Pseudo INDOR Nuclear Magnetic Resonance Spectra Using Double Resonance Difference Spectroscopy and the Fourier Transform Technique

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Summary A method is presented for obtaining the information available from a nuclear magnetic resonance swept INDOR experiment with the advantages of the pulsed Fourier Transform method using Double Resonance Difference Spectroscopy.

In the continuous wave (CW) method for measuring INDOR spectra the intensity of a single transition is monitored while sweeping the second irradiating field ω_2 through connected transitions in the spectrum using low power $[(\gamma H_2)^2 T_1 T_2 \approx 1]$.[1] To carry out a comparable swept double resonance experiment while simultaneously taking advantage of the pulsed Fourier Transform time average method of improving sensitivity presents difficulties. A convenient method of obtaining similar INDOR information in the FT mode is to use nuclear magnetic double resonance difference spectroscopy (DRDS) to measure intensity changes between a single resonance spectrum and one with generalised Overhauser effects from selective irradiation of a single transition.

The Figure (a) shows the CW ^1H resonance spectrum of 1,2-dibromopropionic acid in deuteriobenzene at 100 MHz recorded on a Varian XL100 using the solvent deuterium as the lock signal. In the Figure (b) is shown the INDOR spectrum obtained in the conventional CW mode of operation monitoring line C4 whilst sweeping ω_2 through the other lines in the spectrum: the observed INDOR signals correspond to intensity increases and decreases in C4 as one irradiates the progressively and regressively connected transitions. The Figure (c) shows exactly the same frequency information but obtained in the FT mode using DRDS in the following manner. The single resonance proton spectrum was acquired from Fourier Transformation of 256 pulses and this spectrum was subtracted from that

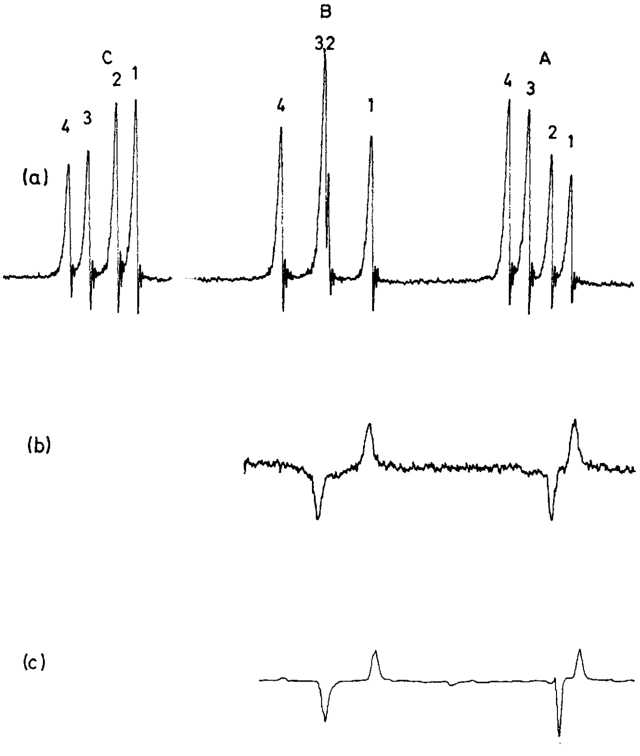

Figure. (a) The ^1H CW spectrum of 1,2-dibromopropionic acid at 100 MHz in deuteriobenzene. (b) The INDOR CW spectrum of 1,2-dibromopropionic acid at 100 MHz *monitoring* line C4. (c) The pseudo INDOR FT spectrum of 1,2-dibromopropionic acid at 100 MHz *irradiating* line C4. The energy level scheme showing the connected transitions is given in ref. 2.

obtained under the same conditions but with a weak irradiating field at the C4 frequency. The observed intensity differences in the A and B multiplets result from the generalised Overhauser effects on the C4 connected transitions. The frequencies of the signals and the sign of their intensities are identical with those observed in the normal CW INDOR spectrum. This is because the progressive or regressive nature of a pair of transitions is manifested regardless of which of the pair is irradiated. However, the actual intensity changes are not necessarily the same.

The difference spectrum is calculated on-line using the standard Varian Block Averaging Program No. 10310-E-XL with minor modification. Care must be taken to maintain a constant sample temperature throughout: thus the single resonance spectrum is obtained with the decoupler power at the required setting for the irradiation experiment but with the frequency offset 10 Hz outside the spectral region.

INDOR spectroscopy has the advantage over other double resonance techniques in that one can carry out consecutive INDOR experiments[1] to locate hidden transitions in complex spectra which are themselves connected only to hidden transitions. Now such experiments should also be feasible using double resonance difference spectroscopy with the Fourier Transform technique. The increased sensitivity now possible by using the Fourier Transform pseudo INDOR method will also enable one to make ^{13}C assignments which require very selective ^{1}H irradiation experiments in cases where the proton spectrum features assigned protons with similar chemical shifts.

At higher power levels ($\gamma H_2/2\pi \approx \Delta\nu_{\frac{1}{2}}$) where spin tickling occurs the DRDS technique can again be used to find connected transitions. Furthermore, it makes possible consecutive tickling experiments between hidden transitions which would be very difficult using the CW technique.

(*Received, 4th July* 1973; *Com.* 958.)

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