A Low-Field Magnetically Affected Reaction Yield (MARY) Spectrometer with Spectral Fluorescence Resolution

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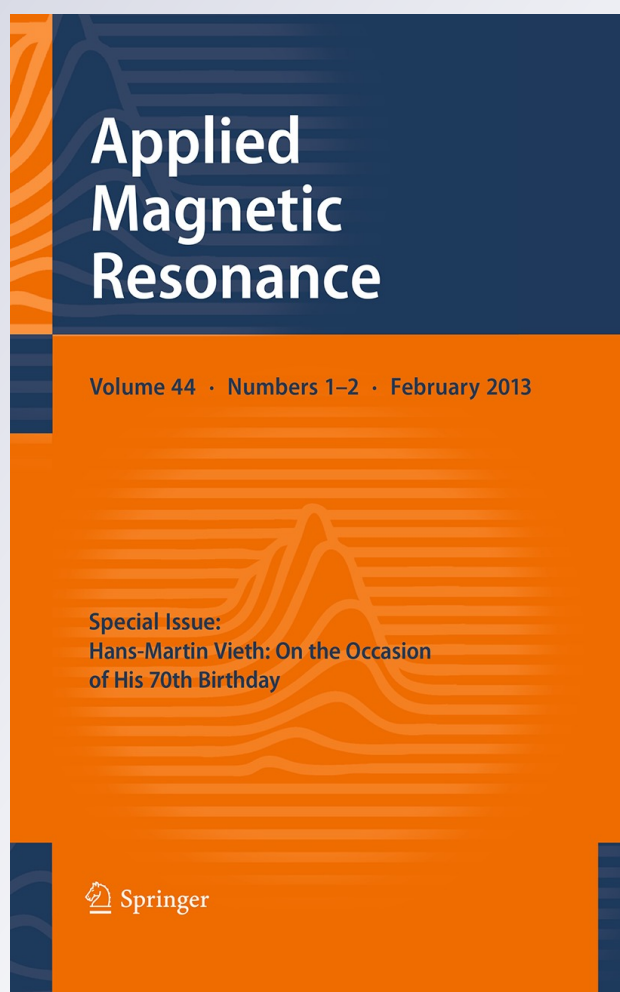# A Low-Field Magnetically Affected Reaction Yield (MARY) Spectrometer with Spectral Fluorescence Resolution

**Evgeny V. Kalneus · Anatoly R. Melnikov ·
Valery V. Korolev · Vladimir I. Ivannikov ·
Dmitri V. Stass**

Abstract A novel spectrometer for low-field studies in magnetically affected reaction yield (MARY) spectroscopy with fluorescence detection is described. The spectrometer is based on a yoke-free magnetic system containing no ferromagnetic elements, uses X-ray or optical excitation, and includes a monochromator to analyze the spectral composition of luminescence. Using the new setup, the effect of transversal residual magnetic field on zero field MARY line is illustrated, formation of exciplexes under X-irradiation in a naphthalene/*N,N*-dimethylaniline solution in alkane is demonstrated, a magnetic field effect on the emission spectrum is shown in field-cycling mode, and modulated MARY spectra in the exciplex and the intrinsic luminophor bands are compared to show that magnetic field sensitivity here is provided at the stage of the recombining radical ion pair, while exciplex formation only transforms the luminescence properties.

1 Introduction

Magnetically affected reaction yield, or MARY, spectroscopy is a spin-chemistry method that allows one to detect radical ions with lifetimes as short as several nanoseconds and to study their reactions [1]. Several implementations of MARY have been realized by now [2–10]. In the authors' implementation [11] the experiments are carried out in warm nonpolar solutions. Irradiation of the sample with X-rays produces primary radical ion pairs of solvent holes and electrons that inherit initial singlet spin correlation of unpaired electrons from the parent

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molecule. The additional electron acceptor and/or donor present in the solution captures the electron and/or the hole to produce the target secondary pair, with the spins remaining correlated in this process. The additional component is commonly a luminophor, and the recombination of the pairs in singlet state leads to observable fluorescence. An applied magnetic field modulates the spin state of the pair and thus the fluorescence signal to produce magnetic field effect (MFE)—the dependence of the steady-state fluorescence intensity on magnetic field [12–14]. In the region of weak magnetic fields, in the mT range, and especially in the vicinity of zero field, these MFE curves can show sharp lines related to energy level crossings in the spin system of the radical pair [15–25]. Such enriched MFE curves are referred to as MARY spectra and bear structural and kinetic information on the recombining radical ions on the nanosecond time scale.

Two aspects that lend MARY spectroscopy its utility are optical detection and low magnetic fields. The former determines the very high concentration sensitivity, with steady-state concentrations of 100 pairs being sufficient for detection [26]. The latter gives MARY its sensitivity to short-lived radical ions, as in the region of low magnetic fields spin evolution conveyed in the observable fluorescence can be driven by much stronger internal hyperfine interactions, rather than by resonance MW pumping [27]. Furthermore, similar to the methods of coherent optical spectroscopy, the detected signal here directly reflects the internal couplings between the electron and nuclei spins, rather than provide a linear response of the system of spins to weak external perturbation, as in conventional continuous-wave (CW) magnetic resonance techniques. The "coupled spins in low field" approach has recently been developed into a novel high-resolution field-cycling NMR method for studies in nuclear hyperpolarization [28, 29]. However, both these aspects bring in accompanying factors that have to be taken into account, and require specialized setup features to be fully realized.

The magnetic field has to be cleanly swept through zero, where the most important MARY line if found, and cover the range of about "−50" to 50 mT. This is an inconvenient range for both standard iron-core magnets, that perform poorly in weak fields due to core nonlinearity, hysteresis, and loss of permeability, and air-core Helmholz-type coils that cannot provide efficient current-to-field conversion if reasonable field homogeneity is required. Furthermore, the experiment requires placing an X-ray tube and a photomultiplier tube (PMT), which are both vacuum tubes and are sensitive to magnetic field, as close to the sample as possible. Hence, certain measures on field confinement are required. A specialized magnetic system for low-field MARY studies is thus highly desirable.

Regarding the optical detection, it is commonly considered that upon recombination of a radical ion pair comprising a luminophor molecule an excited luminophor molecule is generated that emits the detected quantum of fluorescence. However, upon recombination there is always a second molecule next to the excited product, coming from the other partner of the pair, either a molecule of the same compound, or a deliberately introduced second component. This can lead not only to the expected emitting of the quantum of luminescence by the excited molecule, but also to formation of excited complexes, such as exciplexes [30]. Exciplexes can also form via normal diffusion-controlled bulk reaction of the excited molecule with its

partner, so a concentration-dependent competition of the two channels is possible. Although exciplexes are mostly generated optically and studied in polar solutions [31], they have indeed been reported in nonpolar solutions including donor–acceptor systems in alkanes [32] very similar to those used for spin chemistry under X-irradiation, such as TMPD/biphenyl in methylcyclohexane [33], pyrene/N,N-dimethylaniline in n-hexane [34], and anthracene/N,N-dimethylaniline in n-hexane [35]. The concentration-dependent formation of exciplexes with red-shifted luminescence bands, if any, and unpredictable quantum yields of exciplex luminescence can significantly change the luminescence properties of the system and thus the detected signal, especially if spectral limiting or selection of fluorescence is used to improve signal-to-noise ratio. It would be therefore beneficial to be able to study the spectra of radiation-generated luminescence directly in the conditions of MARY experiment.

In this work, we describe a specialized MARY spectrometer with iron-free magnetic system, optical registration system with spectral resolution, and the option of concurrently using X-ray and optical sample excitation, which has just been commissioned in our lab, and discuss first radiation-generated luminescence and MARY spectra taken on the new setup.

2 Experimental Setup

The schematic diagram of the MARY spectrometer is shown in Fig. 1 and will now be described with reference to its several subsystems.
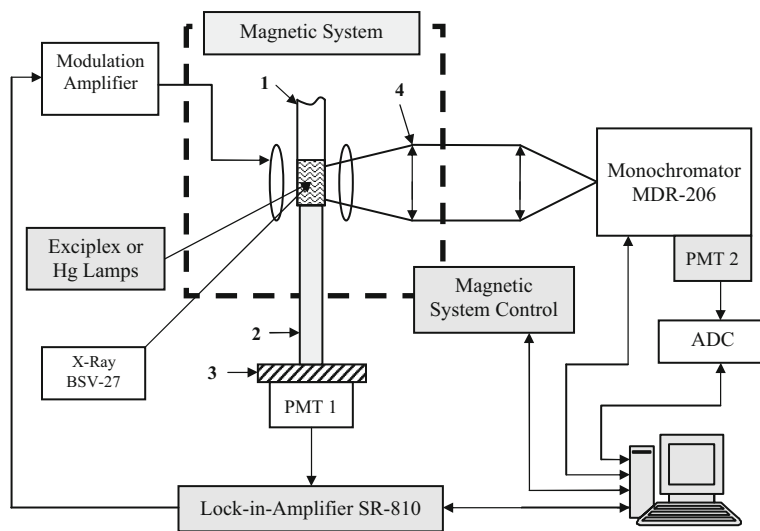

Fig. 1 Schematic diagram of MARY spectrometer with spectral fluorescence resolution. The numbers additionally show degassed ampoule with liquid sample (*1*), light guide (*2*), optional optical filter (*3*), and a two-lens condenser (*4*)

2.1 Magnetic System

The spectrometer is built around a specialized yoke-free magnetic system that creates magnetic field in the range from "−50" to "+50" mT in a cylindrical working region with a length of 8 cm and a diameter of 1 cm with measured relative field homogeneity of about 10^{-4} without using ferromagnetic elements or employing a field-sensing feedback loop. The symmetry axis of the system, along which the magnetic field is swept, will be further referred to as Z axis and is oriented horizontally, with vertical axis designated as Y axis and the other horizontal axis as X axis. The horizontal field sweeping allows a convenient placement of liquid sample from above and between the coils and an access to the sample via the openings in the coils for close placement of the X-ray tube in a region about the Z axis with well-controlled magnetic field. The latter is critical as X-rays cannot be readily focused or otherwise processed like optical radiation, and thus the flux of X-irradiation falling onto a given target area of the sample is inversely proportional to the square of the distance to the tube, which thus has to be placed as close as practical to the sample. On the other hand, the X-ray tube, which is basically a gap across which electrons are accelerated and hit the target producing bremsstrahlung, is sensitive to magnetic field that deflects the electron beam off the target. At a distance of greater than or equal to 15 cm from the center of the system along the sweeping Z axis, the magnetic field does not exceed 10 mT at maximum working field due to active shielding. As experiments with field cycling described later on demonstrate, this is weak enough and introduces no artifacts when the X-ray tube is placed that close to the sample. The other magnetic field-sensitive element of the setup, PMT, poses less of a problem, as optical radiation can be conditioned and transferred away from the sample, so the PMT can be placed farther away from the sample without major loss of sensitivity. The two PMTs used in the described setup are placed more than half a meter away from the sample, well outside the magnetic system. A detailed description of the design, construction and testing of the magnetic system was given in Ref. [36], and here only the key moments will be briefly summarized.

The system is logically and physically divided into several subsystems. The first one is Power system with active shielding consisting of three pairs of coaxial coils. The Power system creates field in the range 2–50 mT in both directions along the Z axis with rather high efficiency (rated power 850 W at 50 mT), steep field roll-off outside the working region, and calculated relative field homogeneity 4.3×10^{-6}. The second one is the scanning system built of two pairs of coaxial coils. It can continuously sweep through the zero of the field covering the range ± 10 mT and provides a better calculated relative field homogeneity of 1.4×10^{-6} at the expense of lower power efficiency (rated power 300 W at 10 mT) and shallower field roll-off profile. The two systems work independently, and their fields simply add up vectorially in space due to the lack of any ferromagnetic elements. In currently used mode of operation the field range of ± 2.5 mT is covered by the scanning system alone, and higher fields are created by the power system alone.

In addition to these two main subsystems that sweep the field along the horizontal Z axis of the system, there is a system for compensation of residual transversal fields to ensure clean and linear passage through the zero of the total field at the sample location. The compensation system consists of two pairs of thin rectangular coils with dedicated power supply units, one pair for each of the Y and X axes, providing up to ± 0.15 mT in both directions. Finally, a pair of coaxial modulation coils is provided to create oscillating field along the sweeping Z axis with amplitude of up to 1.5 mT in frequency range 0.5–40 kHz. The coils are fed from the reference generator of the lock-in amplifier through a home-built power amplifier.

To monitor the swept field a smart A1321 Hall sensor (Allegro MicroSystems) is built into the system at the end of the cylindrical working volume, after a lead plug blocking the incident X-rays. It should be stressed that the sensor is used only for monitoring the field and does not provide feedback signal for field stabilization, which is done solely by stabilizing currents through the coils in the linear system without ferromagnetic elements. This turned out to be the most convenient and reliable way for creation of rather weak static magnetic fields of the order of Earth's field. The compensation of the residual field is performed manually using a home-built magnetic field meter for weak fields based on an HMC1052 2D magnetoresistive sensor (Honeywell) developed as an accessory for the new spectrometer. When compensating out the residual field the probe of the meter is temporarily placed into the sample compartment instead of the sample.

2.2 Control System

The described power, scanning, and compensation subsystem each have a dedicated power supply unit and a microcontroller-based control unit. The overall control of the MARY spectrometer is divided into three levels, as demonstrated schematically in Fig. 2. The low level is the level of executive devices (ED) with embedded dedicated AVR 8-Bit RISC microcontrollers (ATMEL). The low-level controllers provide the required functionality of each ED and ensure its safe operation on the hardware level independent of the incoming stream of commands.

The medium level of control is implemented as intelligent control block (ICB) based on ATmega 128 microcontroller (ATMEL) having two built-in asynchronous transceivers, which coordinates the work of all low-level devices and serves as a bridge between them and the PC. ICB receives the high-level setup sequence from the controlling PC, parses it into individual setup parameters for each ED, generates the actual stream of commands for them providing real-time control and timing of the experimental sequence, and collects and passes upwards the results of measurements and status information on the blocks of the system. After receiving the setup sequence, ICB can provide autonomous work of the system without recurring to the PC. Since a typical spectrum can take hours to complete, this significantly improves reliability of the spectrometer.

Finally, the upper level of control is provided by a PC running main program that only exchanges macrocommands with ICB. The program provides user interface to experiment, as well as gives the operator low-level access to ED for debugging purposes.
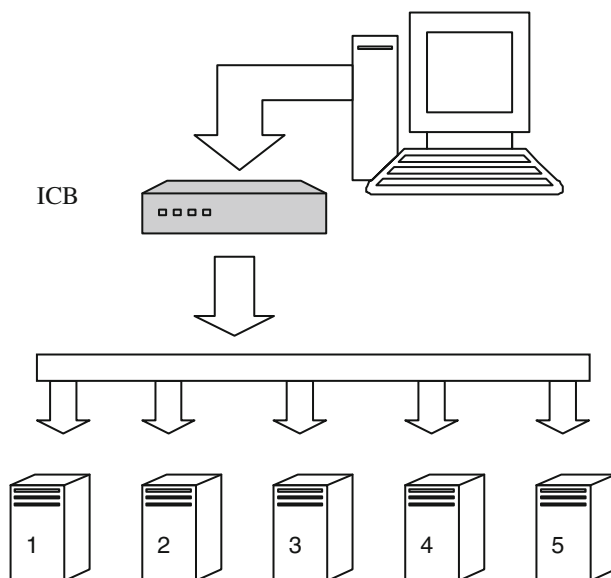
Fig. 2 Three-level control system of the MARY spectrometer: upper level provided by a PC exchanging macro commands with intelligent control block (ICB) implementing the medium level, which coordinates the work of all low-level devices, and lower level provided by executive devices (ED) with embedded microcontrollers that provide the required functionality of each ED (power supply unit for power magnetic system, power supply unit for scanning magnetic system, residual lab field measurement and compensation module, field modulation module, PMT control module)

2.3 Sample Compartment, Excitation and Registration Systems

The internal volume of the magnetic system is a cylinder with five access ports: one along the horizontal scanning Z axis and two along each of the other two axes. The Z axis port has an adapter to directly install an X-ray tube (BSV-27, Svetlana, St. Petersburg, Russia) for X-ray generation of radical ion pairs in nonpolar solutions, or an KrXl (222 nm) or XeCl (308 nm) excilamp (IHCE SB RAS, Tomsk, Russia) [37] for optical generation of radical ion pairs in polar solutions. To compare the spectra of luminescence under X-ray and photo generation from the same sample the X-ray tube can be substituted for a high-pressure mercury lamp DRSh-500 with double monochromator DMR-4 to select spectral line for excitation. The other port along the Z axis houses the field-monitoring sensor and connectors for modulation and compensation coils.

The sample is placed into the top port along the vertical Y axis, the bottom Y port holds a 10-mm OD quarts light guide. In a standard MARY experiment with magnetic field modulation the light guide is used to pass luminescence from the sample onto a PMT FEU-130, if needed through optical filters. Alternatively, the port with light guide can be used as an auxiliary optical excitation port, e.g., for optical system calibration.

The spectrally resolved registration of luminescence is performed through one of the horizontal X ports in the direction normal to both magnetic field and X-ray

excitation flux. A pair of quartz lenses projects the sample image onto the entrance slit of an MDR-206 grating monochromator (LOMO Photonics, St. Petersburg, Russia, objective focus length 180 mm, grating 1,200 lines/mm, inverse linear dispersion 4.3 nm/mm), having a FEU-100 PMT on its exit slit. Although having a lower light sensitivity than FEU-130 used after the light guide, FEU-100 has much broader spectral sensitivity range of 170–830 nm, which is critical for recording luminescence spectra. The signal from the PMT goes to a home-built 16-bit ADC based on AD7705 chip (Analog Devices) and an ATMEGA8 microcontroller (ATMEL), and then is acquired by the controlling PC. The other X port currently houses a spherical mirror to improve light collection from the sample, but is generally not committed and can be used for other purposes. The registration optical system was calibrated by black body radiation using a reference incandescent lamp with known temperature of the filament illuminating a sputtered MgO diffuser. Unfortunately, the low optical efficiency of the grating monochromator precludes taking modulated MARY spectra through the monochromator for anything but the very bright samples, so MARY spectra with fluorescence spectral resolution can be taken by first recording a spectrum of luminescence under X-rays through the monochromator, determining the band of interest, and then using optical filters to select this band from the total light flux falling onto the FEU-130 PMT through the quartz light guide.

2.4 Samples

The standard samples for recording MARY spectra are thin-walled quartz tubes with OD 8 mm holding about 1 mL of degassed alkane solution with the required additives. However, this turned out to be unacceptable for recording the luminescence spectra under X-irradiation, as quartz has a rather strong intrinsic luminescence under X-rays [38, 39] that is furthermore steadily growing due to creation of additional luminescing defect centers under X-rays. Figure 3, traces with open circles and filled triangles, shows typical luminescence spectra of empty thin-walled tubes made of two types of quartz, a Wilmad Suprasil ESR tube and a tube from a Russian equivalent of Suprasil, optical quartz KU-1. The spectrum of quartz is rather prominent, covers the most important region of 250–500 nm, constantly grows stronger, and cannot be completely removed by annealing the tube prior to experiment. The open triangle trace shows a similar spectrum from a Pyrex glass tube, which also shows a prominent emission band masking the spectrally important region.

The best results were obtained for tubes made of molybdenum glass (filled circles), which has a much weaker luminescence band without the tendency to develop with exposition time. To further clean up the spectrum the ampoules of molybdenum glass with outer diameter 5 mm and inner diameter 3.5 mm were placed in a tight lead jacket with outer diameter 9 mm having two 2-mm-wide vertical collimating slits at 90° to each other for the incident radiation and the detected luminescence, which suppresses the residual intrinsic X-ray-generated luminescence of the glass—a spectrum from this arrangement is shown as the trace with open squares. Optical absorption measurements show that these ampoules are transparent above 320 nm and practically do not interfere with the emission
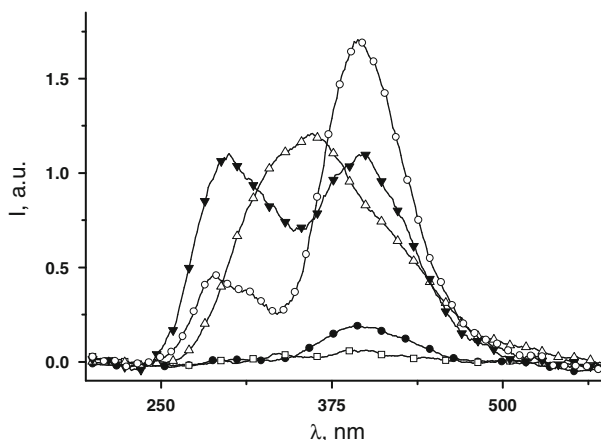
Fig. 3 Luminescence spectra under X-irradiation from a thin-walled tube with OD 5 mm made of Suprasil (*open circle*), optical quartz KU-1 (*filled inverted triangle*), Pyrex glass (*open upright triangle*), molybdenum glass (*filled circle*), molybdenum glass in lead jacket (*square*), see text. X-ray tube 40 kV × 20 mA; monochromator slits 2.2–2.2 mm

spectrum of the sample itself. These tubes also turned out to be mechanically tolerant to thermocycling from liquid nitrogen to room temperature required for repeated freeze–pump–thaw cycles needed to degas the sample. The only inconvenience for their use arises when luminescence spectra under optical excitation need to be taken, as excitation wavelengths shorter than 320 nm are often required, which are blocked by the ampoule. However, in these cases the spectra can be routinely taken in a quartz tube. The conductive lead jacket also interferes with field modulation, so modulated MARY spectra have to taken without it.

Summing up, when a clean luminescence spectrum under X-ray irradiation is required, it is taken in a lead-jacketed tube with OD 5 mm made of molybdenum glass containing about 0.3 mL of degassed sample solution. When a MARY spectrum with magnetic field modulation is required, a thin-walled quartz tube with OD 8 mm is used, holding about 1 mL of degassed sample solution. The same sample can be used for evaluating emission spectra under X-irradiation in preparation for spectrally resolved MARY experiments, if spectral contamination from the tube can be tolerated. Luminescence spectra with optical excitation can be taken either in glass or in quartz tube, as deemed convenient.

All presented experimental spectra were taken using purified *n*-dodecane as solvent provided by (Mrs. Natalia Ivanova or Mrs. Nadezhda) Sergey. *N,N*-dimethylaniline was freshly distilled over zinc powder by (Ms. Maria Davydova), the 193–195 °C fraction was used for sample preparation. Naphthalene, naphthalene-d_8, durene, and *p*-terphenyl-d_{14} were used without additional purification.

2.5 Software

The controlling software of MARY spectrometer supports several modes of operation. The primary mode is standard magnetic field modulation MARY

experiments under X-rays excitation with lock-in detection via Stanford Research Systems SR810 lock-in amplifier, field sweeping and repeated scanning with averaging [11]. A simple but important feature is the possibility of scanning the field not always in the same direction, i.e., increasing, with field rewind between the consecutive scans, but scanning back and forth, which helps avoid spectral skewing. The covered field range is ± 50 mT with minimum field step 10^{-5} T. The second mode is recording the spectra of luminescence under X-ray or optical excitation or without excitation (bioluminescence or chemiluminescence) by sweeping the monochromator (monochromator spectral range 200–1,200 nm, currently used FEU-100 spectral range 170–830 nm) with repeated scanning and averaging. Next, the mode of slow kinetics of light emission was implemented to study biolumi-nescence. The shortest time step is 2 ms and is determined by the bandwidth of the registration ADC. A field-cycling kinetics and luminescence mode has also been implemented and is now under test, when in every point along the time or wavelength axis the luminescence is measured twice, with field on and with field off. The field is ramped on and off relatively slowly (about 1 s for a 0–20 mT transition), and the measurement is performed only after the field has settled. A pair of luminescence spectra or kinetics is thus simultaneously obtained, in field and without field.

3 Experimental Spectra

3.1 MARY Spectra

Figure 4 shows a standard modulated MARY spectrum for solution of 10^{-2} M durene (electron donor) and 10^{-3} M p-terphenyl-d_{14} (electron acceptor and luminophor) in n-dodecane. The two traces differ only in the degree of transversal field compensation. Trace 1 shows the spectrum with completely compensated transversal residual magnetic field (<0.01 mT), and trace 2 corresponds to 0.25 mT of uncompensated transversal field. The presence of transversal field does not allow true passage through zero field and makes the field sweep nonlinear, which results in a broadened and diminished zero field MARY line—the most important feature of this spectrum. Although this example is somewhat exaggerated and is given to demonstrate the problem, it does illustrate the common situation in low-field studies in spin chemistry. In theory the zero field MARY line can be arbitrarily narrow, provided the lifetime of the radical pair is long enough [19], and its most intriguing aspect is the possible effect of Earth's magnetic field (about 0.03 mT) on radical processes in chemistry and biology [40, 41]. Failure to compensate the components of the field transversal to the scanned field can severely corrupt the results. One caveat here is that a common belief that a ferromagnetic core is very effective in aligning the residual field along itself due to its very high magnetic permeability, so there is virtually no transversal field at sample in such a magnet, does not hold in very low fields in the mT range, where the permeability of magnetic alloys drops to low numbers. Although special materials (μ-metals) having high magnetic permeability in very low field are available, they saturate already in very low

fields in the mT range. An air-core magnetic system is much more effective and predicable in compensating the transversal fields in the vicinity of zero field and can provide a field of up to tens of mT.

3.2 X-Ray-Induced Recombination Luminescence Spectra

Figure 5 shows X-ray-induced recombination luminescence spectra for typical solutions used in MARY spectroscopy, or any other type of spin-chemistry experiment under X-rays. The traces shown with open symbols correspond to solutions of either luminescing electron acceptor (naphthalene, open circles) or luminescing electron donor (*N,N*-dimethylaniline, open triangles) in *n*-dodecane at commonly used concentrations of 10^{-2}–10^{-3} M. The luminescence here arises due
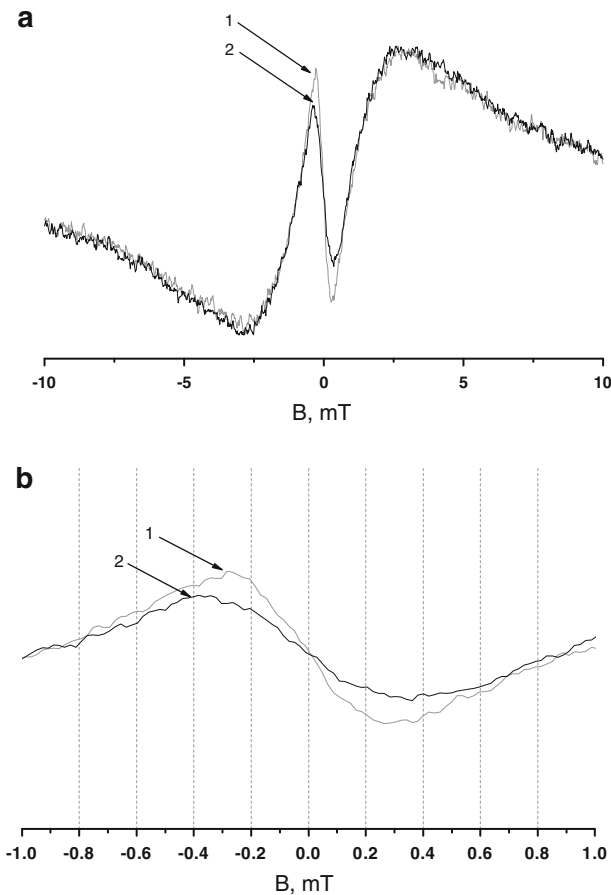

Fig. 4 a Modulated MARY spectra for solution of 10^{-2} M durene and 10^{-3} M *p*-terphenyl-d_{14} in *n*-dodecane, modulation amplitude 0.1 mT. Trace 1 shows spectrum with completely compensated transversal residual magnetic field, trace 2 corresponds to 0.25 mT of uncompensated transversal field; **b** an expanded view of the vicinity of zero field

to recombination of radical ion pairs comprising a radical ion of the luminophor, and the emission bands are where expected for the given luminophor. For this particular pair of molecules the emission bands are both centered at 340 nm and practically overlap. However, when the two acceptors are introduced into solution together (two traces with filled circles and triangles for two sample compositions), a new red-shifted band with a maximum about 380 nm appears, apparently belonging to emission band of naphthalene/N,N-dimethylaniline exciplex in alkane. Thus, an exciplex is indeed forming in this system, and further experiments with varied concentration and optical excitation instead of X-rays show that it forms via both possible channels, directly upon recombination and via bulk reaction of the relatively long-lived excited state of naphthalene with N,N-dimethylaniline. The concentrations of acceptors in such experiments are rather high and often are made much higher than for the shown spectra to improve the efficiency of charge capture to acceptors, and the naphthalene/N,N-dimethylaniline emission band was seen to completely turn into the exciplex emission band at high N,N-dimethylaniline concentration of several tenths of mole per liter. It should also be noted that high concentrations of luminophors and thus high optical densities of solutions pose no problems for taking radiation-induced luminescence spectra as opposed to photoinduced luminescence, as the ionizing radiation penetrates the organic sample and is not confined to thin regions near the wall, as is the case for optical excitation of optically dense samples [32]. Thus, successful experiments were performed in neat N,N-dimethylaniline used as solvent.

3.3 X-Ray-Induced Recombination Luminescence Spectra with Field Cycling

Figure 6 shows two pairs of recombination luminescence spectra, recorded under X-ray excitation using magnetic field cycling from 0 to 20 mT, from degassed
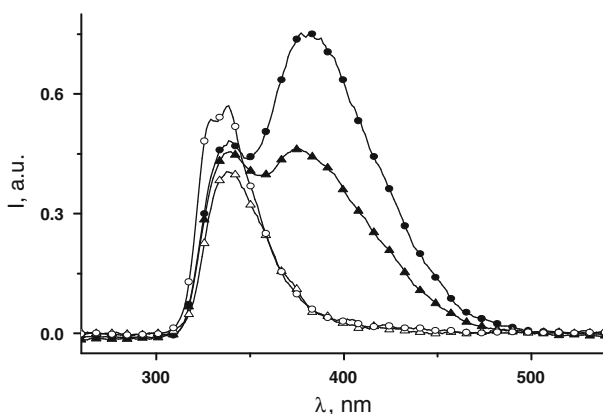

Fig. 5 X-ray-induced recombination luminescence spectra taken in a lead-jacketed molybdenum glass sample tube from degassed *n*-dodecane solutions of 5×10^{-3} M naphthalene (*open circle*), 10^{-2} M *N,N*-dimethylaniline (*open triangle*), 3.2×10^{-3} M naphthalene and 10^{-2} M *N,N*-dimethylaniline (*filled triangle*), and 6.4×10^{-3} M naphthalene and 10^{-2} M *N,N*-dimethylaniline (*filled circle*). Slits 2.2–2.2 mm

n-dodecane solutions of naphthalene-d_8 with (circles) and without (triangles) added *N*,*N*-dimethylaniline. These spectra were taken in a thin-walled quartz tube, so a shoulder of quartz luminescence is present in the region below 300 nm. For comparison, the spectra taken in the same conditions from an empty thick-walled quartz tube (outer diameter 10 mm, wall thickness 1.5 mm) are also shown (squares). For all three pairs of spectra empty symbols correspond to the field of 20 mT and filled symbols correspond to zero field. The things to be noted from this figure are the pronounced magnetic field effect (circa 6 % relative enhancement of emission in the field) on the emission bands of both naphthalene and exciplex, and virtually no magnetic field effect for plain quartz, where it is not expected. The figure also demonstrates the relative magnitudes of the target (solution) and parasitic (quartz) luminescence for a standard sample. The spectra for plain quartz were taken to check for the degree of artifacts due to magnetic field sensitivity of the X-ray tube and PMT. Although close examination shows that the two traces for quartz do separate, the observed effect on the emission from radical pair recombination in identical experimental conditions is about an order of magnitude larger. We also note that in the sample with both electron donor and acceptor magnetic field effect in the field 20 mT is identical for both individual luminophor and exciplex emission bands, indicating that magnetic field effect is generated at the stage of radical ion pair recombination rather than exciplex formation. While the latter is common in optically generated exciplexes in polar media, where the exciplex reversibly interconverts with a separated radical ion pair [42, 43], in nonpolar systems this does not occur, and exciplex formation only redistributes luminescence. Although magnetic field effect curve, i.e., the dependence of emission enhancement on applied field, could have been taken point by point by varying the cycling field in
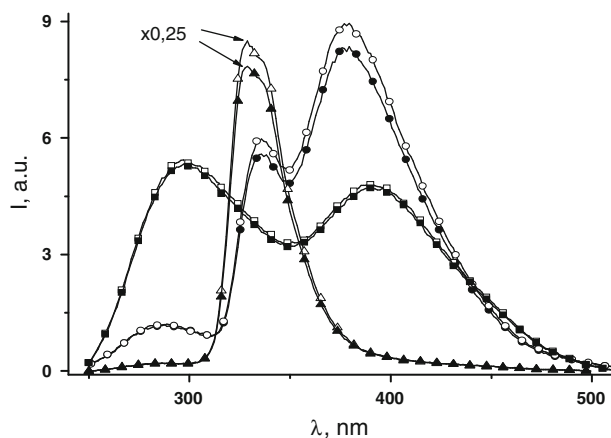

Fig. 6 X-ray-induced recombination luminescence spectra with magnetic field cycling (0–20 mT) taken in a thin-walled quarts tube from degassed *n*-dodecane solutions of 1.1×10^{-2} M naphthalene-d_8 (triangles, both traces divided by 4 for scaling) and 1.1×10^{-2} M naphthalene-d_8 and 10^{-2} M *N*,*N*-dimethylaniline (*circles*). For comparison the spectra taken in the same conditions from a thick-walled quartz tube are also shown (*squares*). For all three pairs empty symbols correspond to field of 20 mT and filled symbols correspond to zero field. Slits 2.2–2.2 mm

this experiment, this is done more conveniently in a modulated MARY with spectral fluorescence resolution as described in the next section.

3.4 Modulated MARY with Spectral Fluorescence Resolution

As noted earlier, the low optical efficiency of the grating monochromator precludes taking modulated MARY spectra through the monochromator for regular samples. Furthermore, the working regime of the PMT at the monochromator was optimized for DC measurement to improve the quality of luminescence spectra. The PMT has a rather high load of 1 MΩ to improve signal-to-noise ratio, but this together with capacitance of the cable going to lock-in amplifier (about 100 pF) creates a low-pass filter attenuating AC signals at frequencies above several hundred Hz. A buffering
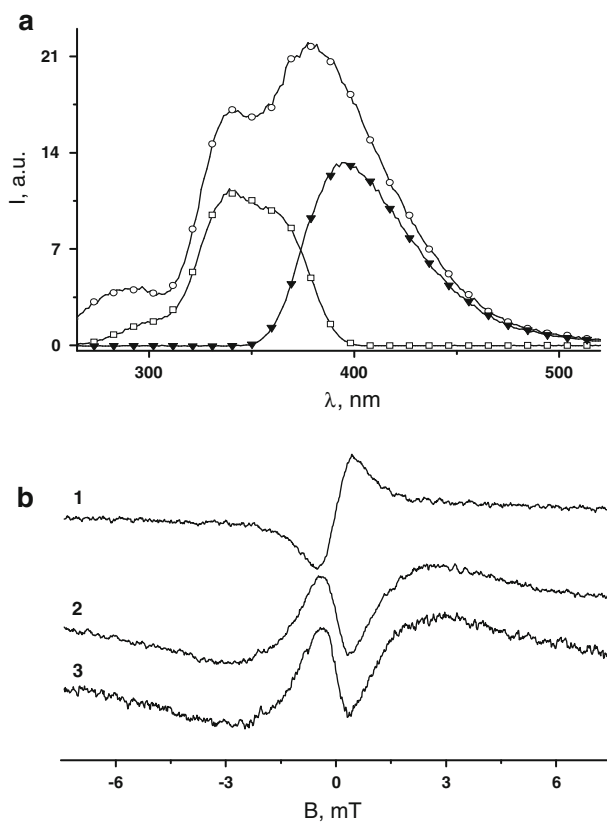

Fig. 7 a X-ray-induced recombination luminescence spectra from degassed *n*-dodecane solution of 1.1×10^{-2} M naphthalene-d_8 and 10^{-2} M *N,N*-dimethylaniline taken without filtering (*open circle*), with an BS-8 filter leaving the exciplex band (*filled inverted triangle*), and with the UFS-2 filter leaving the intrinsic naphthalene or *N,N*-dimethylaniline band (*open square*), slits 4.2–4.2 mm; **b** modulated MARY spectra from *n*-dodecane solution of 1.1×10^{-2} M naphthalene-d_8, full light (1), *n*-dodecane solution of 1.1×10^{-2} M naphthalene-d_8 and 10^{-2} M *N,N*-dimethylaniline in the exciplex band, spectrum (*filled inverted triangle*) from panel *a* (2), and in the intrinsic naphthalene or *N,N*-dimethylaniline band, spectrum (*open square*) from panel *a* (3)

preamplifier directly at PMT was found to introduce quite noticeable drifts as compared to the input amplifier of the ADC used for luminescence measurements without restoring the signal loss through the monochromator and was thus abandoned. Instead, it was decided to take MARY spectra with fluorescence spectral resolution by first recording a spectrum of luminescence under X-rays through the monochromator, determining the band of interest, and then using optical filters to select this band from the total light flux falling onto the FEU-130 PMT (with a higher sensitivity and a lower load of 30 kΩ and thus higher bandwidth) through the quartz light guide.

Figure 7 illustrates this approach for the naphthalene/N,N-dimethylaniline system from the previous section. Panel a shows X-ray-induced recombination luminescence spectra from the sample taken without filtering and through two filters leaving either the exciplex or the intrinsic luminophor bands, and panel b shows modulation MARY spectra from this sample in the two filtered bands (traces 2 and 3), as well as spectrum without optical filtering from a sample containing only naphthalene-d_8 (trace 1). The MARY spectrum (1) is typical [11] for a pair with two partners having weak hyperfine couplings (radical anion and radical cation of deuterated naphthalene), and shows only a narrow magnetic field effect without the zero field MARY line. The two optically band-limited spectra for the naphthalene-d_8/N,N-dimethylaniline system are identical and are typical for a pair with dominant hyperfine couplings on one of the partners (radical cation of N,N-dimethylaniline). The spectrum taken in full light is identical to the two filtered ones and is not shown. This demonstrates that the magnetic field in both exciplex emission band and the intrinsic luminophor emission band is indeed formed in the recombining radical ion pair, and not at the stage of exciplex formation. Rather curiously, no MARY signal of the pure naphthalene-d_8 type (like trace 1) was found in the intrinsic luminophor emission band.

4 Conclusions and Outlook

The described specialized low-field MARY spectrometer with spectral fluorescence resolution and switchable excitation sources turned out to be a versatile experimental system covering several types of experiment that were previously either not available or could not be performed at the same setup. Using the new setup, the effect of transversal residual magnetic field on zero field MARY line was illustrated, formation of exciplexes under X-irradiation in a naphthalene/N,N-dimethylaniline solution in alkane was demonstrated, a magnetic field effect on the emission spectrum was shown in field-cycling mode, and modulated MARY spectra in the exciplex and the intrinsic luminophor bands were compared to show that magnetic field sensitivity here is provided at the stage of the recombining radical ion pair, while exciplex formation only transforms the luminescence properties. The field-cycling mode of spectrometer can be used to study magnetosensitivity of recombination luminescence, chemiluminescence or bioluminescence from unstable samples. The possibility to compare the spectra of luminescence with optical and X-ray excitation from the same sample and their magnetic field sensitivity is a

useful new tool to study recombination luminescence that many spin-chemistry methods are based upon. Finally, the possibility to employ X-ray excitation and 308 nm exciplex lamp excitation on the same sample in identical conditions can help bridge the gap between radiation spin chemistry in nonpolar solutions and exciplex spin chemistry in polar solutions that historically developed via parallel but not overlapping routes.

References

1. D.V. Stass, S.V. Anishchik, V.N. Verkhovlyuk, in *Selectivity, Control, and Fine Tuning in High-Energy Chemistry*, ed. by D.V. Stass, V.I. Feldman (Research Signpost, Kerala, India, 2011), p. 143
2. C.A. Hamilton, J.P. Hewitt, K.A. McLauchlan, U.E. Steiner, Mol. Phys. **65**, 423 (1988)
3. M.M. Triebel, A.K. Morozov, M.M. Totrov, G.E. Zorinyants, E.L. Frankevich, Chem. Phys. Lett. **214**, 321 (1993)
4. D.V. Stass, N.N. Lukzen, B.M. Tadjikov, Y.N. Molin, Chem. Phys. Lett. **233**, 444 (1995)
5. S. Aich, S. Basu, D.N. Nath, J. Photochem. Photobiol. A **109**, 95 (1997)
6. M. Justinek, G. Grampp, S. Landgraf, P.J. Hore, N.N. Lukzen, J. Am. Chem. Soc. **126**, 5635 (2004)
7. J.R. Woodward, C.B. Vink, Phys. Chem. Chem. Phys. **9**, 6272 (2007)
8. S.R.T. Neil, K. Maeda, K.B. Henbest, M. Goez, R. Hemmens, C.R. Timmel, S.R. Mackenzie, Mol. Phys. **108**, 993 (2010)
9. T. Miura, A.M. Scott, M.R. Wasielewski, J. Phys. Chem. C **114**, 20370 (2010)
10. T. Miura, A. Kageyama, S. Torii, H. Murai, J. Phys. Chem. B **114**, 14550 (2010)
11. E.V. Kalneus, D.V. Stass, Y.N. Molin, Appl. Magn. Reson. **28**, 213 (2005)
12. K.M. Salikhov, Y.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, *Spin Polarization and Magnetic Effects in Chemical Reactions* (Elsevier, Amsterdam, 1984)
13. U.E. Steiner, T. Ulrich, Chem. Rev. **89**, 51 (1989)
14. S. Nagakura, H. Hayashi, T. Azumi (eds.), *Dynamic Spin Chemistry: Magnetic Controls and Spin Dynamics of Chemical Reactions* (Kodansha, Tokyo/Wiley, New York, 1998)
15. O.A. Anisimov, V.M. Grigoryants, S.V. Kiyanov, K.M. Salikhov, S.A. Sukhenko, Y.N. Molin, Theor. Exp. Chem. **18**, 256 (1983)
16. S.A. Sukhenko, P.A. Purtov, K.M. Salikhov, Sov. J. Chem. Phys. **2**, 29 (1985)
17. D.V. Stass, B.M. Tadjikov, Y.N. Molin, Chem. Phys. Lett. **235**, 511 (1995)
18. V.O. Saik, A.E. Ostafin, S. Lipsky, J. Chem. Phys. **103**, 7347 (1995)
19. C.R. Timmel, U. Till, B. Brocklehurst, K.A. McLauchlan, P.J. Hore, Mol. Phys. **95**, 71 (1998)
20. E.V. Kalneus, D.V. Stass, K.L. Ivanov, Y.N. Molin, Mol. Phys. **104**, 1751 (2006)
21. V.M. Grigoryants, S.D. McGrane, S. Lipsky, J. Chem. Phys. **109**, 7354 (1998)
22. E.V. Kalneus, D.V. Stass, K.L. Ivanov, Y.N. Molin, Mol. Phys. **104**, 1751 (2006)
23. V.M. Grigoryants, S.D. McGrane, S. Lipsky, J. Chem. Phys. **109**, 7354 (1998)
24. V.O. Saik, S. Lipsky, Chem. Phys. Lett. **264**, 649 (1997)
25. E.V. Kalneus, A.A. Kipriyanov Jr, P.A. Purtov, D.V. Stass, Y.N. Molin, Dokl. Phys. Chem. **415**, 170 (2007)
26. O.A. Anisimov, in *Ion Pairs in Liquids, Radical Ionic Systems*, ed. by A. Lund, M. Shiotani (Kluwer, Dodrecht, 1991), p. 285
27. F.B. Sviridenko, D.V. Stass, Y.N. Molin, Chem. Phys. Lett. **297**, 343 (1998)
28. K.L. Ivanov, K. Miesel, A.V. Yurkovskaya, S.E. Korchak, A.S. Kiryutin, H.-M. Vieth, Appl. Magn. Reson. **30**, 513 (2006)
29. S.E. Korchak, A.S. Kiryutin, K.L. Ivanov, A.V. Yurkovskaya, Yu.A. Grishin, H. Zimmermann, H.-M. Vieth, Appl. Magn. Reson. **37**, 515–537 (2010)

30. J.B. Birks, I.H. Munro, Prog. React. Kinet. **4**, 239 (1967)
31. K. Bhattacharyya, M. Chowdhury, Chem. Rev. **93**, 507 (1993)
32. E.J. Land, J.T. Richards, J.K. Thomas, J. Phys. Chem. **76**, 3805 (1972)
33. M. Ottolenghi, Acc. Chem. Res. **6**, 153 (1973)
34. N. Mataga, T. Okada, K. Ezumi, Mol. Phys. **10**, 203 (1966)
35. Y.H. Lee, M. Lee, Bull. Korean Chem. Soc. **18**, 1054 (1997)
36. E.V. Kalneus, D.V. Stass, Y.A. Grishin, Rev. Sci. Instrum. **76**, 084102 (2005)
37. V.F. Tarasenko, Pure Appl. Chem. **74**, 465 (2002)
38. R. Boscaino, M. Cannas, F.M. Gelardi, M. Leone, Phys. Rev. B **54**, 6194 (1996)
39. M.A. Kasymdzhanov, P.K. Khabibullaev, S.S. Kurbanov, Tr. J. Phys. **22**, 475 (1998)
40. B. Brocklehurst, K.A. McLauchlan, Int. J. Radiat. Biol. **69**, 3 (1996)
41. K. Maeda, K.B. Henbest, F. Cintolesi, I. Kuprov, C.T. Rodgers, P.A. Liddell, D. Gust, C.R. Timmel, P.J. Hore, Nature **453**, 387 (2008)
42. D.R. Kattnig, A. Rosspeintner, G. Grampp, Phys. Chem. Chem. Phys. **13**, 3446 (2011)
43. D.R. Kattnig, A. Rosspeintner, G. Grampp, Angew. Chem. Int. Ed. **47**, 960 (2008)