Line Narrowing in Nitrogen-14 NQR by Non-Resonant Irradiation*, **

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The effect of non-resonant irradiation on the linewidth of ^{14}N NQR lines has been investigated in three cases with zero asymmetry parameter. The characteristic time of the free induction decay (T_2^*) in Trimethylamine (TMA), Triethylenediamine (TED) and Hexamethylenetetramine (HMT) was studied at 77 K. Circularly polarized non-resonant irradiations of 11 kHz were used with intensities of up to 24 G with a geometrical arrangement following Ito and Hashi. The largest effect, a 100% increase in T_2^*, is measured in TMA. No observable effect occurs in HMT. An intermediate result occurs in TED, where the considerable narrowing caused by the non-resonant field serves to provide a greater resolution of the fine structure first reported by Colligiani and Ambrosetti. This fine structure, presumably dipolar in origin, is not itself affected by the non-resonant irradiation. The degree to which the theory of dressing fields can account for these results is discussed.

Introduction

Line broadening is not nearly as serious a problem in NQR spectroscopy as it is in NMR of solids, principally because there is no laboratory frame DC magnetic field imposed on normally polycrystalline samples [1]. Still, line-narrowing schemes are desirable not only because they might reveal previously unresolved structure, but also because they can lead to considerable improvement in detection sensitivity.

In 1977 and 1981 two new multiple pulse NQR techniques were reported [2, 3] which can allow orders of magnitude sensitivity enhancement for ^{14}N NQR. The pulse sequences involved have close analogies with previously well known NMR sequences, but a proper understanding of the evolution of the NQR Hamiltonian during the sequences continues to be the subject of study [4–6]. A common requirement for these sequences to be effective from the point of view of signal-to-noise enhancement is that the pulse spacing be made smaller than T_2, the spin echo decay time. It is not surprising then that the most spectacular enhancements occur only in the special case when the combination of integer spin and a highly asymmetric electric field gradient provides for effective quenching of both homonuclear and heteronuclear spin-spin coupling [7]. Unfortunately, in the majority of NQR cases the spin is half-integer or the asymmetry is small, so that T_2's are short. Then, the inevitable dead times after each pulse make it difficult to shorten the sequence pulse spacings enough to achieve the benefits of multiple pulse irradiation. A very promising way out of this difficulty is offered by cw non-resonant irradiation of the spin system during the multiple pulse experiment. This "dressing" of the spin system with non-resonant photons may provide a very general method of drastically reducing unwanted spin-spin coupling.

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Photon Dressed NQR

If a system has Hamiltonian H_0 with eigenenergies E_n and is subjected to two irradiations, $\mathscr{H}_1 \cos(w_0 t)$ and $\mathscr{H}_2 \cos(w_2 t)$, the traditional spectroscopist might first consider all of the possible transitions which the two irradiations could produce. In contrast, Cohen-Tannoudji and Haroche [8–11] introduced the novel concept of an atom "dressed" by the photons of a non-resonant field $\mathscr{H}_2$, whose more complex energy levels are then probed by the resonant field $\mathscr{H}_1$. The fundamental difference is that one asks what are the energy levels and other properties of the combination "atom plus field". The relevant Hamiltonian then consists of three parts: H_0, the original nude system; H_{qf}, the quantum field operator for the dressing irradiation; and H_{int}, the interaction between the original system and the dressing field.

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Of the several interesting predictions of the theory of dressed atoms the most promising for us here is the result that the effective magnetic moment of a dressed atom can be made to vanish. More specifically, in the presence of a static field H_0, and dressing field $H_2 \cos(w_2 t)$ such that $w_2 \gg \gamma H_0$, the magnetic moment is modulated by the zero order Bessel function $J_0(\gamma H_2/w_2)$. The parameter γ is the usual gyromagnetic ratio of the nucleus. Then, the conditions for a vanishing effective magnetic moment occur when the intensity and frequency of the dressing field obey the relations (for spin $I=1/2$)

$$\gamma H_2/w_2 = 2.4, 5.5, 8.6, \ldots, \quad (1)$$

for the zeroes of the Bessel function, provided that the applied field H_0 is not large ($\gamma H_0 \ll w_2$).

For conventional NMR the above conditions on H_2 and w_2 are technically very difficult to achieve. Nevertheless, Hashi and coworkers showed excellent agreement with theory by cleverly performing the experiment in the rotating frame [12–14]. For optically pumped vapors [15] which served as the first experimental verification of dressed atom effects, and for NQR, the necessary frequency and amplitude of the dressing field can easily be achieved. Ito and Hashi reported [16] the first experimental observation of photon-dressed NQR effects in 1978, and in subsequent work [17–19]. They observed a shift and a splitting of the ^{23}Na NQR line in sodium chlorate and an increase in the ^{35}Cl spin echo time in sodium chlorate and in p-dichlorobenzene. They also worked out the theory for a dressed quadrupolar system with spin $I=3/2$.

In this paper, we will report experimental observations for the case of $I=1$, $\eta=0$. By limiting ourselves to axial symmetry, we are assured that spin-spin coupling is not already quenched [7].

Results and Discussion

Circularly polarized non-resonant irradiation of frequency $w_2/2\pi = 11.1$ kHz and peak magnitude H_2 up to 20 G was applied to NQR samples, using the geometrical arrangement of Ito and Hashi [16]. A Matec pulsed spectrometer was used to detect the NQR induction signals. Three substances were studied at 77 K: Hexamethylenetetramine (HMT), Triethylenediamine (TED), and Trimethylamine (TMA). The relevant NQR parameters are collected in Table 1. In all cases the lineshapes were homogeneously broadened, evidenced by our inability to obtain spin echoes.

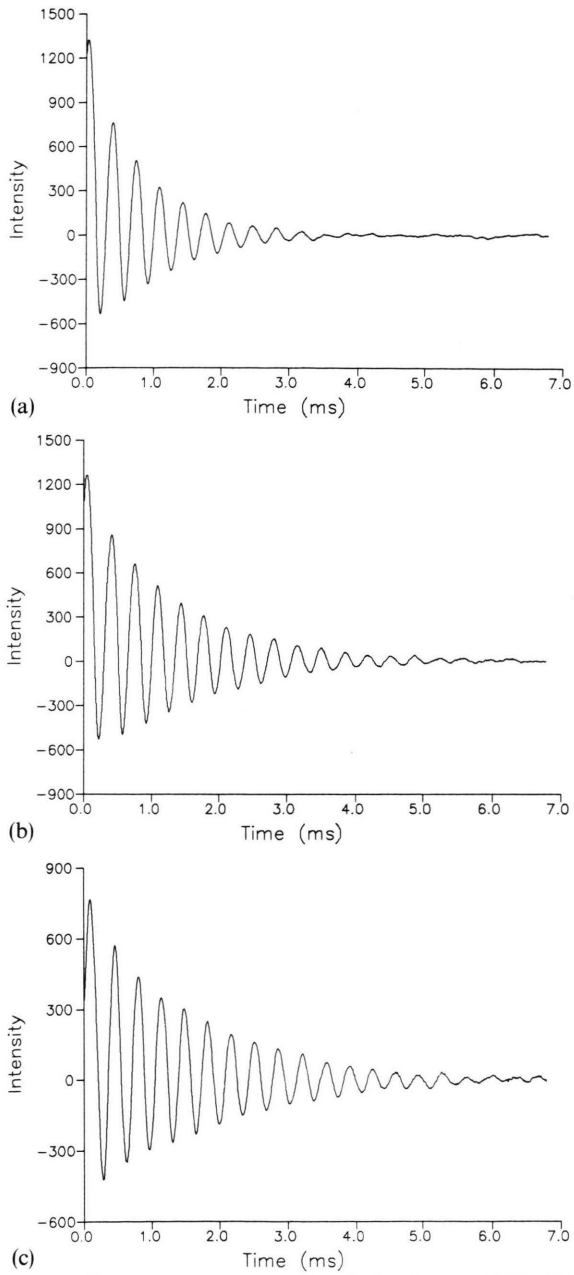

Fig. 1. ^{14}N NQR FID for trimethylamine at 77 K. The sample is also irradiated by an 11.1 kHz circularly polarized dressing field of progressively stronger peak amplitude H_2: (a) $H_2=0$, (b) $H_2=12.8$ G, and (c) $H_2=24.0$ G.

The effect of non-resonant irradiation on TMA is shown in Figure 1. Figure 1a is the free induction decay (FID) obtained without non-resonant irradia-

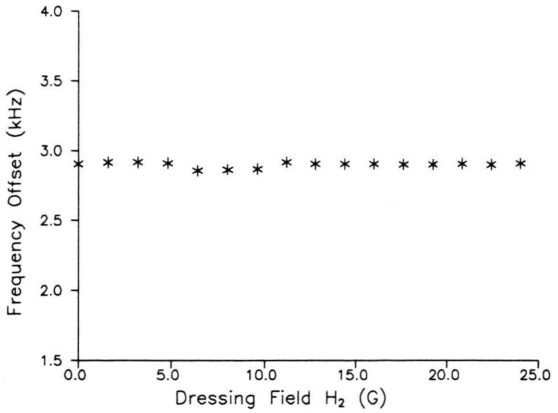

Fig. 2. Frequency offset of ^{14}N NQR FID signal versus dressing field peak amplitude H_2. No frequency shift is observed.

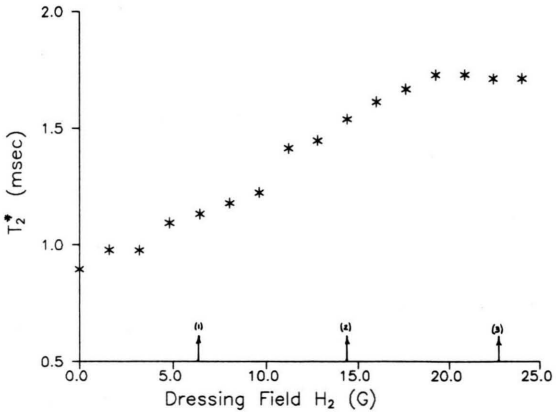

Fig. 3. The inverse linewidth parameter T_2^*, obtained by numerical fit of NQR FID data such as shown in Fig. 1, versus dressing field peak amplitude H_2. The location of the first three predicted zeros of the proton effective magnetic moment are indicated by the numbered arrows.

Table 1. NQR parameters at 77 K for materials discussed in the text. ν_Q is the NQR resonance frequency, e^2qQ/h is the quadrupole coupling constant, and η is the asymmetry parameter of the electric field gradient tensor.

	ν_Q [kHz]	e^2qQ/h [kHz]	η
Trimethylamine (TMA) [a]	3693.5	4924.7	0
Triethylenediamine (TED) [b]	3895.4	5193.9	0
Hexamethylenediamine (HMT) [c]	3407.6	4543.4	0
HMT · 3 phenol [d] ($\eta = 0$ site only)	3499.3	4665.7	0

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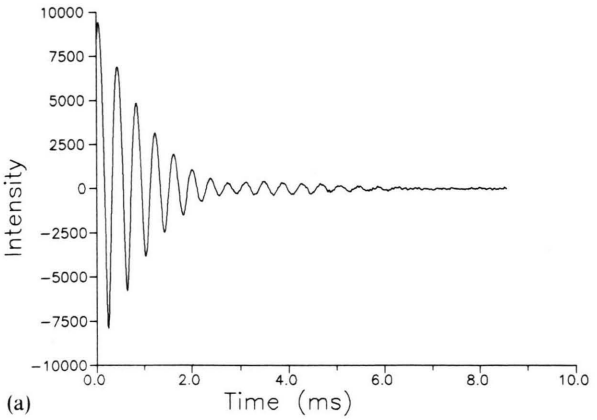
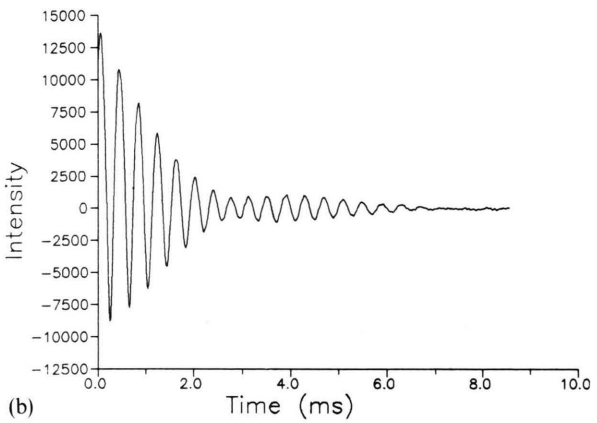
tion. The radio-frequency transmitter was offset by 2.9 kHz above exact resonance, resulting in a characteristic FID pattern. The FID is not symmetric about the time-axis since the receiver was set for a mixture of phase sensitive and amplitude detection. Numerical simulations reveal that the FID is exponential with a characteristic time $T_2^* = 0.90$ msec. Figures 1 b and 1 c show the FID obtained under identical circumstances but with a circularly polarized 11.1 kHz dressing field of peak amplitude $H_2 = 12.8$ and 24.0 G, respectively. The FID is visibly lengthened, indicating line narrowing.

Data were collected for sixteen values of H_2 between zero and 24 G, i.e., $\gamma H_2/2\pi$ up to 100 kHz. In each case numerical fits showed excellent agreement with a Lorenzian lineshape. In Fig. 2 the frequency of the FID is plotted for increasing values of H_2. Within experimental error, the NQR lines are not shifted at all by fields of up to 24 G. Finally, the characteristic FID decay time T_2^*, obtained from numerical fitting of the FID data, is plotted in Fig. 3 as a function of H_2. A monotonic increase is observed, with no discernible features at the zeros of the Bessel function of (1), indicated by numbered arrows in Figure 3. Thus quantitative agreement with dressed atom theory cannot be claimed. Further work is planned, especially taking into account strong coupling between pairs of protons.

As first reported by Colligiani and Ambrosetti [20], both TED and HMT have structure to their NQR lineshape: they each appear to be a partially resolved asymmetric doublet. The structure, presumably dipolar in origin, is revealed for the case of TED at 77 K by the characteristic beat pattern of the FID shown in Figure 4 a. Figures 4 b and 4 c show the NQR FID obtained when an 11.1 kHz dressing field of peak magnitude H_2 is applied to TED, with $H_2 = 12.8$ and 20.8 G, respectively. Numerical analysis of these NQR FID signals, and for those obtained for intermediate values of H_2 yield a rather surprising result. As H_2 is increased from zero to 25.6 G, the *unresolved* line broadening decreases by a factor of two, very much in agreement with observations in TMA reported above. However, the *resolved* splitting does not appear to change at all, within experimental error, so that the result of the non-resonant irradiation is to reveal in progressively sharper resolution the underlying asymmetric doublet structure.

Analogous measurements were performed on polycrystalline HMT at 77 K and in the $\eta = 0$ site [21] of





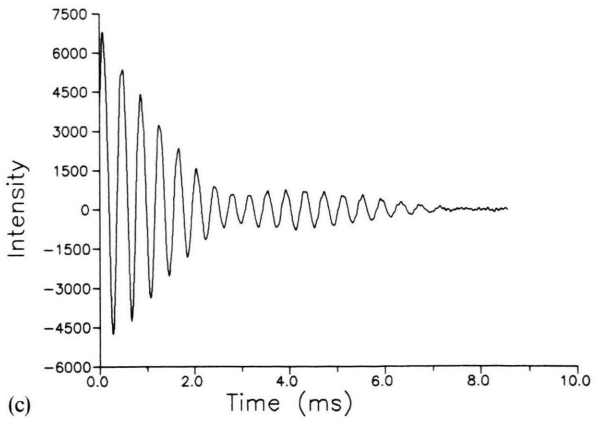


Fig. 4. ^{14}N NQR FID for triethylenediamine at 77 K. The magnitude of the 11.1 kHz dressing field is (a) $H_2 = 0$, (b) $H_2 = 12.8$ G, (c) $H_2 = 20.8$ G.

the hydrogen-bonded complex, HMT · 3 phenol [21]. These two crystals gave indistinguishably similar lineshapes for the ^{14}N NQR, an asymmetric doublet similar to the one observed in TED. This observation strengthens the assumption for dipolar origin of the line structure, since HMT and TED share the same number and arrangement of nearest neighbor protons. This time, however, *no* effect whatever was observed as H_2 was increased from zero to over 25 G peak. Neither the unresolved broadening nor the resolved asymmetric doublet was affected, within our experimental precision. The selective efficacy of audio-frequency irradiation in reducing lineshape broadening leads us to consider thermal effects. Certainly, line broadening due to hindered reorientations about the molecular trigonal axes, kown to occur in both HMT [23] and TED [24], should not be directly affected by proton decoupling. For HMT, however, the correlation time for these motions was reliably [25] measured to be longer than one second at 77 K; so it would appear that thermal motions cannot account for the observed linewidth.

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