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Hydrogen Bonding Systems Containing Hydrogen Fluoride. III.* Infrared Frequency Shifts and CNDO/2 Calculations on HF-Carbonyl Compound Complexes

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CNDO/2 calculations were carried out for the hydrogen bonded complexes between hydrogen fluoride (HF) and a series of organic compounds having a carbonyl group as a proton acceptor. Infrared spectral measurements were also made to obtain the frequency shifts of H–F stretching vibration, $\Delta\nu_{HF}$, for the same complexes in dilute carbon tetrachloride solution. Optimum geometry was obtained on the assumption of planar complex. For all the carbonyl compounds used, the interatomic angles, $\angle$C–O···H, were 120°—123° for the most stable conformation. The changes in the distance between H atom and F atom, ΔR_{HF}, were in good correlation with $\Delta\nu_{HF}$ obtained from IR spectra. Calculated hydrogen bond energies were also in good correlation with $\Delta\nu_{HF}$, though their absolute values were somewhat larger than those derived from experimental observations. This indicates that the CNDO/2 calculations give relatively correct enthalpy values for the hydrogen bond complexes of a given donor with a series of molecules having a common acceptor group. Other correlations of $\Delta\nu_{HF}$ with properties expected to change with the hydrogen bond formation were also confirmed. These include the energies of each bond obtained by the partitioning of the total energy and the force constant of H–F bond. The electron population on the oxygen atom and other atoms participating in the hydrogen bond formation, the charge transfer, ionization potentials and dipole moment enhancements were also calculated and discussed in terms of the measure of hydrogen bond strength.

One of the unique physico-chemical properties of hydrogen fluoride (HF) is a strong tendency to form the hydrogen bonding complexes with various organic molecules. It has been recognized experimentally that the frequency shift of H–F stretching mode due to hydrogen bond formation, $\Delta\nu_{HF}$, and the hydrogen bond energy, ΔH, are unusually larger than the corresponding quantities for any other hydrogen bonding systems.[1–4] On the other hand, HF has a simple geometrical structure and its electronic structure is also relatively simple. To date, many molecular orbital calculations for HF hydrogen bonding systems have been carried out by both non-empirical and semi-empirical methods.[5,6] The results of these calculations give theoretical insight into the nature of hydrogen bonding interactions of HF. However, reliable experimental evidence is often missing and no attempt has been made to compare the well-established experimental data with the calculated results for a series of hydrogen bond complexes consisting of a fixed proton donor (HF) and various proton acceptors.

In the present study, a series of organic compounds which have a carbonyl group were chosen as proton acceptor and the nature of their HF complexes was examined. Reasons for our choice of acceptors are: since the carbonyl group is found in organic molecules such as ketones, aldehydes and amides, their proton accepting ability is distributed over a wide range, making it possible for us to deal with molecules having largely differing pK_a values; the geometry of carbonyl compounds is usually simple and well-defined. The following carbonyl compounds were chosen: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl ethyl ketone, methyl propyl-ketone and *N*,*N*′-dimethylformamide (DMF). CNDO/2 calculations were carried out on the hydrogen bonded structure of HF. Optimized geometry and the corresponding hydrogen bond energy were obtained. The values of $\Delta\nu_{HF}$ were also determined for the same acceptors in dilute carbon tetrachloride solution by the method described previously.[4]

Experimental

The experimental procedures and apparatus used to obtain infrared frequency shift were the same as those reported previously.[3,4] The solubility of aldehydes in CCl_4 was so small that determination of equilibrium constant of complex formation was impossible. Only the $\Delta\nu_{HF}$ could be determined (Table 1).

Method of Calculation

The CNDO/2 calculations were carried out by means of the original parameterization of Pople, Segel and Santry.[7,8] Throughout the calculations, the standard geometries were used and kept constant for all the proton acceptor monomers, and the geometry of proton donor (HF) was fully optimized with respect to the total energy. Figure 1 shows the specifications of geometry for hydrogen bonding complexes.

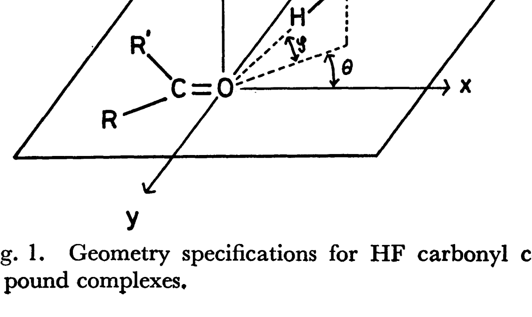

Fig. 1. Geometry specifications for HF carbonyl compound complexes.

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TABLE 1. CALCULATED OPTIMUM GEOMETRIES AND ENERGIES, AND EXPERIMENTAL INFRARED FREQUENCY SHIFT FOR HF–CARBONYL COMPOUND COMPLEXES

Acceptor	Formal-dehyde	Acetal-dehyde	Propioal-dehyde	Butyral-dehyde	Acetone	Methyl ethyl ketone	Methyl propyl ketone	*N*,*N*-Di-methyl-formamide	HF (mono-mer)
Calculated Optimum Geometries									
R(F–O) (Å)	2.434	2.416	2.416	2.416	2.403	2.402	2.403	2.392	
R(H–F) (Å)	1.021	1.024	1.024	1.024	1.027	1.027	1.027	1.030	1.000
ΔR(H–F) (Å)	0.021	0.024	0.024	0.024	0.027	0.027	0.027	0.030	0
	57°	57°	57°	57°	60°	59°	59°	60°	
Calculated Optimum Energies									
ΔE (kcal/mol)	−14.48	−16.53	−16.58	−16.61	−18.44	−18.43	−18.46	−20.73	
ΔE_{corr} (kcal/mol)	−5.4	−6.1	−6.1	−6.2	−6.8	−6.8	−6.8	−7.7	
					(−6.9)[a]			(−7.6)[a]	
E_{HF} (eV)	−19.13	−18.95	−18.95	−18.94	−18.77	−18.77	−18.78	−18.62	−20.42
ΔE_{HF} (eV)	1.30	1.48	1.48	1.48	1.65	1.65	1.65	1.80	0
E^{R}_{HF} (eV)	−18.79	−18.57	−18.56	−18.56	−18.35	−18.35	−18.35	−18.15	−20.33
ΔE^{R}_{HF} (eV)	1.54	1.76	1.77	1.77	1.98	1.98	1.98	2.18	
K(H–F) (mdyn/Å)	17.20	16.90	16.70	16.76	16.42	16.37	16.34	16.17	19.12[b]
Experimental Data									
ν_{HF} (cm^{-1})	3468	3410	3399	3404	3298	3320	3302	3151	3961[c]
$\Delta\nu_{HF}$ (cm^{-1})	493	551	562	557	663	640	658	810	

a) Ref. 4. b) J. A. Pople and D. L. Beveridge, in "Approximate Molecular Orbital Theory," McGraw-Hill Book Company, New York (1970). c) H. Hyman and J.J. Katz, in "Non-Aqueous Solvent System," ed. by T. C. Waddington, Academic Press, New York, N. Y. (1965), Chap. 2.

The optimum geometries and corresponding total energies were obtained by the following procedure.

(1) The HF molecule is first placed on the x-axis in xy-plane. As shown in Fig. 1, the xy-plane is one of the planes of symmetry for the acceptor molecule and the x-axis is the extension line of C=O bond of the acceptor molecule. The distance between fluorine and oxygen atoms, R(F–O), was optimized with respect to the total energy.

(2) On the xy-plane, angular orientation of the HF molecule with respect to C=O bond was optimized by rotating the HF molecule around the origin toward the smaller alkyl group of acceptor molecule by an angle θ.

(3) Keeping R(F–O) and θ constant, the atomic distance R(H–F) is optimized.

(4) Finally R(F–O) is again optimized by keeping R(H–F) and θ constant.

The above procedures seem to be sufficient for obtaining optimum geometries, since the values obtained remain unchanged even when both R(H–F) and θ were again optimized in the same manner. The following comment is given as regards the calculated optimum geometry and energy for each HF complex. The angle ϕ (Fig. 1) was assumed to be zero. For HF–formaldehyde complex, a CNDO/2 calculation has been reported by Schuster.[9] Both θ and ϕ were optimized in his calculation. However, as pointed out by Morokuma[10] and by Kollman and Allen,[5] the angular dependence of hydrogen bond energy was estimated to be very small in CNDO/2 and other empirical calculations, which is in contrast with the results of more refined *ab initio* calculations for the same complex. Optimization with respect to ϕ in the CNDO/2 calculations may not be justified. The structure of hydrogen bonding complex can well be described by means of a general hybridization model.[11,12] Since there should be a trigonal hybrid orbital on the oxygen atom of carbonyl group in the molecular plane, the assumption that $\phi=0$ may be sufficiently reasonable.

According to Schuster's calculation, the hydrogen bond energy, ΔE, for HF–formaldehyde complex is insensitive to ϕ. Our calculated ΔE value was −14.48 kcal/mol for HF–formaldehyde complex. This is almost comparable with those of Schuster[9] for the case that $\phi=0$, a minor discrepancy being due to the difference in the geometry used for formaldehyde monomer.

Results and Discussion

Geometry of HF Hydrogen Bonding Complexes. The optimum geometries calculated for the complexes between HF and a series of carbonyl compounds are summarized in Table 1. The optimum values of θ are 57—60° for all the complexes studied. This is consistent with the general hybridization model for the hydrogen bonds. Since there is a trigonal hybridization on the

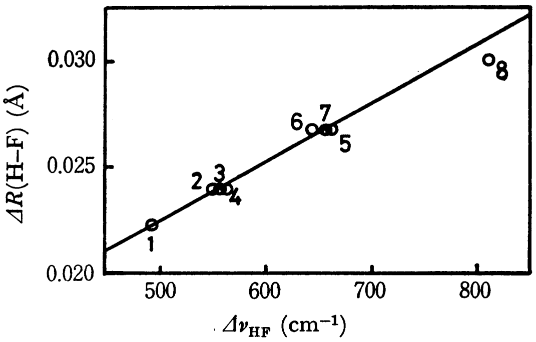

Fig. 2. Plots of ΔR(H–F) *vs.* $\Delta\nu_{HF}$; 1, formaldehyde; 2, acetaldehyde; 3, propionaldehyde; 4, butyraldehyde; 5, acetone; 6, methyl ethyl ketone; 7, methyl propyl ketone; 8, *N*,*N*-dimethylformamide.

oxygen atom of the carbonyl group, the values of θ seem to meet our expectation. It is interesting to examine the possible correlation between the change in atomic distances accompanied by hydrogen bond formation and the infrared frequency shift. As shown in Fig. 2, the change in H–F distance, ΔR(H–F), was found to increase linearly with $\Delta\nu_{\mathrm{HF}}$.

Hydrogen Bonding Energy and the Badger-Bauer Relationship. The hydrogen bonding energy ΔE we obtained are given in Table 1. The partitioning of total molecular energy was also carried out, the results and the force constants of H–F bond also being summarized in Table 1.

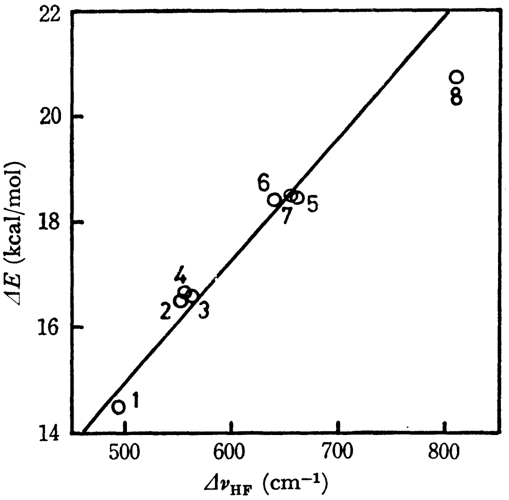

Fig. 3. Plots of ΔE *vs.* $\Delta\nu_{\mathrm{HF}}$. The number of points is the same as that in Fig. 2.

Badger-Bauer Relationship: A linear correlation, called the Badger-Bauer relationship, is known to exist between the hydrogen bond energy and the frequency shift.[13–16] A linear correlation could also be recognized between the calculated hydrogen bond energy ΔE and experimental frequency shift, $\Delta\nu_{\mathrm{HF}}$, except for the case of HF–DMF complex (Fig. 3). The results indicate that relative values of ΔE can be reasonably estimated from the present calculations for HF–aldehyde and HF–ketone complexes. The deviation for HF–DMF complex will not be due to the fact that the relative value for this complex is unjustifiable.

This will be confirmed from the following discussion. The ΔE values for HF–acetone and HF–DMF complexes were calculated to be -18.44 and -20.73 kcal/mol, respectively (Table 1), while the enthalpy of complex formation values, ΔH, for the above two in carbon tetrachloride solution have been estimated to be -6.9 and -7.6 kcal/mol, respectively, from infrared spectroscopic measurement.[4] However, the ratio, $\Delta E/\Delta H$, for HF–acetone complex agrees fairly well with that for HF–DMF complex within experimental error.[17] This indicates that the relative value of ΔE for HF–DMF complex is also as reasonable as those for other complexes. The discrepancy found for HF–DMF complex may be due to the fact that the nature of the hydrogen bond differs from the other since DMF monomer has a conjugated system and its highest occupied orbital is not σ- but π-orbital. The anomaly for HF–DMF complex was observed in all the correlations tested.

It is recognized that semi-empirical calculations such as CNDO/2 overestimate the hydrogen bond energy.[5] The discrepancy between ΔE and ΔH is seriously large, even when the difference between experimental environment and the assumption in theoretical calculation is taken into considerations. However, since the calculated ΔE values are relatively valid, we may define a corrected ΔE value which is normalized so as to satisfy the experimental ΔH values both for HF–acetone and HF–DMF complexes. These normalized energy values (denoted by ΔE_{corr}) are also given in Table 1.

Semi-empirical methods such as CNDO/2 calculation involve optional parameters and the problem of which parameterization is the most suitable for representing such delicate interactions as the hydrogen bond remains.[18] However, the present calculations for the hydrogen bond complexes between a fixed proton donor and a series of proton acceptors with a fixed functional group should provide fairly reasonable (relative) values of hydrogen bond energy probably because of the compensation of various factors concerning parameterization. It is concluded that the present treatment is useful for estimating the hydrogen bond energy which cannot be obtained due to experimental difficulty (*e.g.*, in the case of HF–aldehyde complexes).

Partitioning of Total Energy: The total molecular energy E may be decomposed into one and two center terms;[7]

$$E = \sum_{\mathrm{A}} E_{\mathrm{A}} + \sum_{\mathrm{A}}\sum_{\mathrm{B}} E_{\mathrm{AB}} \tag{1}$$

The two center term, E_{AB}, can be interpreted as a measure of the strength of A–B bond and written as[19]

$$E_{\mathrm{AB}} = E^{\mathrm{R}}_{\mathrm{AB}} + E^{\mathrm{V}}_{\mathrm{AB}} + E^{\mathrm{J}}_{\mathrm{AB}} + E^{\mathrm{K}}_{\mathrm{AB}} + E^{\mathrm{N}}_{\mathrm{AB}}. \tag{2}$$

The leading term of the RHS of Eq. 2, $E^{\mathrm{R}}_{\mathrm{AB}}$, represents the contribution of resonance integral to E_{AB}[20] and is given by[19]

$$E^{\mathrm{R}}_{\mathrm{AB}} = 2\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}} P_{\mu\nu}\beta_{\mu\nu}S_{\mu\nu}. \tag{3}$$

An analysis of $E^{\mathrm{R}}_{\mathrm{AB}}$ is equivalent to a population analysis in which the individual terms are weighted with an energy factor $\beta_{\mu\nu}$. The amounts of change in E_{AB} and $E^{\mathrm{R}}_{\mathrm{AB}}$ for H–F bond,

$$\Delta E_{\mathrm{HF}} = E_{\mathrm{HF}}(\text{monomer}) - E_{\mathrm{HF}}(\text{complex}) \tag{4}$$

$$\Delta E^{\mathrm{R}}_{\mathrm{HF}} = E^{\mathrm{R}}_{\mathrm{HF}}(\text{monomer}) - E^{\mathrm{R}}_{\mathrm{HF}}(\text{complex}) \tag{5}$$

were expected to be more directly correlated with $\Delta\nu_{\mathrm{HF}}$. As shown in Fig. 4, both ΔE_{HF} and $\Delta E^{\mathrm{R}}_{\mathrm{HF}}$ are in good correlation with $\Delta\nu_{\mathrm{HF}}$ values.

Force Constant of H–F Bonds: The force constant K(H–F) of H–F bond can be approximately evaluated from the second derivative of the total energy with respect to H–F distance at an equilibrium geometry (Table 1). It decreases with an increase in the strength of hydrogen bond. A linear correlation holds with ν_{HF} (Fig. 5).

Electron Populations and Charge Transfer. The electron populations on the atoms participating in the formation of hydrogen bond or the charge transfer due to the hydrogen bond formation may be utilized as a measure of hydrogen bond strength. The electron

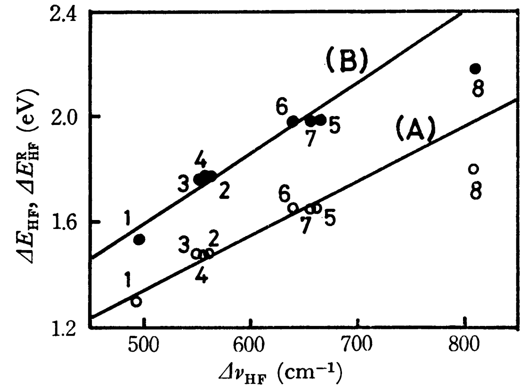

Fig. 4. (A) Plots of ΔE_{HF} vs. $\Delta\nu_{HF}$; (B) plots of ΔE^R_{HF} vs. $\Delta\nu_{HF}$. The number of points is the same as that in Fig. 2.

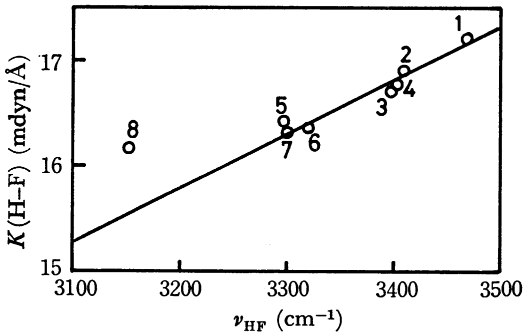

Fig. 5. Plots of K(H–F) vs. ν_{HF}. The number of points is the same as that in Fig. 2.

populations on F, H, O and C atoms for monomers and complexes and the amount of charge transfer from the proton acceptors to the proton donor, ΔQ, are summarized (in Table 2).

Correlations with Hydrogen Bond Energy: Del Bene[11,21] pointed out from the results of *ab initio* calculations that the net electron population on the proton accepting sites (atoms) is a good measure of the hydrogen bond strength. In accordance with this suggestion, the electron population on the oxygen atoms of proton acceptor and ΔQ are plotted against ΔE_{corr}. Good linear correlations have been obtained except for the HF–DMF complex (Fig. 6).

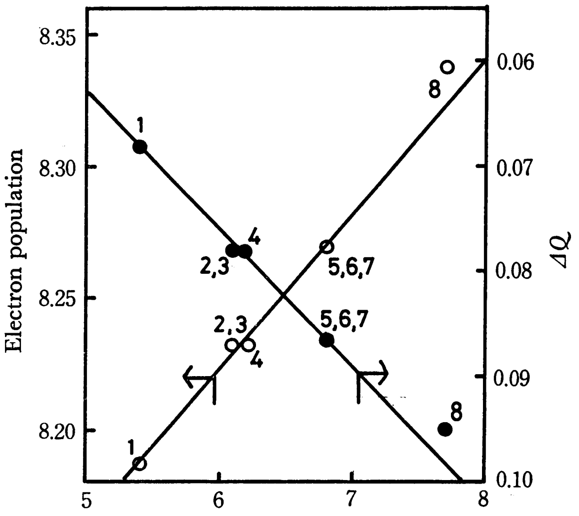

Fig. 6. Plots of electron population on O atom of proton acceptor monomer and the amount of charge transfer by hydrogen bond against ΔE_{corr}. The number of points is the same as that in Fig. 2.

Electron Population on Oxygen Atom: Although the above correlations are successful, more detailed analysis on the electron population on the oxygen atom will give further insight into the nature of the present hydrogen bond systems. First, let us examine the changes in the electron populations on each atom participating F–H···O=C hydrogen bond. The following changes were observed on the electron populations when the hydrogen bonding complex was formed (Table 2): For all the complexes studied, there were an increase in the electron population on the fluorine atom and a decrease in the electron population both on the hydrogen and carbon atoms. On the other hand, a decrease in the electron population on the oxygen atom was observed only for the cases of HF–DMF and HF–formaldehyde complexes. This led us to calculate the contributions of σ- and π-electrons to the total electron population. Table 3 shows, as an example, the amounts of change in the electron populations on the O and C atoms for HF–formaldehyde and HF–acetaldehyde complexes. It is seen that there is a decrease in the σ-electron population and an increase in the π-electron population for each complex, and that the sign of the change in total electron population depends on the relative magnitude of both contributions.

It is thus concluded that, for all the complexes other than HF–formaldehyde and HF–DMF, there are some

TABLE 2. ELECTRON POPULATIONS ON F, H, O, AND C ATOMS AND THE AMOUNTS OF CHARGE TRANSFER ΔQ FOR HF HYDROGEN BONDING COMPLEXES

Acceptor	F	H	O (monomer)	O (complex)	C (monomer)	C (complex)	ΔQ
HF (monomer)	9.2262	0.7738					
Formaldehyde	9.3226	0.7456	8.1868	8.1848	5.7905	5.7590	0.0682
Acetaldehyde	9.3377	0.7400	8.2316	8.2333	5.7605	5.7257	0.0777
Propionaldehyde	9.3381	0.7398	8.2314	8.2340	5.7649	5.7305	0.0779
Butyraldehyde	9.3383	0.7397	8.2320	8.2349	5.7684	5.7341	0.0780
Acetone	9.3518	0.7348	8.2695	8.2751	5.7417	5.7066	0.0866
Methyl ethyl ketone	9.3520	0.7347	8.2690	8.2754	5.7468	5.7121	0.0867
Methyl propyl ketone	9.3518	0.7347	8.2695	8.2761	5.7504	5.7158	0.0865
N,*N*-Dimethylformamide	9.3647	0.7302	8.3389	8.3379	5.6535	5.6252	0.0949

Table 3. Electron population changes on carbon and oxygen atoms of carbonyl group for HF–formaldehyde and HF–acetaldehyde complexes

Atom	Formaldehyde		Acetaldehyde	
	O	C	O	C
$2P_\pi$	+0.0512	−0.0512	+0.0635	−0.0554
$2S_\sigma$	−0.0209	+0.0055	−0.0232	+0.0059
$2P_\sigma$	−0.0323	+0.0142	−0.0386	+0.0146
σ-Total	−0.0532	+0.0197	−0.0618	+0.0206
Total	−0.0020	−0.0315	+0.0017	−0.0348

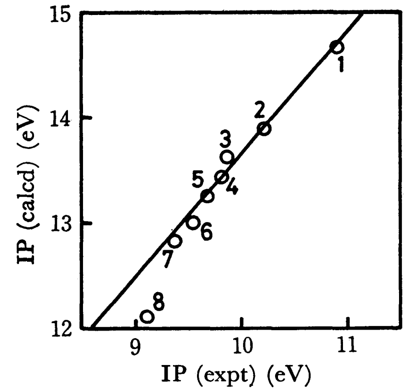

Fig. 7. Plots of calculated ionization potential *vs.* experimental ionization potential for all acceptor monomers. The number of points is the same as that in Fig. 2.

more transfers of π-electrons from methyl-, ethyl-, or propyl group into carbonyl group by the hyperconjugation effect which is accompanied by hydrogen bond formation. The increase in the electron population on the oxygen atom for these complexes should be due to the fact that the increase in the π-electron population by this effect exceeds the decrease in the σ-electron population. The lack of hyperconjugation effect in the HF–formaldehyde and HF–DMF complexes might be responsible for the decrease in the total electron population on the oxygen atom.

Ionization Potential and Dipole Moment Enhancement. The proton accepting abilities of the carbonyl group have been discussed in detail by Cook.[22] It is of interest to calculate the energy, $E_{C=O}$, of the carbonyl group for monomer and complex and the first ionization potential (IP) and to examine possible correlations of the frequency of the C=O stretching vibration, $\nu_{C=O}$, with them. The results of calculation for $E_{C=O}$ and IP are given in Table 4. We see that the calculated $E_{C=O}$ values are parallel with the $\nu_{C=O}$ values given by Cook.[22] A similar parallelism can be confirmed for any pairs from ΔE_{corr}, $\Delta\nu_{HF}$, and $\Delta E_{C=O}$ (the change in the amount of $E_{C=O}$ by the hydrogen bond formation).

IP as a Measure of Hydrogen Bond Strength: The calculated IP values for proton acceptor monomers are compared with those obtained experimentally in Fig. 7.[22,23] A satisfactory correspondence holds between them, though the calculated values are always somewhat larger than the observed ones (DMF is an exception). Cook has pointed out that there is a linear relationship between IP and $\nu_{C=O}$ and the latter can be used as a measure of the hydrogen bond strength. The $\nu_{C=O}$ will exhibit a shift due to the hydrogen bond formation and can also be used as a measure of hydrogen bond strength, though the shift, $\Delta\nu_{C=O}$, could not be detected for HF-complexes.[24] Careful examination of the IP values (Table 4) leads to the conclusion that they cannot always be used as a measure of hydrogen bond strength. The values for $\Delta\nu_{HF}$, $\nu_{C=O}$, $E_{C=O}$, and ΔE_{corr} are almost constant for three aldehydes except formaldehyde and for three ketones, whereas the values of both observed and calculated IP decrease continuously from acetaldehyde to methyl propyl ketone.

The failure of correlation may be interpreted as follows. The first ionization potential of proton acceptor monomer depends on the properties of the highest occupied orbital. This is considered to be a measure of the charge transfer and/or of the proton accepting ability. However, since various kinds of interactions other than the charge transfer (*e.g.*, electrostatic, dispersion, and repulsive) may contribute to the hydrogen bond energy, one cannot always discuss the strength of hydrogen bond in terms of the facility of charge transfer and accordingly the first ionization potential. It is important to evaluate how much the ionization potential of proton acceptor monomer reflects the properties of electrons available for hydrogen bonding.[21,11]

Anomaly in HF–DMF Complex: For all the acceptor monomers except DMF, the highest occupied orbitals are σ-orbital. It consists almost exclusively of the lone pair orbital. In contrast, the highest occupied orbital of DMF monomer is π-orbital. Since the highest

Table 4. Energy of carbonyl group, ionization potential and dipole moment enhancement for HF hydrogen bond complexes

Acceptor	$\nu_{C=O}$ (cm^{-1}) (Monomer)	$E_{C=O}$ (eV)		$\Delta E_{C=O}$ (eV)	IP (eV)		$\Delta\mu$(D)
		(Monomer)	(Complex)		(Expt)	(Calcd)	
Formaldehyde		−45.54	−45.13	0.39	10.90[b]	14.68	1.05
Acetaldehyde	1733[a]	−44.26	−43.78	0.48	10.21[a]	13.90	1.34
Propionaldehyde	1738[a]	−44.29	−43.81	0.48	9.86[a]	13.64	1.36
Butyraldehyde	1729[a]	−44.29	−43.81	0.48	9.81[a]	13.45	1.39
Acetone	1717[a]	−43.11	−42.53	0.58	9.69[a]	13.25	1.41
Methyl ethyl ketone	1722[a]	−43.15	−42.56	0.59	9.54[a]	13.01	1.43
Methyl propyl ketone	1717[a]	−43.14	−42.55	0.59	9.39[a]	12.84	1.46
N,*N*-Dimethylformamide	1684[a]	−43.37	−42.46	0.91	9.11[a]	12.12	1.73

a) Ref. 22. b) Ref. 23.

occupied orbital would take the main part in hydrogen bond, calculations on HF–DMF complex were performed for two models, a π-hydrogen bond model in which the HF molecule approaches perpendicular to the molecular plane of acceptor molecule, and a σ-hydrogen bond model which is the same as that for other complexes. The π-hydrogen bond model was found to have less hydrogen bond energy than the σ-hydrogen bond model. Similar results have been recognized in the *ab initio* calculations on HF–HCN and HF–formaldehyde hydrogen bonds.[11,25] This was ascribed to the fact that the energy of electrons in π-orbital is considered to be more favorable for the charge transfer in hydrogen bond than that in σ-orbital. However, the σ-orbital has a higher electron density on the site of hydrogen bonding and accordingly has a higher probability of interaction with proton donor than the π-orbital. Thus the electrons in the σ-orbital seem to give greater contribution to hydrogen bonding. This may explain the anomaly of HF–DMF complex.

Dipole Moment Enhancement: It is well-known for typical hydrogen bonding that the dipole moment of hydrogen bond complex becomes larger than the sum of the dipole moments of its components.[26] The calculated values for the increase in dipole moment $\Delta\mu$ are given in Table 4. No correlations were recognized between $\Delta\mu$ and ΔE_{corr}. For the HF–aldehyde complexes, with HF–formaldehyde as an exception, the $\Delta\mu$ values increase in the order, acetaldehyde$<$propionaldehyde$<$butyraldehyde, while the ΔE_{corr} values remain almost constant. The $\Delta\mu$ can be divided into two contributions, one due to induced dipole moment, $\Delta\mu_{\mathrm{ind}}$, and the other to charge transfer, $\Delta\mu_{\mathrm{ct}}$.[26] Since the $\Delta\mu_{\mathrm{ct}}$ for these HF–aldehyde complexes would be almost the same, the behavior of overall $\Delta\mu$ can be interpreted as the increase of contributions of $\Delta\mu_{\mathrm{ind}}$ in the order given above.

In conclusion, the present CNDO/2 calculations could give, though semi-quantitative, a fairly good description of the properties of HF hydrogen bond complexes. Correlations with experimental $\Delta\nu_{\mathrm{HF}}$ would serve to overcome the lack of energetic information due to experimental difficulties. Success and failure of correlations with the quantities used as a measure of hydrogen bond strength may furnish further insight to the understanding of HF hydrogen bonds.

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References

1) D. N. Schepkin, *Opt. Spectrosk.*, **19**, 709 (1965).

2) D. N. Schepkin, *Teor. Eksp. Khim.*, **2**, 276 (1966).

3) H. Touhara, H. Shimoda, K. Nakanishi, and N. Watanabe, *J. Phys. Chem.*, **75**, 2222 (1971).

4) M. Tsuda, H. Touhara, K. Nakanishi, and N. Watanabe, *J. Phys. Chem.*, **80**, 362 (1976).

5) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 282 (1972) and earlier papers cited therein.

6) More recent works since that given in Ref. 5 are too numerous to list in full. The following is by no means complete. (a) A. Johansson, P. A. Kollman, and S. Rothenberg, *Theor. Chim. Acta*, **29**, 167 (1973); (b) P. A. Kollman, A. Johansson, and S. Rothenberg, *Chem. Phys. Let.*, **24**, 199 (1974); (c) L. A. Curtiss and J. A. Pople, *J. Mol. Spectrosc.*, **48**, 413 (1973); (d) G. H. F. Diercksen, W. von Niessen, and W. P. Kraener, *Theor. Chim. Acta*, **31**, 205 (1973); (e) W. von Niessen, *Theor. Chim. Acta*, **31**, 297 (1973): (f) see also Refs. 11 and 25.

7) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

8) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

9) P. Schuster, *Theor. Chim. Acta*, **19**, 212 (1970).

10) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).

11) J. E. Del Bene and F. T. Marchese, *J. Chem. Phys.*, **58**, 926 (1973).

12) J. E. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973).

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

14) R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

15) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, Calif. (1960).

16) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding," Van Nostrand Reinhold, New York, N. Y. (1971).

17) The experimental values for ΔH may be somewhat underestimated because of specific and non-specific solvations of carbon tetrachloride for HF and acceptor molecules, but the effect on the ratio is negligible.

18) It is not clear, however, whether any improvement on the parameterization can remove the defect of semi-empirical methods in their application to hydrogen bonds.

19) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

20) For other terms, see Ref. 19.

21) J. E. Del Bene, *J. Chem. Phys.*, **57**, 1899 (1972).

22) D. Cook, *J. Am. Chem. Soc.*, **80**, 49 (1958).

23) F. I. Vilesov, *Dokl. Akad. Nauk SSSR*, **132**, 1332 (1960).

24) In the present infrared measurement, the concentration of proton acceptor was kept much greater than that of HF in order to carry out measurements under the experimental conditions by which only 1 : 1 complex exists. Hence we could not determine accurately the shift of $\nu_{\mathrm{C=O}}$ due to hydrogen bond formation, since the excess proton acceptor monomer band interfered with it.

25) J. E. Del Bene, *Chem. Phys. Lett.*, **24**, 203 (1974).

26) H. Ratajczak and W. J. Orville-Thomas, *J. Chem. Phys.*, **58**, 911 (1973).