Spin Chemistry and Radio- and Microwave Radiations Effects on Living Organisms

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Abstract: During the last decades, the escalated use of various wireless communication devices, which emit non-ionizing radiofrequency (RF) radiation of audio and TV broadcasting and high frequency microwave (MW) electromagnetic fields of wireless communication technology, have raised concerns among the general public regarding the potential adverse effects on human health. In spite of large body of investigation of these effects of *in vitro* and *in vivo*, which exposures of animals and humans or their cells to RF and MW fields, data reported in scientific publications are contradictory. This minireview is an attempt of critical analysis of these data from point of basic conceptions of spin chemistry, which stands on four fundamental phenomena: 1) resonance absorption electromagnetic radiation, 2) triplet state splitting in magnetic field, 3) spin conservation rule and 4) singlet triplet interconversion. From the standpoint of the problem of influence of electromagnetic radiation on biological reactions, spin effects in radical pairs are of special interest. Potential affection of very strong PMF on anisotropic diamagnetic system, say, biological lipid membranes and fluidity biological liquids can be also taken in consideration. The Lorentz magnetic forces of RF and MW fields are very weak and can not provide a magneto-reception mechanism. Therefore all finding which don't fit to "a Procrustean bed" of the spin chemistry can be considered as annoying artefacts or intriguing challenging problem for future.

Key words: radioradiation, microwave radiations, human health

Introduction

The escalated use of various wireless devices (Fig. 1) have raised concerns regarding the potential adverse effects on the humans health and emotional state. [1] Microwave Auditory Effects and Applications. Springfield, Illinois: Charles C. Thomas. Possible effects of Electromagnetic Fields (EMF) on Human Health. Scientific Committee on Emerging and Newly Identified Health Risks. SCENIHR. 2007; International Agency for Research on Cancer-(IARC), "Non-ionizing radiation Part I: static and extremely low frequency (ELF) electric and magnetic fields," Monographs, vol. 120, 2013; Acquisition Safety - Radio Frequency Radiation (RFR) Hazards". Naval Safety Center - United States Navy. 2014; Standard for Safety Level with Respect to Human Exposure to Radio Frequency Electromagnetic Fields, 3KHz to 300GHz". IEEE Std. IEEE. C95.1-2005; Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR). Opinion on Potential health effects of exposure to electromagnetic fields (EMF). 2015; Guidelines for limiting exposure to time-varying electric, magnetic, and electromagnetic fields (up to 300 GHz). International Commission on Non-Ionizing

Radiation, 2010; Protection. International Commission on Non-Ionizing Radiation Protection (ICNIRP). 2013. Exposure to high frequency electromagnetic fields, biological effects and health consequences (100 kHz–300 GHz). ICNIRP 16/2009. http://www.icnirp. de/documents/RFReview.pdf; ICNIRP GUIDELINES FOR LIMITING EXPOSURE TO TIME-VARYING ELECTRIC AND MAGNETIC FIELDS (1 HZ – 100 kHZ) PUBLISHED IN: HEALTH PHYSICS 99(6):818-836; 2010). Despite the many studies conducted and many effects reported, the exact mechanism of the interaction between electromagnetic fields and biological systems still remains elusive.

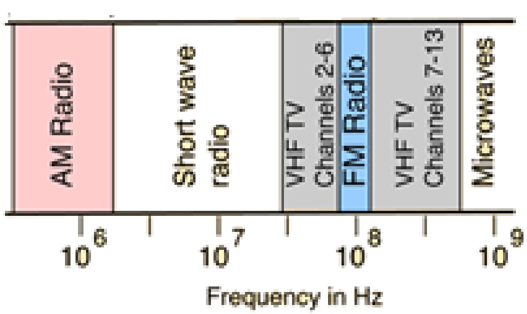

Figure 1. Typical frequencies of the broadcasting and transcontinental microwave relay networks.

Spin chemistry stands on four fundamental phenomena: 1) resonance absorption electromagnetic radiation, 2) triplet state splitting in magnetic field, 3) spin conservation rule and 4) singlet triplet interconversion [2-9] From the standpoint of the problem of influence of electromagnetic radiation on biological reactions, spin effects in radical pairs are of special interest.

Theoretical grounds

The electron spin resonance (ESR) phenomena involve the resonance absorption or dispersion of a microwave frequency (0.3- 250 GHz) of electromagnetic field (υ_{res}) by a system of particles with the intrinsic spin moment of an unpaired electron in a constant magnetic field of strength B_{res} ranged from y 0.034 T to approximately 10.2 T. [10, 11] The absorption leads to magnetization in the exited state of the system and the electron magnetic resonance condition is:

$$h\upsilon_{res} = g_e \beta_B B_{res} \qquad (1)$$

where g_e is a g-factor, characterizing the value of the intrinsic electron spin moment (free electron g-value is 2.002319), β_B is the Bohr magneton (9.27400968×10^{-24} J·T^{-1}), h is the Plank constant (6.6×10^{-34} J·s). Accordingly, if ν_{res} and B_{res} is expressed in Hz and Gauss respectively (T = 10000 Gauss),

$$\nu_{res} = 2.8 \ \mathrm{x}10^6 \ B_{res} \ s^{-1}. \qquad (2)$$

Similar conditions are formulated for the resonant absorption of nuclear systems (for proton, for example):

$$h\upsilon_{res} = g_n\mu_n B_{res} \qquad (3)$$

where g_n = 5.6, μ_n is the magnetic moment (7.6 10^6 Hz/T). Therefore,

$$\nu_{res} 42.6 \ \mathrm{x} \ 10^2$$

if ν_{res} and B_{res} are expressed in Hz and Gauss, respectively

The Zeeman resonance frequencies for transitions of electrons for a single unpaired spin in low magnetic field close to the Earth's magnetic field, 45μT, typically fall in the region between 1 and 10 MHz. The Zeeman frequencies for transitions between the nuclear spin states are in the region around 100–1000 Hz. The coupling between nuclei leads to transition frequencies around 10 Hz [12].

The hyperfine interaction between the electron and the nuclear spins consists of the isotropic Fermi contact interaction and the anisotropic dipole-dipole interaction are in the range 1-10 mT which correspond to frequencies from $4.26\ 10^3$ Hz to $4.26\ 10^4$ Hz.

When a magnetic field is applied to a singlet radical or ion-radical pairs, affected by external magnetic field, the level T splits into three levels: T_{+1}, T_0 and T_{-1}. Fig. 2 illustrates the effect of the external magnetic field strength (H_0) on a process, the rate of which is proportional to the population of the singlet level of a radical pair. As the field strength increases, the T_+ and T_- levels are progressively displaced from the T_0 level, and therefore the influence of magnetic field on the overall rate becomes progressively less, the population of S levels increases and the rate of recombination becomes faster.

In a typical radical pair, coherent evolution of the spin state provides S ↔ T interconversion [2-9, 13, 14] As consequence, the singlet state undergoes spin-selective reaction to produce the singlet initial product in the singlet state (SP) or reacts to give a back-reaction product (Fig. 2).

According to fundamentals of spin chemistry, under resonance microwave pumping, absorption of microwave radiation can effect on the transitions between triplet levels ($T_+ \leftrightarrow T_0$ and $T_0 \leftrightarrow T_-$) leading to a decrease in the population of the singlet state of the pair and, as a consequence, to a drop in the radical reaction yield. Resonance values of magnetic fields and MW frequencies typically range from 1mT to 20 -. mT and from 28 Mhz to 540 Mhz respectively (15, 16)

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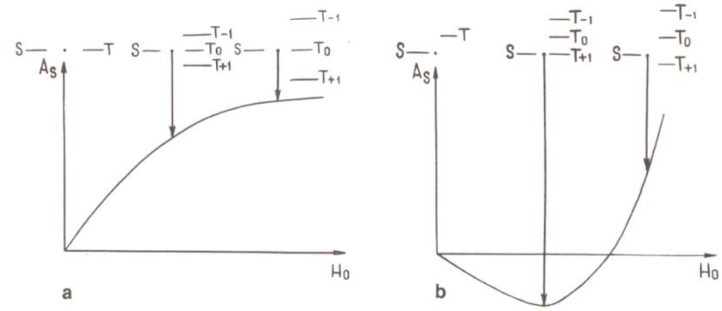

Figure 2. The effect of the field strength (H0) on the population (AS) at the singlet level, which depends on the rate of the S ! T transition (kST) for a radical pair: a without exchange interaction (J = 0) and b with exchange interaction (J > 0). The vertical arrows indicate qualitatively the correspondence between the triplet splitting and the associated behavior of the static magnetic field (H_0) [9].

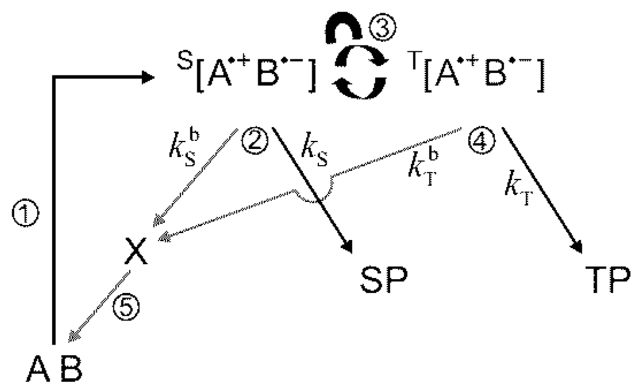

Figure 3. T ↔S spin conversion of the present radical pair generated from a triplet precursor at (a) $B = 0$ T, (b) $0\ T < B < 20$ T, and (c) $20\ T \le B$ (See details in [17])

When the energy of hyperfine couplings is close to the radiofreqency (υ_0 = 5- 5O MHz), a marked effect of the applied RF on the yield of radical reactions in the presence of a 0−4 mT static magnetic field can be expected [6-8, 13,14,17,18,20-23,2] [

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It was demonstrated that radical concentrations can be modified by combinations of weak, steady and alternating magnetic fields, which in turn modify the population distribution of the nuclear and electronic spin state, the energy levels and the alignment of the magnetic moments of the components of the radical pairs in [24,25]. In general, the coupling between the nuclei, nuclei and electrons, and Zeeman shifts in the electron and nuclear energy levels can lead to transitions with resonances spanning frequencies from a few Hertz into the megahertz region.

In a recent review [23] the following factors causing the S ↔ T interconversion have been summarized: the hyperfine and dipolar interactions between the electron and nuclear spins, Zeeman interactions, mixing states of different multiplicities by resonant magnetic fields, zero-order splitting of the singlet state (S) and three triplet states (T_-, T_0, T_+) and radical pair lifetime, τ.

Appraisal of experimental data on electromagnetic effects on living organisms from point of view of the magnetic resonance conditions

In biological systems, the set of chemical processes involving formation of radical pairs effectively proceed. Typical examples of such processes are chain reactions of oxidation липидов and other biomolecules, as well as reactions with participation of superoxide and nitric oxide. On the basis of observed magnetic isotope and magnetic field effects in enzymatic ATP synthesis catalyzed by magnesium, a new, ion-radical mechanism of ATP synthesis was formulated [6-8]

Choisen experimental data on biological effects of electromagnetic radiation of various frequencies in static magnetic field and correspondent resonance values, calculated using Eqs. 2 and 4 are presented in Tables 1-3.

For different groups of healthy volunteers, the effect the 450 MHz microwave radiation modulated at 7 Hz (first group), 14 and 21 Hz (second group), 40 and 70 Hz (third group, 15), 217 and 1000 Hz (fourth group) on n the electroencephalographic (EEG) was examined [26] The calculated spatial peak of the specific absorption rate (SAR) averaged over 1 g was 0.303 W/kg. As an example, Fig 4 shows the relative changes in the EEG energy for the subjects or the subjects at14 and 21Hz modulation. The protocol with exposure lasted 20 -40 min.

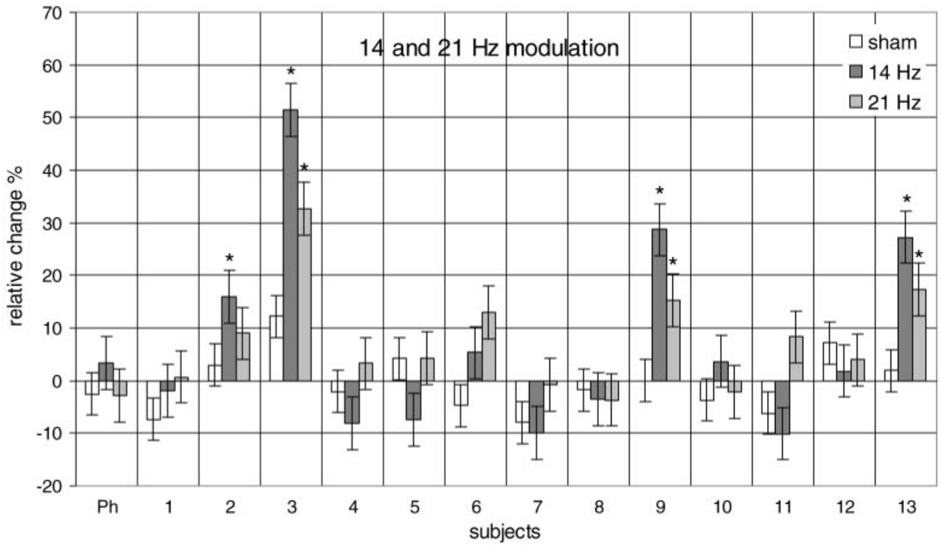

Fig. 4. Relative changes in the EEG energy for the subjects in second group at 14 and 21Hz modulation frequencies as parameter Sn values calculated for a subject [26].

The experimental results showed that exposure to 450 MHz microwaves modulated at different low frequencies caused significant increases in the EEG beta rhythms energy for 13– 31% of the subjects.
Effects of 872 MHz radiofrequency radiation (872 MHz) and menadione on intracellular reactive oxygen species (ROS) production and DNA damage in human SHSY5Yneuroblastoma cells at a relatively high SAR value (5 W/kg) eas investigated [27]. The production of ROS was measured using the fluorescent probe dichlorofluorescein and DNA damage was evaluated by the Comet assay. The cell exposition for 1 h with or without menadione resulted in an enhance chemically induced ROS production and thus cause secondary DNA damage. No effects of the Global System for Mobile Communications (GSM) signal were seen on either ROS production or DNA damage.The cell exposition for 1 h with or without menadione resulted in an enhance chemically induced ROS production and thus cause secondary DNA damage. No effects of the Global System for Mobile Communications (GSM) signal were seen on either ROS production or DNA damage.
The effects of weak magnetic fields (45 μT) radio frequency (7 MHz) at 10 μTRMS) on the production of reactive oxygen species (ROS) from intracellular superoxide (O_2•-) and extracellular hydrogen peroxide (H2O2) were investigated in vitro with rat pulmonary arterial smooth muscle cells (rPASMC) [28]. In these conditions, a decrease in O_2•- and an increase in H_2O_2 concentrations were observed. It was proposed that O_2•- and H_2O_2 production in given metabolic processes occur through singlet-triplet modulation of semiquinone flavin (FADH•) enzymes and O2•- spin-correlated radical pairs, which in leads an increase of H_2O_2 singlet state products. The letter creates cellular oxidative stress and acts as a secondary messenger that affects cellular proliferation.

For geomagnetic storm, with the duration of the main phase 2–24 hours, disturbance – storm time index (Dst) can be between -50 and approximately -600 nT. These values are confirmed with resonance frequencies of either 2.5 Hz and 27 Hz (Eq. 4) or For a solar flare phenomena (https://en.wikipedia.org/wiki/Solar_flare), radiation of frequencies were found starting from ~15 MHz with calculated resonance magnetic field either B_{res} = 3500 G (Eq.4) or B_{res} = 5,4 G (Eq. 2). It is clear that the both calculated values of B_{res} are out the Earth magnetic field.

Table 1. Biological effects of experimental low electromagnetic frequency υ_{exp} in the magnetic fields MF and corresponding resonance electromagnetic frequencies υ_{res} calculated by the resonance equations Eq. 2 for ESR and proton NMR (Eq.4) respectively. The proton NMR resonance frequencies are given in parenthesis.

$\upsilon_{exp\ Hz}$	MF G	$\upsilon_{res\ kHz}$	Object, bioeffect	reference
5	0.5	14.7 (2.1)	rats, lymphocyte	[29]
10	0. 5	14.7 (2.1)	rats, blood enzymes	[30]
25	0.5	14.7 (2.1)	murin, genexpression	[31]
50	5	147 (21)	Gerbils,brain oxidative stress	[32]
50	10	290 (42)	Plateletrich plasma, platelet aggregation	[33]
50	10	290 (42)	THP-1 cells,	[34]
60	20	580 (84)	rat brain, NO levels	[35]
60	0.5	14.7 (2.1)	mices, NO in hyperalgesia	[36]

Table 2. Biological effects of experimental shortwave electromagnetic frequency υ_{exp} in the Earth magnetic fields (MF) and corresponding resonance magnetic field B_{res} (in Gauss) calculated by Eq. 4.

υ_{exp}	MF G	B_{res}	Object, bioeffect	reference
1 MHz	0.5	0.5	cage proteins, iron release	[37].
5 MHz	0.5	2.5	fibrosarcoma cells, cellular growth rates	[38]
7 MHz	0.5	3.5	rats, reactive oxygen species	[28]
27.12MHz	0.5	13.5	motor activity of rabbits	[39]

Table 3. Biological effects of experimental microwave frequency (υ_{exp}) in the Earth magnetic field (0. 5 G) and corresponding resonance magnetic field (B_{res}) calculated by Eq .2.

υ_{exp}	B_{res}	Bioeffects	reference
900-MHz	340	rhizogenesis in plants	[40]
900-MHz	340	oxidative stress in rats	[41]
900-MHz	340	cognitive effects in Alzheimer's mices	[42]
900-MHz	340	reproductive capacity of *Drosophila*	[43]
900-MHz	340	cerebral cortical neurons of rats	[44]
900-MHz	340	promotion oxidation in rat brain	[45]
900-MHz	340	brain metabolism	[46]
872 MHz	329	ROS in human neuroblastoma cells	[27]
1.909 GHz	717	DNA damage	[47]
2.45 GHz	925	oxidative stress in mice	[48]
2.856 GHz	1078	neural cell apoptosis of rats spatial learning of rats	[50] [44].

Table 4 summarizes frequencies used in the broadcasting, radio, VHF TV, and microwave radio relay (MWRR) systems and related resonance magnetic field B_{res} calculated by Eq. 2. As can be seen from the Table, only longwave radio radiation may have an impact on a biological object in magnetic fields close to the Earth MF.

Table 4 Frequencies used in the broadcasting, radio, VHF TV, and microwave radio relay (MWRR) systems and related resonance magnetic field B_{res} calculated by Eq. 2.

Systems	Frequency	B_{res}
Long wave radio Short waves radio	540 -1600 kHz 1.6 –30 MHz	0.2 G - 0.6 G 0.6 - 18 G
FM –radio	88.1 -108,1 MHz	31.5 - 38.7 G

The microwave frequencies (8 to 40 GHz) producing in relay link installations *https://en.wikipedia.org/wiki/Microwave_transmission)* are corresponded to calculated values of B_{res} from 2860 to 14 290 G (Eq. 2) and may be attributed to transition between the three triplet states (T_-, T_0, T_+). Magnetic resonance immerging (MRI) uses magnetic fields of 2000 – 30000 G (typically 15000G), radio waves (for example, 8.5 MHz), and field gradients to generate images of the inside of the body. (https://en.wikipedia.org/wiki/Physics_of_magnetic_resonance_imaging*)*. For given MF strength, resonance frequencies are estimated as ν_{res} = 2.8 - 84 GHz). Frequency of 8.5 MHz falls in the range of short wave radio frequencies (Table 4) and, therefore, may cause the S ↔ T conversion. Commercial magnetic bracelets utilize strong magnetic field B = 300 – 5000 G (www.billythetree.com/magnetic-jewelry-and-gauss.aspx) that correspondent calculated resonance frequencies υ_{res} = 0.8 – 13.2 GHz. . Essential evidences now exist that exposure of strong static high magnetic fields (SMFs) causes marked changes in the properties of a number of biological systems [51].

Police radar guns utilize frequencies of K band (18 to 27 GHz) and K_a band (27 to 40 GHz) (*https://en.wikipedia.org/wiki/Radar).* with calculated resonance magnetic field B_{res} from 2860 to 14290G (Eq. 2), that is out of resonance in the Eath magnetic field and therefore as though is harmless.

Radiation of 2.45 GHz, which may arise at a leak from microwave ovens, is out of resonance in the Eath magnetic field.

The ability of living organism, including birds, mammals, reptiles, amphibians, fish, crustaceans and insects, to use the Earth's magnetic field for orientation and navigation is one of the most intriguing and challenging problem for biochemistry and chemical physics [52]). Based on the finding that electron transfer processes generate radical pairs in coherent electron spin states in weak magnetic fields, Schulten and colleagues [53] suggested a *radical pairs* reaction mechanism for a chemical compass, based on the finding that electron transfer processes generate radical pairs in coherent electron spin states in weak magnetic fields, which allows biological species to orient themselves in the geomagnetic field. Cryptochromes as potential magnetoreceptors were proposed [54-56]. The cryptochrome/photolyase family contains the redox-active cofactor flavin adenine dinucleotide (FAD) triad of trytophans (Trp-triad), which are involved in electron transfer initiated by blue light giving a flavosemiquinone radical, FAD•− or FADH•, and a radical derived from the Trp-triad ([54-57].

Strong evidence in favor of the radical pair mechanism is a finding that oscillating magnetic fields disrupt the magnetic orientation behaviour of migratory birds which were disoriented when exposed to a single-frequency (7-MHz) field in addition to the geomagnetic field. [55]. This effect depended on the angle between the oscillating and the geomagnetic fields.

The valuable information about chemical nature and concentration of radical pairs may be obtained by means of A powerful approach based on modern advanced physical methods including chemically induced electron spin polarization, chemically induced nuclear spin polarization, time resolved ESR, etc can be valuable in investigation of effect electromagnetic fields on chemical nature and concentration of radical pairs [2,4, 5, 16, 59-61]/

Conclusions

Spin chemistry of processes proceeding through intermediated radical pairs imposes strict requirements on effects of magnetic and electromagnetic fields in one cases and predicts these effects for other cases. Selected very low frequency radiation in magnetic fields, close to the Earth MF (EMF), and shortwave radio radiation can influence on a radical process in the EMF. On the other hand, in these conditions longwave and ‘highfrequency electromagnetic radiations from radio receivers mobile telephones, are out of resonance therefore are forbidden.

Spin chemistry rules predict absorption of microwave radiation the MRI installations and magnet bracelets using strong magnetic fields in appropriating conditions. Contrary to it, resonance absorption of microwave radiation generated be radar antennas and police radars in the EMF are forbidden. To solve the challenging problems, spin chemistry experts and biochemists have to cooperate in the investigation of biological radical reactions *in vivo* and *in vitro.*

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