

Homonuclear Selective Population Inversion: An INDOR Equivalent in Fourier Transform Nuclear Magnetic Resonance Spectroscopy

By KLAUS G. R. PACHLER* and PHILIPPUS L. WESSELS

(National Chemical Research Laboratory, Council for Scientific and Industrial Research P.O. Box 395, Pretoria, South Africa)

Summary It is shown how the selective population inversion (SPI) technique can be applied to coupled homonuclear spin systems to give the same information in FT n.m.r. spectroscopy as INDOR in the continuous-wave (CW) mode of operation.

EFFORTS to combine the advantages of the INDOR double resonance technique with those of pulsed Fourier transform n.m.r. spectroscopy have led Feeney and Partington¹ to suggest a pseudo-INDOR experiment. A population transfer between two energy levels is effected by continuously applying a small r.f. field to a single transition

while accumulating spectra in the FT mode. The difference, obtained by subtracting an unperturbed spectrum observed under exactly identical conditions, closely resembles the CW INDOR spectrum.

The selective population inversion technique² achieves the same objective and has been successfully used in heteronuclear ¹³C ··· {¹H} double pulse experiments.³⁻⁵ In this experiment large intensity changes are induced by inverting the populations of two connected ¹H energy levels with a selective π pulse. The ¹³C spectrum is then observed following a non-selective $\pi/2$ pulse. In a homonuclear system, however, the non-selective pulse also affects the in-

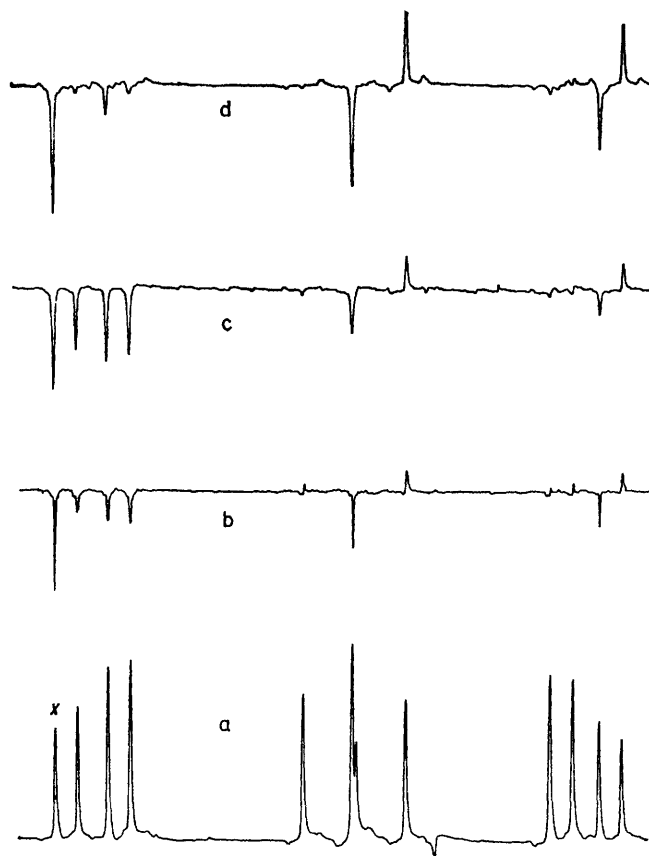


FIGURE. (a) The 100 MHz ^1H FT n.m.r. spectrum of 2,3-dibromopropionic acid in C_6D_6 , and difference spectra obtained (b) by continuously irradiating the transition at lowest field (x) (pseudo-INDOR), (c) by saturating the same line prior to sampling the spectrum, and (d) by inverting the first line with a selective π pulse (SPI).

verted transition and the appearance of the final spectrum is difficult to predict. Recent density matrix calculations⁶ have indicated that the effects due to any population changes are largely eliminated if a non-selective $\pi/2$ pulse is used to observe the spectrum, but are preserved to a

certain extent if smaller flip angles are used. A compromise can be found between the reduced signal amplitude following flip angles smaller than $\pi/2$ and the loss of population transfer effects at larger flip angles.

These considerations apply to all three techniques compared herein. All spectra in the Figure have therefore been obtained under the same experimental conditions. 16 transients have been accumulated (2×16 for difference spectra) with a flip angle of $\pi/6$. Pulse delays between the non-selective pulses allowed the system to return to thermal equilibrium. Difference spectra have been obtained in the previously described manner.⁴ Free induction decays of perturbed and normal spectra are alternately added to or subtracted from computer memory before Fourier transformation. Trace (a) shows the ^1H FT spectrum of 2,3-dibromopropionic acid in C_6D_6 (undegassed; concentrated solution). In the three difference spectra (b–d) the first low-field line (indicated by x) has been perturbed. Trace (b) is a pseudo-INDOR spectrum obtained with a continuous r.f. power of $\bar{\nu}\text{H}_2 = 0.3$ Hz. Trace (c) is a difference spectrum obtained from a saturation experiment⁷ in which the first line was saturated for 10 s with an r.f. power of $\bar{\nu}\text{H}_2 = 2.5$ Hz prior to applying the non-selective observing pulse. Trace (d) shows the homonuclear SPI difference spectrum [$\bar{\nu}\text{H}_2 = 2.5$ Hz.]

The spectra shown in the Figure demonstrate quite convincingly the superiority of the homonuclear SPI technique over the other two techniques. The sensitivity of the pseudo-INDOR experiment is limited by the onset of tickling at higher power levels. The saturation technique could give a maximum effect equal to half the intensity of any observed line. The longer period required to saturate a line increases secondary population transfers to other energy levels as evident in the three transitions following the perturbed line. The SPI experiment shows by far the biggest intensity changes, twice as large as in the saturation experiment. The pseudo-INDOR and the saturation experiments could probably be improved by degassing the sample, while this is less important for the SPI method. The SPI effect is less than expected for a complete inversion because of the compromise between flip angle and transfer effect discussed above.

(Received, 28th October 1974; Com. 1319.)

¹ J. Feeney and P. Partington, *J.C.S. Chem. Comm.*, 1973, 611.

² K. G. R. Pachler and P. L. Wessels, *J. Magnetic Resonance*, 1973, **12**, 337.

³ A. A. Chalmers, K. G. R. Pachler, and P. L. Wessels, *Org. Magnetic Resonance*, 1974, **6**, 445.

⁴ A. A. Chalmers, K. G. R. Pachler, and P. L. Wessels, *J. Magnetic Resonance*, 1974, **15**, 415.

⁵ S. Sørensen, R. Hansen, and H. Jakobsen, *J. Magnetic Resonance*, 1974, **14**, 243.

⁶ P. Meakin and J. P. Jesson, *J. Magnetic Resonance*, 1973, **11**, 182; 1974, **13**, 354; S. Schäublin, A. Höhener, and R. R. Ernst, *ibid.*, p. 191.

⁷ R. R. Ernst, W. P. Aue, E. Bartholdi, A. Höhener, and S. Schäublin, *Pure Appl. Chem.*, 1974, **37**, 47.