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Two-dimensional hyperfine sublevel correlation spectroscopy: Powder features for $S = 1/2$, $I = 1$

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Abstract

The lineshapes of two-dimensional magnetic resonance spectra of disordered or partially ordered solids are dominated by ridges of singularities in the frequency plane. The positions of these ridges are described by a branch of mathematics known as catastrophe theory concerning the mapping of one 2D surface onto another. We systematically consider the characteristics of HYSCORE spectra for paramagnetic centers having electron spin $S = 1/2$ and nuclear spin $I = 1$ in terms of singularities using an exact solution of the nuclear spin Hamiltonian. The lineshape characteristics are considered for several general cases: zero nuclear quadrupole coupling; isotropic hyperfine but arbitrary nuclear quadrupole couplings; coincident principal axes for the nuclear hyperfine and quadrupole tensors; and the general case of arbitrary nuclear quadrupole and hyperfine tensors. The patterns of singularities in the HYSCORE spectra are described for each case.

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1. Introduction

Techniques to allow observation of multidimensional spectra are widely applied in magnetic resonance spectroscopy for better resolution and easier interpretation of experimental data [1,2]. Two-dimensional (2D) displays of spectra are used extensively because they are readily visualized. In both electron paramagnetic resonance and nuclear magnetic resonance (EPR and NMR) spectroscopies, 2D spectra are obtained as slices or projections of higher dimensional spectra or by applying some pulse sequence to the system in question where two time intervals, t_1 and t_2, in the pulse sequence are varied independently, see Fig. 1. The system response (typically spin echo or free induction signal) is stored as a 2D array of data. After 2D Fourier transformation, one obtains the 2D spectral density of the signal in the ω_1, ω_2 plane, where the frequency, ω_j, is the Fourier conjugate of t_j. In solid state measurements, such spectra often have complicated lineshapes because of anisotropic interactions that cause molecules with different orientations to have different spectral frequencies. If the molecules in the sample have complete or partial orientational disorder, (often referred to as 'powder' samples), the detailed lineshapes offer an opportunity to determine the complete, anisotropic magnetic resonance parameters of the molecule (see, e.g. [3,4]).

In 2D Fourier magnetic resonance experiments, the time-domain signal produced by molecules at any single, arbitrary orientation may be presented as

$$V(t_1, t_2) = \sum_{j,k=1}^{N} A_{j,k} \exp(\imath\Omega_j t_1 + \imath\Omega_k t_2), \tag{1}$$

where the frequencies Ω_j depend on the spin Hamiltonian eigenvalues and in simple cases are the transition frequencies of the system. The amplitudes, $A_{j,k}$, depend on the

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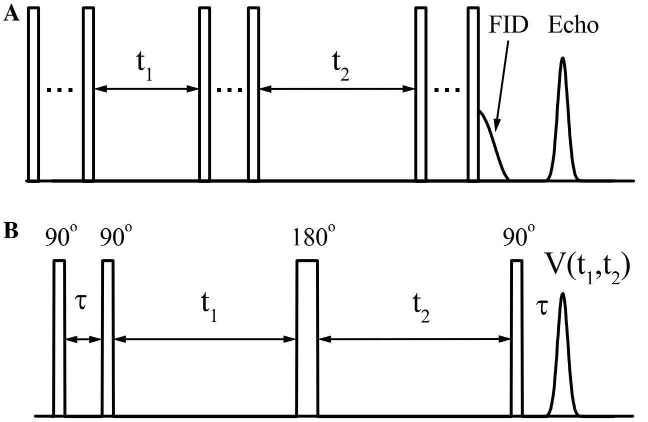

Fig. 1. Pulse sequences used in two-dimensional spectroscopy, (A) the general scheme, and (B) HYSCORE experiment implementation. In the latter case the stimulated echo signal amplitude is measured. It is generated by the first, second and the fourth pulses. The signal amplitude is measured as a function of two delays, t_1 and t_2, between the mixing (third) pulse and second and fourth pulses, respectively. The rotation angles are shown above the pulses.

characteristics of the microwave (mw) pulses in the case of EPR or radiofrequency (rf) pulses in the case of NMR, the particular pulse sequence, and on the parameters of the spin Hamiltonian. Both Ω_j and $A_{j,k}$ implicitly depend on the orientation of the molecule in the magnetic field of the spectrometer because the spin Hamiltonian generally is orientation dependent. In this paper, we use a type of 2D EPR spectroscopy known as HYSCORE [7] as a specific example, although the approach is applicable to other types of 2D EPR [8–10] or NMR methods. For simplicity, we do not consider relaxation in Eq. (1) and assume both frequencies to be non-zero. In general, the signal described by Eq. (1) consists of damped periodic oscillations in the time domain. We ignore the damping here because it is usually negligible compared to damping caused by interference from the distribution of frequencies in a 'powder' sample.

Fourier transformation of Eq. (1) gives

$$V_{\mathrm{F}}(\omega_1,\omega_2)=\sum_{j,k=1}^{N}A_{j,k}\delta(\omega_1-\Omega_j)\delta(\omega_2-\Omega_k), \tag{2}$$

where $\delta(x)$ is Dirac's delta-function. Instead of a smooth function of two variables in the time domain, the transformed signal is a set of discrete points in the frequency domain having infinite amplitude and zero spectral density in the rest of the frequency plane. For an orientationally disordered or 'powder' sample, Eqs. (1) and (2) must be integrated over the orientations of the molecules in the sample with respect to the laboratory frame. Such integration leads to a set of regions or spectral 'lines' having non-zero spectral density, which may partly overlap each other. The boundaries between regions with zero and non-zero spectral density often form rather prominent ridges. Such 2D patterns of ridges allow precise determination of the spin Hamiltonian parameters from which valid inferences of the molecular or electronic structure can be made and is the motivation for the use of 'contour lineshapes' developed by Dikanov [5]. In favorable cases, spin Hamiltonian parameters are determined completely by the positions of the ridges without the need to consider the intensity factors in Eqs. (1) and (2). This paper systematically examines the shapes of these ridges and the question of whether prominent ridges lie only on the boundaries between regions with and without spectral density.

From the point of view of mathematics, each term in Eq. (2) represents a smooth mapping of the hemisphere of possible orientations onto the frequency plane

$$\begin{cases}\omega_1=\Omega_j(\theta,\phi)\\ \omega_2=\Omega_k(\theta,\phi)\end{cases}. \tag{3}$$

Here θ and ϕ are the polar and azimuthal angles relating the external magnetic field to the molecular frame. Because inversion of the magnetic field does not change the eigenvalues of the spin-Hamiltonian, only a hemisphere of possible orientations need be considered. We will make extensive use of the unit hemisphere defined by θ and ϕ in discussing the orientation dependence of the spectral frequencies in the 2D spectra. This smooth mapping generates singularities where many orientations of a paramagnetic center (PC) result in the same set of frequencies so that significant areas of the hemisphere map to a single, intense point in the frequency plane.

These singularities produce a 2D 'powder' spectrum with prominent features where the signal intensity approaches infinity in the ideal case. The branch of mathematics which concerns singularities in the smooth mappings of one metric space onto the other is called catastrophe theory [6]. We used catastrophe theory to predict and understand features in HYSCORE spectra for different classes of spin Hamiltonians but for this paper we try to explain those results with more familiar mathematics. Other approaches have been used with great success (see the excellent discussion of 2D NMR powder lineshapes in [4]).

In HYSCORE spectra, the singularities are modified by the intensity factor, $A_{j,k}$. The intensity factor is strictly bounded, generally, $0 \leqslant |A_{j,k}|^2 \leqslant 1$. These intensity factors may cause part of a singularity to have zero amplitude, but they can never produce a singularity independent of the mapping. Thus, the prominent features in a spectrum correspond to singularities whose locations can be determined without calculating the $A_{j,k}$ although not every singularity will have sufficient intensity to be observed.

This paper considers 2D spectroscopy in 'powder' samples in the context of catastrophe theory and focuses on the features of the spectrum that arise from singularities produced by the mapping because in many cases the locations of these singularities are sufficient to determine the desired spin Hamiltonian parameters. A form of 2D pulsed EPR spectroscopy, known as hyperfine sublevel correlation (HYSCORE) spectroscopy [7], of PCs having electron spin $S = 1/2$ and nuclear spin $I = 1$ is used as a specific spectroscopic example. HYSCORE uses the electron spin for the

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