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The Challenge of the Structure-Function Relations in Chemical and Biophysical Dynamics

By Joshua JORTNER, Tel Aviv
Member of the Academy

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It is a privilege to deliver this lecture in front of the distinguished Members of the Leopoldina Academy. I am deeply grateful for the honor bestowed on me. Over a time span of more than 300 years the Leopoldina Academy has represented scientific tradition on the highest level. Since the origins of modern science, scientific endeavour has been international, both in scope and in intrinsic significance. Modern science also has a unique role in building bridges between nations. Alluding to contemporary history, let us remember that scientific collaboration was of utmost importance in building the bridges between Israel and Germany. In another important context of the service to science, the Leopoldina Academy has served for many years as a bridge between the two parts of Europe. This service to human values is greatly appreciated. It is an honor and privilege to be here.

We shall be concerned with femtosecond dynamics in isolated molecules, clusters, condensed phase and biosystems, which pertains to the elucidation of the phenomena of energy acquisition, storage and disposal as explored from the microscopic point of view. The broad area of nonradiative dynamics, from small molecules to biomolecules, played a central role in the development of modern chemistry during this century. We shall address recent developments in shaping the conceptual framework and perspectives of femtosecond chemistry and biology, which rest on intramolecular, cluster, condensed phase and biophysical dynamics.

In the realm of chemical and biological dynamics ultrafast relaxation can prevail on the time scale of nuclear motion. The exploration of ultrafast chemical and biological dynamics stems from concurrent progress in theory and experiment. The advent of femtosecond lasers allows for the real-time interrogation of the intramolecular and intermolecular nuclear motion during chemical and biophysical transformation (ZEWAIL 1994, CHERGUI 1996). On the theoretical front, the theory and simulations of radiationless processes (JORTNER 1996), wavepacket dynamics (MANZ 1996), coherence effects (MANZ 1996), cluster dynamic size effects (JORTNER 1992), nonadiabatic condensed phase dynamics (JORTNER 1996) and nonlinear optical interactions (MUKAMEL 1995) provide the conceptual framework for intramolecular, cluster, condensed phase and biophysical dynamics.

Perspectives for future studies of »nonreactive« intramolecular dynamics on the time scale of nuclear motion pertain to:

1. High-energy intravalence and Rydberg excitations of large molecules will constitute a hunting ground for femtosecond intramolecular time-resolved dynamics in electronic origins of jet-cooled isolated molecules (JORTNER 1996). Only recently the first time resolved lifetime of ~ 40 fs for the S_2 state of isolated benzene was reported by HERTEL et al. (RANDOLF et al. 1996). These data, which approach or exceed the time scale for intramolecular frequencies, are important in the context of intramolecular dynamics in the Franck-Condon quasicontinuum. Temporal records on the time scale for ultrafast interstate dynamics will be established.
2. Time-resolved chemistry in isolated, solvent-free, supermolecules and model biomolecules, mode selectively and coherent isolated-molecule chemistry. Some of the interesting problems involve charge separation in a single supermolecule resulting in the formation of a giant dipole, hole transfer in an isolated polypeptide, with the possible distinction between transfer and transport, vibrational coherence in intramolecular chemistry, vibrational mode selectivity in electron tranfer (ET) and in electronic energy transfer (EET), and coherent vs incoherent electronic energy transfer.
3. Coherence effects. The time evolution of a coherently excited wavepacket of molecular eigenstates will exhibit interference effects. For large molecules such wavepackets can manifest
   - molecular eigenstates originating from interstate or interstate coupling;
   - Jahn TELLER coupled vibronic manifold in doubly degenerate states of a large molecule;
   - electron-vibrational coherence in mediated coupling;
   - electron-vibrational coherence in intramolecular chemistry.
4. Dynamics of ultrahigh n (=50–250) molecular Rydbergs. Remarkable progress in the elucidation of the dynamics of ultrahigh Rydbergs of molecules was accomplished (BIXON and JORTNER, 1995a,b, 1996, JORTNER and BIXON 1994, 1996). Time scales for the longevity of molecular Rydberg states are being explored by nuclear wavepacket dynamics. Of considerable interest is the coherent excitation and interrogation of an electronic wavepacket of high n molecular Rydbergs (FISCHER et al. 1995). Furthermore, relaxation phenomena in an electronic quasicontinuum (JORTNER and BIXON 1996), will lead to a conceptual unification of vibronic and electronic dissipative channels.

Clusters, i. e., finite aggregates containing $2–10^9$ constituents, provide novel insight into the dynamics of systems with finite density of states, where separation of time scales can be realized (JORTNER and LEVINE 1990). A key concept for the quantification of the unique characteristics of cluster pertains to size effects (JORTNER 1992, 1996). Perspective of future explorations of cluster dynamic size effects pertain to:

1. Real-time probing of adiabatic nuclear motion on multidimensional potential surfaces. These will involve preparation, e. g., (passive) vibrational mode selectivity

and energy storage, e. g., intracluster vibrational energy redistribution. This problem is also central in biophysics, pertaining to protein folding.

2. Real-time dynamics of nuclear configurational changes. Of considerable interest in this context is the dynamics of large local configurational charge which are induced by an extravalence excitation of a probe atom (e. g., ${}^1S_0 \rightarrow {}^3P_1$ excitation of Xe) or a molecule (e. g., Rydberg excitation of NO) in a rare-gas cluster (GOLDBERG and JORTNER in press).
3. Impact-induced vibrational coherence. These are induced by a short-range repulsive interactions with intracluster dissociation fragments in I_2Ar_n or $I_2^- Ar_n$ or by Rydberg excitation, e. g., Xe^*Ar_n, and manifest the excitation of a vibrational wavepacket.
4. Temporal records for nuclear dynamics. These presumably involve the Coulomb explosion of highly charged clusters (PURNELL et al. 1994, LAST et al. 1997), providing some of the fastest (fs) nuclear dynamics, which will be further explored.
5. Real-time dynamics of elementary excitations in finite systems. These will involve collective compression nuclear modes and phonons. Compression models exhibit decay from a collective excitation to single particle excitations. More esoteric elementary excitations constitute rotons (vortex rings) in quantum boson systems, e. g., $({}^4He)_n$ with $n > 100$ or possibly $(H_2)_n$, which can be studied by two-particle excitations in the electronic origin of a probe molecule in the cluster (HARTMANN et al. 1996).
6. Thermal femtosecond chemistry. Cluster impact dynamics *via* high-energy cluster-wall collisions extensively explored (SCHEK et al. 1995) and cluster-cluster collisions open up a new research area of thermal fs chemistry.

Perspectives of future studies of condensed phase dynamics pertain to:

1. Real-time dynamics of elementary excitations, e. g., excitons, phonons, vibrons or rotons, in the context of one-particle and two-particle excitations.
2. Real-time dynamics of configurational relaxation induced by electron solvation in fluids. The interesting adiabatic electron bubble formation equilibrium radius 17 Å at zero pressure in liquid He, Ne or H_2 was theoretically studied (ROSENBLIT and JORTNER 1995, 1997), considering a combination of a quantum mechanical and a hydrodynamic effect, and should be subjected to experimental scrutiny.
3. Dynamics of medium structure. The exploration of the time dependent correlation function g(r, t), following the excitation of a probe ion or molecule in a fluid is novel and interesting.
4. Interstate energy and phase relaxation in the Franck-Condon vibronic quasicontinuum. Nondiabatic femtosecond dynamics is governed by electronic coupling (V) and nuclear Franck-Condon factors. The coupling to the vibronic quasicontinuum is weakly correlated (i. e., small correlations factors $\eta_{ss'} < 0.3$ for multimode model systems) resulting in high rates ($\propto V^2$) and in phase erosion (BIXON and JORTNER 1997). Further exploration of ultrafast femtosecond EET and ET processes (ZINTH, private communication; BRADFORTH et al. 1995, VOS et al 1993, KÜHN and SUNDSTRÖM 1997) will be of interest.

5. Temporal records on rates for nonadiabatic dynamics. Recent experimental studies on ET dynamics (ZINTH, private communication) established time scales of 80–100 fs, while studies of EET between prosthetic groups in the photosynthetic reaction center and EET in photosynthetic antennas (BRADFORTH et al. 1995, VOS et al. 1993, KÜHN and SUNDSTRÖM 1997) established time scales of 50–100 fs. These ultrafast time scales for ET and EET ($\tau = 50$–100 fs) correspond to vibrational frequencies of $(c\tau)^{-1} \cong 300$–$600\ \mathrm{cm}^{-1}$, i. e., being on the time scale of the intramolecular frequencies and considerably exceeding the frequencies of medium (or protein) modes. The theory of radiationless transitions in the (weakly correlated) Franck-Condon quasicontinuum indeed predicts that the characteristic times can exceed the vibrational period (BIXON and JORTNER 1997).
6. The ubiquity of vibrational coherence effects ranging from small to huge systems raises the conceptual question of the distinction between the experimental condition of the preparation and interrogation on one hand, and the intrinsic aspects of relaxation and dephasing dynamics on the other hand. The manifestation of quantum beats is determined by:
   - spectroskopic information, i. e., transition moments and periods, and
   - dynamic information, i. e., modulation amplitudes and (low) correlation parameters (BIXON and JORTNER 1997). For the excited state population probability, weak modulation reflects dynamics information, while the quantum beats in the photon counting rates from the bacteriochlorophyll dimer in the photosynthetic bacterial reaction center just provide spectroscopic information.
7. Homogeneous vs heterogeneous broadening. These pertain to spatial effects, e. g., diagonal Anderson-type and off-diagonal disorder which result in localization, and to temporal effects, which are reflected in the spectral density.

Remarkable progress has been made in biophysical ultrafast dynamics, with the experimental and the theoretical microscopic exploration of the primary processes of EET in photosynthetic antennas and ET in photosynthetic reaction centers (JORTNER 1996). The ultrafast EET processes (time scales from ~ 100 fs to ps) in different (nonuniversal) antenna structures effetively preclude energy waste. The basic issues which pertain to the mechanism and unidirectionality of the primary charge separation in the (univeral) reaction center (RC) structure of photosynthetic bacteria and photosystem II are not yet fully elucidated. These involve:

1. Optimization principles for the primary ET process.
2. Kinetic redundancy for the primary ET process. This will insure the stability of photosynthetic apparatus with respect to mutagenesis, chemical modifications, and environmental perturbation.
3. Structural redundancy. This is manifested in the unique symmetry breaking, i. e., the unidirectionality of the primary charge separation across the »active« A branch of the RC. ET transfer theory implies that unidirectionality is dominated by cumulative effects, i. e., electronic coupling and energetic modification of the energy gap across the »inactive« B branch. Breaking of the symmetry breaking, i. e., inducing

charge separation across the inactive branch, was accomplished by chemical modification of the energetics, which retards the ET process across the active branch.

4. Dynamic information complements and transcendents structural data in photobiology. Structural information alone is not sufficient to understand the function of the RC, which rests on ultrafast dynamics. We should strive towards the unification of structure-dynamics-function relations in ultrafast biophysical and chemical dynamics.

The temporal limits for chemical and biological transformations are attributed to dynamics on the time scale of nuclear motion. Have we indeed reached the temporal borders of the fundamental processes in chemistry and biology? The time scales for intermolecular and intramolecular motion definitely provide the relevant temporal limits for biological transformations. For chemical transformations even shorter time scales of femtoseconds to attoseconds (i. e., 10–0.1 fs) for electron dynamics will be unveiled. Examples which come to mind in the realm of intramolecular and cluster dynamics fascinating processes involve hole migration in He_n^+ clusters (SCHEIDEMAN et al. 1993) on the $10^{-14} - 10^{-12}$ s time scale prior to its trapping, as well as early charge delocalization in isolated large molecules and model biomolecules (HABERSTADT and JANDA, private communication). In the areas of clusters and condensed phase electron dynamics relevant processes involve bulk and surface electron-electron collisions and plasmon dynamics, incipient excess electron localization in liquids, electron-hole coherence of Wannier excitons and exciton wavepacket dynamics in semiconductor clusters and quantum dots, dynamics of excess electron external image states on metals and adsorbants on metal surfaces (HERTEL et al. 1996), and electron tunneling microscopy in real-time (BOTKIN et al. 1996). Such chemical transformations involve changes in electronic state(s) without the involvement of nuclear motion, bypassing the constraints imposed by the Franck-Condon principle.

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Prof. Dr. Dr. h. c. mult. Joshua JORTNER
University of Tel Aviv
School of Chemistry
Ramat Aviv
69978 Tel Aviv
Israel