

V. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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A. NUCLEAR RESONANCE SPECTRA OF HINDERED INTERNAL ROTORS

Previous observation of rotational barriers by means of steady-state nuclear-resonance experiments have depended on the isolation of a single rotational isomer for times that are characteristic of nuclear-moment interactions in molecules – typically 0.1 sec (refs. 1, 2).

In most molecules that are interesting from the viewpoint of the theory of rotational hindrance the barriers are much too low to provide this isolation. Even when interconversion is rapid, however, anisotropy in the averaging of nuclear positions about the principal bond axis can, theoretically, lead to otherwise unexpected splittings in the nuclear resonance spectrum (3). We have observed such splittings in a number of simple molecules and verified that their temperature dependence is qualitatively as would be predicted. We are now attempting to verify that this agreement is quantitative, as well as qualitative, by studying molecules (e.g., $\text{CH}_2\text{Br} - \text{CF}_2\text{Br}$) for which something about the energetics of internal rotation is known from other sources.

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References

1. W. D. Phillips, J. Chem. Phys. 23, 1363 (1955).
2. H. S. Gutowsky and C. H. Holm, J. Chem. Phys. 25, 1228 (1956).
3. D. M. Graham and J. S. Waugh, J. Chem. Phys. (in press).

B. PARAMAGNETIC RESONANCE IN ATOMS ALIGNED BY ELECTRON IMPACT

A method for producing and determining the inequalities in the populations of the magnetic sublevels of the metastable 6^3P_2 state in mercury has been previously reported by us (1). This note describes an experiment in which a resonance between the magnetic sublevels of this state for the even isotopes of mercury was observed. This experiment is similar to an experiment performed by H. G. Dehmelt (2).

The apparatus that was used was described in the last report (1). However, a pair of high-frequency coils was placed around the discharge tube in such a manner that the axis of the coils was perpendicular to the direction of motion of the electrons and midway between the cathode and anode. In order to illuminate only the even isotopes, a lamp filled with Hg^{198} was used as the light source.

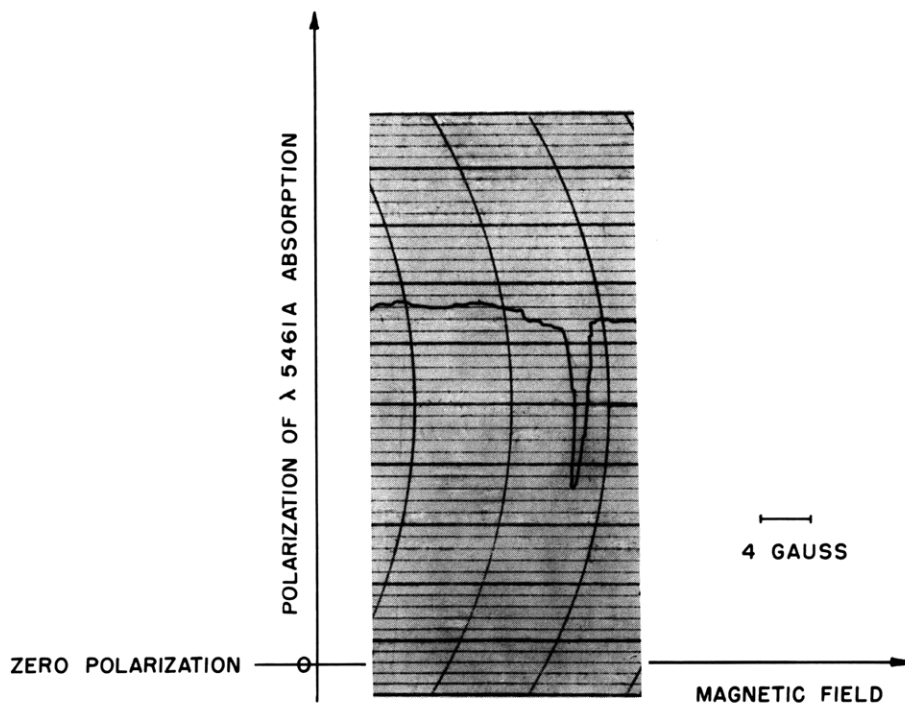


Fig. V-1. Recorder trace of polarization of $\lambda 5461 \text{ \AA}$ absorption by 3P_2 mercury atoms plotted against magnetic field.

The method of observing the resonance is as follows. A rotating polaroid and narrow-band amplifier are used to observe the inequalities in the populations ("polarization") of the magnetic sublevels of the 3P_2 levels. A magnetic field in the direction of the electrons is turned on and set to a value of approximately 24 gauss. This splits the 3P_2 level into five sublevels ($m = \pm 2, \pm 1, 0$) approximately 50 mc apart. Then a small 50-mc magnetic field is applied perpendicular to the "splitting field" by means of the high-frequency coils. This small rf field induces $\Delta m = \pm 1$ transitions in the mercury atoms.

At the resonant frequency, the magnetic sublevels become almost equally populated, so that a decrease in the polarization signal is observed.

Figure V-1 shows a typical resonance curve. The halfwidth of the resonance curve is approximately 0.5 gauss, and is believed to be caused primarily by the inhomogeneity of the splitting field.

Construction of new apparatus is underway for the purpose of scanning all of the hyperfine-structure levels of Hg^{199} and Hg^{201} , in order to determine the polarization of these levels and to observe resonances ($\Delta F = 0$; $\Delta m_F = \pm 1$) in these levels. The field inhomogeneities are being corrected; it is hoped that the resonances will be much

(V. NUCLEAR MAGNETIC RESONANCE)

narrower and consistent with the lifetime of the 3P_2 level in the discharge, which is believed to be of the order of 10^{-5} second.

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References

1. B. B. Aubrey and L. C. Bradley III, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., July 15, 1957, p. 39.
2. H. G. Dehmelt, Phys. Rev. 103, 1125 (1956).