

# Structures of water-CO<sub>2</sub> and methanol-CO<sub>2</sub> cluster ions: [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1–7)

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Infrared photodissociation (IRPD) spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1–7) are measured in the 1100–3800 cm<sup>-1</sup> region. At the same time, the solvation characteristics in the clusters are investigated theoretically; the geometry optimization and the vibrational analysis are carried out for the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1–4) and the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1–3) ions at the MP2/6-31+G\* level of theory. The IRPD spectrum of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion shows the free OH and the hydrogen-bonded OH stretching bands of the H<sub>2</sub>O<sup>+</sup> ion core and the antisymmetric CO stretching band of the solvent CO<sub>2</sub> molecule, indicating that the solvent CO<sub>2</sub> molecule is preferentially solvated to the H<sub>2</sub>O<sup>+</sup> ion core via the O–H•••OCO hydrogen bond. In [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, the free OH stretching band is not observed; both of the OH groups of the H<sub>2</sub>O<sup>+</sup> ion core are hydrogen bonded to the solvent CO<sub>2</sub> molecules. Spectral features of the IRPD spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=3–7) suggest that the third and the fourth CO<sub>2</sub> molecules are bound to the oxygen atom of the H<sub>2</sub>O<sup>+</sup> ion core, and that the first solvation shell of the H<sub>2</sub>O<sup>+</sup> ion core becomes filled with four CO<sub>2</sub> molecules. All the IRPD spectra of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1–7) ions display the hydrogen-bonded OH stretching band of the CH<sub>3</sub>OH<sup>+</sup> ion core, meaning that the solvent CO<sub>2</sub> molecule is preferentially bonded to the OH group of the CH<sub>3</sub>OH<sup>+</sup> ion core, similar to the case of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup>. Quantum chemical calculations for the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1–3</sub>]<sup>+</sup> ions demonstrate that the second and the third solvent CO<sub>2</sub> molecules are bonded to the oxygen atom of the CH<sub>3</sub>OH<sup>+</sup> ion core. © 2009 American Institute of Physics. [DOI: 10.1063/1.3116144]

## I. INTRODUCTION

The charge distribution in molecular cluster ions depends on physical and chemical properties of constituent molecules such as the ionization potential and the proton/electron affinity. The stability of the ion core of molecular cluster ions is controlled also by the solvation structure formed around the ion core. For example, the attachment of one different molecule to homocluster ions can change the charge distribution and the cluster structure drastically. In the case of carbon dioxide homocluster anions, (CO<sub>2</sub>)<sub>n</sub><sup>-</sup>, the negative charge is delocalized over two CO<sub>2</sub> molecules in the n=2–5 ions, forming the C<sub>2</sub>O<sub>4</sub><sup>-</sup> ion core.<sup>1,2</sup> For the (CO<sub>2</sub>)<sub>n</sub><sup>-</sup> ions with n=7–13, the charge is localized in one CO<sub>2</sub> molecule, described as CO<sub>2</sub><sup>-</sup>•(CO<sub>2</sub>)<sub>n-1</sub>. For the n=6 ion, isomers with the CO<sub>2</sub><sup>-</sup> or the C<sub>2</sub>O<sub>4</sub><sup>-</sup> ion core coexist in the experiment. By contrast, the addition of one water (H<sub>2</sub>O) or methanol (CH<sub>3</sub>OH) molecule to the (CO<sub>2</sub>)<sub>n</sub><sup>-</sup> ions substantially affects the stability of the ion cores in the clusters. Photoelectron (PE) spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>-</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>-</sup> demonstrated that the CO<sub>2</sub><sup>-</sup> ion core is stable even in the n=2 ion.<sup>3–6</sup> IR studies of the

[H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>-</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>-</sup> ions showed that the preferential stability of the CO<sub>2</sub><sup>-</sup> ion core over the C<sub>2</sub>O<sub>4</sub><sup>-</sup> ion in these clusters is due to the formation of strong hydrogen bonds between CO<sub>2</sub><sup>-</sup> and H<sub>2</sub>O or CH<sub>3</sub>OH.<sup>7,8</sup> Sanov and co-workers<sup>9–13</sup> extensively studied the electronic structure and the photochemistry of the [(H<sub>2</sub>O)<sub>n</sub>•(CO<sub>2</sub>)<sub>m</sub>]<sup>-</sup> ions by PE imaging and photofragment mass spectroscopy.

For CO<sub>2</sub> cation clusters, (CO<sub>2</sub>)<sub>n</sub><sup>+</sup>, it was reported that the clusters have the C<sub>2</sub>O<sub>4</sub><sup>+</sup> ion core for n=2–26,<sup>14,15</sup> and an IR spectroscopic study of the (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ions showed no sign of the CO<sub>2</sub><sup>+</sup> ion core for n=3–8.<sup>16</sup> By contrast, there are few reports on [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> cluster ions. Heinbuch *et al.*<sup>17</sup> reported a mass spectrometric study on the single photon ionization of (CO<sub>2</sub>)<sub>n</sub> and (CO<sub>2</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> with a soft x-ray laser. They discussed the mechanism and dynamics of the formation of the molecular clusters such as (CO<sub>2</sub>)<sub>n</sub><sup>+</sup>, [(H<sub>2</sub>O)<sub>1,2</sub>•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup>, and (H<sub>2</sub>O)<sub>n</sub>H<sup>+</sup>. However, no comment has been given for the charge distribution and the structure of these cluster ions. Since the ionization potential of H<sub>2</sub>O (12.62 eV) and CH<sub>3</sub>OH (10.94 eV) is lower than that of CO<sub>2</sub> (13.78 eV),<sup>18</sup> a drastic change in the charge distribution of the (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ions is expected by the attachment of H<sub>2</sub>O or CH<sub>3</sub>OH.

In the present study, we investigate the charge distribution and the solvation structure around the ion core for [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> with n=1–7 by IR

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TABLE I. Positions ( $\text{cm}^{-1}$ ) of Lorentzian components used for the reproduction of the IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  in the antisymmetric CO stretching  $[\nu_3(\text{CO}_2)]$  region.

$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	Assignment <sup>a,b</sup>
...	...	2334	2336	2334	2nd $\text{CO}_2$
2332	2342	2343	2343	2343	c2
2356	2356	2354	2353	2353	c1

<sup>a</sup>“2nd” represents the second solvation shell.

<sup>b</sup>The  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core are called c1 and c2, respectively.

photodissociation (IRPD) spectroscopy. The IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  and  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  are measured in the 1100–3800  $\text{cm}^{-1}$  region. These clusters exhibit IR bands assignable to the CO stretching vibration of  $\text{CO}_2$ , the OH stretching vibrations of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  components, and the HOH bending vibration of  $\text{H}_2\text{O}$ . The IRPD spectra show spectral features as characteristic of the geometric and electronic structure of these clusters. By comparing the IRPD spectra with the IR spectra predicted by quantum chemical calculations, we provide definite structures for these cluster ions.

## II. EXPERIMENTAL AND COMPUTATIONAL

The details of our experiment have been given elsewhere.<sup>19</sup> Briefly, a mixture of  $\text{CO}_2$  gas and water or methanol vapor is injected into a source chamber through a pulsed nozzle with a stagnation pressure of 0.4 MPa. The pulsed free jet crosses an electron beam at the exit of the nozzle with an electron kinetic energy of 350 eV, producing  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  or  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$ . Cluster ions produced are accelerated into a flight tube by applying pulsed  $\sim 1.3$  kV potential to the acceleration grids with a width of 10  $\mu\text{s}$ . In the flight tube, only target parent ions can go through a mass gate. After passing through the gate, mass-selected parent ions are irradiated by an output of a pulsed IR laser. Resultant fragment ions are mass analyzed by a reflectron and detected by a multichannel plate. Yields of fragment ions are normalized by the intensity of parent ions and the photodissociation laser. IRPD spectra of parent ions are obtained by plotting normalized yields of fragment ions against wavenumber of the IR laser. The IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  and  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  are observed by

monitoring yields of all the fragment ions due to the loss of  $\text{CO}_2$  molecules. The tunable IR light in the 2000–3800  $\text{cm}^{-1}$  region is an idler output of an optical parametric oscillator (OPO) (LaserVision) pumped by a fundamental output of a Nd:YAG (yttrium aluminum garnet) laser. We obtain the IR laser in the 1100–2100  $\text{cm}^{-1}$  region by using different frequency generations of the idler and the signal outputs of the OPO laser with a  $\text{AgGaSe}_2$  crystal.

In order to analyze the IRPD spectra, we also carry out quantum chemical calculations of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ( $n=1-4$ ) and  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  ( $n=1-3$ ) with GAUSSIAN03 program package.<sup>20</sup> Geometry optimization and vibrational analysis are done at the MP2/6-31+G\* level.

## III. RESULTS AND DISCUSSION

### A. IRPD spectra of $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$ ( $n=1-7$ )

Figure 1 shows the IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  with  $n=1-7$  in the 1100–3800  $\text{cm}^{-1}$  region. Band positions of the IRPD spectra are collected in Tables I–III. No band is observed for the  $n=1$  ion below 2100  $\text{cm}^{-1}$ , indicating that the  $n=1$  ion does not dissociate below this energy. All the IRPD spectra in Fig. 1 display bands at around 2350  $\text{cm}^{-1}$ . Since neutral  $\text{CO}_2$  has the antisymmetric CO stretching vibration ( $\nu_3$ ) at 2349.3  $\text{cm}^{-1}$ ,<sup>21</sup> the bands at around 2350  $\text{cm}^{-1}$  can be assigned to the antisymmetric CO stretching vibration  $[\nu_3(\text{CO}_2)]$  of solvent  $\text{CO}_2$  molecules. The appearance of the  $\nu_3(\text{CO}_2)$  band in the  $n=1$  spectrum indicates that the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_1]^+$  ion has an ion-molecule form,  $\text{H}_2\text{O}^+\cdots\text{CO}_2$ . This result is reasonable because the ionization potential of  $\text{H}_2\text{O}$  (12.62 eV) is lower than that of  $\text{CO}_2$  (13.78 eV).<sup>18</sup>

TABLE II. Positions ( $\text{cm}^{-1}$ ) of Lorentzian components used for the reproduction of the IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  in the region of the  $\nu_1+\nu_3$  and  $2\nu_2+\nu_3$  combination bands of the solvent  $\text{CO}_2$  molecules.

$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	Assignment <sup>a,b</sup>
...	3578	3596	...	...	...	c2
3589	3600	3601	...	...	...	c1
...	...	...	3597	3593	3593	c1 and c2
...	...	...	3609	3609	3608	2nd $\text{CO}_2$
...	3681	3699	...	...	...	c2
3723	3721	3712	...	...	...	c1
...	...	...	3702	3695	3698	c1 and c2
...	...	...	3712	3711	3711	2nd $\text{CO}_2$

<sup>a</sup>2nd represents the second solvation shell.

<sup>b</sup>The  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core are called c1 and c2, respectively.

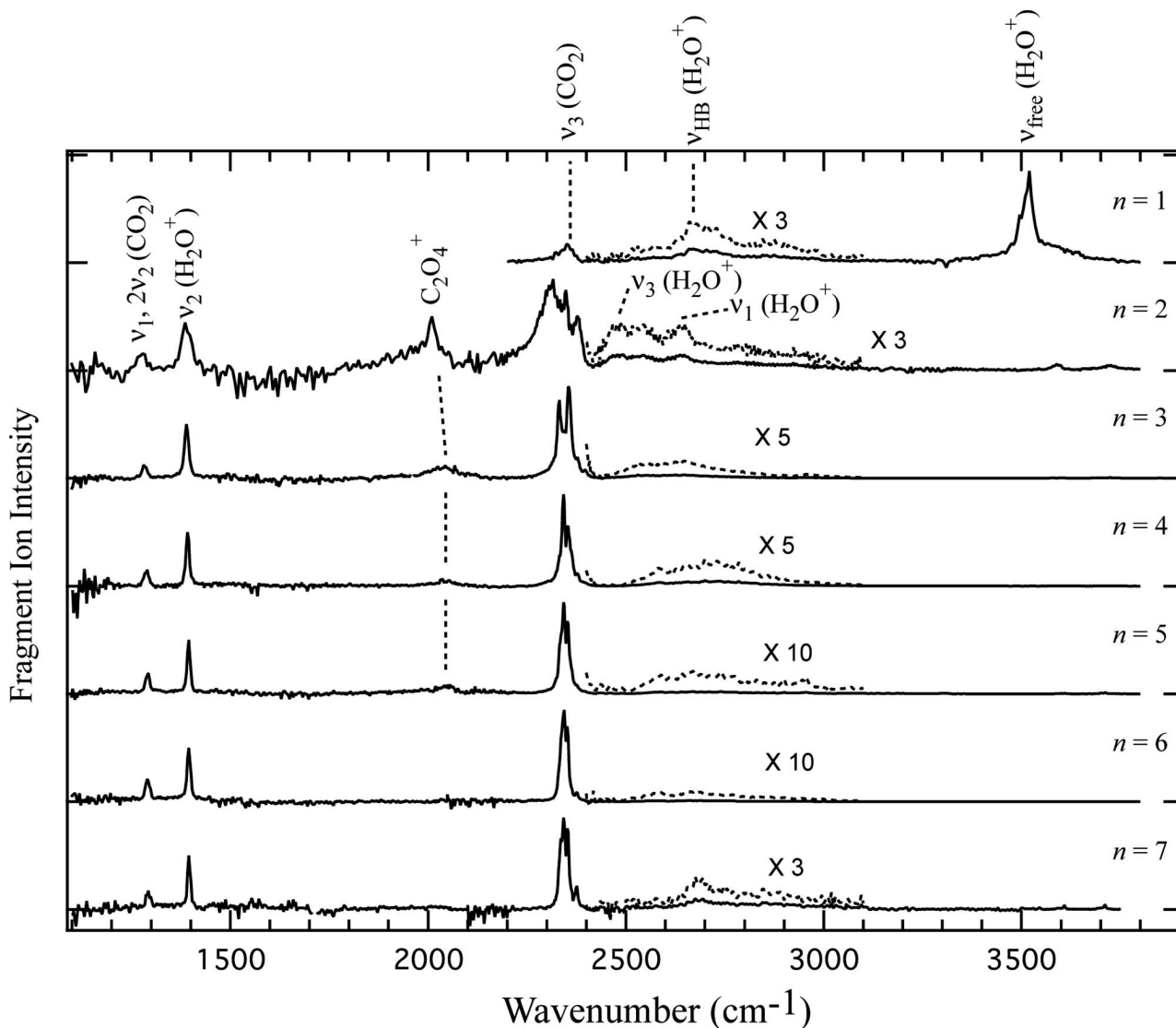


FIG. 1. The IRPD spectra of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ions with  $n=1-7$ . These spectra are observed by monitoring yields of all the fragment ions due to the loss of  $\text{CO}_2$  molecules.

In Fig. 1, there are quite broad bands in the region of 2400–3100  $\text{cm}^{-1}$ . In addition, in the  $n=1$  spectrum, a strong band is observed at 3520  $\text{cm}^{-1}$ . These bands can probably be attributed to the  $\text{H}_2\text{O}^+$  ion core. The  $\text{H}_2\text{O}^+$  monomer ion has the symmetric and the antisymmetric OH stretching vibrations [ $\nu_1(\text{H}_2\text{O}^+)$  and  $\nu_3(\text{H}_2\text{O}^+)$ ] in the 3000–3600  $\text{cm}^{-1}$  region.<sup>22–24</sup> The sharp band at 3520  $\text{cm}^{-1}$  in the IRPD spectrum of the  $n=1$  ion is ascribed to the free OH stretching band of the  $\text{H}_2\text{O}^+$  ion core [ $\nu_{\text{free}}(\text{H}_2\text{O}^+)$ ], and the broad band at around 2700  $\text{cm}^{-1}$  is assignable to the hydrogen-bonded OH stretching vibration [ $\nu_{\text{HB}}(\text{H}_2\text{O}^+)$ ]. In the  $n=2$  spectrum, no strong band is observed in the 3000–3800  $\text{cm}^{-1}$  region, so the two OH groups of the  $\text{H}_2\text{O}^+$  ion core are hydrogen bonded to the solvent  $\text{CO}_2$  molecules. Two maxima at  $\sim 2640$  and  $\sim 2480$   $\text{cm}^{-1}$  in the  $n=2$  spectrum can be assigned to the symmetric [ $\nu_1(\text{H}_2\text{O}^+)$ ] and antisymmetric [ $\nu_3(\text{H}_2\text{O}^+)$ ] OH stretching vibrations of the  $\text{H}_2\text{O}^+$  ion core. Thus, it is concluded that the first and the second solvent  $\text{CO}_2$  molecules are preferentially attached to the OH groups of the  $\text{H}_2\text{O}^+$  ion core. The broad band at around 2700  $\text{cm}^{-1}$

of the  $n=3-7$  ions are due to the  $\nu_1(\text{H}_2\text{O}^+)$  and  $\nu_3(\text{H}_2\text{O}^+)$  bands; the two OH groups of the  $\text{H}_2\text{O}^+$  ion are hydrogen bonded to the solvent  $\text{CO}_2$  molecules also in these clusters.

In the 1100–1500  $\text{cm}^{-1}$  range of the IRPD spectra, two sharp bands are identified at  $\sim 1280$  and  $\sim 1390$   $\text{cm}^{-1}$ . For gaseous  $\text{CO}_2$ , the Fermi resonance between  $\nu_1$  and  $2\nu_2$  provides two Raman active bands at 1285.5 and 1388.3  $\text{cm}^{-1}$ .<sup>21</sup> These vibrations are IR inactive under the isolated condition, but they appear at 1284.3 and 1376  $\text{cm}^{-1}$  in IR spectra of  $\text{CO}_2$  in solid Ne.<sup>25</sup> In addition, the  $(\text{CO}_2)_n^+$  ions also show these Fermi resonance bands at  $\sim 1285$  and  $\sim 1395$   $\text{cm}^{-1}$  in the IRPD spectra.<sup>16</sup> Therefore, the IRPD bands at  $\sim 1280$   $\text{cm}^{-1}$  can be assigned to the low frequency component of the Fermi doublet of solvent  $\text{CO}_2$  molecules. For the band at around 1390  $\text{cm}^{-1}$ , it may be assignable to the high frequency component of the Fermi doublet of solvent  $\text{CO}_2$  molecules. However, the relative intensity of the bands at  $\sim 1280$  and  $\sim 1390$   $\text{cm}^{-1}$  is quite different from that of  $(\text{CO}_2)_n^+$ . For the  $(\text{CO}_2)_n^+$  clusters, the low frequency band is substantially stronger than the high frequency one.<sup>16</sup> In the

TABLE III. Band positions ( $\text{cm}^{-1}$ ) and assignments of the IRPD spectra of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  in the 1100–2100  $\text{cm}^{-1}$  region.

$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	Assignment
1276	1283	1288	1291	1291	1293	$\nu_1, 2\nu_2$ ( $\text{CO}_2$ )
1389	1389	1392	1395	1395	1396	$\nu_2$ ( $\text{H}_2\text{O}^+$ )
1997	2037	2040	2041	...	...	$\text{C}_2\text{O}_4^+$

case of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$ , the former band is weaker than the latter one, as seen in Fig. 1. The other candidate of the 1390  $\text{cm}^{-1}$  band is the HOH bending vibration of the  $\text{H}_2\text{O}^+$  ion [ $\nu_2(\text{H}_2\text{O}^+)$ ]. The  $\text{H}_2\text{O}^+$  ion has a strong band of the  $\nu_2$  vibration at  $\sim 1432$   $\text{cm}^{-1}$  in the gas phase<sup>26,27</sup> and at 1401.7  $\text{cm}^{-1}$  in solid Ne.<sup>28</sup> Therefore, it is highly probable that the  $\sim 1390$   $\text{cm}^{-1}$  band of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ions is assigned to the  $\nu_2$  vibration of the  $\text{H}_2\text{O}^+$  component.

The spectra of the  $n=2-7$  clusters in Fig. 1 show bands at around 3600 and 3700  $\text{cm}^{-1}$ , which are too weak to be recognized (expanded views of the spectra in this region are shown later). Similar to the case of  $\text{CO}_2$  monomer and  $(\text{CO}_2)_n^+$ , the weak bands at  $\sim 3600$  and  $\sim 3700$   $\text{cm}^{-1}$  in the spectra of  $n=2-7$  are ascribed to the Fermi resonance bands of the  $\nu_1+\nu_3$  and  $2\nu_2+\nu_3$  transitions of solvent  $\text{CO}_2$  molecules, where  $\nu_1$  and  $\nu_2$  stand for the symmetric CO stretching vibration and the OCO bending vibration, respectively.<sup>16,21</sup>

Most of the IR bands in Fig. 1 can be explained in terms of the vibrations of the solvent  $\text{CO}_2$  molecules or the  $\text{H}_2\text{O}^+$  ion core. However, the band at around 2030  $\text{cm}^{-1}$  in the spectra of  $n=2-5$  cannot be assigned on the basis of the IR studies of  $\text{CO}_2$  and  $\text{H}_2\text{O}^+$ . The most probable species for the band at  $\sim 2030$   $\text{cm}^{-1}$  is the  $\text{C}_2\text{O}_4^+$  ion core because in the case of the  $(\text{CO}_2)_n^+$  ions the IR bands due to the  $\text{C}_2\text{O}_4^+$  ion core emerge at around 2100  $\text{cm}^{-1}$ .<sup>16</sup> Figure 2 shows an energy diagram regarding the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  system, drawn with the results of the ionization potential of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and the electronic spectrum of the  $\text{C}_2\text{O}_4^+$  ion.<sup>18,29</sup> The vertical axis is given with respect to the energy of one  $\text{H}_2\text{O}$  and two  $\text{CO}_2$  molecules,  $E(\text{H}_2\text{O}+2\text{CO}_2)=0$  eV. The right energy levels represent the system of a  $\text{CO}_2^+$  ion, a neutral  $\text{CO}_2$ , and a neutral  $\text{H}_2\text{O}$  molecule,  $E(\text{CO}_2^++\text{CO}_2+\text{H}_2\text{O})$ .<sup>18</sup> Since there are two  $\text{CO}_2$  molecules in this system, the right

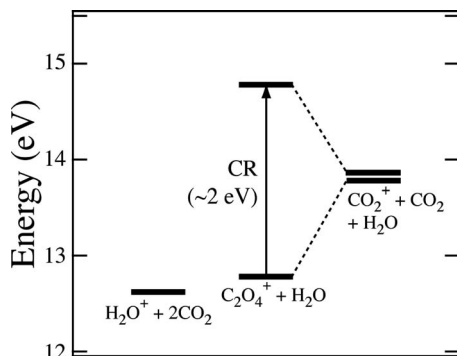


FIG. 2. The energy diagram for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  system. The vertical axis is based on the energy of one  $\text{H}_2\text{O}$  and two  $\text{CO}_2$  molecules,  $E(\text{H}_2\text{O}+2\text{CO}_2)$ . This diagram is drawn with the results of the ionization potential of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and the electronic spectrum of the  $\text{C}_2\text{O}_4^+$  ion.

levels are doubly degenerated.<sup>30</sup> The center levels in the figure correspond to the  $(\text{C}_2\text{O}_4^++\text{H}_2\text{O})$  form, where the charge resonance (CR) interaction between  $\text{CO}_2^+$  and  $\text{CO}_2$  largely stabilizes the  $\text{C}_2\text{O}_4^+$  energy and splits the degenerated levels into two separated levels. The CR transition from the lower level to the higher one was observed at around 2 eV.<sup>29</sup> If the binding energy of the  $\text{C}_2\text{O}_4^+$  ion is mainly due to the CR interaction (this is the case for benzene dimer ion),<sup>31,32</sup> it can be estimated as  $\sim 1$  eV. Therefore, the energy level of the system with one  $\text{C}_2\text{O}_4^+$  ion and one  $\text{H}_2\text{O}$  molecule,  $E(\text{C}_2\text{O}_4^++\text{H}_2\text{O})$ , is located at around 12.78 eV. The left energy level in Fig. 2 represents the energy of the  $\text{H}_2\text{O}^+$  ion and two  $\text{CO}_2$  molecules,  $E(\text{H}_2\text{O}^++2\text{CO}_2)$ .<sup>18</sup> As can be seen in Fig. 2, the energy levels of  $E(\text{C}_2\text{O}_4^++\text{H}_2\text{O})$  and  $E(\text{H}_2\text{O}^++2\text{CO}_2)$  are close to each other with a difference of  $\sim 0.16$  eV. As mentioned in Sec. III B, the 0.16 eV (1290  $\text{cm}^{-1}$ ) energy difference is smaller compared to the internal energy that the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  ion is expected to have in the experiment. Therefore, it is probable that there exist two types of isomers for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  ion: the one having the  $\text{C}_2\text{O}_4^+$  ion core and the other having the  $\text{H}_2\text{O}^+$  core. As seen in Fig. 1, the intensity of the band at  $\sim 2030$   $\text{cm}^{-1}$  relative to that of the  $\text{H}_2\text{O}^+$  band at  $\sim 1390$   $\text{cm}^{-1}$  decreases from  $n=2$  to 3. This result suggests that the abundance ratio of the isomer with the  $\text{C}_2\text{O}_4^+$  ion core decreases with increasing the cluster size. The  $\text{H}_2\text{O}^+$

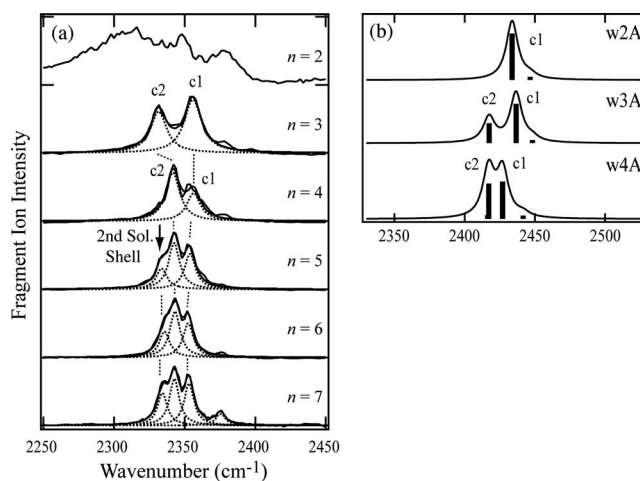


FIG. 3. (a) Expanded views of the IRPD spectra for  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ( $n=2-7$ ) in the 2250–2450  $\text{cm}^{-1}$  region (solid lines) with Lorentzian components for the reproduction of the IRPD spectra (dotted lines). (b) Theoretical IR spectra calculated for the most stable isomers of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ( $n=2-4$ ). The solid curves are produced with applying the Lorentzian component with a full width at half maximum of 10  $\text{cm}^{-1}$  to each of the IR bands. The labels c1 and c2 denote the  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core, respectively.

ion, in which the positive charge is concentrated in one molecule, gains the stabilization energy through the solvation more than the C<sub>2</sub>O<sub>4</sub><sup>+</sup> ion with the charge delocalized over two molecules. Therefore, the more the cluster has solvent molecules, the more stable the H<sub>2</sub>O<sup>+</sup> ion core is. In our IRPD experiment for the  $n=2$  ion, the fragmentation to C<sub>2</sub>O<sub>4</sub><sup>+</sup> and H<sub>2</sub>O was not observed, even for the excitation of the C<sub>2</sub>O<sub>4</sub><sup>+</sup> ion part at 1997 cm<sup>-1</sup>. The quantum chemical calculations in this study at the MP2/6-31+G\* level suggest that the energy of (H<sub>2</sub>O<sup>+</sup>•CO<sub>2</sub>+CO<sub>2</sub>) is lower than that of (C<sub>2</sub>O<sub>4</sub><sup>+</sup>+H<sub>2</sub>O) by 11920 cm<sup>-1</sup>. The cleavage of the C<sub>2</sub>O<sub>4</sub><sup>+</sup> ion core and the formation of the H<sub>2</sub>O<sup>+</sup>•CO<sub>2</sub> fragment ion occur in the photoexcitation of the C<sub>2</sub>O<sub>4</sub><sup>+</sup> ion core of the  $n=2$  ion.

Information on the solvation structure in the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>*n*</sub>]<sup>+</sup> clusters emerges in the IRPD spectra around 2350 cm<sup>-1</sup>. Figure 3(a) shows expanded views of the IRPD spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>*n*</sub>]<sup>+</sup> ( $n=2-7$ ) in the 2250–2450 cm<sup>-1</sup> region. The  $n=2$  ion shows a broad feature in this region, suggesting that the  $n=2$  ion giving the IRPD bands has a large amount of the internal energy. In the  $n=3$  spectrum, the bandwidth becomes narrower than that of the  $n=2$  ion. This result indicates that the binding energy of one CO<sub>2</sub> molecule in the  $n=3$  ion is quite smaller than that in the  $n=2$  ion, and the evaporative cooling process in the ion source provides lower internal energy for the  $n=3$  ion than that for the  $n=2$  ion. The IRPD spectrum of the  $n=3$  ion is reproduced with two Lorentzian components at 2332 and 2356 cm<sup>-1</sup>. The intensity of the former band relative to that of the latter one is about 73 %. Also for the  $n=4$  ion, the IRPD spectrum consists of two components at 2342 and 2356 cm<sup>-1</sup>; the intensity of the low frequency band relative to that of the high frequency one becomes higher (~180%). From the dependence in the relative intensity of these bands on the cluster size, the low frequency component in the  $n=3$  and 4 spectra can be ascribed to the third and the fourth solvent CO<sub>2</sub> molecules. The high and low frequency components are labeled “c1” and “c2,” respectively. As mentioned above, the first and the second CO<sub>2</sub> molecules are preferentially hydrogen bonded to the OH groups of the H<sub>2</sub>O<sup>+</sup> ion core. Therefore, the c1 components correspond to the CO<sub>2</sub> molecules attached to the hydrogen atoms of the H<sub>2</sub>O<sup>+</sup> ion. The c2 components originate from the third and the fourth CO<sub>2</sub> molecules, which are bonded to the position other than the hydrogen atoms. In the  $n=5$  spectrum, a new component emerges on the lower frequency side of the two bands [as highlighted by an arrow in Fig. 3(a)]; these three components are located at 2334, 2343, and 2354 cm<sup>-1</sup>. The  $n=6$  and 7 ions also have three components in the IRPD spectra, but the intensity of the lower frequency component increases with increasing the cluster size. Therefore, the component at ~2335 cm<sup>-1</sup> is attributed to the fifth to seventh solvent CO<sub>2</sub> molecules. The position of the component is almost the same for the  $n=5-7$  ions. This result suggests that the interaction between the H<sub>2</sub>O<sup>+</sup> ion core and the fifth to seventh solvent CO<sub>2</sub> molecules is not as strong as that of the first to fourth CO<sub>2</sub> molecules. It is quite probable that the first four CO<sub>2</sub> molecules are bonded directly to the H<sub>2</sub>O<sup>+</sup> ion core, forming the first solvation shell, and additional solvent molecules are attached outside of the first shell. The lower frequency com-

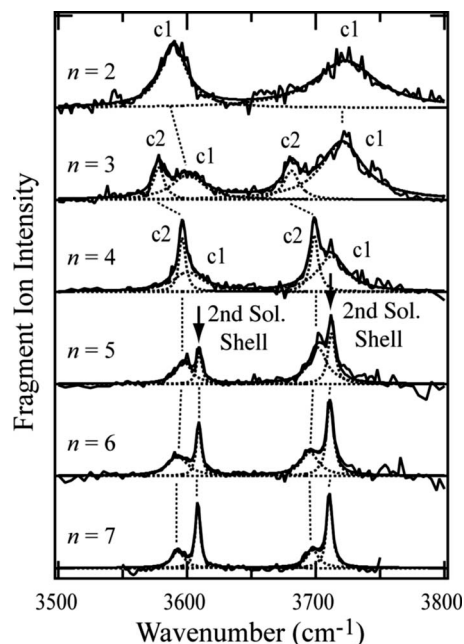


FIG. 4. Expanded views of the IRPD spectra for [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>*n*</sub>]<sup>+</sup> ( $n=2-7$ ) in the 3500–3800 cm<sup>-1</sup> region (solid lines) with Lorentzian components for the reproduction of the IRPD spectra (dotted lines).

ponent in the IRPD spectra of  $n=5-7$  is due to the solvent molecules in the second solvation shell. The stronger the solvent CO<sub>2</sub> molecule is bonded to the H<sub>2</sub>O<sup>+</sup> ion core, the higher the frequency of the antisymmetric CO stretching vibration becomes. Figure 3(b) is the simulated IR spectra of the  $n=2-4$  ions obtained for the geometry optimized clusters. The details of the results of the calculations are explained in Sec. III B.

A similar band feature is seen also in the IRPD spectra in the 3500–3800 cm<sup>-1</sup> region. Figure 4 shows the expanded views of the IRPD spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>*n*</sub>]<sup>+</sup> ( $n=2-7$ ) in the 3500–3800 cm<sup>-1</sup> region. As described above, the bands in this region are the Fermi doublet of  $\nu_1+\nu_3$  and  $2\nu_2+\nu_3$  of solvent CO<sub>2</sub> molecules. The IRPD spectrum of the  $n=2$  ion shows two bands at 3589 and 3723 cm<sup>-1</sup>. In the  $n=3$  spectrum, there are four components at 3578, 3600, 3681, and 3721 cm<sup>-1</sup>. The bands at 3578 and 3681 cm<sup>-1</sup>, which are labeled as c2, are weaker than the 3600 and 3721 cm<sup>-1</sup> ones labeled as c1. For the  $n=4$  ion, the IRPD spectrum can also be reproduced by four components at 3596, 3601, 3699, and 3712 cm<sup>-1</sup>; the 3596 and 3699 cm<sup>-1</sup> bands become comparable to the 3601 and 3712 cm<sup>-1</sup> bands. Therefore, the bands labeled as c2 for the  $n=3$  and 4 ions in Fig. 4 can be assigned to the third and the fourth solvent CO<sub>2</sub> molecules. For the clusters larger than  $n=4$ , two new bands appear at around 3609 and 3711 cm<sup>-1</sup> (highlighted by arrows in Fig. 4) in addition to the components at ~3594 and ~3698 cm<sup>-1</sup>. The ~3594 and ~3698 components correspond to the first to fourth solvent CO<sub>2</sub> molecules. The new bands at 3609 and 3711 cm<sup>-1</sup> become stronger and stronger with increasing the cluster size. Therefore, these bands are ascribed to the solvent molecules in the second solvation shell.

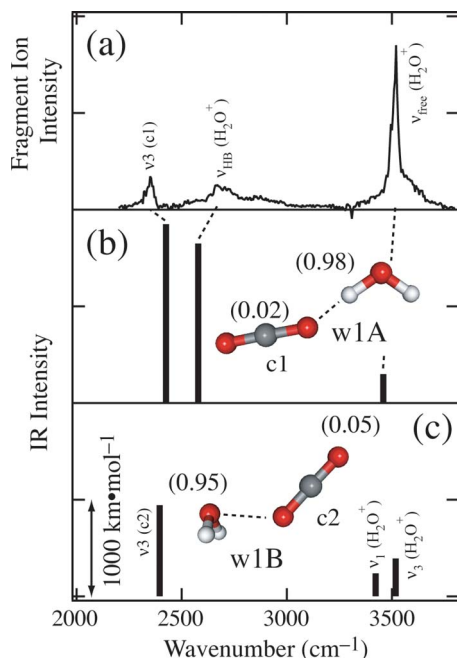


FIG. 5. (Color online) (a) The IRPD spectrum of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_1]^+$  ion. [(b) and (c)] The structure and the IR spectra of stable isomers (w1A and w1B) for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_1]^+$  ion calculated at the MP2/6-31+G\* level of theory. Numbers in parentheses show the charge distribution on the constituent molecules. The labels c1 and c2 stand for the  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core, respectively.

## B. Structure of $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$

In order to demonstrate theoretically the structural features derived from the IRPD spectra, we carry out *ab initio* molecular orbital (MO) calculations for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ions with  $n=1-4$ . In Fig. 5, the IRPD spectrum of the  $n=1$  ion is compared to IR spectra calculated for two optimized structures (isomers w1A and w1B). The characters c1 and c2 in Fig. 5 denote the  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core, respectively. Table IV collects the total energies, binding energies, vibrational frequencies, and IR intensities of these isomers. In both isomers the positive charge is localized on the water part, forming the  $\text{H}_2\text{O}^+$  ion core. The most stable structure for  $n=1$  is isomer w1A [Fig. 5(b)], in which one OH group is hydrogen bonded to the  $\text{CO}_2$  molecule.

Isomer w1B [Fig. 5(c)], where the solvent  $\text{CO}_2$  molecule is located out of the plane of the  $\text{H}_2\text{O}^+$  ion core, is less stable than w1A by  $+2298\text{ cm}^{-1}$ . The large difference in the total energy between w1A and w1B suggests that the most probable solvation of  $\text{CO}_2$  to the  $\text{H}_2\text{O}^+$  ion is the hydrogen bonding to the OH group. Both isomers w1A and w1B have three IR bands in the  $2000-4000\text{ cm}^{-1}$  region, corresponding to one antisymmetric CO stretching vibration of  $\text{CO}_2$  and two OH stretching vibrations of  $\text{H}_2\text{O}^+$ . The CO stretching vibration appears at similar positions for w1A ( $2425\text{ cm}^{-1}$ ) and w1B ( $2395\text{ cm}^{-1}$ ). On the other hand, the frequency and the IR intensity of the OH stretching vibrations are quite different for w1A and w1B. Isomer w1A has the hydrogen-bonded OH stretching vibration at  $2578\text{ cm}^{-1}$  and the free OH band at  $3459\text{ cm}^{-1}$ . In isomer w1B, both of the OH groups are free from the hydrogen bond, showing the symmetric and antisymmetric OH stretching vibrations at  $3423$  and  $3518\text{ cm}^{-1}$ , respectively. As seen in Fig. 5(a), the IRPD spectrum of the  $n=1$  ion shows only one strong band at  $3520\text{ cm}^{-1}$  in the  $3200-3800\text{ cm}^{-1}$  region. This spectral feature well resembles the IR spectrum of isomer w1A. Therefore, the structure of the  $n=1$  ion is attributed to isomer w1A. The binding energy of isomer w1A is calculated to be  $6130\text{ cm}^{-1}$ , which is higher than one-photon energy of the IR laser used for the  $n=1$  ion. The laser power dependence of the IRPD for the  $n=1$  ion shows a linear relationship in our experiment, suggesting that the  $n=1$  ion is dissociated through one-photon absorption with the aid of the internal energy. In the IRPD spectrum, the  $\nu_{\text{free}}(\text{H}_2\text{O}^+)$  band is stronger than the  $\nu_{\text{HB}}(\text{H}_2\text{O}^+)$  and  $\nu_3(\text{c1})$  bands, whereas the former one is predicted to be weaker than the other ones for w1A. The number of the  $n=1$  ions that can be involved in the IRPD process increases with increasing IR photon energy because the higher the IR photon energy is, the less internal energy is necessary for the assist of the IRPD process. Since the calculated energy difference between isomers w1A and w1B is  $2298\text{ cm}^{-1}$ , isomer w1B can exist under the present experimental condition and take part in the IRPD process of the  $n=1$  ion. However, the IRPD spectrum of the  $n=1$  ion displays no clear sign of isomer w1B, which must show two bands in the  $3300-3800\text{ cm}^{-1}$  region. Thus we conclude that only isomer w1A exists in the present experiment. Although we do not have any reasonable explanation for the

TABLE IV. Total energies, binding energies, vibrational frequencies, IR intensities, and assignments for optimized isomers of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_1]^+$ .

Isomer	Total energy <sup>a</sup> ( $\text{cm}^{-1}$ )	Binding energy <sup>a,b</sup> ( $\text{cm}^{-1}$ )	Frequency ( $\text{cm}^{-1}$ )	IR intensity ( $\text{km mol}^{-1}$ )	Assignment <sup>c</sup>
w1A	(0)	6130	2425	1850	$\nu_3(\text{c1})$
			2578	1651	H-bonded OH
			3459	300	free OH
w1B	2298	3832	2395	945	$\nu_3(\text{c2})$
			3423	240	$\nu_1(\text{H}_2\text{O}^+)$
			3518	394	$\nu_3(\text{H}_2\text{O}^+)$

<sup>a</sup>The correction with the zero-point vibrational energy is performed to obtain these values.

<sup>b</sup>The fragment species are  $\text{H}_2\text{O}^+$  and  $\text{CO}_2$ .

<sup>c</sup>The  $\text{CO}_2$  molecules attached to the hydrogen atom of the OH group and out of the plane of the  $\text{H}_2\text{O}^+$  ion core are called c1 and c2, respectively.

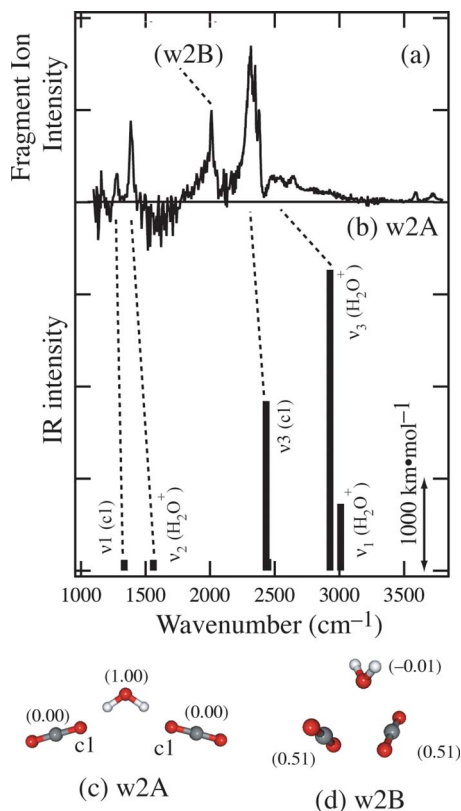


FIG. 6. (Color online) (a) The IRPD spectrum of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  ion. (b) The IR spectrum of the most stable isomer (w2A) for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  ion calculated at the MP2/6-31+G\* level of theory. (c) The structure of isomer w2A. (d) The structure of another stable isomer (w2B), which has a  $\text{C}_2\text{O}_4^+$  ion core. Numbers in parentheses show the charge distribution on the constituent molecules.

absence of isomer w1B in our experiment, it is probable that the potential barrier between w1A and w1B is quite low and w1B is spontaneously converted to w1A in the ion source. The lowest frequency vibration of w1B may imply this potential picture; the frequency of the intermolecular torsional vibration, which moves the CO<sub>2</sub> molecule to the hydrogen atoms, is calculated to be only 36 cm<sup>-1</sup>. Therefore, the potential along the torsional motion is quite shallow, and the potential barrier from w1B to w1A may probably be very low.

The predominance of c1 over c2 is also found in the quantum chemical calculations of the  $n=2$  ion. The geometry optimization of the  $n=2$  ion provides two stable isomers, w2A and w2B (Fig. 6). The most stable isomer (w2A) has a  $\text{C}_{2v}$  form with the CO<sub>2</sub> molecules attached to the OH groups; both of the CO<sub>2</sub> molecules are classified into c1. No isomer with the H<sub>2</sub>O<sup>+</sup> ion core is found other than w2A for the  $n=2$  ion. Isomer w2B has a  $\text{C}_2\text{O}_4^+$  ion core with a solvent H<sub>2</sub>O molecule. The structure of isomer w2B is quite similar to that of the  $(\text{CO}_2)_3^+$  ion, which also has a  $\text{C}_2\text{O}_4^+$  ion core with  $\text{C}_2$  symmetry.<sup>16</sup> Table V collects the total energies, binding energies, vibrational frequencies, IR intensities, and assignments of isomers w2A and w2B. Isomer w2A has the symmetric  $[\nu_1(\text{H}_2\text{O}^+)]$  and antisymmetric  $[\nu_3(\text{H}_2\text{O}^+)]$  OH stretching vibrations of the H<sub>2</sub>O<sup>+</sup> ion core at 3009 and 2928 cm<sup>-1</sup>, respectively. The frequency of  $\nu_1(\text{H}_2\text{O}^+)$  is higher than that of  $\nu_3(\text{H}_2\text{O}^+)$ , opposite to the order of free H<sub>2</sub>O<sup>+</sup> or H<sub>2</sub>O. This tendency was reported also for the H<sub>2</sub>O<sup>+</sup>•••(Ar)<sub>*n*</sub> clusters.<sup>22,23</sup> Two vibrations appearing at around 2440 cm<sup>-1</sup> are the in-phase and out-of-phase combinations of the antisymmetric CO stretching vibrations of the two CO<sub>2</sub> (c1) molecules  $[\nu_3(\text{c1})]$ ; the IR intensity of the out-of-phase band is quite stronger than that of the in-phase one. In addition, isomer w2A has two IR bands at 1335 and 1561 cm<sup>-1</sup>, which are the out-of-phase combination of the symmetric CO stretching vibrations  $[\nu_1(\text{c1})]$  and the bending vibration of the H<sub>2</sub>O<sup>+</sup> ion core  $[\nu_2(\text{H}_2\text{O}^+)]$ , respectively. As seen in Fig. 6, most of the IRPD bands of the  $n=2$  ion can be explained with the IR spectrum of isomer w2A. These assignments are consistent with those derived experimentally in the previous section. The vibrational analysis for w2A predicts an IR intensity for the  $\nu_3(\text{c1})$  vibration weaker than that of the  $\nu_3(\text{H}_2\text{O}^+)$  one, whereas the IRPD band of  $\nu_3(\text{c1})$  is stronger than that of  $\nu_3(\text{H}_2\text{O}^+)$ . This discrepancy in the IR intensity may indicate that the efficiency of the vibrational predissociation is substantially lower for the hydrogen-bonded OH stretching vibrations; the probability of the vibrational predissociation depends on the vibrational mode that is primarily excited. The binding energy of isomer w2A (4790 cm<sup>-1</sup>) is still larger than the IR photon energy, but smaller than that of isomer w1A (6130 cm<sup>-1</sup>). The decrease in the binding energy is the origin of the observation that the

TABLE V. Total energies, binding energies, vibrational frequencies, IR intensities, and assignments for optimized isomers of  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$ .

Isomer	Total energy <sup>a</sup> (cm <sup>-1</sup> )	Binding energy <sup>a,b</sup> (cm <sup>-1</sup> )	Frequency (cm <sup>-1</sup> )	IR intensity (km mol <sup>-1</sup> )	Assignment <sup>c,d</sup>
w2A	(0)	4790	1335	117	$\nu_1(\text{c1})$ -oop
			1337	9	$\nu_1(\text{c1})$ -ip
			1561	117	$\nu_2(\text{H}_2\text{O}^+)$
			2434	1841	$\nu_3(\text{c1})$ -oop
			2447	126	$\nu_3(\text{c1})$ -ip
			2928	3268	$\nu_3(\text{H}_2\text{O}^+)$
w2B	12 417	-7627	3009	727	$\nu_1(\text{H}_2\text{O}^+)$
			N/A	N/A	N/A

<sup>a</sup>The correction with the zero-point vibrational energy is performed to obtain these values.

<sup>b</sup>The fragment species are isomer w1A and CO<sub>2</sub>.

<sup>c</sup>The CO<sub>2</sub> molecule attached to the hydrogen atom of the OH group is called c1.

<sup>d</sup>“oop” and “ip” stand for the out-of-phase and in-phase combinations of the vibrations of the CO<sub>2</sub> molecules.

IRPD process occurs in the lower frequency region for  $n=2$ . The result of the laser power dependence of the IRPD for the  $n=2$  ion indicates that the  $n=2$  ion is dissociated through one-photon absorption. In addition, the  $n=2$  ion shows the IRPD band at  $1276\text{ cm}^{-1}$ . Therefore, the  $n=2$  ion in the experiment with a form like w2A may have the internal energy of at least  $\sim 3500\text{ cm}^{-1}$ . For isomer w2B, the MP2 calculation gives anomalous values for the vibrational analysis; this is similar to the case of  $(\text{CO}_2)_n^+$ .<sup>16</sup> Therefore, it is not possible to compare the IRPD spectrum of the  $n=2$  ion with the IR spectrum of isomer w2B. However, as mentioned in Sec. III A, it is reasonable to ascribe the  $1997\text{ cm}^{-1}$  band to some isomers with the  $\text{C}_2\text{O}_4^+$  ion core; the most probable isomer is w2B. The relative intensity between the  $\text{C}_2\text{O}_4^+$  band at  $1997\text{ cm}^{-1}$  and the  $\nu_3(\text{c}1)$  band at  $\sim 2350\text{ cm}^{-1}$  reflects the relative abundance of the  $\text{C}_2\text{O}_4^+$  ion and the solvent  $\text{CO}_2$  molecules in the ion packet of  $n=2$ , namely, the abundance ratio of w2A and w2B in the experiment. In the case of  $(\text{CO}_2)_3^+$ , which consists of the  $\text{C}_2\text{O}_4^+$  ion core and the solvent  $\text{CO}_2$  molecule, the ratio of the IRPD band intensity of the  $\text{C}_2\text{O}_4^+$  ion core relative to that of the solvent  $\text{CO}_2$  molecule is 2.1.<sup>16</sup> According to the IRPD spectrum of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_2]^+$  ion in Fig. 6(a), the ratio is  $\sim 0.11$ . Therefore, the relative abundance of isomer w2B to w2A is estimated to be  $\sim 10\%$ . From the viewpoint of the calculated total energy in Table V, the abundance ratio of w2B seems very high in the present experiment. This is probably because isomer w2B produced in the ionization process is not converted to w2A due to a very high potential barrier expected to exist between w2A and w2B.

For the  $n=3$  and 4 ions, only one type of stable isomers is found for each cluster in our MO calculations. Figure 7 displays the structure of the stable isomers (isomers w3A and w4A) and their IR spectra with the IRPD spectra for the  $n=3$  and 4 ions. Table VI shows the binding energies, vibrational frequencies, IR intensities, and assignments of w3A and w4A. Both isomers have the  $\text{H}_2\text{O}^+$  ion core. In isomer w3A, two  $\text{CO}_2$  molecules are bound to the OH groups in the plane (c1), and the other one is located out of the plane of the ion core (c2). Isomer w4A has a  $\text{C}_2$  structure, in which there are two c1 molecules and two c2 ones. Apparently, isomers w3A and w4A have the IR spectra similar to that of isomer w2A. The IRPD bands of the  $n=3$  and 4 ions can be explained with the IR spectra of w3A and w4A, as shown in Fig. 7. Figure 3(b) shows the expanded views of the theoretical IR spectra of isomers w2A, w3A, and w4A in the anti-symmetric CO stretching region. The main band for isomer w2A is the out-of-phase combination of the  $\nu_3(\text{c}1)$  vibrations. The agreement of the  $n=2$  ion is poor because of high internal energy of the cluster, but the IR spectra of isomers w3A and w4A well reproduce the feature of the IRPD spectra. As displayed in Fig. 3(b), the normal mode analysis shows that the higher and lower components in the spectra of w3A and w4A are ascribed to the c1 and c2 molecules, respectively. This correspondence is consistent with that experimentally determined in Fig. 3(a).

Here it would be of considerable interest to compare the properties of the  $\text{H}_2\text{O}^+(\text{CO}_2)_n$  ions with those of  $\text{H}_2\text{O}^+(\text{rare gas atom})_n$ . Dopfer and co-workers<sup>22–24,33,34</sup>

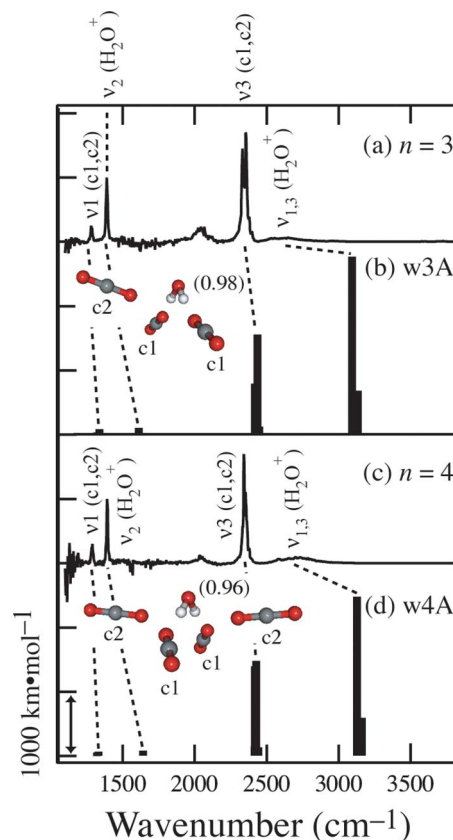


FIG. 7. (Color online) (a) The IRPD spectrum of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_3]^+$  ion. (b) The structure and the IR spectrum of a stable isomer (w3A) for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_3]^+$  ion calculated at the MP2/6-31+G\* level of theory. (c) The IRPD spectrum of the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_4]^+$  ion. (d) The structure and the IR spectrum of a stable isomer (w4A) for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_4]^+$  ion calculated at the MP2/6-31+G\* level of theory. Numbers in parentheses show the charge distribution on the  $\text{H}_2\text{O}$  component.

extensively studied the intermolecular interaction and the microsolvation process of the  $\text{H}_2\text{O}^+$  ion with rare gas atoms. The examination of the intermolecular potential energy surface of the  $\text{H}_2\text{O}^+\cdot\text{Ar}$  dimer complex at the MP2 level demonstrates a planar proton-bound  $\text{H}-\text{O}-\text{H}\cdots\text{Ar}$  global minimum and a local minimum with the  $p$ -bound structure, in which the Ar atom is attached to the  $2p_y$  orbital of the oxygen atom.<sup>22</sup> Indeed this global minimum structure is found in the IRPD experiments of  $\text{H}_2\text{O}^+\cdot\text{Ar}$ ,  $\text{H}_2\text{O}^+\cdot\text{Ne}$ , and  $\text{H}_2\text{O}^+\cdot\text{He}$ .<sup>23,24,33</sup> The quantum chemical calculations and the IRPD result of the  $\text{H}_2\text{O}^+\cdot\text{Ar}_2$  ion show that the most stable form is expected to have two hydrogen bonds leading to a planar  $\text{Ar}\cdots\text{H}-\text{O}-\text{H}\cdots\text{Ar}$  structure with  $\text{C}_{2v}$  symmetry.<sup>22,23</sup> For the  $\text{H}_2\text{O}^+\cdot\text{Ar}_n$  clusters with  $n=3$  and 4, the third and the fourth Ar atoms are expected to be bonded to the  $2p_y$  orbital of the oxygen atom.<sup>22,23</sup> These properties of the intermolecular interaction in the  $\text{H}_2\text{O}^+\cdot\text{Ar}_n$  ions are quite similar to those found for the  $\text{H}_2\text{O}^+(\text{CO}_2)_n$  clusters as mentioned above. The quantum chemical calculations of the  $\text{H}_2\text{O}^+\cdot\text{CO}_2$  ion provide two isomers (w1A and w1B), similar to the isomers of  $\text{H}_2\text{O}^+\cdot\text{Ar}$ . The first and the second  $\text{CO}_2$  molecules are hydrogen bonded to the OH groups, and the third and the fourth ones are located at the oxygen atom. However, there are also some differences between the  $\text{H}_2\text{O}^+\cdot\text{Ar}_n$  and the  $\text{H}_2\text{O}^+(\text{CO}_2)_n$  systems. In the case of the



TABLE VI. Binding energies, vibrational frequencies, IR intensities, and assignments of stable isomers of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>3,4</sub>]<sup>+</sup>.

Isomer	Binding energy <sup>a</sup> (cm <sup>-1</sup> )	Frequency (cm <sup>-1</sup> )	IR intensity (km•mol <sup>-1</sup> )	Assignment <sup>b,c</sup>
w3A	2667 <sup>d</sup>	1322	30	$\nu_1$ (c2)
		1337	85	$\nu_1$ (c1)-oop
		1338	11	$\nu_1$ (c1)-ip
		1610	105	$\nu_2$ (H <sub>2</sub> O <sup>+</sup> )
		2417	794	$\nu_3$ (c2)
		2437	1558	$\nu_3$ (c1)-oop
		2448	126	$\nu_3$ (c1,c2)
		3092	2770	$\nu_3$ (H <sub>2</sub> O <sup>+</sup> )
		3132	681	$\nu_1$ (H <sub>2</sub> O <sup>+</sup> )
		w4A	2566 <sup>e</sup>	1322
1322	0			$\nu_1$ (c2)-ip
1330	67			$\nu_1$ (c1)-oop
1331	13			$\nu_1$ (c1)-ip
1641	85			$\nu_2$ (H <sub>2</sub> O <sup>+</sup> )
2416	148			$\nu_3$ (c1,c2)
2417	1400			$\nu_3$ (c2)-oop
2427	1483			$\nu_3$ (c1)-oop
2442	133			$\nu_3$ (c1,c2)
3128	2481			$\nu_3$ (H <sub>2</sub> O <sup>+</sup> )
3160	593	$\nu_1$ (H <sub>2</sub> O <sup>+</sup> )		

<sup>a</sup>The correction with the zero-point vibrational energy is performed to obtain these values.

<sup>b</sup>The CO<sub>2</sub> molecules attached to the hydrogen atom of the OH group and out of the plane of the H<sub>2</sub>O<sup>+</sup> ion core are called c1 and c2, respectively.

<sup>c</sup>oop and ip stand for the out-of-phase and in-phase combinations of  $\nu_1$  or  $\nu_3$  of the CO<sub>2</sub> molecules.

<sup>d</sup>The fragment species are isomer w2A and CO<sub>2</sub>.

<sup>e</sup>The fragment species are isomer w3A and CO<sub>2</sub>.

H<sub>2</sub>O<sup>+</sup>•Ar<sub>2</sub> ion, the IRPD experiment exhibited the existence of a less stable isomer, in which one Ar atom is hydrogen bonded to the OH group and the other one is attached to the oxygen atom with the *p*-bond.<sup>23</sup> The quantum chemical calculations for the H<sub>2</sub>O<sup>+</sup>•Ar<sub>2</sub> ion also displayed a local potential minimum at this structure.<sup>22</sup> Contrastingly, the H<sub>2</sub>O<sup>+</sup>•(CO<sub>2</sub>)<sub>2</sub> ion shows no sign of such a minor isomer either in the IRPD experiment or in the MP2 calculations. The differences probably originate from the stronger intermolecular interaction for the H<sub>2</sub>O<sup>+</sup>•(CO<sub>2</sub>)<sub>n</sub> system than that for the H<sub>2</sub>O<sup>+</sup>•Ar<sub>n</sub> one. We perform the geometry optimization and the vibrational analysis of the hydrogen-bonded isomer for the H<sub>2</sub>O<sup>+</sup>•CO<sub>2</sub> and H<sub>2</sub>O<sup>+</sup>•Ar ions at the MP2/aug-cc-pVDZ level of theory. The binding energies of the H<sub>2</sub>O<sup>+</sup>•CO<sub>2</sub> and H<sub>2</sub>O<sup>+</sup>•Ar ions are predicted to be 6741 and 2030 cm<sup>-1</sup>, respectively. The stronger interaction for the CO<sub>2</sub> system than the Ar one may probably be due to a larger polarizability of CO<sub>2</sub> (2.91 × 10<sup>-24</sup> cm<sup>3</sup>) than that of Ar (1.64 × 10<sup>-24</sup> cm<sup>3</sup>).<sup>35</sup>

### C. IRPD spectra and structures of [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (*n*=1–7)

Since methanol has the ionization potential (10.94 eV) lower than that of CO<sub>2</sub> (13.78 eV),<sup>18</sup> the ion core of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ions is expected to be CH<sub>3</sub>OH<sup>+</sup>, similar to the case of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup>. Figure 8 shows the IRPD spectra of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (*n*=1–7) clusters in the

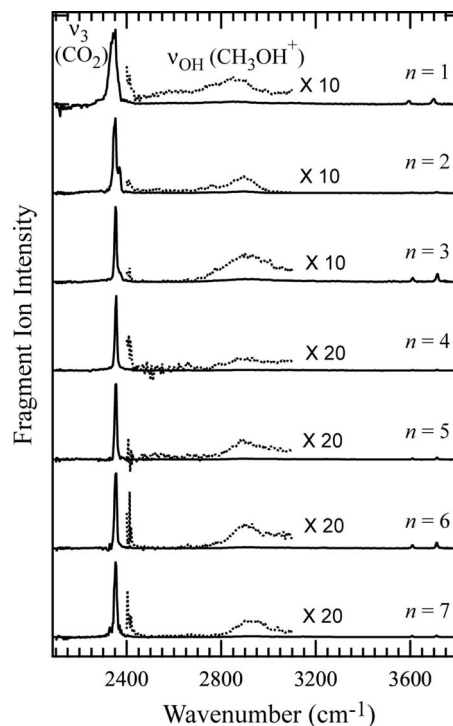


FIG. 8. The IRPD spectra of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ions with *n*=1–7. These spectra are observed by monitoring yields of all the fragment ions due to the loss of CO<sub>2</sub> molecules.

2100–3800 cm<sup>-1</sup> region. All the spectra show a strong band at ~2350 cm<sup>-1</sup> and a broad weak band in the 2400–3100 cm<sup>-1</sup> region. Similar to the case of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ions, the ~2350 cm<sup>-1</sup> band in the IRPD spectra of [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> can be assigned to the anti-symmetric CO stretching vibration of the solvent CO<sub>2</sub> molecules [ $\nu_3$ (CO<sub>2</sub>)]. Since the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion has the band of the solvent CO<sub>2</sub> molecule at ~2350 cm<sup>-1</sup>, the ion core of [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> is the CH<sub>3</sub>OH<sup>+</sup> ion. The IRPD spectra in Fig. 8 show no strong band assignable to the stretching vibration of the free OH group of CH<sub>3</sub>OH<sup>+</sup> in the 3000–3550 cm<sup>-1</sup> region. Therefore, the OH group of the CH<sub>3</sub>OH<sup>+</sup> ion core is hydrogen bonded to the solvent CO<sub>2</sub> molecule in the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ions. The broad bands of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> clusters in the 2400–3100 cm<sup>-1</sup> region are assigned to the hydrogen-bonded OH stretching vibration of the CH<sub>3</sub>OH<sup>+</sup> ion core [ $\nu_{\text{OH}}(\text{CH}_3\text{OH}^+)$ ]. In addition, weak but sharp bands also appear at around 3600 and 3700 cm<sup>-1</sup>. These bands are ascribed to the Fermi doublets of the  $\nu_1 + \nu_3$  and  $2\nu_2 + \nu_3$  vibrations of the solvent CO<sub>2</sub> molecules.

For the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> clusters, the solvation characteristics of the CO<sub>2</sub> molecules to the H<sub>2</sub>O<sup>+</sup> ion core emerge in the IRPD spectra in the 2250–2450 (Fig. 3) and 3500–3800 cm<sup>-1</sup> (Fig. 4) regions. By contrast, the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> clusters do not show such a clear picture of the CO<sub>2</sub> solvation in the IRPD spectra. Figures 9 and 10 display expanded views of the IRPD spectra of [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> in the 2250–2450 cm<sup>-1</sup> and the 3500–3800 cm<sup>-1</sup> regions, respectively. In Fig. 9, the *n*=1 ion shows a broad band at around 2343 cm<sup>-1</sup> with a width of ~33 cm<sup>-1</sup>. The IRPD spectrum of the *n*=2 ion is repro-

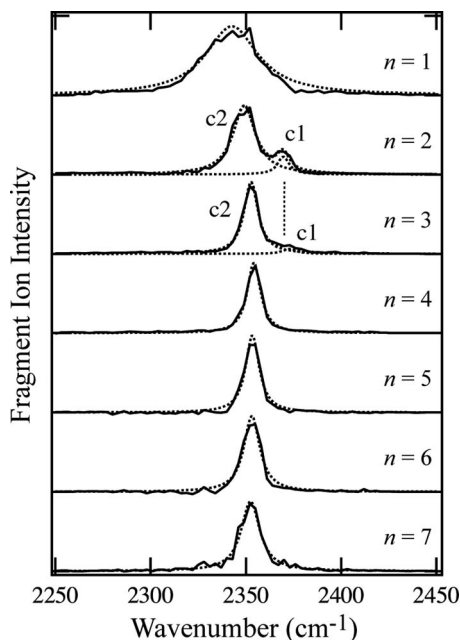


FIG. 9. Expanded views of the IRPD spectra for  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  ( $n=1-7$ ) in the  $2250-2450\text{ cm}^{-1}$  region (solid lines) with Lorentzian components for the reproduction of the IRPD spectra (dotted lines). The labels c1 and c2 denote the  $\text{CO}_2$  molecules attached to the OH group and out of the H-O-C plane of the  $\text{CH}_3\text{OH}^+$  ion core, respectively.

duced by two sharp bands centered at  $2349$  and  $2369\text{ cm}^{-1}$  with a width of  $\sim 15\text{ cm}^{-1}$ . The  $n=3$  ion also has two components at  $2353$  and  $2373\text{ cm}^{-1}$ , but the intensity of the low frequency band relative to the high frequency one becomes higher than that of the  $n=2$  ion. Therefore, one can assign the low frequency component in the spectra of  $n=2$  and 3 to the second and the third solvent  $\text{CO}_2$  molecules (c2). The high frequency component of the  $n=2$  and 3 ions is attrib-

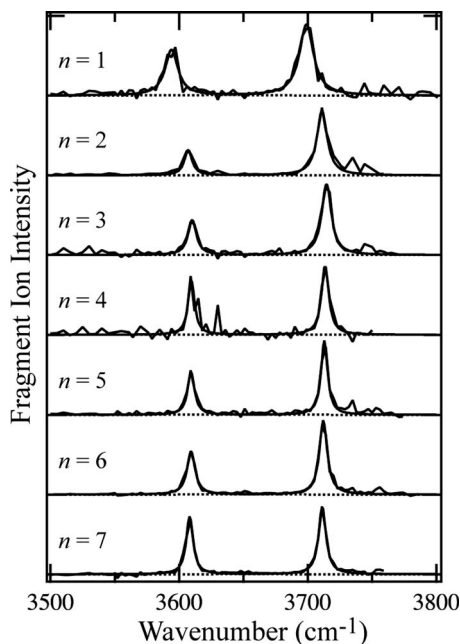


FIG. 10. Expanded views of the IRPD spectra for  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  ( $n=1-7$ ) in the  $3500-3800\text{ cm}^{-1}$  region (solid lines) with Lorentzian components for the reproduction of the IRPD spectra (dotted lines).

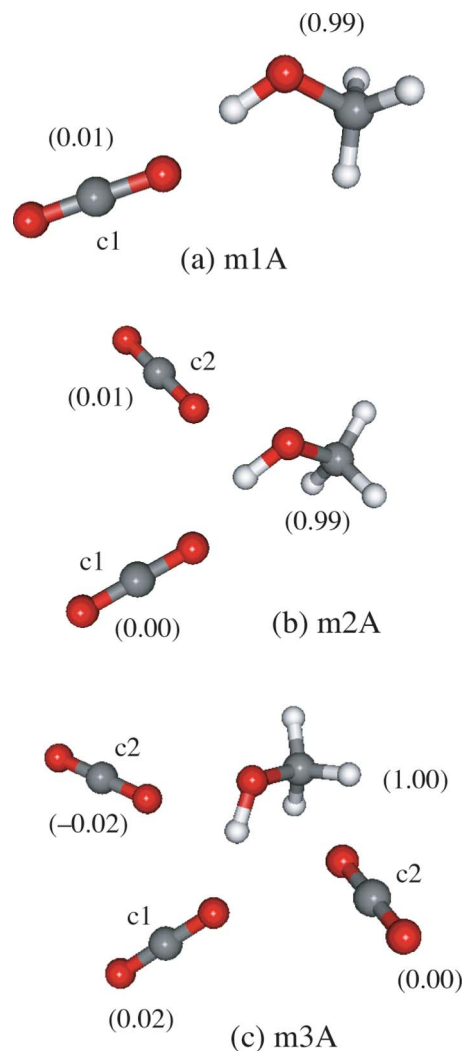


FIG. 11. (Color online) Stable structures of  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  ( $n=1-3$ ) optimized at the  $\text{MP2}/6-31+\text{G}^*$  level. Numbers in parentheses show the charge distribution on the constituent molecules.

uted to the  $\text{CO}_2$  molecule hydrogen bonded to the OH group of the  $\text{CH}_3\text{OH}^+$  ion core (c1). This assignment is consistent with that for the  $[\text{H}_2\text{O}\cdot(\text{CO}_2)_n]^+$  ( $n=3$  and 4) ions; the stronger the intermolecular interaction between the ion core and the solvent  $\text{CO}_2$  molecules is, the higher the frequency of the antisymmetric CO stretching vibration is (see Fig. 3). For the clusters larger than  $n=3$ , the  $\nu_3(\text{CO}_2)$  band can be reproduced by one component at  $\sim 2353\text{ cm}^{-1}$ ; this position is almost the same as that of the c2 components for the  $n=2$  and 3 ions. This result indicates that the interaction between the  $\text{CH}_3\text{OH}^+$  ion core and solvent  $\text{CO}_2$  molecules is strongest for the first  $\text{CO}_2$  molecule, and is similar for additional solvent molecules. Similarly, the IRPD spectra in the  $3500-3800\text{ cm}^{-1}$  region (Fig. 10) show a blueshift of the two bands from  $n=1$  and 2 and the bands keep almost the same position for  $n=2-7$ . This result also implies the drastic change in the intermolecular interaction between the first solvent molecule and the other ones.

The quantum chemical calculations show solvation features similar to those derived experimentally. Figure 11 displays stable structures of the  $[\text{CH}_3\text{OH}\cdot(\text{CO}_2)_n]^+$  ( $n=1-3$ ) ions; the binding energy, vibrational frequency, IR intensity,

TABLE VII. Binding energies, vibrational frequencies, IR intensities, and assignments of stable isomers of [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1-3</sub>]<sup>+</sup>.

Isomer	Binding energy <sup>a</sup> (cm <sup>-1</sup> )	Frequency (cm <sup>-1</sup> )	IR intensity (km mol <sup>-1</sup> )	Assignment <sup>b</sup>
m1A	4580	2435	889	$\nu_3$ (c1)
		2869	299	CH
		3094	1836	H-bonded OH
		3149	41	CH
		3266	22	CH
m2A	2305 <sup>c</sup>	2418	668	$\nu_3$ (c2)
		2436	846	$\nu_3$ (c1)
		2923	191	CH
		3158	1446	H-bonded OH
		3181	95	CH
m3A	2134 <sup>d</sup>	3278	25	CH
		2414	222	$\nu_3$ (c2)
		2416	1452	$\nu_3$ (c2)
		2429	538	$\nu_3$ (c1)
		2968	182	CH
		3118	1460	H-bonded OH
		3185	22	CH
		3278	17	CH

<sup>a</sup>The correction with the zero-point vibrational energy is performed to obtain these values.

<sup>b</sup>The CO<sub>2</sub> molecules attached to the OH group and out of the H–O–C plane of the CH<sub>3</sub>OH<sup>+</sup> ion core are called c1 and c2, respectively.

<sup>c</sup>The fragment species are isomer m1A and CO<sub>2</sub>.

<sup>d</sup>The fragment species are isomer m2A and CO<sub>2</sub>.

and assignment are collected in Table VII. Only isomer m1A is found in our geometry optimization for the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion. The positive charge is localized in the CH<sub>3</sub>OH constituent, and the solvent CO<sub>2</sub> molecule is preferentially bound to the OH group, forming a hydrogen bond. The binding energy between the CH<sub>3</sub>OH<sup>+</sup> ion core and the solvent CO<sub>2</sub> molecule is calculated to be 4580 cm<sup>-1</sup>, which is higher than the IR photon energy used in this study, but substantially lower than that of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion (isomer w1A, 6130 cm<sup>-1</sup>). The intermolecular interaction between the CH<sub>3</sub>OH<sup>+</sup> ion and the CO<sub>2</sub> molecule is weaker than that between the H<sub>2</sub>O<sup>+</sup> ion and CO<sub>2</sub>. The vibrational frequency and the IR intensity of isomer m1A agree with the spectral pattern of the IRPD spectrum for the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion (Table VII). The position of the antisymmetric CO stretching vibration is almost the same as that for isomer w1A, and a band of the hydrogen-bonded OH stretching vibration is predicted to appear at 3094 cm<sup>-1</sup>. In isomer m2A, one CO<sub>2</sub> molecule is hydrogen bonded to the OH group, and the other one is bound to the oxygen atom of the CH<sub>3</sub>OH<sup>+</sup> ion core. The binding energy is estimated as 2305 cm<sup>-1</sup>, which is comparable with the IR photon energy used in this study and quite smaller than that of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ion (isomer w2A, 4790 cm<sup>-1</sup>). The vibrational analysis for isomer m2A shows the antisymmetric CO stretching and the hydrogen-bonded OH stretching vibrations at positions similar to those for m1A. The band of the CO<sub>2</sub> molecule bonded at the hydrogen atom of the OH group (c1) is located at 2436 cm<sup>-1</sup>, which is higher than that of the molecule out of the H–O–C plane of the CH<sub>3</sub>OH<sup>+</sup> ion (c2, 2418 cm<sup>-1</sup>). This vibrational frequency relationship of c1

and c2 agrees with that derived experimentally in Fig. 9. The IR intensities of the c1 and c2 bands calculated for m2A are similar to each other (846 and 668 km/mol, respectively). In the IRPD spectrum of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ion, on the contrary, the c2 band is considerably stronger than that of the c1 one, indicating that the probability of the vibrational predissociation is higher for the excitation of the c2 molecule than that of the c1 one. Isomer m3A has a CH<sub>3</sub>OH<sup>+</sup> ion core; one CO<sub>2</sub> molecule is hydrogen bonded to the OH group, and the other CO<sub>2</sub> molecules are located at the oxygen atom of the ion core. The binding energy of isomer m3A is a bit smaller than that of m2A. Similar to the case of m2A, the  $\nu_3$  (c1) band is located at a frequency (2429 cm<sup>-1</sup>) higher than those of the  $\nu_3$  (c2) bands (2414 and 2416 cm<sup>-1</sup>). Also for the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ions, the solvent CO<sub>2</sub> molecules are preferentially attached to the OH group of the CH<sub>3</sub>OH<sup>+</sup> ion core.

#### IV. SUMMARY

The IRPD spectra of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> and [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n=1-7$ ) ions have been measured in the 1100–3800 cm<sup>-1</sup> region. Moreover, the geometry optimization and the vibrational analysis have been carried out for the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n=1-4$ ) and the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n=1-3$ ) ions at the MP2/6-31+G\* level of theory. Most of the IRPD bands can be attributed to the H<sub>2</sub>O<sup>+</sup> ion, the CH<sub>3</sub>OH<sup>+</sup> ion, and the solvent CO<sub>2</sub> molecules, which is reasonable from the viewpoint of the ionization potential of CO<sub>2</sub> (13.78 eV), H<sub>2</sub>O (12.62 eV), and CH<sub>3</sub>OH (10.94 eV). The IRPD spectrum of the [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>1</sub>]<sup>+</sup> ion shows the free OH and hydrogen-bonded OH stretching bands of the H<sub>2</sub>O<sup>+</sup> ion core at 3520 and ~2700 cm<sup>-1</sup>, respectively, with the antisymmetric CO stretching band of the solvent CO<sub>2</sub> molecule at ~2350 cm<sup>-1</sup>. This spectral pattern is explained with the cluster structure that the CO<sub>2</sub> molecule is solvated to the H<sub>2</sub>O<sup>+</sup> ion core through the O–H•••OCO hydrogen bond. The free OH stretching band is not observed in the IRPD spectrum of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> because the solvent CO<sub>2</sub> molecules are preferentially bonded to the OH groups of the H<sub>2</sub>O<sup>+</sup> ion core. According to the IRPD spectra of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n=3-7$ ), the third and the fourth CO<sub>2</sub> molecules are solvated to the oxygen atom of the H<sub>2</sub>O<sup>+</sup> ion core from out of the plane of H<sub>2</sub>O<sup>+</sup>. The first solvation shell of the H<sub>2</sub>O<sup>+</sup> ion core is closed with the four CO<sub>2</sub> molecules. All the IRPD spectra of the [CH<sub>3</sub>OH•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n=1-7$ ) ions display the hydrogen-bonded OH stretching band of the CH<sub>3</sub>OH<sup>+</sup> ion core at around 2900 cm<sup>-1</sup> even for the  $n=1$  ion. Similar to the case of [H<sub>2</sub>O•(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup>, the first solvent CO<sub>2</sub> molecule is preferentially bonded to the OH group of the CH<sub>3</sub>OH<sup>+</sup> ion core.

#### ACKNOWLEDGMENTS

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