

Survey of Progress in Chemistry

Edited by ARTHUR F. SCOTT

VOLUME 1
1963

Survey of Progress in Chemistry

EDITED BY

ARTHUR F. SCOTT

Department of Chemistry

Reed College

Portland, Oregon

Volume 1

1963



ACADEMIC PRESS
New York and London

COPYRIGHT © 1968, BY ACADEMIC PRESS INC.

ALL RIGHTS RESERVED.

**NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT
WRITTEN PERMISSION FROM THE PUBLISHERS.**

ACADEMIC PRESS INC.

111 Fifth Avenue, New York 8, New York

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 68-22882

PRINTED IN THE UNITED STATES OF AMERICA

Contributors

WILLIAM P. JENCKS, Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts

WILLIAM F. LITTLE, Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina

R. E. RUNDLE, Department of Chemistry, Iowa State University, and Ames Laboratory, U.S. Atomic Energy Commission, Ames, Iowa

RUDOLF M. SALINGER, University of Cincinnati, Cincinnati, Ohio

RILEY SCHAEFFER, Department of Chemistry, Indiana University, Bloomington, Indiana

ALAN W. SEARCY, Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, University of California, Berkeley, California

KENNETH B. WIBERG, Department of Chemistry, Yale University, New Haven, Connecticut

Preface

It is nowadays almost a commonplace that a chemist finds it practically impossible to keep abreast of important developments in chemistry generally, not to mention developments in his own field of special interest. College teachers as a group are perhaps more conscious of this information problem than are some other segments of the chemistry profession. This is really not surprising. Because of their responsibility for the education of chemists-to-be, college teachers feel obliged not only to keep their course materials in step with new developments but also to have some understanding of advances in other areas of chemistry. Yet, as those of us who have been teaching during the past forty years know so well, there has been no significant change in the time available to the teacher for study and assimilation of the steadily increasing flow of new ideas and information. In moments of despair, when a teacher tries to picture the situation which could lie ahead, he is likely to conclude that chemistry instruction might soon lag hopelessly behind the real chemical world—a state of affairs which would be without precedent in academic history. Ways of forestalling such an outcome appear to be rather limited at this point in time. One way would be to improve the means of communication between the research frontier and the teacher; another would be to increase the “study” time available to the teacher; the best of all, however, would be the combination of improved transmission of information to the teacher and the deliberate increase in his “study” time.

The *Survey of Progress in Chemistry* which is being launched with this volume is an attempt to improve the transmission of new material to the college chemistry teacher. Its aim can be expressed neatly in terms of a simile borrowed from J. D. Bernal. We can view the traditional dissemination of chemical information through scientific journals as being on a par with the most primitive level of wind-pollination in certain plants. The more pollen grains released—above a certain number—the more miss the stigmata waiting to catch them. What is needed in the case of chemistry teachers is a more advanced mechanism corresponding

to the selective stage of insect-pollination where, with far less pollen, more gets to the right flowers. It is our hope that the *Survey* will be a definite step toward the more advanced and efficient mechanism, and will serve to bring to the teacher authoritative discussions of recent developments in chemistry that he, as a teacher, should be acquainted with but does not have time to glean from the published literature by himself.

Although the primary "target" of the *Survey* is the chemistry teacher, it is hoped, of course, that the *Survey* will meet the needs of many other groups of chemists who would like to know what is happening in chemistry outside their own fields of activity. For obvious reasons, the series should be helpful also to the beginning graduate student and the ambitious undergraduate who are seeking an introduction to some topic not yet covered in the typical textbook.

In putting together this first volume of the *Survey* the editor naturally faced some interesting policy questions with respect to topics, contributors, and the "level of presentation." In considering topics there seemed to be no good reason to adhere to the traditional subdivisions of chemistry and devote one chapter to physical chemistry, another to organic chemistry, and so on. Indeed, on the frontier of chemical research today there are many points where attack is by a combination of two or more of these divisions; witness, for example, such new fields as "organic photochemistry" and "inorganic biochemistry." Although it is our intention to include, in a single volume, chapters dealing with several areas of chemical activity, the selection of topics for any one volume is dependent to some extent on who can spare the time to write for that particular volume; for it is axiomatic these days that a chemist who is at the forefront of his field of research is an exceedingly busy individual. In preparing his chapter each contributor has kept the college teacher in mind and has employed whatever mode of presentation he deemed best. This is another way of stating that the articles in the *Survey* are not intended to be the usual type of review article which serves another, quite different purpose. To enable the authors to "see" the same group of readers the editor advised them to assume the typical reader to be a college teacher who had completed his graduate studies about ten years ago. It is believed that this description of the potential teacher-reader takes in the major fraction of the present group of chemistry teachers and likewise the major fraction of active chemists.

In conclusion, it is noted with both pleasure and gratitude that many active research chemists have given generous support to the *Survey* project: by encouragement, by suggestions of topics and authors, and by

consenting to prepare chapters for this or future volumes of the *Survey*. The editor is especially indebted to the contributors to this first volume because of their willingness to join in the experiment and also for their full cooperation in carrying it out.

September 1963

ARTHUR F. SCOTT

CONTENTS

LIST OF CONTRIBUTORS	v
PREFACE	vii

New Research Tools of Chemists

RILEY SCHAEFFER

I. Introduction	1
II. Magnetic Resonance Methods	2
III. Mass Spectrometry	11
IV. Diffraction Methods	18
V. Spectroscopic Methods	24
VI. Optical Rotatory Dispersion	29
References	33

High-Temperature Reactions

ALAN W. SEARCY

I. Introduction	35
II. Factors That Determine Equilibrium Reaction Products	36
III. The Displacement of a Metal From Compounds by a Second Metal	47
IV. Displacement of One Nonmetal by a Second Nonmetal	64
V. Conclusion	76
References	77

The Implications of Some Recent Structures for Chemical Valence Theory

R. E. RUNDLE

I. Introduction	81
II. The Rare Gas Rule and Valence Orbitals	85
III. Outer <i>D</i> -Orbital Compounds	117
IV. Summary	127
References	128

Metallocenes**WILLIAM F. LITTLE**

I. Introduction	133
II. Ferrocene	134
III. Other Metallocenes	183
References	203

Oxidation-Reduction Mechanisms in Organic Chemistry**KENNETH B. WIBERG**

I. Introduction	211
II. General Methods of Investigating Oxidation-Reduction Reactions ..	212
III. Ester Mechanisms	219
IV. Hydride Transfer Mechanisms	226
V. Hydrogen Atom Abstraction Mechanisms	229
VI. Electron Abstraction Mechanisms	236
VII. Displacement Mechanisms	238
VIII. Addition-Elimination Mechanisms	241
IX. Conclusion	245
References	246

The Chemistry of Biological Energy Transfer**WILLIAM P. JENCKS**

I. Introduction	249
II. Terminology and Some Examples	251
III. The Source of Useful Energy in Biological Systems	256
IV. Group Transfer Reactions	267
V. Utilizations of Chemical Energy	294
VI. Future Developments	298
References	299

The Structure of the Grignard Reagent and the Mechanisms of Its Reactions**RUDOLF M. SALINGER**

I. Structure of the Grignard Reagent	301
II. Mechanisms of Grignard Reactions	311
References	323
AUTHOR INDEX	325
SUBJECT INDEX	334

New Research Tools of Chemists

RILEY SCHAEFFER

*Department of Chemistry
Indiana University
Bloomington, Indiana**

I. Introduction	1
II. Magnetic Resonance Methods	2
A. Nuclear Magnetic Resonance	2
B. Electron Spin Resonance	10
III. Mass Spectrometry	11
IV. Diffraction Methods	18
A. X-ray Diffraction	18
B. Neutron Diffraction	23
C. Electron Diffraction	23
V. Spectroscopic Methods	24
A. Ultraviolet and Visible Spectroscopy	24
B. Infrared Spectroscopy	26
VI. Optical Rotatory Dispersion	29
References	33

I. Introduction

The development of a totally new research tool is a rare event indeed and has frequently in the past obtained the well-deserved recognition of a Nobel Prize. In the present chapter only magnetic resonance methods have been of such recent development. More often the appreciation by chemists in general of the potent force of a particular tool is the result of improvement and simplification of an instrument which allows broader use by nonspecialists. As more information is obtained with the particu-

lar tool the technique gradually spreads until it is in broad general use. Probably the last area a particular tool reaches is the undergraduate teaching laboratory. The majority of tools described in this chapter have been in limited use by specialists for much or all of the first half of this century but have only recently become available to the majority of workers. In fact we have chosen to include some tools still largely in the hands of specialists in the belief that they will find increasing general use in the coming decade.

The primary purpose of this chapter is to introduce the reader to new tools of the research chemist and some of the newer uses he has made of older tools. The limited space here does not permit detailed treatment of any individual tool and future chapters in this series will be devoted to many of them. Rather we have sought to show some of the major areas of usefulness of a number of common tools and indicate some of the limitations in their use. The reader must consult the references for further details.

* Contribution No. 1101.

II. Magnetic Resonance Methods

A. NUCLEAR MAGNETIC RESONANCE

"I'm sorry, but the electrons don't confide in me" was the answer often given by a well-known professor of chemistry when a question asking for too detailed information was asked by a student. Surely every chemist has wished at times that he had a way of talking directly, or even through a translator, to his favorite molecules and of asking them questions about their structure and chemical behavior. Nuclear magnetic resonance (NMR) affords the chemist a way of asking some very detailed questions of molecules and receiving quite straightforward replies, although he must still learn the "language" to be able to translate the replies into a useful form (see Jackman, 1959; Roberts, 1959, 1961; Brownstein, 1959; Strong, 1959). Typical questions that a molecule might be asked are:

"Do you contain hydrogen (or almost any other element) and, if so, how much?"

"What percentage of an unusual isotope of an element do you contain?"

"What is the arrangement of the atoms within you?"

"Do you exchange atoms with other molecules (of your own chemical type or another) very often?"

'In your travels through solution have you recently had an unpaired electron or come near to a molecule or ion with an unpaired electron?'

Surely a tool that is capable of giving answers to such questions as these well deserve the high regard of the research chemist and also our present attention.

In principle NMR can be used to ask such questions as the foregoing of any molecule that contains an atom of an element of which some isotope exists which is either of odd atomic number or of odd atomic mass. Nearly every element has some stable isotope which satisfies this requirement although, unfortunately, in many cases the isotope may occur in only very low natural abundance. Thus for studies of oxygen compounds only the oxygen-17 isotope is satisfactory, and it is present in normal oxygen only to the extent of 0.037%. Some further limitations apply which will become apparent below, but fortunately some elements of very great chemical interest are well adapted to study using NMR. It is exceedingly fortunate that the method is so readily applied to compounds containing hydrogen since nearly all of the millions of organic compounds will give answers to questions asked by NMR. In addition fluorine, phosphorus, and boron are well adapted to NMR study, and studies of compounds containing a host of other elements (including carbon, nitrogen, oxygen, and silicon) have been carried out.

The equipment necessary for the observation of NMR is simple in principle although, as with most other instruments, the practice is considerably more complex. An NMR spectrometer consists of a magnet capable of producing a highly uniform magnetic field, a radio transmitter operating at a frequency of between 1 and 60 Mc, depending on the isotope to be studied, and a radio receiver carefully tuned to the same frequency. Probably the most difficult condition to achieve is the necessary uniformity of magnetic field (uniform to about one part per hundred million in the frequency range generally used for hydrogen); and the procedures used to assure this uniformity are fairly complex. Nevertheless, the effect itself can be observed with less complicated equipment. Thus it is possible to utilize the magnetic field of the earth itself to observe the effect, and a design that may be copied in the home laboratory and uses only a common permanent magnet has been described by Strong (1959); however, scientific work requires large, and at present costly, equipment.

Several types of spectrometers have been built, but a brief description will be given only of the operation of one of the common commercial types. A small sample of the substance to be studied is placed into a sample tube (thin-walled 5-mm Pyrex tubing is frequently used) and the sample inserted into a "probe" which contains the radio transmitter

coils and receiver coils mounted accurately at right angles to one another and to the applied magnetic field. Adjustments are made to minimize the amount of signal picked up by the receiver. The magnetic field is then slowly increased from lower to higher fields. At certain "resonant" fields the nuclei in the sample are affected by the transmitted frequency and a signal is induced in the receiver coils which is then amplified and recorded. The resultant spectrum is a plot of receiver voltage against applied field. To understand and interpret the spectrum we must look a bit deeper into the source of the effect itself.

The fact is well known to chemists in general that electrons possess a property called spin and behave in many ways as though they were small charged spheres constantly spinning on an axis; it is perhaps less well known that many nuclei also possess the property of spin and may be assigned a quantum number for nuclear spin generally called I . An isotope is suitable for NMR study if its nucleus has nonzero spin. As a general rule the spin of a nucleus is zero only if it is composed of an even number of protons and an even number of neutrons. The spin of the nucleus (or the electron) causes it to behave in many ways as though it were a small bar magnet; that is to say, it possesses a magnetic moment. Consequently, if a nucleus possessing a spin is placed in a magnetic field an interaction takes place which orients the nuclear spin axis with respect to the applied field and causes it to precess about the field axis somewhat like a gyroscope. Quantum restrictions similar to those governing the behavior of electrons apply to nuclei as well; in fact, in the present case there are just $2I + 1$ ways in which the angular momentum of the nucleus may be oriented with respect to the field. In a number of the nuclei useful for NMR (for example, hydrogen and fluorine) the spin of the nucleus is $\frac{1}{2}$ so that the number of possible orientations is $2 \times \frac{1}{2} + 1 = 2$; the nuclear spin precession axis may be aligned with or against the field. In most of the discussion to follow we shall confine ourselves to those nuclei of $I = \frac{1}{2}$.

In the absence of a magnetic field all orientations of nuclear spin are equally likely, but when a magnetic field is applied this degeneracy is removed and a definite energy difference exists between the two possible spin orientations. Unlike most spectroscopic experiments, the energy difference between these two states can be varied at will since it depends directly on the strength of the magnetic field employed according to an equation of the form

$$h\nu = kH_0$$

in which h is Planck's constant, ν is the frequency of the transition (analogous to the frequency of an infrared or ultraviolet transition in ordinary optical spectroscopy), k is a constant which may be expressed

as a combination of more fundamental atomic constants, and H_0 is the applied field. For technical reasons which we need not go into at this time, it is advantageous to work at the highest practical magnetic fields which can be maintained uniform to the necessary degree. With present commercial instruments this is somewhat in excess of 14,000 gauss, and many current instruments operate at about 10,000 gauss. Each nucleus will possess a characteristic absorption frequency, and in fields of the magnitudes mentioned above this is found experimentally to be in the range of a number of megacycles per second—a convenient radiofrequency range. Table I lists characteristic NMR frequencies for some common isotopes in a 10,000 gauss field.

TABLE I

CHARACTERISTIC NMR FREQUENCIES IN Mc/SEC FOR A 10,000 GAUSS FIELD

Isotope	Spin I	Natural abundance (%)	NMR frequency (10,000 gauss)
H ¹	$\frac{1}{2}$	99.98	42.577
B ¹¹	$\frac{3}{2}$	81.2	13.660
N ¹⁴	1	99.635	3.076
N ¹⁵	$\frac{1}{2}$	0.365	4.315
O ¹⁷	$\frac{5}{2}$	0.037	5.772
F ¹⁹	$\frac{1}{2}$	100.00	40.055
P ³¹	$\frac{1}{2}$	100.00	17.235

It would appear from what has thus far been said that all nuclei of a given isotope would respond to an applied radiofrequency at exactly the same applied field and, indeed, this is true to a very high degree; thus, if a sample of ethanol is inserted between the coils, a single, somewhat broad resonance is observed unless the magnetic field is very uniform. Even this single signal can be used, however, since the intensity of an NMR signal depends under normal operating conditions only on the number of nuclei contained between the coils of the probe. Thus through the use of standards a convenient method may be worked out for the analysis of concentration of alcohol (in a nonproton-containing solvent).

In a sensitive spectrometer, however, each chemically different nucleus in the molecule gives rise to a separate resonance (or as will be seen below, several resonances) at slightly different fields. The reason for this is to be found simply in the fact that the phenomenon is a *nuclear* one and the important field in the foregoing equation for resonance is the one *actually effective at the nucleus*. This may be different from the applied field

owing to several different causes: (1) The electrons present in the molecule both in the lower lying levels in the atoms and, of more importance, in the valence shells exert some magnetic effects—the nucleus is “shielded” to a degree from the effects of the applied field. If two nuclei of a given type are not shielded to exactly the same degree there will be a slight “chemical shift” in the position of their resonances. (2) Each of the other nuclei of non-zero spin will slightly alter the field seen by a particular nucleus. This leads to the phenomenon of “spin-spin” coupling and will be discussed further on. To observe the interplay of these two factors in giving useful chemical information the more detailed spectrum of ethyl alcohol is often used as an example and is treated briefly below. (3) The presence of any magnetic particles in the solution studied may effectively change the field at the nucleus of the observed atom. It is this effect which enables one to answer the last question asked in the first paragraph of this section.

As the resolution of the instrument giving only a single absorption for ethanol is improved, the single absorption splits up into three different resonances (one arising from each of the chemically different hydrogen atoms) as shown in Fig. 1. A great benefit of the dependence of signal

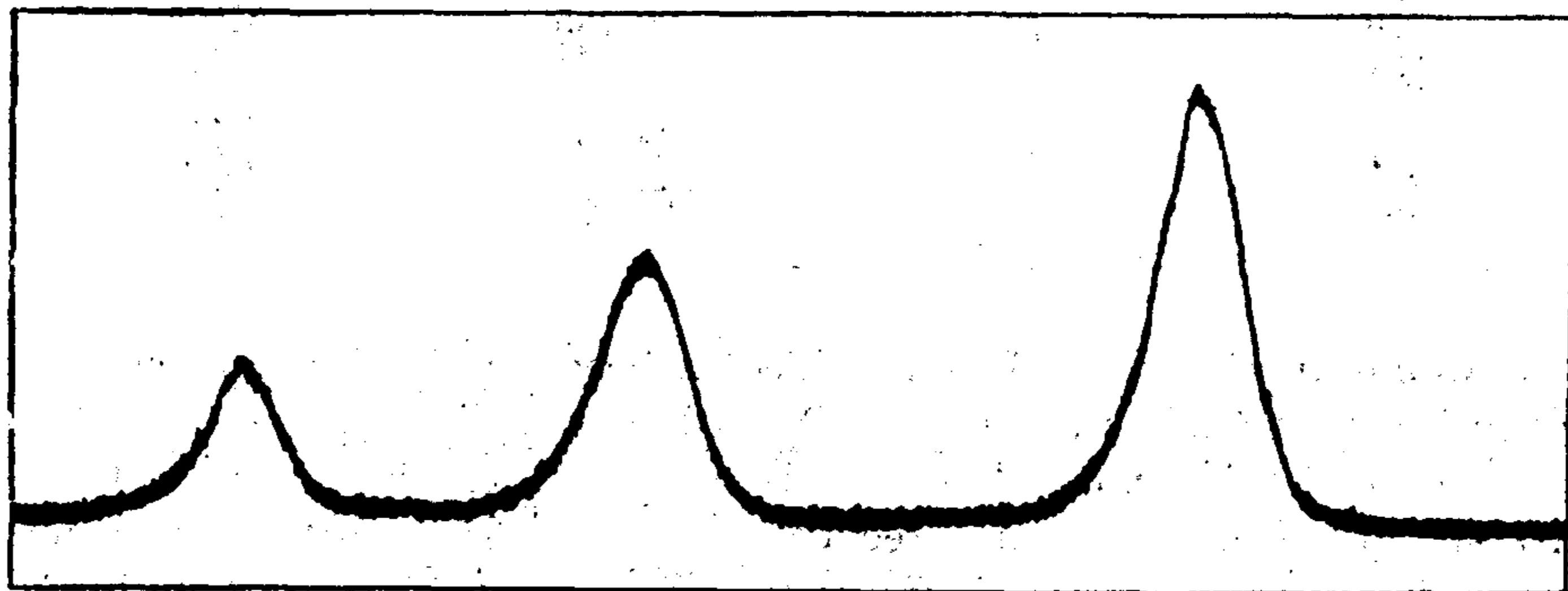


FIG. 1. The low resolution spectrum of ethanol. [Reprinted with permission from Jackman (1959).]

intensity only on the number of nuclei responsible for the signal can be seen at once: the three peaks are in the intensity ratio of 1:2:3 corresponding to one O—H proton, two CH₂ protons, and three CH₃ protons, respectively. It can easily be seen that such a subtle difference as that between a CH₂ and a CH₃ group is sufficient to give a readily apparent chemical shift between the two resonances (the difference does not depend wholly on the presence of the OH group since resonances from both CH₂ and CH₃ groups can readily be observed for even a molecule

such as propane, although it is substantially smaller in such a case). The three signals appear at slightly different values of the field since there are slight differences in the extent of shielding of the different protons by the valence electrons.

As the field homogeneity is improved still further (spinning of the sample tube on an axis through the two sets of coils helps to even out field inhomogeneities), the three basic lines split up once more into more complicated patterns. If the ethanol contains a slight trace of acid the pattern next appears as in Fig. 2. The CH_3 resonance has become a

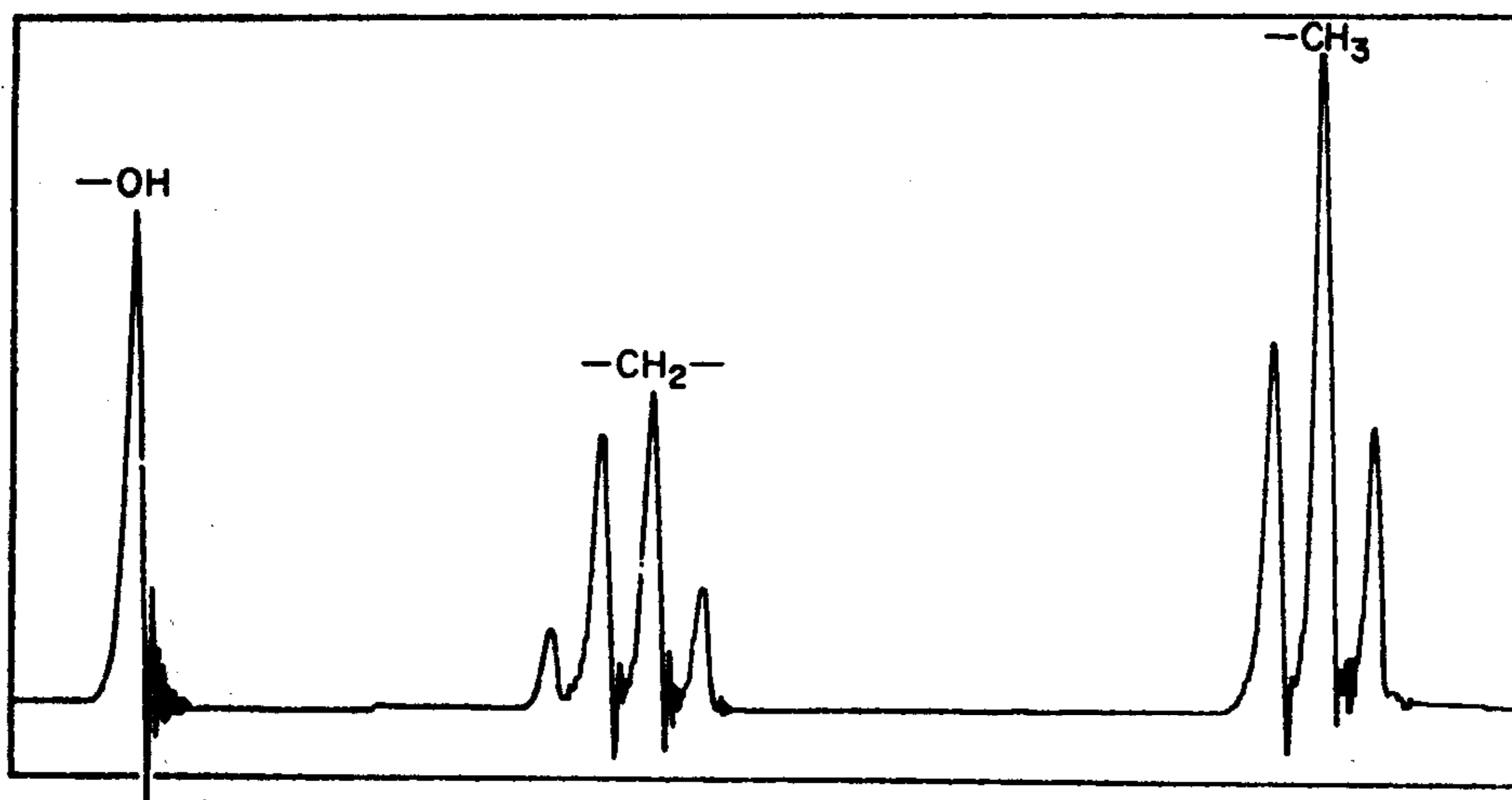


FIG. 2. The high resolution spectrum of ethanol containing a trace of acid. [Reprinted with permission from Jackman (1959).]

triplet of relative intensity 1:2:1, whereas the CH_2 has become a quartet with peaks in the ratio of 1:3:3:1, and the OH line, under these conditions, remains as a single peak. The effect of the nuclear spins of the CH_2 protons is felt by the CH_3 protons and vice versa through spin-spin coupling. The pattern produced is quite predictable: the total spin of the two methylene group protons is $\frac{1}{2} + \frac{1}{2} = 1$ leading to $(2 \times 1) + 1 = 3$ different orientations of their total spin and thus three fields and consequently three lines for the methyl resonances. Since there is only one way for the two methylene resonances both to add or both to subtract from the applied field and there are two ways in which their spins can cancel one another in the effect on the applied field, the central line is of twice the intensity of the outer two. In general, for spin coupling to more than one hydrogen, the intensities will be in the ratio of the binomial coefficients of the same order: equal intensity for two lines if spin coupled to

one hydrogen; 1:2:1 intensities for two; 1:3:3:1 for three; 1:4:6:4:1 for four etc. Thus the peaks arising from the methylene protons reflect the fact that they are spin coupled to the three methyl protons.

If the acid present in the ethanol is now carefully removed, a still more complex spectrum results. The hydroxyl proton splits as it is affected by the two CH_2 protons into a 1:2:1 triplet similar to that of the methyl group, but having only one-third the intensity of the latter since there are only one-third as many protons in the group. At the same time the methylene group protons are split once more by spin-spin coupling to the hydroxyl proton, resulting in the over-all pattern shown in Fig. 3. At this

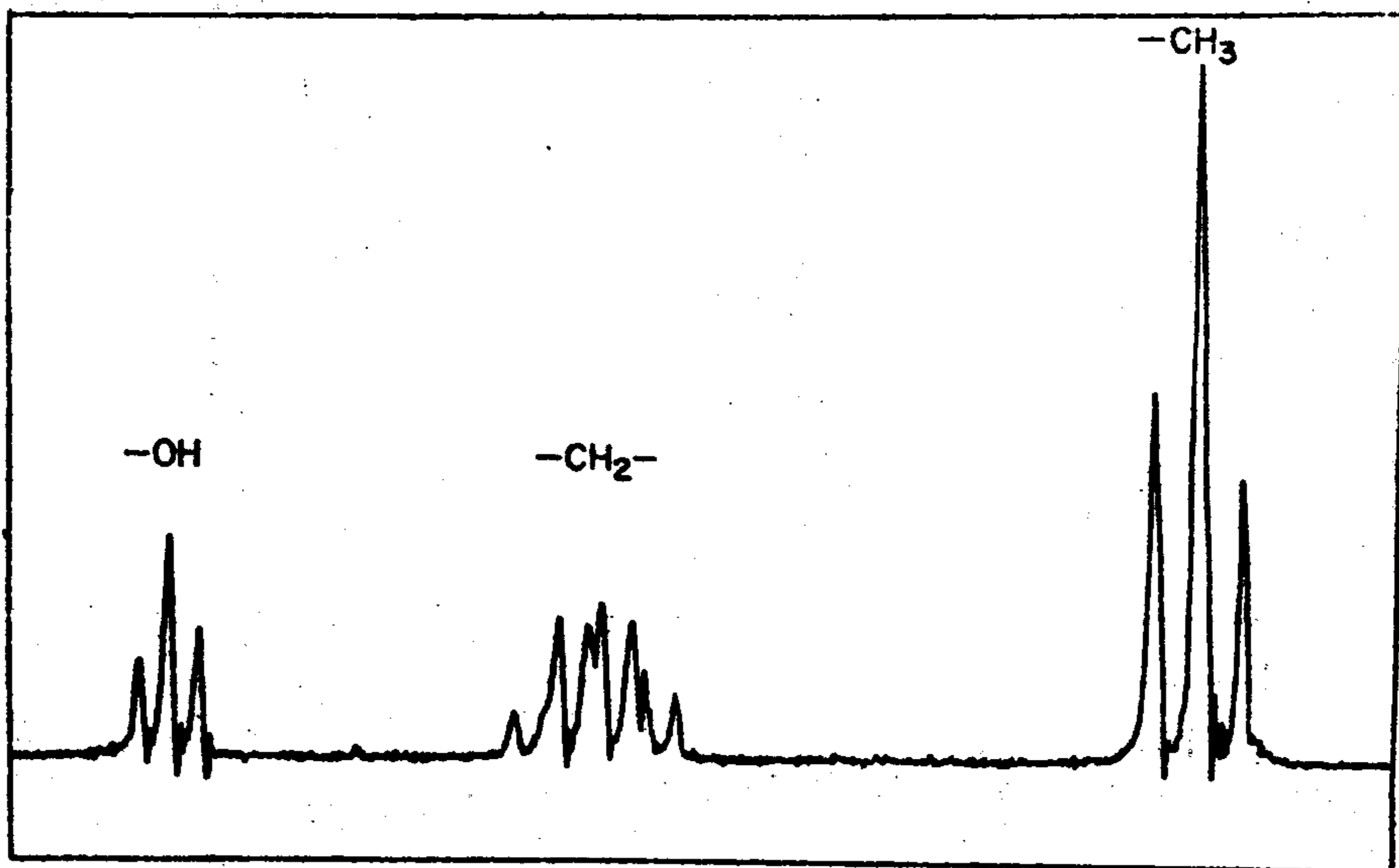


FIG. 3. The high resolution spectrum of highly purified ethanol. [Reprinted with permission from Jackman (1959).]

stage the complete chemical structure of ethanol could be worked out from the NMR spectrum alone, although the details of bond angles and distances are of course not given.

The effect of excess acid on the spectrum of ethanol is striking and leads us naturally to another useful result. In the presence of small amounts of either acid or base, the hydroxyl protons gain lability and begin to be passed between alcohol molecules at a rate which depends on the acid or base concentration. As the acidity is increased slowly, the hydroxyl triplet of pure ethanol begins to gradually change as the outer two lines move in and shrink and the central line grows until one broader line results. The effect arises from a relatively simple cause: if the proton