Glossary

adiabatic approximation | Its original form, due to Max Born and Vladimir Fock (1928), was stated as follows: "A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum." [Wikipedia]

adiabatic dynamics | Evolution occurring on a single electronic state

annihilation operator | Annihilation operators “annihilate” one quantum of energy and shift the eigenstate to the next lower one in energy.

avoided crossing | The phenomenon where two eigenvalues of an Hermitian matrix representing a quantum observable and depending on N continuous real parameters cannot become equal in value ("cross") except on a manifold of N-2 dimensions. [Wikipedia]

Baker–Hausdorff relationship | The statement that only commutators and commutators of commutators, ad infinitum, are needed to express the solution.

Brownian motion | The fluctuating position of a particle under the influence of a thermal environment.

Condon approximation | The assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

conical intersection | The set of molecular geometry points where the potential energy surfaces are degenerate (intersect) and the non-adiabatic couplings between these states are non-vanishing.

creation operator | Creation operators “create” one quantum of energy and shift the eigenstate to the next higher one in energy.

cumulant expansion | An alternative way to *moment expansion* to characterize probability distributions provided all the moments exist.

Davydov splitting | The splitting of states that due to overlapping wavefunctions of two translationally inequivalent molecules.

density matrix | An alternate representation of the state of a quantum system for which we have previously used the wavefunction. Although describing a quantum system with the density matrix is equivalent to using the wavefunction, one gains significant practical advantages using the density matrix for certain time-dependent problems—particularly relaxation and nonlinear spectroscopy in the condensed phase.

dipole correlation function | The function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of E field and contains information on states of system and broadening due to relaxation

electric dipole approximation | The approximation that the wavelength of the type of electromagnetic radiation that induces, or is emitted during, transitions between different atomic energy levels is much larger than the size of the atom or molecule.

exciton | A bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force.

homogeneous broadening | Lind broudening due to dynamic processes intrinsic to the molecular system. This is commonly assigned a time scale T_2.

hot bands | A band associated with the transition between two excited vibrational states, i.e. neither is the overall ground state.

inhomogeneous broadening | Broadened lineshapes by a static distribution of frequencies (on the timescale of the measurement).

ladder operators | Ladder Operators are operators that increase or decrease eigenvalue of another operator. There are two types; raising operators and lowering operators. The raising operator is also called the creation operator because it adds a quantum in the eigenvalue and the annihilation operators removes a quantum from the eigenvalue.

Landau–Zener expression | An analytic solution to the equations of motion governing the transition dynamics of a two-state quantum system, with a time-dependent Hamiltonian varying such that the energy separation of the two states is a linear function of time. [Wikipedia]

mixed state | A state that consists of a statistical ensemble of different state vectors. Density matrix formalism is useful for describing mixed states, because it can be a characterized by single density matrix.

nonadiabatic dynamics | Evolution affected by more than one electronic state. This includes phenomena like intersystem crossing and internal conversion.

orientational relaxation | An ensemble averaged dephasing effect associated with the randomization of the initial dipole orientations.

population relaxation | Decay in the coherence created by the light field as a result of the finite lifetime of the coupled states. It is often assigned a time scale T_1.

potential of mean force | The free energy surface along the chosen coordinate. The PMF examine how a system's energy changes as a function of some specific reaction coordinate parameter.

pure dephasing | A dynamic effect in which memory of the phase of oscillation of a molecule is lost as a result of intermolecular interactions that randomize the phase. It is characterized by a time constant T_2*.

pure state | A system that can be described via a single state vector.

second cumulant approximation | A cumulant expansion that is truncated at second order.

spectral density | A coupling-weighted density of states.

spectral diffusion | The process that a individual chromophore will have a dynamic “instantaneous frequency” that evolves in time as a result of its interactions with a dynamically evolving system.

stochastic | Motion or model that includes a random component to the time-development.