

Variation of ^{13}C NMR Linewidths of Metallocenes as a Function of Magic Angle Sample Spinning Frequency

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1. Introduction

In this paper we report high-resolution solid state ^{13}C NMR investigations of various metallocenes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^5\text{-C}_5\text{H}_5)]$; $\text{M} = \text{Fe}, \text{Ru}, \text{Ni}$], carried out as a function of magic angle sample spinning (MAS) frequency. Specifically, we focus on how the linewidth of the isotropic peak varies with MAS frequency at fixed temperature. Unexpectedly, it has been found that the linewidth increases as the MAS frequency is increased, and it is demonstrated that the underlying reason is that the ^1H decoupling becomes less efficient as the MAS frequency is increased. It is suggested that molecular motion within these solids is an important factor underlying this phenomenon.

It is well known that, at room temperature, there is substantial molecular motion in crystalline metallocenes [1-3]. In ferrocene, for example, it has been shown [4-6] that there is rapid reorientation of the cyclopentadienyl (C_5H_5) rings via a five-fold jump mechanism, with correlation time $\tau_c \approx 5 \times 10^{-12}$ s at 293 K. The correlation time for ring reorientation in nickelocene at room temperature is essentially the same as that for ferrocene, whereas the ring reorientation in ruthenocene is associated with a significantly longer correlation time ($\tau_c \approx 5 \times 10^{-10}$ s at 293 K) [4,5]. It has been suggested [2] that there may be some additional slower molecular motions in crystalline ferrocene at ambient temperature. All experiments reported in this paper were carried out at constant temperature, and hence the correlation time for molecular motion for a given metallocene can be assumed to be constant for the series of experiments discussed here.

Before presenting our results, we discuss briefly relevant aspects of magic angle sample spinning (MAS) and high power ^1H decoupling in relation to the measurement of high-resolution ^{13}C NMR spectra for organic solids, with

particular emphasis on the application of the technique to systems in which there is substantial molecular motion.

2. Theory

In solid state ^{13}C NMR of organic materials, the two major sources of line-broadening are chemical shift anisotropy (CSA) and direct ^{13}C - ^1H dipole-dipole interaction. Magic angle sample spinning (MAS) [7,8] will transform an NMR line broadened by these effects into a set of comparatively narrow, equally-spaced lines comprising an isotropic peak and spinning sidebands. The spacing between adjacent lines in this set is equal to the MAS frequency ν_r . The chemical shift of the isotropic peak is independent of ν_r , and only this line remains when the anisotropic interactions have been averaged completely (i.e. at sufficiently large ν_r).

As discussed fully elsewhere [7-9], there is an important difference concerning the way in which CSA and direct dipole-dipole interaction are affected by MAS. For an NMR line broadened by CSA, relatively slow MAS is generally sufficient to transform this line into the set of narrow, equally-spaced lines discussed above, whereas a line broadened by direct dipole-dipole interaction will be narrowed significantly only if ν_r is in the region of (or greater than) the magnitude of the dipole-dipole interaction. The underlying reason for this difference [9] is that CSA gives rise to inhomogeneous broadening of the spectral line, whereas dipole-dipole interaction is a source of homogeneous broadening; the value of ν_r required to achieve effective line-narrowing is larger (relative to the linewidth of the static sample) in the case of homogeneous broadening. For most organic solids with natural isotopic abundance, the only appreciable dipole-dipole interaction directly affecting the ^{13}C NMR spectrum is that between

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^{13}C and ^1H . Since the magnitude of this interaction (typically *ca.* 30 kHz for rigid organic solids) is generally much larger than the MAS frequencies that can be obtained on conventional instruments, substantial averaging of this interaction cannot be achieved using MAS. For this reason, high power ^1H decoupling is generally applied (in addition to MAS) during acquisition of the ^{13}C spectrum in order to eliminate line-broadening due to direct ^{13}C - ^1H dipole-dipole interaction.

In ^{13}C NMR spectroscopy of many crystalline metallocenes (such as ferrocene and ruthenocene), CSA and direct ^{13}C - ^1H dipole-dipole interaction are the important sources of line-broadening.

A detailed publication [10] has considered, from both theoretical and experimental standpoints, the linewidth of the isotropic peak, recorded under MAS conditions, for a system that is subject to line-broadening by CSA. It was also shown that, at fixed temperature, the linewidth of the isotropic peak decreases as the MAS frequency (ν_r) is increased, approaching a limiting value at sufficiently large ν_r . Another paper [11] has considered the linewidth of a spin system S , dipolar coupled to an unlike spin system I , under conditions of isotropic molecular motion and decoupling of the I spins. Using ω_1 to denote the decoupler field strength, it was shown that, in the limit of long correlation time (i.e. $\omega_1\tau_c \gg 1$) the linewidth is proportional to $(\omega_1)^{-2}$, whereas in the limit of short correlation time (i.e. $\omega_1\tau_c \ll 1$) the linewidth is independent of ω_1 . Thus, for a sample at fixed temperature (and hence fixed τ_c), the linewidth should either decrease as the decoupler field strength is increased (long correlation limit) or remain independent of the decoupler field strength (short correlation limit). The effects of anisotropic molecular motion on the measured spectrum were also discussed briefly in ref. 11.

In the studies discussed in this paper, both MAS frequency and ^1H decoupler field strength are important in controlling the linewidth of the isotropic peak in the ^{13}C NMR spectrum. If the separate effects discussed above can be combined in a simple way, then it should be expected that: (a) at fixed temperature and fixed decoupler field strength, the linewidth should decrease with increasing MAS frequency (up to a limiting value, beyond which the linewidth should be effectively independent of the MAS frequency); and (b) at fixed temperature and fixed MAS frequency, the linewidth should either decrease or remain constant as the decoupler field strength is increased, depending on the motional regime (i.e. long or short correlation limit) of the sample at the temperature of interest.

It is shown here that, for ferrocene and ruthenocene at room temperature, the effects of MAS frequency and ^1H decoupler field strength on the ^{13}C NMR linewidth cannot be combined in this simple way, since the effective decoupler field strength is modulated by altering the MAS frequency. Nickelocene is paramagnetic, and for this

reason it is not valid to consider nickelocene in the same way as ferrocene and ruthenocene in relation to the NMR properties discussed here.

3. Experimental

^{13}C NMR spectra were recorded at 125.758 MHz on a Bruker MSL500 spectrometer using a Bruker double-bearing magic angle spinning probe capable of MAS frequencies between *ca.* 1 kHz and 12 kHz with stability better than *ca.* ± 10 Hz. All spectra were recorded at room temperature (293 ± 2 K) with the samples contained in zirconia rotors (4 mm external diameter).

The ^{13}C "single pulse" sequence was used to record the spectra, with high power ^1H decoupling applied during acquisition. Typical parameters were: ^{13}C 90° pulse length = 3.5 μs ; recycle delay = 10 s for ferrocene and 20 s for ruthenocene.

The ^1H decoupler field was set on resonance for the ^1H of each metallocene. An accurate assessment of the decoupler field strength was made by measuring (for adamantane) the length of the ^1H 90° pulse ($\tau_{90}(^1\text{H})$) for the ^1H r.f. power level used in the experiments involving ^1H decoupling. For the discussion of results, $\tau_{90}(^1\text{H})$ has been converted to a decoupling frequency ν_1 via:

$$\nu_1 = \frac{1}{4 \tau_{90}(^1\text{H})}$$

ν_1 is related to the decoupler field strength H_1 and to the parameter ω_1 used in ref. 11 by the equations:

$$\nu_1 = \frac{\gamma(^1\text{H}) H_1}{2 \pi} = \frac{\omega_1}{2 \pi}$$

The linewidth of the isotropic peak in the ^{13}C NMR spectrum was measured as the full width at half maximum height, and the experimental error in the measured linewidth is estimated to be less than *ca.* ± 5 Hz.

4. Results and Discussion

Initially we present the main results for ferrocene [12], and then consider the other metallocenes studied. High-resolution ^{13}C NMR spectra of ferrocene were recorded initially at two different decoupler field strengths ($\nu_1 = 64.9$ kHz and 26.6 kHz), and at several MAS frequencies (ν_r) ranging from *ca.* 1 kHz to 11 kHz. The spectrum at $\nu_r \approx 5$ kHz was recorded both at the start and at the end of the series of experiments to confirm that there were no irreversible changes in the spectrum due to subjecting the sample to high rotation rates. The variation of linewidth (Δ) of the isotropic peak as a function of ν_r is shown in Fig. 1. Clearly, at a given decoupler field strength, Δ

increases as ν_r is increased. The relationship between Δ and ν_r is approximately linear, particularly at the higher decoupler field strength, and the gradient is greater at the lower decoupler field strength. At fixed ν_r , the linewidth Δ is smaller at higher decoupler field strength, as shown in Fig. 1.

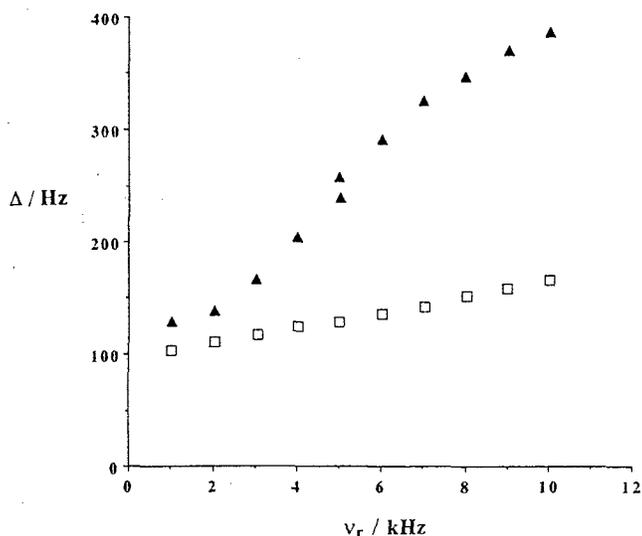


Fig. 1 Linewidth (Δ) versus MAS frequency (ν_r) for the isotropic peak in the ^{13}C NMR spectrum of ferrocene. The spectra were recorded at ^1H decoupler field strengths corresponding to $\nu_1 = 64.9$ kHz (\square) and $\nu_1 = 26.6$ kHz (\blacktriangle).

Our observation that the linewidth of the isotropic peak increases as the MAS frequency is increased conflicts with the discussion in Section 2 that, under conventional conditions, Δ should decrease, or remain constant, as ν_r is increased. We propose that the observed increase in Δ with increasing ν_r for ferrocene arises as a result of MAS indirectly modulating the efficiency of the ^1H decoupling in such a way that the *effective* decoupler field strength is decreased, leading to line-broadening, as ν_r is increased. This conclusion is supported by the results of three further experiments.

(1) ^{13}C NMR spectra of ferrocene were recorded for a series of different decoupler field strengths (with ν_1 in the range 20 kHz to 80 kHz) at fixed ν_r . As expected, Δ decreases as ν_1 is increased at fixed ν_r (Fig. 2). Furthermore, in the limit of sufficiently high decoupler field strength, Δ becomes essentially independent of both ν_r and ν_1 , and converges to a limiting value of *ca.* 100 Hz. From this it can be concluded that both values of ν_r (5.06 kHz and 9.05 kHz) used to record the data shown in Fig. 2 are sufficiently rapid to remove any ν_r -dependent sources of line-broadening due to CSA; i.e. at sufficiently high decoupler field strength, Δ is essentially independent of ν_r at these values of ν_r . This is consistent with the view that, under the conditions of the experiments shown in Fig. 1, the property that *does* depend on ν_r is the efficiency of the ^1H decoupling (and not the ability of MAS to remove

the line-broadening effects due to CSA). As discussed fully elsewhere [12], there is a linear relationship between Δ and $(\nu_1)^{-2}$.

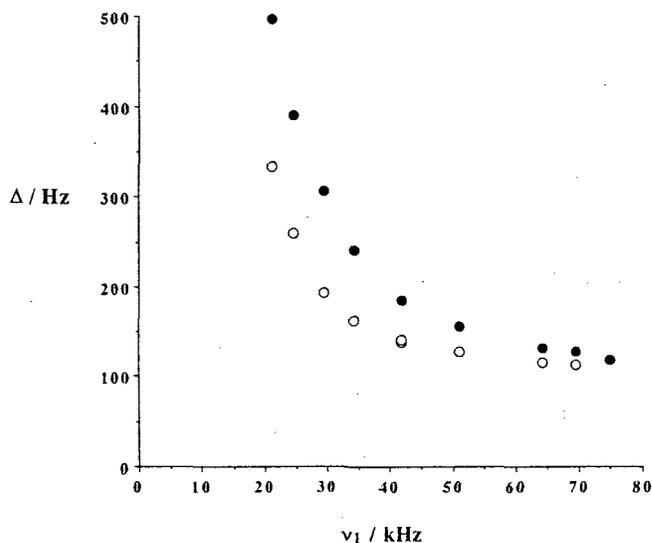


Fig. 2 Linewidth (Δ) versus ν_1 for the isotropic peak in the ^{13}C NMR spectrum of ferrocene. The spectra were recorded at MAS frequencies $\nu_r = 5.06$ kHz (\circ) and $\nu_r = 9.05$ kHz (\bullet).

(2) ^{13}C NMR spectra of ferrocene were recorded as a function of ν_r , but with no ^1H decoupling field applied; the variation of Δ with ν_r in these experiments is shown in Fig. 3. Under these conditions, Δ decreases as ν_r is increased, as predicted from the discussion in Section 1 and from ref. 10. This relationship between Δ and ν_r reflects the direct effect of MAS on the linewidth of the isotropic peak for a system that is subject to line-broadening by CSA and by direct ^{13}C - ^1H dipole-dipole interaction. At the lowest value of ν_r studied (*ca.* 3 kHz), Δ is *ca.* 592 Hz, and it is clear that slow MAS alone can substantially average the dipole-dipole interaction (as well as CSA) in

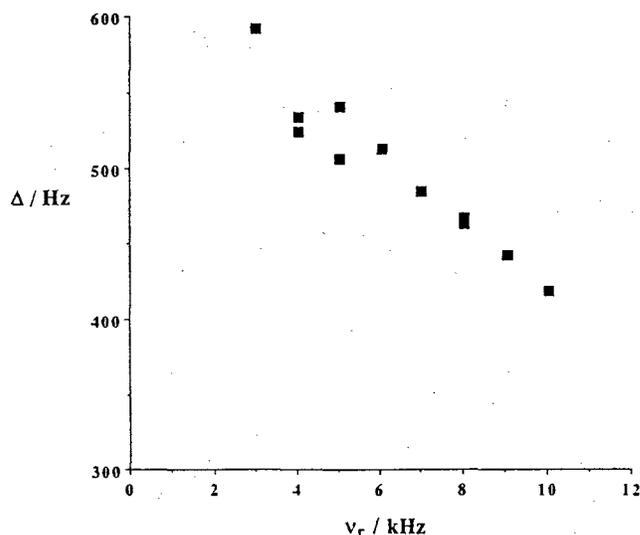


Fig. 3 Linewidth (Δ) versus MAS frequency (ν_r) for the isotropic peak in the ^{13}C NMR spectrum of ferrocene, with no ^1H decoupling applied.

this system. Undoubtedly, this is a consequence of the fact that the direct ^{13}C - ^1H dipole-dipole interaction is already extensively averaged by molecular motion.

(3) ^{13}C NMR spectra were recorded (using the ^{13}C "single pulse" method with no ^1H decoupling field applied) for perdeuterated ferrocene (denoted ferrocene- d_{10}) as a function of MAS frequency. Over the range $\nu_r \approx 1$ kHz to 12 kHz, the linewidth of the isotropic peak is independent of ν_r (Fig. 4), and the value ($\Delta \approx 117$ Hz) is close to the limiting linewidth obtained in our experiments for undeuterated ferrocene. In ^{13}C NMR spectroscopy of ferrocene- d_{10} , the principal source of line-broadening is CSA and, furthermore, the CSA should be substantially the same in ferrocene- d_{10} and in undeuterated ferrocene. The fact that Δ is essentially independent of ν_r for ferrocene- d_{10} thus strongly supports the view that the increase of Δ with ν_r for undeuterated ferrocene is *not* arising from CSA being modulated by MAS.

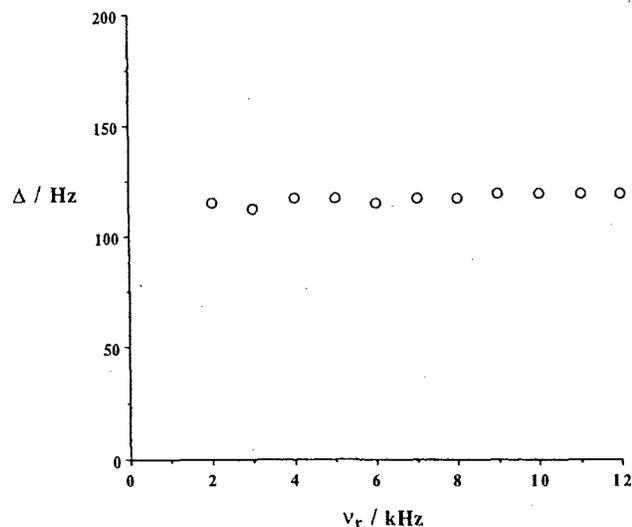


Fig. 4 Linewidth (Δ) versus MAS frequency (ν_r) for the isotropic peak in the ^{13}C NMR spectrum of ferrocene- d_{10} , with no ^1H decoupling applied.

High-resolution ^{13}C NMR spectra of ruthenocene and nickelocene were also recorded as a function of MAS frequency in order to establish whether the behaviour observed for ferrocene is also exhibited by other structurally-related systems. In Fig. 5, the relationships between Δ and ν_r for ruthenocene and ferrocene are compared, with all spectra recorded at the same ^1H decoupler field strength ($\nu_1 = 64.9$ kHz).

It is clear that ruthenocene exhibits the same general trend as ferrocene, with Δ increasing as ν_r is increased, although the relationship for ruthenocene is apparently less linear than that for ferrocene. At the higher values of ν_r studied, the gradient $\partial\Delta/\partial\nu_r$ is larger for ruthenocene. These small differences in behaviour between ferrocene and ruthenocene presumably reflect small differences in the

dynamic properties of these solids at 293 K (as suggested in ref. 5).

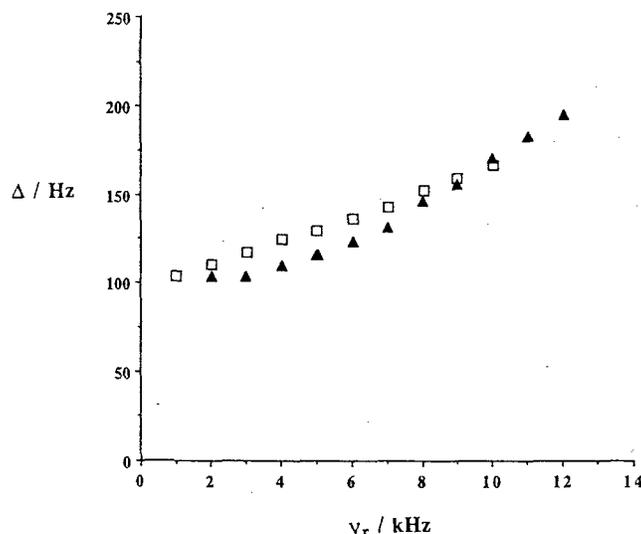


Fig. 5 Linewidth (Δ) versus MAS frequency (ν_r) for the isotropic peak in the ^{13}C NMR spectra of ferrocene (□) and ruthenocene (▲), at fixed ^1H decoupler field strength corresponding to $\nu_1 = 64.9$ kHz.

The linewidth in the ^{13}C NMR spectrum of nickelocene is substantially greater ($\Delta = 15.7$ kHz at $\nu_r = 5$ kHz) than that in spectra recorded for ferrocene and ruthenocene under the same conditions. The linewidth for nickelocene is not significantly affected by increasing the MAS frequency, although there is a measurable decrease to $\Delta = 15.4$ kHz at $\nu_r = 11$ kHz. The very large ^{13}C NMR linewidth observed for nickelocene, even under conditions of MAS and high power ^1H decoupling, is due to the paramagnetic properties of this molecule (which contains two unpaired electrons). For this reason, it is not expected that the NMR properties of nickelocene will be comparable, in any way, to those of ferrocene and ruthenocene.

5. Conclusions

The increase in linewidth of the isotropic peak in the ^{13}C NMR spectra of ferrocene and ruthenocene as the MAS frequency is increased (at fixed temperature and fixed ^1H decoupler field strength) is due to an indirect effect in which the *effective* ^1H decoupler field strength is decreased as ν_r is increased. Considering the results of high-resolution ^{13}C NMR experiments for several crystalline organic solids carried out in our laboratory, it is clear that, for systems in which there is no appreciable molecular motion, Δ is essentially independent of ν_r . This fact tends to suggest that the molecular motions present within crystalline ferrocene and ruthenocene are important in relation to the observed increase in the linewidth of the isotropic peak with increasing MAS frequency.

A similar anomalous relationship between isotropic ^{13}C NMR linewidth and temperature has been observed recently by Muller [13] in studies of thiourea inclusion compounds; in this case, linewidths for ^{13}C environments in the guest molecules (which undergo substantial molecular motion) have been observed to increase with increasing temperature, and again this effect has been attributed to an "interference" between the molecular motion and the efficiency of the ^1H decoupling.

In view of the fact (see Section 1) that cyclopentadienyl ring reorientation occurs on a timescale of the order of *ca.* 10^{-12} s for ferrocene and *ca.* 10^{-10} s for ruthenocene at room temperature, it is not clear whether ring reorientation is indeed the dynamic process responsible for influencing the value of Δ in our experiments; it might be expected that a motion occurring at a frequency comparable to ν_1 and/or ν_r (and thus in the approximate frequency range 10^3 Hz to 10^6 Hz) would be required. At present, we make no attempt to assign the dynamic process that is important in giving rise to the observed NMR phenomena for ferrocene and ruthenocene at room temperature. However, it may be that the slower motion in ferrocene alluded to in ref. 2 is influential in this regard. Future experiments, at different temperatures, will investigate the variation of Δ with ν_r at different values of the correlation time for this motion, and other experimental investigations of the dynamic properties of crystalline metallocenes are in progress. We are also currently investigating various theoretical implications of the results reported here.

Finally, it is relevant to strike a cautionary note in regard to recording high-resolution solid state ^{13}C NMR spectra for systems that are subject to line-broadening by CSA and direct ^{13}C - ^1H dipole-dipole interactions. In view of the results reported here, it is clear that there are circumstances under which optimum resolution can be obtained by recording the spectrum at high ^1H decoupler field strength and low MAS frequency, rather than at high ^1H decoupler field strength and high MAS frequency.

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