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Singularities in the lineshape of a second-order perturbed quadrupolar nucleus. The magic-angle spinning case

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ABSTRACT

For a nucleus with a half-integral spin and a strong quadrupole coupling, the central transition (from magnetic quantum number $-1/2$ to $+1/2$) in the spectrum shows a characteristic lineshape. By strong coupling, we mean an interaction strong enough so that second-order perturbation theory is needed, yet still sufficient. The spectrum of a static sample is well-known and the magic-angle-spinning (MAS spectrum) is different, but still can be calculated. The important features of both these spectra are singularities and steps in the lineshape, since these are the main tools in fitting the calculated spectrum to experimental data. A useful tool in this investigation is a plot of the frequency as a function of orientation over the surface of the unit sphere. These plots have maxima, minima and saddle points, and these correspond to the features of the spectrum. We used these plots to define both the positions and derive new formulae for the heights of the features and we now extend this to the magic-angle spinning case. For the first time, we identify the orientations corresponding to the features of the MAS spectra and derive formulae for the heights. We then compare the static and MAS cases and show the relationships between the features in the two spectra.

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1. Introduction

The lineshape for the central transition of a half-integral spin quadrupolar nucleus is very familiar to NMR spectroscopists. For many cases, the quadrupole interaction is treated as a perturbation to the main Zeeman interaction. In absolute terms, the perturbation is small (much less than a percent), but because NMR lines are remarkably narrow, the effects can be easily seen. In particular, the central transition (the transition from the state with magnetic quantum number $-1/2$ to that with quantum number $+1/2$) of a half-integral spin is not perturbed to first (or third) order by the quadrupole interaction. If the quadrupole coupling is appropriately strong, compared to the Zeeman interaction, then second-order perturbation theory can be used to calculate the position of the central transition.

Since the quadrupole interaction is molecule-fixed, this will depend on the orientation of the molecule [1–3] in the magnetic field. The spectrum of a powdered sample (Fig. 1) will be a probability density function: the limit of a histogram of the number of crystallites that have a frequency within a given range. Recently, we reviewed this lineshape for a static system [4], with emphasis on the steps and singularities and their relation to a

contour plot of the frequency as a function of orientation on the unit sphere [5]. The formula for the frequency, as a function of orientation, is well known and can be used to calculate the lineshape directly. However, it is also useful to plot the frequency on the surface of the unit sphere. This plot helps in deriving, for the first time, simple analytical formulae for the heights of these features. These formulae were for a static sample, and we now extend these results to a spectrum acquired with fast magic-angle sample spinning (MAS).

For second-order perturbed spectra, the magic angle is no longer magic [6]. Spinning narrows the lineshape somewhat, but does not reduce it to a single line. The lineshape depends on the spinning angle, and the magic angle does not necessarily give the narrowest line. This has prompted more sophisticated methods, such as multiple-quantum MAS (MQMAS) [7], double rotation [8] and dynamic angle spinning [9–12] which can produce sharp lines. However, there is still much information that can be gleaned from a simple one-dimensional spectrum, and the purpose of this paper is to reveal this.

Spinning the sample at the magic angle has the advantage that, to a good approximation, other interactions are “spun out”. We are then dealing with a single interaction, whereas a static spectrum usually has contributions from dipolar coupling and chemical shielding anisotropy (CSA). In our previous paper, we dealt mostly with the quadrupole lineshape in isolation, but included contributions from CSA in a particular special case. The general case of a

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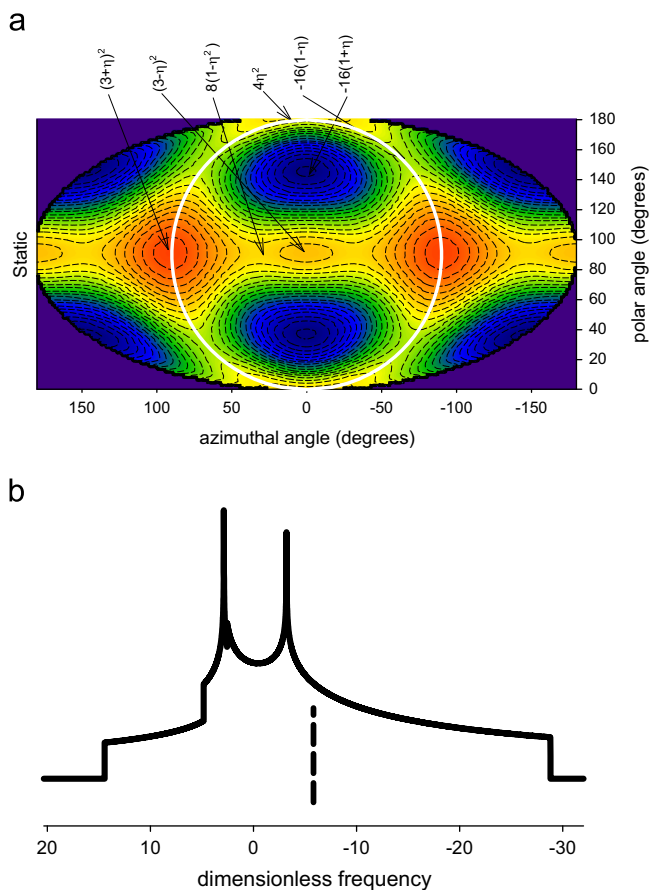


Fig. 1. (a) Contour plot of the second-order perturbed frequency of the central transition of a quadrupolar nucleus with a half-integral spin, as a function of orientation of the nucleus for a static sample. The orientation is uniform over the surface of the unit sphere, which is displayed here using the Mollweide map projection. In this projection, the lines of latitude are horizontal and the lines of longitude are ellipses through the poles. The solid white line corresponds to longitudes of $\pm\pi/2$ (in geographical terms), which generates a circle on this scale. The scale for the azimuthal angle strictly applies only to the equator. The reduced frequency, as a function of polar and azimuthal angles is given by Eq. (4) in the dimensionless units defined there. The frequencies at the critical points, which correspond to the features in the spectrum, (b) are in dimensionless units and calculated using a value of the asymmetry parameter, η , of 0.8. (b) Spectrum lineshape derived from the contour plot in (a) for a value of $\eta=0.8$. The x axis is given in dimensionless units given by Eq. (4) and are the same as figure 7 in Ref. [17]. The vertical dashed line at -5.824 represents the center of mass of the spectrum at $-(8/5)(3+\eta^2)$ in these units. The features (steps and singularities) are in order of decreasing frequency (left to right in the spectrum) and given by $(3+\eta)^2$, $(3-\eta)^2$, $8(1-\eta^2)$, $4\eta^2$, $-16(1-\eta)$ and $-16(1+\eta)$. For this particular value of η , the third and fourth features are almost coincident. These formulae are appropriate for $\eta > 1/3$ and there is one fewer step for the case of $\eta < 1/3$.

CSA tensor with an arbitrary orientation to the quadrupole tensor is still unsolved (except numerically) [13]. However, since the MAS case is common, important and quite easy to solve, we present the relation between frequency and orientation and derive formulae for the heights of the features along with an example of experimental data.

A key tool is the contour plot of the perturbed frequency as a function of the orientation of the molecule, presented on a projection of the unit sphere. This contour plot shows maxima, minima and saddle points, which correspond to the features of the lineshape [4,5]. For the static sample case, we showed how we cannot only locate these features, but also calculate their heights. For the MAS case, the formulae for the frequency as a function of orientation are well-known, but details of the correlation of the features of the spectrum with the contour plot, and formulae for

the heights of the features have not been published, to the best of our knowledge.

If the positions of the features in the spectrum are clear enough, then the quadrupole parameters can be extracted directly from them [14], without the need for a powder average. However, many spectra are poorly resolved, so having both the positions and the heights of the features greatly extends the possibilities for spectral analysis without a powder pattern.

1.1. Theory

The theory presented here is much the same as in our previous paper—just the equation for the frequency is different. The spectrum we measure is a probability density function of the frequency over the orientations of the crystallites in a random powder—the limit of a histogram of the distribution of frequencies. Since the quadrupole interaction is defined by the molecule, different orientations (represented by different points on the unit sphere) will have different frequencies. We can plot these frequencies (Fig. 1(a)) as a projection of the unit sphere onto a flat surface (in this case, we used the Mollweide projection [15]). The contours of this three-dimensional plot represent the frequencies (z axis) as a function of polar and azimuthal angles (x and y axes), so if we consider a thin slice defined between closely-spaced contours (a narrow range of frequencies, which would define a bin in the histogram), the area of this slice corresponds directly to the height of the histogram at that range of frequencies. The shapes of any particular slice can be quite complex, so we cannot define an explicit function for its area and hence, its height in the full lineshape, but we can define the area for important parts of it.

The contour plots show typical critical points: maxima, minima and saddle points which play two important roles. These correspond to obvious features in the spectrum (Fig. 1(b)), where the finite steps in the lineshape function correspond to maxima and minima, and the saddle points correspond to the singularities. The other role is that, near these critical points, the shape of the contours is better defined – for instance, near a maximum or a minimum they are elliptical – and we can calculate their areas analytically. We used this technique to define the heights of the features for some lineshapes for static samples. We now move on to the lineshapes of samples acquired under magic-angle spinning (MAS) conditions.

There are a number of ways of writing the formula for the second-order-perturbed quadrupole frequency as a function of orientation [16–18]. For the static samples, the effect of the perturbation can be clearly seen from looking directly at the mixing of the central single-quantum transition with other transitions [19], rather than the classic perturbation of the wavefunctions [20]. This approach is known as the direct method [21,22] in NMR and has recently been reviewed in a wider context [23]. Although all the transitions can be mixed together by the perturbation, selection rules restrict the mixing to just a few [19,22]. Once the formula is defined, it is often convenient to collect terms, either in terms of η , the asymmetry parameter, or in powers of $\cos(\theta)$, the polar angle. It is also convenient to write the frequency in a set of reduced units [17], where the overall factor contains the Larmor frequency, ν_0 , the quadrupole coupling and the spin quantum number, S , and the other part depends only on the geometry and the asymmetry factor.

The quadrupole interaction is well described in the literature. It is the interaction of the electrical quadrupole moment of the nucleus with the local electric field gradient of the electrons. This electric field gradient is a symmetric traceless second-order tensor, and is usually defined in its principal axis frame (PAF), V^{PAF} , in which it is diagonal. In this frame, it is often specified by its largest element (conventionally V_{zz} , the component along the

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