

Figure 3. Heat of adsorption of CO and N₂ on alumina: open points are from low-pressure adsorption data and solid points from high-pressure data.

it was confirmed that there was no change in the helium density, surface area, or X-ray structure of the alumina sample taken out of the piezometer after finishing all high-pressure measurements.⁸) The full reversibility of the adsorption and the quickness with which adsorption equilibrium is established, as indicated by steady pressure within 1 hr. of changing to a new contact of the piezometer, indicate that only physical adsorption, and no chemisorption or any such slow activated process is involved in this case.

The adsorption of CO on alumina at pressures below atmospheric, however, involves much stronger adsorbent-adsorbate interactions. A conventional volumetric adsorption apparatus has been used to measure the adsorption at -78, 0, and 20° for both CO and N₂ on the alumina sample. The isosteric heats of adsorption as a function of surface coverage by the two gases from the 0 and 20° low-pressure isotherms and from the

0 and 25° high-pressure isotherms (ΔG vs. P) are plotted together in Figure 3, which shows the high heat of adsorption for the first amounts of CO adsorbed.

Calculation of entropy change on adsorption of CO and N₂ on alumina both at low pressures and at high pressures gives an idea of the thermodynamic behavior of the gases in the adsorbed state, in particular the mobility of the adsorbed molecules.⁸ Until the surface coverage θ reaches about 0.003, the adsorption of CO seems to involve strong interactions with the surface with the consequence that the adsorbed molecules seem to be quite immobile and fixed to definite sites on the surface. The small dipole moment of CO, its larger quadrupole moment, and greater polarizability, as compared to N₂, apparently seem to have a profound influence on the first amounts of CO adsorbed on alumina, making it a case of stronger physical adsorption. But at about $\theta = 0.011$, the CO adsorption conforms more to the mobile than to the fixed-site type. At high pressure it shows supermobile adsorption, just as for N₂ on alumina at the same coverage and temperature. When the total number of molecules on the surface (the amount adsorbed together with the amount present in a surface layer due to the applied high gas density only) reaches about 60-65% of the v_m value from the B.E.T. equation, restrictions on the mobility of the adsorbed CO molecules become gradually noticeable.

A detailed analysis of these results and a tentative explanation for the second ascending and endothermic part of the high-pressure N₂ adsorption isotherms will be published separately.

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(8) J. H. de Boer and P. G. Menon, *Proc. Roy. Acad. Sci. (Amsterdam)*, B65, 17 (1962).

The Direct Measurement of Centroids of High-Resolution Nuclear Magnetic Resonance Spectra

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The direct measurement of the average chemical shift from the centroid of a high-resolution n.m.r. spectrum is accomplished by a simple extrapolation of the double integral. The technique is justified, described, tested, and applied.

Anderson and McConnell have shown how the lower moments of high-resolution magnetic resonance spectra are expressly related to the magnetic parameters, particularly the chemical shifts, which are involved.¹

(1) W. A. Anderson and H. M. McConnell, *J. Chem. Phys.*, 26, 1496

In the simplest instance the centroid, or normalized first moment, was equated to the average value of the chemical shifts regardless of complications in the spectrum due to spin couplings. In addition to being thereby an accessible quantity, the mean chemical shift is in several ways a useful one. It serves as a convenient starting point for the assignment of transitions in complex spectra,² gives a direct way of measur-

(1957); see also, J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 156-160.

(2) E. B. Whipple and Y. Chiang, *J. Chem. Phys.*, 40, 713 (1964).

ing by difference the chemical shifts of hydrogen replaced by deuterium in complicated spin systems, and can sometimes be itself a sufficient criterion for the solution of a chemical structure problem.

The n th moment of the spectrum from a single group of nuclei was defined in the work of Anderson and McConnell by eq. 1, where the displacements

$$\langle \nu^n \rangle = \sum_{pq} (\nu_{pq})^n L_{pq} / \sum_{pq} L_{pq} \quad (1)$$

ν_{pq} are in units of frequency measured from some arbitrary reference, and the intensities, L_{pq} , are in any convenient units.¹ Equation 1 and the relations derived from it assume a line spectrum. Since the actual absorptions have finite widths and may be incompletely resolved, the measured moments are more generally defined by eq. 2, where the spectral density

$$\bar{G}_n = \int_{\nu_1}^{\nu_2} \nu^n G(\nu) d\nu / \int_{\nu_1}^{\nu_2} G(\nu) d\nu \quad (2)$$

function, $G(\nu)$, is assumed to vanish outside the region $\nu_1 < \nu < \nu_2$. While it is clear that results derived from (1) are not generally true for (2), the substitution is valid for the first moment ($n = 1$) provided that $G(\nu)$ is the composite of individual line shapes, $g_{pq}(\nu)$, each of which is symmetrical about a frequency corresponding to the respective line in (1), and has the area L_{pq} . This is proved by translating the origin of each component of $G(\nu)$ in eq. 2 to obtain eq. 3. If the

$$\bar{G}_1 = \frac{\sum_{pq} \int_{\nu_1}^{\nu_2} (\nu - \nu_{pq}) g_{pq}(\nu) d\nu + \sum_{pq} \nu_{pq} L_{pq}}{\sum_{pq} L_{pq}} \quad (3)$$

line shapes are even functions about their center frequencies, ν_{pq} , then the odd functions comprising the first term of eq. 3 all vanish as long as the range of integration includes enough of the signals to approximate a symmetrical interval about each. Equation 3 then reduces to eq. 1.

The sweep rates employed in most practical measurements exceed the conditions for slow passage under which the assumption of a symmetrical line-shape function is justified. Even then the displacement of the centroid from the center resonance frequency is inappreciable; less, for instance, than the corresponding displacement of the maximum absorption. This can be verified from calculated line shapes³ or demonstrated experimentally by measuring the centroids of a single line under opposing sweep directions.

1. Technique

The essential prerequisites for accurate instrumental measurements of the moments of a spectrum are a drift-free scanning system and a stable base line, both of which are satisfied in commercially available spectrometers. Most are also equipped with electronic integrating systems,⁴ so that the only modification necessary is to insert a scaling device which is proportional to the magnetic field between the spectrometer output and the integrator input. One very simple device consists of a linear potentiometer mechanically

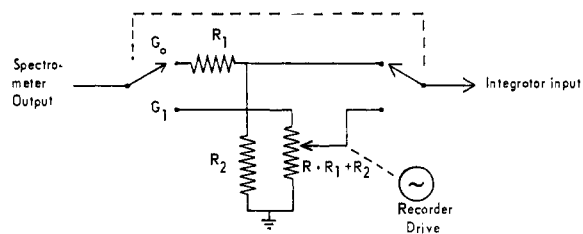


Figure 1. A-60 spectrometer modification for direct measurement of first moments.

coupled to the recorder drive system of a Varian A-60 spectrometer. This is illustrated in the G_1 switch position of Figure 1. The G_0 position provides a separate measurement of the integral at a fixed attenuator position, which is necessary for normalization. An example is shown in Figure 2. With proper buffering this method can be extended to the higher moments.

A better method for direct measurement of the centroid utilizes double integration. Once an entire spectrum is traversed ($\nu > \nu_2$), its double integral enters a linear region described by eq. 4. The constant

$$\int_{\nu_1}^{\nu > \nu_2} \int_{\nu_1}^{\nu} G(x) dx d\nu = G_0 \nu + c \quad (4)$$

in eq. 4 can be identified with the unnormalized first moment by integrating the defining equation of the latter by parts (eq. 5). Making this substitution and

$$G_1 = \int_{\nu_1}^{\nu > \nu_2} \nu G(\nu) d\nu = G_0 \nu - \int_{\nu_1}^{\nu > \nu_2} \int_{\nu_1}^{\nu} G(x) dx d\nu \quad (5)$$

solving (4) for its horizontal intercept, ν_0 , gives $\nu_0 = G_1/G_0 = \bar{G}_1$, which implies that an extrapolation of the linear region of the double integral back to its intersection with the base line gives a direct determination of the centroid. An example is shown in Figure 2, where it can be compared with the direct method. The double integral has the obvious advantage of requiring a single measurement rather than the ratio of two.

Double integration of an n.m.r. spectrum can be accomplished either by connecting two single integrators⁴ in series or by modifying the integrating circuit to accumulate the double integral with a single operational amplifier.⁵ The circuit in Figure 3 gave satisfactory results under conditions similar to those in Table I, although as a matter of convenience most of the experiments described here used the series integration method.

In passing, it is of interest to note that eq. 5 can be applied to broad-line and e.p.r. spectrometers employing field modulation and synchronous detection to show that the double integral and unnormalized first moment have equal magnitudes. This follows simply from the fact that the integral over the signal vanishes in this mode of detection. The result is of interest inasmuch as the first moment, and hence the double integral, remains simply proportional to the absorption

(3) B. A. Jacobsohn and R. K. Wangness, *Phys. Rev.*, **73**, 942 (1948).

(4) Varian Associates Staff and Consultants, "NMR and EPR Spectroscopy," Pergamon Press, New York, N. Y., 1960.

(5) Technical Data for Model UPA-2 Utility Packaged Amplifier, George A. Philbrick Researches, Inc., Boston 16, Mass.

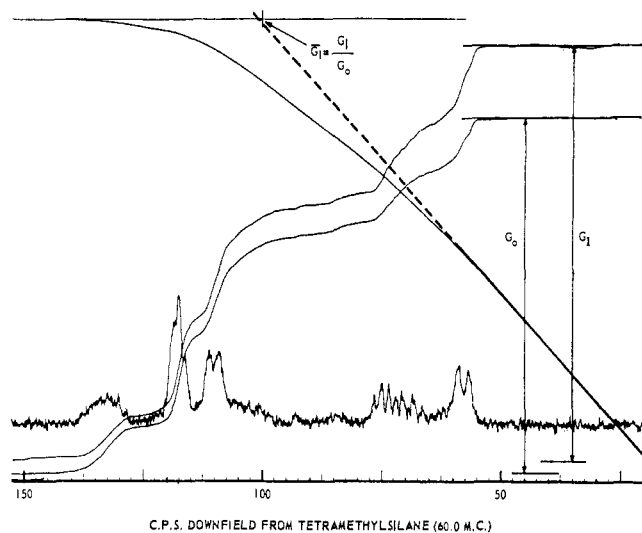


Figure 2. N.m.r. spectrum with its integral, first moment, and double integral displayed. The spectrum is of the protons in *exo-trans-endo-pentacyclo*[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecane-*exo-5,6,11,12-d₄*.

intensity even when the instrument distorts the signals from their limiting derivative shapes.⁶

2. Applications

In order to determine chemical shifts and spin coupling constants uniquely from an experimental spectrum, it is necessary to assign the observed transitions to a set of energy levels.⁷ This task is facilitated by the use of frequency sum and difference rules.^{7,8} One of the simplest of these is that the sum of the frequencies of any set of transitions which connect progressively the uppermost and lowermost energy levels of a system equals the sum of the chemical shifts. This follows from the fact that all intermediate levels in the sum will cancel, and the coupling terms, which depend on the relative orientations of the individual spins, will be the same for both extreme levels. A systematic approach to the complete analysis of a spectrum from N spins might begin, therefore, by picking out all sums of N frequencies which are equal to $N\bar{G}_1$.² Conversely, one can use the sum rule for an assigned spectrum to determine a precise value for its first moment, thereby testing the applicability of eq. 2 under a variety of experimental conditions. A vinyl chloride sample whose spectrum had been previously analyzed² was chosen for this purpose. Using an external Miller integrator⁴ in place of the voltage dividers in the experimental arrangement of Figure 1, the centroids in Table I were measured under varying sweep conditions and field homogeneity as indicated.

Random errors, which are due largely to uncertainties in extrapolation and to spectrometer and/or integrator drift, are of the order of 0.5% of the total sweep. Determinate errors, by virtue of eq. 3, include all effects which tend to product an asymmetric line shape. These errors can be operationally subdivided according to whether or not they depend on the conditions of

(6) P. H. Verdier, E. B. Whipple, and V. Schomaker, *J. Chem. Phys.*, **34**, 118 (1961).

(7) J. D. Swalen and C. A. Reilly, *ibid.*, **37**, 21 (1962).

(8) S. Castellano and J. S. Waugh, *ibid.*, **34**, 295 (1961).

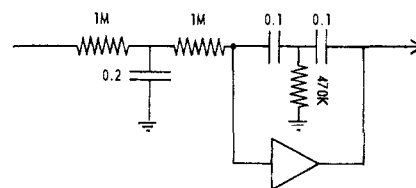


Figure 3. Typical circuit for double integration using an H. A. Philbrick Researches, Inc., Type UPA-2 operational amplifier.

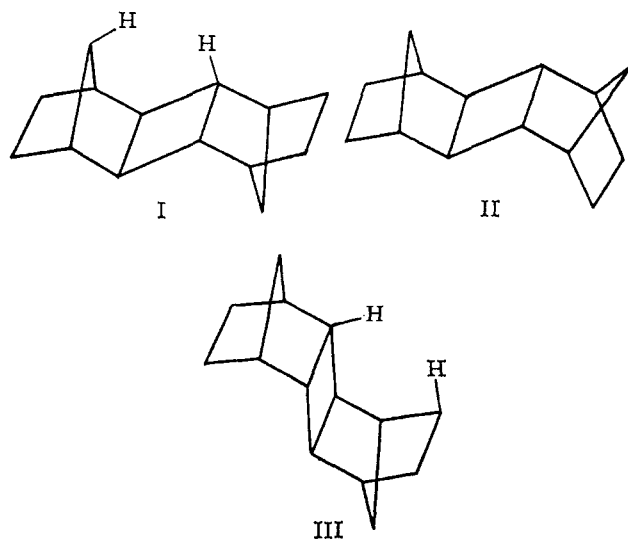
passage through resonance. The data in Table I might appear to indicate that systematic errors of both kinds occur, but are small. As mentioned earlier,

Table I. Measured Centroids of Vinyl Chloride N.m.r. Spectrum^a

Sweep rate, ^b c.p.s./sec.	Obsd. centroid, ^c c.p.s.	Sample spinner
0.4	343.1	Off
1.0	342.5	Off
	342.7	On
2.5 ^d	343.3	Either
-0.4	344.1	On
-1.0	343.9	On
-2.0	343.4	On

^a Observed centroid = 342.8 c.p.s. ^b Positive sense toward increasing applied field. ^c C.p.s. downfield from tetramethylsilane at 60.0 Mc. ^d Scanning range of 250 c.p.s. rather than 100 c.p.s.

graphical integration of theoretical³ line shapes confirms that rapid-passage line-shape errors are of minor consequence, and the same is true of errors due to the measuring system response, determined here by the integrator RC time constants of 0.01 sec. Even the apparent experimental difference between centroids measured under opposite sweep directions is not consistently observed in other measurements, so that its significance here is questionable. At any rate, these errors can be averaged over opposing sweep directions. Two sources of line-shape errors which cannot be averaged are field inhomogeneity and detector phasing. The effect of the latter is to admix some of the second moment⁹ and should be affected by sample spinning.



(9) This is based on the assumption that the dispersion mode signal is proportional to $\nu G(\nu)$, which is valid for the slow-passage solution to the Bloch equations.

Field homogeneity errors are apparent in the measured centroids of single lines in undercycled and overcycled⁴ fields, and a slightly overcycled field is the most likely source of the low-field average in Table I.

In many cases it should be possible to utilize the centroids of spectra to distinguish among alternative solutions to a chemical structure problem. To do so, it is necessary that some predictable difference in chemical shifts be of sufficient magnitude to deflect the average. For example, a detailed study of the proton magnetic resonance spectra of *trans*-norbornene dimers has established¹⁰ that the pairwise interactions depicted below cause mutual, paramagnetic shifts of about 0.3 p.p.m. in the case of I and 0.6 p.p.m. in the

(10) D. R. Arnold, D. T. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

case of III. Apart from these, the only shifts which vary appreciably with configuration are those resulting from exocyclic or endocyclic environments for the protons on the four-membered ring. In I there are four endocyclic protons and four interacting pairs of the first type, in III there are four exocyclic protons and four interacting pairs of the second type, while II has two protons and two interactions of each type. The shifts combine to displace the centroid of I to higher field than II and III to lower field than II by approximately $1.8/N$ p.p.m., where N is the number of protons per molecule.

This situation is not altered by substitution in positions not involved directly in the interactions I or III, so that the configurations of various dimers of substituted norbornenes could be assigned simply by comparing the centroids of their n.m.r. spectra.

The Ionic Bond

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The model chosen to define the ionic bond is that of two oppositely charged spheres, each slightly polarized by the electric field of the other. The properties of the one-electron density distribution obtained from the Hartree-Fock wave function for LiF are compared with those of the model to determine how closely the bond in LiF approaches the ionic case. This comparison is carried out in terms of the forces exerted on the nuclei and by a direct comparison of the molecular density distribution with that of the ions Li^+F^- .

Introduction

An increasing number of Hartree-Fock wave functions are being made available for simple molecules. While the molecular binding energies predicted by these wave functions are too small by an amount equal to the correlation energy of the electrons, the derived one-electron density distribution and those properties which are determined by this distribution are correct to the second order.² Thus, a meaningful discussion of chemical bonding can be carried out in terms of Hartree-Fock one-electron density distributions and their dependent properties. The force acting on a nucleus in a molecule is an example of such a property, and, since this force is rigorously determined by classical electrostatics,³ it provides an excellent basis for the discussion of chemical binding.⁴ What is indeed available through these quantum mechanically determined density distributions is a classical description of the chemical bond.

(1) A. P. Sloan Research Fellow.

(2) For a recent review of this matter see C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964).

(3) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939); H. Hellmann, "Einführung in die Quantenchemie," F. Deuticke, Leipzig, 1937, p. 285.

(4) R. F. W. Bader, *Can. J. Chem.*, **41**, 2303 (1963); R. F. W. Bader and G. A. Jones, *ibid.*, **41**, 2251 (1963).

We shall apply such an analysis to the bond in the lithium fluoride molecule.

The lithium fluoride molecule possesses a dipole moment of 6.284 D.⁵ The separation of equal and opposite charges at the observed lithium fluoride bond length gives a dipole moment of 7.51 D. It is obvious that this molecule will possess a highly ionic bond by any previous definition of the word "ionic." According to Pauling's⁶ definition of ionicity as the ratio of the observed dipole moment to that obtained for complete charge separation, the lithium fluoride molecule is 84% ionic and 16% covalent. With a Hartree-Fock density distribution available for this molecule, such useful but ambiguous definitions of bonding should be improved upon. The simplest physically realizable model of an ionic bond is that of two oppositely charged ions in contact, each necessarily polarized to a slight extent by the electric field of the other. We choose this as our definition of an ionic bond. This definition relates a purely ionic bond to the *complete transfer* of one or more units of negative charge. Slight distortions of the spherical charge distributions of the ions must be allowed for, or the ionic bond becomes a physically unrealizable situation. These small polarizations reduce the dipole moment due to the complete transfer of charge. Thus, as Rittner has pointed out,⁷ the observation of a dipole moment less than that calculated for complete charge separation does not rule out the possibility that the transfer of one electronic charge from one atom to the other is complete. We shall investigate how closely the Hartree-

(5) L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *J. Chem. Phys.*, **38**, 1203 (1963).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(7) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).