Magic angle spinning (MAS) NMR linewidths in the presence of solid-state dynamics

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Abstract

In solid-state NMR, the magic angle spinning (MAS) technique fails to suppress anisotropic spin interactions fully if reorientational dynamics are present, resulting in a decay of the rotational-echo train in the time-domain signal. We show that a simple analytical model can be used to quantify this linebroadening effect as a function of the MAS frequency, reorientational rate constant, and magnitude of the inhomogeneous anisotropic broadening. We compare this model with other theoretical approaches and with exact computer simulations, and show how it may be used to estimate rate constants from experimental NMR data.

1. Introduction

Magic angle spinning (MAS) is widely used in solid-state NMR to refocus the effects of anisotropic interactions, such as dipolar coupling, chemical shift anisotropy and quadrupolar coupling, permitting in favourable cases the recording of high-resolution spectra [1, 2]. However, it has long been known that MAS can fail in the presence of reorientational dynamics, causing linewidths to increase dramatically [3]. For example, we have recently shown that the combination of solid-state dynamics on the microsecond timescale with the large quadrupolar interaction causes considerable broadening in the isotropic dimension of ^{27}Al satellite-transition MAS (STMAS) NMR spectra of as-synthesized aluminophosphates; by contrast, the corresponding isotropic ^{27}Al multiple-quantum MAS (MQMAS) NMR spectra remain relatively narrow in the presence of motion, since the spin transitions involved are unaffected by the quadrupolar interaction to first order [4, 5].

This dynamic broadening effect can be viewed as an obstacle to resolution or as a useful probe of molecular motion [6-11]. However, it is sometimes possible to select experiments that exhibit linebroadening in one dimension while retaining high-resolution in a second dimension. As shown in our recent study of dynamics by ^{2}H double-quantum (DQ) MAS NMR spectroscopy [10], this allows motion to be probed without loss of resolution.

In previous work, we have briefly introduced a simple analytical model to illustrate and quantify the effects of dynamics on linewidths in MAS NMR spectra [4]. The purpose of this Letter is to justify our use of this model and to widen its application: in section 2 we describe the model and compare it with more conventional theoretical approaches; in section 3, by comparison with exact numerical simulations, we show that the model provides a surprisingly quantitative description; finally, in sections 4 and 5, we show how MAS NMR spectroscopy, in conjunction with a simple model for linebroadening, can be used to estimate timescales for dynamic processes in solids.

2. Theories of motional broadening under MAS

A. Overview

For an NMR transition experiencing a traceless second-rank inhomogeneous interaction under sample rotation at a frequency ν_R, the contribution to the frequency of a transition can be written as a Fourier series [12]:

$$\nu(t) = \sum_{m=-2}^{2} \nu^{(m)} \exp\left(2\pi i m \nu_R t\right) \quad . \tag{1}$$

The coefficient $\nu^{(0)}$ is equal to zero when spinning is performed at the magic angle and, as a result, the net phase accrued during a complete rotor period is zero. The effect of the anisotropy is therefore eliminated if spectra are acquired in a rotor-synchronized, or "stroboscopic", manner.

In the presence of reorientational dynamics, this conclusion is no longer valid, since the coefficients $\nu^{(m)}$ become time-dependent. The result is that the evolution is no longer refocused and the rotor-synchronized MAS linewidth becomes dependent on the size of the interaction, the kinetics of the motion, and the spinning rate.

B. Maricq and Waugh approximation

An early description of motional linebroadening under MAS was provided by Maricq and Waugh [3]. Their analysis is valid in the fast-spinning regime, where the spinning rate ν_R is large compared with the size of the anisotropy ν_{an}. In this regime, the full MAS linewidth at half-height $\Delta\nu_{1/2}$ is small compared with the spinning rate and the signal from a single crystallite at the end of a rotor period can be approximated by a power series truncated to first order:

$$\begin{aligned} s(\tau_R) &= s(0)\exp\left(-\pi\Delta\nu_{1/2}\tau_R\right) \\ &\approx s(0)\left(1-\pi\Delta\nu_{1/2}\tau_R\right) \end{aligned} \quad , \tag{2}$$

where $\tau_R = 1/\nu_R$. This signal can also be written in terms of the phase $\phi(\tau_R)$ acquired by a spin, which under solid-state dynamics is randomly distributed with a mean of zero:

$$\begin{aligned} s(\tau_R) &= s(0)\overline{\exp\left(i\phi(\tau_R)\right)} \\ &\approx s(0)\left(1-\tfrac{1}{2}\overline{\phi^2(\tau_R)}\right) \end{aligned} \quad , \tag{3}$$

where the overbar implies ensemble averaging and we have assumed the phase acquired by any spin during a rotor period is small. By comparing eqs (2) and (3), an expression for the MAS linewidth is obtained:

$$\begin{aligned} \Delta\nu_{1/2} &= \frac{\nu_R}{2\pi}\overline{\phi^2(\tau_R)} \\ &= 2\pi\nu_R \int_0^{\tau_R}\int_0^{\tau_R} \overline{\nu(t')\nu(t)}\,dt'dt \end{aligned} \quad . \tag{4}$$

The value of this expression depends on the details of the spin interaction and solid-state dynamics. In their analysis, Maricq and Waugh assume an axially symmetric anisotropy ν_{an}, the principal axis system (PAS) of which is oriented at 90° to the rotor axis. Random molecular motion is modelled by allowing the azimuthal angle of the PAS with respect to the rotor-fixed frame, α^{PR}, to be time dependent, with rate constant k and the following correlation function:

$$\overline{\cos 2\alpha^{PR}(t)\cos 2\alpha^{PR}(t')} = \overline{\sin 2\alpha^{PR}(t)\sin 2\alpha^{PR}(t')} = \tfrac{1}{2}\exp\left(-k\left|t-t'\right|\right) \quad . \tag{5}$$

Using this formula, eq (4) is evaluated to yield a simple analytical expression for the linewidth in the fast-spinning regime:

$$\Delta\nu_{1/2} = \frac{\pi\nu_{an}^2}{2\nu_R\left(16\pi^2+x^2\right)^2}\left(-16\pi^2 e^{-x}+16\pi^2+16\pi^2 x+x^2 e^{-x}-x^2+x^3\right) \quad , \tag{6}$$

where $x = k/\nu_R$. In the slow-motion limit $x << 1$, this reduces to the expression given in ref [3]:

$$\Delta\nu_{1/2} = \frac{k\nu_{an}^2}{16\pi\nu_R^2} \quad . \tag{7}$$

According to eq (6), maximum linebroadening occurs when $2\pi\nu_R/k \approx 0.55$. In the regime close to this maximum, we can neglect all but the two largest terms to obtain a formula with the same form as the (order-of-magnitude) expression quoted by Virlet [13]:

$$\Delta\nu_{1/2} = \frac{k\pi\nu_{an}^2}{2k^2+32\pi^2\nu_R^2} \quad . \tag{8}$$

C. Extension of Maricq and Waugh approximation

Although the approach taken by Maricq and Waugh provides a qualitative description of motional broadening in the fast-spinning regime, the calculation assumes a single-crystal sample and the characteristics of the motion are somewhat arbitrary. However, it is easy to extend their methodology to take into account both powder averaging and a specific motional model, and still obtain analytical expressions for the linewidth.

For ^{2}H (spin $I = 1$) nuclei in D_2O molecules undergoing 180° flips about the C_2 symmetry axis, and experiencing an axially symmetric quadrupolar interaction, it is straightforward to evaluate eq (4):

$$\Delta\nu_{1/2} = \frac{27\pi C_Q^2 \sin^2\theta}{320\nu_R\left(4\pi^4+5\pi^2x^2+x^4\right)^2}\begin{pmatrix} 12\pi^6-12\pi^6e^{-2x}+24\pi^6x-3\pi^4x^2+3\pi^4x^2e^{-2x} \\ +38\pi^4x^3-4\pi^2x^4+4\pi^2x^4e^{-2x}+16\pi^2x^5 \\ -x^6+x^6e^{-2x}+2x^7 \end{pmatrix} \quad (9)$$

where $x = k/\nu_R$ and $C_Q = e^2qQ/h$ is the ^{2}H quadrupolar coupling constant (for the case of a spin $I = 1$ nucleus experiencing the first-order quadrupolar interaction $\nu_{an} = \frac{3}{4}C_Q$) and θ is the DOD angle. In the limit of slow motion, the MAS linewidth is given by the following equation, which has the same form as eq (7):

$$\Delta\nu_{1/2} = \frac{81k\,C_Q^2\sin^2\theta}{320\pi\nu_R^2} \quad . \quad (10)$$

D. Spin-echo model

In an attempt to describe motional broadening under *all* regimes, Wimperis and co-workers introduced a new model, in which MAS is approximated by a spin-echo train with the spacing between π pulses defining the "rotor period" $\tau_R = 1/\nu_R$; reorientational motion is modelled by two-site exchange [4]. Mathematically, this is most easily described in the interaction representation using the stochastic-Liouville equation, with the coherences on the two sites represented by a vector $\mathbf{M}(t)$:

$$\mathbf{M}(\tau_R) = \exp\left(\mathbf{L}^+\tau_R/2\right)\exp\left(\mathbf{L}^-\tau_R/2\right)\mathbf{M}(0) \quad , \quad (11)$$

where the time-independent Liouvillians $\mathbf{L}^-$ and $\mathbf{L}^+$ describe evolution during the first and second halves of the rotor period respectively:

$$\mathbf{L}^{\pm} = \begin{pmatrix} -k\pm i2\pi\nu_A & k \\ k & -k\pm i2\pi\nu_B \end{pmatrix} \quad , \quad (12)$$

where ν_A and ν_B are the frequencies of the two sites. An average Liouvillian can then be calculated for the rotor period:

$$\mathbf{M}(\tau_R) = \exp\left(\mathbf{L}^{av}\tau_R\right)\mathbf{M}(0) \quad . \tag{13}$$

The resulting spectrum is the sum of two Lorentzian lines, with linewidths $\Delta\nu_{1/2}^{(i)}$ directly proportional to the eigenvalues of the average Liouvillian, L_i^{av}:

$$\Delta\nu_{1/2}^{(i)} = \frac{-1}{\pi\tau_R} L_i^{av}. \tag{14}$$

In most cases, the two components either have nearly equal linewidth, or the line is dominated by just one of the components. The MAS linewidth can therefore be expressed by a single analytical formula:

$$\Delta\nu_{1/2} = \frac{k}{\pi} - \frac{\nu_R}{\pi}\ln\left[\frac{1}{z^2}\left(\begin{array}{l}-\pi^2\Delta\nu_J^2+k^2\cosh\dfrac{z}{\nu_R} \\ +\sqrt{2}k\,\mathrm{sgn}\left(z^2\right)\sqrt{\left(k^2-2\pi^2\Delta\nu_J^2+k^2\cosh\dfrac{z}{\nu_R}\right)\sinh^2\dfrac{z}{2\nu_R}}\end{array}\right)\right] \tag{15}$$

where $z=\sqrt{k^2-\pi^2\Delta\nu_J^2}$ and $\Delta\nu_J=\nu_A-\nu_B$ is the magnitude of the "frequency jump" resulting from reorientation (and fulfills the same role as that of ν_{an} in the Maricq and Waugh model).

Fig. 1 shows the variation of $\Delta\nu_{1/2}$ as a function of k for different values of the MAS rate and frequency jump. Two regimes can be identified: (i) in the *fast-spinning regime* ($\nu_R >> \Delta\nu_J$), the anisotropy is efficiently suppressed by magic angle spinning. However, exchange interferes with this process and the value of k that maximizes the linewidth depends on the spinning rate (see Fig. 1(b)) rather than on the frequency jump (see Fig. 1(a)). Nevertheless, the actual linewidth depends on both spinning rate and frequency jump. (ii) In the *slow-spinning regime* ($\nu_R << \Delta\nu_J$), analogy may be drawn with chemical exchange in liquids and static solids, where the value of k that causes maximum broadening is determined by the magnitude of the frequency jump (see Fig. 1(c)); the linebroadening is almost independent of the spinning rate (see Fig. 1(d)).

Although eq (15) is a rather complicated expression, it simplifies in the obvious limits. In the *slow-exchange* ($k << \Delta\nu_J$) and *slow-spinning regime* ($\nu_R << \Delta\nu_J$), the expression for liquid (or static single-crystal) samples in slow exchange is recovered:

$$\Delta\nu_{1/2} \approx \frac{k}{\pi} \quad . \tag{16}$$

In the *slow-exchange* ($k << \Delta\nu_J$) and *fast-spinning regime* ($\nu_R >> \Delta\nu_J$), the reduced expression agrees with that of Maricq and Waugh (eq (7)) to within a numerical factor:

$$\Delta\nu_{1/2} \approx \frac{k\pi\Delta\nu_J^2}{24\nu_R^2} \quad . \tag{17}$$

And, finally, for all MAS rates, in the fast-exchange limit ($k >> \Delta\nu_J$), the expression applied to liquid (or static single-crystal) samples is obtained:

$$\Delta\nu_{1/2} \approx \frac{\pi\Delta\nu_J^2}{2k} \quad . \tag{18}$$

E. Calculation of $\Delta\nu_J$

One of the main limitations of the spin-echo model described above is that a single frequency jump is assumed while, in a real powder under MAS, the frequency jump is both orientation- and time-dependent. Since the frequency jump cannot exceed the width of the static powder pattern, the latter gives an order-of-magnitude value for the frequency jump. A better estimate can be made by calculating the root-mean-square (RMS) frequency jump for a static powder. In ^{2}H NMR of D_2O molecules undergoing 180° flips about the C_2 symmetry axis and experiencing a quadrupolar coupling, the RMS frequency jump is given by:

$$\Delta\nu_J^{RMS} = C_Q\sqrt{\frac{27}{80}}\sin\theta \quad , \tag{19}$$

where the quadrupolar coupling tensor is assumed to be axially symmetric and aligned with its principal axis co-linear to the OD bond.

3. Comparison with exact simulations

The spin-echo model described above makes plausible predictions of MAS linewidths in the presence of motion. To determine the extent to which these predictions are quantitative, comparison was made with exact numerical simulations of ^{2}H MAS NMR spectra, assuming the dynamic D_2O system described in section 2E. To properly take into account MAS and molecular flips, the spin dynamics were modelled using a time-dependent Liouville equation:

$$\frac{d\mathbf{M}(t)}{dt} = \begin{pmatrix} i2\pi\nu_Q^A(t) - k - R & k \\ k & i2\pi\nu_Q^B(t) - k - R \end{pmatrix} \mathbf{M}(t) \quad , \qquad (20)$$

where R/π is the linewidth in the absence of exchange; $\nu_Q^A(t)$ and $\nu_Q^B(t)$ represent the time-dependent quadrupolar frequencies of the two possible orientations of the molecule in the molecular frame of reference (the two orientations are related by 180° rotation about the C_2 axis) and are of the form given by eq (1). The Liouville equation was solved by dividing the rotor period into ten equal time periods, during each of which the rotor is assumed to be stationary, and calculating the evolution in a stepwise manner. Since ideal pulses are assumed, the initial state is given by $\mathbf{M}(0) = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$.

The resulting data were then averaged over a set of 300 powder orientations determined by the ZCW algorithm [14-17], and the resulting signal Fourier transformed. $\Delta\nu_{1/2}$ values measured directly from the spectra are shown in Fig. 2, together with theoretical predictions as described in section 2.

There is a high level of agreement between the linewidths obtained from exact simulations (crosses) and those predicted by the spin-echo model (solid lines), especially

in the slow-spinning regime. The difference is greater in the fast-spinning regime, but the level of agreement is nevertheless remarkable given the primitive nature of the model.

Fig. 2 also displays linewidth predictions obtained using the Maricq and Waugh model (dashed lines). These predictions compare relatively poorly with the simulated data, which is not too surprising given the approximations used in the calculation. The modified version of this theory (dotted lines) described in section 2C shows better agreement in the fast-spinning regime (Fig. 2c) for which it is derived. It is also noteworthy that for large values of k, the predictions agree closely with the simulation data in all three graphs. This is a consequence of the small phase approximation in eq (3). For small k, most spins will experience either no "reorientational jumps" or only a small number of these; evolution of the former will be fully refocussed, while the latter are likely to acquire large phases in the intermediate- or slow-spinning regimes, invalidating the approximation. For large values of k, however, most spins will flip many times during a rotor period, so any phase acquired is likely to be small, and the approximation is valid.

It should be noted that simulated linewidth data is absent for some values of k, C_Q and ν_R. This occurs when the width of the line approaches the spinning rate: in the rotor-synchronized spectrum, this means that the spectrum is not wide enough to accommodate the peak shape; in the non-rotor-synchronized spectrum, this corresponds to a merging (and hence disappearance) of the spinning sidebands.

4. Experimental details

Experiments were performed at T = 335 K on a Bruker Avance NMR spectrometer equipped with a widebore 9.4 T magnet and 4-mm MAS probe generating a radiofrequency field strength of approximately 100 kHz. ^{2}H (ν_0 = 61.4 MHz) single- and double-quantum MAS spectra were obtained using a two-dimensional correlation experiment as described in ref [10]; the MAS rate was 10 kHz and a double-quantum

excitation time of 4 μs was used. The static spectrum was acquired using the Exorcycled quadrupolar-echo experiment [18], with a free-precession interval between pulses of 30 μs.

5. Experimental results

Rotor-synchronized single- and double-quantum ^{2}H MAS NMR spectra of sodium tetrathionate dihydrate-d_4 are shown in Figs. 3a and 3b. For the single-quantum transitions, the largest anisotropic interaction is the quadrupolar coupling, which is therefore expected to be the dominant cause of motional linebroadening. The double-quantum transition, however, is not affected by the quadrupolar interaction to first order, and so any line broadening effects are likely to be small and caused by other interactions such as the chemical shift anisotropy and dipolar coupling [10]. We assume the motion responsible for the broadening to be 180° flips about the C_2 axes of the D_2O molecules.

As expected, the single-quantum spectrum in Fig. 3a shows much greater broadening than the double-quantum spectrum in Fig. 3b. Determination of the reorientational rate constant by the conventional method of static lineshape fitting (Fig. 3c) using the quadrupolar-echo technique [19] yields $k = 10^{6.83\pm0.05}$ s^{-1}. Fig. 3d shows the linewidth predicted by the spin-echo model as a function of the rate constant k for the D_2O reorientation. The measured single-quantum linewidth (2.8 kHz), corresponds to $k = 10^{7.11\pm0.03}$ s^{-1} using this model (the model allows for two possible k values at this linewidth, but variable-temperature measurements suggest the upper value is correct; i.e., linewidth decreases with increasing temperature). If the single-quantum MAS lineshape is fitted directly using exact numerical simulations, a value of $k = 10^{6.95\pm0.02}$ s^{-1} is obtained. The difference in rate constant determined from static and MAS data is consistent with ~5 K frictional heating caused by sample rotation.

At the exchange rate estimated from the single-quantum linewidth, the dashed line in Fig. 3d predicts negligible motional broadening of the double-quantum lineshape. The 290 Hz measured linewidth is likely to be due to sources other than motion on the

microsecond timescale, including B_0 inhomogeneity, non-secular relaxation contributions, and 150 Hz exponential damping applied during data processing.

6. Conclusions

Motionally-induced linebroadening in MAS spectra can be described analytically by modelling MAS as a series of spin echoes. This intentionally simplistic, but very general, model shows qualitative agreement with the earlier approach of Maricq and Waugh under certain conditions. However, comparison with exact numerical simulations suggests that our spin-echo model is applicable to both fast-spinning and (unlike Maricq and Waugh) slow-spinning regimes and that there is a reasonable level of quantitative agreement between the two.

The spin-echo model is, therefore, a useful tool for (i) estimating rate constants, (ii) predicting whether a particular resonance will be observable in a given MAS experiment, and (iii) judging how the experimental parameters may be modified to obtain narrower (or broader) MAS resonances. The model is applicable to any inhomogeneous interaction that is refocused, wholly or partially, by MAS (e.g., quadrupolar coupling, chemical and paramagnetic shift anisotropy, heteronuclear dipolar coupling), and to the whole range of MAS NMR experiments (including, e.g., MQMAS, STMAS and DQMAS spectroscopy).

Finally, it is interesting to speculate if the results shown here are applicable to homogeneously broadened ^{1}H NMR spectra of solids. The use of fast (> 25 kHz) MAS to obtain relatively high-resolution ^{1}H NMR spectra is increasingly popular and yet, with individual ^{1}H-^{1}H dipolar couplings often as large as 30 kHz, the spin-echo model predicts motionally broadened MAS linewidths in the range 10^2-10^4 Hz if dynamics-driven large-amplitude modulations of dipolar couplings are occurring on the appropriate timescale. This would have implications for the spectral resolution ultimately achievable in ^{1}H MAS NMR of dynamic solids and, indeed, for the observability of some ^{1}H resonances using this technique.

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Figure Captions

Fig. 1. Single-quantum ^{2}H MAS NMR linewidths, $\Delta\nu_{1/2}$, predicted by the spin-echo model in eq. (15). The linewidth in the absence of exchange is 50 Hz. (a, b) Fast-spinning regime ($\nu_R >> \Delta\nu_J$); (c, d) slow-spinning regime ($\nu_R << \Delta\nu_J$). The effect of changing the frequency jump $\Delta\nu_J$ is shown in (a, c) while that of changing the MAS rate ν_R is shown in (b, d).

Fig. 2. Comparison of analytical MAS linewidth models with results from exact simulations in the (a) slow- ($\nu_R << C_Q$), (b) intermediate- ($\nu_R \sim C_Q$) and (c) fast-spinning ($\nu_R >> C_Q$) regimes. Single-quantum ^{2}H MAS NMR linewidths, $\Delta\nu_{1/2}$, are calculated for deuterium nuclei experiencing an axially symmetric quadrupolar interaction in D_2O molecules that have a DOD bond angle of 104.5° and are undergoing 180° flips about the C_2 symmetry axis; a MAS rate of 10 kHz and intrinsic linewidth of 50 Hz are assumed. Exact simulations (+) were performed by stepwise integration of eq (20). The spin-echo model (solid lines) uses eq (15) with $\Delta\nu_J^{RMS}$ calculated from eq (19). The Maricq and Waugh approximation (dashed lines) uses eq (6) with $\nu_{an} = \frac{3}{4}C_Q$. The extended version of the Maricq and Waugh approximation (dotted lines) uses eq (9).

Fig. 3. (a) Single-quantum and (b) double-quantum ^{2}H MAS NMR spectra of sodium tetrathionate dihydrate-d_4 together with lineshape fitting (using exact numerical simulations) of single-quantum spectrum (dashed line). (c) Static quadrupolar-echo ^{2}H NMR spectrum of sodium tetrathionate dihydrate-d_4 and lineshape fitting (dashed line). (d) Single-quantum (solid line) and double-quantum (dashed line) linewidths predicted using the spin-echo model. For the single-quantum linewidth, eq (19) was used to estimate the RMS frequency jump, assuming a DOD bond angle of 105.5° and C_Q = 266 kHz; for the double-quantum linewidth a much smaller frequency jump of 2 kHz was assumed. Intrinsic linewidths of 3.7 kHz and 50 Hz are assumed for static and MAS simulations, respectively, while 150 Hz exponential damping was applied in (b).

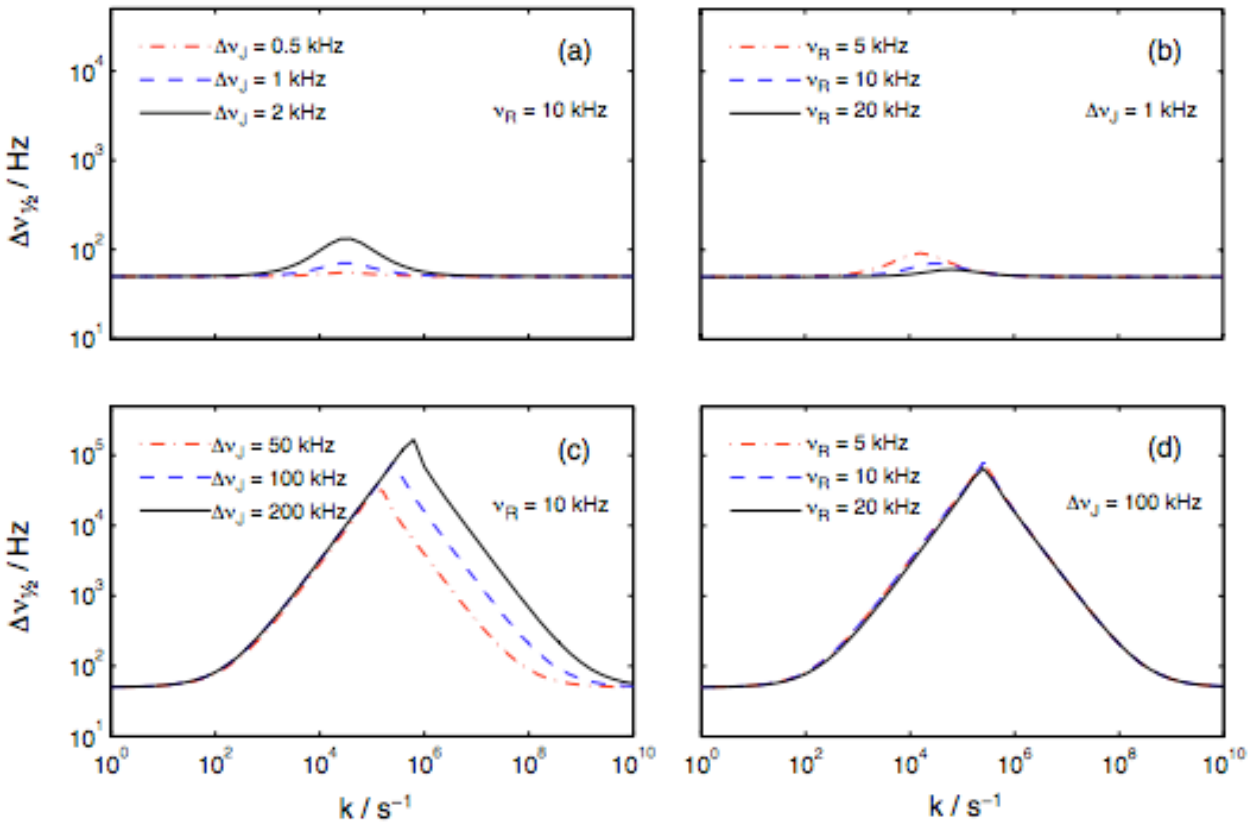

Figure 1: Thrippleton et al.

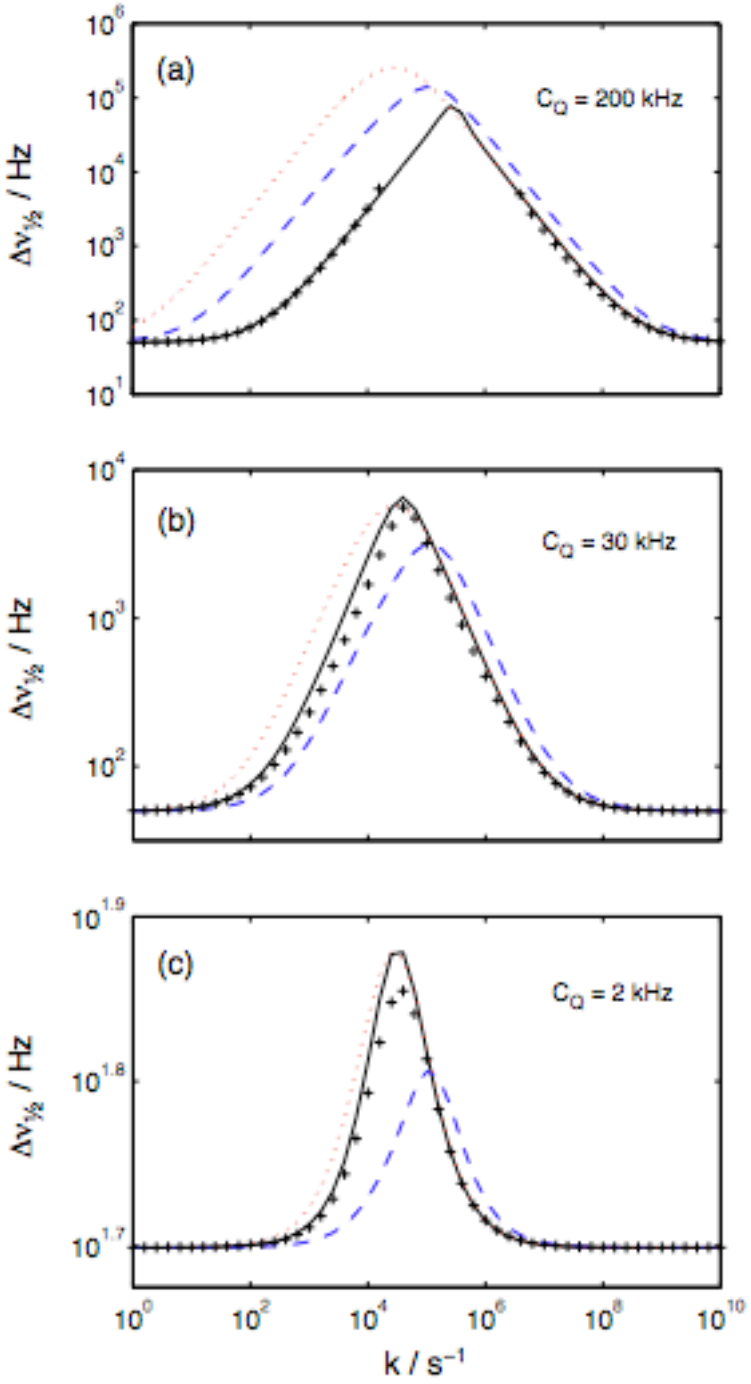

Figure 2: Thrippleton et al.

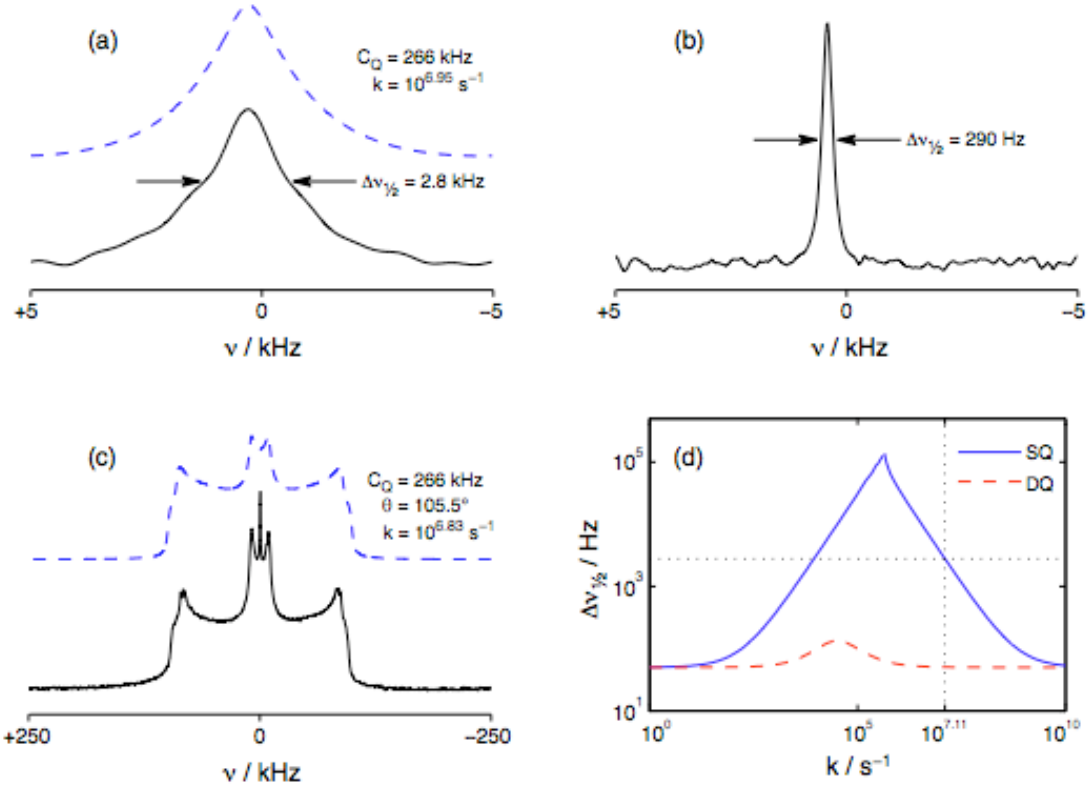

Figure 3: Thrippleton et al.