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A Simple Method for the Calibration of the Decoupler Radiofrequency Field Strength

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A simple experiment is proposed which provides a convenient way to calibrate the decoupler radiofrequency field strength over a wide range of magnitudes and with high accuracy. The calibration can be performed on the sample to be investigated and an example is shown for sucrose.

During the past decade a large number of new experiments have been proposed in the literature where either 90 or 180° pulses or a combination of these are applied to a nonobserved nuclide (called here the *heteronucleus*, S) coupled to the nuclei under investigation (I). Some of those experiments are the "proton-flip experiment" (*1*, *2*), the heteronuclear shift correlation experiment (*3–6*), indirect J spectroscopy (*7*), the INEPT experiment (*8*, *9*), and the composite pulse decoupling experiments (*10–11*). The radiofrequency pulses applied to the heteronuclei are usually generated by using the decoupler channel in the coherent mode for a suitable length of time.

The method for determining the decoupler rf field strength described in this paper has already been used in some laboratories for a number of years and has been briefly mentioned in the literature (*12*). However, it has appeared to us that most users of the newer-type pulse experiments are unaware of its existence, and are still using the old and, in practice, more cumbersome method of coherent off-resonance decoupling (*13*) for this purpose.

THE CALIBRATION SEQUENCE

In the discussions given below ^{13}C will be used as an example of the observed nuclide, while ^{1}H will be taken as the heteronuclide. The strength of the decoupler rf field will be indicated in hertz, i.e., it is the reciprocal of the time needed to rotate the heteronucleus through 360°. The sequence described below allows convenient calibration for all rf field strengths larger than about twice the heteronuclear coupling constant (J_{IS}). The scheme for the pulse sequence is displayed in Fig. 1. The proton noise irradiation just before the carbon pulse is optional and just serves to improve the ^{13}C sensitivity. Although, for convenience, a heteronuclear ^{13}C–^{1}H pair is chosen, the sequence works for any pair of nuclei with a resolvable mutual spin coupling.

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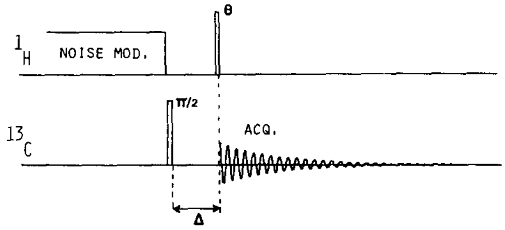

FIG. 1. The calibration pulse sequence. The delay Δ has to be set to $1/(2J)$. If the flip angle θ of the proton pulse equals $\pi/2$, no carbon magnetization will be observed.

The delay Δ has to be adjusted to $1/(2J)$, where J is the proton carbon spin coupling constant for a directly bonded ^{13}C–^{1}H pair. The value of J does not have to be known very accurately; a deviation of 5% still gives satisfactory results. The decoupler transmitter frequency must have a frequency offset of less than about 30% of the rf decoupler field strength from the proton resonance of the ^{13}C–^{1}H pair under consideration. As will be shown below, if the flip angle θ of the proton pulse is adjusted to be equal to $\pi/2$, no ^{13}C magnetization can be detected after this proton pulse. Hence, this offers an extremely simple method for calibrating the proton pulse to correspond to a $\pi/2$ flip angle.

An oversimplified, but instructive explanation of this phenomenon goes as follows. At a time $1/(2J)$ after the ^{13}C pulse the ^{13}C multiplet vectors, with angular frequencies $\Omega_C \pm \pi J$, are in antiphase in the transverse plane (Fig. 2A). One of those vectors corresponds to a proton in the $|\alpha\rangle$ spin state ($M_{C\alpha}$), while the other one corresponds to a $|\beta\rangle$ spin state ($M_{C\beta}$). If at this point a proton pulse with flip angle $\pi/2$ is applied, half the $|\alpha\rangle$ protons change to the $|\beta\rangle$ spin state and the other half stays in the $|\alpha\rangle$ state. Hence the ^{13}C magnetization component, $M_{C\alpha}$, originally corresponding to protons in the $|\alpha\rangle$ state splits into two components with frequencies $\Omega_C \pm \pi J$ (Fig. 2B). A similar argument holds for the other magnetization vector, $M_{C\beta}$. Therefore the new components have a net resultant of zero at all times after the proton $\pi/2$ pulse (Fig. 2C), and no transverse ^{13}C magnetization can be detected.

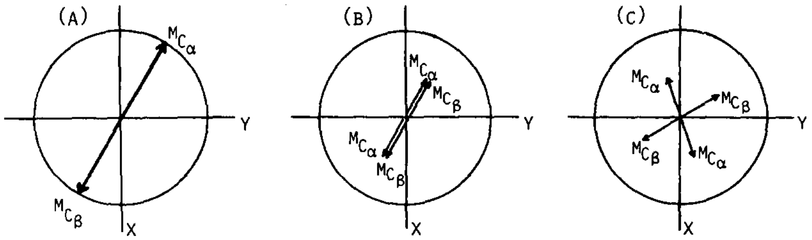

FIG. 2. The position of the carbon magnetization vectors in the transverse plane during the sequence of Fig. 1. (A) Just before the proton $\pi/2$ pulse, (B) just after the proton $\pi/2$ pulse, and (C) during the detection when the ^{13}C components are pairwise in antiphase. M_{C_α} and M_{C_β} are the ^{13}C multiplet components corresponding to the proton in the $|\alpha\rangle$ and the $|\beta\rangle$ state, respectively.

A more rigorous explanation involves using the density matrix formalism to describe the behavior of the spin system. Just before the proton θ pulse in the sequence shown in Fig. 1, when the ^{13}C multiplet components are in antiphase, the density matrix σ' is given by

$$\sigma' = D\begin{bmatrix} 0 & a & 0 & 0 \\ a^* & 0 & 0 & 0 \\ 0 & 0 & 0 & -a \\ 0 & 0 & -a^* & 0 \end{bmatrix} + 1/4\mathbb{1}, \qquad [1]$$

where D equals $\hbar\Omega_C/(kT)$ and $\hbar$, k, and T have their usual meaning. The factor a is given by the expression: $\exp\,[i(\Omega_C + \pi J)/2J]$. A proton pulse with a flip angle of θ radians is described by the operator, R_x, given by

$$R_x(\theta) = \exp(i\theta I_{xH}) = \cos(\theta/2)\mathbb{1} + 2\sin(\theta/2)I_x, \qquad [2]$$

where I_{xH} is the I_x operator for the proton considered (*14*). The proton pulse, applied to the spin system described by the density matrix σ' (Eq. [1]), creates a new state described by the matrix σ, given by

$$\sigma = R_x^{-1}(\theta)\sigma' R_x(\theta)$$

$$= D\begin{bmatrix} 0 & a(c^2 - s^2) & 0 & -2isca \\ a^*(c^2 - s^2) & 0 & -2isca^* & 0 \\ 0 & 2isca & 0 & -a(c^2 - s^2) \\ 2isca^* & 0 & -a^*(c^2 - s^2) & 0 \end{bmatrix} + 1/4\mathbb{1}, \qquad [3]$$

where $s = \sin(\theta/2)$ and $c = \cos(\theta/2)$. As can be seen from this density matrix, the elements σ_{12} and σ_{34} are zero for $\theta = \pi/2$, and all ^{13}C magnetization has been transferred into zero-quantum (σ_{23} and σ_{32}) and double-quantum (σ_{14} and σ_{41}) coherence. Similar density matrix calculations show that also for a $^{13}CH_2$ and for a $^{13}CH_3$ group the transverse magnetization disappears if a proton pulse with flip angle $\pi/2$ is applied at time $1/(2J)$ after the initial ^{13}C pulse.

EXPERIMENTAL

Experiments were performed on a Nicolet 360-MHz spectrometer equipped with a Nicolet 293A′ pulse programmer. The decoupler power was approximately 3.5 W. The sample used was a 1.5 *M* solution of sucrose in D_2O in a 12-mm sample tube. The results of four scans were coaveraged in order to improve the signal-to-noise ratio. The delay Δ was optimized for the multiplet from carbon C1 of the glucose ring which has a spin coupling constant of about 170 Hz with its directly bonded proton, and was set to 3 msec.

RESULTS AND DISCUSSION

Figure 3 shows the conventional proton-coupled ^{13}C spectrum of sucrose and the ^{13}C spectra obtained with the sequence of Fig. 1 for different durations of the proton

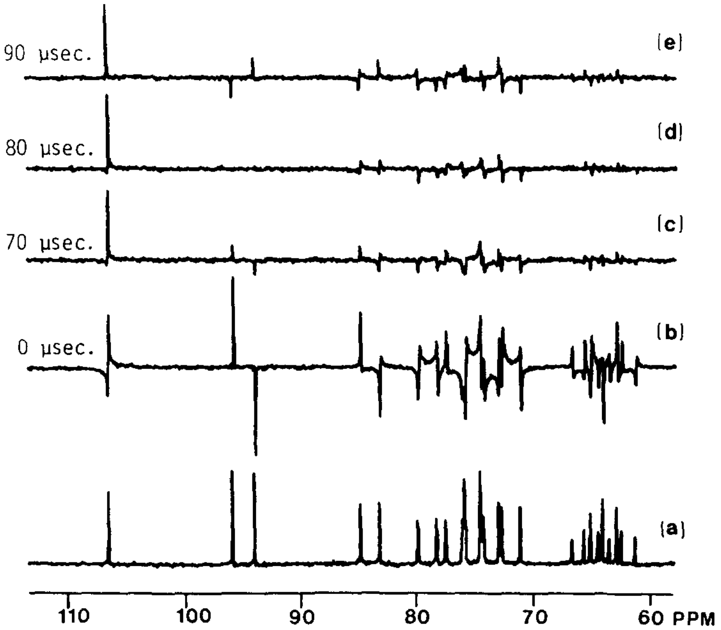

FIG. 3. (a) The conventional proton-coupled ^{13}C spectrum of sucrose, and (b)–(e) the spectra obtained with the sequence of Fig. 1 for durations of the proton pulse of 0, 70, 80, and 90 µsec, respectively. The delay Δ has been optimized for the carbon C1 of the glucose ring (at about 95 ppm) and its directly attached proton.

pulse. As can be seen from this figure, a proton pulse length of 80 µsec corresponds in this case to a proton flip angle of $\pi/2$. As has been pointed out by Freeman and co-workers (*15*), a pulse with flip angle $\pi/2$ is largely self-compensating for errors due to off-resonance effects. Therefore, a proton transmitter frequency offset from the two ^{13}C satellites in the proton spectrum equal to 30% of the proton rf field strength still causes hardly any change in the measured results. Hence this calibration method is extremely simple to use and gives very reliable results. By performing the experiment on a sample with a quarternary carbon with only one long-range coupling like, for example, acetic acid, one can calibrate the rf field strength for even much lower values, down to about 25 Hz which can be useful in, e.g., setting up a selective *J*-spectroscopy experiment (*16*).

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