
Concluding Remarks

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This *Faraday Discussion* has been stimulating, exciting and broad in scope. We are all greatly indebted to the Chairman of the Organizing Committee, Professor Klaus Müller-Dethlefs and to the members of the Committee for having arranged this most interesting scientific endeavour on the frontlines of modern chemical physics.

The goals of this *Faraday Discussion* were well established by the Organizing Committee—exploring new insights into molecular ionization dynamics originating from: (1) the invention of zero-electron kinetic energy (ZEKE) spectroscopy as a very high-resolution spectroscopic tool; (2) the advancement of theoretical approaches for a quantitative understanding of ionization dynamics. In what follows we shall attempt to unify these ‘two cultures’.

I. Novel features of electron-vibrational level structure and dynamics

In the area of photoionization spectroscopy and dynamics progress was made in three major experimental directions.

(1) ZEKE spectroscopy advanced by Müller-Dethlefs, Schlag and co-workers^{1–4} and developed by Mackenzie and Softly,⁵ Vrakking and Lee,⁶ Even and co-workers,^{7,8} Merkt,⁹ Neusser *et al.*¹⁰ and Boesl *et al.*,¹¹ among others, constitutes a remarkable advance in photoelectron spectroscopy (PES). While standard PES allowed for a spectral resolution of $\sim 1000\text{ cm}^{-1}$, the ZEKE method allows for a standard spectral resolution of $0.1\text{--}1.0\text{ cm}^{-1}$ and pulsed field ionization (PFI), in conjunction with ion counting, allows for a spectral resolution of $5 \times 10^{-3}\text{ cm}^{-1}$.⁶

(2) Time-resolved ZEKE spectroscopy, using a time-delayed extracting electric field, was advanced by Even *et al.*,⁷ Schlag *et al.*^{12,13} and Zhang *et al.*,¹⁴ allowing for time-resolved studies of the lifetime and dynamics of ultrahigh Rydbergs located $5\text{--}10\text{ cm}^{-1}$ below the ionization potential. The time-resolution is 10 ns, while PFI time-resolved studies allow for a temporal resolution of 1 ns.⁶

(3) Time-resolved PES,¹⁵ achieving ultrafast femtosecond temporal resolution, allowing for the interrogation of intracluster and intramolecular dynamics on the time scale of nuclear motion.

The remarkable progress in ZEKE spectroscopy allowed for the exploration of fundamental problems, *e.g.*, the dynamic Jahn–Teller effect in CH_4^+ .¹⁶ Radicals, *e.g.*, the allyl C_3H_5 , propargyl C_3H_3 , ethyl C_2H_5 ,¹⁷ and radical ions C_2H_5^+ ,¹⁸ are characterized by low-lying excited electronic states, possessing low barriers to intramolecular reactions and exhibiting parallel internal conversion and reactive intramolecular decay channels. Radicals became amenable to study by energy and time-resolved PES, unveiling novel features of energetics and intramolecular dynamics.¹⁷ Photoionization of negative molecules and cluster ions,^{19–24} to yield neutrals far away from

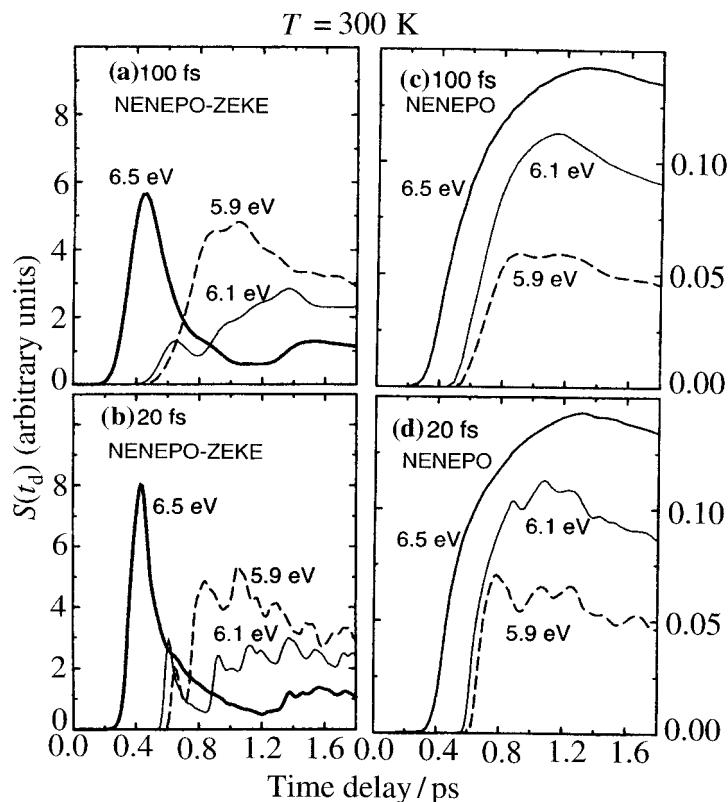


Fig. 1 The enhancement of the temporal resolution in the pump-probe signals for NENEPO-ZEKE (curves a and b) relative to the energy averaged NENEPO signals (curves c and d). The simulations of the femto-second dynamics were reported in ref. 47 for the $\text{Ag}_3^-/\text{Ag}_3/\text{Ag}_3^+$ molecular cluster with pump and probe pulses of 20 fs and 100 fs duration (marked on each panel) and the pulse probe energies in the range 5.9–6.1 eV (marked on the curves).

nuclear equilibrium configuration, constitutes significant progress in the field of transition state nuclear dynamics. PES of ‘exotic’ anions pertain to dipole-bound excess electron states^{25–27} of molecules (CH_3CN^- , adenine⁻) and aggregates $(\text{H}_2\text{O})_2^-$, $(\text{HF})_n^-$, their bound electronic excitations (CH_2CN^-* ,²⁸ $\text{I}^-(\text{H}_2\text{O})_n^*$ for low n ,²⁹ $\text{I}^-\text{CH}_3\text{CN}^*$ ³⁰) and Feshbach resonances ($\text{I}^-\text{CH}_3\text{NO}_2^*$ ³⁰). A surprising result referred to the marginal stability or instability of anions of isolated large aromatic molecules (naphthalene⁻) or heterocyclic molecules in the gas phase,^{27,31,32} in contrast to the solution data. This led to the exploration of solvent stabilization of such spatially diffuse ($\langle r \rangle \sim 10\text{--}100 \text{ \AA}$), weakly dipole bound ($\text{EA} = 5\text{--}100 \text{ meV}$) excess electron states in heterocyclic molecules (pyridine, pyrimidine) and in dimethyl uracil and methyl cytosine,³³ which are of some biophysical interest. Microsolvation effects on the stability of large anions and the gradual ‘transition’ from diffuse dipole bound to tight valence type anion states should be further explored by ZEKE spectroscopy. Time-resolved ps and fs PES studies of electronically excited states of solvated anion clusters, which are dipole bound for small systems, and of the CTTS type for larger clusters, are actively explored,³⁴ where cluster nuclear reorganization dynamics is of interest. Moving towards large clusters, ZEKE spectroscopy of van der Waals clusters and of hydrogen bonded molecular aggregates^{35–37} is of considerable chemical, physical and biophysical interest and relevance in the context of future exploration of nonrigid, multistate, floppy systems, which will constitute a central research area in chemical physics and biophysics. PES, in conjunction with dissociation dynamics of small polypeptides in the gas phase,³⁸ unravels features of charge migration in model biophysical systems. Regarding molecular systems of potential astrophysical interest, PES and spectroscopy of carbon chain anions (C_n^- , $n = 3, 5$) exhibit

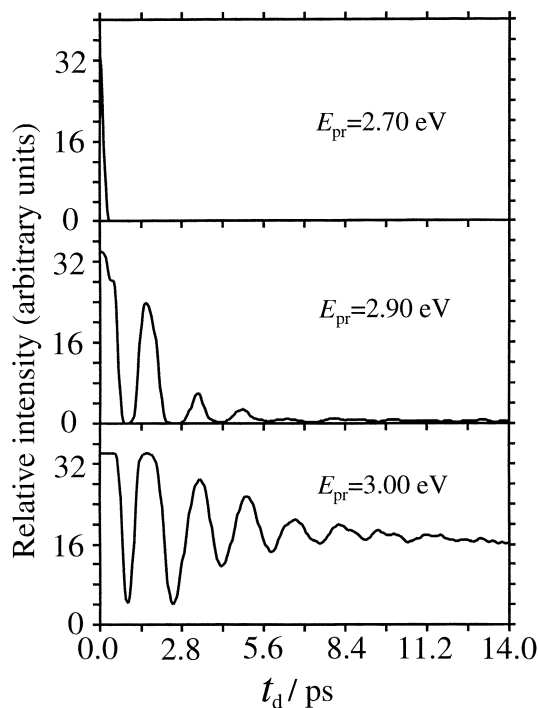


Fig. 2 Predictions for the dynamics of microscopic bubble formation around the extravalence impurity excitation in rare-gas heteroclusters as investigated by fs PES (ref. 48). The simulated NEEXP0 pump-probe signals (pulse widths 100 fs) for $\text{Xe}(\text{So})\text{Ar}_{54} \rightarrow \text{Xe}({}^3\text{P}_1)\text{Ar}_{54} \rightarrow \text{Xe}^+({}^2\text{P})\text{Ar}_{54}$ (at the probe pulse energies shown in the figure) reveal: (1) the initial bubble formation (at the time scale of 100 fs), (2) vibrational coherence effects for the bubble boundary motion and (3) completion of 1 VR at 8–10 ps.

long-lived Feshbach resonances above the electron affinity,³⁹ which may be relevant for the resolution of the long-standing mystery of the unidentified diffuse interstellar bands.⁴⁰ Expanding the borderlines of ZEKE spectroscopy, a notable development involves threshold ion-pair productions (TIPPS),⁴¹ a novel technique,^{41,42} which was named ZIKE (zero-ion kinetic energy) spectroscopy, shedding new light on the old problem of photodissociative ion-pair production by the interrogation of long-lived states just below the dissociation threshold. This selective overview reflects on the remarkable progress of modern high-resolution and time-resolved PES, allowing for the exploration of level structure and dynamics from ‘small’ systems, *e.g.*, diatomic radicals of atmospheric chemistry interest,⁴³ to large complex systems, *e.g.*, clusters and polypeptides.^{35–38}

II. Experimental progress and theoreticians’ proposals

Novel experimental techniques were advanced and presented at this meeting. The new TIPPS-ZIKE method^{41,42} allows for the spectral resolution of 1 cm^{-1} . A velocity imaging technique was developed to examine energetic and angular correlations between the several particles formed in dissociative single and double photoionization.⁴⁴ Further molecular alignment studies of photoelectron angular distribution, which are expected to provide detailed information for the partial wave analysis of the ionization process, are called for. Another novel technique involves slow photoelectron imaging,^{45,46} which provides direct information on electron scattering by the ionic core. This experimental progress, in the realm of spatial and velocity imaging, reflects on progress in exploring vector correlations in photoionization dynamics.

Interplay between theory and experiment led to the proposal of some new experimental approaches. Time-resolved pump-probe femtosecond ZEKE spectroscopy was proposed⁴⁷ (Fig. 1) for NENEPO (negative-neutral-positive)²³ and for NEEXP0 (neutral-excited-positive)⁴⁸ studies

of molecular and van der Waals clusters to explore vibrational coherence effects far from equilibrium,⁴⁷ and in microscopic bubble formation around excited low n Rydberg electronic excitations⁴⁸ (Fig. 2). Another interesting proposal pertains to the stabilization of exotic systems (e^+e^- or H^+H^-) in crossed electric and magnetic fields.⁴⁹ The potential has an outer minimum at $x = -4F/w_c^2$, where F is the electric field and w_c the cyclotron frequency. For the H^+H^- pair with $F = 1 \text{ V cm}^{-1}$ and a magnetic field of 1 T one estimates $x = -2 \text{ }\mu\text{m}$, giving rise to a spatially huge ground state. These proposals constitute, for the time being, ‘theoreticians’ dreams’.

III. Rydberg states and ionization dynamics

New concepts were advanced and tested in the realm of the dynamics of ultrahigh ($n = 10\text{--}300$) Rydberg states of atoms, and of diatomic and polyatomic molecules and clusters.^{50–62} The radiationless decay channels involve autoionization (atoms and molecules), predissociation (molecules) and internal conversion (large molecules). One expects resonances in single-channel or multi-channel decay and interferences between resonances. The new phenomena in ultrahigh Rydberg manifold(s) involve level coupling and splitting due to external perturbations in conjunction with weak Rydberg-core coupling. This leads to dramatic lifetime dilution effects, and level mixing in near-degenerate level structure induced by internal perturbations (Fig. 3).^{50–62} In the absence of external perturbations the temporal response of the system to coherent (optical) excitation is manifested by interference effects, *i.e.*, quantum beats.^{63,64}

Starting with the applications of the traditional theory of resonances to the lifetimes of ultrahigh Rydbergs $|nlJ\alpha\rangle$, (where n , l and α represent the principal quantum number (qn), the orbital qn, the total angular momentum qn and all other qns, respectively). The partial widths $\Gamma_{IJ\alpha}^I(n)$ for each channel I are determined by the n^3 scaling law $\Gamma_{IJ\alpha}^I = \Gamma_0^I [n - \delta(l\alpha)]^{-3}$, where $\delta(l\alpha)$ is the quantum defect, while the total width is $\Gamma \approx \Gamma_0 n^{-3}$, with $\Gamma_0 = \sum_I \Gamma_0^I$. Furthermore, overlap between the resonances is negligible as the density of Rydberg states in $\rho(n) = n^3/2Ry$, whereupon $\Gamma\rho(n) \approx \Gamma_0/2Ry$, being smaller than unity and independent of n . Accordingly, the Rydberg lifetimes are expected to be $\tau(n) \approx n^3\hbar/\Gamma_0$. This scaling law is obeyed only over a limited range of n ($< n_M$). The breakdown of the n^3 scaling law is exhibited for $n > n_M$, with the lengthening of the lifetimes being expressed by the dilution factor $D(n) = \tau(n)/(n^3\hbar/\Gamma_0)$. For atoms, diatomics and large molecules, typical values of n_M fall in the range of 60–120, while the $D(n_M)$ parameters fall in

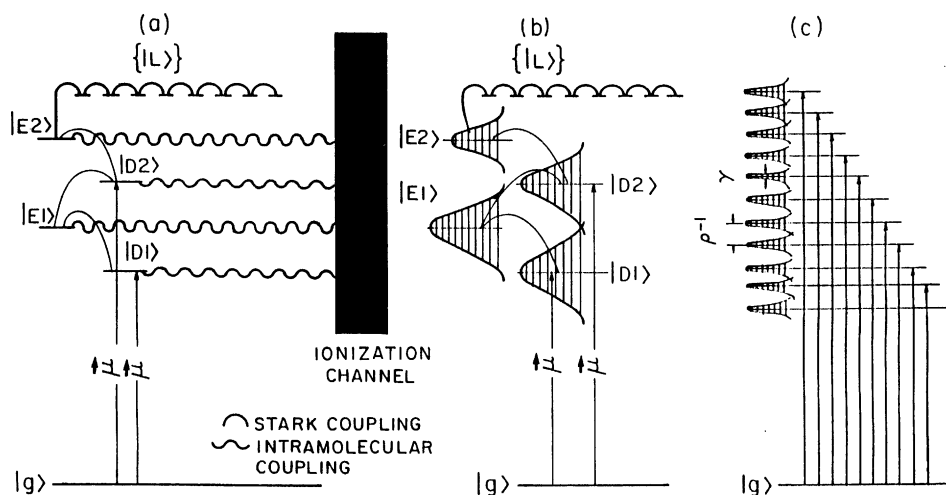


Fig. 3 An energy level scheme for the splitting, mixing and decay (by autoionization) of ultrahigh Rydberg states in an electric field (ref. 55). The zero-order (low l) doorway states $|D1\rangle$, $|D2\rangle$ for excitation are coupled to (low l) escape states $|E1\rangle$, $|E2\rangle$, and separated from the high l manifold (case (a)). In the field-free situation (case (b)) resonances are exhibited. Switching a weak (homogeneous) electric field (case (c)) results in level mixing, giving rise to independently decaying levels.

the range of $15\text{--}10^3$ for different systems, demonstrating the universality of the lifetime dilution effects. The Stark coupling and mixing model (prevailing at the weak fields in the ZEKE apparatus) provided an adequate physical picture for the dilution effect.^{50–62} The onset of l diluted lifetimes is manifested at $n_M \simeq 80[\delta(l)(\text{mod}1)]^{1/5} (F/V \text{ cm}^{-1})^{-1/5}$, *i.e.*, for typical values of $\delta(l)$, $n_M \sim 10^2$ at the (homogeneous) electric field strength of $F = 0.05 \text{ V cm}^{-1}$, with an l dilution factor of $D \sim n_M$. The dilution effect provided the experimental basis for the time-resolved ZEKE spectroscopy of high Rydbergs. Of considerable interest is the analogy between l mixing of ultrahigh Rydbergs⁵³ and intramolecular coupling within a bound vibronic level structure of a polyatomic molecule.^{65–68} The Rydberg dilution effect is analogous to the Douglas coupling effect in a bound level structure of triatomic molecules, which gives rise to anomalously long radiative lifetimes.^{65–68} The effective Hamiltonian formalism^{65–68} was applied to single channel or multichannel decay, focusing on the dynamics in a (bound) subspace of the Hilbert space. The dynamics of np' and nd' autoionizing Rydbergs of Ar was treated using Stark and spin-orbit coupling,⁵⁵ while the nf ($N^+ = 2$) and np ($N^+ = 0$) predissociating Rydbergs of NO were treated introducing Stark and dipolar interactions.⁵⁶ This treatment, which incorporates long-range coupling, accounts well for the gross features of l mixing and for accidental resonances in the Rydberg level structure. An extension of the formalism for the Rydbergs of NO, including both long-range dipolar interactions and short-range core coupling *via* the quantum defect method, was provided,⁵⁷ leading to a comprehensive picture of l dilution effects. (l, m) mixing of ultra or high Rydbergs (giving rise to a dilution factor of $\sim n_M^2$) induced by an inhomogeneous electric field was proposed,⁵² experimentally observed^{69,70} and subjected to scrutiny.⁷¹ Another class of lm mixing effects involves the control of Rydberg stabilization in inhomogeneous fields by Rydberg state tagging and adiabatic following in pulsed electric fields.⁷² Another potential source of rich spectral and dynamic information will involve ultrahigh Rydbergs in magnetic fields. The hydrogen atom in a magnetic field serves as a prototype for so called “quantum chaos”, implying a nonseparable quantum system whose classical dynamics is chaotic.⁷³

The level structure of a field-free high n metastable Rydberg manifold corresponds to isolated (sparse) resonances, *i.e.*, $\Gamma\rho(n) < 1$. The Rydberg series constitute a regular spacing of levels with an average spacing $\rho(n)^{-1} \propto n^{-3}$. A coherent excitation of a Rydberg wavepacket^{74,75} will result in time-evolution, which is characterized by two time scales: (i) the quantum beat time $\tau \propto \rho(n) \propto n^3$, which is identical with the classical result for the Kepler motion involving the wavepacket oscillation time between the core and the turn point in the Coulomb potential; (ii) the revival time of the wavepacket $\tau_R \propto n\tau$. Experimental studies⁶³ interrogate the two time scales for atomic and molecular Rydbergs. Wavepacket Rydberg dynamics in the ‘reactive’ autoionizing (and predissociating) level structure of H_2 has just been presented using the multichannel quantum defect theory.⁶⁴ These calculations predict the occurrence of interference effects between the components of the complex resonances and the Kepler motion,⁶⁴ calling for further experimental and theoretical studies of coherent excitation of metastable Rydbergs. Another, yet unexplored, aspect of Rydberg dynamics will involve time evolution of wavepackets of ultrahigh n ($> n_M$) ‘diluted’ Rydbergs in a homogeneous electric field. For a given n , the product of the density of diluted states and their decay width is $(\Gamma_0/2\delta(l)\text{Ry})(n/n_M)^5$, still corresponding to the sparse level structure. Multiple time scales for quantum beats will exhibit slow intra-Rydberg and fast inter-Rydberg interference components, a problem deserving further scrutiny. Although the time-resolved information on wavepacket dynamics (coherently excited by a weak radiation field) and on the energy-resolved spectroscopy is equivalent, the former information will be useful to disentangle physical information for a congested level structure.

Moving from Rydberg states to photoionization dynamics, the problem of nuclear adiabatic and nonadiabatic nuclear wavepacket dynamics by energy-resolved and angle-resolved PES, as masterfully explored and presented by McKoy,⁷⁶ marks significant progress. Interrogating temporal, energetic and angular resolution of PES provides information on the nature and dynamics of the doorway states and on the characterization of the final ionization channels. Notable progress in time-resolved PES involves the interrogation of adiabatic nuclear dynamics of transition states of chemical reactions. These are prepared by vertical photoionization from a stable negative ion state whose ground state nuclear configuration is closed to the geometry of the transition state of the neutral and interrogated by PES.^{19–24} A typical example involved the NENEPO spectroscopy of $\text{Ag}_3^-/\text{Ag}_3/\text{Ag}_3^+$ (Fig. 1),^{23,24,47} where the adiabatic nuclear dynamics of the Ag_3 in its linear

transition state involves distinct configurational relaxation, intracluster collisions and onset of IVR, resonant and dissipative IVR and nuclear equilibration in a three atom, finite temperature cluster. The Wigner representation of the density matrix⁴⁷ and nuclear wavepacket dynamics⁷⁷ were utilized to simulate the NENEPO-ZEKE signals and the total (energy integrated) PES signals. As evident from Fig. 1, the NENEPO-ZEKE signals provide considerably more detailed temporal information on vibrational coherence effects. PES probing of nonadiabatic dynamics of polyatomics will allow for disentangling electronic from vibrational processes.⁷⁸ Time-resolved photoelectron angular distribution will constitute a sensitive probe for field-induced alignment and intramolecular coupling mechanisms.⁷⁸ The dependence of the laboratory frame photoelectron angular distribution on the symmetry of the parent state will provide a probe for non-adiabatic internal conversion in large molecules. Further information on nonadiabatic dissociative dynamics of polyatomics will result from time- and angle-resolved photoelectron-photoion coincidence methods.⁷⁸

The dynamics of ionization of 'exotic' negative ions in their ground or electronically excited states is interesting. Examples which come to mind involve ground states of dipole bound negative ions (adenine⁻), electronically excited dipole-bound solvated anion and solvated electron clusters and CTTS states of the corresponding large clusters. How does one distinguish between the dipole-bound spatially diffuse, weakly bound dipole state and a tightly bound anion state? Angular distribution of photoelectrons from anions of molecular aggregates is expected to constitute a criterion for the distinction between dipole-bound and valence electron states.⁷⁹

IV. Perspectives

We proceed to highlight some facets of the dynamics of ultrahigh Rydbergs and ionization in complex systems. Complexity is viewed as an energetic, phase and/or temporal structure with variations. Adopting this definition, complexity is expected to prevail in ionization dynamics from small systems (autoionizing atoms or predissociating diatomics) to huge systems (charge separation in proteins and in DNA).

Focusing briefly on 'small' systems, the statistics of resonance structure and widths in atomic and molecular 'reactive' spectra has been of interest in the context of the 'fingerprint of chaos' in quantum mechanical systems.⁷³ The statistical distribution of energy level spacings and of atomic autoionizing resonances obey in some cases the Wigner distribution, implying strong level repulsion resulting in nearly uniform level spacings. Concurrently, these survive profound regularities in the pattern of Rydberg resonance energies and decay widths.⁷³ Accordingly, it is still an open question whether "quantum irregularity" reflects on "classical chaos" in autoionizing small systems.⁷³

Alluding to nuclear dynamics in large molecular systems, it is appropriate to address the question raised by McKoy: "Will (nuclear) wavepackets survive in large molecular systems?" Thirty years ago the concept of molecular quantum beats was predicted for the coherent excitation of a mixed intramolecular vibronic level structure in large molecules.^{68,80} The appropriate level structure should correspond to the intermediate level structure of mixed, separated (relative to their decay widths) molecular eigenstates. A coherently excited wavepacket of such molecular eigenstates will exhibit interference effects (quantum beats) in the temporal decay. These wavepackets were manifested for interstate nonadiabatic coupling and intrastate adiabatic coupling (analogous to multistate Fermi resonances) in the intermediate level structure. In a large molecule, these quantum beats will survive in the intermediate vibronic level structure, but will be washed out in the statistical limit of overlapping resonances, where the level structure collapses to a Lorentzian lineshape⁶⁵⁻⁶⁸ and the temporal decay pattern is exponential. It took ten years (awaiting the development of supersonic seeded molecular jets) until these theoretical predictions were confirmed experimentally with molecular quantum beats being observed for coherent excitation of intermediate level structures arising from the S_1 -{T} interstate coupling in methyl glyoxal⁸¹ and intrastate coupling in the S_1 state of anthracene.⁸²

The intermediate level structure and the statistical limit manifest interstate and intrastate coupling and relaxation within an intramolecular vibronic manifold, where the level structure is discrete. Can an analogous, mixed, sparse or dense discrete level structure be exhibited for ultrahigh electronic Rydberg states? Here we have to distinguish between coupling and relaxation. On the

basis of general arguments we can argue that the large density of states ($\propto n^3$) and the strength of the intramolecular inter Rydberg coupling (*e.g.*, long-range electron–core multipole and polarizability interactions) warrants the occurrence of inter-Rydberg coupling. Indeed, accidental degeneracies for $np(N^+ = 0) - n'd (N^+ = 1)$ Rydbergs of NO for $n = 92, n' = 80$ and $n = 95, n' = 82$ (analogous to vibrational Fermi resonances),^{6,56} and the coupling of a doorway state $nd (n \simeq 50)$ Rydberg with a $n'p (n' \approx 300)$ manifold in H_2O ,^{83,84} manifest inter-Rydberg coupling phenomena. Can a dense Rydberg manifold serve as an electronic statistical quasicontinuum for Lorentzian line broadening and for intramolecular relaxation of a doorway Rydberg state? The statistical limit is accomplished under the conditions of strong coupling $V\rho > 1$ and overlapping resonances $\gamma\rho \gg 1$, where V is the inter-Rydberg coupling strength and ρ and γ the decay width of a state within the molecular eigenstates manifold. The conditions for the realization of an electronic quasicontinuum for intramolecular inter-Rydberg relaxation were explored⁸⁵ for dipole coupling $V = C_D(mn')^{-3/2}$ (or with a more accurate expression⁶²) of a doorway Rydberg state $|n, l, N^+, N\rangle$ with a dense $|\{n', l', N^+ \pm 1, N\}\rangle$ manifold ($n' > n$) of bound Rydberg states, which are described by Hund's coupling case (d) with the nonradiative decay widths given by the n^3 scaling law, *i.e.*, $\gamma = \Gamma_0/n^3$. The statistical limit for an electronic quasicontinuum is realized for a certain range of the coupling strength domain (Figs. 4 and 5), establishing how the characteristics of the level structure and dynamics are determined by the rotational constant B , by the molecular dipole moment ($C_D \propto \mu$), by the decay width constant Γ_0 , and by l . The statistical limit within an electronic quasicontinuum is expected to be amenable for experimental observation in large polar molecules, while the $np(N^+ = 0) - n'd(N^+ = 1)$ coupling in H_2O ^{83,84} corresponds to the sparse level structure. This analysis provides a first step towards the generalization and unification of the theory of intramolecular coupling and dynamics for an electronic quasicontinuum. From the point of view of general methodology, the family of intramolecular decay channels (Fig. 6) has to be extended. The traditional channels involved reactive nonradiative decay in autoionization and predissociation (introduced in 1928–1930 with the genesis of quantum mechanics), together with the vibronic Franck–Condon quasicontinuum for interstate and intrastate relaxation (of 1968 vintage). We have now added a new decay channel involving the electronic Rydberg quasicontinuum. These four dissipative channels (Fig. 6) for intramolecular dynamics can be characterized in terms of state specificity of the coupling matrix elements, which fall into two categories of smooth coupling (for autoionization, predissociation and electronic quasicontinuum) and ‘bumpy’

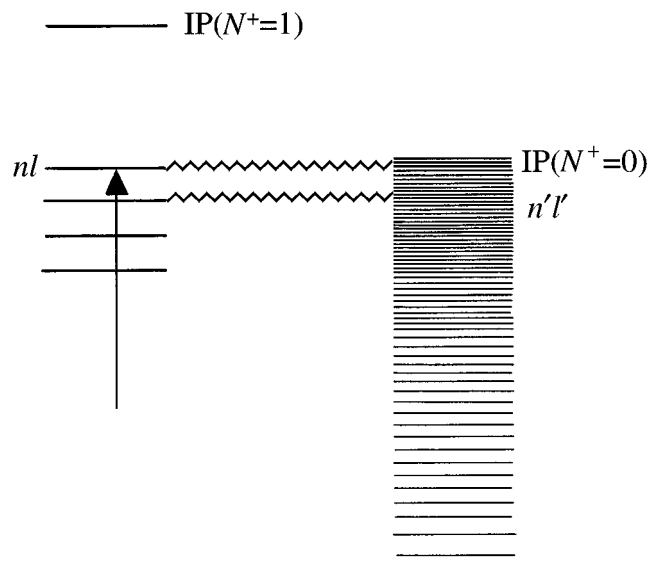


Fig. 4 Realization of the electronic quasicontinuum. Energy level scheme for the coupling of the doorway Rydberg state(s) $|n, l, N^+ = 1, N\rangle$ to the background Rydberg manifold $\{|n', l', N^{+'} = 0, N\rangle\}$. V denotes the intramolecular core multipole (or anisotropic polarizability)–Rydberg electron coupling.

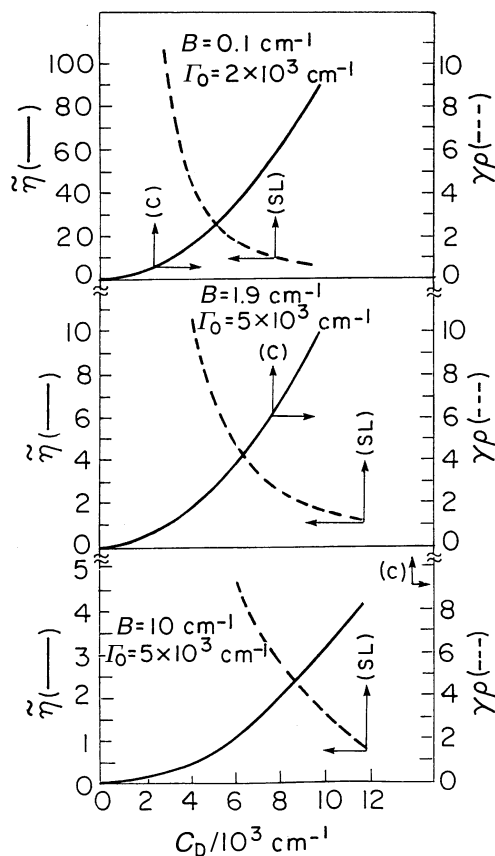


Fig. 5 Conditions for the realization of strong coupling and of the statistical limit in the electronic quasi-continuum. The dependence of the coupling parameters V_p and $\tilde{n} = 2\pi V^2 p^2$, and of the linewidth parameter $\gamma\rho$ on the strength C_D of the dipole coupling are simulated for model diatomics. The vertical arrow marked (C) denotes the onset of strong coupling for $C_D > C_D^{(C)}$. The vertical arrow marked (SL) denotes the upper limit $C_D < C_D^{(SL)}$ for the statistical limit. Note that the statistical limit can be realized for molecules containing heavy atoms, with moderately low B values.

weakly correlated coupling for the vibronic quasicontinuum. These correlations determine the features of vibrational coherence in nonradiative dynamics and govern the fastest temporal limits for relaxation.

Dynamics in a congested, bound electronic Rydberg level structure constitutes one example of dynamics in spatially huge pseudo-one-particle systems. Other examples of ‘isotheric’ spatially huge systems involve the following.

(i) Rydberg type electron-hole pair Wannier states in the condensed phase, where the Coulomb potential is dielectrically screened and the ionization to the conduction band can be controlled by external field ionization.⁸⁶ ZEKE studies in the low-temperature condensed phase will be of considerable interest.

(ii) High Rydberg-type states of charge-transfer ion-pairs where the ionic (Rittner type) potential gives rise to nuclear Rydberg states near the dissociation limit.⁸⁷ These nuclear states were explored by TIPPS giving rise to ZIKE spectroscopy.

(iii) The dynamics of the decay of the antiproton (\bar{p}) in truly exotic atoms, *i.e.*, $\alpha\bar{p}e(\bar{p}\text{He}^+)$. This ‘atomcule’, consisting of the alpha particle (α), an electron (e) and an antiproton (\bar{p}), is initially produced in a high Rydberg state ($n = 38$, $l = 37$) of the antiproton and exhibits surprisingly long (μs) lifetimes for $\bar{p} + p$ annihilation, which originates from l mixing.⁸⁸ The dynamics of this truly exotic system is in striking analogy with the dynamics of ultrahigh Rydberg states.

INTRAMOLECULAR DYNAMICS

ISOLATED MOLECULES

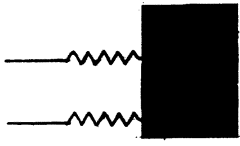
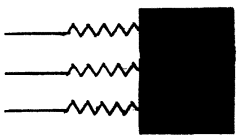
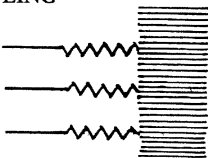
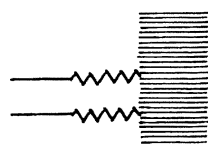
RELAXATION PROCESS	DISSIPATIVE CHANNEL
AUTOIONIZATION (1930-)	IONIZATION CONTINUUM "SMOOTH" COUPLING 
PREDISSOCIATION (1928-)	DISSOCIATION CONTINUUM "SMOOTH" COUPLING 
RADIATIONLESS TRANSITIONS BOUND LEVEL STRUCTURE (1968-)	VIBRONIC FRANCK-CONDON QUASICONTINUUM "BUMPY" WEAKLY CORRELATED COUPLING 
ELECTRONIC RELAXATION ULTRAHIGH RYDBERGS (1996-)	ELECTRONIC QUASICONTINUUM "SMOOTH" COUPLING 

Fig. 6 Decay channels for intramolecular dynamics.

New aspects of ionization dynamics were recently accomplished *via* multielectron ionization of molecules and clusters in strong laser fields ($I = 10^{14}$ – 10^{16} W cm⁻²).^{89–93} Multielectron dissociative ionization^{94–101} leads to Coulomb explosion¹⁰² and to production of high-energy (10–200 eV) multicharged ions. When large clusters, *e.g.*, Xe₁₀₀₀, are subjected to multielectron dissociative ionization, the kinetic energy of multicharged Xe⁸⁺ ions is in the energy range 100 KeV–1 MeV, attaining the domain of nuclear physics. As the multielectron ionization involved hundreds (or thousands) of photons, the radiation field is treated classically. Theoretical studies^{94–101} of these novel phenomena focused on the quasi-resonance mechanism, the charge-resonance induced ionization and its dynamic enhancement during the Coulomb explosion, the ignition model, and the response of electronic to ultrahigh laser fields.

Moving from strong to extremely weak radiation fields, ionization of high n Rydberg states by black-body radiation¹⁰³ is interesting. This mechanism may be important for the production of cold plasmas. While in conventional plasmas the electron kinetic energies are in the range of 1–10 eV, being comparable to the Coulomb interactions, in cold plasmas the strength of the Coulomb interactions dominates, giving rise to new phenomena.¹⁰⁴ A cold plasma was already produced by the near-threshold photoionization of Xe atoms held in a magneto-optical trap at the temperature of 30 μ K, with the resulting electrons attaining the temperature of 100 mK (0.1 cm^{-1}).¹⁰⁵

Low temperature dense samples of Rydberg atoms in a magneto-optical trap ($T = 300 \mu\text{K}$, $p \sim 10^9 \text{ cm}^{-3}$ and $R_0 \sim 10^{-3} \text{ cm}$) are analogous to an amorphous metallic solid, where many-body effects prevail.¹⁰⁶ Energy exchange in a frozen Rydberg gas was shown to give rise to spectral line broadening and splitting.¹⁰⁷ The analogy of these phenomena to spectral diffusion in solids, the possible localization in a band and the nature of dissipation processes, constitute some of the outstanding questions in this fascinating field.

We touched on the rich dynamic processes relevant to ionization in atoms, diatomic molecules, large molecules, clusters, ultracold gases and cold plasmas. The last type of interesting and most relevant processes pertains to charge transfer and transport (CTT) involving charge separation migration, shift, recombination and localization in isolated supermolecules, clusters, condensed phase, interfaces and biophysical systems. This rich field of CTT, from isolated molecules to biomolecules,¹⁰⁸ was alluded to at this meeting in the context of hole transfer in gas-phase polypeptide molecules,³⁸ which serve as biophysically relevant systems for the identification of binding sites, transfer specific electronic interactions, energetics selective solvation and dynamics.

Two classes of biophysical systems, the photosynthetic RC and DNA are of considerable interest in the context of CTT. The primary charge separation in the photosynthetic RC, which ensures life on earth, proceeds *via* a sequence of well-organized, highly efficient, directional and specific electron transfer processes between the prosthetic groups across the membrane protein.¹⁰⁸ The central open problem in the electron transfer dynamics of the unidirectionality of the primary charge separation across the A branch of the (A and B symmetric) RC, manifesting symmetry breaking, was recently resolved.¹⁰⁹ Charge separation in the photosynthetic RC is of direct biological relevance and impact. In contrast, charge transfer and transport in DNA¹¹⁰ is relevant in nanoscience and nanoelectronics for the development of DNA based molecular technologies, *e.g.*, functional nanoscale electronic devices and biosensors. Biological applications pertain to implications of radiation damage and also DNA repair by charge (hole) migration. Thus CTT in biophysical systems leads to the elucidation of basic elementary processes in biology and to opening of new avenues in molecular electronics. This brings us to future trends in the rich and diverse area of ionization and charge transfer dynamics, exploring elementary processes in large complex systems from the microscopic point of view.

The *Faraday Discussions* have a long and distinguished tradition of central, seminal contributions to physical chemistry and other areas of science. It was told that in the 1930s when a topic for a *Faraday Discussion* was announced, the leading physical chemists started working on the subject. This tradition of the contributions to high-quality science was continued and perpetuated in our *Faraday Discussion* meeting.

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