Ab initio MO Study of Hydrogen Bonding and Spectral Characteristics of HCN-H$_2$O-HCN Trimer: Comparison between Dimer and Trimer

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Hydrogen bonding of HCN-H$_2$O-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-H$_2$O or H$_2$O-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 + H$_2$O + HCN). This is opposite of the previous result for H$_2$O-HCN-H$_2$O. 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 H$_2$O-HCN part of the trimer is remarkably red-shifted from that of the H$_2$O-HCN dimer. This information is expected to be useful for experimental detection of the trimer.

Key Words: HCN-H$_2$O-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-H_2O with C_{s} symmetry in which the two molecules are binding with N-H hydrogen bond. The H_2O-HCN dimer is more stable in energy than the HCN-H_2O dimer. This agrees with the previous calculation reported by Rivelino and Canuto [3]. The structures of HCN and H_2O 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 H_2O) to 108.6°.

The stable form of HCN-H_2O-HCN trimer is a bent one with C_{s} symmetry. The nitrogen atom of a HCN orients toward the hydrogen atom of central H_2O, and the hydrogen atom of another HCN orients toward the oxygen atom of H_2O. 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-H_2O and 2.130 Å for H_2O-HCN. The effect of HCN addition on the hydrogen bond distances is hence confirmed.

**Fig. 1.** Illustration of structures of isolated molecules (H_2O and HCN ), dimers (H_2O-HCN and HCN-H_2O ) and HCN-H_2O-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

|        | H\_2O (symmetry: C\_2v) | H\_2O (symmetry: C\_2v) |
|--------|-------------------------|-------------------------|
| r(O-H) | 0.995                   | 0.995                   |
| \(\theta\) (H-O-H) | 103.5                  | 103.5                  |

|        | HCN (symmetry: C\_s) |
|--------|----------------------|
| r(C-H) | 1.068                |
| r(C-N) | 1.171                |
| \(\theta\) (H-C-N) | 180.0                |

|        | H\_2O-HCN (symmetry: C\_2v) |
|--------|-----------------------------|
| r(O5-H4) | 0.960                       |
| r(O5-H6) | 0.960                       |
| r(O5-H7) | 2.130                       |
| r(C8-H7) | 1.075                       |
| \(\theta\) (H6bO5bH7) | 119.3                  |
| \(\theta\) (O5bH7bC8) | 178.0                  |
| \(\theta\) (H7bC8bN9) | 180.0                  |

|        | HCN-H\_2O (symmetry: C\_s) |
|--------|-----------------------------|
| r(C2-H1) | 1.069                       |
| r(C2-N3) | 1.170                       |
| r(N3-H4) | 2.224                       |
| r(O5-H4) | 0.963                       |
| r(O5-H6) | 0.959                       |
| \(\theta\) (C2bN3bH4) | 167.8                  |
| \(\theta\) (N3bH4bO5) | 179.2                  |

|        | HCN-H\_2O-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                       |
| \(\theta\) (H6bO5bH7) | 119.3                  |
| \(\theta\) (O5bH7bC8) | 178.0                  |
| \(\theta\) (H7bC8bN9) | 180.0                  |

|        | H\_2O (symmetry: C\_2v) |
|--------|-------------------------|
| r(O-H) | 0.959                   |
| \(\theta\) (H-O-H) | 103.5                  |
| HCN (symmetry: C\_s) |
| r(C-H) | 1.068                |
| r(C-N) | 1.171                |
| \(\theta\) (H-C-N) | 180.0                |
| H\_2O-HCN (symmetry: C\_2v) |
| r(O5-H4) | 0.960                       |
| r(O5-H6) | 0.960                       |
| r(O5-H7) | 2.130                       |
| r(C8-H7) | 1.075                       |
| \(\theta\) (H6bO5bH7) | 119.3                  |
| \(\theta\) (O5bH7bC8) | 178.0                  |
| \(\theta\) (H7bC8bN9) | 180.0                  |

**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, \(\theta\): bond angle in degree)
Table 2. Total energies of isolated molecules, dimers and trimer (in Hartree)

| Specie         | MP2        | MP4SDQ      | MP4SDTQ     |
|----------------|------------|-------------|-------------|
| HCN            | –93.203290 | –93.209724  | –93.226962  |
| H₂O            | –76.274972 | –76.281474  | –76.287305  |
| H₂O-HCN        | –169.485984| –169.498518 | –169.521821 |
| HCN-H₂O        | –169.483912| –169.496282 | –169.519737 |
| trimer         | –262.697391| –262.715616 | –262.756603 |

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 \( E_{\text{HB}}(\text{N-H}) = 19.36 - 21.31 \) kJ mol\(^{-1}\) and \( E_{\text{HB}}(\text{O-H}) = 25.23 - 26.75 \) kJ mol\(^{-1}\), respectively. The hydrogen bond energies of the corresponding dimers are calculated to be \( E_{\text{HB}}(\text{N-H}) = 13.35 - 14.83 \) kJ mol\(^{-1}\) and \( E_{\text{HB}}(\text{O-H}) = 19.22 - 20.27 \) 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 \( E_{\text{HB}} \) 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 \( E_{\text{add}} \) are also listed. The \( E_{\text{add}} \) are defined as

\[
E_{\text{add}}(\text{N-H}) = E_{\text{HB}}(\text{N-H}) \text{ of HCN-H₂O-HCN} - E_{\text{HB}}(\text{N-H}) \text{ of HCN-H₂O} \\
E_{\text{add}}(\text{O-H}) = E_{\text{HB}}(\text{O-H}) \text{ of HCN-H₂O-HCN} - E_{\text{HB}}(\text{O-H}) \text{ of H₂O-HCN}
\]
The $E_{\text{add}}$ corresponds to the change of $E_{\text{HH}}$ induced by addition of an HCN molecule to another side. The values of $E_{\text{add}}$ are calculated to be 6.01 – 6.48 kJ mol$^{-1}$. The $E_{\text{add}}$(N-H) and $E_{\text{add}}$(O-H) calculated at the same level of theory are equal to each other. These results of $E_{\text{add}}$ 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$_2$O molecule reported previously [4], but the mechanism of the difference in the effect of HCN and H$_2$O 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 HCN-H$_2$O (+0.468). Similarly, the positive charge on H atom included in O-H bond (H7, +0.238) is larger than that of H$_2$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$_2$O 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 HCN-H$_2$O are 3307 (asymmetric mode) and 1930 (symmetric mode) cm$^{-1}$;
the frequencies for $\text{H}_2\text{O}-\text{HCN}$ are 3223 and 1915 cm$^{-1}$. When HCN-$\text{H}_2\text{O}$-$\text{HCN}$ trimer is formed by addition of H$_2$O 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-$\text{H}_2\text{O}$, the frequency is calculated to be 1930 (dimer) and 1935 (trimer) cm$^{-1}$; for H$_2$O-HCN, the frequency is 1915 (both dimer and trimer) cm$^{-1}$. The frequency of the asymmetric stretching band of HCN-$\text{H}_2\text{O}$ is also kept constant. In contrast, the frequency of the asymmetric stretching of H$_2$O-HCN moiety is red-shifted by the trimer formation. For H$_2$O-HCN dimer, the frequency is 3223 cm$^{-1}$. When HCN-H$_2$O-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-$\text{H}_2\text{O}$ moiety to an antibonding orbital of HCN of H$_2$O-HCN moiety; when trimer is formed by addition of HCN to H$_2$O-HCN dimer, negative charge on HCN of H$_2$O-HCN increases (–0.013 → –0.016), while positive charge on H$_2$O decreases (+0.013 → +0.009). HCN of H$_2$O-H$_2$O side is positively charged (0 → +0.008). These results mean that HCN at H$_2$O-HCN side gains electron from HCN-$\text{H}_2\text{O}$ 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 H$_2$O-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 H$_2$O-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-$\text{H}_2\text{O}$-$\text{HCN}$, H$_2$O-HCN-H$_2$O, 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 H$_2$O and HCN has been found by the present calculations. The hydrogen bonds of H$_2$O-HCN and HCN-$\text{H}_2\text{O}$ 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 H$_2$O-HCN is remarkably red-shifted when the trimer is formed; the absorption based on the HCN asymmetric stretching of H$_2$O-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 H$_2$O 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 H$_2$O 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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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4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、実験的な観測例がないものの、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り期待される。

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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