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Theory of Multiple NMR Spin Echoes of HD Impurities in Solid Para-H_2

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The theory of the formation of NMR multiple echoes for isotopic impurities (HD) in solid para-H_2 has been developed for the case of weak quantum tunneling of the impurities. The results show that even for low tunneling rates (100–1000 Hz), NMR multiple echoes can be observed for experimentally accessible nuclear spin polarizations and can be used to provide an independent test for the existence of tunneling in the solid hydrogens.

INTRODUCTION

Quantum solids such as solid heliums and solid hydrogens are unique among solids because of the relatively strong delocalization of the atoms or molecules about the lattice positions (*1, 2*). This quantum zero point motion is a result of the weak interactions between the particles and of their low mass. As a result of the overlap of the particle wave functions, particles at neighboring sites can tunnel from one site to another at detectable rates, leading to a motional narrowing of the NMR lineshape that is independent of temperature.

The line narrowing is very significant for solid ^3He, reducing the rigid-lattice line width by factors of up to 10^3, depending on the density (*3*), and is clearly observable in NMR studies of ^3He impurities in solid ^4He (*4–7*). The NMR lineshape observed for HD impurities in solid para-H_2 is similarly narrowed (*8*) compared to the calculated rigid-lattice lineshape. This phenomenon has been attributed to quantum tunneling in solid para-H_2. The tunneling rates for solid H_2 are much smaller than those for solid ^3He, $\omega_t(H_2)$ ~kilohertz compared to $\omega_t(^3He)$ ~megahertz. Demonstrating the existence of tunneling in solid H_2 or placing limits on its possible values has been an experimental challenge and has not to this date been fully resolved.

The most recent theories of tunneling in quantum solids involve multiple particle exchange with 2-, 3-, 4-, $\cdots$ cyclic particle exchanges (*9*). In solid ^3He, this results in the remarkable nuclear-spin-ordered phases at millikelvin temperatures. These phases are very different from the simple Heisenberg antiferromagnets predicted by a simple two-particle exchange model. The multiple-particle exchange model predicts that the exchange in solid para-H_2 would be comparable to that observed in solid ^3He when the solid ^3He is compressed to a density such that the effective free volume available for cyclic particle exchange is the same as that for solid H_2. This condition occurs at a molar volume of $V_m \sim 15$ cm^3/mol and corresponds to exchange rates in the range 1–10 kHz (*6*). These estimates are very close to the values (~1 kHz) needed to explain the observed narrowing of the HD NMR lineshapes (*8*). The line-narrowing effect for solid H_2 is, however, weak and the interpretation in terms of quantum tunneling is not firmly established (*8, 10*). New tests for the existence of quantum tunneling in solid H_2 are therefore of considerable importance, not only for the understanding of the ground-state properties of solid H_2 in particular, but also for testing the theoretical models for quantum crystals in general.

One consequence of the quantum tunneling in solid helium and the resulting long nuclear spin–spin relaxation times, T_2, is the observation of multiple nuclear spin echoes that occur at times $t = n\tau$ for $n = 1, 2, 3, \cdots$ after a standard $\pi/2$—τ—$\pi/2$ RF pulse sequence (*11*). (The higher-order echoes are not a memory effect associated with short times between pulse sequences and are seen if a time equal to several values of T_1 elapses between sequences.) The observation of multiple echoes in solid ^3He led to an important new result: it showed for the first time that the magnetization deviated appreciably from that of the Heisenberg nearest-neighbor antiferromagnetic model.

The multiple echoes occur because of the nonlinearities of the nuclear spin dynamics in the presence of the nuclear demagnetization field associated with the intermolecular dipole–dipole interactions (*12–14*). The effects are very general and could, in principle, be observed in any system if the values of the equilibrium nuclear spin polarization M_0 are sufficiently high and if the values of T_2 are sufficiently long. The general condition for obtaining multiple spin echoes is $4\pi\gamma M_0 T_2 > 1$. If T_2 has the rigid-lattice value, this condition is not satisfied except for very low (submillikelvin) temperatures. Motional lengthening of T_2, due to tunneling in the present

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case, is therefore necessary to be able to observe multiple spin echoes in practical applications for solid samples.

The purpose of this paper is to determine the exact conditions for the formation of multiple NMR echoes for isotopic impurities in solid H_2 with the intention of obtaining a new and independent test for the existence of quantum tunneling in the solid hydrogens. The possibility of such a test exists because the amplitude of the echoes depends critically on the value of the nuclear demagnetization field and the lifetime T_2 of the transverse magnetization, which in turn is determined by the quantum tunneling. The interpretation of the measurements of T_2 of HD impurities in solid hydrogen using traditional techniques has been questioned (*10*), and an independent test of the apparent lengthening of the transverse magnetization relaxation time due to motion has become important. In the next section, we give a brief review of the theory of formation of NMR multiple spin echoes, and in the following section, we give the specific theoretical conditions for their observation for HD in solid para-H_2.

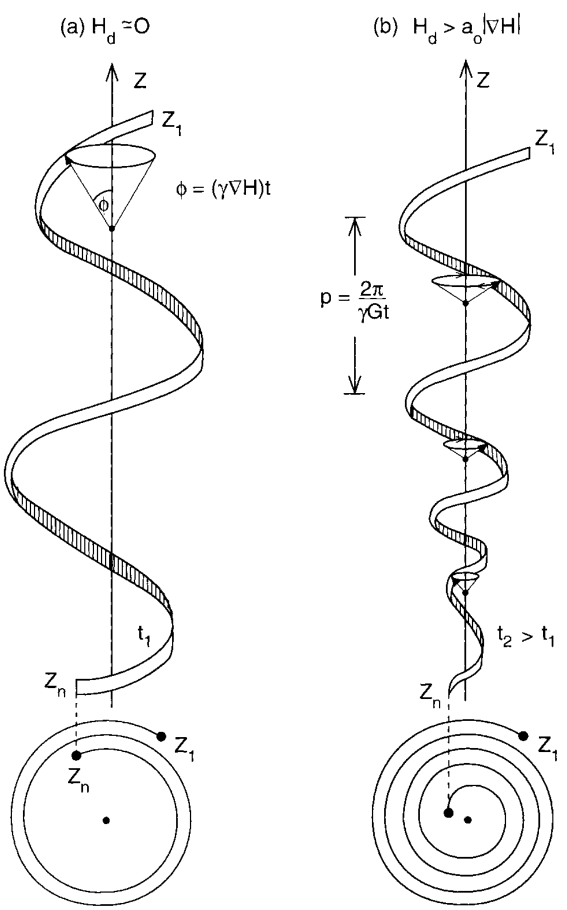

FIG. 1. Schematic representation of the precession of nuclear spins located at different positions along the z axis for (a) dipolar fields, $H_d \sim 0$, and (b) $H_d \geqslant a_0|\nabla H|$ for field gradient ∇H and lattice spacing a_0.

THEORY OF MULTIPLE ECHOES

NMR spin echoes are a well-known phenomenon in liquids (*15*). After a two-RF-pulse sequence at times 0 and τ, a single echo is observed at time 2τ. This occurs because the second pulse acts as a time reversal operator, and part (or all) of the loss of coherence of the precessing magnetization in the time $0 < t < \tau$ is reversed in the interval $\tau < t < 2\tau$, leading to a focusing of the magnetization to form an echo at 2τ. The same type of spin echo can be observed in solid ^{3}He; however, instead of only one echo, multiple echoes are observed at times 2τ, 3τ, . . . , $n\tau$ (*16*). In fact, NMR multiple echoes can in principle be observed in any material if the values of the transverse relaxation time T_2 are sufficiently long and if the demagnetization field produced by the nuclear spins is strong enough to produce observable nonlinear components in the evolution of the magnetization for times $t < T_2$. In ^{3}He, for example, the large zero-point motion of the atoms leads to a large nuclear-spin-exchange frequency and consequently a motionally narrowed NMR lineshape, which in turn leads to large values of T_2 (a fraction of a second, compared to tens of microseconds in the absence of motion) (*11, 17*). The demagnetizing field H_d is strong enough to produce observable effects when $\gamma H_d T_2 \geqslant 1$. We will summarize below the essential features of the general theory given by Abragam and Goldman (*17*).

Following an initial $\pi/2$ pulse, the transverse magnetization M_t precesses at the Larmor frequency in a spiral about the direction of the local applied field and its gradient. A second $\pi/2$ pulse will convert the transverse magnetization into a longitudinal magnetization $M_z(t)$ that will have a space variation (*a fingerprint*) reflecting the inhomogeneity of the DC magnetic field. The dipolar field produced by this spatial variation of $M_z(t)$ is responsible for the formation of the multiple echoes.

Neglecting diffusion and relaxation effects, and considering the case of high fields, the dipolar interactions are (*17*)

$$\mathcal{H}_D = \frac{1}{2}\sum_{ij} A_{ij}\left[2I_z^i I_z^j - \frac{1}{2}[I_+^i I_-^j + I_-^i I_+^j]\right]. \qquad [1]$$

The demagnetization field $H_d(r)$ is found from the sum $\int d^3\mathbf{r}\mathcal{H}_D(\mathbf{r}, \mathbf{r}')$. The deviation of the resonance frequency from the central frequency is then given by $\boldsymbol{\omega}_d = -\gamma\mathbf{H}_d$ with components

$$\omega_d(z) = \sum_j A_{ij} p_{jz} \qquad [2a]$$

$$\omega_d(x, y) = -\frac{1}{2}\sum_j A_{ij} p_{jx,y}, \qquad [2b]$$

where $\mathbf{p}$ is the polarization of the spins. Using space Fourier transforms, these can be written as

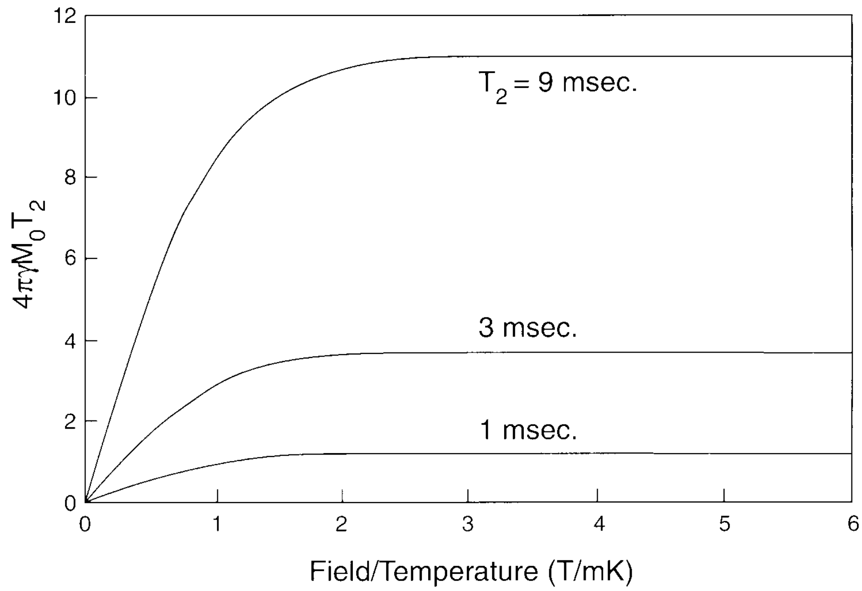

FIG. 2. Variation of the condition $\beta\tau = 4\pi\gamma M_0 T_2 \geqslant 1$ for the observation of multiple echoes as a function of applied field H and temperature for different values of T_2 for HD impurities (~1%) in solid para-H_2.

$$\omega_d(z) = A(\mathbf{k})p_z(\mathbf{k}) \quad [3a]$$

$$\omega_d(x, y) = -\frac{1}{2}A(\mathbf{k})p_{x,y}(\mathbf{k}). \quad [3b]$$

If the field gradient $G = \nabla H_d$ is parallel to the local magnetic field H_0, the transverse magnetization will spiral around that particular direction. This is illustrated in Fig. 1. For $H_d = 0$, the spins at each site precess in phase with their neighbors and do not change with time. For nonnegligible values of H_d, the precessional frequency changes from site to site, and along the z axis the tips of the magnetization vectors trace out a helix whose pitch $p = 2\pi/\gamma Gt$ increases with time. The helix literally wraps itself up as time evolves (Fig. 1b). It can be shown that (*17*)

$$A(\mathbf{k}) = A = \frac{4}{3}\pi\gamma^2\hbar n \quad [4]$$

for spins with gyromagnetic ratio γ and spin density n. In this special case, where the nuclear spin polarization is homogeneous, Eqs. [3a] and [3b] can be written as

$$\omega_d(z) = Ap_z(k) \quad [5a]$$

$$\omega_d(x, y) = -\frac{1}{2}Ap_{x,y}(k). \quad [5b]$$

The inverse Fourier transform leads to

$$\boldsymbol{\omega}_d = -\frac{1}{2}Ap_{x,y} + \frac{3}{2}Ap_z\hat{z}. \quad [6]$$

It is the second term in this expression that leads to the precession around H_0. The first term simply represents the field parallel to the spins.

Consequently, in the simplest case, where the nuclear spin polarization is homogeneous, the effective part of the dipolar field is

$$\omega_d(z) = \frac{3}{2}Ap_z, \quad [7]$$

where p_z is the nuclear spin polarization component along the direction of the field. The purely longitudinal precession frequency is

$$\omega_z = \omega_0 + \Delta + \frac{3}{2}Ap_z, \quad [8]$$

where ω_0 is the central Larmor frequency $\omega_0 = -\gamma H_0$ and Δ is the additional shift from this frequency due to the gradient of the applied field.

In the rotating frame, the transverse magnetization at time τ_- after the first pulse (and just before the second pulse) is (*11*)

$$M_t(\tau_-) = M_x(\tau_-) + iM_y(\tau_-) = M_0 e^{i\Delta\tau}, \quad [9]$$

where $M_0 = \frac{1}{2}\gamma\hbar N \tanh(\gamma\hbar H/2k_B T)$ is the thermal equilibrium polarization in magnetic field H_0 at temperature T. Immediately after the second pulse, at time τ_+, which rotates the spins around the y axis, we have

$$M_t(\tau_+) = R_y\left(\frac{\pi}{2}\right)M(\tau_-)R_y^{-1}\left(\frac{\pi}{2}\right) \quad [10]$$

$$M_t(\tau_+) = iM_0\sin(\Delta\tau) \quad [11a]$$

$$M_z(\tau_+) = -M_0\cos(\Delta\tau). \quad [11b]$$

The precession frequency in the rotating frame is now given by

$$\omega' = \Delta + \gamma M_z(\tau_+) = \Delta - \beta\cos(\Delta\tau) \quad [12]$$

with $\beta = \frac{3}{2}Ap_0 = 4\pi\gamma M_0$. At time t after the second pulse, the transverse magnetization is

$$M_t(t) = M_t(\tau_+)\exp(i\omega' t)$$
$$= iM_0\sin(\Delta\tau)\exp\{i[\Delta - \beta\cos(\Delta\tau)]t\}. \quad [13]$$

The term $\exp\{i[\Delta - \beta\cos(\Delta\tau)]t\}$ leads to multiple echoes. This can be seen by expanding the exponential in terms of the Bessel functions J_n and writing M_t as

$$M_t(t) = \frac{1}{2}(e^{i\Delta\tau} - e^{-i\Delta\tau})e^{i\Delta t}\sum_{n=-\infty}^{\infty}(-i)^n J_n(\beta\tau)e^{in\Delta\tau}. \quad [14]$$

Echoes occur when the phase factors cancel, i.e., for

$$t = -(n \pm 1)\tau. \quad [15]$$

The amplitude of the echo of order m produced at time $t = m\tau$ is

$$I_m = (-i)^{m+1}M_0(\beta\tau)^{-1}J_m(m\beta\tau). \quad [16]$$

The condition for observation of an echo is, from Eq. [16], $\beta\tau > 1$. As the time interval τ must be less than the transverse relaxation time T_2, this condition becomes

$$\beta T_2 = 4\pi\gamma M_0 T_2 > 1 \quad [17]$$

and is shown as a function of applied field and temperature in Fig. 2 for a range of values of T_2.

DISCUSSION

We have calculated the complex amplitude of the multiple echoes for conditions where the polarization is sufficiently high that the associated demagnetization field will lead to detectable nonlinear dynamics for the evolution of the nuclear magnetization. The time scale of this local spin dynamics is tied fundamentally to the natural microscopic lifetime of the transverse magnetization, and can therefore provide a very basic test for the occurrence of quantum tunneling of the atoms or molecules from one site to neighboring sites.

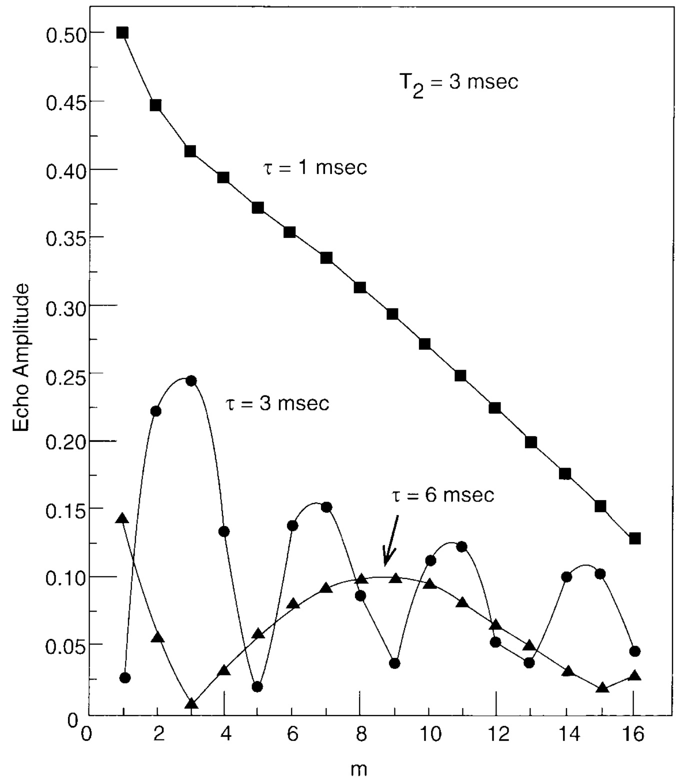

FIG. 3. Magnitude $|I_m|$ of the mth order multiple echo for three different repetition times: $\tau = 0.33T_2$, T_2, and $2T_2$.

It is particularly important to note that the echo amplitudes vary in a complex fashion with the order m of the echo (Eq. [16]). This is illustrated in Figs. 3–5. In Fig. 3, we plot the magnitude of each echo as a function of m for three selected pulse sequences, corresponding to repetition times $\tau = 1$, 3, and 6 ms, for a transverse relaxation time $T_2 = 3$ ms. (This is a typical value for dilute (1%) HD mixtures in solid para-hydrogen.) This choice corresponds to a value of 3.77 for the critical factor $\beta\tau$ which determines the condition for the observation of multiple echoes. For this value of T_2, this value of β requires that the ratio $H/T \geqslant 10$ T K^{-1}.

The calculations show that there is a rapid change in the oscillations of the amplitude of the echoes I_m with the value of m as $\beta\tau$ changes from 1 through 2π. This change is due to the quasi-periodic behavior of the Bessel function $J_m(m\beta\tau)$ in Eq. [16]. This feature is particularly useful for providing an independent measurement of T_2 or M_0 because the identification of the sharp minimum in the amplitude $|I_m|$ (e.g., for $\tau = 3$ ms in Fig. 3), or detailed fits to the amplitude as a function of m or τ, can be used to determine the demagnetization factor β quite accurately. This application of the analysis would be especially useful as a probe

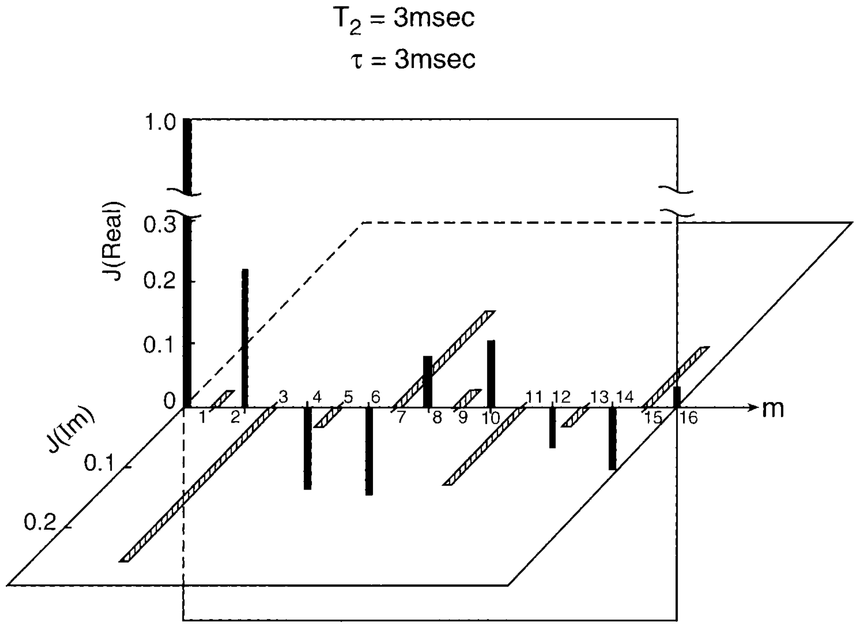

FIG. 4. Variation of the amplitude and the phase of the mth order multiple-echo response $I_m(\tau)$ for $\tau = T_2 = 3$ ms. (These are normalized to unity at $\tau = 0$ and are the Bessel functions, $J_m(m\beta\tau)$.)

for testing for quantum tunneling in dilute solid H_2 mixtures. It would provide a measure of the lifetime of the transverse magnetization, using a method that is distinctly different from the standard T_2 measurements which are subject to the incompletely understood spin–spin correlations (*10*) in the very dilute systems. For the studies of dilute HD solid mixtures, we can use this test in a regime where M_0 is perfectly calculable because the solid remains paramagnetic down to nanokelvin temperatures where nuclear spin ordering effects are predicted.

Not only do the amplitudes of the multiple echoes vary rapidly with the order m of the multiple echo, but a well-characterized variation of the phase ϕ is also predicted by these calculations, and this is shown in Figs. 4 and 5. There is also the dependence on m that can be used to determine both T_2 and M_0. This test has not been used in experimental studies up to the present time because the NMR configuration used did not detect the phase of the multiple echoes. The additional information offered by measuring both the phase and the amplitude of the echoes I_m would provide an even more stringent test for the existence of the motional narrowing of the NMR lineshape due to quantum tunneling.

The overall dependence of the mth echo on the polarization and the condition for the observation of nonlinear effects is shown in Figs. 4 and 5. The experiments reported by Deville *et al.* (*11*) were carried out for two regimes, low H and high H, with $H/T = 1.5 \times 10^{-3}$ and 25, respectively. The condition for multiple echoes for the full range of experimental conditions is

$$2\pi\gamma^2\hbar N T_2 \tanh\left[\frac{\hbar\gamma H}{2k_B T}\right] > 1. \qquad [18]$$

We would like to test the full range of the above condition by exploring the echoes as a function of H/T systematically from the linear region (high T, low H) to the high polarization limit for which the tanh factor saturates (high H, low T). These tests and detailed fits of both the amplitudes and the phases of the multiple echoes should provide reliable values of the true *memory* time, which is the motionally averaged T_2, and thereby test the models of quantum tunneling for the solid hydrogens. Deville *et al.* (*11*) have tested for the existence of multiple echoes in solid ^3He for both very low and very high values of H/T, but the theory of multiple echo formation has not been tested for other quantum solids. Systematic studies of the variation of the phase and the amplitude of the echoes needs to be carried out.

The detection of multiple echoes for ortho-H_2 molecules (total nuclear spin $I = 1$, orbital angular momentum $J = 1$) as impurities in solid para-H_2 would also be very interesting, but would not be observable in practice because of the *quenching* of the tunneling rates. This quenching results from the anisotropic interactions between the $J = 1$ molecules and the lattice which lead to a broad band of energy levels ($\Delta E \sim V_{aniso} \sim 1$ K). For tunneling for a molecule with a given orientation to a neighboring site where its new orientation will correspond to a different anisotropic interaction energy, only a small fraction of final states are allowed because of the conservation of energy. The effective tunnel-

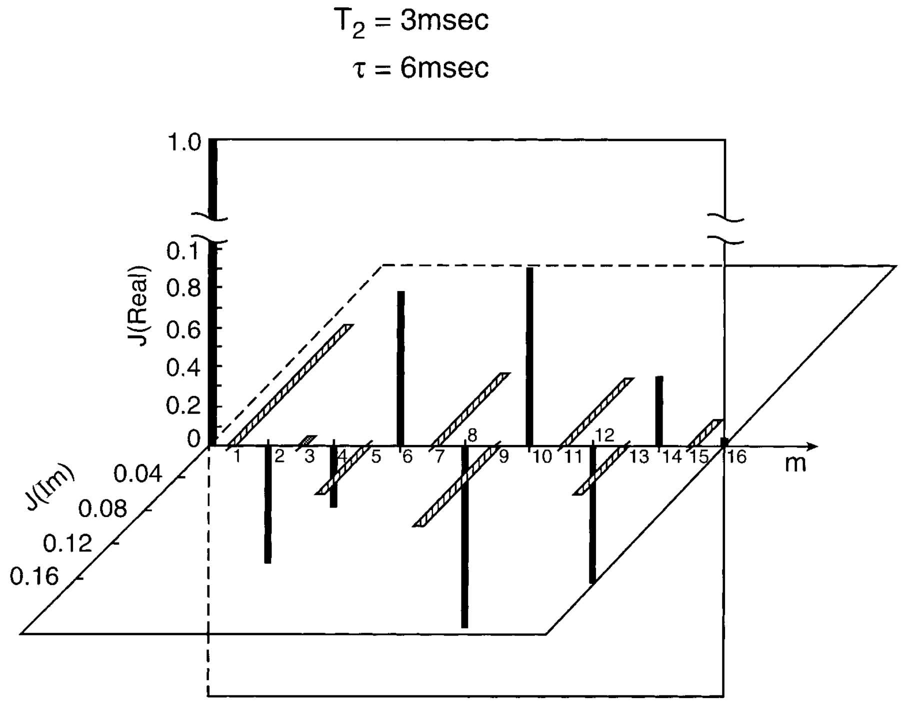

FIG. 5. Variation of the amplitude and the phase of the *m*th order multiple-echo response $I_m(\tau)$ for $\tau = 2$ and $T_2 = 6$ ms.

ing rate is therefore considerably reduced, with $J_{\text{ortho}} \sim 10^{-7} J_{\text{HD}}$. The rate is, however, nonzero and should contribute to the rate of formation of ortho pairs. The tunneling of para molecules cannot be observed by NMR because the total nuclear spin $I = 0$.

The observation of multiple echoes for HD or HT and a detailed analysis of the dependence of the amplitude and the phase on the order m of the echo would provide a valuable test for the existence of tunneling of isotopic impurities in solid para-H_2. Previous experiments have been limited to simple T_2 measurements and while distinct deviations from rigid-lattice behavior were observed, the interpretation of the results is uncertain because of the unreliability of the theory of relaxation in this system for very dilute mixtures. Multiple-echo formation, on the other hand, depends crucially on the local dynamics and the true microscopic lifetime of the transverse magnetization, thereby allowing one to determine if tunneling does occur.

CONCLUSION

Calculations have been carried out to determine the conditions for the formation of multiple echoes from HD molecules in solid para-H_2. The amplitude and phase of the echoes have been determined as a function of the order of the echo and the initial polarization. It is shown that the echoes depend strongly on the intrinsic *coherent* memory time for the transverse magnetization, and as a consequence can provide stringent tests for the existence of quantum tunneling of the HD molecules from site to site in the lattice. Such experiments would provide a crucial test of our current theory of tunneling in the quantum crystals. The theoretical models depend on the fact that the tunneling is limited by the amount of free space available for cyclical permutation of the particles. This free-space model leads to a prediction of observable tunneling for HD, in contrast to the results of the previous two-particle tunneling models.

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