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An Intermolecular Perturbation Approach to Hydrogen Bondings in Systems in the Ground and Excited Electronic States

Shigeru Nagase and Takayuki Fueno

Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka, Japan

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The intermolecular interaction energy for binary systems in the ground and excited electronic states was partitioned into the Coulomb, exchange-repulsion, induction, dispersion and charge-transfer interaction terms by the perturbation expansion method. The various interaction terms were evaluated for the hydrogen bondings in $(HF)_2$, $(H_2O)_2$, $(CH_3OH)_2$, $(RCOOH)_2$, and $HF \cdot H_2O$ in various geometrical configurations. It has been found that the Coulombic interaction plays a dominant role in the stability of these hydrogen bonded systems. The method was further applied to the $HCOOH \cdot H_2O$ codimer in both the ground and excited singlet electronic states. The results were in accord with the well-known water solvent effects on the shifts of absorption spectral bands.

Key words: Intermolecular perturbation – Hydrogen bond – Energy partitioning – Spectral shifts

1. Introduction

Efforts to theoretically elucidate the nature of the intermediate-range intermolecular interactions involved in the hydrogen bonding still appear to be rewarding, particularly because the specific roles and relative importances of various types of interaction energies to be involved there have not yet been fully understood. Recently, Duijneveldt *et al.* [1–3] have attempted to evaluate some of these contributing factors, using the intermediate-overlap perturbation formalism developed by Murrell *et al.* [4, 5]. Admittedly, however, their treatments are somewhat limited in scope because they have oversimplified the hydrogen bonded systems into a model in which only three centers with four electrons are considered. Still less is known of the hydrogen bonding of excited species, even though some CNDO/2 [6, 7] and *ab initio* [8, 9] calculations are available.

In this paper, we will apply the intermolecular perturbation method to hydrogen-bonded systems in the electronically excited states as well as in the ground state. Our primary purpose is to clarify the factors which should govern the geometrical orientations of hydrogen-bonded dimers or codimers. To this end, we will partition the total hydrogen bond energy into the Coulomb, exchange-repulsion, induction, dispersion and charge-transfer interaction terms, and will assess the relative importances of these terms to given binary systems in various spatial orientations. Variations in the magnitudes of these energies upon electronic excitation and the accompanying changes in spatial orientation of the systems will also be treated and discussed.

2. Molecular Orbital Formalism

2.1. Ground States

To begin with, let us briefly consider the interaction energy between two ground-state molecules whose wave functions are $\Phi_0(\mathrm{A})$ and $\Phi_0(\mathrm{B})$, respectively. The wave functions can be represented by the Slater determinants built up of orthonormal molecular orbitals (MO):

$$\Phi_0(\mathrm{A}) = |\cdots i\bar{i} \cdots| , \tag{1}$$

and

$$\Phi_0(\mathrm{B}) = |\cdots j\bar{j} \cdots| . \tag{2}$$

When the two molecules approach each other, the wave function of the entire interaction system Ψ can be considered to be represented as the superposition of the ground (AB), locally excited (A*B and AB*), doubly excited (A*B*) and charge-transfer ($\mathrm{A}^+\mathrm{B}^-$ and $\mathrm{A}^-\mathrm{B}^+$) configurations, each of which is antisymmetrized with respect to electron exchange between the components. Other highly-transferred and highly-excited configurations can be neglected, provided the interaction is not too strong.

Derivations of the total interaction energy has already been worked out by Murrell *et al.* [4, 5], and its intramolecular zero-differential-overlap (ZDO) version given in our previous paper [10]. Suffice it to mention here that the total interaction energy is expressible as a sum of the five interaction terms, i.e., the Coulomb (E_Q), exchange-repulsion (E_K), induction (E_I), dispersion (E_D) and charge-transfer (E_{CT}) energies, which are so termed according to the characteristics of the configurations from which they originate. To the approximation up to the second order of both the interaction potential (U) and overlap (S), they are given by the general formulas as follows:

$$E_Q = 2\sum_i^{\mathrm{A}} \langle \varrho_{ii} | V(\mathrm{B}) \rangle + 2\sum_j^{\mathrm{B}} \langle \varrho_{jj} | V(\mathrm{A}) \rangle - 4\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} \langle \varrho_{ii} | \varrho_{jj} \rangle + \sum_\mu^{\mathrm{A}}\sum_\nu^{\mathrm{B}} Z_\mu Z_\nu / R_{\mu\nu} , \tag{3}$$

$$E_K = -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} [\langle \varrho_{ij} | \varrho_{ji} \rangle + S_{ij}\{\langle \varrho_{ij} | V(\mathrm{B}) \rangle + \langle \varrho_{ji} | V(\mathrm{A}) \rangle\}] , \tag{4}$$

$$E_I = 2\sum_i^{\mathrm{A}}\sum_k^{\mathrm{A}} \langle \varrho_{ik} | V(\mathrm{B}) \rangle^2 / (E_0 - E_{i\to k}) + 2\sum_j^{\mathrm{B}}\sum_l^{\mathrm{B}} \langle \varrho_{jl} | V(\mathrm{A}) \rangle^2 / (E_0 - E_{j\to l}) , \tag{5}$$

$$E_D = 4\sum_i^{\mathrm{A}}\sum_k^{\mathrm{A}}\sum_j^{\mathrm{B}}\sum_l^{\mathrm{B}} \langle \varrho_{ik} | \varrho_{jl} \rangle^2 / (E_0 - E_{i\to k, j\to l}) , \tag{6}$$

$$E_{CT} = 2\sum_i^{\mathrm{A}}\sum_l^{\mathrm{B}} \langle \varrho_{il} | V(\mathrm{B}) \rangle^2 / (E_0 - E_{i\to l}) + 2\sum_j^{\mathrm{B}}\sum_k^{\mathrm{A}} \langle \varrho_{jk} | V(\mathrm{A}) \rangle^2 / (E_0 - E_{j\to k}) , \tag{7}$$

where the interaction density (ϱ_{mn}), as we call it tentatively, and the interaction potential fields ($V(\mathrm{A})$ and $V(\mathrm{B})$) of the component molecules A and B are defined as

$$\varrho_{mn} = \begin{cases} mm\,, & \text{when} \quad m = n \\ mn - S_{mn} mm\,, & \text{when} \quad m \neq n\,, \end{cases} \tag{8}$$

$$V(\mathrm{A}) = 2 \sum_{i}^{\mathrm{A}} \int i(2) i(2) (1/r_{12})\, d\tau_2 - \sum_{\mu}^{\mathrm{A}} Z_\mu / r_{1\mu}, \tag{9}$$

and

$$V(\mathrm{B}) = 2 \sum_{j}^{\mathrm{B}} \int j(2) j(2) (1/r_{12})\, d\tau_2 - \sum_{\nu}^{\mathrm{B}} Z_\nu / r_{1\nu}\,. \tag{10}$$

In Eqs. (3) through (7) we have used the following notations. The indices i (and j) and k (and l) specify the occupied and unoccupied MO's of molecule A (and B), respectively. S_{mn} is the overlap integral between MO's m and n; Z_μ and Z_ν the nuclear charge of the atoms μ and ν, respectively; and $R_{\mu\nu}$ the distance between atoms μ and ν. E_0 is the electronic energy of the ground state configuration while $E_{i\to k}$ etc. are the electronic energies of the configurations resulting from the electron transition indicated. The integrals involved in the above equations are denoted by

$$\langle \varrho_{mn} | V \rangle = \int \varrho_{mn}(1)\, V(1)\, d\tau_1\,, \tag{11}$$

$$\langle \varrho_{mn} | \varrho_{nm} \rangle = \int \varrho_{mn}(1)\, (1/r_{12})\, \varrho_{nm}(2)\, d\tau_1\, d\tau_2\,. \tag{12}$$

2.2. *Excited States*

Next, let us consider the case in which molecule B has a closed-shell structure, but molecule A has an open-shell structure due to the electronic excitation from the $a-th$ occupied MO to the $b-th$ unoccupied MO. The wave function of molecule A in the excited singlet state is now written as

$$\Phi_0(\mathrm{A}^*_{a\to b}) = \{ |\text{- - -} i\bar{i} \text{- -} a\bar{b} \text{- - -}| - |\text{- - -} i\bar{i} \text{- -} \bar{a}b \text{- - -}| \} / \sqrt{2}\,. \tag{13}$$

Then, the wave function (Ψ^*) of the interacting system comprising the excited singlet state molecule ($\mathrm{A}^*_{a\to b}$) and the ground state molecule (B) may be represented by a linear combination of the form:

$$\begin{aligned} \Psi^* = {} & \mathscr{A} \Phi_0(\mathrm{A}^*_{a\to b})\, \Phi_0(\mathrm{B}) \\ & + \mathscr{A} \sum_{i}^{\mathrm{A}} \sum_{k}^{\mathrm{A}} C_{i\to k} \Phi_{i\to k}(\mathrm{A}^{**}_{a\to b})\, \Phi_0(\mathrm{B}) + \mathscr{A} \sum_{j}^{\mathrm{B}} \sum_{l}^{\mathrm{B}} C_{j\to l} \Phi_0(\mathrm{A}^*_{a\to b})\, \Phi_{j\to l}(\mathrm{B}^*) \\ & + \mathscr{A} \sum_{i}^{\mathrm{A}} \sum_{k}^{\mathrm{A}} \sum_{j}^{\mathrm{B}} \sum_{l}^{\mathrm{B}} C_{i\to k, j\to l} \Phi_{i\to k}(\mathrm{A}^{**}_{a\to b})\, \Phi_{j\to l}(\mathrm{B}^*) \\ & + \mathscr{A} \sum_{i}^{\mathrm{A}} \sum_{l}^{\mathrm{B}} C_{i\to l} \Phi_i(\mathrm{A}^{*+}_{a\to b})\, \Phi_l(\mathrm{B}^-) + \mathscr{A} \sum_{j}^{\mathrm{B}} \sum_{k}^{\mathrm{A}} C_{j\to k} \Phi_k(\mathrm{A}^{*-}_{a\to b})\, \Phi_j(\mathrm{B}^+) \end{aligned} \tag{14}$$

where $\mathscr{A}$ is the antisymmetrizing operator to permit electron exchange between the molecules A and B, and where the locally excited ($\mathrm{A}^{**}_{a\to b}\mathrm{B}$ and $\mathrm{A}^*_{a\to b}\mathrm{B}^*$), doubly excited ($\mathrm{A}^{**}_{a\to b}\mathrm{B}^*$), and charge-transfer ($\mathrm{A}^{*+}_{a\to b}\mathrm{B}^-$ and $\mathrm{A}^{*-}_{a\to b}\mathrm{B}^+$) configurations are allowed to mixed with the locally excited configuration ($\mathrm{A}^*_{a\to b}\mathrm{B}$), as shown in Fig. 1. Again, other highly-transferred and highly-excited configurations can be omitted for the cases of not very strong interaction.

By using Eq. (14), the total interaction energy between the excited and ground state molecules is obtained as a sum of five interaction terms (E_Q^*, E_K^*, E_I^*, E_D^*, and E_{CT}^*) in the same way as that described above for the interactions between the ground state molecules. The derivations were somewhat tedious but straightforward. The resultant expressions for the interaction terms in the excited state are as follows:

$$E_Q^* = E_Q - \langle \varrho_{aa}|V(\mathrm{B})\rangle + \langle \varrho_{bb}|V(\mathrm{B})\rangle \,, \tag{15}$$

$$\begin{aligned} E_K^* = & -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} [\langle \varrho_{ij}|\varrho_{ji}\rangle + S_{ij}\{\langle \varrho_{ij}|V(\mathrm{B})\rangle + \langle \varrho_{ji}|V(\mathrm{A}_{a\to b}^*)\rangle] \\ & + \sum_j^{\mathrm{B}} [\langle \varrho_{aj}|\varrho_{ja}\rangle + S_{aj}\{\langle \varrho_{aj}|V(\mathrm{B})\rangle + \langle \varrho_{ja}|V(\mathrm{A}_{a\to b}^*)\rangle\}] \\ & - \sum_j^{\mathrm{B}} [\langle \varrho_{bj}|\varrho_{jb}\rangle + S_{bj}\{\langle \varrho_{bj}|V(\mathrm{B})\rangle + \langle \varrho_{jb}|V(\mathrm{A}_{a\to b}^*)\rangle\}] \,, \end{aligned} \tag{16}$$

$$\begin{aligned} E_I^* = & \sum_{i\neq a}^{\mathrm{A}} \{\langle \varrho_{ia}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{i\to b}) + \langle \varrho_{ib}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to b,i\to b}) \\ & + 2\sum_{k\neq b}^{\mathrm{A}} \langle \varrho_{ik}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to b,i\to k})\} \\ & + \sum_{k\neq b}^{\mathrm{A}} \{\langle \varrho_{bk}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{i\to k}) + \langle \varrho_{ak}|V(\mathrm{B})^2/(E_{a\to b} - E_{a\to b,a\to k})\} \\ & + 2\langle \varrho_{ab}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to b,a\to b}) + 2\langle \varrho_{ba}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_0) \\ & + \sum_j^{\mathrm{B}}\sum_l^{\mathrm{B}} \langle \varrho_{jl}|V(\mathrm{A}_{a\to b}^*)\rangle^2/(E_{a\to b} - E_{a\to b,j\to l}) \,, \end{aligned} \tag{17}$$

$$\begin{aligned} E_D^* = & \, 2\sum_j^{\mathrm{B}}\sum_l^{\mathrm{B}} \Bigg[\sum_{k\neq b}^{\mathrm{A}} \{\langle \varrho_{bk}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{a\to k,j\to l}) \\ & + \langle \varrho_{ak}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{a\to b,a\to k,j\to l})\} \\ & + \sum_{i\neq a}^{\mathrm{A}} \{\langle \varrho_{ia}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{i\to b,j\to l}) + \langle \varrho_{ib}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{a\to b,i\to b,j\to l})\} \\ & + 2\sum_{i\neq a}^{\mathrm{A}}\sum_{k\neq b}^{\mathrm{A}} \langle \varrho_{ik}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{a\to b,i\to k,j\to l}) \\ & + 2\langle \varrho_{ab}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{a\to b,a\to b,j\to l}) + 2\langle \varrho_{ba}|\varrho_{jl}\rangle^2/(E_{a\to b} - E_{j\to l}) \Bigg] \,, \end{aligned} \tag{18}$$

$$\begin{aligned} E_{CT}^* = & \sum_j^{\mathrm{B}} \{\langle \varrho_{ja}|V(\mathrm{A}_{a\to b}^*)\rangle^2/(E_{a\to b} - E_{j\to b}) + \langle \varrho_{jb}|V(\mathrm{A}_{a\to b}^*)\rangle^2/(E_{a\to b} - E_{a\to b,j\to b}) \\ & + 2\sum_{k\neq b}^{\mathrm{A}} \langle \varrho_{jk}|V(\mathrm{A}_{a\to b}^*)\rangle^2/(E_{a\to b} - E_{a\to b,j\to k})\} \\ & + \sum_l^{\mathrm{B}} \{\langle \varrho_{bl}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to l}) + \langle \varrho_{al}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to b,a\to l}) \\ & + 2\sum_{i\neq a}^{\mathrm{A}} \langle \varrho_{il}|V(\mathrm{B})\rangle^2/(E_{a\to b} - E_{a\to b,i\to l})\} \,, \end{aligned} \tag{19}$$

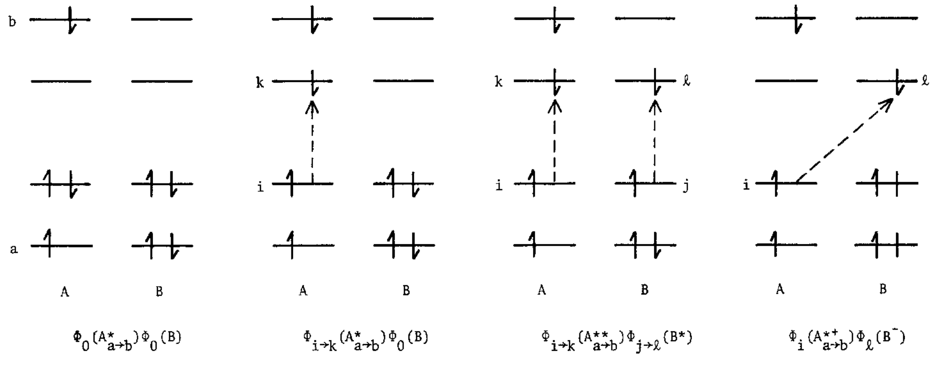


Fig. 1. Various electronic configurations which are assumed to mix as an excited molecule A^*_{a-b} interacts with a ground-state molecule B

where the interaction potential field of the excited molecule ($A^*_{a\to b}$) is defined as

$$V(A^*_{a\to b}) = V(A) - \int a(2)a(2)\,(1/r_{12})\,d\tau_2 + \int b(2)b(2)\,(1/r_{12})\,d\tau_2 . \qquad (20)$$

Here, it should be noted that the various interaction energy terms [Eqs. (15) through (19) as well as Eqs. (3) through (7)] are all expressible only as the products of the interaction densities (ϱ) and potentials (V), and hence can clearly provide conceptually useful interpretations.

3. Method of Calculation

In evaluating the various interaction energies numerically, we further expanded them into the formulas represented in terms of atomic orbitals. We adopted similar approximations as used in our previous paper [10] for the sake of computational economy. Thus, the zero-differential-overlaps were assumed within the component molecules, but intermolecular overlaps were all retained. Atomic orbital integrals such as the electron-core attraction, interelectronic repulsion, and atomic overlap integrals were evaluated by using the Slater valence-shell *s* atomic orbitals, and the multicenter atomic integrals were approximated by Mulliken's formula [11]. The energies and wave functions of the isolated molecules were calculated by the CNDO/2 method [12]. All computations were performed on a FACOM 230–60 at the Kyoto University Computation Center.

4. Results and Discussion

4.1. Hydrogen Bond Energy as a Function of the Intermolecular Distance

We here take up the $(HF)_2$ linear dimer in order to investigate the dependence of the various energy components on the F- - -F distance. The calculation results are given in Fig. 2.

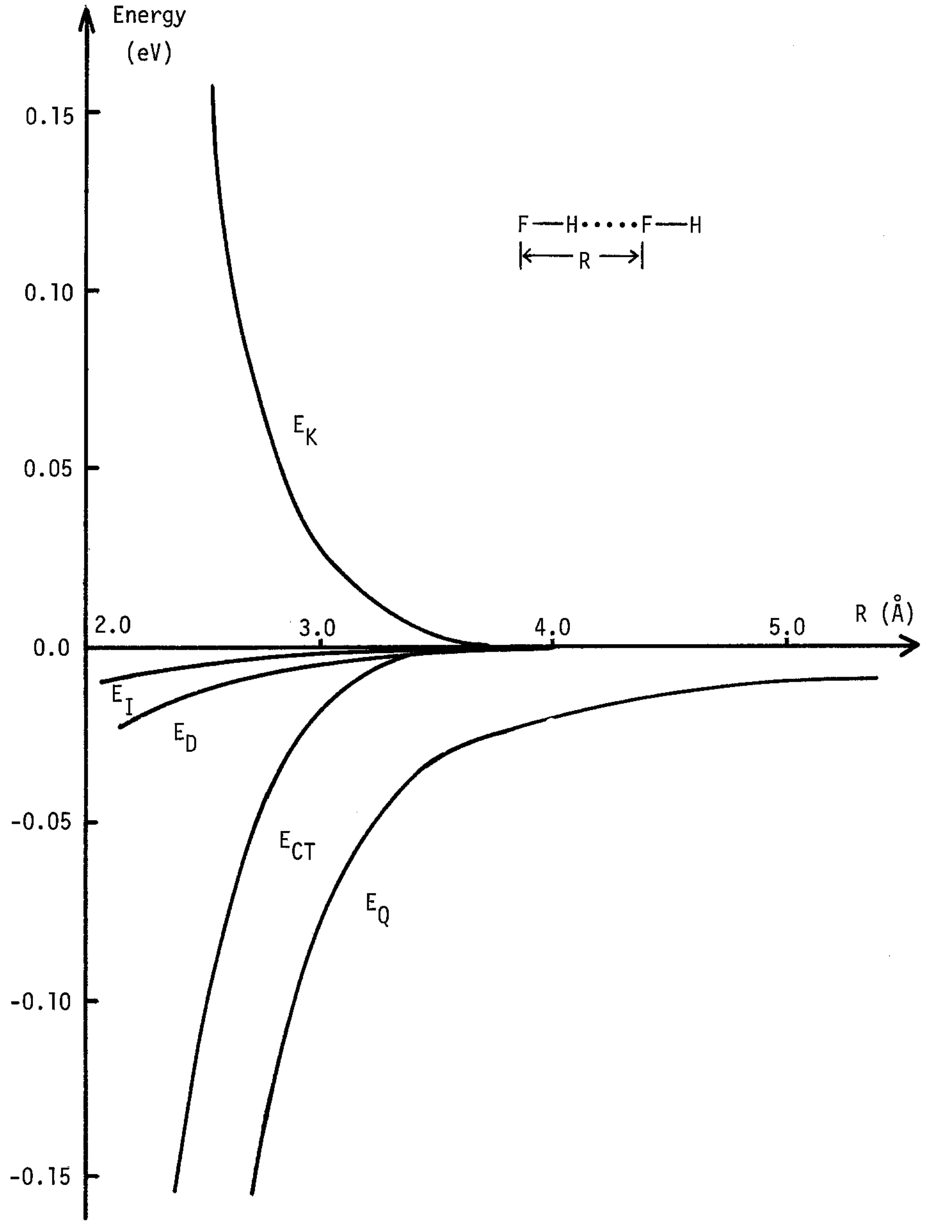


Fig. 2. Variations in various types of interaction energies in the linear HF dimer with the F - - - F distance

At large distances, the main contribution to the hydrogen bond is the electrostatic Coulomb interaction term (E_Q) and the contributions of the other interaction terms are almost negligible. As the distance decreases, the Coulomb interaction term increases dramatically because of the interpenetration of the charge clouds [1–3]. On the other hand, the exchange-repulsion (E_K) and charge-transfer (E_{CT}) interaction terms become significant at the F- - -F distance of about 3.6 Å or less, and make a considerable contribution to the hydrogen bonding at shorter distances. However, the former increases somewhat more sharply than the latter, and hence the stabilization due to the latter is overshadowed by the destabilization due to the former. This may be one of the distinctive features of hydrogen bonding. In the usual chemical reaction (or in a new-bond formation process), the contribution of the charge-transfer interaction is larger than that of the exchange-repulsion interaction and the net effects are to put more charge clouds in the intermolecular region. Although further detailed analyses may be demanded, we believe that the sum of the exchange-repulsion and charge-transfer interaction terms roughly cancel mutually and that the net small destabilization is surpassed by the large stabilization due to the Coulomb interaction term in the region of the F- - -F distances of our interest.

4.2. Geometrical Configurations of Hydrogen Bonded Dimers in the Ground State

4.2.1. Hydrogen Fluoride Dimer. Theoretical calculations on the HF dimer have been carried out by *ab initio* [13–15] and semiempirical [16, 17] methods. All the calculations show a near-linear HF dimer to be the most stable. As is shown in Table 1, our calculation results also show that the linear dimer is

Table 1. Hydrogen bond energy as a function of the F---F distance in the dimer

(eV)

$(HF)_2$ dimer	R(Å)[a]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
Linear dimer	5.0	-0.0104	0.0000	-0.0001	-0.0002	-0.0000	-0.0107
	4.5	-0.0144	0.0000	-0.0002	-0.0003	-0.0000	-0.0150
	4.0	-0.0211	0.0004	-0.0003	-0.0007	-0.0004	-0.0222
	3.5	-0.0346	0.0032	-0.0008	-0.0017	-0.0027	-0.0365
	3.0	-0.0783	0.0264	-0.0019	-0.0044	-0.0195	-0.0775
	2.5	-0.3295	0.2002	-0.0047	-0.0137	-0.1130	-0.2606
Cyclic dimer	5.0	-0.0043	0.0000	-0.0000	-0.0000	-0.0000	-0.0043
	4.5	-0.0064	0.0001	-0.0000	-0.0001	-0.0000	-0.0064
	4.0	-0.0099	0.0003	-0.0001	-0.0002	-0.0002	-0.0100
	3.5	-0.0167	0.0020	-0.0002	-0.0004	-0.0009	-0.0162
	3.0	-0.0330	0.0121	-0.0006	-0.0013	-0.0033	-0.0261
	2.5	-0.0895	0.0751	-0.0017	-0.0045	-0.0098	-0.0304

a) R is the distance between fluorine atoms.

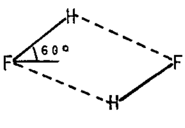
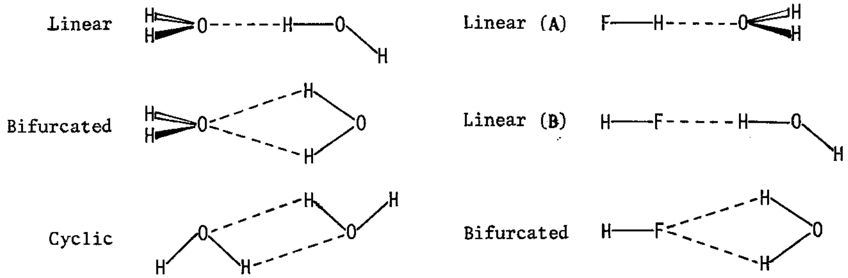


Table 2. Contributions to the hydrogen bond energies for the H_2O-H_2O and H_2O-HF systems (eV)

Dimer	Geometry	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
H_2O-H_2O[a]	Linear	-0.2178	0.2046	-0.0025	-0.0194	-0.0831	-0.1181
	Bifurcated	-0.0730	0.0756	-0.0010	-0.0033	-0.0239	-0.0256
	Cyclic	-0.0889	0.1280	-0.0013	-0.0095	-0.0363	-0.0081
H_2O-HF[b]	Linear (A)	-0.2117	0.1515	-0.0052	-0.0145	-0.0817	-0.1616
	Linear (B)	-0.1733	0.1371	-0.0013	-0.0082	-0.0443	-0.0900
	Bifurcated	-0.0588	0.0385	-0.0007	-0.0021	-0.0202	-0.0443

a) The O---O distance is 2.7 Å. b) The F---O distance is 2.7 Å.



more stable than the cyclic dimer. As the F- - -F distance decreases, both linear and cyclic dimers tend to be stabilized, but the linear dimer is more effectively stabilized because of the Coulomb (E_Q) and charge-transfer (E_{CT}) interaction terms. However, the exchange-repulsion term (E_K) favors the cyclic dimer rather than the linear one.

4.2.2. Water Dimer. The linear, bifurcated, and cyclic water dimers with an O- - -O distance 2.7 Å were examined (Table 2). Of the three geometrical configurations, the linear dimer is the most stable because of the Coulomb (E_Q), charge-transfer (E_{CT}), and dispersion (E_D) terms. Their relative stability decreases in the order of linear > bifurcated > cyclic dimers. The recent experimental investigation [18] as well as many theoretical investigations [13, 19–24] support the linear dimer.

4.2.3. Water-Hydrogen Fluoride Codimer. Three geometrical configurations at an F- - -O distance 2.7 Å were calculated (Table 2). Again, the linear $H_2O \cdot HF$ codimer is the most stable because of the E_Q, E_{CT}, and E_D interaction terms. In the linear codimers, hydrogen fluoride participates in the hydrogen bonding as a proton donor [linear (A)] more effectively than as a proton acceptor [linear (B)].

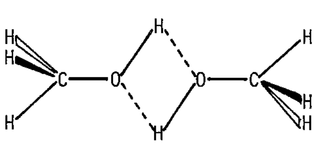
4.2.4. Methanol Dimer. Although earlier experimental work seemed to indicate that the methanol dimer had a cyclic structure [25–27], more recent experiments [28] as well as calculations [16, 29] support the view that the

Table 3. Contributions to the hydrogen bond energy for the CH_3OH dimer

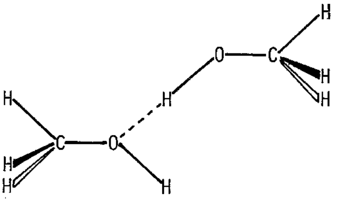
(eV)

Dimer	Geometry	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
CH_3OH-CH_3OH[a)]	Cyclic	-0.0192	0.0264	-0.0009	-0.0101	-0.0102	-0.0139
	Linear	-0.2234	0.2282	-0.0030	-0.0325	-0.0974	-0.1286

a) The O---O distance is taken to be 2.7 Å.



Cyclic



Linear

linear dimer is more stable than the cyclic one. Our calculation results obtained at an O- - -O distance 2.7 Å clearly show a greater stability of the linear dimer (Table 3). The linear dimer is destabilized more effectively by the repulsion-interaction term (E_K), but the attractive terms especially owing to the E_Q and E_{CT} terms can overcome the destabilization due to the E_K term.

4.2.5. Carboxylic Acid (RCOOH) *Dimer.* Reliable experimental data are available for the carboxylic acids. They demonstrate that the cyclic dimer is the most stable [30, 31] and that, of the linear dimers, the *s-cis* form is more stable than the *s-trans* form [32]. The cyclic dimer of formic acid was also predicted by the calculations [16, 29, 33, 34]. Our calculations for the formic acid dimer show that the relative stability decreases in the order of cyclic $\gg$ *s-cis* $>$ *s-trans* dimers (Table 4). The stability of the cyclic dimer relative to the linear ones owes mainly to the Coulombic attraction term (E_Q), while the repulsion interaction term (E_K) destabilizes the cyclic dimers more greatly. The difference in stabilization between the *s-cis* and *s-trans* forms is also ascribable to the Coulomb interaction term (E_Q).

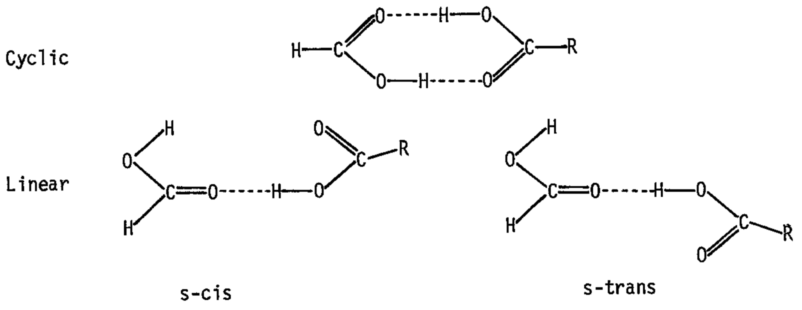
At this point, it may be interesting to examine the influence of substituents (R) with different electronegativities upon the hydrogen bonding formed. We considered CH_3 and CF_3 as substituents. The former is an electron-donating substituent while the latter an electron-accepting one. In other words, CF_3 strengthens the acidity of HCOOH while CH_3 weakens it. The calculation results obtained for the *s-cis* dimers in which the substituted acids operate as proton-donors are also shown in Table 4. The hydrogen bond strength decreases in the order of $CF_3COOH > HCOOH > CH_3COOH$. This order may be anticipated from the property of the substituents mentioned above.

Table 4. Contributions to the hydrogen bond energies for the carboxylic acid codimers

(eV)

HCOOH-RCOOH	Geometry[a]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
R = H	Cyclic	-0.4979	0.4277	-0.0215	-0.0941	-0.1770	-0.3629
	s-cis	-0.2568	0.1826	-0.0090	-0.0489	-0.1063	-0.2385
	s-trans	-0.2469	0.1830	-0.0082	-0.0475	-0.1060	-0.2256
R = CF_3	s-cis	-0.2728	0.1777	-0.0133	-0.0500	-0.1105	-0.2690
R = H	s-cis	-0.2568	0.1826	-0.0090	-0.0489	-0.1063	-0.2385
R = CH_3	s-cis	-0.2469	0.1817	-0.0069	-0.0505	-0.1033	-0.1152

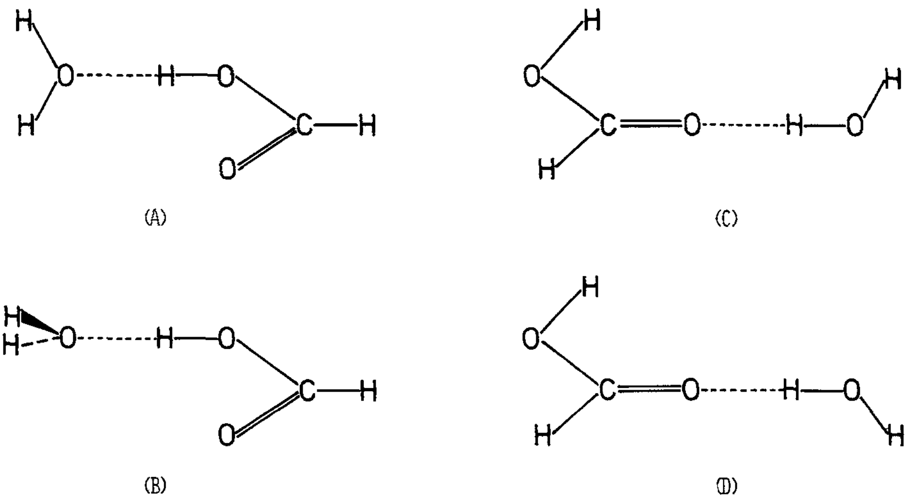
a) The O---O distance is taken to be 2.7 Å.



However, the stabilization due to the dispersion term (E_D) decreases in the order of $CH_3COOH \geq CF_3COOH \geq HCOOH$, and the destabilization due to the exchange repulsion term (E_K) increases in the order of $CF_3COOH < CH_3COOH < HCOOH$. Contrary to these, the stabilization due to the attraction terms (E_Q, E_{CT}, and E_I in which E_Q is the dominant factor) decrease in the order or $CF_3COOH > HCOOH > CH_3COOH$. Thus, the effect of the substituents considered here may be ascribed mainly to the Coulomb interaction term.

4.3. Hydrogen Bonding in the Electronically Excited States

As our calculation method does provide reasonable and useful results for the hydrogen bonding in the ground state, it seems that its applications to the hydrogen bonding in the electronically excited state is meaningful in order to grasp the essential features of the changes in the interaction energy terms due to excitation. One of the most important phenomena affected by hydrogen bond formation is the experimentally observed shift of the absorption band of a molecule in a hydrogen-bonding solvent [35].



(A) (C) (B) (D)

Fig. 3. Geometrical configurations of the linear HCOOH–H_2O hydrogen bonded codimer

We carried out the intermolecular interaction calculations on the water-formic acid codimer in the $n-\pi^*$ and $\pi-\pi^*$ excited states as well as in the ground state. For the hydrogen bonded system, four geometrical configurations with an O- - -O distance 2.7 Å were considered as shown in Fig. 3. In the geometries (**A**) and (**B**), formic acid is a proton-donor and water is a proton-acceptor. In the geometries (**C**) and (**D**), on the other hand, the former is a proton-acceptor and the latter a proton-donor.

It has generally been considered that solute molecules are stabilized in solutions by the interactions with the solvent molecules. As is clear from Table 5, formic acid participates in hydrogen bonding as both proton-acceptor and -donor in the ground state and thus the formic acid-water system is stabilized. In the excited state, however, formic acid acts chiefly as a proton-donor [geometries (**A**) and (**B**)] because of the great stabilization due to the Coulomb interaction term (E_Q^*), even though other interaction terms (E_K^*, and E_D^*) stabilize more effectively the hydrogen bond in which the formic acid partakes as a proton-acceptor [geometries (**C**) and (**D**)]. From these results, we may conjecture that the solute and solvent molecules undergo considerable reorientation upon the excitation of solute. Probably, the reorientation process will play an important role in photochemical reactions.

As for the stabilization in the ground relative to excited states, Table 5 shows that it decreases in the order of $\pi-\pi^*$ excited state > ground state > $n-\pi^*$ excited state in all the geometries [(**A**), (**B**), (**C**), and (**D**)]. On the other hand, Table 6 shows that the vertical $n-\pi^*$ transition energies for the hydrogen bonded codimers calculated by our modified INDO method [36] are greater than the energy obtained for HCOOH, while the vertical $\pi-\pi^*$ transition energies for the hydrogen bonded codimers are smaller than the energy for HCOOH.

Table 5. Contributions to the hydrogen bond energy for the HCOOH-H_2O codimer in the ground and excited states

(eV)

Geometry	State[a]	E_Q^*	E_K^*	E_I^*	E_D^*	E_{CT}^*	E_{total}^*
(A)	ground	-0.2481	0.1477	-0.0051	-0.0247	-0.1110	-0.2410
	n-π*	-0.2402	0.1461	-0.0044	-0.0247	-0.0760	-0.1992
	π-π*	-0.2911	0.1423	-0.0105	-0.0452	-0.0846	-0.2892
(B)	ground	-0.2432	0.1473	-0.0044	-0.0215	-0.1107	-0.2325
	n-π*	-0.2394	0.1458	-0.0042	-0.0215	-0.0758	-0.1952
	π-π*	-0.2858	0.1418	-0.0091	-0.0425	-0.0844	-0.2800
(C)	ground	-0.2166	0.1317	-0.0047	-0.0410	-0.1069	-0.2374
	n-π*	-0.1644	0.1269	-0.0041	-0.0410	-0.0800	-0.1625
	π-π*	-0.2072	0.1334	-0.0044	-0.0823	-0.0785	-0.2390
(D)	ground	-0.2208	0.1318	-0.0046	-0.0407	-0.1071	-0.2414
	n-π*	-0.1674	0.1270	-0.0042	-0.0407	-0.0802	-0.1655
	π-π*	-0.2240	0.1335	-0.0040	-0.0855	-0.0787	-0.2586

a) See Fig. 4.

Table 6. The effect of the hydrogen bond on the n-π^* and π-π^* transitions[a]

Acceptor-Donor	Geometry	$\Delta E_{n-\pi^*}$[b]	f[c]	$\Delta E_{\pi-\pi^*}$[b]	f[c]
HCOOH		5.024	0.256	9.129	0.808
H_2O-HCOOH	(A)	5.104	0.225	9.013	0.807
	(B)	5.092	0.225	9.014	0.808
HCOOH-H_2O	(C)	7.907	0.002	9.106	0.800
	(D)	7.744	0.018	9.125	0.800

a) Calculations were carried out by using a Modified INDO method [36].

b) Vertical transition energy in eV. c) Oscillator strength in Å.

It seems apparent from these calculated results that there is a correlation between the hydrogen-bond strength and the magnitude of the absorption band shift caused by water. That is, the blue shift of the $n-\pi^*$ transition of HCOOH must be due to the lesser stability of the $HCOOH \cdot H_2O$ codimer in the $n-\pi^*$ excited state than in the ground state, while the red shift of the $\pi-\pi^*$ transition could be attributed to the increase in the hydrogen bond energy upon the $\pi-\pi^*$ excitation. The directions of the shifts predicted are in accord with the well-known experimental results on the water solvent effects [35].

The magnitude of the blue shift of the $n-\pi^*$ transition is larger in the geometries (**C**) and (**D**) than in the geometries (**A**) and (**B**). This is ascribable mainly to the greater decrease in E_Q^* in (**C**) and (**D**) as a consequence of the promotion of electrons in the n-orbital (which is localized around the carbonyl oxygen atom as the hydrogen bond center) to the strongly delocalized π^*-orbital (which is polarized toward the carbonyl carbon atom). On the other hand, the magnitude of the red shift of the $\pi-\pi^*$ transition is larger in the geometries (**A**) and (**B**) than in the geometries (**C**) and (**D**). This is attributed to the larger stabilization of (**A**) and (**B**) due principally to the E_Q^* term. Thus, the important role of the Coulomb interaction term in hydrogen bonding should be emphasized in relation to the water solvent effects on the electronic excitation energies of carboxylic acids.

5. Concluding Remarks

The partitioning of the hydrogen bond energy into five interaction terms appears to shed insight into the factors governing the geometrical configurations of hydrogen-bonded dimers or codimers. Reorientation of the hydrogen-bonded systems upon electronic excitation of the component molecule is also noteworthy. However, because of the approximate nature of the perturbation formalism here used, we have been unable to discuss the absolute magnitudes of the hydrogen bond energies at equilibrium orientations. For that purpose, structural changes of the component molecules upon hydrogen bonding would have to be duly taken into consideration. Nevertheless, the conclusion that the Coulombic interaction energy is the most important contribution to hydrogen bondings both in the ground and excited states would probably remain unaltered.

Another point which might be raised is that we have represented the excited states of component molecules by the wave functions [$\Phi_0(A^*_{a\to b})$ as in Eq. (13)] constructed with virtual orbitals (for example, MO b). In order for the perturbation technique to be reliable enough, the first term [which is the antisymmetrized product of $\Phi_0(A^*_{a\to b})$ and $\Phi_0(B)$] in Eq. (14) must be as exact as possible. Obviously, it will be more advantageous to utilize the self-consistent field orbitals which minimize the excited state energy. Recent *ab initio* calculations by Iwata and Morokuma [37] based on the electron-hole potential method are noteworthy in this respect. It is gratifying that the bulk of the results of our present study is well in accord with theirs.

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Professor Dr. T. Fueno
Department of Chemistry
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka, Japan