Dynamic Tunneling Polarization as a Quantum Rotor Analogue of Dynamic Nuclear Polarization and the NMR Solid Effect

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The populations of the tunneling states of CH_3 are manipulated by rf irradiation of weakly allowed sideband transitions within the manifold of tunneling-magnetic levels. Substantial positive and negative CH_3 tunneling polarizations are observed, providing a quantum rotor analogue of dynamic nuclear polarization and the solid effect in NMR. The field-cycling NMR technique used in the experiments employs level crossings between tunneling and Zeeman systems to report on the tunneling polarization. The tunneling lifetimes are measured and the field dependence investigated.

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Nuclear spin isomers are identified in symmetric molecules that possess identical nuclei with finite spin. They arise as a result of the antisymmetry principle which is the most general form of the Pauli exclusion principle (PEP). A well-known case is that of molecular hydrogen with its spin isomers of orthohydrogen (o-H_2) and parahydrogen (p-H_2), the former having total nuclear spin $I = 1$ while the latter has $I = 0$. Because of the entanglement of space and spin degrees of freedom, spin isomers are distinct species that generally possess little capacity to interconvert. The transitions that would enable them to equilibrate are spin restricted and can only be mediated by a time dependent magnetic interaction connecting space and spin. Therefore, in practice it can be challenging to manipulate the relative proportions of spin isomers present in a material in a prescribed manner, although one may envisage situations in which it would be desirable to do so. For example, a spin isomer can act as a store of energy and angular momentum that could be made available as an agent to hyperpolarize nuclear spins to enhance the sensitivity of NMR [1–6]. Alternatively, analogous to singlet states [7], they may be used as long-lived storage reservoirs of nuclear spin order.

We will describe experiments that facilitate a customized manipulation of the populations of two spin isomers. These are the spin-symmetry species of methyl rotors, CH_3, labeled A and E. In addition to the PEP, this system exhibits another quantum effect with the two species being separated in energy by a quantum tunneling splitting $\hbar\omega_t$. The spin-symmetry species have very long lifetimes, and interconversions are accompanied by a change in nuclear spin state. By rendering the interproton dipole-dipole interaction time dependent, it has proved possible to drive transitions between the A and E species directly using radio frequency radiation [8]. We shall show how, by suitable design of the experiment, this can result in a dynamic polarization of CH_3 spin-symmetry states, analogous to dynamic nuclear polarization in NMR. Depending upon the experimental conditions, the rf field may pump either $A \rightarrow E$ or $E \rightarrow A$ transitions, so the long-lived states created exhibit population inversion as well as positive excursions from equilibrium.

The existence of spin isomers is a quantum effect that has no classical analogue. The phenomenon is associated with the rotational energy of a molecule, naturally connected with its symmetry properties. For example, the ground states of o-H_2 and p-H_2 are split in energy by twice the rotational constant. While H_2 is a three-dimensional rotor, the rotations of CH_3 are constrained by the molecular structures in which they are found, so their rotation is one dimensional with the hydrogen atoms being confined to a plane. The spin-symmetry species have symmetry properties isomorphous with the group C_3 and are labeled A and E according to the irreducible representations [9]. The rotation of the CH_3 rotor is generally hindered by a potential barrier determined by interatomic interactions of H with the molecular environment. At low temperature the CH_3 rotation is governed by quantum tunneling through the barrier with the angular frequency ω_t. The latter is an exponential function of the barrier height and is therefore characteristic of a particular material. Whereas in H_2 the energy splitting between spin isomers is governed by the rotational constant of order 2 THz, the splitting between the spin-symmetry species of CH_3 is governed by a tunneling interaction and can vary in the range 100 GHz to <1 kHz [10].

Because of space-spin entanglement a change in spin-symmetry state involves simultaneous changes in space and spin eigenfunctions. Therefore, on its own, electromagnetic radiation does not have the requisite symmetry properties to mediate such transitions. However, the nuclear dipole-dipole interaction does have the required properties, being determined by products of space and spin variables [11]. By operating at low field, where the applied static B field, the rf field, and the dipolar field all have similar magnitude, spin forbidden transitions are observed to become weakly allowed [8], enabling $A \leftrightarrow E$ transitions to be driven in response to rf irradiation.

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A schematic of the CH_3 energy levels is shown in Fig. 1. The A species is a nuclear spin quartet with spin $I = 3/2$ and there are two degenerate E species labeled E^a and E^b which are nuclear spin doublets with spin $I = 1/2$. The A and E species exhibit the splitting $\hbar\omega_t$, while the magnetic energy levels fan out in proportion to the applied B field, displaying the Zeeman splitting $\hbar\omega_Z$ where ω_Z is the ^{1}H Larmor frequency. As a consequence of the zero field splitting, $\hbar\omega_t$, it transpires there are two special B-field values where the magnetic levels (anti)cross. These occur where $\omega_Z = \omega_t$ and $\omega_Z = \omega_t/2$ [12,13].

We define the tunneling polarization as the population difference of the A and E species,

$$P_{\text{tun}} = (p_A - p_E)/(p_A + p_E).$$

Given the longevity of these tunneling states, we may define the inverse tunneling temperature β_{tun} of the tunnel system in terms of these populations using Boltzmann statistics. The ^{1}H spin polarization P_Z together with the inverse Zeeman temperature β_Z may be defined similarly in terms of the populations of the $m_I = \pm 1/2$ Zeeman levels.

While the tunneling polarization P_{tun} is an important property of the spin-isomer system, it is not one that is readily accessible to direct measurement. In contrast, the Zeeman polarization P_Z can be readily measured using pulsed NMR. The aim is to manipulate the spin-isomer populations by electromagnetic irradiation and to detect those changes in a measurement. The experiments described here are designed to utilize the level crossings as the means of detecting the tunneling polarization. First, the ^{1}H spins are polarized in high field, which creates a population gradient among the ^{1}H Zeeman levels. This order can then provide the reservoir that drives differences in spin-isomer population when pumping specified tunneling-magnetic transitions within the manifold of levels depicted in Fig. 1. To observe P_{tun} the ^{1}H Zeeman polarization is first saturated, destroying Zeeman order and rendering $P_Z = 0$. Then the tunneling and Zeeman systems are brought into contact by tuning the applied static field to a level crossing. Here the ^{1}H spins can act as a proficient sensor of P_{tun} as polarization in the tunneling system is transferred to the previously saturated ^{1}H Zeeman system. A measurement of P_Z then accurately reports that value of the tunneling polarization.

The experiment is founded in field-cycling NMR where field switches are adiabatic [14]. To manipulate the spin-isomer populations requires the facility to make rapid adjustments to the magnitude of the applied B field in concert with secondary rf irradiation at the frequency ω_{rf}. The latter is applied using broadband Helmholtz coils. The applied B field is provided by a superconducting solenoid with low inductance, enabling switches between field values at the rate 1.5 T s^{-1}.

The field-cycling pulse sequence is shown in Fig. 2 and comprises the following steps. (1) ^{1}H polarization is set to zero using a burst of $\pi/2$ pulses at the resonant field B_{NMR}. (2) The ^{1}H spins are polarized for the time τ_{pol} at the field B_{pol}. (3) The applied field is reduced to the low-field value B_{lf} where the sample undergoes rf irradiation at the frequency ω_{rf} for the time τ_{lf}. (4) The field returns to B_{NMR} where the ^{1}H polarization is destroyed. (5) The field is set to the level-crossing field B_{LC} for the time τ_{LC} where the Zeeman and tunneling systems equilibrate and tunneling order is converted to Zeeman order. (6) The tunneling polarization created during step (3) is monitored by a measurement of the ^{1}H spin polarization using a $\pi/2$ pulse.

To record a spectrum the sequence was repeated with a sequential scan of ω_{rf}. The sample studied was 2-butanone at 4.2 K with tunnel frequency $\omega_t/2\pi = 492$ kHz [15].

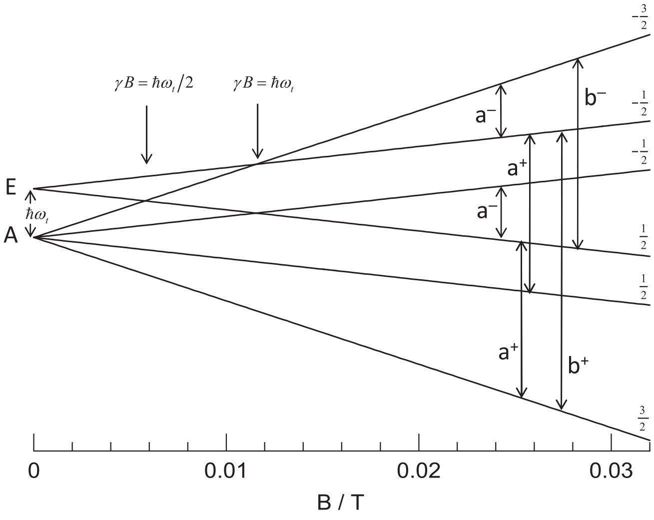

FIG. 1. The tunneling-magnetic energy levels of CH_3 identifying the level crossings and the "forbidden" sideband transitions that interconvert spin-symmetry species.

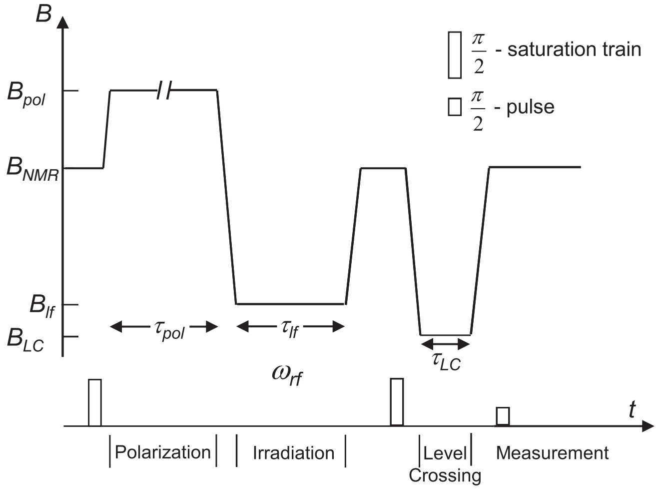

FIG. 2. The DTP field-cycling NMR pulse sequence.

The spectrum recorded using the field $B_{\mathrm{lf}} = 0.028$ T is shown in Fig. 3 where the polarization time was $\tau_{\mathrm{pol}} = 270$ s at the field $B_{\mathrm{pol}} = 1$ T. The level-crossing field is $B_{\mathrm{LC}} = \hbar\omega_t/\gamma = 0.0115$ T. The rf irradiation time was $\tau_{\mathrm{lf}} = 5$ s and $\tau_{\mathrm{LC}} = 2$ s. Positive and negative peaks are observed in the spectrum which plots the ^{1}H polarization in inverse temperature units, defined at the field B_{LC}. The peak at 697 kHz (labeled a^-) is positive, coinciding with rf irradiation at the "negative" tunneling sideband $\omega_Z - \omega_t$. Here the rf irradiation pumps $E \rightarrow A$ transitions, leading to a net cooling of the tunneling system; see Fig. 1. Its partner peak at 1680 kHz (labeled a^+) is negative and coincides with rf irradiation at the "positive" tunneling sideband $\omega_Z + \omega_t$ where $A \rightarrow E$ transitions are pumped leading to a net heating of the tunnel system and population inversion. The nonequilibrium tunnel states created are long lived and the information on their state that is "readout" by level-crossing transfer of polarization to the ^{1}H Zeeman system results in the observed spectrum. The effect is reminiscent of dynamic nuclear polarization and indeed is analogous to the solid effect [11,16] where transitions are conventionally pumped between the levels of two coupled Zeeman systems. In this new experiment the irradiation pumps polarization within the tunnel system, so we assign the phrase dynamic tunneling polarization (DTP) to describe it.

Another pair of DTP features appears centered on the $\Delta m = \pm 2$ spectrum. The positive peak at 1882 kHz (labeled b^-) arises from pumping $E \rightarrow A$ transitions at the negative tunneling sideband $2\omega_Z - \omega_t$. Its negative partner at 2865 kHz (labeled b^+) arises from pumping $A \rightarrow E$ transitions at the positive tunneling sideband $2\omega_Z + \omega_t$. Other features in the spectrum will be discussed later.

The ^{1}H spin-lattice relaxation time at $B_{\mathrm{pol}} = 1$ T is approximately $T_1 = 2600$ s, so with $\tau_{\mathrm{pol}} = 270$ s the initial ^{1}H polarization is 23% of equilibrium. Larger tunneling polarizations can be achieved when the ^{1}H polarization times are of order T_1. In Fig. 3 another spectrum has been recorded in the immediate vicinity of the DTP peaks using polarization times $\tau_{\mathrm{pol}} = 2000$ s which provides ^{1}H polarization of 61% of equilibrium. The DTP peaks are proportionally more intense. With initial ^{1}H polarization 2.65 times larger, the DTP peaks a^-, a^+, and b^- are 2.62 times more intense while b^+ is 3.4 times more intense. In a further series of experiments, the DTP intensity of peak b^- has been monitored as a function of τ_{pol} and it faithfully mirrors a curve of initial ^{1}H Zeeman polarization versus time.

The lifetime of the tunneling states has been investigated in an adaptation to the DTP field-cycling sequence. A relaxation interval τ_{rel} at the field B_{rel} was inserted between the end of the rf irradiation period and the saturation of the ^{1}H spins. During this interval the nonequilibrium tunneling polarization could relax. By monitoring the amplitude of DTP peak b^- as a function of τ_{rel}, a measure of the tunneling lifetime T_{tun} was obtained. In Fig. 4 the data recorded at three B_{rel} values are presented. The DTP peak amplitude decays with increasing τ_{rel} exhibiting only small deviation from exponential behavior. There is a systematic dependence upon relaxation field. Fitting to an exponential decay, we obtain $T_{\mathrm{tun}} = 4200$ s at $B_{\mathrm{rel}} = 0.799$ T and $T_{\mathrm{tun}} = 1085$ s at 0.029 T. These values are approximately twice the ^{1}H T_1's measurement. The measurement at 0.019 T with $T_{\mathrm{tun}} = 70$ s is within the level-crossing region that we will consider next.

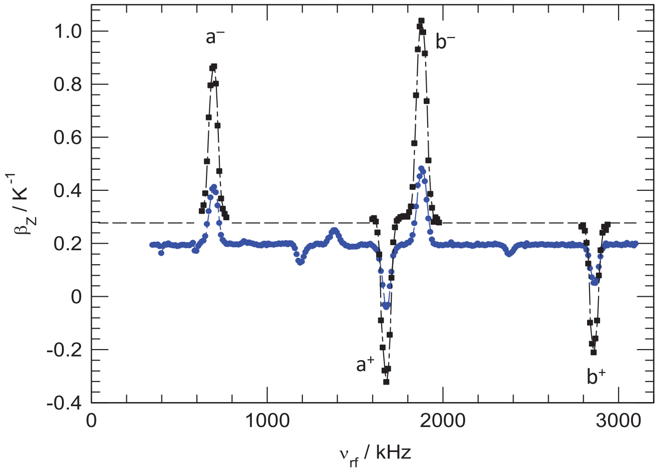

FIG. 3 (color). The DTP spectrum of 2-butanone, where β_Z reports the tunneling polarization of CH_3 following equilibration of tunneling and Zeeman systems at the level crossing. Strong positive and negative peaks in tunneling temperature are observed, centered on the $\Delta m = \pm 1, \pm 2$ NMR transitions. (●) $\tau_{\mathrm{pol}} = 270$ s; (■) $\tau_{\mathrm{pol}} = 2000$ s. $B_{\mathrm{lf}} = 0.028$ T

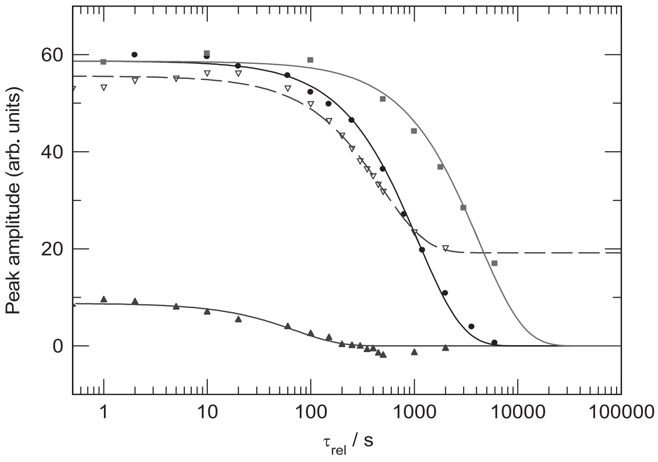

FIG. 4. The relaxation of the tunneling system measured as a function of τ_{rel} via the amplitude of the b^- DTP peak. (■) $B_{\mathrm{rel}} = 0.799$ T; (●) $B_{\mathrm{rel}} = 0.029$ T; (▲) $B_{\mathrm{rel}} = 0.019$ T. The baseline of the $B_{\mathrm{rel}} = 0.019$ T spectrum (▽) is significantly higher as the relaxation is conducted within the level-crossing region.

The amplitude of the b^- DTP peak has been monitored as a function of the field B_{LC}. As expected, the amplitude peaks at 0.0115 T where $\gamma B_{\mathrm{LC}} = \hbar\omega_t$, and at fields outside the level-crossing region there is no DTP effect. The extension of the level-crossing region to fields corresponding to $\gamma B_{\mathrm{LC}} = 2\hbar\omega_t$ is unexpected. This feature indicates the existence of a coupling between two CH_3 rotors [17,18]. That such a coupling exists is reinforced by the observation of a DTP peak at $2\omega_Z - 2\omega_t = 1384$ kHz in Fig. 3. It is established experimentally that the tunnel-Zeeman level-crossing contact is fast on the time scale of the field switches.

Given that the relative heat capacity of Zeeman and tunneling systems is of order 6–8 (including nonmethyl ^{1}H) at the level crossing, we estimate that the peak inverse tunneling temperatures achieved in Fig. 3 during rf irradiation are of order $\beta_{\mathrm{tun}} \approx \pm 6\ \mathrm{K}^{-1}$. Approximately 30% larger tunneling polarizations have been achieved by preparing initial ^{1}H Zeeman states at equilibrium at 1 T, and higher polarizations still can be achieved with higher field and lower temperature. The lifetimes of the tunneling states are longer than, but still of the order of, the ^{1}H T_1, which probably reflects the similar role played by the fluctuating local dipolar field in both relaxation mechanisms. However, to quantify this effect will require more detailed investigation due to the multiexponential character. We have shown how, using resonant pumping, substantial, long-lived nonequilibrium tunneling populations may be created, including inversion. This principle may have applications in schemes involving this and other spin-isomer systems, exploiting the entanglement of space and spin and the PEP in developing methods to hyperpolarize nuclear spin systems.

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