(14) The pK of nitromethane in water is 10.2; that of acetone is estimated to be 20.[15]

(15) R. P. Bell, *Trans. Faraday Soc.*, **39**, 253 (1943).

(16) We are grateful to Dr. D. J. Peterson for supplying us with a pure sample of $(C_6H_5)_2PCH_2SO_2C_6H_5$.

(17) Measurements were made in pure DMSO at 25°.[1,11] As a consequence of anchoring our pK scale to "absolute" measurements made in the 5–12 pK region, the values given in earlier papers in this series[1,11] must be adjusted upward by a little over 2 pK units. Details will be given in a full paper now in preparation.

(18) The Δ pK's relative to the hydrogen compound (statistically corrected).

(19) For example, the effect of phenyl in increasing the ion pair acidities of hydrocarbons in cyclohexylamine is generally 2 pK units, or less, the largest value (4.4) being observed with fluorene as the parent acid.[20]

(20) A. Streitwieser, Jr., J. R. Murdoch, G. Häfelinger, and C. J. Chang, *J. Amer. Chem. Soc.*, **95**, 4248 (1973).

(21) This is true also for other parent carbon acids. Details will be presented in a full paper now in preparation.

(22) This value should be regarded as tentative since it is above the limit for accurate measurements.

(23) Another example of the misleading information relative to carbanion stabilities sometimes given by kinetic acidities is the observation that $(PhS)_3CH$ and $(PhS)_2CH_2$ exchange at almost the same rate under NH_3 catalysis in liquid NH_3.[8,24] In contrast, we find $(PhS)_3CH$ to be more acidic than $(PhS)_2CH_2$ in DMSO by 8.3 pK units.

(24) On the other hand, $(EtS)_3CH$ has been reported to undergo *t*-BuOK catalyzed exchange in *t*-BuOH at a rate 379 times that for $(EtS)_2CH_2$.[25]

(25) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964).

(26) National Science Foundation Postdoctoral Fellow, 1971–1972.

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An Application of Fourier Transform Techniques in the Proton Homo Double Resonance Mode. Internuclear Double Resonance

Sir:

Internuclear double resonance (INDOR)[1] is well accepted as one of the convenient methods to find hidden resonance lines and/or to determine relative signs of spin coupling constants in high resolution nmr studies. In this method, the change in level populations as the result of spin pumping is detected through the monitor line as the intensity variation which occurs when the frequency, ω_2, of the perturbing field H_2 coincides with the frequency of a line that has an energy level in common with the monitor line transition at ω_1.

For simplicity, assume a spin coupled two-spin system AB. The energy level diagram is shown in Figure 1. Quantitatively, the intensity of the monitor line corresponding to the transition B_1, for example, increases when the population at the level q increases through spin pumping by the effect of the swept irradiation frequency ω_2. Spin pumping to the level r reduces the intensity of the monitor line. The rf level at the frequency ω_1 for monitoring is adjusted below saturation in an INDOR experiment.[2]

However, consider the spectrum to be measured after the transition B_1 is irradiated by frequency ω_2. The irradiation must be sufficient to perturb the population in levels q and r but be short in time so as not to cause the rearrangement of the population in p and s. The difference in peak intensity of lines corresponding to transitions A_1 and A_2 as measured by conventional single resonance methods and the peak intensities measured using the procedure outlined above must be analogous to the INDOR spectrum.

This kind of peak intensity is maximized if it is observed in a spectrum measured just after the level populations in r and q are interchanged. This measurement, however, is difficult to make using conventional swept mode nmr equipment because the required time to span the whole spectral range is usually long enough to reach thermal equilibrium.

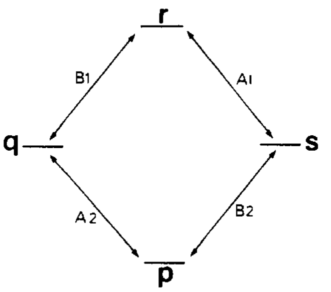

Figure 1. Energy level diagram for AB two spin system. p, q, r, and s show energy levels, respectively, and A_1, A_2, B_1 and B_2 represent allowed transitions, respectively.

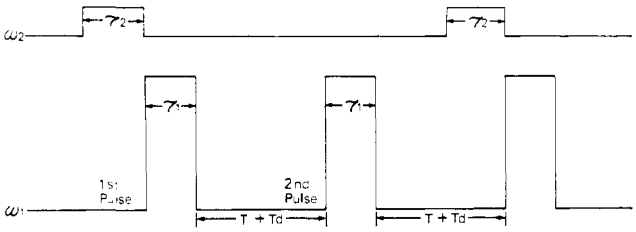

Figure 2. Time sequence of the pulse trains. Pulse at ω_2 is used for irradiation, pulses at ω_1 are observed.

The Fourier transform technique is the best way to solve this difficulty. The information on peak intensity in the frequency domain is available at the beginning of the free induction decay. That is, the information may be correct if data acquisition time is comparable to relaxation time T_1 and if relaxation times of each of lines are not equal.

Figure 2 is a schematic representation of pulse train. To obtain optimum effects at frequency ω_2, the irradiation field strength H_2 and the pulse width τ_2 must meet the relationship $\gamma H_2 \tau_2 = \pi$, where γ is gyromagnetic ratio of a proton, and, in addition, the frequency distribution must be narrow enough so as not to perturb other transitions. In extreme cases, these conditions can be achieved by using continuous wave irradiation; however, this mode of operation causes generalized Overhauser effects[3] or spin tickling,[4] depending on the spin system involved.

The first pulse at frequency ω_1 is used to observe the effect on the irradiation at ω_2. The second pulse at frequency ω_1 is used to measure the spectrum of the spin system at thermal equilibrium in the external magnetic field. The difference in free induction decays after these two kinds of pulses occur is then accumulated and transformed into frequency domain. For a meaningful measurement, the sum of the aquisition time T and the pulse delay time T_d must be long enough compared to all of relaxation times T_1 of the spin system under study.

An experiment to illustrate this principle was carried out on a Varian NV-14 high resolution nmr spectrometer modified for proton FT use. The data system used was a Varian Data Machine's ADAPTS computer system. An internal deuterium lock was used to hold the field/frequency ratio constant. The output frequency of the NV-14's standard spin decoupler was pulsed and amplified to obtain an appropriate pulse for sample irradiation purposes.

The result of one experiment is reproduced in Figure 3. The bottom trace is a part of a normal spectrum of a deuteriochloroform solution of Maltol (Figure 4) measured by using the Fourier transform technique. The middle shows the effect of ω_2 on the same part of the spectrum. The upper one is the result of using the procedure described above. The line at the far left of the trace was irradiated in this ex-

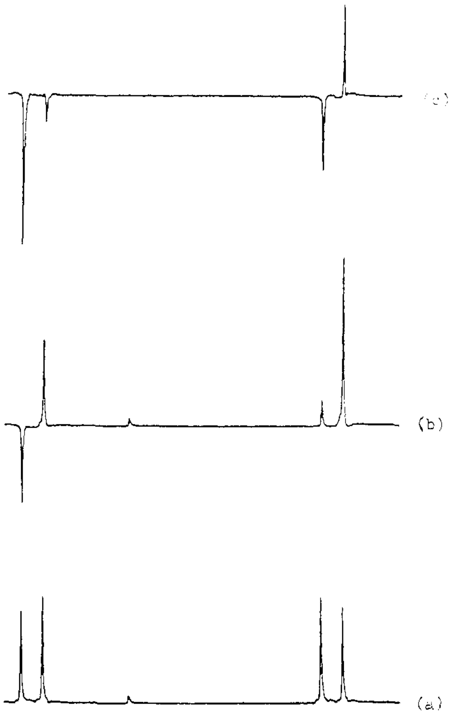

Figure 3. A part of spectrum of Maltol in $CDCL_3$: (a) normal spectrum; (b) the same part of the spectrum with ω_2 irradiation; and (c) difference of (a) and (b). Middle small singlet corresponds $CHCL_3$ in the solvent used.

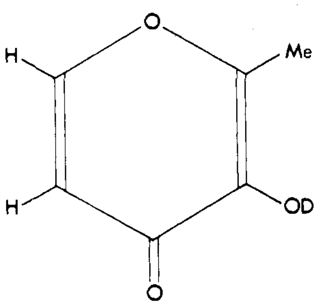

Figure 4.

ample. All traces are the result of five transient accumulations and are read out with absolute intensity mode.

As expected, the line corresponding to the regressive transition[4a] appears negative[3b] and the one due to the progressive transition appears positive, respectively.

The intensity of the partner line of the irradiated doublet can be interpreted in terms of the relaxation during a period between the time irradiated at ω_2 and that observed at ω_1.[5] The intensity estimated by making use of the equation developed by Wangsness and Bloch[6] under appropriate assumptions gives the same result as obtained from simple consideration based on the level population difference. However, the effect of the pulse at the frequency ω_1 must be small enough to act as the perturber for an unperturbed state which is established by the external field and the pulse at the frequency ω_2. Generally, the sensitivity seems still much higher in this method than conventional INDOR even under this condition.

In summary, the method described has benefits which include short experimental time, higher sensitivity, and ease of accumulation. There is promise of wide application to the analysis of many organic compounds, even in very dilute solutions.

References and Notes

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(2) Ferretti and Freeman reported ("Transient Nutation Technique") the experimental procedure was the same as INDOR except for a much higher rf level for monitoring. J. A. Ferretti and R. Freeman, *J. Chem. Phys.*, **44**, 2054 (1966).
(3) (a) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **37**, 85 (1962); (b) R. Kaiser, *ibid.*, **39**, 2435 (1963).
(4) (a) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962); (b) R. Freeman, *ibid.*, **53**, 457 (1970).
(5) Details will be reported elsewhere shortly.
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Compressed Tetragonal Distortion in $Rb_2PbCu(NO_2)_6$ at 295°K

Sir:

We wish to report the first example of *compressed* tetragonal distortion for six-coordinate Cu(II) with *equivalent* ligands. Single-crystal X-ray diffraction shows the rubidium lead hexanitrocuprate(II) crystals to be orthorhombic with space group, *Fmmm*. The crystallographic site symmetry for Cu(II) is D_{2h} (*mmm*), but two of the three pairs of Cu-N distances are equal within experimental error. Thus, Cu(II) has a compressed tetragonal environment with an average Cu-N bond length of 2.171 (5) Å for the long bonds and 2.063 (4) Å for the short bonds. The bond distances and bond angles are given in Table I, and the hexanitrocuprate(II) anion is shown in Figure 1.

Crystal data for the greenish black crystals are: a = 10.8296 (7), b = 10.8196 (7), and c = 10.6113 (7) Å; V = 1243.35 $Å^3$ (λ = 0.70926 Å for the cell determination); orthorhombic, with space group *Fmmm* ($D_{2h}{}^{23}$, No. 69); four formula units (M = 717.7 daltons) per cell; D_x = 3.834 g cm^{-3}; μ = 223.9 cm^{-1} for Mo Kα radiation.

Intensity data were collected with an automated four-circle diffractometer, a NaI scintillation detector, and Mo Kα radiation with a Nb incident beam filter. The θ-2θ scan technique was used to measure all 5313 reflections out to 2θ = 90° ($\pm h$, $+k$, $\pm l$). The data were corrected for absorption and averaged to give 1427 independent reflections. Full-matrix least-squares refinement gave a conventional R factor of 0.026 based on all reflections.

Examples of Cu(II) in a compressed tetragonal environment cited by other authors are potassium tetrafluorocu-

Table I. Bond Distances (Å) and Bond Angles (deg) for $Rb_2PbCu(NO_2)_6$ at 295°K[a]

Cu-N(1)	2.063 (4)
Cu-N(2)	2.176 (5)
Cu-N(3)	2.166 (5)
N(1)-O(1)	1.241 (3)
N(2)-O(2)	1.241 (4)
N(3)-O(3)	1.250 (4)
Pb-O(1)	2.808 (3)
Pb-O(2)	2.789 (3)
Pb-O(3)	2.783 (3)
Rb-O(1)	3.168 (1)
Rb-O(2)	3.127 (1)
Rb-O(3)	3.145 (1)
O(1)-N(1)-O(1)	117.5 (3)
O(2)-N(2)-O(2)	116.6 (4)
O(3)-N(3)-O(3)	114.8 (4)

[a] Standard deviations of last significant figure are given in parentheses.