Ab initio MO Study of Hydrogen Bonding and Spectral Characteristics of HCN-H₂O-HCN Trimer: Comparison between Dimer and Trimer

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Hydrogen bonding of HCN-H₂O-HCN trimer has been studied by means of ab initio molecular orbital (MO) calculations. The changes in intermolecular interaction energy and vibrational frequency induced by addition of HCN molecule to HCN-H₂O or H₂O-HCN dimer are especially focused. The distances of hydrogen bonds in the trimer are calculated to be shorter than those in the corresponding dimers. The hydrogen bond distances are hence shortened by addition of another HCN. The interaction energies of the hydrogen bonds are also increased by addition of HCN. The dipole moment of the trimer is smaller than the sum of the dipole moments of the separate moieties (HCN + H₂O + HCN). This is opposite of the previous result for H₂O-HCN-H₂O. The spectral shift of the stretching modes induced by hydrogen bond formation has been predicted by vibrational frequency analysis. The vibrational frequency of the asymmetric stretching mode of HCN included in the H₂O-HCN part of the trimer is remarkably red-shifted from that of the H₂O-HCN dimer. This information is expected to be useful for experimental detection of the trimer.

Key Words: HCN-H₂O-HCN trimer, hydrogen bonding, vibrational frequency, ab initio MO calculation

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Introduction

Complexes consisted of some small molecules formed by hydrogen bonding are of interest in various fields such as physical chemistry, geochemistry, astrochemistry, and biology. For example, complexes of hydrogen cyanide (HCN) and water (H₂O) are considered to play an important role in the formation of organic molecules on the ancient earth. These complexes are also important in the formation of interstellar molecules.

Studies on dimers consisted of HCN and H₂O have been reported by several authors from both experimental and theoretical viewpoints. For example, Gutowsky et al. reported the results of their microwave studies on H₂O-HCN dimer [1]. They measured the rotational constants of the dimer. Heikkilä et al. reported that H₂O-HCN dimer could be formed by 193 nm photolysis of matrix-isolated formamidoxime (CH₂NOH) in solid argon [2]. They also reported the theoretical results on the energetics of four isomers of the dimer (H₂O-HCN, H₂O-HNC, HCN-H₂O and HNC-H₂O). Rivelino and Canuto reported the results of theoretical analysis of H₂O-HCN and HCN-H₂O dimers [3]. They have analyzed the structures, binding energies and vibrational frequencies.

In contrast to the dimers, trimers consisted of H₂O and HCN have not been paid much attention. Rivelino and Canuto reported the theoretical results on binding energies of H₂O-HCN-H₂O trimer and H₂O-HCN-HCN-H₂O tetramer [4]. They have reported that the hydrogen bond distances of the O-H and N-H parts of the trimer are shorter than those of the corresponding dimers. The binding energies of the trimer are also larger than those of dimers. These results indicate that the original hydrogen bonds of the dimers are strengthened by the addition of another H₂O molecule. This kind of induction effect is often called "cooperative effect". However, no other trimers have been studied. Additionally, any experimental detection of trimers consisted of HCN and H₂O has not been succeeded. If HCN and H₂O can alternately bind to form larger polymeric complexes (...H₂O-HCN-H₂O-HCN...), knowledge of energetics of possible trimers and larger complexes is important to understand the structures and the formation mechanism of the polymeric complexes. As described above, the characteristics of H₂O-HCN-H₂O trimer has been studied. However, another alternately bound structure of trimer, i.e. HCN-H₂O-HCN, has not been studied. To experimentally detect the various trimers and larger complexes, their spectral features, especially the difference between the spectra of dimers and larger

complexes, should be known in advance.

In this study, the structure, binding energies and vibrational frequencies of HCN-H₂O-HCN trimer are studied by means of Møller-Plesset (MP) ab initio molecular orbital calculations. The change in the interaction between dimer and trimer induced by addition of an HCN molecule to dimers consisted of HCN and H₂O is investigated theoretically and compared with the effect on the hydrogen bonding of H₂O-HCN-H₂O reported previously. Mechanism of the effect is discussed on the basis of the analysis of atomic charge distribution. The harmonic vibrational frequencies of the trimer are calculated, and the infrared absorption (IR) spectrum of the trimer is simulated using the calculated frequencies. The information on the spectroscopic features of the trimer will be useful for experimental detection of the trimer.

Computational Methods

All calculations were done with the Gaussian 03 program package [5]. The optimized geometries, total energies, dipole moments and harmonic vibrational frequencies of the isolated molecules (H₂O and HCN), dimers (H₂O-HCN and HCN-H₂O) and trimer (HCN-H₂O-HCN) were calculated at the MP2 / 6-311++G(d,p) level of theory. The total energies were calculated also at the MP4SDQ / 6-311++G(d,p) // MP2/6-311++G(d,p) and MP4SDTQ / 6-311++G(d,p) // MP2 / 6-311++G(d,p) levels. Binding energies of the hydrogen bonds were calculated as the differences between the total energies of the complexes and the total energies of the separate moieties. The binding energies were corrected for basis set superposition error (BSSE) by counterpoise method [6]. NPA (Natural Population Analysis) atomic charge distributions were analyzed on the basis of calculations at the MP2 / 6-311++G(d,p) level. The IR spectra of the dimers and the trimer were visualized using the GaussView program [7] on the basis of the calculated vibrational frequencies.

Results and Discussion

Optimized structures and total energies of isolated molecules, dimers, and trimer

The structures of the isolated molecules, dimers, and trimer are shown in Fig. 1. The optimized geometrical parameters are listed in Table 1. The total energies of the dimers and trimer are summarized in Table 2. The two stable forms of the dimer are obtained; i.e. H₂O-HCN

with C_{2v} symmetry in which the two molecules are binding with O-H hydrogen bond, and HCN-H₂O with C_s symmetry in which the two molecules are binding with N-H hydrogen bond. The H₂O-HCN dimer is more stable in energy than the HCN-H₂O dimer. This agrees with the previous calculation reported by Rivelino and Canuto [3]. The structures of HCN and H₂O themselves are found to be hardly deformed by the complex formation, while when the trimer forms H-O-H angle is changed from 103.5° (free H₂O) to 108.6°.

The stable form of HCN-H₂O-HCN trimer is a bent one with C_s symmetry. The nitrogen atom of a HCN orients toward the hydrogen atom of central H₂O, and the hydrogen atom of another HCN orients toward the oxygen atom of H₂O. Comparing the hydrogen bond distances of the dimers and trimer, the distances of both hydrogen bonds of the trimer are found to be shorter than those of the corresponding dimers. The N-H and O-H hydrogen bond distances of the trimer are 2.117 and 2.064 Å, respectively. The corresponding distances of the dimers are 2.224 Å for HCN-H₂O and 2.130 Å for H₂O-HCN. The effect of HCN addition on the hydrogen bond distances is hence confirmed.

Fig. 1. Illustration of structures of isolated molecules (H₂O and HCN), dimers (H₂O-HCN and HCN-H₂O) and HCN-H₂O-HCN trimer. Atom labeling of the complexes has been defined to be common.

Hydrogen bond energies of N-H and O-H bonds of dimers and trimer

The hydrogen bond energies of the dimers and trimer are listed in Table 3. The hydrogen bond energies are calculated as the differences in the total energy of a

dimer or trimer and the total energies of the

Table 1. Optimized geometrical parameters for isolated molecules, dimers and trimer obtained at the MP2 / 6-311++G(d,p) level (r: bond length in Å, θ : bond angle in degree)

H ₂ O (symmetry: C_{2v})	
r(O-H)	0.959
θ (H-O-H)	103.5
HCN (symmetry: $C_{\infty v}$)	
r(C-H)	1.068
r(C-N)	1.171
θ (H-C-N)	180.0
H ₂ O-HCN (symmetry: C_{2v})	
r(O5-H4)	0.960
r(O5-H6)	0.960
r(O5-H7)	2.130
r(C8-H7)	1.075
r(C8-N9)	1.172
θ (H4-O5-H6)	104.0
θ (H7-C8-N9)	179.7
θ (H6-O5-H7)	127.9
HCN-H ₂ O (symmetry: C_s)	
r(C2-H1)	1.068
r(C2-N3)	1.170
r(N3-H4)	2.224
r(O5-H4)	0.963
r(O5-H6)	0.959
θ (H1-C2-N3)	179.7
θ (C2-N3-H4)	167.8
θ (N3-H4-O5)	179.2
θ (H4-O5-H6)	103.2
HCN-H ₂ O-HCN (symmetry: C_s)	
r(C2-H1)	1.069
r(C2-N3)	1.169
r(N3-H4)	2.117
r(O5-H4)	0.965
r(O5-H6)	0.959
r(O5-H7)	2.064
r(C8-H7)	1.077
r(C8-N9)	1.072
θ (H1-C2-N3)	180.0
θ (C2-N3-H4)	169.0
θ (N3-H4-O5)	169.8
θ (H4-O5-H6)	108.6
θ (H6-O5-H7)	119.3
θ (O5-H7-C8)	178.0
θ (H7-C8-N9)	180.0

Table 2. Total energies of isolated molecules, dimers and trimer (in Hartree)

Specie	MP2	MP4SDQ	MP4SDTQ
HCN	-93.203290	-93.209724	-93.226962
H ₂ O	-76.274972	-76.281474	-76.287305
H ₂ O-HCN	-169.485984	-169.498518	-169.521821
HCN-H ₂ O	-169.483912	-169.496282	-169.519737
trimer	-262.697391	-262.715616	-262.756603

corresponding separate moieties. The equations for the calculation of hydrogen bond energies are as follows.

For dimer:

$$E_{\text{HB}}(\text{N-H}) = E(\text{HCN-H}_2\text{O}) - \{ E(\text{H}_2\text{O}) + E(\text{HCN}) \}$$

$$E_{\text{HB}}(\text{O-H}) = E(\text{H}_2\text{O-HCN}) - \{ E(\text{H}_2\text{O}) + E(\text{HCN}) \}$$

For trimer:

$$E_{\text{HB}}(\text{N-H}) = E(\text{HCN-H}_2\text{O-HCN}) - \{ E(\text{H}_2\text{O-HCN}) + E(\text{HCN}) \}$$

$$E_{\text{HB}}(\text{O-H}) = E(\text{HCN-H}_2\text{O-HCN}) - \{ E(\text{HCN-H}_2\text{O}) + E(\text{HCN}) \}$$

where E_{HB} stands for the hydrogen bond energies ($E_{\text{HB}}(\text{N-H})$ and $E_{\text{HB}}(\text{O-H})$ corresponds to the energies of N-H and O-H hydrogen bonds, respectively), and E stands for the total energies of the species indicated in their parenthesis.

The similar tendency for the hydrogen bond energies is commonly observed by the calculations at the MP2, MP4SDQ and MP4SDTQ levels of theory; the O-H and N-H hydrogen bond energies of the trimer are higher than the energies of the corresponding dimers. The N-H and O-H hydrogen bond energies of the trimer are calculated to be $E_{\text{HB}}(\text{N-H}) = 19.36 - 21.31 \text{ kJ mol}^{-1}$ and $E_{\text{HB}}(\text{O-H}) = 25.23 - 26.75 \text{ kJ mol}^{-1}$, respectively. The hydrogen bond energies of the corresponding dimers are calculated to be $E_{\text{HB}}(\text{N-H}) = 13.35 - 14.83 \text{ kJ mol}^{-1}$ and $E_{\text{HB}}(\text{O-H}) = 19.22 - 20.27 \text{ kJ mol}^{-1}$. Hence a HCN is bound more strongly to the dimers rather than to isolated H₂O with either N-H or O-H bond. Comparing the total energies of two dimers, it is found that H₂O-HCN is stable one and N-H hydrogen bond is newly formed when the trimer forms. The results of E_{HB} show that this N-H bond formation strengthens both of the O-H and N-H hydrogen bonds of the trimer. This result suggests that the trimer can exist as a stable form of the complex containing HCN and H₂O.

In the Table 3 the difference in the hydrogen bond energy between dimers and trimer E_{add} are also listed. The E_{add} are defined as

$$E_{\text{add}}(\text{N-H}) = \{ E_{\text{HB}}(\text{N-H}) \text{ of HCN-H}_2\text{O-HCN} \} - \{ E_{\text{HB}}(\text{N-H}) \text{ of HCN-H}_2\text{O} \}$$

$$E_{\text{add}}(\text{O-H}) = \{ E_{\text{HB}}(\text{O-H}) \text{ of HCN-H}_2\text{O-HCN} \} - \{ E_{\text{HB}}(\text{O-H}) \text{ of H}_2\text{O-HCN} \}$$

Table 3. Hydrogen bond energies E_{HB} of dimers and trimer and difference in hydrogen bond energy E_{add} (in kJ mol^{-1})

	MP2	MP4SDQ	MP4SDTQ
$E_{\text{HB}}(\text{O-H})$			
H ₂ O-HCN	-20.27	-19.22	-19.83
HCN-H ₂ O-HCN	-26.75	-25.23	-26.00
$E_{\text{HB}}(\text{N-H})$			
HCN-H ₂ O	-14.83	-13.35	-14.36
HCN-H ₂ O-HCN	-21.31	-19.36	-20.53
E_{add}	-6.48	-6.01	-6.17

Table 4. NPA atomic charges of isolated molecules, dimers and trimer obtained at the MP2 / 6-311++G(d,p) level

	Atomic charge
free H ₂ O	
H4	+0.447
O5	-0.894
H6	+0.447
free HCN	
H1, H7	+0.207
C2, C8	+0.092
N3, N9	-0.300
H ₂ O-HCN	
H4	+0.463
O5	-0.913
H6	+0.463
H7	+0.232
C8	+0.082
N9	-0.326
HCN-H ₂ O	
H1	+0.213
C2	+0.127
N3	-0.337
H4	+0.468
O5	-0.914
H6	+0.442
HCN-H ₂ O-HCN	
H1	+0.216
C2	+0.142
N3	-0.350
H4	+0.486
O5	-0.935
H6	+0.458
H7	+0.238
C8	+0.083
N9	-0.337

The E_{add} corresponds to the change of E_{HB} induced by addition of an HCN molecule to another side. The values of E_{add} are calculated to be $6.01 - 6.48 \text{ kJ mol}^{-1}$. The $E_{\text{add}}(\text{N-H})$ and $E_{\text{add}}(\text{O-H})$ calculated at the same level of theory are equal to each other. These results of E_{add} also support the formation of the trimer as a stable complex. This effect of HCN molecule on the hydrogen bond energy seems to be more significant than the effect of H_2O molecule reported previously [4], but the mechanism of the difference in the effect of HCN and H_2O will be a subject for further research.

Atomic charge distributions of isolated molecules, dimers, and trimer

The NPA atomic charges on atoms of the isolated molecules, dimers, and trimer obtained at the MP2 level are listed in Table 4. The positive charge on H atom included in N-H hydrogen bond of the trimer (H4, +0.486) is larger than that of $\text{HCN-H}_2\text{O}$ (+0.468). Similarly, the positive charge on H atom included in O-H bond (H7, +0.238) is larger than that of $\text{H}_2\text{O-HCN}$ (+0.232). The negative charges on N and H atoms included in these hydrogen bonds are larger than those of the corresponding dimers. From these results, it is found that charge separation between the atoms joining in the hydrogen bonds is more significant for trimer. This local charge redistribution seems to be the origin of the effect of molecule addition on hydrogen bonding.

Spectral shifts induced by complex formation

To obtain the simulated IR spectra of the complexes consisted of H_2O and HCN, harmonic vibrational frequency analysis was performed and the spectra of the dimers and trimer were visualized using the calculation results. For all optimized structures, no imaginary frequency was found; the obtained optimized structures were confirmed to be stable ones. Here, the asymmetric and symmetric stretching modes of HCN moiety are especially focused. To predict experimentally expected vibrational frequencies, the frequencies calculated at the MP2 / 6-311++G(d,p) level were scaled using the scaling factor of 0.9502 reported by Irikura et al [8]. This factor is the value reported for MP2 / 6-311G(d,p) calculation and the value for MP2 / 6-311++G(d,p) calculation has not been reported. However, Irikura et al. reported that the scaling factor does not significantly depend on the basis set used. On the basis of this conclusion, we used the value for MP2 / 6-311G(d,p) calculation in this study.

The vibrational frequencies of the HCN asymmetric and symmetric stretching modes of $\text{HCN-H}_2\text{O}$ are 3307 (asymmetric mode) and 1930 (symmetric mode) cm^{-1} ;

Table 5. Harmonic vibrational frequencies of symmetric and asymmetric stretching modes of HCN included in dimers and trimer obtained at the MP2 / 6-311++G(d,p) level (in cm^{-1}) ^{a)}

	$\text{H}_2\text{O-HCNHCN-H}_2\text{O}$	$\text{HCN-H}_2\text{O-HCN}$
symmetric stretching		
H1-C2-N3	2031(1930)	2036(1935)
H7-C8-N9	2015(1915)	2015(1915)
asymmetric stretching		
H1-C2-N3	3480(3307)	3480(3307)
H7-C8-N9	3392(3223)	3358(3191)

a) Both the vibrational frequencies before and after scaling are listed. The frequencies indicated in the parenthesis are the values after scaling. The scale factor used is 0.9502.

Fig. 2. Simulated IR spectra of dimers and trimer: (a) $\text{HCN-H}_2\text{O}$ dimer, (b) $\text{H}_2\text{O-HCN}$ dimer and (c) $\text{HCN-H}_2\text{O-HCN}$ trimer. The vertical axis corresponds to the infrared absorbance (in arbitrary unit). In this figure, the values of the frequencies before scaling are shown.

the frequencies for H₂O-HCN are 3223 and 1915 cm⁻¹. When HCN-H₂O-HCN trimer is formed by addition of H₂O or HCN to the dimers, the frequencies of the symmetric stretching of HCN moiety are almost equal to that of the corresponding dimer. For HCN-H₂O, the frequency is calculated to be 1930 (dimer) and 1935 (trimer) cm⁻¹; for H₂O-HCN, the frequency is 1915 (both dimer and trimer) cm⁻¹. The frequency of the asymmetric stretching of HCN-H₂O is also kept constant. In contrast, the frequency of the asymmetric stretching of H₂O-HCN moiety is red-shifted by the trimer formation. For H₂O-HCN dimer, the frequency is 3223 cm⁻¹. When HCN-H₂O-HCN trimer is formed, the frequency is remarkably shifted to 3191 cm⁻¹. These results are summarized in Table 5. This red-shift can be understood on the basis of electron transfer from HCN-H₂O moiety to an antibonding orbital of HCN of H₂O-HCN moiety; when trimer is formed by addition of HCN to H₂O-HCN dimer, negative charge on HCN of H₂O-HCN increases (-0.013 → -0.016), while positive charge on H₂O decreases (+0.013 → +0.009). HCN of HCN-H₂O side is positively charged (0 → +0.008). These results means that HCN at H₂O-HCN side gains electron from HCN-H₂O moiety and the electron occupies the antibonding orbital of HCN. This would be the origin of the spectral shift.

The simulated IR spectra of the dimers and the trimer visualized using the GaussView program are shown in Fig. 2. In the spectra of the dimers, intense absorption peaks based on the asymmetric stretching mode of H₂O-HCN are clearly confirmed. On the other hand, the absorption bands based on the symmetric stretching are quite weak. In the spectra of the trimer, the red-shift of the asymmetric stretching band of H₂O-HCN described above can be confirmed. This shift will be a useful evidence for the detection of trimer because observation of the red-shift of the large absorption band will be easily done by means of high-resolution IR measurement using rare-gas matrix. The experimental detection of trimer has not been achieved at the moment; although the IR spectra of dimers have been measured previously by matrix isolation technique [2], the spectra of trimers (HCN-H₂O-HCN, H₂O-HCN-H₂O, etc.) and larger complexes have not been known. However, judging from the present results on hydrogen bond energies, trimer will exist as a stable form and the observation of trimer will be revealed by accurate measurements of IR spectra employing matrix isolation technique and novel experimental conditions for generation of the trimers. The authors believe that the results of this study will be experimentally applied in the future.

Concluding remarks

The findings obtained in this study can be summarized as follows:

- (1) The effect of HCN addition on hydrogen bonding between H₂O and HCN has been found by the present calculations. The hydrogen bonds of H₂O-HCN and HCN-H₂O dimers are strengthened by addition of another HCN and their bond distances are shortened. This result indicates that the trimer can exist as a stable complex. This effect would be due to the local charge redistribution induced by trimer formation.
- (2) The asymmetric stretching mode of HCN included in H₂O-HCN is remarkably red-shifted when the trimer is formed; the absorption based on the HCN asymmetric stretching of H₂O-HCN of trimer appears at the lower frequency than the corresponding dimers. This information on the spectral shift is useful for the experimental detection of the trimer that has not been achieved at the moment.

The similar investigation on larger complexes will be interesting; the alternate complexes consisted of H₂O and HCN can exist also as cyclic ones and their effects of molecule addition on the cyclic hydrogen bonding are still ambiguous. Polymer chain consisted of many HCN and H₂O molecules may also be able to form. Molecular orbital calculation results on the effects of molecule addition and IR spectra for larger (linear and cyclic) complexes will be reported in the future.

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References and Notes

- [1] H. S. Gutowsky, T. C. Germann, J. D. Augspurger, C. E. Dykstra, *J. Chem. Phys.*, **96**, 5808 – 5816 (1992).
- [2] A. Heikkilä, M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *J. Phys. Chem. A*, **103**, 2945 – 2951 (1999).
- [3] R. Rivelino, S. Canuto, *Chem. Phys. Lett.*, **322**, 207 – 212 (2000).
- [4] R. Rivelino, S. Canuto, *J. Phys. Chem. A*, **105**, 11260 – 11265 (2001).
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.

- Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucchi, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03 Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.
- [6] S. F. Boys, F. Bernaldi, *Mol. Phys.*, **19**, 553 – 566 (1970).
- [7] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, GaussView Version 3.09, Semichem, Inc., Shawnee Mission, KS, 2007.
- [8] K. K. Irikura, R. D. Johnson III, R. N. Kacker, *J. Phys. Chem. A*, **109**, 8430 – 8437 (2005).

ab initio分子軌道法によるHCN-H₂O-HCN 3 量体の水素結合とスペクトルに関する研究：2 量体と 3 量体の比較

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H₂OとHCNからなる錯体については、2 量体 (H₂O-HCNおよびHCN-H₂O) は低温マトリックス中での実験的観測に成功しているが、それよりも大きな多量体については観測例がない。本研究では、H₂OとHCNからなる 3 量体の実験的観測のための基礎的知見を得るために、HCN-H₂O-HCN 3 量体の水素結合および赤外吸収 (IR) スペクトルについてab initio分子軌道法により研究した。本研究では特に、H₂O-HCNおよびHCN-H₂O 2 量体へのHCN付加による分子間相互作用エネルギーおよび振動数の変化に注目した。3 量体の水素結合距離は、O-HおよびN-Hのいずれの水素結合においてもそれぞれ対応する 2 量体の水素結合距離よりも短く、水素結合エネルギーも 3 量体のほうが大きいことがわかった。従って、実験的な観測例はないものの、H₂OとHCNの 3 量体は安定に存在し得るものと予想される。振動数解析により 2 量体と 3 量体のHCNの伸縮振動モードの振動数を比較したところ、対称伸縮モードについては 2 量体と 3 量体ではほぼ等しく、非対称伸縮モードについてもHCN-H₂O 2 量体とこれに対応する 3 量体のHCNではほぼ等しかった。対照的に、H₂O-HCN 2 量体とこれに対応する 3 量体のHCNの非対称伸縮モードの比較では、3 量体の形成 (HCNの付加) に伴う顕著なレッドシフトが確認できた。この結果は、3 量体の実験的観測のための有効な情報となると期待される。

キーワード: HCN-H₂O-HCN 3 量体, 水素結合, 振動数, ab initio分子軌道計算

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