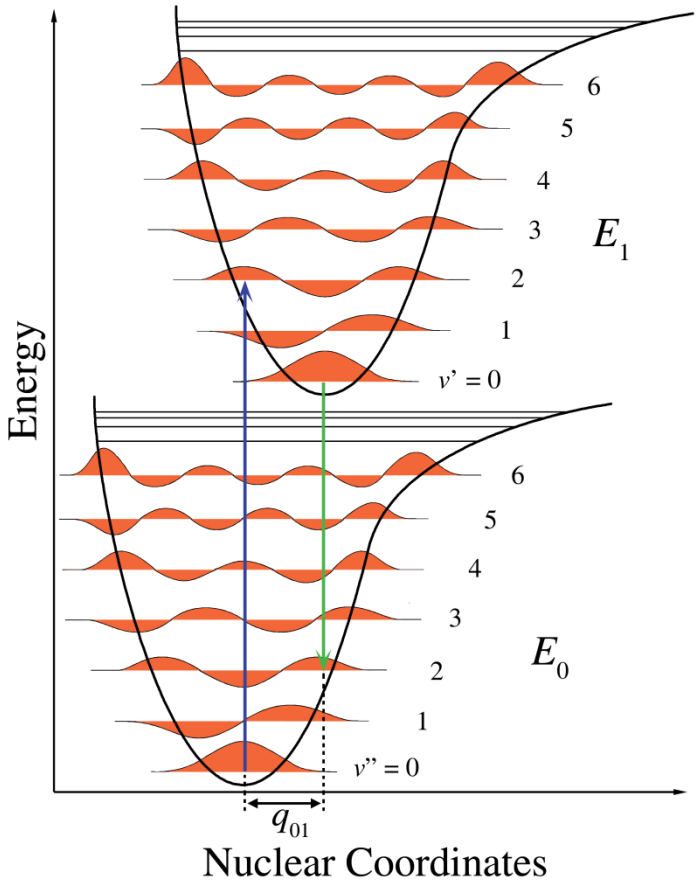


Figure 2-2 A schematic representation of the Franck-Condon principle (reproduced from http://en.wikipedia.org/wiki/Franck-Condon_principle). The upward arrow indicates the most favored vibronic (i.e., both vibrational and electronic) transition predicted by the Franck-Condon principle.

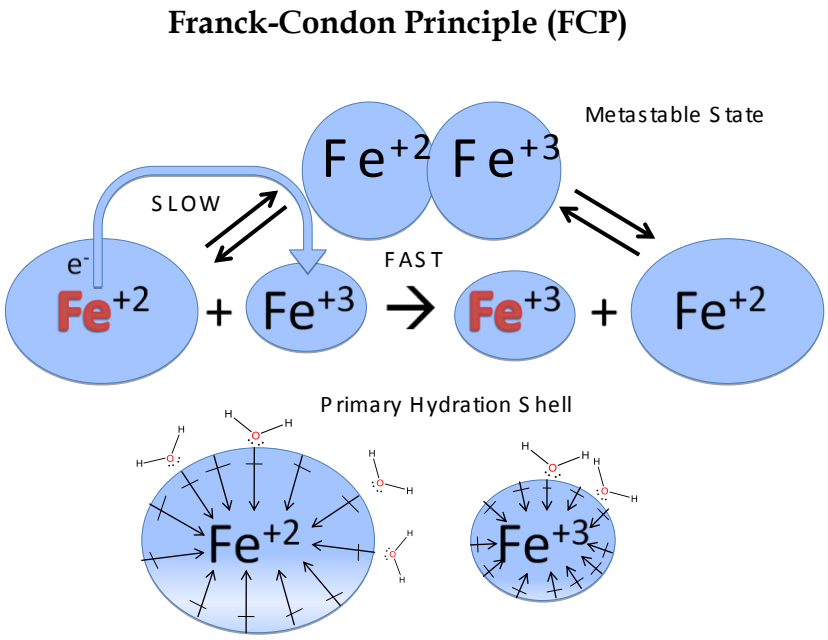
2.2.2 Franck-Condon Principle in Chemistry

It is well established in inorganic electron transfer reactions that electron transfer processes must be preceded by the reorganization of the solvation (also called hydration) shells surrounding reactants (Reynolds and Lumry 1966). It was Libby (1952) who accounted for this phenomenon based on the Franck-Condon principle, suggesting that, *before the fast electron transfer can occur, the slower nuclear rearrangements of water molecules in the hydration shells must take place*, the proton being 1,836 times as massive as the electron. This is schematically illustrated in Figure 2-3. The overall reaction involves the transfer of one electron from the ferrous ion, Fe^{+2}, to the ferric ion, Fe^{+3}. Due to the charge difference, the hydration shell around the ferric ion is more compact than the hydration shell around the ferrous ion. Despite this, there is a finite probability that the two hydration shells assume similar sizes at some time points as depicted by the two identically sized spheres partially overlapping in the upper portion of Figure 2-3. Such a transient, metastable state is known as the *Franck-Condon state* or the *transitions state*, and it is only in this state that one electron can be transferred from Fe^{+2} to Fe^{+3} resulting in the electron

being on either of the iron ions. That is, in the Franck-Condon state, the two iron ions are chemically equivalent, within the limits set by the Heisenberg Uncertainty Principle (Reynolds and Lumry 1966). The Franck-Condon complex (i.e., the reaction system at the Franck-Condon state) can now relax back to the reactant state or relax forward to the product state, depending on the sign of the Gibbs free energy change, ΔG, accompanying the redox reaction. If ΔG given by Eq. (2-23) is negative, the reaction proceeds forward (from left to right), and if it is positive, the reaction proceeds backward (from right to left).

$$\Delta G = G_{final} - G_{initial} = \Delta G^{0} - RT \log (Fe^{+2})/(Fe^{+3}) \quad \ldots\ldots\ldots\ldots \quad (2\text{-}23)$$

where G_{final} and $G_{initial}$ are the Gibbs free energy levels of the final and initial states of the reaction system, ΔG^{0} is the standard Gibbs free energy (i.e., ΔG at unit concentrations of the reactants and products), R is the universal gas constant, T is the absolute temperature of the reaction medium, and (Fe^{+2}) and (Fe^{+3}) are the concentrations of the ferrous and ferric ions.



(*Drawn by Julie Bianchini, 2008*)

Figure 2-3 The Franck-Condon Principle in action in one of the simplest chemical reactions known, i.e., the one-electron redox reaction of the iron ions. (*Lower*) Due to the greater charge density around the ferric ion (Fe^{+3}), as compared with that around the ferrous ion (Fe^{+2}), water dipoles (depicted as crossed arrows) are more strongly attracted to the former than to the latter, forming smaller and tighter primary hydration shell around Fe^{+3} than around Fe^{+2}. (*Upper*) The electron transfer process is much faster than the nuclear rearrangements accompanying hydration shell changes (due to the proton being ~ 2000 times more massive than the electron). The hydration shells around both the Fe^{+3} and Fe^{+2} ions contract and expand (i.e., "breath") periodically as a consequence of thermal fluctuations or Brownian motions (not shown).

2.2.3 The Generalized Franck-Condon Principle (GFCP)

It was postulated in (Ji 1974a) that the *Franck-Condon principle* need not be restricted to electron transfer processes in molecular spectroscopy or inorganic electron transfer reactions but could be extended to any physicochemical processes that involve coupling between two processes whose rates differ significantly. The generalized version of the Franck-Condon p-principle was also referred to as the *Principle of Slow and Fast Processes* (PSFP) (Ji 1991, p. 52-56), which states that

> "Whenever an observable process, P, results from the coupling of two partial processes, one slow (S) and the other fast (F), with F proceeding faster than S by a factor of 10^2 or more, then S must precede F." (2-24)

Statement (2-24) as applied to enzymic catalysis can be schematically represented as follows:

$$(A^\circ + B)_r \text{ <--> } [(A^\circ + B)^\ddagger \Leftrightarrow (A + B^\circ)^\ddagger] \text{ <--> } (A + B^\circ)_p \qquad (2\text{-}25)$$

where A and B are the donor (or source) and the acceptor (or sink) of a particle denoted by ° (which can be any material entities, either microscopic or macroscopic), and the parentheses indicate the immediate environment (also called microenvironment) surrounding the reactant system, i.e., $(A^\circ + B)_r$, or the product system, i.e., $(A + B^\circ)_p$, where the subscripts r and p stand for reactant and product, respectively. The superscript ‡ denotes the so-called Franck-Condon state which is intermediate between the reactant and product states so that the particle now loses its preference for either A or B and can be associated with A or B with equal probability within the constraints imposed by the Heisenberg uncertainty principle (Ryenolds and Lumry 1966). The Franck-Condon states, connected by a double-headed arrow, ⇔, and enclosed within the square brackets, can be either two distinct states separated by a free energy barrier large relative to thermal energies or may be two aspects of a common resonance state (Ji 1974a), in which case the free energy barrier between the two states are less than or comparable to thermal energies (i.e., 0.6 Kcal/mole at physiological temperatures).

So generalized, the Franck-Condon principle can be applied to a wide range of biological processes as pointed out in Table 1.12 in (Ji 1991), which is reproduced below as Table 2-1:

Table 2-1 The application of the generalized Franck-Condon principle to biological processes at different levels of organization. Reproduced from (Ji 1991, p. 54).

Table 1.12. The application of the generalized Franck-Condon Principle to various biological rate processes.

	Partial Processes	
Overall Process (P)	Fast (F)	Slow (S)
1. Enzymic catalysis	Covalent bond rearrangements (i.e., electronic transitions)	Conformational rearrangements of catalytic groups (i.e., nuclear rearrangements)
2. Gene expression	Enzymic reactions	Conformational rearrangements of double-stranded DNA
3. Memory	Input of signals to neurons	Rearrangements of genes in DNA(?)
4. Morphogenesis	Gene expression	Rearrangements of the connections between cells and between cells and extracellular matrix(?)
5. Evolution	Events in individual organisms	Rearrangements of physical and social environments of organisms

The processes accounted for by GFCP include ligand binding to receptors, enzymic catalysis (Section 10.2), ion pumping, action of molecular motors (Sections 11.1 and 15.2), gene expression, cell migration, morphogenesis (Section 18.3), and biological evolution itself.

After over two decades since the list in Table 2-1 was prepared, the list of the fields where GFCP has been found to apply has grown from 5 to 10 (see Table 2-2).

Table 2-2 The universality of the Generalized Franck-Condon Principle, GFCP (or the Principle of Slow and Fast Processes, PSFP). GFCP (or PSFP) has been postulated to act the levels of molecules, chemical reactions, the origin of life, receptors, enzymes, photosynthesis, cells, brain processes, and the biological evolution.

Level	Fast (F)	Slow (S)	Overall Process (P)
1. Molecules (*Figure 2-2*)	Electronic transitions (intramolecular)	Nuclear movements (intramolecular)	Absorption or emission of photons
2. Chemical Reactions (*Figure 2-3*)	Electron transfer (intermolecular)	Nuclear movements (intermolecular)	Reduction-oxidation reactions
3. Origin of Life (*Figure 13-3*)	Thermal motions	Heating-cooling cycle attending the rotation of the Earth	Self-replication
4. Ligand Receptors (*Figure 7-2*)	Ligand diffusion into and out of the binding pocket	Conformational change of the receptor	Molecular recognition by receptors and enzymes
5. Enzymes (*Figures 7-6)*	Electronic rearrangements	Conformational changes of enzymes,	Enzymic catalysis
6. Photon Receptors	Light-induced electronic excitation of chromophores	Conformational change of reaction center proteins	Photosynthesis (Conversion of radiation energy to chemical energy)
7. Metabolic Network (*Figure 15-3*)	Local metabolic fluctuations	Intracellular microenvironmental changes	gene-directed intracellular processes
8. Cells (*Figure 15-2)*	Intracellular metabolic fluctuations	Extracelllular environmental changes	Goal-directed cell functions (i.e., space- and time-dependent gene expression)
9. Brains (*Figure 17-1)*	Neuronal firings	Neural assembling and disassembling	Micro-macro coupling through neural synchrony

10. Evolution (Figure 15-13)	a) DNA/RNA polymerization reactions (Devo) b) Life cycles of organisms (Evo)	a) Conformational changes of DNA and chromatins b) Geological and environmental changes	a) Gene expression b) Natural selection

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