Indirect Phase Detection of NMR Spinor Transitions

D. Suter and A. Pines
Department of Chemistry, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

M. Mehring
Physikalisches Institut II, Universität Stuttgart, D-7000 Stuttgart, West Germany
(Received 14 April 1986)

The behavior of quantum mechanical state functions under selective rotations is discussed. If a two-level transition is phase shifted with composite z pulses, the component state function shared with a connected transition can be multiplied by i, thereby shifting the corresponding coherence into an orthogonal channel. Application to the sensitive indirect detection of NMR transitions is demonstrated.

PACS numbers: 76.70.Dx, 03.65.Bz, 76.70.Fz

If a half-integer spin is rotated through an angle 2π it does not return to its original state, but its state function is multiplied by -1. According to the analogy of Feynman, Vernon, and Hellwarth[1] the same holds for any two-level system. Although this change of sign is not observable in an isolated particle, it can be observed if the two levels are part of a larger system. The effect has been demonstrated in neutron interferometry,[2,3] molecular-beam resonance,[4] and nuclear magnetic resonance (NMR) interferometry.[5] In addition it has been shown recently that this spinor rotation may be utilized for enhanced-sensitivity electron-nuclear double-resonance (ENDOR) experiments.[6] The typical situation is depicted in Fig. 1. Suppose we wish to detect the NMR transition 2-3 by means of its effect on transition 1-2 which may be an electron-spin resonance (ESR) or optical transition, or another NMR transition. The experiment, shown schematically in Fig. 2(b), starts with the preparation of a coherent superposition of states $|1\rangle$ and $|2\rangle$, followed by a pulse on the 2–3 transition which rotates the state vector through 2π rad.[1] The associated sign change inverts the coherence in transition 1–2, thereby changing the detected signal amplitude by -200%. In crowded ESR spectra, however, the ESR transition which is used in the ENDOR experiment often coincides with resonances of electrons which are not coupled to nuclear spins and therefore create an unmodulated background signal which makes the observation of the spinor-ENDOR effect less sensitive. We propose here to circumvent this problem by a modified experiment which does not affect the amplitude, but the phase of the 1-2 signal. By use of phase-sensitive detection it is then possible to observe exclusively those electrons which are coupled to nuclear spins.

The scheme is described by Fig. 2(c). The coherent superposition and echo of states $|1\rangle$ and $|2\rangle$ may be written

$$\Psi = c_1|1\rangle + c_2|2\rangle. \tag{1}$$

In Fig. 2(b), showing the normal spinor-ENDOR experiment,[6] the 2-3 transition is rotated by 2π before the echo, thereby multiplying the coefficient of state function $|2\rangle$ by -1,

$$c_2|2\rangle \rightarrow -c_2|2\rangle, \tag{2}$$

and so inverting the 1-2 coherence.

Suppose, however, that we rotate transition 2-3 by an angle ϕ around its z axis. This corresponds to a phase shift of the 2-3 transition by ϕ and may be accomplished by a composite pulse,[7] off-resonance irradiation, or differential precession.[3] The effect on c_2 in

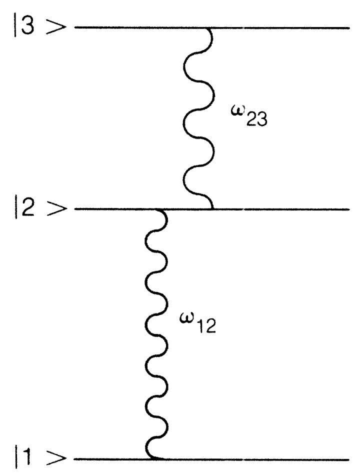

FIG. 1. Energy-level scheme of the totally symmetric part of a dipolar-coupled system of two spins $\frac{1}{2}$, equivalent to a single spin 1. A similar energy-level scheme applies also to spinor-ENDOR effect.

the 1-2 superposition is then

$$c_2|2\rangle \rightarrow e^{i\phi/2}c_2|2\rangle. \quad (3)$$

If $\phi=\pi$, as in Fig. 2(c), the 1-2 coherence is shifted by $-\pi/2$ into the orthogonal, otherwise empty detection channel:

$$\Psi=c_1|1\rangle+ic_2|2\rangle. \quad (4)$$

With use of phase-sensitive detection, it is therefore possible to observe in one of the two channels exclusively magnetization from transitions which are coupled to the irradiated NMR transitions. The effect could also be observed on the 1-3 transition, which is phase shifted by $+\phi/2$.

An NMR version of the experiment was performed as follows. The system of Fig. 1 was used, consisting of the totally symmetric part of two magnetically equivalent protons, coupled by dipolar interaction. This system allows observation not only of transition 1-2, but also the irradiated transition 2-3, and thereby direct experimental comparison of the effect of the phase shift on the two transitions. The experimental scheme of Fig. 2(c) with variable ϕ was applied. The nonselective $(\pi/2)_y$ pulse creates 1-2 coherence. After free precession for a time τ and a nonselective π pulse the density operator of the system is given by

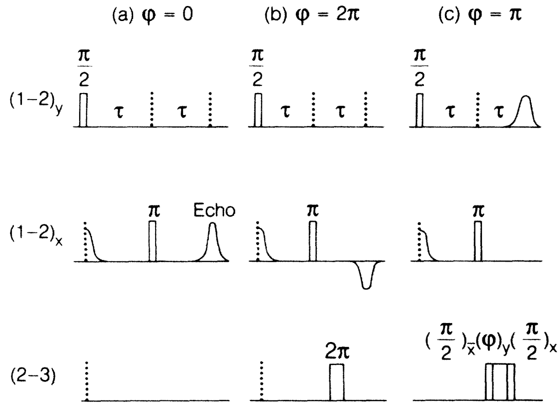

FIG. 2. Experimental scheme used for indirect phase detection of NMR spinor transitions. The top row shows pulses and signals in the y channel of the 1-2 transition, the second row corresponds to the x channel, and the bottom row shows the pulses applied to the 2-3 transition. (a) Spin-echo sequence applied to transition 1-2. The excitation pulse is applied along the y axis; echo pulse and signal appear in the x channel. (b) Spinor-ENDOR effect: During the spin-echo sequence a 2π pulse is applied to the 2-3 transition; its effect on the 1-2 transition is an inversion of the echo signal. (c) Application of a composite z pulse onto the 2-3 transition can shift the echo signal from the $(1\text{-}2)_x$ into the otherwise empty y channel.

$$\rho(\tau+)=\exp(-i\pi S_x)\exp(-iH\tau)S_x\exp(iH\tau)\exp(i\pi S_x), \quad (5)$$

where the three-level system is described as a virtual spin 1. During the second half of the experiment we apply a composite z pulse selectively to the 2-3 transition. At the time of the echo we therefore have

$$\rho(2\tau)=\exp(-iH\tau)\exp(-i\phi S_z^{(2\text{-}3)})\rho(\tau+)\exp(i\phi S_z^{(2\text{-}3)})\exp(iH\tau), \quad (6)$$

which is evaluated as

$$\rho(2\tau)=\sqrt{2}[S_x^{(1\text{-}2)}\cos(\phi/2)-S_y^{(1\text{-}2)}\sin(\phi/2)+S_x^{(2\text{-}3)}\cos(\phi)+S_y^{(2\text{-}3)}\sin(\phi)], \quad (7)$$

showing the ϕ shift in 2-3 and the $-\phi/2$ shift in 1-2. The resulting spectra are shown in Fig. 3 together with the amplitude of the echo signal in the y channel of the 1-2 transition, which is empty if no phase shift or 2-3 irradiation is applied. The observed amplitudes and phases agree well with the theoretical expression if the inhomogeneity of the rf field is taken into account.

In summary, we have shown that it is possible to change the phase of coherence by applying a composite z rotation to a connected transition. This experimental scheme may be used for indirect detection in a variety of applications such as ENDOR, indirect detection of low-γ nuclei, multiple quantum transitions,[8] or optically detected magnetic and optical transitions.[9,10] The technique allows indirect detection with high sensitivity since the signal which is obtained, as in the case of spinor-ENDOR experiment, is independent of the population difference across the irradiated 2-3 transition. Prerequisites for its applicability are a relaxation time of the 1-2 transition longer than the time needed to perform the z rotation and quadrature detection of the echo signal. Alternative methods to shift the phase of the 2-3 transition include two π pulses, phase shifted by $(\pi-\phi)/2$ or separated by a period of free precession. In the latter case the phase shift is proportional to the resonance offset of the π pulses and the length of the free-precession period. This may therefore be the evolution time of a two-dimensional experiment which would combine high sensitivity with high resolution, avoiding the power broadening of the original method.[6,11] The technique may also be used for spectral assignment and the sign of the observed phase shift contains information about the connectivity of the transitions. Generalization to spins (or pseudospins) $S>\frac{1}{2}$ is also possible.[5] While half-integer

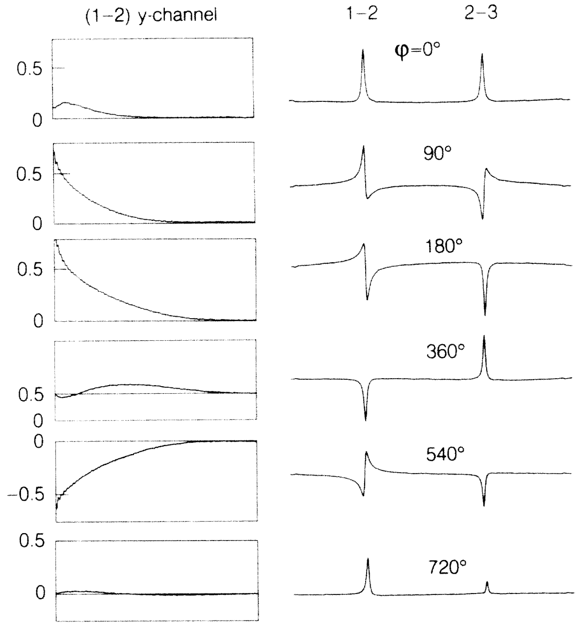

FIG. 3. NMR spectra of dichloromethane as a function of the flip angle ϕ of the composite z pulse in Fig. 2(c). The full phase shift ϕ appears in the low-frequency line while the high-frequency line shows only half of the phase shift $-\phi/2$. The left-hand column shows the amplitude of the 1-2 signal in one of the two quadrature channels of the phase-sensitive NMR detector. The phases have been adjusted such that the amplitude is zero if no z pulse is applied.

spins exhibit a 4π periodicity, integer spins return to the original state after a rotation through 2π. A rotation by an angle ϕ around the z axis multiplies the component wave functions by a phase factor $\exp(-i\phi m)$, where m represents the magnetic quantum number characterizing the particular substate.

We gratefully acknowledge helpful discussions with E. L. Hahn and R. A. Harris. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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