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Mass-Independent Isotope Effects

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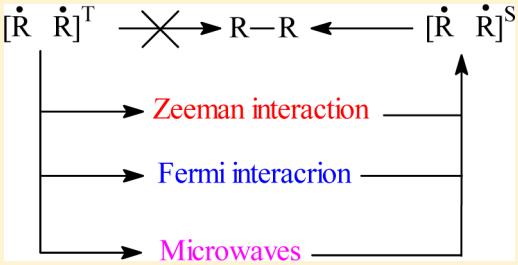
ABSTRACT: Three fundamental properties of atomic nuclei—mass, spin (and related magnetic moment), and volume—are the source of isotope effects. The mostly deserved and popular, with almost hundred-year history, is the mass-dependent isotope effect. The first mass-independent isotope effect which chemically discriminates isotopes by their nuclear spins and nuclear magnetic moments rather than by their masses was detected in 1976. It was named as the magnetic isotope effect because it is controlled by magnetic interaction, i.e., electron−nuclear hyperfine coupling in the paramagnetic species, the reaction intermediates. The effect follows from the universal physical property of chemical reactions to conserve angular momentum (spin) of electrons and nuclei. It is now detected for oxygen, silicon, sulfur, germanium, tin, mercury, magnesium, calcium, zinc, and uranium in a great variety of chemical and biochemical reactions including those of medical and ecological importance. Another mass-independent isotope effect was detected in 1983 as a deviation of isotopic distribution in reaction products from that which would be expected from the mass-dependent isotope effect. On the physical basis, it is in fact a mass-dependent effect, but it surprisingly results in isotope fractionation which is incompatible with that predicted by traditional mass-dependent effects. It is supposed to be a function of dynamic parameters of reaction and energy relaxation in excited states of products. The third, nuclear volume mass-independent isotope effect is detected in the high-resolution atomic and molecular spectra and in the extraction processes, but there are no unambiguous indications of its importance as an isotope fractionation factor in chemical reactions.



INTRODUCTION

A majestic role of isotopes in physics and chemistry, in biochemistry and biology, in the dating of ancient climate and global events in the natural history of the Earth, in determining geological age of ores, minerals, and historical relics, in art and archeology, in medicine and tracing of pollutants in environmental ecology, etc. is well-known. Isotopes carry the memory of the birth and transformation of molecules and their distribution traces chemical history of the matter. There are two facets in the service of isotope memory: first, isotopes function as its source, they participate in its creation and accumulation through the isotope effects in the reactions; second, they serve as the labels certifying and tracing chemical events and their sequence. This paper treats the first, more important function, i.e., fractionation of isotopes induced by isotope effects based on the three fundamental properties of atomic nuclei—mass, spin (and related magnetic moment), and volume.

MASS-DEPENDENT ISOTOPE EFFECT

The well-known and highly deserved mass-dependent isotope effect (MDE) separates isotopic nuclei on their masses. It originates from the difference in energy (mostly vibrational) of molecules with light and heavy nuclei: the latter have lower energy and react lazier. For this reason, the sign of MDE is always positive: the heavy nuclei are accumulated in reactants, and the light ones are transferred in products. The effect is large only for hydrogen; for all others, it does not exceed several tenths of percent and even much less for heavy elements. It characterizes energy-expensive processes and arises in chemical reactions of substitution or chemical bond scission. Its magnitude only slightly depends on the reaction mechanism and carries rather restricted information on its details. Despite this fact, the MDE is a phenomenon of paramount importance for many fields of human activity—from superconductivity in physics to enzymatic transfer of phosphate groups in the ATP synthesis in biology. There is no need to comment on it in detail because mechanisms of the MDE are well-known and described in many books.[1−7]

MDE is known to be certified as classical and quantum. The former is controlled by zero-energy difference of isotopic molecules which results in an activation energy difference of their reactions; the latter follows from the wave properties of atoms and occurs as a quantum mass-dependent tunneling of atoms (predominantly, hydrogen) under barrier. Dexter Northrop[8] suggested an elegant and physically perfect high-pressure technology isotope experiment to distinguish these two effects. It is based on the fact that the zero-energy difference of isotopic molecules does not depend on pressure, while the tunneling transmission coefficient strongly depends on it.

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The most reliable and almost unambiguous test for MDE is the isotope ratios in triads (^{16}O−^{17}O−^{18}O, ^{32}S−^{33}S−^{34}S, ^{24}Mg−^{25}Mg−^{26}Mg, ^{42}Ca−^{43}Ca−^{44}Ca, ^{198}Hg−^{199}Hg−^{200}Hg, etc.). In terms of the commonly accepted values of isotope fractionation, these ratios look like relations $\delta^{17}O = 0.5\delta^{18}O$, $\delta^{33}S = 0.5\delta^{34}S$, $\delta^{25}Mg = 0.5\delta^{26}Mg$, $\delta^{43}Ca = 0.5\delta^{44}Ca$, $\delta^{199}Hg = 0.5\delta^{200}Hg$, etc. (further we will nominate these ratios as a one-half-rule). Here, in particular, for ^{17}O

$$\delta^{17}O = (R_x/R_{st} - 1) \times 10^3$$

$R_x = (^{17}O/^{16}O)$ is a content of ^{17}O in the analyzed material; R_{st} is that in a certain standard; both values are usually expressed in pro mil (0.1%). The one-half-rule is confirmed in many experiments; there are no doubts about its validity, so that now it is generally accepted.

Hulsten and Thode[9] were the first who observed a noticeable deviation of sulfur isotope contents from the one-half-rule in the iron meteorites. This discovery was a historical start of the mass-independent isotope effect (MIE). Later, in 1973, Clayton et al.[10] detected a similar deviation for oxygen in calcium−aluminum inclusions from carbonaceous chondrite Allende; they had found $\delta^{17}O = \delta^{18}O$ in contrast to $\delta^{17}O = 0.5\delta^{18}O$ as the one-half-rule was expected to predict. Both deviations were nominated as isotope anomalies. Since there were no other ideas, with the exception of MDE, both isotope anomalies mentioned above were attributed to the nuclear processes (in particular, cosmic ray induced spallation) or invasion of the matter with anomalous isotopic composition into the Solar System from outside. In other words, isotope anomalies were assumed to belong to the matter with different nuclear genesis; any chemical sources of these anomalies were excluded.

SHORT HISTORY OF MIE

The first observation of *chemically induced* MIE was announced in 1976 by Buchachenko et al. in the paper[11] entitled "*Isotope enrichment induced by magnetic interactions in chemical reactions*" and later was widely recognized (see, for instance, refs 12−14). The ^{13}C isotope enrichment in the photochemical decomposition of dibenzyl ketone at 20 °C in benzene was shown to strongly exceed that expected for MDE. Even more convincing was the magnetic field dependence of the effect which was direct evidence of its magnetic nature (on this basis, the new effect was christened by Buchachenko as the *magnetic* isotope effect).

The discovery of the new, nuclear spin-dependent MIE started the race in search of the magnetic isotope effect. In 1977, Sagdeev et al.[15] confirmed it in triplet sensitized photolysis of benzoyl peroxide. Nicholas Turro in 1978 was the first who used micelles as the microreactors[16] for the photolysis reactions; he has shown that the reactions in micelles result in enormously large isotope separation.[17−20] In 1980 Pines and co-workers[21] showed that in viscous solutions the magnetic isotope effect markedly increases (see, for details, ref 7). Later this nuclear spin and, therefore, nuclear magnetic moment dependent isotope effect was discovered for oxygen,[22−26] silicon,[27,28] sulfur,[29,30] germanium,[31,32] tin,[33−35] mercury,[36,37] magnesium,[38,39] calcium,[40] zinc,[41] and uranium.[42] In all these cases, the one-half-rule was never satisfied.

In 1983 Thiemens et al.[43] discovered another MIE; it was detected in the gas-phase synthesis of ozone from molecular oxygen. In contrast to the magnetic isotope effect, the new effect was convincingly proved to be nuclear spin independent. It appeared to be a paradoxically remarkable phenomenon: being unambiguously mass-dependent, it nevertheless results in the mass-independent isotope fractionation. The resolution of the paradox is very simple: the mass-independent isotope effect discovered by Thiemens et al. is in fact mass-dependent, but it results in isotope fractionation which deviates from that predicted by the one-half-rule of MDE.

Both these effects, nuclear spin-dependent, *magnetic* MIE and nuclear spin-independent, *nonmagnetic* MIE, are the most chemically significant, the most contributing in chemistry and related sciences (geochemistry, space chemistry, life sciences). As the powerful mechanisms of isotope fractionation, they should be taken into account to accurately reconstruct genesis and pathways of chemical evolution of the matter and of its components (minerals, oils, ores, coals, interstellar substances, etc.). Any isotope anomalies and deviations trace chemical evolution, like an echo of chemical fate of nature. Both these effects will be further discussed and exemplified by the most prominent results to outline the scope of their functioning.

MAGNETIC MIE IN CHEMISTRY AND BIOCHEMISTRY

Magnetic MIE as a highlight in spin chemistry is based on the fundamental and universal principle: all chemical reactions are spin selective, they are allowed only for those spin states of reactants whose total spin is identical to that of products.[44,45] It is unique, and it introduces in chemistry magnetic interactions. Contributing almost nothing in chemical energy and being negligibly small and traditionally ignorable, magnetic interactions are the *only ones* which are able to change the electron spin of reactants and switch over the reaction between spin-allowed and spin-forbidden channels, controlling chemical reactivity. Magnetic MIE, i.e., *nuclear spin selectivity* of chemical reactions, is the dependence of the reaction rates on the nuclear spin and nuclear magnetic moment of the reactants.[7,46,47] It bears also new ideas on how to control chemical reactions by selective spin manipulation using magnetic fields and microwave pumping.[48]

In contrast to nonmagnetic MIE, which is controlled by the chemical energy of reactant molecules and exhibits itself in energy-expensive reactions, magnetic MIE dominates in energy-cheap reactions of radicals and ion-radicals. The vast number of reactions with participation of radicals, ion-radicals, paramagnetic metal ions, and molecules (such as NO, O_2) is spin selective. In these reactions, a pair of reactants is a spin-selective nanoreactor, in which the reaction chooses spin-allowed channels. Particularly, the triplet radical pair (R· ·R) prepared by photolysis, radiolysis, or encounter of freely diffusing radicals is not able to recombine and produce the diamagnetic, zero-spin molecule RR (Figure 1). To recombine a triplet−singlet spin conversion of the pair is required. Three magnetic interactions transform the nonreactive triplet radical pair $(R\cdot\ \cdot R)^T$ into the reactive singlet pair $(R\cdot\ \cdot R)^S$. If triplet−singlet spin conversion is driven by electron−nuclear Fermi interaction (well-known in ESR spectroscopy as a hyperfine coupling), the reaction probability is a function of hyperfine coupling and nuclear magnetic moment. Evidently, *the radical pair functions as an electron and nuclear spin-selective chemical nanoreactor*, which sorts magnetic and nonmagnetic nuclei and directs them into the different reaction products. It is the key idea how magnetic MIE functions (for details, see refs 7 and 47).

The quantitative measure of the magnetic MIE is determined by the rate of triplet−singlet spin conversion of the pair. For

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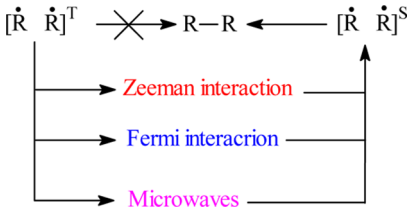

Figure 1. Three magnetic interactions induce spin conversion. The radical pair functions as a spin-selective nanoreactor in which the reaction probability is a function of hyperfine coupling and nuclear magnetic moment of the radicals.

the simplest case of conversion between two states with zero-spin projections, S and T_0, it may be estimated by solving the Schrodinger equation with the wave functions

$$S = 1/\sqrt{2}(\alpha\beta - \beta\alpha)$$

$$T_0 = 1/\sqrt{2}(\alpha\beta + \beta\alpha)$$

and spin Hamiltonian

$$\mathbf{H} = \beta\mathbf{H}(g_1S_1 + g_2S_2) + aS_1I$$

Here, α and β are spin functions of unpaired electrons on the radicals of the pair; S_1 and S_2 are spins of these radicals; g_1 and g_2 are their g-factors; I and a are nuclear spin and hyperfine coupling constant for one of the radicals carrying a magnetic nucleus; β is the Bohr magnetic moment; and $\mathbf{H}$ is a magnetic field strength. The rate of triplet−singlet spin conversion ω is determined as a matrix element $<T_0|\mathbf{H}|S>$; it results in the equation

$$\omega = 1/2(\Delta g\beta\mathbf{H} + am) \quad (1)$$

Here Δg is a difference of the g-factors of radicals in the pair, and m is a nuclear spin projection. According to this equation, there are two contributions into the triplet−singlet spin conversion. The first one is controlled by the difference of Zeeman energies $\Delta g\beta\mathbf{H}$, and the second contribution operates only in pairs with magnetic nuclei and is quantitatively described by the second term in eq 1 (for details of the theory see ref 7). The remarkable property of magnetic MIE is that the fractionation of magnetic and nonmagnetic isotopes is much more efficient than that of light and heavy isotopic nuclei and exceeds fractionation induced by MDE by 1 or even 2 orders of magnitude. It is worthy to compare characteristic features of magnetic MIE and MDE as shown in Table 1.

Table 1

feature	MDE	magnetic MIE
fundamental nuclear property	mass	spin and magnetic moment
electron−nuclear magnetic interaction	no effect	strong dependence
magnetic field	no effect	strong effect
viscosity, diffusion	no dependence	strong dependence
size of a microreactor	no effect	strong effect
lifetime of the radicals	no dependence	strong dependence
temperature dependence	weak	strong
spin multiplicity	no effect	strong effect

Since the time of discovery of magnetic MIE, it was detected for many isotopes in numerous reactions; here only some typical aspects of the effect will be emphasized.

The biogeochemical cycle of mercury compounds in the environment is a subject of special attention. By monitoring isotope composition of these compounds inside and outside of living organisms as well as in enzymatic reactions, isotopic anomalies for magnetic nuclei ^{199}Hg and ^{201}Hg with respect to nonmagnetic ones ^{198}Hg and ^{200}Hg were discovered which unambiguously indicate that both chemical and biochemical transformation of mercury compounds follows radical spin-selective mechanisms. This new technology is a powerful tool to trace the sources and fate of mercury pollutants in soil, water, plants, nutrients, and living organisms.[49−53]

Recently, magnetic MIE was shown to fractionate oxygen isotopes in the photo-oxidation of water by molecular oxygen.[54] Photolysis of ^{17,18}O-labeled water in the presence of molecular oxygen is accompanied by transfer of ^{17}O and ^{18}O isotopes from water to oxygen, demonstrating that the photoinduced oxidation of water does occur. The reaction exhibits a magnetic isotope effect: oxidation of $H_2{}^{17}O$ is faster by 3.3% (in the Earth magnetic field) and by 3.7% (in the field of 0.5 T) than that of $H_2{}^{18}O$. The key reaction which produces fractionation of oxygen isotopes is that of HO_2 radical coupling. Photo-oxidation of water by molecular oxygen is thought to be important for the elucidation of the global process of oxygen production and consumption in nature; the monitoring of isotope composition is known to be the best way to do that.[55]

Certainly magnetic MIE was observed in thermo-chemical sulfate reduction. The large ^{33}S enrichment (13‰), beyond what would be expected from MDE, was detected in the polysulfide fraction of products. This effect is thought to contribute substantially to the Archean sulfur isotope anomalies observed in geochemistry.[14,56,57]

Magnetic MIE on the oxidation of silicon crystals was recently observed.[58,59] Silicon atoms ^{29}Si with magnetic nuclei were shown to be oxidized two times faster than atoms ^{28}Si and ^{30}Si with spinless, nonmagnetic nuclei. This effect, as well as the magnetic field effect, unambiguously certifies solid state silicon oxidation as an electron and nuclear spin-selective process in which paramagnetic intermediates—radicals, ion-radicals, and radical pairs—are involved. The dominating oxidizing species were assumed to be oxygen molecules in the triplet spin state. The insertion of the oxygen molecule into the Si−Si bond as a key primary reaction of silicon oxidation generates triplet radical pairs. Hyperfine coupling with ^{29}Si nuclei in these pairs stimulates triplet−singlet spin conversion and transforms nonreactive triplet pairs into the reactive singlet ones. In terms of this mechanism, both magnetic interactions, Zeeman and hyperfine, accelerate silicon oxidation in agreement with experimental observations. In favor of this statement is the fact that there is no difference in the rate of oxidation of ^{28}Si and ^{30}Si atoms with nonmagnetic nuclei. These effects were demonstrated for the Czhochralsky-grown silicon crystals with natural ^{29}Si abundance (4.7%) and for the float zone crystals highly enriched with the ^{29}Si isotope (72.8%).

The remarkable feature of magnetic MIE is that it can be enhanced by selective and controllable microwave pumping of the radical pairs carrying magnetic nuclei. Microwave pumping stimulates their triplet−singlet spin conversion, increasing recombination probability and, ultimately, the yield of product with magnetic nuclei.[48] This microwave magnetic isotope effect was predicted in 1981[60] and experimentally illustrated in

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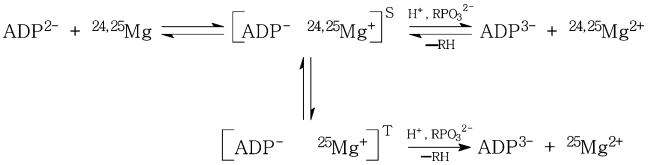
1991[61] by microwave pumping of the ^{13}C radical pairs generated by dibenzyl ketone photolysis. Even at a rather low amplitude of the pumping, the recombination probability of the magnetic pairs was shown to increase at least by 6% with respect to that without pumping. It must be noted that the tremendous perspectives of the microwave magnetic isotope effect remain so far virtually unexplored.

ISOTOPE CATALYSIS

In 2004 a new function of magnetic isotopes was revealed[38] in biochemical reactions: the activity of magnesium-dependent ATP-producing enzymes (ATPase and phosphorylating kinases), in which the Mg^{2+} ion has a magnetic isotopic nucleus ^{25}Mg, was found to be 2−3 times higher than that of enzymes in which the Mg^{2+} ion has nonmagnetic, spinless isotopic nuclei ^{24}Mg or ^{26}Mg. There was no difference in the ATP yield for enzymes with ^{24}Mg and ^{26}Mg; it gives evidence that in this reaction magnetic MIE operates rather than mass-dependent MDE.[39,62−66] A discovery of such an unusual mass-independent, nuclear-magnetic isotope effect reliably evidences that the ATP synthesis is a radical (or ion-radical) process in which paramagnetic intermediates, ion-radicals, and ion-radical pairs participate.[7] This new mechanism is shown below for the particular case of transfer of the phosphate group from the phosphorylating substrate RPO_3^{2-} to ADP



As a first step, it implies electron transfer from the terminal phosphate group of ADP to the Mg^{2+} ion; it generates a primary ion-radical pair, composed of the radical-cation Mg^+ and oxy-radical of ADP. Due to the total spin conservation, this pair being generated from the diamagnetic molecules is in a singlet spin state. The next step is the phosphorylation itself in which the ADP oxy-radical attacks the P═O chemical bond of the substrate phosphate, generating ATP and regenerating the Mg^{2+} ion.[67,68]

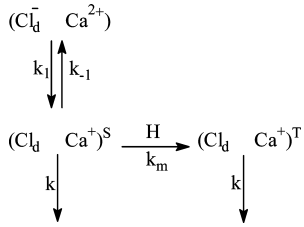
The rate of phosphorylation and the ATP yield along this singlet channel are suppressed by spin-allowed reverse electron transfer in the primary ion-radical pair which regenerates starting reactants. However, in the presence of $^{25}Mg^{2+}$ ions, hyperfine coupling of the unpaired electron with the magnetic nucleus ^{25}Mg in the radical-cation Mg^+ stimulates singlet−triplet spin conversion of the primary ion-radical pair and transforms it into the triplet pair, in which back electron transfer is spin forbidden. This new triplet channel of phosphorylation provides an additional yield of ATP which increases the total production of ATP by 2−3 times. Thus, the essence of the magnetic isotope effect in the ATP synthesis is that the magnetic interaction of the unpaired electron in the $^{25}Mg^+$ radical with a magnetic nucleus induces singlet−triplet spin conversion and switches on a new, additional reaction channel of the ATP synthesis. It certifies nuclear spin control of chemical reactivity. The ion-radical mechanism is definitely proved by the existence of the magnetic isotope effect on the ATP synthesis catalyzed also by calcium and zinc ions: the yield of ATP increases by 2−3 times when the catalytic site carries magnetic nuclei ^{43}Ca and ^{67}Zn in $^{43}Ca^{2+}$ and $^{67}Zn^{2+}$ ions instead of nonmagnetic, spinless nuclei ^{40}Ca and ^{64}Zn;[40,41] another confirmation of the ion-radical mechanism follows from the magnetic field dependence of the ATP synthesis.[66] This effect was shown to function in isolated mitochondria and in living organisms (rats, rabbits, goats).[69,70] This in vivo biomedical effect is used to stimulate ATP synthesis in heart muscle to prevent hypoxia and other pathologies related to the deficiency of ATP (for details, see review 73 and references therein).

As the ions in this process are regenerated and conserved, this phenomenon is in fact *nuclear spin catalysis* which is similar to the well-known *electron spin catalysis*;[71,72] it may be considered as a new type of mass-independent isotope effect.

PREDICTED BUT NOT YET DISCOVERED NUCLEAR SPIN ISOTOPE EFFECTS

The influence of the magnetic fields (permanent and oscillating) on the micromechanics and plasticity of diamagnetic crystals seems to be an unbelievable phenomenon; nevertheless, it exists as a magneto-plasticity. The essence underlying this enigmatic phenomenon is that the magnetic field accelerates the motion of dislocations which are known to be responsible for plasticity. An atomic mechanism of the phenomenon was suggested[74] to be a spin-dependent process in the ion-radical pairs generated by electron transfer between dislocations and stoppers. It may be exemplified by Scheme 1

Scheme 1. Chemical Evolution of Dislocation in the Magnetic Field



for the particular case of NaCl crystals with Ca^{2+} ions as the stoppers. A dislocation stops when it meets the Ca^{2+} ion. Electron transfer from dislocation (more exactly, from the Cl^- ion shown in Scheme 1 as Cl_d^-, an atomic element of dislocation) to the Ca^{2+} ion generates an ion-radical pair in the singlet spin state with the rate constant k_1. It is remarkable that in this pair the Coulomb interaction which holds trapped dislocation is switched off so that released dislocation is able to move again. This process is known in solid state physics as the depinning. Its rate is restricted by return of the electron with the rate constant k_{-1} which regenerates the initial state of trapped dislocation.

The magnetic field induces spin conversion of the pair from the singlet state into the triplet one with the rate constant k_m; in the latter back electron transfer is spin forbidden. It means that the magnetic field increases the lifetime of the pair in the state with switched off Coulomb potential and, therefore, stimulates liberation of trapped dislocation from the Coulomb prison with the rate constant k.

This mechanism predicts softening of ionic crystals and strengthening of covalent crystals in the magnetic field; it is supported by observation of microwave stimulation of dislocation mobility on the resonant Zeeman frequencies.[75] A quantitative theory of the magnetic plasticity in terms of kinetic parameters of Scheme 1 is developed in ref 76.

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Now it is easy to predict nuclear spin control of the dislocation mobility by the presence of ions (Ca^{2+}, Mg^{2+}, etc.) with magnetic nuclei (^{43}Ca, ^{25}Mg, etc.).[77] Singlet−triplet spin conversion in the ion-radical pairs will be induced by hyperfine electron−nuclear coupling, so that the inclusion of such ions into the crystal even in trace amounts is expected to modify mechanical properties of diamagnetic crystals, both ionic and covalent.

Yakov Zeldovich, the famous Russian theoretical physicist, has predicted two remarkable isotope effects. In cooperation with Maksimov,[78] he has shown that the diffusion coefficients of the molecules in gases at low pressure depend on the nuclear spin. The idea is that in the molecules with spinless nuclei the rotational angular moment is conserved, so that the diffusion coefficient is determined by averaging of the free flight distances on the cross sections of collisions. In the molecules with nuclear spin isotopes, the rotational angular moment is not conserved during the time-of-flight because of spin-rotational interaction $H_{IJ} = ICJ$, where I is the nuclear spin; J is the rotational angular momentum; and C is a tensor of spin-rotational interaction. It means that the flying molecule tumbles. In this case it is necessary to average collision cross sections on the free flight distances. The results of these two physically different procedures are not identical; i.e., the diffusion coefficients of the molecules with spin-carrying and spinless nuclei are different. This idea was suggested to be used for the fractionation of the nuclear isomers, i.e., nuclei with identical masses and magnetic moments.

Another idea is based on the nuclear spin-selective optical excitation of the atoms (Ca, Zn, Mg, Hg, Cd, etc.).[79,80] For the spinless atoms, the radiation transitions $ns^2\ ^1S_0-nsnp\ ^3P_0$ are strictly forbidden. However, for the nuclear spin-carrying atoms, the radiation transition probability is nonzero because hyperfine electron−nuclear coupling mixes $^1P_1$ and $^3P_0$ states and makes the $^1S_0-^3P_0$ transition partly allowed. Its probability is proportional to the coefficient $a[I(I+1)]^{1/2}\Delta E^{-1}$,where a is the hyperfine coupling constant in the $^3P_0$ state; I is the nuclear spin; and ΔE is an energy splitting between the excited states $^1P_1$ and $^3P_0$. These transitions in fact were observed by spectroscopy for $^{199,201}Hg$ atoms (2655.8 Å) but not for $^{200,202}Hg$. This effect was not yet explored for the magnetic isotope separation in atomic gases; possibly, it functions in the space chemistry.

NONMAGNETIC MIE

Both MIEs, magnetic and nonmagnetic, ascertain that there is no need to postulate a nuclear origin (but does not exclude it) of isotopic anomalies; they are most likely to be the results of the chemistry. Nonmagnetic MIE discovered by Thiemens[43] was extensively testified in many reactions, where isotopic anomalies in meteorites were successfully explained in terms of this effect; the results are summarized in exhaustive reviews by Thiemens[81,82] and Weston.[83]

There are two theories explaining the unusual deviation of isotope fractionation produced by the effect discovered by Thiemens from that predicted by the one-half-rule. According to the theory proposed by Marcus et al.,[84,85] isotope fractionation is assumed to arise due to the fact that the density of quantum states in vibrationally excited molecules, born in the reaction of atom addition, is greater for symmetric (such as $^{18}O^{17}O^{18}O$) than for asymmetric (such as $^{17}O^{18}O^{18}O$) molecules. Then, it immediately follows that symmetric and asymmetric molecules will decay with different rates, producing isotope discrimination.

Robert et al.[86,87] suggested a molecular model in which the same isotope effect is supposed to arise from the competition of scattering and reactive collisions for the molecules with distinguishable and indistinguishable isotopes. The differential cross sections of these processes were shown to depend on the angular and impact parameters. The model was extended by Robert to explain or predict isotopic anomalies in meteorites for such elements as xenon, silicon, titanium, barium, etc.

An unusual isotope effect was discovered by Miller et al.[88,89] The thermally induced decomposition of calcium carbonate produces anomalous depletion of ^{17}O in the solid oxide and an equivalent enrichment of ^{17}O in the CO_2. This phenomenon is extremely enigmatic because it has a reasonable explanation neither in terms of magnetic MIE nor in terms of nonmagnetic MIE. As a feasible mechanism, an electron transfer was considered to generate an ion-radical pair ($M^+\ \bullet OCO_2^-$) in MCO_3 where M is Ca, Mg, Ba, etc. Then magnetic MIE in this pair is supposed to fractionate oxygen isotopes. However, $CuCO_3$ exhibited isotope fractionation similar to that in $CaCO_3$ despite the fact that the pair ($Cu^+\ \bullet OCO_2^-$) in $CuCO_3$ is not able to fractionate oxygen isotopes because the Cu^+ ion is diamagnetic.[90] Nevertheless, even decomposition of $CuCO_3$ was accompanied by isotope fractionation.

NUCLEAR VOLUME ISOTOPE EFFECT

In the fractionation of heavy elements, for which MDE is small, not only mass but also the volume (more exactly the radius) of the nucleus may appear to be significant. The first nuclear volume isotope effect (NVI effect) was mentioned by Nishizava et al.;[91] it stemmed from the experimental observation of strontium isotope effect on the liquid−liquid extraction of strontium chloride by crown ether. Later, Nomura et al.[92] have found isotopic ^{233}U anomaly in the $U^{4+}-U^{6+}$ exchange reaction; they noted that the isotope effect was correlated with isotope shifts in the atomic spectra of uranium isotopes. Bigeleisen[93] has developed the theory of the effect and suggested a method to calculate the isotopic separation factor from the parameters of molecular spectra of isotopic molecules.[94] Extended calculations[95−98] of the NVI effect later resulted in additional arguments in favor of the effect. A review of the NVI effect was recently presented by Malinovsky et al.[99] with special emphases on the analytical techniques.

Unlike MDE which originates mostly from the vibrational energy difference of isotopic molecules, the NVI effect is due to the electronic energy difference. Its magnitude is evident from the following considerations. Electron potential in the nuclear Coulomb field of the central point symmetry is

$$\varphi_0 = \frac{ze}{r}$$

where z and e are charges of nucleus and electron, respectively; and r is the electron−nucleus distance. For a nucleus of radius R, the potential has the form

$$\varphi = ze\left(\frac{3}{2R}\right) - \left(\frac{r^2}{2R^3}\right)$$

The difference in potentials for isotopes with nuclei of different volumes results in the shift of energy levels for s electrons having nonzero density on the nucleus. Its magnitude is proportional to $(R/a)^2$ where a is the Bohr radius ($a = 0.525$

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Å). Even for the 1s electron, closest to the nucleus, this energy correction for the hydrogen nucleus (proton) is only

$$\left(\frac{R}{a}\right)^2 \cong \left(\frac{0.9 \times 10^{-13}}{0.5 \times 10^{-8}}\right)^2 \cong 4 \times 10^{-10}$$

For a larger nucleus ^{196}Hg the correction is larger

$$\left(\frac{R}{a}\right)^2 \cong \left(\frac{5.44 \times 10^{-13}}{0.5 \times 10^{-8}}\right) \cong 10^{-8}$$

and increases proportionally to the square of the nuclear radius.

Presumably, for the p, d, and f electrons whose density on the nucleus is strictly equal to zero as well as for the high-lying s electrons, these corrections may be totally ignored. However, due to the spin polarization, even p, d, and f electrons have a small but nonzero density on the nucleus. For this reason, the nuclear volume isotope effect is detected reliably in the atomic spectra as the shifts of spectral lines about 10^{-6} of the line frequencies.

The contribution of the NVI effect into the fractionation of isotopes seems to depend on the type of chemical process. It is certainly detected in the chemical systems which are maintained in the state of equilibrium or near it (exchange reactions or extraction processes). However, there are no unambiguous indications of its importance as an isotope fractionation factor in chemical reactions; at least, even for mercury isotopes the inversion of the sign of isotope effect observed for ^{199}Hg[53,100] is incompatible with the NVI effect.

CONCLUSION

Both MIEs, magnetic and nonmagnetic, function independently but in physically different conditions. The latter dominates in reactions occurring in energy-rich and short-living collisions of atoms and molecules; the former exhibits itself in the low-energy and long-living reactive encounters of paramagnetic species. In the collision reactions, both electron and nuclear spins are conserved because the collision time is about 10^{-13}–10^{-14} s, so that to change spin during this short time a powerful magnetic energy of 10^{13}–10^{14} Hz (about 4×10^5 J/mol) is required; there are no such strong magnetic forces in chemistry. Despite the fact that the electron system of chemical bonds is the fastest, their spin system is very slow and inertial. A time of about 10^{-10}–10^{-7} s is required to change spin, so spin is changed only in the long-living pairs of spin carriers.

The sign of MDE is unambiguously controlled by the mass ratio of isotopes, whereas the sign of magnetic MIE depends on the spin multiplicity of the radical pair. It depends on the direction of spin conversion (from triplet to singlet or vice versa), so the inversion of the spin multiplicity is accompanied by inversion of the sign of magnetic MIE. Such dependence is an excellent test for the identification of the spin multiplicity of the reactive intermediates and, therefore, for the elucidation of reaction mechanism. The MDE is well-known to decrease only slightly as temperature increases, while the temperature dependence of the magnetic MIE is much more complicated and irregular, because it involves temperature dependence of the radical lifetime, diffusion coefficients, and other parameters of molecular and chemical dynamics of the radical pair. The magnitudes of magnetic MIE are known to be about 2 or even 3 orders of magnitude larger than those of MDE and nonmagnetic MIE. At last, magnetic field dependence is the most individual characteristic feature of magnetic MIE.

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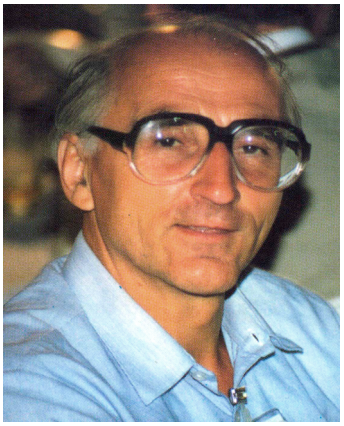
Notes

The authors declare no competing financial interest.

Biography



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