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Femtochemistry

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Abstract. The review is devoted to a new field of chemistry — femtochemistry. New, in principle, possibilities of investigation and control of chemical reactions by means of ultrashort coherent light pulses are considered. The general concepts are illustrated by numerous examples of femtochemical studies of the dynamics and kinetics of elementary chemical reactions in the gas and condensed phases. The prospects of femtochemistry are discussed.
The bibliography includes 172 references.

I. Introduction

How does an elementary chemical reaction occur? What are intermediate configurations of a reacting system? How can the route and the rate of a chemical reaction be controlled? Chemists have asked themselves these questions throughout the history of the development of chemistry. However, the profundity of both the questions and the answers depends on the level of understanding of elementary processes and on the experimental capabilities.

Until quite recently, in all experiments dealing with elementary reactions the time evolution of either reactants or reaction products has been recorded. However, on the path from reactants to products, the molecular system passes through various structures (states) which can no longer be considered as reactants but cannot yet be regarded as products. From the experimenter's viewpoint, the range of interatomic distances corresponding to these structures is a 'black box' because the experiment does not provide any information about these structures or their change. Chemists call this range of interatomic distances the transition state,[1] and the time evolution of atom configurations in this 'black box' is called transition state dynamics. The passage of a reacting molecular system through the transition state represents an elementary step of a chemical reaction. The reaction path is usually characterised by the dependence of the potential energy on interatomic distances.

Theorists try to reconstruct the transition state dynamics from the results of investigations of the kinetics of reactants and products. However, it turned out that this often cannot be done unambiguously; experimental data are needed. The problem lies in the fact that the residence time of a molecular system in the 'black box' is very short, ~ 100 fs (1 fs = 10^{-15} s). Therefore, special laser equipment is required to detect the events taking place over this 100-fs period.

The appearance of a new tool — light pulses with durations of 10 – 100 fs — provided the possibility of detecting tiny changes, about 0.1 Å, in the distances between atoms in a molecular system; this triggered a new line of research in chemical physics, namely, femtochemistry. This field of investigations makes it possible to answer the questions posed above at a new, in principle, level; to verify some fundamental assumptions which we use; to distinguish the regions where they are no longer valid; and to discover new ways of controlling a chemical transformation. In 1999, an American scientist A Zewail was awarded the Nobel Prize for studies in the field of femtochemistry. Although femtochemistry is 'young' (its age can be estimated as 12 years), several reviews have been published (see, for example, publications [2–6]). In this review, we attempt to examine, from different standpoints, the rapidly developing approaches and concepts as well as new problems arising in this field.

II. Characteristic features of femtosecond pulses

Before discussing the problems of femtochemistry, let us consider characteristic features of ultrashort light pulses and new experimental capacities brought about by these features.

In a system of coordinates the z axis of which coincides with the direction of propagation of a laser pulse, the components of the electric field strength $E(t) = [E_x(t),E_y(t),E_z(t)]$ of a femtosecond light pulse for a specified point in space can be written in the form

$$E_x(t) = E_{x0}\mathrm{f}(t)\cos[\omega_0 t + \delta_x + \alpha(t)],$$
$$E_y(t) = E_{y0}\mathrm{f}(t)\cos[\omega_0 t + \delta_y + \alpha(t)], \quad (1)$$
$$E_z(t) = 0.$$

In these equations, E_{x0} and E_{y0} are the maximum values of the x and y components of the field strength, respectively, f(t) is the

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time dependence of the envelope of the pulse, t is the current time, ω_0 is the carrier light frequency related to the carrier wavelength λ_0 in the following way:

$$\lambda_0 = \frac{2\pi c}{\omega_0},$$

δ_x and δ_y are the phase constants and $\alpha(t)$ is the function describing the frequency modulation over the pulse duration. The polarisation of light in the pulse is characterised by the ratio E_{x0}/E_{y0} and by the δ_x and δ_y values. The pulse envelope $f(t) \propto \sqrt{I(t)}$, where $I(t)$ is the time dependence of light intensity in the pulse, can have different forms. However, irrespective of this, it is determined by pulse duration (τ).

Most often, Gaussian pulses with the envelope

$$f(t) = \exp\left(-\frac{t^2 2\ln 2}{\tau^2}\right), \tag{2}$$

and the frequency modulation

$$\alpha(t) = \frac{1}{2}\gamma t^2, \tag{3}$$

where γ is the temporal chirp (the parameter determining the rate of phase modulation) are considered. When $t = \pm\tau/2$, the light intensity in the pulse is equal to half its maximum.

Thus, parameters characterising a femtosecond pulse include pulse duration τ, field amplitude, carrier frequency and the function $\alpha(t)$ (expressed in most cases in terms of the temporal chirp γ).

It is known that a field can also be specified by spectral characteristics

$$\mathscr{E}_j(\omega) = \int_{-\infty}^{+\infty} E_j(t)\exp(i\omega t)\mathrm{d}t, \tag{4}$$

where $j = x, y$. Usually, the functions $f(t)$ and $\exp[i\alpha(t)]$ vary much more slowly than $\exp(i\omega_0 t)$; therefore, it can be written that

$$\mathscr{E}_j(\omega) = \frac{1}{2}\exp(-i\delta_j)F_j(\omega-\omega_0), \tag{5}$$

where

$$F_j(\omega-\omega_0) = E_{j0}\int_{-\infty}^{+\infty} f(t)\exp\{i[(\omega-\omega_0)t-\alpha(t)]\}\mathrm{d}t. \tag{6}$$

The function $F_j(\omega-\omega_0)$ is complex-valued and can be represented in the form

$$F_j(\omega-\omega_0) = |F_j(\omega-\omega_0)|\exp[i\varphi(\omega-\omega_0)], \tag{7}$$

where

$$|F_j(\omega-\omega_0)| \propto \sqrt{S(\omega)},$$

$S(\omega)$ is the the pulse power spectrum measured experimentally. The spectral phase $\varphi(\omega-\omega_0)$ is related to the functions $f(t)$ and $\alpha(t)$ in a complex manner. For Gaussian pulses, these functions are determined by relations (2) and (3), respectively. Therefore,

$$\varphi(\omega-\omega_0) = \frac{1}{2}\beta(\omega-\omega_0)^2,$$
$$\beta = \frac{4\gamma\tau^4}{16(\ln 2)^2 + \gamma^2\tau^4}. \tag{8}$$

The β parameter is called spectral chirp.

An important spectral characteristic of a femtosecond pulse is the width of its spectrum at the half-height of the amplitude ($\Delta\omega$). The spectral width is determined by the uncertainty relation

$$\tau\Delta\omega = \text{const}. \tag{9}$$

The value of const depends on the shape of the pulse and the chirp envelope. For a Gaussian pulse with $\gamma = 0$ (this pulse is usually referred to as transform-limited), const = 2.773. In the case of chirped pulses (*i.e.*, those with $\gamma \neq 0$), the constant can acquire arbitrarily large values depending on the chirp value.

Now we shall list the main experimental capacities resulting from the properties of femtosecond pulses.

First, due to the short pulse duration, evolution of processes can be studied with a temporal resolution even higher than the duration of the pulse itself. When the velocity of an atom is 10^5 cm s^{-1} and $\tau = 10^{-14}$ s, changes in the internuclear distances of about 0.1 Å can be detected. This means that not only the formation of products but also the time evolution of the nuclear configuration can be monitored with high accuracy in real time within the time scale of vibrational motion.

Second, since the spectral width of femtosecond pulses is rather large, several quantum states with different energies can be excited simultaneously. For example, a transform-limited pulse with $\tau = 10^{-14}$ s has the spectral width $\Delta\omega = 1100$ cm^{-1}. This light pulse can excite simultaneously several vibrational quantum states.

Third, a coherent light pulse can be obtained. In combination with the aforesaid, this means that coherent excitation of several vibrational or rotational states is possible. This new type of an excited state is called a non-stationary quantum state or a coherent nuclear wave packet.†

A specific feature of these states is that several eigen energy states with definite relative phases of atomic motion in a molecule can be subjected simultaneously to coherent excitation. The scheme of non-stationary and stationary quantum states of a molecule is shown in Fig. 1.

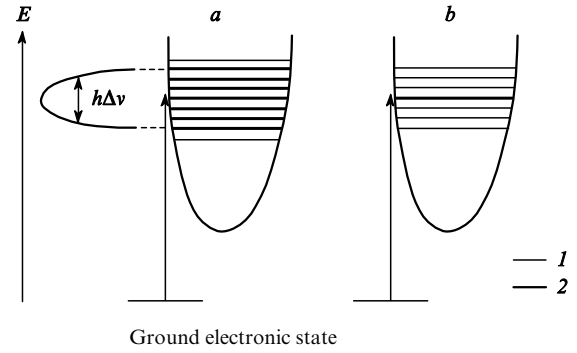


Figure 1. Non-stationary (*a*) and stationary (*b*) vibrational quantum states of a molecule. The horizontal lines mark unoccupied (*1*) and occupied (*2*) stationary vibrational states.

Fourth, due to high intensity (peak power) of femtosecond pulses with the pulse energy being relatively low, multiphoton absorption processes giving rise to highly excited molecular systems can be easily accomplished and numerous methods of non-linear spectroscopy can be used without heating the sample. Under the action of such pulses on a gas or a solid, light pulses with a broad spectral range (supercontinuum) and X-ray and electron pulses are generated. It should also be noted that light field intensities (10^{10} V cm^{-1}) exceeding even the intensities of intramolecular fields can be attained rather easily.

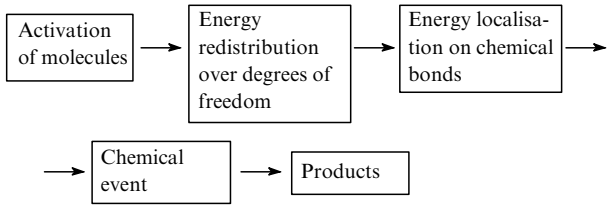
Thus, the use of femtosecond light pulses makes it possible to attain high temporal resolution, to create coherent non-stationary quantum states, to produce highly excited molecules, to act upon the potential energy surface (PES) and to generate ultrashort light, electron and X-ray pulses.

† The notion of wave packet was introduced in 1926 by E Schrödinger; however, it has virtually not been used in chemistry.

III. The main objectives of femtochemistry

How does the study of reactions within the femtosecond time scale pertain to practical chemistry? Indeed, the duration of an elementary reaction in practical chemistry is much longer than 100 fs. This is due to the fact that an elementary reaction includes both a fast chemical event and the preceding slower intra- and intermolecular energy exchange processes.

For an unimolecular chemical event to occur, the following processes should take place:



Activated molecules should possess a sufficiently high energy, which can be acquired either upon collisions, or due to a chemical reaction, or upon absorption of photons. Usually, this energy is redistributed very rapidly (in about 0.1 – 1 ps) over different vibrational degrees of freedom of the molecule. Then a fluctuation should occur, after which a certain energy is concentrated in the required site of the molecule, for example, in the form of vibrations of atoms of the bond to be cleaved. Only after this, does the chemical event take place. The time scale of the chemical event itself is 10 – 100 fs.

The specific features of new instrumentation noted above determine the following lines of research in femtochemistry: study of the dynamics of intramolecular processes and the transition state in a chemical transformation; study of the kinetics of ultrafast chemical reactions; control of the intramolecular dynamics and of the path of an elementary chemical reaction.

Now we shall briefly explain what is the purpose of each of these lines of investigation.

The goal of the first line is to obtain more detailed and substantiated views on the nuclear dynamics in a molecular system (either reacting or not). This refers both to the dynamics of intramolecular processes (coherent motion of nuclei, energy redistribution or localisation, *etc*.) and time evolution of the configurations of the molecular system on passing from reactants to products. In this connection, the possibility of creating a coherent wave packet (rotational, vibrational or electronic) in the molecular system is of fundamental importance. The most significant for chemistry is the vibrational wave packet in which several vibrational states undergo simultaneously coherent excitation. In this case, it can be said that intramolecular dynamics of nuclei is the time evolution of the vibration-rotational wave packets. A significant feature of this description is that phase characteristics of the nuclear motion are taken into account. However, it is known that after some time, dephasing takes place; as a consequence, the nuclear dynamics becomes incoherent and the regular nuclear motion switches to stochastic motion.

The purpose of the second line is to gain information on the kinetics of ultrafast reactions. Within the framework of this line of research, investigators are interested in the time evolution of the reactant or product concentration rather than in the phase characteristics of the nuclear motion. The features of femtosecond pulses most significant for this line of research include short duration, which allows implementation of techniques with high temporal resolution (using these techniques, one can study ultrafast reactions), and high intensity (this allows excitation of molecules with visible light to high energies).

The third line of research in femtochemistry is the most 'ambitious'. In this case, all the above-mentioned features of femtosecond pulses are significant. The possibility of creating femtosecond pulses opens new, in principle, opportunities for controlling intramolecular processes and the path of elementary chemical reactions. The idea of this control is based on the fact that, by using femtosecond pulses, one can switch the reacting system to a transition state with a definite initial wave function and then control the time evolution of this state. Due to the coherence of the light pulse, the initial state of the system can be created as a well-defined coherent wave packet. By changing the carrier frequency and the amplitude and phase characteristics of a femtosecond light pulse, it is possible to create in the initial (zero) instant of time different nuclear wave packets, the dynamics of which can be substantially different. The high temporal resolution allows researchers to 'monitor' the evolution of the transition state in order to act upon the system PES by one more femtosecond light pulse at the required point in time.

IV. Experimental methods of femtochemistry

Typical experimental methods of femtochemistry are based on the use of two femtosecond pulses according to the 'pump – probe' pattern (Fig. 2). The first pulse (λ_1) creates a wave packet in the electronically excited state. After some period of time, a second pulse (λ_2) probes the changes that have taken place. After the probe pulse, the molecular system passes into a different electronic state [either upper (Fig. 2 *a*) or lower (Fig. 2 *b*) in energy] and, owing to this transition, the response of the system to the action of the pump and probe pulses as a function of the time delay between them is recorded. The 'pump – probe' pattern makes it possible to detect both the dynamics of the motion of atoms (wavelength λ_2) and the kinetics of product formation (wavelength λ_2').

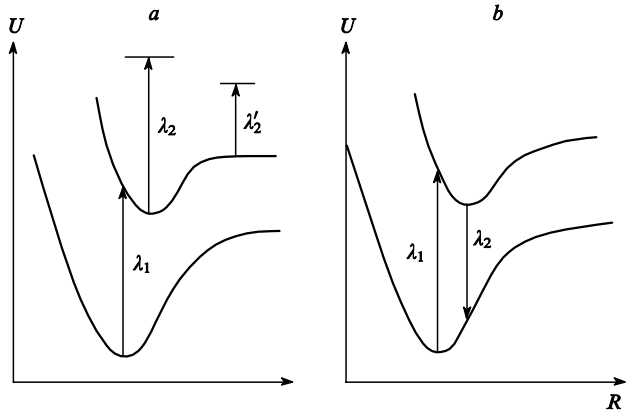


Figure 2. Simplest patterns of the 'pump – probe' technique. U is potential energy, R is the distance between the nuclei, λ_1 is the wavelength at the centre of the pump pulse spectrum, λ_2 is the wavelength at the centre of the spectrum of the pulse probing the transition state dynamics; λ_2' is the wavelength at the centre of the spectrum of the pulse probing the reaction products.

A typical scheme of the setup is shown in Fig. 3. A laser (as a rule, a dye or titanium-sapphire laser) usually pumped by a continuous-wave argon or solid-state laser generates consecutive femtosecond light pulses. The energy of these pulses is increased in a laser amplifier. The amplified pulse passes through a compensator of the envelope velocity dispersion (not shown in the Figure) and is then split into two components. One component is used as the pump pulse and the other, as the probe pulse. Both pulses pass through facilities which allow one to change the pulse parameters (carrier frequency, chirp, duration). The variable time delay between the pump and probe pulses is ensured by an optical delay line in which the optical path length of one of the pulses can vary. The pump and probe pulses are focussed on the specimen. The response to the two pulses as a function of the delay between them is recorded using a detector. The characteristics recorded as the response can include photoinduced absorption,[7–9] fluorescence,[10–12] stimulated radaiation,[13] miltiphoton ionisation[14]

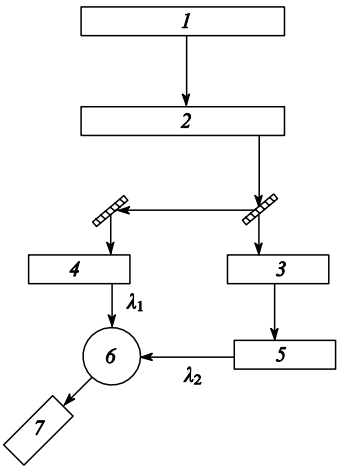


Figure 3. Experimental setup used for the 'pump – probe' experiments. (*1*) generator of femtosecond pulses; (*2*) optical amplifier of the pulse energy; (*3*, *4*) devices for changing the parameters of femtosecond light pulses, (*5*) optical line of the time delay between the pump and probe pulses; (*6*) reaction zone, (*7*) device for recording the response of the molecular system to the action of two pulses.

(often recorded using time-of-flight mass spectrometry techniques [15, 16]), rotation of the polarisation plane, [17] *etc*.

It is worth noting that the high intensity of femtosecond pulses permits utilisation of any non-linear spectroscopy technique developed to date in which several pulses are used.[18, 19] A special group of methods includes those in which the second pulse is focussed onto a target in order to generate ultrashort supercontinuum,[20, 21] electron [22–25] or X-ray [26, 27] pulses, which then serve as the probe pulses.

Supercontinuum pulses are used most effectively to study solutions. Primary processes in solutions result in broad absorption spectra of reactants, intermediate states and products. These spectra overlap, which markedly hampers interpretation of experimental data obtained at a particular wavelength. Regarding the time evolution of the intermediate states, more information is provided by an approach according to which time evolution of a broad spectrum of photoinduced absorption is recorded. This requires an ultrashort pulse which emits light over a broad spectral range. A supercontinuum the spectrum of which covers the whole visible region can serve as the source of such a pulse in femtochemistry. The methods that make use of this approach are documented.[20, 21]

Ultrashort pulses of electrons and X-rays are also used as probe pulses. In this case, diffraction of electrons or X-rays after reflection from the specimen under study is detected. By recording the diffraction pattern of electrons or X-rays at various points in time after the action of the pump light pulse, one can gain information on the structure of intermediates and the dynamics of structural changes. The methods based on electron diffraction are applicable only to gas media, while those based on X-ray diffraction are suitable also for condensed media. For example, electron diffraction has been used to determine the structure of an intermediate species.[22] The diffraction of X-rays has been used as yet only to detect the dynamics of structural changes in the absence of a chemical reaction. Thus time evolution of the arrangement of cadmium atoms in films of organic compounds heated by femtosecond light pulses has been studied.[26] There are publications in which absorption of the probe X-ray pulse is used to investigate photochemical reactions. For example, a study by Raksi *et al*.[27] deals with photodissociation of SF_6 molecules.

V. Dynamics of intramolecular processes and of transition states in a chemical transformation

It has been noted above that, due to the great spectral width, a coherent femtosecond light pulse excites a non-stationary quantum state, *viz*., a coherent wave packet (rotational, vibrational or electronic). The dynamics of nuclear motion shows itself in the time evolution of this packet. High temporal resolution permits real-time detection of the dynamics of wave packets.

A great number of theoretical studies devoted to the dynamics of coherent nuclear wave packets both in di- and polyatomic systems have been published.[28–36] Let us consider some properties of vibrational wave packets in relation to diatomic molecules in the absence of a chemical transformation.

Usually wave packets of this type are formed in some electronically excited state $|1\rangle$, to which dipole radiation transitions from the ground electronic state $|0\rangle$ are allowed. For simplicity, we assume that the pump pulse has a Gaussian shape, carrier frequency ω_0, duration τ and temporal chirp γ. Let us also assume that the crucial contribution to the wave packet is made by the ground vibrational state (the state with the vibrational quantum number $\upsilon = 0$) of the ground electronic state. Then at the instant of termination of the action of the light pulse ($\tau_f \approx \tau$), the vibrational wave packet $\Psi_1(R, \tau_f)$ (R is the distance between the nuclei) in the electronically excited state $|1\rangle$ has the form

$$\Psi_1(R, \tau_f) = \sum_{\upsilon} \varphi_{1\upsilon}(R) C_{\upsilon}(\tau_f, \tau, \gamma). \tag{10}$$

Here $\varphi_{1u}(R)$ are the vibrational wave functions of the molecule in the electronic state $|1\rangle$ corresponding to the vibrational quantum number υ and the vibration energy $\varepsilon_{1\upsilon}$ measured in relation to the minimum of the electronic potential curve of the state $|1\rangle$, while the complex coefficients are

$$C_{\upsilon}(\tau_f, \tau, \gamma) \approx S_{00,1\upsilon} \exp\left\{-i\frac{\varepsilon_{1\upsilon}\tau_f}{\hbar} - i\frac{\beta(\tau,\gamma)[\varepsilon_{1\upsilon} - (\omega_0 - T_{e1})]^2}{2\hbar^2}\right\} \times \times \exp\left[-\frac{\varepsilon_{1\upsilon} - (\omega_0 - T_{e1})^2}{2\Gamma^2(\tau,\gamma)}\right], \tag{11}$$

where $S_{00,1u}$ are the overlap integrals of the wave function of the ground vibrational state of the $|0\rangle$ electronic term and the wave functions $\varphi_{1\upsilon}(R)$, T_{e1} is the distance between the bottom of the ground state and the first excited state, the spectral chirp $\beta(\tau, \gamma)$ is defined by the formula (8), and

$$\Gamma^2(\tau,\gamma) = \gamma^2 \frac{\tau^2}{4\ln 2} + \frac{4\ln 2}{\tau^2}. \tag{12}$$

The evolution of the wave packet $\Psi_1(R, \tau_f)$ that has formed by the instant τ_f at $t > \tau_f$ obeys the temporal Schrödinger equation for a free molecule and, hence, the corresponding non-stationary wave function has the form

$$\Psi_1(R, t) = \sum_{\upsilon} \varphi_{1\upsilon}(R) C_{\upsilon}(\tau_f, \tau, \gamma) \exp\left[-i\frac{(t - \tau_f)\varepsilon_{1\upsilon}}{\hbar}\right]. \tag{13}$$

The probability of obtaining in measurements the value ε_υ for the vibrational energy of the molecule the state of which is described by the non-stationary wave function $\Psi_1(R, t)$ is equal to $|C_\upsilon(\tau_f, \tau, \gamma)|^2$ and does not depend on time t. A significant feature of the wave packet is the fact that the probability density for finding a molecule with the distance R between the nuclei

$$|\Psi_1(R,t)|^2 = \sum_{\upsilon} |C_\upsilon|^2 \varphi_{1\upsilon}^2(R) + \sum_{\upsilon > \upsilon'} 2|C_\upsilon| \times \tag{14}$$

$$\times \left\{\cos\left[\frac{(t - \tau_f)(\varepsilon_{1\upsilon} - \varepsilon_{1\upsilon'})}{\hbar} + \mathrm{Arg}(C_{\upsilon'}) - \mathrm{Arg}(C_\upsilon)\right]\right\} \times$$

$$\times \varphi_{1\upsilon}(R)\varphi_{1\upsilon'}(R)$$

(unlike the stationary states) depends on time t. This can be interpreted as movement of the wave packet along the PES.

The dynamics of wave packets in model anharmonic oscillators has been studied theoretically in detail.[28–36] It was found that it consists of two stages. The first stage is spreading of the packet with splitting into several sub-packets. Subsequently these sub-packets can be completely restored, owing to interference, to give the initial wave packet within time T/x, where T is the period of classical vibrations and x is the anharmonicity parameter. Similar results are obtained in numerical calculations for real systems, for example, for the I_2 molecule. Figure 4 shows the $|\Psi(R,t)^2|$ functions for the I_2 molecule in the electronically excited state $B0_u^+$ for three delay times calculated in relation to experimental data obtained by Sarkisov *et al.*[12] It can be seen that in the initial time instant, the vibrational wave packet is localised in space; then motion of the centre of gravity and spreading of the packet take place. The spreading is due to the fact that the phases of the Fourier components of the packet become less correlated with one another.

A vivid description of wave packet dynamics can be obtained by using representation of the quantum state of the system in terms of the Wigner distribution function in the phase space (see, for example, Ref. 37). The Wigner function for an anharmonic molecular oscillator is written as

$$W(R,P,t)=\frac{1}{\pi\hbar}\int_{-\infty}^{+\infty}\exp\left(i\frac{Px}{\hbar}\right)\rho_1^{(\mathrm{vib})}(R+x,R-x,t)\mathrm{d}x, \quad (15)$$

where P is the momentum conjugate to the coordinate R, $\rho_1^{(\mathrm{vib})}(R+x,R-x,t)$ is the density matrix for the molecular oscillator in a coordinate representation (the definition for the notion of a density matrix can be found, for example, in Ref. 31); in particular, if the state of the molecular oscillator is described by the wave function $\Psi_1(R,t)$, then

$$\rho_1^{(\mathrm{vib})}(R+x,R-x,t)=\Psi_1(R+x,t)\Psi_1^*(R-x,t). \quad (16)$$

The Wigner distribution function is an analogue of the classical distribution function in the phase space. However, this analogy should not be understood literally because, due to quantum fluctuations, $W(R,P,t)$ is not a positively defined function. To get rid of the 'non-classical' behaviour of the Wigner distribution function for quasi-classical quantum states (for example, vibrational wave packets of diatomic molecules in typical femtosecond experiments), it is averaged over regions of the phase space (about $2\pi\hbar$). The function used most often is the following 'coarse-grained' distribution function (it is called sometimes the Husimi function):

$$W_{\mathrm{H}}(\bar{R},\bar{P},\sigma,t)=\frac{1}{\pi}\int_{-\infty}^{+\infty}\mathrm{d}R\int_{-\infty}^{+\infty}W(R,P,t)\times \quad (17)$$

$$\times\exp\left[-\frac{(\bar{R}-R)^2}{\sigma^2}-\frac{(\bar{P}-P)^2\sigma^2}{\hbar^2}\right]\mathrm{d}P,$$

where σ is a parameter expressed in units of length. The variables $\bar{R}$ and $\bar{P}$ can be regarded as the classical coordinate and the momentum of the molecular oscillator, respectively.

Lozovoy *et al.*[37] calculated, in relation to experiments described in other publications,[12,38] the Husimi distribution functions for the vibrational wave packets formed by the pump pulse in the $B0_u^+$ electronic state of the I_2 molecule. The results of calculations for two delay times show that at $\Delta t = 149$ fs, the packet is still localised, while at $\Delta t = 4944$ fs, it has split into four sub-packets. At longer times, interference takes place, resulting in the restoration of the initial wave packet. The physical pattern of the dynamics of the vibrational wave packet in a diatomic molecule in the absence of bond rupture can be described as follows. The packet is first spread, which is due to the 'disturbance' of the relative phases of various Fourier components of the wave packet. Then it is divided into sub-packets, the Fourier components of which have similar phases. These packets interfere either constructively or destructively; this may result in more localised wave packets. Thus, for diatomic molecules, the intramolecular dynamics can be represented as splitting and restoration of wave packets.

The dynamics of vibrational wave packets in the absence of chemical transformations of the diatomic iodine molecule in the electronically excited state $B0_u^+$ is manifested as time oscillation of the response in the 'pump–probe' experiment. This response is a dependence of the signal intensity (I) on the delay between the pump and probe pulses (Δt). Figure 5 shows the experimental data and the results of calculations of the response function in accordance with the theory developed by Sarkisov and co-workers.[39] This theory allows one to derive the response function of the 'pump–probe' experiment for diatomic molecules at various parameters of the pump and probe light pulses. The

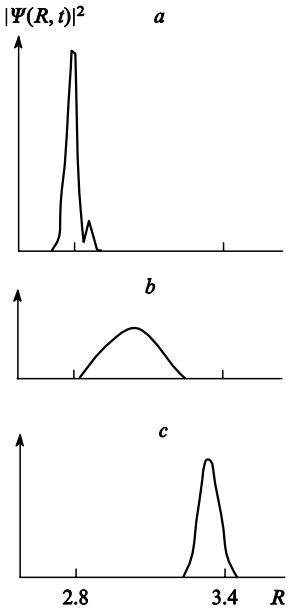


Figure 4. Dynamics of the vibrational wave packets in the bound electronic state $B0_u^+$ of the iodine molecule: distribution of the probability density $|\Psi(R,\mathrm{t})|^2$ of the occurrence of nuclei at distances R for time delays $\Delta t = 0$ (*a*), 30 (*b*), 60 fs (*c*).

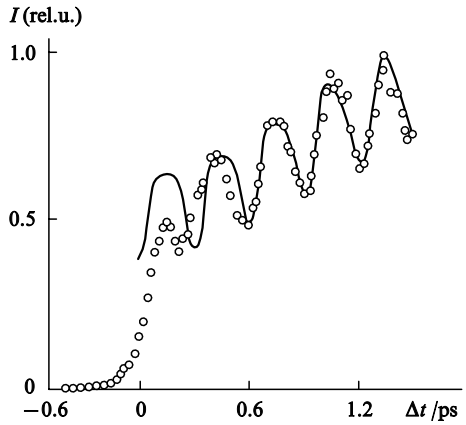


Figure 5. Superimposed oscillation signals in 'pump–probe' experiments for an iodine molecule in an electronically excited state.[12]
The dots show experimental data and the curve corresponds to calculations.

calculated response function for the detection of fluorescence is in good agreement with the experimental data without adjustable parameters. The deviation of the theoretical curve from the experimental points at short Δt values is due to overlap of these pulses (the theory used [39] does not imply this overlap.)

In terms of the classical theory, the vibrations of atoms in a diatomic molecule are represented as vibrations of two masses connected by a spring. Within the framework of the theory of stationary quantum states, the vibrations of nuclei are not considered at all. Only introduction of the notion of wave packets does provide a view on the vibrations from the quantum standpoint.

What are the dynamics of wave packets for polyatomic molecules? To answer this question, the dynamics of nuclear wave packets in a triatomic molecule (NO_2) has been studied.[40] In experimental studies, the author utilised the resonance variant of the stimulated scattering. The pump pulse had a circular polarisation; this made it possible to eliminate the influence of molecular rotation on the detected response. First, a coherent vibrational wave packet in an adiabatic electronically excited state was formed. The lifetime of this packet is determined by the interaction of the electronically excited and ground states. As a result of this interaction, the intramolecular non-adiabatic electron-vibrational dynamics switches from a regular to a stochastic mode. The experiments showed (and calculations confirmed) that this transition takes place over a period of 500 fs.

In the NO_2 molecule, the terms of the electronically excited and ground states undergo strong interaction; this provides grounds for regarding it as a model of a complex molecule. Therefore, it can be assumed that for polyatomic molecules, transition from a regular dynamic mode to the stochastic mode will take place in approximately the same time period (500 fs – 2 ps). Indeed, the wave packet dynamics manifested in the oscillations of the recorded signals has been observed for many complex molecules (see, for example, a number of studies [41–44]); in all cases, the time of oscillations did not exceed several picoseconds. As an example, we shall consider the results of a study [42] devoted to intramolecular vibrational dynamics of the azulene molecule during the internal conversion from the electronic state S_1 to the ground electronic state. In the experiments, both probe and pump pulses were shorter than 20 fs. Damped oscillations of the signal upon excitation of the molecule to the S_1 state with an excess of vibrational energy of >1300 cm^{-1} were observed. The damping time was 0.7 ps. Analysis showed that the main contribution to oscillations is made by only two (the corresponding frequencies are 160 and 200 cm^{-1}) of the 48 vibration modes. Thus, for large molecules, femtosecond pump pulses can generate vibrational wave packets consisting of a limited number of vibration modes. This example shows that the coherence of the atomic motion in a molecular system can also be retained on a picosecond scale.

Experimental methods have now been developed which provide the generation of rotational wave packets and recording of their dynamics not only in the excited but also in the ground electronic state.[17,45] The dynamics of the rotational wave packets observed experimentally for the NO_2 molecule in the ground electronic state is illustrated by Fig. 6. It can be seen that the signal reflecting the evolution of the rotational wave packet has the form of beats. Experiments were carried out using the method of non-resonance stimulated Raman light scattering. The pump and probe pulses are linearly polarised at an angle of 45° with respect to each other. The variation of the rotation angle of the plane of polarisation of the probe pulse as a function of Δt was detected. The rotational constants determined from this dependence coincide with the rotational constants determined by conventional microwave spectroscopy techniques.

Currently, approaches are being formed aimed at the formation and detection of vibrational wave packets in the ground electronic state. For example, as applied to diatomic molecules, methods for four-wave mixing of three pulses with a femtosecond

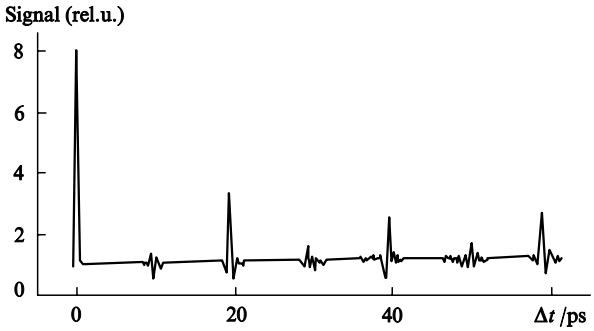


Figure 6. Experimentally observed dynamics of rotational wave packets for the NO_2 molecule in its ground electronic state.[17]

temporal resolution are being developed.[46–48] Methods for generation of vibrational wave packets in polyatomic molecules in the ground electronic state with excitation energies of either higher or lower than the dissociation threshold of these molecules have been proposed.[49,50]

Now we shall consider the intramolecular dynamics in the presence of a chemical transformation beginning also with a diatomic molecule. The most interesting example is pre-dissociation of the NaI molecule (Fig. 7). This system is characterised by avoided crossing of the covalent and ionic potential curves (Fig. 7 *a*). Both the dynamics of the transition state $[Na\cdots I]^{\#}$ and

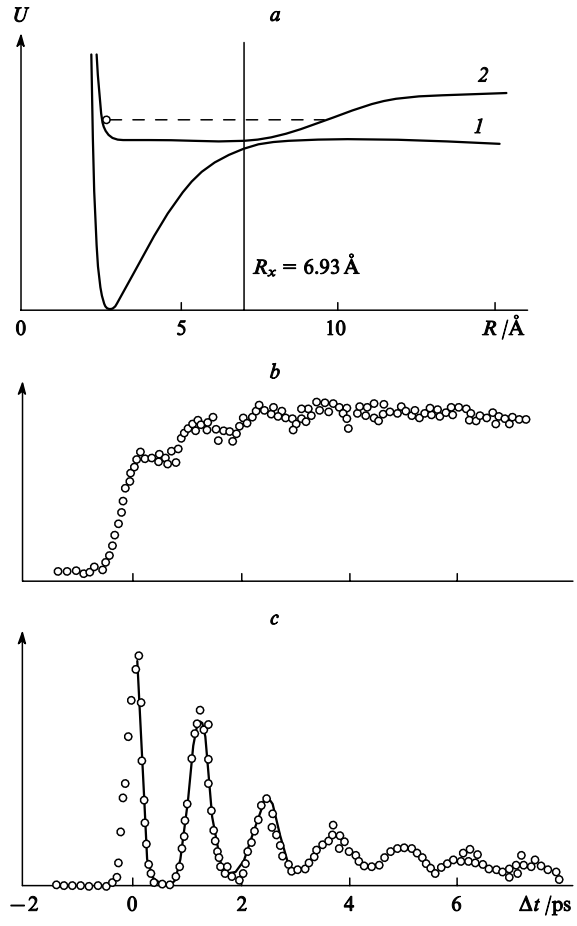


Figure 7. Dynamics of NaI dissociation.[51]
(*a*) potential energy curves for the ground (*1*) and excited (*2*) electronic states; (*b*) kinetics of accumulation of free Na atoms; (*c*) experimental monitoring of the $[Na\cdots I]^{\#}$ transition state.

the coherent kinetics of the formation of the pre-dissociation product, a sodium atom, were measured. The transition state dynamics gives an oscillating response with a decreasing amplitude. The decrease in the amplitude is related to 'skipping' of a part of the wave packet to a different electronic potential curve. Apparently, this is the first example of experimental real-time monitoring of the dynamics of intramolecular motion accompanied by non-adiabatic electron transitions. The product (sodium atom) is formed when the wave packet approaches the avoided crossing point. If we dealt with stationary states, the kinetics would be exponential with a rate constant equal to the vibration frequency multiplied by the probability of the non-adiabatic transition. However, in this case, the situation is different. When the wave packet is far from the avoided crossing region, the product yield does not increase. This type of kinetics is due to coherence; therefore, we call it coherent kinetics. By averaging the kinetics over all phases of wave packets, we shall obtain exponential kinetics.

It should be noted than the vibrationally coherent reactions induced by femtosecond pulses can take place in complex systems in various media. When these reactions occur, coherent wave packets can in some cases be observed experimentally in the products. Three reactions can be considered as examples, namely, decomposition of CH_2I_2 upon multiphoton absorption,[52] proton transfer in the 2-(2′-hydroxyphenyl)benzothiazole molecule [42] and the reaction responsible for the primary stage of vision.[53]

In the first reaction, the CH_2I_2 molecules were excited due to two-photon absorption on exposure to a femtosecond pulse with a carrier wavelength of 308 nm. Over a period of less than 100 fs, the carbene CH_2 and the iodine molecule in a non-stationary vibrationally excited state of the electronic state D' are formed.

In the case of proton transfer in the 2-(2′-hydroxyphenyl)benzothiazole molecule,[42] clear-cut damped oscillations of stimulated fluorescence were observed 60 fs after excitation with the probe pulse. The authors consider that the observed oscillations occur after the proton transfer has taken place. Analysis showed that only four of the 69 vibration modes (118, 254, 289 and 529 cm^{-1}) are involved in the formation of the vibrational wave packet, the predominant contribution to oscillations being made by only two vibration modes (118 and 254 cm^{-1}). The damping time for the contribution of the mode with a frequency of 118 cm^{-1} is 0.3 ps; that for each of other modes is $\sim$1 ps.

The third reaction is photoinduced isomerisation of the retinal chromophore in rhodopsin; more precisely, isomerisation of the excited 11-*cis*-retinal in the ground electronic state.[53] The 11-*cis*-retinal molecule was excited by a femtosecond pulse and the oscillating time dependence of the absorption of the product with a period of 550 fs was recorded. Two important experimental facts are worth mentioning: (i) the reaction occurs over a period of 200 fs; (ii) the reaction product was formed in a non-stationary vibrationally excited state of the ground electronic state. The researchers cited [53] give the affirmative answer to the question 'Does the vibrational coherence play an important role in the primary stage of vision?' They consider that avoided crossing of PES takes place and the wave packet can 'skip' from one PES to another and attribute the effective quantum yield of the reaction (0.67) to the reaction time (200 fs). The probability of this skip depends on the wave packet velocity in the avoided crossing region. If the velocity of the wave packet motion is decreased, the quantum yield of photoisomerisation should diminish. To confirm this hypothesis, femtosecond experiments on photoisomerisation of isorhodopsin were carried out. It was found that isorhodopsin isomerisation affords the same product, bathorhodopsin. It was suggested that the initial velocity of wave packet motion after excitation is lower in the case of isorhodopsin than in the case of rhodopsin. This was confirmed in experiments: the reaction proceeds more slowly (over 600 fs) and has a lower quantum yield (0.22). Therefore, the investigators concluded that the quantum yield is determined by the reaction dynamics rather than by the vibrational relaxation processes, as had been considered previously.

There are several publications in which the coherent wave packets have been observed when investigating elementary reactions within the femtosecond and sub-picosecond time scales. For example, vibrational coherence was observed in the photodissociation of OCS in the gas phase,[54] photodissociation of $Mn_2(CO)_9$ [55] and $Cr(CO)_6$,[41] intramolecular proton transfer,[56] femtosecond processes in proteins [57] and electron transfer.[58–62] For example, in a study of the hexamethylbenzene complex with tetracyanoethylene (TCE), oscillations were detected both in absorption and in fluorescence.[59, 60, 62] In a study of donor–acceptor interactions, Rubtsov and Yoschihara [61] have used various electron donors (carbazole, 1-chloronaphthalene, *N*-methylaniline) and acceptors (TCE, chloranil, fluoranil). It was shown that for each particular acceptor, irrespective of the nature of the donor, the same oscillation frequency in the fluorescence signal is observed: 155 cm^{-1} for TCE (oscillation period 215 fs), 178 cm^{-1} for chloranil (oscillation period 187 fs) and 212 cm^{-1} for fluoranil (oscillation period 157 fs). Hence, the oscillations are due to the formation of the vibrational wave packet associated with the excitation of a particular electron acceptor in the donor–acceptor complex.

It should be noted that the use of laser spectroscopy with ultrahigh temporal resolution often makes it possible to gain information on not only the product formation and the reactant decay but also on the transition state dynamics without observing the vibrational coherence. These studies also made a substantial contribution to the development of the views on the transition state dynamics. First of all, this refers to the study of electron transfer processes in molecular systems with intervalent transitions in organometallic compounds,[63, 64] charge recombination in photoexcited donor–acceptor complexes without covalent bonds,[59–70] charge separation and recombination in donor–acceptor supramolecules with covalent bonds.[70–75]

Studies of electron transfer in non-covalent donor–acceptor complexes and intervalent transitions in metal complexes provided important information on the dynamics of relaxation of their dipole environment.[61–68] These studies showed that, in addition to orientational relaxation, an important role is played by the libration motion of the medium dipoles.[60, 63, 64] In the same publications, it is noted that the single-mode approximation (when one average frequency of intramolecular vibrations is taken) is insufficient for describing the internal re-organisation of the system.

A situation typical of covalently bonded supramolecules is that an optical transition from the ground state gives rise to a locally excited state, which passes subsequently into a charge transfer state. The covalently bonded donor–acceptor supramolecules 'mimic' the charge separation process in a photosynthetic centre.[71, 72] Charge separation can take place both on the pico- and on the femtosecond time scale. This has been demonstrated [75] in relation to charge separation in the tetra-*meso*-substituted ferrocenylporphyrin molecules. The researchers studied the relaxation dynamics in various tetra-*meso*-substituted ferrocenylporphyrins, Fc_4PH_2, $ZnFc_4P$, $Fc_4PH_4^{2+}$ and $TCE:Fc_4PH_2$ (Fc is ferrocene, P is porphyrin), by the 'pump–probe' method. A supercontinuum was used as the probe pulse. The differential absorption in the 380–600 nm spectral range was recorded. Under the action of a femtosecond pulse with a wavelength of 610 nm, the $Q^1(\pi^*-\pi)$ state of the electron acceptor (porphyrin molecule) was excited, the ferrocene molecule serving as the electron donor. The formation of the charge transfer state $P^- - Fc^+$ from the locally excited $Q(\pi^*-\pi)$ state takes place over a period of $\sim$200–210 fs in the case of Fc_4PH_2 and $ZnFc_4P$. However, in the case of $Fc_4PH_4^{2+}$ and $TCE:Fc_4PH_2$, transition to the charge transfer state requires at least 10 ps. The different time scales of transition are, apparently, due to different conformation flexibilities of the porphyrin ring. Note that the transition to the charge transfer state occurs faster than the relaxation of solvent

molecules. A higher rate of electron transfer compared to the rate of relaxation of solvent molecules is also observed for complexes containing no covalent bonds.[62, 65] To interpret these facts, it is necessary to use new approaches to the standard views on electron transfer.

Other examples of investigation into transition state dynamics without observing the coherent wave packets can be found in a number of publications devoted to elucidation of the problem whether a reaction follows a stepwise or a concerted mechanism. Stepwise reactions differ from concerted ones in that the potential curves along the reaction coordinate have an intermediate minimum between the minima corresponding to reactants and products. In some cases, the reaction mechanism can be established rather easily. For example, photodecomposition reactions of acetone,[76] fluoroethane [77] and cyclic ketones [78] occur by stepwise mechanisms. This is proved (by experiment) by the fact that the primary and secondary bond ruptures occur at different time instants. The decomposition of CH_2I_2 upon multiphoton excitation [52] follows a concerted mechanism, which is confirmed by the short reaction time (< 50 fs) and by the product being formed in a non-stationary coherent state. However, it is often difficult to elucidate the reaction mechanism; this requires methods with a very high temporal resolution. Examples of reactions that follow stepwise and concerted mechanisms are listed in Table 1.

Table 1. Examples of reactions occurring by stepwise and concerted mechanisms.

Reaction	λ_1 /nm	Mechanism	t /fs	Ref.
$Fe(CO)_5 + 2\,h\nu \rightarrow$ $\rightarrow FeCO + 4\,CO$	400	concerted	~ 100	79
$Fe(CO)_5 + h\nu \rightarrow$ $\rightarrow Fe(CO)_4^* + CO$, $Fe(CO)_4 \rightarrow Fe(CO)_3 + CO$	267	stepwise	~ 100 ~ 3000	80
cyclo-$C_4H_8 \rightarrow 2\,C_2H_4$ (in the ground electronic state)	–	the same	~ 700	81
Cyclohexene $\rightarrow$ $\rightarrow$ ethylene + butadiene (in the ground electronic state)	–	concerted, stepwise	~ 200	82
Two-proton transfer in 2,2′-bipyridine-3,3′-diol	300 – 400	the same	~ 50 $\sim 10\,000$	83, 84

The first example is related to the photochemistry of metal carbonyls, which are widely used as photocatalysts and for the production of high-purity metallic films on various surfaces. Photodecomposition of these compounds has been studied using femtosecond spectroscopy techniques. For example, the ultrafast dynamics of photofragmentation of $Mn_2(CO)_{10}$, namely, rupture of the metal – metal and metal – ligand bonds occurring over hundreds of femtoseconds, has been studied.[85] The dynamics of $M(CO)_6$ dissociation (M = Cr, W, Mo) in solutions has been investigated [86] using femtosecond IR spectroscopy. It was found that the primary reaction in the UV photolysis is ejection of one CO group, which takes place over a period of less than 240 fs. Let us analyse decomposition of $Fe(CO)_5$ in the gas phase in more detail. Two groups of researchers [79, 80] have considered an important point, namely, whether the molecule loses one or several CO ligands after photoexcitation. The viewpoints of the researchers cited are appreciably different.

In experiments described in one of these publications,[79] the 'pump – probe' procedure was used. The pump pulse had a carrier wavelength of 400 nm. Upon the absorption of two photons, a transition state with an excitation energy of 50 000 cm^{-1} was formed. The probe pulse had a carrier wavelength of 800 or 400 nm. Using a time-of-flight mass spectrometer, the ions of both the starting compound and all the fragments of $Fe(CO)_n^+$ decomposition ($n = 0 - 5$) were detected. The experiments showed that the decay times of all the $Fe(CO)_n^+$ cations ($n = 2 - 4$) were nearly equal and amounted to ~ 100 fs. (Time characteristics of the growth of signals of the cations were not detected.) The maxima of signals of these cations are shifted in time relative to the maximum of the $Fe(CO)_5^+$ signal by 20 ± 5 fs for $Fe(CO)_4$, by 30 ± 5 fs for $Fe(CO)_3$ and by 60 ± 15 fs for $Fe(CO)_2$. Only for FeCO and Fe, were the kinetic characteristics of the growth of signals observed, the formation kinetics of iron atoms being correlated with the kinetics of the decay of FeCO. This means that dissociation of FeCO is a subsequent reaction which occurs with a characteristic time of 230 fs. The following model was proposed to interpret the experimental data. The excitation is followed by structural rearrangement of the transition state during the first 20 ± 5 fs; consequently, the distance between the centers of gravity of $Fe(CO)_4$ and CO increases relative to the equilibrium distance. With this transition state geometry, after absorption of the photons from the probe pulse, the parent molecule is converted into the corresponding ion, which decomposes to give the detectable $Fe(CO)_4^+$ ion and CO. Within 30 ± 5 fs after the pump pulse, a new configuration of the transition state appears (apparently, two CO ligands are separated from the Fe atom by distances greater than the equilibrium distance). The probe pulse induces the transformation of the parent molecule into the corresponding ion, which decomposes to give the detectable $Fe(CO)_3^+$ ion and two CO molecules. The origin of the detectable $Fe(CO)_2^+$ and $FeCO^+$ cations is explained in approximately the same way. Within the framework of this model, the observable ions are 'fingerprints' of the time evolution of the transition state. Thus, upon absorption of two photons with a wavelength of 400 nm, the reagent loses four CO ligands in ~ 100 fs. Since this value corresponds to the time scale of the period of the Fe – CO bond vibrations (the typical range is 80 – 100 fs), the researchers concluded that the reaction

$$Fe(CO)_5 + 2\,h\nu \longrightarrow FeCO + 4\,CO$$

occurs by a concerted mechanism.

The same reaction was studied by similar methods in another study.[80] Five consecutive processes with time constants of 21, 15, 30, 47 and 3300 fs were detected after the pump pulse. However, the four faster processes were attributed to intermediate intramolecular processes taking place in the excited $Fe(CO)_5$ molecule and in the primary product $Fe(CO)_4$ formed in an electronically excited state. In the opinion of the researchers cited, the second step of CO elimination, *i.e.*, transition of $Fe(CO)_4$ to $Fe(CO)_3$, occurs in the ground electronic state over a longer period (3.3 ps). They discussed the possibility of a concerted reaction mechanism and concluded that it does not take place.

The conclusions made in the two studies discussed above are contradictory. However, it should be noted that Trushin *et al.*[80] performed excitation of the $Fe(CO)_5$ molecule by one-photon absorption at a wavelength of ~ 267 nm, while in the study by Banares *et al.*,[79] this was done by two-photon excitation at ~ 400 nm. Therefore, in the latter case, the $Fe(CO)_5$ molecule could have a much greater excitation energy and, perhaps, different parameters of the initial vibrational wave packet. In addition, both groups of scientists did not control the structure of the pump pulse, although it is known, for example, that the chirp of the pump pulse can result in an increase in the product yield in the channel corresponding to the concerted mechanism. Thus, the question of the mechanism of this reaction remains open.

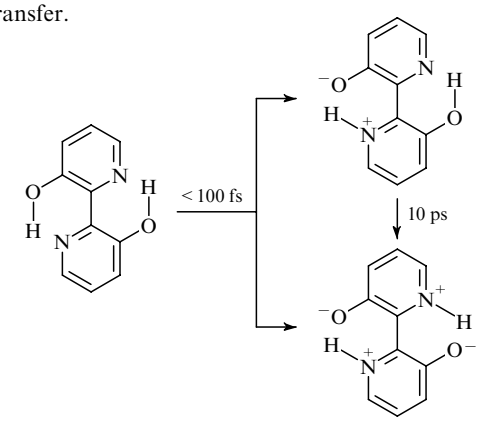
The second example is opening of the cyclobutane ring giving rise to two ethylene molecules.[81] Two mechanisms of this reaction are discussed in the literature — concerted (described by the Woodward – Hoffman rule) and stepwise (a biradical two-step mechanism). By investigating the kinetics of the decay of biradicals, the authors [81] arrived at the conclusion that the reaction follows the stepwise biradical mechanism. They believe that a

small potential well (4 kcal mol^{-1}) corresponding to the intermediate species, biradicals, is present near the top of the barrier.

The third example is represented by decomposition of cyclohexene and other cyclic compounds.[82] Experimental data and trajectory calculations showed that the reactions follow two mechanisms, a concerted and a stepwise biradical mechanism. In the researchers' opinion, the contributions of the two types of mechanisms to the overall reaction rate are dictated by the asymmetry of the molecular structure, localisation of the activated complex and the height of the potential barrier.

The problem of the search for an experimental criterion which would be indicative of a concerted reaction mechanism has been discussed.[82,87] It is generally accepted that several bonds are modified simultaneously in a concerted reaction — some of them are cleaved and some new bonds are formed. However, the notion of simultaneity for the experimenter has not been defined. The authors of the publications considered believe that a well-posed criterion should be related to the time scale of the movement along the reaction coordinate. This means that only the real-time dynamics of intermediate structures can substantiate the concept of concertness. It should be emphasised that the notion of concerted reactions has usually been related only to the structure of PES. In femtochemistry, realisation of either concerted or stepwise mechanism can also depend on the way of production of the wave packet, in particular, on the degree of its coherence.

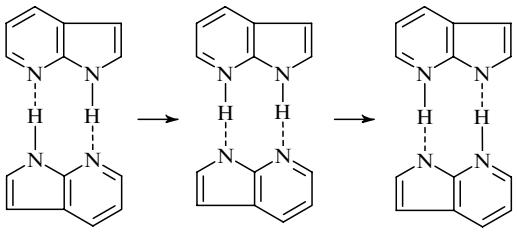
The last-mentioned example refers to the studies of intramolecular two-proton transitions in electronically excited states. Two-proton transfer in the 2,2′-bipyridine-3,3′-diol molecule has been studied.[83,84] It was found that this transfer can follow two mechanisms, namely, a one-step concerted mechanism and a two-step mechanism comprising two successive steps of one-proton transfer.



The concerted reaction and the first step in the stepwise process occur in less than 100 fs, while the last step requires ~10 ps.

One of the studies cited [84] is devoted to the dependence on the excitation energy of the ratio of the reaction yields obtained from the different channels. It was shown that an increase in the vibrational energy in the electronically excited state S_1 results in a higher ratio of the yields of mono- and diketo tautomeric products. The predominance of the concerted mechanism at low excitation energies was attributed to the fact that there exists a potential barrier for the first step, which affords the monoketo tautomer. Due to presence of an electrophilic substituent in these molecules, the one-proton transfer takes place.[88] This was demonstrated using tautomerisation of 6-methoxycarbonyl-2,2′-bipyridine-3,3′-diol as an example. The one-proton transfer in this molecule takes < 150 fs.

Yet another example is provided by the proton transfer processes in 7-azaindole dimers. They can be regarded as model processes mimicking tautomerisation in DNA pairs. Time evolution during the intramolecular tautomerisation of 7-azaindole dimers containing two N—H bonds has been investigated.[89] The molecular structures in which the transfer of one or two protons takes place are shown below



On exposure to a femtosecond pulse at 305–310 nm, the dimers formed in a molecular beam passed to an electronically excited state. Ionisation of various structures under the action of the probe pulse (wavelength 605 nm) took place at different points in time after the pump pulse. The result of ionisation was recorded by a time-of-flight mass spectrometer. The femtosecond temporal resolution made it possible to follow the motion of protons in each intermediate and to determine the characteristic times of this motion in the absence of a solvent. It was found that the first step of proton transfer occurs in several hundreds of femtoseconds, while the second step, which yields tautomer, is much slower, it proceeds over a period of several picosends. When the hydrogen atoms are replaced by deuterium atoms, the time scales of tautomerisation reactions change substantially. The mechanism of these processes has been discussed,[89] in particular, the role of quantum tunnelling in it. Nevertheless, the question of whether the two-proton transfer follows a concerted or a stepwise mechanism has been brought up in subsequent studies.[90–92] In these publications, the possibility of existence of active and inactive dimers with respect to tautomerisaton reactions and the role of solvation effects are discussed. It was shown [91] that clustering of water does not induce the formation of reaction-inactive dimers; the researchers concluded that the two-proton transfer follows a stepwise mechanism. However, Catalan *et al.*[92] believe that this transfer in 7-azaindole dimers occurs by a concerted mechanism. The conclusions made in this study provoked scientific discussion. Remarks concerning the publication cited [92] can be found in a study by Folmer *et al.*[93] The authors investigated this reaction using the 'Coulomb explosion' technique and concluded that it follows a stepwise mechanism.

VI. The kinetics of ultrafast chemical reactions

Study of the kinetics of a process includes monitoring of the time evolution of the concentration of a reactant or a product. This means that the populations of quantum levels rather than the dynamics of wave packets should be detected (we are not interested in the phase caracteristics of the nuclear motion). The features of femtosecond pulses significant for this line of femtochemistry include high temporal resolution and high intensity. Using these pulses with multiphoton absorption, it is possible to produce and to study molecules in high electronic states the lifetimes of which are very short.

Currently, vigorous studies dealing with the chemistry of highly excited molecules are being carried out. It is obvious that the rates and the ratios of channels of these reactions depend substantially on intramolecular processes such as conversion from highly excited electronic states, S_n, energy redistribution over vibrational modes and vibrational relaxation caused by intermolecular energy transfer to the solvent.

In a study of electron relaxation, it has been shown [94,95] that excitation of high electronic states in, for example, coumarin 481, oxazine 1 and sulforhodamine, is accompanied by internal conversion processes ($S_n \rightarrow S_1$), which occur in 180–280 fs. This conclusion is based [94] on the results of the following experiments. Coumarin 481 molecules in cyclohexane were excited by a pulse (duration 100 fs, wavelength 267 nm) to some electronic state S_n, the energy level of which is 12 000 cm^{-1} higher than the energy level S_1. From measurement of the kinetics of fluorescence (the up-conversion) related to the $S_1 \rightarrow S_0$ transition, the researchers reached a conclusion about the time characteristics of the $S_n \rightarrow S_1$

internal conversion. By investigating intramolecular processes for various porphyrins, it was found that the lifetime of the porphyrin molecule as the free base (H_2P) in the S_3 state is shorter than 40 fs, while that in the S_2 state is 90 fs. These and other data attest that the time scale of these processes is < 300 fs.

In some publications (see, for example, Refs 96–100), it is concluded that intramolecular energy redistribution occurs much faster, namely, in tens of femtoseconds. A somewhat different opinion was expressed by Hasche *et al.*,[100] who consider that redistribution of vibrational energy is faster (30–200 fs) for approximately iso-energetic vibrational levels and slower (200–1000 fs) for vibrational levels with appreciably different frequencies. Much longer times are required for relaxation of vibrational energy, *i.e.*, for the transfer of vibrational energy to the molecules of the environment. The time scale of these processes is about tens of picoseconds.[94, 101]

Let us consider examples of kinetic measurements for reactions of the following classes: bond rupture in electronically excited molecules, elimination of electronically excited molecules, decomposition of vibrationally excited molecules in the ground electronic state, photoisomerisation, bimolecular reactions in van der Waals complexes, bimolecular association reactions (*i.e.,* reactions in which the reactants are free and no chemical transformations take place upon collision; however, for definite distances between the reactants, photon absorption can take place; this induces the formation of a bond).

Examples of unimolecular reactions proceeding within femto- and sub-picosecond time scales are presented in Table 2. Below we discuss these reactions in more detail.

Table 2. Characteristic times (τ) of some ultrafast unimolecular reactions.

Reaction number	Reaction	t /fs	Ref.
Bond rupture in electronically excited molecules			
1	$(ICN)^e \rightarrow I + CN$	200	102
2	$(CH_3I)^e \rightarrow CH_3 + I$ (see [a])	100–200	103
3	$(CD_3I)^e \rightarrow CD_3 + I$ (see [a])		
4	$(C_2F_4I_2)^e \rightarrow (C_2F_4I)^* + I^*$ (see [b])	200	77
5	$(C_2F_4I_2)^e \rightarrow (C_2F_4I)^* + I$		
Elimination from electronically excited molecules			
6	$(CH_2I_2)^e \rightarrow CH_2 + I_2(D')$ (see [a])	< 100	52
7	$(NH_3)^e \rightarrow NH(c^1) + H_2$ (see [c])	< 50	104
Isomerisation of electronically excited molecules			
8	Isomerisation of spironaphthooxazine, multistep process	3000	21, 105, 106
Tautomerisation of electronically excited molecules			
9	$A^e \rightarrow T^e$	60	107
10	$T^e \rightarrow$ decay (A^e is the ketone form of methyl salicylate, T^e is the enol form of methyl salicylate)	> 1000	107
Decomposition of vibrationally excited radicals in the ground electronic state			
11	$(C_2F_4I)^* \rightarrow C_2F_4 + I$ (see [c])	25 000	77
12	$(CH_3CO)^* \rightarrow CH_3 + CO$	500	76
13	$[CH_2(CH_2)_{n-2}C{=}O]^* \rightarrow CH_2(CH_2)_{n-2} + CO$ (n = 4, 5, 6, 10)	100	78

Note. The superscript '*e*' designates electronically excited species, and '*' marks vibrationally excited species. Excitation energy/eV: [a] 8; [b] 4.7; [c] 10.

Dissociation of ICN from an electronically excited state (see Table 2, reaction *1*) takes place on the repulsive term. The kinetics of formation of the CN product has been measured experimentally.[102] The time of bond rupture was determined by comparing experimental data (obtained with ultrahigh temporal resolution) with the results of calculations in terms of the diatomic approximation.

After decomposition of the $(CH_3I)^e$ and $(CD_3I)^e$ molecules (see Table 2, reactions *2* and *3*) (each molecule gained an excitation energy of 8 eV due to two-photon absorption) from Rydberg states, the time evolution of processes was recorded for 100–200 fs.[103] An appreciable isotope effect was observed.

The electronically excited $(C_2F_4I_2)^e$ molecule is formed after exposure of $C_2F_4I_2$ to a femtosecond light pulse with a wavelength of 277 nm. Decomposition of the electronically excited molecule takes place along two channels over a period of 200 fs giving rise to the vibrationally excited $(C_2F_4I)^*$ radical in the ground electronic state and a iodine atom. One channel provides an electronically excited iodine atom, and the other channel, a non-excited iodine atom (see Table 2, reactions *4* and *5*, respectively).

Both mechanisms of decomposition of $(C_2F_4I_2)^e$ and the mechanism of decomposition of the $(C_2F_4I)^*$ radicals formed in the ground electronic state have been studied.[77] The results of this study are discussed in more detail below, when considering the processes with participation of vibrationally excited radicals in the ground electronic state.

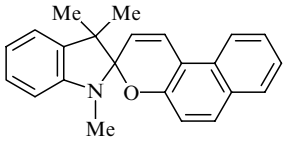
Elimination reactions of highly excited molecules occur due to multiphoton absorption. Femtosecond pulses have a high on-peak power; therefore, multiphoton processes readily take place. An example is reaction *6* (see Table 2), namely, gas-phase decomposition of a CH_2I_2 molecule excited by multiphoton absorption, induced by absorption of two photons with a wavelength of 310 nm (excitation energy 8 eV).[52] One product of this reaction is molecular iodine, which exists in a non-stationary quantum state; reaction time < 100 fs. Note that for low excitation energies, rupture of the C–I bond to give an iodine atom is the main reaction channel.

Yet another example is decomposition of ammonia induced by five-photon absorption ($\lambda = 615$ nm).[104] If the excitation energy of the ammonia molecule is 10 eV, decomposition by reaction *7* takes place (see Table 2); if it amounts to ~ 8 eV, the following reaction proceeds:

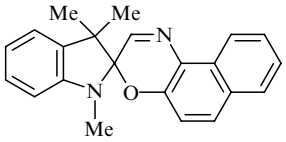
$$NH_3 \longrightarrow NH_2 + H.$$

These examples illustrate the potential of methods with the use of femtosecond pulses for the development of the chemistry of electronically excited molecules.

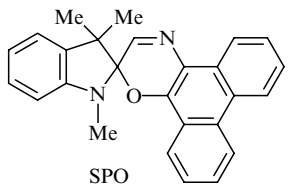
A large number of publications are devoted to photoisomerisation induced by femtosecond pulses (see, for example, papers [9, 21, 105–117]). In particular, many studies deal with isomerisation of electronically excited molecules of various photochromic compounds in solutions. On exposure to light, photochromic compounds can undergo reversible intramolecular transformations accompanied by a change in the absorption spectrum. This property of photochromic compounds can be used for generation of various optico-electronic devices. In particular, the possibility of using them for three-dimensional optical memory is discussed.[115, 116] Let us consider photoisomerisation of unsubstituted indoline spiro compounds, namely, spironaphthopyran (SNP), spironaphthooxazine (SNPO) and spirophenanthrooxazine (SPO).



SNP

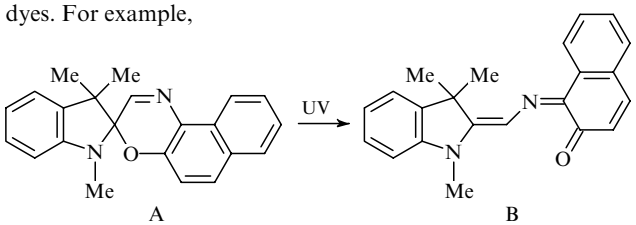


SNPO



SPO

Photoisomerisation is transition of form A into form B, which has a planar structure similar to the structure of merocyanine dyes. For example,



A B

Femtosecond pulses with durations of 170–400 fs have been used.[112–114] It was found that isomerisation proceeds *via* singlet states and is completed within a picosecond time scale.

The mechanism of these reactions has been studied in more detail in several publications.[21, 105, 106] The pump pulse centred at a wavelength of 308 nm had a duration of 70 fs. Probing was performed using a supercontinuum in the spectral range of 420–590 nm. For each of the three compounds, the dynamics of the photoinduced absorption spectra was recorded with a high temporal resolution for different time intervals after the action of the pump pulse. Figure 8 illustrates the dynamics of the photoinduced absorption spectra recorded experimentally for spirophenanthrooxazine. It was found that the reaction mechanism does not change when the position of the aromatic rings changes. On the basis of experimental data and quantum-chemical calculations, a photoisomerisation mechanism including the following processes was proposed:

(0) $A(S_0) + h\nu \longrightarrow A(S_2)$,

(1) $A(S_2) \longrightarrow A(S_1)$,

(2) $A(S_1) \longrightarrow X^*$,

(3) $X^* \longrightarrow B$.

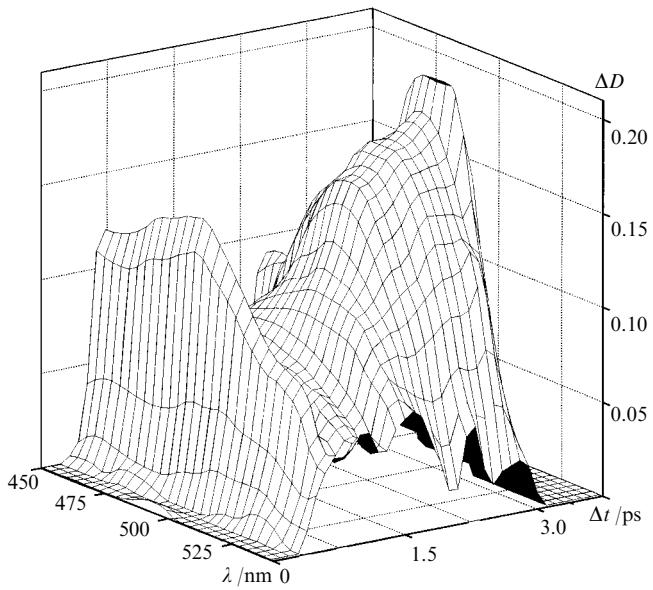


Figure 8. Dynamics of the photoinduced absorption spectra for SPO.[106] ΔD is the optical density change.

Here $A(S_i)$ ($i = 1, 2$) is molecule A in the singlet electronic state S_i; X is an intermediate species, which is characterised by rupture of the bond between spiro carbon and oxygen. It is worth noting that the experimental approach developed in a series of publications[21, 104] made it possible to observe the time evolution of the $S_2 \rightarrow S_1$ transition, vibrational relaxation in the S_1 electronic state, the formation of the intermediate species X*, which is the *cis*-cisoid isomer in the electronically excited state, and the formation of X and of the reaction products — forms B of the corresponding spiro compounds. The last-mentioned reaction includes the following steps: non-adiabatic $X^* \rightarrow X$ transition and the transition of X into species B. However, it was impossible to separate these steps in time, due to the superposition of the absorption spectra for species X and B. Therefore, both steps are written as a single reaction, which appears to be limited by the rotation of the molecule about bonds of the opened ring. The results of experimental studies for SNPO are shown in Fig. 9. Absorption of a light quantum brings the molecule to the S_2 excited state. This is followed by transition to the vibrational levels of the S_1 electronic state. This transition shows itself as accumulation of molecules $A(S_1)$; this is detected by a change in the absorption spectra observed for delays of up to 110 fs (Fig. 9 *a*). The next stage is transition of molecule $A(S_1)$ into the state X* (this intermediate state was observed by low-temperature phosphorescence[109]), which is characterised by rupture of the bond between the spiro carbon atom and the oxygen atom. The species X* is detected on the basis of absorption spectra in the spectral range of 420–450 nm; the variation of the concentration of X* is illustrated by Fig. 9 *b*. The next step is non-adiabatic transition of the system from the excited state X* to the ground electronic state X. The molecule acquires the possibility of rotating around the

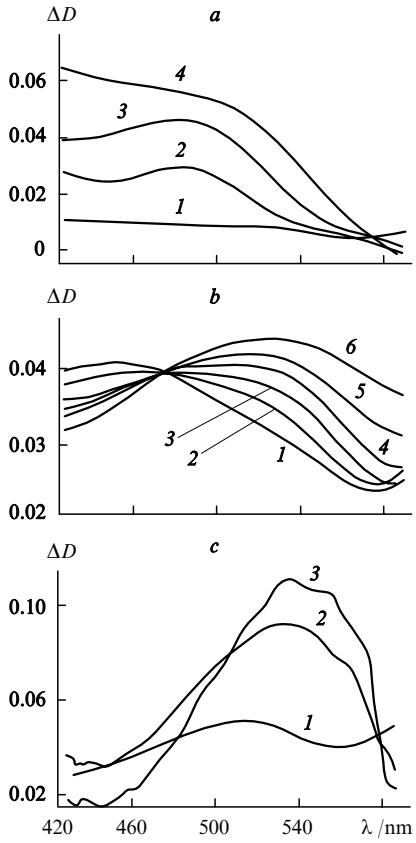


Figure 9. Photoinduced absorption spectra of SNPO for various time delays between the pump and probe pulses.
Δt /fs: (*a*) −110 (*1*), 0 (*2*), 73 (*3*), 185 (*4*); (*b*) 665 (*1*), 739 (*2*), 812 (*3*), 886 (*4*), 960 (*5*), 1034 (*6*); (*c*) 960 (*1*), 3600 (*2*), stationary absorption spectrum of the reaction product (*3*).

bonds of the opened ring. Figure 9 *c* shows the variation of the absorption spectra associated with this process. The absorption spectrum for a delay of 3.6 ps shown in the same figure is similar to the known steady-state absorption spectrum of form B.

The calculation of the dynamics of this reaction is as yet too complicated; therefore, the experimental data were processed within the framework of the kinetic scheme presented above. This processing made it possible to describe quantitatively the three-step mechanism of photoisomerisation of the compounds under consideration in terms of the rate constants k_i (i = 1, 2, 3). The following values were obtained (fs):

Compound	k_1^{-1}	k_2^{-1}	k_3^{-1}
SNP	100	250	1800
SNPO	80	230	1000
SPO	100	300	2000

It can be seen that the rate constants found for the three compounds are virtually equal. Only the k_3 value, which, as noted above, is determined by the rate of rotation around the C–C and C–N bonds, does differ substantially in the case of SNPO. This is apparently due to the fact that rotation around the C–C bonds occurs more easily than rotation around the C–N bonds.[118]

Of substantial interest for researchers are tautomerisation reactions in which intramolecular proton transfer takes place. These reactions are involved in many chemical and biological systems; in some systems, these processes are photochromic, although no pronounced structural changes take place.

Tautomerisation has been studied in the vapour phase,[119] in supersonic molecular beams [89] and in solutions.[83, 84, 90–92, 120, 121] Herek *et al.*[119] investigated the methyl salicylate system in which a proton migrates from one oxygen atom to the other. This process is accompanied by the change of the structure from the ketone form (before the transfer) to the enol form (after the transfer). The authors consider that the proton transfer takes place over a period of 60 fs. At longer times (picosecond time scale), non-radiative decay of the resulting structure takes place, caused by intramolecular energy relaxation or dissociation. In the studies mentioned above [83, 84, 89, 90–92] dealing with one- and two-proton transfer reactions in bipyridinediols and 7-azaindole dimers, it was found that the transfer of two protons can occur both as a synchronous process and as two consecutive steps. Each step includes the transfer of one proton, the first proton migrating much faster than the second one. Neuwahl *et al.*[120] studied the same processes but employed other experimental methods. This work confirmed the results of a previous study;[83] according to these estimates, primary processes of one- and two-proton transfer in bipyridinediols occur over periods of < 50 fs.

The researchers cited above consider that the proton transfer takes place in electronically excited states. A different point of view is expressed by Takeda *et al.*,[121] who studied intramolecular proton transfer in 2-(2′,4′-dinitrophenyl)pyridine; they assumed that no intermediate or final products in excited states are formed. Only three different intermediate photoinduced absorption spectra were observed in the experiments. To interpret experimental data, they proposed a model which is often used to describe photochromic reactions. Under the action of excitation, the molecule passes into the singlet excited state S_1 (the $S_1 \rightarrow S_n$ transition was observed experimentally); relaxation of the excited state gives rise to an intermediate product in its ground electronic state, and subsequently, the final product is formed. According to author's estimate, the intramolecular proton transfer requires 320–500 fs. This is several times longer than the duration of proton transfer in other systems.[122, 123] In our opinion, the absence of excited intermediate species is unlikely. The assumption of the researchers cited [121] is based on the fact that they did not observe any luminescence. However, we have considered above a model of photoisomerisation of spiro compounds in which photoinduced absorption by the intermediate electronically excited product without luminescence was recorded.

Most of unimolecular reactions with photoactivation proceed in accordance with statistical laws. This is due to the fact that intramolecular redistribution of energy occurs in 0.1–1 ps, *i.e.*, over a period much shorter than the characteristic time of decomposition of the molecule. For a reaction not to obey the statistical laws, decomposition must be faster than the intramolecular redistribution of the vibrational energy. This requires a very fast excitation of the molecule to high energies. This process has been realised.[68] The molecule passed into an electronically excited state upon the action of a femtosecond pulse. Fast decomposition of the electronically excited molecule gave rise to vibrationally excited radicals in the ground electronic state. The degree to which the vibrational excitation surpasses the potential barrier to radical decomposition in the ground electronic state depends on the height of the barrier and on the wavelength of the pump light pulse. By adjusting the wavelength of the pump light pulse and by choosing an appropriate molecular system, one can obtain radicals with either slight or substantial vibrational excitation exceeding the potential barrier. The above-mentioned decomposition of vibrationally excited $(C_2F_4I)^*$ radicals generated in reactions *4* and *5* can be considered as an example of the former situation. The vibrationally excited radical decomposes along two pathways to give C_2F_4 together with excited or non-excited iodine atoms

$$(C_2F_4I)^* \longrightarrow C_2F_4 + I, \qquad \text{(reaction } 14\text{)}$$

$$(C_2F_4I)^* \longrightarrow C_2F_4 + I^*. \qquad \text{(reaction } 15\text{)}$$

The reaction was studied in a supersonic molecular beam using a time-of-flight mass spectrometer (multiphoton ionisation was induced by a second femtosecond pulse with a wavelength of 304 nm). The kinetics of product formation, the velocity distribution of I and I* atoms and the anisotropy of product dispersion in reactions *4*, *5* (see Table 2) and *14*, *15* were measured. The yields of I and I* atoms were 0.7 and 0.3, respectively. The average proportion of the translational energy was 59% for reaction *4* and 67% for reaction *5*. With allowance for the energy conservation law, the distribution of internal energy in the intermediate $(C_2F_4I)^*$ radical was determined. This distribution proved to be broad and to have two maxima located at 12 and 17 kcal mol^{-1}.

The vibrationally excited radical decomposes over a period of 25 ps. The measurements showed that only 30% of the excited radicals formed in reaction *4* decompose by channels *14* and *15*. On the basis of this result and of the distribution of internal energy in the radical, the potential barrier to reaction *14* was estimated to be $\sim$15 kcal mol^{-1}. Preliminary calculations resorting to the statistical theory indicate that decomposition by pathway *14* takes place within a picosecond time scale, which is in line with experimental results (although analysis of the velocity distribution of I and I* atoms showed that some molecules decompose faster than it follows from calculations).

Yet another example is decomposition of highly vibrationally excited $(RCO)^*$ radicals in the ground electronic state.[76] On exposure to a femtosecond pulse, electronically excited acetone molecules R^1COR^2 (R^1 = Me, R^2 = Et) are formed. Decomposition of electronically excited molecules (excitation energy 186 kcal mol^{-1}) takes place over a period of $\sim$100 fs. This affords vibrationally excited $(R^1CO)^*$ and $(R^2CO)^*$ radicals in the ground electronic state. Decomposition of the acetyl radical requires 500 fs (that of the propionyl radical lasts 750 fs) for an excitation energy of $\sim$65 kcal mol^{-1}. This time of decomposition is much shorter than the time calculated in terms of the Rice–Ramsperger–Kassel–Marcus (RRKM) statistical theory. This low rate of radical decomposition has been attributed [76] to the fact that upon photoexcitation, only a minor part of vibrational energy (less than the equilibrium energy) is evolved on the reaction coordinate, namely, the C–C bond.

The next example refers to the research into highly vibrationally excited radicals of the $[CH_2(CH_2)_{n-2}C=O]^*$ type in their ground electronic state.[78] The number of carbon atoms n in these

radicals was 4, 5, 6 and 10. These radicals were formed upon photodissociation (which took 100 fs) of the corresponding cyclic ketones. Decomposition of the vibrationally excited radicals does not obey statistical laws. This is proved by two facts. First, the reactions occur over a period of ~ 100 fs, which is several orders of magnitude shorter than the values calculated in terms of the statistical theory. Second, the reaction time barely depends on the number of carbon atoms in the radical and hence, on the number of vibrational degrees of freedom.

Thus, using femtosecond procedures, it is possible to generate vibrationally excited radicals with various, including non-statistical, distributions of intramolecular energy and to study decomposition of these radicals. An approach to the investigation of intramolecular processes at high vibrational energies and new ways of conducting reactions to circumvent the statistical laws have been considered.[76]

A complicated experimental problem of femtochemistry is fixing the zero point of time. Therefore, the question of the possibility of investigation of bimolecular reactions in van der Waals complexes has long remained open. The following approach has been proposed.[85] A weakly bonded van der Waals complex (VDWC) incorporating a molecule of one reactant is assembled in a supersonic molecular beam. Under the action of a femtosecond pulse, the second reactant is formed in the VDWC. In this case, the instant of action of the light pulse which generates the reacting system can be taken to be zero. Some examples of bimolecular reactions studied by femtosecond spectroscopy techniques are listed in Table 3.

Table 3. Examples of bimolecular reactions in VDWC.

Reaction number	Reaction	VDWC	t /fs	Ref.
Exchange reaction				
16	$H + CO_2 \rightarrow OH + CO$	$IH\cdots CO_2$	1000	124
Reactions with electron transfer				
17	$PhH + I_2 \rightarrow PhHI + I$	$PhH\cdots I_2$	1000	125
18	$PhH + I_2 \rightarrow PhHI + I^*$	$PhH\cdots I_2$	200	
Photoassociation reaction				
19	$Hg + Hg + h\nu \rightarrow Hg_2$	–	–	126

The first example is bimolecular reaction *16* in the $IH\cdots CO_2$ VDWC. On exposure to the light pulse, the I–H bond is cleaved. This point in time is taken to be zero. The hydrogen atom starts to move and then reacts with CO_2 to give the OH radical. If the structure of the complex is known, it becomes possible to study the bimolecular reaction that takes place with a specified rate and a specified impact parameter. In this particular case, it was shown [124] that reaction *16* proceeds *via* the step of formation of a long-lived complex over several picoseconds. A similar technique has been utilised to study [127] the bimolecular reaction

$$Br + I_2 \longrightarrow BrI + I.$$

The second example includes charge transfer reactions *17* and *18*. These reactions have been studied using various electron donors (D), for example, $D = C_6H_6$,[125] C_2H_5S.[128] A common feature of these reactions is a correlation between the ionic and covalent terms. In these reactions, the weakly bonded D···I complex consists of electron-donor molecules D and iodine. The complex was irradiated by a femtosecond pulse; as a consequence, the molecular system passed to a transition state in the ionic part of the potential curve (Fig. 10). This means that an electron has passed from the donor to the acceptor. The system moves along the term, enters the area of Coulomb attraction and approaches the avoided crossing point at which two channels of product

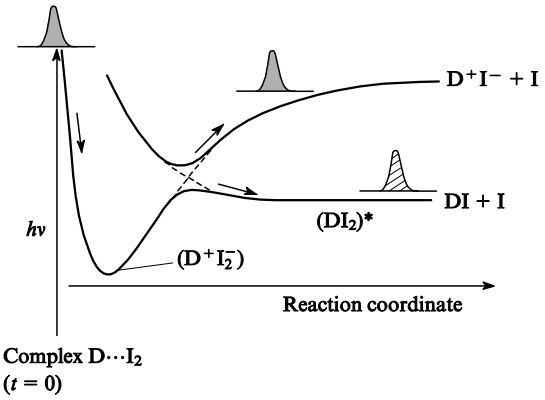


Figure 10. Chart of the potential energy change along the coordinate of the reaction $D\cdots I_2 \rightarrow DI + I$ (or $D^+I^- + I$).
After absorption of light by a weakly bound complex, the nuclei start to move towards the pseudo-crossing point of the ionic and covalent terms; after the pseudo-crossing point has been passed, two reaction channels appear.

formation appear. In the studies under consideration, the iodine atom was detected and its velocity was measured by time-of-flight mass spectrometry. As a rule, the formation of iodine atoms with two different velocities corresponding to the two channels was observed (for example, if benzene is used as the electron donor, these velocities are 400 and 1000 m s^{-1}). The channel yielding the excited iodine atom (the faster iodine atoms) is implemented over a period of 200 fs, while the channel giving rise to the non-excited iodine atom is performed in 1000 fs.

The third example is bimolecular photoassociation *19* in which an excited Hg_2 molecule is produced from two mercury atoms under the action of a femtosecond pulse. The potential curve for the Hg_2 molecule is repulsive. The femtosecond pulse allows the system to switch from the repulsive state to the binding state. The resonance character of this transition is determined by the pulse wavelength and the distance (the impact parameter) separating the mercury atoms in the ground electronic state. Thus, by varying the pulse wavelength, the mercury atoms participating in the reaction can be selected according to their impact parameters. The dynamics of the excited molecules thus formed can be studied by time-resolved fluorescence methods.

In the examples discussed above, the molecular systems were considered to be isolated. However, if the chemical reaction occurs in solution, the solvent has a substantial influence on it. After excitation of the molecular system by a femtosecond pulse, two types of fast dynamic processes can take place, namely, intramolecular processes (redistribution of electronic and vibrational energy) and intermolecular processes (vibrational relaxation and solvation of excited molecules). Information concerning these processes is gained most often from the shifts of time-resolved absorption, fluorescence and stimulated emission spectra for times of less than several picoseconds.[129–131] It was found that in many cases, the dynamics of solvation includes two steps, a faster step with a duration of < 200 fs and a slower step occurring within the picosecond time scale. The fast step is often attributed to intramolecular processes, while the slow step is ascribed to intermolecular relaxation, the formation and destruction of hydrogen bonds, *etc*.

The interaction of the solvent with the dissolved substance has a substantial influence on not only intermolecular but also intramolecular processes in the latter. Thus in a study of the dynamics of formation and rupture of a hydrogen bond and its influence on the rate of relaxation of the *trans*-retinal molecule in the S_3 and S_2 electronic states in a butan-1-ol–cyclohexane mixture,[132] it was found that the lifetime of the molecule in the S_3 state in pure cyclohexane is 30 fs, while that in the S_2 state is 0.7 ps; upon the

addition of butanol, these periods increase by factors of ~ 7 and ~ 2.5, respectively. The increase in the lifetime of the molecule in the S_2 state resulted in higher quantum yields of fluorescence and isomerisation. In another publication,[131] bithiophene, tertiophene and quaterthiophene oligomers have been studied in solution and photoinduced absorption and fluorescence spectra have been detected. For time periods of < 1 ps after excitation, spectral shifts were observed; they were interpreted as relaxation processes, resulting in an equilibrium between the excited oligomers and their solvation shells.

Femtosecond vibrational spectroscopy can serve as an efficient tool for the study of solvation mechanisms. For example, coumarin 102 has been studied (using C_2Cl_4 and $CHCl_3$ as solvents).[133] The carbonyl group of coumarin dyes was found to be linked to a solvent molecule by a hydrogen bond; the researchers showed how the presence of this bond is manifested in the dynamics. In the experiment, coumarin 102 was transferred to the electronically excited S_1 state by the action of a 100-fs light pulse with a frequency of 1500 to 1750 cm^{-1}, and the evolution of the absorption vibrational spectrum in the ground and in excited states and in polar ($CHCl_3$) and non-polar (C_2Cl_4) solvents was detected with a temporal resolution of 200 fs. In the spectrum of a coumarin solution in a non-polar solvent, the absorption band of the C=O bond was located at 1735 cm^{-1}, which is a characteristic frequency for a free carbonyl group. For the electronically excited state, a decrease in the dipole moment of the transition was observed; however, no significant shift of the C=O vibration band was found. In the case of a coumarin solution in a polar solvent, the absorption frequency of the C=O vibrations is markedly displaced, namely, to 1700 cm^{-1} for the coumarin molecule in its ground electronic state. This shift is attributed to the presence of a hydrogen bond between the $CHCl_3$ molecule and the C=O group of coumarin in its ground electronic state. For the electronically excited state, the frequency of the C=O mode shifts to 1740 cm^{-1}, *i.e.*, it is close to that in a non-polar solvent. This points to the absence of a hydrogen bond in the electronically excited state.

In the examples considered above, we virtually did not mention studies dealing with femtosecond processes in proteins. Detailed information concerning these processes has been reported.[53, 57, 134–138]

VII. Control of intramolecular dynamics and an elementary chemical event

Chemical reactions are controlled at the macroscopic level by changing reaction conditions — pressure, temperature and other parameters. Attempts at controlling an elementary reaction by changing the character of the interaction of light with reactants have been undertaken long ago.[139]

The development of femtosecond pulses, which permit one to change the transition state dynamics, opens new, in principle, opportunities of controlling an elementary chemical reaction and, hence, the product yield. Let us consider various approaches which can be helpful in developing this line of research.

1. Non-statistical unimolecular reactions. The approach using non-statistical unimolecular reactions is based on the generation of vibrationally excited molecules with such an intramolecular distribution of vibrational energy that the unimolecular reaction proceeds to give desired products. The attempts to perform selective reactions in this way have been made for one-photon[140] and infrared multiphoton excitation.[141] However, it was found that unimolecular reactions induced by photoactivation took place in line with statistical laws, according to which the rate constants for these reactions do not depend on intramolecular energy distribution but are dictated by the total vibrational energy. This was due to the fact that intramolecular energy redistribution occurs faster (within 0.1–1 ps) than decomposition of the molecule. In order to control the decomposition route and to obtain desired products, it is necessary to localise the excitation energy in a particular fragment of the molecule; this should be done during the reaction.

This method of control can be realised using femtosecond pulses. Under the action of these pulses, the molecules are excited very rapidly; due to multiphoton absorption, the excitation energy can be so high that decomposition occurs faster than the intramolecular energy redistribution; the initial intramolecular distribution of the excitation energy can be changed by varying the amplitude and phase characteristics of the femtosecond light pulse.

The reactions considered above can serve as examples of processes in which femtosecond pulses are used to study non-statistical decomposition of vibrationally excited radicals. The first example is decomposition of the highly vibrationally excited $(R^1CO)^*$ and $(R^2CO)^*$ radicals (R^1 = Me, R^1 = Et) in their ground electronic state.[76] These radicals are formed upon decomposition of ketone molecules R^1COR^2 induced by a femtosecond pulse and taking 50–100 fs. When the vibrational excitation energy is ~ 65 kcal·mol^{-1}, rupture of the C–C bond in the acetyl radical takes place in 500 fs. This decomposition period is ten times as long as that calculated in terms of the RRKM statistical theory. According to the researchers' viewpoint, upon decomposition of the parent ketone molecule, the vibrational energy in the resulting $(R^1CO)^*$ and $(R^2CO)^*$ radicals is distributed non-uniformly; more precisely, only a minor portion of this energy has evolved onto the reaction coordinate along the C–C bond. During 500 fs, the vibrational energy does not have time to be redistributed; therefore, this coordinate receives less vibrational energy than expected in accordance with the statistical law.

The second example is stepwise decomposition of cyclic ketones with various numbers of carbon atoms (n = 4, 5, 6 and 10). After excitation of the molecules of cyclic ketones by a femtosecond pulse, the first C–C bond is cleaved to give radicals of the $[CH_2(CH_2)_{n-2}C=O]^*$ type in their ground electronic state. This cleavage requires ~ 50 fs. The species thus formed contains a store of non-statistically distributed vibrational energy, which is much greater than the energy needed to split off the carbon oxide. It was shows[78] that the rates of decomposition calculated by the statistical theory are two to four orders of magnitude lower than the measured rates. It was also noted that the measured decomposition rates virtually do not depend on the number of atoms in the decomposing species, whereas calculations in terms of statistical theory predict a decrease in the rate of decomposition by orders of magnitude following the change in the number of carbon atoms from 4 to 10. These results can be interpreted only by assuming that biradicals formed in the ground electronic state have a substantial energy of vibrational excitation in the reaction coordinate sufficient for their subsequent decomposition. Since decomposition proceeds faster than the energy redistribution over various vibrational modes, initially, there is much more energy in the reaction coordinate than would be there after statistical redistribution of the vibrational energy.

Hence, if decomposition can follow two channels, then, using femtosecond pulses, it is possible to create molecules in which the vibrational energy located on the reaction coordinate of one channel exceeds the threshold value, while that on the reaction coordinate of the other channel is lower than the threshold value. Thus, by varying the fraction of the vibrational energy on one or another reaction coordinate, one can direct the reaction along one channel.

2. Dynamics of wave packets. The known methods for laser separation of isotopes proposed by Letokhov[141] are based on small isotope shifts in the spectra of atoms and molecules. To implement these methods, monochromatic laser sources with tuned wavelength are required. An experiment dealing with the laser separation of bromine isotopes using femtosecond pulses has been described.[142]

The new approach to the separation of isotopes makes use of specific features of the wave packet dynamics. If wave packets for the isotopes of bromine molecules ($^{79}Br_2$ and $^{81}Br_2$) are created,

the wave packet dynamics in the two isotopic molecules will be different. During short periods of time, the differences related to the dissimilar vibration frequencies are insignificant. However, the time evolution of wave packets goes through periodic destructions and revivals.[37] Therefore, the deviations of the wave packet dynamics are accumulated in the isotopic molecules, and at times of the order of tens of nanoseconds, they would be sufficient for choosing the instant for acting upon the molecule of only one isotope by another femtosecond pulse. Averbukh *et al.*[142] employed a 100-fs pulse tunable in the region of 550 – 590 nm for the formation of wave packets. The second femtosecond pulse having the same duration and a wavelength of 340 nm was used for ionisation. The delay between the pulses was varied up to 50 ps. Ionised molecules were detected using a time-of-flight mass spectrometer. An isotope ratio of ~250% was attained.

3. Action on the PES. Femtosecond pulses can be used to control the dynamics of the transition state by changing the PES at the required time instant. Let us consider a simple example. Suppose that there are two crossing terms with different types of symmetry; a wave packet moves along one of the terms, without 'feeling' the other term, and forms products C and D. At the instant the wave packet approaches the crossing point of the terms, a femtosecond pulse acts upon the PES. The pulse would induce splitting of the terms. As a consequence, the wave packet continues moving but along the other potential term; this may give products A and B. This approach to the control of the reaction has been proposed and implemented in experiments on photodissociation of OClO.[143] The reaction proceeds by two channels

$$\mathrm{OClO} + h\nu \begin{cases} \rightarrow \mathrm{O} + \mathrm{ClO} \\ \rightarrow \mathrm{Cl} + \mathrm{O_2} \end{cases}$$

For low intensities of the pump pulse, both products are formed in a ratio corresponding to known published data. However, as the intensity of the pump pulse increases, the rate along the channel resulting in molecular oxygen starts to increase non-linearly, while the rate along the channel yielding ClO decreases. The time delay between the pump and probe pulses in these experiments was 40 ps. In the authors' opinion, these changes are due to distortions of the potential energy surface. The following model is possible: the pulse induces the formation of the electronically excited state $^2A_2$ ($^2A_2 \leftarrow X\,^2B_1$). This is followed by internal conversion to the $^2A_1$ electronic state, from which dissociation of OClO takes place to give ClO. Transition to the $^2B_2$ state is hindered; therefore, the amount of molecular oxygen formed is small. Upon an increase in the intensity of the pump pulse, the PES is distorted and transition to the $^2B_2$ state occurs much more easily; therefore, the fraction of the molecular oxygen increases. The yield of molecular oxygen increases following an increase in the pump pulse intensity (I) in proportion to I^4. In the study cited, the $\mathrm{ClO} : \mathrm{O_2}$ ratio varied by a factor of 12 and the intensity of the excitation field reached a value of 1.5×10^{12} W cm^{-2}.

It should be noted that intensities of 10^{18} W cm^{-2} can be attained in a field of focussed femtosecond pulses; therefore, the light field strength can reach 10^{10} V cm^{-1}. Thus, we can deal with fields exceeding the intraatomic fields (10^9 V cm^{-1} for the hydrogen atom). Under the action of so strong fields, distortion of PES can take place for a short period. The use of strong fields for the target-directed distortion of PES would apparently be an object of the future studies.

4. Dynamics of non-adiabatic transitions. A scheme for controlling the molecular evolution with the use of non-adiabatic transitions up and down in energy was first proposed by Tanor and Rice.[144] The scheme assumes the possibility of acting at a required instant upon the wave packet, generated by a pump pulse, by another pulse in order to bring the system to a different state. This approach is illustrated by Fig. 11, which shows the variation of the potential energy along the reaction coordinate for two electronic terms. Let us consider the molecule ABC. If there is

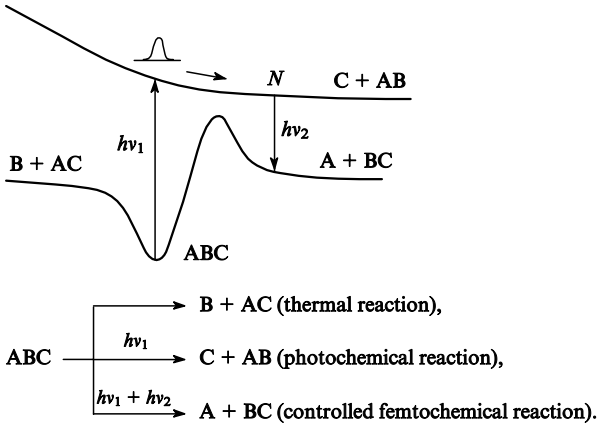


Figure 11. Scheme for the control of the reaction using non-adiabatic transitions performed at definite time instants.

a high potential barrier on the right, only B and AC can be formed as the reaction products in the case of thermal activation. Upon photoactivation by stationary light, the reaction yields C and AB. Irradiation with a femtosecond pulse gives a wave packet, which moves along the direction marked by the arrow. In femtochemistry, the wave packet dynamics is controlled in the real-time mode. By acting on the molecular system by a femtosecond pulse at the instant the wave packet reaches point N (to shift it down in energy to the right slope of the potential barrier), the reaction can be directed at the selective formation of only products A and BC. It should be emphasised that in terms of the model considered, these products cannot be obtained using other activation methods. The formation of iodine molecules in different electronically excited states[145] and the formation of Na^+ or Na^{2+} ions induced by a pair of femtosecond pulses with different time delays between the pulses[146] can be regarded as experimental illustrations of this approach. However, no convincing examples of the experimental use of this type of control can be found in the literature yet.

5. Orientation dynamics — control of the geometry of reactant approach. The efficiency of a reaction both in the gas and in the condensed phases is known to depend substantially on the mutual orientation of the colliding partners. In the gas phase, a specified orientation of one reactant with respect to the other is usually attained in crossed molecular beams on application of uniform or non-uniform electric fields. In recent years, attempts to use electromagnetic field pulses for creation of molecules with a predominant direction of the dipole moment have been made more and more often. Femtosecond pulses are used for the formation of coherent rotational wave packets in the ground electronic state.[17, 147, 148] In this case, the orientation varies with time while repeating the previous orientations rather than remaining static, as in the case where conventional techniques are used. The control of the geometry of reactant approach can be clearly demonstrated in relation to bimolecular reactions in VDWC. An example is provided by bimolecular reaction *16* in the IH···CO_2 van der Waals complex (see Table 3) considered above. Under the action of the first femtosecond pulse, the I—H bond is cleaved, and the hydrogen atom starts moving towards CO_2. At a certain instant, the second femtosecond pulse creates a coherent rotational packet in the CO_2 molecule. By changing the time delay between the first and second pulses, one can control flying of the hydrogen atom towards CO_2 molecules having different orientations, *i.e.*, study the dependence of the product yield on the geometry of reactant approach. Naturally, there can be any other molecule in place of CO_2.

6. Coherent dynamics. The approaches being developed most successfully are those in which phase characteristics of the laser pulses are used. Several theoretical approaches have been elaborated; they envisage the use of phase characteristics of the exciting

light for controlling the yield of products in an elementary reaction. Shapiro and Brumer [149] proposed a scheme similar to the scheme of the interference of light which had passed along two channels and had arrived at the initial point with different phases. Similarly, two wave packets characterised by the wave functions ψ_1 and ψ_2 can follow different paths. If they come to the same final state, the probability of occurrence in this state is proportional to the total wave function squared. Hence, the amplitudes of the two wave functions should be summed up before squaring. The probability of the occurrence of the system in a particular state depends on the cross term which includes the phases of different wave functions. This approach has been implemented experimentally, for example, by Zhu *et al.*[150] A beam of DI molecules was excited by two laser beams, by one photon ($\lambda = 118$ nm) from the first beam and three photons ($\lambda = 354$ nm) from the second beam. The phase correlation between these beams was varied by passage of both light beams through a transparent gas medium: the refractive indices at different wavelengths are different; therefore, by varying the pressure inside the gas cell, one can control the phase. The excited DI molecules decay along two channels, $DI^+ + e^-$ and $D + I(^2P_{1/2})$. As expected, the relative yield is a sinusoidal function of the difference between the phases.

For creating a nuclear wave packet with definite phase and amplitude characteristics, the use of chirped femtosecond pulses has been proposed;[151] this would markedly simplify the control schemes for elementary chemical processes. First, under the influence of these pulses, multiphoton processes of light absorption occur more easily. Second, a femtosecond pulse is spectrally broad and it becomes possible to generate vibrational and rotational wave packets with different initial phases of the Fourier components by changing the phase characteristics of the pulse. Third, two wave packets with the wave functions ψ_1 and ψ_2 can be produced. The probability that the system occurs in a particular state depends on the cross term, which includes phases of different wave functions.

The influence of the chirp on the intramolecular dynamics and on photophysical and photochemical processes involving diatomic molecules is illustrated by examples presented in Table 4. It can be seen that the quantum yields in the processes considered above depend on the chirp of the pump pulse. When the pump pulse intensity is high (strong fields), the quantum yield of fluorescence of dyes in solution depends on the sign of the chirp (see the last example in Table 4).

Let us illustrate the variation in the vibrational dynamics for the iodine molecule in the electronically excited state as a function of the chirp sign.[37] For this purpose, we shall consider the results of calculations of the wave packet dynamics in the Wigner representation of the quantum state of the system, *via* the 'coarse-grained' Wigner distribution function in the phase space using relation (15). These calculations utilised the results of experiments performed under conditions where all the parameters including the magnitude of β remained invariant, only the sign of the chirp being changed. The dependence of the Husimi function W_H on the classical coordinate and the momentum (characterised by the change in the degree of blackening) for different times elapsed after absorption of the pump pulse is illustrated in Fig. 12. The density maps corresponding to wave packets formed by the pump pulse with $\beta = -2000$ fs^2 are shown at the left; those for the pulse with $\beta = 2000$ fs^2 are on the right. It can be seen that the wave packets formed by the pulse with a negative chirp retain localisation for much longer periods. This means that the intramolecular dynamics of atoms can be influenced by controlling phase characteristics of the pulses. By changing synchronisation of the atomic motion in the transition state and by varying phase characteristics of the pump pulse, one can control the transition state dynamics, *i.e.*, the product yields in an elementary chemical reaction.

Table 4. Examples of influence of the chirp on some physicochemical processes.

Process	Result	Ref.
$Na_2 + n\,h\nu \rightarrow Na^+ + e$ $Na_2 + n\,h\nu \rightarrow Na_2^+ + e$	the quantum yield of the ions depends on the chirp	152
$NaI + h\nu_1 \rightarrow NaI$ $(NaI)^* \rightarrow Na + I$ $(NaI)^* + h\nu_2 \rightarrow Na^* + I$	the Na*/Na ratio depends on the chirp	153
The vibrational dynamics of I_2 in the electronically excited state	the vibrational dynamics depends on the chirp	37, 154
The rotational dynamics of D_2 and N_2 in the ground electronic state	the rotational dynamics depends on the chirp	17, 147
Fluorescence of LD690 dye molecules	the fluorescence quantum yield depends on the chirp	155

In recent years, experimental works have been published, which demonstrated that the phase characteristics of the pulse can influence appreciably the channels of product yields in photodissociation of polyatomic molecules.

Multiphoton photodissociation of CH_2I_2 has been studied.[156] The normal channel for the photodissociation of this molecule is the formation of iodine atoms in the electronically excited and ground states and the CH_2I radical. However, it is known that in the case of one-photon absorption in the vacuum ultraviolet region (> 9 eV), one more channel exists ($\sim$1%), which affords molecular iodine in the $D'^3\Pi_g$ state and, to a small extent, in the electronically excited *f* states. In the study cited, the dependence of the multiphoton photodissociation of CH_2I_2 on the sign and the magnitude of the linear chirp was measured. Pulses with a carrier wavelength of 624 nm and with a duration of 47 fs were used in the experiments. Excitation was performed both by pulses centred at 624 nm and by pulses obtained by doubling the frequency, *i.e.*, centred at 312 nm. The value of the spectral chirp β was varied from -2000 to 2400 fs^2. The well-known fluorescence of the molecular iodine at 342 nm is a consequence of multiphoton absorption of light with a wavelength of 624 nm. The maximum yield of molecular iodine in the electronically excited state D' was observed at $\beta = -500$ fs^2, while the minimum yield was found at $\beta = -2400$ fs^2. The yield of molecular iodine varied by a factor of 2.9. The dependence of the product yield on the chirp value was also observed when the CH_2I_2 molecule was excited by pulses with a wavelength of 312 nm. However, the variation of the yield of molecular iodine in the excited state followed the opposite pattern: the highest yield was observed at $\beta = -2400$, whereas the lowest yield was observed at $\beta = -500$ fs^2. The chirp follows a quadratic dependence on the pulse duration. The absence of symmetry in the dependence of the product yields on the chirp relative to the zero chirp indicates that the observed variations of the yields are related to the phase characteristics of the pump pulse rather than to the pulse duration.

The second example is multiphoton photodissociation of ammonia. One-photon excitation with an energy higher than $\sim$6 eV is known to induce decomposition of ammonia to give the NH_2 radical in the ground state X^2B_1 and the hydrogen atom (the first channel).

Excitation of an ammonia molecule to 9.4 eV gives rise to the second channel, reaction *7* (see Table 2).[157]

Multiphoton photodissociation of ammonia under the action of femtosecond pulses centred at 615 nm (2 eV) has been studied.[104] The duration of the transform-limited pulse was 50 fs. To have an energy of excitation of the molecule higher than 9.4 eV, five photons should be absorbed. Since the excitation energy equal to 10 eV is still insufficient for ionisation, the molecule decomposes according to the two above-noted channels. The NH radical formed in photodissociation *7* occurs in the

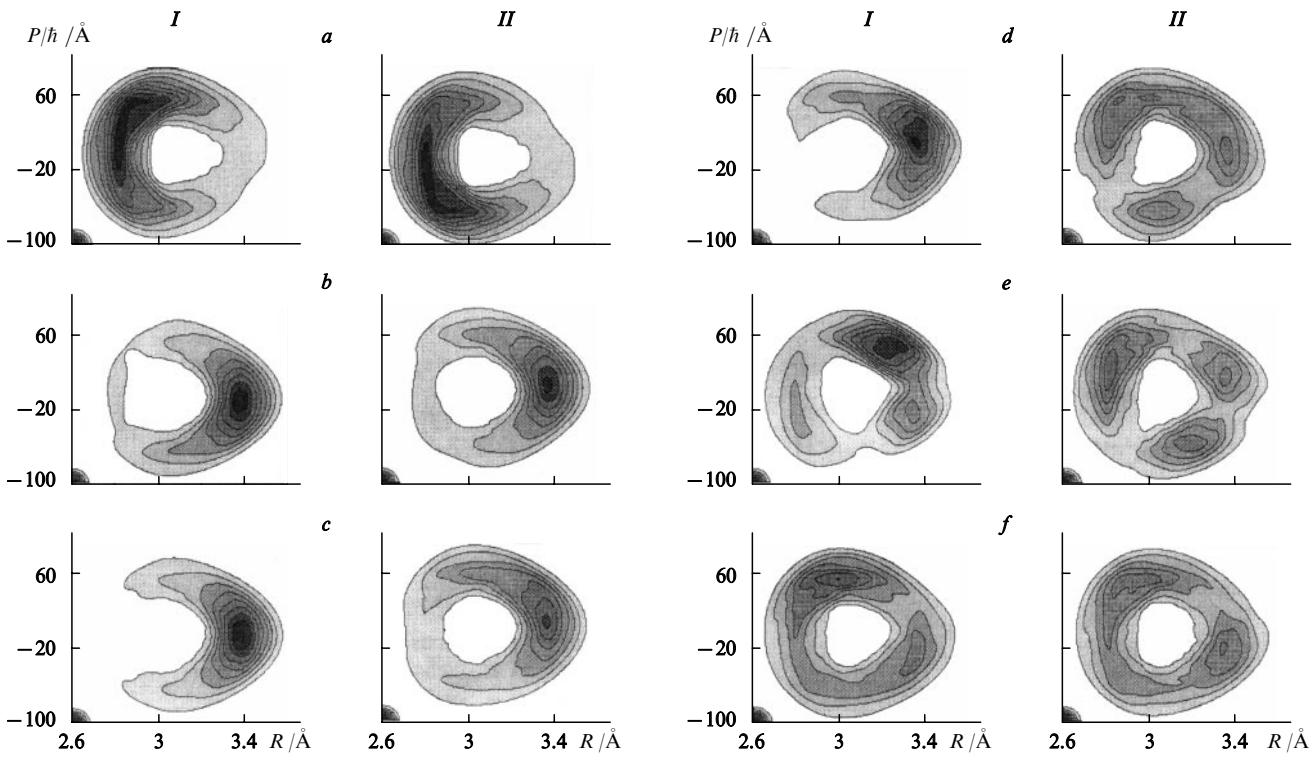


Figure 12. Dependence of the Husimi function on the classical coordinate (abscissa) and the momentum (ordinate) at different times (t) after absorption of the pump pulse for $\beta = -2000$ fs^2 (I), 2000 fs^2 (II).[37]
t /fs: (*a*) 0, (*b*) 150, (*c*) 750, (*d*) 1950, (*e*) 3150, (*f*) 4960.

electronically excited state $c^1\Pi$, from which fluorescence related to the $c^1\Pi \rightarrow a^1\Delta$ transition is observed at 324 nm.[157] Thus, the quantum yield of the ammonia decomposition according to the second channel can be judged by fluorescence intensity, which is proportional to the concentration of the NH($c^1\Pi$) radical. In the study cited, the variation of the integral fluorescence (F) in the spectral region of 300–340 nm was recorded as a function of the intensity of pump pulses (I). It was shown that experimental data are described adequately by the equation

$$F = A(\beta)(I)^5,$$

where $A(\beta)$ is the coefficient depending on the spectral chirp. This relation was used to determine the coefficient $A(\beta)$, expressed in relative units and reflecting the influence of the chirp on the photodissociation of ammonia by the second channel. Figure 13 presents the $A(\beta)$ dependences normalised to the $A(\beta = 0)$ values. The fluorescence intensity is proportional to the number of NH($c^1\Pi$) radicals formed; therefore, the plot in Fig. 13 reflects the dependence of the quantum yield of these radicals in relative units on the value of the spectral chirp. The ratio of the maximum quantum yield to the minimum quantum yield equals 12. It should also be noted that the variation of the quantum yield is non-symmetric with respect to the zero chirp; this implies that the observed changes are mainly related to the phase characteristics of the femtosecond pulse rather than to the pulse duration.

Taking these two reactions as examples, it was demonstrated that the product yields can be controlled using phase characteristics of the pump pulses. However, it has already been noted that the characteristic times of coherence of nuclear wave packets are normally 100–1000 fs. Hence, the reactions of excited molecules should occur over even shorter periods of time; this requires relatively high excitation energies (in the examples considered above, the excitation energies were 10–12 eV). The PES parameters for these energies are unknown; therefore, there arises the problem of determining and analysing these parameters for complex molecular systems for which quantum-chemical calcu-

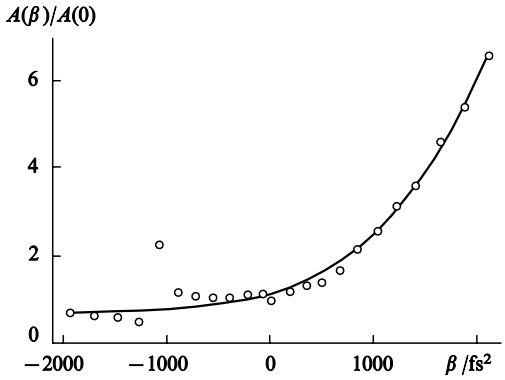
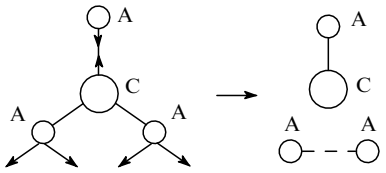


Figure 13. Yield of the product NH($c^1\Pi$) *vs.* the value of the spectral chirp.

lations are difficult to perform. In this connection, some researchers are developing a different approach. Thus it has been found [158] that a scheme with the use of a feedback with the product yields can be implemented within the framework of optimal control theory; this method permits determination of pulse shape and spectral content. This scheme maximises the yield of a definite product. Experiments of this type have been carried out;[159] the researchers performed automated optimisation of the control of the reaction channels using photodissociation of the $LFe(CO)_2Cl$ molecule (L is cyclopentane) as an example. This molecule contains different bonds between the metal and the ligands (Fe–CO, Fe–Cl and Fe–L). On exposure to femtosecond pulses, products are formed *via* two channels; one channel implies rupture of only one Fe–CO bond, while according to the other channel, all the ligands, except Cl, are detached. Both products are detected by means of a mass spectrometer. The measured ratio of the product weights is fed to a computer and is processed in terms of a definite

algorithm. An instruction is devised according to which the phase characteristics of a femtosecond pulse change in such a way as to ensure a higher ratio of product weights. The minimum ratio is 1.2, and the maximum ratio is 4.9. In the opinion of the authors, the global minimum has not yet been found. Therefore, it is expected that this range of ratios can be markedly extended.

The effects caused by the chirp are related to the characteristics of the PES and to the wave packet dynamics. The change in the chirp of the pump pulse results in different distributions of the initial phases of the steady states (the superposition of which makes the wave packet); this influences the dynamics of the atomic motion in the transition state. The qualitative scheme for the control of the product yields by phase characteristics of the femtosecond pulse is shown below in relation to a planar tetraatomic molecule CA_3:



The standard photodissociation channel for molecules of this type involves rupture of the C–A bond where the vibrational energy is evolved on the stretching vibration, which determines the reaction coordinate. Let as assume that the wave packet consists of antisymmetric and bending vibrations, which determine the reaction coordinate by a concerted mechanism. If the motion of A atoms is so synchronised that two bonds are synchronously stretched and their bending vibrations, occurring in parallel with stretching, participate in the formation of the new A–A bond, the concerted mechanism would be realised more efficiently. It appears that synchronisation of the motion of atoms can be used to make a fairly large class of reactions follow a concerted mechanism.

Examples of control of reactions proceeding in condensed media upon one-photon absorption have been considered above. Studies [83, 84] of one- and two-proton transfer in the 2,2′-bipyridine-3,3′-diol molecule induced by femtosecond pulses in solutions was considered in Section V. Since these processes take place over periods of $< 50-100$ fs, it is reasonable to assume that the two-proton transfer follows a concerted mechanism. Then, by changing the chirp of the pump pulse, one can change the ratio of the channels of one- and two-proton transfer. Petrukhin and coworkers [160, 161] studied one- and two-proton transfer in 2,2′-bipyridine-3,3′-diol induced by femtosecond pulses in a hexane solution. The pumping was performed by pulses centred at a wavelength of 308 nm, while probing was accomplished by a supercontinuum pulse in the spectral range of 400–620 nm. The time evolutions of the photoinduced absorption spectra in the 400–470 nm range and of the photoinduced 'brightening' in the 470–620 nm range were monitored in experiments. It was found that photoinduced 'brightening' at a wavelength of 500 nm was due to stimulated emission from the excited diketo tautomer under the action of the probe pulse, while the photoinduced absorption at $\sim$450 nm is due to the $S_n \rightarrow S_1$ transitions in both the monoketo and diketo tautomers. It was found that the time evolution of brightening and absorption depends on the chirp of the pump pulse. In the opinion of the researchers, this is indicative of the fact that the ratio of the channels of one- and two-proton transfer is determined by both the sign and the magnitude of the chirp of the pump pulse. Hence, the reaction can also be controlled in the condensed phase.

VIII. The prospects of femtochemistry

In our opinion, the research in femtochemistry will develop vigorously in the near future according to four main lines.

The first line is the control of chemical reactions. We believe that the control of chemical reactions and physical processes aimed at obtaining desired products will be among the most promising fields of development of femtochemistry. In the majority of studies which have been considered in this review, pulses with durations of several tens of femtoseconds have been employed. Only a few studies operating with femtosecond pulses shorter than 10 fs are available. Obviously, chemical laboratories would be gradually equipped with lasers able to generate pulses with ever decreasing durations. This means that the coherent chemistry will cover more and more objects; it will become possible to use coherent wave packets even for those systems in which stochastisation occurs very rapidly. First, due to the shortening of a pulse, its spectral width increases; hence, the number of steady states included in the nuclear wave packet formed and the set of the initial phase distributions will increase. This markedly extends the range of variation of the amplitude and phase characteristics of the femtosecond pulse and thus enhances the capacity of controlling the dynamics of the molecular system in the transition state. Second, for very short pulse durations, localisation of the nuclear wave packet can reach even 0.005 Å. This makes it possible to increase the accuracy of controlling the orientation dynamics and non-adiabatic transitions. In other words, shortening of femtosecond pulses would provide the possibility of extending the number of molecular systems suitable for realisation of coherent reactions and of increasing substantially the selectivity. It is by virtue of femtosecond pulses that new schemes of controlling the processes such as photoionisation, fluorescence and light absorption would be implemented experimentally and substantiated theoretically in the near future. It appears that these schemes would include several femtosecond pulses (with different chirps) and time delays between them. Schemes of this type have already been proposed (see, for example, studies [162, 163]). We expect that the development of the above-considered approaches to the control of chemical reactions would result in the near future in the development of selective environmentally clean chemical technologies. Apparently, these technologies would be economically rational only for the preparation of expensive materials in small quantities. The approaches in question will become especially promising for the control of functional properties of nanostructures.

The shortening of the duration of pump pulses down to values at which the 'energy span' (ΔE) will be comparable with the bond energy (for a pulse duration of 1 fs, the ΔE value is $\sim$40 kcal mol^{-1}) will result in the development of new schemes for the control of chemical reactions. With sufficiently short pulses, it will be possible to generate electron wave packets in which several electronic quantum states are excited simultaneously. One can hope that schemes for controlling the electron motion in these packets would be designed.

The second line is the wave packet dynamics in the ground electronic state. Most of the examples considered in this review, especially for coherent chemistry, referred to reactions in which the reactant was in the electronically excited state. This is due to the fact that it is much more difficult to form vibrational packets in the ground electronic state than in an electronically excited state. As noted above, experimental methods are being currently developed [46–50] for the formation of coherent vibrational wave packets with excitation energies both higher and lower than the dissociation threshold. In this connection, two factors are significant: the decrease in the duration of femtosecond pulses and development of multi-pulse methods. The setting of shorter pulses in the practice of chemical experiment would substantially improve the possibilities of formation of coherent vibrational wave packets in the ground electronic state. Indeed, in this case, it is easier to use several femtosecond pulses to generate the required wave packets due to downward non-adiabatic transitions. The possibility of creating vibrational wave packets in the ground electronic state would appear as a result of multiphoton absorption of infrared femtosecond pulses. The increase in the probability of this

absorption is due to the fact that it would be possible to form a wave packet on the basis of high-frequency symmetrical vibration modes; consequently, the multiquantum factor for absorption would markedly decrease. We believe that the number of investigations into the coherent dynamics of the transition state for reactions in the ground electronic state will essentially increase in the near future.

The third line is the time evolution of the structural changes with femtosecond temporal resolution. Femtosecond pulses with a duration of 10^{-14} s allow the detection of shifts equal to 0.1 Å; however, conversion of the response function into the distance between the atoms is rather easy for diatomic molecular systems but very difficult for polyatomic molecular systems. In other words, the values measured in spectroscopic experiments cannot be transformed in the general case into the coordinates of moving atoms. An alternative variant is to develop methods that allow determination of the structures of intermediate species with a femtosecond temporal resolution.

By irradiating a target with a powerful femtosecond pulse, one can generate electron or X-ray pulses; measurement of electron or X-ray diffraction provides information on the time evolution of the positions of nuclei. Electron diffraction occurs only in the gas phase; X-ray diffraction can also be studied in condensed media. At present, these approaches are used in procedures with picosecond and sub-picosecond temporal resolution.

Time-resolved ultrafast electron diffraction has been used to study photodissociation of CF_2I_2 on irradiation with light pulses ($\lambda = 307$ nm).[22] It was found that abstraction of two iodine atoms is completed within $\sim$4 ps; the structure of the resulting CF_2 radical was determined. The radical is formed in the ground electronic state with the following interatomic distances: C–F 1.30 ($\pm$0.02) Å, F···F 2.06 ($\pm$0.06) Å.

No convincing examples of using time-resolved X-ray diffraction have been reported yet. Therefore, study of the dynamics of positions of the cadmium atoms in a film containing 83 layers of cadmium atoms after heating the film by a femtosecond light pulse[26] can be referred to as an example. In this study, the dependence of the intensity of the diffraction signal on the delay between the heating light pulse and the probe X-ray pulse was measured. The experimental results obtained bear information on the time evolution of the shift of cadmium atoms from the corresponding layers with a sub-picosecond temporal resolution.

Evidently, spectroscopic measurements in dynamic investigations would be gradually replaced by measurements of this type.

The fourth line of research is femtochemistry with spatial resolution. Femtosecond spectroscopy has provided methods that allow investigations to be performed with high temporal resolution. Using scanning tunnelling microscopy, surface images (including those containing single adsorbed species) with angstrom spatial resolution were obtained for the first time; the energy distribution of surface electrons and the migrations of surface atoms have been measured; new nano-scale surface structures have been assembled. New spectroscopic techniques were developed which allow measurement of the vibrational spectra of single adsorbed species using a scanning tunnelling microscope, detection of single paramagnetic centres on the surface of oxidised metals, study of photoisomerisation of individual molecules, *etc.*[164–166] However, the number of problems the solution of which requires methods with high temporal and spatial resolution constantly increases. In recent years, several approaches to the development of these methods have been used.

The first approach is aimed at creating the possibility of performing detection by light pulses with high spatial resolution. However, the light pulses in the conventional optics are subject to a diffraction limit, which makes impossible a spatial resolution of less than $\sim\lambda/2$. In several recent years, so-called 'near-field optics' which permits a substantial improvement of the spatial resolution has been developed. The simplest implementation of the near-field optics is to replace the set of lenses by pointed optical light guide with the hole diameter d at the tip smaller than the wavelength. The near field decays rapidly with an increase in the distance from the light guide. Therefore, the specimen is mounted at distances less than d. Within the framework of this approach, it is possible to perform femtochemical investigations with a spatial resolution of tens of nanometers. The schemes used for the excitation of molecules have been reported.[167, 168]

Another approach is based on combination of femtosecond pulses with photoelectron spectroscopy. Light pulses generate electrons, which can be detected with high spatial resolution. This approach has been realised by Secatskii *et al.*[169] The researchers used very sharp silicone pins at the end of which femtosecond pulses were focused. These pulses induced two-photon emission of electrons, which was detected by a microscope. It was demonstrated that femtosecond two-photon laser photoelectron microscopy can ensure a spatial resolution of up to 3 nm.

An approach representing an attempt to combine femtosecond pulses with scanning tunnelling microscopy has been reported.[170, 171] Illumination of the tunnel gap with femtosecond pulses was combined with detection of components of the tunnelling current, which follow a non-linear dependence on the intensity of light pulses. In the opinion of the authors, this route could provide both high spatial and high temporal resolutions.

It has been noted[172] that modern chemistry cannot be conceived without coherence and high spatial and temporal resolutions. It is these points that appear to become important factors in the development of chemistry.

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