

VII. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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RESEARCH OBJECTIVES

The aims of this group are twofold: first, the investigation of chemical structural problems by nuclear magnetic-resonance techniques; and second, the investigation of the structure of atomic nuclei, particularly of radioactive nuclei, by nuclear magnetic-resonance techniques and by the investigation of atomic hyperfine structure and isotope shift. In order to get information from the relatively small numbers of atoms with radioactive nuclei that can be prepared, the emphasis in this group has been on the optical properties of atomic vapors. In addition to straightforward spectroscopic investigations that make use of gratings and interferometers, and especially designed light sources requiring very few atoms, techniques have been developed for eliminating Doppler broadening, especially by the use of radiofrequency and microwave absorption, and also of atomic-beam light sources.

The work of some members of the group on spectroscopic light sources, and on mercury-rare-gas plasmas more generally, has led to new directions of investigation. These are concerned primarily with the detailed analysis of light from plasmas to give data on collision processes, and with high-field magnetic effects.

The major part of the chemical work is being done through studies of nuclear magnetic resonance line shape versus temperature in solids and of fine structure in the nuclear resonance spectra of liquids. However, to an increasing extent, we are relying on transient nuclear resonance methods, including spin-echo and free induction decay techniques, to give more direct measures of the relaxation times T_1 and T_2 . Present problems include (a) the mechanism of nuclear spin relaxation in gases, (b) self-diffusion of simple hydrocarbon molecules in the liquid phase, (c) the phase behavior of solid methane, hydrogen sulfide, hydrogen selenide, and hydrogen chloride, (d) the nature of the ferroelectricity in potassium ferricyanide trihydrate and some other materials, and (e) the structures of the complexes between alkaline earth ions and adenosine di- and triphosphates.

Experiments are also getting under way on the Mössbauer effect (thus far, only of Fe^{57}) in various transition metal compounds, including the spinels.

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A. MOLECULAR REORIENTATION AND NUCLEAR SPIN RELAXATION IN HYDROGEN GAS

In one of the earliest nuclear magnetic-resonance experiments Purcell, Pound, and Bloembergen (1) observed the absorption signal of hydrogen gas at pressures of 10-30 atm. They also measured the nuclear relaxation time, T_1 , by the saturation method. Later they compared their results with values calculated from an equation derived by Schwinger (2). Schwinger's equation, which is given below, expresses the

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fact that the internal magnetic interactions of the hydrogen molecule can be averaged out by molecular reorientation. For $\omega_o \tau_c \ll 1$, T_1 is given by

$$\frac{1}{T_1} = 2\gamma^2 \tau_c \left[\frac{1}{3} H'^2 J(J+1) + \frac{3H''^2 J(J+1)}{(2J-1)(2J+3)} \right]$$

where

γ is the gyromagnetic ratio for protons

τ_c is the correlation time for m_J state (that is, time between changes in m_J)

ω_o is the Larmor frequency

H' is the field at proton caused by molecular rotation, ≈ 27 gauss

H'' is the field at proton caused by other proton, ≈ 34 gauss

Some more recent experimental results are given in Table VII-1 which indicate that the theoretical situation is far from satisfactory.

Table VII-1. Observed and calculated relaxation times.
(Hydrogen gas at 10 atm and 300°K.)

| T_1 | T_2 | |
|------------------------------|----------------------------------|----------------------|
| $\sim 50 \times 10^{-3}$ sec | $\sim 50 \times 10^{-3}$ sec | Calculated (ref. 2) |
| $\sim 15 \times 10^{-3}$ sec | | Bloembergen (ref. 2) |
| | $1.2 \pm 0.2 \times 10^{-3}$ sec | Packard (ref. 3) |
| | $1.0 \pm 0.1 \times 10^{-3}$ sec | Present work |

Complete definitions of T_1 and T_2 have been given by Bloembergen, Purcell, and Pound (2). In all of the cases investigated experimentally $T_1 = T_2$, and T_1 was directly proportional to the pressure. The formula for $1/T_1$ simply reduces to a statement of proportionality between $1/T_1$ and τ_c when all of the known constants are substituted. Then it is possible to determine τ_c from T_1 measurements and to calculate collision cross sections for the change of m_J . We have observed the nuclear relaxation of hydrogen gas in mixtures of many other gases by both linewidth and spin-echo measurements. Some of these results are shown in Fig. VII-1. Also, extrapolations were made to infinite dilution of H_2 in each of the foreign gases, and the resulting values of T_1 were used to calculate effective collision cross sections.

Drastically different values of T_1 were found in the various gas mixtures; however, the startling fact was that the effective collision frequencies from T_1 measurements were much smaller than expected. The magnitudes in some cases were as much as 10^2 times smaller than those calculated from kinetic theory. These effective collision

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frequencies and hence the corresponding cross sections were also found to increase with decreasing temperature.

Interesting information about the probability of changing m_J in a collision

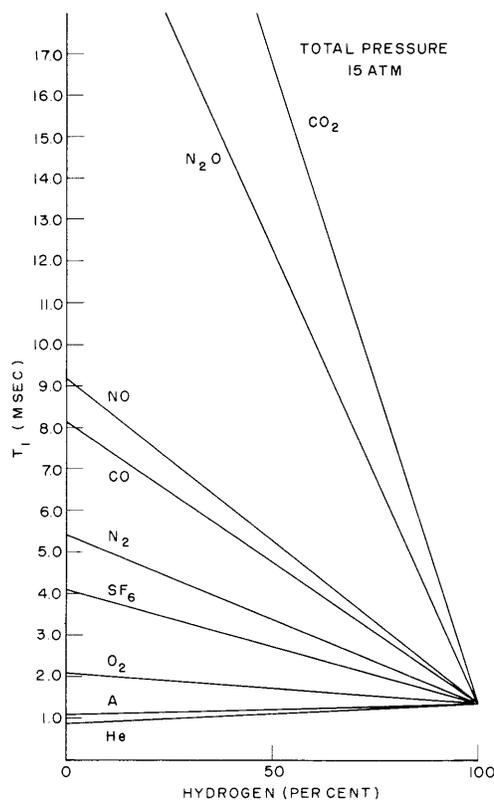


Fig. VII-1. Relaxation times for protons in ortho-hydrogen molecules in mixtures with various gases.

can be obtained from our results if Schwinger's equation is correct; however, this information is required to verify the equation. The relative cross sections are interesting, but we need their absolute magnitudes. In order to resolve these difficulties we are following two courses of action: (a) The temperature dependence of the collision cross sections is being determined from room temperature down to liquid-nitrogen temperature; (b) the nuclear relaxation times will be measured for H^1 and F^{19} in a number of molecules for which the molecular correlation times are known from nonresonant absorption measurements (4). When these measurements are completed, we hope to develop a satisfactory theory for the mechanism of nuclear relaxation in gases.

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B. NUCLEAR RESONANCE LINEWIDTH IN SOLID HYDROGEN SELENIDE

A study has been completed of the second moment of the proton resonance in H_2Se between $65^\circ K$ and the melting point (J. H. Loehlin, Ph. D. thesis, Department of Chemistry, M. I. T., 1960). The experimental results, together with the previously measured heat capacity (1), are summarized in Fig. VII-2. At the lowest temperatures (phase III) the

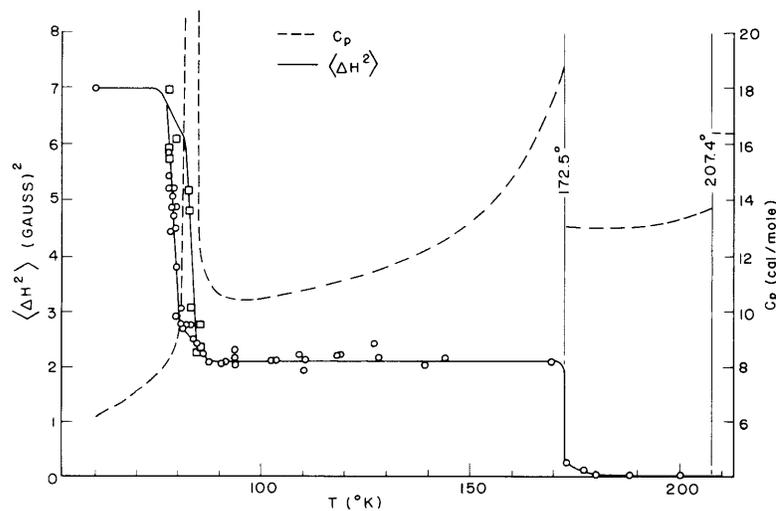


Fig. VII-2. Second moment of the proton resonance in H_2Se .

second moment is consistent only with a rigid structure composed of H_2Se molecules not unlike those found in the gas phase. In the intermediate-temperature region (phase II) the molecules apparently reorient rapidly in situ, and at higher temperatures (phase I) rapid self-diffusion occurs. It is noteworthy that the change in second moment at the III-II transition shows hysteresis, but is not discontinuous, and coincides with the lambda point in the heat capacity, and that the II-I transition is abrupt and also coincides with a heat-capacity anomaly. X-ray powder photographs show that phases I and II are face-centered cubic (as far as the Se atoms are concerned) and that phase III is of lower symmetry. It is probable, but still not certain, that both transitions

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are similar in nature to those in hydrogen sulfide and have to do primarily with changes in the orientational ordering of molecules in the lattice. A detailed argument about the natures of both transitions will soon be submitted for publication to the Journal of Chemical Physics.

This work represents a repetition and refinement of some measurements originally performed by Alpert (3).

J. H. Loehlin

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C. PARITY CONSERVATION IN ATOMS AND MOLECULES

It is well known that the parity of an isolated atom or molecule is a good quantum number, at least approximately, in the absence of external fields. But the recent discovery that parity is not conserved in the weak interactions raises the possibility that some small parity nonconserving interaction (electron-electron or electron-nucleon) may be present in atoms and molecules, so that each state of an atom would actually contain a small admixture of the "wrong" parity.

We are searching for such an effect by trying to detect circular polarization in the absorption of light by an isotopic medium. Since circular polarization reverses its sign upon reflection in a mirror, the presence of circular polarization would clearly show that parity was not conserved, although the converse is not necessarily true. In order to make the experiment sensitive to such an effect, we are looking at a forbidden magnetic-dipole transition; this method measures the first power of the mixing coefficient, and is sensitive to a very small admixture of allowed electric dipole radiation. The particular transition that is being studied is in the spectrum of O_2 , from the ground state $^3\Sigma_g^-$ to $^1\Sigma_g^+$, a transition that gives rise to the well-known atmospheric absorption bands at approximately 7600 Å. We have already determined that any polarization is small (probably less than 5 per cent), and we hope to have a considerably more accurate value soon. Later, we hope to study another similar transition in O_2 , $^3\Sigma_g^- \rightarrow ^1\Delta_g$, and perhaps to continue with a study of the molecule $O^{16}O^{17}$.

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D. HYPERFINE STRUCTURE AND ISOTOPE SHIFT IN Tl^{201} , Tl^{202} , AND Tl^{204}

The hyperfine structure (hfs) and isotope shifts of thallium 201, 202, and 204 have been measured spectroscopically, with the use of techniques previously described (1,2). The only change is in the method of production. These new isotopes were produced by deuteron bombardment of liquid mercury in the external beam of the M. I. T. cyclotron. Two separate bombardments were required: the first was 10 hours long at 35 μ a, the second was 20 hours long at 30 μ a.

In the first run, the hyperfine structures of thallium 201 and thallium 202 were observed. There was an intentional delay of one week between the second bombardment and observation of the spectrum, in order to allow most of the shorter-lived thallium 201 (half-life, 3 days) to die away – leaving thallium 202 and thallium 204 (12 days and 4 years, respectively) in the lamp.

The hfs separations in the $^2P_{1/2}$ and $^2S_{1/2}$ states of thallium 201 are $0.696 \pm 0.004 \text{ cm}^{-1}$ and $0.402 \pm 0.004 \text{ cm}^{-1}$. From these values the magnetic moment of thallium 201 is found to be 1.58 nm. The configuration-mixing model of Arima and Horie (3) yields a value of 1.36 nm, when the contributing proton configuration is $(1h_{11/2})^{12} s_{1/2}$ and the neutron contribution is from the $(1i_{13/2})^{10} (3p_{3/2})^4$ configuration. The value predicted by the single-particle model is 2.79 nm.

The isotope shift 201-205 is $0.124 \pm 0.004 \text{ cm}^{-1}$ in the 3775 A line, and $0.115 \pm 0.004 \text{ cm}^{-1}$ in the 5350 A line. The isotope shifts of thallium 202 and thallium 204 could be measured only in the green line because of overlapping with thallium 205 in the ultraviolet line. The values are $0.104 \pm 0.004 \text{ cm}^{-1}$ for the 202-205 shift, and $0.036 \pm 0.004 \text{ cm}^{-1}$ for the 204-205 shift. In each case the shift is in the direction of the normal volume effect, that is, the heavier isotope has the lower binding energy.

R. J. Hull, H. H. Stroke

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E. HYPERFINE STRUCTURE AND ISOTOPE SHIFT IN NATURAL THALLIUM

The $^2S_{1/2}$ hyperfine structure splittings and isotope shift in the $^2S_{1/2} \rightarrow ^2P_{1/2}$ transition (3776 A) in natural thallium ($_{81}Tl^{203}$, $_{81}Tl^{205}$) have been measured. Increased accuracy over existing values (1) was obtained by using an atomic beam in

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absorption, and a Fabry-Pérot interferometer, in conjunction with a 10-inch reflection grating. The light source was a commercial Osram thallium lamp. The combined apparatus gave absorption linewidths of approximately 10 mK. Fabry-Pérot patterns were reduced by the rectangular array reduction method (2). The $^2P_{1/2}$ splittings for the two isotopes were previously determined quite accurately (3) by atomic-beam magnetic-resonance experiments. The $^2S_{1/2}$ splittings and component separations were determined as ratios of these known values. The results obtained can be listed as follows:

$$Tl^{203} \Delta \nu \ 7^2S_{1/2} = 407.9 \pm 1.4 \text{ mK}$$

$$Tl^{205} \Delta \nu \ 7^2S_{1/2} = 410.9 \pm 1.2 \text{ mK}$$

$$3776 \text{ A line isotope shift} = 55.1 \pm 1.4 \text{ mK.}$$

C. J. Schuler

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F. LEVEL CROSSINGS IN A MERCURY ELECTRODELESS-DISCHARGE LAMP

An Hg^{199} electrodeless-discharge lamp has shown changes in the intensity of the 2537 Å light which it emits while in a magnetic field that is swept through the point of degeneracy of two states in the 3P_1 Zeeman pattern.

The lamp is a quartz and vycor cube, 1 cm on a side, containing argon at 2-mm pressure and approximately 1 mg of enriched Hg^{199} . The mercury atoms are excited by 3-kmc microwave power, which in some cases is delivered to a rectangular cavity containing the lamp. In other cases, the lamp is simply placed adjacent to the open end of the coaxial waveguide of 7/8-inch diameter that carries the power. The cavity, operated in its lowest mode, is oriented so that the microwave electric field is parallel to the dc magnetic field.

The sigma polarized component of the 2537 Å light is observed with a 1P28 photomultiplier placed at right angles to the magnetic field. The field can be swept and simultaneously modulated at 30 cps. The photomultiplier output is amplified, phase-detected, filtered, and displayed on a chart recorder.

The level-crossing effect is observed in emission at a magnetic field that is within a few gauss of that reported by Hirsch and Stager (1) for $Hg^{199} \ ^3P_1$ crossings in

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absorption. However, the line shapes are difficult to interpret. If the 30-cps modulation were small compared with the natural width of the crossing levels, the output of the phase detector would be proportional to the derivative of the light intensity versus magnetic field curve. In the work reported here, it is necessary to use modulation of the same order of magnitude as the natural linewidth in order to achieve an adequate signal-to-noise ratio. While the experimental results can be regarded approximately as first-derivative curves, it would clearly be desirable to be able to do away with the field modulation and measure intensities directly.

Two distinct line shapes, A and B, are observed as shown in Fig. VII-3. Which shape is observed depends on conditions in the discharge that are unknown at the present time. Shape A is to be expected because it is a reasonable approximation to the derivative of the Lorentzian line observed (1) in level-crossing absorption experiments.

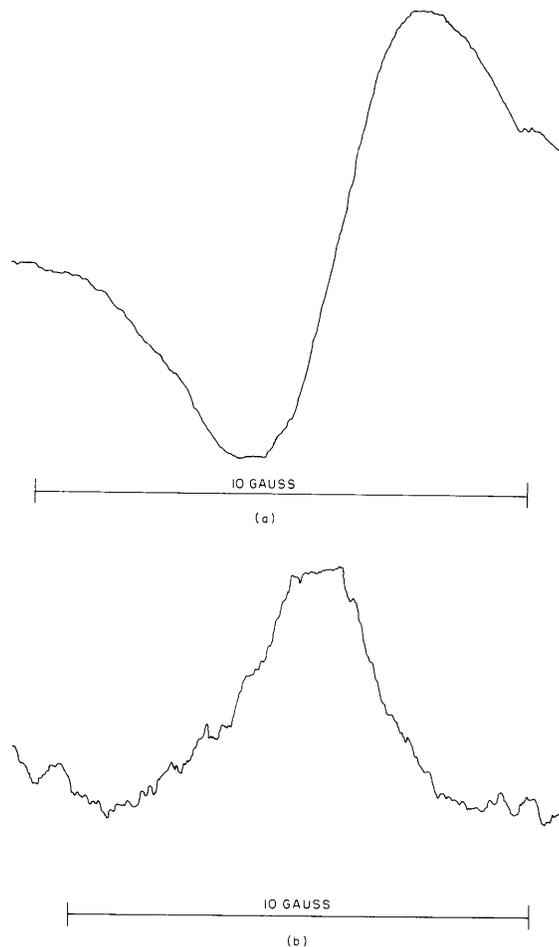


Fig. VII-3. Hg^{199} level crossing in emission:
(a) shape A; (b) shape B.

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Shape B is novel and may be the derivative of a very asymmetric curve. Both shapes are seen with cavity excitation of the lamp, but only shape B has been observed with the lamp excited by the coaxial line.

The atoms in the lamp that display the level-crossing effect may be excited through bombardment by electrons in the gas discharge, or through optical excitation by photons emitted from other radiating atoms. If the primary excitation process is by electron bombardment, a wide variety of line shapes may result, since the electric field at each point in the lamp depends strongly on the behavior of the discharge. On the other hand, our failure to observe level crossings in the nonresonance lines of the mercury discharge is most easily explained on the hypothesis that the excitation is primarily optical.

H. R. Hirsch, W. W. Smith

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