

Transient Nutations in $^{19}\text{F}-\{^{13}\text{C}\}$ Double Resonance

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Summary A new method of measuring ^{13}C resonance positions in fluorinated organic compounds is described.

RECENTLY it has been pointed out that Torrey oscillations (transient nutations^{1,2}) in $\text{H}-\{^{13}\text{C}\}$ double resonance provide a sensitive detection method for ^{13}C resonances.³ Typical applications are measurements of $^{13}\text{C}-^{13}\text{C}$ coupling constants and ^{13}C dilution shifts in molecules containing ^{13}C in natural abundance. The simple experimental set-up makes this approach a worthwhile alternative to recently advanced ^{13}C n.m.r. techniques.^{4,5}

It seemed useful to investigate other combinations of nuclei, $\text{X}^1-\{\text{X}^2\}$, in order to extend the applicability and

to surmount the restrictions of ^{13}C measurements. Apart from the proton, the most promising X^1 nucleus is ^{19}F . Owing to its high natural abundance and gyromagnetic ratio, indirect ^{13}C observation, utilizing $^{19}\text{F}-\{^{13}\text{C}\}$ Torrey oscillations, is expected to give a similar increase in sensitivity as that for protons. Preliminary experiments on fluorinated hydrocarbons confirmed this. A typical example (Figure) shows the four Torrey signals of the A_3X spin system of $^{13}\text{CF}_3\cdot\text{CO}_2\text{H}$. The oscillations were generated by sweeping the perturbing r.f. field H_2 through the four ^{13}C transitions so as to satisfy the adiabatic rapid-passage conditions. The observing field, H_1 , was saturating the low-frequency satellite signal of the trifluoromethyl group. The resulting intensities resemble those observed in A_3X spin systems with $\text{A} = \text{H}$. The same applies to AX and A_2X systems studied so far. Assuming equal populations for those levels which are affected by the observing field, H_1 , and a Boltzmann distribution for the population of the remainder the relative intensities in a A_nX spin system are given by formula (1).⁶ For $^{13}\text{CF}_3\cdot\text{CO}_2\text{H}$, the calculated

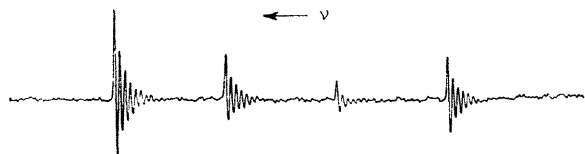


FIGURE. $^{19}\text{F}-\{^{13}\text{C}\}$ Torrey oscillations in $^{13}\text{CF}_3\cdot\text{CO}_2\text{H}$ (80% v/v in C_6F_6) at 84.6 MHz. The spectrum was obtained by saturating the low-frequency ^{19}F doublet line with the observing field while sweeping the second r.f. field to lower frequency over the four ^{13}C transitions. The trace was recorded in 100 s. The spacings between the first peak excursion of the four Torrey signals correspond to the coupling $|\text{J}_{\text{CF}}| = 283$ Hz.

$$I_p \sim \binom{n}{p} \left(\frac{\gamma_{\text{A}}}{\gamma_{\text{X}}} m_p^2 - m_p \right); m_p = -n/2 + p, \\ p = 0, 1, \dots, n \quad (1)$$

intensities are 7.6, 3.3, 1.0, and 5.3, whereas the experimental ones are 5.9, 2.9, 1.2, and 2.8, respectively. As for protons,

predictions approximately agree with measurement, particularly with samples which have not been degassed. In view of the approximations underlying the derivation of the equation this fact is of limited physical significance. Information on relaxation mechanisms can be deduced in principle but this requires a more sophisticated treatment.⁶ However, in measurement of ¹³C resonance positions, formula (1) indicates the transitions which should be chosen in order to achieve an optimal signal-to-noise ratio. In A_nX systems (*n* = 1,2,3) for example, which are usually encountered in ¹³C studies, the ¹³C multiplet at highest frequency, X_{*n*+1}, gives the strongest signal when the low-frequency ¹⁹F doublet is saturated (see Figure). Depending upon the generation of the signal, the maximum of the first peak excursion is displaced from the exact line position X_{*n*+1}. By sweeping the r.f. field H₂ to lower as well as to higher frequency a symmetrical pattern of transient nutations is obtained. The intersection of both signals yields the line frequency X_{*n*+1} from which the ¹³C chemical shift is calculated by subtracting *n*/2 × J_{FC}. Precision is

determined by the half width of the first peak excursion which is simply the product $dv_2/dt \times \Delta t_{1/2}$. $\Delta t_{1/2}$ is inversely proportional to the nutation frequency $\Omega = \gamma_F H_1 / 2\pi$, a relationship which holds for exact resonance of the observing field H₁ with the ¹⁹F doublet line. As for H-¹³C double resonance, measurements with high sensitivity can be reproduced to within ±0.3 Hz (for more experimental details see ref. 3).

The ¹⁹F-¹³C double resonance method is advantageous in that while observing fluorine resonance it is possible to decouple protons from ¹³C. Further, because of the relatively large F-C-¹³C coupling constants, tertiary carbon atoms can be studied; these, even with ¹³C Fourier transformation techniques, usually give poor signal-to-noise ratio owing to long relaxation times T₁.

Spectra were measured on a Bruker KIS-HFX 10. The author is indebted to Bruker Scientific, Elmsford, New York, for measuring time.

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