Site- and geometry-specific CH⋯O interaction in small acetaldehyde clusters studied with core-electron excitation spectroscopy in the carbon K-edge region

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Abstract. Site-dependent C1s-core excitation spectra of small acetaldehyde (AAL) clusters have been studied under the cluster regime of beam conditions. The excitation spectra of the clusters were generated by monitoring the partial-ion-yields of cluster-origin fragments. Comparison of the cluster bands with the monomer bands revealed that the band intensities of C1s core-to-Rydberg transitions come to be strongly excitation-site dependent upon cluster formation showing significant reduction of C1sHCO→Ryd bands relative to the monomer bands. Computer modeling of X-ray absorption spectra using a density functional theory calculation demonstrated that the intensity reduction is the outcome of the site- and geometry-specific CH⋯O interaction where hydrogen-bonding association between the aldehyde (HCO) sites of different AAL molecules takes place exclusively within the clusters. As the representatives of small AAL clusters (n≥3), two types of molecular complexes (a planar cyclic trimer and a tetramer with a stack of two dimers) were derived to rationalize the site-dependence of the experimental C1s excitation spectra. Spectral simulation of the above complexes could reproduce the experimental site-dependence of the core-to-Rydberg band-features upon clusterization, indicative of significant contribution of these clusters under the present beam-stagnation condition.

1. Introduction

Inner-shell excitation spectra of small hydrogen bonding (HB) clusters have been studied in the beam condition [1-6], and they provided new spectroscopic findings on the local HB interaction within the molecular clusters as well as the fragmentation mechanism upon H-bond cluster formation. Formic-acid (FA) has two oxygen sites available for strong H-bond formation and forms a stable cyclic-dimer
configuration in the gas phase, with doubly bridged (OH⋯O) H-bonds with a binding energy of ~15 kcal/mol [1,7]. The configuration is exclusively the most stable unit-structure among the molecular complexes and provides a major source of building blocks for the FA cluster formation. The comparison of the cluster excitation-bands with those of molecular FA showed that the first resonance O1s_{CO}→π^*_{CO} band shifts upwards (to a higher energy) by ~0.31 eV whereas the second O1s_{OH}→π^*_{CO} band shifts downwards by ~0.82 eV [1]. The π^*_{CO} orbital is actually insensitive to the H-bonding due to the out-of-plane character, the band shifts of O1s_{CO(OH)}→π^*_{CO} are strongly attributable to the change in core electron binding energies (CEBEs) of these oxygen atoms upon H-bond formation. In contrast, the antibonding σ^*_{OH} orbital is directly related to the HB to give higher excitation energies and reduced band-intensities relative to the monomer band. The band-structures of FA clusters have been well supported by a recent density functional theory (DFT) calculation [7].

Acetaldehyde (AAL) has a relatively high dipole moment, larger than those of typical polar solvents such as water and methanol [8]. Quantum chemical calculation shows that the charge distribution of AAL is mostly localized on the carbonyl C=O site that actually defines the molecular dipole moment. Although AAL has both hydrogen donor C sites and lone-pair acceptor O site within the molecule, strong H-bonds such as the O−H⋯O are not expected in neutral cluster species due to a lower H-bond donor strength of C–H [9]. It is thus natural to postulate that the overall structures of small AAL clusters are actually determined and that the weak CH⋯O interactions are largely influenced, by the strong multipole interactions. Governed by such electrostatic interactions, it can be assumed to constitute nearly anti-parallel CO of dimer configurations within AAL clusters.

Recently, we have studied O1s_{HCO}→π^*_{CO} excitation of AAL clusters [5,6] in the smallest cluster regime of beam conditions. The intense O1s_{HCO}→π^*_{CO} band of clusters was found to shift to a high energy by 0.15 eV relative to the monomer band. Computer modeling of X-ray absorption spectra based on the DFT calculation was carried out to rationalize the experimental results. The simulation of the most stable dimer with a non-planar T-shaped geometry could reproduce the experimental cluster-band shift. The band shift was interpreted as being both due to the HOMO-LUMO (n→π^*) interaction within the complex and the stabilization upon dimerization. The CH⋯O interaction was also identified by the appearance of vibrationally blue-shifting hydrogen bonding [10] in the AAL complex.

Here, we have extended inner-shell excitation studies to small AAL clusters in the Carbon K-edge region, and the effects of such intermolecular interactions on the core-excitation spectra have been examined. C1s site-specific band probing of AAL clusters is promising since AAL has two different CH sites (the methyl and the aldehyde (carbonyl) carbon sites) available for CH⋯O interaction and their distinct core-to-Rydberg bands detectable in the Carbon K-edge region. The band-structures of core-to-Rydberg transitions observed in small AAL clusters were also compared with those predicted by the DFT calculation.

2. Experiments and theoretical calculations

The experiments were performed using a cluster-photochemistry apparatus [3,11] mounted to a high-resolution plane-grating monochromator at the soft X-ray beamline BL27SU in the SPring-8 facility. Cluster beams were generated in a beam source chamber by supersonic expansion of gaseous mixtures of 4.9−13.5% AAL/He via a 50 μm nozzle, under the stagnation pressures of P0 = 0.11−0.3 MPa. The mixtures were prepared by bubbling helium gas through the liquid AAL sample in a cylinder. The stagnation pressures were kept constant with immersing the sample cylinder in a thermostated refrigerant. The beams were collimated with a 1.0mm skimmer and directly introduced into a main chamber of the apparatus [11], where it was crossed with a monochromatized soft X-ray beam at the ionization region of a double-field type TOF spectrometer. For comparison with the inner-shell excitation measurements of AAL clusters, effusive (monomeric) gas was prepared by direct introduction [1] of pure AAL through a 1/16 in. (o.d.) stainless-steel tube into the ionization region. 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 C1s→3p/4pπ
Rydberg transitions of CO$_2$ at 294.938/296.364 eV [12]. The resolution of the monochromator was $E/\Delta E = 5000$–7500 at the energy corresponding to the carbon K-edge. The details of the procedure have been described elsewhere [1].

Acetaldehyde (AAL: CH$_3$CHO) was supplied by Aldrich at a purity of $\geq 99.5\%$ and helium by Nihon-Sanso at $\geq 99.99\%$. They were used without further purification.

In order to examine the molecular configurations and intermolecular interactions within AAL clusters and support the analysis of core-excitation spectra, ab initio molecular orbital (MO) and DFT calculations were carried out for AAL molecule and its complexes. Initial geometries of the small complex were generally optimized using the Gaussian 03 program [13] at the MP2/cc-pVTZ level of approximation. The vibrational frequencies were calculated at the same level to confirm the stationary structures and correct the zero-point vibrational energies (ZPVEs). The frequencies were further scaled [14] with multiplying by 0.9832 after the MP2 calculations. The basis set superposition error (BSSE) was corrected using the procedures proposed by Boys and Bernardi [15]. The molecular complexes larger than the dimer were optimized at the MP2/cc-pVDZ level and their stabilization energies were estimated without BSSE correction.

The calculation of core-excited states was performed with the StoBe-deMon code [16], based on the 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 the 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, the $\Delta Kohn$–Sham calculations [17] that allow full relaxation of core-hole ionization states were performed to derive the ionization energy (IP). The relativistic correction of 0.08 eV [18,19] was added to the IP of the C1s 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. [20], whereas (6311/311/1) and (311/1) basis sets were used for 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 the DFT calculations were performed using the gradient-corrected exchange and correlation functionals developed by Perdew and Wang [21,22]. Further details of the calculations have been given elsewhere [17,23].

3. Results and Discussion

3.1. Core excitation measurements of AAL molecule and clusters in the carbon K-edge region

3.1.1. Total-ion-yield (TIY) spectra of AAL molecule and clusters

Prior to the measurements of AAL clusters, the total-ion-yield (TIY) of AAL was observed under the effusive condition. Figure 1 shows a typical overview TIY spectrum of AAL molecule recorded in the 285–295 eV energy range that covers carbon K-edge transitions. Publications on the X-ray absorption and excitation spectra of free AAL molecule are available in the ISEELS [24] and NEXAFS [25] measurements. The carbon K-edge excitation of AAL molecule are available in the ISEELS [24] and NEXAFS [25] measurements. The carbon K-edge excitation of AAL involves the electron transitions from the aldehyde (carbonyl) HC=O and methyl CH$_3$ carbon sites. An intense core-to-$\pi^*$ valence band with excitation from C1$_{s\,\text{HCO}}$ site occurs at 286.1 eV; moderate and/or weak Rydberg (3s and 3p) transitions from C1$_{s\,\text{CH}_3}$ site exist at 287–289 eV whereas those from C1$_{s\,\text{HCO}}$ site appear in the 290–292 eV range. The Rydberg transitions of AAL from both C1s sites are fairly well resolved amongst the carbonyl compounds. The CEBEs of C1$_{s\,\text{CH}_3}$ and C1$_{s\,\text{HCO}}$ have been determined to be 291.35 and 294.00 eV in the X-ray photoelectron spectroscopy [26]. Based on the previous band assignments, we reassigned the C1s excitation bands from the TIY as listed in table 1, where low-lying Rydberg transitions...
relevant to the present study are indicated. In our measurement, the band energies are in closer agreement (with an average discrepancy of 0.06 eV) with the results of Prince et al. [25].

Figure 1. TIY spectrum of free acetaldehyde (AAL) molecule observed with core-excitation in the carbon K-edge region. Prominent valence and lower-Rydberg excited states are indicated. The band assignment is given in table 1.

Table 1. Representative band-assignment of free AAL molecule in the carbon K-edge region.

| Band No. | Photon energy E / eV | Assignment | Quantum Defect / δ |
|----------|----------------------|------------|-------------------|
| C1s_{CO} excitation | | | |
| 1 | 286.08 | 286.17 (+0.09) | 286.30 (+0.22) | π^*_{CO} | 0.69 |
| | 286.26 | 286.32 (+0.06) | +Δν (+0.18) | |
| | 286.42 | 286.48 (+0.06) | +2Δν (+0.16) | |
| 6 | 290.14 | 290.21 (+0.07) | 290.12 (-0.02) | 3σ(CO) | 1.12 |
| 7 | 290.96 | 291.02 (+0.06) | 290.90 (-0.06) | 3pσ(CO) | 0.88 |
| 8 | 291.36 | 291.40 (+0.04) | 291.20 (-0.16) | 3pπ(CO) | 0.73 |
| 9 | 292.05 | 292.10 (+0.05) | 292.00 (+0.05) | 4sσ(CO) | 1.39 |
| | (294.00) | (294.00) | | |
| C1s_{CH3} excitation | | | |
| 2 | 287.26 | 287.33 (+0.07) | 287.2 (-0.06) | 3sσ(CH3) | 1.17 |
| | 287.62 | 287.69 (+0.07) | +Δν (+0.36) | |
| 3 | 288.30 | 288.36 (+0.06) | 288.30 (0) | 3pπ(CH3) | 0.89 |
| 4 | 288.98 | 289.05 (+0.07) | 289.00 (+0.07) | 3pσ(CH3) | 0.60 |
| 5 | 289.20 | 289.26 (+0.06) | 289.5 (+0.30) | 4s(CH3) | 1.48 |

Prince K C et al. (Ref. [25])
Hitchcock A P and Brion C E (Ref. [24])
difference from the present work
Jolly W L, Bomben K D and Eyerman C J (Ref. [26])
Jolly W L and Schaaf T F (Ref. [27])
3.1.2. Partial-ion-yield (PIY) spectra of AAL molecules and clusters

As was the case for previous O1s excitation of AAL clusters [5,6], we recorded an intense series of protonated clusters $\text{M}_n\text{H}^+$ ($\text{M}: \text{CH}_3\text{CHO}$) in the TOF fragment-mass measurement of the present cluster beams (figure 2(a)). Pressure variations of the product distribution important for the AAL beam characterization have been recently described [5], where atomic and smaller fragments than the parent molecule such as $\text{C}^+$, $\text{O}^+$, and $\text{C}_2^+$ in the cluster beam were attributed to the free AAL origin whereas the protonated clusters $\text{M}_n\text{H}^+$ were originated from AAL clusters. Figure 2(b) shows the variations of fractional intensities of the monomer-origin ($\text{C}^+$/C$_2^+$) and cluster-origin ($\text{M}_n\text{H}^+$) products with beam stagnation pressure. While the pressure dependences similar to the previous beam characterization (Figure 2(b) in Ref. 5) were given, larger back-ground intensities were admitted in the present monomer-origin ($\text{C}^+$/C$_2^+$) products. This is only the difference in the cluster beam-characteristics found for the cluster photochemistry apparatus in the SPring-8 facility.

By monitoring PIY intensities of the $\text{M}_n\text{H}^+$ products originating from the clusters, excitation spectra of AAL clusters could be recorded without any contribution of free molecule. In contrast, the PIYs of atomic and small fragments actually have the same band-features and peak-energies as those observed in the TIY of the effusive beam, it is also reasonable to conclude that they come from free AAL molecule. Figure 3 compares the PIY spectra in the C1s edge region for the monomer- and cluster-origin cations simultaneously recorded at the same energy points. In the present case where a fair amount of back-ground AAL can be admitted, we chose a moderate cluster-beam condition of $P_0 = 0.20$ MPa in order to facilitate our signal accumulation over the entire C1s edge region (285–295 eV) with step-widths of $\Delta E = 0.05–0.10$ eV. The beam stagnation pressure is higher than that ($P_0 = 0.10$ MPa) used in the previous O1s excitation (PIY) measurement where the cluster beam was found to have the smallest cluster-size distribution with a prominent dimer-contribution [5,28].

The PIYs of the cluster-specific products, $\text{MH}^+$/M$_2\text{H}^+$ show distinct band-characteristics other than the first valence ($\text{C1s}_{\text{HCO}} \rightarrow \pi^*_{\text{CO}}$) transition; the $\text{C1s}_{\text{HCO}} \rightarrow \text{Rydberg}$ transitions at $\sim 290$ eV and higher energies are found to lose their intensities whilst the $\text{C1s}_{\text{CH}_3} \rightarrow \text{Rydberg}$ transitions merely broaden their bands as the cluster-Rydberg bands generally show. Although the core-to-Rydberg ($\text{C1s}_{\text{CH}_3} \rightarrow 3p\pi: \sim 288.3$ eV)/($\text{C1s}_{\text{HCO}} \rightarrow 3s\sigma: \sim 290.1$ eV) excitations in the present monomer system have relatively weak oscillator-strengths in origin, structural changes upon cluster formation could be thus extracted in the site-selective PIY measurement, under the present beam-stagnation condition. The present PIY spectra of small AAL clusters clearly show that there appears significant intensity

![Figure 2](image-url)
reduction of the C1s$_{\text{HCO}}$ core-to-Rydberg transitions, indicating that the site-dependent intermolecular interactions of AAL molecule are involved within the clusters.

3.2. Computer modeling of XA spectra of AAL molecule and clusters by DFT calculations

3.2.1. CH···O interactions derived for the representative AAL dimers

In order to compare the experimental results with theoretical expectations and to give an interpretation for the intensity reduction of the “cluster” C1s$_{\text{HCO}}$→Rydberg bands from the “monomer” bands, model XA spectra were generated for the representative (AAL)$_n$ clusters using the DFT calculation. In the first stage, several dimer complexes with stable minima were examined to understand the outcomes of the interaction of C1(HCO)/C2(CH$_3$) core-atoms that appear in the calculated XAS. Examples of the dimer structures are shown in figure 4(a); i.e. dimer 1: the most stable non-planar (spatial) structure, and dimer 2/dimer 3: the planar structures with configurations of different types of CH···O interaction, optimized at the MP2/cc-pVTZ level of approximation. Some other configurations for AAL dimer have also been reported using ab initio MO and DFT calculations [29]. Among these dimers, non-planar structures were found to be more stable than the planar ones by ~0.5−1.0 kcal/mol depending on the level of calculation. We have generated several model XA spectra for the respective dimer configurations, and the representative cases are given in figure 4. It should be noted that the stabilization energy of the most stable dimer 1 is calculated to be $\Delta E_b = -2.70$ kcal/mol and those for planar dimer 2/dimer 3 are $\Delta E_b = -2.04/\sim -1.87$ kcal/mol [30], respectively, including the BSSE and ZPVE corrections.

The overview XA spectra in the C K-edge region calculated for the representative dimers are shown in figure 4(b), where the comparison is also made with that of free molecule without any intermolecular interaction (top panel). Vertical bars represent the oscillator strengths of individual transitions from the constituent C atoms in the system. Although the low oscillator strengths of the core-to-higher Rydberg transitions are also reproduced in the calculated spectra, we focus our attention on the lowest-lying Rydberg transitions so that reliable comparison with the experimental transitions can be made. Since the C1(C2) atoms in non-planar dimer 1 and planar dimer 2 are not equivalent to the C3(C4) atoms under their chemical surroundings, their excitation energies have different
magnitudes depending on the different influence of intermolecular (electrostatic etc.) multipoles and local interactions such as the H-bonding. The C1(C2) atom in planar dimer 3, in turn, is equivalent to the C3(C4) atom within the C2v symmetry, so that their excitation energies are actually degenerate.

Following the argument in section 3.1.2, close inspection of the core-to-lower Rydberg transitions among the representative dimers reveals the following characteristics under the intermolecular CH⋯O H-bonding interaction. Firstly, relative intensity of the C1s(\text{CH})→3p\pi transition is mostly comparable to the monomer one, whether any methyl hydrogen of the C2(C4) site interacts with the carbonyl oxygen atom of the counterpart molecule or methyl hydrogen atoms of the site are free from the intermolecular CH⋯O interaction. Secondly, in contrast, oscillator strength of the C1s(\text{HCO})→3s\sigma transition in the aldehyde C1(C3) site decreases significantly in the complex when its aldehyde hydrogen directly associates with the counterpart oxygen atom. Summarizing the above, the intensity of the C1s core-to-Rydberg transition has such site-specific character that the distinct reduction of the band intensity takes place at the aldehyde carbon site, derived from the definite CH⋯O interaction [30]. In the dimer complex where both aldehyde sides of the molecules sit facing antiparallel each other to give a planar ring structure with doubly bridged CH⋯O bonds (such as the case of planar dimer 3), the C1s core-to-Rydberg bands actually disappear in the computer modeling XA spectra. In this respect, the XA spectrum given for the most stable (T-shaped) dimer 1 shows a less favorable comparison with the C1s excitation spectra observed. This is not surprising since the present C1s core-excitation spectra were recorded under the moderate beam-stagnation condition where the major contribution of clusters larger than the dimer can be expected. As far as the present fundamental analysis (between the molecular configurations and spectral patterns in the representative dimers) is concerned, the experimental C1s excitation spectra of AAL clusters strongly favour the unit-structures such as cyclic dimer 3 obtained in the computer modeling calculation.

In the OH⋯O interaction that affects on the O1s excitation of H-bonded FA clusters [1,7], the intensity reduction as well as the energy shift of core-to-\sigma^*(OH) transition have been described. The antibonding \sigma^*(OH) orbital of H-donor oxygen site is strongly perturbed upon H-bond formation and the state is destabilized due to the n→\sigma^* interaction. Charge transfer made upon complexation induces delocalization of the \sigma^* orbital to reduce the core-to-\sigma^* band-intensities. The low-lying C-Rydberg states such as the 3s and 3p\sigma have more or less antibonding \sigma^*(CH) character in the orbitals, so that...
the band-characteristics similar to the above transition can be realized in the C1s_{HCO}→Ryd bands. In figure 4(b), in fact, one may find the quenching and blue-shifting of the core-to-3s Rydberg band in each of the C1 sites in the representative dimers where the distinct CH--O interaction can be admitted. It should be added that we have not examined the core-to-valence transition, C1s_{HCO}→π* and its vibrational progression in the present calculation since the simulation program is not incorporated with those other than the electronic transition. The energy shift of the band involves explicitly both vibrational and electronic transitions within the specified molecular complex with a definite size and configuration, so that the details on the structural change of the C1s_{HCO}→π* band upon cluster formation are separated here and will be given in a future publication.

### 3.2.2. Interpretation of CH--O interactions in small AAL clusters

**Figure 5.** (a) Representative AAL trimer and tetramer structures employed for the XAS modeling in the carbon K-edge region. The structures were optimized using the MP2/cc-pVDZ level of approximation. (b) Comparison of the calculated XAS among the AAL molecule (top panel) and representative (AAL)$_3$ and (AAL)$_4$ clusters (lower panels); Vertical (colored) bars denote the band positions and transition intensities from the respective C1(HCO) and C2(CH$_3$) carbon sites of the constituent molecules.

To our knowledge, geometry optimization analyses of AAL clusters larger than the dimer are not available up to this time since AAL molecule has such a low symmetric structure and is expected to form a number of configurations as the $n$(≥3)-isomers. In order to rationalize the core-to-Rydberg band-disappearance observed in the small cluster regime of beam conditions, however, contributions of several clusters larger than AAL dimer are examined based on the representative unit-structures described in the previous analysis. Figure 5(a) shows the examples of the representative complexes (trimer 1 and tetramer 1) exceedingly compatible with the above requirement, optimized at the MP2/cc-pVDZ level of approximation. Figure 5(b) compares the calculated XAS of these complexes with that of free molecule, where the intensities of the important transitions are scaled relative to that of the first C1s_{HCO}→π* band.

**Trimer 1** extended from **dimer 3** in figure 4 has a planar cyclic structure of $C_{3h}$ symmetry with an interaction energy of $\sim -8.5$ kcal/mol; three equivalent CH--O contacts (at each aldehyde site) are established in this minimum. Since the stabilization energy of **dimer 3** amounts to $\Delta E_{st} = -4.14$ kcal/mol calculated with the same level of MP2/cc-pVDZ, the addition of a molecule to **dimer 3** to form **trimer 1** gains a larger energy-increment for a single CH--O interaction than that obtained for the formation of **dimer 3**. From a geometrical point of view, one could find a shortening of intermolecular CH--O distance in **trimer 1** with respect to the value obtained in **dimer 3**. In fact, the
CH⋯O distance (2.375 Å) in trimer 1 is shortened by 0.073 Å from that (2.448 Å) derived in dimer 3 [30], indicative of the increased strength of CH⋯O interaction. Such non-additive effect is due to the multipole interaction characteristic of the constituent molecule. In the case of cyclic dimer with doubly bridged H-bonds, it has been known that closer distance between the donor-hydrogen atoms (the acceptor-oxygen) of the counterpart-molecules destabilizes the system [31] via electrostatic repulsion to give weaker intermolecular interaction. Dimer 3 is then the example that could not lead to the most stable structure. The cyclic structures of trimers, however, are often found to be the ones of the most favourable configurations (on the thermochemical ground) for the simple polar molecules such as acetonitrile [32], formic acid [1,7,33], formamide [31], etc. An analogue of these complexes cyclic trimer 1 is expected to be the most stable one of AAL trimer that may effectively contribute to the excitation spectra under the present cluster-beam condition. One can easily recognize that the calculated XAS of trimer 1 (figure 5(b)) gives a satisfactory correspondence of the intensity-reduction features to the observed C1s core-to-Rydberg bands.

A representative of AAL tetramer was also obtained by geometry optimization starting from a planar cyclic structure, according to the analogy given for the lower member complexes as above. Tetramer 1 shown in figure 5(a) gave the minimum of a stack-of-two dimers structure as a result. We tried the optimization several times by changing initial guess of the cyclic geometries to lead the same stacking structure. This strongly implies that the cyclic structure, if any, is less stable than the stacking structure in AAL tetramer. The cyclic dimer unit in the stacked complex has a configuration similar to that of dimer 3 and the units are oriented in a twisted form; the unit is just a typical arrangement to meet the spectral requirements (figure 5(b)). Taking into account the stabilization energy (ΔE_b=−4.14 kcal/mol) of dimer 3 and the complexation energy (ΔE_c=−16.50 kcal/mol) of tetramer 1 calculated at the same level of approximation, significant magnitude of interaction is expected between the dimer pairs in the complex. Since the closest four CH⋯O distances between the stacking molecules are around 3.43 Å whilst those between the molecules in the cyclic dimers are ~2.45 Å, both H-donor and acceptor interactions between two monomers in the different pairs make tiny contributions to the total stabilization energy. As we alluded earlier, the charge distribution within AAL molecule is generally localized on the carbonyl C=O site that actually defines the relatively large dipole moment, so that the antiparallel oriented dipole interaction between the molecules in the different pairs plays important roles in energetics. Another interaction to be mentioned is “through space” π-π interactions between the CO sites of the molecules in the different pairs. The dimer pairs in the complex are twisted such that the favourable contacts of the CO sites in the different pairs are doubly realized (figure 5(a)). The stabilization by stacking is thus interpretable as being both due to these multipole and through-space interactions between the opposite dimers. The significant stabilization given in tetramer 1 leads to another strong candidate of the cluster to contribute to the site-specific C1s excitation spectra, observed under the present beam-stagnation condition.

The present interpretation of the quenching of the C1s core-to-Rydberg states for the aldehyde site is based primarily on the calculated XA spectra (figure 4) where the representative AAL dimer configurations are used as the unit-structures to model the cluster bonding and its geometric structures. The unit-structure of the planar cyclic dimer where both hydrogen and oxygen at the aldehyde site associate with those at the corresponding site leads to very weak oscillator strengths, due to the CH⋯O hydrogen-bonding interaction, for the excitation to the cluster-Rydberg states. In the present study, the cluster PIYs (figure 3) of the C1s core-to-Rydberg were recorded at a slightly higher stagnation pressure (P_0=0.20 MPa) than the previous O1s measurements (P_0=0.10 MPa), in order to facilitate the signal accumulation of the relatively weak core-to-Rydberg bands. Since cluster size distribution shifts to larger clusters with increasing stagnation pressure (i.e. increasing condensation parameter Γ* [34]), predominant contribution of larger clusters than the dimer could be expected to the cluster PIYs observed. A less favorable agreement between the observed PIYs and calculated XA spectrum of the most stable dimer 1 can be thus understood by the above argument. Here, we propose trimer 1 and tetramer 1 extended from the unit-structure of the planar cyclic dimer to account for the major
sources of cluster that may contribute significantly to the present PIY spectra. These beam-stagnation conditions are both near the threshold of cluster formation, so that the present C1s excitation spectra reflect mostly the electronic properties of such small AAL clusters.

4. Conclusions
C1s core-electron excitation spectra of small acetaldehyde (AAL) clusters have been studied in the beam conditions. The band intensities of C1s core-to-Ryd transition of AAL clusters are found to change site-dependently upon cluster formation showing significant intensity reduction of C1sHCO→Ryd bands relative to the monomer bands. Computer modeling XA spectra demonstrated that the band reduction is the outcome of the site- and geometry-specific CH⋯O interaction where the planar association between the HCO sites of different molecules takes place exclusively within the clusters. The intensity reduction of the bands is interpreted as being due to the antibonding σ*CH character in the Rydberg orbitals of HCO carbon site that may participate in the weak CH⋯O hydrogen bonds. As the representatives of small acetaldehyde clusters (n≥3), two types of molecular complexes (a planar cyclic trimer and a tetramer with a stack of two dimers) with head(HCO site)-to-head association between AAL molecules were derived to rationalize the site-dependent core-to-Ryd band-features observed in the C1s excitation spectra. Significant contribution of the above mentioned complexes to the spectra could be justified under the present cluster-beam stagnation condition.

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