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CNDO/2 Calculations on the Configurations of the Ion-molecule Complexes. The NH_4^+-CH_4, H_3O^+-CH_4 and NH_4^+-H_2 Systems

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The optimized configurations of several ion-non polar molecule complexes (NH_4^+–CH_4, H_3O^+–CH_4 and NH_4^+–H_2) have been discussed by the use of the CNDO/2 method. The results for NH_4^+–CH_4 and H_3O^+–CH_4 turn out to be quite different from those previously proposed by the calculations based on the classical electrostatic model. It may be demonstrated that these systems are stabilized by a kind of hydrogen bond where the charge transfer effect from a neutral molecule to a cation plays an important role, according to the configuration analysis.

In the field of intermolecular forces, there has been recent progress in the theoretical development of weak interactions, such as hydrogen bonds or ion-molecule bonds, based on *ab initio* calculations or fairly reliable semi-empirical calculations.[1,2)]

Of these, ion-molecule bonds consist of interaction between ions and neutral molecules in the singlet ground state. Such bonds have usually been investigated in order to comprehend the solvation process of ions in polar solvents, such as H_2O and NH_3.[1a,1b)] In contrast with the extensive studies of these ion-polar molecule complexes, there have been only a few studies of ion-non polar molecule complexes.

Recently it has become possible to obtain direct thermodynamical data on some ion-non polar molecule complexes in the gaseous state through the mass spectrometry of ion beams at low temperatures. Bennett, Field, and Beggs have obtained the equilibrium constants and thereby evaluated the ΔG_{300}, ΔH^0 and ΔS^0 values of the following reactions:[3–5)]

$$CH_5^+ + CH_4 \rightleftharpoons CH_5^+\text{-}CH_4 \qquad \Delta H^0 = -4.14\,\text{kcal/mol}$$

$$NH_4^+ + CH_4 \rightleftharpoons NH_4^+\text{-}CH_4 \qquad \Delta H^0 = -3.59 \pm 0.11\,\text{kcal/mol}$$

$$CF_3^+ + CH_4 \rightleftharpoons CF_3^+\text{-}CH_4 \qquad \Delta H^0 = -4.55 \pm 0.05\,\text{kcal/mol}$$

$$H_3O^+ + CH_4 \rightleftharpoons H_3O^+\text{-}CH_4 \qquad \Delta H^0 = -8.0\,\text{kcal/mol}$$

The $-\Delta H^0$ means the interaction energy needed to stabilize such an ion-molecule complex. They have also calculated the classical electrostatic interaction energy in order to discuss the stable configurations of these complexes.

Geometries suggested by the popular semi-classical electrostatic model[6)] are often consistent with the experimental results or those calculated by MO method[7)] for small ion-non polar molecule complexes, such as H_5^+ and He–H_3^+. It is, however, questionable whether this method yields reliable results for larger complexes such as the NH_4^+–CH_4 system, since it quite neglects the effect of charge transfer, which seems to play an important role in stabilizing these complexes. Indeed, the models proposed by the experimentalists are far from those conjectured from the reliable geometries of the H_3O^+–H_2O and NH_3–NH_3 systems.[1a,1b)]

It may, therefore, be worthwhile to discuss the geometries of some typical ion-non polar molecule systems. In this paper, we will calculate the interaction energies in order to predict the stable configurations of the NH_4^+–CH_4, H_3O^+–CH_4 and, additionally, NH_4^+–H_2 systems by means of the CNDO/2 method.** This method has yielded considerably reliable results on the interaction energies and stable configurations for neutral molecule systems and for cationic systems as well.[8)] Furthermore, we will carry out the configuration analysis by expanding the MO of the optimized configuration in order to show the contribution factors which stabilize each complex.

Method of Calculation

The bond distances and angles in the isolated cations and molecules are optimized individually by the CNDO/2 calculation; they are shown in Table 1.

TABLE 1. BOND DISTANCES AND ANGLES USED FOR ISOLATED SYSTEMS

Species	Bond	Distance (Å)	Angle	Size. deg
CH_4	C-H	1.115	H-C-H	109°28′
H_2	H-H	0.741[a)]	—	—
NH_4^+	N-H	1.077	H-N-H	109°28′
H_3O^+ [b)]	O-H	1.045	H-O-H	114°45′

a) Assumed. b) Pyramidal form.

For the NH_4^+–CH_4 system, in which both NH_4^+ and CH_4 have the C_2 axis and the C_3 axis, ten different kinds of configurations within the probable symmetries have been selected. The optimized configuration is determined for each interacting system by changing the intermolecular distance between NH_4^+ and CH_4; subsequently, several prominent parameters are optimized in the order of their magnitudes for the interaction energy.

For the H_3O^+–CH_4 system and the NH_4^+–H_2 system, details will be described later.

The method of configuration analysis[9)] is applied to the most optimized configuration of each complex. Here we will briefly outline a CI wavefunction:

$$\Psi = C_0\Psi_0 + \sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}\Psi_{i\to l} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}\Psi_{k\to j} + \sum_i^{\text{occ}}\sum_j^{\text{uno}} C_{i\to j}\Psi_{i\to j} + \sum_k^{\text{occ}}\sum_l^{\text{uno}} C_{k\to l}\Psi_{k\to l} + \cdots \qquad (1)$$

** As to CF_3^+-CH_4 and CH_5^+-CH_4 systems, it is doubtful whether the CNDO/2 method is suitable to treat CF_3^+ and CH_5^+ isolated systems. Thus the reliable MO calculation results of these systems are of further indices.

where i, j, k, and l represent the i-th occupied MO of an isolated system, A, the j-th unoccupied of A, the k-th occupied of B, and the l-th unoccupied of B respectively, and where the sign $i \rightarrow l$ indicates the one-electron shift from MO i to MO l and so on. We can thus make the CI wavefunction of the complexes if the coefficients are known. In order to see the contributing factors to the stabilization of the complexes, we construct a wavefunction:

$$\begin{aligned}\Psi = C_0\Psi_0 &+ [\sum_{i}^{\text{occ}}\sum_{l}^{\text{uno}}(C_{i\rightarrow l})^2]^{1/2}\Psi(\text{A}^+\cdot\text{B}^-)\\ &+ [\sum_{k}^{\text{occ}}\sum_{j}^{\text{uno}}(C_{k\rightarrow j})^2]^{1/2}\Psi(\text{A}^-\cdot\text{B}^+)\\ &+ [\sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}}(C_{i\rightarrow j})^2]^{1/2}\Psi(\text{A}^*\cdot\text{B})\\ &+ [\sum_{k}^{\text{occ}}\sum_{l}^{\text{uno}}(C_{k\rightarrow l})^2]^{1/2}\Psi(\text{A}\cdot\text{B}^*) + \cdots\cdots\cdots \end{aligned} \tag{2}$$

where, for instance, $\Psi(\text{A}^+\cdot\text{B}^-)$ and $\Psi(\text{A}^*\cdot\text{B})$ represent all of the one-electron transferred configurations from A to B, and all of the one-electron excited configurations in A, respectively.

Results and Discussion

The NH_4^+-CH_4 System. The selected configurations are shown in Fig. 1, while the changes in the interaction energies with varying the distance between NH_4^+ and CH_4 are drawn in Fig. 2. The optimized configuration turns out to be (A). The starred hydrogen atom in (A), (B), and (C) seems to play an important role in binding the systems. The values of the net charge of the hydrogen atoms are as follows; (A) +0.300, (B) +0.296, and (C) +0.289. It can easily be seen that the (A) configuration is the most advantageous for bonding, since the positively charged hydrogen contributes to bind the system as a bridging center through Coulomb interaction with the carbon atom in CH_4. Henceforth, it may be said that the optimized configuration for the ion-molecule complex is mainly guaranteed by the existence of a positively charged hydrogen atom in the cation situated on the bonding axis of the complex as a bridging center. Furthermore, the neutral molecule retains its highest symmetry and avoids the form in which a hydrogen atom in the molecule confronts the positively charged hydrogen atom in the cation. Such a tendency coincides with the previous calculation results as to, for instance, the H_3O^+-H_2O and the H_2O-H_3O^+-H_2O systems.[1a]

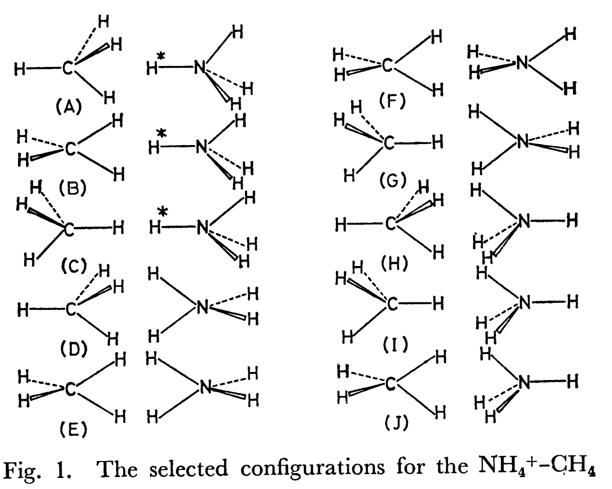

Fig. 1. The selected configurations for the NH_4^+-CH_4 system.

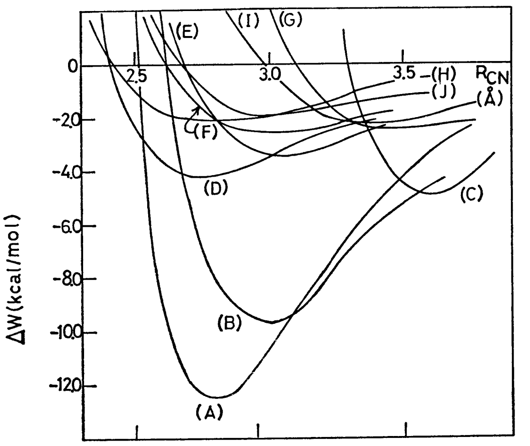

Fig. 2. Potential curves of the selected configurations for the NH_4^+-CH_4 system. The 90° rotation of either fragment along the C-N axis in (B), (D), (G), and (J) and 180° rotation in (A) yield no energy change within an error.

The (A) configuration is next treated so as to be optimized with other parameters. The optimized (A) configuration in Fig. 3 shows that R_{6N7H} stretches toward 1C as far as 1.117 Å and that ∠3H1C4H *etc.* open a little to be 112°. Thus, the optimized energy of this system is 14.49 kcal/mol (experimental: 3.59 kcal/mol). We need not further optimize the (B) configuration and those following in Fig. 1, since they would not exceed the optimized (A) in Fig. 3 in interaction energy. Interestingly, the configuration in Fig. 4 proposed by Bennett and Field[5] is converse in the direction of the CH_4 and NH_4^+ from the optimized

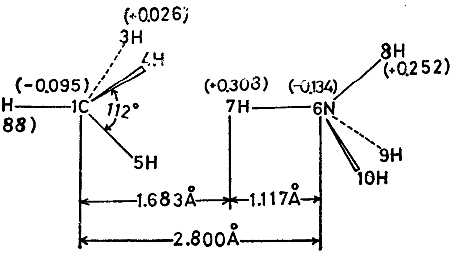

Fig. 3. The optimized configuration of the NH_4^+-CH_4 system. R_{4H7H} = 1.729 Å and other bond distances remain unchanged.

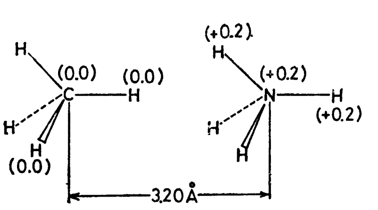

Fig. 4. Bennett and Field's model for the NH_4^+-CH_4 system.

configuration predicted here. The E_{AB} analysis in the CNDO/2 method shows that the E_{1C7H} and E_{6N7H}-attractive energies have the largest effect in stabilizing the complex among the other attractive and repulsive energies. In fact, the eclipsed form yields the same $-\Delta W$ as that of the staggered form in Fig. 3. Therefore, in this configuration, CH_4 and NH_4^+ seem to rotate along their bonding axis. The values of atomic net charge are also given in Fig. 3; the quantity of the transferred charge from CH_4 to NH_4^+ is estimated to be -0.071.

The H_3O^+–CH_4 System. For this system, five kinds of configurations are treated. The (A) configuration in Fig. 5 is selected by the criterion noted above, and others that have C_{3v} geometries in both fragments are compared with (A). In Fig. 6 the optimized configuration is shown to be (A), as was expected. The other configurations are far less stable than (A) in spite of their symmetries. A further optimized form of (A) is shown in Fig. 7, where R_{6O7H} stretches toward 1C to be 1.115 Å and where ∠3H1C4H *etc.* in CH_4 open until 114°. This is also quite the same pattern as in the NH_4^+–CH_4 system in Fig. 3. The calculated interaction energy gives 31.56 kcal/mol (experimental: 8.0 kcal/mol). The configurations in Fig. 8, previously proposed by Bennett and Field,[4] are quite different from the most optimized one predicted here.

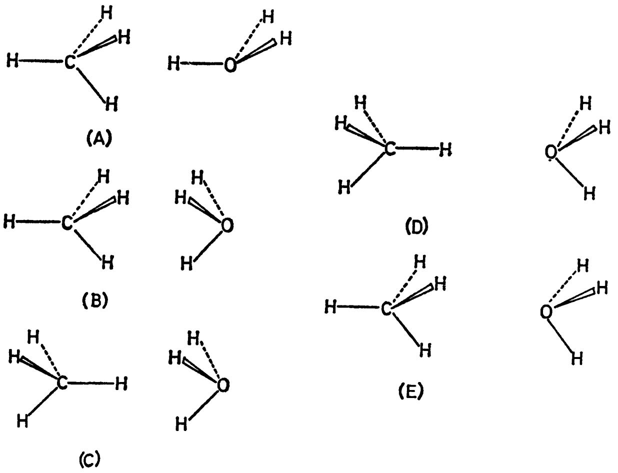

Fig. 5. The selected configurations for the H_3O^+-CH_4 system.

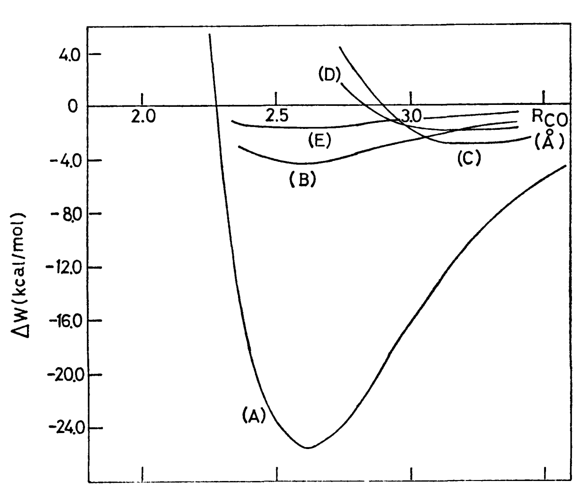

Fig. 6. Potential curves of the selected configurations for the H_3O^+-CH_4 system. The 90° and 180° rotation of either fragment along the C-O axis in (A) yields no energy change within an error.

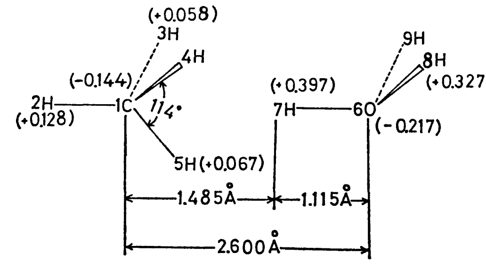

Fig. 7. The optimized configuration for the H_3O^+-CH_4 system. $R_{4H7H}=1.619$ Å and other bond distances remain unchanged.

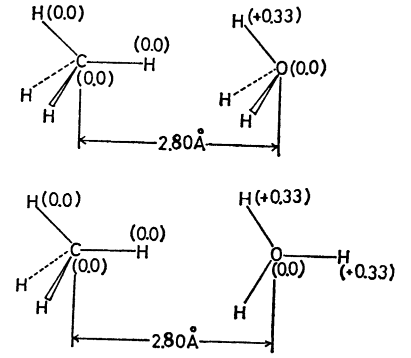

Fig. 8. Bennett and Field's model for the H_3O^+-CH_4 system.

As to the E_{AB} values, E_{1C7H} and E_{6O7H} are the dominant attractive energies, and the 90° and 180° rotations of either fragment along the C–H–O axis yield no energy change as in the NH_4^+–CH_4 system. Therefore, this system should also rotate freely along the C–H–O axis. The quantity of the transferred charge from CH_4 to H_3O^+ is -0.166, which is considerably larger than that in the NH_4^+–CH_4 system.

The NH_4^+–H_2 System. This system is considered to be a simple model of the ion-molecule complexes, although there are no previous experimental data available. Therefore, it seems that it would be

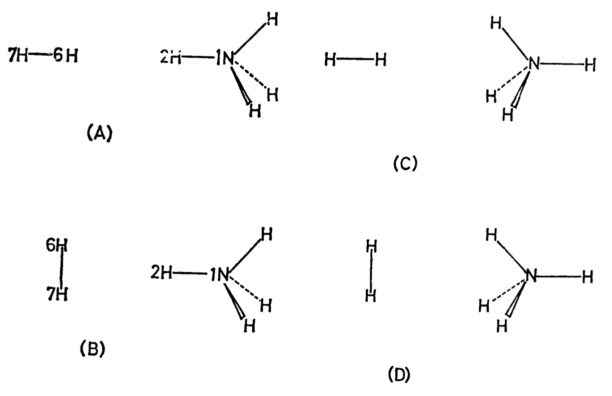

Fig. 9. The selected configurations for the NH_4^+-H_2 system.

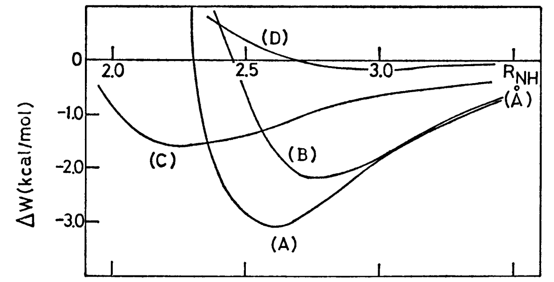

Fig. 10. Potential curves of the selected configurations for the NH_4^+-H_2 system.

TABLE 2. THE INTERACTION ENERGY OF THE NH_4^+-H_2 SYSTEM

Configuration	Parameters		Interaction energy (kcal/mol)
(A) Configuration	R_{6H7H}[a]	=0.641 Å	−7.45 (Repulsive)
		0.741 Å	3.07
		0.841 Å	2.45
	R_{1N2H}	=0.977 Å	−9.98 (Repulsive)
		1.077 Å	3.07
		1.117 Å	−3.70 (Repulsive)
(B) Configuration	R_{6H7H}	=0.721 Å	1.57
		0.741 Å	2.13
		0.761 Å	2.13
		0.781 Å	1.51
	R_{1N2H}	=1.067 Å	1.88
		1.077 Å	2.13
		1.087 Å	2.26
		1.097 Å	2.20

a) 7H is fixed.

interesting to predict the interaction energy and the optimized configuration for this system by MO theoretical treatment. In order to do so, four kinds of configurations were selected and their maximum interaction energies were calculated. The selected configurations and the potential curves are shown in Fig. 9 and Fig. 10 respectively. The interaction energy, $-\Delta W$, of the optimized (A) configuration is 3.07 kcal/mol, while that of the secondary optimized (B) configuration is 2.13 kcal/mol. Since these values are very close, both (A) and (B) should be further optimized. The results, presented in Table 2, show that the $-\Delta W$ in (A) remains unchanged, while that in (B) becomes 2.26 kcal/mol. Therefore, the (A) configuration is still most stable. In Fig. 11 the detailed form of the (A) configuration is presented. The quantity of the transferred charge from H_2 to NH_4^+ is −0.013, much less than those of the NH_4^+–CH_4 and the H_3O^+–CH_4 systems, and it produces less stabilization energy. The result that the difference in $-\Delta W$ values between (A) and (B) is only 0.81 kcal/mol, which is the same order as kT at room temperature, implies that H_2 rotates in the space near NH_4^+. Furthermore, the experimental data of $-\Delta H^0$ of this system, if any, would be about 0.5~0.75 kcal/mol, referring that the calculated $-\Delta W$ values for both the NH_4^+–CH_4 and the H_3O^+–CH_4 systems are four times the respective experimental values. If so, the $-\Delta W$ values for the (A), (B), (C), and (D) configurations will become closer, and (A) may change into (B), (C) or (D) in rapid succession, at least in the range of room temperature.

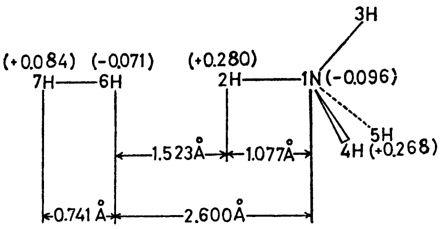

Fig. 11. The optimized configuration for the NH_4^+-H_2 system.

Thus, the NH_4^+–H_2 system is far from being a rigid complex. The two fragments, NH_4^+ and H_2, retain most of their individual integrity in the cluster. H_2 should be considered as distributed on a sphere about NH_4^+, with only a slight maximum probability at the calculated equilibrium configuration.

Configuration Analysis. Table 3 shows the results of the configuration analysis for the optimized configurations of the above systems. The values represent the weights (*i.e.*, the square of the coefficients in Eq. (2)) of the wavefunctions of various configurations. It can easily be seen that the more the weights of the charge transfer terms increase and that of the ground state decreases, the larger the stabilization energy appears, namely, the NH_4^+–H_2, the NH_4^+–CH_4, and the H_3O^+–CH_4 system, in order. The percentage contribution of the charge transfer term from the neutral molecule to the cation is particularly remarkable—that is, 1.47%, 7.22%, and 15.44% in the NH_4^+–H_2, NH_4^+–CH_4, and H_3O^+–CH_4 systems respectively, compared with the contributions from the other configurations. The weight of the polarization term of the cation is larger than that of the neutral molecule in the NH_4^+–CH_4 and H_3O^+–CH_4 system, while for the NH_4^+–H_2 system the weight in H_2 is 0.0030, surpassing that of NH_4^+.

In conclusion, it turns out that the previous results for these complexes obtained by the classical electrostatic method are deficient, since that method apparently

TABLE 3. THE WEIGHTS OF VARIOUS CONFIGURATIONS FOR EACH SYSTEM

Configurations	NH_4^+-CH_4	H_3O^+-CH_4	NH_4^+-H_2
Ground state	0.9130	0.8048	0.9797
Neutral→Cation charge transfer	0.0722	0.1544 (0.0074)[a]	0.0147
Cation→Neutral charge transfer	0.0049	0.0058	0.0022
Polarization of neutral molecule	0.0031	0.0089	0.0030
Polarization of cation	0.0044	0.0140	0.0002
Sum of the above values	0.9977	0.9964[b]	0.9999

a) Two-electron transfer configuration. b) All contributions from two-electron transfer are added.

neglects the charge transfer, which has a significant effect in stabilizing the complexes. On the contrary, the MO treatment allows us to predict the optimized configurations and display the essential factors which stabilize the complexes, as has been mentioned above. Lastly, it is interesting that the ion-molecule complexes reported here are held by a kind of hydrogen bond, X···H–Y, in which X represents a carbon atom, and Y, a nitrogen or an oxygen atom. Since the H bears most of the positive charge in the cation, this X···H–Y bond is strong enough to hold the complex, and it yields a larger interaction energy than those of the ordinary hydrogen bond systems. Either fragment of the systems treated here is able to rotate freely along the axis of the X···H–Y because of the dominance of the E_{XH} and E_{HY}-attractive energies, which are isotropic with regard to this type of rotation. Furthermore, in the NH_4^+–H_2 system H_2 would rotate three-dimensionally near NH_4^+, according to the CNDO/2 calculation. In the present calculation we have used the convenient semi-empirical MO method. An *ab initio* MO treatment for these complexes would be further expected.

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