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Solvent Effects on $n \rightarrow \sigma^*$ Transitions, Hydrogen Bonding between Ethylamines and Aliphatic Alcohols

BY D. P. STEVENSON

RECEIVED FEBRUARY 7, 1962

The long wave length edges of the $n \rightarrow \sigma^*$ absorption bands of the ethylamines are shown to undergo marked blue shift in prototropic solvents from their position in aprototropic solvents. It is shown that these blue shifts are due to the formation of specific, one to one, presumably hydrogen bonded, complexes between the amines and the proton donors. The magnitude of the changes in absorptivity at a given "long wave length" can be used to quantitatively compare the electron donor power of bases toward a particular (protonic) acceptor or to compare the proton donor power of a series of donors toward a given base. It is found that the tendency of the amines, NH_3, $EtNH_3$, Et_2NH and Et_3N to complex with water is completely anti-parallel to the basicity of these amines as measured by K_b. It is shown that the tendency of triethylamine to complex with the alcohols, methyl-, ethyl-, *s*-propyl- and *t*-butyl in isoöctane solution decreases in the given order, and approximate values for the association constants are, 3.4, 2.6, 1.4 and 1.0 in liter/mole, respectively, at 25°.

In this paper there are presented the results of a systematic study of the ultraviolet ($\lambda \geq 2000$ Å.) absorption spectra of the ethyl (mono-, di- and tri-) amines in the variety of solvents, diethyl ether, isoöctane, tertiary butyl alcohol, methanol and water. This work was undertaken with the object of illustrating the applicability of measurements of the apparent blue shifts of the $n \rightarrow \sigma^*$ absorption bands of bases in prototropic solvents as a means of studying the extent of hydrogen bonding between base and solvent[1] and between base and prototropic solute in inert solvent.

All spectroscopic measurements were made with an Applied Physics Corp. (Cary) Model 14 spectrophotometer. Matched 1 cm. quartz cells were used throughout, and by means of matched quartz inserts, the optical path in the solutions and reference cell could be varied in steps from 1.00 cm. to 0.010 cm. By gas–liquid chromatography the ethylamines were shown to be better than 99.5% pure, with the impurities if any, other ethylamines. The spectroscopic quality of the solvents was checked in each case by comparison of the transmission of 1 cm. thickness against distilled water and the distilled water was checked against dry air in the reference cell.

The spectra of the three ethylamines in isoöctane and water solution are shown in Figs. 1 and 2. In these Figs. there are shown as "points" the results of measurements of the absorption spectra of diethylamine in hexane and water, respectively, reported by Ley and Arends,[2] the only previous reports of the spectra of aliphatic amines in solution that we have been able to find. The data of Ley and Arends for hexane solution are in quite reasonable agreement with our results when consideration is given to the very different spectrophotometric techniques employed. For $\lambda \geq 2200$ Å. our data on the water solutions and those of Ley and Arends are again in good agreement. We do not understand and offer no explanation of the "high" absorptivities found by the earlier workers at shorter wave lengths ($\lambda < 2200$ Å.).

In Table I there are shown the wave lengths, λ_{100} and λ_{10}, at which the amine solutions in diethyl ether have absorptivities equal to 100 and 10 l./mole cm., and the absorptivities of the vapors and the solutions in other solvents at these wave lengths (λ_{100} and λ_{10}). The data on the vapor spectra are from the paper of Tannenbaum, *et al.*[3] These data of Table I make it evident that the absorption curves for the amines in ether solution are shifted to the blue from the vapor and slightly

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[1] D. P. Stevenson, G. M. Coppinger and J. W. Forbes, *J. Am. Chem. Soc.*, **83**, 4350 (1961). See also, G. J. Brealey and M. Kasha, *ibid.*, **77**, 4462 (1955), for the results of studies of blue shifts of $n \rightarrow \pi^*$ transitions and hydrogen bonding.

[2] H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

[3] E. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

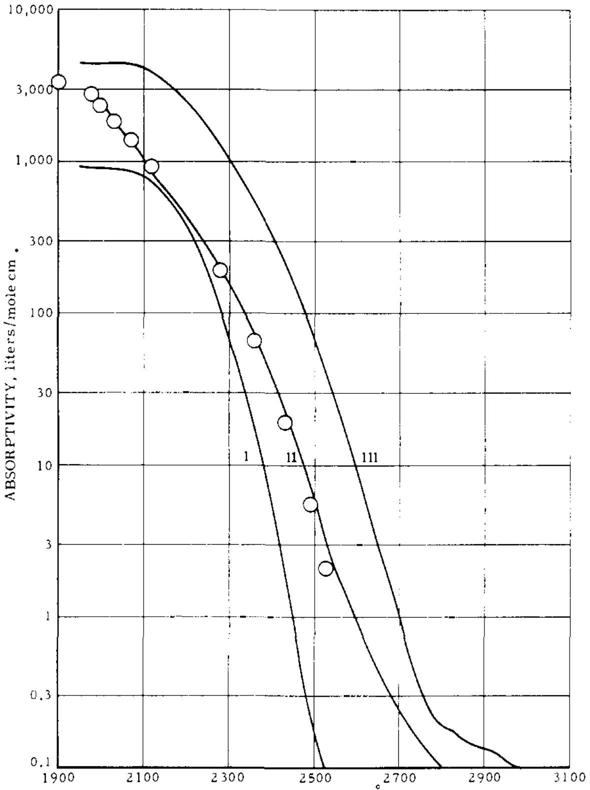

Fig. 1.—The absorption of ethylamines in isoöctane solution. Smooth curves, this research; circle points, diethylamine in hexane solution from Ley and Arends.[2] I, $EtNH_2$; II, Et_2NH; III, Et_3N.

to the red from isoöctane solution spectra. In the alcohol and water solutions the spectra show a greater or smaller blue shift from the diethyl ether spectrum like that shown by the NH_3 in water spectrum.[1] Interpreting the spectra of the solutions in the prototropic solvents as due to amine molecules not engaged in specific, hydrogen bond complexes with the solvent of the type —$\rangle$N:----H-O-, we calculate the upper limits to the per cent of free base molecules in the solvents shown in Table II.

TABLE I

SOLVENT EFFECTS ON THE ETHYLAMINE SPECTRA

Solvent	Absorptivities, liter/mole cm.					
	$EtNH_2$		Et_2NH		Et_3N	
	λ_{100}, 2280 Å.	λ_{10}, 2380 Å.	λ_{100}, 2347 Å.	λ_{10}, 2484 Å.	λ_{100}, 2495 Å.	λ_{10}, 2621 Å.
Diethyl ether	100	10.0	100	10.0	100	10.0
Vapor	250	~10	160	18	145	..
t-Butyl alcohol	9.0	0.71	17.0	1.9	43	4.2
Methyl alcohol	2.2	.23	3.4	0.44	5.8	0.70
Water	1.4	.14	4.0	0.43	3.1	0.24
Isoöctane	104	8.9	85	8.0	73	5.6
Acetonitrile	..	..	..	..	112	15.0

TABLE II

UPPER LIMITS TO FREE BASE (PER CENT) IN ALCOHOLS AND WATER. 25°

Solvent	Base: NH_3	$EtNH_2$	Et_2NH	Et_3N
t-Butyl alcohol	...	≤ 8.0	≤ 18.0	≤ 42.5
Methanol	...	≤ 2.2	≤ 3.9	≤ 6.4
Water	≤ 0.7	≤ 1.4	≤ 4.1	≤ 2.7
$K_b \times 10^5$ (H_2O)	1.8	47	100	53

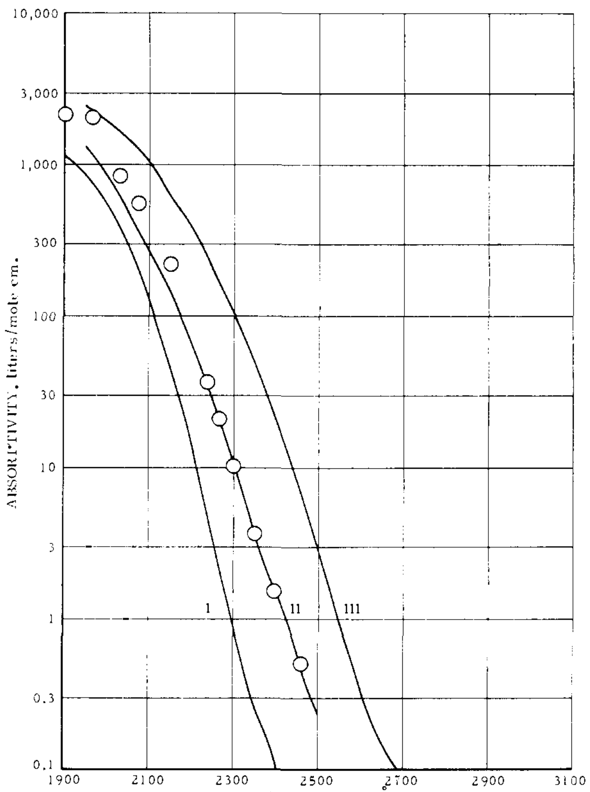

Fig. 2.—The absorption spectra of the ethylamines in water solution. Smooth curves, this research; circle points, diethyl amine, Ley and Arends.[2] I, $EtNH_2$; II, Et_2NH; III, Et_3N.

It has been found that the absorption band of triethylamine in acetonitrile solution is almost coincident with that in diethylether solution. This observation is convincing proof that the blue shift of the amine spectra in alcohol solutions from those in diethylether solutions is not due to a general "medium effect," or simply due to the presence of large permanent dipoles in the solvent molecules. The dielectric constant of acetonitrile is 36.7,[4] somewhat greater than that of methanol (31.5)[5] while the dielectric constants of diethyl ether and isoöctane are 4.3[6] and 2.0,[6] respectively. The permanent dipole moment of acetonitrile is 3.9 D.[7] while those of diethyl ether and isoöctane are 1.3 and 0.0 D.[7]

Two points of interest with respect to the data assembled in Table II are to be noted: (1) That while the degree of association of the amines with water and methanol are about equal, there is considerably less association with tertiary butyl alcohol, and (2) that the degree of association of the bases with water is completely anti-parallel the basicity of the bases as measured by the equilibrium constant shown in the bottom row of Table II.

$$K_b = \frac{(BH^+)(OH^-)}{\text{total B}} \qquad (1)$$

[4] C. J. F. Böttcher, *Physica*, **6**, 59 (1939).

[5] R. J. W. LeFevre, *Trans. Faraday Soc.*, **34**, 1127 (1938).

[6] "Handbook of Chemistry and Physics," C. D. Hodgman Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 37th Ed., page 2324.

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, Chap. III.

In order to demonstrate that the spectral blue shift is indeed due to a specific one to one complex between base and proton donor, there were measured spectra of the ternary systems, triethylamine and water in diethylether as shown in Table III. In columns 2, 3 and 4 of this table there are shown the absorbances (1.00 cm.) of the solutions of the indicated composition at 25 Å. intervals from 2700–2500 Å. In column 5 and 6 there are shown the concentrations of free base calculated from the absorbance data at each wave length under the assumption that the absorbance of the water containing solutions is due solely to free base. The complete absence of systematic variation in apparent free base concentration with wave length indicates that either our assumption[1] that the complex, $\geqslant N$:----H-O-, is effectively transparent in the wave length range is correct, or that the absorptivity of the complex is simply proportional to that of the free base. In the absence of other evidence we are inclined to the first explanation since the second explanation seems improbable.

From the average concentrations of free base for each solution containing water, there were calculated the apparent association constants, shown

$$K_c = \frac{B^0 - B}{B(A^0 + B - B^0)} \qquad (2)$$

B^0 = total amine concentration
B = average free amine concentration
A^0 = total water concentration

at the bottom of both columns 5 and 6 of Table III. Since the apparent K_c's from the two solutions agree within their respective uncertainties and there is a factor of 3 difference in the ratios B^0/A^0 for the two solutions, we have adequate evidence of the reality of the one to one complex, amine·H_2O.

TABLE III

EFFECT OF WATER ON THE SPECTRUM OF TRIETHYLAMINE IN DIETHYL ETHER

25°

Et_3N^0, mole/liter	1.00_0	0.750	0.500	0.750	0.500
H_2O	0.000	0.257	0.513	0.257	0.513
λ, Å.	Absorbance, 1.00 cm.			Free Et_2N mole/liter	
2500	92.2	67.8	43.9	0.736	0.476
2525	61.2	44.2	28.4	.722	.465
2550	38.9	28.0	18.4	.721	.475
2575	23.9	17.5_0	11.3_7	.732	.476
2600	14.7_7	10.8_0	6.8_3	.731	.462
2625	8.9_0	6.5_7	4.1_6	.738	.467
2650	5.4_0	4.9_5	2.50	.732	.463
2675	2.90	2.1_1	1.39_5	.728	.481
2700	1.65_0	1.22_0	0.78_2	.739	.474
			Average, B	.731	.471
				± .006	± .006
			K_c (liter/mole)	.109	.127
				± .035	± .035

From the data shown in Table II, it appears that in water solution ammonia is about four times as associated as is triethylamine. In diethyl ether, on the other hand, ammonia appears to have about thirty times the tendency of triethylamine to hydrogen bond with dissolved water. This follows from the comparison of the water–ammonia association constant equal to about 3 in diethyl ether solution[1] with that given in Table III of the present work, *i.e.*, a triethylamine–water association constant of about 0.1 in diethyl ether. The difference in the relative tendencies of ammonia and triethylamine to associate with water in water solution and in dilute diethylether solution is probably the consequence of the fact that in water solution the amine–water association is in competition with water–water association while in diethyl ether solution the competitive association is that of water with the base ether.[8]

In order to demonstrate the utility of measurements of the apparent blue shifts of $n \rightarrow \sigma^*$ transitions in the study of the proton donor strengths, we have measured the spectra of isoöctane solutions of triethylamine containing approximately equivalent concentrations of each of the four alcohols, (1) methanol, (2) ethanol, (3) *s*-propanol and (4) *t*-butanol. Representative absorbance data for the various solutions are shown in Table IV. Concentrations of free amine were computed from the absorbances by means of the absorptivities of the amine in alcohol free isoöctane, and the average free amine concentrations are shown in column 7 of Table IV. Apparent association constants, shown in column 8 of Table IV were calculated by means of eq. 2. As would be expected, the apparent K_c increases with dilution, because in the use of eq. 2 we assume that the effective concentration of available proton donors equals the total concentration of alcohol less the concentration of complexed amine. Actually, of course the effective concentration of available protons is reduced by the self-association of the alcohol and the reduction of this error with dilution is the source of the increase in the apparent association constant for the amine–alcohol complex. The studies of the n.m.r. spectra of methanol and *t*-butanol in carbon tetrachloride solution of Saunders and Hyne,[9] indicates that for total alcohol concentrations in the range of 0.6 to 0.1 mole/liter the ratio of free proton to total alcohol varies from ~0.3 to 0.9.

In order to demonstrate the essential validity of the foregoing qualitative explanation of the systematic inconstancy of the apparent association constant K_c shown in Table IV, and to obtain estimates of the actual association constants, given in the column K_c(corr) of Table IV, the following further experiments and calculations were made. The absorption band that occurs at about 1.40 μ[10] in the near infrared spectra of solutions of alcohols in inert solvents is attributed to the first overtone of the "free hydroxyl" O–H stretching motion. There were measured the absorbances (at $\lambda_{max} = 1.403\mu$) of methanol solutions in isooctane for 0.01 to ~1 mole/liter as shown in Table V. The proton magnetic resonance data[10] on methanol in carbon tetrachloride solution indicate methanol to be >90% monomeric for concentrations < 0.1 mole/liter. Thus assuming a similar degree of polymerization to obtain in isoöctane solution (<0.1 *M*), the absorptivity of the free hydroxyl can be

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(8) See the discussion in the last paragraph of this paper.

(9) M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

(10) G. E. Hilbert, *et al.*, *Nature*, **135**, 147 (1935); *J. Am. Chem. Soc.*, **58**, 548 (1936).

TABLE IV

EFFECT OF ALCOHOLS ON THE SPECTRUM OF TRIETHYLAMINE IN ISOÖCTANE

25°

R	Moles liter: ROH	Moles liter: Et_3N	Absorbance (1 cm.) at: 2500 Å.	Absorbance (1 cm.) at: 2575 Å.	Absorbance (1 cm.) at: 2650 Å.	Free Et_3N	K_c (liters mole)	K_c (corr.)
Me	0.548	0.358	15.17	3.84	0.68$_2$	0.229	1.32	3.04
Me	.274	.179$_0$	7.94	1.954	.37$_3$	.123$_2$	2.06	3.06
Me	.137$_0$	.089$_5$	4.2$_6$	1.10$_5$	.18$_8$	.064$_2$	3.53	3.92
Et	.430	.358	16.1$_1$	3.74	.74$_1$	.244	1.12	2.84
Et	.265	.179$_0$	8.5$_8$	2.067	.38$_9$	.131$_0$	1.69	2.86
Et	.137$_5$	.089$_5$	4.4$_9$	1.11$_6$	.204	.072$_1$	2.10	2.34
s-Pr	.488	.352	19.8$_5$	4.5$_1$	.80$_0$	.286	0.54$_6$	1.39
s-Pr	.294	.176$_0$	10.1$_1$	2.20	.39$_8$	.143$_9$	1.05	1.62
t-Bu	.449	.358	20.7$_1$	4.6$_5$	.90$_8$	.305	0.43$_9$	1.07
t-Bu	.224$_5$	.179$_0$	10.9$_2$	2.47	.46$_1$	.159$_2$	0.60$_5$	1.06
t-Bu	.112$_2$	.089$_5$	5.24	1.26$_9$	.20$_0$	.079$_2$	1.27^9	1.38
..	.00	1.00$_0$	68.2	15.5$_0$	2.91	....	...	

estimated from the absorbance of dilute (<0.05 *M*) solutions and then employing this absorptivity the concentration of "free hydroxyl" can be calculated as a function of gross methanol concentration, C^0(MeOH), from the absorbance data for solutions of higher concentrations. The results of our measurements are summarized in Table V in the form of a tabulation of graphically smoothed C^0(MeOH), absorbance and free hydroxyl (C(MeOH)) values in columns 1, 2 and 3. In column 4 there are given for comparison the concentrations of free hydroxyl estimated from the n.m.r. data of Saunders and Hyne.[9]

By associating the quantity $(A^0 - B^0 + B)$ with the gross methanol concentration of a solution containing methanol and amine, there could be made an estimate of "free hydroxyl" concentration for the solution from an appropriate graph of the data in Table V. Then the "corrected" association constant is

$$K_c(\text{corr.}) = K_c \frac{A^0 - B^0 + B}{(\text{Free OH})} \qquad (3)$$

with the values shown in column 9 of Table IV.

It will be seen that the trend of K_c with concentration virtually disappears in K_c(corr), *i.e.*, is reduced for the concentration range involved in the case of the methanol–triethylamine in isoöctane system from about a factor of 3 to less than 20%.

TABLE V

1.402 μ ABSORBANCE OF METHANOL IN ISOÖCTANE SOLUTION AND THE "FREE HYDROXYL" CONCENTRATION

C^0(MeOH), mole/l.	O.D., cm.$^{-1}$	C(MeOH),[a] mole/l.	C(MeOH),[b] mole/l.
0.010	0.014$_2$	0.009$_8$	~0.01
.050	.063	.043	.048
.100	.111	.076	.089
.200	.164	.113	.137
.400	.217	.150	.168
.800	.271	.187	.178

[a] Concentration of "free-OH" from the absorptivity at infinite dilution, A = 1.45 liter/mole cm. This A, as would be expected for the difference in solvent, is lower than that reported for carbon tetrachloride solutions, 2.16 liter/mole cm., by R. O. Crisler and A. M. Burrill, *Anal. Chem.*, **31**, 2055 (1959). [b] For CCl_4 solutions from data in ref. 8 of text. Assumed that $\nu(\text{OH}) = \alpha\nu_f(\text{OH}) + (1 - \alpha)\,\nu(\text{OHO})$.

The correlation curve for free hydroxyl *vs.* alcohol concentration based on the data shown in Table V was employed without modification to estimate free hydroxyl concentration for the experiments in the other three alcohols (Table IV). As justification for this procedure, we cite the proton magnetic resonance data of Saunders and Hyne[9] that indicate for concentrations below 0.5 mole/liter the concentrations of free hydroxyl in tertiary butyl alcohol solution in carbon tetrachloride are approximately equal to those of methanol solution of the same concentration and essentially equal to those of the methanol in isoöctane solutions.

Essential confirmation of the naive interpretation of the proton magnetic resonance data was obtained from measurements of the absorbance of the 1.414μ band of solutions of *t*-butyl alcohol in isoöctane. Because of the overlapping doublet character of the "free hydroxyl" absorption band of the spectra of ethanol and *s*-propanol,[11] we have not attempted a similar interpretation of measurements on isoöctane solution spectra of these alcohols.

It will be noted that there is little dependence of the apparent association constant for the triethylamine–water complex in ether solution upon water concentration and that this association constant appears to be at least an order of magnitude smaller than that for triethylamine–alcohol complexes in isooctane. At first sight these observations may appear to be incompatible and inconsistent with the relative degrees of association of the amines with solvent deduced from the spectra of the amines in alcohol. Actually there is neither incompatibility nor inconsistency of the various observations. In the case of water in ether solutions the total concentration of water is probably a direct measure of the effective water activity. The water molecules in dilute ether solution should have little tendency toward self-association since they can bridge ether molecules with hydrogen bonds, R_2O—HOH—OR_2, which accounts for the concentration independence of the apparent association constant, while this same hydrogen bridging will reduce the availability (activity) of water molecules for complexing with the amines and thus result in the calculation of an apparently low association constant. The association constant, K_c, for the triethylamine–water complex in diethyl ether solution found from the data of

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[11] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **4**, 711 (1936). See also R. Piccolini and S. Winstein, *Tetrahedron Letters*, **13**, 4 (1959).

Table III, is to be associated with a reaction of the form

$$\mathrm{Et_3N + Et_2O{\cdot}HOH \rightleftarrows Et_3NHOH + Et_2O} \quad (4)$$

rather than the reaction

$$\mathrm{Et_3N + H_2O \rightleftarrows Et_3NHOH{\cdot}} \quad (5)$$

That is, the apparent association constants for ammonia–water (Table II of ref. 1) and triethylamine–water (Table III above) in diethyl ether are really measures of the basicity of the amine relative to that of ether.

ADDED JUNE 21, 1962.—Since the paper was accepted for publication the author has learned that Barrow and Yerger, *J. Am. Chem. Soc.*, **76**, 5247 (1954), found for the triethylamine–ethanol association constant in carbon tetrachloride solution the value, 2.9 ± 0.3 liters/mole at ambient temperature, from measurements of the intensity of the alcohol OH band at 3630 cm.$^{-1}$. The average value for this equilibrium constant in isoöctane solution according to the data in our Table IV, is $2.6_8 \pm 0.2$ liters/mole. The excellent agreement with the previous value provides further substantiation of the validity of our interpretation of the blue shifts of the absorption spectra of amines in prototropic solvents, and the utility of such measurements in the study of "hydrogen bond" complexes.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON]

Anomalous Shapes of Hybrid Orbitals[1]

BY WILLIAM T. SIMPSON

RECEIVED JANUARY 22, 1962

In the framework of the ligand field theory it is shown that hybridization diminishes a higher p orbital in the direction of a ligand while augmenting a lower s orbital in this same direction.

Second-order perturbation theory contains the result that when levels mix, the higher ones push a lower one down, while the lower ones push a higher one up. It is possible to apply this fact in such a way as to lead to conclusions about hybridization which are quite unexpected. For example, it is possible to argue that hybridization in hydrogen fluoride (HF) affects the fluoride p orbital directed towards the proton so as to *decrease* electron density in the region of the proton and increase density correspondingly in the region along the proton-fluoride line away from the proton.

To go into the matter further, we shall look at a bond from the point of view of a closed-shell model —here, the ligand field theory. For example, for HF we may think about the electrons in a closed-shell fluoride ion as perturbed by the ligand: a proton. For convenience we may regard the central ion as containing two orbitals only, like $2s$ and $2p_x$, called s and p. The former is symmetric and the latter anti-symmetric with respect to reflection in the yz-plane. A proton placed out on the x-axis will lower the energy of s and p, and because of the directional properties, p somewhat more than s. With V representing the influence of the proton we have

$$|\langle p|V|p\rangle| > |\langle s|V|s\rangle|$$

The energy level scheme which shows the effect of a bond between the atom s^2p^1 and a hydrogen atom is, according to the ligand field picture, simply the orbital energy level scheme of the ion s^2p^2 as perturbed. To the first order there is the level shift indicated in Fig. 1, going from the zeroth column to the first (I). The energy of the "molecule" is lowered by

$$\Delta E_{\mathrm{I}} = 2\langle p|V|p\rangle + 2\langle s|V|s\rangle$$

where the factors of two arise because the orbitals are doubly filled.

The perturbation will mix s and p, corresponding to which there is a further change in the energy of the molecule

$$\Delta E_{\mathrm{II}} = -\frac{2\langle s|V|p\rangle^2}{\mathrm{W_p}^0 - \mathrm{W_s}^0} - \frac{2\langle p|V|s\rangle^2}{\mathrm{W_s}^0 - \mathrm{W_p}^0}$$

Going along with the second-order energies are the first order functions (normalized to the first order)

$$\bar{\mathrm{s}} = s + \epsilon p$$

$$\bar{\mathrm{p}} = p - \epsilon s$$

where $\epsilon = -\langle s|V|p\rangle/(\mathrm{W_p}^0 - \mathrm{W_s}^0)$. Actually $\Delta E_{\mathrm{II}} = 0$ because the p level goes up as much as the s level goes down. (As a matter of fact the Slater determinant based on the configuration $\bar{s}^2\bar{p}^2$ is the same as the one based on s^2p^2.) Up to a point, hybridization is irrelevant with the ligand field description of the molecule; because one closed-shell many-electron function based on certain orbitals is the same as another based on different orbitals which have been obtained from the first ones by a unitary transformation. In the Fig., I is as good as II.

When we consider spectra, ionization potentials, etc., the hybridization becomes relevant. It makes a lot of difference whether we base our description of the singly-ionized molecule on scheme I or II in Fig. 1. Of course here we are dealing with an open-shell configuration. The correct description of the ionized species requires us to use II—the orbital from which the electron is to be removed is $\bar{p}$, not p.

Let us now inquire into the shapes of the hybrid orbitals. If for definiteness the phases are picked so that s and p are both positive in the vicinity of the proton, then $\langle s|V|p\rangle$ will be negative, making ϵ positive. Keeping in mind the phases, we can therefore picture $\bar{s}$ as distorted so as to put extra density (comparing with s) in the region of the proton. This is consonant with the fact that the energy of $\bar{s}$ is lower than the energy of s. According to a similar argument, $\bar{p}$ is distorted so as to take electron density away from the proton. Al-

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[1] Supported in part by contract with the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.