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Chemistry on the border of two centuries — achievements and prospects †

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Abstract. Chemistry is on the threshold of a new flight; new ideas and lines of research are originating now; new directions arise, which form a new face of chemistry. The bibliography includes 79 references.

I. Introduction

Chemistry ultimately formed as a fundamental science only in the early XXth century when it got a reliable and solid physical basis made of three main concepts of quantum mechanics, namely

— the Schrödinger equation, which is the quantum successor of the classical mechanics equations (Hamilton – Jacobi equations);

— Pauli's exclusion principle, which governs the distribution of electrons among spin states and energy levels and

— wave function, which carries information on the charge and spin distribution.

It is these concepts that have imparted physical meaning to the D. I. Mendeleev Periodic Table, an outstanding discovery of the XIX century the significance of which goes far beyond chemistry. From the viewpoint of these three concepts, a chemical reaction should be regarded as a physical process involving rearrangement of electron shells and nuclei.

The understanding and realisation of the significance of these quantum-mechanics principles for chemistry makes chemical science clear and predictable as regards its main features; they give rise to the diversity and richness as well as to the elegant logic and beauty of chemistry.

In the XX century chemistry became an exact science; many quantitative regularities and precise laws have been established (including the 'electron periodicity' of the Mendeleev law); a very high metrological level of determination of atomic, molecular, thermodynamic and kinetic constants, characterising both substances and chemical processes, has been attained.

During this century, chemistry has developed into a branched science. Nowadays, many fields of chemistry exist as separate branches of science — inorganic, organic and physical chemistry; radiochemistry, biochemistry, analytical chemistry, geochemistry, *etc*. Each of them has its own subject and the scope of investigations as well as its own problems and experimental techniques. However, by the 80s, the professional separation of the chemistry branches has started to be replaced by attempts to tackle jointly the general fundamental problems of chemical science.

The first attempt to identify the most important 'integration' lines in chemistry was made in a paper by Legasov and Buchachenko,[1] in which chemistry was classified at a new level. The chemical science was structured according to the targets and problems rather than according to the names of various 'chemistries,' which now number more than four dozen. This classification follows the logic inherent in chemistry, which does not separate chemistry into 'chemical counties' but instead organises it as a unified science and also unites chemists as a community.

Nowadays, at the end of the XXth century, the classification proposed in the publication mentioned above [1] has not changed much, and the hierarchy of general problems of chemistry can be presented as follows.

— the art of chemical synthesis;
— chemical structure and function;
— control of chemical processes;
— chemical materials science;
— chemical technology;
— chemical energetics;
— chemical analytics and diagnostics;
— chemistry of living matter.

These are the main 'arterial roads' which direct the development of modern chemistry and reflect its achievements and progress.

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Chemical synthesis is the key direction in the development of chemistry and the source of all its treasures. This route makes chemistry the most constructive branch of science. Chemistry provides other branches of science and industry with materials; in this sense, one can say that it stands in the middle of natural sciences. It is especially intriguing that, despite the existence of theoretical principles of chemical synthesis, there still remains scope for the freak of imagination and intuition. This brings chemical synthesis closer to an art.

The atomic and molecular architecture and the electronic structures of newly synthesised compounds are infinitely diverse, so are their physical and chemical properties and, therefore, functions. The relationship *between the structure and functional behaviour* of a substance is the subject of the second line of research.

The control of chemical processes and their molecular mechanisms and the use of chemical factors (complex formation, solvation, molecular organisation, catalysis) and physical treatment (ranging from light to mechanical treatment) for controlling chemical processes constitute the essence of the third line.

A substance is not a material yet but only the precursor of a material. People have to 'teach' substances to work as materials and to estimate their operation characteristics and ranges of applicability. These are the tasks of the *chemical materials science*.

The aim of *chemical technology* is to design, optimise and scale a technological process as well as to ensure its low energy expenditures and safety and to make it environmentally clean.

The development of efficient ways of transformation of chemical energy into other kinds of energy, accumulation of energy in energy-storing substances and materials (including lasers with chemical and solar pumping), transformation of solar energy, chemical cells and coupling of energy-producing and energy-consuming processes constitute the subject of *chemical energetics*.

The progress in chemical materials science and chemical technology would be impossible without reliable *chemical analytics and diagnostics*. This is a vigorously developing line of research (which includes chemical sensors and the chemistry of odour) having links to lots of branches, ranging from technical monitoring systems to medicine or ecology.

There is no question that all these lines of research are related not only logically. They are intrinsically connected by the methodology of chemical research itself — elements of several lines can be found in a good scientific article. The remarkable combination of differentiation and integration makes up the efficient and creative style of modern chemistry.

Finally, the *chemistry of living matter* is an enormous chemical galaxy, which is still to be explored. It assimilates the results of biochemistry, chemistry of natural products, phytochemistry, enzyme science, medical and pharmaceutical chemistry, genetic engineering, biotechnology and many other fields of chemistry. This line of research is associated with great expectations; it undoubtedly possesses an exceptionally high potential, indisputable prospects and a highly promising future. Even today, its outlines and significance can be traced by looking at the transgene technology.

II. Novel chemical structures and materials

Each arterial road of chemistry has its own events and discoveries, which can be both regular and unexpected. However, the most significant events still occur in the first, key arterial road. Development of methods for the synthesis and design of new substances and materials are the main goals of chemistry. It should be noted that the number of compounds that have been created chemically (artificially and skilfully) is permanently increasing. The molecular architecture of newly formed compounds is infinitely variable and fabulously abundant. For example, the following unusual structures have been obtained: rhombic molecules — structural units of one-dimensional metals; proton 'sponges' and 'tubes' (molecularly organised proton-carrying reservoirs and channels); toroidal molecules; polymetal rotaxanes; catenanes; crowns and anticrowns, capable of separating cations and anions; hypervalent radicals such as NH_4, CH_5, H_3O, some of which are long-lived species, for example, $(CH_2)_2NH_2$ (lifetime ~ 3 μs);[2] high-spin molecules containing tens of unpaired electrons within a single species [for example, the complex $Mn_6^{2+}(R_2NO^{\bullet})_6$ has 36 unpaired electrons]; multi-deck polyaromatic molecules; molecules with large numbers of chiral centres, *etc*. Some of the compounds obtained artificially may remain exotic species for good, but some others would trigger new lines of research.

The adoption of new principles of radial synthesis in which molecules unite according to the fractal pattern to give an enormous molecule, *dendrimer*, has been an important event in chemistry. Nature has used this principle to produce glycogen, amylopectin and some other polysaccharides and proteins. Many remarkable discoveries have been made in the chemistry of dendrimers, especially in the polymer chemistry.[3] The architectures of dendrimer structures are virtually infinite; the same is true for their functions and applications. In particular, it has been predicted that dendrimers based on polyconjugated molecules could serve as energetic antennas collecting the energy of optical (including solar) excitation and transforming it into photoelectric current.

Impressive results have been attained in the synthesis of organometallic polymers. The preparation of ladder, tape and rod-like organometallic polymers can be formally classified as 'one-dimensional' or 'two-dimensional' radial synthesis. Thus Fig. 1 shows two projections of an unusual organometallic ladder polymer $[(CuL_2)PF_6]_\infty$, prepared by polymerisation of 2,7-diazapyrene (L) and $[Cu(MeCN)_4]PF_6$ in the MeCN – PhCN system.[4] It can be seen from the Figure that a monomer unit of this polymer is

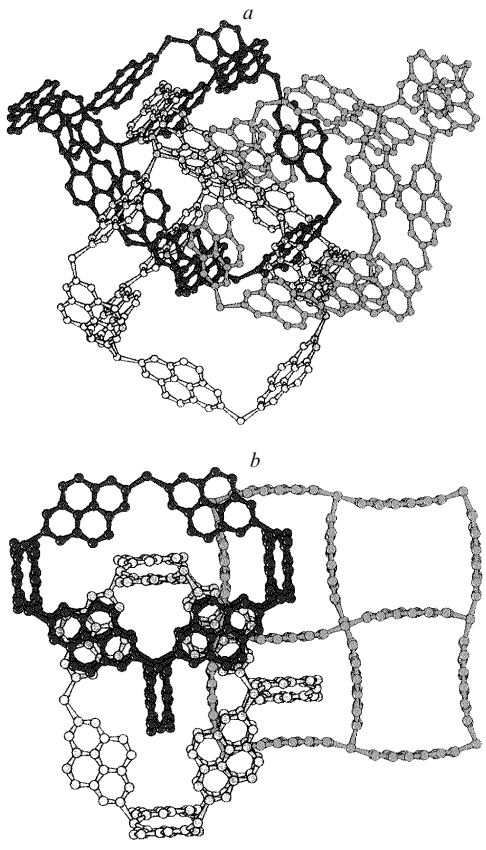


Figure 1. Two projections of the organometallic ladder-type polymer $[(CuL_2)PF_6]_\infty$ (L = 2,7-pyrene) with polycatenane and adamantane structural units.[4]

formed by three interpenetrating adamantane networks arranged at angles of 90° relative to one another. Examples of three-dimensional organometallic dendrimers have been reported (see below).

The discovery of *superconducting ceramics* has stirred up not only physicists and engineers but also chemists. These compounds had been prepared well before their superconducting properties were discovered, but it was this intriguing and unexpected feature of ceramics that aroused most enthusiasm and hope. The achievements in this field proved to be modest compared to the expectations; although the progress along this line has now substantially slowed, some pleasant surprises are still possible (note the startling publication [5] dealing with superconductivity of inorganic composites at room temperature, the value of which is still unclear). It is about this type of situation that Niels Bohr said that problems are more important than solutions. In fact, solutions can become obsolete to leave the problems, which stimulate the search for new solutions.

After a great number of paramagnetic organic compounds (stable radicals and high-spin molecules) had been synthesised, attempts to prepare *molecular ferromagnets* were undertaken. The principle of design of organic ferromagnets had been formulated long before they were discovered in 1989.[6,7] The exchange interaction of the unpaired electrons in paramagnetic organic molecules is known to be negative; it accounts for the antiparallel arrangement of the magnetic moments of the electrons. It has been suggested that macroscopic ferromagnetism in ferromagnets is attained *via* pairwise antiferromagnetic interactions. This hypothesis immediately received experimental support.[8]

Figure 2 shows the crystal structure of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-*N*′-oxyl *N*-oxide.

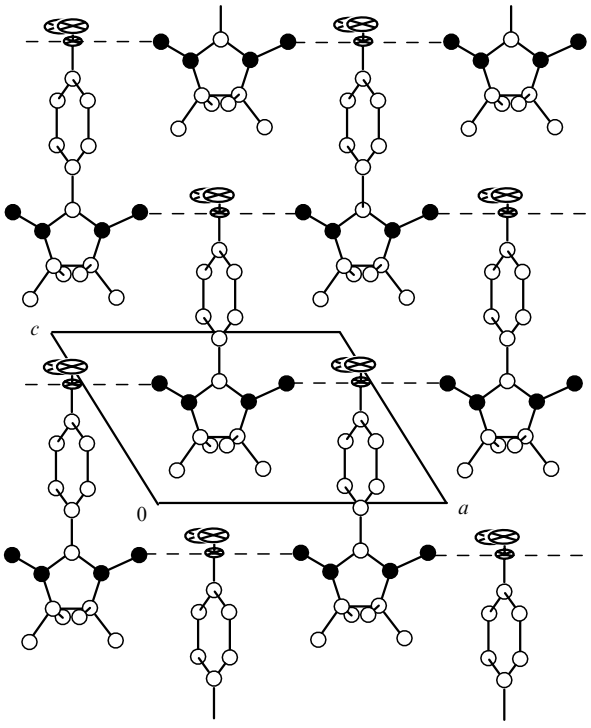
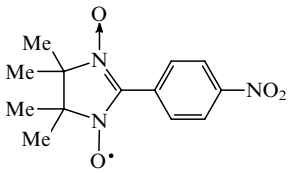


Figure 2. Two-dimensional representation of the crystal lattice of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-*N*′-oxyl *N*-oxide.
The $NO^{\bullet}$ groups (areas with high spin density) are coloured black, while the NO_2 groups (areas with small negative spin density) are designated by crosses.[8]



It can be seen that the nitroxides are arranged in the crystal in such a way that fragments with high spin density ($NO^{\bullet}$ groups) are located close to fragments where the spin density is low and negative (NO_2 groups). Owing to the pairwise exchange interaction of the neighbouring spins with positive and negative electron density, spins with positive density align in one direction, while those with negative density align in the opposite direction; this creates macroscopic ferromagnetism in the crystal. This is only one of the numerous examples of organic ferromagnets.[9]

One should not, however, create illusions about this class of compound. The specific spin density and the degree of magnetisation in these substances are very low; correspondingly, the temperatures of ferromagnetic phase transitions are also very low ($\sim$1 K). Mixed organometallic ferromagnets are more promising (and therefore more attractive). Figure 3 presents the structure of an organometallic ferromagnet, $\{[FeCr(ox)_3].(NBu_4)\}_\infty$ (ox is oxalate anion). The structure consists of the $Cr(ox)_3$ fragments being joined together by the Fe ions to form a huge ferromagnetic molecule. In the crystal, the compound $\{[FeCr(ox)_3](NBu_4)\}_\infty$ has a layered structure.[10,11]

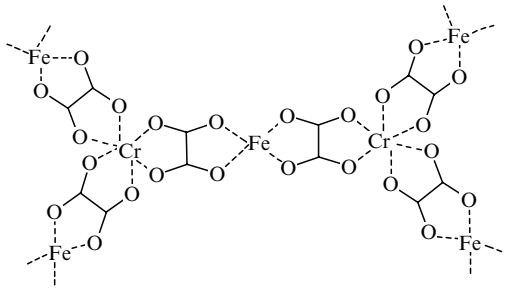


Figure 3. Structure of the organometallic ferromagnet $\{[FeCr(ox)_3](NBu_4)\}_\infty$ (T_c = 12 K). For the sake of simplicity, the tetrabutylammonium cation is not shown.[10]

Fullerenes have become a real treasure for chemistry. The most daring and optimistic forecasts are associated with fullerenes. Fullerenes C_{60}, C_{70}, *etc*. can be prepared in macroscopic quantities by the arc method. However, the mechanism of their formation still remains obscure. The perception of this fact stimulates experimental and theoretical (molecular dynamics) studies of the formation of fullerenes from atoms, pairs of atoms and clusters under the conditions of gas discharge, plasma, electric arc, *etc*. The main goal of these studies is to understand the mechanism of polyhedral clustering and the arrangement of atoms to give a fullerene structure (see, for example, Ref. 12). The search for catalysts of this process is also perfectly reasonable. It is beyond doubt that this route would bring both predicted discoveries and godsends.

At present, in addition to traditional chemistry, targeted chemistry of these compounds is in progress. In particular, it is of interest to perform polymerisation of fullerenes with retention of the spherical cage units (*via* cross-linking). According to predictions, these polymers would possess high electron 'capacity,' which would permit them to be used in chemical and storage cells. Thermal polymerisation of the most readily available C_{60} fullerene is known to be forbidden from the symmetry viewpoint. Therefore, it requires some sort of treatment which would stimulate distortion of the icosahedral symmetry of C_{60} and

eliminate the prohibition (high pressure,‡ shear deformations, shock waves, *etc*.). This is a key problem.

Among other lines of research in the targeted chemistry of fullerenes, mention should be made of fullerene modification aimed at producing materials for microelectronics (the easy construction of integral circuits, simple and clean nano-technologies and other advantages) and synthesis of fullerene-based organometallic and organic complexes to be used as superconductors.

Thus it was found that M_3C_{60} and $M_2M'C_{60}$ fullerides (M, M′ = K, Na, Rb, Cs) exhibit superconducting properties. The compound $RbCs_2C_{60}$ still remains the record holder, T_c = 33 K. A remarkable feature of the superconducting fullerides is the dependence of the temperature of superconductivity transition T_c on the crystal lattice parameter (Fig. 4).[13] This dependence proved to be opposite to that observed for organic superconductors based on tetrathiafulvalene and its derivatives, which were famous in the 60s – 70s (for details, see Ref. 1). In the latter case, compression of the crystal lattice by external pressure results in higher T_c values; conversely, in the case of fullerides, compression decreases T_c. This unusual behaviour has stimulated the search for new superconducting fullerides based on the expansion of the fullerene crystal lattice (by intercalation by NaN_3 and NaH, introduction of NH_3, *etc*). In particular, the compound $(NaH)_4C_{60}$ obtained by intercalation of C_{60} by NaH exists as two crystal phases, cubic and orthorhombic. The cubic β-phase conducts electricity, while the orthorhombic α-phase does not.[14] Within the framework of the same idea (crystal lattice expansion), synthesis of charge transfer complexes based of fullerenes and tetrathiafulvalene and its derivatives (the latter served as 'bricks' in the construction of organic superconductors) is being developed.

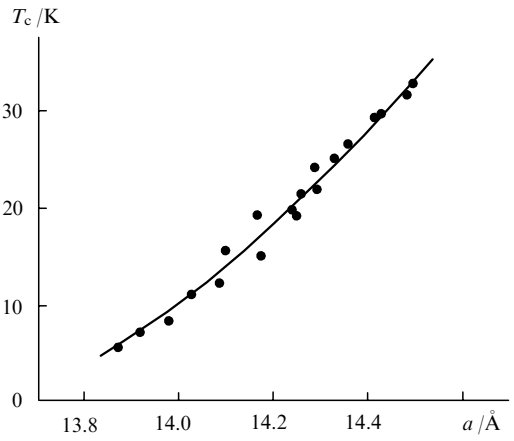


Figure 4. Dependence of the superconductivity transition temperature T_c on the crystal lattice parameter a in the series of fullerides M_3C_{60} with a face-centered cubic structure.[13]

The mechanism of superconductivity still remains an intriguing question. Does the consideration of this problem go beyond the canonical electron pair theory, according to which the movement of electron pairs is governed by the lattice phonon spectrum (the Bardeen, Cooper, Shrieffer — BCS — theory)? This question has stimulated the synthesis of $^{13}C_{60}$ fullerene (with 99% replacement of ^{12}C by ^{13}C) and the corresponding fullerides, $K_3{}^{12}C_{60}$ and $K_3{}^{13}C_{60}$.[15] In qualitative agreement with the BCS theory, the superconduction point decreased from 19.2 to 18.8 K on passing from $K_3{}^{12}C_{60}$ to $K_3{}^{13}C_{60}$. This important result confirms participation of phonons in the formation and movement of the Cooper pairs.

According to the canonical BCS theory, the superconduction point $T_c \propto M^{-\alpha}$, where M is the mass of the particle responsible for the phonon spectrum (in this particular case, $^{12}C_{60}$ and $^{13}C_{60}$), and α is a characteristic parameter, equal to 0.5. Taking account of the isotope effect and proceeding from the value T_c = 18.8 K, one can easily find that $\alpha = 0.3$ (rather than 0.5 as predicted by the BCS theory) for the fulleride $K_3{}^{12}C_{60}$. This could prompt the conclusion that the BCS theory requires modification. However, this conclusion is not ultimate. In particular, there are no grounds for claiming that the phonons responsible for the Cooper pairing are generated by vibrations of C_{60} as a whole; the pairing might be due to the part of the phonon spectrum created by internal vibrations of C_{60} (for example, the breathing vibration of the sphere). In this case, a mass smaller than the mass of C_{60} should be substituted into the expression $T_c \propto M^{-\alpha}$ and thus the resulting α would move towards 0.5. These conclusions are consistent with the results obtained for Rb_3C_{60} with partial substitution of ^{13}C atoms for ^{12}C. The α value found for this fullerene (0.37) is closer to 0.5.

Endofullerenes constitute one of the most exotic and remarkable classes of chemical compounds created by chemistry. They are formed upon insertion and capture of atoms or ions inside the fullerene sphere. However, it is not the insertion into the fullerene sphere itself that makes these compounds unique but rather the fact that capture of these species by fullerenes is a virtually irreversible process (unlike, for example, the capture of species by cyclodextrins, which is reversible).

A great number of endofullerenes have already been synthesised: $T@C_{60}$ (tritium atoms are formed from ^6Li ions on irradiation with neutrons in the presence of C_{60}), $(^3He,^4He)@C_{60}$, $K@C_{59}B$, $La@(C_{60},C_{70},C_{74},C_{82})$, *etc*.; endofullerenes with two or even three captured atoms have been obtained, for example, $He_2@C_{70}$, $La_2@(C_{72},C_{74},C_{80})$, $(Gd_2,Y_2)@C_{90}$, $(Sc_2,Er_2)@C_{82}$, $Sc_3@C_{82}$, *etc*.[16] It should be noted that in the synthesis of $La_2@(C_{72},C_{74})$ in the arc of graphite implanted with La_2O_3, only endofullerenes $La_2@C_{72}$ and $La_2@C_{74}$ are intensively formed, no 'empty' C_{72} and C_{74} being observed. This fact may prove significant from the viewpoint of catalysis of fullerene synthesis.

Some answers to the question of what is the mechanism of the endofullerene synthesis have already been found. As was to be expected, the early idea that the carbon shell is permeable for high-energy atoms proved to be naive. This idea might (although not for sure) be valid in the case of hydrogen atoms; however, even for He direct insertion into C_{60} (without violation of the cage structure) would require ~10 eV, and He^+ would be able to penetrate through a six-membered ring upon an orthogonal collision only if it has an energy of 35 – 45 eV. This is much larger than the energy required for dissociation of the C – C bonds in the fullerene shell (70 – 80 kcal mol^{-1}). It is clear that rupture of the C – C bonds to open a 'window' in the shell followed by insertion of the guest atom and closure of the 'window' upon restoration of the C – C bonds is energetically much cheaper than direct insertion.

This mechanism is not at variance with the experimental results. Thus helium slowly (over a period of several weeks) enters the C_{60} sphere at a pressure of ~3000 atm and a temperature of 600 – 650 °C.[17] The endofullerene $Ne_2@C_{70}$ is obtained by heating C_{70} under a high pressure of neon, the C_{70} : $Ne@C_{70}$: $Ne_2@C_{70}$ ratio being dependent on the number of the synthesis cycles and reaching a limiting value of 1000 : 1 : 0.02.[18] These findings led to the important conclusion that there exists a promoter or catalyst which facilitates the insertion of He atoms into C_{70}. This might be a radical, which adds to fullerene and thus weakens the adjacent chemical bonds and promotes the opening of a 'window'. Certainly, discovery of a catalyst able to reversibly open and close a 'window' in the fullerene sphere would ensure a breakthrough into this new class of compound.

‡ The report that at high pressures and temperatures the hardness of the fullerene polymerisation product exceeds that of diamond has not been supported.

Probably, a reversibly appearing 'window' as a capture mechanism is important for small neutral atoms (such as He and Ne). In the case of large atoms (*e.g.*, lanthanides), trapping of atoms (or ions) during the formation of the carbon sphere is apparently more significant. The search for appropriate catalysts which would facilitate this process is also worth efforts.

Both mechanisms can act simultaneously; apparently, this is the case for trapping of an N atom by C_{60} (when C_{60} is heated in a nitrogen plasma).[19] In the $N@C_{60}$ molecule, the nitrogen atom with three unpaired electrons (one electron in each *p* orbital) is chemically inert (this is also true for hydrogen in $H@C_{60}$ and for phosphorus in $P@C_{60}$). The unique chemical inertness of an inner π-electron shell in fullerenes is in sharp contrast with the high reactivity of the outer π shell. Thus reactions involving the outer shell (Fig. 5) barely affect the inner nitrogen atom; only slight distortion of its EPR spectrum is observed, which is manifested as weak satellite lines, indicating that the spherical symmetry of C_{60} has been somewhat distorted. This makes the nitrogen *p* orbitals energetically slightly non-equivalent (by ~0.003 eV) and stimulates dipole spin splitting of the Zeeman levels.

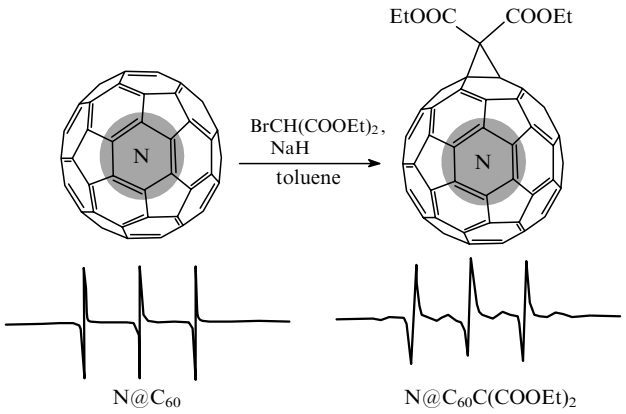


Figure 5. Scheme of the $N@C_{60}$ molecule and the product of its cyclopropanation. The corresponding EPR spectra are shown below.

Yet another feature of endofullerenes, which is of fundamental importance, is noteworthy, namely, contraction of the electron shell inside the fullerene sphere. The constant of hyperfine (electron–nucleus) coupling in a free N atom is 3.7 Œ, that in the KN_3 crystal is 5.0 Œ and the same value for $N@C_{60}$ is 5.7 Œ. This indicates that atoms inside the fullerene sphere experience substantial pressure, which results in contraction of the *p* orbitals of valence electrons. In terms of quantum chemistry, this means perturbation of the wave function resulting in an increase in the contribution of the *s* orbital to the superposition of atomic orbitals. Contraction of the electron shell of the inner atom has also been found in the endofullerenes $(Sc,La,Y)@C_{60}$. In these compounds, anisotropy of the *g*-factor of the unpaired electron was observed,[20] which points unambiguously to hindered rotation of the atoms inside the sphere.

It is not difficult to find a relationship between the electron shell contraction and the behaviour of 'onion' fullerenes such as $C_{60}@C_{240}@C_{540}$..., which consist of several spherical molecules arranged one inside the other, the distance between the sphere surfaces being $\geqslant$ 0.34 nm. This is a new class of endofullerenes. The inner spheres experience enormous pressure of the outer spheres, and this accounts for the fact that the inner spheres are converted into diamond even upon weak photo or radiation treatment.

Synthesis of *cylindrical carbon nanotubes* (~100 Å in diameter), which are formed according to the same principle as fullerenes, has become a prominent event in modern chemistry. They can be doped with metals (both on the inside and on the outside) and are characterised by high solubility of hydrogen (owing to capillary condensation); therefore, they can be used in chemical cells. Young's moduli of carbon nanotubes are close to that of graphite (in one plane). The first experimental data on the use of nanotubes as probing tips in scanning force tunnelling microscopy were reported. Development of methods for the preparation of oriented nanotubes on thin metallic films using laser etching is in progress. Polymerisation of nanotubes opens up ways to new porous materials such as organic zeolites. Multilayer nanotubes consisting of molecular cylinders enclosed one into another have been obtained.

Technologies that enable manipulation of nanotubes by virtue of atomic force tunnelling microscopy are being developed.[21] One can lay, bend, cut, straighten, cross and move nanotubes thus arranging molecular electronic devices. Thus, it becomes possible to pass from fine words to impressive deeds.

Preparation of *metallic hydrogen* represents one more important achievement of recent years. It can be debated whether it was done by chemists or physicists; however, the transformation of hydrogen into metallic hydrogen is undoubtedly a chemical process, resulting in a rearrangement of the electron shells of hydrogen molecules. Metallic hydrogen is obtained by shock compression of a 0.5-mm thick liquid film of molecular hydrogen placed between single-crystal Al_2O_3 anvils at a pressure of 2 Mbar.[22] The electrical conductivity of this material ($\sim 2000\ \Omega^{-1}\ cm^{-1}$) is close to those of molten cesium and rubidium; in this sense, metallic hydrogen resembles liquid alkali metals. The mechanism of its formation is unknown; it involves either immediate complete release of the electrons from a hydrogen molecule or dissociation of the molecule into atoms followed by the discharge of electrons to the conduction band. In order to decide between these variants, non-stationary reaction regimes need to be studied.

III. Chemistry in micro- and macro-reactors

It should be admitted that the chemistry created by the mind and hands of Man is only a minor fraction of chemistry created by Nature. The vast majority of reactions implemented by humans are 'non-organised' reactions in which species (molecules, ions, atoms or radicals) react when they meet by chance (in space and time). Meanwhile, the 'natural' chemistry is highly organised, *i.e.* almost all the chemical transformations occur in systems with molecular or supermolecular order. Large sets of biochemical reactions are organised both in space and in time. Thus, during photoreception each light quantum absorbed by the retina of an eye triggers a cascade of reactions yielding ultimately cyclic guanosine monophosphate (quantum yield 10^4), which induces an electric potential on the membrane. This signal is then recorded in the brain as the signal for light reception (other examples can be found in a review[1]). It is owing to the high degree of organisation that the selectivity and productivity of biochemical reactions reach very high levels, which are yet inaccessible in conventional chemistry.

The realisation of this fact and the turning of chemistry as a science to molecular and supermolecular organisation of reactants started in the second half of this century; now this is a leading line in the intrinsic self-organisation of chemistry directed towards the future.

The simplest microreactor in which reactants can be organised in space is a van der Waals molecule. A large number of microreactors of various natures and sizes and various degees of molecular ordering exist. They include complexes, crystal solvates, gas (for example, methane) hydrates, inclusion compounds (in which 'hosts', represented by cyclodextrins, semispherands, calixarenes, *etc.*, organise reactions of 'guest' molecules), macromolecules, (helices or rigid zigzag-like rods), the cavities of zeolites and other porous media, micelles and vesicles. Microreactors change the molecular dynamics of reactants, mechanisms and rates of chemical transformations, the p*K* values of acids and

bases, local charges and charge distributions, ionisation potentials, electron affinities, conformations and reactivities. Reactions in microreactors follow new 'forced' pathways, and other anomalous features can also be observed.

Two-dimensional microreactors are represented by the electric double layer, monomolecular layers (of the Langmuir–Blodgett type), membranes (both biological and artificial), interfaces (they are used in phase transfer catalysis, especially in reactions involving ordered and directed exchange by substances and electric charges between the phases), adsorption layers of reactants on solids ('two-dimensional' zone reactions) and so on.

A classical two-dimensional microreactor — electric double layer — has now a new lease on life, associated with high time resolution regimes ($\sim 10^{-12}$–10^{-9} s), which are brought about by the laser-induced chemistry at solid–liquid interfaces. The main character in such a microreactor is an electron, either solvated or free. Its chemical behaviour is the subject of special interest regarding generation of electric potentials and modelling of the potentials existing in 'natural' chemistry. Potentials at a liquid–liquid interface also deserve attention.

The interest in 2D monolayers on solids is due not only to their use as heterogeneous catalysts (this topic is already out of date) but also to the new opportunities offered by synthetic chemistry on the surface. For example, 1,5-cyclooctadiene, which binds to the surface of an Si(001) single crystal upon rupture of one C=C bond, forms a two-dimensional molecular lattice.[23] The highly ordered monolayer consisting of grafted molecules exhibits high reactivity and can participate in further chemical functionalisation leading to any chemical architecture.

Cluster microreactors are highly diverse. They can be atomic, molecular, ionic, ion-molecular and organometallic, either charged or neutral. Clusters are formed in gases (for example, in expanding supersonic atomic-molecular beams), in zeolite channels (for example, the In_8 clusters), in liquids, on solid surfaces, in solid matrices (such as solid argon or xenon), *etc*. They play an important role in the chemical materials science (cluster materials with unusual physics and mechanics), in chemical analytics and diagnostics (detectors and sensors) and in other fields of applied chemistry.

The main, fundamental problem in the chemistry of clusters is associated with dimension effects. This is an intriguing question — how do the properties of separate species evolve on their combination into the properties of a new phase; how are the bridges between the world of a separate molecule and the world of macroscopic matter being built? The dimension effects are so diverse and unexpected that no general solution of this problem exists. Quantum chemistry and molecular dynamics methods provide partial answers only to some questions.

Clusters still remain enigmatic objects (for unusual properties of clusters, see for example, Ref. 24). Thus Re atom is inert towards CH_4, whereas the Re_3 cluster is active; the linear clusters Cu_3 and Ni_3 do not react with H_2 or CH_4, whereas triangular clusters react readily and rapidly; the Co_n clusters are reactive towards H_2 at $n = 3$, 10 and 12 and are inert at any other n; the Nb_n clusters with $n = 3$, 4 and 5 react with H_2, whereas other Nb clusters are relatively inert; Nb clusters with $n = 5$, 6 and 11 are active in dehydrogenation of benzene; the Ag_n clusters exhibit metallic properties starting from $n = 6$, whereas Na_n do not exhibit any signs of a metal phase even at $n = 14$. The $I_2(C_6H_6)_m$ cluster is polyhedral and $V_n(C_6H_6)_m$ has a multi-deck sandwich structure.

The MoO^+ cation does not react with NH_3, whereas the $Mo_3O_8^+$ and $Mo_3O_9^+$ clusters dehydrogenate NH_3 to give complexes with the nitrogen formed upon dehydrogenation. The same clusters oxidise CO to CO_2. The $V_3O_7^+$ and $V_3O_{12}^+$ clusters are efficient in dehydrogenation of butadiene and destruction of butane, while $V_3O_6^+$ and $V_3O_{11}^+$ are inert in these reactions but they are active in the addition and oxidative cyclisation reactions.[25]

In the cluster of α-naphthol with $(H_2O)_n$ (these compounds are called crystal hydrates), proton transfer from excited α-naphthol to water has been detected only for $n \geqslant 20$; in the case of α-naphthol clusters with $(NH_3)_n$ this process occurs even at $n \geqslant 4$. In the clusters of univalent magnesium (or calcium) with $(H_2O)_n$ and $(CH_3OH)_n$, the electron transfer and hydrogen reduction

$$Mg^+(CH_3OH)_n \longrightarrow (MgOCH_3)^+(CH_3OH)_{n-1} + H,$$

$$Mg^+(H_2O)_n \longrightarrow (MgOH)^+(H_2O)_{n-1} + H$$

occur for $6 \leqslant n \leqslant 15$; at any other n the reaction does not occur, and hydrogen elimination is not observed.[26]

The rate of photoinduced isomerisation of *trans*-stilbene placed in the $(hexane)_n$ cluster was measured in molecular beams by picosecond spectroscopy.[27] The rate constant for this process decreases in the sequence 9.7×10^9 ($n = 0$, free molecule), 3×10^9 ($n = 1$), 1×10^9 ($n = 2$), 0.8×10^9 ($n = 3$), 0.5×10^9 s^{-1} ($n = 4$). Unexpectedly, all these constants proved to be smaller than the observed isomerisation constant of *trans*-stilbene in pure liquid hexane at the same temperatures and energies (11.5×10^9 s^{-1}); *i.e.* immersion of *trans*-stilbene into the $(hexane)_n$ cluster decreases its reactivity. The cluster shell fixes the molecule even more strongly than a 'liquid-phase' shell; it abnormally increases the kinetic (Kramers) friction, which accompanies the movement of the reacting molecule along the reaction coordinate.

Special interest is aroused by the dimension effects in semiconducting nanocrystals the size of which is smaller than the Bohr radius of an exciton. Quantum capture of an electron and a hole (generated by photochemical or radiation-chemical treatment) in the confined space of these nanoclusters (called quantum dots) results in an increase of the band gap following a decrease in the cluster size; hence, recombination luminescence shifts to the blue region (to higher energies). A striking example is provided by nanocrystals of CdSe 'coated' by one or two ZnS monolayers. When the diameter of the inner CdSe nucleus increases stepwise from 23 to 55 Å, the bright blue luminescence passes into green, yellow, orange and, finally, bright red luminescence.[28]

In addition, cluster chemistry opens up the way to a new strategy in heterogeneous catalysis, especially when combined with scanning tunnelling microscopy. The tip of the microscope is able to apply any number of any atoms on the faces, edges or terraces of any crystal, thus creating diverse catalytic microreactors and providing conditions for testing various reactions on them. This is a new wind in the fundamental science of catalysis and its future.

Clusters are much more widespread and, hence, much more significant than it has been believed until recently. Thus it has been found experimentally (by cold-neutron and X-ray scattering) that liquid ammonia is clustered — it consists of the $(NH_3)_7$ clusters containing one molecule in the centre and six molecules at the periphery.[29] The cluster structure of liquid water is well known: water molecules are united into hexa-, penta- and tetramers, having close energies and forming prismatic, cage, 'open-book' and adamantane structures, and also into dodecahedra and other big clusters. Liquid aqueous solutions of ethanol are also non-uniform; they consist of water and ethanol clusters.[30] It is noteworthy that when the content of the alcohol in water is ~40%, the proportions of ethanol and water clusters are equal. Perhaps, this accounts for the special receptive-gustatory properties of the well-known and popular water-ethanolic drink. Indications of clustering have also been found in liquid benzene. This might prove to be a general phenomenon; if this is really so, all liquid-phase reactions should be interpreted as occurring in microreactors.

Furthermore, a chemical reaction can itself stimulate molecular organisation of a microreactor. Thus a colourless molecule of spiropyran having a long hydrocarbon 'tail' is converted upon photochemical treatment into a coloured bipolar form with separated charges; it is in this form that spiropyran molecules

unite to form micelles. Here photochemical reaction acts as the trigger for micelle formation.

Brain is a macroreactor of enormous complexity. There occur a tremendous number of chemical reactions, responsible for the synthesis of the memorising molecular structures, which form memory and the whole control system of a living organism. Brain is of key importance in the entire chemistry of living matter; chemistry of brain is the chemistry of the XXI century.

The main purpose of brain is to transform chemical energy into electric energy; this task is accomplished by neuromediators. They stimulate enzymic synthesis in synaptic membranes and ensure communication between neurons, formation of electric potentials and transfer of electric signals *via* recharge of the membrane. They control a cobweb of impulses and potentials, which govern all functions of a living organism. Neuroprotectors act *via* chemical mechanisms.

Many neuromediators have long been known. Thus dopamine and its chemical functions have been studied comprehensively; however, only recently it has been found that its deficiency in an organism is responsible for dotage. One reason for the reduction of the dopamine level with advance in age is that it is destroyed under the action of the enzyme monoamino oxidase B. Another reason is that the number of dopamine-receiving neurons in an organism decreases with time (a low level of these neurons is also characteristic of those who suffer from parkinsonism). In addition, it has been found that some narcotics trap neurons and remove them from the functioning of brain. It is clear that the understanding of the chemical mechanisms of the operation of neuromediators opens up ways for eliminating disorders in the work of the brain macroreactor.

Other neuromediators are also known; among these, mention should be made of versatile nitrogen oxide with a broad spectrum of chemical and physiological action and Semaks – a neuropeptide consisting of seven amino acids.

Study of a macroreactor such as the human brain requires delicacy, which sharply restricts the range of possible direct experiments. Nevertheless, these studies are carried out within the framework of neurophysiology in combination with medicine and clinical surgery. The studies widely use microelectrode equipment, which permits estimation of the behaviour of the electric potentials formed and their response to chemotherapy and physiological treatment. Enormous opportunities are also provided by positron-emission tomography, in which the ^{11}C isotope and ^{11}C-labelled chemical compounds being tested are used as the positron sources. At present, researchers have realised that wide use of experimental modelling of brain elements can help in the understanding of the operation of this macroreactor. The main goal of modelling is to answer the question how does the brain perform its primary task, *i.e.* how does it transform chemical energy into electric energy. By the way, as a 'side result' of this modelling, one could expect design of molecular devices characterised by high coefficients of conversion of chemical energy into electric energy (within the framework of chemical energetics).

The Earth is a huge *geochemical macroreactor*. This mechanochemical reactor is the source of earthquakes. It covers the whole of mechanochemistry and its consequences: chemical bond rupture induced by mechanical treatment, formation and migration of dislocations, generation and multiplication of cracks, shears and shear waves, generation of electric potentials and their gradients, radio waves, magnetic fields and chemical emission. Now scientists have understood that the key to the diagnostics and prediction of earthquakes lies in mechanochemistry. All events that take place in the geochemical macroreactor echo in the ionosphere as electic field gradients and are detected there as forerunners of earthquakes. Mechanochemistry, a field of science in which chemistry occupies a prominent place, is directed towards the XXI century.

IV. Coherent chemistry

Coherent chemistry is a 'new face' of chemistry. Coherence is the ability of chemical systems to generate oscillation regimes of reactions. The coherence (time synchronisation) of a chemical reaction is manifested as cyclic variations of the reaction rate and can be detected as oscillating product yields, luminescence emission, electrochemical currents or potentials, *etc.*

Chemical coherence exists at two levels, quantum and macroscopic levels. In the former case, the coherence refers to the reactivity of an assembly of reacting particles generated by a laser pulse. Such an assembly oscillates between states with different reactivities, these oscillations modulating the yields of the reaction products. The vibrational and spin types of coherence are of the quantum origin. In the case of macroscopic coherence, the concentrations of active reagents (or intermediates) periodically change. The best known example of macroscopic coherence is the Belousov – Zhabotinsky reaction.

The coherence introduces new notions into chemistry, such as wave packet, phase, loss of phase coherence (dephasing), interference, bifurcation and bifurcation diagrams, phase portrait, strange attractor and phase turbulence. This is not simply a new language of chemistry; this reflects a new level of thinking and a new level of chemical research practice. In the coherent chemistry, the random, statistical behaviour of molecules is replaced by organised, ordered and synchronous behaviour; thus, chaos turns into order.

A short (10^{-14} – 10^{-13} s) laser pulse (with a duration shorter than the period of vibrations of atoms) 'excites' a molecule and 'throws' it onto a new potential. In this new potential, an assembly of molecules prepared by the laser pulse behaves coherently, *i.e.* vibrations of atoms of all of the members of the assembly are synchronised, the whole assembly being a wave packet.

When moving on the potential surface, a wave packet can disperse into several smaller packets (with different vibration amplitudes and phases); some of them can go out of phase (lose the coherence) and disappear, while some other can interfere to restore partially the initial packet, *etc.*

A classical illustration of the coherent behaviour of a wave packet is provided by an assembly of NaI molecules (Fig. 6).[31] Molecules of NaI excited by a short ($\sim$50 fs) pulse are 'transferred' from the surface of the ground (ionic) state to the surface of an excited 'covalent' state; this creates a wave packet localised on a potential surface. This wave packet slides in an adiabatic potential (Fig. 6 *a*, the upper curve), in which it oscillates between the covalent and ionic states and crosses at some intervals the point of intersection of the ionic and covalent terms (when the interatomic distance is 6.93 Å). Due to the non-adiabatic connection of these two terms, there is a finite probability of penetration of the packet from the upper curve to the lower one. As this takes place, a part of the penetrated packet dissipates to generate Na atoms (they can be detected experimentally) and the rest becomes a new wave packet, which moves coherently in the lower valley.

The point of intersection of the ionic and covalent terms (where the upper and the lower potential curves contact with each other) is the bifurcation point in which the wave packet splits into two packets, one of which is partially irreversibly destroyed. In principle, it is clear that the packet situated in the lower potential curve can return to the upper potential curve *via* the same bifurcation point and restore the initial packet (interference), although in this particular case, the probability of this event is low. For other systems characterised by a different configuration of the potential energy surface, this probability can be substantial and the packet interference can be manifested fairly clearly.

These qualitative considerations can be converted into a quantitative picture by calculating the probabilities of dissipation of the packet at the bifurcation point (according to Landau – Zener). Fig. 6 *b* shows the pattern of the packet movement on the time and space coordinates. It can be readily seen that the coherent movement of the packet in the upper valley generates a stream of

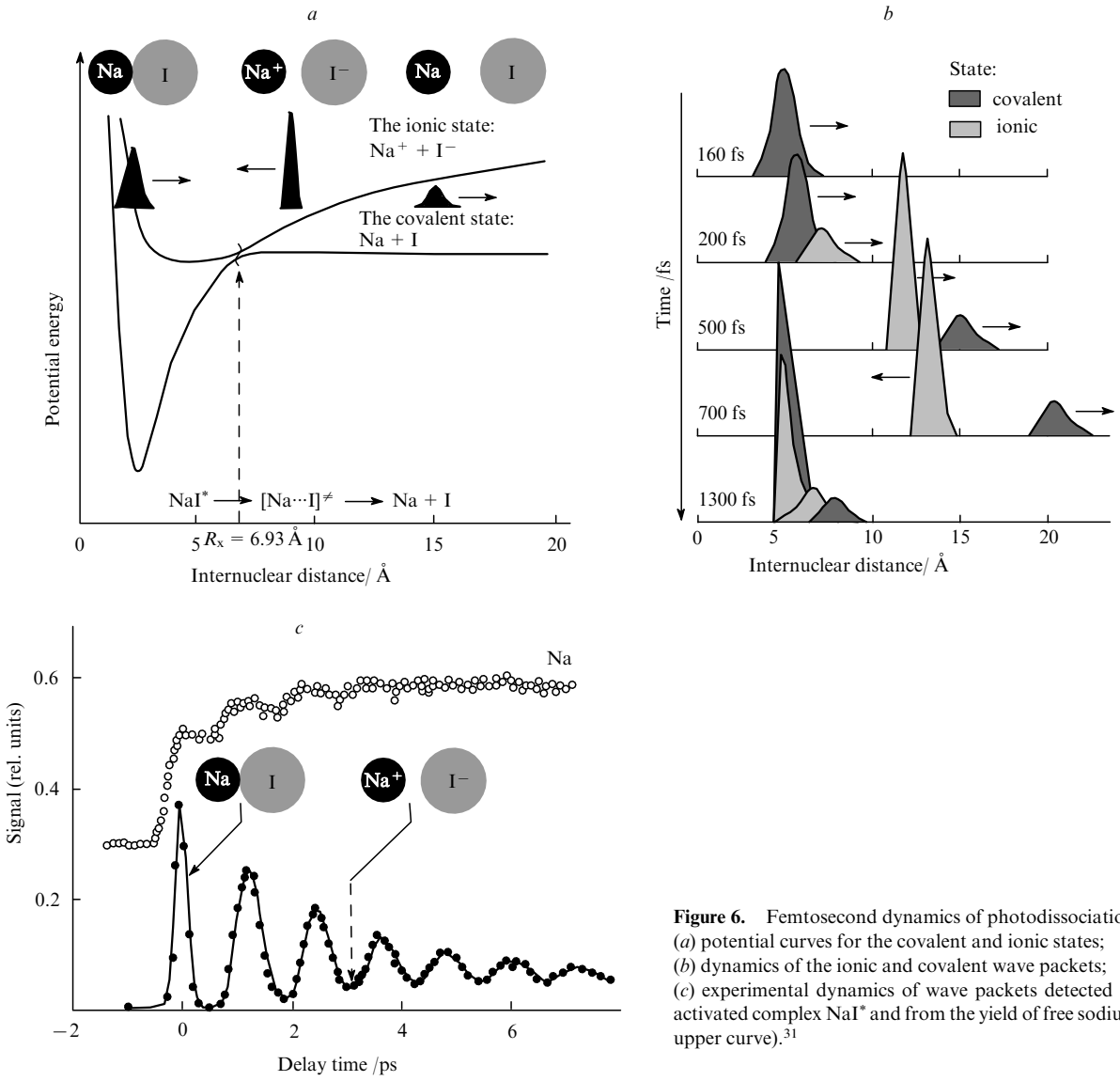


Figure 6. Femtosecond dynamics of photodissociation of NaI; (*a*) potential curves for the covalent and ionic states; (*b*) dynamics of the ionic and covalent wave packets; (*c*) experimental dynamics of wave packets detected based on the activated complex NaI^* and from the yield of free sodium atoms (the upper curve).[31]

Na atoms (reaction product) at the bifurcation point. The density of this stream oscillates with time, the oscillation frequency being equal to the frequency of packet oscillation in the upper valley; the density amplitude attenuates due to the packet dissipation, dephasing and falling into the deep lower valley (Fig. 6 *c*).

The coherence created initially is retained during the reactions and is transferred to the products. This indicates that the molecular assembly undergoes a collective, synchronous and phase coherent chemical transformation.

This coherence can be found not only in simple reactions such as dissociation of the NaI, I_2, HgI_2, *etc*. molecules but also in complex systems. Thus phototransformation of rhodopsin and its analogues occurs in parallel *via* a coherent and a non-coherent § channel over a wide spectral range (400–1100 nm).[32] The key process in the phototransformation of rhodopsin — a molecular system consisting of an apoprotein (opsin) and 11-*cis*-retinene attached to it — is the *cis*–*trans*-isomerisation of retinene around the C(11) = C(12) bond. The direct coherent formation of the first intermediate (bathorhodopsin from rhodopsin and hR_K from halorhodopsin hR) occurs over a period of ~200 fs, the coherence being retained in the reaction product. The fact that even in a complex molecular system such as rhodopsin, the degree of coherence remains remarkably high (~20%) merits attention. When the hydrogen atoms at C(11) and C(12) are replaced by deuterium, the isotope effect is not observed over a short period of time (up to 110 fs); it appears only in the range 110–170 fs, when rocking around the C(11) = C(12) bond is characterised by a large amplitude and leads to full rotation. This means that the coherence of the whole process (it takes ~200 fs) is a stable characteristic, which is retained at any amplitude along the coordinate of isomerisation.[33]

Vibrational coherence can also be detected in the chemical transformations of such a bulky molecular system as the bacterial photosynthetic centre.[34] Moreover, coherence has been found in the antennae of photosynthesising centres, its degree and 'length' (*i.e*. the length of the 'coherent' accumulation of energy) being dependent on the molecular order and spatial arrangement of the light-collecting complexes near the the energy-collecting photosynthesising centre.

It is not the coherence itself that is the most remarkable feature of the coherent chemistry but rather new and non-traditional methods for controlling chemical reactivity. When the first pulse throws a wave packet onto a potential surface, the second pulse can influence its evolution: either throw it further onto a new surface or bring it back onto the initial surface (the Raman process). This can be done either before or after the wave packet has passed the bifurcation point by changing the delay between the first (pump) pulse and the second (probe) control pulse. In

§ Phototransformation *via* a non-coherent channel implies statistical thermalisation of the excited state followed by slow (2–4 ps) statistical formation of the product.

other words, the dynamics of wave packets and their chemical fate can be controlled; the ratio of the channels of their transformation and the yields of the reaction products can be altered. Thus a new tool for controlling a chemical reaction appears, *i.e*. the phase of a coherent assembly. By affecting a wave packet in various phases of its evolution, one can change its chemistry.

For example, in the electronically coherent assembly of HD^+ molecules, prepared from HD by a short ionising laser pulse (pump pulse), the electron oscillates between the H and D atoms. Using the second (control) pulse, one can attain the coherent control of the HD^+ dissociation, which gives either $H + D^+$ or $H^+ + D$, depending on the instant when the second pulse acts. To induce the former dissociation pathway, the second pulse should be switched on when the electron resides on the hydrogen atom, whereas for the latter pathway, it should occur when the electron is on deuterium. This is the highest level of coherence in chemistry, the prospects of which are being discussed even now.[35]

An even finer and a more elegant way of controlling the chemical fate of a wave packet is embodied in the phase relationship between the packet and the probe pulse. The current state of optics makes it possible to control the frequency-dependent phase of laser pulses. The delay $\tau(\omega)$ of the group velocity of a particular frequency component of the optical spectrum is known to depend on the phase of this component Φ by the relation $\tau(\omega) = \partial\Phi(\omega)/\partial\omega$. For a pulse with a given spectrum, all the frequency components should be in phase and should arrive simultaneously at the destination point, *i.e*. $\tau(\omega)$ does not depend on frequency. In this case, $\Phi(\omega)$ includes no frequency-dependent quadratic terms (or terms with higher exponents). However, one can change $\Phi(\omega)$ in a specified way (by virtue of optical grids and prisms) in order to introduce frequency-dependent quadratic terms (they are called chirps). In these chirped pulses, phase velocities become frequency dependent. Thus when the chirps are negative, the red component of the pulse lags behind and arrives at the destination point (*e.g.,* at a wave packet) later than the high-energy blue component. Conversely, in the case of positive chirps, the red light is ahead of the blue one. It is clear that by changing the chirp of an optical pulse, one can control the relationship between the phases of the wave packet and the control pulse and thus 'catch' the packet in various positions on the potential surface by either red, or blue, or another appropriate light.

Certainly, this is a simplified picture illustrating in a clear form the main principles and chemical effects of the vibrational quantum coherence. The main idea is that the coherent chemistry brings about a new factor controlling chemical reactions, namely, the phase. By changing the phase (this can be attained by delaying the control pulse relative to the generating pulse or by chirping), one can manipulate the chemical behaviour of assemblies of reacting species without changing the energy or angular momentum.

The next level of coherence is quantum periodicity in a system consisting of two species, each carrying an electron spin (for example, a pair of radicals). Such a spin pair can exist in two states — singlet (reactive) and triplet (chemically inert). An assembly of these pairs, prepared by a pulsed method (photolysis or radiolysis) in a specified spin state (*e.g*., in the triplet state), oscillates synchronously between the two states. The driving force of this oscillation is the difference between the Zeeman energies of the two partner spins or the hyperfine electron–nuclear coupling (if the radicals contain magnetic nuclei). The magnitude of these interactions is of the order of several megahertz (it is with this frequency that the assembly oscillates between the signlet and triplet states). It is clear that the yield of the products of a chemical reaction (which are formed only when the species occur in the singlet state) is time-modulated at the same frequency (Fig. 7). The periodicity in the product formation is a consequence of the coherence of the behaviour of spin pairs; this is an example of electron-spin quantum beats in chemical reactions (as opposed to the vibrational quantum beats, considered in the previous Section).

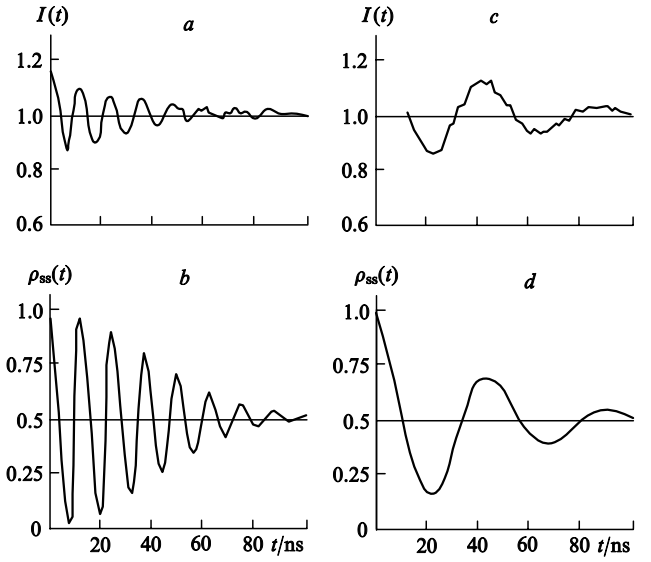


Figure 7. Quantum beats in the recombination of the (diphenyl sulfide)$^+$/(*p*-terphenyl-d_{14})$^-$ radical-ion pair in *cis*-decalin at $H = 1200$ (*a*, *b*) and 3000 G (*c*, *d*). The product of recombination of *p*-terphenyl-d_{14} was detected by fluorescence.
(*a*, *c*) Experimental data, (*b*, *d*) theoretical calculations; $I(t)$ is the fluorescence intensity, $\rho_{ss}(t)$ is the content of the singlet state in the radical-ion pair.

The electron-spin coherence has been found in photochemical and radiation-induced chemical reactions of radical pairs [36] and in the primary photochemical event of charge (and electron spin) separation in the photosynthetic reaction centres. In these systems coherence originates due to the synchronous oscillation of spin pairs between the singlet and triplet states. Moreover, in addition to the electron-spin coherence, nuclear-spin coherence has been found in these systems (ordered in-phase precession of the system of polarised nuclei occurs).[37]

The advantage of spin coherence is that it provides new methods of investigation and identification of fine and accurate details of the structure and dynamics of chemically generated spin systems. Furthermore, even when the chemical reaction producing spin systems occurs statistically (non-coherently), spin coherence exists in these systems, which opens up a way to the new field of science, chemical radiophysics (see Section V).

The oscillating regimes of chemical reactions were first observed rather long ago. At that time, oscillations were considered to be an exotic rather than a regular feature. Nowadays the Belousov–Zhabotinsky reaction and oscillations of pH and electrochemical potentials in heterogeneous systems such as oil–water systems, Liesegang rings and wave combustion, have become classical examples. However, the fact that macroscopic coherence is a fundamental property has been realised only recently. The science of chemical oscillators has been revived owing to two important facts.

Firstly, it became clear that coherent regimes could increase the yields of reaction products and the process selectivity and could lead to self-cleaning of surfaces from catalytic poisons, *etc*. These expectations have been confirmed, especially for chemical oscillators with forced oscillations.[38]

Secondly, the interest in chemical oscillators has been aroused again owing to biochemical oscillating processes occurring in nerve cells, muscles, and mitochondria. This resulted in active assimilation of new systems of oscillators, *i.e*. in combination of several chemical oscillators into a common unified system. It is believed that such a system would be a prototype (although yet primitive) of the future models of neuron networks.[39] However, even now, studies are in progress on the oscillator excitation thresholds in such a combined system and on the influence of the

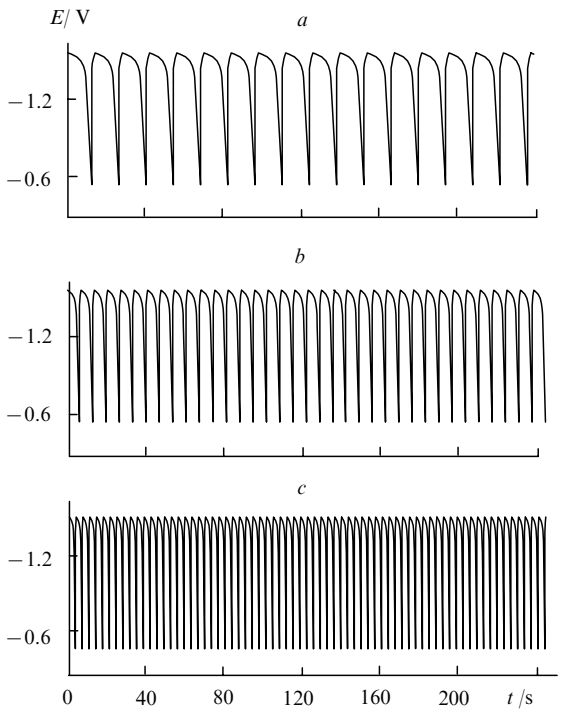


Figure 8. Periodic potential oscillations during the reduction of bromate ions in a solution of NaOH at a silver electrode and at the current 1.5 (*a*), 2.5 (*b*) and 3.0 mA (*c*).[42]

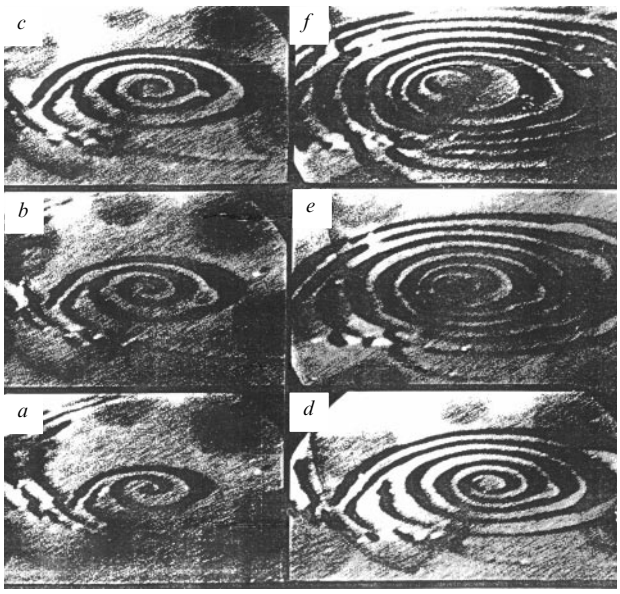


Figure 9. Helical wave on the Pt(110) surface which develops during oxidation of CO with oxygen (434 K). The light sections are areas occupied by CO; the dark sections are areas occupied by oxygen. The photographs were taken consecutively at times 0 (*a*), 10 (*b*), 21 (*c*), 39 (*d*), 56 (*e*) and 74 s (*f*) on a 0.2×0.2 mm^2 area.[44]

number of oscillators, the way of their connection (a linear or a circulating system) and the connection parameters (mass exchange, control of electrochemical potential and currents) on the excitation of collective oscillations, *etc*.

New chemical oscillators have been discovered. Thus the potential of a platinum electrode in the $ClO_2 - I_2 - CH_3C(O)CH_3$ system varies as a periodic function of time. When formaldehyde and methanol are oxidised under galvanostatic conditions, the oscillation frequency repeatedly doubles, resulting in the break-down to chaos at the bifurcation points.[40] This type of behaviour resembles that observed in some enzymic reactions and biological systems.[41] Oxidation of bromate ions in alkaline solutions is also an oscillating process (Fig. 8). Oscillations are due to the concentration effects at the electrode surface and, therefore, they vary as a function of the surface geometry (roughness, presence of islets, *etc*.).[42] Another bromate oscillator catalysed by tris(bipyri-dine)ruthenium is, in addition, a photo-controlled system displaying different bifurcation diagrams in the light and in the dark. A strange bifurcation behaviour of the order and chaos regimes and doubling of frequency are also observed in the peroxidase-catalysed oxidation of dihydro(nicotinamide)adenine dinucleotide (NADN).[43]

In heterogeneous catalytic oscillators, oscillations may arise due to a non-linear relationship between the rates of chemical reaction and heat exchange, concentration gradients, periodic modulations of the composition of a 'two-dimensional' reactant, 'breathing' of the surface (when atoms go down and up, similarly to waves in a two-dimensional lattice), *etc*. Examples of chemically oscillating processes are provided by the reduction of NO with hydrogen (when the pressure of H_2 decreases, the period of oscillations repeatedly doubles until break-down to chaos occurs), oxidation of CO with oxygen on platinum, accompanied by generation of time-and-space helical waves (Fig. 9)[44] and some other processes.

The brain is a striking and a unique example of a system self-organised in space and time. The chemical activity of enzymes and, as a consequence, the electric potentials in the system of synaptic membranes and neurons in brain are remarkably synchronised (coherent). It is also clear that the scales of coherence (*i.e*. the sizes of synchronised areas in brain) are different for different levels of brain functioning. In other words, the brain consists of biochemical oscillators of various sizes connected to one another and combined into a unified control system.

Order is the normal state of this system, while chaos implies severe pathologies (such as Alzheimer's disease). Perfect order is the property of a brilliant genius brain (this idea is only hypothetical but looks like being true).

V. Spin chemistry and chemical radiophysics

Yet another new field of modern chemistry is spin chemistry concerned with the behaviour of angular momenta (spins) of electrons and nuclei during chemical reactions. Spin chemistry is based on the fundamental law: in adiabatic chemical reactions the electron and nuclear spins are strictly retained. Only those reactions are allowed which do not require spin change. In other words, all the chemical reactions are spin-selective, *i.e*. they are allowed only for those spin states of reactants the total spin of which is equal to the total spin of products, and they are completely forbidden when the reactant spin is not equal to the product spin.

A simple example is provided by a radical pair comprising methyl and hydroxyl radicals. Recombination of these radicals to give methanol occurs only in the singlet state, because this ensures that the electron spin of the pair ($S = 0$) is identical to that of CH_3OH. However, disproportionation of the same radicals in the singlet state to yield H_2O and triplet methylene (the total spin of the products $S = 1$) is forbidden for spin reasons. For the triplet radical pair ($S = 1$), on the contrary, recombination is forbidden, whereas disproportionation is allowed, although its activation energy is relatively high, ~ 6 kcal mol^{-1}.

One should be conscious of the fact that chemistry is governed by two fundamental factors — energy and spin (as shown in the previous Section, one more factor, phase, appears in the coherent chemistry).

Unlike the prohibition for energy reasons (it appears when the energy of reactants is lower than the energy barrier to the

reaction), which can be overcome *via* tunnelling under the barrier, the spin prohibition is insurmountable.

Spin can be changed upon non-chemical magnetic interactions; only they can transform spin-forbidden (non-reactive) states of reactants (*e.g.*, radical pairs) into spin-allowed (reactive) states. Magnetic interactions, the energy of which is negligibly small, switch reaction channels — they can open closed channels and, conversely, close the open (allowed) ones, depending on the initial state of the reactants. Actually, they write a new, magnetic script of a chemical reaction.

The spin selectivity and, hence, the magnetic sensitivity of chemical reactions has served as the source of three generations of magnetic effects discovered during the last two decades.[45] Fig. 10 illustrates the origin of these effects in relation to a particular example, which is, however, frequently encountered in chemistry, namely, a radical pair able to exist in either the singlet or the triplet spin state. In the case where triplet – singlet transitions are induced by static magnetic fields (external fields or internal fields of magnetic nuclei), first-generation magnetic effects arise. Magnetic effects of the second generation appear when the spin conversion of pairs occurs on exposure to microwave fields. Finally, when the conversion is induced by the influence of a third paramagnetic species, a remarkable phenomenon, spin catalysis, can be observed, which represents the third generation of magnetic effects. The third species (a radical or a paramagnetic ion) acts as a spin catalyst.

First-generation magnetic effects. An external magnetic field exerts two types of influence on the spin conversion of radical pairs and, hence, on the chemical reactivity. Firstly, the field switches off two of the three channels of spin conversion, namely, $S-T_+$ and $S-T_-$, so that only the $S-T_0$ channel is left (T_+ , T_0 and T_- are triplet states which differ in the projection of the total spin). Secondly, it accelerates the $S-T_0$ conversion if the partners of the pair have different Zeeman energies. Depending on the initial spin state and magnetic parameters (hyperfine coupling energy, *g*-factors, dipole interaction) of the reactants, chemical reactions can be accelerated or decelerated by an external magnetic field.

Magnetic field effects have been found in a great number of chemical and biochemical reactions, their range constantly extending. A reliable theory capable of predicting the significance

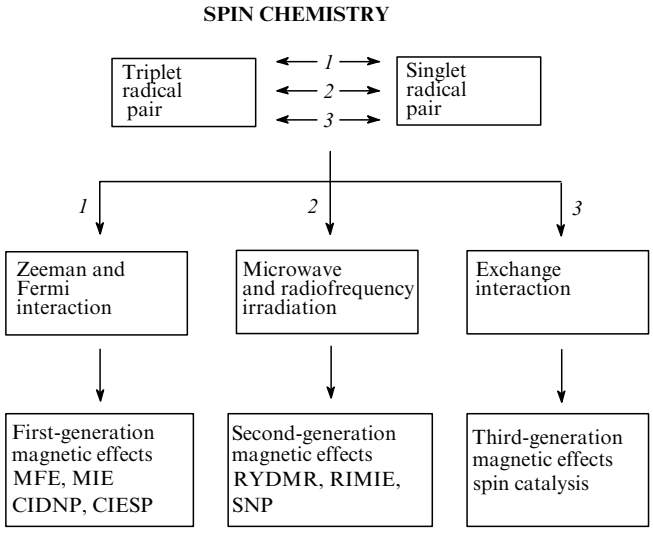


Figure 10. Spin evolution of radical pairs. The following designations are used: MFE is magnetic-field effect, MIE is magnetic isotope effect, CIDNP and CIESP are chemically induced dynamic nuclear polarisation and electron spin polarisation, RYDMR is reaction yield detected magnetic resonance, RIMIE is radio-induced magnetic isotope effect and SNP is stimulated nuclear polarisation.

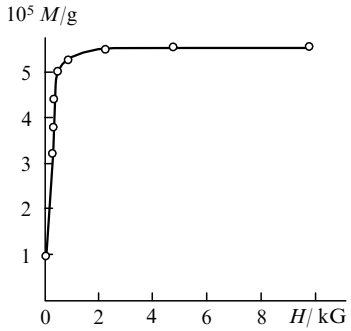


Figure 11. Molecular mass of the polymer obtained by emulsion polymerisation of styrene (dibenzyl ketone as a photoinitiator; sodium dodecylsulfate as an emulsifier; constant polymerisation time) *vs* magnetic field intensity.[46]

and behaviour of magnetic effects has been developed. The magnitudes of these effects are often quite large. Thus the rate of photoinduced aqueous-emulsion polymerisation of styrene and the molecular mass of the resulting polymer increase 6 – 8-fold even in weak magnetic fields, ~100 G (Fig. 11).[46] An even more pronounced effect (20 – 25-fold increase) is attained in the light scattering by colloidal particles subjected to photochemical cross-linking.[47] This strong effect can be used for visualisation of magnetic fields and their gradients.

Being selective regarding the electron spin, chemical reactions between spin carriers (radicals, paramagnetic ions and molecules, carbenes, *etc.*) are also selective as regards the nuclear spin. If the two spin subsystems (electronic and nuclear) are related by the Fermi hyperfine coupling (FHC), the nuclear subsystem can affect the behaviour of the electronic subsystem *via* the FHC and thus modify the chemical reactivity of spin carriers. The nuclear-spin selectivity is manifested as different rates of spin-selective reactions of radicals (or other spin carriers) with magnetic and non-magnetic nuclei. This is a new phenomenon referred to as magnetic isotope effect (MIE), which differs fundamentally from the classical isotope effect (CIE), resulting from nuclear-mass selectivity of reactions. Both effects sort the isotope nuclei: the CIE selects nuclei according to their weights, while the MIE selects them according to their spins and magnetic moments.

The discovery of the magnetic isotope effect is a prominent event of the last quarter of the XX century, its significance being comparable with that of the discovery of the classical isotope effect. In addition, the magnitude of this effect substantially exceeds that of the CIE (Fig. 12) and, unlike the magnitude of the CIE, it depends on the magnetic field, temperature, molecular and chemical dynamics and the spin state of the reactants. The magnetic isotope effect results in fractionation of magnetic and non-magnetic isotopes in chemical, biochemical, geochemical and interstellar processes.[48]

The third effect belonging to the group of first-generation magnetic effects is chemically induced dynamic nuclear polarisation (CIDNP). Unlike the MIE, in this case the nuclei are sorted not only according to their magnetic moments but also according to their orientations. During a chemical reaction, nuclei with different orientations are sent into different products and this creates non-equilibrium populations of the Zeeman nuclear levels in these products. An excessive population of the lower Zeeman level corresponds to the positive nuclear polarisation, whereas overpopulation of the upper level implies negative polarisation. The latter case is especially remarkable: when the overpopulation of the upper level exceeds some permissible limit, the populations are inverted; this provides the basis for chemical radiophysics.

An assembly of product molecules with inverted populations accumulates energy in the Zeeman storage reservoir; the energy can either be consumed as heat (*via* spin – lattice magnetic relaxation) or be converted into stimulated emission at a Zeeman

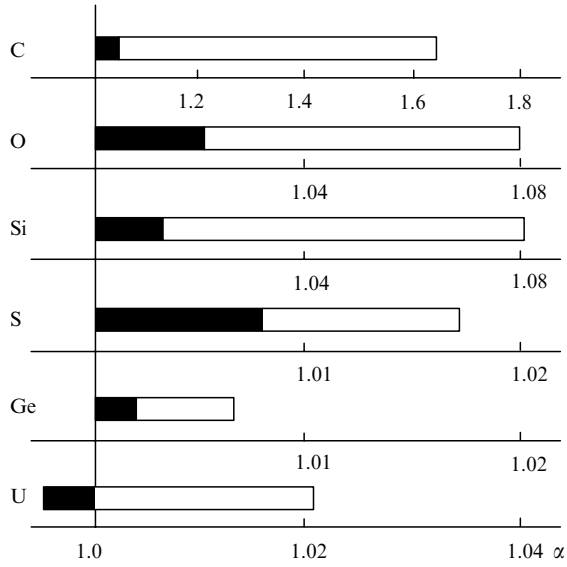


Figure 12. Comparison of the magnitudes of the magnetic (white areas) and classical isotope effects (black areas) in the separation of the $^{13}C/^{12}C$, $^{17}O/^{16}O$, $^{29}Si/^{28}Si$, $^{33}S/^{32}S$, $^{73}Ge/^{72}Ge$ and $^{235}U/^{238}U$ isotope pairs. The coefficient α of one-stage isotope separation (a universal measure of isotope effect) is plotted as the abscissa.

nuclear frequency. In this case, the reaction becomes a radio-frequency emitter, *i.e.* a quantum generator with chemical pumping (similar to chemical lasers). This new phenomenon — radio-frequency emission of chemical reactions — was first predicted theoretically and later found experimentally.[49] It appears when the energy stored in the Zeeman storage reservoir exceeds the generation threshold, the movement of nuclear spins spontaneously becomes coherent, and this coherent set of nuclei functions as a quantum generator.

Chemically induced electron spin polarisation (CIESP) is the fourth effect. It arises due to the electron-spin selection during the reaction and results in non-equilibrium population of the Zeeman electron levels in radicals and paramagnetic molecules (in this respect, CIESP resembles CIDNP).

The two latter effects are widely used in chemistry and biochemistry as new investigation methods (diagnostics of reaction mechanisms, detection of radicals, and chemical kinetics and chemical physics techniques).

Second-generation magnetic effects. The microwave emission of chemical reactions is only one aspect of chemical radiophysics. A chemical reaction can be not only a generator but also a receiver of microwaves. The reception at the chemical level follows from the principles of spin chemistry: the resonance microwave radiation stimulates the triplet–singlet conversion of radical pairs (or pairs of other spin carriers) and changes the yields of chemical products, which can be detected by chromatography, luminescence, electrical conductivity, *etc*. Thus, owing to the second-generation magnetic-spin effects, a reaction becomes a chemical receiver of microwave radiation.[50] Moreover, this expedient can be performed selectively. If the microwave pumping affects all the radical pairs, the final outcome reduces to the change in the product yield at resonance frequencies. This effect has been called reaction yield detected magnetic resonance (RYDMR). Selective pumping involving only radical pairs with magnetic nuclei brings about a remarkable phenomenon, radio-induced magnetic isotope effect (RIMIE). Finally, when the microwave pumping is also selective regarding the orientation of nuclear spins (involves only assemblies of radical pairs with selected orientations of nuclear spins), stimulated nuclear polarisation (SNP) appears.

Third-generation magnetic effects. Spin catalysis is the first example of purely physical catalysis.[41] This phenomenon is notable because the spin conversion of reactants is induced by a paramagnetic species, a spin catalyst. Conversion occurs as a result of exchange interaction of the catalyst with the reactants. Spin catalysis accelerates radical recombination, *cis–trans* isomerisation of compounds with double bonds (by seven to eight orders of magnitude), recombination of spin-polarised atoms, *etc*. Spin catalysis might also be effective in biochemical processes.

The spin chemistry and the chemical radiophysics are based on electron- and nuclear-spin manipulation. When manipulation is accomplished by the chemical reaction itself, interesting first-generation magnetic-spin effects arise; they include microwave generation, which transforms a chemical reaction into a molecular radio station. When spin manipulation is induced by microwaves, even more elegant second-generation magnetic effects originate. They serve as an indicator of microwave reception.

The spin chemistry and the chemical radiophysics are tightly connected; nevertheless, each of them solves independent problems. The former develops new principles of the control of chemical reactions (including that by virtue of microwaves), while the latter is significant practically for biomedical purposes.

VI. Chemistry under extreme and exotic conditions

Nowadays, the scope of chemistry is expanding, modern chemistry is actively encroaching upon fields that have not been of interest or have been inaccessible for classical chemistry. Transition from the 'explored' reaction conditions to extreme, non-classical and even exotic conditions occurs more and more swiftly. These conditions include intense electric and magnetic fields, superhigh pressures, shear deformations, light fields with intensities comparable with those of the electric fields inside the molecules, supercritical conditions, powerful gravitation, sonic and microwave fields, *etc*.[52]

Ultrashort laser pulses (duration 10 fs or shorter) carry enormously powerful optical radiation and electric fields. This immediately gave impetus to the search for new possible effects. In fact, the interaction of optical and electric fields with the electron shells of molecules gives rise to lots of unusual effects.

Picosecond pulses with a power of up to 10^9 W cm^{-2} induce 'orbital' excitations in molecules, which lead mainly to the molecule fragmentation. However, when the power is higher (about $10^{14}-10^{15}$ W cm^{-2}), multielectron ionisation of molecules occurs, which is followed by Coulomb explosion of the atomic-nuclear core. This type of behaviour is observed, for example, for clusters: an intense laser pulse (120 fs, 10^{15} W cm^{-2}) induces efficient ionisation of the NH_3 molecular clusters, which is accompanied by Coulomb explosion, yielding charged nitrogen atoms (N^{2+}, N^{3+}, N^{4+}).[53] Fullerene C_{60} is also ionised by an intense laser beam (100 fs, 10^{16} W cm^{-2}) to give C_{60}^{4+}, which is split into fragment ions *via* Coulomb explosion.[54]

The Lorentz forces, which accompany the passage of a laser pulse through a substance, induce several other effects. Thus they ensure the formation of microparticles in polymer solutions. The photon pressure of the Lorentz forces in a concentrated beam captures polymer chains and condenses them into microparticles with diameters of $\sim$10 nm or larger.[55] In addition, laser beams cause ablation of atoms and atomic-molecular clusters from solid surfaces, thus performing molecular etching. Each of these effects can provide the basis for not only new chemical research methods but also new high-end chemical technologies.

High-power laser pulses are an excellent means for generating powerful short shock waves (in particular, they are used in physics for laser compression of deuterium aimed at attaining controlled nuclear fusion). In chemistry, laser shock waves are employed to study the behaviour of substances under extreme conditions (high temperatures, high pressures, shear deformations). Thus laser-induced shock waves ensure a pressure of up to 5 GPa in the front; the duration of the leading front can reach several hundred picoseconds for reversible compression and $\sim$20–25 ps for irreversible compression. The temperature drop behind the shock front occurs at enormous rates (about 10^{11} K s^{-1}).

Laser-stimulated shock waves provide great scope for 'extreme' chemistry; they actually give rise to a 'new wave' in the use of shock waves. Onion fullerenes and the transformation of fullerene spheres into diamond have been already mentioned. The same occurs with multilayer nanotubes: at pressures of ~ 50 GPa, their outer shells are torn and twisted to give graphite structures (diamond nanocrystals have also been detected).[57] The synthesis of diamond according to the known explosion technology might occur (at least, partly) *via* onion fullerenes and nanotubes, which are then converted into diamond under the action of a shock wave.

The supercritical state of matter is a source of unexpected and, hence, 'anomalous' effects. For example, near the critical point, highly developed density fluctuations are observed, which implies fast reversible clustering of the substance. Perhaps, it is this feature that accounts for the considerable technological advantages of the supercritical state for extraction and other processes.[58]

Synthesis of metallic hydrogen (which has been mentioned above) and the reaction of tritium with hydrogen and deuterium in normal liquid helium and in superfluid quantum helium should be noted as the latest achievements of the 'extreme' chemistry.[59] It was found that the exceptionally large isotope effects observed in this reaction (this is predictable) are different for normal and quantum helium (this is unexpected). If this finding is confirmed, new and unusual evidence for chemical coherence will be thus obtained.

Magnetic-field effects in chemistry have been already discussed within the framework of spin chemistry. All the effects observed in spin chemistry arise as a response of the electron and nuclear magnetic moments to magnetic treatment (a magnetostatic field or the magnetic component of a microwave field). In a system of moving electric charges (solvated electrons or ions), the magnetic fields create Lorentz forces, which, in turn, induce a number of other effects. Therefore, the range of magnetic-field effects may prove to be even broader than predicted by pure spin chemistry.

Magnetic fields have considerable influence on the rate of migration of dislocations in ionic and atomic crystals such as NaCl and Si (the rate increases 3–6-fold in 4–5 Œ magnetic fields),[60] on the plastic deformation rate and on the strength of ionic crystals[61] (Fig. 13). These effects are of interest for chemistry and solid-state mechanics. Despite the fact that they can find a reasonable and non-contradictory explanation in terms of the concepts of spin chemistry (spin-dependent recombination of dislocations on paramagnetic stoppers, affecting the rate of migration of dislocations), a contribution of Lorentz forces also cannot be ruled out, even more so because the effects themselves depend on low-frequency (about hundreds of hertz) electric fields.

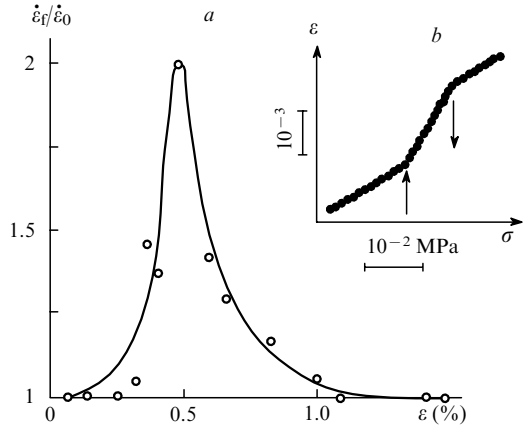


Figure 13. Rate of plastic deformation of a single crystal of NaCl $\dot{\varepsilon}_f$ in a 0.7 T magnetic field (in relation to the rate of deformation $\dot{\varepsilon}_0$ in a zero field) as a function of deformation ε (*a*), and deformation ε as a function of stress σ (*b*) (the up arrow shows the instant when the magnetic field is switched on, and the down arrow shows the instant of switching off the field).

The influence of magnetic fields on the electrodeposition of silver on copper is apparently also associated with Lorentz forces (the yield of the reaction in a ~ 80 Œ field at a field gradient of 4×10^3 kŒ m^{-1} increases to 45%; in addition the density of the dendrites of the deposited metal increases and their quality improves).[62] In this case, the magnetic field influences the microdynamics and microturbulence of the electric double layer at the electrode–solution interface *via* the Lorentz force. (It would be pertinent to evaluate the prospects of this new phenomenon).

Unlike chemical radiophysics, based on the magnetic component of a microwave field, *microwave chemistry* utilises the electric component of this field. In microheterogeneous systems with localised polar and non-polar regions (*e.g.* when polar reagents are concentrated in microreactors), microwaves are absorbed by polar and polarisable areas. Actually, these areas function as miniature microwave ovens with addressed supply of heating energy; therefore, reactions which occur in these reactors are highly selective.[63]

Chemical reactions initiated by ultrasound also occur in microreactors (cavitations). Although the chemical effects in them are specific, they largely resemble those induced by low-temperature plasma and shock waves. Both microwave and ultrasound chemistry are regarded (for good reason) as providing new means for synthetic chemistry.

Finally, the chemistry in intense gravitation fields (as well as the chemistry in the state of weightlessness) undoubtedly belongs to the 'extreme' chemistry. A sharp increase in the gravitational force of molecules, clusters and associates in these fields should generate new effects; the magnitudes and signs of the concentration gradients change, equilibria shift, the arrangement of phases in accordance with density is inverted and the rates and competition of processes alter.[64] The opportunities provided by these effects are virtually unlimited; the problem lies only in the availability of technical means needed to implement them in practice. Of course, this would be possible only for high-end technology rather than for large-scale chemical production.

The low-temperature region (near 4 K) was assimilated by chemistry relatively long ago. The most outstanding result is the discovery of the quantum mechanism of chemical reactions, *i.e.* tunnelling through the barrier, and its consequences (enormous isotope effects, temperature-independent limiting rates of reactions). Certainly, this also can be classified as 'extreme' chemistry.

The chemistry dealing with temperatures of 10^{-4}–10^{-6} K should be regarded as 'exotic'. The preparation of ultracold atoms is based on the fact that the velocity of their movement changes upon the absorption of an optical quantum (laser cooling of atoms). If atoms and laser photons are selected in such a way that the absorption occurs in the low-frequency region of the spectrum ('red' edge), then the resonance absorption by an atom moving towards the photons shifts to the line centre and is enhanced, due to the Doppler shift. In the case of 'accompanying' atoms, the Doppler effect shifts the resonance away from the centre and attenuates the absorption; consequently, the atoms experience a decelerating force directed along the photon stream. Atoms placed in orthogonal laser beams are decelerated in all the three directions; this creates an optically viscous medium in which the movement of atoms stops, their kinetic temperature being 10^{-4}–10^{-6} K (even temperatures of 10^{-10} K can be attained).

From ultracold ^{85}Rb atoms, a crystal lattice has been constructed (it proved to be a body-centred cubic lattice), the lattice parameters were measured by optical diffraction and the frequencies of collective lattice vibrations were determined.[65] In other words, scientists succeeded in creating a new state of matter — crystalline gas.

Ultracold atoms, devoid of kinetic energy, are of interest for precise spectroscopy and metrology, for probing the atom – atom and atom – surface potentials, for experimental verification of the postulates of quantum electrodynamics of a single-atomic maser.

Optical excitation of atoms in the crystalline gas affords electronically excited atoms, which react with other atoms to give excimer molecules implanted into the crystalline gas. The first steps in the chemistry of the energy-free cold atoms and molecules have already been made; its future starts today. Furthermore, the possibility of laser cooling of molecules in liquids is being discussed.[66]

VII. Once again about cold fusion

In the late 80s of the outgoing century, the scientific world was overwrought by a dramatic event — discovery of nuclear reactions accompanying electrochemical synthesis. The brilliant horizons of the cold nuclear fusion immediately became visible; indirect evidence supporting this finding (neutrons, γ-radiation, excess thermal effects) was even obtained. However, the euphoria has soon come to an end; experimental mistakes and non-reproducibility of the observed effects were found. Consequently, 'cold fusion' was wittily renamed to 'confusion'. At present, both experimental research and debates concerning cold nuclear fusion have transformed into sluggish processes continued by a small group of enthusiasts.

However, the curiosity of this 'discovery' has not disappeared. The questions of whether a chemical reaction can induce nuclear fusion and whether transformations of the electron shell can stimulate nuclear transformations still remain open.

Probably, the answer is that generation of neutrons can accompany a chemical process; however, neutrons do not result directly from this process but are formed as a secondary product. They can arise upon nuclear decay induced by γ- and X-radiation emitted by the electron shell, *i.e.* they have a chemical nature.

Although direct chemonuclear fusion was not accomplished, it has given rise to a new strategy of chemical energetics — coupling of a mechanochemical reaction with a non-branched (or slightly branched) chain photonuclear reaction.

This strategy is based on the following idea: mechanically stimulated reactions result in excited electron shells and give rise to γ- and X-rays, which are captured by nuclei (photonuclear reaction); the nuclei excited in this way decay to generate new γ-quanta and/or neutrons. A chain (or partially branched) chemonuclear reaction with energy evolution can occur. The problem is that the mechanical treatment must excite inner electrons; only in this case, conversion of outer electrons to inner vacancies (such as the Auger process) would generate hard X-rays or γ-rays. It is clear that shock waves would be the most suitable type of mechanochemical treatment for this purpose. It is also necessary to elucidate theoretically the appropriate type of electron shell compression (this has already been mentioned in relation to endofullereners and diamond synthesis) that would enable excitation of high-lying electronic levels of inner electrons (excitation of the outer electrons followed by ionisation would imply escape and inefficient consumption of the mechanical energy).

Another problem is to choose an atomic composition of molecules (or mixtures of molecules) that would permit complete capture of γ- and X-rays by the nuclei. The capture cross-section in photonuclear reactions is known to be relatively large, its spectrum being fairly broad. This provides grounds for believing that the second problem could be solved more easily than the first one (effective mechanochemical generation of hard radiation).

Obviously, this is a strategic goal; on the way to its solution, one can face insurmountable and yet unpredictable obstacles. However, the aim deserves development (at least theoretically, to start with).

VIII. Physics of chemical reactions

Chemistry, like any other highly developed branch of science, has become a high-risk science. This means that the problems of chemistry are complicated and it is not always possible to solve them by existing methods; therefore, the probability of failures and wasted labour, time and resources becomes fairy high. The risks can be reduced only on the basis of deep insight into the physical aspect of chemical reactions, which is the most important and elitist part of chemical physics.

The physics of chemical reactions is based on four types of dynamics:

— molecular dynamics and molecular organisation;

— energy dynamics (energy dynamics in gases, energy migration in clusters, energy transformation in liquids, energy relaxation in solids);

— chemical dynamics (potential energy surfaces, energetics in the chemical dynamics, theory of chemical reactions);

— angular momentum dynamics and spin dynamics.

The physics of chemical reactions is a field of science involving both experimental and theoretical research; its advances are natural and the problems are traditionally clear (they are analysed in Ref. 24). The main point in this field of science is chemical dynamics, the most important aspect of which is the theory of chemical reactions.

Chemical dynamics have grown out of chemical kinetics; the latter include a general knowledge that has penetrated into all the branches of chemistry and has promoted the development of universal chemical criteria for reaction mechanisms.

However, chemical kinetics deal with the number of chemical events (*i.e.* the interval between the events), whereas chemical dynamics are concerned with the course of the events themselves (movement of the reactants over the potential energy surface). This is the central event in the circle of which the whole chemistry moves and which lies at the heart of a chemical reaction. Chemical dynamics are the 'cardiogram' of this 'chemical' heart.

The advances in the theory of chemical reactions constitute an individual and broad subject.[67, 68] Actually, two large problems need to be solved: the construction of potential energy surfaces and the calculation of the movement of the reactant nucleus in the calculated potential fields (the proper dynamics of a chemical event).

Both problems can be solved in various modifications, with several levels of approximation and with different degrees to which the quantum nature of the movement is taken into account. In principle, it is now possible to construct a potential surface for any reaction with any degree of accuracy (taking account of the capabilities of modern computers, one has to be able to reduce a reaction of any desired complexity to a simple one without losing its physical or chemical contents). Reliable methods for the calculation of the dynamic trajectories of the reactant movement over the potential surfaces have now been developed. They include methods of classical trajectories (based on the Hamilton – Newton – Lagrange laws of classical mechanics), semiclassical trajectories (taking account of quantum effects *via* superposition of the initial quantum states of the reactants) and purely quantum trajectories (based on the solution of the Schrödinger equation, which presents the probabilities of reactant transformations *via* all reaction channels as an *S*-matrix or scattering matrix). The resulting set of trajectories is used to calculate the canonical $k(T)$ and microcanonical $k(E)$ rate constants (T and E are temperature and energy). Two examples of such calculations are presented in Figs 14 and 15.

General methods for the solution of the dynamic problem have been developed: the method of the reaction path Hamiltonian, the method of the trajectory curvature, multidimensional quantum dynamics and quantum transition state theory. The main idea of the dynamical methods is to distinguish the movement of the reactants along the reaction coordinate and to take into account the influence of all the other types of movement (both 'assisting' and retarding). The interaction of all the types of movement (both those directed along the coordinate and others) is considered to be 'dynamic friction' and, among other tasks, the modern theory should provide calculation of its value.

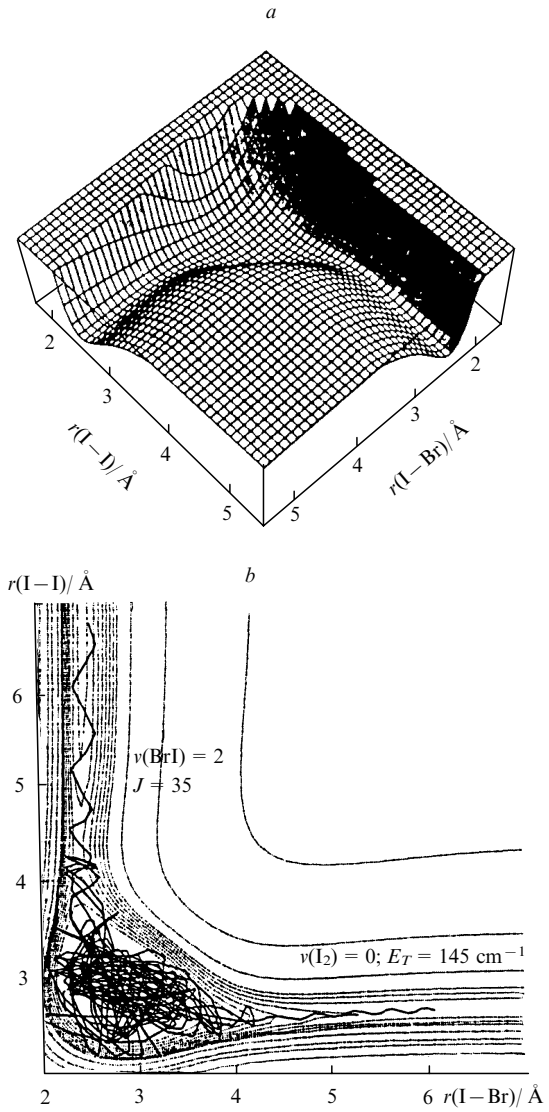


Figure 14. Potential energy surface for the reaction $Br + I_2 \rightarrow BrI + I$ (*a*) and one of the trajectories on this surface (*b*) with a duration of 17.6 ps; *v* are vibrational states, *J* is the rotation moment and E_T is the kinetic energy.

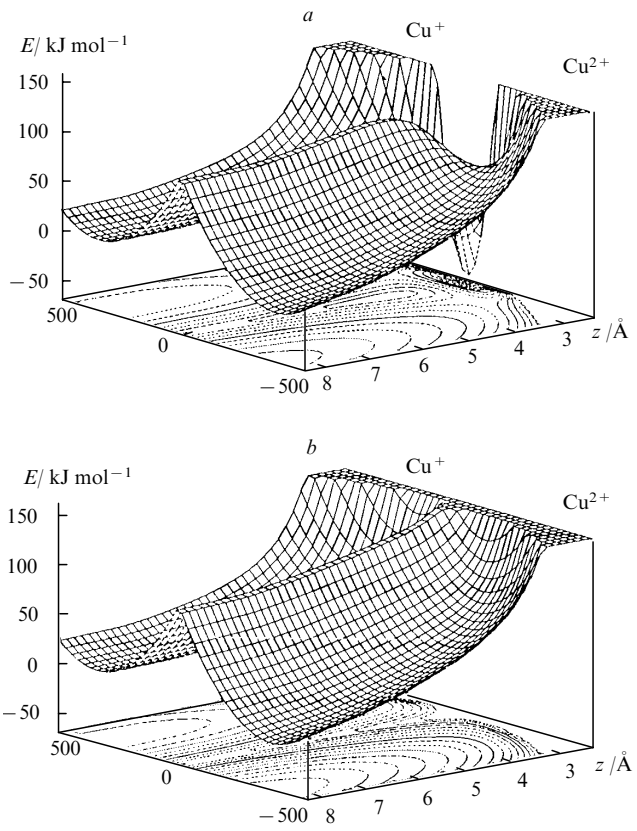


Figure 15. Free energy surfaces for the reaction $Cu^{2+} \rightarrow Cu^{+}$ at an electrode for adiabatic (*a*) and nonadiabatic (*b*) transformation; *z* is the distance of the ion from the electrode, *E* is the energy of solvent reorganisation.

However, the great theoretical power of chemistry has an unpleasant aspect. Owing to the broad and successful application of quantum chemistry and molecular dynamics methods, researchers tend to avoid science-dependent and expensive experiments, this tendency becoming more and more pronounced. This is objective reality and the general trend of development of world's chemistry (perhaps, not only chemistry).

The theory of chemical reactions is closely related to the theory of nuclear reactions (this is true not only for the diffusion regime in which the kinetic equations and their solutions are absolutely identical). A system that undergoes a chemical reaction in a liquid or in a solid is similar to the reacting nucleons surrounded by the medium, *i.e.* other nucleons in a nucleus. In this case, too, chemistry occupies an advantageous position: it is simple in the sense that only one type of interaction operates, namely, the Coulomb interaction with a known energy–distance relationship. This is a fundamental statement, which follows from quantum mechanics (the accuracy of its laws is beyond controversy, like that of the laws of classical mechanics). However, there is also direct experimental evidence supporting this statement. The case in point is the experimental probing of atomic wave functions, which are the basis for the entire chemistry.

This experiment is very simple: an atomic (Ca or Cu) beam is excited by polarised light to the p_z or d_{z^2} state; after that, this beam with spatially oriented p_z or d_{z^2} orbitals is exposed to a crossed beam of He atoms; scattering of the He beam is detected, the scattering pattern being used to reconstruct the scattering potential. The result proved to be very vivid: the scattering profile exactly reproduced the shapes of the atomic orbitals.

One can argue that this result is trivial (in the sense that no other result was to be expected); however, it leads to the understanding of the fact that only the Coulomb potential operates in chemistry (a part of it, the exchange interaction, is spin-dependent). Moreover, if we recall the fact that the atomic wave functions have originated on the tip of a pen from the quantum-mechanics postulates and the Schrödinger equation with a centrosymmetrical Coulomb potential, we can feel the triumph of the human mind.

The magic and fascination of chemistry are due to the fact that the Coulomb potential gives rise to a variety of chemical bonds (ionic, covalent, donor–acceptor, dative, hydrogen and van der Waals bonds), chemical species (atoms, carbenes, ions, molecules, exciplexes, Rydbergs, excimers, van der Waals molecules, complexes, radicals, *etc.*), states (ground, excited, charge, spin, orbital, differing in symmetry, *etc.*), mechanisms of chemical transformations and controlling factors (energy, spin, phase, orbital symmetry). With this diversity and wealth, chemistry is always new. The discovery of new states of hydrogen molecules can serve as an example (Fig. 16). They are matched by adiabatic potential minima located in the vicinity of the points of intersection of the binding term $H^+ + H^-(1s^2)$ and the repulsive terms $H(1s) + H(np)$, where $n = 1, 2, 3,\ldots$. These species are not Rydberg molecules having 'plump' electron shells with principal quantum numbers reaching hundreds but 'normal' molecules with

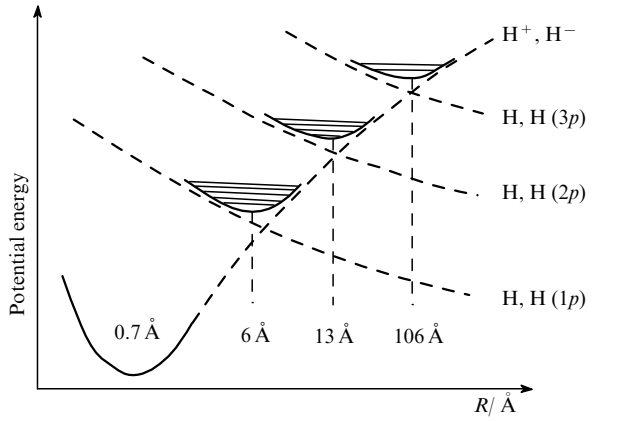


Figure 16. Terms of metastable hydrogen molecules with interatomic distances 6, 13 and 106 Å. They are located in adiabatic valleys at the intersection of the ionic term (H^+, H) with the terms corresponding to the orbitally excited states H (1*p*), H (2*p*) and H (3*p*).

equilibrium interatomic distances of 6, 13, 106 Å, *etc*. characterised by their own vibrational-rotational spectra. Similar molecules can also exist for other atoms. They can be detected in low-temperature or rarefied plasma or in the huge interstellar chemical reactor.

IX. Atomic-resolution spectroscopy and chemistry

This field of modern chemistry is being vigorously developed; it assumes detection of chemical reactions with high time resolution (about $\leqslant$10 fs, which is shorter than the period of vibrations of an atom in a molecule) or with high space resolution ($\sim$1–5 Å, which is about the size of a single atom or a molecule). Both values correspond to atomic resolution.

The adoption of short laser pulses has extended the scope of chemistry and introduced into chemistry new ideas, which have been embodied in *femtochemistry*.[69]

Firstly, the time periods of 10–100 fs are so short in relation to the period of nuclear vibrations that the nuclei remain virtually fixed at their positions during this period. For example, the interatomic distances in a iodine molecule in the ground state oscillate between 2.5 Å (contracted bond) and 5 Å (stretched bond). A femtosecond pulse 'catches' a molecular assembly with a particular interatomic distance and a particular motion phase and throws it almost instantly onto a new potential surface. On this potential, atoms start a new movement, which is now synchronous (coherent). Thus the femtosecond pulse has created a wave packet — an assembly of molecular oscillators with a fixed vibration phase, a given interatomic distance and a definite energy. In other words, femtochemistry opens up the way for production of coherent wave packets.

Secondly, a time resolution of 1–100 fs corresponds to a coordinate resolution of 0.1–0.01 Å. This means that the movement of the nuclei over the potential surface, including that on the top of the barrier and near it, is monitored with this coordinate resolution. It is clear that we are dealing with spectroscopy and chemistry of the transition state, which has always been an object for investigation by theorists but now has become the subject of experimental research. Femtochemistry deals with the time of movement of reaction systems on the potential surface and introduces into chemistry the experimental chemical dynamics.

Thirdly, by monitoring the movement of nuclei over the potential surface, one can interfere in the dynamics of the transition state by its energy or phase pumping and thus change the transformation pathways of the transition state itself. In this sense, one can say that femtochemistry is the chemistry of the transition state.

As an example of the control of chemical reaction channels, let us consider decomposition of a chlorine dioxide molecule OClO. When the pumping energy is $\sim 0.3 \times 10^{12}$ W cm^{-2}, decomposition follows predominantly the O + ClO pathway; when the energy exceeds 0.8×10^{12} W cm^{-2}, the second channel leading to O_2 + Cl, starts to predominate and at an energy of 1.4×10^{12} W cm^{-2}, the rate of decomposition *via* the second channel is 12 times greater than that according to the first channel.[70] Chemical approaches also permit complete switching of the reaction from the first channel to the second one, for example, this can be attained by adding a water molecule to chlorine dioxide or by placing chlorine dioxide in an $(H_2O)_n$ cluster.[71] Although the chemical method leads to the same result as femtochemistry, this result is achieved by an absolutely different mechanism. In fact, when the initial state of the reactants changes, the reaction switches to a new potential surface; thus, the chemical approaches represent a classical example of changing the reactivity upon complex formation or solvation.

Fourthly, femtochemistry has opened a new chapter in the structural analysis of short-lived species including transition states. Instruments which permit ultrafast diffraction of electrons on these species have been designed. The first femtosecond pulse from a photocathode generates an ultrashort electron beam accelerated by an intense electric field ($\sim$30 kW cm^{-1}). After that, the second femtosecond pulse (with a controlled delay) generates a wave packet or a transition state for a chemical system under study. After that, electron beam diffraction on the transition state or on the reaction product is recorded.

In the future, this remarkable equipment would permit probing of the transition state geometry.[72] A resolving power of $\sim$1 ps with respect to the electron beam (which is the factor limiting the capability of the instruments) has already been attained, and this limit can undoubtedly be overcome. This would enable not only time (spectroscopic) but also geometrical monitoring of the transition state (based on the electron diffraction).

Finally, fifthly, femtochemistry provides great possibilities for investigating ultrafast reactions such as proton (electron) transfer in acid–base (donor–acceptor) pairs; tautomerisation; *cis*–*trans*-isomerisation with detection of *twist*-conformations; photogeneration and relaxation of an electron–hole pair in semiconductors; elementary steps of photosynthesis; decomposition of molecules (*e.g*., decomposition of iodine in clusters near the gas–liquid phase transition or under supercritical conditions, *etc*.).

Femtochemistry reveals important new facts concerning heterogeneous processes, in particular, desorption of molecules and desorption mechanism. A femtosecond pulse heats an electron gas to a temperature of several thousand degrees but leaves phonons in metal almost cold (heated to a temperature of only several hundred degrees). The low phonon temperature cannot account for either the high rates of desorption or the high vibrational temperature ($\sim$2000 K) of diatomic molecules. It is clear that the fast desorption of molecules (not more than 10 vibrations on the surface after a femtosecond pulse) is stimulated by the hot electron gas (apparently, *via* generation of an electron–hole pair followed by its fast annihilation at the adsorption site).[73] Independent experiments with generation of a surface electromagnetic wave, which probes the surface and its adsorption coverage, has confirmed that, after a femtosecond pulse has been initiated, a molecule remains on the surface only for 3–5 vibrations.

Apparently, femtochemistry would enable detection of fast electronic events such as electron exchange between the protons in the H_2^+ cation (these events take $\sim$2 fs), π-electron migration in the Kekule structures of benzene, electron revolution round the nucleus, electron transfer to upper orbitals upon excitation, *etc*. However, this would require lasers of the next generation with a resolving power in the attosecond range (1 attosecond = 10^{-18} s).

The progress in the design of photodetectors and scanning optical microscopes has given access to *observation of single*

molecules (such as rhodamine 6G, and terrylenediimine). By exciting and monitoring stationary luminescence of single molecules (molecular 'fireflies'), one can study lateral diffusion of molecules on solid surfaces and bulk diffusion in solids (such as polymers). When polarised light is used for excitation and polarised luminescence is recorded, it becomes possible to measure reorientation of molecules and monitor their trajectories. The first wonderful phenomena have already been discovered. Thus an unusual type of behaviour of rhodamine 6G molecules deposited on glass was found; some of the molecules remain still, some other move without rotating and some other rotate without moving.[74] The behaviour of terrylenediimine on an SiO_2 surface proved to be even more surprising: luminescence of some molecules was found twice modulated by a low frequency (10 and 100 Hz), the luminescence bands of 'modulated' molecules being shifted to higher frequency.[75] Even these two examples demonstrate that probing of a surface by molecular 'fireflies' promises a lot of new discoveries.

The capability of optical detection using single molecules is not limited to investigations of molecular dynamics. A 'flickering' (non-statistical) behaviour of single molecules associated with spectral diffusion has been found; it is also possible to measure directly the rate of energy transfer to neighbouring molecules and to elucidate the dependence of the energy on the distance (by changing the number of 'fireflies' per unit surface; normally several molecules are located on one square micron).[76]

It is obvious that the potentialities of detection using single molecules are substantially increased by using pulse excitation. This brings about new opportunities in the investigation of ergodicity and new methods for direct measurement of quantum yields in the photodecay of single molecules, *etc*.

The discovery of *tunnelling vibrational spectroscopy* of single molecules is a new great breakthrough in chemistry.[77] The tunnelling current, which flows between the tip of a tunnelling scanning microscope and a solid surface on which an adsorbed molecule 'sits' under the tip, has a clear-cut resonance character. The resonance always occurs in the case where the tip potential (and, hence, the energy of tunnelling electrons) corresponds to the vibronic levels of an adsorbed molecule. Examples of vibrational spectra for several single molecules are shown in Fig. 17.

Vibrational spectroscopy of a single molecule exactly reproduces its portrait and permits one to follow its dynamics (rest time) and chemical fate.[78] This opens up new prospects for the science of catalysis. The ways for detecting electron paramagnetic resonance of a single spin are clear and have already been theoretically substantiated.[79] A great number of new ideas are originating in *atomic-resolution chemistry*.

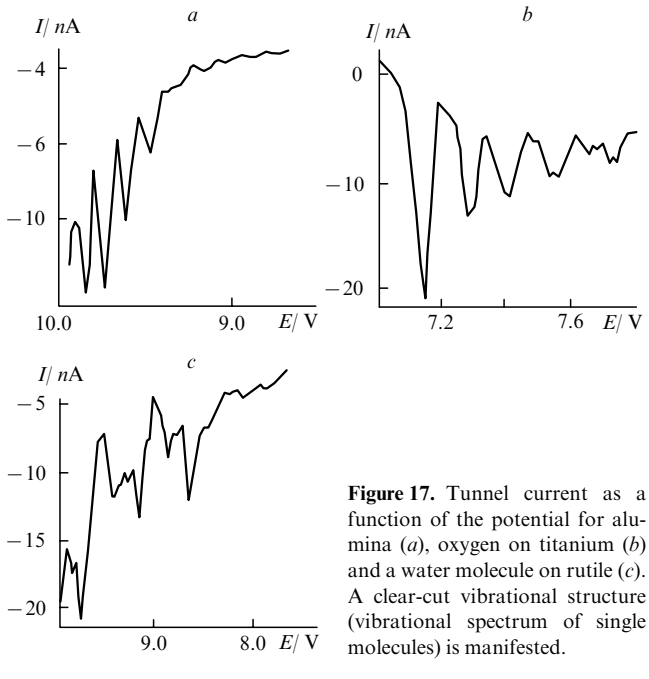


Figure 17. Tunnel current as a function of the potential for alumina (*a*), oxygen on titanium (*b*) and a water molecule on rutile (*c*). A clear-cut vibrational structure (vibrational spectrum of single molecules) is manifested.

X. Conclusion

Chemistry as a fundamental science has no limits; it is impossible to represent even its outline within one paper. The face of chemistry is being permanently renewed; new beautiful features appear, which include coherence, atomic resolution (in time and in space), magnetic script of chemical reactions, chemical radiophysics, new ideas in molecular architecture and new molecular assemblies. A special part in the modern chemistry is assigned to the coherent chemistry, which introduces a third controlling factor, the phase (in addition to the energy and spin). In this review, we have discussed the quantum vibrational coherence, the quantum spin coherence and the macroscopic coherence with characteristic times of 10^{-15}–10^{-13}, 10^{-9}–10^{-7} and 10^{-1}–10^{-3} s, respectively. A new level of this field of science would be associated with the generation of electron coherence, *i.e*. creation of electronically coherent wave packets with characteristic times of 10^{-18}–10^{-15} s.

The intrinsic order and the structure of chemistry and also everything created by chemistry display the charm of strict logic, substantiation and perfection. This is yet another feature of chemistry, which makes it a fundamental science. The scope of chemical research is constantly expanding; it is possible (and useful) to make predictions only regarding the tendencies of development. We cannot foresee the particular events in science; this is clearly demonstrated by the achievements of the last three decades (fullerenes, telomerase, superconducting ceramics, *etc*.). However, we can make use of our scientific intuition, foresight and professional sense of understanding of the general movement of science and thought.

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