Unique Deuteron Spin Echoes from HD and o-D_2 in Large Crystal Fields

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Novel deuteron multiple spin echoes are observed from HD and o-D_2 molecules trapped in hydrogenated amorphous-silicon samples. The echo locations result from the combined action of intramolecular quadrupole and dipole couplings. Using molecular-beam values of the interactions, the observed echo times are predicted to within a few percent. For o-D_2, the echoes demonstrate mixing of $I=0$ and $I=2$, $m=0$ states. The existence of the HD and o-D_2 echoes at low temperatures requires crystal-field admixture of higher J states into the rotational ground state of the molecules.

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We report the first observations of molecule-specific deuteron NMR (DMR) multiple spin echoes for HD and o-D_2 molecules. The molecules are trapped in an amorphous-silicon (a-Si) matrix and experience large crystal fields.

Solomon[1] described multiple echoes in the case of the spin $I > \frac{1}{2}$ and an electric quadrupole interaction. Because the $2I$ degenerate resonances are split by the quadrupole interaction, a spin can have different frequencies before and after the second pulse. That is, the spins will rephase faster or slower than they dephased. This leads to echoes at times $k\tau$ after the second pulse, with k taking on values other than unity. However, for spin 1 only $k=1$ echoes are predicted.

Figure 1 shows examples of the 90-τ-90 multiple echoes discovered for deuteron ($I=1$) nuclei in HD molecules in a-Si:D,H. The a-Si sample also contains H_2 and D_2 molecules, as well as a larger quantity of H and D atoms covalently bonded to silicon atoms in the amorphous framework. At 20.9 K the signal from the covalently bonded D has a much longer T_1 (1000 sec) than the deuterons of HD (5 sec). By acquiring data at a 0.6-sec recovery interval, only the signals from HD and D_2 contribute significantly in Fig. 1. The 500-μsec traces are averages of 8000 digitized acquisitions and start 80 μsec after the second rf pulse.

The pulse spacing τ in Fig. 1 is 204 μsec. The three echoes at times $k\tau$ after the second pulse with $k=0.56$, 1.00, and 1.78. The k values are constant for τ varying between 50 and 1000 μsec. The reciprocal relation $(1.78)^{-1}=0.56$ indicates that the observed echoes are Solomon-like. The HD $k\neq 1$ echoes have been observed in the silicon sample (H541) from 4 K to more than 200 K and in several other high-quality a-Si:D,H samples. The molecules responsible for the unique HD echoes in sample H541 correspond to one-eighth of the 4 at.% deuteron population in a high-quality plasma-deposited a-Si:D,H sample. The film sample (H541) was deposited at 0.12 W/cm^2 onto a 230°C Al substrate, subsequently removed with dilute HCl. The reaction gases were SiH_4 (4 sccm) and D_2 (76 sccm) at 0.7 Torr. The sample contained 4 at.% D and 5.8 at.% H, determined by DMR and by gas-evolution studies.

The relevant deuteron spin Hamiltonian of HD is

$$H/\hbar = -\gamma H_0 I_z + \mathbf{a}[I_z^2 - \tfrac{1}{3}I(I+1)] + \mathbf{b}I_z\,, \qquad (1)$$

where **a** and **b** depend on the rotational state of the molecule. The terms are the Zeeman and intramolecular

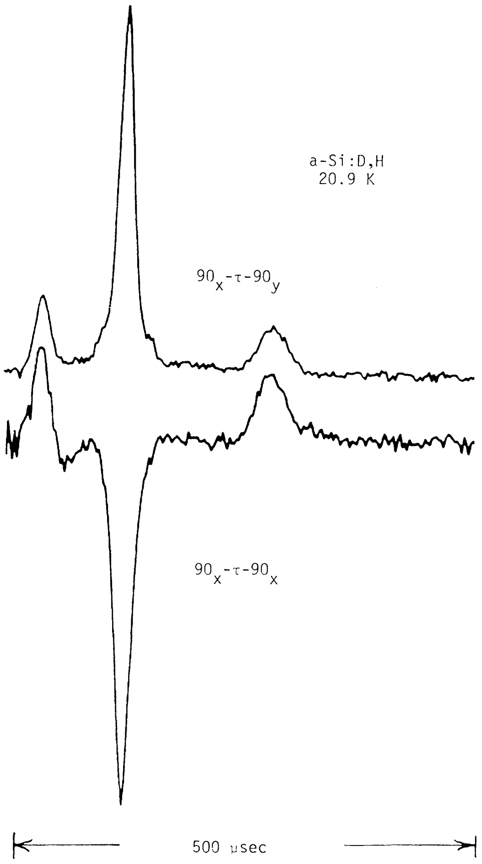

FIG. 1. Deuteron multiple echoes for HD in a-Si:D,H at 20.9 K. Two rf-pulse sequences are shown with $\tau=204$ μsec. The traces start 80 μsec after the second pulse.

quadrupole and dipole interactions, respectively. In what follows we assume the molecule is isolated from other nuclear spins so the proton spin state is fixed. The sign of $\mathbf{b}$ depends on the proton spin state. Defining $\omega_0 \equiv \gamma H_0$, the three deuteron energy levels are given by

$$E_1/\hbar = -\omega_0 + \mathbf{a} + \mathbf{b}\,, \quad E_0/\hbar = 0\,, \\ E_{-1}/\hbar = \omega_0 + \mathbf{a} - \mathbf{b}\,, \tag{2}$$

where terms involving $I(I+1)$ are dropped because they do not affect the transition frequencies. The transitions occur at

$$\omega_+ = \omega_0 + \mathbf{a} - \mathbf{b}\,, \quad \omega_- = \omega_0 - \mathbf{a} - \mathbf{b}\,. \tag{3}$$

The nuclear quadrupole moment interacts with an electric field gradient of intramolecular origin. The electric field gradient and the proton-deuteron dipole interaction are both second-rank tensors with the same axis of (uniaxial) symmetry. That is, the quadrupole and dipole interactions have the same angular dependence. Thus, the *ratio* $\mathbf{b}/\mathbf{a}$ will be constant although $\mathbf{a}$ and $\mathbf{b}$ have distributions of values, because of the various crystal-field environments of the HD molecules. The distribution of $\mathbf{a}$ and $\mathbf{b}$ values leads to the dephasing of the free induction decay. Because of the low temperatures and large rotational constant (64 K) of HD, quantum mechanics is required to describe the molecular orientations. Nevertheless, the ratio of $\mathbf{b}/\mathbf{a}$ will be the same for all molecules, whether they are in rotational eigenstates, are rapidly averaging between several rotational states, or are at sufficiently high temperatures for a classical description of orientation and rotation to be appropriate.

We note that both $\mathbf{a}$ and $\mathbf{b}$ are zero in the spherically symmetric $J=0$ state and also are zero when averaged over equally weighted m_j states for any fixed J. However, a crystal field acting on the molecule will produce a nonspherically weighted admixture of $J=2$ states into the $J=0$ ground state, thus leading to nonzero values of $\mathbf{a}$ and $\mathbf{b}$. This mechanism affects $\mathbf{a}$ and $\mathbf{b}$ in exactly the same way. However, the quantity $\mathbf{a}$ is also affected by the crystal field acting directly on the quadrupole moment of the deuteron. This direct effect is only about $\frac{1}{34}$ of the indirect effect acting through the rotational wave function, from our perturbation calculation starting with a $J=0$ ground state. This factor of 34 acts as an antishielding factor and is vital in producing the relatively invariant ratio $\mathbf{b}/\mathbf{a}$.

The times of the HD echoes can be obtained from the following simple, physical argument. A spin with an initial coherence at frequency ω_+ [Eq. (3)] accumulates phase $\omega_+\tau$ during the time τ between pulses. After the second pulse, the spin coherence will be at ω_- or ω_+. The quantum component that remains at the same frequency can only give rise to a $k=1$ echo. If the coherence switches to ω_-, the net phase ϕ at time t after the second pulse is

$$\phi = \pm\omega_+\tau + \omega_- t\,. \tag{4}$$

The ± sign indicates that the second pulse serves to phase invert part of the initial coherence, and leaves part unchanged. The detailed behavior depends upon pulse nutation angles and the relative rf phases of the pulses.

Echo locations are determined by the values of $k \equiv t/\tau$ for which ϕ is independent of $\mathbf{a}$ and $\mathbf{b}$ (but at fixed $\mathbf{b}/\mathbf{a}$ ratio; in HD, $|\mathbf{b}/\mathbf{a}| < 1$). Considering initial coherences at both ω_+ and ω_- and including cases in which the frequencies do and do not change at the second pulse, Eqs. (3) and (4) yield echoes at positive times given by

$$k = \frac{t}{\tau} = \frac{1-\mathbf{b}/\mathbf{a}}{1+\mathbf{b}/\mathbf{a}}\,,\ 1,\ \frac{1+\mathbf{b}/\mathbf{a}}{1-\mathbf{b}/\mathbf{a}}\,. \tag{5}$$

These correspond to the modified echo times described by Butterworth,[2] by Mehring and Kanert,[3] and by Boden *et al.*[4,5] for the addition of a dipolar term to the spin Hamiltonian. In their work, however, the dipolar term was not correlated to the quadrupolar term and produced a damping of the Solomon echoes rather than new echoes.

A density-matrix treatment predicts the same times for the multiple echoes. Following the application of two radio-frequency pulses (for which $\gamma H_1 \gg \mathbf{a}$ and $\mathbf{b}$, and characterized by a rotation operator R) the time evolution of the density matrix yields a deuteron free precession signal

$$S(t) = \sum_{m,m',m''} \langle m|R|m''\rangle\langle m'|R^{-1}|m+1\rangle\langle m''|\rho_{(0)}|m'\rangle \\ \times [I(I+1)-m(m+1)]^{1/2}\exp[i(t-\tau)\{(2m+1)\mathbf{a}+\mathbf{b}\}+i\tau\{\mathbf{a}(m'+m'')+\mathbf{b}\}(m'-m'')]\,. \tag{6}$$

The free precession signal will be nonzero and echoes can occur at times t following the second pulse such that[2] S is independent of $\mathbf{a}$ and $\mathbf{b}$ at fixed $\mathbf{a}/\mathbf{b}$,

$$k = \frac{t}{\tau} = \frac{[\mathbf{a}(m'+m'')+\mathbf{b}](m''-m')}{\mathbf{a}(2m-1)+\mathbf{b}}\,. \tag{7}$$

For allowed echoes $m''-m=\pm 1$ and for $I=1$ this yields allowed echoes at the times given in Eq. (5) above. The relative widths of these echoes are predicted to be

$$1-\mathbf{b}/\mathbf{a}\,,\ 1,\ 1+\mathbf{b}/\mathbf{a}\,. \tag{8}$$

Molecular-beam measurements by Code and Ramsey[6] have determined $\mathbf{a}$ and $\mathbf{b}$ for isolated HD in the $J=1$, $m=0$ state to be $\mathbf{a}=33.681$ kHz and $b=8.880$ kHz. With these couplings Eq. (5) predicts echoes at k values of 0.583, 1, and 1.716. The good agreement with the observed echoes at $k=0.56$, 1.00, and 1.78 demonstrates that the $k\neq 1$ echoes do arise from HD molecules. The ~4% difference between the observed and predicted echo formation times probably reflects the $\frac{1}{34}$ direct quadrupolar factor discussed above. A 3% reduction of **a** in the ratio **a**/**b** produces a 2% increase in the satellite-echo $k > 1$ value predicted for HD by Eq. (5). The negative signal just before the large $k=1$ echo in Fig. 1 is part of a $\Delta m=2$ forbidden echo which occurs at $k=2\mathbf{b}/(\mathbf{a}-\mathbf{b})$.

The $k\neq 1$ echoes should only occur when the HD proton spin state is constant for times of order 2τ or longer. Nearby protons in HD or H_2 molecules or covalently bonded to silicon can produce proton-spin-state interchanges (flip-flops) because of their mutual dipole interaction. The damping of the $k\neq 1$ echoes as τ is increased occurs with an envelope $T_2 \sim 600$ μsec in sample H541 near 15 K. This T_2 could arise from a proton located on the average 5 Å away from the HD.

The density-matrix calculation of the echoes formed under the Hamiltonian of Eq. (1) indicates that, for a 90° relative phase shift between the rf pulses, all three echoes have the same polarity, as at the top of Fig. 1. For pulses of the same rf phase, the $k\neq 1$ echoes are of the opposite polarity from the $k=1$ echo, as at the bottom of Fig. 1. The sum of the calculated amplitudes for the three like-phase echoes is predicted to be zero, when extrapolated to $\tau=0$. The experimental amplitudes do not add to zero, showing that the $k=1$ echo arises in part from deuteron spins not in HD molecules. The echo intensities are all predicted and observed experimentally to vary as $\sin^2\theta$, where θ is the nutation angle of the second pulse.

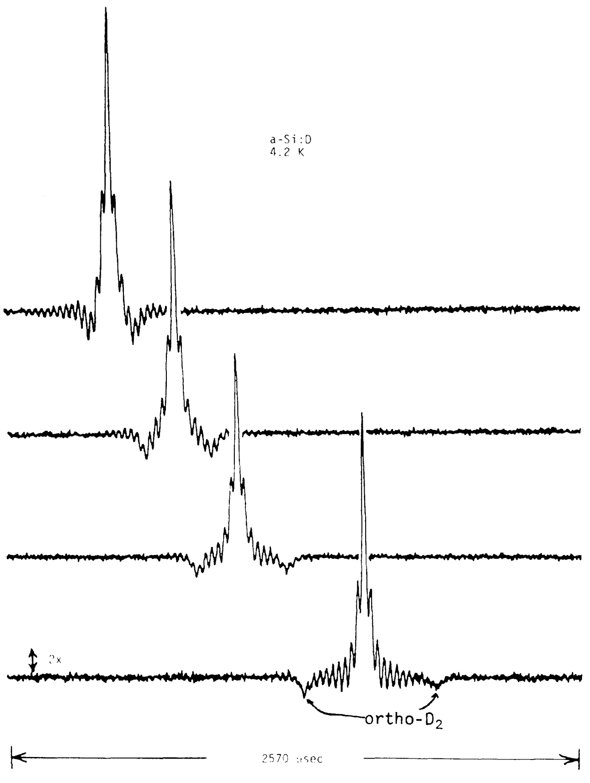

FIG. 2. Deuteron multiple echoes from o-D_2 in a-Si:D with τ values 600, 900, 1200, and 1800 μsec. The pulse sequence is 90_x-τ-24_y. The beats on the main echo arise from p-D_2.

Multiple echoes with $k\neq 1$ are also observed for an amorphous-silicon sample prepared exclusively with deuterium, as shown in Fig. 2. The sample was deposited from SiD_4 by F. Jansen and M. Machonkin at the Xerox Webster J. C. Wilson Center. We attribute these echoes to o-D_2 (even J). The odd-J p-D_2 has total nuclear spin 1 and can only give rise to a single echo at $k=1$. Because the magnetic moment of the deuteron is smaller than that of the proton, one expects the o-D_2 k values to be closer to unity than in HD. Indeed, the observed k values in Fig. 2 are 0.85, 1, and 1.19. The transients in Fig. 2 are the sums of 256 digitized acquisitions (except for the $\tau=1800$-μsec trace, which is 512 acquisitions) with a 30-sec recovery time. The displayed sweeps are 2570 μsec long and start 84 μsec after the second rf pulse in a 90_x-τ-24_y sequence.

The reasoning leading to Eq. (5) is not correct for o-D_2, where *like* spins are dipolar coupled. The molecule with even J is symmetry restricted to states of total nuclear spin 0 and 2. It has been common to treat the $I=0$ and $I=2$ fractions as independent and uncoupled. For many purposes this gives correct answers. However, for the present experiment it is completely wrong: The $I=2$ component alone would give rise to the Solomon echoes at $k=\frac{1}{3}$, 1, and 3, quite different from the observed values.

The Hamiltonian for the two deuterons is

$$\begin{aligned}H/\hbar = &-\gamma H_0 I_{1z} - \gamma H_0 I_{2z} + \mathbf{a} I_{1z}^2 + \mathbf{a} I_{2z}^2 \\ &+ \mathbf{b}\left(I_{1z}I_{2z} - \tfrac{1}{4} I_{1+}I_{2-} - \tfrac{1}{4} I_{1-}I_{2+}\right). \qquad (9)\end{aligned}$$

Here the like-spin dipole interaction includes transverse or "flip-flop" terms. The two spins have the same quadrupole interaction **a**, by symmetry. Since $\gamma H_0 \gg 2\pi|\mathbf{a}|$ and $|\mathbf{a}|$ exceeds $|\mathbf{b}|$ by a factor ~ 10, we first treat the Zeeman and quadrupole interactions, leaving the spins uncoupled. Using ordered pairs to denote the m states of each spin, the states and energies are the following:

$$\begin{aligned}&\psi_2 = (1,1)\,, \quad E_2/\hbar = -2\omega_0 + 2\mathbf{a}\,, \\ &\psi_1 = (1,0) + (0,1)\,, \quad E_1/\hbar = -\omega_0 + \mathbf{a}\,, \\ &\psi_x = (1,-1) + (-1,1)\,, \quad E_x/\hbar = 2\mathbf{a}\,, \\ &\psi_y = (0,0)\,, \quad E_y/\hbar = 0\,, \\ &\psi_{-1} = (-1,0) + (0,-1)\,, \quad E_{-1}/\hbar = \omega_0 + \mathbf{a}\,, \\ &\psi_{-2} = (-1,-1)\,, \quad E_{-2}/\hbar = 2\omega_0 + 2\mathbf{a}\,.\end{aligned} \qquad (10)$$

The omitted antisymmetric combinations of spin states are those for total spin 1, p-D_2. The four states in Eq. (10) with total $m\neq 0$ are just states of total spin 2. ψ_x and ψ_y are linear combinations of $I=0$ and $I=2$, $m=0$. The six $\Delta m = \pm 1$ transitions in Eq. (10) all have frequencies $\omega_0 \pm \mathbf{a}$; thus only $k=1$ echoes can be formed, as expected for uncoupled spins 1.

The dipole interaction is treated in nondegenerate first-order perturbation (the splitting of 2**a** between ψ_x and ψ_y is large compared to **b**). The new energies are[7]

$$E_2/\hbar = -2\omega_0 + 2\mathbf{a} + \mathbf{b}\,,\quad E_1/\hbar = -\omega_0 + \mathbf{a} - \mathbf{b}/2\,,$$
$$E_x/\hbar = 2\mathbf{a} - \mathbf{b}\,,\quad E_y/\hbar = 0\,, \tag{11}$$
$$E_{-1}/\hbar = \omega_0 + \mathbf{a} - \mathbf{b}/2\,,\quad E_{-2}/\hbar = 2\omega_0 + 2\mathbf{a} + \mathbf{b}\,.$$

$\Delta m = \pm 1$ transitions all can be shown[7] to have the same order-of-magnitude matrix elements. The frequencies are now $\omega_0 \pm (\mathbf{a} + 3\mathbf{b}/2)$ and $\omega_0 \pm (\mathbf{a} - \mathbf{b}/2)$. Unlike the HD case, **b** has only one sign.

Using these frequencies for ω_+ and ω_- in Eq. (4) yields predicted echoes at

$$k = \frac{t}{\tau} = \frac{1+3\mathbf{b}/2\mathbf{a}}{1-\mathbf{b}/2\mathbf{a}}\,,\ 1,\ \frac{1-\mathbf{b}/2\mathbf{a}}{1+3\mathbf{b}/2\mathbf{a}}\,. \tag{12}$$

A density-matrix calculation yields the same result. The **a** and **b** values for D_2 are $\mathbf{a} = 33.681$ kHz and $\mathbf{b} = 2.719$ kHz, yielding predicted echoes at $k = 0.855$, 1, and 1.169. This agrees with the observations to within $\sim 2\%$. The crystal-field direct effect on **a** and **b**/**a** corresponds to a small shift in the satellite-echo k values predicted for o-D_2 by Eq. (12). The remarkable echoes provide an unambiguous signature of o-D_2 molecules. Damping of the $k \neq 1$ echoes (Fig. 2) shows that the molecules are isolated on a time scale of the envelope dipolar T_2, here about 2 msec.

Clearly, the $k \neq 1$ echoes in HD and o-D_2 cannot occur in the spherically symmetric $J = 0$ state, because **a** and **b** both would vanish. Since the echoes are observed at low temperatures (well below the $J = 0$ to $J = 1$ splitting), the molecules are in their rotational ground states. The ground states must have admixtures of higher J states. Thus, we infer that the molecules are located in sites with substantial crystal fields in the amorphous silicon. The Fourier transform of the $k \neq 1$ echoes has a full width at half maximum near 35 kHz. This requires the admixture coefficient of $J = 2$ states to be of order $\frac{1}{3}$.

The $k \neq 1$ echoes in HD and o-D_2 arise from the combined action of quadrupole and dipole interactions in each molecule. Because the two interactions have the same angular dependence, the echoes are present in "powder average" as well as with partial motional narrowing. The analysis of the echoes in o-D_2 emphasizes that the $I = 0$ and $I = 2$ nuclear spins are coupled by the degenerate $m = 0$ levels. Such echoes may occur in other spin systems. The $k \neq 1$ echoes can generate serious distortions in line shapes obtained by Fourier transformation of the $k = 1$ echo.

The spectroscopically unique deuteron multiple echoes provide a definitive signature for HD and o-D_2 molecules trapped in the presence of large electric field gradients. The $k \neq 1$ echoes arise from that part of the amorphous-silicon DMR spectrum previously identified as the broad central component (the weakly bound fraction) which is observed in high-quality deuterated a-Si samples and which disappears upon post-deposition annealing to 350 °C. The population of translationally immobile and rather isolated HD and D_2 apparently goes into an increasing population of more mobile molecules in microvoids which appear in the annealed and deteriorated samples. The new multiple echoes may be particularly useful for the study of HD and o-D_2 adsorbed on surfaces and contained in porous media.

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