this comparison. As mentioned previously, the act of coordination by the donor atom lone pair results in increased binding energy in the $\sigma$ systems in both molecules. The stabilization effect is much larger for $CH_3CN$. On the other hand, the $\pi$ systems in both molecules are destabilized, this effect being much larger for $CH_3NC$.

Further evidence for the greater "basicity" of the carbon lone pair comes from a comparison of the $H_3C$–C and $H_3C$–N bonds, respectively. The overlap energies for these links are $-9.70$ and $-8.65$ ev while the overlap populations are 0.84 and 0.70.

Comparison of the energies of the C and N lone-pair orbitals in these two compounds indicates $CH_3NC$ should be the stronger base in agreement with experiment.[10]

In the case of $CH_3NC$ we find a situation with regard to the $\pi$ orbitals very analogous to that of acyl group donors such as ketones and amides. These Lewis bases undergo a marked decrease in C=O bond strength upon coordination of the oxygen lone pair. This has generally been attributed to strong polarization of the $\pi$ cloud resulting in a more singly bonded nature for the C–O link. Coordination of the N lone pair of $CN^-$ by $CH_3^+$ appears to nearly produce the same effect. The $\pi$-bond weakening, moreover, nearly offsets the $\sigma$-system strengthening, and very little change in CN binding energy occurs. Note the small increase in $F_{CN}$ relative to the parent $CN^-$.

**D. $C_2^{2-}$, $H_2C_2$.** Calculations were carried out for $C_2^{2-}$ and $H_2C_2$ with essentially the same trends as noted for $CN^-$ and HCN. The redistribution of electron density in the lone pairs and C–C $\sigma$ orbital of $C_2^{2-}$ upon protonation is quite similar to the cyanide case. One exception here, however, is a slight *decrease* in $\pi$ overlap energy, where before a slight increase in overlap energy was found. This, perhaps, is not unexpected. No comparison with $F_{CC}$ is possible here since the Raman spectrum of $C_2^{2-}$ has not been reported. Our molecular orbital calculations predict an increase in $F_{CC}$.

## Conclusions

To summarize our findings we note the following. (1) A good correlation is found between $F_{CN}$ and $\Omega_{CN}$ when coordination of *either* lone pair of $CN^-$ occurs. Within the series of substituted cyanides both overlap energies and overlap populations afford a good correlation with the CN force constant and the C–N internuclear distance. (2) Analysis of the overlap energies at the subtotal level indicates that stronger binding occurs within the CN $\sigma$ system as a result of electron-pair donation, and this effect, through an increase in CN force constant, explains the observed increase in $\nu_{CN}$ upon coordination. The increased strength of the $\sigma$ bonds arises from a greater dominant contribution from the donor atom s orbital. The $\pi$-orbital perturbation is subordinate to this. (3) The effect of coordination of the C lone pair of $CN^-$ on the N lone pair appears to be such as to make the N lone pair more basic in the Lewis sense since this orbital is found to lie at higher energy in HCN and $CH_3CN$, for example, than in $CN^-$. A similar statement may be made for the C lone pair in $CH_3NC$. (4) Comparison of $CH_3CN$ and $CH_3NC$ shows the carbon lone pair in $CH_3NC$ is more readily available for coordination than the N lone pair of $CH_3CN$. This greater basicity of $CH_3NC$ is masked to some extent in practice by its general instability relative to $CH_3CN$. Both the C—C and C≡N links are stronger in $CH_3CN$ than the C—N and N≡C links of $CH_3NC$.

**Acknowledgment.** The author wishes to thank the Bell Telephone Laboratories of Winston-Salem for their generous donation of IBM 7040/7044 computer time. He also expresses his appreciation to Mrs. J. Boone of Bell Laboratories for her assistance in performing these computations.

---

[10] P. von R. Schleyer and A. Allerhand, *J. Am. Chem. Soc.*, 84, 1322 (1962).

---

# A Study of the $HF_2^-$ Ion by Fluorine Magnetic Resonance[1a]

**Rizwanul Haque and L. W. Reeves**

*Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada.* *Received September 9, 1966*

**Abstract:** Studies of the fluorine chemical shift changes in the following salts have been measured in water as a function of concentration: $KHF_2$, $NH_4HF_2$, $NaHF_2$, KF, $NH_4F$, and NaF. The changes in chemical shift observed for the salt $KHF_2$ can be satisfactorily interpreted according to the equilibrium: $HF_2^- \rightleftharpoons HF + F^-$. An equilibrium constant has been obtained for this dissociation, and chemical shifts of the species $HF_2^-(H_2O)_x$, $HF(H_2O)_y$, and $F^-(H_2O)_z$ are compared. The subscripts $x$, $y$, and $z$ denote unknown solvation numbers in water.

A study of $KHF_2$[2] in the solid state by infrared spectroscopy was followed by detailed measurements of heat capacity and dielectric properties.[3] The linearity of the $HF_2^-$ ion has been shown by Ketelaar and Vedder[4a] and Newman and Badger.[4b] Pimentel[5] has sug-

---

[1] (a) This research was supported by the National Research Council of Canada and Petroleum Research Fund of the American Chemical Society in grants to L. W. R.

[2] J. A. A. Ketelaar, *Rec. Trav. Chim.*, 60, 523 (1941).

[3] E. F. Westrum and K. S. Pitzer, *J. Am. Chem. Soc.*, 71, 1941 (1949).

[4] (a) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, 19, 654 (1951); (b) R. Newman and R. M. Badger, *ibid.*, 19, 654 (1951).

[5] G. C. Pimentel, *ibid.*, 19, 446 (1951).

gested a molecular orbital model for the $HF_2^-$ ion involving a three-center orbital. Neutron diffraction studies of the $HF_2^-$ ion confirm the symmetric arrangement of the linear ion.[6] Broad-line nmr studies of the proton and fluorine signals from powdered $KHF_2$ samples[7] further confirm the symmetric structure.

A qualitative study of the $^{19}F$ nmr spectra of $KHF_2$ solutions has been made previously[8] with a precision of ±2.0 ppm quoted for the chemical shifts. Since large $^{19}F$ chemical shifts are observed in solutions of the bifluoride ion, an interpretation of these shifts in terms of an equilibrium constant for dissociation of the ion has been the object of this study.

## Experimental Section

The following salts of the bifluoride ion, $Na^+$, $K^+$, and $NH_4^+$, were supplied as analytical reagents by B.D.H. Solutions of these salts at various concentrations were made up in doubly distilled water. Nmr spectra were recorded using freshly prepared solutions. A conventional Varian HR spectrometer operating at 40 mHz was used to record spectra and a 10 *M* KF solution in a capillary was used as an external standard. Volume susceptibility measurements were made on all solutions using pure water as a reference by the method of Frei and Bernstein.[9] Diamagnetic susceptibility corrections were then applied appropriate for a cylindrical sample shape.

## Results and Discussion

In Figure 1, $^{19}F$ chemical shifts of the three bifluoride ion salts are plotted as a function of concentration. These can be compared with the dilution chemical shifts observed in the corresponding fluorides, also remeasured in this work. Unfortunately the solubility of $NaHF_2$ prevents extensive investigation of this salt. The $^{19}F$ chemical shift in $KHF_2$ solutions can be measured over sufficient concentration range to compute an equilibrium constant for the reaction

$$HF_2^- \rightleftharpoons HF + F^- \tag{1}$$

We assume the single $^{19}F$ resonance to be a time average of the three environments represented in eq 1.[10] Representing the chemical shift with respect to the $F^-$ ion at infinite dilution as zero, the observed chemical shift $\delta_{obsd}$ can be written

$$\delta_{obsd} = \frac{(1-\alpha)}{(1+\alpha)}\delta_{HF_2^-} + \frac{\alpha}{1+\alpha}\delta_{HF} \tag{2}$$

where $\alpha$ and $\delta_{HF_2^-}$ are the degree of dissociation and chemical shift of the $HF_2^-$ ion, respectively. The chemical shift of HF, $\delta_{HF}$, is estimated to be 20.5 ppm to high field from the chemical shift of the $F^-$ ion. This estimate can be justified by considering the equilibrium for the dissociation of HF in water

$$H_2O + HF \rightleftharpoons H_3O^+ + F^- \tag{3}$$

The value[11] of $K_D$ is $3.53 \times 10^{-4}$ mole $l.^{-1}$. At the lowest concentration of $HF_2^-$ ion observed, the dissociation according to eq 1 is almost complete, but the HF produced in process 1 is still only ~2.5% dissociated according to eq 3. The extrapolation of the chemical shift of the $^{19}F$ resonance to infinite dilution, therefore, in $KHF_2^-$ solutions corresponds to the time-averaged chemical shift of an equimolar solution of $F^-$ and HF at infinite dilution in water. Since the chemical shift of the $F^-$ ion at infinite dilution is known and represented in Figure 1, one can derive a chemical shift of hypothetical undissociated HF at infinite dilution in water.

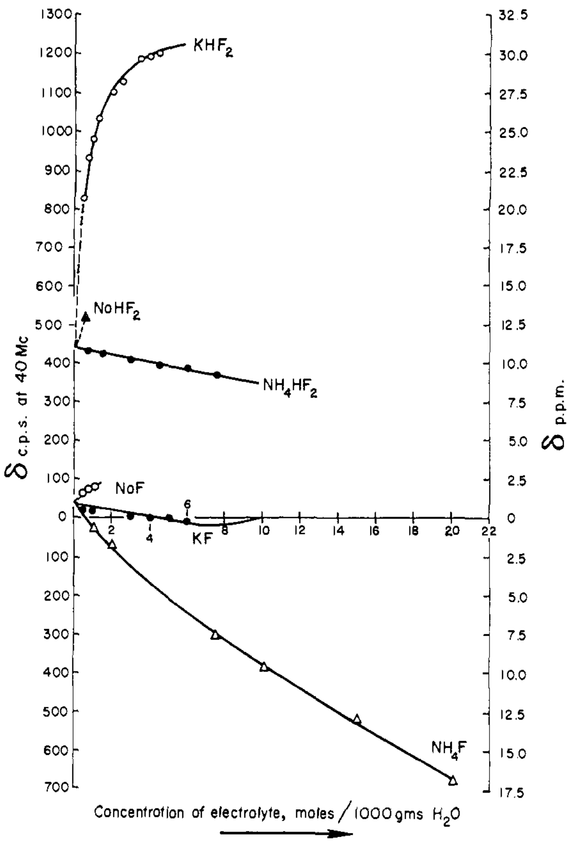

Figure 1. $^{19}F$ chemical shift changes for the aqueous solutions of $KHF_2$, $NaHF_2$, $NH_4HF_2$, NaF, KF, and $NH_4F$ at 40 Mcps.

The chemical shift, $\delta_{HF_2^-}$, and $\alpha$, the degree of dissociation of the $HF_2^-$ ion at various concentrations, are to be derived from the dilution chemical shift changes. The equilibrium constant for eq 1 can be written in the usual way

$$K_e = \frac{\alpha^2 c}{(1-\alpha)}\frac{\gamma_{HF}\gamma_{F^-}}{\gamma_{HF_2^-}} = K_c\frac{\gamma_{HF}\gamma_{F^-}}{\gamma_{HF_2^-}} \tag{4}$$

where $\gamma$'s are activity coefficients. We are able to derive $K_c$ and its dependence on concentration. The value of $\delta_{HF_2^-}$ has been estimated by plotting $\delta_{obsd}$ against $C^{-1/2}$, which is a reasonably linear dependence, and we accept a value of $\delta_{obsd}$ when $C^{-1/2} = 0$. This estimate gives $\delta_{HF_2^-} = +36.4$ ppm from the $F^-$ ion at infinite dilution. The degree of dissociation, $\alpha$, and the values of $K_c$ can now be calculated using eq 2 and 4. The values of $K_c$ are listed in Table I from the best fit line for experimental points. By plotting $pK_c$ as a function of $C^{1/2}$, the value $pK_e$ is found to be 0.47 by extrapolation. This can be compared to a previous[12] determination of 0.708.

---

(6) J. A. Ibers, *J. Chem. Phys.*, **40**, 402 (1964).

(7) J. S. Waugh, F. B. Humphrey, and D. M. Yost, *J. Phys. Chem.*, **57**, 486 (1963).

(8) I.-T. Vang and F. I. Skripov, *Dokl. Akad. Nauk SSSR*, **136**, 58 (1961).

(9) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **37**, 1891 (1962).

(10) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.*, **21**, 279 (1953).

(11) "Handbook of Physics and Chemistry," 43rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

(12) F. A. Cotton and G. Wilkinson, "Inorganic Chemistry," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1962.

Table I. Computed Values of the Equilibrium Constant, $K_c$, for the Dissociation of the $HF_2^-$ Ion at Different Concentrations of $KHF_2$ in Water

| Concn of $KHF_2$, $C^a$ | $K_c{}^a$ | Concn of $KHF_2$, $C^a$ | $K_c{}^a$ |
|---|---|---|---|
| 0.25 | 0.246 | 2.25 | 0.105 |
| 0.50 | 0.240 | 2.50 | 0.104 |
| 0.75 | 0.220 | 2.75 | 0.100 |
| 1.00 | 0.137 | 3.00 | 0.100 |
| 1.25 | 0.135 | 3.25 | 0.097 |
| 1.50 | 0.120 | 3.50 | 0.090 |
| 1.75 | 0.105 | 3.75 | 0.085 |
| 2.00 | 0.106 | 4.00 | 0.083 |

[a] In moles/kg of water.

The chemical shift changes of $^{19}F$ in solutions of $NH_4HF_2$ do not depend entirely on the equilibrium represented by eq 1. It is evident from the dilution shift in $NH_4F$ solutions that solutions containing the $NH_4^+$ ion which can hydrolyze and form hydrogen bonds with $F^-$ are much more complex. The hydrolytic equilibria and hydrogen-bonding effects which lead to a low-field shift in $NH_4F$ solutions also effect in a more complex manner the chemical shift changes in the $NH_4HF_2$ solutions. It is interesting to note, however, that the chemical shift of $^{19}F$ at infinite dilution is probably about the same for $NH_4HF_2$ and $KHF_2$ solutions. From this study we are able to compare chemical shifts of $^{19}F$ in different hydrogen-bonded environments. If we take the shift of $F^-$ ion at infinite dilution in water as zero (some hydrogen-bonded solvation is occurring in this case), then the chemical shift of a hypothetical isolated HF molecule in water is $+20.5$ ppm to high field, the $HF_2^-$ ion is $+36.4$ ppm to high field, and the chemical shift in anhydrous liquid HF is $+76.1$ ppm.[13] If, as seems reasonable, we assume that the chemical shift becomes diamagnetic monotonically as the hydrogen bond strength to a fluorine atom increases, then this indicates hydrogen bond strengths in the order: $(HF)_n$(anhydrous liquid) $> HF_2^-(H_2O)_x > HF(H_2O)_y > F^-(H_2O)_z$. The subscripts $n$, $x$, $y$, and $z$ can be regarded as unknown solvation numbers.

---

[13] 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.

---

# Intensities of Forbidden Transitions in Octahedral Complexes

**Richard F. Fenske**

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.* *Received August 8, 1966*

**Abstract:** This work concerns the relative intensities of Laporte forbidden ligand field transitions of octahedrally coordinated transition metal complexes in which the charge-transfer transitions are from the ligand to the metal. Within the framework of a one-electron approximation, it is shown from theoretical considerations that the ligand field transitions in such complexes vibronically mix with those ligand-to-metal transitions in which the final states involve the $e_g$ and not the $t_{2g}$ orbital of the metal. Relative intensities of ligand field transitions within a complex are correlated with the observed ligand-to-$e_g$ transition. Correlations of intensities between corresponding transitions for analogous chloro and bromo complexes are also obtained.

It has long been recognized[1] that the portions of the absorption spectra of octahedral transition metal complexes associated with the ligand field transitions are Laporte forbidden since both the ground and excited states are of the same parity (g → g). That weak absorptions are actually observed has been attributed to vibrational perturbations which "mix" electronic states of even and odd parity. The forbidden dipole transition is said to "borrow" intensity from an allowed g → u transition.

Early explanations[2,3] of the Laporte forbidden transitions in metal complexes were carried out in the framework of a crystal-field model. Consequently, the state of odd parity was presumed to be the metal p orbital above the partially filled d orbitals, *e.g.*, the 4p level for the first transition row. Englman[4] was the first to attempt a calculation on the basis of a molecular orbital (MO) model in which the g → u transition involved a "charge transfer," that is, the molecular orbitals of even and odd parities were primarily associated with the metal and ligand atomic orbitals, respectively. Although Englman concluded that the allowed transitions in aquo complexes were from the metal to the ligand, there is substantial agreement that in complexes with electron-donor ligands it is the ligand-to-metal transitions which give rise to the observed absorptions. One can say only that his correlation of ligand field transitions with the *edge* of the first intense absorption band was possibly fortuitous. In this connection, it should be noted that in Englman's tabulation, he presumes that all first observed transitions occur from the $2t_{2g}$ metal orbital which is not reasonable for those ions, $Fe^{+2}$ through $Cu^{+2}$, in which the $2e_g$ metal orbital is occupied (see Figure 1).

It is worthwhile to reexamine Englman's postulates in the light of ligand-to-metal charge-transfer transitions involving electron-donor ligands. According to first-order perturbation theory, the contribution of odd parity states, $C_i$, to the even parity ground and excited

---

[1] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and references therein.

[2] C. J. Ballhausen and A. D. Liehr, *Mol. Phys.*, 2, 123 (1959).

[3] S. Koide and M. H. L. Pryce, *Phil. Mag.*, 3, 607 (1959).

[4] R. Englman, *Mol. Phys.*, 3, 48 (1960).