Hydrogen bonding interaction of small acetaldehyde clusters studied with core-electron excitation spectroscopy in the oxygen K-edge region

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Abstract. In order to examine inner-shell electron excitation spectra of molecular clusters with strong multipole interactions, excitation spectra and time-of-flight (TOF) fragment-mass spectra of small acetaldehyde (AA) clusters have been studied under the beam conditions. The TOF spectra at the oxygen K-edge region showed an intense growth of the protonated clusters, MnH+ (M=CH3CHO) in the cluster beams. "cluster-specific" excitation spectra could be generated by monitoring partial-ion-yields of the protonated clusters. The most intense band of O1s→π*CO was found to shift to a higher energy by 0.15 eV relative to the monomer band upon clusterization. X-ray absorption spectra (XAS) were also calculated for the representative dimer configurations using a computer modelling program based on the density functional theory. The XAS prediction for the most stable (non-planar) configuration was found to give a close comparison with the cluster-band shift observed. The band shift was interpreted as being due to the HOMO−LUMO interaction within the complex where a contribution of vibrationally blue-shifting hydrogen bonding could be identified.

1. Introduction

Using a synchrotron radiation source, we previously observed inner-shell excitation spectra of formic-acid (HC(O)OH) molecules and small clusters [1] in the beam conditions, and obtained new spectroscopic findings on the local hydrogen bonding (HB) interaction within the molecular clusters as well as fragmentation mechanism upon HB cluster formation. Formic-acid has two oxygen sites available for the strong H-bond formation and forms a stable cyclic-dimer configuration in the gas phase with doubly bridged H-bonds with a binding energy of ~15 kcal/mol [1,2]. The configuration is exclusively the most stable unit-structure among the formic-acid complexes, it may provide the major source of building blocks for the cluster formation. By monitoring partial-ion-yields (PIYs) of the cluster-origin products upon O1s excitation, “cluster-specific” excitation spectra with no contribution

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from molecular excitation could be studied. Comparison of the cluster bands with those of molecular formic-acid showed that the first resonance O1s→π*CO band shifts upwards (to a higher energy) by ~0.31 eV whereas the second O1sOH→π*CO band shifts downwards by ~0.82 eV. The band shifts of the core-to-valence transitions in the clusters have been interpreted as being due to the change in core electron binding energy (CEBE) of the oxygen atoms upon HB formation. The O1sCO/O1sOH→π*CO band-shifts of the formic-acid clusters have been well supported by a recent density functional theory (DFT) calculation [3].

Acetaldehyde (AA) has a simple structure of C₃ symmetry and a high dipole moment, larger than those of typical polar solvents such as water and methanol [4]. Although AA has both hydrogen donor C and lone-pair acceptor O sites within the molecule, strong H-bonds such as the O−H···O are not expected in neutral cluster species. In the case of A−H···O for comparison, strengths of H-bond donor are qualitatively characterized as the differences in electronegativities of the constituent atoms in the associated A−H covalent bond, leading to the classification as F−H > O−H > N−H > C−H [5]. It is thus natural to postulate that the overall structures of small AA clusters are considered as being largely determined by the strong multipole interactions. Governed by such electrostatic interactions, it can be assumed to constitute nearly anti-parallel dimer configurations within the AA clusters.

Here, we have extended inner-shell excitation studies to small acetaldehyde (AA) clusters in the oxygen K-edge region, then the effects of such intermolecular interactions on the excitation spectra upon clusterization have been examined. The band-shift of core-to-valence O1s→π*CO transition observed in the small AA clusters was also compared with those predicted by the DFT calculation using a computer modeling program [6].

2. Experiments and theoretical calculations
The experiments were carried out in a cluster beam-photoreactive scattering apparatus [7] mounted toa plane-grating monochromator on the soft X-ray beam line BL-6 of the HiSOR facility at Hiroshima University. Two types of sample beams were used; cluster and effusive beams. The cluster beams were generated by supersonic expansion of gaseous mixtures of 1.7−5.0%AA/He via a φ 50 μm nozzle, under the stagnation pressures up to 0.3 MPa. The mixtures were prepared by bubbling the He gas through a liquid sample in a cylinder. An effusive beam was prepared by direct introduction of neat AA under the stagnation pressure of P₀ = ~5.0 kPa through a φ 200μm nozzle. The stagnation pressures were kept constant by immersing the sample cylinder in a thermostated refrigerant. Either beam was collimated with a φ 1.0mm skimmer and allowed to enter the scattering chamber of the apparatus, where it was crossed with a monochromatized soft X-ray beam at the ionization region of a Wiley–MacLaren type [8] TOF spectrometer. Photoelectron-photoion coincidence (PEPICO) signals were recorded using a fast multihit digitizer with a time resolution typically set to 4 ns. The photon energy was calibrated using the O1s→4p/5s Rydberg transition of CO₂ at 540.01 eV [9]. The resolution of the monochromator was E/ΔE ≥ 2000 at the energy corresponding to the oxygen K-edge. Details of the procedure have been described elsewhere [7].

Acetaldehyde (AA: CH₃CHO) was supplied by Aldrich at a purity of ≥ 99.5% and helium by Nihon-Sanso at ≥ 99.99%. They were used without further purification.

In order to examine the molecular configurations and intermolecular interactions within the AA clusters and support the analysis of core-excitation spectra, ab initio molecular orbital (MO) and DFT calculations were carried out for the AA molecule and clusters. Initial geometries of the system were optimized using the Gaussian 03 program [10] at the MP2/cc-pVTZ level of approximation. Vibrational frequencies were calculated at the same level to confirm their stationary structures and correct the zero-point vibrational energies (ZPVEs). The frequencies were further scaled [11,12] with multiplying by 0.9832 after the MP2 calculations. The basis set superposition error (BSSE) was corrected using the procedures proposed by Boys-Bernardi [13] to estimate the stabilization energies of the clusters.
The calculation of core-excited states was performed with the StoBe-deMon code [6], based on a solution of the Kohn–Sham DFT equations. The theoretical X-ray absorption spectra (XAS) were generated by the transition potential (TP) method combined with a double basis set technique. The orbital energies and oscillator strengths were calculated to obtain the transition energies and absorption intensities in the theoretical XA spectrum. The TP method describes most of the relaxation effects on core-excitation states and provides a single set of orthogonal orbitals for the spectrum calculation. In determining the absolute energy positions of the XA spectrum, ∆Kohn–Sham calculations [14] that allow the full relaxation of core-hole ionization states were performed to derive the ionization energy (IP). The relativistic correction of 0.33 eV [15,16] was added to the IP of the O1s electrons. Electron interactions of C and O atoms without any core-electron excitation (core-hole) were described with effective core potentials. The ionized center was described using the IGLO-III basis of Kutzelnigg et al. [17], whereas (6311/311/1) and (311/1) basis sets were used for the other heavy atoms and hydrogen atoms. The spectrum was generated by a Gaussian convolution of discrete transition lines by adjusting their broadenings to simulate the experimental spectrum. All DFT calculations were performed using the gradient-corrected exchange and correction functionals developed by Perdew and Wang [18,19]. Further details of the calculations have been given elsewhere [14,20].

3. Results and Discussion

3.1. Core-electron excitation measurements of AA molecule and clusters at the oxygen K-edge

![Figure 1](#)

**Figure 1.** (a) TIY overview spectra of AA molecule (top trace) and clusters (lower three traces) under the stagnation conditions designated in the figure. The band assignment is given in Table 1. (b) Comparison of the PIY spectra between monomer-origin (C⁺, C₂⁺) and cluster-origin (MH⁺, M₂H⁺) products at the O1s→π⁺CO band.

**Figure 1(a)** shows the typical overview total-ion-yield (TIY) spectra of AA molecule and clusters observed under the beam conditions, recorded in the 528–550 eV excitation energy range that covers oxygen K-edge transitions. Publications on the X-ray absorption and excitation spectra of free AA molecule are available in the ISEELS [21] and NEXAFS [22] measurements. The oxygen K-edge excitation of AA involves the electron transition from the oxygen −C=O site. Its CEBE has been determined in the X-ray photoelectron spectroscopy [23,24]. Based on the Gaussian deconvolution analysis and previous band assignments, we reassigned the O1s excitation bands from the TIY of AA as listed in Table 1. In our measurement, closer agreement of the band energies could be obtained with those by Hitchcock and Brion [21]. When comparison of the TIYs in the cluster beams was made with that in the effusive beam, no definite change of the cluster band features for the Rydberg transitions could be admitted under the stagnation pressures up to $P_0 = 0.3$ MPa, although they are
weak and there appears some smoothness in the cluster bands. This is partly because cluster beams are in the small cluster regime where the beams contain significant amounts of uncondensed free molecules as well as the clusters of small sizes.

In the TOF fragment-mass measurements of cluster beams, we observed an intense series of protonated clusters $M_nH^+$ ($M=\text{CH}_3\text{CHO}$) under the beam stagnation conditions shown in Figure 1(a). The pressure variation of the product distributions important for the beam characterization has been recently described [25]. It should be added here that, in the effusive beam, trace amounts of $\text{MH}^+$ above the background TOF level could be singly identified as the cluster-origin product. Atomic and smaller fragments such as $\text{C}^+$, $\text{O}^+$, and $\text{C}_2^+$ in the cluster beam show a TOF pattern similar to that of the effusive beam, indicating that they are substantially free AA origin since the beam is again in the small cluster regime. By monitoring the PIY intensities of the $M_nH^+$ products originating from the clusters, “cluster-specific” excitation spectra could be recorded without any contribution of free molecules. In contrast, the PIYs of atomic and small fragments actually have the same band-peak energy as that observed in TIY of the effusive beam, it is thus reasonable to conclude that they come from free AA molecules. Figure 1(b) compares the PIY spectra of the $\text{O}_1s \rightarrow \pi^*_\text{CO}$ band for the monomer- and cluster-origin cations simultaneously obtained at the same energy points under the lowest stagnation pressure of $P_0 = 0.1$ MPa. We chose the cluster beam condition of $P_0 = 0.1$ MPa since it provides as small cluster size distribution as possible. Since exclusive intensity of the $\text{MH}^+$ product has been observed over the $M_3\text{H}^+$ and $M_2\text{H}^+(\approx 0)$, it is natural to postulated that the cluster beam at $P_0 = 0.1$ MPa has a smallest cluster size distribution with prominent dimer-contribution. The “cluster-specific” band position was determined with the aid of the deconvolution analysis [26]. A least squares Gaussian-curve fitting of the monomer- and cluster-bands at $P_0 = 0.1$ MPa showed that the cluster $\text{O}_1s \rightarrow \pi^*_\text{CO}$ band is broadened slightly and shifted to a higher energy by 0.154 ± 0.010 eV relative to the monomer band. While we tried to examine the upper PIY bands (Rydberg transitions) other than the $\text{O}_1s \rightarrow \pi^*_\text{CO}$, reliable data on the relative change of the bands could not be extracted due to low oscillator strengths.

### Table 1. Band assignment of acetaldehyde molecule in the oxygen K-shell region.

| Band No. | Photon energy $E$ / eV | Assignment |
|----------|------------------------|------------|
| 1 | 531.02 | 531.53 (+0.51) | 531.14 (+0.12) | $\pi^*_\text{CO}$ |
| 2 | 535.03 | 535.42 (+0.39) | 535.10 (+0.07) | 3s$a'$ |
| 3 | 535.81 | 536.32 (+0.51) | 535.84 (+0.03) | 3p |
| 4 | 536.77 | 537.05 (+0.28) | 536.68 (-0.09) | 4s |
| 5 | 538.58$^c$ | 538.58$^c$ | 538.43$^a$ | IP |
| 6 | 541.34 | 541.0±0.3 | 542.0 | double exc. |
| 7 | 547.56 | 545.2±0.3 | 544.5 | $\sigma^*_{\text{CO}}$ |

$^a$Prince K C et al. (Ref. [18])

$^b$Hitchcock A P and Brion C E (Ref. [19])

$^c$Jolly W L, Bomben K D and Eyerman C J (Ref. [20])

$^d$Jolly W L and Schaaaf T F (Ref. [21])

### 3.2. Computer simulation of XA spectra of AA molecule and dimers derived by DFT calculations

In order to compare the experimental results with the theoretical expectations, and to give an interpretation for the energy shift of the “cluster-specific” $\text{O}_1s \rightarrow \pi^*$ band from the “monomer” band, some model XA spectra were generated for the representative (AA)$_2$ dimers using the DFT calculation, since the experimental cluster band was recorded under the smallest cluster regime of beam conditions. Examples of the dimer configuration are shown in Figure 2(b); i.e. dimer 1: the most stable non-planar (spatial) structure, and dimer 2: a planar structure with anti-parallel molecular configuration, optimized at the MP2/cc-pVTZ level of approximation. Some other configurations have also been
reported for the dimers using the ab initio MO and DFT calculations [27]. Among these dimers, non-planar spatial structures were found to be more stable than the planar ones by ~0.5−1.0 kcal/mol depending on the level of calculation. Here, electrostatic interactions are firstly important between the AA molecules in determining the stability of the dimer configurations. Under such low symmetric molecules, the system can actually have the closest molecular contact in the non-planar dimer configurations with high electrostatic stabilization energies. The stability has been attributed to the combination of electrostatic and van der Waals interactions as well as rather weak C−H⋯O interaction. The binding energy for the most stable dimer 1 calculated here is \( \Delta E_b = -2.70 \) kcal/mol and that for the planar dimer 2 is \( \Delta E_b = -1.98 \) kcal/mol, including the BSSE and ZPVE corrections.

![Figure 2](image)

**Figure 2.** (a) Comparison of the calculated XA spectra between the free molecule and representative dimers (dimer1 and dimer2) in the oxygen K-edge region. (b) Comparison of the calculated O1\( s \rightarrow \pi^*_{CO} \) band-spectra between the free molecule and representative dimers.

| System | Interaction | \( d_{CH \cdots O} \)/Å | \( \theta_{CH \cdots O} \)/deg. | \( \Delta \text{CEBE} \)/eV | \( \Delta (\text{Term v.})^a \)/eV | Band-shift\(^b\)/eV |
|--------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| dimer 1 | O1−H21      | 2.386           | 124.1           | −0.78           | −0.96           | 0.18            |
|        | O2−H11      | 2.740           | 75.1            | −0.27           | −0.36           | 0.09            |
|        | O2−H12      | 2.891           | 106.6           | −0.27           | −0.36           | 0.09            |
| dimer 2 | O1−H22      | 2.425           | 179.2           | −0.46           | −0.44           | 0.07            |

\(^a\) Variation of O1\( s \rightarrow \pi^*_{CO} \) energy

\(^b\) O1\( s \rightarrow \pi^*_{CO} \) band component

**Figure 2(a)** shows the overview XA spectra calculated for the free molecule and the representative dimers in the O K-edge region. Vertical bars represent the oscillator strengths of individual transitions from the constituent O atom in the system. Although the low oscillator strengths of the core-to-Rydberg transitions are reproduced in the calculated spectra, we presently focus on the O1\( s \rightarrow \pi^*_{CO} \) transition since reliable comparison with the upper experimental transitions could not be made. **Figure**
compares the O\textsubscript{1s}→\pi^\textsubscript{CO}\* transitions of the representative dimers (dimer 1 and dimer 2) with that of the free molecule. Since O atoms in the non-planar dimer 1 are not equivalent under their chemical surroundings, their excitation energies have different magnitudes depending on the different influence of the intermolecular (electrostatic etc.) multipoles and local interactions such as the H-bond. The oxygen atoms in the planar dimer 2, in turn, are equivalent within the $C_2h$ symmetry, so that their excitation energies are actually degenerate. Table 2 summarizes the molecular parameters (O···H–C) around the O atoms to be core-excited in the dimers, and the excitation energies from the individual O1s orbitals. The energetics are given relative to those of free molecule. In the dimer 1 configuration, the O\textsubscript{1s}→\pi^\textsubscript{CO}\* energies of inequivalent O sites are calculated to be larger than the monomer one (blue-shift) by 0.18 and 0.09 eV, respectively. The largest spectral shift corresponds to the core-excitation of the O atom with the closest O···H contact (Fig. 2(a)). These energy shifts are closely consistent with the experimental peak shift (~ 0.15 eV). In contrast, the O\textsubscript{1s}→\pi^\textsubscript{CO}\* energy of the planar dimer 2 shows degenerate transition with a smaller blue-shift by 0.07 eV. The experimental shift cannot be rationalized by the contribution from O\textsubscript{1s} core-excitation of the planar dimer 2. It is thus clear that the experimental results can be strongly explained by the significant contribution from the most stable configuration of the dimer 1.

It is notable here that structural optimization analysis of AA clusters larger than the dimers is not available up to this time since AA molecule has such a low symmetric structure and is expected to form a number of configurations as the n-isomers. Recent site-dependent C1s excitation spectra of AA clusters [28], however, shows strongly perturbed C1s\textsubscript{CO}→Ryd transitions under the relatively higher stagnation pressures at $P_0 = 0.2$ MPa, indicating the contribution of basic configurations with HCO functional group of the molecule contacting with each other within the clusters. Such configurations of n-isomer should be on a line with that of the dimer 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Molecular orbitals showing the HOMO–LUMO interaction within the most stable non-planar dimer 1.}
\end{figure}

From a geometrical view point, the strength of H-bond is formally characterized by H-bond length (or distance) and its directional property [5]. A strong H-bond geometry favours a linear H-bond structure and a O···H–C distance less than the van der Waals contact. The shortest O···H distance (O1–H21) in the dimer 1 is around ~2.4 Å that shows less than the sum (2.72 Å) of the van der Waals radii of O and H atoms [29]. The C–H···O bond is chemically categorized as a weak H-bond due to the low H-bond donor strength, then its geometries are easily deformed under other strong interactions.
However, the closer O1–H21 contact than the others (O2–H11/O2–H12) may reflect a stronger H-bonding interaction of O1 than the O2, and probably lead to a larger component for the O1 excitation energy. It is notable, in this connection, that the planar dimer 2 configuration has a favourable geometry despite the weak C–H⋯O bonds but that sufficient contribution from multipole interaction cannot be gained for the binding energy, due to a longer molecular separation than the dimer 1. The definite H-bonding contribution to the O1s→π*CO band could not be evaluated since the configuration would be the outcome of the interactions of several types as described above.

Presently, we have observed the spectral band-shift of core-to-valence O1s→π*CO transition of small AA clusters in the PIYs of the cluster-origin products. The DFT calculations were applied to the representative dimers to rationalize these experimental results, since the band-shift was determined in the smallest cluster regime of beam conditions. The XAS calculation by DFT showed that the most stable non-planar dimer configuration (dimer 1) could well reproduce the blue-shift of the O1s→π*CO transition observed. Here, we will focus our attention more details on the O1s→π*CO transition in the most stable dimer 1.

Table 3. Bond length and vibrational frequency (stretching) calculated by MP2/cc-pVTZ level.

| Bond (functional group) | Monomer | The most stable dimer (non-planar) |
|-------------------------|---------|----------------------------------|
|                         |         | M2 molecule                      | M1 molecule                      |
|                         |         | Length/Å                         | Length/Å                         | Length/Å                         | Length/Å |
| C–H (CHO)               | 1.1054  | 1.1022(−)                        | 1.1028(−)                        | 1.1022(−)                        | 1.1028(−) |
| C=O                    | 1.2130  | 1.2166(+)                        | 1.2156(+)                        | 1.2166(+)                        | 1.2156(+) |
| C–C                    | 1.4987  | 1.4969(−)                        | 1.4965(−)                        | 1.4969(−)                        | 1.4965(−) |

|                         | Freq.α/cm⁻¹ | Freq.α/cm⁻¹ | Freq.α/cm⁻¹ | Freq.α/cm⁻¹ |
|                         |             |             |             |             |
|                         | 2829        | 2876(+       | 2855(+)     | 1706        |
|                         |             | 1706        | 1695(−)     | 1704        |
|                         |             | 1093        | 1096        | 1097        |

* Scaling factor of 0.9575 is employed (Ref. [12]).

In order to consider the origin of the spectral band-shift in the O1s→π*CO band, we examined the HOMO–LUMO structures between the constituent molecules M1 and M2 in the most stable dimer 1. Figure 3 shows the HOMO–LUMOs given by StoBe-deMon calculation that expand within the configuration upon dimerization where the π*CO orbital of O1 site, corresponding the larger component of the O1s→π*CO shift, is designated (the π*CO orbital of O2 site is not shown). One may easily realize the orbital mixing between the nonbonding nO and antibonding π*CO of the present non-planar configuration. The band-shift of the O1s→π*CO transition could be thus interpreted as being due to the augmentation of the HOMO–LUMO energy gap as well as the stabilization energy upon dimerization. It is quite important to note that electron transfer to the LUMO, viz. M1 to M2 molecule, is expected to take place under the HOMO–LUMO interaction. Since the LUMO in M2 has a weak σ-bonding nature between the H and C atoms, and another weak π*CO antibonding nature between the C and O atoms in the CHO functional group, electron transfer to M2 leads to slightly a shorter C–H bond and a longer C=O bond via the HOMO–LUMO interaction. These MO structures of the dimer 1 imply that there involves the blue-shifting (in vibrational frequency) hydrogen bonding [30] in the interaction. In the ab initio MO calculation, in fact, the present complex (dimer 1) formation is found to be accompanied by blue-shifts of the C–H and red-shifts of the C=O stretching frequencies in the HCO functional group in M2/M1. Table 3 summarizes the bond length and vibrational frequency of the associated bond, where the comparison between the monomer and the most stable dimer 1 can be made. In the dimer 1 configuration, O1 atom in M1 molecule interacts with C–H (HCO) in M2 molecule and O2 atom in M2 interacts with C–H (CHO) in M1 and so on. The present vibrationally blue-shifting H-bonding causes the contraction of such C-H bond by 0.0016–0.0022 Å and blue-shifts of the C–H stretch frequencies by 26 - 47 cm⁻¹ relative to the free molecule. In this respect, the closer
O···H–C contact (in O1–H21 in Table 2) is found to lead a stronger blue-shifting H-bond. It is also notable that the configuration of the dimer 2 has a “proper” (red-shifting) H-bond, although the weak one, where the elongation of the C–H (CH3) bond by 0.0007 Å and a red-shift of the C–H stretching frequency by 7 cm⁻¹ are identified.

Figure 4(a) compares the energy levels of core-excited states from individual O atoms in the most stable non-planar dimer 1, with those of AA monomer. Their energetics are given from the DFT calculation. A stable multipole-configuration of the neutral dimer occasionally induces a strong charge-multipole interaction upon core-electron ionization, and stabilizes the core-hole final states. Figure 4(b) shows the charge-dipole interaction as a zero-th approximation in the core-ionization states. This simple approximation leads to a larger stabilization energy of O1 ionization than the O2 ionization. The similar trend is also expected for higher Rydberg states. In the core-to-valence transition, however, valence orbitals are not at all diffusing over to the neighbouring molecule, so that interaction between the orbitals is realized when the close contact with the neighbouring molecule can be made. In the present case, it is only when the system forms the non-planar (nearly T-shaped) structure that the n_CO−π*CO (HOMO–LUMO) interaction comes to be important. As described above, the O atoms are not equivalent under their chemical surroundings, and then their excitation energies have different magnitudes depending on the different influence of the intermolecular interactions. With O1 excitation to the O1s→π*CO state (Figure 4 (c)), the system has the closest O1–H21 contact under the stronger influence of the n_CO−π*CO interaction, leading to the larger O1s→π*CO excitation energy. With O2 excitation to the O1s→π*CO state, however, less intense mixing of MOs within the dimer can be observed; this is clearly corresponding to the weaker n_CO−π*CO interaction. In the present system where chemical interaction is involved, although the weak one, it is concluded that significant
contributions of such orbital interaction to the stabilities of the core-to-valence excited states are made preferentially over the core-hole final state interactions.

4. Conclusions
Core-electron excitation spectra of small acetaldehyde clusters have been studied in the small cluster regime of beam conditions. The “cluster-specific” excitation spectra could be generated by monitoring the PIY spectra of the fragments originating from the clusters. Comparison of the “cluster-specific” band with the “monomer” band revealed that the O1s→π*CO band of clusters shifts to a high energy by 0.15 eV. The density functional theory calculation was applied to rationalize the experimental results. As the representative of small acetaldehyde clusters, two types of dimers (the most stable non-planar dimer and anti-parallel aligned planar dimer) were chosen to derive the spectral simulation of the O1s→π*CO transitions. The simulation of the most stable dimer with a non-planar geometry could reproduce the experimental band-energy shift upon dimerization, indicative of a significant contribution of the most stable dimer 1. The energy shift of the band was interpreted by the augmentation of the HOMO–LUMO energy gap induced in the non-planar complex, where the interaction of vibrationally blue-shifting hydrogen bonding is identified.

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