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Reviews

Dynamic NMR spectroscopy in studies of the kinetics of photoinduced chemical exchange in solutions

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Modern NMR-based methods of studying the kinetics and mechanisms of reversible photochemical reactions in solutions are surveyed. Detailed consideration of peculiar features of the experimental techniques based on NMR lineshape analysis and double resonance NMR and used for the determination of the effective rate constants for and quantum yields of photoinduced chemical exchange processes is presented.

Key words: dynamic NMR spectroscopy, nuclear Overhauser effect, biresonance NMR, double resonance NMR spectroscopy, photochemistry, photoisomerization, quantum yield, photoinduced molecular dynamics, photoinduced chemical exchange, NMR lineshape, spin saturation transfer, nuclear spin magnetization transfer, inverse fractional nuclear spin population transfer, kinetics of photoinduced chemical exchange, reversible chemical reactions; spin-lattice relaxation.

Introduction

Modern photochemistry is a rapidly developing branch of chemical science. The kinetics of photochemical processes can be determined using a variety of methods that have well been documented in original studies, monographs, and reviews.[1—18] Particularly, mention should be made of femtochemistry.[2,7] Considerable progress made in this avenue of photochemical research in the last two decades is due to intensive advancement of pulsed laser technologies that made it possible to investigate very fast photochemical processes with the characteristic times from a few to a few hundred femtoseconds.[2,7] Lasers designed at the moment will allow processes with a characteristic time of $8 \cdot 10^{-16}$ s (attosecond time scale) to be studied.

Modern photochemistry includes a number of methods that are based on spectrophotometric detection of both initial compounds and reaction products[1—8,10,14,15,17,19—24] and on luminescence studies[8,12,15,25—27] in the UV, visible, and IR spectral regions.[6,12,15,28,29]

Yet another group of methods for investigation of the kinetics of photochemical processes can conditionally be termed "magnetic-resonance" techniques for detection of products and initial reactants because they are based

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on ESR[11,13,16,30] and NMR[30,31] spectroscopies. We will consider the NMR-based methods in more detail.

Determination of the quantum yields of irreversible photochemical reactions[19,30,31] (in particular, photoisomerization reactions[20—22]) is an efficient application of NMR spectroscopy. Using photochemically induced dynamic nuclear polarization, one can study the physicochemical properties of short-lived radical species and the kinetics of radical chemical reactions (photodecomposition of molecules, phototransfer of electrons, *etc*.).[30—32] Without dwelling on details and specific features of particular radiospectroscopic techniques, it should be noted that, by and large, they concede to the methods based on other principles (see above). For instance, a rather large duration of the radiofrequency probe pulses in modern high-resolution NMR spectrometers (a few microseconds) imposes a limitation. Nevertheless, radiospectroscopic techniques are successfully used in those cases where photochemical methods of investigation are inefficient. Additionally, radiospectroscopic methods of investigation of photoprocesses offer unique possibilities compared to other physicochemical techniques, which makes them a valuable and actual tool of modern physical chemistry.

The aim of this work was to review modern magnetic resonance methods of studying the kinetics and mechanisms of reversible photochemical processes, namely, photoinduced chemical exchange (PICE) reactions. The simplest reactions are shown in Scheme 1.

Scheme 1

$$\mathrm{A} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} \mathrm{B} \qquad (a)$$

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{B} \xrightarrow{k} \mathrm{A} \qquad (b)$$

$$\mathrm{A} + \mathrm{B} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} \mathrm{C} \qquad (c)$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{h\nu} \mathrm{C} \xrightarrow{k} \mathrm{A} + \mathrm{B} \qquad (d)$$

A, B, and C are molecules, isomers, conformers, *etc*.;
k is the rate constant for the dark chemical reaction.

Particular attention is paid to the description of the NMR-based methods of determination of the effective rate constants for PICE using NMR lineshape analysis, biresonance inverse fractional nuclear spin population transfer, and spin saturation transfer. NMR studies of PICE are aimed at solving problems in molecular electronics (design of photoswitches, memory devices, photosensors, *etc*.[33—37]). They can also favor the understanding of the mechanisms of cyclic chemical reactions in living organisms upon perception of light information[25,38,39] and be useful in dose estimation and location of X-ray irradiated regions in living organisms.

1. Determination of the kinetics of photoinduced chemical exchange: theoretical and methodological background

1.1. Terminology

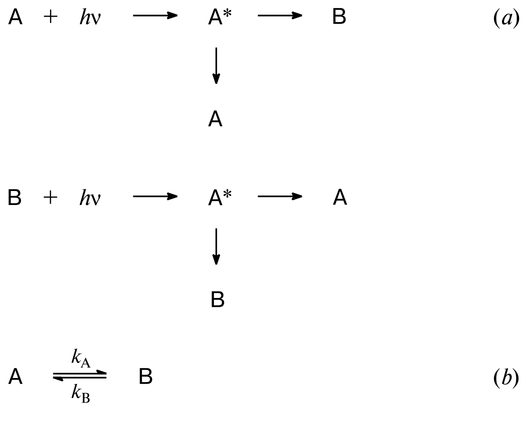
Traditionally, dynamic NMR spectroscopy is used to determine the kinetic characteristics of dark reversible chemical processes in solutions.[32,40] In a narrow (classical) sense dynamic NMR spectroscopy is used for studying the kinetics of reversible processes under the conditions where the reactants are in themodynamic equilibrium.[31,32,40—47] Two decades ago, an extended interpretation of dynamic NMR spectroscopy was proposed (see monograph[31]). In particular, a general formalism of the description of complex spin systems involved in nonstationary chemical reactions of arbitrary order was developed based on the density operator.[31] Thus, NMR spectroscopy can be used for studying reversible and irreversible stationary and non-stationary processes occurring under equilibrium and, which is of paramount importance, nonequilibrium conditions. The equations describing the dynamics of spin systems in the framework of general formalism and the classical modified Bloch equations for the chemical systems characterized by first-order reactions[31] have the same form. This fact is of fundamental value because it indicates a high degree of generalization of the modified Bloch equations and substantiates their use for solving a wide range of problems, in particular, studying the kinetics of reversible first-order photochemical reactions. At the same time, determination of the kinetics of reversible photochemical processes using NMR techniques were not considered in detail in the monograph mentioned above.[31] Original studies in this field were reported only very recently.[48—54] Analytical expressions relating the NMR lineshape and the integrated intensities of NMR signals to the effective rate constants for PICE were derived using the modified Bloch equations. We believe that progress in this avenue[48—54] of research on the PICE kinetics based on NMR methods of lineshape analysis, biresonance[55] (*i.e.*, using double resonance NMR spectroscopy) inverse fractional nuclear spin population transfer,[53] and spin saturation transfer[21,33,50,52] can lead to its transformation to a particular branch of dynamic NMR spectroscopy, namely, photodynamic NMR spectroscopy. It should be emphasized that photodynamic NMR spectroscopy is a branch of NMR spectroscopy, which covers various experimental techniques for studying the kinetics, determination of the quantum yields and mechanisms of essentially reversible photoinduced processes. In other words, we use the term "photodynamic NMR spectroscopy" in a narrow sense (methods of investigation of PICE processes, excluding the available NMR methods of studying irreversible photochemical reactions) by analogy with the classical meaning of dynamic NMR spectroscopy as a variety of methods for studying the kinetics of dark reversible chemical processes.[40,41]

1.2. Two-site PICE in the presence of dark chemical exchange: a kinetic scheme

A possible way of extending methodological scope and elaboration of new methods is to use a combination of some known physicochemical methods of investigations. Examples of successful development are provided by such methods as laser magnetic resonance (technique based on ESR, microwave, and IR spectroscopies); optically detected magnetic resonance; and chemically induced, stimulated, and dynamic nuclear polarizations that are based on magnetic-resonance and photochemical methods.[11–13,15–18,28,30,31,38] Recently,[28] a combined approach was proposed, which involves IR and NMR spectroscopies. Dynamic NMR techniques used in the PICE studies can also be treated as specific joint approach. This implies the use of a combination of NMR spectroscopy and IR, UV, or X-ray spectroscopies depending on the aim and scope of a particular study. NMR spectroscopy is used for monitoring photochemical reactions, whereas IR, UV, or X-ray spectroscopy is used for monitoring the power and spectral compositon of the light influencing the substance under study and for "extra" monitoring of photochemical reactions.

Two-site PICE reactions involving fast interconversion of molecular forms A and B under irradiation[50,51] are shown in Scheme 2.

Scheme 2



k_A and k_B are the rate constants for monomolecular dark chemical exchange.

It is assumed that the transition-state (A*) lifetime is 10^{-10}—10^{-12} s. The power of light radiation absorbed by the form A per unit volume solution (W_A) is such that the optical density within the sample under study is $D \ll 1$. A magnetic nucleus X in the molecular form A has a magnetic environment ***a*** or occupies the site ***a***; in molecular form B it is placed in site ***b***. Under photostationary conditions it is required that $d[A]/dt = 0$ (see Refs 50 and 51) in expression (1):

$$d[A]/dt = -W_A\varphi_{AB}\lambda h^{-1}c^{-1} - k_A[A] + \\ + W_B\varphi_{BA}\lambda h^{-1}c^{-1} + k_B[B], \quad (1)$$

where φ_{AB} is the quantum yield of B formation and φ_{BA} is the quantum yield of A formation in reaction (*a*) (see Scheme 2); λ is the laser emission wavelength; *h* is the Planck constant; and *c* is the speed of light. The negative contribution to expression (1) transformed to describe the first-order reactions[40,41] is as follows[50,51]:

$$d[A]/dt = -\tilde{k}_A[A], \quad (2)$$

$$\tilde{k}_A = k'_A + k_A,$$

$$k_A' = W_A\varphi_{AB}\lambda h^{-1}c^{-1}[A]^{-1}, \quad (3)$$

where k_A' is the effective rate constant for PICE and $\tau_A = \tilde{k}_A{}^{-1}$ is the characteristic lifetime of the ***a***-spins. Under photostationary conditions the loss of magnetization in site ***a*** as a result of transformations of the chemical forms A to B (see Scheme 2) is exactly compensated by "jumps" (in terms of the hopping model for elementary acts of chemical reactions)[32,40] from site ***b*** to site ***a*** (*i.e.*, as a result of B→A transformation). The expressions for the site ***b*** have a similar form

$$d[B]/dt = -\tilde{k}_B[B], \quad (4)$$

$$\tilde{k}_B = k'_B + k_B,$$

$$k_B' = W_B\varphi_{BA}\lambda h^{-1}c^{-1}[B]^{-1}. \quad (5)$$

1.3. NMR lineshape for two-site PICE under photostationary conditions

The NMR lineshape for a chemical system with two-site PICE (see Scheme 2) under ptotostationary conditions is given by[50,51]

$$V(\nu) = -C_0\{P[1 + \tau(P_B/T_{2A} + P_A/T_{2B})] + QR\}/(P^2 + R^2), \quad (6)$$

where C_0 is the signal amplitude and

$$\delta\nu = \nu_A - \nu, \qquad \Delta\nu = 0.5(\nu_A - \nu_B) - \nu,$$

$$P = \tau[1/T_{2A}T_{2B} - 4\pi^2\Delta\nu^2 + \pi^2(\delta\nu)^2] + P_A/T_{2A} + P_B/T_{2B},$$

$$Q = \tau[2\pi\Delta\nu - \pi\delta\nu(P_A - P_B)],$$

$$R = 2\pi\Delta\nu[1 + \tau(1/T_{2A} + 1/T_{2B})] + \\ + \pi\delta\nu\tau(1/T_{2B} - 1/T_{2A}) + \pi\delta\nu(P_A - P_B).$$

Here ν is the resonance frequency at which the signal amplitude is determined; τ is the fitting parameter; ν_A and ν_B are the frequencies of maxima of two signals in the NMR spectrum, associated with the sites ***a*** and ***b***, respectively, in the absence of chemical exchange; T_2 is the transverse spin relaxation time; P_A and P_B are the populations of the states A and B, respectively; $P_A + P_B = 1$, and $\tau = P_A/\tilde{k}_B = P_B/\tilde{k}_A$.

It should be noted that expression (6) is given here in the form suitable for writing programs for analyzing the NMR lineshape in order to determine the rate constants and effective rate constants from experimental data[54] (P, Q, and R are intermediate terms and C_0 is the signal amplitude). In this connection τ can be treated as a fitting parameter when using relationship (6) for calculating the NMR lineshape to determine the $\tilde{k}_B$ and $\tilde{k}_A$ values.

By analyzing the changes in the NMR lineshape (6) under irradiation with respect to the initial spectrum recorded in the dark one can estimate the $k_A{'}$ and φ values. Figure 1 shows the pulse sequence for the PICE kinetic studies $(\mathrm{D1{-}P1{-}(FID)}_{(h\nu)})_N$, where D1 is the relaxation delay, P1 is the duration of the radiofrequency probe pulse (its value can be in the range from 0 to 90°), $(\mathrm{FID})_{(h\nu)}$ denotes the irradiation of the chemical system during acquisition of the free induction decay signal, and N is the number of accumulations of the NMR signal. These notations are the same as those used in the handbook.[56] The theoretical changes in the NMR lineshape for degenerate PICE are illustrated in Fig. 2 (calculated using Eq. (6)).

Now we will estimate the lower and upper bounds of the range of effective rate constants for PICE; they can be determined using the technique in question by measuring the ^{1}H NMR spectra. The lower bound is $k'_{\min} \approx 0.1\ \mathrm{s}^{-1}$, which is due to error in determination of the half-width of the NMR line (for diamagnetic compounds, one has ~0.1 Hz). Assuming an NMR spectrometer operating at a frequency of 100 MHz (^{1}H nuclei), $\delta\nu = 10^3$ Hz (corresponds to 10 ppm), and an error in the determination of the line half-width lying between 0.1 to 1 Hz, the maximum theoretically possible effective rate constant for PICE is $k'_{\max} \approx 10^5$—$10^6\ \mathrm{s}^{-1}$. However, so high constants k' correspond to too high power W. For instance, for $k' \approx 10^5\ \mathrm{s}^{-1}$ one should have $W = 25$ kW; this power should be absorbed in a volume of nearly 0.3 mL provided that $\lambda = 300$ nm, $\varphi = 0.5$, and $[\mathrm{A}] = 10^{-3}\ \mathrm{mol\ L}^{-1}$. We believe that the maximum practically attainable effective rate constant is $k'_{\max} \approx 10^2\ \mathrm{s}^{-1}$.

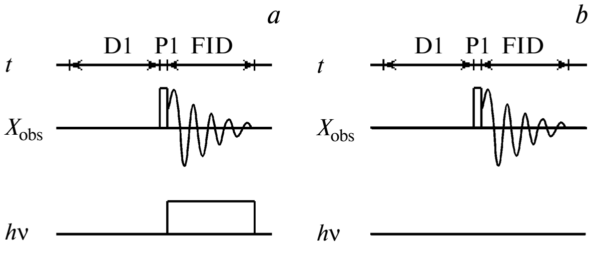


Fig. 1. Pulse sequence for the PICE kinetic studies using NMR lineshape analysis under irradiation with light (*a*) and in the dark (*b*). X_{obs} denotes the radiospectroscopic observation channel (^{1}H, ^{13}C, ^{19}F nuclei, *etc.*) and *h*ν denotes the irradiation channel (electromagnetic radiation in the visible, IR, or UV spectral region) for the system under study.

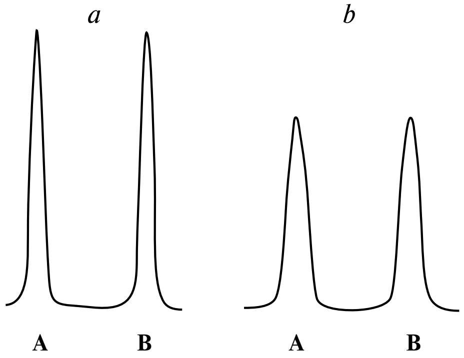


Fig. 2. Theoretical changes in the NMR lineshape for degenerate two-site PICE: initial spectrum ($\nu_A - \nu_B = 10$ Hz, $T_{2A} = T_{2B} = 2.7$ ms) (*a*) and spectrum obtained under irradiation of the system ($k_A{'} = 3.7\ \mathrm{s}^{-1}$) (*b*).

The changes in the NMR lineshape due to PICE and other methodological features were considered in more detail elsewhere.[23,39,54,57—60] The method of PICE studies based on NMR lineshape analysis was evaluated[60] taking *cis*- and *trans*-photoisomerization of planar (β-diketonato)platinum complexes as examples (processes in this system are described by Scheme 1, reaction (*a*)). Technical aspects of the application of NMR spectroscopy to PICE studies have been reported in more detail in the studies mentioned above.[39,50,58—60]

1.4. NMR lineshape in the case of multisite PICE

The NMR lineshape in the case of N-site PICE is given by[54]

$$v(\nu) = \mathrm{Im} - [iC_0 I(i2\pi\nu \mathrm{I} - i\Omega + T_2 + K^{\mathrm{eff}})\vec{P}], \qquad (7)$$

where ν is the resonance frequency at which the signal amplitude is determined; I is the column vector (all N elements of this vector are equal to unity); I is a diagonal unity matrix of dimension $N \times N$; Ω is a diagonal matrix with the elements $\omega_i = 2\pi\nu_i$ (ν_i is position of the ith maximum of the NMR signal in the absence of exchange); T_2 is the diagonal matrix with the elements $T_{21}{}^{-1}$, $T_{22}{}^{-1}$, $T_{23}{}^{-1}$; $\vec{P}$ is the column vector describing the populations of positions 1, 2, ..., N with the elements $p_1, p_2, ..., p_N$; and K^{eff} is the effective PICE rate matrix of dimension $N \times N$ with the elements

$$K_{ii}^{\mathrm{eff}} = \sum_{j \neq i}^{N} k_{ij}^{\mathrm{eff}}; \qquad K_{ij}^{\mathrm{eff}} = -k_{ji}^{\mathrm{eff}}, \qquad j \neq i.$$

Expression (7) can be used in experimental studies of reversible photoprocesses (nondegenerate and degenerate PICE) in multicomponent chemical systems similar to, *e.g.*, degenerate dark twelve-site chemical exchange in lanthanide complexes $[Ln(NO_3)_3(D18C6)]$ and $[Ln(NO_3)_3(18C6)]$ (Ln = La, Pr, and Nd; D18C6 = diaza-18-crown-6, and 18C6 = 18-crown-6).[44—46]

1.5. Dependence of the integrated intensity of NMR signal on the effective rate constants for photoprocesses when using the spin saturation transfer technique under PICE conditions

The Forsen—Hoffmann double resonance NMR (or spin saturation transfer technique) is used for studying the kinetics of reversible dark chemical reactions.[61] A modified version of this technique was employed[62] for qualitative investigations of the mechanisms of irreversible photochemically induced processes. The method[62] consists in effective radiofrequency saturation of the nuclei occupying one position in the molecule of the initial compound due to selective rotation by 90° followed by selective demagnetization due to a magnetic field inhomogeneity pulse[56] (short-term violation of the magnetic field homogeneity along the z axis) and subsequent monitoring of the redistribution of this saturation over the sites corresponding to molecules of the products of the irreversible photoreactions under study. This is a version of the radiofrequency label technique. Then, the field of application of the spin saturation transfer techniques was extended[21,33,50,52] to quantitative determination of the effective rate constants for PICE. In this case, radiofrequency saturation of the nuclei occupying a particular position in the molecule of the initial chemical compound is also used and the distribution of the radiofrequency label among the molecules of products of the processes studied that occur in the probe of the NMR spectrometer is monitored.

The temporal dependence of the longitudinal magnetization in position ***a*** (M_{zA}, which is associated with the chemical form A under two-site exchange described by Scheme 2) can be derived from the modified Bloch equations ignoring the secondary radiofrequency field[50,52]

$$dM_{zA}/dt = (M_{0A} - M_{zA})/T_{1A} - M_{zA}/\tau_A + M_{zB}/\tau_B. \qquad (8)$$

When the magnetization M_{zB} is completely suppressed by the secondary radiofrequency field applied at the corresponding resonance frequency ν_B, the expression for M_{zA} has the form

$$dM_{zA}/dt = M_{0A}/T_{1A} - M_{zA}/\tau_{1A}, \qquad (9)$$

$$1/\tau_{1A} = 1/T_{1A} + 1/\tau_A. \qquad (10)$$

Integration of relationship (9) gives the following dependence of M_{zA} on the duration of irradiation with light $t_{h\nu}$

$$M_{zA}(t_{h\nu}) = M_{0A}[C \cdot \exp(-t_{h\nu}/\tau_{1A}) + \tau_{1A}/T_{1A}], \qquad (11)$$

where the constant C is governed by the M_{zA} value at $t_{h\nu} = 0$. The parameter M_{zA} exponentially decreases until a new constant value

$$M_{zA}(\infty) = M_{0A}\tau_{1A}/T_{1A} = M_{0A}/[1 + T_{1A}(k_A' + k_A)]. \qquad (12)$$

Manifestation of radiofrequency label effects requires meeting certain conditions. This can be illustrated taking reaction (a) in Scheme 2 as an example. Here A* is an intermediate, whose lifetime τ_{A*} should be shorter than the spin-lattice relaxation time T_{1A*}. The stationary version of this technique also requires accumulation of a sufficient number of radiofrequency-labeled nuclei prior to acquisition of the NMR spectrum of the product ($t_{det} \le T_{1B}$).

The field of application of the spin saturation transfer technique is governed by the τ_{1A}/T_{1A} ratio (relative decrease in the observed signal in expression (12)). Assuming that this ratio can vary from 0.9 to 0.1, the parameter τ_{1A} will lie between $0.1 \cdot T_{1A}$ and $9 \cdot T_{1A}$. Usually, one has $T_1 \approx 20$ s for protons, although sometimes the times T_1 can be much shorter (~0.1 s) even for diamagnetic compounds. Therefore, the double resonance technique provides access to a new range of PICE rates and can serve as a counterpart to the method based on NMR lineshape analysis. To estimate the lower bound of applicability of this method, let us set $T_{1A} = 0.1$ s and, hence, $\tau_{A,min} = 0.1 \cdot T_{1A} = 0.01$ s. The upper bound can be estimated assuming $T_{1A} = 30$ s. For instance, the experimentally T_1 value for the hydride protons in complex $[(\mu\text{-H})Os_3(\mu\text{-NH}_2)(CO)_{10}]$ in $CDCl_3$ appeared to be 28 s. Therefore, $\tau_{A,max} = 9 \cdot T_{1A} = 270$ s ≈ 300 s. Thus, the double resonance NMR technique provides access to the effective rate constants for PICE lying between $3 \cdot 10^{-3}$ and 10^2 s^{-1}.

Three experimental methods of k_A' estimation were analyzed in detail.[52] We will briefly outline one of them, namely, a "pseudo-1D nuclear Overhauser effect" (with the pulse sequence D1—$HG_{(h\nu)}$—P1—FID). Here D1 is the relaxation delay, $HG_{(h\nu)}$ is the selective single-frequency decoupling under irradiation of the chemical system with light, P1 is the radiofrequency probe pulse, and FID is the free induction decay. The pulse sequence is shown in Fig. 3. This technique is based on measurements of the limiting values (at $HG_{(h\nu)} > T_1$) of the integrated intensities of NMR signals, $\nu(\infty,\nu_A)$, under and in the absence of irradiation $\nu_D(\infty,\nu_A)$. The corresponding ratio has the form[52]

$$\nu(\infty,\nu_A)/\nu_D(\infty,\nu_A) = (1 + T_{1A}k_A)/[1 + T_{1A}(k_A' + k_A)]. \qquad (13)$$

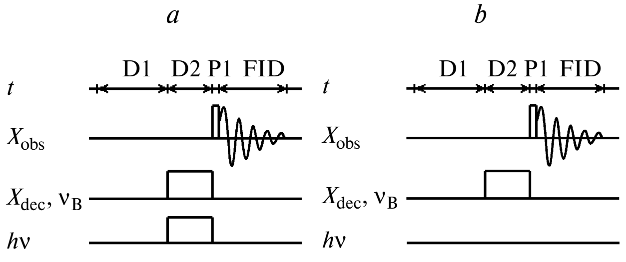


Fig. 3. Pulse sequence for PICE studies using the spin saturation transfer technique under irradiation with light (*a*) and in the dark (*b*). X_{obs} denotes the radiospectroscopic observation channel (^{1}H, ^{13}C, ^{19}F nuclei, *etc.*), X_{dec} denotes the homonuclear decoupling channel, and $h\nu$ denotes the irradiation channel (electromagnetic radiation in the visible, IR, or UV spectral region) for the chemical system under study.

By experimentally measuring the $\nu(\infty,\nu_A)/\nu_D(\infty,\nu_A)$ ratio it is possible to estimate the constant k_A' provided that T_{1A} is determined independently, *e.g.*, using the inversion—recovery (180°—τ—90°) technique.[31,42–45,63] The following essential distinction of this technique from the "pure" 1D nuclear Overhauser effect should be pointed. In the former case, the NMR signal intensity decreases in the course of experiments, whereas in the latter case it increases. One should keep in mind that when using expression (13), the signal from site ***a*** (at the frequency ν_A) is monitored and the secondary radiofrequency field is applied at the frequency ν_B. The spectral changes for the case of the spin saturation transfer technique are illustrated in Fig. 4. The first model spectrum corresponds to a system without chemical exchange. The second spectrum was obtained under suppression of the second signal (at the frequency ν_B) and two-site PICE conditions. The third spectrum is the difference spectrum.

In the case of the dark chemical exchange, expression (13) is transformed into an anamorphosis with $k_A' = 0$ (see Refs 43 and 52). Thus, by measuring ratio (13) under irradiation and in the dark one can estimate the k_A' and k_A values.

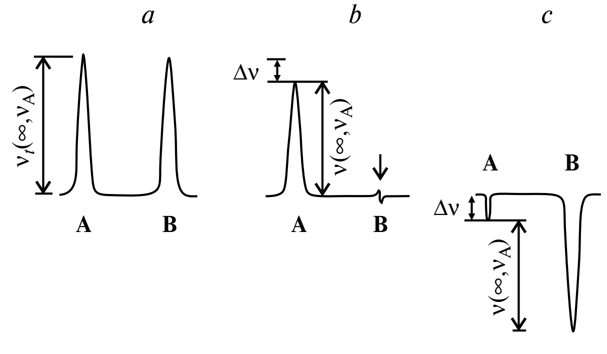


Fig. 4. Theoretical changes in the NMR lineshape for degenerate two-site chemical exchange under different conditions illustrating the spin saturation transfer technique: initial spectrum (*a*), spectrum obtained under homonuclear decoupling of the second signal (at frequency ν_B) and irradiation of the chemical system (*b*), and the difference spectrum (*c*) ($\nu_A - \nu_B = 100$ Hz, $T_{2A} = T_{2B} = 27$ ms, $k_A' = 7.4$ s^{-1}).

The spin saturation transfer technique was successfully used in studies of dark chemical exchange caused by rotation of the phenyl fragments of tetraphenylporphyrin molecules in diamagnetic and paramagnetic sandwich complexes of porphyrins with lanthanides[43] and in studies of dark conformational dynamics of lanthanide complexes with eighteen-membered crown ethers.[44–46]

1.6. Dependence of the integrated intensities of NMR signals on the effective rate constants for photoprocesses when using the inverse fractional nuclear spin population transfer technique under the PICE conditions

When studying the PICE kinetics, the inverse fractional nuclear spin population transfer technique can be practically implemented using the pulse sequence D1—P1(selective)—D2$_{(h\nu)}$—D3—P2—FID shown in Fig. 5. Under these conditions in the system with two-site chemical exchange (with equal populations) the ratio of the integrated intensities of NMR signals under irradiation and in the dark (M_{1z}^{light} and M_{1z}^{dark}, respectively) is proportional to the following expression[21,33,53]:

$$\frac{M_{1z}^{\text{light}}(t = \text{D2})}{M_{1z}^{\text{dark}}(t = \text{D2})} = \frac{1 - e^{-T_1^{-1}\text{D2}} + e^{-(T_1^{-1}+2k^{\text{eff}})\text{D2}}}{1 - e^{-T_1^{-1}\text{D2}} + e^{-(T_1^{-1}+2k)\text{D2}}}, \qquad (14)$$

where $k^{\text{eff}} = k + k^{\text{photo}}$ is the sum of the effective rate constants for dark chemical exchange and PICE, respectively; D1 is the relaxation delay, D2$_{(h\nu)}$ is the time delay for irradiation of the chemical system; for simplicity, we assume the delay D3 = 0; P1 is the selective 180° pulse, P2 is the duration of the probe radiofrequency pulse.[55,63,64]

The essential features of the technique are shown in more detail in Fig. 6. The first model spectrum corresponds to a system without chemical exchange. The second spectrum corresponds to inversion of the population of the second signal without PICE. The third spectrum corresponds to a two-site system with inversion of the nuclear spin population of the second signal in the presence of PICE. The next is the difference spectrum between the second and third ones. The ratio of the integrated intensities of the signals M_{2z} and M_{2z}' is given by Eq. (14).

It should be noted that, according to our estimates, the inverse fractional nuclear spin population transfer technique allows the range of determination of the effective rate constants for photoprocesses to be extended by tens of per cent compared to the spin saturation transfer technique.

The inverse fractional nuclear spin population transfer method was successfully used[21,33] in the NMR studies of chemical exchange due to *cis—trans*-photoisomerization

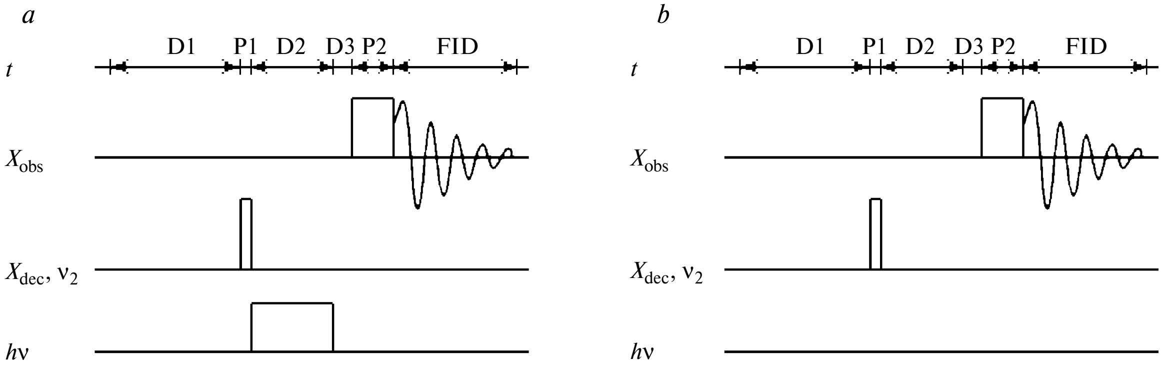


Fig. 5. Pulse sequence for PICE studies using the inverse fractional nuclear spin population transfer technique under irradiation with light (*a*) and in the dark (*b*). X_{obs} is the radiospectroscopic observation channel (^1H, ^{13}C, ^{19}F nuclei, *etc.*), X_{dec} is the radiospectroscopic channel of selective homonuclear decoupling of the second signal at the frequency ν_2, and $h\nu$ denotes the irradiation channel (electromagnetic radiation in the visible, IR, or UV spectral region) for the chemical system under study.

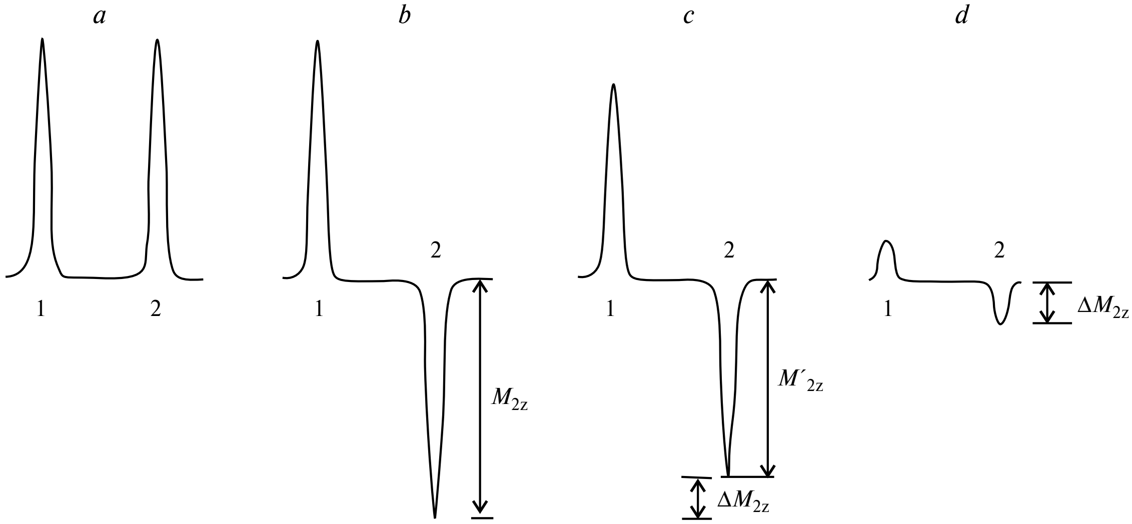
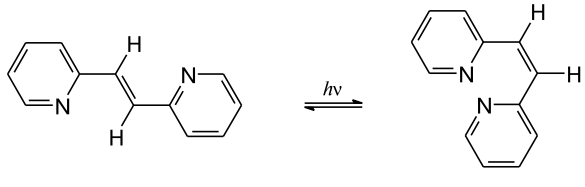


Fig. 6. Theoretical changes in the NMR lineshape for degenerate two-site chemical exchange under different conditions illustrating the inverse fractional nuclear spin population transfer technique: initial spectrum (*a*), spectrum under inversion of the fractional nuclear spin population of the second signal (no irradiation of the chemical system with light) (*b*), spectrum under inversion of the fractional nuclear spin population of the second signal and irradiation of the chemical system (*c*), and the difference spectrum between *b* and *c* (*d*) ($\nu_1 - \nu_2 = 100$ Hz, $T_{21} = T_{22} = 27$ ms, $k_{12}' = 10$ s^{-1}, irradiation for a period of 0.01 s).

of 1,2-(2,2′-dipyridyl)ethene (**1**) (Scheme 3). Detailed consideration of the results obtained is given in Section 2.

Scheme 3



trans-**1** *cis*-**1**

A distinctive feature of the spin saturation transfer and inverse fractional nuclear spin population transfer techniques compared to NMR lineshape analysis is the possibility of studying the PICE kinetics under both photostationary and non-stationary conditions.

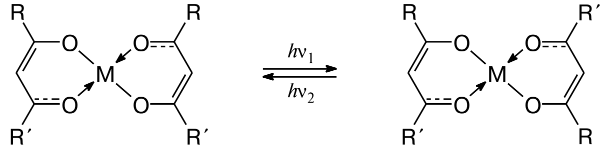
The advantage of these NMR-based methods over the methods based on recording of IR or UV absorption and luminescence spectra consists in the possibility of determining the kinetics of photoprocesses under the photostationary conditions. The NMR-based methods also provide a unique possibility of studying photoinduced interconversions in degenerate systems (*e.g.*, photoinduced interconversions of enantiomers).

2. Specific features of experimental procedures and prospects for elaboration of NMR-based methods of determination of the PICE kinetics

2.1. NMR spectroscopy in studies of reversible photochemical processes

An efficient application of NMR spectroscopy is the determination of the quantum yields of irreversible photochemical reactions,[19,30,31] which is based on the NMR monitoring of photolysis of the chemical compounds under study (see above). It was used for detailed studies of *cis—trans*-photoisomerization of the planar nickel(II), palladium(II), and platinum(II) bis(β-diketonate) complexes[19] (Scheme 4) under irreversible conditions in dichloromethane and alcohol solutions. The NMR spectra of the *cis*- or *trans*-isomers of these complexes were recorded *in situ* with extending the duration of irradiation of the solutions. This was accompanied by a decrease in the initial isomer concentration and an increase in the photolysis product concentration. Then, the initial isomer was replaced and the reverse photochemical reaction was studied in a similar manner. This made it possible to estimate the quantum yield of the direct and reverse *cis—trans*-photoisomerization reactions. For instance, the quantum yield *of cis—trans*-photoisomerization of $[Pt(BA)_2]$ (BA is benzoylacetone) upon irradiation at λ = 254 nm was $\varphi = 3 \cdot 10^{-3}$ (see Scheme 4).

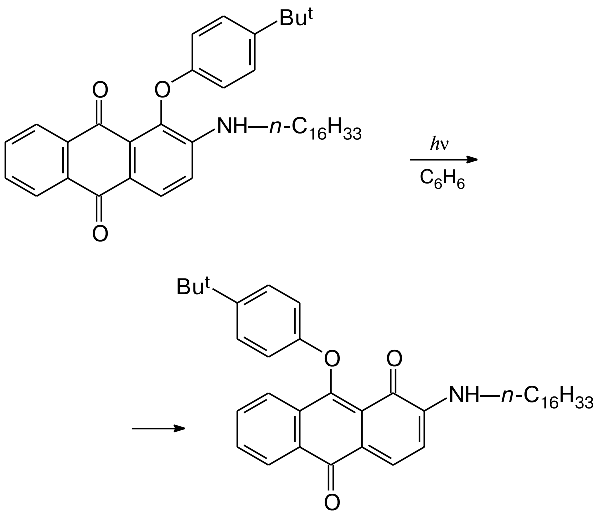
Scheme 4



M = Ni, Pt, Pd; R = Me, R′ = Ph

Similarly, ^{1}H NMR spectroscopic and UV spectrophotometric studies revealed that 1-(4-*tert*-butylphenoxy)-2-cetylamino-9,10-anthraquinone undergoes photoisomerization to 9-(4-*tert*-butylphenoxy)-2-cetylamino-1,10-anthraquinone with the quantum yield $\varphi = 0.4 \pm 0.1$ under irradiation within the UV/visible absorption band with a maximum at λ = 441 nm (Scheme 5).[22] The light sources used in these experimental studies were a c.w. argon laser[59,60] (power 2.5 W) emitting at 488 and 514 nm and a DRSh-250 high-pressure mercury lamp (nominal power 250 W).

Scheme 5



An interesting example of application of NMR spectroscopy to investigations of photochemical reactions is provided by the study of the photoisomerization of compound **1** (see Scheme 3).[21,33] Direct ^{1}H NMR and UV spectrophotometric monitoring of photolysis allowed the quantum yield of *trans—cis*-photoisomerization of compound **1** under irreversible conditions to be estimated ($\varphi_{trans \to cis} = 0.35 \pm 0.04$). These experiments were carried out with deoxygenated CD_3CN as solvent and a pulsed excimer xenon—chlorine laser (λ = 308 nm, average power 0.6 W) as a light source. In particular, it was found that in the study of photolysis of the initial *trans*-isomer under particular experimental conditions the photosystem reaches the region of photostationary regime after 600 laser pulses. This allowed the inverse fractional nuclear spin population transfer technique to be used[21,33] under the photostationary conditions for independent determination of the quantum yields of the direct and reverse *trans—cis*-photoisomerization of compound **1** (Fig. 7).[33] The first spectrum in Fig. 7 was recorded in the dark. The second plot is the difference spectrum between the first spectrum and the spectrum recorded under irradiation with a gas laser at λ = 308 nm. The signal at δ 7.68 corresponds to the C=CH group of the *trans*-isomer, while the signal at δ 6.81 corresponds to the C=CH group of

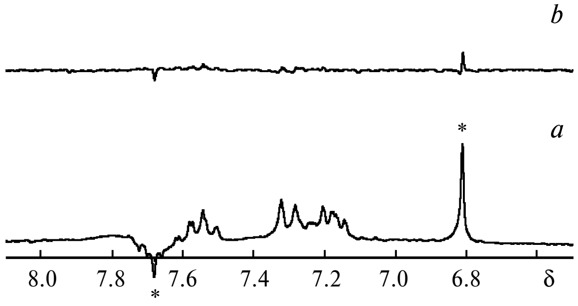


Fig. 7. ^{1}H NMR spectra (200 MHz) of the *cis*- and *trans*-isomers of 1,2-(2,2′-dipyridyl)ethene in CD_3CN under inversion of the C=CH group signal of the *trans*-isomer (δ 7.68) in the dark (*a*) and the difference spectrum between the spectra recorded under irradiation with a gas laser (λ = 308 nm) and in the dark (*b*) (volume 0.5 mL, concentration 0.005 mol L^{-1}).

the *cis*-isomer. Exchange occurs between the astrisked sites. It should be noted that the second spectrum in Fig. 7 corresponds to spectrum *d* in Fig. 6 and indicates transfer of the inverse fractional nuclear spin population as a result of PICE between the *cis*- and *trans*-isomers of compound **1**. The study of signal intensities under irradiation with light and in the dark gave estimates of $\varphi_{trans\to cis}$ and $\varphi_{cis\to trans}$ ($\varphi_{trans\to cis} = 0.34\pm0.04$ s^{-1} and $\varphi_{cis\to trans} = 0.17\pm0.03$ s^{-1}). The $\varphi_{trans\to cis}$ values experimentally determined by two methods are consistent with each other and with the published data on *trans—cis*-photoisomerization of related compounds (stilbene derivatives[6,18]). Therefore, the inverse fractional nuclear spin population transfer technique can be used for experimental investigations of PICE in other chemical compounds.

2.2. Prospects for development of modern experimental NMR-based techniques for studying the kinetics of photoinduced chemical exchange

Modern 2D NMR spectroscopy methods made it possible to perform a complete assignment of all signals in such complex organic reagents, as retinoids and, in particular, in the 11-*cis*-retinal Schiff base, which plays an important role for perception of light information in biosystems.[65,66] Therefore, successful development of dynamic NMR-based methods of investigation of PICE would allow one to use these methods for *in situ* studies on the kinetics of photoprocesses in biological systems in the nearest future. In combination with other photochemistry methods[2,15,67,68] this undoubtedly will permit obtaining new information on specific features of the kinetics and mechanisms of photochemical reactions and, therefore, on the physicochemical properties of these biosystems. Of course, the field of application of the NMR-based methods of PICE studies will not be limited to the investigations of retinoids. In the future, (with an increase in sensitivity of NMR spectrometers due to the use of stronger constant magnetic fields) these techniques will possibly be used in studies of indigoids, phthalocyanines, porphyrins, anthraquinones, stilbene derivatives, and photosensitive crown ethers (and their coordination compounds),[21,22,43,67] as well as many other classes of chemical compounds (in particular, those reported in Refs 35—37 and 69—114).

2.3. Radiation sources for initiation of PICE processes emitting in the visible, UV, and IR spectral regions

The following remarks should be made when we concern modern radiation sources that emit in the visible, UV, and IR spectral regions, are used for initiation of photochemical processes,[70,115—117] and can be used in the setups for PICE studies in combination with NMR spectrometers. Continuous irradiation of the chemical system in the presence of PICE can be achieved using

(1) traditional sources, namely, low-pressure and high-pressure hydrogen and mercury lamps emitting in the range 170—2000 nm (nominal power from 250 W to 3 kW);

(2) c.w. solid-state, liquid, and gas lasers (including semiconductor lasers, dye lasers, chemical lasers, parametric lasers, and thermally pumped gas dynamic lasers (total average power from 100 mW to 100 kW at different harmonics) emitting in the range 300—1500 nm (depending on the working substance);

(3) orotrons (average power from 10 mW to 1 W) emitting in the range 800—1600 μm and gyrotrons (average power up to 8 kW) emitting in the range 900—1700 μm.

In the absence of c.w. light sources with the necessary parameters one can use various types of pulsed lasers,[33,64,70,116—118] in particular, an X-ray laser or a free-electron laser (*e.g.*, a laser designed recently at the Novosibirsk Research Center of the Russian Academy of Sciences; its average power reaches up to 50 W, the emission wavelength is 128 μm, and the pulse repetition rate is 5.6 MHz), if the average power of such sources meets the experimental requirements.

Conclusion

Modern NMR methods based on the lineshape analysis, biresonance spin saturation transfer, and inverse fractional nuclear spin population transfer are applicable to studies of the kinetics and mechanisms of reversible photochemical processes in solutions characterized by the effective rate constants for the photoprocesses varying between 10^{-3} and 10^{2} s^{-1}. They offer unique possibilities of studying the PICE kinetics immediately under the photostationary conditions and analyzing the interconversions of molecular forms in degenerate systems (*e.g.*, photoisomerization of enantiomers).

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