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Proton resonance for oscillating field of the order of static magnetic field

Clemar Schurrer, Silvina Pérez *, Alberto Wolfenson [1]

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, IFEG—CONICET, Medina Allende s/n, Ciudad Universitaria, 5000 Córdoba, Argentina

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ABSTRACT

A spin decoupling method in nuclear quadrupole resonance spin echo experiment is used to detect the proton magnetic resonance absorption spectrum. The behavior of proton resonance in α phase of polycrystalline *p*-dichlorobenzene as a function of the intensity of the proton decoupling oscillating field (H_2) is measured. Good agreement between the experimental resonance frequency and Shirley's theory for a non-interacting 1/2 spin system is observed. To our knowledge this is the first time the NMR proton frequency dependence on linear polarized excitation field intensity for H_2/H_o as high as 1.8 is measured.

1. Introduction

The NMR proton frequency dependence on linear polarized excitation field intensity is a phenomenon that has been analyzed in the beginnings of NMR by Bloch and Siegert [1]. They particularly treated the problem of the magnetic resonance for a particle with spin 1/2 in a constant field H_o under the action of an alternating field, H_2, of arbitrary intensity with frequency ω and perpendicular to H_o. They solved the problem by a method of successive approximations which converges the better the smaller the ratio of the varying field to the magnitude of the constant field ($H_2/H_o \ll 1$).

Later, in 1965 a theoretical work by Shirley [2] analyzed the interaction of a two-state system excited by a linearly polarized oscillating field in a formalism which replaced the semiclasical time-dependent Hamiltonian with a time-independent Hamiltonian represented by an infinite matrix (Floquet Hamiltonian). In this treatment no restriction on H_2 intensity is needed.

In NMR experiments, usually, the relative intensity H_2/H_o is lower than 10^{-3} and Bloch–Siegert correction to the resonance frequency is applied [1]. However NMR experiments at low fields are more common nowadays and the condition $H_2 \sim H_o$ is more easily achieved (for example when H_o is of the order of tens of Gauss or lower). In fact, some effects, induced by the rf field intensity, have been observed at low static external magnetic fields (~40 G), in Double Nuclear Resonance experiment in solids [3] and in solid state proton imaging detected by NQR [4]. In these experiments $H_2 \sim H_o$ and it becomes important to know the correct resonance frequency to set the spin decoupling experiment properly.

In the present work a decoupling method [3] is used to study the proton resonance as a function of proton decoupling oscillating field intensity (H_2) by affecting the NQR echo signal of the ^{35}Cl spins. Floquet's theory is used to explain the behavior of the experimental resonance frequency.

2. Decoupling method

To perform proton decoupling in a ^{35}Cl NQR experiment, an external static magnetic field H_o has to be applied to define a proton resonance. A constant, linearly polarized, excitation proton field H_2 at a fixed frequency (ν = 90.48 kHz corresponding to $H_{res} = \omega/\gamma$ = 21.25 G) is applied. This affects the ^{35}Cl echo signal intensity acquired using a Hahn echo sequence at τ = 500 μs. Then, the occurrence of a proton resonance can be measured by observing the effect on the chlorine quadrupole echo intensity, as it will be shown in Section 6. This resonance is studied as a function of both H_2 and H_o magnetic fields.

3. Experimental

The experiments were carried out on α phase of polycrystalline p-dichlorobenzene using a home-made NQR spectrometer equipped with a Tecmag NMRkit II multi nuclei observe unit and a Tecmag Macintosh-base Real Time NMR station.

High purity *p*-dichlorobenzene in polycrystalline form was used to perform the experiments. The sample 5 mm in diameter and 10 mm height was sealed under vacuum in a cylindrical glass sample holder.

Probe-head schematic drawing is shown in Fig. 1. Two solenoid coils provide the static magnetic field with a homogeneity better than 1/1000. Two solenoid coils, each one of 40 mm in diameter

* Corresponding author. Address: FaMAF—UNC Medina Allende s/n, Ciudad Universitaria, 5000 Córdoba, Argentina. Fax: +54 351 4334054.
E-mail address: clyde@famaf.unc.edu.ar (S. Pérez).
[1] Fellow of CONICET, Argentina.

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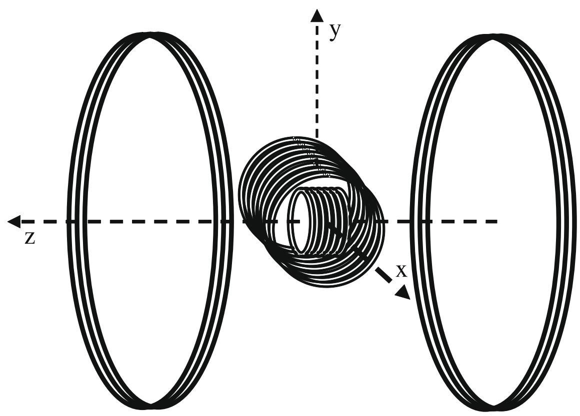

Fig. 1. Spin decoupling probe head schematics drawing in perspective.

and 27 mm long, placed 15 mm apart and perpendicular to the Zeeman coils provide the proton irradiation field H_2 at v = 90.48 kHz. A solenoid coil 8 mm in diameter and 26 mm long tuned at 34.348 MHz, parallel to the static magnetic field, was used to transmit and detect at the ^{35}Cl NQR frequency.

The temperature was kept at 273 K using an ice thermal bath.

The H_2 magnetic fields determinations were carried out with a Leybold gaussmeter. The calibration of the gaussmeter Hall probe and the measurement of the static magnetic field H_o were done measuring the frequency splitting between lines of a sodium chlorate NQR spectrum. To do this a sodium chlorate single crystal of $20 \times 14 \times 14\ \text{mm}^3$ was used. The angle θ_0 between the principal direction of the electric field gradient tensor and the static magnetic field satisfied $\cos\theta_0 = \frac{1}{\sqrt{3}}$. The relative uncertainties of magnetic field measurements were 1/300.

4. Theory

As mentioned above Shirley [2] developed a formal theory that relates the solution of a Schrödinger equation with a periodic Hamiltonian for a quantum system with two discrete states α and β to the solution of another Schrödinger equation with a time-independent Hamiltonian (Floquet Hamiltonian) represented by an infinite matrix.

The interaction of the quantum system with the oscillating field evolves according to the Schrödinger equation ($\hbar = 1$)

$$i\frac{d}{dt}\begin{pmatrix} a_\alpha(t) \\ a_\beta(t) \end{pmatrix} = \begin{pmatrix} E_\alpha & 2b\cos\omega t \\ 2b\cos\omega t & E_\beta \end{pmatrix}\begin{pmatrix} a_\alpha(t) \\ a_\beta(t) \end{pmatrix}$$
$$\text{or} \quad i\left(\frac{d}{dt}\right)F(t) = \mathscr{H}_c(t)F(t) \tag{1}$$

In matrix notation Floquet's theorem asserts the existence of a solution of Eq. (1) in the form:

$$F(t) = \Phi(t)e^{-iQt} \tag{2}$$

where Φ is a matrix of periodic functions of t and Q is a constant diagonal matrix. The diagonal elements q_α of Q are called characteristic exponents and follow the relation:

$$\sum_\alpha q_\alpha = \frac{1}{T}\int_o^T Tr\ \mathscr{H}_c(t)dt \qquad (\text{mod}\ \omega) \tag{3}$$

Substituting the Fourier series expansions of $\Phi(t)$ and $\mathscr{H}_c$ into the Schrödinger equation allows obtaining an infinite set of recursion relations, which can be rewritten in the form of a matrix eigenvalue equation for the q's:

$$\sum_{\gamma k}\left(H^{n-k}_{\alpha\gamma} + n\omega\delta_{\alpha\gamma}\delta_{kn}\right)F^k_{\gamma\beta} = q_\beta F^n_{\alpha\beta} \tag{4}$$

The operator will be denoted by $\mathscr{H}_f$ and called the Floquet Hamiltonian associated with the semi classical Hamiltonian $\mathscr{H}_c$

$$\mathscr{H}_f = \begin{pmatrix}
\bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet \\
\bullet & E_\beta-2\omega & b & 0 & 0 & 0 & 0 & 0 & 0 & \bullet \\
\bullet & b & E_\alpha-\omega & 0 & 0 & b & 0 & 0 & 0 & \bullet \\
\bullet & 0 & 0 & E_\beta-\omega & b & 0 & 0 & 0 & 0 & \bullet \\
\bullet & 0 & 0 & b & E_\alpha & 0 & 0 & b & 0 & \bullet \\
\bullet & 0 & b & 0 & 0 & E_\beta & b & 0 & 0 & \bullet \\
\bullet & 0 & 0 & 0 & 0 & b & E_\alpha+\omega & 0 & 0 & \bullet \\
\bullet & 0 & 0 & 0 & b & 0 & 0 & E_\beta+\omega & b & \bullet \\
\bullet & 0 & 0 & 0 & 0 & 0 & 0 & b & E_\alpha+2\omega & \bullet \\
\bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet
\end{pmatrix} \tag{5}$$

For an isolated proton spin system, $E_\alpha = 1/2\omega_o$, $E_\beta = -1/2\omega_o$ and $b = \gamma H_2/4$. The Floquet Hamiltonian has a periodic structure and its eigenvalues (λ) have also periodic properties. If λ is an eigenvalue, also is $\lambda + n\omega$ for any integer n. It is then possible to label the eigenvalues $\lambda_{\alpha n} = q_\alpha + n\omega$, where $q_\alpha = \lambda_{\alpha o}$ is chosen as that member of the set having the smallest absolute value. They represent physical energy levels of the proton-radiation field system in interaction and much information can be learned from them. In fact, Shirley found a relationship between the time average transition probability and $\frac{\partial q_\alpha}{\partial \omega_o}$ [2].

$$\overline{P} = \frac{1}{2}\left(1 - 4\left(\frac{\partial q}{\partial \omega_o}\right)^2\right) \tag{6}$$

Particularly, if the plot of q_α as a function of $\omega_o \equiv E_\alpha - E_\beta$ is made, using ω as a scaling parameter, the resonances (maximum time average of the transition probability between the two-states) occur where the curves for two eigenvalues approach each other closely but do not cross [5] (see Fig. 2). These extreme values for the eigenvalues can be found by solving

$$\frac{\partial q_\alpha}{\partial \omega_o} = 0 \tag{7}$$

In this simple case of only two atomic states in the Floquet Hamiltonian, $q_\alpha + q_\beta = E_\alpha + E_\beta = 0$ and only one characteristic exponent, called q, need to be determined.

Unfortunately it is only possible to find analytical expressions of the eigenvalues for matrix with 2^n elements. For this reason, numerical calculations of Floquet matrix eigenvalues are needed. In Fig. 2, 6×6 (up to first term Fourier component), 10×10 (up to second term Fourier component) and 14×14 (up to third term Fourier component) Floquet matrix eigenvalues q are shown as a function of ω_o/ω for (a) $b/\omega = 1/8$ y (b) $b/\omega = 1/2$. It is observed that the first resonance is very close to $\omega_o/\omega = 1$ when $b/\omega = 1/8$ but it is shifted to lower frequencies when b/ω increases ($b/\omega = 1/2$ or $H_2 \sim 42$ G in the present work). Moreover the shift is more evident when higher terms are included. It is also observed that for $n = 1$ only one resonance is predicted, while $n = 2, 3$ predict higher resonances ($\omega_o/\omega \sim 3, 5$) as should be expected [6]. Therefore Floquet matrix including up to first term Fourier component is not a good approximation to the problem and at least Floquet matrix including up to second term Fourier component should be considered to describe the proton resonance dependence with H_2 (see Fig. 4).

Since in this work H_2 is varied from *0* to around *40* G, the q obtained from Floquet matrix including up to second term Fourier component will be considered to explain experimental data. In this case, Fig. 3 shows q as a function of ω_o/ω for different values of b/ω. It is easily observed that the resonance frequency diminishes as b/ω increases unless for $b/\omega \leqslant 1/2$. Numerical calculation of

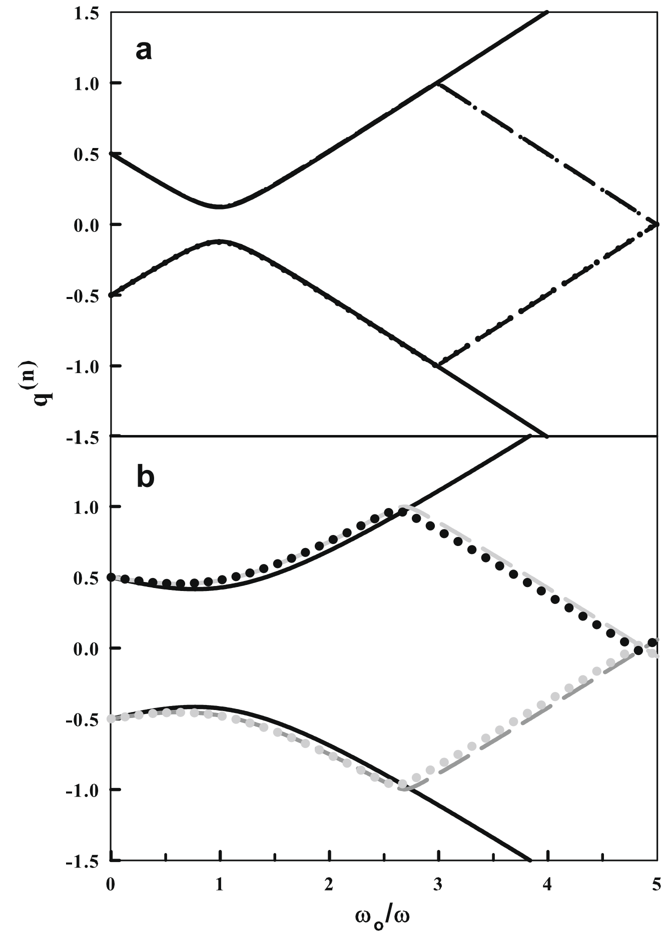

Fig. 2. Two branches of the characteristic exponent $q^{(n)}$ as a function of ω_o/ω. n indicates the order of the approximation (a) $b/\omega = 1/8$ where (----) $n = 1$, (– –) $n = 2$ and (·····) $n = 3$ (b) $b/\omega = 1/2$ where (—) $n = 1$, (– –) $n = 2$ and (·····) $n = 3$.

$\frac{\partial q}{\partial \omega_o} = 0$ allows then to determine ω_o/ω as a function of b/ω. This behavior is shown in Fig. 4.

From Eq. (6) it is also possible to calculate the proton resonance line width dependence with H_2. This dependence can be compare to the experimental data and to the expected line width calculated from the steady state power absorbed by the proton system in a rotating field [6], $P = 2\omega H_2^2 \chi''$, where:

$$\chi''(H_o, H_2) = \frac{M_o \gamma^2 H_o}{2\omega T_1} \frac{(H_2^2 + (1/\gamma T_2)^2)}{H_2^2} \times \frac{1}{\left[H_2^2 + (1/\gamma T_2)^2 + (\omega/\gamma - H_o)^2\right]} \quad (8)$$

which is a Loretzian line with a width $\left(H_2^2 + (1/\gamma T_2)^2\right)^{\frac{1}{2}}$.

Half line width calculated from Eqs. (6) and (8) are shown in Fig. 5. The value assigned to $\left(\frac{1}{\gamma T_2}\right)$ is *1.6* G and it was obtained fitting the experimental data as a function of H_o for low H_2 and it corresponds to $T_2 \sim 150$ µs.

5. Experimental results and discussion

In a standard Hahn echo experiment, the echo amplitude can be written as:

$$E(\tau) = E_o e^{-2\tau/T_2} \quad (9)$$

where T_2 is the spin–spin relaxation time of the ^{35}Cl spin due to all species of nuclear neighbors. In the present work the homonuclear and heteronuclear contribution are written as:

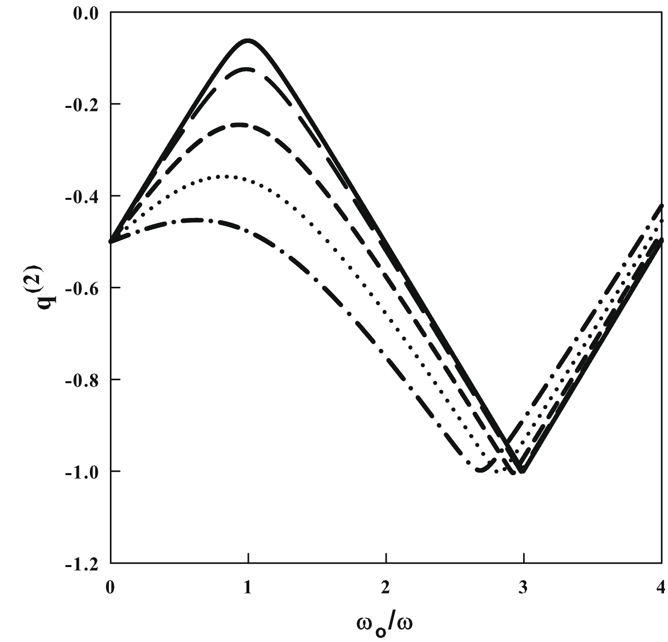

Fig. 3. $q^{(2)}$ as a function of ω_o/ω for: (—) $b/\omega = 1/16$, (– –) $b/\omega = 1/8$, (---) $b/\omega = 1/4$, (····) $b/\omega = 3/8$ and (– · –) $b/\omega = 1/2$.

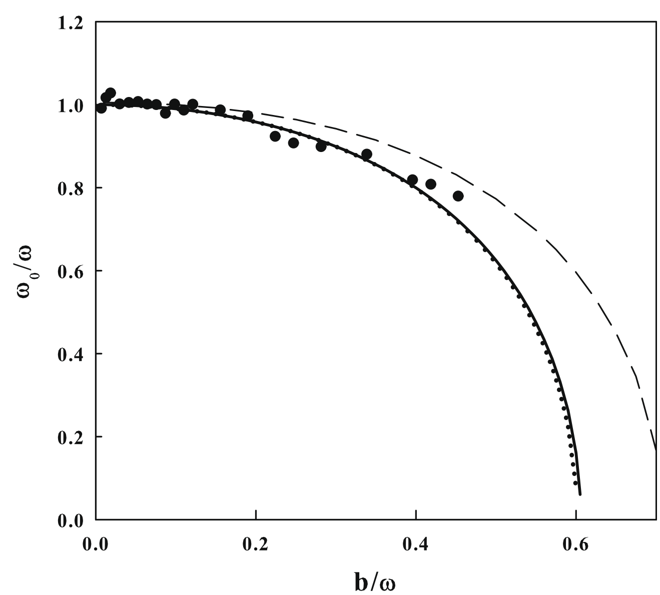

Fig. 4. Proton resonance frequency (ω_o) as a function of excitation field intensity (H_2) (•) experimental data, (----) Shirley's theory considering up to first term Fourier components (—) Shirley's theory considering up to second term Fourier components and (·····) Shirley's theory considering up to third term Fourier components.

$$\frac{1}{T_2} = \left(\frac{1}{T_2}\right)_{Cl—Cl} + \left(\frac{1}{T_2}\right)_{Cl—H} \quad (10)$$

Then, let the ^{35}Cl echo amplitude in the Hahn echo experiment with proton decoupling be expressed as:

$$E'(H_2, H_o, \tau) = E_o e^{-2\tau/T_2'} \quad (11)$$

E_o can be obtained from the echo amplitude when no external magnetic field and no proton irradiation are present. In this case:

$$E'(H_2, H_o, \tau) = E e^{-2\tau\left(\frac{1}{T_2'} - \frac{1}{T_2}\right)} \quad (12)$$

As stated before, $(1/T'_2)$ will have two contributions. The first one, due to Cl—Cl dipolar interactions, can be assumed independent of H_o and H_2. The second one, due to Cl—H dipolar coupling, will change in the presence of H_o and H_2 since proton spin can also be flipped by the electromagnetic field H_2. From a phenomenological point of view, if W is the probability that a spin is flipped by H_2, then the probability that a proton contributes to $(1/T'_2)$ will be $(1 - W)$. Therefore:

$$\frac{1}{T'_2} = \left(\frac{1}{T_2}\right)_{\text{Cl—Cl}} + (1 - W)\left(\frac{1}{T_2}\right)_{\text{Cl—H}} \tag{13}$$

The probability W should be proportional to the proton absorption line shape [6] $W = kP/\omega H_2 = kH_2\chi''(\omega,H_o,H_2)$. Replacement of Eqs. (10) and (13) in Eq. (12) gives place to the following expression:

$$E'(H_2, H_o, \tau) = Ee^{2\tau W\left(\frac{1}{T_2}\right)_{\text{Cl—H}}} \tag{14}$$

Then:

$$\ln(E'(H_2, H_o, \tau)) = \ln(E(\tau)) + kH_2\chi''(\omega, H_o, H_2) \tag{15}$$

Therefore the logarithm of the experimental echo amplitude is proportional to the proton absorption line.

Fig. 6 shows the echo amplitude as a function of the external magnetic field (H_o) for three different excitation field intensities. When $H_2 = 5.5$ G one resonance is observed at $H_o \cong 21.2$ G ($\nu \cong 90.26$ kHz) which is a single quantum transition resonance. If $H_2 = 16.1$ G, the single quantum resonance is shifted to lower fields and broadened. An extra resonance is also detected around half the irradiation frequency, $H_0 \sim 11$ G. For $H_2 > 33$ G, the proton resonance exhibits a multiplicity of peaks. These peaks are related to what Bloom et al. [7] called slow beats. They predicted the existence of beat modulation effects in the quadrupolar free precession

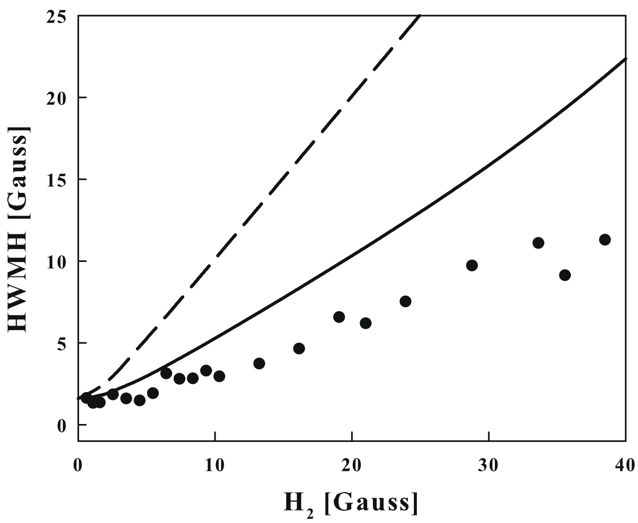

Fig. 5. Proton resonance half-width as a function of H_2. (•) experimental data (—) line width calculated using Eq. (6), (---) line width calculated using Eq. (8).

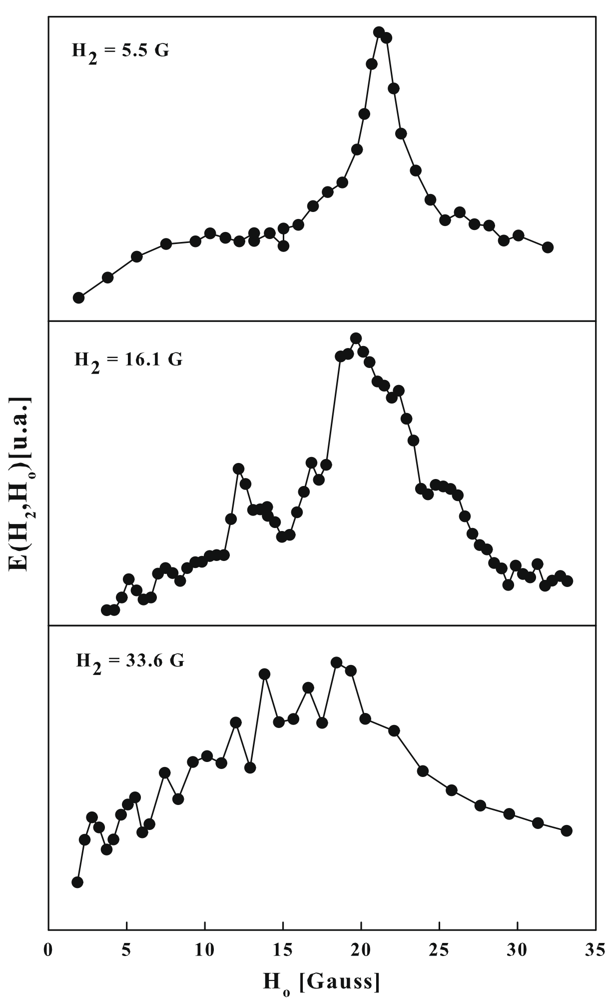

Fig. 6. Experimental echo intensity as a function of H_o for three different values of H_2.

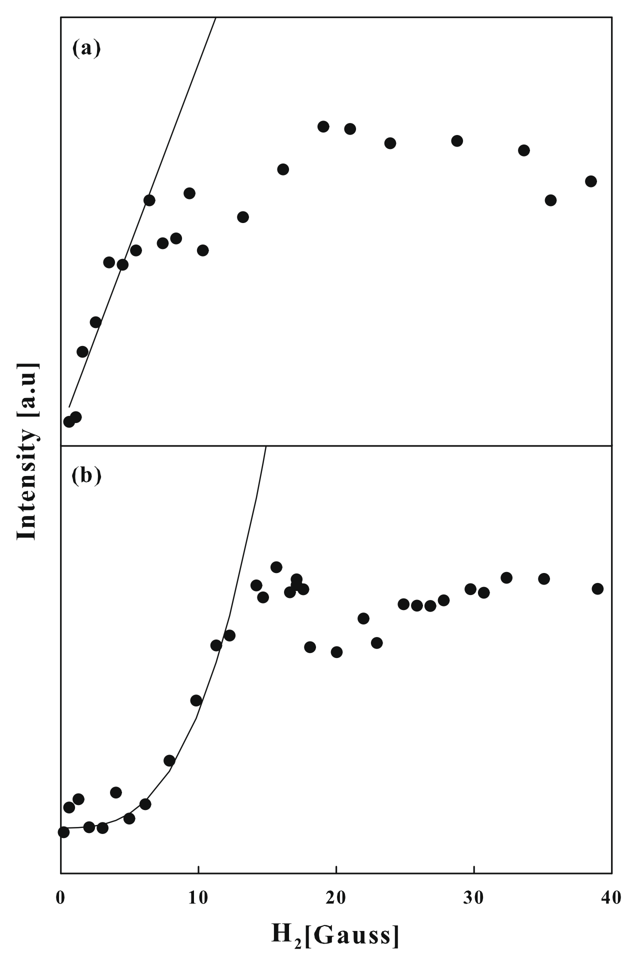

Fig. 7. (a) SQT resonance intensity as a function of H_2. (b) DQT resonance intensity as a function of H_2.

signal in a small constant external magnetic field. They detected slow beats in $NaClO_3$. In the present work it was found that slow beats are only observed in *p*-dichlorobenzene when spin proton decoupling is used, because of the strong Cl—H coupling.

The secondary resonance could be associated to a double quantum transitions ($\Delta m = \pm 2$) in which a pair of nuclear spins are flipped when a photon of energy $\hbar\omega$ is absorbed. The dipole–dipole interaction is the key to understand this otherwise forbidden interaction between H_2 and the proton spin system [8]. Fig. 7a shows the H_2 dependence of the single quantum transition (SQT) resonance intensity while Fig. 7b despites the double quantum transition (DQT) resonance intensity dependence with H_2. It is observed that the first one grows linearly with H_2 and the second one increases proportionally to H_2^3 according to the expression [9]:

$$I \propto (\gamma H_2)^{2p-1} \qquad p = 1\ (SQT), 2(DQT) \tag{16}$$

Eq. (16) is obtained under the assumption of $H_2 \ll H_o$, when this condition is not fulfilled saturation effects appears and Eq. (16) is not longer valid [10,11].

The excitation field intensity dependence of the experimental main proton resonance is shown in Fig. 4. The solid, dotted and dash lines are the values predicted by Shirley's theory. Good agreement between experimental data and Shirley's theory including up to second term Fourier component is observed for the whole range of measured H_2,

According to Shirley's theory as well as stated by Abragam, resonances at 3ω, 5ω, etc. should also be observed. They were not detected because H_o higher than *60* G would have been necessary in the present experiment.

Finally theoretical line width predictions are not in good agreement with experimental data as shown in Fig. 5. The experimental line width is even lower than the one stated by Shirley's theory. This could be due to the fact that protons in the sample are not really isolated. In the presence of two interacting spin, the total simplified Hamiltonian becomes:

$$H = H_z + H_d^o + H_{rf}(t) \tag{17}$$

$$H = \begin{bmatrix} \omega_o - A & 0 & \sqrt{2}b\cos\omega t & 0 \\ 0 & 0 & 0 & 0 \\ \sqrt{2}b\cos\omega t & 0 & 2A & \sqrt{2}b\cos\omega t \\ 0 & 0 & \sqrt{2}b\cos\omega t & -\omega_o - A \end{bmatrix} \qquad A = \frac{\gamma^2\hbar^2}{4r^3}(1 - 3\cos^2\theta) \tag{18}$$

This Hamiltonian is equivalent to:

$$H = \begin{bmatrix} E_\alpha & \sqrt{2}b\cos\omega t & 0 \\ \sqrt{2}b\cos\omega t & E_\beta & \sqrt{2}b\cos\omega t \\ 0 & \sqrt{2}b\cos\omega t & E_\gamma \end{bmatrix} \tag{19}$$

where:

$$E_\alpha = \omega_o - A \qquad E_\beta = 2A \qquad E_\gamma = -\omega_o - A \tag{20}$$

and the so-called Floquet Hamiltonian is:

$$\mathscr{H}_f = \begin{bmatrix} \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet \\ \bullet & E_\gamma - 2\omega & 0 & c & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet \\ \bullet & 0 & E_\alpha - \omega & 0 & 0 & 0 & c & 0 & 0 & 0 & 0 & 0 & \bullet \\ \bullet & c & 0 & E_\beta - \omega & 0 & c & 0 & c & 0 & 0 & 0 & 0 & \bullet \\ \bullet & 0 & 0 & 0 & E_\gamma - \omega & 0 & c & 0 & 0 & 0 & 0 & 0 & \bullet \\ \bullet & 0 & 0 & c & 0 & E_\alpha & 0 & 0 & 0 & c & 0 & 0 & \bullet \\ \bullet & 0 & c & 0 & c & 0 & E_\beta & 0 & c & 0 & c & 0 & \bullet \\ \bullet & 0 & 0 & c & 0 & 0 & 0 & E_\gamma & 0 & c & 0 & 0 & \bullet \\ \bullet & 0 & 0 & 0 & 0 & 0 & c & 0 & E_\alpha + \omega & 0 & 0 & 0 & \bullet \\ \bullet & 0 & 0 & 0 & 0 & c & 0 & c & 0 & E_\beta + \omega & 0 & c & \bullet \\ \bullet & 0 & 0 & 0 & 0 & 0 & c & 0 & 0 & 0 & E_\gamma + \omega & 0 & \bullet \\ \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & c & 0 & E_\alpha + 2\omega & \bullet \\ \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet \end{bmatrix} \tag{21}$$

where $c = \frac{b}{\sqrt{2}}$.

In the case of *p*-dichlorobenzene the shortest distance between two protons is $r \sim 2.3$ Å. This corresponds to a dipolar interaction $A \sim 3.5$ *G*. Using ω as a scaling parameter results that $A/\omega \approx 1/6$. With these numbers it is possible to find the Floquet eigenvalues $q_\alpha = \lambda_{\alpha 0}$ and eigenvectors $|\lambda_{\alpha 0}\rangle$ as a function of ω_o/ω for different values of c/ω and calculate the average transition probabilities $\overline{P}_{\beta\to\alpha}, \overline{P}_{\beta\to\gamma}$ using Shirley's equations.

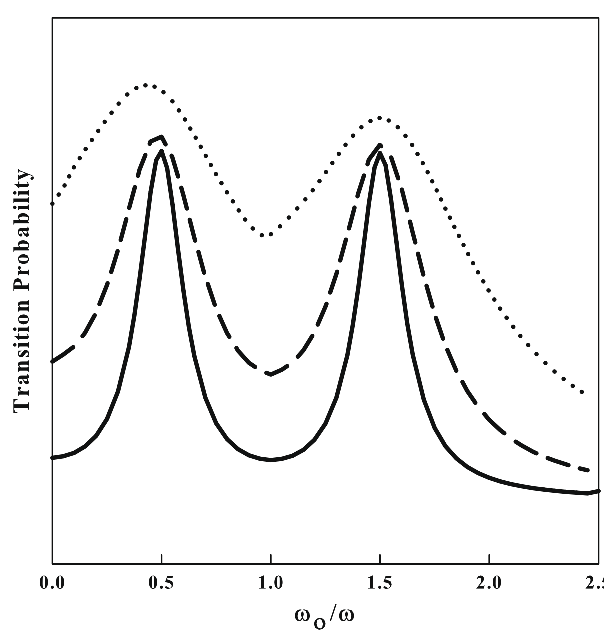

Fig. 8. Numerical computed time-averaged transition probability, including up to third term Fourier components, as a function of ω_o/ω. (—) $c/\omega = 1/16$, (----) $c/\omega = 1/8$ and (·····) $c/\omega = 1/4$.

$$\overline{P}_{\beta\to\alpha} = \sum_{\delta} T_{\alpha\delta} T_{\beta\delta} \qquad \delta = \alpha, \beta, \gamma \tag{22}$$

where the matrix T is defined to be a partial sum of the squares of the eigenvector components

$$T_{\alpha\beta} = \sum_{k} \left| \langle \alpha k | \lambda_{\beta 0} \rangle \right|^2 \tag{23}$$

The results (Fig. 8) show that two resonances should be observed when spin pair interaction is considered. The peak separation increases as c/ω increases and the line, as a whole, is shifted to lower frequencies. If A/ω is too small compared to ω_0/ω that it can be neglected, then the problem is equivalent to solve an isolated $I = 1$ spin system. This problem was solved by Hermann and Swain [12] and they found the same qualitative behavior reported here.

In solids, more than two spins are involved and the net effect would be the observation of a line broadening. Since the observed line width is narrower than the expected one, it is reasonable to assume that this effect is due to the indirect detection method.

6. Conclusions

In this paper we present the first experimental determination of the proton resonance as a function of oscillating field intensities as high as the static magnetic field. Good agreement between experimental data and Shirley's theory is found for the proton resonance frequency as a function of H_2 intensity. The curve ω_o/ω vs. b/ω should be used to correct the proton frequency when a spin decoupling experiment is set at low field, especially when $H_2 \sim H_o$ or higher.

A secondary resonance, that could be associated to a double quantum transition, is also observed around half the irradiation frequency and with an oscillating field intensity dependence following a power law H_2^3 as it is expected at $H_2 < H_o$.

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