Inner-shell excitation spectroscopy and fragmentation of small hydrogen-bonded clusters of formic acid after core excitations at the oxygen *K* edge

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Inner-shell excitation spectra and fragmentation of small clusters of formic acid have been studied in the oxygen *K*-edge region by time-of-flight fragment mass spectroscopy. In addition to several fragment cations smaller than the parent molecule, we have identified the production of $HCOOH \cdot H^+$ and H_3O^+ cations characteristic of proton transfer reactions within the clusters. Cluster-specific excitation spectra have been generated by monitoring the partial ion yields of the product cations. Resonance transitions of $O1s(C{=}O/OH)$ electrons into π_{CO}^* orbital in the preedge region were found to shift in energy upon clusterization. A blueshift of the $O1s(C{=}O) \rightarrow \pi_{CO}^*$ transition by ~ 0.2 eV and a redshift of the $O1s(OH) \rightarrow \pi_{CO}^*$ by ~ 0.6 eV were observed, indicative of strong hydrogen-bond formation within the clusters. The results have been compared with a recent theoretical calculation, which supports the conclusion that the formic-acid clusters consist of the most stable cyclic dimer and/or trimer units. Specifically labeled formic acid-*d*, HCOOD, was also used to examine the core-excited fragmentation mechanisms. These deuterium-labeled experiments showed that HDO^+ was formed via site-specific migration of a formyl hydrogen within an individual molecule, and that HD_2O^+ was produced via the subsequent transfer of a deuterium atom from the hydroxyl group of a nearest-neighbor molecule within a cationic cluster. Deuteron (proton) transfer from the hydroxyl site of a hydrogen-bond partner was also found to take place, producing deuteronated $HCOOD \cdot D^+$ (protonated $HCOOH \cdot H^+$) cations within the clusters. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2387949]

I. INTRODUCTION

Inner-shell electron excitation in the near-edge regime of molecular clusters can provide unique information[1] on the size-dependent changes in the electronic and geometric structures upon cluster formation as well as on the reaction mechanisms and dynamics of core-excited clusters from fragment mass distributions. Since the excitation involves the transition of an inner-shell electron localized closely to a nucleus into unoccupied electronic levels and/or ionized continuum states, transition energies are sensitive to the change in local electronic structures around the core atom and spatial orbital correlations with neighboring molecules when intermolecular interaction is significant in the clusters.[2] In order to obtain new insights into the local hydrogen bond (HB) configuration within the molecular clusters, we have performed inner-shell excitation measurements of the total-ion-yield (TIY) and partial-ion-yield (PIY) spectra of small formic-acid (FA) clusters, where the constituent FA molecules interact strongly through the HBs.

Inner-shell excitation spectra of some organic molecules (alcohols, carboxylic acids, and esters) including molecular FA were first reported using electron-energy-loss spectroscopy (EELS) by Ishii and Hitchcock.[3,4] They analyzed the spectra in comparison with near-edge-x-ray-absorption-fine-structure (NEXAFS) spectra[5] of multilayer molecules on Si surfaces and discussed spectroscopic properties based on the

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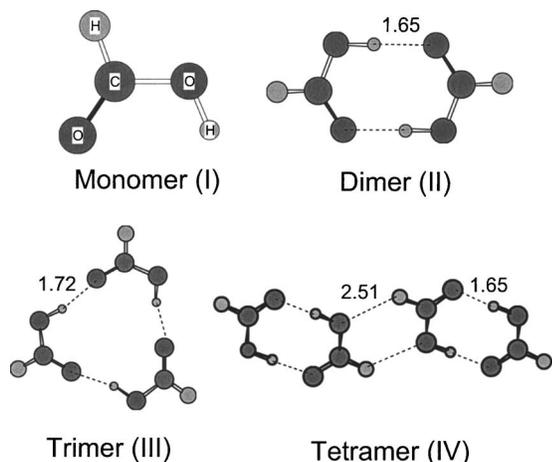
FIG. 1. Examples of the most stable configurations for free FA molecule and small $(FA)_n$ clusters. These configurations were obtained with the calculations of Ref. 11. Hydrogen bond lengths are given in units of angstroms.

chromophore or functional group concept. Fairly good comparisons between the gas-phase EELS and multilayer NEXAFS spectra have been given except for the carboxylic acids, where the second resonance peak due to $O1s_{OH}$ electron transitions into the π^*_{CO} orbital, $O1s_{OH} \rightarrow \pi^*_{CO}$, in the multilayer NEXAFS spectra could not be resolved. To elucidate the spectral changes of $O(1s)$ excitation upon condensation of carboxylic acids it is thus of fundamental importance to examine the evolution in soft x-ray absorption/excitation spectra from monomer acids[6] to their small clusters under high-resolution conditions.

The FA molecule [Fig. 1(I)], the prototype carboxylic acid, has two sites available for strong HB formation and forms a cyclic dimer in the gas phase, with doubly bridged $(-OH \cdots O = C <)$ hydrogen bonds. Since the cyclic dimer [Fig. 1(II)] has the most stable structure with a complexation energy (~ 15 kcal/mol) larger than any other dimer configuration, it can be assumed to constitute planar-complexes-of-dimers structures and/or stack-of-dimers units within the clusters. In fact, recent structural studies by *ab initio* molecular orbital (MO) and density functional theory (DFT) calculations[7–9] have demonstrated that small H-bonded clusters of formic acid strongly favor planar structures consisting of such stable cyclic dimer(s) and/or trimers [Figs. 1(II)–1(IV)] on thermochemical grounds.[10]

We have performed inner-shell excitation studies of free FA and its clusters $(FA)_n$ in order to investigate the changes in electronic and geometric structures as well as the fragmentation mechanisms upon H-bonded cluster formation. The TIY and PIY excitation spectra of free FA molecules and clusters were interpreted in comparison with the theoretical x-ray absorption (XA) spectra presented in a previous publication[11] based on DFT calculations. In order to elucidate the fragmentation mechanisms for core-excited clusters, effusive (predominantly monomer) and cluster beams of specifically labeled formic acid-*d* (FAD) were also studied. A photoelectron-photoion-coincidence (PEPICO) technique was applied to time-of-flight (TOF) measurements of the charged species generated under effusive and cluster beam conditions. The photoinduced fragmentation of these proto-

type H-bonded clusters in the O *K*-edge region is discussed based on the PIYs and branching ratios (BRs) of the product cations originating from small FA clusters.

II. EXPERIMENT

The experiments were performed using the cluster-photochemistry apparatus connected to a high-resolution plane-grating monochromator[12] at the *c* branch of the soft x-ray beamline BL27SU of the SPring-8 facility. The apparatus has been described in detail elsewhere,[13,14] and only a minimal description of the major components and procedures is given here. A continuous cluster beam was generated by supersonic expansion of a gaseous mixture of 2%–6% FA(FAD) with He through a $\phi 30 \mu m$ nozzle under stagnation pressures of $P_0 = 0.1 - 0.3$ MPa, the mixture being prepared by bubbling He gas through a liquid FA(FAD) sample in a cylinder. The beam was collimated with a $\phi 1.0$ mm skimmer and allowed to enter the main chamber of the apparatus, where it was crossed with a beam of monochromatized soft x rays at the ionization region of a double-field-type TOF mass spectrometer.[15] An "effusive" (monomeric) beam was prepared by direct introduction of pure FA(FAD) through a 1/16 in.o.d. stainless-steel tube into the ionization region. A constant electrostatic field of 400 V/cm was applied across the interaction region throughout the TOF measurements, which served to accelerate photoions into the TOF spectrometer (with a drift length of $L = 679$ mm) and photoelectrons directly to a microsphere plate (MSP) electron detector. The detector signals were processed with Ortec NIM modules controlled by a personal computer, and the PEPICO signals were recorded using a fast multihit digitizer (FAST ComTec 7886) with a time resolution typically set to 4 ns.

The bandwidth of the monochromator for the soft x-ray radiation was $E/\Delta E = 8000$ ($\Delta E = 0.07$ eV) at the energy corresponding to the oxygen *K* edge. TIY spectra were recorded using a step width of 0.05 eV, while PIY spectra in the preedge resonance region were typically recorded with a 0.10 eV step width. The peak positions listed in Tables I and II were determined with the aid of a deconvolution analysis. The photon energy was calibrated using the $O1s \rightarrow 4p/5s$ Rydberg transition of molecular CO_2 (Ref. 16) at 540.01 eV.

The samples used were of commercial quality. Formic acid (HCOOH) and formic acid-*d* (HCOOD) were supplied by Aldrich at purities of $\geq 98\%$, and helium by Taiyo Toyo Sanso at $\geq 99.99\%$. In preliminary experiments a baked molecular sieve was immersed into the liquid FA(FAD) sample in the cylinder to minimize any possible H_2O impurities, but no change was observed in the TOF fragment-mass patterns so for the experiments described below both the FA and FAD samples were used without further purification.

A special precaution was taken for the effusive sample condition to ensure reliable spectral measurements for free FA(FAD) molecules. Due to the HB interaction, the concentration of dimers in equilibrium increases when the system is at high pressures or low temperatures. Refined thermochemical data[17,18] predict that less than 1% of FA(FAD) molecules are dimerized at an equilibrium vapor pressure of

TABLE I. Peak assignments of molecular FA and FAD in the oxygen K-shell region.

Band No.	Energy (eV)			Term value (eV)	Assignment
	Present work	Calc.[a]	Other experiment[b]		
1	532.01	532.38 (0.014)[c]	532.17	6.94	$O1s_{CO} \rightarrow \pi^*_{CO}$
#	$\cdots$	535.04 (0.001)			$O1s_{CO} \rightarrow \sigma^*_{O-H}$
2	534.8	535.16 (0.005)	535.37	5.85	$O1s_{OH} \rightarrow \pi^*_{CO}$
3	535.8	535.18 (0.007)	535.37	4.85	$O1s_{OH} \rightarrow \sigma^*_{O-H}$
4	537.14	536.24	537.16	1.81	$O1s_{CO} \rightarrow 4s$
*			537.34		$4s + \nu_3$
*			537.54		$4s + 2\nu_3$
5	538.13	538.16	538.37	2.52	$O1s_{OH} \rightarrow 3p$
IP(C=O)	$\cdots$		[538.95, 539.02][d]		
IP(OH)	$\cdots$		[540.65, 540.69][d]		
6	542.48		542.3		$O1s_{OH} \rightarrow \sigma^*_{C-OH}$

[a]Takahashi *et al.* (Ref. 11).
[b]Prince *et al.* (Ref. 6).
[c]The value in the parentheses is oscillator strength calculated in Ref. 23.
[d]IP values in the brackets were experimentally determined in Ref. 31.

$\sim$1 Pa ($\sim$0.01 Torr) in a collision cell. The FA(FAD) sample was introduced upstream of the interaction region via a leak valve and stainless-steel tubing of $\sim$1.5 m in length to ensure that equilibrium at low pressures was reached through wall collisions. Since the FA(FAD) molecules were kept at pressures below 10^{-4} Pa and no fragment cations originating from clusters (dimers) were observed in the TOF spectra of effusive FA(FAD), we conclude that FA(FAD) clusters do not contribute to the spectroscopic measurements under the effusive condition.

III. RESULTS AND DISCUSSION

A. Total ion yield (TIY) spectra

The top trace in Fig. 2 shows a TIY spectrum of free FA molecules obtained under the effusive condition. The spectrum was recorded in the 530–550 eV energy region, covering the oxygen K-edge transitions. The spectral features resemble the EELS spectra[3,4] and closely accord with the recent high-resolution NEXAFS spectrum,[6] characterized by two intense $O1s_{CO/OH} \rightarrow \pi^*/\sigma^*$ (532.2 and 535.4 eV) and $O1s_{CO/OH} \rightarrow 4s/3p$ (537.2 and 538.4 eV) Rydberg transitions in the preedge region, as denoted in the figure. The TIY spectra of FA clusters observed under stagnation pressures of

$P_0 = 0.1$ and 0.3 MPa are also shown in Fig. 2 (middle and lower traces). They were found to have almost the same spectral features. The three main TIY peaks of the FA clusters in the preedge region appear at energies of 532.1, 535.1, and 538.5 eV, and a broad transition above the ionization edge occurs at $\sim$542.5 eV. The preedge TIY cluster bands have broader bandwidths and show appreciable spectral band shifts within the accuracy of the present photon energy scale. For example, the first TIY resonance peak is shifted by $\sim$0.1 eV to a higher energy, and the second resonance peak by $\sim$0.3 eV to a lower energy. These shifts are interpreted as being due to the contributions from small H-bonded clusters and free molecules involved within the cluster beam. Further discussion on the band structures in the preedge region will be given in the later sections. As can be seen in the several core-excited clusters,[19,20] the relative intensity in the $O1s$ continuum region increases with increasing stagnation pressure of the cluster beam. This intensity increase in the continuum has been explained[20] as the effective formation and fragmentation of multiple-charged clusters at higher energies.

The TIY spectrum of the cluster beam showed no apparent changes in the peak positions and relative peak intensities as the stagnation pressure was increased up to $P_0 = 0.3$ MPa,

TABLE II. Peak assignments of FA and FAD clusters in the oxygen K-shell region.

Band No.	Energy (eV)		Term value (eV)	Assignment
	Present work	Theor./Calc.[a]		
1′	532.36	532.7 (0.012)[b]	6.67	$O1s_{CO} \rightarrow \pi^*_{CO}$
2′	534.46	534.5 (0.006)	5.57	$O1s_{OH} \rightarrow \pi^*_{CO}$
#	$\cdots$	536.5 (0.0005)		$O1s_{CO} \rightarrow \sigma^*_{O-H}$
#	(537.0)	537.1 (0.0007)	(3.03)	$O1s_{OH} \rightarrow \sigma^*_{O-H}/3s$Ryd.
IP(C=O)	$\cdots$	539.03 [539.05][c]		
IP(OH)	$\cdots$	540.03 [540.07]		

[a]Takahashi *et al.* (Ref. 11).
[b]The value in the parentheses is oscillator strength calculated in Ref. 23.
[c]IP value in the brackets was also theoretically determined by Aplincourt *et al.* (Ref. 33).
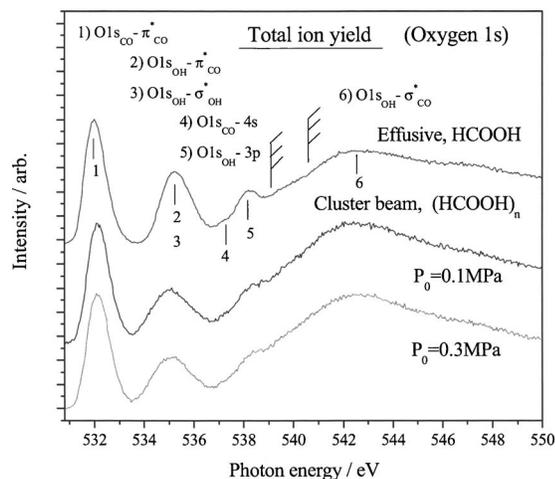
FIG. 2. Comparison of the TIY spectra between free FA molecules and $(FA)_n$ clusters observed with core excitation at the O K edges; (a) effusive condition and (b) cluster beams. For details, see the text.

FIG. 3. Comparison of the TOF spectra between free FA and FAD molecules observed with $O1s_{CO} \rightarrow \pi^*_{CO}$ excitation at 532.1 eV.

indicating that the beam is in the small cluster regime.[21] In this regime the beam contains a certain amount of uncondensed free FA molecules, and effective production of large-sized clusters is not achieved due to the low sample densities (2%–6% FA in He) under such beam conditions. As will be alluded to later on, protonated clusters $(FA)_n H^+$ with $n \geq 3$ could not be detected upon core excitation even at a stagnation pressure of $P_0 = 0.3$ MPa. It is of interest to consider the *ab initio* MO calculation data[23] with basis-set-superposition-error (BSSE) and zero-point-vibrational-energy (ZPVE) corrections, obtained at the MP2/cc-pVTZ level of theory. These data predict that the binding energy between the FA monomers in the stable dimer (~12.4 kcal/mol) is significantly larger than that between the dimers in the tetramer (~1.5 kcal/mole), regardless of the orientation of the constituent dimers. Since the magnitude of the latter is much smaller than the binding energies between molecules with protic hydrogen and lone-pair acceptor sites such as methanol[24] (~5.6 kcal/mol) and water[25] (~5.2 kcal/mol), significant growth of FA clusters larger than the stable dimers and trimers is considered to be suppressed on thermochemical grounds. Under the small cluster regime beam conditions, we thus assume that the stable dimers and trimers are present in the highest concentrations, but in the discussion which follows we also assume the presence of clusters of sizes up to $n = 5–6$.

B. PEPICO spectra

1. TOF spectra of molecular FA (HCOOH/HCOOD)

Figure 3(a) shows a typical PEPICO spectrum of molecular FA obtained in the effusive condition. The spectrum was recorded at 532.1 eV excitation energy, corresponding to the carbonyl oxygen $O1s_{CO} \rightarrow \pi^*_{CO}$ transition. At this energy H^+, CH_n^+, OH_n^+, and COH_n^+ fragments are produced at higher rates than larger fragments with masses of $CO_2H_n^+$. This is a general characteristic of fragment-mass distribution of PEPICO spectra recorded at the oxygen-core excitation of molecular FA. Among the mass groups, CH_n^+, OH_n^+, COH_n^+, and $CO_2H_n^+$, TOF peaks without hydrogen ($n = 0$) are usually
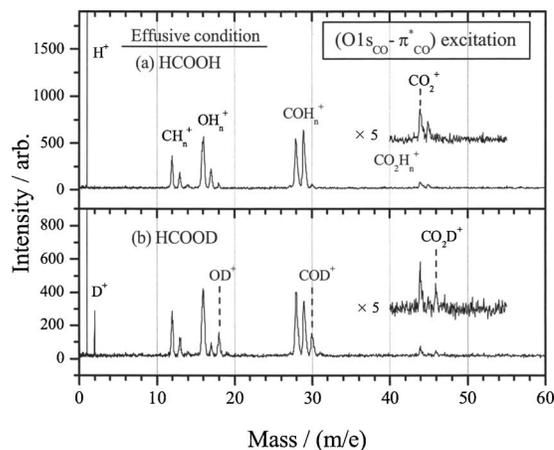
the largest, except for COH^+ and CO_2H^+. The latter intensities are found to be dependent on the excitation energy. The COH^+ peak intensity decreases from the CO^+ level at high excitation energies above the $O1s_{CO} \rightarrow \pi^*_{CO}$ excitation, whereas the CO_2H^+ intensity reaches to the CO_2^+ level above the ionization thresholds[26] (~540 eV). A trace amount of H_2O^+ production is also seen in the core excitation of molecular FA, indicating that a H/H^+ transfer process is involved in its deexcitation mechanism.

Figure 3(b) shows a similar TOF spectrum from molecular FAD at 532.1 eV obtained under the same effusive condition. Since a hydrogen atom in the hydroxyl group is replaced with a deuterium atom in FAD, most of the $COH^+ (m/e = 29)$ fragments can be identified as being formyl (HCO^+) cations. In a similar manner, the $CO_2H^+ (CO_2D^+)$ products are not attributable to formate cations but are assigned to carboxylic cations. Besides the $OD^+ (m/e = 18)$ cation, we also observe the appearance of $OH^+ (m/e = 17)$ and $HDO^+ (m/e = 19)$; formation of the latter indicates that the formyl hydrogen is mobile enough to undergo H migration in the FAD molecule,

$$HC(O)OD^+ \rightarrow [CO \cdots HOD]^+ \rightarrow CO + HDO^+. \quad (1)$$

This shows a noticeable correspondence to the decay process found in the previous study[19] of inner-shell excitation of methyl formate $[HC(O)OCH_3]$, where CH_3OH^+ production by the loss of CO was explained by H transfer from the formyl group to the migrating moiety. It is also notable that the formation of parent FA/FAD cations could not be appreciably identified in the TOF spectra of molecular FA/FAD.

2. TOF spectra of small FA clusters [(HCOOH)$_n$/(HCOOD)$_n$]

Using cluster beams with 2% FA/He and 2%FAD/He mixtures, TOF spectra of core-excited formic acid clusters were recorded under a stagnation pressure of 0.3 MPa. The spectra observed at an excitation energy of 532.1 eV are given in Fig. 4 for comparison with those obtained under the effusive condition (Fig. 3). Although the signal intensities of $CO_2H_n^+$ ($CO_2H_p D_q^+$) cations were found to be still relatively weak, as was the case for the free molecules (Fig. 3), spectral
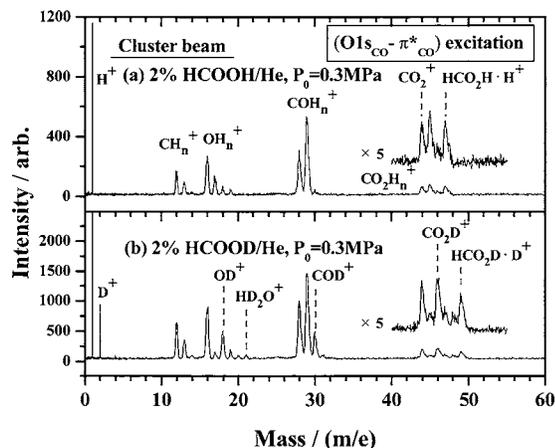
FIG. 4. Comparison of the TOF spectra between FA and FAD clusters observed with $O1s_{CO} \rightarrow \pi^*_{CO}$ excitation at 532.1 eV.

growth of the $CO_2H_3^+$ ($CO_2HD_2^+$) peaks can be ascertained. The production of these cations in the FA(FAD) cluster beams indicates that they are protonated $HCOOH \cdot H^+$ and deuteronated $HCOOD \cdot D^+$ that originate in formic-acid clusters. The deuterium-labeled experiment also showed that $HCOOD \cdot D^+$ could be formed via site-specific deuteron (proton) transfer from the hydroxyl group of the neighboring molecule in the cationic clusters, indicating a reaction center at one of the strong HB sites,

$$(HCOOD)_n^+ \rightarrow HCOOD \cdot D^+ + HCOO$$
$$+ (n-2)HCOOD. \tag{2}$$
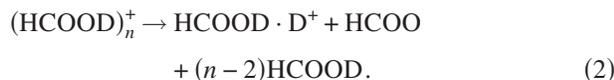
Such site-specific proton (deuteron) transfer processes have previously been observed in the core-excited clusters of specifically labeled methanol[27] and methyl formate.[19] It has been also demonstrated[19,28] that the proton (deuteron) transfer reaction occurs on the lowest energy pathways after the intracluster energy transfer via molecular evaporation following the electronic relaxation. It is also notable here that no apparent cluster cations $(HCOOH)_nH^+$ and $(HCOOD)_nD^+$ with $n \geq 3$ could be identified with beam-stagnation pressures below $P_0 = 0.3$ MPa.

The oxonium ions H_3O^+ ($m/e = 19$) produced from FA clusters and HD_2O^+ ($m/e = 21$) from FAD clusters seen in Fig. 4 are also regarded as being of cluster origin. The intensities of the above cations are not particularly high but are evidence of the H(D) transfer reaction in the FA(FAD) clusters, with H_3O^+ (HD_2O^+) being formed via H_2O^+ (HDO^+) precursors. H_2O^+ (HDO^+) can be formed by the loss of CO via the site-specific process (1) in the molecular level, interacting with the nearest-neighbor molecule within the clusters,

$$(HCOOD + HDO^+) \rightarrow (HC(O)O \cdots DOHD^+)$$
$$\rightarrow HCOO + HD_2O^+. \tag{3}$$
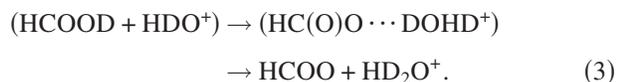
In a similar study of core excitation of methyl-formate clusters,[19] the production of the methyl-oxonium cation was interpreted as being due to the successive transfer of another deuterium (hydrogen) atom from a neighboring molecule within the clusters. The energetics predicted by an *ab initio*

MO calculation showed that once the ROH^+ precursor was produced in the clusters then the formation of oxonium cation could proceed with an activation barrier as high as ~ 15 kcal/mol, when the cationic system was generated in the electronic ground state.

Product distribution in the FA(FAD) clusters has been examined in detail by comparison of the TOF spectra from the free FA(FAD) molecules (Fig. 3) and clusters (Fig. 4). The TOF spectra of FA(FAD) clusters showed that (A) the production of atomic and small fragments such as C^+, O^+, and CO^+ was generally suppressed in the cluster beams but had a TOF pattern similar to that of the effusive condition. This indicates that the fragments are largely produced from free FA(FAD) molecules since the cluster beam produced under the present stagnation condition still contains a certain amount of uncondensed free FA(FAD) molecules. We also observed that (B) the relative intensities for CHO^+ and $COOH^+$ ($COOD^+$) were enhanced significantly in the cluster beams. These products are not always cluster in origin but show strong characteristics of fragments produced from molecules within the clusters through the suppression of further fragmentation due to the transfer of their excess energies to surrounding molecule(s), including the HB partner. We previously showed that the excitation center[11] actually appears in a molecule site within the HB clusters where core excitation is made. Since the present cluster-size distribution is in the small cluster regime, then enhanced production of these fragments (CHO^+ and $COOH^+$) with low $(HCOOH)_nH^+$ and $(HCOOD)_nD^+$ yields suggests that excess energy transfer by evaporation is not sufficiently achieved and that *local* fragmentation of the center molecule is strongly favored, along with the elimination of the HB partner, in the deactivation of the formic-acid clusters. Further discussion on the formation mechanisms of the oxonium and protonated cluster cations will be continued in the later sections.

C. Partial ion yield (PIY) spectra and branching ratios (BRs)

1. PIY spectra of molecular FA (HCOOH/HCOOD)

The PIY spectra of some representative cations for molecular FA are shown in Fig. 5, where the TIY spectrum is also indicated for comparison. Most of their spectral patterns are generally similar to the TIY, although the relative intensities of the band peaks (at ~ 532.1, ~ 535.1, and ~ 542.5 eV) are different in individual fragment spectra. Close inspection shows that the second peak of each PIY spectrum has a different energy position and shape from those in the TIY spectrum. This is particularly noticeable in the PIY of the COO^+ fragment, indicative of the second band structures made up by superposition of different transitions of core excitation. The second TIY peak being noticeably broader than the first resonance can be thus interpreted as being due to the mixture of band structures.

Figure 6 shows the BRs of several fragment cations for molecular FA(FAD), in comparison with the TIY spectrum. Significant increase in the CHO^+/COH^+ ratios at the $O1s_{CO} \rightarrow \pi^*_{CO}$ excitation in the middle panel shows that it contributes much to the production of CHO^+/COH^+ in mo-
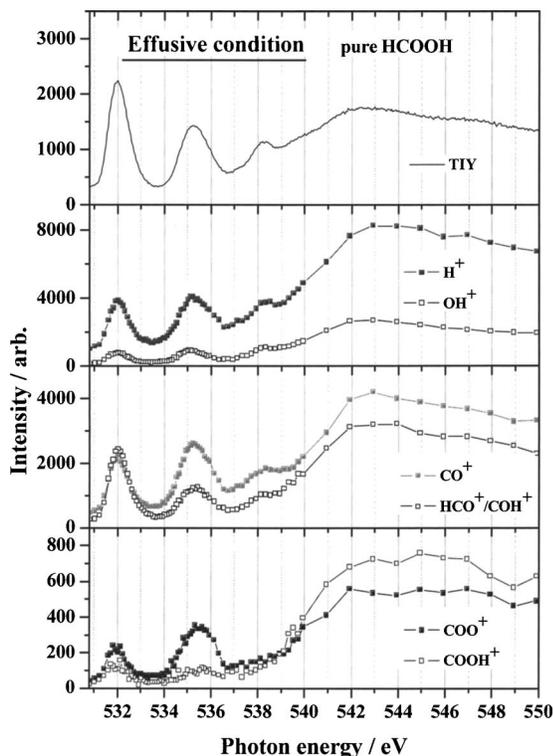
FIG. 5. Comparison among the PIY spectra for some representative cations, H^+, OH^+, CO^+, HCO^+/COH^+, COO^+, and $COOH^+$, produced in the $O(1s)$ core excitation of free FA molecules. TIY is shown at the top panel.

lecular FA. The deuterium-labeled experiment reveals that both CHO^+ and COD^+ productions are dominant at the $O1s_{CO} \rightarrow \pi^*_{CO}$ transition but the former showed a preferential relative importance throughout the core excitation. Their productions are interpreted as being due to the π^*_{CO} orbital that has an antibonding π character both between C and carbonyl O, and C and hydroxyl O atoms, as were discussed in studies
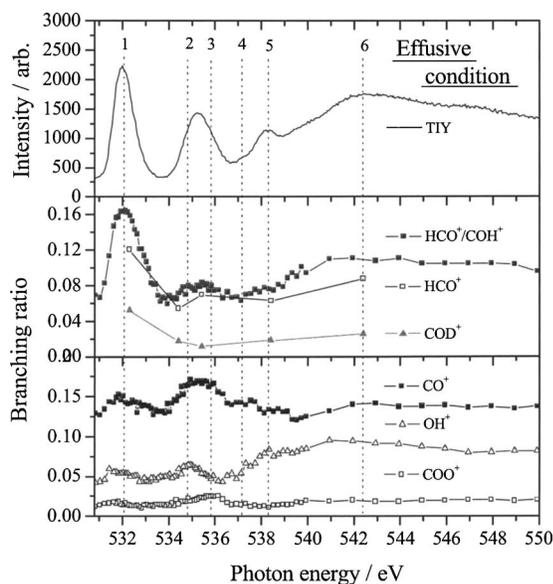
FIG. 6. Comparison among the BRs for some representative cations, HCO^+/COH^+, CO^+, OH^+, and COO^+, formed in the $O(1s)$ core excitation of free FA molecules. The BRs for the CHO^+ and COD^+ formation in the free FAD molecules are also plotted for comparison at several excitation energies. TIY is shown at the top panel.

of the core excitation of methyl formate.[29] The relative stability of HCO^+ at the first $O1s_{CO} \rightarrow \pi^*_{CO}$ excitation comes from the bound nature of C=O that still remains after the core excitation to the antibonding π^* orbital; this is less likely to cause significant C=O dissociation.

An interesting band structure is found in the region of the second TIY peak, where it is possible to identify double peaks for the BR of CHO^+/COH^+ in Fig. 6. We here assigned the band located at the lower energy of $\sim$534.8 eV to the $O1s_{OH} \rightarrow \pi^*_{CO}$ transition and that at the higher energy of $\sim$535.8 eV was assigned as the $O1s_{OH} \rightarrow \sigma^*_{O-H}$ transition. The energy step width used in the PIY spectra may not be small enough to observe any double peaks due to the limited number of data points; the BR of CO^+ has also a single peak wider than the second TIY peak. The peak at $\sim$534.8 eV and the valley at $\sim$536 eV of the BR for OH^+ can be interpreted as the enhancement in $[HC(O)-OH]^+$ dissociation at the $O1s_{OH} \rightarrow \pi^*_{CO}$ transition and the blocking of OH^+ formation by $[HC(O)O-H]^+$ fission at the $O1s_{OH} \rightarrow \sigma^*_{O-H}$ band. The latter observation is supported[30] by the increase of the BR for COO^+ at the $O1s_{OH} \rightarrow \sigma^*_{O-H}$ band.

The broadening of the second band of the NEXAFS (Ref. 6) and EELS (Refs. 3 and 4) spectra has so far suggested that there exists an overlapping structure for the different transitions with similar energies. We here observed the PIYs and photon energy dependences of BRs for fragment cations and identified a new feature in the band that can be assigned to the $O1s_{OH} \rightarrow \pi^*_{CO}$ and $O1s_{OH} \rightarrow \sigma^*_{O-H}$ transitions. The assignments of molecular FA are summarized in Table I, where comparisons with those from the recent NEXAFS (Ref. 6) and theoretical x-ray absorption spectroscopy (XAS) works[11] are made. Assignments other than those mentioned above follow the NEXAFS results. A Gaussian deconvolution analysis was used to confirm the peak positions and the peak energies listed in Table I were determined by adjusting the peak parameters to give the best fit to the observed TIY spectra.

2. PIY spectra of small FA clusters $[(HCOOH)_n/(HCOOD)_n]$

Figure 7 compares the PIY spectra of the representative cations from $(HCOOD)_n$ clusters observed at a pressure of $P_0 = 0.3$ MPa, along with the TIY spectrum under the same beam condition. The cluster beam produced under the condition still contains a certain amount of uncondensed free molecules, but "cluster-specific" excitation spectra can be recorded without contribution of free molecules by monitoring the PIYs of the fragments originating from FA(FAD) clusters. Following the arguments in Sec. III B 2, atomic and small fragment cations such as C^+, CO^+, and $OD^+(OH^+)$ that primarily come from molecular FA(FAD) have actually the same PIY peak patterns and positions as those in Fig. 5. In contrast, the PIYs of the cluster-specific products, $HCOOD \cdot D^+$ and HD_2O^+, have different resonance peaks from the monomer bands; the first band peak is slightly shifted to the high-energy side by $\sim$0.2 eV and the second band to the lower-energy side by $\sim$0.6 eV from the monomer band. The PIYs (i.e., the excitation spectra) of HCO^+ and $COOD^+$ show peak patterns very close to the cluster-
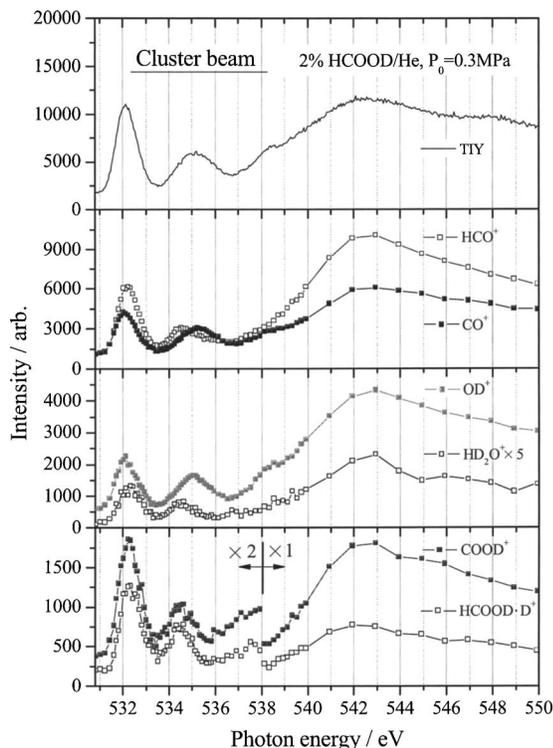
FIG. 7. Comparison of the PIY spectra for some representative cations, CO^+, HCO^+, OD^+, HD_2O^+, $COOD^+$, and $HCOOD \cdot D^+$, produced in the $O(1s)$ core excitation of FAD clusters. TIY is shown at the top panel.

FIG. 8. Comparison among photon energy dependences of the BRs for some representative cations, CO^+, OD^+, HCO^+, $COOD^+$, $HCOOD \cdot D^+$, and HD_2O^+, formed in the $O(1s)$ core excitation of FAD clusters. TIY is shown at the top panel.

specific bands, clearly consistent with the arguments given in Sec. III B 2. It may thus be concluded that the formation of fragments HCO^+ and $COOH^+$ ($COOD^+$) increases when the system is condensed upon clusterization.

The photon energy dependences of BRs for the cluster-specific cations ($HCOOD \cdot D^+$ and HD_2O^+) are quite distinct when they are compared with those of the molecular-origin cations (C^+ and CO^+), as shown in Fig. 8. The BRs of HCO^+ and $COOD^+$ formation again show similar spectral patterns but have larger magnitudes than those of the apparent cluster-specific products ($HCOOD \cdot D^+$ and HD_2O^+). These results support the argument that decay processes following the core excitation of FA(FAD) clusters may take place locally by direct dissociation at the hot molecule site[32] in such small HB clusters where the first excitation is made, and that H^+/D^+ transfer processes with low internal energies are considerably suppressed to give such low yields of the cluster-specific products when the system is in the small cluster regime. Based on the PIYs and BRs of these product cations, we determined the cluster peak positions to be 532.4 and 534.5 eV for the core-valence transitions $O1s_{CO} \rightarrow \pi_{CO}^*$ and $O1s_{OH} \rightarrow \pi_{CO}^*$, respectively. The parameters of the cluster bands are listed in comparison with those theoretically predicted in Table II. Theoretical peak energies were adopted from the XA spectrum[11] calculated for the most stable dimer structure, under the assumption that small FA clusters actually consist of the most stable dimer and/or trimer units.[10]

The core-electron binding energy (CEBE) depends heavily on the electron density around the particular atom to which the core electron is localized. It has been demonstrated that the electron density around the hydroxyl oxygen is more strongly perturbed than that of the carbonyl oxygen when FA(FAD) is dimerized by the formation of HBs.[11,33] As a consequence, the ionization potential (IP) (or CEBE) of $O1s(CO)$ in the dimer was calculated to be slightly shifted to a higher energy, whereas the IP of $O1s(OH)$ was found to be shifted to a lower energy by ~0.6 eV compared to molecular FA(FAD) (Table II). The $\pi^*(CO)$ orbital to be excited is actually insensitive to dimerization via HBs due to its out-of-plane character; the peak shifts of the $O1s_{CO/OH} \rightarrow \pi_{CO}^*$ excitations are then responsible for the difference in CEBEs for these two oxygen atoms in the FA(FAD) clusters. Both experimental peak energies for the π_{CO}^* excitations are very close to the theoretical predictions (532.7 and 534.5 eV) and the variation in transition energies upon clusterization can be understood by the above interpretations. Due to the in-plane character of the $\sigma^*(OH)$ orbital, in contrast, the excitation energies to the $(O1s_{CO/OH}^{-1}\sigma_{OH}^*)$ states are strongly perturbed by the dimerization via HBs. The σ_{OH}^* excitations shift their peak positions to higher energies because of the induction of additional antibonding interaction between two formic acids, and concurrently reduce their transition intensities due to the significant decrease in Franck-Condon densities for core excitation. The DFT calculation[11] predicts the excitation energies of the stable dimers for the $O1s_{CO/OH} \rightarrow \sigma_{OH}^*$ transitions to be higher by 1.4–1.9 eV compared to the molecular formic acid, if their oscillator strengths are within the detectable limit. The broad augmentation of the BRs at ~537.0 eV that appears in the fragments from clusters (Fig. 8) may suggest the existence of $O1s_{CO/OH} \rightarrow \sigma_{OH}^*$ transitions upon clusterization of formic acid. In the small clusters of formic acid, however, Rydberg transitions to the $(O1s_{CO}^{-1}4s)$ and
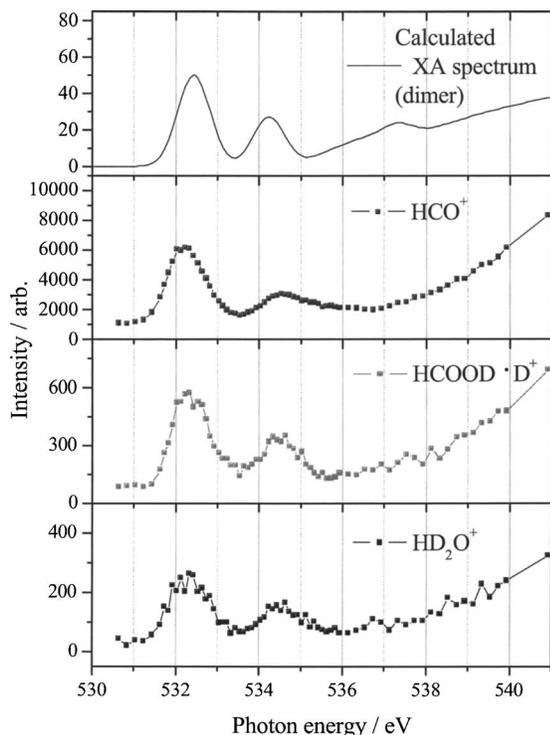
FIG. 9. Comparison of the PIY spectra for some representative cations, HCO^+, $HCOOD \cdot D^+$, and HD_2O^+, with the XA spectrum of FA dimer predicted by Takahashi *et al.* (Ref. [11]).

FIG. 10. Schematic diagrams of [(a) and (b)] local fragmentation and (c) H^+/D^+ transfer channels induced after the inner-shell excitation of $(HCOOD)_2^+$ dimer. (a) HCO^+ ($+OD+HCOOD$) formation, (b) $COOD^+$ ($+H+HCOOD$) formation, and (c) $HCOOD \cdot D^+$ ($+HCOO$) formation. The ΔH values are given relative to the energy of vertically ionized $[(HCOOD)_2^+]_{ver}$ dimer.

$(O1s_{OH}^{-1}3p)$ states cover the same region and overlap the $O1s_{CO/OH} \rightarrow \sigma_{OH}^*$ transitions, so a definite assignment for the ~537.0 eV region cannot be made here.

The excitation spectra for the cluster-specific products and their analogs (HCO^+ and $COOD^+$) are compared with the calculated XA spectrum for stable dimers in Fig. 9. In contrast to the HCO^+ excitation spectrum that involves a certain amount of molecular contribution, the PIYs of $HCOOD \cdot D^+$ and HD_2O^+ make good comparisons with the calculated XA spectrum at the resonant core-valence transitions. It has been shown that small FA clusters are made up mostly of stable dimer(s) and/or trimer(s), and that their calculated XA spectra are actually very similar due to the strong HB ($-OH \cdots O=C<$) formation.[11] Therefore, the present good comparison of the cluster-specific spectra with the calculated XA spectrum verifies that they originate from such small FA clusters with the most stable conformations.

D. Fission mechanisms of molecular FA and small FA clusters

Significant production (high BR) of HCO^+ at the $O1s_{CO} \rightarrow \pi_{CO}^*$ resonance was observed in effusive FA molecules (Fig. 6). Also seen are some other fragment cations such as CO^+, OH^+, and COO^+ that increase at the second and/or third resonance band. The increase (or decrease) in the fragment BR at the resonance can be understood by the antibonding character of the valence orbital produced in each core-valence transition. Recent resonance Auger spectra of formic acid[34] have demonstrated the predominance of spectator Auger transitions compared to weak participant Auger decays, so we can conclude that most of the dissociative

ionization of molecular FA in the resonance region takes place from the spectator Auger final states, which have one electron left in an antibonding orbital and two valence holes.

In the case of the cluster beam, we found that the HCO^+ product strongly comes from small clusters since its BR also increases at the cluster-specific $O1s_{CO/OH} \rightarrow \pi_{CO}^*$ bands. Also note that the system favors the HCO^+ production rather than CO^+ at the second $O1s_{OH} \rightarrow \pi_{CO}^*$ cluster band (Fig. 8), when it is compared with those in the effusive condition (Fig. 6). The present contrast between the effusive and cluster conditions indicates that the secondary dissociation of HCO^+ is suppressed in the cluster bands due to the subsidiary energy transfer to the surroundings, especially to the HB partner. A BR behavior similar to the above could also be seen in the $COOH^+$ ($COOD^+$) production. Under the interaction with surrounding molecules, photoreaction within the clusters takes place in competition with the intracluster energy transfer processes. In order to explain the reaction dynamics in the core-excited HB clusters, $(HCOOD)_2$ dimer was chosen as a representative of the clusters of small sizes. The schematic reaction channels that indicate [(a) and (b)] local fragmentation and (c) H^+/D^+ transfer in the case of core-excited $(HCOOD)_2^+$ dimer are shown in Fig. 10. Here, the energetics (ΔH) of the channels[35] are given relative to the energy of vertically ionized $[(HCOOD)_2^+]_{ve}$ dimer from the most stable $(HCOOD)_2$ in the electronic ground state. Since the excitation spectra (PIYs) of fragments HCO^+ and $COOD^+$ have spectral patterns similar to the cluster-specific bands, this finding suggests that the fragmentation processes [(a) and (b)] of the HB cluster occur locally at the hot molecule site[32] that remains after the Auger electronic decays, when the cluster size is small and excess energy transfer in the cluster is not effectively achieved. The cluster-specific excitation spectra could be measured without molecular contribution by monitoring the PIYs for $HCOOH \cdot H^+$ ($HCOOD \cdot D^+$) and H_3O^+ (HD_2O^+) products. Since their production is consid-

ered not to involve the fast dissociation dynamics on the high-energy surfaces [Fig. 10(c)] and shows similar PIY and BR patterns although they are of minor importance, we can conclude that they are produced via intermediate precursors in the electronic ground state which have enough excess energy to react with the HB partner by the H^+/D^+ transfer process, after the evaporation of neutral molecules[19] in clusters probably larger than dimers or trimers.

IV. CONCLUSIONS

Inner-shell excitation spectra of small hydrogen-bonded (HB) formic-acid (FA) clusters in the O K-edge region have been recorded for the first time using a synchrotron radiation source. In order to examine the influence of different hydrogen sites on the photoinduced process, deuterium-labeled formic acid-d (FAD), HCOOD was also studied. By monitoring the PIYs of the products $HCOOH \cdot H^+$ ($HCOOD \cdot D^+$) and H_3O^+ (HD_2O^+), "cluster-specific" excitation with no contribution from molecular excitation could be studied. Comparison of the cluster bands with those of molecular FA showed that the first $O1s_{CO} \to \pi^*_{CO}$ band shifts upwards (to a higher energy) by ~ 0.2 eV while the second $O1s_{OH} \to \pi^*_{CO}$ shifts downwards by ~ 0.6 eV. The core-excitation spectra to the resonance excited-valence orbitals compared well with theoretical predictions. The photon energy dependences of the product branching ratios exhibit distinct production of fragment cations HCO^+ and $COOH^+$ in the cluster bands. The efficient formation of HCO^+ suggests that local fragmentation at a hot molecule site is also involved within the HB clusters after Auger relaxation.

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