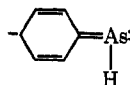


be ascribed to a stabilization of the acid, relative to its conjugate base. There is little such stabilization of the conjugate base because the $p\pi$ - $d\pi$ interaction would cause a shift of electron density toward an atom with a formal charge of $1-$. For the cases of phenylgermane⁶ and phenylarsine, the effect probably has a similar magnitude, and contributing resonance structures of the following type can be written



The acid-strengthening effect of the phenyl group in $C_6H_5MH_x$ is due (in addition to a relatively weak σ inductive effect) to a stabilization of the anion by interaction of an empty $p\pi$ molecular orbital of the phenyl ring with a filled $p\pi$ "nonbonding" orbital of the M atom. The effect is operative in the phenyl derivatives of methane and of the hydrides of elements of groups V and VI.⁷ For example, in the case of phenylarsine, resonance structures of the following type can be written for the anion



We assume that the valence orbitals of the arsenic atom in the anion are involved in bonding as follows: one $p\sigma$ orbital in the As-H bond, a $p\sigma$ orbital and a $p\pi$ orbital in the As-C bond, and an s orbital for the completely nonbonding lone pair. On this basis the ion should be completely planar, with a 90° C-As-H bond angle. Presumably there is little such $p\pi$ - $p\pi$ stabilization of phenylarsine; the lone-pair orbital on the arsenic atom in phenylarsine probably has very little p character because of the high s^2p^3 - sp^4 promotion energy.⁸ (The H-As-H bond angle of 91.8° in arsine⁹ is structural evidence of the "inertness" of the lone pair).

The acid-strengthening effect is inoperative in phenylgermane¹⁰ because the lone-pair orbital on the germanium atom of the $C_6H_5GeH_2^-$ ion (like that on the arsenic atom of the isoelectronic $C_6H_5AsH_2$) has little p character. Consequently there can be no significant $p\pi$ - $p\pi$ interaction between the phenyl ring and the germanium atom in the anion without an energetically unfavorable hybridization of the germanium orbitals. These conclusions are consistent with the facts that no compound is known containing a $p\pi$ - $p\pi$ bond between

(6) Birchall and Drummond⁴ have observed slight downfield nmr shifts for the ortho and para hydrogens of phenylgermane, relative to benzene. Because various complicated factors can influence the chemical shifts of ring protons, these results are difficult to interpret in terms of $p\pi$ - $d\pi$ bonding. Indeed, it is not even known whether $p\pi$ - $d\pi$ bonding sufficient to account for the observed acidity effects would involve enough electron withdrawal from the phenyl ring to cause a significant chemical shift in the nmr of the phenyl protons.

(7) The nonbonding electrons of the conjugate bases of these hydrides have considerable p character. This feature is a prerequisite for the π acid-strengthening effect.

(8) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, p 122.

(9) W. L. Jolly, "The Chemistry of the Non-Metals," Prentice-Hall, Englewood Cliffs, N. J., 1966, p 91.

(10) Birchall and Drummond⁴ have observed a slight downfield nmr shift for the ortho hydrogens of the phenylgermane anion. They have interpreted the nmr spectrum as evidence for the absence of conjugation between germanium and the ring.

carbon and germanium and that the germacyclopentadienide ion shows no aromatic character.¹¹

Apparently whenever the π acid-strengthening effect of a phenyl group is operative, it overpowers any possible acid-weakening effect. The latter effect wins by default in the case of phenylgermanes; it probably will be found to do likewise in the case of phenylsilanes—and perhaps in the case of phenylstannanes. It should be pointed out that possibly the acid-weakening effect of a phenyl group can be ascribed partly or completely to a cause other than $p\pi$ - $d\pi$ bonding; whatever the cause, the explanation of the weak acidity of the phenylgermanes remains intact.

Acknowledgment.—This work was supported by the U. S. Atomic Energy Commission.

(11) M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

CHEMISTRY DEPARTMENT
UNIVERSITY OF CALIFORNIA AND
INORGANIC MATERIALS RESEARCH DIVISION
LAWRENCE RADIATION LABORATORY
BERKELEY, CALIFORNIA 94720

WILLIAM L. JOLLY

RECEIVED FEBRUARY 5, 1971

Fundamental Nature of the Correlation of ΔH vs. ΔS . Lanthanide Fluoride Complexes

Sir:

In a recent communication, Fay and Purdie¹ discussed the "correlation of ΔH and ΔS for a series of analogous metal complexes" with respect to "common structure throughout the series" and illustrated the confusion which has evolved in this subject. Their stated intent was "to point out the incorrect reasoning of this interpretation—in order to prevent any later misguidance in the interpretation of these approximately linear relationships." By examining two linear relations between ΔH and ΔS constructed from measured values for several lanthanide and alkaline earth complexes, they suggested that either a linear least-squares fit or a linear fit with $d\Delta H/d\Delta S = 0.298$ (*i.e.*, corresponding to the temperatures of the measurements) is satisfactory. Accordingly they concluded with two statements: (1) "Since the linear correlation is contingent upon a certain restriction on ΔG and since ΔG tells us nothing about the structure of the complexes in solution, then conversely the linear dependence of ΔH - ΔS should be independent of the structural properties of the complexes." (2) "The reason for the correlation is more fundamental than one of structure."

In this communication we shall attempt to indicate the significance of the "fundamental" part of the second conclusion by Fay and Purdie (FP) but at the same time try to demonstrate the fallacy of accepting without qualification the second part (*i.e.*, "one of structure") and the last part of the first conclusion (*i.e.*, " ΔH - ΔS should be independent of the structural properties..."). In fact, the potential rationale and theory underlying the correlation is a fundamental one which if investigated and understood in this perspective is intimately

(1) D. P. Fay and N. Purdie, *Inorg. Chem.*, **9**, 195 (1970).

associated with structure.^{2,3} However, to appreciate and recognize these implications, one must set aside the empirical situation and the attempts to derive the significance and meaning *via* logical empiricism; rather one must examine the situation on the basis of statistical thermodynamics so that the fundamental principle and the theoretical implications involved can be established first and then applied to derive information from the empirical facts. To identify these objectives briefly, we cite some relevant facts essentially of a theoretical thermodynamic nature.

1. To prove that the "correlation is no more informative than the free energy" it is more meaningful to employ the theoretical structure of thermodynamics⁴ as contained in the Legendre transformation rather than to express the values of ΔH vs. ΔS for the lanthanide complexes in two linear forms as FP have done especially when the lines have been derived in such grossness to have obscured the information (see last paragraph). Starting with any one of the sets of thermodynamic variables, for instance (G ; p , T , N_i 's), one can derive any other set such as (H ; p , S , N_i 's). Each of these sets constitutes for a pure-phase space a thermodynamic equation of state with a well-defined monotonic character. Since this transformation is measure preserving, any information contained in $G(T)$ is also contained in $H(S)$. For a set of chemical reactions, one can define similarly an equation for a sequence of sufficiently equivalent configurations of reactants and products on the basis of the monotonic character of (ΔE ; ΔV , ΔS , ΔN_i 's).² This situation implies one potential energy function at the molecular or atomic level which is parametrically scaled.^{2,3} By transformations equivalent to that cited above, one can derive other sets involving the Δ 's. Thus any information contained in $\ln K$ vs. T^{-1} is also contained in ΔH vs. ΔS . The value of accepting the correlation of ΔH vs. ΔS is that it appears to be more amenable to theoretical treatment² especially since the meaning and significance of entropy has been expanded into information theory.

2. The principle involved in the correlation can be readily comprehended in terms of the following relations. If ΔH and ΔS are functions of T and some unknown variable x , then one can write that

$$\Delta H(x, T) = \Delta G(x, T) + T\Delta S(x, T) \quad (1)$$

In the frequently employed experimentation, one generates ΔH and ΔS from the slope and intercept of $\ln K$ vs. T^{-1} with T viewed as the independent variable, or at least the probing variable, and without, in some cases, at least, knowing whether x is constant. The pairs of values ΔH and ΔS generated by repeated experimentation with the series studied can be examined for correlation. For any correlation linear or otherwise, one can derive the slope

$$\frac{d\Delta H}{d\Delta S} = \frac{d\Delta G}{d\Delta S} + T + \Delta S \frac{dT}{d\Delta S} \quad (2)$$

At constant T , this slope is

$$\left(\frac{\partial \Delta H}{\partial \Delta S}\right)_T = \left(\frac{\partial \Delta G}{\partial \Delta S}\right)_T + T \quad (3)$$

(2) R. J. Thorn, *J. Chem. Phys.*, **51**, 3582 (1969).

(3) See for instance, H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **205**, 247 (1951).

(4) H. Chen, J. Loter, and R. J. Thorn, unpublished work.

Hence the slope of the correlation relation consists of the two terms $(\partial \Delta G / \partial \Delta S)_T$ and T . This slope thus represents a virtual or hidden "temperature" associated with some scaled atomic or molecular parameter. The first term in eq 3 corresponds to the feature which FP were trying to examine. The second term can explain why many of the correlations yield slopes nearly the same as the midtemperatures of the measurements when the first term is sufficiently small. Attempts to establish empirically the principle involved in the correlation and the significance of the slope in terms of an isokinetic temperature^{5,6} have created much confusion, in part because exact linearity is implied in the arguments and in part because the correlation is associated with random and systematic errors.⁷

3. The statements that " ΔG tells us nothing about the structures" and that " $\Delta H - \Delta S$ should be independent of the structural properties of the complexes" are limitations of the data (actually in the present case they are limitations of the analysis of the data as shown below) and not limitations of thermodynamics per se nor of the principle associated with the correlation. The structure of a system investigated thermodynamically is manifest in the variously ordered derivatives in thermodynamics or in the variously ordered moments in statistical thermodynamics.⁸ To the extent that a theoretical study of the correlation of $\Delta H(\Delta S)$ has been accomplished,^{2,3} one anticipates that for a given structure it must be monotonically increasing with all the derivatives finite rather than linear. Thus for the unknown characterized monotonicity, if two or more sufficiently equivalent configurations are present in the series or sequence investigated, then an examination of ΔH vs. ΔS should accomplish an ordering such that items corresponding to the two structures can be separated, the two groups are connected discontinuously or through a transitional sequence displaying a different monotonic character, and a significant ordering of the items with a common structure should occur.

Within the context of these facts and the general subject at hand and with a more complete statistical analysis, one can reexamine the correlation cited by Mesmer and Baes⁹ (MB) and recover the information which originally is contained in the data and particularly in Figures 1 and 2 given by Walker and Choppin¹⁰ (WC) but which was lost in the analyses given both by MB and by FP. A replot of the values for ΔH and ΔS for the lanthanide fluoride complexes yields the results displayed in Figure 1. Both MB and FP interpreted the correlation represented by the plotted points in terms of one linear relation such as that represented by least squares with scatter which they thought was within the errors. With a small number of subsets it is, of course, a not improbable event that the line given by MB was as they state within experimental error. (Only four points of fourteen are more than 1σ away from the line and only two points are away by more than 2σ . The one point away by 4σ does question the situation slightly.) In a

(5) See O. Exner, *Nature (London)*, **201**, 488 (1964).

(6) See R. McGregor and B. Milicevic, *ibid.*, **211**, 523 (1966).

(7) R. J. Thorn, *High Temp. Sci.*, **3**, 197 (1971).

(8) See for instance R. J. Thorn in "The Chemistry of Extended Defects in Non-Metallic Solids," L. Eyring and M. O'Keefe, Ed., North-Holland, Amsterdam, 1970, pp 395-424.

(9) R. E. Mesmer and C. F. Baes, Jr., *J. Phys. Chem.*, **72**, 4720 (1968).

(10) J. B. Walker and G. R. Choppin, *Advan. Chem. Ser.*, **No. 71**, 127-138 (1967).

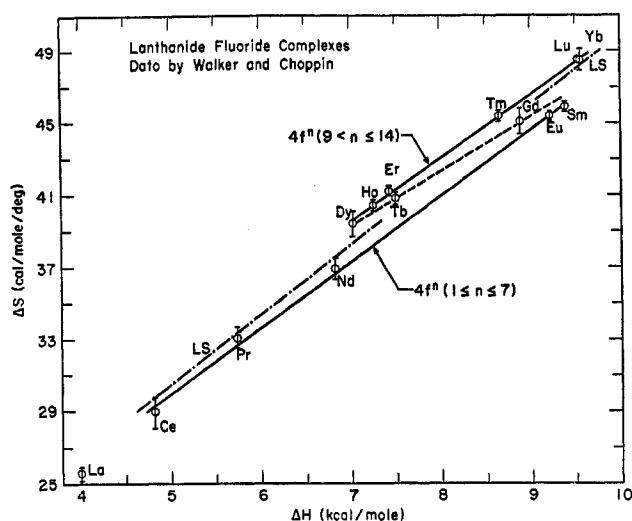


Figure 1.—Correlation of entropic and enthalpic changes for formation of complexes between lanthanide and fluoride ions.¹⁰ The least-squares line corresponds to the interpretation by Fay and Purdie¹ and by Mesmer and Baes.⁹ On the basis of analysis of covariance, the separation into the two indicated subsets ($1 < n < 7$) and ($9 < n < 14$) is established. The probability that the two lines have the same value of ΔS at $\Delta H = 8$ kcal/mol is 4×10^{-6} ; the probability that they have the same slope is 0.59.

private communication from WC it was disclosed that the standard deviations of a single measurement were reported in their article. To obtain standard deviations of the mean as required in correlation studies, one can divide the enthalpy standard deviations by $\sqrt{20}$ and the free energy standard deviation by $\sqrt{4}$, according to the number of determinations WC performed to obtain a value. In doing so, one finds that only six of the fifteen points remain within 1σ of the MB line and four points are away from the MB line $>3.5\sigma$ with one point as much as 9σ away. No longer is it reasonable to consider the line of MB within experimental error, and the fine structure reported in this paper should be sought. Furthermore, the selection of the standard deviation as a basis for errors is somewhat arbitrary, and one must recognize that errors can be compensating. Therefore, any conclusion obtained on such bases is conditioned, and it is more meaningful to accept the values for ΔS and ΔH , to calculate quantitatively on the basis of analysis of covariance¹¹ the probability that a resolution into the indicated subsets exists, and then to examine its plausibility. Accordingly, a more detailed analysis has been accomplished with the following results.

1. The linear least-squares analyses yield the following equations. For $1 < n < 7$ for the $4f^n$ orbitals

$$\Delta S = (40.94 \pm 0.17) + (3.629 \pm 0.085)(\Delta H - 8)$$

and for $9 < n < 14$

$$\Delta S = (43.04 \pm 0.063) + (3.563 \pm 0.059)(\Delta H - 8)$$

in which the intercept at $\Delta H = 8$ kcal/mol is used as a zero rather than $\Delta H = 0$ because it is within the range of values in which the errors are standard deviations. Comparing these errors, one observes that the intercepts do not agree but the slopes do agree; the

reciprocals of the slopes do not agree with 0.298. By accepting some other level of confidence besides the standard deviation, one could make the intercepts, slopes, and 0.298, respectively, agree or disagree. This ambiguity can be eliminated through an analysis of covariance for the two lines. From such a statistical analysis one finds that the probability that the two lines have the same intercept at $\Delta H = 8$ is 4×10^{-6} ; the probability that they have the same slope is 0.59. Therefore the resolution of the data into two subsets is well established. The same analysis of Nancollas¹² data on the alkaline earth formates and acetates (cited by FP) demonstrates a separation into two subsets, the formates and the acetates. In this case the probabilities are 0.011 and 0.62 for the same intercepts ($\Delta H = 0$ is the reference since the measured values span this value) and slopes, respectively. Thus to the extent that one compares the two probabilities for the intercepts, the two subsets for the rare earth fluoride complexes are more dissimilar than are the alkaline earth formates and acetates.

2. If one examines Figures 1 and 2 by WC, then one recognizes that the separations effected herein are only a manifestation of the structure in the ΔH and ΔS vs. atomic numbers, Z . The resolution of WC's data established by the analysis of covariance resembles that reported by Spedding, Pikal, and Ayers¹³ for the variation with ionic radii of apparent molal volumes of rare earth chlorides and nitrates in aqueous solutions.

In all three cases cited above, the primary effect of a significant change in configuration or structure within the set produces two subsets with linear correlations which are approximately parallel. In a survey of entropic and enthalpic changes for a variety of processes involving small molecules in aqueous solutions, Lumry and Rajender¹⁴ cited several examples of pairs of linear correlation which are nearly parallel. In a study of systematic errors encountered in the measurement of vapor pressures of inorganic compounds, McCreary and Thorn¹⁵ found subsets of nearly parallel linear correlations. All these observations are undoubtedly significant. However, attempts to derive these significances from a purely empirical perspective may be unproductive because from the theoretical perspective cited above and discussed elsewhere^{2,3,7} the pertinent facts appear to be that the correlation is never exactly linear but rather is monotonic with a well-defined character² and the analysis of covariance indicates that the approximately linear correlations are not exactly parallel.

The pertinent point in this communication is that the correlation and appropriate statistical analysis could have accomplished the separation of the two subsets of rare earth fluoride complexes and even most of the ordering within the two subsets without prior knowledge of Z , the electronic configuration, or ionic radii. Whether, in the absence of the known electronic structures, one would have effected the resolution given in Figure 1 depends apparently on one's interest, conviction, confidence in the theoretical basis for the correlation, and the statistical analysis effected. Both MB and FP obscured the resolution, but they did appreciate

(12) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(13) F. H. Spedding, M. J. Pikal, and B. O. Ayers, *J. Phys. Chem.*, **70**, 2440 (1966).

(14) R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).

(15) J. R. McCreary and R. J. Thorn, submitted for publication.

(11) See C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and Chemical Industry," Wiley, New York, N. Y., 1954.

the fundamental nature of the correlation. We believe not only that the reason for the correlation is a fundamental one but also that its origin can be identified with sufficiently and significantly equivalent configurations or essentially in chemistry with conservation of orbital symmetry and that, once its theoretical basis and ramifications are established, it can be incorporated into statistical thermodynamics as a general principle² and used not only in the systematics of complex reaction but also in the analysis of systematic errors.^{2,7,15,16}

(16) J. R. McCreary, S. A. Rassoul, and R. J. Thorn, *High Temp. Sci.*, **1**, 412 (1969).

GULF GENERAL ATOMIC
SAN DIEGO, CALIFORNIA 92112

JOHN H. NORMAN
PERRIN WINCHELL

ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439

R. J. THORN*

RECEIVED FEBRUARY 17, 1971

Direct Evaluation of Dipolar Nuclear Magnetic Resonance Shifts from Single- Crystal Magnetic Measurements. Paramagnetic Anisotropy of Bis(2,4-pentanedionato)bis(pyridine)cobalt(II)

Sir:

A fundamental aspect of the study of isotropic nuclear magnetic resonance (nmr) shifts $\Delta\nu^{iso}$ in paramagnetic systems¹ is the separation of the Fermi contact $\Delta\nu^{con}$ and dipolar² $\Delta\nu^{dip}$ contributions to these shifts. Contact shifts provide a measure of the unpaired electron spin density at the resonating nucleus, whereas dipolar shifts arise from a through-space dipolar interaction between the electronic magnetic moment and the nuclear spin moment, which does not vanish in magnetically anisotropic systems. In one of the earliest attempts to separate contact and dipolar shifts, Happe and Ward,³ in 1963, studied the labile pyridine-type base adducts of bis(2,4-pentanedionato)cobalt(II) and -nickel(II), hereafter Co(acac)₂ and Ni(acac)₂. They observed a difference in the proton isotropic shift ratios between the cobalt and nickel systems and attributed this difference to the presence of a dipolar interaction in the case of the cobalt adducts. They achieved a quantitative separation, assuming that the dipolar shifts conformed to the geometric factors⁴ estimated for an axially symmetric system. The method of spin-isolated nuclei was employed wherein it was assumed that the shift of the para proton of 4-phenylpyridine coordinated to Co(acac)₂ was purely dipolar in origin. The contact shift ratios for both the cobalt and nickel systems so obtained agree quite well, and the contact shift was attributed to spin delocalization in the σ systems of these heterocyclic amine ligands.

Subsequently, Horrocks and coworkers employed the *ratio method* to achieve the separation in similar sys-

tems.⁵⁻⁸ This latter method has recently been discussed in detail by one of us in an article⁹ which also pointed out that dipolar shifts may properly be evaluated from magnetic susceptibility anisotropy data rather than g -tensor anisotropy as had been attempted previously.^{10,11} Equations for dipolar shifts, valid for axial symmetry, for the two most probable averaging conditions^{10,11} were derived inductively⁹ from the analogous expressions involving g -tensor anisotropy.^{4,10,11} The validity of one of these equations has recently been verified by independent theoretical derivations.^{12,13}

In the present Correspondence we report single-crystal magnetic susceptibility anisotropy data for Co(acac)₂(py)₂, py = pyridine, and the direct evaluation of dipolar shifts therefrom. Only for Co(bipy)₃Br₂·6H₂O, bipy = 2,2'-bipyridyl, has such an evaluation previously been made.⁹ The recent publication of ¹³C isotropic shift data for the Co(acac)₂(py)₂¹⁴ and Ni(acac)₂(py)₂^{14,15} systems renders the present report particularly timely and allows the importance of dipolar shifts for nuclei other than protons to be assessed for the first time.

In their paper,¹⁴ Doddrell and Roberts assume that dipolar shifts are of little importance for ¹³C nuclei and, on the basis of ratio differences between the cobalt and nickel systems, conclude that the spin delocalization mechanisms are significantly different for the two systems and that a degree of π -spin delocalization is present. Our results indicate that dipolar shifts *do* contribute importantly to ¹³C isotropic shifts in Co(acac)₂(py)₂ and, within the fairly large experimental uncertainties, show that no difference in spin delocalization mechanism is necessary to explain the observed differences between the cobalt and nickel systems.

Magnetic Anisotropy.—Large orthorhombic¹⁶ single crystals of Co(acac)₂(py)₂ were grown by slow evaporation of a benzene solution. Single-crystal magnetic anisotropies were measured as a function of temperature from 77 to 293°K by Krishnan's critical-torque method, the technique, theory, and methodology of which is described in detail by us elsewhere.¹⁷ The bulk average susceptibility $\bar{\chi}$ was measured on a powdered sample by the Gouy method, and for both types of measurement a variable-temperature cryostat of published design¹⁸ was employed. The torsion fiber was calibrated with tetragonal nickel sulfate hexahydrate ($\Delta\chi_a^{19} = 80.8$ VVk/²⁰ mol at 27°). The results at 293°K are $\chi_a - \chi_b = 2310$, $\chi_c - \chi_b = 3820$, and $\bar{\chi} = 9569$ VVk/mol,²¹ which yielded $\chi_a = 9836$, $\chi_b = 7526$,

(5) W. DeW. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

(6) R. W. Kluijber and W. DeW. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

(7) R. W. Kluijber and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

(8) R. W. Kluijber and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **6**, 166 (1967).

(9) W. DeW. Horrocks, Jr., *ibid.*, **9**, 690 (1970).

(10) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

(11) J. P. Jesson, *ibid.*, **47**, 582 (1967).

(12) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(13) B. R. McGarvey, *J. Chem. Phys.*, **53**, 86 (1970).

(14) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970).

(15) I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, **92**, 6651 (1970).

(16) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(17) W. DeW. Horrocks, Jr., and D. DeW. Hall, *Coord. Chem. Rev.*, in press.

(18) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

(19) A. Bose, S. C. Mitra, and S. K. Datta, *Proc. Roy. Soc., Ser. A*, **248**, 153 (1958).

(20) 1 Van Vleck (VVk) = 10⁻⁶ cgsu; see ref 17.

(21) Includes a diamagnetic correction of -146 VVk/mol.

(1) For reviews see (a) E. deBoer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (b) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(2) Sometimes referred to as pseudocontact.

(3) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(4) H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).