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ELECTRONIC STRUCTURE STUDY OF HYDROGEN-BONDED WATER CLUSTERS AND LINEAR-CHAIN ICE CRYSTAL USING A MODIFIED MNDO

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Abstract: A revised version of MNDO is employed particularly for the treatment of hydrogen-bonded water clusters and linear-chain ice. The computed results of the average hydrogen-bond energies and the first ionization energies for large water clusters and ice are found to correlate well with observation. In addition, using the tight-binding crystal orbital method of LCAO, the band structure of the linear-chain ice is reported.

I. Introduction

Various levels of direct lattice vector approaches associated with SCF HF (self-consistent field Hartree-Fock) LCAO (linear combination of atomic orbitals) CO (crystal orbital) have been used[1-16]. In order to avoid excessive computational time, semi-empirical valence-electron methods[17-20] are often employed. Among these semi-empirical methods, MNDO[20] (modified NDDO[18] (neglect of diatomic differential overlap)) is the most recent development and has become one among the most widely used tools for studying organic molecules, clusters and polymers.

Here we introduce a modified treatment of MNDO to specifically study molecular clusters and crystals. The molecular cluster is the aggregated state of molecules as a bound system due to attractive intermolecular interaction. Thus it will be of great interest how physical properties of hydrogen-bonded water clusters vary due to the intermolecular interaction as cluster size increases. Recently, linear-chain water clusters as model clusters have been a subject of great interest due to their relevance to solution electrochemistry, solitonic mechanism for proton transfer bioenergetics and atmospheric chemistry involving ice. Thus particular systems of present interest are the finite linear-chain water clusters of large size, $(H_2O)_n$ and the infinite linear-chain ice crystal, $(H_2O)_\infty$. Using a modified treatment[21,22] of MNDO particularly suited for hydrogen-bonded linear-chain water clusters, we report the computed results of the average hydrogen-bond energies and the first ionization energies for water clusters, including the electronic band structure of the linear-chain ice crystal. In addition, we will examine the convergence of the hydrogen-bond energies and the first ionization energies to the predicted bulk limit of ice as cluster size increases.

II. Modification of MNDO for the Treatment of Water Clusters and Ice Crystal

In general, the k-th block diagonalized matrix for the effective one-electron Hamiltonian (between the atomic Bloch functions) is written for infinite linear-chain crystals (i.e., $N \to \infty$),[1]

$$\mathbf{F}(k) = \sum_{q=-\infty}^{\infty} \exp(ikqa)\ \mathbf{F}(q) \quad , \qquad (II.1)$$

where k is the crystal wave number, q, the cell index and a, the primitive translation. Here the matrix elements of $\mathbf{F}(q)$ between the atomic orbitals, ${}_\mu 0$ belonging to the reference unit cell 0 and ${}_\nu q$ belonging to the unit cell q and the matrix elements are explicitly,

$$F_{\mu^o\nu^q} = \int \phi_{\mu^o}(\vec{r}_\alpha) h(\vec{r}_\alpha) \phi_{\nu^q}(\vec{r}_\alpha) d\vec{r}_\alpha + \sum_{s,t}\sum_{\lambda\sigma} D_{\lambda^s\sigma^t}\left[\int \phi^*_{\mu^o}(\vec{r}_\alpha)\phi^*_{\lambda^s}(\vec{r}_\beta)\, V_{\alpha\beta}\, \phi_{\nu^q}(\vec{r}_\alpha)\phi_{\sigma^t}(\vec{r}_\beta) d\vec{r}_\alpha d\vec{r}_\beta - \frac{1}{2}\int \phi^*_{\mu^o}(\vec{r}_\beta)\phi^*_{\lambda^s}(\vec{r}_\beta)\, V_{\alpha\beta}\, \phi_{\sigma^t}(\vec{r}_\alpha)\phi_{\nu^q}(\vec{r}_\beta) d\vec{r}_\alpha d\vec{r}_\beta\right] \tag{II.2}$$

with

$$D_{\lambda^s\sigma^t} = \sum_j \frac{a}{\pi}\int_{-\pi/a}^{\pi/a} C^*_{\lambda^s j}(k) C_{\sigma^t j}(k)\; e^{i(t-s)ka} dk \; . \tag{II.3}$$

Here $D_{\mu\nu}$ is the charge density matrix element for the one-dimensional crystal. μ, ν, λ, and σ are the atomic orbital indices. q, s, and t are the cell indices. $C(k)$ is the expansion coefficient for crystal orbitals. $V_{\alpha\beta}$ is the Coulomb interaction between electrons α and β.

Now writing

$$<\mu^o|h|\nu^q> \; = \int \phi^*_{\mu^o}(\vec{r}_\alpha)\, h(\vec{r}_\alpha)\, \phi_{\nu^q}(\vec{r}_\alpha) d\vec{r}_\alpha \tag{II.4}$$

and

$$\Gamma^{\nu^q\sigma^t}_{\mu^o\lambda^s} = \int \phi^*_{\mu^o}(\vec{r}_\alpha)\, \phi^*_{\lambda^s}(\vec{r}_\beta)\, V_{\alpha\beta}\, \phi_{\nu^q}(\vec{r}_\alpha)\, \phi_{\sigma^t}(\vec{r}_\beta) d\vec{r}_\alpha d\vec{r}_\beta \tag{II.5}$$

the expression (II.2) is simply,

$$F_{\mu^o\nu^q} = \; <\mu^o|h|\nu^q> \; + \sum_{s,t}\sum_{\lambda\sigma} D_{\lambda^s\sigma^t}\left[\Gamma^{\nu^q\sigma^t}_{\mu^o\lambda^s} - \frac{1}{2}\Gamma^{\sigma^t\nu^q}_{\mu^o\lambda^s}\right] \tag{II.6}$$

Here the first term is the familiar one-electron integral and the second term, the two-electron integrals Γ. The two-electron integrals Γ are determined by parameterization.

We now devide the matrix elements (II.6) of F into two sets, namely intramolecular and intermolecular elements and introduce the NDDO approximation[18]. Thus we obtain for the intramolecular matrix elements,

$$F_{\mu_a^o\nu_a^o} = \; <\mu_a^o|h|\nu_a^o> + \sum_{\lambda_a^o\sigma_a^o} D_{\lambda_a^o\sigma_a^o}\left[\Gamma^{\nu_a^o\sigma_a^o}_{\mu_a^o\lambda_a^o} - \frac{1}{2}\Gamma^{\sigma_a^o\nu_a^o}_{\mu_a^o\lambda_a^o}\right] \; . \tag{II.7}$$

which represents the matrix element between the atomic orbitals μ_a^o and ν_a^o both belonging to the same atom a in the same cell o, and

$$F_{\mu_a^o\nu_b^o} = \; <\mu_a^o|h|\nu_b^o> - \frac{1}{2}\sum_{\lambda_b^o\sigma_a^o} D_{\lambda_b^o\sigma_a^o}\Gamma^{\sigma_a^o\nu_b^o}_{\mu_a^o\lambda_b^o} \; . \tag{II.8}$$

which represents the matrix element between an atomic orbital μ_a^o belonging to an atom a and an orbital ν_b^o belonging to a different atom b in the same cell o. Now for the intermolecular matrix elements we obtain

$$F_{\mu_a^o\nu_b^q} = \; <\mu_a^o|h|\nu_b^q> - \frac{1}{2}\sum_{\lambda_b^q\sigma_a^o} D_{\lambda_b^q\sigma_a^o}\Gamma^{\sigma_a^o\nu_b^q}_{\mu_a^o\lambda_b^q} \; . \tag{II.9}$$

representing the matrix element between an atomic orbital μ_a^o belonging to an atom a in the cell o and an orbital ν_b^q belonging to a different atom b in cell q.

Parameters in the conventional semi-empirical methods are selected by fitting physical properties for isolated molecules (monomers), based on geometries wherein their equilibrium intra-atomic distances are much shorter compared to intermolecular separations between molecular units in the molecular clusters or molecular crystals. For this reason semi-empirical methods are likely to fail in reproducing the observed properties of molecular clusters or crystals whose building blocks are the molecular units. Thus in our treatment we divide parameters into two sets; one for the intramolecular interaction and the other for the intermolecular interaction in accordance with the expressions (II.7) through (II.9).

Beside the separation of the intramolecular and intermolecular interactions mentioned earlier, in our treatment we introduce only the core-core repulsion energy differently from the original MNDO[20]. It is written[21,22]

$$E_{ab} = Z_a Z_b (s_a s_a|s_b s_b)\,[1 + \gamma_{ab} e^{-\alpha_{ab} r_{ab}}] \quad . \qquad (II.10)$$

for the pairs of atoms a and b. Here r_{ab} is the interatomic distance between a and b. γ and α are the parameters to be chosen by fitting measurements (See ref. 21 for details). Z_a and Z_b are the core charges of atoms a and b respectively. $(s_a s_a|s_b s_b)$ above is the two-electron two center integrals involving the s atomic orbitals in the two different atoms a and b. Despite the employment of the two sets of parameters, it was encouraging to find[21] that the values of the intramolecular parameters converged close to the orignal MNDO parameters. For the details of parameterization for water, we refer the readers to ref. 21. It is of note that the AM1 method[23] of Dewar and coworkers yielded a reasonably good but relatively small hydrogen-bond energy ~ 3.3 Kcal/mole for water dimer. To the best of our knowledge, no further application to the clusters of larger size has appeared. Other MNDO modification for water was recently reported by Burstein and Isaev[24] but no application to the systems of water clusters have appeared.

Finally, the crystal orbital energy or the energy band $\epsilon(k)$ is obtained[1]

$$F(k)\,C(k) = \epsilon(k)\,S(k)\,C(k) \quad . \qquad (II.11)$$

$S(k)$ is the k-th block of the block diagonalized matrix for atomic overlap integral. The electronic band structure of infinite linear-chain ice, $(H_2O)_\infty$ will be reported in the next section.

III. Computed Results of Hydrogen-bonded Water Clusters and Ice

Here we avoid formal description of treating molecular clusters and the parameterization procedure as they appeared elsewhere[21,22]. All the calculated results below are based on optimized geometries.

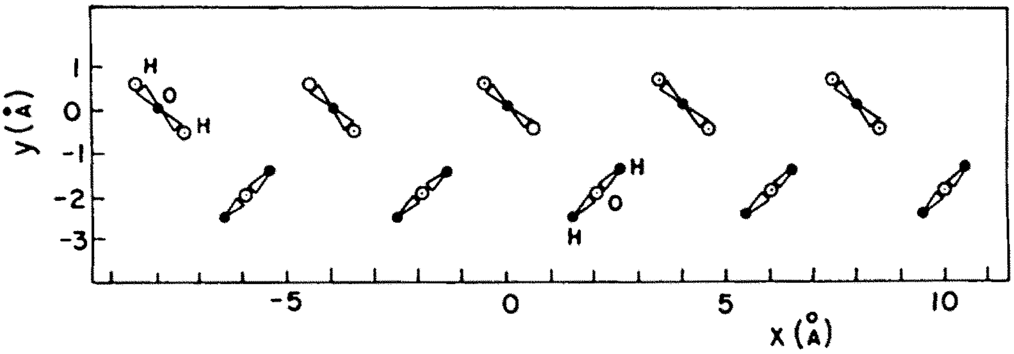

Fig. 1
Optimized geometry for 1-D ice linear chain. H denotes hydrogen and O denotes oxygen. The circled atoms are at z = 0.58 Å, others are at z = 0.

The predicted[22] heats of formation for the water clusters taken from portions of the hexagonal ice I were found to be in good agreement with the ab initio calculations of Tomoda and Kimura[25]. In the present study we consider both the finite and infinite linear-chain clusters. Thus, in order to make direct comparison with the linear-chain ice crystal, we first pay attention to linear-chain water clusters shown in Fig. 1. The hydrogen ($O-H\cdots O$) bond length is 2.88 Å, the $O\cdots O\cdots O$ bond angle, 88° and the $H-O-H$ bond angle, 105Å, the $O-H$ bond length is 0.95 Å.

As shown in Fig. 2, the first ionization energy is predicted to decrease as cluster size n increases. Further we note that there exists the propensity of linearity between the ionization energy ϵ and $1/n$. The numerical results for the first ionization energies (ϵ) are well represented by the analytic expression ϵ = 0.879 eV ($1/n$) + 11.69 eV. In the large size limit the ionization energy converges to a value of 11.7 eV. This is satisfactorily close to the observed value[26] (work function of ~ 11.0 eV) of bulk ice. The predicted first ionization energies of the finite linear-chain clusters $(H_2O)_n$ are generally larger than those[22] of non-linear clusters, as expected. Further the ionization energy (or work function) of the infinite linear-chain cluster, $(H_2O)_\infty$, is found to be greater than observation. This value is expected to be smaller when the complete dimensionality of ice, namely the three-dimensional ice is fully taken into account. This is because the additional dimensions enhance the dispersion of electron cloud in all directions and thus the reduction of electron binding energy, i.e., the first ionization energy.

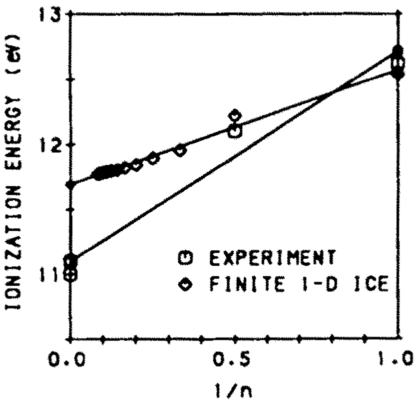

Fig. 2
First ionization energy as a function of the inverse of critical size, i.e., 1/n.

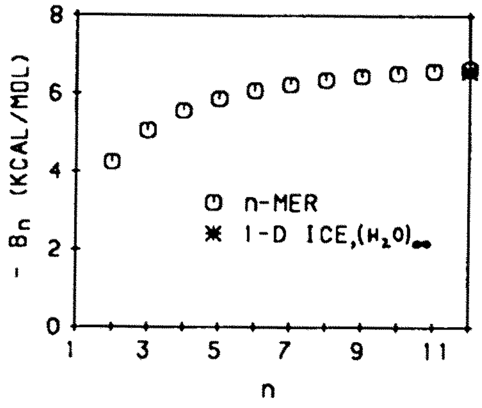

Fig. 3
Binding energy per bond vs. cluster size n for finite chain segments (ʘ), and for the infinite 1-D crystal (-✱-).

In Fig. 3 we show variation of the hydrogen-bond energy, B_n, (binding energy / bond) as a function of cluster size. Also shown is the hydrogen bond energy for the case of the infinite 1-D ice chain. At the large size limit, the hydrogen bond energy for the finite clusters reaches a value of 6.65 Kcal/mol, which is within 1% of the infinite crystal result of 6.59 Kcal/mol. This shows excellent convergence to the bulk value as the cluster size n increases. Finally in Fig. 4 we introduce the band structure of the linear-chain ice crystal $(H_2O)_\infty$. Calculations performed with one and two nearest neighbor approximations yielded results with insignificant differences. The predicted band gap is ~ 15.9 eV. The optimized geometry of $O-H\cdots O$ bond length is found to be 2.88 Å for the linear crystal. Predicted valence band widths are narrow as expected. The predicted band gap is in qualitative agreement with the earlier CNDO/2 calculations of Ladik[27], in that both calculations show the 1-D ice crystal to be an insulator. However the CNDO/2 calculations yielded a much greater value of 20.4 eV for the band gap.

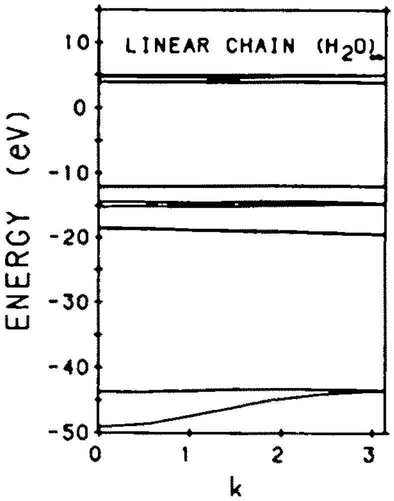

Fig. 4
Energy band structure for our linear-chain ice crystal.

IV. Summary

There has been a great interest in both the finite and infinite linear-chain water clusters[27-31]. In the the present study we have systematically examined the first ionization energies and average hydrogen-bond energies of the linear water clusters as a function of cluster size. The salient features found from this study are a decrease of the first ionization energy with cluster size *n* obeying closely a linear relationship with 1/*n*. The predicted band gap of the linear-chain ice was large with 15.9 eV. Due to the economy of computational time with the modified MNDO treatment presented here, it will be of great interest to examine the water clusters of larger size and the three-dimensional ice crystal in order to realistically understand the bulk electronic properties of hydrogen-bonded water systems.

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