Unlike the case of Ni(gma)$^-$, the differential mixing of $\pi_L^*(a_2)$ and $\pi_L^*(b_2)$ with metal orbitals will depend nearly completely on overlap, rather than on a combination of overlap and relative energy factors. This situation will almost certainly lead to the energy order $\pi^*(a_2) > \pi^*(b_2)$ for *sym*-Ni(H$_2$gma)$^-$, compared to $\pi^*(b_2) > \pi^*(a_2)$ for Ni(gma)$^-$. Further, the epr results for the former require $\sigma^*(b_1) > \pi^*(a_2)$ inasmuch as the observed g tensor does not reveal the near-axial symmetry expected from the $\sigma^{*1}(b_1)$ configuration. Therefore, the $\ldots\pi^2(b_2)$, $2\sigma^{*4}(a_1)$, $\pi^{*2}(b_2)$, $\pi^{*1}(a_2)$ ground configuration is assigned to *sym*-Ni(H$_2$gma)$^-$, with the order of orbitals more stable than $\pi^*(a_2)$ unknown. The proposed appreciable admixture of d_{yz} in this MO results in a situation analogous to the $^2B_{3g}$ states of [Ni–S$_4$]$^-$ and [Ni–N$_4$]$^-$ and to the ^2B_g state of *trans*-[Ni–S$_2$N$_2$]$^-$, and on this basis could account for the observed g-tensor anisotropy.

Summary

The principal result of this work is the experimental establishment of g-tensor properties for coordinated radical anions. For those complexes assigned the csfr formulation, the measured g tensors suggest the following order of decreasing metal orbital involvement in the odd-electron wave functions: Ni(gma)$^-$ > Ni(dtbh)$^-$ ~ Ni(dbh)$^-$ > Zn(gma)$^-$ ~ Zn(dtbh)$^-$ ~ Cd(gma)$^-$ ~ Cd(dtbh)$^-$. The persisting problem is the establishment of the quantitative degree of metal orbital involvement in these series of complexes which possess, in the phraseology of Schrauzer and Mayweg,[14] "delocalized ground states." In an experimental epr sense, all that can be presently done is to measure the departure of the g tensor from its properties in a cation-stabilized free-radical complex toward those expected for a complex in which the electron is essentially metal-localized. At what point the description is changed from ligand free radical to metal-localized radical is currently a subjective matter.[18] As already emphasized, either description is inadequate and neither supplants a complete molecular orbital treatment including configuration interaction and spin–orbit coupling, which produces a ground state demonstrably reconcilable with experiment.

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Theoretical Aspects of the Linear Enthalpy Wavenumber Shift Relation for Hydrogen-Bonded Phenols[1]

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Contribution from the William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois, and Salem Hall, Wake Forest College, Winston-Salem, North Carolina. *Received November 4, 1966*

Abstract: The approximation involved in using the observed OH wavenumber shift of phenol upon hydrogen-bond formation as a measure of the magnitude of the interaction has been examined. The equation $-\Delta H = 0.016\Delta\bar{\nu}_{O-H} + 0.63$ has been recast in terms of the change in the OH bond energy of phenol on adduct formation, δE_{OH}, and the energy of formation of the new bond between the donor and the hydrogen E_{HB}. The results of molecular orbital calculations (extended Hückel variety) have been analyzed in terms of the bond-energy relationship for the original bond to hydrogen and the hydrogen to base bond. These results provide theoretical justification for the original relationship. Furthermore, this treatment has yielded a parameter which is a quantitative measure of the response of the OH bond of the acid to perturbation by an approaching lone pair of electrons.

In 1962 an enthalpy–OH wavenumber shift ($\Delta\bar{\nu}_{OH}$) relationship[2] for phenol adducts was presented which involved a wide range of electron-pair donors. The two experimental quantities were related by the equation

$$-\Delta H\ (\pm 0.5\ \text{kcal mole}^{-1}) = 0.016\Delta\bar{\nu}_{O-H} + 0.63 \quad (1)$$

The work verified, at least for phenol adducts, the earlier prediction[3] of a linear relationship between the enthalpy of hydrogen-bond formation and OH wavenumber shift. Lippencott and Schroeder[4] several years ago presented a semiempirical model of the hydrogen bond which also predicted a linear relationship between these two quantities over an enthalpy range of −1 to approximately −14 kcal mole^{-1}. A very slight curvature near the origin was predicted which implied a nonzero intercept on the enthalpy axis upon extrapolation of the linear portion of the curve.

More recently, other workers[5,6] have questioned the validity of this linearity. They have studied weak donor systems which apparently do not obey this relationship. In addition it has been stated[5] that there is no theoretical basis for the existence of such a relationship. This uncertainty has stimulated us to examine the theory of frequency shifts from the point of view

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(1) (a) Presented at the 5th National Meeting of the Society for Applied Spectroscopy, Chicago, Ill., 1966; (b) abstracted in part from the doctoral dissertation of K. F. Purcell, University of Illinois, 1965.

(2) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

(3) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

(4) E. R. Lippencott and R. Schroeder, *ibid.*, **23**, 1099 (1955).

(5) R. West, D. L. Powell, L. S. Whately, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(6) D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964).

of the approximations involved in the vibrational aspects of the problem and also to examine the changes in the molecular orbitals defining the A–H···B hydrogen-bond system as the H···B interaction is altered. By so doing we hoped to find theoretical justification for the large amount of data which is in accord with this relationship.

Calculations

The molecular orbital calculations are lcao–mo calculations of the extended Hückel type[7] including a procedure for adjusting valence-state ionization energies and orbital exponents for core charge. A calculation is iterative with respect to a self-consistent set of atom charges.[8] Off-diagonal H matrix elements were taken as

$$H_{ij} = -1.75S_{ij}(H_{ii}H_{jj})^{1/2}$$

and neutral atom valence-state ionization energies are those of Hinze and Jaffé.[9] Slater atomic functions have been used.

The simple valence force constant calculations were carried out by hand using the GF formulation described by Wilson, *et al.*[10]

Results and Discussion

In studying the wavenumber shift–enthalpy relation for hydrogen-bonding acids, one is faced with the question of what does the wavenumber shift actually measure and how is this related to the total enthalpy for the formation of a hydrogen bond. It is certainly true that the change in the force constant of the O–H bond (in phenol, for example) is a better measure of the change in the strength of that bond than the wavenumber shift because the frequency assigned as the "O–H stretching vibration" is that determined by at least a three-body–two-force constant oscillating system. One approximation normally made is that kinematic coupling of the O–H stretching coordinate with other vibrational coordinates within the acid itself is negligible or at least invariant under the conditions of adduct formation. Owing to the high energy of the OH stretching vibration and the large mass of the oxygen atom, this is a good approximation for C–O, O–H coupling. Phenol, for example, would be considered as a two-body system with the phenyl ring and the oxygen or the oxygen alone acting as a single "atom." The hydrogen-bonded adduct may then be represented as

$$\mathrm{O{-}H\cdots B}$$

where B represents the donor atom or molecule and O represents the remainder of the acid molecule. A second approximation that has been made is[3] to ignore the force constant of the H···B bond and, hence, to treat the hydrogen-bonded adduct as a diatomic molecule. This approximation is significantly poorer than the first because of the small mass of the hydrogen atom but is the one which leads to the use of frequency shift itself as a measure of the change of OH force constant or strength of the O–H bond.

Recently, data have become available which allow an assessment of this last approximation. Ginn and Wood[11] have obtained spectra for carbon tetrachloride solutions of phenol containing trimethylamine, triethylamine, and pyridine in the region 380–80 cm^{-1}. They find vibrations in this region which they attribute to stretching of the H···B bond: trimethylamine at 143 cm^{-1}, triethylamine at 123 cm^{-1}, and pyridine at 134 cm^{-1}.

Using the experimental values of 5.508 sec^{-2} for λ_{OH}[2] and 0.012 sec^{-2} for λ_{HB}[11] in the trimethylamine adduct and 7.681 sec^{-2} for the O–H vibration of the phenol monomer,[2] the vibrational secular equations were solved for the corresponding force constants.

The solutions to these equations are given in Table I. According to these results there is a pronounced decrease in the O–H force constant of phenol upon hydrogen-bond formation with trimethylamine.

Table I

	F_{OH}, mdynes/A	$F_{OH}^{1/2}$, mdynes/A$^{1/2}$
F_{OH}[a]	7.660	2.76
F'_{OH}[b]	5.026	2.24
F''_{OH}[c]	5.493	2.34
F_{HB}	0.478	...

[a] F_{OH} is the monomer phenol force constant. [b] F'_{OH} is the "true" adduct phenol force constant. [c] F''_{OH} is the adduct phenol force constant ignoring the H···B bond.

In comparing F'_{OH} and F''_{OH} we find that in ignoring the H···B force constant a 10% error in F_{OH} results and that the error in $F_{OH}^{1/2}$ is only about 5%. However, the difference between these two calculated changes in O–H force constant is ~20% (for $F_{OH}^{1/2}$ −0.52 *vs.* −0.42). The importance of $F_{OH}^{1/2}$ will be seen shortly. Trimethylamine is one of the strongest bases to have been studied with phenol, and this force constant may be taken as an approximate upper limit for H···B bonds in phenol adducts used in the correlation.

It is interesting to compare this value with the N–B force constant[12] for $(CH_3)_3NBH_3$ (=2.4 mdynes/A) and with the N–H force constant for $(CH_3)_3NH^+$ which will be[10] on the order of 5 mdynes/A.

The relationship between the O–H wavenumber shift or force constant and enthalpy of adduct formation (in a poorly solvating solvent) may now be examined. The enthalpy change for the reaction of phenol with a Lewis base may be thought of as consisting of two contributions: the change in the phenol O–H bond energy, δE_{O-H}, and the bond energy of forming the new hydrogen bond to the base, E_{HB}.

$$\Delta H = \delta E_{OH} + E_{HB} \qquad (2)$$

Any nonbonded repulsions which occur between the oxygen atom and the base are implicitly absorbed in E_{HB}. This contribution to ΔH will be small but varies with the base and is properly considered as one of the factors affecting the basicity of a lone-pair donor toward a hydrogen-bonding acid. Now a relationship between the change in O–H bond energy and the wavenumber shift or force constant change is needed as well as a

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(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(8) P. C. Van Der Voorn, Doctoral Dissertation, University of Illinois, 1965.

(9) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(10) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(11) S. G. Ginn and J. L. Wood, *Proc. Chem. Soc.*, 884 (1965).

(12) R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 59.

relationship between E_{HB} and the O–H wavenumber shift. Several authors[13,14] discuss the relationship between D_0, the bond dissociation energy, and ω_e (the harmonic oscillator vibrational energy in cm^{-1}) and x_e (the anharmonicity constant for that oscillator) for an anharmonic diatomic oscillator

$$D_0 = D_e(1 - 2x_e) = \frac{\omega_e^2}{4\omega_e x_e}(1 - 2x_e)$$

where D_e equals D_0 plus the zero-point energy. A change in oscillator frequency may then be related to a change in D_0 by

$$\delta D_0 = \frac{\delta\omega_e}{4x_e}(1 - 2x_e)$$

for no change in x_e.[15] Since ω_a (the anharmonic energy in cm^{-1}) is given by

$$\omega_a = \omega_e(1 - 2x_e)$$

δD_0, in terms of $\delta\omega_a$, is simply

$$\delta D_0 = \frac{\delta\omega_a}{4x_e} \text{ or } \delta E_0 = -\frac{\delta\omega_a}{4x_e} \qquad (3)$$

E_0 is meant, here, to be the bond energy, and $\delta\omega_a < 0$ implies that $\delta E_0 > 0$. For δE_0 in kcal mole^{-1}, the above relation is

$$\delta E_0 = -\frac{hcN}{4x_e}\,\delta\omega_a \qquad (4)$$

with Planck's constant in units of kcal molecule^{-1} sec. Since ω_e is given by

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu}}$$

it follows that $\delta\omega_a$ and $\Delta k_e^{1/2}$ are related by

$$\delta\omega_a = \frac{1}{2\pi c}\Delta\sqrt{\frac{k_e}{\mu}}(1 - 2x_e)$$

Rewriting this in terms of an anharmonic force constant, k_a, one obtains

$$\delta\omega_a = \frac{1}{2\pi c\sqrt{\mu}}\Delta(k_a)^{1/2}$$

The last two equations are identical when $x_e = 0$. The relationship for change in E_0 and change in $k_e^{1/2}$ is given by

$$\delta E_0 = -\frac{hcN}{4x_e}\left(\frac{1 - 2x_e}{2\pi c\sqrt{\mu}}\right)\Delta k_e^{1/2}$$

Some experimental justification for the linear relationship between E_0 and ω_a or $k_a^{1/2}$ for a given bond type has been given by Fox and Martin.[16] Our problem lies in evaluating δE_0 for the OH bond in phenol from $\Delta\tilde{\nu}_{\mathrm{obsd}}$ (the observed wavenumber change) which differs from $\delta\omega_a$ by virtue of vibrational coupling of the OH and H···B coordinates in the "OH" normal coordinate. Ideally one would try to observe both $\tilde{\nu}_{\mathrm{OH}}$ and $\tilde{\nu}_{\mathrm{H\cdots B}}$ and carry out a normal coordinate analysis for each adduct as was done for phenol–trimethylamine above. Each analysis would yield k_a (or $k_a^{1/2}$) and allow the calculation of $\delta\omega_a$ and δE_0 directly for the OH bond. As noted earlier, both vibrational energies are generally not available. Until such data become available one is left to approximate $\delta\omega_a$ by $\Delta\tilde{\nu}_{\mathrm{obsd}}$. The seriousness of the ensuing error is judged by the data in Table I which show that the use of $\tilde{\nu}_{\mathrm{obsd}}$ for the adduct constitutes a 5% error in approximating ω_a in the adduct while the error in using $\Delta\tilde{\nu}_{\mathrm{obsd}}$ (the change in wavenumber) for $\delta\omega_a$ underestimates the latter by *ca.* 20%.

It is interesting to consider at this point the cumulative errors introduced by the Birge–Sponer relationship as applied here (eq 4) and that introduced by setting $\Delta\tilde{\nu}_{\mathrm{obsd}} = \delta\omega_a$. The Birge–Sponer method of obtaining E_0 is known[13,14] to overestimate E_0 by *ca.* 20%. As noted above, $\Delta\tilde{\nu}_{\mathrm{obsd}}$ is *ca.* 20% smaller than $\delta\omega_a$. The two approximations made here, therefore, will cancel one another to within a few per cent and will, therefore, result in a cumulative error of *ca.* 5%, say in the value of δE_{OH} calculated using eq 6 below. The error limits in eq 1 range from ~20% for low ΔH to ~5% for the larger ΔH. It is therefore seen that this method of obtaining δE_{OH} from $\Delta\tilde{\nu}_{\mathrm{obsd}}$ is valid to well within the limits of the original empirical relationship.

It appears that if a more accurate determination of $\delta\omega_a$ should be made, it must be accompanied by a more accurate relation between δE_0 and $\delta\omega_a$ (that resulting from the Rydberg potential function, for example) if one wishes to maintain an uncertainty of ~5% in the calculated δE_{OH}.

In order for eq 1 to be theoretically sound there must be a linear relationship between the energy of the base to the hydrogen bond, E_{HB}, and the destabilization of the O–H bond. From the equations, in which Planck's constant has units of kcal sec/molecule

$$\Delta H = -\left(\frac{hcN}{4x_e}\right)\delta\omega_{\mathrm{OH}} + E_{\mathrm{HB}} \qquad (5)$$

and

$$\delta E_{\mathrm{OH}} = -\left(\frac{hcN}{4x_e}\right)\delta\omega_{\mathrm{OH}} \qquad (6)$$

one can determine E_{HB} and δE_{OH}. This has been done[17] for some literature data[2,5] using $\Delta\tilde{\nu}_{\mathrm{OH}}$ for $\delta\omega_{\mathrm{OH}}$. The results are shown in Figure 1 and Table II. The dotted lines in the figure are the error limits (±0.5 kcal/mole) reported[2] for the 90% confidence level of the $\Delta\tilde{\nu}_{\mathrm{OH}}$–$\Delta H$ relationship. It is seen that E_{HB} is linearly related to δE_{OH}, as is required, with a nonzero intercept on the E_{HB} axis of ~−0.6. It is interesting to note also the reasonable magnitudes of the E_{HB} for coordinate bonds.

Equation 1 may now be recast as

$$\Delta H = \left(\frac{1}{k'} - \frac{hcN}{4x_e}\right)\Delta\tilde{\nu}_{\mathrm{OH}} + \text{constant}$$

where k' is the slope of the E_{HB}, $\Delta\tilde{\nu}_{\mathrm{OH}}$ relationship. In terms of δE_{OH} ($\delta E_{\mathrm{OH}} = kE_{\mathrm{HB}} + $ constant, $k = (hcN/4x_e)k'$) this constant ($k = -0.682$ for phenol) measures the response of the O–H bond to the effect of an ap-

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[13] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p 100.

[14] G. W. King, "Spectroscopy and Molecular Structure," Holt, Rinehart and Winston, New York, N. Y., 1964, p 163.

[15] Unfortunately, we are frustrated by both a lack of proper data and a theoretical means to account for variation in x_e in the adducts.

[16] G. Fox and A. Martin, *Trans. Faraday Soc.*, **36**, 897 (1940); *J. Chem. Soc.*, 884 (1939).

[17] The anharmonicity constant for *p*-chlorophenol was determined in this laboratory to be 0.0229; the value 0.0227 for phenol was calculated from data in ref 6.

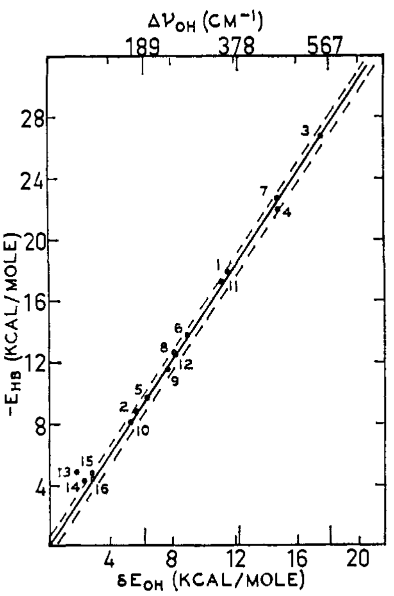

Figure 1. Energy of the H· · ·B bond as a function of the change in energy of the O–H bond of phenol.

proaching lone pair of electrons. It is tempting to anticipate a correlation of this quantity with other measures of acidity. The pK_a's, OH proton chemical shifts, and substituent constants of OH acids might be expected to bear a direct relationship to this parameter. This quantity is unique in that it measures a *bond* property. It is a measure of the susceptibility of the O–H bond to distortion by a Lewis base.

Table II. Data for Figure 1

		$\delta E_{OH}{}^a$	$E_{HB}{}^a$	$\Delta\bar{\nu}_{OH}$, cm^{-1}
1	DMA	10.9	−17.3	345
2	CH_3CN	5.6	−8.8	178
3	Et_3N	17.4	−26.6	553
4	Me_3PO	14.6	−22.0	470
5	Me_2CO	6.1	−9.4	193
6	Et_2O	8.8	−13.8	279
7	H_3N	14.6	−22.6	462
8	Et_2S	7.9	−12.5	250
9	Bu_2Se	7.6	−11.3	240
10	EtOac	5.2	−8.0	154
11	DMSO	11.3	−17.8	359
12	Bu_2S	8.0	−12.3	254
13	$C_6H_{11}F$	1.7	−4.8	53
14	$C_6H_{11}Cl$	2.1	−4.3	66
15	$C_6H_{11}Br$	2.6	−4.6	82
16	$C_6H_{11}I$	2.7	−4.4	86

[a] Energies in kcal/mole.

Preliminary data are available[18] for *p*-chlorophenol and allow a similar calculation for this acid. The ΔH *vs.* $\Delta\bar{\nu}_{OH}$ plot for this acid has a slope of 0.021, *i.e.*

$$\Delta H = 0.021\Delta\bar{\nu}_{OH}$$

This may be interpreted in terms of a larger dipolar contribution to the total enthalpy than with phenol adducts. The value of k for this acid is −0.592 (*cf.* −0.682 for phenol), a fact which also indicates that the OH bond energy change is smaller for this more polar acid for a given E_{HB} than in the case of phenol. This may be interpreted in the following ways. (1) The OH bond in *p*-chlorophenol is more resistant to distortion by a lone-pair donor. (2) There is a large contribution to E_{HB} from dipolar interaction in the case of *p*-chlorophenol. That is, the greater electron-withdrawing property of the *p*-chlorophenyl group results in a higher positive charge on the proton. Both an increased dipolar interaction with electron-pair donors and a less polarizable or less easily perturbed OH bond results. It is interesting to note that this interpretation is very similar to the currently popular "hard and soft" acid concept in that phenol is the softer more distortable acid *in the vicinity of the acid site.* It is this ability of "k" to reflect the distortability of the electrons in the bond containing the acid atom that makes it such a useful quantity.

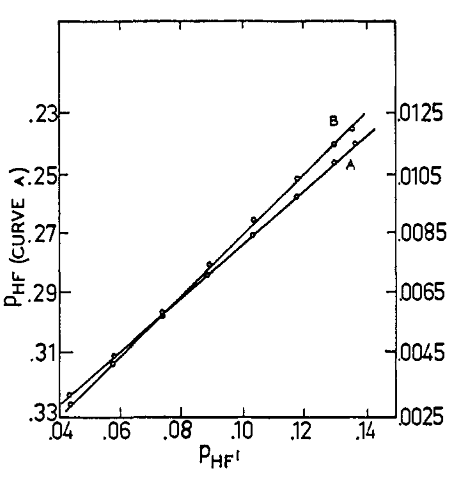

Figure 2. The overlap populations of the H–F bond and the F–F′ "bond" as a function of the overlap population of the H· · ·F′ bond: (A) H–F *vs.* H· · ·F′, (B) F–F′ *vs.* H· · ·F′.

While these results are interesting, the question as to why the energy of the hydrogen bond should be linearly related to the change in the energy of the O–H bond still remains. It was decided to attempt an extended Hückel calculation on the hydrogen-bond system $(FHF)^-$ and to examine the effect on the two fluorine to hydrogen bonds of gradually removing one of the fluorines from the other atom.[5] The use of F^- was felt to be more realistic and representative of actual hydrogen-bonding situations involving alcohols than the use of O^{2-} since the oxygen atoms in alcohols most certainly do not carry a net charge as large as two. The curve derived by Lippencott and Schroeder for O–H· · ·O systems was used to allow for contraction of the HF bond as the second fluorine was removed. The results of our calculations are given graphically in Figures 2, 3, and 4. In Figure 2 we have plotted the overlap population[19] of the short HF bond (ρ_{HF}) against the overlap population of the long HF bond ($\rho_{HF'}$). Also included for comparision is the nonbonded F–F′ repulsion ($\rho_{FF'}$) (*i.e.*, the negative FF′ overlap population). Over the range of F–F′ distances 2.49 to 2.80 A (a range which covers enthalpies of −1 to −14 kcal/mole on the Lippencott–Schroeder curve), these quantities are *linearly* related.

According to Mulliken's formulation,[19] ρ_{ij} is proportional to Ω_{ij} ("the overlap energy") and the relation-

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(18) F. Henneike, private communication.

(19) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955); (b) *ibid.*, **36**, 3428 (1962).

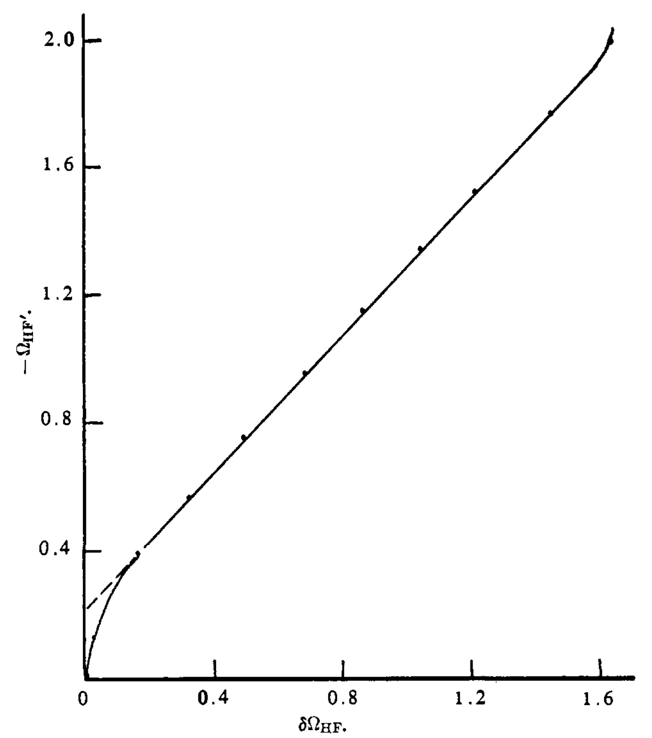


Figure 3. The change in overlap energy of the original hydrogen bond as a function of the overlap energy of the new hydrogen bond.

ship is $\Omega_{ij} = \rho_{ij}\beta_{ij}/S_{ij}$, where $\beta_{ij} = H_{ij} - {}^1/_2S_{ij}(H_{ii} + H_{jj})$. We can determine the nature of the Ω_{HF} *vs.* $\Omega_{HF'}$ relationship by calculating the β_{ij}/S_{ij} values from the results of our iterative calculations. Here we use the definitions

$$\Omega_{HF} = \sum_k(\sum_i\Omega_{iH})k$$

$$\Omega_{HF'} = \sum_k(\sum_j\Omega_{jH})k$$

where the summations are over the k-occupied molecular orbitals and the i and j ao's of F and F′, respectively. The results of these calculations are presented graphically in Figure 3 as a plot of $\delta\Omega_{HF}$ $(=\Omega_{HF} - \Omega_{HF}{}^0)$ *vs.* $\Omega_{HF'}$. The slope is −0.94 and the dotted lines are drawn at *ca.* ±3% tolerance on $\delta\Omega_{HF}$. Another point of consistency relates to the behavior of the curve near the origin. Figuure 3 indicates that a nonzero intercept is expected for the linear portion of the curve in agreement with the experimental data and the Lippencott–Schroeder model.

It appears that the experimentally determined linearity between δE_{OH} and E_{HB} is theoretically sound. The slope calculated for the $(FHF)^-$ model is in essential agreement with that for phenol when one recalls that this slope is sensitive to the nature of the AH bond in the acid (*vida supra*). These results are extremely encouraging and do suggest that the original relationship (eq 1) is not just a fortuitous situation. The linear frequency shift–enthalpy relation originally proposed by Badger and Bauer appears to be valid for phenol when sufficient care is taken to obtain accurate enthalpy data for the hydrogen-bonding interaction.

In this treatment we have been thus far concerned only with the covalent contribution to the bond energies and have neglected, in an explicit sense, any ionic contributions to these energies. Such contributions are extremely difficult to determine with any accuracy and, moreover, some ionic bond character has been included through the lcao–mo treatment itself. However, in an attempt to gain a qualitative estimate of the nature of the relation of the electrostatic potential energy of one fluorine relative to the other during the retraction of a fluorine, we have calculated the Coulombic potential energies for each fluorine atom with the other and the hydrogen atom for each step in the retraction process. The atomic charges used in this calculation were the atomic charges found in mo calculations. When plotted one against the other (Figure 4), the potential energies are found to be very closely linearly related, and the slope of this line is −0.6, to be compared with the others.

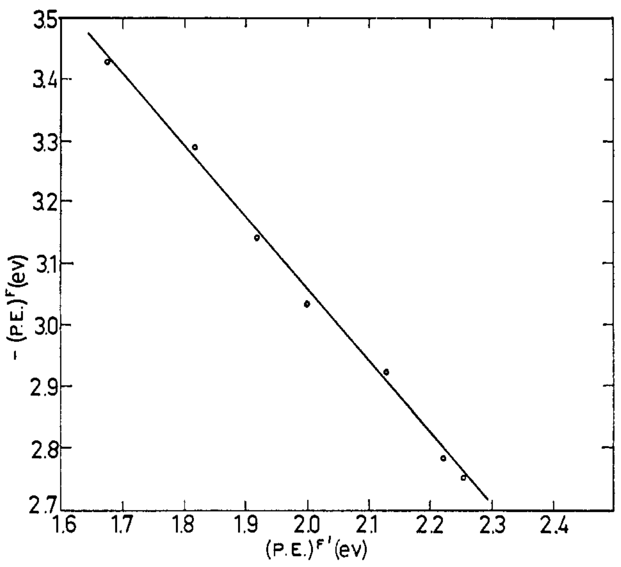
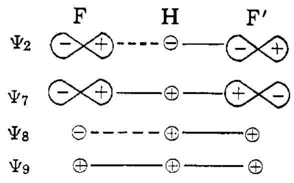


Figure 4. The Coulombic energy relationship of the two fluorine "atoms."

A qualitative description of the occupied σ molecular orbitals in terms of ao's is given below.

∞ represents a fluorine 2p orbital and
○ represents an s orbital (2s for F, 1s for H).



The σ mo's are found, on the basis of the eigenvectors[20] (see Table III for the eigenvectors for the case $R_{FF'}$ = 2.49 A), to involve primarily either fluorine 2p or 2s orbitals with little "hybridization" of the two in any one mo. A series of dots between two ao's indi-

Table III. Eigenvectors for the Case $R_{FF'}$ = 2.49 A

	F_s	$F_{p\sigma}$	H_s	F'_s	$F'_{p\sigma}$
Ψ_2	0.015	0.587	−0.007	−0.006	0.817
Ψ_7	−0.125	0.728	0.250	−0.096	−0.511
Ψ_8	−0.539	0.004	0.005	0.846	0.003
Ψ_9	0.811	−0.007	0.083	0.508	0.003

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[20] Recall that the basis set ao's have charge adjusted orbital exponents.

Table IV. One-Electron Orbital Energies (ev) of HF_2^-

	$R_{FF'}$ = 2.49 A	$R_{FF'}$ = 2.79 A	ΔE
$E(2)$	−18.97	−18.93	−0.04
$E(7)$	−20.24	−20.26	0.02
$E(8)$	−36.37	−36.31	−0.06
$E(9)$	−36.92	−36.98	0.06
E_F	−19.28	−19.43	0.15
$E_{F'}$	−19.08	−18.93	−0.15

cates an "antibonding" interaction of the orbitals; a straight line connecting two ao's represents a bonding interaction. The mo's labeled ψ_7 and ψ_9 are bonding with respect to both H–F and $H\cdots F'$; ψ_2 and ψ_8 are $H\cdots F'$ bonding and H–F antibonding. The unoccupied fifth mo is not shown. This result is obtained whenever the HF′ distance is greater than the HF distance.

It may also be noted (from the magnitudes of the eigenvectors) that ψ_2 and ψ_8 correspond to "nonbonding" orbitals *in the sense that there is little hydrogen 1s involvement*. This description is misleading, however, since these orbitals contribute significantly to the HF, HF′ overlap populations and energies.

In Table IV are given the one-electron energies of the mo's for F–F′ internuclear distances of 2.49 and 2.79 A. The effect of shortening the F–F′ distance is as follows: ψ_2 is stabilized, ψ_7 is destabilized, ψ_8 is stabilized, ψ_9 is destabilized. The stabilization of the molecule by changes in ψ_2 and ψ_8 is larger than the destabilization of the molecule by ψ_7 and ψ_9. The change in H–F bond energy must then be less than the change in $H\cdots F'$ bond energy. We note that the formation of the new bond is more important than destabilization of the old bond and this, of course, is the prime reason for stability of the hydrogen-bonded adduct. Note that ψ_7 and ψ_9 include contributions from the new bond as well as the original bond. Contributions from the strength of the new bond in these molecular orbitals are less than the destabilization of the original bond since the net change in energy of both of these molecular orbitals is in a positive direction.

A comment on the nonbonding $2p_x$, $2p_y$ orbitals can be made. The data in Table IV indicate that these filled nonbonding π-type orbitals on F are destabilized to the same extent that these nonbonding orbitals on F′ are stabilized (move to lower energy). The directions of the changes are a consequence of the decreasing negative charge on F′ and the increasing negative charge on F as $R_{FF'}$ is decreased.

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Contact-Shift Studies and Delocalization Mechanisms of Nickel(II)–Benzylamine Complexes

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Abstract: The proton nmr contact shifts of $[Ni(bz)_6]^{2+}$ (bz = benzylamine, $C_6H_5CH_2NH_2$) have been investigated to ascertain whether or not unpaired spin can be delocalized in the phenyl π system when the ligand–metal interaction is essentially σ. The amino, methylene, and aromatic protons are assigned in the nmr spectrum of the complex. The contact shifts and electron spin–nuclear spin coupling constants for these protons are reported. Results obtained from the nmr data show that electron spin is delocalized into the π system of the phenyl group of the ligand. Since the bonding to the ligand is σ, this study shows that contrary to several literature reports one may not assume *a priori* that π delocalization in a phenyl ring is evidence for metal–ligand π-type bonding. A delocalization mechanism which accounts for the observed shifts is presented. The complex with the formula $[Ni(bz)_5BF_4](BF_4)$ was isolated as a solid. Spectral and conductance data are presented to substantiate that $[Ni(bz)_6]^{2+}$ is the species present when the previously mentioned complex is dissolved in nitromethane solutions containing an excess of benzylamine.

The general theory and interpretation of nmr contact shifts has been extensively discussed in a previous publication from this laboratory[2] and should be consulted along with the references therein for background information. In this paper, we are specifically concerned with using both the signs and magnitudes of the contact shift for the ligand protons to deduce information about the metal–ligand bonding. The unpaired spin in most complexes is in a molecular orbital which is essentially a metal d orbital. The extent of mixing of the ligand orbitals with this essentially d metal orbital to form a nonbonding or antibonding mo is taken as an indication of the mixing of the d orbitals with the ligand orbitals in forming the bonding molecular orbital. Hence, by looking at the contact shift, one infers information about the bonding.

Happe and Ward[3] have found proton contact shifts indicating a σ mechanism for delocalizing spin onto pyridine. There have been many reports in the literature,

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