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Application of Spectrometry and Spectroscopy to Time Scale Analysis in Astrochemistry

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ABSTRACT
Application of numerous quantum concepts and principles of the well-developed theories of rate coefficients in the velocity of chemical reactions, including quantum tunneling and various equilibriums, to the development of nanotechnology beyond nanometer-accuracy in distance measurements at the single molecule level extends the analysis of results from distance measurements to time scale analysis that with combination of spectrometry and spectroscopy extends the knowledge of percentage distribution of elements that are heavier than iron in the birth of super-novae and are too heavy to be produced by stellar fusion in comparison to lighter elements, like oxygen, carbon, or helium to time scale investigation of chemical reactions in neutron stars and supernovae to imply Rayleigh-Taylor and Richtmyer-Meshkov instabilities, and break of spherical symmetry, consequently indicating concentration of pressures and energies in small regions. In combination with Kolmogorov's turbulence 5/3 time-scale law and loophole free Bell tests that can result in thousands times difference could be applied to time differences evaluation. Further application of these and similar theoretical approaches can extend research to nano-level investigations of the multitude of polymers' shapes and could be further applied to DNA and RNA analysis.

Keywords: Quantum Effects, Nanometer Accuracy, Transitional State Theory, Supernovae, Time-Scale Law

The rate of chemical reactions is a very complicated subject." (H. S. Johnson, 35 years after Eyring, Polanyi, and Evans introduced Transitional State Theory) "The overall picture is that the validity of the transition state theory has not yet been really proved and its success seems to be mysterious." (Raymond Daudel, Georges Leroy, Daniel Peeters, and Michael Sana, 17 years later in "Variational Transition State Theory with Multidimensional Tunneling" by Antonio Fernandez-Ramos, Benjamin A. Ellingson, Bruce C. Garrett, and Donald G. Truhlar)." The advent of quantum mechanics in 1926 brought a unifying view of the particle-wave duality that permitted a straightforward understanding of puzzling phenomena such as tunneling. Nobel prizes awarded for applying the concept of tunneling have since included those for the theory of alpha decay, the invention of tunnel junctions, and the invention of the electron scanning tunneling microscope. Tunneling may occur when two media are separated by a third medium and a wave description is appropriate for determining the propagation of energy. If only ordinary traveling waves are required for the analysis prior to looking at tunneling, the desired results are the reflection and transmission, or refraction, coefficients at each boundary" (T. L. Ferrell, J. P. Goudonnet, R. C. Reddick, S. L. Sharp, and R. J. Warmack "The Photon Scanning Tunneling Microscope").

Quantum tunneling is a quantum phenomenon, where subatomic particle passes through potential barrier and is important for nuclear fusion in stars like Sun. The concept of quantum tunneling is closely related to quantum bottleneck states near reaction barriers that is subject to recent experiments in chemical reactions.

100 years ago Arthur Eddington proposed hydrogen-helium fusion as source of stellar energy that was supported by experiments with light elements 10 years later.

"The calculation of rate coefficients is a discipline of nonlinear science of importance to much of physics, chemistry, engineering, and biology. Fifty years after Kramers' seminal paper on thermally activated barrier crossing, the authors report, extend… to theories of noise-activated escape, for which many of the notable contributions are originating from the communities both of physics and of physical chemistry. Theoretical numerical approaches for single- and many-dimensional metastable systems (including fields) in gases and condensed phases. The role of many-dimensional transition-state theory is contrasted with Kramers' reaction-rate theory for moderate-to-strong friction. The rate theory accounting for memory friction with turnover theory. The peculiarities of noise-activated escape in a variety of physically different metastable potential configurations are elucidated in terms of the mean-first-passage-time technique. At lower temperatures, quantum tunneling effects start to dominate

the rate mechanism. The early quantum approaches as well as the latest quantum versions of Kramers' theory are discussed, thereby providing a description of dissipative escape events at all temperatures…to indicate the most important areas for future research in theory and experiment [1]."

Introduction

The mathematical structure of the models of Boltzmann type kinetic equations for reacting gas mixtures for particles undergoing inelastic interactions with reactions of bimolecular and dissociation-recombination type is very complicated, because of the collisional operators that usually in the full Boltzmann equations are expressed by 5-fold integrals. Consequently direct numerical applications of these models present several computational difficulties. The search for the simpler solution had its long way till the introduction of the equation for the Brownian motion by Albert Einstein.

Jacobus van't Hoff, who laid foundations of stereochemistry and was the first winner of the Nobel Prize in Chemistry, and Arrhenius, who also was awarded Nobel Prize in Chemistry 2 years later were the first to introduce equations for the equilibrium and rate constants 135 and 130 years ago. Van 't Hoff equation for the temperature dependence of the equilibrium constant for a reversible reaction:

$$A \rightleftharpoons B$$
$$\mathrm{d}(lnK) / \mathrm{d}T = \Delta U / RT^2$$

where K is the equilibrium constant of the reaction, ΔU is the change in internal energy, R is the universal gas constant, and T is thermodynamic temperature.

Arrhenius equation was one of the earliest attempts to find rate constant:

$$k = Ae^{\frac{-E_a}{RT}}$$

where k is the rate constant, E_a is the activation energy barrier, R is the gas constant, T is temperature in Kelvin, A is frequency factor constant or Arrhenius factor for the rate of collision. With kb denoting Boltzmann constant and h Plank's constant.

$$A = \frac{k_b T}{h}$$

that does not consider the state of equilibrium of the reactants.

Eyring, Polanyi, and Evans introduced Transitional State Theory (TST) some 75 years ago that gives functional expression for the connection between equilibrium and rate constants. TST does not require the reactants and products to be in equilibrium, but the activated complexes are in quasi- equilibrium with the reactants.

The equilibrium constant was supposed to be proportional to the exponent of Gibbs free energy.

$$k \propto \exp(\Delta G/RT)$$

where ΔG is Gibbs energy of activation and difference between energy of reactants and activated complexes and equals in terms of entropy of activation ΔS and enthalpy of activation ΔH to:

$\Delta G = \Delta H - T\Delta S$, it follows that $k \propto \exp(\Delta S/R) \exp(-\Delta H/RT)$,

Considering that equilibrium constant k_1 for the quasi- equilibrium is the essential component in the above equation and the rate constant is expressed through the equilibrium constant for

the quasi- equilibrium and some constant k_2 that is directly proportional to the frequency v of the vibrational mode in converting the activated complex to the products of the reaction, the rate constant can be written as:

$$k = k_1 k_2$$

where $k_2 = k'v$

where k' is a proportionality constant, and from the statistical mechanics considerations the equilibrium constant k_1 for the quasi- equilibrium can be written as:

$$k_1 = \frac{k_b T}{hv} \widehat{k_1}$$

where $\widehat{k_1} = \exp(-\Delta G/RT)$ and the expression for the rate constant becomes $k = \frac{k_b T}{hv} \exp(-\Delta G/RT)$, Combining all the

$$A = k' \frac{k_b T}{h} (\Delta S/R) \exp(-\Delta H/RT).$$

After the adjustment for dimensionality depends on standard concentration c and molecularity parameter m, the equation becomes:

$$A = k' \frac{k_b T}{h} \exp(\Delta S/R) \exp(-\Delta H/RT) c^{(1-m)}.$$

Kramers used newly discovered concepts of quantum tunneling and other quantum phenomena, when he introduced his approach to the velocity of chemical reactions based on Bohr-Kramer-Slater "The quantum Theory of Radiation":

Historical development of Bohr-Kramers-Slater theory of equilibrium, Eyring-Polanyi-Evans transitional state theory, and Rice-Ramsperger-Kassel-Marcus rate theory on quantum matter level, and their subsequent application to Fokker-Plank equation for the velocity of chemical reactions with further extension to multidimensional approach with various problems arising in their applications that should be accounted for before being extended further to different more complicated applications including proteins.

Next year after Kramers applied Smoluchowski equation that uses such concepts as memory friction, quantum tunneling, and equilibrium with other quantum concepts to velocity of chemical reactions [2].

A.N. Kolmogorov introduced 5/3 law using considerations of dimensionality and statistical isotropy for spatial independence of directions of low scale turbulence motions that imply loss of geometrical and directional information in Richardson's energy cascade for energy spectrum function [3-10].

$$E(K) \approx C\varepsilon^{2/3}k^{-5/3}$$

where ε is energy flow and k is a wave number, and C is some dimensionless constant that can be determined from experiments and is close to 1.

This derivation is considered heuristical, even though Zakharov in the middle 60-es, 3 years after Kolmogorov's attempt to approach the problem of intermittency (pattern of chaotic dynamic during only a fraction of the time that decreases with the scale) has shown that wave kinetic equations (closed integro-differential equations for the spectrum) have exact power-law solutions which are similar to Kolmogorov's spectrum of hydrodynamic turbulence [11,12].

Kramers' theory of the velocity of chemical reactions introduced diffusion equation based on assumption that the reactants are in the state of equilibrium, or quasi- equilibrium (chemical equilibrium) in the following form of Fokker-Plank equation:

$$m\frac{\partial^2 x}{\partial t^2} = \frac{\partial U(x)}{\partial x} - \gamma m\frac{\partial x}{\partial t} + f(t)$$

where m is reduced mass in the potential of mean force U, and F is a noise of a random fluctuating force, originating from the thermal motion, is a viscosity, or so called memory friction for Smoluchowski equation and one of the essential components of many kinetical systems.

It was based on the assumptions about a particle that moves in an external field of force and additionally is subject to the irregular forces of a surrounding medium in temperature equilibrium, which he called Brownian motion. The conditions are such that the particle is thought of as caught in a potential hole but may escape in the course of time by passing over a potential barrier. The problem is to calculate the probability of escape in its dependency on temperature and viscosity of the medium.

The Stochastic Differential Equation for the transport of a particle is given by:

$$dX_t = \mu(X_t, t)\,dt + \sigma(X_t, t)\,dWt$$

where $\mu(X_t, t)$ and $\sigma(X_t, t)$ are the mean and covariance matrices of the process and dWt is Brownian or white noise.

For Brownian motion and Langevin Equations:

$$m\frac{\partial^2 x}{\partial t^2} = -\gamma\frac{\partial x}{\partial t} + f(t)$$

From Langevin Equation follows 1-D Fokker-Planck Equation

$$m\frac{\partial^2 x}{\partial t^2} = -\frac{\partial U(x)}{\partial x} - \gamma m\frac{\partial x}{\partial t} + f(t)$$

by considering Brownian noise F (t) as a differential in time of Brownian process depending on x coordinate and time and composing PDE

$$\left[\frac{\partial^2 W(x,t)}{\partial t} = \frac{\partial U'(x)}{\partial x} + D\frac{\partial^2}{\partial x^2}\right] W(x,t)$$

Modifications
7 years later Grote and Hynes applied Langevin equation to model the motion along the reaction coordinate and derived expressions for the rate constant for different friction values.

Their approach was based on later modifications to Kramers approach used 1-D, 2-D, 3-d, and multi-D Fokker-Planck Equations. For 3-D

$$\frac{\partial f(r,t)}{\partial t} = \left[-\sum_{i=1}^{3}\frac{\partial}{\partial x_i}D_i^1(r) + \sum_{i=1}^{3}\sum_{j=1}^{3}\frac{\partial^2}{\partial x_i \partial x_j}D_{ij}^1(r)\right]f(r,t)$$

Inverse dependence of the rate constant on friction in Kramers' theory that increases with increasing γ when γ is small and decreases with increasing γ when γ is large with expectation that k reaches maximum at some value of γ and decreases to zero with approaching either zero or infinity is known as Kramers' turnover problem [13].

Kramers derived expressions for the rate constant for different ranges of the friction coefficient. The friction arises from coupling of the reaction coordinate to other degrees of freedom of the reactant molecule and to solvent molecules, serving as a thermal bath. A simple model for a thermal bath consists of a set of n harmonic oscillators with the potential energy [13].

The study had the following problems, pointed out in his original paper:
1. The study for the sake of simplicity was only a one-dimensional model.
2. However, as long as no perfect temperature equilibrium is attained, the equation of Maxwell velocity distribution holds only approximately. This is even the case when the external force is zero. According to his description, the Brownian forces of the medium illustrate the mechanism which strives to bring about temperature equilibrium. The value of the viscosity coefficient γ (which may depend on T even in the manner of an exponential function) is a measure for the intensity with which the molecules in the different states react with the surrounding medium.
3. The model illustrates also the ambiguity involved in the conception, transition state".
4. Quantum mechanical, tunnel-effects" for which there is no room in our model, could also play a part.
5. Both Kramers and Grote-Hynes improvement give a well-defined rate constant, and therefore cannot account for dispersed kinetics or dynamic disorder. Such a clear separation of time scale is no longer true for proteins, which are sluggish systems as demonstrated by the fluctuation observed at the slow and broad range of time scales.

Dispersed kinetics and dynamic disorder has been the subject of intensive theoretical investigations. The first approach assumes the fluctuating rate constant is phenomenologically dependent on a time-varying control parameter, such as the activation barrier height, or the area of the bottleneck. Although this approach is conceptually straightforward, the control parameters are usually not experimentally accessible. As a result, their dynamics is often assumed empirically on an ad hoc basis. One of the examples is Brownian motion governed by Langevin dynamics [14-20].

The second one assumes a kinetic scheme involving multiple discrete conformational states with different rate constants. However, there is often no sufficient information about the kinetic parameters or the connection topology among the multiple states.

The other approach could be RRKM (Rice-Ramsperger-Kassel-Marcus) rate theory developed about the time of BKS (Bohr, Kramers, and Slater) theory that uses notions of active and inactive molecules is a good introduction to the use of well developed mathematical apparatus of multi-dimensional approaches using Boolean algebra and fuzzy logic [12].

Kramers reaction rate theory predicts that the solvent dynamics will always decrease the reaction rate, or that in the most favorable situation no barrier recrossings take place and the rate constant corresponds with that of RRKM rate theory, which gives the Transition State Theory rate as a function of the collision rate for independent polyatomic molecules.

However, for general realistic applications, Kramers' theory (and RRKM theory) fails when the time scale of barrier crossing (which is of course much faster than 1/k) is in the same order or even slower than the time scale of the correlations in the random solvent fluctuations. Both theories BKS and RRKM depend on time scale of barrier escaping and both fail in many particular and experimental cases [21-25].

In order to obtain a good agreement between experiment and theory, one of the first propositions was to consider smaller value for the total number of the vibrational degrees of freedom in the classical RRKM theory.

Forthcoming of tunneling phenomena in optics and thermal physics 33 years after Kramers' work Ivar Giaever was awarded the Nobel Prize in Physics with Leo Esaki and Brian Josephson for their work on the tunneling phenomena in solids. Arthur Ashkin's work in Bell Laboratories on optical trapping was awarded with Nobel Prize in Physics together with Donna Strickland and Gérard Mourou for similar discoveries in optics. Ashkin's work helped Steven Chu in his investigations on cooling and trapping atoms with Nobel Prize in Physics 10 years after Nobel Prize in Physics was awarded to Hans Dehmelt and Wolfgang Paul for the development of the ion trap technique and 3 years before the Nobel Prize in Chemistry was awarded to John Bennett Fenn for the development of electrospray ionization (ESI) and Koichi Tanaka for the development of soft laser desorption (SLD) that results in ion formation without breaking chemical bonds and their application to the ionization of biological macromolecules, especially proteins [26-30].

Limit for the Resolution of the Optical Microscopy
10 years before the introduction of van't Hoff equation, Ernst Abbe stated a limit for the resolution of the optical microscopy, not better than half the wavelength of light or 0.2 micrometers because of the diffraction resolution limit.

9 years ago Eric Betzig, S. W. Hell and William E. Moerner were awarded the Nobel Prize in Chemistry for the development of super-resolved fluorescence microscopy with ability to visualize pathways of individual molecules inside living cells on nanolevel [31].

One of the ways stimulated emission depletion (STED) is related to ultraviolet–visible spectrophotometry (UV/VIS) the name that refers to absorption spectroscopy or fluorescence spectroscopy. Ashkin's ability to use the radiation pressure of light to move particles, atoms, viruses, living cells, and other physical objects was called "an old dream of science fiction".

These all major discoveries are related to spectroscopy with application of tunneling effect that was main part of Kramers theory. Because of the theoretical difficulties with different numerous states and variables for investigation there is a real necessity in special experimental approach that would allow measurements during the reaction time.

Connections between the Theory of the Velocity of Chemical Reactions and Mass Spectrometry
One of such experimental tools that could serve for these reasons is Mass Spectrometry. It was mentioned above that there are

numerous bridges between the Theory of the Velocity of Chemical Reactions and Mass Spectrometry. One of them is an observation of anode or canal rays traveling in the opposite direction of negatively charged cathode rays that travel from cathode to anode by Eugen Goldstein 2 years after introduction of van't Hoff's equation with about that time the word "spectrograph" becoming widespread. Later improvements by W. Wien and J. J. Thomson led to the development of the Mass Spectrometry. Though the Mass Spectrometry is defined as analytical tool that measures the mass-to-charge ratio of ions, in quadrupole mass analyzers the mass filter is used to filter ions with different charge-to-mass ratios by use of oscillating electrical fields to stabilize or destabilize the paths of ions passing quadrupole field created between 4 parallel rods, where the ions in a certain range of mass to charge ratio are passed through the system at any time, can play an important role in determining the transmission probability of a specific ion passing through the mass filter. Such model computes even the ion trajectories [32-35].

Mass spectrometry (MS) is a powerful technique for identifying and quantifying molecules within complex mixtures, or the system of sticky particles. The following abilities of Mass spectrometry contribute to its importance for the Analytical Chemistry:
1. Shifting and Rearranging
2. Sampling and Filtering.
3. Time–frequency analysis
4. Correlation analysis
5. The ultrahigh resolving power
6. Methods of measuring spectra, e.g. atomic emission spectrometry (AES) and the newer techniques of atomic fluorescence (AFS)

Astronomical Spectroscopy
The application of the above mentioned methods can be further extended to the different concepts and areas of chemical research, e.g. Astronomical spectroscopy that is the study of astronomy using the techniques of spectroscopy to measure the spectrum of electromagnetic radiation, including visible spectrum, radio, and X-ray. A stellar spectrum can reveal many properties of stars, such as their chemical composition, temperature, density, mass, distance, luminosity, and relative motion using Doppler shift (redshift or blueshift) measurements. For different signals depending on frequency there are different methods that are required for the observations of spectral and dark lines in the spectrum that are very closed to diffraction limit. Around 200 years ago Joseph von Fraunhofer developed production of very pure prisms that allowed observation of dark lines in continuous spectrum and in combination with the telescope to observe the stellar and planets' spectrum and led to finding element Hellium in the Sun's spectrum 150 years ago, a year before publication of the first Periodic Table of Elements by Mendeleev. Only after 27 years this colorless and odorless element was found on Earth [36,37].

Connections between the Theory of the Velocity of Chemical Reactions and Astronomical Spectroscopy
Richard Chace Tolman, who was mathematical physicist, physical chemist and authority on statistical mechanics with focus on the so-called pre-Schrödinger quantum theory, based on the old version of Max Planck, Niels Bohr and Arnold

Sommerfeld, thus relating him to Bohr-Kramers-Slater theory is one of the best examples of connection between Astronomical spectroscopy that was applied in finding Astronomical proof of Tolman Oppenheimer Volkoff limit and the Theory of the Velocity of Chemical Reactions in the application to the theoretical background on the chemistry of supernovae stars that during impulsively acceleration of different fluids with different densities that are caused by a blast wave and are followed by the development of Rayleigh–Taylor instabilities with their limit of Richtmyer–Meshkov instabilities and are leading to intensive interfacial mixing of materials inside stars that break spherical symmetry of stars and provides conditions for synthesis of heavy mass elements in addition to light mass elements synthesized in the star previously.

Hydrodynamical considerations based on assumptions of spherical symmetry in stars with very high Reynolds numbers of plasma requires the plasma motion to be turbulent. The last notion is based on the diversity of percentage of different elements that were found experimentally through application of mass spectrometry in the spectrum of super novae. Another consideration is a loss of directional information in plasma dynamics.

Application of turbulent motion theory would lead to Kolmogorov's 5/3 time scale law stated 1 year after Kramers introduction of Fokker-Planck Equation to the investigation in the Theory of the Velocity of Chemical Reactions with further application of Kolmogorov's principal by Tatarsky to Astrophysics.

Supernovae births are not perfectly symmetrical. Stars have density irregularities before the formation of supernovae, and the blasting forces are not perfectly regular. The irregularities produce extremely dense and hot regions within superhot fluid of the exploding star. The supernova's pressures and energies get especially concentrated in small regions that were called "chemical factories" for elements from cobalt to nickel to copper, up through iodine and xenon, and including uranium and plutonium that are too heavy to be produced by stellar fusion.

This allows to observe and theoretize on the formation of many elements, e.g. calcium, iron, silver, gold, uranium, and thorium with latter elements also being production of neutron star mergers in the "r-process". Lighter elements, like oxygen, carbon, helium, and nitrogen that exist because of very high fusion energies accounting for "protons-proton chain reaction" inside stars according to Eddington's theory that considered the temperature inside stars to be too low to overcome the Coulomb barrier.

The development of quantum mechanics led to the discovery of tunneling effect of the wave functions of the protons through the repulsive barrier that allows for fusion at a lower temperature. Though these are partially produced by supernovae, but mostly are in planetary nebulae, which are the cast-off shells of red giants. For example the so-called "Cosmic Soccer Balls" could be mentioned that are another name for very unique kind of carbon molecule, nicknamed "Buckyballs" that are spherical molecules made up of 60 carbon atoms. Their similarity to soccer balls is very astonishing. The structure was first produced chemically in the lab during simulating conditions of the outer envelopes of red giant stars some 35 years ago, and 10 years ago were found in planetary nebulae with the unique set of spectral lines appearing in the infrared part of the spectrum.

Almost 80 years ago A.N. Kolmogorov applied dimensionality considerations to the equations of turbulence with very large Reynolds number to obtain equations for spatial time scale analysis with actually multidimensional and fractal spatial time Because of the conditions and wave behavior the derivation is highly applicable to astronomical observations characterized by multifractal and multidimensional space and time analyses. 20 years later Kolmogorov applied his theory again to intermittency in turbulence with very large gradients and velocity differences, where almost periodic system exhibits chaotic motion with irregular intervals [38-40].

This phenomenon is a multiscale phenomenon with possible ratio of largest and the smallest lengths of 10^5 - 10^6, where waves are composed from:
1. Unstable large eddies (energy-containing length scale that break up into small ones and
2. The energy is transferred from large scales to smaller until such length scale (dissipation scale η) that the memory friction of the fluid dissipate the kinetic energy. Kolmogorov considered them to be probabilistically and statistically independent. The motion of dissipation scale η is close to statistical equilibrium ("equilibrium range"), and statistics in the equilibrium range are uniquely determined by the memory friction γ and the rate of energy dissipation or energy flow ε.

From physical, invariance, and isotropy at different scales and directions considerations $E(k) = C \, \varepsilon^x \, k^y$, where C is dimensionless constant. Solving system of equations for lengths and times gives the Kolmogorov's 5/3 law:

$$E(k) = C \, \varepsilon^{2/3} \, k^{-5/3}$$

where constant C is determined by experiments.

Though the assumptions are heuristic and results slightly vary in different experiments, the theory of multifractal spatial time scale in multidimensional problems was further developed in the 60-es and 70-es by Tatarski and after application to astronomical seeing with effects of apparent burring in optical observations (e.g. "Martian canals") was applied in the 80-es to Galaxy observations.

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