1. Introduction

Spin exchange is a change of spin states of paramagnetic particles in colli-
sions which is induced by exchange interaction of partners that occurs when
their electron orbitals overlap. Exchange interaction arises as a result of
the dependence of the Coulomb repulsion of electrons on the orientation of
their spins (see, e. g. [1.1,2]). According to the Pauli exclusion principle
the spatial distributions of electrons are different depending on whether
their spins are parallel or antiparallel. Two electrons with antiparallel
spins can be simultaneously found at the same point of space, while two elec-
trons with parallel spins can not. As a result the Coulomb repulsion is
stronger for the first case. When the energy of exchange interaction is small
enough, exchange interaction between two particles A and B can be described
by a well-known Hamiltonian [1.1,2]

$$\hat{V} = \hbar J_{AB}(r)\hat{S}_A \hat{S}_B \qquad (1.1)$$

where $J_{AB}(r)$ is the so-called exchange integral, $\hat{S}_A$ and $\hat{S}_B$ are spin operators
of interacting particles A and B, r is the distance between the particles,
$\hbar$ is the Planck constant divided by 2π. For the simplest case $S_A = S_B = 1/2$
Hamiltonian (1.1) has two eigenstates corresponding to the total spin value
$S = 0$ (the singlet state) and $S = 1$ (the triplet state), the energy splitting
between them being $\hbar J_{AB}(r)$.

The spin dependence of the electron interaction energy becomes important
only when their orbitals overlap. Since the overlap of the electron wave
functions decreases rapidly with the distance r between the interacting atoms,
the energy of exchange interaction also decreases rapidly with the increase
of r.

At short distances, such as those between atoms in molecules, when the
overlap is substantial and the energy of exchange interaction is large enough
as compared to the energy of thermal motion, this interaction results in the

formation of chemical bonds between atoms. In solids such interactions, when their energy exceeds the energy of thermal motion, result in the appearance of ferromagnetic or antiferromagnetic properties.

Spin exchange in solutions is induced by far weaker exchange interactions that occur when the particles approach to a Van der Waals distance. This energy is much smaller than the energy of chemical bonds. In this situation exchange interaction is quite well described by Hamiltonian (1.1). This simplifies essentially the theoretical treatment of spin exchange.

Moreover, at Van der Waals distances J_{AB} is usually smaller than the energy of thermal motion. Thus spin exchange practically does not perturb the character of the thermal motion of interacting molecules. This circumstance furthermore simplifies the theoretical description of spin exchange kinetics.

Though exchange interactions between paramagnetic particles during their collisions are very small, they can nevertheless essentially change the states of the spins of these particles. Usually these changes consist in an exchange of spin states between the partners, i. e., a change in the state of electron spin of one of the particles is fully compensated by an opposite change in the electron spin state of its partner. In this most common situation spin exchange can be represented by a scheme shown in Fig.1.1.
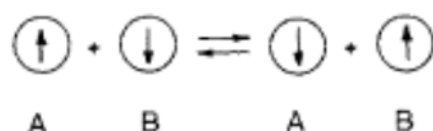

Fig.1.1. Schematic representation of a spin exchange process between two paramagnetic particles. The vertical arrows indicate the spin orientations and their exchange as a result of a collision

In dilute solutions spin exchange takes place via binary collisions of paramagnetic particles:

$$A(\uparrow) + B(\downarrow) \rightleftharpoons A(\downarrow) + B(\uparrow) \qquad (1.2)$$

and by analogy with bimolecular chemical reactions its rate can be represented as

$$W = K_e C_A C_B \qquad (1.3)$$

where C_A and C_B are the concentrations of particles A and B, and K_e is the rate constant.

Most simply the rate constants of spin exchange can be measured from the ESR spectra of interacting particles. (For introduction to ESR spectroscopy see [1.3,4]). Depending on specific conditions the ESR lines can be broadened, shifted, or narrowed by spin exchange. Reliable methods have been developed

that allow one to measure the rate constants of spin exchange in all those situations. From ESR spectra one can measure even extremely large rate constants of spin exchange (up to 10^{11} 1/mol $\cdot$ s), but the smallest values of rate constants that can be measured by this method usually do not exceed 10^7 1/mol $\cdot$ s.
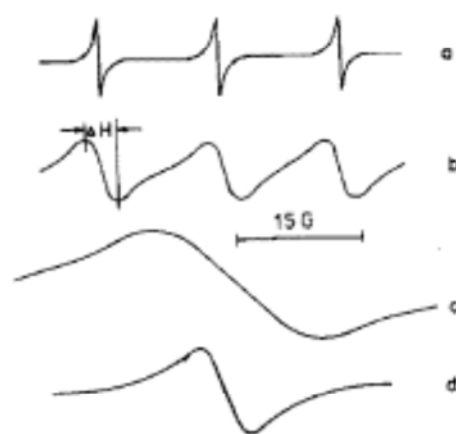

Fig.1.2a-d. The influence of spin exchange on the ESR spectrum of a nitroxide free radical. The rate of spin exchange increases from the top to the bottom spectrum as a result of increase of the radical concentration: (a) no spin exchange; (b) exchange broadening; (c) collapse of the hyperfine structure; (d) exchange narrowing

Figure 1.2 represents a typical example of the change of the ESR spectra as a result of spin exchange. In this figure the ESR spectra of a stable nitroxide free radical are given for different concentrations of this compound in solution. Free radicals of this type are often used in studies of spin exchange. The spectrum (a) corresponds to very dilute solutions of the free radical, when the influence of spin exchange on the spectrum can be neglected. The spectrum consists of three lines due to hyperfine interaction of the unpaired electron with the nuclear magnetic moment of the nitrogen atom. The increase in the rate of spin exchange at larger free radical concentrations results in broadening of the ESR lines (see spectrum b) and in a small shift of the outer lines towards the center of the spectrum.

Further increase in free radical concentration leads to the collapse of the three hyperfine lines into a broad single line (spectrum c) and then to the narrowing of this single line (spectrum d).

The rate constant K_e can be most easily found from the dependence of the line broadening on the concentration of paramagnetic particles. This broadening occurs as a result of shortening of the lifetime of the electron spin states due to spin exchange in agreement with the uncertainty principle. The magnitude of this broadening can be related to the rate constant of spin exchange K_e and the concentration of paramagnetic particle, C, as

$$A \cdot (\Delta H - \Delta H_0) = K_e \cdot C \qquad (1.4)$$

Reference - Molin, Yu. N.; Salikhov, K. M.; Zamaraev, K. I. *Spin Exchange Principles and Applications in Chemistry and Biology*; Springer−Verlag: Berlin, 1980.: