Fourier transformation of rf discrete saturation in ESR

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A Fouier-transformed analog of the pulsed method of rf discrete saturation is proposed.

Schweiger *et al.*[1] recently carried out a Fourier transformation of a discrete-saturation spectrum.[2,3] They showed that this technique is superior to the widely used spectroscopy based on modulation of the development of the electron spin echo. In this method, the first, selective, "soft" microwave pulse excites a discrete-saturation spectrum, while a second, intense, short $\pi/2$ pulse generates a signal representing the decay of free precession, which is transformed by a computer into a discrete-saturation spectrum. The same investigators[4] studied the resonant effect of an rf field on the Fourier-transformed discrete-saturation spectrum, applying an rf field pulse between the two microwave pulses.

We wish to propose a slight modification of the experimental layout, described in Ref. 4, in order to implement a Fourier-transformed analog of the method of rf discrete saturation,[5,6] which is in turn one of the pulsed versions of electron–nuclear double resonance.[7]

Years of experience in the use of the method of rf discrete saturation (e.g., Refs. 8–10) have shown that the important factor is not the suppression of the central hole in the discrete-saturation spectrum but, on the contrary, the restoration of this hole. For this purpose, the frequencies of the two microwave pulses—the selective and nonselective pulses—must be shifted with respect to each other. The spectrum of rf discrete saturation is used basically in connection with the effect of an rf field on the central hole. Unless this approach is taken, it is essentially impossible to study the angular distribution of the spectrum of the rf discrete saturation, since the discrete-saturation spectrum itself has a strong angular dependence. The central hole in pulsed rf-discrete-saturation experiments plays the same role as is played by the stimulated-echo signal in the Mims[11] and Davies[12] methods of electron–nuclear double resonance, which are based on an electron spin echo.

The reconstructed amplitude of the central hole must be stored, and then its dependence on the frequency of the rf field must be constructed. In the spectra of discrete saturation and rf discrete saturation, the intensities of the burnt-out holes play a secondary role. Comprehensive information on the hyperfine interaction is contained in the resonant frequencies (the positions of the holes in the case of discrete saturation) and in the hyperfine-interaction tensors found from them.

What basic advantages can we expect from a Fourier-transformed method of rf discrete saturation?

1. The rf pulse can be increased in duration without bound, to avoid causing a

broadening of the spectral lines of electron–nuclear double resonance, as in pulsed electron–nuclear double resonance based on the electron spin echo, because of the strict time limitation $t < T_{2e}$, where t is the duration of the rf pulse, and T_{2e} is the transverse electron relaxation time. The role played by the time T_{2e} in rf-discrete-saturation experiments is played by the cross-relaxation time within an ESR line, which determines the lifetime of the discrete-saturation spectrum and which is several orders of magnitude longer than T_{2e}.

2. The rf-discrete-saturation spectrum is more informative than other electron–nuclear double resonance methods. The presence of a discrete-saturation spectrum leads to an integrated picture of the regions of resonant radio frequencies expected in the spectrum of rf discrete saturation. In addition, because of the different effect on the discrete saturation, resonant radio frequencies from each nucleus are separated into two subsystems ν_+^α and ν_-^α, where α specifies the number of the nucleus in the surroundings of the magnetic center, and the sign specifies the electron state.

3. The resolution of the rf-discrete-saturation spectrum for lines belonging to different electron states is better than that of other electron–nuclear-double-resonance methods because they are received separately (from the discrete-saturation spectrum), even if they overlap. This circumstance is particularly important for the spectrum of nuclei of distant coordination spheres, since these lines accumulate near the Larmor frequency and overlap.

Both in experiments on a Fourier-transformed discrete-saturation spectrum[1] and in the Fourier-transform method of rf discrete saturation, the first, selective microwave pulse must be a saturating pulse, not a coherent pulse (a π pulse). In other words, its duration must be greater than or on the order of T_{2e}. As we have established previously,[13] a coherent pulse, instead of a saturating pulse, causes a pronounced broadening of the burnt-out holes. After a time T_{2e}, it leads to the formation of undesirable ESR wiggles or a parabolic structure of the dips in the ESR line. The time T_{2e} can be determined easily from the minimum width of the burnt-out holes in the ESR line.[13] The same is true of the rf pulse. If the resonant lines in the spectrum of pulsed electron–nuclear double resonance (rf discrete saturation) are not to be broadened, the duration of the pulse must satisfy the condition $t > T_{2N}$, where T_{2N} is the transverse nuclear relaxation time or the reciprocal of the width of the steady-state NMR at these nuclei.

The spectrum of multiple holes in nonuniformly broadened ESR lines, whose width is governed by the nuclei surrounding the magnetic center, can be burnt in two independent ways. The discrete-saturation spectrum is burnt because of a reorientation of the effective magnetic field acting on the nucleus in the course of an electronic transition.[2,3] In this case it is not possible to burn out a single hole, regardless of the degree of saturation of the ESR line. The discrete-saturation spectrum is burnt out simultaneously and constitutes a single spin packet of complex shape. The state of a magnetic center corresponding to the central hole, say $|+1/2, M\rangle$, where M is the z projection of the resultant nuclear moment of the surrounding nuclei, may be, for a time on the order of T_{2e}, in a state $|-1/2, M'\rangle$, belonging to any of the side holes in the discrete saturation spectrum, because of a flip-flop exchange with a neighboring magnetic center. The spectrum of the multiple holes behaves in a completely different way. We explained that spectrum in Ref. 14 on the basis of the saturation of a forbidden transition. In that study we investigated the ESR of a nitrogen donor impurity in silicon carbide. At low and intermediate degrees of saturation, a single central hole was burnt out in the ESR line. As the degree of saturation was raised (as the duration or amplitude of the alternating field was increased), side holes appeared in the ESR line. This type of spectrum of multiple holes in the ESR line of a phosphorus donor impurity in silicon was first observed by Feher.[15] However, because of the distinctive feature of the burning of the spectrum discussed above, that spectrum was erroneously attributed to discrete spin diffusion. An explanation of the saturation of a forbidden transition was first offered by Kozhushner *et al.*[16]

It can be hoped that the simplicity of the sequence of pulses and the great amount of information which can be obtained in a Fourier-transformed rf-discrete-saturation method, along with advanced technical capabilities, will allow this method to become an important part of magnetic rf spectroscopy.

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