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Analytical potential of Mössbauer spectroscopy

V G Semenov, L N Moskvin, A A Efimov

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Abstract. Basic knowledge about Mössbauer spectroscopy, necessary for gaining qualitative and quantitative information on the substance composition from Mössbauer spectra, is considered. Methods of Mössbauer spectra processing are discussed and databases ensuring the search for information on objects under study are described. Applications of Mössbauer spectroscopy in various fields of chemistry, mineralogy, biology and materials science are considered. The bibliography includes 135 references.

I. Introduction

More than 45 years ago Rudolf Mössbauer discovered the phenomenon of resonant nuclear fluorescence of γ-radiation in ^{191}Ir.[1] A spectral method based on the phenomenon was named Mössbauer spectroscopy (more rarely, it is also called nuclear gamma-resonance spectroscopy). The technique immediately became a powerful tool for studying the structural and chemical state of solids and found wide application in various areas of science and technology,[2] such as materials science, chemistry, biology, geology, mineralogy, *etc*. At present, a number of monographs devoted to Mössbauer spectroscopy are available (see, *e.g*., monographs [3–9]). In these books, the emphasis is placed on consideration of the physical principles and theoretical aspects of the method and on the most interesting objects of investigation. The number of such objects continuously increases, especially in connection with increasing interest in the materials science. Now we can say with certainty that Mössbauer spectroscopy is no longer an exotic physical method of investigation. At present, this is a routine analytical method with its specific methodology and objects of analysis.

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Comprehensive information on Mössbauer spectroscopy studies and their results can be found on the Website of the Mössbauer Effect Data Centre (MEDC) at the University of North Carolina (USA) at URL http://www.unca.edu/medc. The MEDC database includes about 40 000 records, including a reference to the discovery of the Mössbauer effect. New references are published on a regular basis in *Mössbauer Effect Reference and Data Journal* (MERDJ, ten issues per year).[10] MEDC publications also include collections of works aimed at summarising information concerning various avenues and objects of Mössbauer spectroscopy studies (mineralogy, materials science, analytical chemistry, catalysis, *etc*.).[11]

Until recently, Mössbauer spectroscopy took a back seat among other analytical chemistry methods. Often, analyst chemists simply had no information on the analytical potential of Mössbauer spectroscopy. Recently, the situation has become better. In particular, two Mars exploration rovers, 'Spirit' and 'Opportunity', were equipped with Mössbauer spectrometers, which is evidence of increasing interest in the analytical potential of Mössbauer spectroscopy. This made it possible to obtain reliable information on water-driven chemical processes on Mars. The aim of this review is to attract the attention of analytical chemists to the title method. We will consider the key methodological issues of Mössbauer spectroscopy, methods of processing of Mössbauer spectra in order to obtain qualitative and quantitative information and the most typical objects of analysis in chemistry, geology, mineralogy, biology and materials science. In considering the results of analysis of particular objects, the emphasis will be placed on the experimental design depending on the nature of the object under study.

II. Physical principles of Mössbauer spectroscopy and its modifications

Mössbauer spectroscopy is based on recoilless resonant absorption of γ-quanta with energy E_0, emitted by nuclei of Mössbauer isotopes in an excited state (source of radiation), by corresponding nuclei in an object under study (absorber) that are in the ground state. After absorption of γ-quanta, the latter nuclei undergo transition to the excited state of energy E_0'. Resonant absorption is only possible at $E_0 = E_0'$. Mössbauer's merit consisted in that he found the conditions suitable for observation of resonant absorption of γ-quanta by atomic nuclei. He found that if the

emitting nuclei are incorporated into a solid,† it becomes highly probable that emission will occur in a recoilless fashion (without energy loss), because energy is transferred to the entire crystal rather than a particular atom, thus converting into energy of crystal lattice vibrations. In this case the emission and absorption lines have the same natural width (Γ) that is determined by the quantum-mechanical Heisenberg uncertainty relation:

$$\Gamma = \frac{\hbar}{\tau},$$

where $\hbar = h/2\pi$ and τ is the excited-state lifetime of the Mössbauer nucleus. Typical lifetimes of excited nuclear states lie between 10^{-10} and 10^{-6} s, which corresponds to linewidths $\Gamma = 10^{-5}$–10^{-9} eV. The relative linewidths of nuclear transitions with energies in the range 10^4–10^5 eV are 10^{-10} to 10^{-15} eV, being responsible for extremely high resolution of Mössbauer spectroscopy with respect to energy, which much exceeds the resolution of all other physical methods.

In real situations one should allow for a change in the γ-quantum energy due to thermal motion of atoms. Therefore, measurements of Mössbauer absorption (scattering) spectra require a controllable variation of the γ-quanta energy of the source of radiation in the range from a few neV to tens of neV. Most often, this is achieved by mounting the source of radiation on a Doppler modulator that provides continuous motion of the source relative to absorber (sample under study). The Doppler energy change, ΔE_D, due to the motion of the source of radiation with controllable speed υ, is calculated as follows:

$$\Delta E_D = \frac{E_0 \upsilon}{c},$$

where c is the speed of light. In this case the energy of γ-quanta emitted towards the absorber is given by

$$E(\upsilon) = E_0\left(1 + \frac{\upsilon}{c}\right) = E_0 + \Delta E_D, \qquad (1)$$

where $E(\upsilon)$ is the energy of the γ-quantum emitted by the source moving at velocity υ and E_0 is the energy of the γ-quantum emitted by the immobile source.

The Mössbauer absorption spectrum is usually represented as the dependence of the relative intensity of radiation passed through or scattered by the sample on the velocity of the source of radiation relative to the sample (Fig. 1). In fact this means that the Mössbauer spectrum represents the dependence of the γ-quanta absorption section on the Doppler energy (ΔE_D) added to the energy E_0 of these quanta. In order to obtain a convenient quantitative estimate of the signal, the effect (relative difference between the signal and background) is used instead of the relative intensity. Additional information on the object under study can usually be obtained by varying external parameters that affect the resonant absorption effect (*e.g.*, temperature, pressure and external magnetic field and electric field).

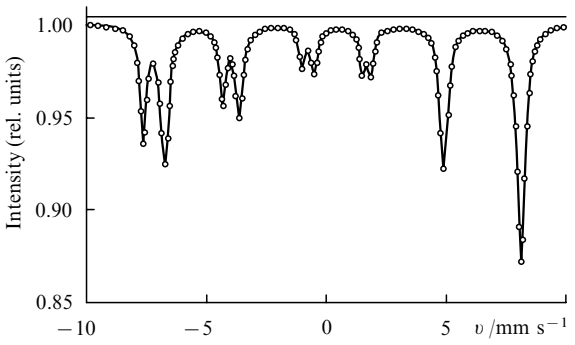


Figure 1. Mössbauer spectrum of Fe_3O_4.

Measuring Mössbauer spectra includes registration of either γ-radiation that has passed through the absorber (absorption geometry) or radiation associated with resonance processes and scattered by the absorber (scattering geometry). Since the Mössbauer transitions are to some extent converted, experiments with the scattering geometry allow not only the resonance γ-radiation but also X-ray radiation or conversion electrons accompanying resonant scattering of γ-rays to be detected. X-Ray radiation contains information on the state of a thin (several tens of micrometres) surface layer of the sample and conversion electrons contain information only on the state of the surface layer 200–300 nm thick, which is determined by the short distance they travel within the sample material. The corresponding modification of Mössbauer spectroscopy is called conversion electron Mössbauer spectroscopy.[7] Since recently, ultrathin surface layers (2–200 nm thick) have been studied using a new modification of conversion electron Mössbauer spectroscopy, namely, small-angle conversion electron Mössbauer spectroscopy.[14–16] By varying the angle of incidence of γ-quanta it is possible to vary the depth to which γ-rays penetrate the surface layers of the sample under study.

Conventional sources of radiation represent long-lived parent radionuclides that are necessary for creating an intense flux of monochromatic resonant γ-radiation, which is then used for studying the state of corresponding Mössbauer nuclei in the absorber or in the scatterer. However, yet another experimental geometry is possible. Here, the sample to be analysed contains an incorporated Mössbauer isotope and acts as the source of γ-quanta and a known compound containing the same isotope characterised by a single monochromatic line for corresponding Mössbauer radiation acts as absorber or scatterer. This modification is called emission Mössbauer spectroscopy.[17] This type of Mössbauer spectra is sensitive to specific features of the chemical environment of the resonance atom and of the structure that contains the resonance atom. The sensitivity of emission Mössbauer spectroscopy is as high as 10^{12} atoms per cm^2 of the surface area of the sample, which is much higher than the sensitivity of the scattering and absorption Mössbauer spectroscopies. An important feature and limitation of emission Mössbauer spectroscopy is the need of non-protected manipulation of radioactive substances. Therefore, this modification of Mössbauer spectroscopy is of limited practical use.

The possibility of studying certain objects by Mössbauer spectroscopy is determined by their elemental composition. At present, the Mössbauer effect is documented for more than 40 elements whose isotopes can be used in Mössbauer spectroscopy studies. However, physical and technological limitations reduce the number of isotopes suitable for being used for analytical purposes to at most seven (^{57}Fe, ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, ^{151}Eu and ^{197}Au). The ^{57}Fe and ^{119}Sn isotopes are of the greatest practical value. In spite of a relatively small number of 'Mössbauer' isotopes, numerous objects can be studied by Mössbauer spectroscopy, because the 'Mössbauer' elements are constituents of many objects to be analysed. For instance, iron belongs to the most abundant elements on Earth; therefore, ^{57}Fe Mössbauer spectroscopy has been intensively employed in geochemical and materials science studies of iron-containing solid samples.

^{119}Sn Mössbauer spectroscopy is of lesser use, because tin is 1000 times less abundant than iron. Nevertheless, numerous studies of tin-containing materials and minerals were carried out and tailor-made instruments for geological exploration for tin were designed in the early stage of development of Mössbauer spectroscopy.

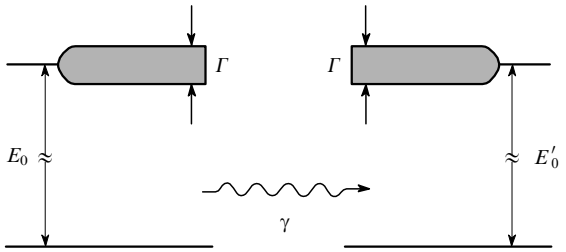
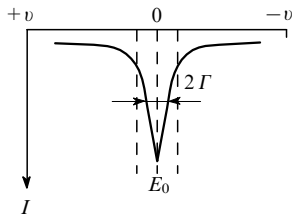
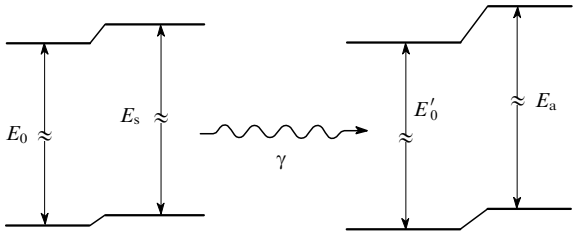
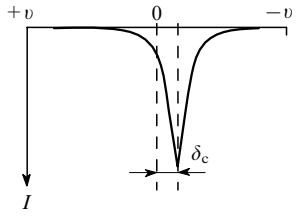
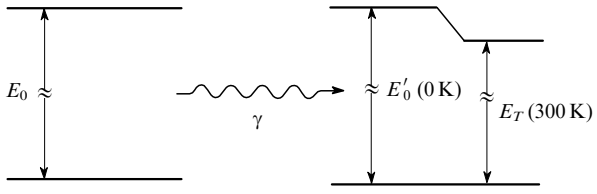
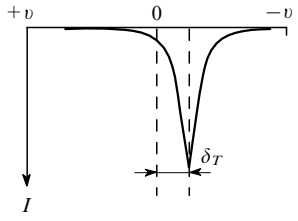
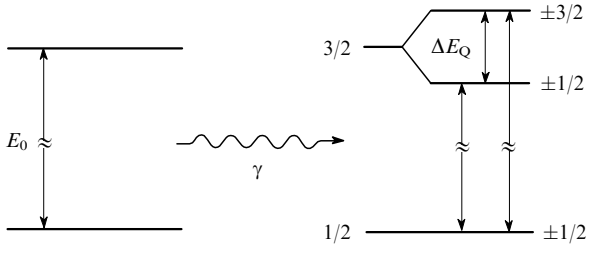
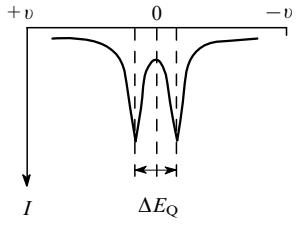
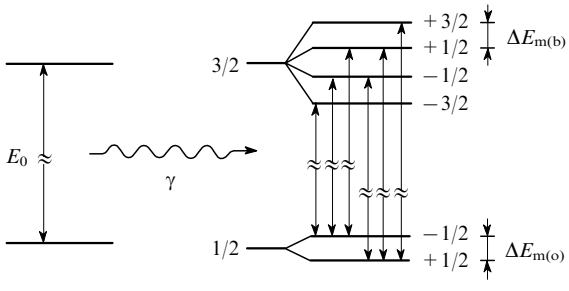
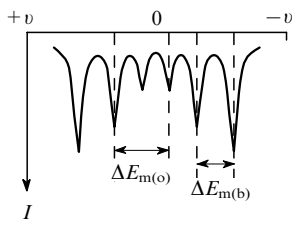
† More recently, it was shown that Mössbauer effect can be observed not only in solids (regular crystals), but also in amorphous solids or solutions.[12,13]

III. Mössbauer spectra as a source of analytical information

The nucleus of a Mössbauer atom is a highly sensitive probe, namely, the energies of nuclear sublevels vary depending on the electronic environment of the nucleus and on the internal and external electric and magnetic fields.

The Mössbauer spectra bear information on various interactions, many of which are indirectly related to the chemical nature of the Mössbauer atom and its nearest environment. The relation is indirect because the chemical properties of an atom are determined by its outer electrons, which are shielded from the Mössbauer nucleus by inner electrons. Table 1 lists the most important parameters that can be extracted from Mössbauer spectra and used for qualitative analysis. We also present here the energy diagrams that demonstrate the influence of the parameters in question and the corresponding patterns of Mössbauer spectra. As resonance nuclei we consider those of the most widely

Table 1. Most important parameters of ^{57}Fe and ^{119}Sn Mössbauer spectra.

Characteristics of Mössbauer spectra	Schemes of energy levels and transitions for ^{57}Fe (or ^{119}Sn) isotopes in		Mössbauer spectral pattern
	source of radiation (s)	absorber (a)	
Resonance linewidth (Γ)			
Isomer (chemical) shift (δ_c)			
Second-order temperature (Doppler) shift (δ_T)			
Quadrupole energy splitting (ΔE_Q)			
Magnetic splitting			

used Mössbauer isotopes, ^{57}Fe and ^{119}Sn, having the ground- and excited-state nuclear spins of $I_g = 1/2$ and $I_e = 3/2$, respectively.

Each parameter of the Mössbauer spectra listed in Table 1 has its own physical nature and bears analytical information. Detailed consideration of these parameters is available in the literature.[4–9] The set of parameters listed in Table 1 should be augmented with the probability of Mössbauer effect (f_M), which plays an important role in quantitative analysis using Mössbauer spectroscopy.

Quantitative analysis is based on the assumption that the area, S, under a line in the spectrum of a thin absorber is proportional to the number, n, of the atoms containing Mössbauer nuclei:

$$S = kf_M n,$$

where k is the factor including the resonant absorption cross section, emission intensity, time taken to collect the spectral data, energies of γ-quanta, effect of background emission and the angle between the direction of the γ-quanta flux and the normal to the absorber surface; and f_M is the Mössbauer effect probability (*i.e.*, probability of recoilless elastic processes). The f_M value depends on the root-mean-square displacement of the absorber nuclei from their equilibrium positions $\langle x^2 \rangle$ at temperature T

$$f_M = \exp\left(\frac{-p^2\langle x^2\rangle}{\hbar}\right),$$

where $p = E_\gamma/c$ is the momentum of the γ-quantum ($E_\gamma = \hbar\nu$ is the photon energy).

The stronger the coupling between atoms in the crystal lattice, the higher the characteristic (Debye) temperature of the substance Θ_D and the smaller the root-mean-square nuclear displacement at a given temperature and, hence, the higher the probability of the Mössbauer effect. This dependence of the area under the spectral curve on the number of resonance nuclei is valid in the thin absorber approximation where $n\sigma \ll 1$ (σ is the resonant absorption cross section), *i.e.*, when the shape of the resonance line is undistorted by saturation effect.

Resonance linewidth. In the thin absorber approximation an experimental Mössbauer spectral line has a Lorentzian shape [1] (see Table 1) and the minimum linewidth is given by the doubled natural width of the absorption line, Γ. It was theoretically shown and experimentally proved that there exists line broadening due to diffusion of atoms. The linewidth is influenced by crystal lattice defects that cause changes in the local environment of resonance atoms. Line broadening is most pronounced in the spectra of amorphous and glassy materials.

Isomer (chemical) shift (δ_c) arises in the case where Mössbauer nuclei in the source and in the absorber are in different chemical environments. The isomer shift manifests itself as a shift of the resonant absorption line relative to the absorption line at $v = 0$. The δ_c value is given by:

$$\delta_c = \frac{4\pi}{5}e^2ZR^2\frac{\Delta R}{R}\left\{|\Psi(0)|_a^2 - |\Psi(0)|_s^2\right\}, \quad (2)$$

where e is the charge of electron, Z is the charge of the nucleus, R is the average radius of the nucleus, ΔR is the change in the nuclear radius on going from excited state to the ground state and $|\Psi(0)|_a^2$ and $|\Psi(0)|_s^2$ are the electron densities at the nuclei of the resonance atoms in the absorber (a) and source (s), respectively. For a particular nucleus, the $\Delta R/R$ ratio is a constant and the chemical shift is determined only by the difference between the electron densities at the resonance nuclei in the source and in the absorber, which in turn mainly depends on the s-state populations. Electrons from other shells (p, d, f) can indirectly affect the δ_c value through partial shielding of s-electrons or formation of hybrid states with the s-orbitals (generally, this should be allowed for when interpreting the chemical shift values). The δ_c values obtained by Mössbauer spectroscopy make it possible to draw conclusions about the character of a chemical bond, its degree of covalence, coordination, degree of electron delocalisation, *etc*.

Second-order temperature (Doppler) shift (δ_T) is due to the energy difference between emitted and absorbed γ-quanta (owing to temperature difference between the source and absorber) and manifests itself as a shift of the resonant absorption line. The shift value is calculated as follows

$$\delta_T = -\frac{\langle v^2\rangle}{2c^2}E_0, \quad (3)$$

where $\langle v^2\rangle$ is the temperature-dependent root-mean-square velocity that characterises atomic motions in solids.

Thus, the energy shift δ observed in Mössbauer spectra is the sum of two contributions

$$\delta = \delta_c + \delta_T.$$

Quadrupole splitting (ΔE_Q) is a result of the interaction between the quadrupole moment of non-spherical resonance nucleus with the gradient of the electric field created at the nucleus by the electron shell and ligands. This interaction leads to splitting of a nuclear energy level into sublevels. For ^{57}Fe nuclei the separation, ΔE_Q, is calculated as follows:

$$\Delta E_Q = \frac{eQ}{2}V_{zz}\sqrt{1+\frac{\eta^2}{3}}, \quad (4)$$

where eQ is the quadrupole moment of the nucleus, V_{zz} is the principal component of the electric field gradient at the nucleus along the z axis and $\eta = (V_{zz} - V_{yy})/V_{xx}$ is the asymmetry parameter (V_{xx} and V_{yy} are the electric field gradients along the x and y axes). The coordinate axes are chosen in such a way that $0 \leqslant \eta \leqslant 1$. The electric field gradient at the nucleus is determined by the environment geometry, by the effective charges of ions surrounding the resonance nucleus in the object under study and by the presence of partially filled non-spherical electron shells (p, d, f) in the resonance atom. Thus, in the general case the quadrupole interaction of a Mössbauer nucleus bears information on the structure of the atomic environment of the nucleus in the crystal lattice and on the state of its valence shells.

If the Mössbauer spectrum simultaneously exhibits the chemical shift and quadrupole splitting (these parameters are affected by s- and p-electrons in different fashion), it is possible to obtain more diverse information on the state of the electron shell of the resonance atom and on the local structure of the crystal lattice.

Magnetic (Zeeman) splitting (ΔE_m) arises due to the interaction between the magnetic moment of the nucleus (in both ground and excited states) with the effective magnetic field (B) created by the electron shell at the nucleus. The Zeeman splitting is given by

$$E_m = -g_I\mu_N B\Delta m_I, \quad (5)$$

where g_I is the nuclear gyromagnetic ratio for a given nuclear level (I is the nuclear spin), μ_N is the nuclear magneton, m_I is the magnetic quantum number and Δm_I is the change in the magnetic quantum number corresponding to transition of a ^{57}Fe, ^{119}Sn or ^{125}Te nucleus from excited state (spin $I_e = 3/2$) to the ground state ($I_g = 1/2$). Emission of a γ-quantum from each of the four excited-state sublevels ($+3/2$, $+1/2$, $-1/2$, $-3/2$) causes a transition of the nucleus to one out of two ground-state sublevels ($+1/2$, $-1/2$). The transition occurs in accordance with the selection rule for dipole transitions ($\Delta m = 0, \pm 1$) and results in the appearance of magnetic hyperfine structure (magnetic sextet) in the Mössbauer spectrum (see Table 1). If the nucleus in question is simultaneously involved in the magnetic and quadrupole interactions, energy level calculations are complicated. The magnetic field strength B is a function of structural and electronic parameters, namely, the number of unpaired d-electrons, the type of the chemical bond formed by the resonance atom, the environment geometry, *etc*. Therefore, the appearance of hyperfine magnetic splitting makes the Mössbauer spectra much more informative and allows one to reveal peculiar features of the electronic, crystal and magnetic structures of compounds analysed.

The informativity of the key parameters of Mössbauer spectra (see above) shows that this relatively simple (from experimental standpoint) method not only has a great potential for studies of the structure and electronic properties of solids but is also an efficient method of analysis of solid samples in spite of a limited number of Mössbauer isotopes. A proof of this statement is provided by numerous examples of solution of complex analytical problems using Mössbauer spectroscopy.

The possibility of obtaining unique information on the local chemical state of a resonance atom and on the electric and magnetic fields at the atomic nucleus led to setting up emission Mössbauer spectroscopy experiments in which the resonance atoms were introduced into the sample as specific probes (see, *e.g.*, Ref. 18). This approach was employed, in particular, in a study of high-temperature superconductors. For instance, the copper atoms in the crystal lattices of $Tl_2Ba_2CuO_6$ and $Tl_2Ba_2CaCu_2O_8$ superconductors were replaced by ^{67}Cu isotopes by diffusion doping and then the ^{67}Cu (^{67}Zn) Mössbauer spectra were measured at 4.2 K with ^{67}ZnS as absorber.[18] In this case the main problem is to confirm the fact that the resonance (dopant) atoms occupy the substitution sites in the crystal lattice.

IV. Methods of processing of Mössbauer spectra and databases

An important moment in Mössbauer spectroscopy is processing of experimental spectra using special programs that permit theoretical description of an experimental spectrum using a set of resonance lines. The aim of the spectral data processing is to determine the physical parameters considered in the previous Section.

The Mössbauer spectra are usually processed by the least squares method.[19–21] The functional to be minimised has the form

$$\chi^2 = \sum_{i=1}^{n} \frac{1}{N_i} [N_i - S_i(p_0, p_1, ..., p_k)]^2 \qquad (6)$$

where p_0, p_1, ..., p_k are parameters, N_i is the number of counts in the ith channel ‡ of the experimental spectrum, $S_i(p_0, p_1, ..., p_k)$ is the model spectral amplitude for the ith channel and n is the total number of channels. Processing of an experimental spectrum is preceded by the choice of the model spectral shape. The choice is based on *a priori* information on the object analysed. A model spectrum is assumed to be a spectrum comprising a set of resonance lines corresponding to a particular type of the hyperfine structure of resonance nuclei.§ The model spectrum of a thin absorber can be represented by superposition of Lorentzian lines with negative (absorption spectra) or positive (scattering spectra) amplitudes with respect to the baseline.

The model spectrum of a thick absorber is represented by either convolution of a Lorentzian and a Gaussian function [22] or the transmission integral,[23] which describes the motion of the resonance γ-quantum through an absorber containing resonance nuclei. This approach is best for quantitative analysis.

In a large class of substances, such as amorphous solids, alloys, ultradisperse media, *etc*. the nearest spatial and elemental environment of the atoms containing resonance nuclei continuously changes. The spectra of such substances represent superpositions of continuous series of subspectra and cannot be processed using the algorithms considered above, because the problem becomes ill-posed (no unique solution exists). The approach employed in this case is based on representation of the model spectrum by convolution of k elementary subspectra $L_i^k(p_0, p_1, ..., p_k)$ with one or two continuously varying hyperfine interaction parameters and the weight function $P^k(p_0, p_1, ..., p_k)$ of these subspectra, which is often called the hyperfine field distribution function.[24,25] This function provides information on the distribution of chemical bonds and electric or magnetic fields at nuclei of the resonance atoms in the substance under study.

An alternative approach to solution of ill-posed problems is based on the principle of limited density of spectral lines depending on the statistical significance of the spectrum.[26] The efficiency of this approach was demonstrated taking analysis of complicated Mössbauer spectra of high-temperature superconductors as examples.

Informativity of Mössbauer spectra for qualitative and quantitative analysis can be exemplified by the processing of a γ-ray scattering spectrum of oxidised surface of metallic iron (conversion electrons were detected). Figure 2 presents the experimental Mössbauer spectrum (points) and its decomposition into subspectra corresponding to iron atoms in different phases. Using the Mössbauer parameters of the subspectra, it is possible to identify iron-containing phases (qualitative analysis), while measuring the areas under individual lines provides a quantitative estimate of the relative content of these phases. To obtain a more correct estimate, the surface areas should be corrected for the f_M factor (probability of resonant absorption in each phase). However, determination of the f_M factor faces practical and theoretical difficulties and therefore the relative content of phases is estimated to an accuracy of the f_M factor.

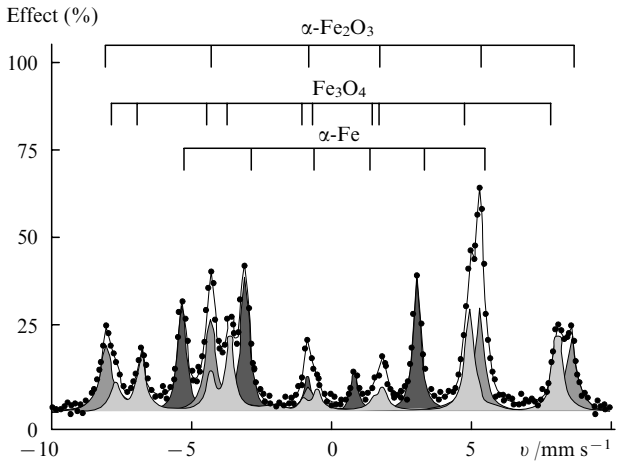


Figure 2. Decomposition of experimental Mössbauer spectrum into subspectra corresponding to iron atoms belonging to a particular phase.

V. Geochemical and cosmochemical analyses

Applications of Mössbauer spectroscopy in chemical analysis mainly concern solution of topical problems of geochemistry and cosmochemistry. They include determination of the oxidation states and coordination numbers of iron and tin atoms in minerals,[27–35] phase analysis of rocks,[36–39] meteorites [40–42] and lunar soil [43] and determination of the age and genesis of minerals.[44,45]

Among the last-named group of research avenues, of special interest are the Mars surface studies,[46–48] in particular, investigations of the mineralogical composition of Martian soil using tailor-made Mössbauer spectrometers MIMDS II. These studies are aimed at understanding the evolution of the planet and answering the question on the existence of water on Mars. Iron-based minerals were studied. Analysis was carried out using the conversion resonant radiation backscatter geometry. The results of analysis of Martian soil near the Gusev crater and on the plain were different. The detection of olivine and pyroxene (silicate

‡ The intensity of γ-quanta flux is fixed using a multichannel analyser. The channel number is proportional to the velocity of the source of radiation.
§ If resonance nuclei are in inequivalent positions, the shape of the model spectrum corresponds to superposition of hyperfine structures.

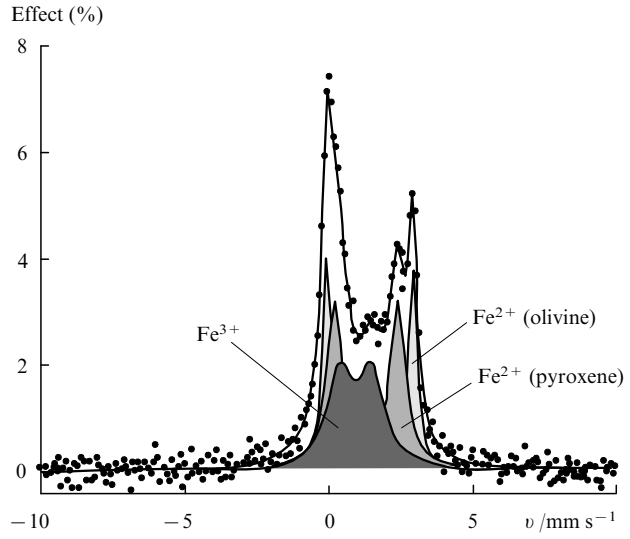


Figure 3. First Mössbauer spectrum taken on the Mars surface near the Gusev crater (points) and its decomposition into subspectra corresponding to iron atoms in different environments.

minerals that are usually contained in volcanic rocks, Fig. 3) near the Gusev crater appeared to be unexpected. The greatest portion (~95%) of the Mössbauer spectra of Martial soil taken on the plain falls on the component corresponding to such a highly abundant Earth mineral as hematite, Fe_2O_3 (Fig. 4). The formation of hematite is usually preceded by hydrolytic transformations of water-soluble forms of Fe(III), which provides indirect evidence for the existence of water on Mars. Confirmation of conclusions about the genesis of Martian minerals requires continuous research involving drilling in order to obtain soil from greater depth.

Mössbauer spectroscopy belongs to the main methods of investigation of the genesis of minerals in the Earth crust. In the last decade there has been a rapidly increasing interest in studies of microbiological pathways of formation of iron-containing minerals *via* anaerobic dissimilatory iron-reducing bacteria involved in reduction of iron oxides. It was assumed that these bacteria could participate in formation of pre-Cambrian iron–silicon formations. Being a highly sensitive method of analysis of

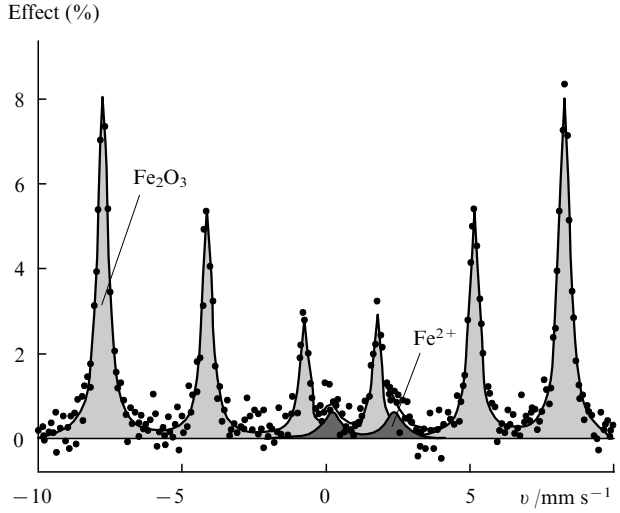


Figure 4. Mössbauer spectrum of Martian soil taken on the plain and its decomposition into subspectra corresponding to iron atoms of hematite Fe_2O_3 (sextet) and olivine Fe^{2+} (doublet).

iron-containing objects, Mössbauer spectroscopy allowed not only the kinetics of the phase transformations induced by iron-reducing bacteria to be studied but also factors affecting this process to be determined.[49–54] The results obtained suggested the existence of various pathways of biosynthesis of iron-containing minerals by micro-organisms that favour the reduction of Fe(III) to Fe(II). At present, the biosynthesis mechanisms are still to be clarified and there has been intensive accumulation of experimental information.

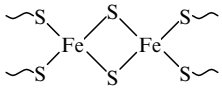
VI. Mössbauer spectroscopy in the analysis and investigations of biological objects

Iron atoms play an important role of active centres in such vitally important proteins as hemoglobin, myoglobin, cytochromes, *etc.* These proteins are responsible for reversible binding and transfer of oxygen and participate in photosynthetic redox chains owing to electron transport. The possibility of application of Mössbauer spectroscopy in studies of biomolecules (mainly proteins) has been best considered in Refs 55–57. An important avenue of biological research is comparison of the Mössbauer parameters obtained in studies of healthy (normal) organisms and the organisms with various diseases or affected by external factors.[58–61]

Methods of measuring the Mössbauer spectra of biological objects are generally identical to those employed in the studies of inorganic objects. However, the concentration of iron in the samples under study (except for ferredoxin) is so low that obtaining statistically significant results requires enrichment with ^{57}Fe isotope. Therefore, an important aspect of the studies and analysis of biological objects is establishing sample preparation conditions suitable for directed exchange of iron atoms in the sample by the ^{57}Fe isotope without destruction of the initial protein structure. This can be attained using incubation of microorganisms in ^{57}Fe-containing media or by injecting a ^{57}Fe salt solution into living organisms.

Using Mössbauer spectroscopy, heme and non-heme proteins (*e.g.*, constituents of photosynthetic centres), iron–sulfur, iron-transport and iron-accumulating proteins were studied. Fine details of the electronic and spin transformations of iron in heme and in sulfur-containing proteins were investigated. In particular, the Fe(II) atom in heme is responsible for reversible binding of oxygen in hemoglobin (Hb) and the operation of hemoglobin. Mössbauer spectroscopy studies showed that violation of normal heme functions is accompanied by oxidation of Fe(II) to Fe(III). Iron(II) in heme is in two spin states, a high-spin ($I = 2$) and a low-spin state ($I = 0$). The high-spin state is observed only for the Fe(II) atom of the deoxy form of Hb in a pentaligand environment. The low-spin state is characteristic of the Fe(II) compound with six ligands, with an O_2 or CO molecule as the sixth ligand. The spectra of Hb, HbO_2 and HbCO are significantly different. The addition of O_2 to Hb is accompanied by dramatic change in the chemical shift value, which is due to transition of Fe^{2+} from the high-spin state in Hb to the low-spin state in HbO_2. The addition of CO to hemoglobin causes the formation of a symmetrical structure HbCO (as indicated by a decrease in the quadrupole splitting) with the Fe(II)–CO bond being stronger than the Fe(II)–O_2 bond. Since CO adds to Hb irreversibly and thus prevents Hb from doing oxygen exchange, poisoning with carbon monoxide leads to fatal case.[55]

Iron-sulfur proteins were among the first biological objects studied by Mössbauer spectroscopy, because they contain a relatively large number of iron atoms in the molecule. The active centre of sulfur-containing proteins comprises the iron and sulfur atoms.[62–66]



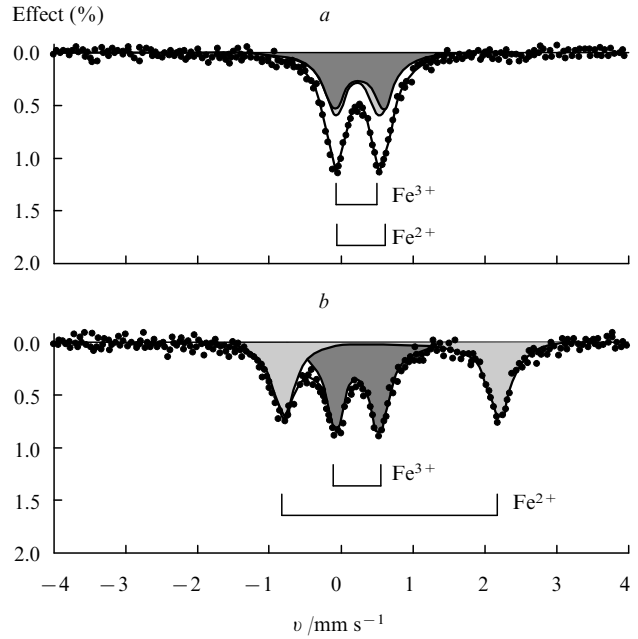


Figure 5. Mössbauer spectra of plant ferredoxin measured at 195 K. Oxidised Fd (*a*) and reduced Fd (*b*). Vertical lines denote positions of the doublet lines.

Usually, the Fe(II) and Fe(III) atoms in sulfur-containing proteins are in the high-spin state. Figure 5 presents the classical Mössbauer spectra of plant ferredoxin (Fd)¶ in the oxidised [Fe(III)] and reduced [Fe(II)] states.

The Mössbauer spectrum of oxidised Fd containing two tetrahedrally coordinated Fe(III) atoms exhibits two doublets with nearly identical parameters ($\delta = 0.22-0.25$ mm s^{-1} and $E_Q = 0.6-0.7$ mm s^{-1}) at a measurement temperature of 195 K. The low δ value indicates a high degree of covalence of Fe–S bonds. In spite of the same ligand composition, it is clear that positions of the iron(III) atoms in the active centre of Fd are inequivalent. This is probably due to the effect of polypeptide chains, resulting in changes in the bond lengths and bond angles in the active centre. This inequivalence is well pronounced in the reduction of Fd. Transfer of an electron to Fd leads to its localisation on a Fe(III) ion and to reduction of this ion to Fe(II) ($\delta \approx 0.7$ mm s^{-1} and $E_Q = 3.0$ mm s^{-1}), the electronic state of the other Fe(III) ion being changed insignificantly.

In pharmacology, Mössbauer spectroscopy is used in studies of the state of iron atoms in iron-containing pharmaceuticals used in medical practice. Most of the preparations contain divalent iron, because in this case [in contrast to Fe(III)] the side effects characteristic of iron compounds are less pronounced. Besides, specific biological activity of the Fe(II)-containing preparations is higher than that of the preparations containing Fe(III) ions. Therefore, for pharmaceutical analysis it is important to determine the oxidation state of iron in iron-containing drugs. Mössbauer spectroscopy is also used for the determination of the oxidation state of iron on storage of drugs. The results of Mössbauer spectroscopy tests of iron-containing vitamins produced by the leading pharmaceutical companies were reported.[67,68] It was shown that all vitamins contain small amounts of trivalent iron; however, in some samples the content of Fe(III) exceeded the permissible rates. This suggests that Mössbauer spectroscopy should be included in the group of methods for control of iron-containing pharmaceuticals.[68]

¶ Ferredoxin is an iron-containing protein acting as electron carrier in many biological redox processes.

In addition to conventional absorption Mössbauer spectroscopy, biological objects are also analysed by emission Mössbauer spectroscopy [12,69–72] (here, a radioactive isotope ^{57}Co is introduced into the object to be analysed). Despite the fact that this technique allows the sensitivity of Mössbauer spectroscopy to be improved by several orders of magnitude, it is rarely used due to the need of unprotected operation with radioactive preparations (see above).

Mössbauer spectroscopy studies of the molecular mobility of proteins, biopolymers and their fragments occupy a special position. These experiments are carried out using the Rayleigh scattering of Mössbauer radiation. The technique made it possible to reveal various groups of motions and to determine corresponding frequency ranges and vibrational amplitudes.[55,73–77]

VII. Mössbauer spectroscopy in structural studies

Mössbauer spectroscopy has been an efficient tool for structural analysis in studies of structural and magnetic phase transitions in organic and inorganic compounds [78–87] containing such Mössbauer isotopes as ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{151}Eu, ^{155}Gd or ^{197}Au. In this case Mössbauer spectroscopy makes it possible to significantly complement the results obtained from IR and NMR spectroscopies. High structural sensitivity of Mössbauer spectroscopy is due to the fact that parameters of the hyperfine structure of the Mössbauer spectrum (chemical shift, quadrupole splitting and magnetic hyperfine splitting) depend on the population of the valence states of the Mössbauer atom in the compound under study and on the spatial structure of this compound. Changes in the parameters of Mössbauer spectra depending on the external factors, affecting the samples under study (temperature, pressure, magnetic fields, *etc.*), provide additional information on the structural and phase transitions in such compounds. The application of Mössbauer spectroscopy to structural studies of Fe(II) complexes can be exemplified by the investigation of the spin-transition state (so-called spin-crossover [88–90]), *i.e.*, an equilibrium state between the high-spin (HS) and low-spin (LS) states. Spin-crossover can occur in d^4-, d^5-, d^6-, d^7- and d^8-transition metal complexes. Depending on the ratio of the splitting energy of the transition metal atom in the ligand field (Δ) to the spin pairing energy (P) the ground state of the transition metal complex can be high-spin (for weak ligand field $\Delta < P$) or low-spin (for strong ligand field $\Delta > P$). If the difference $|\Delta - P|$ becomes comparable in magnitude with the thermal energy k_BT, the equilibrium coexistence of the high-spin and low-spin states becomes possible. Figure 6 presents the energy diagram of Fe(II) 3d-AO energy levels ($3d^6$-electron configuration) in octahedral complex for the high- and low-spin states and for the spin equilibrium state.

The Mössbauer spectra of $[Fe(phen)_2(NCS)_2]$ measured at different temperatures are shown in Fig. 7. The spectrum obtained at 300 K (see Fig. 7 *f*) exhibits a single doublet with

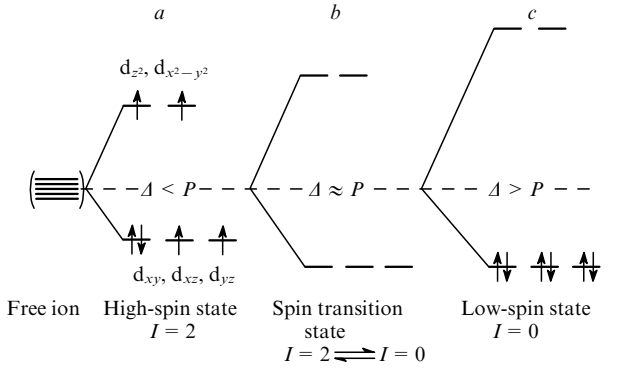


Figure 6. Fe(II) 3d-orbital levels in octahedral complex at weak (*a*), intermediate (*b*) and strong (*c*) ligand field. Fe^{2+} : $Fe_{tot} \approx 0.6$.

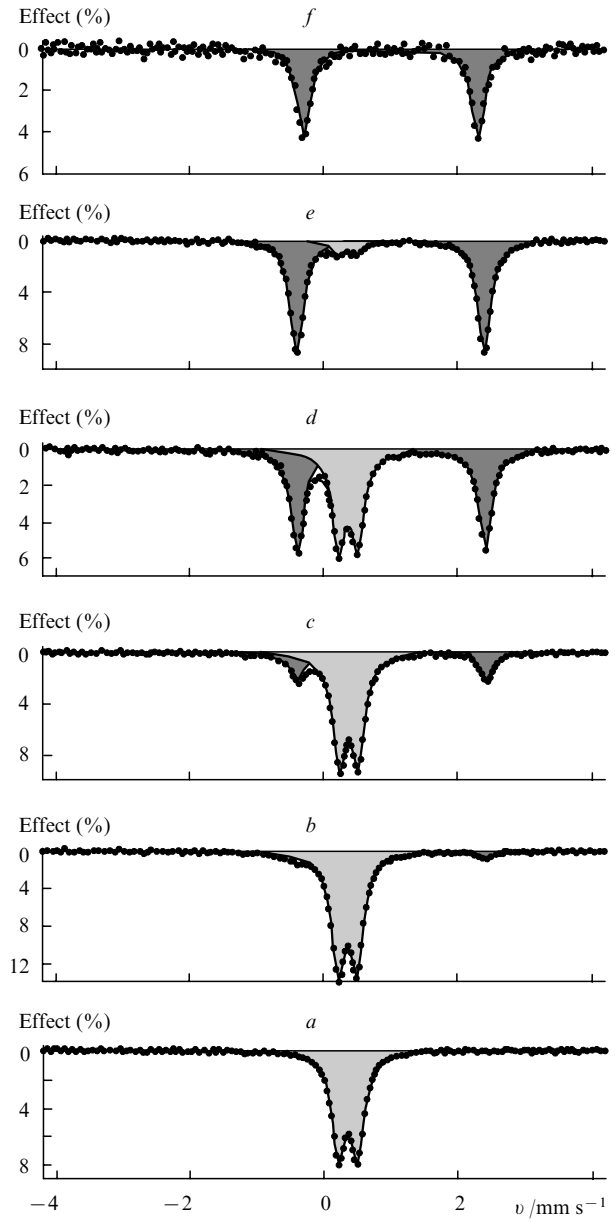


Figure 7. Mössbauer spectra of $[Fe(phen)_2(NCS)_2]$ measured at different temperatures. The subspectra corresponding to iron atoms in the low-spin and high-spin states are bright and dark shaded, respectively. Temperature /K: 77 (*a*), 180 (*b*), 184 (*c*), 186 (*d*), 188 (*e*), 300 (*f*).

the parameters corresponding to a pure HS state of Fe(II) ($\delta \approx 1$ mm s^{-1} and $E_Q = 2.6$ mm s^{-1}) while the spectrum at 77 K (Fig. 7 *a*) exhibits a single doublet with the parameters corresponding to pure LS state ($\delta \approx 0.35$ mm s^{-1} and $E_Q = 0.25$ mm s^{-1}). The spectra obtained in the temperature range 180–188 K exhibit two quadrupole doublets corresponding to two spin states (HS and LS). As the temperature decreases, the proportion of Fe(II) atoms in the HS state decreases and in the LS state increases. Transition from one state to the other occurs jumpwise in a narrow temperature range (180–188 K).

Spin transitions in Fe(III) complexes were studied by measuring the magnetic susceptibility using Mössbauer spectroscopy.[91–93] At present, Mössbauer spectroscopy is employed in studies of spin transitions under the action of electromagnetic radiation, in magnetic field and under pressure.[94–96]

Recently, the emphasis in structural studies of tin compounds has been placed on determination of the charge states and possible crystallographic positions of tin atoms.[97–99] The possibility of simultaneous determination of the chemical shift and quadrupole splitting allows Mössbauer spectroscopy to be used in studying the structure, reactivity and mechanisms of transformations of organotin compounds (see Refs 100–103).

VIII. Mössbauer spectroscopy and the studies and monitoring of corrosion and catalytic processes

The first chemical application of Mössbauer spectroscopy was the study of iron oxides as corresponding corrosion products. Qualitatively, the phase composition of corrosion products can be established by comparing the parameters of Mössbauer spectra with the parameters of the reference spectra of artificially synthesised oxides and hydroxides. Comprehensive information on the structure, magnetic properties and Mössbauer parameters of iron oxides, hydroxides and ferrihydrides was reported by Murad and Johnston.[104] The advantages of Mössbauer spectroscopy as a method of investigation of corrosion processes are as follows:

— uniqueness of information on the chemical and structural transformations during corrosion (in many cases different phases can be identified based on the spectral pattern);

— minimum requirements for sample preparation for analysis and studies;

— possibility of *in situ* studies in aggressive atmosphere and in aggressive liquids;

— possibility of layer-by-layer and phase analyses under coating (thickness of the layers under study can vary over a very wide range);

— the same types of contributions of X-ray amorphous and ultradisperse substances to the Mössbauer spectrum (similar to the contributions of well-crystallised compounds).

Owing to the advantages listed above, Mössbauer spectroscopy has found wide application in studies of corrosion processes, such as corrosion in gases,[105–109] in water and aqueous solutions,[110–112] in aggressive media,[113] in studies of inhibition and passivation,[114–116] internal oxidation and electrode reactions. The availability of Mössbauer spectroscopy also allows it to be employed in solving problems of analytical control, such as monitoring of corrosion of bridges[117,118] and ship hulls,[118] thermal and nuclear power plant circuits,[117,119,120] *etc*. Here, the use of Mössbauer spectroscopy made it possible not only to determine the phase composition of oxide films that grow on the surface of pearlitic steels contacting the aqueous phase but also establish the interrelation between different forms of iron existing in the aqueous phase and the compositions of the films grown on the steel surfaces.[119,120] Using Mössbauer spectroscopy, it was shown that the quality of protective corrosion films on the steel surfaces can be improved by targeted choice of the composition and structure of the dissolved iron compounds involved in film formation.[119,120]

Mössbauer spectroscopy is a highly informative method of research on such surface phenomena as the catalytic activity, dynamics and chemical state of atoms in highly disperse particles, resins, zeolites, on the surface of sorbents and on surface-modified materials.[17,121] The possibilities of using Mössbauer spectroscopy in studies of nanoclusters and nanocluster systems have been considered.[122]

Mössbauer spectroscopy is employed in production of heterogeneous catalysts and in their characterisation, in analysis of the chemical state of the catalyst surface, in analysis of chemisorption products and in the course of catalyst operation. The use of X-ray diffraction methods in studies of real catalysts is complicated by the fact that catalysts are ultradisperse particles. Mössbauer spectroscopy is free from this limitation, which makes it possible to obtain information on the size and distribution of catalytic particles over the catalytically active phase.

Most often, solid catalysts comprise an active component coated on a support. The latter operate various functions, namely, provide the largest surface area to be coated with the active component, stabilise an unstable structure and interact, through

electron exchange, with the active component, thus forming a unique catalytic system. If the active component of a catalyst includes atoms with Mössbauer nuclei, information on the oxidation state of these atoms can be obtained from the chemical shift in the Mössbauer spectra. For instance, Mössbauer spectroscopy data show that iron supported by zeolite LTL is more catalytically active than iron supported by SiO_2, Al_2O_3, C and MgO.[123] The effect of the annealing temperature on the state of ^{191}Au atoms for two types of catalysts, Au/TiO_2 and $Au/TiO_2/SiO_2$, was studied,[124] as well as the mechanism of low-temperature oxidation of CO using Au/Fe_2O_3 as catalyst.[125] Recently, there has been new interest in studies of tin-containing catalysts. For instance, ^{119}Sn Mössbauer spectroscopy was employed to study the catalytic properties of the $Pd-SnO/Al_2O_3$ and $Pd-SnO/SiO_2$ systems designed for water denitration.[126–128]

IX. Conclusion

Summing up, it should be noted that the examples given above do not exhaust the list of analytical applications of Mössbauer spectroscopy that can be found in special publications on the subject (see above). But it is almost impossible to draw a line between applications of Mössbauer spectroscopy in scientific research and in chemical analysis, because distinctions between these fields are rather conditional. Here, the method remains the same, the main goals being different. The results of basic research into outworld can appear to be in demand for chemical analysis after a very short time they have been obtained. For instance, information on the mechanisms of corrosion processes is necessary for control of technological processes. Therefore, in this review we deliberately do not draw this line. The examples given above illustrate the main avenues of applications of Mössbauer spectroscopy in chemistry, mineralogy, biology and materials science. Undoubtedly the list of examples will be appreciably extended in the future. Here, objects in which the Mössbauer effect was observed for the ^{57}Fe isotope were chosen to be the main part of illustrative material. This can be explained by not only high abundance of iron-containing objects (see above) but also the fact that in the last decade the vast majority of studies ($\sim$90%) were carried out with this isotope and therefore they are best to exemplify the range of analytical applications of Mössbauer spectroscopy. The next place is occupied by ^{119}Sn Mössbauer spectroscopy studies with $\sim$6%–7% of the total number of publications. A total of 3%–4% of the overall number of communications falls on the studies with other isotopes.

In connection with advances made in the field of excitation of nuclear resonance levels using synchrotron radiation one can hope that this will open new prospects for applications of nuclear γ-resonance for analytical purposes.[129, 130] First, the use of nuclear resonant scattering of synchrotron radiation eliminates problems associated with preparation of Mössbauer sources, especially short-lived ones. Second, auxiliary equipment on facilities for nuclear resonant scattering of synchrotron radiation makes it possible to carry out measurements in a wide range of temperatures, pressures, magnetic fields, in high vacuum, *etc*., and thus obtain a greater body of information on the object analysed. Particular information on great potential of nuclear resonant scattering of synchrotron radiation for obtaining analytical information can be found in recent literature.[131–135]

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