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Chemically Induced Dynamic Nuclear Polarization

Experiments in Unmodified NMR Spectrometers

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Photoexcitation of chemically induced dynamic nuclear polarization (CIDNP) has generally required either construction of special probes or extensive modifications of commercial probes to admit the illuminating beam of light.¹ In many instances this course is either undesirable or impossible because of the internal structure of the probes. The latter situation obtains in the Varian A-60 class of instruments.

Experiments of this type may be executed readily without any probe modifications whatsoever by the simple expedient of conveying the light into the sample via a lightguide. A schematic diagram of the disposition of elements which we have found satisfactory is given in Figure 1. Light from a high pressure Hg-Xe arc is collected by lens, L1, relayed to a front surface mirror, M, and focused by lens, L2, on the end of the light guide, G, which is contained in the NMR sample tube, T. As usual, the tube is supported in the sample spinner, S. Water filter and other optical components can be introduced at will between L1 and M.

The light guide is fabricated from quartz rod of diameter slightly smaller than the internal diameter of the NMR tube. Its length is uncritical. The length of the column of sample solution will be that normally used in the spectrometers; the product of concentration times the molar absorption at the excitation wavelength should be adjusted so that the sample volume residing in the receiver coil is illuminated optimally.

Too concentrated a solution will attenuate the light before it reaches the sensitive volume. It is necessary for the light guide to enter the solution; otherwise the light emerging from the guide will diverge rapidly and significant flux will be lost. Solutions whose indices of refraction are greater than that of air will themselves act as light guides and help to contain and direct some of the flux. The light guide, incidentally, prevents vortex formation in the spinning samples.

Some experimentation is required to achieve the optimum placement of the light guide in the sample volume, the length and concentration of the sample, and the relative position of the bottom of the light guide with respect to the sample coil. Naturally, the field homogeneity controls will require optimization for each position.

In Figure 2 are shown spectra obtained in a ten year old A-60 from a one percent solution of Di t Butyl ketone in CCl_4 in the absence and presence of actinic light introduced by a light guide as described above. The results obtained in this manner with this and other compounds whose CIDNP spectra have been obtained under previously established conditions compare favorably in the degree of nuclear polarizations achieved.² In some instances, the present arrangement is more attractive as the effects of heating encountered previously seem to be absent.

In situations where it may be necessary to exclude O_2 from the samples, they may be prepared in a dry box and the light guide sealed to the sample tube with an O-ring or Wilson seal. If experiments at variable temperatures using high pressure of flowing gas are contemplated, it will be necessary to modify or fabricate a new pressure cap which will be transparent to the actinic light.

FOOTNOTES AND REFERENCES

*N.I.G.M.S. Postdoctoral Fellow.

¹ M. Cocivera, J. Amer. Chem. Soc. 90, 3261 (1968).

² M. Tomkiewicz, A. Groen, and M. Cocivera, Chem. Phys. Letters 10,
39 (1971).

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. A schematic diagram showing the disposition of elements essential to observe CIDNP in an NMR spectrometer.

L1 and L2 - lenses

M - mirror

G - light guide

"O" - O-ring

T - NMR tube

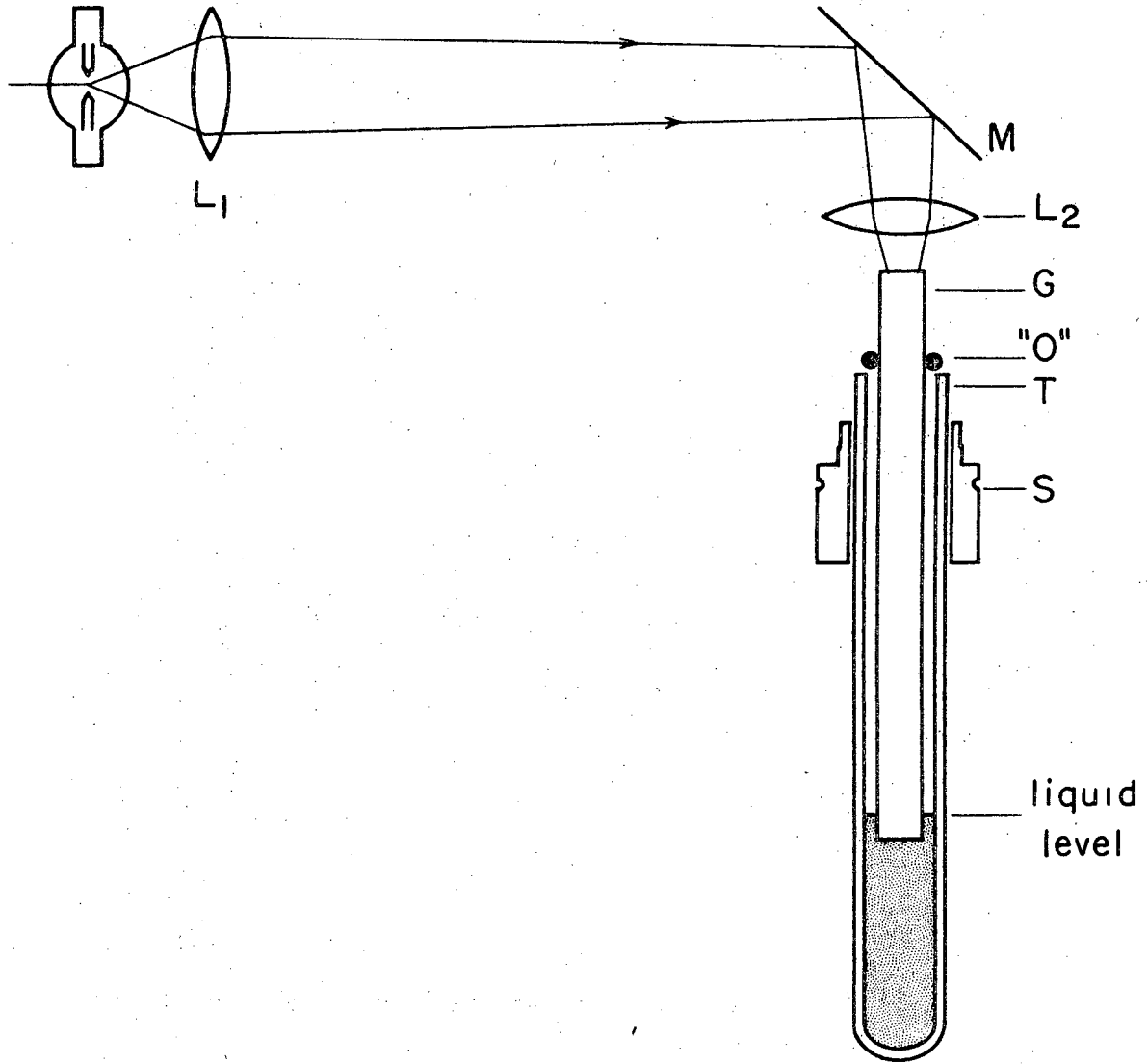
S - spinner

Fig. 2. A - NMR spectrum (at 60 MHz) of 1% of Di t Butyl ketone dissolved in CCl_4 , before irradiation. The sweep time is 250 sec. The separation between markers is 60 Hz.

B - during irradiation - first scan

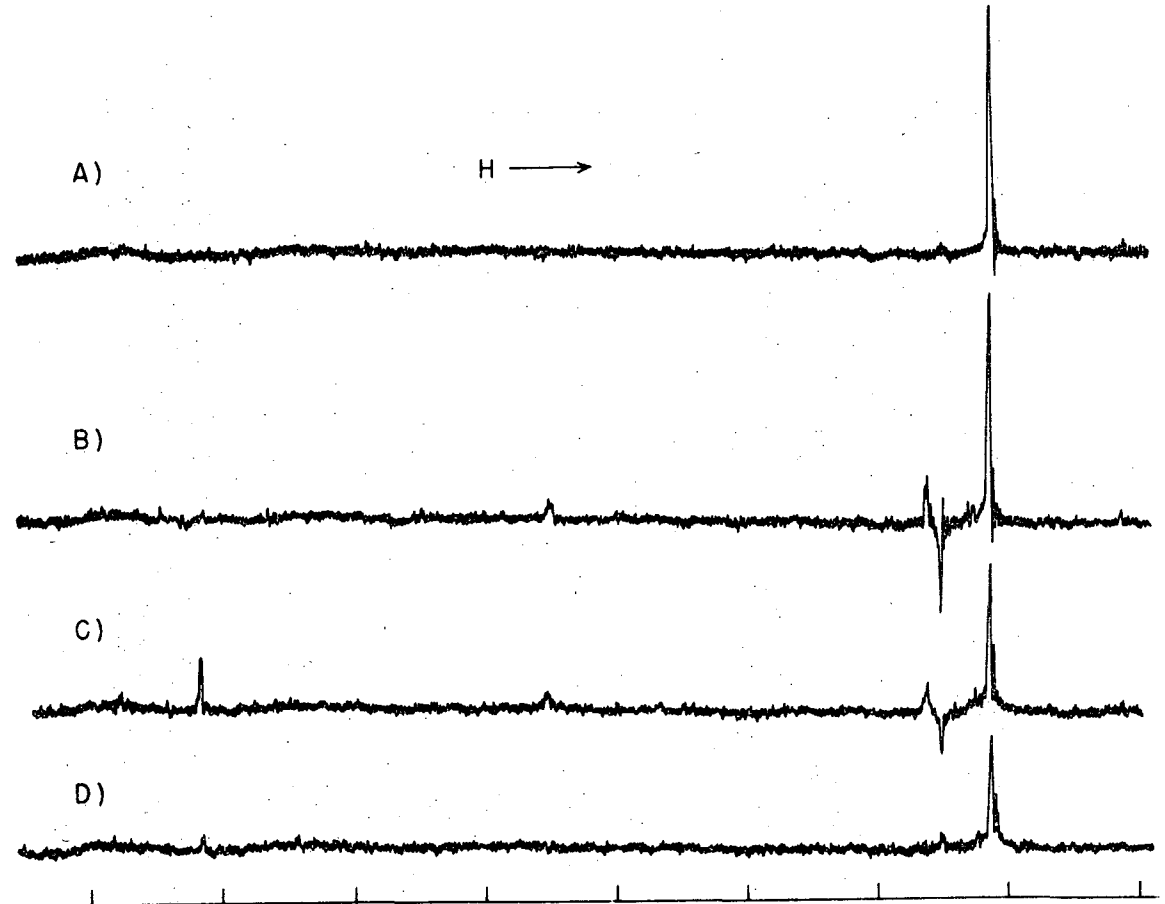
C - during irradiation - second scan

D - after irradiation



XBL723-4556

Fig. 1



XBL 723-4557

Fig. 2

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